Statistical and Thermal Physics

With Computer Applications

Harvey Gould and Jan Tobochnik

Chapter 1

Preface

This text is about two closely related subjects: thermodynamics and statistical mechanics. Thermodynamics is a general theory of macroscopic systems which provides limits on allowable physical processes involving energy transformations and relations between various measurable quantities. Its power is in its generality. Its limitation is that all quantitative predictions require empirical inputs. Statistical mechanics provides a microscopic foundation for thermodynamics and can be used to make quantitative predictions about macroscopic systems. Thermodynamics has always been important, but is of particular relevance at present because of important policy and engineering issues that require an understanding of thermal systems. These issues include global climate change, the search for new sources of energy, and the need for more efficient uses of energy. Statistical mechanics has become much more important in physics and related areas because its tools can now be implemented on computers and are much more widely applicable. These applications include lattice gauge theories in high energy physics, many problems in astrophysics, biological physics and geophysics, as well as topics traditionally considered outside of physics such as social networks and finance.

Although statistical mechanics and thermodynamics are central to many research areas in physics and other sciences, both have had less of a presence in the undergraduate curriculum than classical mechanics, electromagnetism, and quantum mechanics. It wasn't many years ago that statistical mechanics was not even part of the undergraduate physics curriculum at many colleges and universities. Our text is part of an effort to bring some of the recent advances in research into the undergraduate curriculum.

Thermodynamics and statistical mechanics are difficult to teach and to learn. The reasons for these difficulties include the following.

- There is not much emphasis on thermodynamics and statistical mechanics in the introductory physics course sequence, and what is taught in this context is typically not done well.
- Thermodynamics involves phenomenological reasoning without using microscopic information. This approach is little used in other undergraduate courses.

- Students have had little experience making the connection between microscopic and macroscopic phenomena.

- Many calculations are unfamiliar and involve the use of multivariable calculus. The usual notation is confusing because physicists use the same symbol to denote a physical quantity and a functional form. For example, S represents the entropy whether it is written as a function of the energy E, volume V, and particle number N, or if we replace E by the temperature T. Also the distinction between total and partial derivatives is sometimes confusing. These issues arise in other physics courses, but are more important in thermodynamics because of the many variables involved.

- A deep understanding of probability theory is important. Probability concepts often seem simple, and we usefully apply them in our everyday experience. However, probability is subtle as evidenced by the frequent misuse of statistics in news stories and the common tendency to attribute causality to events that are random.

- The solution of a single equation or set of equations such as Newton's laws in mechanics, Maxwell's equations in electrodynamics, and Schrödinger's equation in quantum mechanics is not central to statistical physics. Hence there are no standard procedures that work for a large class of problems, and many of the calculations are unfamiliar to students.

- There are few exactly solvable problems.

- There are many diverse applications of statistical and thermal physics, and hence the nature of undergraduate and graduate courses in this area vary more than courses in other subjects.

Our text deals with these difficulties in various ways which we discuss in the following. However, we emphasize that learning thermodynamics and statistical mechanics is not easy. Understanding is a personal achievement, won only at the cost of constant intellectual struggle and reflection. No text can replace a good instructor and neither can replace disciplined thinking.

One of the features of our text is its use of computer simulations and numerical calculations in a variety of contexts. The simulations and calculations can be used as lecture demonstrations, homework problems, or as a laboratory activity. Instructors and students need not have any background in the use of simulations, and all the simulations are given in a context in which students are asked to think about the results. Our experience is that it is important to discuss various models and algorithms so that students will more easily replace their naive mental models of matter by more explicit ones. For example, many students' mental model of a gas is that the molecules act like billiard balls and give off "heat" when they collide. A discussion of the nature of the interactions between molecules and the algorithms used to simulate their motion according to Newton's second law can show students why the billiard ball model is inadequate and can help them replace their naive model by one in which the total energy is conserved. The simulations also provide useful visualizations of many of the ideas discussed in the text and help make abstract ideas more concrete. For example, Monte Carlo simulations help make the different ensembles more meaningful.

We use simulations in the rich context of statistical physics, where discussion of the physics provides motivation for doing simulations, and consideration of various algorithms provides insight into the physics. In addition, the animations provide both motivation and another way of obtaining understanding. We also discuss some simple numerical programs that calculate various integrals that cannot be expressed in terms of well known functions.

It is possible to use the text without ever running a program. The standard results that appear in other texts are derived in our text without the use of the computer. However, the simulations provide a concrete and visual representation of the models that are discussed in statistical mechanics, and thus can lead to a deeper understanding. Texts and physics courses frequently overemphasize the results obtained from physical theory and underemphasize physical insight. We have attempted to provide a balance between these two goals and provide different resources (simulations, various kinds of problems, and detailed discussion in the text) to help students learn to think like physicists.

Suggested problems appear both within and at the end of each chapter. Those within the chapter are designed mainly to encourage students to read the text carefully and provide immediate reinforcement of basic ideas and techniques. Problems at the end of the chapters are designed to deepen student understanding and allow students to practice the various tools that they have learned. Some problems are very straightforward and others will likely not be solved by most students. The more difficult problems provide a useful starting point for stimulating student thinking and can be used as the basis of class discussions. We have tried to provide a wide range of problems for students with various backgrounds and abilities.

We do not assume any special background in thermal physics. Chapter 1 discusses the important ideas of thermodynamics and statistical physics by appealing to everyday observations and qualitative observations of simple computer simulations. A useful prop during the first several weeks of classes is a cup of hot water. Students are not surprised to hear that the water always cools and are pleased that they are already on their way to understanding one of the basic ideas of thermal systems – the need for a quantity (the entropy) in addition to energy for explaining the unidirectional behavior of macroscopic systems.

It has become fashionable since the 1960s to integrate thermodynamics and statistical mechanics. (Before then, thermodynamics was taught separately, and statistical mechanics was not offered at the undergraduate level at many colleges and universities.) The result of this integration is that many undergraduates and graduate students are not exposed to the phenomenological way of thinking exemplified by thermodynamics. We devote all of Chapter 2 to this way of reasoning without resorting to statistical mechanics, although we often refer back to what was discussed in Chapter 1. Besides the intrinsic importance of learning thermodynamics, its phenomenological way of reasoning using a few basic principles and empirical observations is as important as ever.

Most thermal physics texts discuss the ideas of probability as they are needed to understand the physics. We are sympathetic to this approach because abstract ideas are usually easier to understand in context. However, there is much that is unfamiliar to students while they are learning statistical mechanics, and it is important that students have a firm understanding of probability before tackling problems in statistical mechanics. Our discussion of probability in Chapter 3 includes discussions of random additive processes and the central limit theorem. The latter plays an essential role in statistical mechanics, but it is hardly mentioned in most undergraduate texts. Because the ideas of probability are widely applicable, we also discuss probability in other contexts including Bayes' theorem. These other applications can be skipped without loss of continuity. We include them because a topic such as Bayes' theorem and traffic flow can excite some students and motivate them to delve deeper into the subject.

There is a tendency for thermal physics books to look like a long list of disconnected topics. We have organized the subject differently by having just two chapters, Chapter 2 and Chapter 4 on the essential methodology of thermodynamics and statistical mechanics, respectively. These chapters also contain many simple applications because it is difficult to learn a subject in the abstract. In particular, we consider the Einstein solid (a system of harmonic oscillators), discuss the demon algorithm as an ideal thermometer, and use the ideal gas as a model of a dilute gas.

After discussing the conceptual foundations of statistical mechanics, most thermal physics texts next discuss the ideal classical gas and then the ideal Fermi and Bose gases. One problem with this approach is that students frequently confuse the single particle density of states with the density of states of the system as a whole and do not grasp the common features of the treatment of ideal quantum gases. We follow Chapter 4 by applying the tools of statistical mechanics in Chapter 5 to the Ising model, a model that is well known to physicists and others, but seldom encountered by undergraduates. The consideration of lattice systems allows us to apply the canonical ensemble to small systems for which students can enumerate the microstates and apply the Metropolis algorithm. In addition, we introduce mean-field theory and emphasize the importance of cooperative effects.

Chapter 6 discusses the ideal classical gas using both the canonical and grand canonical ensembles and the usual applications to ideal Fermi and Bose gases. We discuss these topics in a single chapter to emphasize that all treatments of ideal gases involve the single particle density of states. We include programs that calculate numerically several integrals for the ideal Bose and Fermi gases so that the chemical potential as a function of the temperature for fixed density can be determined. In addition we emphasize the limited nature of the equipartition theorem for classical systems and the general applicability of the Maxwell velocity and speed distributions for any classical system, regardless of the nature of the interactions between particles and the phase.

The first part of Chapter 7 discusses the nature of the chemical potential by considering some simple models and simulations. We then discuss the role of the chemical potential in understanding phase transitions with a focus on the van der Waals equation of state.

Most of the material in the first six chapters and Chapter 7 through Section 7.3 would form the core of a one semester course in statistical and thermal physics. Starred sections in each chapter can be omitted without loss of continuity. It is unlikely that Chapter 8 on classical gases and liquids and Chapter 9 on critical phenomena can be discussed in a one semester course, even in a cursory manner. We hope that their presence will encourage some undergraduates to continue their study of statistical physics. Their main use is likely to be as material for special projects.

It is possible to start a course with the development of statistical mechanics in Chapter 4 after a review of the first three chapters. The key results needed from Chapters 1–3 are the fundamental equation $dE = TdS - PdV + \mu dN$, definitions of thermodynamic quantities such as temperature, pressure, and chemical potential in terms of the various thermodynamic potentials, the definitions of the heat capacity and compressibility, and an understanding of how to obtain average quantities from a knowledge of the probability distribution. Of course, knowing these results is not the same as understanding them.

Besides including more material than can be covered in a one semester course, our text has some deliberate omissions. Many undergraduate thermal physics texts invoke kinetic theory arguments to derive the ideal gas pressure equation of state. In contrast, our text does not discuss kinetic theory at all. One of the themes of our text is that time is irrelevant in equilibrium statistical mechanics. We suspect that kinetic theory arguments confuse students if presented early in their learning of statistical mechanics. Part of the confusion is probably associated with the fact that the ideal gas pressure equation of state is derived in statistical mechanics by ignoring the interactions between particles, but the kinetic theory derivation of the same equation of state explicitly includes these interactions. Similarly, many derivations of the Maxwell velocity distribution give the misleading impression that it is applicable only to a dilute gas.

A solutions manual for instructors is available from Princeton University Press.

In addition to the chapters available via the Princeton University Press website, `<press.princeton.edu/titles/9375` we plan to add more chapters on topics in statistical physics to the STP (Statistical and Thermal Physics) collection of the ComPADRE digital library (`<www.compadre.org/stp>`). In particular, we plan to add a chapter on kinetic theory and other dynamical phenomena and a chapter on applications of statistical physics to nonthermal systems. The emphasis of the latter will be on applications to current research problems. In addition, there are resources for the teaching of statistical and thermal physics from other teachers on the ComPADRE website. The latter is a network of free online resource collections supporting faculty, students, and teachers in physics and astronomy education. We encourage others to submit materials on statistical and thermal physics to `<www.compadre.org/stp>`.

The software associated with our text is available in several formats and can be downloaded from `<www.compadre.org/stp>` or `<press.princeton.edu/titles/9375.html>`. All the programs are open source. The compiled programs are jar files and can be run like any other program on your computer by double-clicking on the file. The applications can also be run in applet mode when embedded into an html page and run within a browser. (Directions for doing so are available on both websites.) Java 1.5 or greater must be installed on your computer to run the programs. Java can be downloaded at no cost from `<java.com>` for Windows and Linux and is included with Mac OS X.

All of the programs mentioned in the text and a few others are packaged together with related curricular material in the STP Launcher. This convenient way of organizing and running other Java programs was developed by Doug Brown. Alternatively, you can download the programs individually. The STP programs generally have a wider range of inputs and outputs, but cannot be modified without downloading the source code and recompiling it. The EJS (Easy Java Simulations) programs usually have a simpler interface, but the source code is part of the jar file and can be easily modified. To do the latter it is necessary to download EJS from `<www.um.es/fem/Ejs/>`.

We have many people to thank. In particular, we are especially grateful to Louis Colonna-Romano for drawing almost all of the figures. Lou writes programs in postscript the way others write programs in Java or Fortran.

Milton Cole originally encouraged us to write a text on statistical and thermal physics and to apply for a National Science Foundation grant. The two NSF grants, PHY-98-01878 and DUE-0442481, we have received have given us and our students the resources to write the software associated with the text and the opportunity to attend conferences and workshops where we have been stimulated by discussions with many colleagues. We would like to thank Jill Larkin and Fred Reif for their useful advice and encouragement at the beginning of the STP project. We used Fred Reif's classic thermal physics text for many years and our text shows its strong influence.

We owe a special debt to Wolfgang Christian, Anne Cox, Doug Brown, Francisco Esquembre, and Mario Belloni of the Open Source Physics Project, `<http://www.compadre.org/osp/>` for their many direct and indirect contributions to the STP project. The software would not have been possible without Wolfgang Christian's yeoman work developing and managing the Java-based Open Source Physics Library and its many APIs. Anne Cox helped convert most of the STP curricular material to EJS, set up the STP collection on ComPADRE, and provided many of the solutions to the first three chapters with the help of her student Chris Bauer.

We thank Anne Cox, Bill Klein, and Beate Schmittman for using drafts of our text as their course textbook. We also would like to thank Milton Cole, Don Lemons, Jon Machta, Irwin Oppenheim, Sid Redner, and Royce Zia for reading individual chapters and making useful suggestions. Our students have been patient (not that they had much choice), and many of them gave us valuable feedback. In particular, we would like to thank Kipton Barros, Sarah Brent, Ranjit Chacko, Andy Coniglio, Jake Ellowitz, Michael Robitaille, Chris Sataline, Hui Wang, Laurel Winter, and Junchao Xia for their questions and suggestions. Jake Ellowitz also wrote many of the solutions.

Drafts of the text have been available online for several years. We have benefited from the feedback that we have received from people who have written to us to correct typos and unclear passages. These people include Bernard Chasan, Pedro Cruz, Oscar R. Enriquez, Jim Fox, Rob Kooijman, Matus Medo, Nedialko M. Nedeltchev, Pouria Pedram, Jan Ryckebusch, and Oruganti Shanker. We also appreciate the general comments that we have received about the usefulness of the online text. Individual chapters of the text will remain freely available online at `<www.compadre.org/stp>`. (The page numbers of the online version will differ from the printed copy.)

We remember Lynna Spornick who worked for many years at The Johns Hopkins University Applied Physics Laboratory, and who first worked with us on incorporating computer simulations into the teaching of statistical mechanics and thermodynamics.

It has been a pleasure to work with Ingrid Gnerlich of Princeton University Press. Her encouragement and flexibility have made it possible for us to complete this project and see it in print. We would also like to thank Brigitte Pelner for her patience in correcting the many errors we found after submitting our manuscript.

We thank our colleagues at Clark University and Kalamazoo College for their encouragement. In particular, we would like to thank Sujata Davis and Peggy Cauchy without whom our departments would cease to function.

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In this day of easy internet access, it is still difficult to get feedback other than general comments. We would be grateful for emails regarding corrections (typos and otherwise) and suggestions for improvements. Despite the comments and suggestions we have received, there are probably still more typos, errors, and unclear explanations. Blame them on entropy.

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Chapter 1

From Microscopic to Macroscopic Behavior

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We explore the fundamental differences between microscopic and macroscopic systems, note that bouncing balls come to rest and hot objects cool, and discuss how the behavior of macroscopic systems is related to the behavior of their microscopic constituents. Computer simulations are introduced to demonstrate the general qualitative behavior of macroscopic systems.

1.1 Introduction

Our goal is to understand the properties of *macroscopic* systems, that is, systems of many electrons, atoms, molecules, photons, or other constituents. Examples of familiar macroscopic objects include systems such as the air in your room, a glass of water, a coin, and a rubber band – examples of a gas, liquid, solid, and polymer, respectively. Less familiar macroscopic systems include superconductors, cell membranes, the brain, the stock market, and neutron stars.

We will find that the type of questions we ask about macroscopic systems differ in important ways from the questions we ask about systems that we treat microscopically. For example, consider the air in your room. Have you ever wondered about the trajectory of a particular molecule in the air? Would knowing that trajectory be helpful in understanding the properties of air? Instead of questions such as these, examples of questions that we do ask about macroscopic systems include the following:

1. How does the pressure of a gas depend on the temperature and the volume of its container?
2. How does a refrigerator work? How can we make it more efficient?
3. How much energy do we need to add to a kettle of water to change it to steam?

4. Why are the properties of water different from those of steam, even though water and steam consist of the same type of molecules?

5. How and why does a liquid freeze into a particular crystalline structure?

6. Why does helium have a superfluid phase at very low temperatures? Why do some materials exhibit zero resistance to electrical current at sufficiently low temperatures?

7. In general, how do the properties of a system emerge from its constituents?

8. How fast does the current in a river have to be before its flow changes from laminar to turbulent?

9. What will the weather be tomorrow?

These questions can be roughly classified into three groups. Questions 1–3 are concerned with macroscopic properties such as pressure, volume, and temperature and processes related to heating and work. These questions are relevant to , *thermodynamics* which provides a framework for relating the macroscopic properties of a system to one another. Thermodynamics is concerned only with macroscopic quantities and ignores the microscopic variables that characterize individual molecules. For example, we will find that understanding the maximum efficiency of a refrigerator does not require a knowledge of the particular liquid used as the coolant. Many of the applications of thermodynamics are to engines, for example, the internal combustion engine and the steam turbine.

Questions 4–7 relate to understanding the behavior of macroscopic systems starting from the atomic nature of matter. For example, we know that water consists of molecules of hydrogen and oxygen. We also know that the laws of classical and quantum mechanics determine the behavior of molecules at the microscopic level. The goal of *statistical mechanics* is to begin with the microscopic laws of physics that govern the behavior of the constituents of the system and deduce the properties of the system as a whole. Statistical mechanics is a bridge between the microscopic and macroscopic worlds.

Question 8 also relates to a macroscopic system, but temperature is not relevant in this case. Moreover, turbulent flow continually changes in time. Question 9 concerns macroscopic phenomena that change with time. Although there has been progress in our understanding of time-dependent phenomena such as turbulent flow and hurricanes, our understanding of such phenomena is much less advanced than our understanding of time-independent systems. For this reason we will focus our attention on systems whose macroscopic properties are independent of time and consider questions such as those in Questions 1–7.

1.2 Some Qualitative Observations

We begin our discussion of macroscopic systems by considering a glass of hot water. We know that if we place a glass of hot water into a large cold room, the hot water cools until its temperature equals that of the room. This simple observation illustrates two important properties associated with macroscopic systems – the importance of *temperature* and the *"arrow" of time.* Temperature is familiar because it is associated with the physiological sensations of hot and cold and is important in our everyday experience.

The direction or arrow of time raises many questions. Have you ever observed a glass of water at room temperature spontaneously become hotter? Why not? What other phenomena exhibit a direction of time? The direction of time is expressed by the nursery rhyme:

Humpty Dumpty sat on a wall
Humpty Dumpty had a great fall
All the king's horses and all the king's men
Couldn't put Humpty Dumpty back together again.

Is there a direction of time for a single particle? Newton's second law for a single particle, $\mathbf{F} = d\mathbf{p}/dt$, implies that the motion of particles is *time reversal invariant*; that is, Newton's second law looks the same if the time t is replaced by $-t$ and the momentum $\mathbf{p}$ by $-\mathbf{p}$. There is no direction of time at the microscopic level. Yet if we drop a basketball onto a floor, we know that it will bounce and eventually come to rest. Nobody has observed a ball at rest spontaneously begin to bounce, and then bounce higher and higher. So based on simple everyday observations, we can conclude that the behaviors of macroscopic bodies and single particles are very different.

Unlike scientists of about a century or so ago, we know that macroscopic systems such as a glass of water and a basketball consist of many molecules. Although the intermolecular forces in water produce a complicated trajectory for each molecule, the observable properties of water are easy to describe. If we prepare two glasses of water under similar conditions, we know that the observable properties of the water in each glass are indistinguishable, even though the motion of the individual particles in the two glasses is very different.

If we take into account that the bouncing ball and the floor consist of molecules, then we know that the total energy of the ball and the floor is conserved as the ball bounces and eventually comes to rest. Why does the ball eventually come to rest? You might be tempted to say the cause is "friction," but friction is just a name for an effective or phenomenological force. At the microscopic level we know that the fundamental forces associated with mass, charge, and the nucleus conserve total energy. Hence, if we include the energy of the molecules of the ball and the floor, the total energy is conserved. Conservation of energy does not explain why the inverse process, where the ball rises higher and higher with each bounce, does not occur. Such a process also would conserve the total energy. So a more fundamental explanation is that the ball comes to rest consistent with conservation of the total energy and with some other principle of physics. We will learn that this principle is associated with an increase in the *entropy* of the system. For now, entropy is just a name, and it is important only to understand that energy conservation is not sufficient to understand the behavior of macroscopic systems.[1]

By thinking about the constituent molecules, we can gain some insight into the nature of entropy. Let us consider the ball bouncing on the floor again. Initially, the energy of the ball is associated with the motion of its center of mass, and we say that the energy is associated with one degree of freedom. After some time the energy becomes associated with the individual molecules near the surface of the ball and the floor, and we say that the energy is now distributed over many degrees of freedom. If we were to bounce the ball on the floor many times, the ball and the

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[1] We will learn that as for most concepts in physics, the meaning of entropy in the context of thermodynamics and statistical mechanics is very different from its meaning as used by nonscientists.

floor would each feel warm to our hands. So we can hypothesize that energy has been transferred from one degree of freedom to many degrees of freedom while the total energy has been conserved. Hence, we conclude that the entropy is a measure of how the energy is distributed.

What other quantities are associated with macroscopic systems besides temperature, energy, and entropy? We are already familiar with some of these quantities. For example, we can measure the air *pressure* in a basketball and its *volume*. More complicated quantities are the *thermal conductivity* of a solid and the *viscosity* of oil. How are these macroscopic quantities related to each other and to the motion of the individual constituent molecules? The answers to questions such as these and the meaning of temperature and entropy will take us through many chapters.[2]

1.3 Doing Work and the Quality of Energy

We already have observed that hot objects cool, and cool objects do not spontaneously become hot; bouncing balls come to rest, and a stationary ball does not spontaneously begin to bounce. And although the total energy is conserved in these processes, the *distribution* of energy changes in an irreversible manner. We also have concluded that a new concept, the entropy, needs to be introduced to explain the direction of change of the distribution of energy.

Now let us take a purely macroscopic viewpoint and discuss how we can arrive at a similar qualitative conclusion about the asymmetry of nature. This viewpoint was especially important historically because of the lack of a microscopic theory of matter in the 19th century when the laws of thermodynamics were being developed.

Consider the conversion of stored energy into heating a house or a glass of water. The stored energy could be in the form of wood, coal, or animal and vegetable oils for example. We know that this conversion is easy to do using simple methods, for example, an open flame. We also know that if we rub our hands together, they will become warmer. There is no theoretical limit to the efficiency at which we can convert stored energy to energy used for heating an object.

What about the process of converting stored energy into work? Work, like many of the other concepts that we have mentioned, is difficult to define. For now let us say that doing work is equivalent to the raising of a weight. To be useful, we need to do this conversion in a controlled manner and indefinitely. A single conversion of stored energy into work such as the explosion of dynamite might demolish an unwanted building, but this process cannot be done repeatedly with the same materials. It is much more difficult to convert stored energy into work and the discovery of ways to do this conversion led to the industrial revolution. In contrast to the primitiveness of an open flame, we have to build an *engine* to do this conversion.

Can we convert stored energy into useful work with 100% efficiency? To answer this question we have to appeal to observation. We know that some forms of stored energy are more useful than others. For example, why do we burn coal and oil in power plants even though the atmosphere and the oceans are vast reservoirs of energy? Can we mitigate global climate change by extracting energy from the atmosphere to run a power plant? From the work of Kelvin, Clausius, Carnot and others, we know that we cannot convert stored energy into work with 100% efficiency, and we must necessarily "waste" some of the energy. At this point, it is easier to understand the reason

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[2] Properties such as the thermal conductivity and viscosity are treated in the online supplement (see `<www.compadre.org/stp>` or `<press.princeton.edu/titles/9375.html>`).

for this necessary inefficiency by microscopic arguments. For example, the energy in the gasoline of the fuel tank of an automobile is associated with many molecules. The job of the automobile engine is to transform this (potential) energy so that it is associated with only a few degrees of freedom, that is, the rolling tires and gears. It is plausible that it is inefficient to transfer energy from many degrees of freedom to only a few. In contrast, the transfer of energy from a few degrees of freedom (the firewood) to many degrees of freedom (the air in your room) is relatively easy.

The importance of entropy, the direction of time, and the inefficiency of converting stored energy into work are summarized in the various statements of the *second law of thermodynamics*. It is interesting that the second law of thermodynamics was conceived before the first law of thermodynamics. As we will learn, the first law is a statement of conservation of energy.

Suppose that we take some firewood and use it to "heat" a sealed room. Because of energy conservation, the energy in the room plus the firewood is the same before and after the firewood has been converted to ash. Which form of the energy is more capable of doing work? You probably realize that the firewood is a more useful form of energy than the "hot air" and ash that exists after the firewood is burned. Originally the energy was stored in the form of chemical (potential) energy. Afterward the energy is mostly associated with the motion of the molecules in the air. What has changed is not the total energy, but its ability to do work. We will learn that an increase in entropy is associated with a loss of ability to do work. We have an entropy problem, not an energy problem.

1.4 Some Simple Simulations

So far we have discussed the behavior of macroscopic systems by appealing to everyday experience and simple observations. We now discuss some simple ways of *simulating* the behavior of macroscopic systems. Although we cannot simulate a macroscopic system of 10^{23} particles on a computer, we will find that even small systems of the order of a 100 particles are sufficient to illustrate the qualitative behavior of macroscopic systems.

We first discuss how we can simulate a simple model of a gas consisting of molecules whose internal structure can be ignored. In particular, imagine a system of N particles in a closed container of volume V and suppose that the container is far from the influence of external forces such as gravity. We will usually consider two-dimensional systems so that we can easily visualize the motion of the particles.

For simplicity, we assume that the motion of the particles is given by classical mechanics, and hence we need to solve Newton's second law for each particle. To compute the total force on each particle we have to specify the nature of the interaction between the particles. We will assume that the force between any pair of particles depends only on the distance between them. This simplifying assumption is applicable to simple liquids such as liquid argon, but not to water. We will also assume that the particles are not charged. The force between any two particles is repulsive when their separation is small and weakly attractive when they are far apart. For convenience we

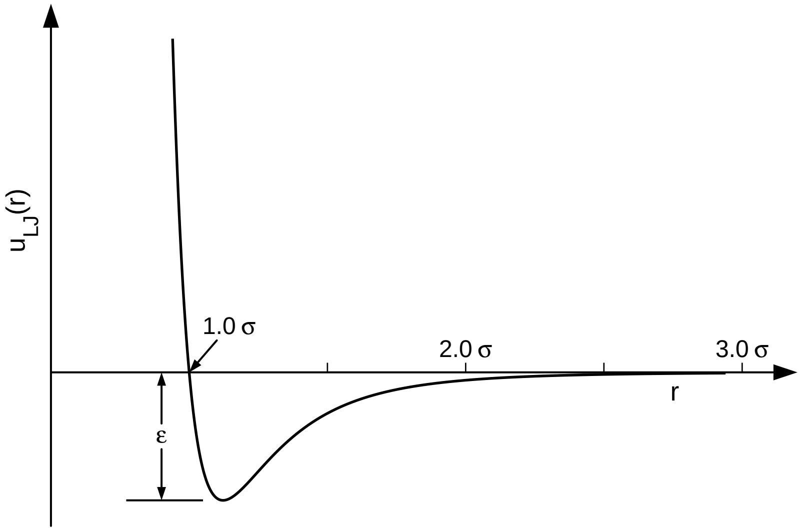

Figure 1.1: Plot of the Lennard-Jones potential $u_{\rm LJ}(r)$, where r is the distance between the particles. Note that the potential is characterized by a length σ and an energy ϵ.

will usually assume that the interaction is given by the Lennard-Jones potential given by[3]

$$u_{\rm LJ}(r) = 4\epsilon\Big[\Big(\frac{\sigma}{r}\Big)^{12} - \Big(\frac{\sigma}{r}\Big)^{6}\Big], \tag{1.1}$$

where r is the distance between two particles. A plot of the Lennard-Jones potential is shown in Figure 1.1. The r^{-12} form of the repulsive part of the interaction was chosen for convenience only and has no fundamental significance. The attractive $1/r^6$ behavior at large r is the van der Waals interaction.[4] The force between any two particles is given by $f(r) = -du/dr$.

In macroscopic systems the fraction of particles near the walls of the container is negligibly small. However, the number of particles that can be studied in a simulation is typically 10^3–10^6. For these small systems the fraction of particles near the walls of the container would be significant, and hence the behavior of such a system would be dominated by surface effects. The most common way of minimizing surface effects and to simulate more closely the properties of a macroscopic system is to use what are known as toroidal boundary conditions. These boundary conditions are familiar to computer game players. For example, a particle that exits the right edge of the "box," reenters the box from the left side. In one dimension this boundary condition is equivalent to taking a piece of string and making it into a loop. In this way a particle moving on the wire never reaches the end (the surface).

Given the form of the interparticle potential, we can determine the total force on each particle due to all the other particles in the system. We then use Newton's second law of motion to find

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[3] This potential is named after John Lennard-Jones, 1894–1954, a theoretical chemist and physicist at Cambridge University. The Lennard-Jones potential is appropriate for closed-shell systems, that is, rare gases such as Ar or Kr.

[4] The van der Waals interaction arises from an induced dipole-dipole effect. It is present in all molecules, but is important only for the heavier noble gas atoms. See for example, Brehm and Mullin.

the acceleration of each particle. Because the acceleration is the second derivative of the position, we need to solve a second-order differential equation for each particle (in each direction) given the initial position and velocity of each particle. (For a two-dimensional system of N particles, we would have to solve $2N$ differential equations.) These differential equations are coupled because the acceleration of a particular particle depends on the positions of all the other particles. Although we cannot solve the resultant set of coupled differential equations analytically, we can use straightforward numerical methods to solve these equations to a good approximation. This way of simulating dense gases, liquids, solids, and biomolecules is called *molecular dynamics*.[5]

In the following two problems we will explore some of the qualitative properties of macroscopic systems by doing some simple simulations. Before you actually do the simulations, think about what you believe the results will be. In many cases the most valuable part of the simulation is not the simulation itself, but the act of thinking about a concrete model and its behavior.

The simulations are written in Java and can be run on any operating system that supports Java 1.5^{+}. You may download all the programs used in this text from `<press.princeton.edu/titles/9375.html>` or `<www.compadre.org/stp>` as a single file (the STP Launcher) or as individual programs. Alternatively, you can run each simulation as an applet using a browser.

Problem 1.1. Approach to equilibrium

Suppose that we divide a box into three equal parts and place N particles in the middle third of the box.[6] The particles are placed at random with the constraint that no two particles can be closer than the length parameter σ. This constraint prevents the initial force between any two particles from being too big, which would lead to the breakdown of the numerical method used to solve the differential equations. The velocity of each particle is assigned at random and then the velocity of the center of mass is set to zero. At $t = 0$, we remove the "barriers" between the three parts and watch the particles move according to Newton's equations of motion. We say that the removal of the barrier corresponds to the removal of an internal constraint. What do you think will happen?

Program `ApproachToEquilibriumThreePartitions` implements this simulation.[7] Double click on the jar file to open the program, and click the `Start` button to begin the simulation. The program shows the motion of the particles in the box and plots the number of particles in the left (n_1), center (n_2), and right (n_3) part of the box as a function of time. The input parameter is N, the number of particles initially in the center cell, so that $n_1 = 0$, $n_2 = N$, and $n_3 = 0$ at $t = 0$.

Give your answers to the following questions before you do the simulation.

(a) Does the system appear to show a direction of time for $N = 6$?

(b) What is the nature of the time dependence of n_1, n_2, and n_3 as a function of the time t for $N = 27$? Does the system appear to show a direction of time? Choose various values of N that are multiples of 3 up to $N = 270$. Is the direction of time better defined for larger N?

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[5] The nature of molecular dynamics is discussed in Gould, Tobochnik, and Christian, Chap. 8.

[6] We have divided the box into three parts so that the effects of the toroidal boundary conditions will not be as apparent as if we had initially confined the particles to one half of the box.

[7] We will omit the prefix `stp_` whenever it will not cause confusion.

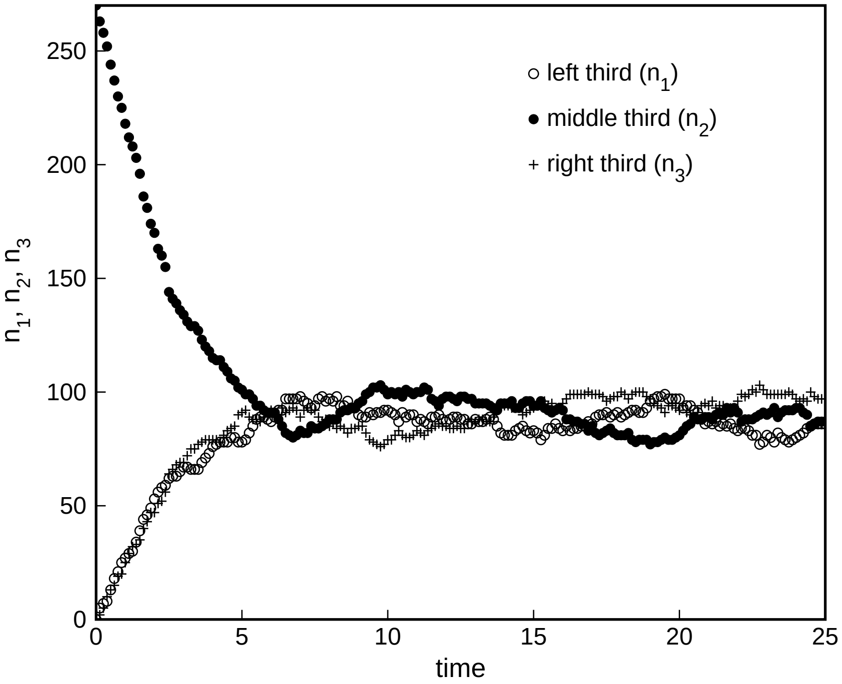

Figure 1.2: Evolution of the number of particles in each third of the box for $N = 270$. The particles were initially restricted to the middle third of the box. Toroidal boundary conditions are used in both directions. The initial velocities are assigned at random such that the center of mass velocity is zero.

(c) The time shown in the plots is in terms of $\sigma(m/\epsilon)^{1/2}$, where σ and ϵ are the length and energy parameters of the Lennard-Jones potential in (1.1) and m is the mass of a particle. Verify that this combination has units of time. For argon $\sigma = 3.4 \times 10^{-10}\,$m, $\epsilon = 1.65 \times 10^{-21}\,$J, and $m = 6.69 \times 10^{-26}\,$kg. What is the value of $\sigma(m/\epsilon)^{1/2}$ for argon? How much real time has elapsed if the program shows that $t = 100$?

(d) To better understand the direction of time make a video[8] of the motion of the positions of 270 particles starting from $t = 0$. Run the simulation until the particles are approximately equally divided between the three regions. Run the video both forward and backward. Can you tell by just looking at the video which direction is forward? Repeat for increasing values of N. Does your conclusion about the direction of time become more certain for larger N?

(e) Repeat part (d) but start the video after the particles are distributed equally among the three regions, say at $t = 20$ as in Figure 1.2. Is the direction of time obvious now? Repeat for various values of N.

(f) *After n_1, n_2, and n_3 first become approximately equal for $N = 270$, reverse the time and

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[8] Choose `Video Capture` under the `Tools` menu. Save the video in QuickTime. The video can be run using the QuickTime Player and played forward or backward by using the command key and the right or left arrow key.

continue the simulation. Reversing the time is equivalent to letting $t \to -t$ and changing the signs of all the velocities. Do the particles return to the middle third of the box? Do the simulation again, but let the system evolve longer before the time is reversed. What happens now? Are your results consistent with the fact that Newton's equations of motion are deterministic and time reversal invariant so that reversing the velocities should exactly retrace the original particle trajectories? (See Problem 1.9 for a discussion of the extreme sensitivity of the trajectories to very small errors.)

(g) Program `ApproachToEquilibriumTwoPartitions` initially divides the box into two partitions rather than three. Run the program and verify that the simulation shows similar qualitative behavior. Explain the use of toroidal boundary conditions. □

The results of the simulations in Problem 1.1 might not seem surprising until you think about them. Why does the system exhibit a direction of time when the motion of each particle is time reversible? Do the particles fill up the available space simply because the system becomes less dense?

To gain some more insight into why there is a direction of time, we consider a simpler model which shows similar behavior. Imagine a closed box that is divided into two parts of equal areas. The left half initially contains N identical particles and the right half is empty. We then make a small hole in the partition between the two halves. What happens? Instead of simulating this system by solving Newton's equations for each particle, we adopt a simpler approach based on a probabilistic model. We assume that the system is so dilute that the particles do not interact with one another. Hence, the probability per unit time that a particle goes through the hole in the partition is the same for all particles regardless of the number of particles in either half. We also assume that the size of the hole is such that only one particle can pass through in one unit of time.

One way to implement this model is to choose a particle at random and move it to the other half. This procedure is cumbersome, because our only interest is the number of particles on each side. That is, we need to know only n, the number of particles on the left side; the number on the right side is $N - n$. Because each particle has the same chance to go through the hole in the partition, the probability per unit time that a particle moves from left to right equals the number of particles on the left side divided by the total number of particles; that is, the probability of a move from left to right is n/N. The algorithm for simulating the evolution of the model is given by the following steps:

1. Generate a random number r from a uniformly distributed set of random numbers in the unit interval $0 \leq r < 1$.
2. If $r \leq n/N$, a particle is moved from left to right, that is, let $n \to n-1$; otherwise, $n \to n+1$.
3. Increase the "time" by 1.

Program `ApproachToEquilibriumPariclesInBox` implements this algorithm and plots the evolution of n.

Problem 1.2. Particles in a box

(a) Before you run the program describe what you think will be the qualitative behavior of $n(t)$, the time-dependence of the number of particles on the left side of the box.

(b) Run the program and describe the behavior of $n(t)$ for various values of N. Does the system approach equilibrium? How would you characterize equilibrium? In what sense is equilibrium better defined as N becomes larger? Does your definition of equilibrium depend on how the particles were initially distributed between the two halves of the box?

(c) When the system is in equilibrium, does the number of particles on the left-hand side remain a constant? If not, how would you describe the nature of equilibrium?

(d) If $N \gtrsim 32$, does the system return to its initial state during the time you have patience to watch the system?

(e) How does $\overline{n}$, the mean number of particles on the left-hand side, depend on N after the system has reached equilibrium? For simplicity, the program computes various averages from the time $t = 0$. Why would such a calculation not yield the correct equilibrium average values? Use the `Zero Averages` button to reset the averages.

(f) Define the quantity σ by the relation[9]

$$\sigma^2 = \overline{(n - \overline{n})^2}. \tag{1.2}$$

What does σ measure? What would be its value if n were constant? How does σ depend on N? How does the ratio $\sigma/\overline{n}$ depend on N? We say that σ is a measure of the fluctuations of n about its mean, and $\sigma/\overline{n}$ is a measure of the relative fluctuations of n. □

From Problems 1.1 and 1.2 we conclude that the mean values of the macroscopic quantities of interest will eventually become independent of time. We say that the system has reached equilibrium, and the macroscopic quantities exhibit fluctuations about their average values. We also learned that the relative fluctuations become smaller as the number of particles is increased, and the details of the dynamics are irrelevant to the general tendency of macroscopic systems to approach equilibrium. These properties of macroscopic systems are independent of the dynamics, the nature of the particles, and many other details.

How can we understand why the systems considered in Problems 1.1 and 1.2 exhibit a direction of time? There are two general methods. One way is to study the dynamics of the system as it approaches equilibrium.[10] A much simpler way is to change the question and take advantage of the fact that the equilibrium state of a macroscopic system is independent of time on the average, and hence time is irrelevant in equilibrium. For the model considered in Problem 1.2 we will see that counting the number of ways that the particles can be distributed between the two halves of the box will give us much insight into the nature of equilibrium. This information tells us nothing about how long it takes the system to reach equilibrium. However, it will give us insight into why there is a direction of time.

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[9] This use of σ should not be confused with the length σ in the Lennard-Jones potential.

[10] The time dependence of the number of particles on the left half of the box in Problem 1.2 is discussed in Section 1.13.1.

microstate		n	$W(n)$	$P(n)$
L	L	2	1	1/4
L	R	1	2	1/2
R	L			
R	R	0	1	1/4

Table 1.1: The four possible ways in which $N = 2$ particles can be distributed between the two halves of a box. The quantity $W(n)$ is the number of microstates corresponding to the macroscopic state characterized by n, the number of particles on the left-hand side. The probability $P(n)$ of macrostate n is calculated assuming that each microstate is equally likely.

A given particle can be in either the left or right half of the box. Let us call each distinct arrangement of the particles between the two halves of the box a *microstate*. For $N = 2$ the four possible microstates are shown in Table 1.1. Because the halves are equivalent, a given particle is equally likely to be in either half when the system is in equilibrium. Hence, for $N = 2$ the probability of each microstate equals 1/4 when the system is in equilibrium.

From a macroscopic point of view, we do not care which particle is in which half of the box, but only the number of particles on the left. Hence, the macroscopic state or *macrostate* is specified by n. Are the three possible macrostates listed in Table 1.1 equally probable?

Now let us consider $N = 4$ for which there are $2 \times 2 \times 2 \times 2 = 2^4 = 16$ microstates (see Table 1.2). Let us assume as before that all microstates are equally probable in equilibrium. We see from Table 1.2 that there is only one microstate with all particles on the left and the most probable macrostate is $n = 2$.

For larger N the probability of the most probable macrostate with $n = N/2$ is much greater than the macrostate with $n = N$, which has a probability of only $1/2^N$ corresponding to a single microstate. The latter microstate is "special" and is said to be nonrandom, while the microstates with $n \approx N/2$, for which the distribution of the particles is approximately uniform, are said to be "random." So we conclude that the equilibrium macrostate corresponds to the most probable state.

Problem 1.3. Counting microstates

(a) Calculate the number of possible microstates for each macrostate n for $N = 8$ particles. What is the probability that $n = 8$? What is the probability that $n = 4$? It is possible to count the number of microstates for each n by hand if you have enough patience, but because there are a total of $2^8 = 256$ microstates, this counting would be very tedious. An alternative is to obtain an expression for the number of ways that n particles out of N can be in the left half of the box. Motivate such an expression by enumerating the possible microstates for smaller values of N until you see a pattern.

(b) The macrostate with $n = N/2$ is much more probable than the macrostate with $n = N$. Why? ☐

Approach to equilibrium. The macrostates that give us the least amount of information about the associated microstates are the most probable. For example, suppose that we wish to know

microstate				n	$W(n)$	$P(n)$
L	L	L	L	4	1	1/16
R	L	L	L	3	4	4/16
L	R	L	L	3		
L	L	R	L	3		
L	L	L	R	3		
R	R	L	L	2	6	6/16
R	L	R	L	2		
R	L	L	R	2		
L	R	R	L	2		
L	R	L	R	2		
L	L	R	R	2		
R	R	R	L	1	4	4/16
R	R	L	R	1		
R	L	R	R	1		
L	R	R	R	1		
R	R	R	R	0	1	1/16

Table 1.2: The 2^4 possible microstates for $N = 4$ particles which are distributed in the two halves of a box. The quantity $W(n)$ is the number of microstates corresponding to the macroscopic state characterized by n. The probability $P(n)$ of macrostate n is calculated assuming that each microstate is equally likely.

where particle 1 is, given that $N = 4$. If $n = 4$, we know with certainty that particle 1 is on the left. If $n = 3$, the probability that particle 1 is on the left is 3/4. And if $n = 2$, we know only that particle 1 is on the left with probability 1/2. In this sense the macrostate $n = 2$ is more random than macrostates $n = 4$ and $n = 3$.

We also found from the simulations in Problems 1.1 and 1.2 that if an isolated macroscopic system changes in time due to the removal of an internal constraint, it tends to evolve from a less random to a more random state. Once the system reaches its most random state, fluctuations corresponding to an appreciably nonuniform state are very rare. These observations and our reasoning based on counting the number of microstates corresponding to a particular macrostate leads us to conclude that

> *A system in a nonuniform macrostate will change in time on the average so as to approach its most random macrostate where it is in equilibrium.*

This conclusion is independent of the nature of the dynamics. Note that the simulations in Problems 1.1 and 1.2 involved the dynamics, but our discussion of the number of microstates corresponding to each macrostate did not involve the dynamics in any way. Instead we counted (enumerated) the microstates and assigned them equal probabilities assuming that the system is isolated and in equilibrium. It is much easier to understand equilibrium systems by ignoring the dynamics altogether.

In the simulation of Problem 1.1 the total energy was conserved, and hence the macroscopic quantity of interest that changed from the specially prepared initial state with $n_2 = N$ to the most random macrostate with $n_2 \approx N/3$ was not the total energy. So what macroscopic quantities changed besides the number of particles in each third of the box? Based on our previous discussions, we can tentatively say that the quantity that changed is the entropy. We conjecture that the entropy is associated with the number of microstates associated with a given macrostate. If we make this association, we see that the entropy is greater after the system has reached equilibrium than in the system's initial state. Moreover, if the system were initially prepared such that $n_1 = n_2 = n_3 = N/3$, the mean value of $n_1 = n_2 = n_3 = N/3$ and hence the entropy would not change. Hence, we can conclude the following:

> *The entropy of an isolated system increases or remains the same when an internal constraint is removed.*

This statement is equivalent to the second law of thermodynamics. You might want to look at Chapter 4, where this identification of the entropy is made explicit.

As a result of the two simulations that we have considered and our discussions, we can make some additional preliminary observations about the behavior of macroscopic systems.

Fluctuations in equilibrium. Once a system reaches equilibrium, the macroscopic quantities of interest do not become independent of the time, but *exhibit fluctuations about their average values.* In equilibrium only the *average* values of the macroscopic variables are independent of time.[11] For example, in Problem 1.2 the number of particles $n(t)$ changes with t, but its average value $\overline{n}$ does not.[12] If N is large, fluctuations corresponding to a very nonuniform distribution of the particles almost never occur, and the relative fluctuations, $\sigma/\overline{n}$ [see (1.2)] become smaller as N is increased.

History independence. The properties of *equilibrium systems are independent of their history.* For example, $\overline{n}$ in Problem 1.2 would be the same whether we had started with $n(t = 0) = N$ or $n(t = 0) = 0$. In contrast, as members of the human race, we are all products of our history. One consequence of history independence is that we can ignore how a system reached equilibrium. We will find that equilibrium statistical mechanics is equivalent to counting microstates. The problem is that this counting is usually difficult to do.

Need for statistical approach. A macroscopic system can be described in detail by specifying its *microstate.* Such a description corresponds to giving all the possible information. For a system of classical particles, a microstate corresponds to specifying the position and velocity of each particle.

From our simulations we see that the microscopic state of the system changes in a complicated way that is difficult to describe. However, from a macroscopic point of view the description is much

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[11] In this introductory chapter some of our general statements need to be qualified. Just because a system has time-independent macroscopic properties does not necessarily mean that it is in equilibrium. If a system is driven by external forces or currents that are time-independent, the observable macroscopic properties of the system can be time independent, and the system is said to be in a *steady state.* For example, consider a metal bar with one end in contact with a much larger system at temperature T_{hot} and the other end in contact with a large system at temperature T_{cold}. If $T_{\text{hot}} > T_{\text{cold}}$, energy will be continually transported from the "hot" end to the "cold" end and the temperature gradient will not change on the average.

[12] We have not carefully defined how to calculate the average value $\overline{n}$. One way to do so is to average $n(t)$ over some interval of time. Another way is to do an ensemble average. That is, run the same simulation many times with different sets of random number sequences and then average the results at a given time (see Section 1.8).

simpler. Suppose that we simulated a system of many particles and saved the trajectories of each particle as a function of time. What could we do with this information? If the number of particles is 10^6 or more or if we ran long enough, we would have a problem storing the data. Do we want to have a detailed description of the motion of each particle? Would this data give us much insight into the macroscopic behavior of the system? We conclude that the presence of a large number of particles motivates us to adopt a statistical approach. In Section 1.7 we will discuss another reason why a statistical approach is necessary.

We will find that the laws of thermodynamics depend on the fact that the number of particles in macroscopic systems is enormous. A typical measure of this number is Avogadro's number which is approximately 6×10^{23}, the number of atoms in a mole. When there are so many particles, predictions of the average properties of the system become meaningful, and deviations from the average behavior become less important as the number of atoms is increased.

Equal a priori probabilities. In our analysis of the probability of each macrostate in Problem 1.2, we assumed that each microstate was equally probable. That is, each microstate of an isolated system occurs with equal probability if the system is in equilibrium. We will make this assumption explicit in Chapter 4.

Existence of different phases. So far our simulations of interacting systems have been restricted to dilute gases. What do you think would happen if we made the density higher? Would a system of interacting particles form a liquid or a solid if the temperature or the density were chosen appropriately? The existence of different phases is explored in Problem 1.4.

Problem 1.4. Different phases

(a) Program `LJ2DMD` simulates an isolated system of N particles interacting via the Lennard-Jones potential. Choose $N = 144$ and $L = 18$ so that the density $\rho = N/L^2 \approx 0.44$. The initial positions are chosen at random except that no two particles are allowed to be closer than the length σ. Run the simulation and satisfy yourself that this choice of density and resultant total energy corresponds to a gas. What are your criteria?

(b) Slowly lower the total energy of the system. (The total energy is lowered by rescaling the velocities of the particles.) If you are patient, you will be able to observe "liquid-like" regions. How are they different from "gas-like" regions?

(c) If you decrease the total energy further, you will observe the system in a state roughly corresponding to a solid. What are your criteria for a solid? Explain why the solid that we obtain in this way will not be a perfect crystalline solid.

(d) Describe the motion of the individual particles in the gas, liquid, and solid phases.

(e) Conjecture why a system of particles interacting via the Lennard-Jones potential in (1.1) can exist in different phases. Is it necessary for the potential to have an attractive part for the system to have a liquid phase? Is the attractive part necessary for there to be a solid phase? Describe a simulation that would help you answer this question. □

It is remarkable that a system with the same interparticle interaction can be in different phases. At the microscopic level, the dynamics of the particles is governed by the same equations of motion. What changes? How does a phase change occur at the microscopic level? Why doesn't a liquid crystallize immediately after its temperature is lowered quickly? What happens when it does begin to crystallize? We will find in later chapters that phase changes are examples of *cooperative* effects. Familiar examples of phase transitions are the freezing and boiling of water. Another example with which you might be familiar is the loss of magnetism of nickel or iron above a certain temperature (358°C for nickel). Other examples of cooperative effects are the occurrence of gridlock on a highway when the density of vehicles exceeds a certain value, and the occurrence of an epidemic as a function of immune response and population density.

1.5 Measuring the Pressure and Temperature

The obvious macroscopic quantities that we can measure in our simulations of many interacting particles include the average kinetic and potential energies, the number of particles, and the volume. We know from our everyday experience that there are at least two other macroscopic variables that are relevant for a system of particles, namely, the pressure and the temperature.

You are probably familiar with force and pressure from courses in mechanics. The idea is to determine the force needed to keep a freely moving wall stationary. This force is divided by the area A of the wall to give the pressure P:

$$P = \frac{F}{A}, \tag{1.3}$$

where the force F acts normal to the surface. The pressure is a scalar because it is the same in all directions on the average. From Newton's second law, we can rewrite (1.3) as

$$P = \frac{1}{A}\frac{d(p_x)}{dt}, \tag{1.4}$$

where p_x is the component of the momentum perpendicular to the wall. From (1.4) we see that the pressure is related to the rate of change of the momentum of all the particles that strike a wall.[13]

The number of particles that strike a wall of the box per second is huge. A pressure gauge cannot distinguish between the individual frequent impacts and measures the average force due to many impacts. We will discuss many examples of the relation of the macroscopic properties of a system to an average of some microscopic quantity.

Before we discuss the nature of temperature consider the following questions.

Problem 1.5. Nature of temperature

(a) Summarize what you know about temperature. What reasons do you have for thinking that it has something to do with energy?

(b) If you add energy to a pot of boiling water, does the temperature of the water change?

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[13] Because most of our simulations are done using toroidal boundary conditions, we will use the relation of the force to the *virial*, a mechanical quantity that involves all the particles in the system, not just those colliding with a wall. See Gould, Tobochnik, and Christian, Chap. 8. The relation of the force to the virial is usually considered in graduate courses in mechanics.

(c) Discuss what happens to the temperature of a hot cup of coffee. What happens, if anything, to the temperature of its surroundings? ☐

Although temperature and energy are related, they are not the same quantity. For example, one way to increase the energy of a glass of water would be to lift it. However, this action would not affect the temperature of the water. So the temperature has nothing to do with the motion of the center of mass of the system. If we placed a glass of water on a moving conveyor belt, the temperature of the water would not change. We also know that temperature is a property associated with many particles. It would be absurd to refer to the temperature of a single molecule.

The most fundamental property of temperature is not that it has something to do with energy. More importantly, *temperature is the quantity that becomes equal when two systems are allowed to exchange energy with one another.* In Problem 1.6 we interpret the temperature from this point of view.

Problem 1.6. Identification of the temperature

(a) Consider two systems of particles A and B which interact via the Lennard-Jones potential in (1.1). Use Program `LJThermalEquilibrium`. Both systems are in a square box with linear dimension $L = 12$. In this case toroidal boundary conditions are not used and the particles also interact with fixed particles (with infinite mass) that make up the walls and the partition between them. Initially, the two systems are isolated from each other and from their surroundings. We take $N_A = 81$, $\epsilon_{AA} = 1.0$, $\sigma_{AA} = 1.0$, $N_B = 64$, $\epsilon_{BB} = 1.5$, and $\sigma_{BB} = 1.2$. Run the simulation and monitor the kinetic energy and potential energy until each system appears to reach equilibrium. What is the mean potential and kinetic energy of each system? Is the total energy of each system fixed (to within numerical error)?

(b) Remove the barrier and let the particles in the two systems interact with one another.[14] We choose $\epsilon_{AB} = 1.25$ and $\sigma_{AB} = 1.1$. What quantity is exchanged between the two systems? (The volume of each system is fixed.)

(c) After equilibrium has been established compare the average kinetic and potential energies of each system to their values before the two systems came into contact.

(d) We seek a quantity that is the same in both systems after equilibrium has been established. Are the average kinetic and potential energies the same? If not, think about what would happen if you doubled the number of particles and the area of each system. Would the temperature change? Does it make more sense to compare the average kinetic and potential energies or the average kinetic and potential energies per particle? What quantity becomes the same once the two systems are in equilibrium? Do any other quantities become approximately equal? What can you conclude about the possible identification of the temperature in this system? ☐

From the simulations in Problem 1.6 you are likely to conclude that the temperature is proportional to the average kinetic energy per particle. You probably knew about this relation already. We will learn in Chapter 4 that the proportionality of the temperature to the average kinetic

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[14] To ensure that we can continue to identify which particle belongs to system A and which to system B, we have added a spring to each particle so that it cannot wander too far from its original lattice site.

energy per particle holds only for a system of particles whose kinetic energy is proportional to the square of its momentum or velocity.

How can we measure the temperature of a system? After all, in an experiment we cannot directly measure the mean kinetic energy per particle. Nevertheless, there are many kinds of thermometers. These thermometers exchange energy with the system of interest and have some physical property that changes in a way that can be calibrated to yield the temperature. In Problem 1.7 we ask you to think about the general characteristics of thermometers. We then consider a simple model thermometer that is useful in simulations. We will discuss thermometers in more detail in Chapter 2.

Problem 1.7. Thermometers

(a) Describe some of the simple thermometers with which you are familiar.

(b) On what physical principles do these thermometers operate?

(c) What requirements must a thermometer have to be useful? □

To gain more insight into the meaning of temperature we consider a model thermometer known as a "demon." This demon is a special particle that carries a sack of energy and exchanges energy with the system of interest. If the change lowers the energy of the system, the demon puts the extra energy in its sack. If the change costs energy, the demon gives the system the needed energy with the constraint that E_d, the energy of the demon, must be nonnegative. The behavior of the demon is given by the following algorithm:

1. Choose a particle in the system at random and make a trial change in one of its coordinates.
2. Compute ΔE, the change in the energy of the system due to the trial change.
3. If $\Delta E \leq 0$, the system gives the surplus energy $|\Delta E|$ to the demon, $E_d \to E_d + |\Delta E|$, and the trial change is accepted.
4. If $\Delta E > 0$ and the demon has sufficient energy for this change (remember that E_d is nonnegative), then the demon gives the necessary energy to the system, $E_d \to E_d - \Delta E$, and the trial change is accepted. Otherwise, the trial change is rejected and the microstate is not changed.
5. Repeat steps 1–4 many times.
6. Compute the averages of the quantities of interest once the system and the demon have reached equilibrium.

Note that the total energy of the system and the demon is fixed.

We consider the consequences of these simple rules in Problem 1.8. The nature of the demon is discussed further in Section 4.9.

Problem 1.8. The demon and the ideal gas

Program `IdealThermometerIdealGas` simulates a demon that exchanges energy with an ideal gas of N particles in d spatial dimensions. Because the particles do not interact, the only coordinate of interest is the velocity of the particles. In this case the demon chooses a particle at random and changes each component of its velocity by an amount chosen at random between $-\Delta$ and $+\Delta$. For simplicity, we set the initial demon energy $E_d = 0$ and the initial velocity of each particle equal to $+v_0\hat{x}$, where $v_0 = (2E_0/m)^{1/2}/N$. E_0 is the desired total energy of the system, and m is the mass of the particles. We choose units such that $m = 1$; the energy and momentum are measured in dimensionless units (see Section 1.11).

(a) Run the simulation using the default parameters $N = 40$, $E = 40$, and $d = 3$. Does the mean energy of the demon approach a well-defined value after a sufficient number of energy exchanges with the system? One Monte Carlo step per particle (mcs) is equivalent to N trial changes.

(b) What is $\overline{E}_d$, the mean energy of the demon, and $\overline{E}$, the mean energy of the system? Compare the values of $\overline{E}_d$ and $\overline{E}/N$.

(c) Fix $N = 40$ and double the total energy of the system. (Remember that $E_d = 0$ initially.) Compare the values of $\overline{E}_d$ and $\overline{E}/N$. How does their ratio change? Consider other values of $N \geq 40$ and E and determine the relation between $\overline{E}_d$ and $\overline{E}/N$.[15]

(d) You probably learned in high school physics or chemistry that the mean energy of an ideal gas in three dimensions is equal to $\frac{3}{2}NkT$, where T is the temperature of the gas, N is the number of particles, and k is a constant. Use this relation to determine the temperature of the ideal gas in parts (b) and (c). Our choice of dimensionless variables implies that we have chosen units such that $k = 1$. Is $\overline{E}_d$ proportional to the temperature of the gas?

(e) Suppose that the energy momentum relation of the particles is not $\epsilon = p^2/2m$, but is $\epsilon = cp$, where c is a constant (which we take to be 1). Consider various values of N and E as you did in part (c). Is the dependence of $\overline{E}_d$ on $\overline{E}/N$ the same as you found in part (d)? We will find (see Problem 4.30) that $\overline{E}_d$ is still proportional to the temperature.

(f) *After the demon and the system have reached equilibrium, we can compute the histogram $H(E_d)\Delta E_d$, the number of times that the demon has energy between E_d and $E_d + \Delta E_d$. The bin width ΔE_d is chosen by the program. This histogram is proportional to the probability $p(E_d)\Delta E$ that the demon has energy between E_d and $E_d + \Delta E$. What do you think is the nature of the dependence of $p(E_d)$ on E_d? Is the demon more likely to have zero or nonzero energy?

(g) *Verify the exponential form of $p(E_d) = Ae^{-\beta E_d}$, where A and β are parameters.[16] How does the value of $1/\beta$ compare to the value of $\overline{E}_d$? We will find that the exponential form of $p(E_d)$ is *universal*, that is, independent of the system with which the demon exchanges energy, and that $1/\beta$ is proportional to the temperature of the system.

(h) Discuss why the demon is an ideal thermometer. ☐

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[15] Because there are finite-size effects that are order $1/N$, it is desirable to consider $N \gg 1$. The trade-off is that the simulation will take longer to run.

[16] Choose `Data Tool` under the `Tools` menu and click OK.

1.6 Work, Heating, and the First Law of Thermodynamics

As you watch the motion of the individual particles in a molecular dynamics simulation, you will probably describe the motion as “random” in the sense of how we use random in everyday speech. The motion of the individual molecules in a glass of water exhibits similar motion. Suppose that we were to expose the water to a low flame. In a simulation this process would roughly correspond to increasing the speed of the particles when they hit the wall. We say that we have transferred energy to the system *incoherently* because each particle continues to move more or less at random.

In contrast, if we squeeze a plastic container of water, we do *work* on the system, and would see the particles near the wall move *coherently*. So we can distinguish two different ways of transferring energy to the system. *Heating transfers energy incoherently and doing work transfers energy coherently.*

Let us consider a molecular dynamics simulation again and suppose that we have increased the energy of the system by either compressing the system and doing work on it or by randomly increasing the speed of the particles that reach the walls of the container. Roughly speaking, the first way would initially increase the potential energy of interaction and the second way would initially increase the kinetic energy of the particles. If we increase the total energy by the same amount, can you tell by looking at the particle trajectories after equilibrium has been reestablished how the energy was increased? The answer is no, because for a given total energy, volume, and number of particles, the kinetic energy and the potential energy each have unique equilibrium values. We conclude that the total energy of the gas can be changed by doing work on it or by heating it or by both processes. This statement is equivalent to the *first law of thermodynamics* and from the microscopic point of view is simply a statement of conservation of energy.

Our discussion implies that the phrase “adding heat” to a system makes no sense, because we cannot distinguish “heat energy” from potential energy and kinetic energy. Nevertheless, we frequently use the word “heat ” in everyday speech. For example, we might say “Please turn on the heat” and “I need to heat my coffee.” We will avoid such uses, and whenever possible avoid the use of “heat” as a noun. Why do we care? Because there is no such thing as heat and the words we use affect how we think. Once upon a time, scientists thought that there was a fluid in all substances called *caloric* or heat that could flow from one substance to another. This idea was abandoned many years ago, but we still use it in our everyday language.

1.7 *The Fundamental Need for a Statistical Approach

In Section 1.4 we discussed the need for a statistical approach when treating macroscopic systems from a microscopic point of view. Although we can compute the trajectory (the position and velocity) of each particle, our disinterest in the trajectory of any particular particle and the overwhelming amount of information that is generated in a simulation motivates us to develop a statistical approach.

We now discuss the more fundamental reason why we must use probabilistic methods to describe systems with more than a few particles. The reason is that under a wide variety of conditions, even the most powerful supercomputer yields positions and velocities that are meaningless! In the following, we will find that the trajectories in a system of many particles depend sensitively on the

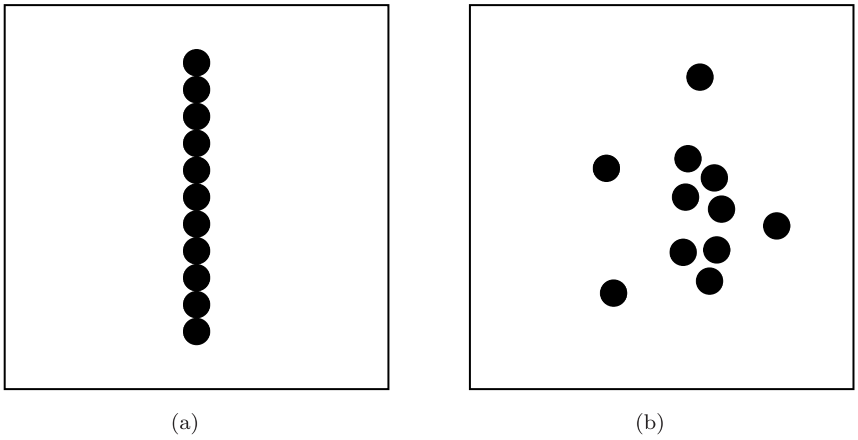

Figure 1.3: (a) A special initial condition for $N = 11$ particles such that their motion remains parallel indefinitely. (b) The positions of the particles shortly after a small change in $v_x(6)$. The only change in the initial condition from part (a) is that $v_x(6)$ was changed from 1 to 1.000001.

initial conditions. Such a system is said to be *chaotic*. This behavior forces us to take a statistical approach even for systems with as few as three particles.

As an example, consider a system of $N = 11$ particles moving in a box of linear dimension L (see Program `SensitivityToInitialConditions`). The initial conditions are such that all particles have the same velocity $v_x(i) = 1$, $v_y(i) = 0$, and the particles are equally spaced vertically, with $x(i) = L/2$ for $i = 1, \ldots, 11$ [see Figure 1.3(a)]. Convince yourself that for these special initial conditions, the particles will continue moving indefinitely in the x-direction (using toroidal boundary conditions).

Now let us stop the simulation and change the velocity of particle 6, such that $v_x(6) = 1.000001$. What do you think will happen? In Figure 1.3(b) we show the positions of the particles at $t = 8.0$ after the change in velocity of particle 6. Note that the positions of the particles are no longer equally spaced. So in this case a small change in the velocity of one particle led to a big change in the trajectories of all the particles.

***Problem 1.9.** Irreversibility

Program `SensitivityToInitialConditions` simulates a system of $N = 11$ particles with the special initial condition described in the text. Confirm the results that we have discussed. Perturb the velocity of particle 6 and stop the simulation at time t after the change and reverse all the velocities. Confirm that if t is sufficiently short, the particles will return approximately to their initial state. What is the maximum value of t that will allow the particles in the system to return to their initial positions if t is replaced by $-t$ (all velocities reversed)? ☐

An important property of chaotic systems is their *extreme sensitivity to initial conditions*, that is, the trajectories of two identical systems starting with slightly different initial conditions will diverge exponentially. For such systems we cannot predict the positions and velocities of the particles very far into the future because even the slightest error in our measurement of the initial conditions would make our prediction entirely wrong if the elapsed time is sufficiently long. That is, we cannot answer the question "Where is a particular particle at time t?" if t is sufficiently long. It might be disturbing to realize that our answers are meaningless if we ask the wrong questions.

Although Newton's equations of motion are time reversible, this reversibility cannot be realized in practice for chaotic systems. Suppose that a chaotic system evolves for a time t and all the velocities are reversed. If the system is allowed to evolve for an additional time t, the system will not return to its original state unless the velocities are specified with infinite precision. This lack of practical reversibility is related to what we observe in macroscopic systems. If you pour milk into a cup of coffee, the milk becomes uniformly distributed throughout the cup. You will never see a cup of coffee spontaneously return to the state where all the milk is at the surface because the positions and velocities of the milk and coffee molecules would need to have exactly the right values to allow the milk to return to this very special state. Even the slightest error in the choice of the positions and velocities will ruin any chance of the milk returning to the surface. This sensitivity to initial conditions provides the foundation for the arrow of time.

1.8 *Time and Ensemble Averages

Although a computed trajectory might not be the one that we thought we were computing, the positions and velocities that we compute are consistent with the constraints we have imposed, in this case, the total energy E, the volume V, and the number of particles N. Because of the assumption of equal probabilities for the microstates of an isolated system, all trajectories consistent with the constraints will contribute equally to the average values of macroscopic quantities. Thus, the trajectories computed in a simulation are useful even though they are very different from the exact trajectories that would be calculated with an infinite precision computer.

Solving Newton's equations numerically as we have done in our molecular dynamics simulations allows us to calculate a time average. If we do a laboratory experiment to measure the temperature and pressure, our measurements also would be equivalent to a time average. Because time is irrelevant for a system in equilibrium, we will find that it is easier to do calculations by using an *ensemble* average. In brief, an ensemble average is taken over many mental copies of the system that satisfy the same known conditions. A simple example might clarify the nature of these two types of averages. Suppose that we want to determine the probability that the toss of a coin results in "heads." We can do a time average by taking one coin, tossing it in the air many times, and counting the fraction of heads. In contrast, an ensemble average can be found by obtaining many similar coins and tossing them into the air at one time. We will discuss ensemble averages in Chapter 3.

It is reasonable to assume that the two ways of averaging are equivalent. This equivalence is called the *ergodic hypothesis*. The term "hypothesis" might suggest that the equivalence is not well accepted, but it reminds us that the equivalence has been shown to be rigorously true in only a few cases. The sensitivity of the trajectories of chaotic systems to initial conditions suggests that a classical system of particles moving according to Newton's equations of motion passes through many different microstates corresponding to different sets of positions and velocities. This property is called *mixing*, and it is essential for the validity of the ergodic hypothesis.

We conclude that macroscopic properties are averages over the microscopic variables and give predictable values if the system is sufficiently large. One goal of statistical mechanics is to determine these averages and give a microscopic basis for the laws of thermodynamics. In this context it is remarkable that these laws depend on the fact that the macroscopic systems we encounter in our everyday experience are chaotic.

1.9 Models of Matter

There are many models of interest in statistical mechanics, corresponding to the wide range of macroscopic systems found in nature and made in the laboratory. So far we have discussed a simple model of a classical gas and used the same model to simulate a classical liquid and a solid.

One approach to understanding nature is to develop models that can be understood theoretically, but that are rich enough to show the same qualitative features that are observed in nature. Some of the more common models that we will consider include the following.

1.9.1 The ideal gas

The simplest models of macroscopic systems are those for which there are no interactions between the individual constituents of the system. For example, if a system of particles is very dilute, collisions between the particles will be rare and can be neglected under most circumstances. In the limit that the interactions between the particles can be neglected completely, the system can be modeled as an *ideal gas.* The ideal classical gas allows us to understand much about the behavior of dilute gases, such as those in the Earth's atmosphere. The quantum versions will be useful in understanding blackbody radiation, electrons in metals, the low temperature behavior of crystalline solids, and a simple model of superfluidity.

The historical reason for the use of the term "ideal" is that the neglect of interparticle interactions allows us to do some calculations analytically. However, the neglect of interparticle interactions raises other issues. For example, how does an ideal gas reach equilibrium if there are no collisions between the particles?

1.9.2 Interparticle potentials

As we have mentioned, the most common form of the potential between two neutral atoms is the Lennard-Jones potential given in (1.1) and Figure 1.1. This potential is a very important model system and is the standard potential for studies where the focus is on fundamental issues, rather than on the properties of a specific material.

An even simpler interaction is purely repulsive and is given by

$$V(r) = \begin{cases} \infty & (r \leq \sigma) \\ 0 & (r > \sigma). \end{cases} \tag{1.5}$$

A system of particles interacting via (1.5) is called a system of hard spheres, hard disks, or hard rods depending on whether the spatial dimension is three, two, or one, respectively. The properties of dense gases and liquids will be discussed in Chapter 8.

1.9.3 Lattice models

In another class of models, the positions of the particles are restricted to a lattice or grid and the momenta of the particles are irrelevant. In the most popular model of this type the "particles" correspond to magnetic moments. At high temperatures the magnetic moments are affected by external magnetic fields, but the interaction between the moments can be neglected.

The simplest, nontrivial lattice model that includes interactions is the *Ising model*, the most important model in statistical mechanics. The model consists of magnetic moments or spins which are located on the sites of a lattice such that each spin can take on one of two values designated as up and down or ± 1. The interaction energy between two neighboring spins is $-J$ if the two spins point in the same direction and $+J$ if they point in opposite directions. One reason for the importance of this model is that it is one of the simplest to have a phase transition, in this case, a phase transition between a ferromagnetic state and a paramagnetic state. The Ising model will be discussed in Chapter 5.

We will focus on three classes of models – the ideal classical and quantum gas, classical systems of interacting particles, and the Ising model and its extensions. These models will be used in many contexts to illustrate the ideas and techniques of statistical mechanics.

1.10 Importance of Simulations

Only simple models such as the ideal gas or special cases such as the one- and two-dimensional Ising model can be analyzed by analytical methods. Much of what is currently done in statistical mechanics is to establish the general behavior of a model and then relate it to the behavior of another model. This way of understanding is not as strange as it might appear. How many examples of systems in classical mechanics can be solved exactly?

Statistical mechanics has grown in importance over the past several decades because powerful computers and new algorithms have made it possible to explore the behavior of more complex systems. As our models become more realistic, it is likely that they will require the computer for understanding many of their properties. Frequently the goal of a simulation is to explore the qualitative behavior of a model so that we have a better idea of what type of theoretical analysis might be possible and what type of laboratory experiments should be done. Simulations also allow us to compute many different kinds of quantities, some of which cannot be measured in a laboratory experiment. Simulations, theory, and experiment each play an important and complementary role in understanding nature.

Not only can we simulate reasonably realistic models, we also can study models that are impossible to realize in the laboratory, but are useful for providing a deeper theoretical understanding of real systems. For example, a comparison of the behavior of a model in three and four spatial dimensions can yield insight into why the three-dimensional system behaves the way it does.

Simulations cannot replace laboratory experiments and are limited by the finite size of the systems and by the short duration of our runs. For example, at present the longest simulations of simple liquids are for no more than 10^{-6} s.

1.11 Dimensionless Quantities

The different units used in science can be confusing. One reason is that sometimes the original measurements were done before a good theoretical understanding was achieved. For example, the calorie was created as a unit before it was understood that heat transfer was a form of energy transfer. So even today we frequently become confused using small calories, big calories, and converting each to joules.

It is frequently convenient to use dimensionless quantities. These quantities can be defined by taking the ratio of two quantities with the same units. For example, the angle θ in radians is the ratio of the arc length s on a circle subtended by the angle to the radius r of the circle: $\theta = s/r$. Similarly, the solid angle in statradians is the ratio of the surface area on a sphere subtended by a cone to the square of the radius of the sphere.

It is also useful to have another quantity with the same dimensions to set the scale. For example, for particles moving with speed v near the speed of light c, it is convenient to measure v relative to c. (You might recognize the notation $\beta \equiv v/c$.) The use of dimensionless variables makes the relevant equations simpler and make it easier to perform algebraic manipulations, thus reducing the possibility of errors. A more important reason to use dimensionless variables is to make it easier to evaluate the importance of quantities in making approximations. For example, if $\beta \ll 1$, we know that relativistic corrections are not needed in most contexts.

We will frequently consider the high and low temperature behavior of a thermal system. What characterizes high temperature? To answer this question we need to find a typical energy ϵ in the system and consider the dimensionless ratio $\tilde{T} \equiv kT/\epsilon$. For example, ϵ might be a measure of the potential energy per particle in the system. If $\tilde{T} \ll 1$, the temperature of the system is low; if $\tilde{T} \gg 1$ the system is in the high temperature regime. An important example is the behavior of electrons in metals at room temperature. We will find in Chapter 6 that the temperature of this system is low. Here ϵ is chosen to be the maximum kinetic energy of an electron at zero (absolute) temperature. In quantum mechanics no two electrons can be in the same state, and hence ϵ is nonzero.

Although $\tilde{T}$ is dimensionless, it is frequently convenient to call $\tilde{T}$ a temperature and sometimes even to denote it by T, with the understanding that T is measured in terms of ϵ. We already did so in the context of Problems 1.6 and 1.8.

Another important reason to use dimensionless quantities is that computers do not easily manipulate very small or very large numbers. Thus, it is best that all quantities be within a few orders of magnitude of one. In addition, the use of dimensionless quantities allows us to do a simulation or an analytical calculation that is valid for many systems. To find the value of a quantity for a specific system, we just multiply the dimensionless quantity by the relevant quantity that sets the scale for the system of interest.

Every measurement is a ratio and is based on a comparison to some standard. For example, if you want a certain time interval in seconds, it is given by the ratio of that interval to 9,192,631,770 periods of the radiation from a certain transition in a cesium atom. This number of periods comes from using a very accurately characterized frequency of this transition and keeping the definition of the second close to its historical definition.

1.12 Summary

The purpose of this introductory chapter is to whet your appetite. At this point it is not likely that you will fully appreciate the significance of such concepts as entropy and the direction of time. We are reminded of the book, *All I Really Need to Know I Learned in Kindergarten.*[17] In principle, we have discussed most of the important ideas in thermodynamics and statistical physics, but it will take you a while before you understand these ideas in any depth.

We also have not discussed the tools necessary to solve any problems. Your understanding of these concepts and the methods of statistical and thermal physics will increase as you work with these ideas in different contexts. However, there is no unifying equation such as Newton's second law of motion in mechanics, Maxwell's equations in electrodynamics, and Schrödinger's equation in nonrelativistic quantum mechanics. The concepts are universal, but their application to particular systems is not.

Thermodynamics and statistical mechanics have traditionally been applied to gases, liquids, and solids. This application has been very fruitful and is one reason why condensed matter physics, materials science, and chemical physics are rapidly evolving and growing areas. Examples of new systems of interest include high temperature superconductors, low dimensional magnets and conductors, composites, and biomaterials. Scientists are also taking a new look at more traditional condensed systems such as water and other liquids, liquid crystals, polymers, granular matter (for example, sand), and porous media such as rocks. In addition to our interest in macroscopic systems, there is growing interest is *mesoscopic* systems, systems that are neither microscopic nor macroscopic, but are in between, that is, between $\sim 10^2$ and $\sim 10^6$ particles.

Thermodynamics might not seem to be as interesting to you when you first encounter it. However, an understanding of thermodynamics is important in many contexts including societal issues such as global climate change and the development of alternative energy sources.

The techniques and ideas of statistical mechanics are now being used outside of traditional condensed matter physics. The field theories of high energy physics, especially lattice gauge theories, use the methods of statistical mechanics. New methods of doing quantum mechanics convert calculations to path integrals that are computed numerically using methods of statistical mechanics. Theories of the early universe use ideas from thermal physics. For example, we speak about the universe being quenched to a certain state in analogy to materials being quenched from high to low temperatures. We already have seen that chaos provides an underpinning for the need for probability in statistical mechanics. Conversely, many of the techniques used in describing the properties of dynamical systems have been borrowed from the theory of phase transitions, an important area of statistical mechanics.

In recent years statistical mechanics has evolved into the more general field of *statistical physics*. Examples of systems of interest in the latter area include earthquake faults, granular matter, neural networks, models of computing, and the analysis of the distribution of response times to email. Statistical physics is characterized more by its techniques than by the problems that are of interest. This universal applicability makes the techniques more difficult to understand, but also makes the journey more exciting.

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[17] Robert Fulghum, *All I Really Need to Know I Learned in Kindergarten*, Ballantine Books (2004).

1.13 Supplementary Notes

1.13.1 Approach to equilibrium

In Problem 1.2 we learned that $n(t)$, the number of particles on the left side of the box, decreases in time from its initial value to its equilibrium value in an almost deterministic manner if $N \gg 1$. It is instructive to derive the time dependence of $n(t)$ to show explicitly how chance can generate deterministic behavior.

We know that, if we run the simulation once, $n(t)$ will exhibit fluctuations and not decay monotonically to equilibrium. Suppose that we do the simulation many times and average the results of each run at a given time t. As discussed in Section 1.8, this average is an ensemble average, which we will denote as $\overline{n}(t)$. If there are $\overline{n}(t)$ particles on the left side after t moves, the change in $\overline{n}$ in the time interval Δt is given by

$$\Delta\overline{n} = \Big[\frac{-\overline{n}(t)}{N} + \frac{N - \overline{n}(t)}{N}\Big]\Delta t, \tag{1.6}$$

where Δt is the time between moves of a single particle from one side to the other. Equation (1.6) is equivalent to assuming that the change in $\overline{n}$ in one time step is equal to the probability that a particle is removed from the left plus the probability that it is added to the right. (In the simulation we defined the time so that the time interval Δt between changes in $n(t)$ was set equal to 1.) If we treat $\overline{n}$ and t as continuous variables and take the limit $\Delta t \to 0$, we have

$$\frac{\Delta\overline{n}}{\Delta t} \to \frac{d\overline{n}}{dt} = 1 - \frac{2\overline{n}(t)}{N}. \tag{1.7}$$

The solution of the differential equation (1.7) is

$$\overline{n}(t) = \frac{N}{2}\Big[1 + e^{-2t/N}\Big], \tag{1.8}$$

where we have used the initial condition $\overline{n}(t=0) = N$. We see that $\overline{n}(t)$ decays exponentially to its equilibrium value $N/2$. How does this form (1.8) compare to your simulation results for various values of N?

From (1.8) we can define a *relaxation time* τ as the time it takes the difference $[\overline{n}(t) - N/2]$ to decrease to $1/e$ of its initial value. Because $\tau = N/2$, $\overline{n}(t)$ for large N varies slowly, and we are justified in rewriting the difference equation (1.6) as a differential equation.

Problem 1.10. Independence of initial conditions

Show that if the number of particles on the left-hand side of the box at $t = 0$ is equal to $n(0)$ rather than $N/2$, the solution of (1.7) is

$$\overline{n}(t) = \frac{N}{2} - \frac{N}{2}\Big[1 - \frac{2n(0)}{N}\Big]e^{-2t/N}. \tag{1.9}$$

Note that $\overline{n}(t) \to N/2$ as $t \to \infty$ independent of the value of $n(0)$. □

1.13.2 Mathematics refresher

As discussed in Section 1.12, there is no unifying equation in statistical mechanics such as Newton's second law of motion to be solved in a variety of contexts. For this reason we will use many mathematical tools. Section 2.24.1 summarizes the mathematics of thermodynamics which makes much use of partial derivatives. The Appendix summarizes some of the mathematical formulas and relations that we will use. If you can do the following problems, you have a good background for much of the mathematics that we will use in the following chapters.

Problem 1.11. Common derivatives

Calculate the derivative with respect to x of the following functions: e^x, e^{3x}, e^{ax}, $\ln x$, $\ln x^2$, $\ln 3x$, $\ln 1/x$, $\sin x$, $\cos x$, $\sin 3x$, and $\cos 2x$. □

Problem 1.12. Common integrals

Calculate the following integrals:

$$\int_1^2 \frac{dx}{2x^2}, \int_1^2 \frac{dx}{4x}, \int_1^2 e^{3x} dx, \text{ and } \int x^{-\gamma}\, dx. \tag{1.10}$$

□

Problem 1.13. Partial derivatives

Calculate the partial derivatives of $x^2 + xy + 3y^2$ with respect to x and y. □

Problem 1.14. Taylor series approximations

Calculate the first three nonzero terms of the Taylor series approximations about $x = 0$ for the following functions:

$$e^{ax}, \ln(1 + x), \text{and} (1 + x)^n, \tag{1.11}$$

where a and n are constants. □

Vocabulary

thermodynamics, statistical mechanics

macroscopic system, microstate, macrostate

specially prepared state, most probable macrostate

equilibrium, fluctuations, relative fluctuations

thermal contact, temperature

sensitivity to initial conditions, chaos

models, computer simulations, molecular dynamics

Additional Problems

Problem 1.15. The dye is cast

(a) What would you observe when a small amount of black dye is placed in a glass of water?

(b) Suppose that a video were taken of this process and the video run backward without your knowledge. Would you be able to observe whether the video was being run forward or backward?

(c) Suppose that you could watch a video of the motion of an individual ink molecule. Would you be able to know that the video was being shown forward or backward? □

Problem 1.16. Fluid as metaphor

Why is "heat" treated as a fluid in everyday speech? After all, most people are not familiar with the caloric theory of heat. □

Problem 1.17. Do molecules really move?

Cite evidence from your everyday experience that the molecules in a glass of water or in the surrounding air are in seemingly endless random motion. □

Problem 1.18. Temperature

How do you know that two objects are at the same temperature? How do you know that two bodies are at different temperatures? □

Problem 1.19. Time-reversal invariance

Show that Newton's equations are time-reversal invariant. □

Problem 1.20. Properties of macroscopic systems

Summarize your present understanding of the properties of macroscopic systems. □

Problem 1.21. What's in a name?

Ask some of your friends why a ball falls when released above the Earth's surface. Then ask them what makes rolling balls come to rest. Are the answers of "gravity" and "friction" satisfactory explanations? What would be a more fundamental explanation for each phenomena? □

Problem 1.22. Randomness

What is your present understanding of the concept of "randomness"? Does "random motion" imply that the motion occurs according to unknown rules? □

Problem 1.23. Meaning of abstract concepts

Write a paragraph on the meanings of the abstract concepts "energy" and "justice." (See the Feynman Lectures, Vol. 1, Chap. 4, for a discussion of why it is difficult to define such abstract concepts.) □

Problem 1.24. Bicycle pump

Suppose that the handle of a plastic bicycle pump is rapidly pushed inward. Predict what happens to the temperature of the air inside the pump and explain your reasoning. (This problem is given here to determine how you think about this type of problem at this time. Similar problems will appear in later chapters to see if and how your reasoning has changed.) ☐

Problem 1.25. Granular matter

A box of glass beads is an example of a macroscopic system if the number of beads is sufficiently large. In what ways is such a system different from the macroscopic systems such as a glass of water that we have discussed in this chapter? ☐

Suggestions for Further Reading

P. W. Atkins, *The Second Law*, Scientific American Books (1984). A qualitative introduction to the second law of thermodynamics and its implications.

John J. Brehm and William J. Mullin, *Introduction to the Structure of Matter*, John Wiley & Sons (1989).

Manfred Eigen and Ruthild Winkler, *How the Principles of Nature Govern Chance*, Princeton University Press (1993).

Richard Feynman, R. B. Leighton, and M. Sands, *Feynman Lectures on Physics*, Addison-Wesley (1964). Volume 1 has a very good discussion of the nature of energy and work.

Martin Goldstein and Inge F. Goldstein, *The Refrigerator and the Universe*, Harvard University Press (1993).

Harvey Gould, Jan Tobochnik, and Wolfgang Christian, *An Introduction to Computer Simulation Methods*, third edition, Addison-Wesley (2006).

J. G. Oliveira and A.-L. Barabási, "Darwin and Einstein correspondence patterns," Nature **437**, 1251 (2005). The authors find that the probability that Darwin and Einstein responded to a letter in τ days is well approximated by a power law, $P(\tau) \sim \tau^{-a}$ with $a \approx 3/2$. How long does it take you to respond to an email?

Jeremy Rifkin, *Entropy: A New World View*, Bantam Books (1980). Although this book raises some important issues, it, like many other popular books and articles, it misuses the concept of entropy. For more discussion on the meaning of entropy and how it should be introduced, see `<www.entropysite.com/>` and `<www.entropysimple.com/>`.

Robert H. Romer, "Heat is not a noun," Am. J. Phys. **69** (2), 107–109 (2001). See also Art Hobson, "The language of physics," Am. J. Phys. **69** (6), 634 (2001); David T. Brookes and Eugenia Etkina, "Using conceptual metaphor and functional grammar to explore how language used in physics affects student learning," Phys. Rev. ST Phys. Educ. Res. **3** (1), 010105-1–16 (2007).

A listing of many of the textbooks on statistical mechanics and thermodynamics can be found at `<www.compadre.org/stp>`. Some of our favorites are listed in the following. It is a good idea to look at several books while you are learning a subject for the first time. Sometimes the same argument with slightly different wording can seem clearer.

Daniel J. Amit and Yosef Verbin, *Statistical Physics*, World Scientific (1999).

Ralph Baierlein, *Thermal Physics*, Cambridge University Press, New York (1999).

Stephen Blundell and Katherine Blundell, *Thermal Physics*, 2nd ed., Oxford University Press (2009).

Craig F. Bohren and Bruce A. Albrecht, *Atmospheric Thermodynamics*, Oxford University Press (1998).

Debashish Chowdhury and Dietrich Stauffer, *Principles of Equilibrium Statistical Mechanics*, Wiley-VCH (2000). This text is more advanced than ours, but contains many accessible gems.

F. Mandl, *Statistical Physics*, second edition, John Wiley & Sons (1988).

F. Reif, *Statistical Physics*, Volume 5 of the Berkeley Physics Series, McGraw-Hill (1967). This text was probably the first to make use of computer simulations to explain some of the basic properties of macroscopic systems.

F. Reif, *Fundamentals of Statistical and Thermal Physics*, McGraw-Hill (1965). Our presentation owes a large debt to the two books by Reif on statistical physics.

Daniel V. Schroeder, *An Introduction to Thermal Physics*, Addison-Wesley (2000). Schroeder's text has many interesting applications.

Chapter 2

Thermodynamic Concepts and Processes

3 June 2011

We introduce the concepts of temperature, energy, work, heating, entropy, engines, and the laws of thermodynamics and related macroscopic concepts.

2.1 Introduction

In this chapter we will discuss ways of thinking about macroscopic systems and introduce the basic concepts of thermodynamics. Because these ways of thinking are very different from the ways that we think about microscopic systems, most students of thermodynamics initially find it difficult to apply the abstract principles of thermodynamics to concrete problems. However, the study of thermodynamics has many rewards as was appreciated by Einstein:

> A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made to me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts.[1]

The essence of thermodynamics can be summarized by two laws:[2] (1) Energy is conserved and (2) entropy increases. These statements of the laws are deceptively simple. What is energy? You are probably familiar with the concept of energy from other courses, but can you define it?

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[1] A. Einstein, *Autobiographical Notes*, Open Court Publishing Company (1991).

[2] The nature of thermodynamics is summarized in the song "First and Second Law" by Michael Flanders and Donald Swann.

Abstract concepts such as energy and entropy are not easily defined nor understood. However, as you apply these concepts in a variety of contexts, you will gradually come to understand them.

Because thermodynamics describes the macroscopic properties of macroscopic systems without appeal to arguments based on the nature of their microscopic constituents, the concepts of energy and entropy in this context are very abstract. So why bother introducing thermodynamics as a subject in its own right, when we could more easily introduce energy and entropy from microscopic considerations? Besides the intellectual challenge, an important reason is that the way of thinking required by thermodynamics can be applied in other contexts where the microscopic properties of the system are poorly understood or very complex. However, there is no need to forget the general considerations that we discussed in Chapter 1. And you are also encouraged to read ahead, especially in Chapter 4 where the nature of entropy is introduced from first principles.

2.2 The System

The first step in applying thermodynamics is to select the appropriate part of the universe of interest. This part of the universe is called the *system.* In this context the term system is simply anything that we wish to consider. The system is defined by a closed surface called the boundary (see Figure 2.1). The boundary may be real or imaginary and may or may not be fixed in shape or size. The system might be as obvious as a block of steel, water in a container, or the gas in a balloon. Or the system might be defined by an imaginary fixed boundary within a flowing liquid.

The *surroundings* are the rest of the universe that can in any significant way affect or be affected by the system. For example, if an ice cube is placed in a glass of water, we might take the ice to be the system and the water to be the surroundings. In this example we would usually ignore the interaction of the ice cube with the air in the room and the interaction of the glass with the table on which the glass is set. However, if the size of the ice cube and the amount of water were about the same, we would need to consider the ice cube and water to be the system and the air in the room to be the surroundings. The choice depends on the questions of interest. The surroundings need not surround the system. An *open system* can exchange matter with its surroundings; a *closed system* cannot.

2.3 Thermodynamic Equilibrium

Macroscopic systems often exhibit some memory of their recent history. A stirred cup of tea continues to swirl for a while after we stop stirring. A hot cup of coffee cools and takes on the temperature of its surroundings regardless of its initial temperature. The final macrostates of such systems are called *equilibrium* states, which are characterized by their time independence, history independence, and relative simplicity.

Time independence means that the measurable macroscopic properties (such as the temperature, pressure, and density) of equilibrium systems do not change with time except for very small fluctuations that we can observe only under special conditions. In contrast, nonequilibrium macrostates change with time. The time scale for changes may be seconds or years, and cannot be determined from thermodynamic arguments alone. We can say for sure that a system is not in equilibrium if its properties change with time, but time independence during our observation

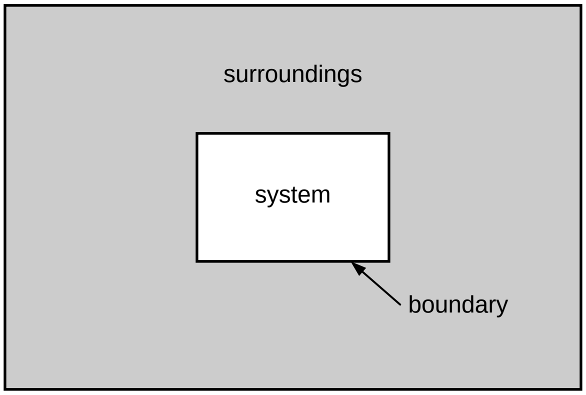

Figure 2.1: Schematic of a thermodynamic system.

time is not sufficient to determine if a system is in equilibrium. It is possible that we just did not observe the system long enough.

As we discussed in Chapter 1 the *macrostate* of a system refers to bulk properties such as temperature and pressure. Only a few quantities are needed to specify the macrostate of a system in equilibrium. For example, if you drop an ice cube into a cup of coffee, the temperature immediately afterward will vary throughout the coffee until the coffee reaches equilibrium. Before equilibrium is reached, we must specify the temperature everywhere in the coffee. Once equilibrium is reached, the temperature will be uniform throughout and only one number is needed to specify the temperature.

History independence implies that a system can go to the same final equilibrium macrostate through an infinity of possible ways. The final macrostate has lost all memory of how it was produced. For example, if we put several cups of coffee in the same room, they will all reach the same final temperature, regardless of their different initial temperatures or how much milk was added. However, there are many cases where the history of the system is important. For example, a metal cooled quickly may contain defects that depend on the detailed history of how the metal was cooled.

It is difficult to know for certain whether a system is in equilibrium because the time it takes a system to reach equilibrium may be very long and our measurements might not indicate whether a system's macroscopic properties are changing. In practice, the criterion for equilibrium is circular. Operationally, a system is in equilibrium if its properties can be consistently described by the laws of thermodynamics.

The circular nature of thermodynamics is not fundamentally different from that of other fields of physics. For example, the law of conservation of energy can never be disproved, because we can always make up new forms of energy to make it true. If we find that we are continually making up new forms of energy for every new system we find, then we would discard the law of conservation of energy as not being useful. For example, if we were to observe a neutron at rest decay into an electron and proton (beta decay) and measure the energy and momentum of the decay products, we would find an apparent violation of energy conservation in the vast majority of decays. Historically, Pauli did not reject energy conservation, but instead suggested that a third particle (the neutrino) is also emitted. Pauli's suggestion was made in 1930, but the (anti)neutrino was not detected until 1956. In this example our strong belief in conservation of energy led to a new prediction and discovery.

The same is true for thermodynamics. We find that if we use the laws of thermodynamics for systems that experimentally appear to be in equilibrium, then everything works out fine. In some systems such as glasses that we suspect are not in thermal equilibrium, we must be very careful in interpreting our measurements according to the laws of thermodynamics.

2.4 Temperature

The concept of temperature plays a central role in thermodynamics and is related to the physiological sensation of hot and cold. Because such a sensation is an unreliable measure of temperature, we will develop the concept of temperature by considering what happens when two bodies are placed so that they can exchange energy. The most important property of the temperature is its tendency to become equal. For example, if we put a hot and a cold body into *thermal contact*, the temperature of the hot body decreases and the temperature of the cold body increases until both bodies are at the same temperature and the two bodies are in *thermal equilibrium*.

Problem 2.1. Physiological sensation of temperature

(a) Suppose you are blindfolded and place one hand in a pan of warm water and the other hand in a pan of cold water. Then your hands are placed in another pan of water at room temperature. What temperature would each hand perceive?

(b) What are some other examples of the subjectivity of our perception of temperature? □

To define temperature more carefully, consider two systems separated by an *insulating* wall.[3] A wall is said to be *insulating* if there is no energy transfer through the wall due to temperature differences between regions on both sides of the wall. If the wall between the two systems were *conducting*, then such energy transfer would be possible. Insulating and conducting walls are idealizations. A good approximation to the former is the wall of a thermos bottle; a thin sheet of copper is a good approximation to the latter.

Consider two systems surrounded by insulating walls, except for a wall that allows energy transfer. For example, suppose that one system is a cup of coffee in a vacuum flask and the other system is alcohol enclosed in a glass tube. The glass tube is in thermal contact with the coffee. If energy is added to the alcohol in the tube, the fluid will expand, and if the tube is sufficiently narrow, the change of the column height of the alcohol will be noticeable. The alcohol column height will reach a time-independent value, and hence the coffee and the alcohol are in equilibrium. Next suppose that we dip the alcohol-filled tube into a cup of tea in another vacuum flask. If the height of the alcohol column remains the same, we say that the coffee and tea are at the same temperature. This conclusion can be generalized as follows:

> If two bodies are in thermal equilibrium with a third body, they are in thermal equilibrium with each other (zeroth law of thermodynamics).

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[3] An insulating wall is sometimes called an *adiabatic wall*.

This conclusion is sometimes called the *zeroth law of thermodynamics*. The zeroth law implies the existence of a universal property of systems in thermal equilibrium and allows us to identify this property as the temperature of a system without a direct comparison to some standard. This conclusion is not a logical necessity, but an empirical fact. If person A is a friend of B and B is a friend of C, it does not follow that A is a friend of C.

Problem 2.2. Describe some other properties that also satisfy a law similar to the zeroth law. ☐

Any body whose macroscopic properties change in a well-defined manner can be used to measure temperature. A *thermometer* is a system with some convenient macroscopic property that changes in a simple way as the equilibrium macrostate changes. Examples of convenient macroscopic properties include the length of an iron rod and the electrical resistance of gold. In these cases we need to measure only a single quantity to indicate the temperature.

Problem 2.3. Why are thermometers relatively small devices in comparison to the system of interest? ☐

To use different thermometers, we need to make them consistent with one another. To do so, we choose a standard thermometer that works over a wide range of temperatures and define reference temperatures which correspond to physical processes that always occur at the same temperature. The familiar gas thermometer is based on the fact that the temperature T of a dilute gas is proportional to its pressure P at constant volume. The temperature scale that is based on the gas thermometer is called the *ideal gas temperature scale*. The unit of temperature is called the *kelvin* (K). We need two points to define a linear function. We write

$$T(P) = aP + b, \tag{2.1}$$

where a and b are constants. We may choose the magnitude of the unit of temperature in any convenient way. The gas temperature scale has a natural zero — the temperature at which the pressure of an ideal gas vanishes — and hence we take $b = 0$. The second point is established by the *triple point* of water, the unique temperature and pressure at which ice, water, and water vapor coexist. The temperature of the triple point is *defined* to be exactly 273.16 K. Hence, the temperature of a fixed volume gas thermometer is given by

$$T = 273.16\frac{P}{P_{\rm tp}} \qquad \text{(ideal gas temperature scale)}, \tag{2.2}$$

where P is the pressure of the ideal gas thermometer, and $P_{\rm tp}$ is its pressure at the triple point. Equation (2.2) holds for a fixed amount of matter in the limit $P \to 0$. From (2.2) we see that the kelvin is defined as the fraction 1/273.16 of the temperature of the triple point of water.

At low pressures all gas thermometers read the same temperature regardless of the gas that is used. The relation (2.2) holds only if the gas is sufficiently dilute that the interactions between the molecules can be ignored. Helium is the most useful gas because it liquefies at a temperature lower than any other gas.

The historical reason for the choice of 273.16 K for the triple point of water is that it gave, to the accuracy of the best measurements then available, 100 K for the difference between the ice point

triple point	273.16 K	definition
steam point	373.12 K	experiment
ice point	273.15 K	experiment

Table 2.1: Fixed points of the ideal gas temperature scale.

(the freezing temperature at standard pressure[4]) and the steam point (the boiling temperature at the standard pressure of water). However, more accurate measurements now give the difference as 99.97 K (see Table 2.1).

It is convenient to define the *Celsius* scale:

$$T_{\text{celsius}} = T - 273.15, \tag{2.3}$$

where T is the ideal gas temperature. Note that the Celsius and ideal gas temperatures differ only by the shift of the zero. By convention the degree sign is included with the C for Celsius temperature (°C), but no degree sign is used with K for kelvin.

Problem 2.4. Temperature scales

(a) The Fahrenheit scale is defined such that the ice point is at 32°F and the steam point is 212°F. Derive the relation between the Fahrenheit and Celsius temperature scales.

(b) What is body temperature (98.6°F) on the Celsius and Kelvin scales?

(c) A meteorologist in Canada reports a temperature of 30°C. How does this temperature compare to 70°F?

(d) The *centigrade* temperature scale is defined as

$$T_{\text{centigrade}} = (T - T_{\text{ice}})\frac{100}{T_{\text{steam}} - T_{\text{ice}}}, \tag{2.4}$$

where T_{ice} and T_{steam} are the ice and steam points of water (see Table 2.1). By definition, there are 100 centigrade units between the ice and steam points. How does the centigrade unit defined in (2.4) compare to the Kelvin or Celsius unit? The centigrade scale has been superseded by the Celsius scale. □

Problem 2.5. What is the range of temperatures that is familiar to you from your everyday experience and from your prior studies? □

2.5 Pressure Equation of State

As we have discussed, the equilibrium macrostates of a thermodynamic system are much simpler to describe than nonequilibrium macrostates. For example, the pressure P of a simple fluid (a gas

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[4] Standard atmospheric pressure is the pressure of the Earth's atmosphere under normal conditions at sea level and is defined to be $1.013 \times 10^5\,\text{N/m}^2$. The SI unit of pressure is N/m^2; this unit has been given the name *pascal* (Pa).

or a liquid) consisting of a single species is uniquely determined by its (number) density $\rho = N/V$, and temperature T, where N is the number of particles and V is the volume of the system. That is, the quantities P, T, and ρ are not independent, but are connected by a relation of the general form

$$P = f(T, \rho). \tag{2.5}$$

This relation is called the *pressure equation of state*. Each of these three quantities can be regarded as a function of the other two, and the macrostate of the system is determined by any two of the three. Note that we have implicitly assumed that the thermodynamic properties of a fluid are independent of its shape.

The pressure equation of state must be determined either empirically or from a simulation or from a theoretical calculation (an application of statistical mechanics). As discussed in Section 1.9 the *ideal gas* represents an idealization in which the potential energy of interaction between the molecules is very small in comparison to their kinetic energy and the system can be treated classically. For an ideal gas, we have for fixed temperature the empirical relation $P \propto 1/V$, or

$$PV = \text{constant} \qquad \text{(fixed temperature)}. \tag{2.6}$$

The relation (2.6) is sometimes called Boyle's law and was published by Robert Boyle in 1660. Note that the relation (2.6) is not a law of physics, but an empirical relation. An equation such as (2.6), which relates different macrostates of a system all at the same temperature, is called an *isotherm*.

We also have for an ideal gas the empirical relation

$$V \propto T \qquad \text{(fixed pressure)}. \tag{2.7}$$

Some textbooks refer to (2.7) as Charles's law, but it should be called the *law of Gay-Lussac*.[5]

We can express the empirical relations (2.6) and (2.7) as $P \propto T/V$. In addition, if we hold T and V constant and introduce more gas into the system, we find that the pressure increases in proportion to the amount of gas. If N is the number of gas molecules, we can write

$$PV = NkT \qquad \text{(ideal gas pressure equation of state)}, \tag{2.8}$$

where the constant of proportionality k in (2.8) is found experimentally to have the same value for all gases in the limit $P \to 0$. The value of k is

$$k = 1.38 \times 10^{-23}\,\text{J/K} \qquad \text{(Boltzmann's constant)}, \tag{2.9}$$

and is called *Boltzmann's constant*. The equation of state (2.8) will be derived using statistical mechanics in Section 4.5.

Because the number of particles in a typical gas is very large, it sometimes is convenient to measure this number relative to the number of particles in one (gram) mole of gas.[6] A mole of any substance consists of Avogadro's number $N_A = 6.022 \times 10^{23}$ of that substance. If there are ν moles, then $N = \nu N_A$, and the ideal gas equation of state can be written as

$$PV = \nu N_A kT = \nu RT, \tag{2.10}$$

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[5] See Bohren and Albrecht, pages 51–53.

[6] A mole is defined as the quantity of matter that contains as many objects (for example, atoms or molecules) as the number of atoms in exactly 12 g of ^{12}C.

where

$$R = N_A k = 8.314\,\mathrm{J/K\,mole} \tag{2.11}$$

is the gas constant.

Real gases do not satisfy the ideal gas equation of state except in the limit of low density. For now we will be satisfied with considering a simple phenomenological[7] equation of state of a real gas with an interparticle interaction similar to the Lennard-Jones potential (see Figure 1.1, page 6). A simple phenomenological pressure equation of state for real gases that is more accurate at moderate densities is due to van der Waals and has the form

$$(P + \frac{N^2}{V^2}a)(V - Nb) = NkT \qquad \text{(van der Waals equation of state)}, \tag{2.12}$$

where a and b are empirical constants characteristic of a particular gas. The parameter b takes into account the nonzero size of the molecules by decreasing the effective available volume to any given molecule. The parameter a is associated with the attractive interactions between the molecules. We will derive this approximate equation of state in Section 8.2.

2.6 Some Thermodynamic Processes

A change from one equilibrium macrostate of a system to another is called a *thermodynamic process*. Thermodynamics does not determine how much time such a process will take, and the final macrostate is independent of the amount of time it takes to reach the equilibrium macrostate. To describe a process in terms of thermodynamics, the system must be in thermodynamic equilibrium. However, for any process to occur, the system cannot be exactly in thermodynamic equilibrium because at least one thermodynamic variable must change. If the change can be done so that the system can be considered to be in a succession of equilibrium macrostates, then the process is called *quasistatic*. A *quasistatic process* is an idealized concept. Although no physical process is quasistatic, we can imagine real processes that approach the limit of quasistatic processes. Usually, quasistatic processes are accomplished by making changes very slowly. That is, a quasistatic process is defined as a succession of equilibrium macrostates. The name thermodynamics is a misnomer because thermodynamics treats only equilibrium macrostates and not dynamics.

Some thermodynamic processes can go only in one direction and others can go in either direction. For example, a scrambled egg cannot be converted to a whole egg. Processes that can go only in one direction are called *irreversible*. A process is *reversible* if it is possible to restore the system and its surroundings to their original condition. (The surroundings include any body that was affected by the change.) That is, if the change is reversible, the status quo can be restored everywhere.

Processes such as stirring the cream in a cup of coffee or passing an electric current through a resistor are irreversible because, once the process is done, there is no way of reversing the process. But suppose we make a small and very slow frictionless change of a constraint such as an increase in the volume, which we then reverse. Because there is no "friction," we have not done any net work in this process. At the end of the process, the constraints and the energy of the system

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[7] We will use the word *phenomenological* often. It means a description of phenomena that is not derived from first principles.

return to their original values and the macrostate of the system is unchanged. In this case we can say that this process is reversible. No real process is truly reversible because it would require an infinite time to occur. The relevant question is whether the process approaches reversibility.

Problem 2.6. Are the following processes reversible or irreversible?

(a) Squeezing a plastic bottle.

(b) Ice melting in a glass of water.

(c) Movement of a real piston (where there is friction) to compress a gas.

(d) Pumping of air into a tire. □

2.7 Work

During a process the surroundings can do work on the system of interest or the system can do work on its surroundings. We now obtain an expression for the mechanical work done on a system in a quasistatic process. For simplicity, we assume the system to be a fluid. Because the fluid is in equilibrium, we can characterize it by a uniform pressure P. For simplicity, we assume that the fluid is contained in a cylinder of cross-sectional area A fitted with a movable piston (see Figure 2.2). The piston allows no gas or liquid to escape. We can add weights to the piston causing it to compress the fluid. Because the pressure is defined as the force per unit area, the magnitude of the force exerted by the fluid on the piston is given by PA, which also is the force exerted by the piston on the fluid. If the piston is displaced quasistatically by an amount dx, then the work done *on* the fluid by the piston is given by[8]

$$dW = -(PA)\,dx = -P\,(Adx) = -PdV. \tag{2.13}$$

The negative sign in (2.13) is present because, if the volume of the fluid is decreased, the work done by the piston is positive.

If the volume of the fluid changes quasistatically from an initial volume V_1 to a final volume V_2, the system remains very nearly in equilibrium, and hence its pressure at any stage is a function of its volume and temperature. Hence, the total work is given by the integral

$$W_{1\to 2} = -\int_{V_1}^{V_2} P(T,V)\,dV \qquad \text{(quasistatic process)}. \tag{2.14}$$

Note that the work done on the fluid is positive if $V_2 < V_1$ and negative if $V_2 > V_1$.

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[8] Equation (2.13) can be written as

$$dW/dt = -P(dV/dt),$$

if you wish to avoid the use of differentials (see Section 2.24.1, page 88).

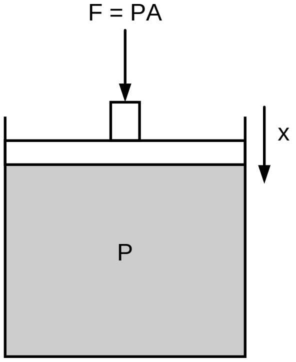

Figure 2.2: Example of work done on a fluid enclosed within a cylinder fitted with a piston when the latter moves a distance Δx.

For the special case of an ideal gas, the work done on a gas that is compressed at constant temperature (an *isothermal process*) is given by

$$W_{1\to 2} = -NkT\int_{V_1}^{V_2} \frac{dV}{V} \tag{2.15}$$

$$= -NkT \ln \frac{V_2}{V_1} \qquad \text{(ideal gas at constant temperature).} \tag{2.16}$$

We have noted that the pressure P must be uniform throughout the fluid when it is in equilibrium. If compression occurs, then pressure gradients are present. To move the piston from its equilibrium position, we must add (remove) a weight from it. Then for a brief time the total weight on the piston will be greater (less) than PA. This difference is necessary if the piston is to move and do work on the gas. If the movement is sufficiently slow, the pressure departs only slightly from its equilibrium value. What does "sufficiently slow" mean? To answer this question, we have to go beyond the macroscopic reasoning of thermodynamics and consider the molecules that comprise the fluid. If the piston is moved a distance Δx, then the density of the molecules near the piston becomes greater than in the bulk of the fluid. Consequently, there is a net movement of molecules away from the piston until the density again becomes uniform. The time τ for the fluid to return to equilibrium is given by $\tau \approx \Delta x/v_s$, where v_s is the mean speed of the molecules. For comparison, the characteristic time τ_p for the process is $\tau_p \approx \Delta x/v_p$, where v_p is the speed of the piston. If the process is quasistatic, we require that $\tau \ll \tau_p$ or $v_p \ll v_s$. That is, the speed of the piston must be much less than the mean speed of the molecules, a condition that is easy to satisfy in practice.

Problem 2.7. Work

To refresh your understanding of work in the context of mechanics, look at Figure 2.3 and explain whether the following quantities are positive, negative, or zero:

(a) The work done on the block by the hand.

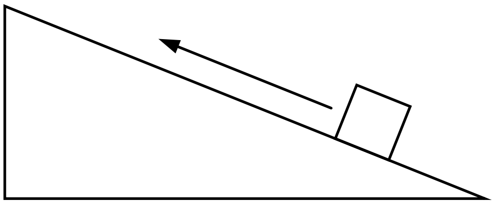

Figure 2.3: A block on an frictionless incline. The arrow indicates the direction of motion. The figure is adapted from Loverude et al. (see references)

(b) The work done on the block by the Earth.

(c) The work done on the hand by the block (if there is no such work, state so explicitly). □

Work depends on the path. The solution of the following example illustrates that the work done on a system depends not only on the initial and final macrostates, but also on the intermediate macrostates, that is, on the path.

Example 2.1. Cyclic processes

Figure 2.4 shows a cyclic path in the P-V diagram of an ideal gas. How much work is done on the gas during this cyclic process? (Look at the figure before you attempt to answer the question.)

Solution. During the isobaric (constant pressure) expansion 1 → 2, the work done on the gas is

$$W_{1\to 2} = -P_{\rm high}(V_{\rm high} - V_{\rm low}). \tag{2.17}$$

No work is done from 2 → 3 and from 4 → 1. The work done on the gas from 3 → 4 is

$$W_{3\to 4} = -P_{\rm low}(V_{\rm low} - V_{\rm high}). \tag{2.18}$$

The net work done on the gas is

$$\begin{aligned} W_{\rm net} &= W_{1\to 2} + W_{3\to 4} = -P_{\rm high}(V_{\rm high} - V_{\rm low}) - P_{\rm low}(V_{\rm low} - V_{\rm high}) && (2.19a)\\ &= -(P_{\rm high} - P_{\rm low})(V_{\rm high} - V_{\rm low}) < 0. && (2.19b) \end{aligned}$$

The result is that the net work done on the gas is the negative of the area enclosed by the path. If the cyclic process were carried out in the reverse order, the net work done on the gas would be positive. ♢

Problem 2.8. Work in a cyclic process

Consider the cyclic process as described in Example 2.1.

(a) Because the system was returned to its original pressure and volume, why is the net amount of work done on the system not zero?

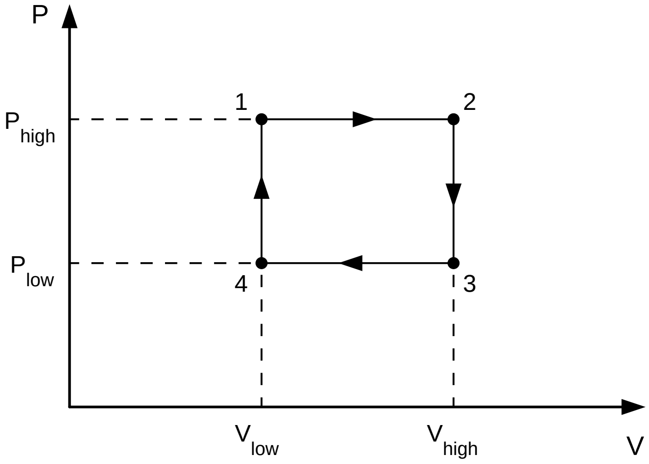

Figure 2.4: A simple cyclic process from 1 → 2 → 3 → 4 → 1. The magnitude of the net work done on the gas equals the enclosed area.

(b) What would be the work done on the gas if the gas were taken from 1 → 2 → 3 and then back to 1 along the diagonal path connecting 3 and 1? □

Example 2.2. Work changes the total energy

Consider two blocks sitting on a table that are connected by a spring. Initially the spring is unstretched. The two blocks are pushed together by a force on *each* block of magnitude F through a distance d. What is the net work done on the two blocks plus spring system. How much does the energy of the system change? How much does the kinetic energy of the system change? How much does the potential energy of the system change?

Solution. Your initial thought might be that because there is no net force on the system, the work done is zero. That answer is incorrect – understanding mechanics isn't easy. To calculate the work you need to add the work done by each force separately. In this case each force does an amount of work equal to Fd, and thus the total work done on the system is $2Fd$. You might think that the change in the kinetic energy of the system is equal to $2Fd$ from the work-kinetic energy theorem that you learned in mechanics. That's also incorrect because the work-kinetic energy theorem is applicable only to a single particle, not to a composite system as we have here. All we can say in this case is that the total energy of the two blocks plus spring system changes by $2Fd$. We cannot answer questions about the change in kinetic or potential energies because not enough information is given.

This example is analogous to a system of many particles. When we do work on it, the total energy of the system changes, but we cannot say anything about how the internal kinetic energy or potential energy changes. It is important to realize that systems of many particles contain both kinetic and potential energy. ♢

2.8 The First Law of Thermodynamics

If we think of a macroscopic system as consisting of many interacting particles, we know that it has a well defined total energy which satisfies a conservation principle. This simple justification of the existence of a thermodynamic energy function is very different from the historical development because thermodynamics was developed before the atomic theory of matter was well accepted. Historically, the existence of a macroscopic conservation of energy principle was demonstrated by purely macroscopic observations as outlined in the following.[9]

Consider a system enclosed by insulating walls. Such a system is *thermally isolated*. An *adiabatic process* is one in which the macrostate of the system is changed only by work done on the system. That is, no energy is transferred to or from the system by temperature differences. We know from overwhelming empirical evidence that the amount of work needed to change the macrostate of a thermally isolated system depends only on the initial and final macrostates and not on the intermediate states through which the system passes. This independence of the path under these conditions implies that we can define a function E such that for a change from macrostate 1 to macrostate 2, the work done on a thermally isolated system equals the change in E:

$$W = E_2 - E_1 = \Delta E \qquad \text{(adiabatic process)}. \tag{2.20}$$

The quantity E is called the internal energy of the system.[10] The internal energy in (2.20) is measured with respect to the center of mass and is the same as the total energy of the system in a reference frame in which the center of mass velocity of the system is zero.[11] The energy E is an example of a *state* function, that is, it characterizes the state of a macroscopic system and is independent of the path.

If we choose a convenient reference macrostate as the zero of energy, then E has a unique value for each macrostate of the system because the work done on the system W is independent of the path for an adiabatic process. (Remember that in general W depends on the path.)

If we relax the condition that the change be adiabatic and allow the system to interact with its surroundings, we find in general that $\Delta E \neq W$. (The difference between ΔE and W is zero for an adiabatic process.) We know that we can increase the energy of a system by doing work on it or by heating it as a consequence of a temperature difference between it and its surroundings. In general, the change in the (internal) energy of a closed system (fixed number of particles) is given by

$$\boxed{\Delta E = W + Q} \qquad \text{(first law of thermodynamics)}. \tag{2.21}$$

The quantity Q is the change in the system's energy due to heating ($Q > 0$) or cooling ($Q < 0$) and W is the work done *on* the system. Equation (2.21) expresses the law of conservation of energy and is known as the *first law of thermodynamics*. This equation is equivalent to saying that there are two macroscopic ways of changing the internal energy of a system: doing work and heating (cooling).

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[9] These experiments were done by Joseph Black (1728–1799), Benjamin Thompson (Count Rumford) (1753–1814), Robert Mayer (1814–1878), and James Joule (1818–1889). Mayer and Joule are now recognized as the co-discoverers of the first law of thermodynamics, but Mayer received little recognition at the time of his work.

[10] Another common notation for the internal energy is U.

[11] Microscopically, the internal energy of a system of particles equals the sum of the kinetic energy in a reference frame in which the center of mass velocity is zero and the potential energy arising from the interactions of the particles.

One consequence of the first law of thermodynamics is that ΔE is independent of the path, even though the amount of work W depends on the path. And because W depends on the path and ΔE does not, the amount of heating also depends on the path. From one point of view, the first law of thermodynamics expresses what seems obvious to us today, namely, conservation of energy. From another point of view, the first law implies that, although the work done and the amount of heating depend on the path, their sum is independent of the path.

Problem 2.9. Pumping air

A bicycle pump contains one mole of a gas. The piston fits tightly so that no air escapes and friction is negligible between the piston and the cylinder walls. The pump is thermally insulated from its surroundings. The piston is quickly pressed inward. What happens to the temperature of the gas? Explain your reasoning. □

So far we have considered two classes of thermodynamic quantities. One class consists of *state functions* because they have a specific value for each macrostate of the system. An example of such a function is the internal energy E. As we have discussed, there are other quantities, such as work done on a system and energy transfer due to heating that are not state functions and depend on the thermodynamic process by which the system changed from one macrostate to another.

The energy of a system is a state function. The mathematical definition of a state function goes as follows. Suppose that $f(x)$ is a state function that depends on the parameter x. If x changes from x_1 to x_2, then the change in f is

$$\Delta f = \int_{x_1}^{x_2} df = f(x_2) - f(x_1). \tag{2.22}$$

That is, the change in f depends only on the end points x_1 and x_2. We say that df is an exact differential. State functions have exact differentials. Examples of inexact and exact differentials are given in Section 2.24.1.

Originally, many scientists thought that there was a fluid called *heat* in all substances which could flow from one substance to another. This idea was abandoned many years ago, but it is still used in everyday language. Thus, people talk about adding heat to a system. We will avoid this use and whenever possible we will avoid the use of the noun "heat" altogether. Instead, we will refer to heating or cooling processes. These processes occur whenever two bodies at different temperatures are brought into thermal contact. In everyday language we say that heat flows from the hot to the cold body. In the context of thermodynamics we will say that energy is transferred from the hotter to the colder body. There is no need to invoke the noun "heat," and it is misleading to say that heat "flows" from one body to another.

To understand better that there is no such thing as the amount of heat in a body, consider the following simple analogy adapted from Callen. A farmer owns a pond, fed by one stream and drained by another. The pond also receives water from rainfall and loses water by evaporation. The pond is the system of interest, the water within it is analogous to the internal energy, the process of transferring water by the streams is analogous to doing work, the process of adding water by rainfall is analogous to heating, and the process of evaporation is analogous to cooling. The only quantity of interest is the amount of water, just as the only quantity of interest is energy in the thermal case. An examination of the change in the amount of water in the pond cannot tell us how the water got there. The terms rain and evaporation refer only to methods of water transfer, just as the terms work, heating, and cooling refer only to methods of energy transfer.

Another example is due to Bohren and Albrecht. Take a small plastic container and add just enough water to it so that its temperature can be conveniently measured. Let the water and the bottle come into equilibrium with their surroundings. Measure the temperature of the water, cap the bottle, and shake it until you are too tired to continue further. Then uncap the bottle and measure the water temperature again. If there were a "whole lot of shaking going on," you would find the temperature had increased a little.

In this example, the temperature of the water increased without heating. We did work on the water, which resulted in an increase in its internal energy as manifested by a rise in its temperature. The same increase in temperature could have been obtained by bringing the water into contact with a body at a higher temperature. It is impossible to determine by making measurements on the water whether shaking or heating was responsible for taking the system from its initial to its final macrostate. (To silence someone who objects that you heated the water with "body heat," wrap the bottle with an insulating material.)

Problem 2.10. Distinguishing different types of water transfer

How could the owner of the pond distinguish between the different types of water transfer assuming that the owner has flow meters, a tarpaulin, and a vertical pole? ☐

Problem 2.11. Convert the statement "I am cold, please turn on the heat," to the precise language of physics. ☐

Before the equivalence of heating and energy transfer was well established, a change in energy by heating was measured in calories. One calorie is the amount of energy needed to raise the temperature of one gram of water from 14.5°C to 15.5°C. We now know that one calorie is equivalent to 4.186 J, but the use of the calorie for energy transfer by heating and the joule for work still persists. Just to cause confusion, the calorie we use to describe the energy content of foods is actually a kilocalorie.

2.9 Energy Equation of State

In (2.8) we gave the pressure equation of state for an ideal gas. Now that we know that the internal energy is a state function, we need to know how E depends on two of the three variables, T, ρ, and N (for a simple fluid). The form of the *energy equation of state* for an ideal gas must also be determined empirically or calculated from first principles using statistical mechanics (see Section 4.5, page 194). From these considerations the energy equation of state for a monatomic gas is given by

$$E = \frac{3}{2}NkT \qquad \text{(ideal gas energy equation of state).} \tag{2.23}$$

Note that the energy of an ideal gas is independent of its density (for a fixed number of particles).

An approximate energy equation of state of a gas corresponding to the pressure equation of state (2.12) is given by

$$E = \frac{3}{2}NkT - N\frac{N}{V}a \qquad \text{(van der Waals energy equation of state).} \tag{2.24}$$

Note that the energy depends on the density $\rho = N/V$ if the interactions between particles are included.

Example 2.3. Work done on an ideal gas at constant temperature

Work is done on an ideal gas at constant temperature. What is the change in the energy of the gas?[12]

Solution. Because the energy of an ideal gas depends only on the temperature [see (2.23)], there is no change in its internal energy for an isothermal process. Hence, $\Delta E = 0 = Q + W$, and from (2.15) we have

$$Q = -W = NkT \ln \frac{V_2}{V_1} \qquad \text{(isothermal process, ideal gas)}. \tag{2.25}$$

We see that if work is done on the gas ($V_2 < V_1$), then the gas must give energy to its surroundings so that its temperature does not change. ♢

Extensive and intensive variables. The thermodynamic variables that we have introduced so far may be divided into two classes. Quantities such as the density ρ, the pressure P, and the temperature T are *intensive* variables and are *independent* of the size of the system. Quantities such as the volume V and the internal energy E are *extensive* variables and are *proportional* to the number of particles in the system (at fixed density). As we will see in Section 2.10, it often is convenient to convert extensive quantities to a corresponding intensive quantity by defining the ratio of two extensive quantities. For example, the energy per particle and the energy per unit mass are intensive quantities.

2.10 Heat Capacities and Enthalpy

We know that the temperature of a macroscopic system usually increases when we transfer energy to it by heating.[13] The magnitude of the increase in temperature depends on the nature of the body and how much of it there is. The amount of energy transfer due to heating required to produce a unit temperature rise in a given substance is called the *heat capacity* of the substance. Here again we see the archaic use of the word "heat." But because the term "heat capacity" is common, we will use it. If a body undergoes an increase of temperature from T_1 to T_2 due to an energy transfer Q, then the average heat capacity is given by the ratio

$$\text{average heat capacity} = \frac{Q}{T_2 - T_1}. \tag{2.26}$$

The value of the heat capacity depends on what constraints are imposed. We introduce the heat capacity at constant volume by the relation

$$C_V = \Big(\frac{\partial E}{\partial T}\Big)_V. \tag{2.27}$$

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[12] We mean the internal energy, as should be clear from the context. In the following we will omit the term internal and simply refer to the energy.

[13] What is a common counterexample?

Note that, if the volume V is held constant, the change in energy of the system is due only to the energy transferred by heating. We have adopted the common notation in thermodynamics of enclosing partial derivatives in parentheses and using subscripts to denote the variables that are held constant. In this context, it is clear that the differentiation in (2.27) is at constant volume, and we will write $C_V = \partial E/\partial T$ if there is no ambiguity.[14] (See Section 2.24.1 for a discussion of the mathematics of thermodynamics.)

Equation (2.27) together with (2.23) can be used to obtain the heat capacity at constant volume of a monatomic ideal gas:

$$C_V = \frac{3}{2}Nk \qquad \text{(monatomic ideal gas)}. \tag{2.28}$$

Note that the heat capacity at constant volume of an ideal gas is independent of the temperature.

The heat capacity is an extensive quantity, and it is convenient to introduce the *specific heat* which depends only on the nature of the material, not on the amount of the material. The conversion to an intensive quantity can be achieved by dividing the heat capacity by the amount of the material expressed in terms of the number of moles, the mass, or the number of particles. We will use lower case c for specific heat; the distinction between the various kinds of specific heats will be clear from the context and the units of c.

The enthalpy. The combination of thermodynamic variables $E + PV$ occurs sufficiently often to acquire its own name. The *enthalpy* H is defined as

$$\boxed{H = E + PV} \qquad \text{(enthalpy)}. \tag{2.29}$$

We can use (2.29) to find a simple expression for C_P, the heat capacity at constant pressure. From (2.13) and (2.21), we have $dE = dQ - PdV$ or $dQ = dE + PdV$. From the identity $d(PV) = PdV + VdP$, we can write $dQ = dE + d(PV) - VdP$. At constant pressure $dQ = dE + d(PV) = d(E + PV) = dH$. Hence, we can define the heat capacity at constant pressure as

$$C_P = \Big(\frac{\partial H}{\partial T}\Big)_P. \tag{2.30}$$

We will learn that the enthalpy is another state function which often makes the analysis of a system simpler. At this point, we see that C_P can be expressed more simply in terms of the enthalpy.

We can find C_P for an ideal gas by writing $H = E + PV = \frac{3}{2}NKT + NkT$ and using the relation (2.30) to find that $C_P = \frac{5}{2}Nk$, and thus

$$C_P = C_V + Nk \qquad \text{(ideal gas)}. \tag{2.31}$$

Note that we used the two equations of state, (2.8) and (2.23), to obtain C_P, and we did not have to make an independent measurement or calculation.

Why is C_P greater than C_V? Unless we prevent it from doing so, a system normally expands as its temperature increases. The system has to do work on its surroundings as it expands. Hence, when a system is heated at constant pressure, energy is needed both to increase the temperature of

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[14] Although the number of particles also is held constant, we will omit the subscript N in (2.27) and in other partial derivatives to reduce the number of subscripts.

the system and to do work on its surroundings. In contrast, if the volume is kept constant, no work is done on the surroundings and the heating only has to supply the energy required to raise the temperature of the system. We will derive the general relation $C_P > C_V$ for any thermodynamic system in Section 2.22.

Problem 2.12. Heat capacities large and small

Give some examples of materials that have either a small or a large heat capacity relative to that of water. You can find values of the heat capacity in books on materials science and on the internet. □

Example 2.4. Heating water

A water heater holds 150 kg of water. How much energy is required to raise the water temperature from 18°C to 50°C?

Solution. The (mass) specific heat of water is $c = 4184\,\mathrm{J/kg\ K}$. (The difference between the specific heats of water at constant volume and constant pressure is negligible at room temperatures.) The energy required to raise the temperature by 32°C is

$$Q = mc(T_2 - T_1) = 150\,\mathrm{kg} \times (4184\,\mathrm{J/kg\,K}) \times (50^\circ\mathrm{C} - 18^\circ\mathrm{C}) = 2 \times 10^7\,\mathrm{J}. \tag{2.32}$$

We have assumed that the specific heat is constant in this temperature range. ♢

Note that, when calculating temperature *differences*, it is often more convenient to express temperatures in Celsius, because the kelvin is exactly the same magnitude as a degree Celsius.

Example 2.5. Cooling a brick

A 1.5 kg glass brick is heated to 180°C and then plunged into a cold bath containing 10 kg of water at 20°C. Assume that none of the water boils and there is no heating of the surroundings. What is the final temperature of the water and the glass? The specific heat of glass is approximately 750 J/kg K.

Solution. Conservation of energy implies that

$$\Delta E_{\mathrm{glass}} + \Delta E_{\mathrm{water}} = 0, \tag{2.33a}$$

or

$$m_{\mathrm{glass}} c_{\mathrm{glass}} (T - T_{\mathrm{glass}}) + m_{\mathrm{water}} c_{\mathrm{water}} (T - T_{\mathrm{water}}) = 0. \tag{2.33b}$$

The final equilibrium temperature T is the same for both. We solve for T and obtain

$$\begin{aligned} T &= \frac{m_{\mathrm{glass}} c_{\mathrm{glass}} T_{\mathrm{glass}} + m_{\mathrm{water}} c_{\mathrm{water}} T_{\mathrm{water}}}{m_{\mathrm{glass}} c_{\mathrm{glass}} + m_{\mathrm{water}} c_{\mathrm{water}}} & \text{(2.34a)} \\ &= \frac{(1.5\,\mathrm{kg})(750\,\mathrm{J/kg\,K})(180^\circ\mathrm{C}) + (10\,\mathrm{kg})(4184\,\mathrm{J/kg\,K})(20^\circ\mathrm{C})}{(1.5\,\mathrm{kg})(750\,\mathrm{J/kg\,K}) + (10\,\mathrm{kg})(4184\,\mathrm{J/kg\,K})} & \text{(2.34b)} \\ &= 24.2^\circ\mathrm{C}. & \text{(2.34c)} \end{aligned}$$

□

Example 2.6. Energy needed to increase the temperature

The temperature of two moles of helium gas is increased from 10°C to 30°C at constant volume. How much energy is needed to accomplish this temperature change?

Solution. Because the amount of He gas is given in moles, we need to know its molar specific heat. Helium gas can be well approximated by an ideal gas so we can use (2.28). The molar specific heat is given by [see (2.11)] $c_V = 3R/2 = 1.5 \times 8.314 = 12.5\,\mathrm{J/mole\,K}$. Because c_V is constant, we have

$$\Delta E = Q = \int C_V\,dT = \nu c_V \int dT = 2\,\mathrm{mole} \times 12.5\,\frac{\mathrm{J}}{\mathrm{mole\,K}} \times 20\,\mathrm{K} = 500\,\mathrm{J}. \tag{2.35}$$

♢

Example 2.7. A solid at low temperatures

At very low temperatures the heat capacity of an insulating solid is proportional to T^3. If we take $C = AT^3$ for a particular solid, what is the energy needed to raise the temperature from T_1 to T_2? The difference between C_V and C_P can be ignored at low temperatures. (In Section 6.9, we will use the Debye theory to express the constant A in terms of the speed of sound and other parameters and find the range of temperatures for which the T^3 behavior is a reasonable approximation.)

Solution. Because C is temperature dependent, we have to express the energy transferred as an integral:

$$Q = \int_{T_1}^{T_2} C(T)\,dT. \tag{2.36}$$

In this case we have

$$Q = A\int_{T_1}^{T_2} T^3\,dT = \frac{A}{4}(T_2^4 - T_1^4). \tag{2.37}$$

♢

Problem 2.13. In Example 2.1 we showed that the net work done on the gas in the cyclic process shown in Figure 2.4 is nonzero. Assume that the gas is ideal with N particles and calculate the energy transfer by heating in each step of the process. Then explain why the net work done on the gas is negative and show that the net change of the internal energy is zero. □

2.11 Quasistatic Adiabatic Processes

So far we have considered processes at constant temperature, constant volume, and constant pressure.[15] We have also considered *adiabatic processes* which occur when the system does not exchange energy with its surroundings due to a temperature difference. Note that an adiabatic process need not be isothermal.

Problem 2.14. Give some examples of adiabatic processes. □

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[15] These processes are called *isothermal*, *isochoric*, and *isobaric*, respectively.

We now show that the pressure of an ideal gas changes more for a given change of volume in a quasistatic adiabatic process than it does in an isothermal process. For an adiabatic process the first law reduces to

$$dE = dW = -PdV \qquad \text{(adiabatic process)}. \tag{2.38}$$

In an adiabatic process the energy can change due to a change in temperature or volume and thus

$$dE = \Big(\frac{\partial E}{\partial T}\Big)_V dT + \Big(\frac{\partial E}{\partial V}\Big)_T dV. \tag{2.39}$$

The first derivative in (2.39) is equal to C_V. Because $(\partial E/\partial V)_T = 0$ for an ideal gas, (2.39) reduces to

$$dE = C_V dT = -PdV \qquad \text{(adiabatic process, ideal gas)}, \tag{2.40}$$

where we have used (2.38). The easiest way to proceed is to eliminate P in (2.40) using the ideal gas law $PV = NkT$:

$$C_V dT = -NkT\frac{dV}{V}. \tag{2.41}$$

We next eliminate Nk in (2.41) in terms of $C_P - C_V$ and express (2.41) as

$$\frac{C_V}{C_P - C_V}\frac{dT}{T} = \frac{1}{\gamma - 1}\frac{dT}{T} = -\frac{dV}{V}. \tag{2.42}$$

The symbol γ is the ratio of the heat capacities:

$$\gamma = \frac{C_P}{C_V}. \tag{2.43}$$

For an ideal gas C_V and C_P and hence γ are independent of temperature, and we can integrate (2.42) to obtain

$$TV^{\gamma-1} = \text{constant} \qquad \text{(quasistatic adiabatic process)}. \tag{2.44}$$

For an ideal monatomic gas, we have from (2.28) and (2.31) that $C_V = 3Nk/2$ and $C_P = 5Nk/2$, and hence

$$\gamma = 5/3 \qquad \text{(ideal monatomic gas)}. \tag{2.45}$$

Problem 2.15. Use (2.44) and the ideal gas pressure equation of state in (2.8) to show that in a quasistatic adiabatic processes P and V are related as

$$PV^\gamma = \text{constant}. \tag{2.46}$$

Also show that T and P are related as

$$TP^{(1-\gamma)/\gamma} = \text{constant}. \tag{2.47}$$

□

The relations (2.44)–(2.47) hold for a quasistatic adiabatic process of an ideal gas.[16] Because $\gamma > 1$, the relation (2.46) implies that for a given volume change, the pressure changes more for an adiabatic process than it does for a comparable isothermal process for which $PV = \text{constant}$. We

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[16] An easier derivation is suggested in Problem 2.24.

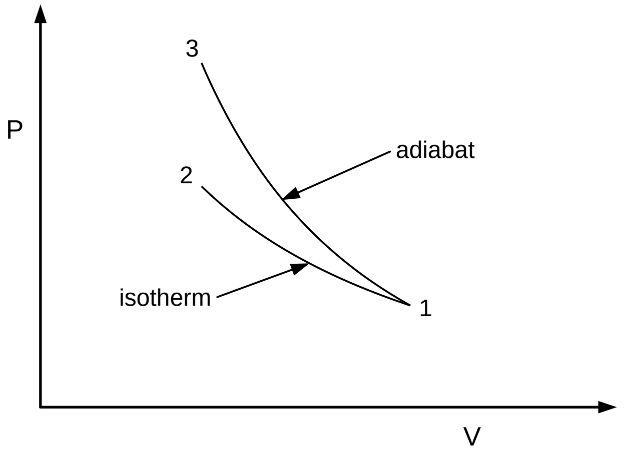

Figure 2.5: Comparison of an isothermal and an adiabatic process. The two processes begin at the same volume V_1, but the adiabatic process has a steeper slope and ends at a higher pressure.

can understand the reason for this difference as follows. For an isothermal compression the pressure increases and the internal energy of an ideal gas does not change. For an adiabatic compression the energy increases because we have done work on the gas and no energy can be transferred by heating or cooling by the surroundings. The increase in the energy causes the temperature to increase. Hence, in an adiabatic compression, both the decrease in the volume and the increase in the temperature cause the pressure to increase more.

In Figure 2.5 we show the P-V diagram for both isothermal and adiabatic processes. The adiabatic curve has a steeper slope than the isothermal curves at any point. From (2.46) we see that the slope of an adiabatic curve for an ideal gas is

$$\Big(\frac{\partial P}{\partial V}\Big)_{\text{adiabatic}} = -\gamma\frac{P}{V}, \tag{2.48}$$

in contrast to the slope of an isothermal curve for an ideal gas:

$$\Big(\frac{\partial P}{\partial V}\Big)_{T} = -\frac{P}{V}. \tag{2.49}$$

How can the ideal gas relations $PV^\gamma = \text{constant}$ and $PV = NkT$ both be correct? The answer is that $PV = \text{constant}$ only for an isothermal process. A quasistatic ideal gas process cannot be both adiabatic and isothermal. During an adiabatic process, the temperature of an ideal gas must change. Note that $PV = NkT$ is valid for an ideal gas during any process, but care must be exercised in using this relation because any of the four variables P, V, N, and T can change in a given process.

Problem 2.16. Although we do work on an ideal gas when we compress it isothermally, why does the energy of the gas not increase? □

Example 2.8. Adiabatic and isothermal expansion

Two identical systems each contain $\nu = 0.1$ mole of an ideal gas at $T = 300\,\mathrm{K}$ and $P = 2.0 \times 10^5\,\mathrm{Pa}$. The pressure in the two systems is reduced by a factor of 2, allowing the systems to expand, one adiabatically and one isothermally. What are the final temperatures and volumes of each system? Assume that $\gamma = 5/3$.

Solution. The initial volume V_1 is given by

$$V_1 = \frac{\nu R T_1}{P_1} = \frac{0.1\,\mathrm{mole} \times 8.3\,\mathrm{J/(K\,mole)} \times 300\,\mathrm{K}}{2.0 \times 10^5\,\mathrm{Pa}} = 1.245 \times 10^{-3}\,\mathrm{m}^3. \tag{2.50}$$

For the isothermal system, PV remains constant, so the volume doubles as the pressure decreases by a factor of 2, and hence $V_2 = 2.49 \times 10^{-3}\,\mathrm{m}^3$. Because the process is isothermal, the temperature remains at 300 K.

For adiabatic compression we have

$$V_2^\gamma = \frac{P_1 V_1^\gamma}{P_2}, \tag{2.51}$$

or

$$V_2 = \Big(\frac{P_1}{P_2}\Big)^{1/\gamma} V_1 = 2^{3/5} \times 1.245 \times 10^{-3}\,\mathrm{m}^3 = 1.89 \times 10^{-3}\,\mathrm{m}^3. \tag{2.52}$$

We see that for a given pressure change the volume change for the adiabatic process is greater. We leave it as an exercise to show that $T_2 = 250\,\mathrm{K}$. ♢

Problem 2.17. Compression of air

Air initially at 20°C is compressed by a factor of 15.

(a) What is the final temperature assuming that the compression is adiabatic and $\gamma \approx 1.4$,[17] the value of γ for air in the relevant range of temperatures? By what factor does the pressure increase?

(b) By what factor does the pressure increase if the compression is isothermal?

(c) For which process does the pressure change more? □

How much work is done in a quasistatic adiabatic process? Because $Q = 0$, $\Delta E = W$. For an ideal gas, $\Delta E = C_V \Delta T$ for any process. Hence for a quasistatic adiabatic process

$$W = C_V (T_2 - T_1) \qquad \text{(quasistatic adiabatic process, ideal gas).} \tag{2.53}$$

In Problem 2.18 you are asked to show that (2.53) can be expressed in terms of the pressure and volume as

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}. \tag{2.54}$$

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[17] The ratio γ equals 5/3 for an ideal gas of particles when only translational motion is important. We will learn in Section 6.2.1 how to calculate γ for molecules with rotational and vibrational contributions to the energy.

Problem 2.18. Work done in a quasistatic adiabatic process

(a) Use the result that we derived in (2.53) to obtain the alternative form (2.54).

(b) Show that another way to derive (2.54) is to use the relations (2.14) and (2.46). □

Example 2.9. Compression ratio of a diesel engine

Compression in a diesel engine occurs quickly enough so that very little heating of the environment occurs, and thus the process may be considered adiabatic. If a temperature of 500°C is required for ignition, what is the compression ratio? Assume that the air can be treated as an ideal gas with $\gamma = 1.4$, and the temperature is 20°C before compression.

Solution. Equation (2.44) gives the relation between T and V for a quasistatic adiabatic process. We write T_1 and V_1 and T_2 and V_2 for the temperature and volume at the beginning and the end of the piston stroke. Then (2.46) becomes

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}. \tag{2.55}$$

Hence the compression ratio V_1/V_2 is

$$\frac{V_1}{V_2} = \Big(\frac{T_2}{T_1}\Big)^{1/(\gamma-1)} = \Big(\frac{773\,\mathrm{K}}{293\,\mathrm{K}}\Big)^{1/0.4} = 11. \tag{2.56}$$

It is only an approximation to assume that the compression is quasistatic in a diesel engine. ♢

2.12 The Second Law of Thermodynamics

The consequences of the first law of thermodynamics are that energy is conserved in thermal processes and heating is a form of energy transfer. We also noted that the internal energy of a system can be identified with the sum of the potential and kinetic energies of the particles.

As was discussed in Chapter 1, there are many processes that do not occur in nature, but whose occurrence would be consistent with the first law. For example, the first law does not prohibit energy from being transferred spontaneously from a cold body to a hot body, yet it has never been observed. There is another property of systems that must be taken into account, and this property is called the *entropy*.[18]

Entropy is another example of a state function. One of the remarkable achievements of the nineteenth century was the reasoning that such a state function must exist without any idea of how to measure its value directly. In Chapter 4 we will learn about the relation between the entropy and the number of possible microscopic states, but for now we will follow a logic that does not depend on any knowledge of the microscopic behavior.

It is not uncommon to use heating as a means of doing work. For example, power plants burn oil or coal to turn water into steam, which in turn turns a turbine in a magnetic field, creating electricity which then can do useful work in your home. Can we completely convert all the energy

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[18] This thermodynamic variable was named by Rudolf Clausius in 1850 who formed the word *entropy* (from the Greek word for transformation) so as to be as similar as possible to the word energy.

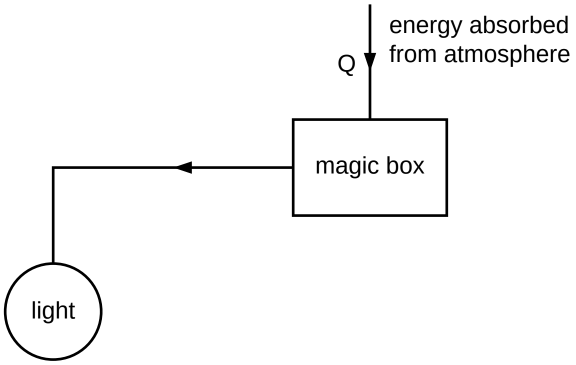

Figure 2.6: A machine that converts energy transferred by heating into work with 100% efficiency violates the Kelvin statement of the second law of thermodynamics.

created by chemical reactions into work? Can we cool a system and use *all* the energy lost by the system to do work? Our everyday experience tells us that we cannot. If it were possible, we could power a boat to cross the Atlantic by cooling the sea and transferring energy from the sea to drive the propellers. We would need no fuel and travel would be much cheaper. Or instead of heating a fluid by doing electrical work on a resistor, we could consider a process in which a resistor cools the fluid and produces electrical energy at its terminals. The fact that these processes do not occur is summarized in one of the statements of the second law of thermodynamics:

> *It is impossible to construct an engine which, operating in a cycle, will produce no other effect than the extraction of energy from a reservoir and the performance of an equivalent amount of work* (Kelvin-Planck statement).[19]

This form of the second law implies that a *perpetual motion machine of the second kind* does not exist. Such a machine would convert energy completely into work (see Figure 2.6).

What about the isothermal expansion of an ideal gas? Does this process violate the second law? When the gas expands, it does work on the piston which causes the gas to lose energy. Because the process is isothermal, the gas must absorb energy so that its internal energy remains constant. (The internal energy of an ideal gas depends only on the temperature.) We have

$$\Delta E = Q + W = 0. \tag{2.57}$$

We see that $W = -Q$, that is, the work done on the gas is $-Q$ and the work done by the gas is Q. We conclude that we have completely converted the absorbed energy into work. However, this conversion does not violate the Kelvin-Planck statement because the macrostate of the gas is different at the end than at the beginning; that is, the isothermal expansion of an ideal gas is not a cyclic process. We cannot use this process to make an engine.

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[19] The original statement by Kelvin is "It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects." Planck wrote "It is impossible to construct an engine, which working in a complete cycle, will produce no effect other than the raising of a weight and the cooling of a heat reservoir." See Zemansky and Dittman, p. 147.

Another statement of the second law based on the empirical observation that energy does not spontaneously go from a colder to a hotter body can be stated as follows:

> *No process is possible whose sole result is cooling a colder body and heating a hotter body* (Clausius statement).

The Kelvin-Planck and the Clausius statements of the second law look different, but each statement and the first law implies the other so their consequences are identical.

We will adopt a more abstract version of the second law that is not based directly on experimental observations, but is more convenient in many contexts:

> *There exists an additive function of state known as the entropy S that can never decrease in an isolated system.*

Because the entropy cannot decrease in an isolated system, we conclude that the entropy is a *maximum* for an isolated system in equilibrium.[20] The term *additive* means that if the entropy of two systems is S_A and S_B, respectively, the total entropy of the combined system is $S = S_A + S_B$. In the following we show that the Kelvin and Clausius statements follow from this version of the second law.

The statement of the second law in terms of the entropy is applicable only to isolated systems (a system enclosed by insulating, rigid, and impermeable walls). Most systems of interest can exchange energy with their surroundings. In many cases the surroundings may be idealized as a large body that does not interact with the rest of the universe. For example, we can take the surroundings of a cup of hot water to be the air in the room. In this case we can treat the *composite* system, system plus surroundings, as isolated. For the composite system, we have for any process

$$\Delta S_{\text{composite}} \geq 0, \tag{2.58}$$

where $S_{\text{composite}}$ is the entropy of the system plus its surroundings.

If a change is reversible, we cannot have $\Delta S_{\text{composite}} > 0$, because if we reverse the change, we would have $\Delta S_{\text{composite}} < 0$, a violation of the Clausius statement as we shall soon see. Hence, the only possibility is that

$$\Delta S_{\text{composite}} = 0 \qquad \text{(reversible process)}. \tag{2.59}$$

To avoid confusion, we will use the term reversible to be equivalent to a constant entropy process. The condition for a process to be reversible requires only that the total entropy of a closed system is constant; the entropies of its parts may increase or decrease.

2.13 The Thermodynamic Temperature

The Clausius and Kelvin-Planck statements of the second law arose from the importance of heat engines to the development of thermodynamics. A seemingly different purpose of thermodynamics

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[20] Maximum and minimum principles are ubiquitous in physics. Leonhard Euler wrote that "Nothing whatsoever takes place in the universe in which some relation of maximum and minimum does not appear."

is to determine the conditions of equilibrium. These two purposes are linked by the fact that whenever there is a difference of temperature, work can be done.

In the following we derive the properties of the thermodynamic temperature from the second law. In Section 2.16 we will show that this temperature is the same as the ideal gas scale temperature introduced in Section 2.2.

Consider an isolated composite system that is partitioned into two *subsystems* A and B by a fixed, impermeable, insulating wall. For the composite system we have

$$E = E_A + E_B = \text{constant}, \tag{2.60}$$

$V = V_A + V_B = \text{constant}$, and $N = N_A + N_B = \text{constant}$. Because the entropy is additive, we can write the total entropy as

$$S(E_A, V_A, N_A, E_B, V_B, N_B) = S_A(E_A, V_A, N_A) + S_B(E_B, V_B, N_B). \tag{2.61}$$

Most divisions of the energy E_A and E_B between subsystems A and B do not correspond to thermal equilibrium.

For thermal equilibrium to be established we replace the fixed, impermeable, *insulating* wall by a fixed, impermeable, *conducting* wall so that the two subsystems are in thermal contact and energy transfer by heating or cooling may occur. We say that we have removed an *internal constraint.* According to our statement of the second law, the values of E_A and E_B will be such that the entropy of the composite system becomes a maximum. To find the value of E_A that maximizes S as given by (2.61), we calculate

$$dS = \Big(\frac{\partial S_A}{\partial E_A}\Big)_{V_A,N_A} dE_A + \Big(\frac{\partial S_B}{\partial E_B}\Big)_{V_B,N_B} dE_B. \tag{2.62}$$

Because the total energy of the system is conserved, we have $dE_B = -dE_A$, and hence

$$dS = \Big[\Big(\frac{\partial S_A}{\partial E_A}\Big)_{V_A,N_A} - \Big(\frac{\partial S_B}{\partial E_B}\Big)_{V_B,N_B}\Big] dE_A. \tag{2.63}$$

The condition for equilibrium is that $dS = 0$ for arbitrary values of dE_A, and hence

$$\Big(\frac{\partial S_A}{\partial E_A}\Big)_{V_A,N_A} = \Big(\frac{\partial S_B}{\partial E_B}\Big)_{V_B,N_B}. \tag{2.64}$$

Because the temperatures of the two systems are equal in thermal equilibrium, we conclude that the derivative $\partial S/\partial E$ must be associated with the temperature. We will find that it is convenient to define the thermodynamic temperature T as

$$\boxed{\frac{1}{T} \equiv \Big(\frac{\partial S}{\partial E}\Big)_{V,N}} \qquad \text{(thermodynamic temperature)}, \tag{2.65}$$

which implies that the condition for thermal equilibrium is

$$\frac{1}{T_A} = \frac{1}{T_B}, \tag{2.66}$$

or $T_A = T_B$.

We have found that, if two systems are separated by a conducting wall, energy will be transferred until the systems reach the same temperature. Now suppose that the two systems are initially separated by an insulating wall and that the temperatures of the two systems are almost equal with $T_A > T_B$. If this constraint is removed, we know that energy will be transferred across the conducting wall and the entropy of the composite system will increase. From (2.63) we can write the change in entropy of the composite system as

$$\Delta S \approx \Big[\frac{1}{T_A} - \frac{1}{T_B}\Big]\Delta E_A > 0, \tag{2.67}$$

where T_A and T_B are the initial values of the temperatures. The condition that $T_A > T_B$ requires that $\Delta E_A < 0$ in order for $\Delta S > 0$ in (2.67) to be satisfied. Hence, we conclude that the definition (2.65) of the thermodynamic temperature implies that energy is transferred from a system with a higher value of T to a system with a lower value of T.

We can express (2.67) as follows: *No process exists in which a cold body becomes cooler while a hotter body becomes still hotter and the constraints on the bodies and the state of its surroundings are unchanged.* We recognize this statement as the Clausius statement of the second law.

Note that the inverse temperature can be interpreted as the response of the entropy to a change in the energy of the system. In Section 2.17 we will derive the condition for *mechanical equilibrium*, and in Chapter 7 we will discuss the condition for *chemical equilibrium*. These two conditions complement the condition for thermal equilibrium. All three conditions must be satisfied for *thermodynamic equilibrium* to be established.

The definition (2.65) of T is not unique, and we could have replaced $1/T$ by other functions of temperature such as $1/T^2$ or $1/\sqrt{T}$. However, we will find in Section 2.16 that the definition (2.65) implies that the thermodynamic temperature is identical to the ideal gas scale temperature.

2.14 The Second Law and Heat Engines

A body that can change the temperature of another body without changing its own temperature and without doing work is known as a *heat bath*. The term is archaic, but we will adopt it because of its common usage.[21] A heat bath can be either a heat source or a heat sink. Examples of a heat source and a heat sink, depending on the circumstances, are the Earth's ocean and atmosphere. If we want to measure the electrical conductivity of a small block of copper at a certain temperature, we can place it into a large body of water that is at the desired temperature. The temperature of the copper will become equal to the temperature of the large body of water, whose temperature will be unaffected by the copper.

For pure heating or cooling the increase in the entropy is given by

$$dS = \Big(\frac{\partial S}{\partial E}\Big)_{V,N} dE. \tag{2.68}$$

In this case $dE = dQ$ because no work is done. If we express the partial derivative in (2.68) in terms of T, we can rewrite (2.68) as

$$dS = \frac{dQ}{T} \qquad \text{(pure heating)}. \tag{2.69}$$

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[21] The terms thermal bath and heat reservoir are also used.

We emphasize that the relation (2.69) holds only for quasistatic changes. Note that (2.69) implies that *the entropy does not change in a quasistatic, adiabatic process.*

We now use (2.69) to discuss the problem that motivated the development of thermodynamics – the efficiency of heat engines. We know that an engine converts energy from a heat source to work and returns to its initial state. According to (2.69), the transfer of energy from a heat source lowers the entropy of the source. If the energy transferred is used to do work, the work done must be done on some other system. Because the process of doing this work may be quasistatic and adiabatic, the work done need not involve a change of entropy. But if all of the energy transferred were converted into work, the total entropy would decrease, and we would violate the entropy statement of the second law. Hence, we arrive at the conclusion summarized in the Kelvin-Planck statement of the second law: no process is possible whose sole result is the complete conversion of energy into work. We need to do something with the energy that was not converted to work.

The simplest possible engine works in conjunction with a heat source at temperature $T_{\rm high}$ and a heat sink at temperature $T_{\rm low}$. In a cycle the heat source transfers energy $Q_{\rm high}$ to the engine, and the engine does work W and transfers energy $Q_{\rm low}$ to the heat sink (see Figure 2.7). At the end of one cycle, the energy and entropy of the engine are unchanged because they return to their original values.

We have defined the work W done on a system as positive. However, in the context of engines, it is more natural to define the work done by the system as positive because that work is the output of the system. Hence, in this section we will take $Q_{\rm high}$, $Q_{\rm low}$, and W to be positive quantities, and explicitly put in minus signs where needed. From the arrows in Figure 2.7 we see that the input to the engine is $Q_{\rm high}$ and the output is W and $Q_{\rm low}$. Hence, we have $Q_{\rm high} = W + Q_{\rm low}$, or $W = Q_{\rm high} - Q_{\rm low}$. From the second law we have that

$$\Delta S_{\rm total} = \Delta S_{\rm high} + \Delta S_{\rm low} = -\frac{Q_{\rm high}}{T_{\rm high}} + \frac{Q_{\rm low}}{T_{\rm low}} \geq 0. \tag{2.70}$$

We rewrite (2.70) as

$$\frac{Q_{\rm low}}{Q_{\rm high}} \geq \frac{T_{\rm low}}{T_{\rm high}}. \tag{2.71}$$

The *thermal efficiency* η of the engine is defined as

$$\begin{aligned} \eta &= \frac{\text{what you obtain}}{\text{what you pay for}} && (2.72)\\ &= \frac{W}{Q_{\rm high}} = \frac{Q_{\rm high} - Q_{\rm low}}{Q_{\rm high}} = 1 - \frac{Q_{\rm low}}{Q_{\rm high}}. && (2.73) \end{aligned}$$

From (2.73) we see that the engine is most efficient when the ratio $Q_{\rm low}/Q_{\rm high}$ is as small as possible. Equation (2.71) shows that $Q_{\rm low}/Q_{\rm high}$ is a minimum when the cycle is reversible or

$$\Delta S_{\rm total} = 0, \tag{2.74}$$

and

$$\frac{Q_{\rm low}}{Q_{\rm high}} = \frac{T_{\rm low}}{T_{\rm high}}. \tag{2.75}$$

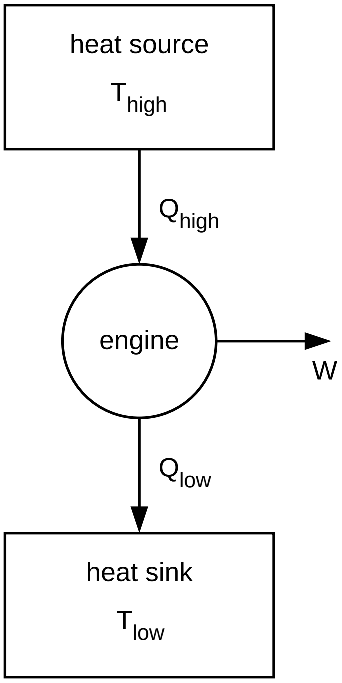

Figure 2.7: Schematic energy transfer diagram for an ideal heat engine. The convention when analyzing energy transfers in the context of engines is that the quantities $Q_{\rm high}$, $Q_{\rm low}$, and W are taken to be positive.

For these conditions we find that the maximum thermal efficiency is

$$\eta = 1 - \frac{T_{\rm low}}{T_{\rm high}} \qquad \text{(maximum thermal efficiency).} \tag{2.76}$$

Note that the temperature in (2.76) is the thermodynamic temperature. A reversible engine of this type is known as a *Carnot engine*.

The result (2.76) illustrates the remarkable power of thermodynamics. We have concluded that all reversible engines operating between a heat source and a heat sink with the same pair of temperatures have the same efficiency and that no irreversible engine working between the same pair of temperatures may have a greater efficiency. This statement is known as *Carnot's principle.* We have been able to determine the maximum efficiency of a reversible engine without knowing anything about the details of the engine.

Real engines never reach the maximum thermodynamic efficiency because of the presence of mechanical friction and because the processes cannot really be quasistatic. For these reasons, real engines seldom attain more than 30–40% of the maximum thermodynamic efficiency. Nevertheless, the basic principles of thermodynamics are an important factor in their design.

Example 2.10. A Carnot engine

A Carnot engine extracts 250 J from a heat source and rejects 100 J to a heat sink at 15°C in one cycle. How much work does the engine do in one cycle? What is its efficiency? What is the temperature of the heat source?

Solution. From the first law we have

$$W = 250\,\mathrm{J} - 100\,\mathrm{J} = 150\,\mathrm{J}. \tag{2.77}$$

The efficiency is given by

$$\eta = \frac{W}{Q_{\rm high}} = \frac{150}{250} = 0.6 = 60\%. \tag{2.78}$$

We can use this result for η and the general relation (2.76) to solve for $T_{\rm high}$:

$$T_{\rm high} = \frac{T_{\rm low}}{1-\eta} = \frac{288\,\mathrm{K}}{1-0.6} = 720\,\mathrm{K}. \tag{2.79}$$

Note that we must use the thermodynamic temperature to calculate the efficiency. ♢

Example 2.11. The efficiency of a hypothetical engine

The cycle of a hypothetical engine is illustrated in Figure 2.8. Let $P_{\rm low} = 1 \times 10^6\,\mathrm{Pa}$, $P_{\rm high} = 2 \times 10^6\,\mathrm{Pa}$, $V_{\rm low} = 5 \times 10^{-3}\,\mathrm{m}^3$, and $V_{\rm high} = 25 \times 10^{-3}\,\mathrm{m}^3$. If the energy absorbed by heating the engine is $5 \times 10^4\,\mathrm{J}$, what is the efficiency of the engine?

Solution. The magnitude of the work done by the engine equals the area enclosed:

$$W = \frac{1}{2}(P_{\rm high} - P_{\rm low})(V_{\rm high} - V_{\rm low}). \tag{2.80}$$

(Recall that the convention in the treatment of heat engines is that all energy transfers are taken to be positive.) Confirm that $W = 1 \times 10^4\,\mathrm{J}$. The efficiency is given by

$$\eta = \frac{W}{Q_{\rm absorbed}} = \frac{1 \times 10^4}{5 \times 10^4} = 0.20. \tag{2.81}$$

Note that, even if the engine operated reversibly, we cannot use the Carnot efficiency because we have no assurance that the engine is operating between two heat baths. ♢

The maximum efficiency of a Carnot engine depends on the temperatures $T_{\rm high}$ and $T_{\rm low}$ in a simple way and not on the details of the cycle or working substance. The *Carnot cycle* is a particular sequence of idealized processes that yields the maximum thermodynamic efficiency given in (2.76). The four steps of the Carnot cycle (two adiabatic and two isothermal steps) are illustrated in Figure 2.9. The initial state is at 1. The system is in contact with a heat bath at temperature $T_{\rm high}$ so that the temperature of the system also is $T_{\rm high}$. The system volume is small and its pressure is high.

$1 \to 2$, *isothermal expansion.* The system expands while it is in contact with the heat source. During the expansion the high pressure gas pushes on the piston and the piston turns a crank. This step is a power stroke of the engine and the engine does work. To keep the system at the same temperature, the engine must absorb energy from the heat source.

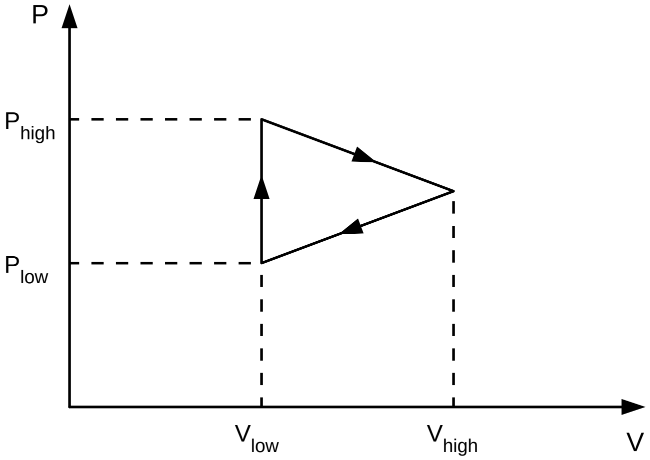

Figure 2.8: The cycle of the hypothetical engine considered in Example 2.11. Take $P_{\rm low} = 1 \times 10^6\,$Pa, $P_{\rm high} = 2 \times 10^6\,$Pa, $V_{\rm low} = 5 \times 10^{-3}\,$m^3, and $V_{\rm high} = 25 \times 10^{-3}\,$m^3.

We could compress the system isothermally and return the system to its initial state. Although this step would complete the cycle, exactly the same amount of work would be needed to push the piston back to its original position and hence no net work would be done. To make the cycle useful, we have to choose a cycle so that not all the work of the power stroke is lost in restoring the system to its initial pressure, temperature, and volume. The idea is to reduce the pressure of the system so that during the compression step less work has to be done. One way of reducing the pressure is to lower the temperature of the system by doing an adiabatic expansion.

$2 \to 3$, *adiabatic expansion.* We remove the thermal contact of the system with the hot bath and allow the volume to continue to increase so that the system expands adiabatically. Both the pressure and the temperature of the system decrease. The step $2 \to 3$ is also a power stroke, but now we are cashing in on the energy stored in the system, because it can no longer take energy from the heat source.

$3 \to 4$, *isothermal compression.* We now begin to restore the system to its initial condition. At 3 the system is placed in contact with the heat sink at temperature $T_{\rm low}$ to ensure that the pressure remains low. Work is done on the system by pushing on the piston and compressing the system. As the system is compressed, the temperature of the system would rise, but the thermal contact with the heat sink ensures that the temperature remains at $T_{\rm low}$. The extra energy is dumped into the heat sink.

$4 \to 1$, *adiabatic compression.* At 4 the volume is almost what it was initially, but the temperature of the system is too low. Before the piston returns to its initial state, we remove the contact with the heat sink and allow the work of adiabatic compression to increase the temperature of the system to $T_{\rm high}$.

These four steps represent a complete cycle, and the idealized engine is ready to go through another cycle. Note that a net amount of work has been done, because more work was done *by* the system during its power strokes than was done *on* the system while it was compressed. The reason is that the work done during the compression steps was against a lower pressure. The result is

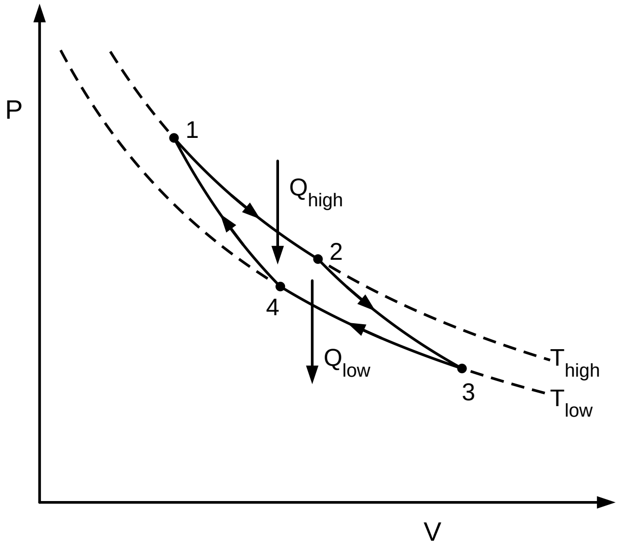

Figure 2.9: The four steps of the Carnot cycle.

that we have extracted useful work, and some of the energy of the system was discarded into the heat sink while the system was being compressed. The price we have had to pay to do work by having the system heated by the heat source is to throw away some of the energy to the heat sink.

Example 2.12. The Carnot cycle for an ideal gas

Determine the changes in the various thermodynamic quantities of interest during each step of the Carnot cycle and show that the efficiency of a Carnot cycle whose working substance is an ideal gas is given by $\eta = 1 - T_{\rm low}/T_{\rm high}$.

Solution. We will use the P-V diagram for the engine shown in Figure 2.9. During the isothermal expansion $1 \to 2$, energy $Q_{\rm high}$ is absorbed by the gas by heating at temperature $T_{\rm high}$. The expanding gas does positive work against its environment, which lowers the energy of the gas. However, $\Delta E = 0$ for an ideal gas along an isotherm and thus the gas must receive energy by heating given by

$$Q_{\rm high} = |W_{1\to 2}| = NkT_{\rm high} \ln \frac{V_2}{V_1}, \tag{2.82}$$

where $W_{1\to 2} = -\int_{V_1}^{V_2} P\,dV$ is the work done on the gas, which is negative. The work done by the gas is thus positive.

During the adiabatic expansion $2 \to 3$, $Q_{2\to 3} = 0$ and $W_{2\to 3} = |C_V(T_{\rm low} - T_{\rm high})|$. Similarly, $W_{3\to 4} = -NkT_{\rm low} \ln V_4/V_3$, and because $Q_{\rm low}$ is positive by convention, we have

$$Q_{\rm low} = \left| NkT_{\rm low} \ln \frac{V_4}{V_3} \right| = NkT_{\rm low} \ln \frac{V_3}{V_4}. \tag{2.83}$$

Finally, during the adiabatic compression $4 \to 1$, $Q_{4\to 1} = 0$ and $W_{4\to 1} = |C_V(T_{\rm low} - T_{\rm high})|$. We also have $W_{\rm net} = Q_{\rm high} - Q_{\rm low}$, where $W_{\rm net}$, $Q_{\rm high}$, and $Q_{\rm low}$ are positive quantities.

Because the product $TV^{\gamma-1}$ is a constant in a quasistatic adiabatic process, we have

$$T_{\rm high}V_2^{\gamma-1} = T_{\rm low}V_3^{\gamma-1} \tag{2.84a}$$

$$T_{\rm low}V_4^{\gamma-1} = T_{\rm high}V_1^{\gamma-1}, \tag{2.84b}$$

which implies that

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}. \tag{2.85}$$

The net work is given by

$$W_{\rm net} = Q_{\rm high} - Q_{\rm low} = Nk(T_{\rm high} - T_{\rm low}) \ln \frac{V_3}{V_4}. \tag{2.86}$$

The efficiency is given by

$$\eta = \frac{W_{\rm net}}{Q_{\rm high}} = \frac{T_{\rm high} - T_{\rm low}}{T_{\rm high}} = 1 - \frac{T_{\rm low}}{T_{\rm high}}, \tag{2.87}$$

as we found previously by general arguments. ♢

Problem 2.19. A Carnot refrigerator

A refrigerator cools a closed container and heats the outside room surrounding the container. According to the second law of thermodynamics, work must be done by an external body for this process to occur. Suppose that the refrigerator extracts the amount $Q_{\rm cold}$ from the container at temperature $T_{\rm cold}$ and transfers energy $Q_{\rm hot}$ at temperature $T_{\rm hot}$ to the room. The external work supplied is W (see Figure 2.10). We define the *coefficient of performance* (COP) as

$$\text{COP} = \frac{\text{what you get}}{\text{what you pay for}} = \frac{Q_{\rm cold}}{W}. \tag{2.88}$$

Show that the maximum value of the COP corresponds to a reversible refrigerator and is given by

$$\text{COP} = \frac{T_{\rm cold}}{T_{\rm hot} - T_{\rm cold}}. \tag{2.89}$$

Note that a refrigerator is more efficient for smaller temperature differences. □

Problem 2.20. Heat pump

A heat pump works on the same principle as a refrigerator, but the goal is to heat a room by cooling its cooler surroundings. For example, we could heat a building by cooling a nearby body of water. If we extract energy $Q_{\rm cold}$ from the surroundings at $T_{\rm cold}$, do work W, and deliver $Q_{\rm hot}$ to the room at $T_{\rm hot}$, the coefficient of performance is given by

$$\text{COP} = \frac{\text{what you get}}{\text{what you pay for}} = \frac{Q_{\rm hot}}{W}. \tag{2.90}$$

What is the maximum value of COP for a heat pump in terms of $T_{\rm cold}$ and $T_{\rm hot}$? What is the COP when the outside temperature is 0°C and the interior temperature is 23°C? Is it more effective to operate a heat pump during the winters in New England where the winters are cold or in the Pacific Northwest where the winters are relatively mild? (It is too bad that the maximum efficiency of a heat pump occurs when it is needed least.) □

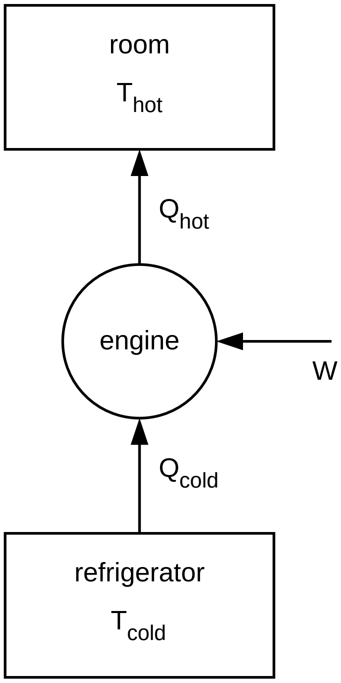

Figure 2.10: The transfer of energy in an idealized refrigerator (see Problem 2.19).

2.15 Entropy Changes

The impetus for developing thermodynamics was the industrial revolution and the efficiency of engines. The key to thermodynamics is understanding the role of entropy changes. In this section we apply the techniques of thermodynamics to calculating entropy changes to a variety of macroscopic systems. We begin with an example.

Example 2.13. Change in entropy of a solid

The heat capacity of water and solids at room temperatures is independent of temperature to a good approximation. A solid with the constant heat capacity C is taken from an initial temperature T_1 to a final temperature T_2. What is its change in entropy? (Ignore the small difference in the heat capacities at constant volume and constant pressure.)

Solution. We assume that the temperature of the solid is increased by putting the solid in contact with a succession of heat baths at temperatures separated by a small amount such that we can use the quasistatic result $dS = dQ/T$. Then the entropy change is given by

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} C(T)\,\frac{dT}{T}. \tag{2.91}$$

Because the heat capacity C is assumed to be constant, we find

$$\Delta S = S_2 - S_1 = C\int_{T_1}^{T_2} \frac{dT}{T} = C \ln \frac{T_2}{T_1}. \tag{2.92}$$

Even though we used a specific quasistatic process, the change in entropy would be the same for any process that took the solid from the same initial state to the same final state. Note that if $T_2 < T_1$, the entropy of the solid is decreased. In Example 2.15 we consider the change in entropy of a larger composite system consisting of a liquid and a heat bath. ♢

How can we measure the entropy of a solid? We know how to measure the temperature and the energy, but we have no entropy meter. Instead we have to determine the entropy *indirectly*. If the volume is held constant, we can determine the *entropy difference* between two temperatures by doing many successive measurements of the heat capacity and by doing the integral in (2.91). Note that such a determination gives only the entropy difference. We will discuss how to determine the absolute value of the entropy under certain conditions in Section 2.20.

Example 2.14. Entropy change due to thermal contact

A solid with heat capacity C_A at temperature T_A is placed in contact with another solid with heat capacity C_B at a lower temperature T_B. What is the change in entropy of the system after the two bodies have reached thermal equilibrium?

Solution. Assume that the heat capacities are independent of temperature and the two solids are isolated from their surroundings.

From Example 2.5 we know that the final equilibrium temperature is given by

$$T = \frac{C_A T_A + C_B T_B}{C_A + C_B}. \tag{2.93}$$

Although the process is irreversible, we can calculate the entropy change by considering any process that takes a body from one temperature to another. For example, we can imagine that a body is brought from its initial temperature T_B to the temperature T in many successive infinitesimal steps by placing it in successive contact with a series of heat baths at infinitesimally greater temperatures. At each contact the body is arbitrarily close to equilibrium and has a well-defined temperature. For this reason, we can apply the result (2.92), which yields $\Delta S_A = C_A \ln T/T_A$. The total change in the entropy of the system is given by

$$\Delta S = \Delta S_A + \Delta S_B = C_A \ln \frac{T}{T_A} + C_B \ln \frac{T}{T_B}, \tag{2.94}$$

where T is given by (2.109). Substitute real numbers for T_A, T_B, C_A, and C_B and convince yourself that $\Delta S \geq 0$. Does the sign of ΔS depend on whether $T_A > T_B$ or $T_A < T_B$? ♢

Example 2.15. Entropy change of water in contact with a heat bath

One kilogram of water at $T_A = 0°\text{C}$ is brought into contact with a heat bath at $T_B = 50°\text{C}$. What is the change of entropy of the water, the heat bath, and the combined system consisting of the water and the heat bath?

Solution. The change in entropy of the water is given by

$$\Delta S_A = C \ln \frac{T_B}{T_A} = 4184\,\mathrm{J/K} \ln \frac{273+50}{273+0} = 704\,\mathrm{J/K}. \tag{2.95}$$

Why does the number 273 enter in (2.95)? The amount of energy transferred to the water from the heat bath is

$$Q = C(T_B - T_A) = 4184\,\mathrm{J/K} \times 50\,\mathrm{K} = 209,000\,\mathrm{J}. \tag{2.96}$$

The change in entropy of the heat bath is

$$\Delta S_B = \frac{-Q}{T_B} = -\frac{209200\,\mathrm{J}}{323\,\mathrm{K}} = -648\,\mathrm{J/K}. \tag{2.97}$$

Hence the total change in the entropy is

$$\Delta S = \Delta S_A + \Delta S_B = 704\,\mathrm{J/K} - 648\,\mathrm{J/K} = 56\,\mathrm{J/K}. \tag{2.98}$$

Note that ΔS is positive. ♢

Problem 2.21. Water in contact with two heat baths in succession

The temperature of 1 kg of water at 0°C is increased to 50°C by first bringing it into contact with a heat bath at 25°C and then with a heat bath at 50°C. What is the change in entropy of the entire system? How does this change in entropy compare with the change that was found in Example 2.15? □

Example 2.16. More on the nature of a heat bath

A heat bath is a large system whose temperature remains unchanged when energy is added to or subtracted from it. As an example we first consider two systems with constant volume heat capacities C_A and C_B that are initially at different temperatures T_A and T_B. What happens when the two systems are placed in thermal contact (and are isolated from their surroundings)? The volume of the two systems is fixed and the heat capacities are independent of temperature. We will consider the general case and then take the limit $C_B \to \infty$.

From (2.93) the final temperature T can be written as

$$T = \frac{C_A}{C_A + C_B} T_A + \frac{C_B}{C_A + C_B} T_B. \tag{2.99}$$

We define the ratio

$$\lambda = \frac{C_A}{C_B}, \tag{2.100}$$

and rewrite (2.99) as

$$T = \frac{C_A}{C_B(1 + C_A/C_B)} T_A + \frac{1}{(1 + C_A/C_B)} T_B \tag{2.101a}$$

$$= \frac{1}{1+\lambda}\big(\lambda T_A + T_B\big). \tag{2.101b}$$

In the limit $\lambda \to 0$ corresponding to system B becoming a heat bath we see from (2.101b) that $T = T_B$.

The total change in the entropy is given by (2.94). The first term gives

$$\Delta S_A = C_A \ln \frac{T}{T_A} \to C_A \ln \frac{T_B}{T_A}, \tag{2.102}$$

in the limit that system B is treated as a heat bath. To evaluate the second term in (2.94) we write

$$\frac{T}{T_B} = \frac{1}{1+\lambda}\Big(1 + \lambda \frac{T_A}{T_B}\Big) \approx (1-\lambda)\Big(1 + \lambda \frac{T_A}{T_B}\Big) \tag{2.103a}$$

$$\approx 1 + \lambda\Big(\frac{T_A}{T_B} - 1\Big), \tag{2.103b}$$

where we have used the approximation $(1+x)^{-1} \approx 1 - x$, and kept terms through order λ. We have

$$\Delta S_B = C_B \ln \frac{T}{T_B} \to C_A \frac{1}{\lambda} \ln \Big[1 + \lambda\Big(\frac{T_A}{T_B} - 1\Big)\Big] \to C_A\Big(\frac{T_A}{T_B} - 1\Big), \tag{2.104}$$

where we have used the approximation $\ln(1+x) \approx x$. Hence, the total change in the entropy of the system is given by

$$\Delta S = C_A\Big[\ln \frac{T_B}{T_A} + \frac{T_A}{T_B} - 1\Big]. \tag{2.105}$$

In Problem 2.61 you will be asked to show that ΔS in (2.105) is always greater than zero for $T_A \neq T_B$. ♢

Problem 2.22. Use the numerical values for various quantities from Example 2.15 to show that (2.105) gives the same numerical result as (2.98). ☐

Example 2.17. Melting of ice

A beaker contains a 0.1 kg block of ice at 0°C. Suppose that we wait until the ice melts and then comes to room temperature. What is the change of entropy of the ice to water? (It takes 334 kJ to melt 1 kg of ice.)

Solution. If we add energy to ice by heating at its melting temperature $T = 273.15\,\mathrm{K}$ at atmospheric pressure, the effect is to melt the ice rather than to raise its temperature.

We melt the ice by supplying $0.1\,\mathrm{kg} \times 334\,\mathrm{kJ/kg} = 33,400\,\mathrm{J}$ from a heat bath at 273.15 K, assuming that the ice is in equilibrium with the air in the room which acts as a heat bath. Hence, the entropy increase due to the melting of the ice is given by $\Delta S = 33,400/273.15 = 122.2\,\mathrm{J/K}$.

The change in the entropy to bring the water from 0°C to room temperature, which we take to be 22°C, is $(0.1 \times 4184) \ln 295/273 = 32.4\,\mathrm{J/K}$. Thus, the total change in entropy of the ice to water at room temperature is $122.2 + 32.4) = 154.6\,\mathrm{J/K}$. ♢

Example 2.18. Entropy change in a free expansion

Consider an ideal gas of N particles in a closed, insulated container that is divided into two chambers by an impermeable partition (see Figure 2.11). The gas is initially confined to one

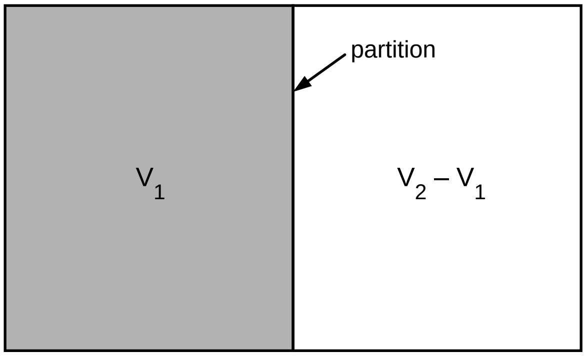

Figure 2.11: The free expansion of an isolated ideal gas. The second chamber is initially a vacuum and the total volume of the two chambers is V_2.

chamber of volume V_1 at a temperature T. The gas is then allowed to expand freely into a vacuum to fill the entire container of volume V_2. What is the change in entropy?

Solution. Because the composite system of two chambers has rigid impermeable walls, no energy leaves or enters the composite system either by heating or by work. Hence, there is no change in the internal energy of the gas. It might be argued that $\Delta S = Q/T = 0$ because $Q = 0$. However, this conclusion would be incorrect because the relation $dS = dQ/T$ holds only for a quasistatic process.

The expansion from V_1 to V_2 is an irreversible process. Left to itself, the system will not return spontaneously to its original state with all the particles in the left container. Because the entropy is a state function, we can consider another process that takes the system to the same final state. This process should be quasistatic so that we can use thermodynamics, and also should take place at constant energy because there is no change in energy during the free expansion of an ideal gas. Suppose that the two chambers are separated by a movable partition with a nonzero mass. Because the partition has mass, the gas does work on the partition to increase its volume by an amount ΔV; that is, work $-P\Delta V$ is done on the gas. Because we want the final state of the gas to have the same energy as the initial state, we need to simultaneously add energy to the gas by heating. Because the gas is ideal, the internal energy depends only on the temperature, and hence the temperature of the ideal gas is unchanged. Hence, $dE = TdS - PdV = 0$, or

$$\Delta S = \frac{1}{T}\int_{V_2}^{V_1} P\,dV = \frac{1}{T}\int_{V_2}^{V_1} \frac{NkT}{V}\,dV = Nk\ln\frac{V_2}{V_1}. \tag{2.106}$$

Hence, the entropy increases as expected. ◊

The discussion of the free expansion of an ideal gas illustrates two initially confusing aspects of thermodynamics. As mentioned, the name thermodynamics is a misnomer because thermodynamics treats only equilibrium states and not dynamics. Nevertheless, thermodynamics discusses processes that must happen over some interval of time. It is also confusing that we can consider processes that did not actually happen. In this case the calculation of ΔS in Example 2.18 is identical to what we would do for an isothermal nonadiabatic quasistatic process where the gas does work, even though in the actual process no work was done by the gas and no heating or cooling occurred. However, the initial and final states and the change in the entropy are the same for the actual process and the calculated process.

Quasistatic adiabatic processes. We have already discussed that quasistatic adiabatic processes have the special property that the entropy does not change, but we repeat this statement here to emphasize its importance. If a process is adiabatic, then $Q = 0$, and if the process is also quasistatic, then $\Delta S = Q/T = 0$, and there is no change in the entropy.

Quasistatic processes are subtle. Consider again the free expansion of an ideal gas. Initially the gas is confined to one chamber and then allowed to expand freely into the second chamber to fill the entire container. It is certainly not quasistatic, and thus $\Delta S > 0$, even though $Q = 0$. Suppose that we imagine this process to be performed very slowly by dividing the second chamber into many small chambers separated by partitions and puncturing each partition in turn, allowing the expanded gas to come into equilibrium. It might seem that in the limit of an infinite number of partitions that such a process would be quasistatic. However, this conclusion is incorrect because it would imply that $dS = dQ/T = 0$.

Note that an infinitesimal process is not necessarily quasistatic. The puncture of a partition would cause the wall to move suddenly, thus creating turbulence and causing changes that are not near equilibrium. Also the work done by the gas in a quasistatic process is $dW = PdV$, but no work is done even though $PdV \neq 0$. The expansion of a gas into a vacuum is not quasistatic no matter how slowly it is performed, and the process is not reversible, because the gas will never return to its original volume.

Example 2.19. Maximum work

When two bodies are placed in thermal contact, no work is done, that is, $W = 0$ and $\Delta E = Q_A + Q_B = 0$. How can we extract the maximum work possible from the two bodies?

Solution. From our discussion of heat engines, we know that we should not place them in thermal contact. Instead we run a Carnot (reversible) engine between the two bodies. However, unlike the heat baths considered in the Carnot engine, here the heat capacities of the two bodies are finite, and hence the temperature of each body changes as energy is transferred from one body to the other.

To extract the maximum work we assume that the process is reversible and write

$$\Delta S = \Delta S_A + \Delta S_B = 0. \tag{2.107}$$

If we assume that the heat capacities are constant, it follows using (2.91) that

$$C_A \ln \frac{T}{T_A} + C_B \ln \frac{T}{T_B} = 0. \tag{2.108}$$

We solve (2.108) for T and find that

$$T = T_A^{C_A/(C_A+C_B)}\, T_B^{C_B/(C_A+C_B)}. \tag{2.109}$$

We see that the final temperature for a reversible process is the geometrical average of T_A and T_B weighted by their respective heat capacities. ♢

Problem 2.23. More work

(a) Show that the work performed *by* the heat engine in Example 2.19 is given by

$$W = C_A(T_A - T) + C_B(T_B - T), \tag{2.110}$$

where C_A and C_B are constants and T is given by (2.109) if the process is reversible. (Recall that our convention is to consider the work done on a system, except when we are discussing heat engines.)

(b) Suppose that $C_A = C_B = C$ (a constant independent of T) in (2.93) and (2.109). Compare the form of the expressions for the final temperature.

(c) Suppose that $T_A = 256\,\mathrm{K}$ and $T_B = 144\,\mathrm{K}$. What are the relative values of the final temperatures in (2.93) and (2.109) assuming that the heat capacities of the two bodies are equal? For which process is the final temperature lower? Why?

(d) Suppose that the heat capacities of both bodies depend linearly on the temperature T rather than being constant; that is, $C_A = AT$ and $C_B = BT$, where A and B are constants. What is the final temperature assuming that the two bodies are placed in thermal contact? What is the final temperature for the case when the maximum work is extracted? What is the maximum work done? ☐

Are all forms of energy equivalent? If you were offered 100 J of energy, would you choose to have it delivered as compressed gas at room temperature or as a hot brick at 400 K? If you are not sure what you want to do with the energy, you should take the form of the energy that can be most directly converted into work, because there is no restriction on the efficiency of using stored energy for heating. What is different is the *quality* of the energy, which we take to be a measure of its ability to do work. We can readily convert energy from higher to lower quality, but the second law of thermodynamics prevents us from going in the opposite direction with 100% efficiency.

As an example consider the adiabatic free expansion of an ideal gas from volume V_1 to volume V_2. As we found in Example 2.18, the entropy increase is $\Delta S = Nk \ln V_2/V_1$. If we had instead let the gas undergo a quasistatic isothermal expansion, the work done by the gas would have been $W = NkT \ln V_2/V_1$, which is the same as $T\Delta S$ for the adiabatic free expansion. Thus, an increase in entropy implies that some energy has become unavailable to do work.

2.16 Equivalence of Thermodynamic and Ideal Gas Scale Temperatures

So far we have assumed that the ideal gas scale temperature that we introduced in Section 2.4 is the same as the thermodynamic temperature defined by (2.65). We now show that the two temperatures are proportional and can be made equal if we choose the units of S appropriately.

The ideal gas temperature scale, which we denote as θ in this section to distinguish it from the thermodynamic temperature T, is defined by the relation

$$\theta = PV/Nk. \tag{2.111}$$

That is, θ is proportional to the pressure of a gas at a fixed low density and is equal to 273.16 K at the triple point of water. The fact that $\theta \propto P$ for a dilute gas is a matter of definition. Another important property of ideal gases is that the internal energy depends only on θ and is independent of the volume.

To show the equivalence between T and θ we need to consider a process for which we have a general result involving the thermodynamic temperature that is independent of the nature of the system involved in the process. We can then specialize to the ideal gas. The only example we have so far is the Carnot cycle. At every stage of the cycle we have

$$\frac{dQ}{\theta} = \frac{dE - dW}{\theta} = \frac{dE + PdV}{\theta}, \tag{2.112}$$

or

$$\frac{dQ}{\theta} = \frac{dE}{\theta} + Nk\frac{dV}{V}. \tag{2.113}$$

The first term on the right-hand side of (2.113) depends only on θ and the second term depends only on the volume. If we integrate (2.113) around one cycle, both θ and V return to their starting values, and hence the loop integral of the right-hand side of (2.113) is zero. We conclude that

$$\oint \frac{dQ}{\theta} = 0. \tag{2.114}$$

Because the only places where Q is nonzero are at the hot and cold heat baths which are held at constant temperatures, we have

$$0 = \frac{Q_{\rm cold}}{\theta_{\rm cold}} - \frac{Q_{\rm hot}}{\theta_{\rm hot}} = 0. \tag{2.115}$$

In Section 2.14 we showed that $Q_{\rm cold}/Q_{\rm hot} = T_{\rm cold}/T_{\rm hot}$ for a Carnot engine [see (2.75)]. If we combine this result with (2.115), we find that

$$\frac{T_{\rm cold}}{T_{\rm hot}} = \frac{\theta_{\rm cold}}{\theta_{\rm hot}}. \tag{2.116}$$

It follows that the thermodynamic temperature T is proportional to the ideal gas scale temperature θ. From now on we shall assume that we have chosen suitable units for S so that $T = \theta$.

2.17 The Thermodynamic Pressure

In Section 2.13 we showed that the thermodynamic definition of temperature follows by considering the condition for the thermal equilibrium of two subsystems. In the following, we show that the pressure can be defined in an analogous way and that the pressure can be interpreted as a response of the entropy to a change in the volume.

As before, consider an isolated composite system that is partitioned into two subsystems. The subsystems are separated by a movable, insulating wall so that the energies and volumes of the subsystems can adjust themselves, but N_A and N_B are fixed. For simplicity, we assume that E_A and E_B have already changed so that thermal equilibrium has been established. For fixed total volume V we have one independent variable, which we take to be V_A; V_B is given by $V_B = V - V_A$. The value of V_A that maximizes $S = S_A + S_B$ is given by

$$dS = \frac{\partial S_A}{\partial V_A}\, dV_A + \frac{\partial S_B}{\partial V_B}\, dV_B = 0. \tag{2.117}$$

Because $dV_A = -dV_B$, we can use (2.117) to write the condition for *mechanical equilibrium* as

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}. \tag{2.118}$$

We define the thermodynamic pressure P as

$$\boxed{\frac{P}{T} \equiv \Big(\frac{\partial S}{\partial V}\Big)_{E,N}} \qquad \text{(definition of thermodynamic pressure).} \tag{2.119}$$

Note that the presence of $1/T$ in the definition of pressure makes the units come out correctly. We will see in the next section that the factor of $1/T$ is needed for consistency with the relation $dE = TdS - PdV$.

For completeness, we define the *chemical potential* as the response of the entropy to a change in the number of particles:

$$\boxed{\frac{\mu}{T} \equiv -\Big(\frac{\partial S}{\partial N}\Big)_{E,V}} \qquad \text{(definition of the chemical potential).} \tag{2.120}$$

We will discuss the interpretation of μ in Section 4.12. You probably won't be surprised to learn that if two systems can exchange particles, then the equality of the chemical potential μ is the condition for *chemical equilibrium*.

We will sometimes distinguish between thermal equilibrium, mechanical equilibrium, and chemical equilibrium for which the temperatures, pressures, and chemical potentials are equal, respectively. When all three conditions are satisfied, a system is in thermodynamic equilibrium.

2.18 The Fundamental Thermodynamic Relation

The first law of thermodynamics implies that the internal energy E is a function of state. For *any* change of state, the change in E is given by (2.21)

$$\Delta E = Q + W \qquad \text{(any process).} \tag{2.121}$$

To separate the contributions to E due to heating and work, the constraints on the system have to be known. If the change is quasistatic, then the infinitesimal work done is

$$dW = -PdV, \qquad \text{(quasistatic process)} \tag{2.122}$$

and

$$dQ = TdS. \qquad \text{(quasistatic process)} \tag{2.123}$$

Thus, for an infinitesimal quasistatic change in the energy we have

$$dE = TdS - PdV. \tag{2.124}$$

There are two ways of thinking about (2.124). As our derivation suggests this equation tells us the relation between changes in the energy, entropy, and volume. Alternatively, we can interpret (2.124) as the differential form (for fixed N) of the fundamental equation $E = E(S, V, N)$. Because $S = S(E, V, N)$ is also a state function and because we defined T, P, and μ in terms of derivatives of S, we may rewrite (2.124) as

$$dS = \frac{1}{T}dE + \frac{P}{T}dV. \tag{2.125}$$

We also have

$$dS = \Big(\frac{\partial S}{\partial E}\Big)_{V,N} dE + \Big(\frac{\partial S}{\partial V}\Big)_{E,N} dV + \Big(\frac{\partial S}{\partial N}\Big)_{E,V} dN. \tag{2.126}$$

A comparison of (2.125) and (2.126) gives the familiar results $1/T = (\partial S/\partial E)_{V,N}$ and $P/T = (\partial S/\partial V)_{E,N}$ [see (2.65) and (2.119)]. If we allow N to vary we can use (2.120) and write

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN. \tag{2.127}$$

If we know the entropy S as a function of E, V, and N, we can determine the corresponding responses T, P, and μ. For this reason we shall refer to E, V, and N as the natural variables in which S should be expressed. In this context S can be interpreted as a *thermodynamic potential* because its various partial derivatives yield the equations of state of the system. In Section 2.21 we shall discuss thermodynamic potentials that have different sets of natural variables.

We can alternatively consider E as a function of S, V, and N and rewrite (2.127) as

$$\boxed{dE = TdS - PdV + \mu dN} \quad \text{(fundamental thermodynamic relation).} \tag{2.128}$$

Equation (2.128) is a mathematical statement of the combined first and second laws of thermodynamics. There are very few equations in thermodynamics that are necessary to memorize, but (2.128) is one of the few equations that you should know without thinking.

Many useful thermodynamic relations can be derived using (2.128). For example, if we regard E as a function of S, V, and N, we can write

$$dE = \Big(\frac{\partial E}{\partial S}\Big)_{V,N} dS + \Big(\frac{\partial E}{\partial V}\Big)_{S,N} dV + \Big(\frac{\partial E}{\partial N}\Big)_{S,V} dN. \tag{2.129}$$

If we compare (2.128) and (2.129), we see that

$$T = \Big(\frac{\partial E}{\partial S}\Big)_{V,N}, \qquad P = -\Big(\frac{\partial E}{\partial V}\Big)_{S,N}, \qquad \mu = \Big(\frac{\partial E}{\partial N}\Big)_{S,V}. \tag{2.130}$$

Note that $E(S, V, N)$ also can be interpreted as a thermodynamic potential.

2.19 The Entropy of an Ideal Classical Gas

Because we know two equations of state of an ideal gas, (2.8) and (2.23), we can find the entropy of an ideal classical gas as a function of various combinations of E, T, P, and V for fixed N. If we substitute $1/T = \frac{3}{2}Nk/E$ and $P/T = Nk/V$ into (2.127), we obtain

$$dS = \frac{3}{2}Nk\frac{dE}{E} + Nk\frac{dV}{V}. \tag{2.131}$$

We can integrate (2.131) to obtain the change in the entropy from state E_1, V_1 to state E_2, V_2:

$$\Delta S = \frac{3}{2}Nk\ln\frac{E_2}{E_1} + Nk\ln\frac{V_2}{V_1}. \tag{2.132}$$

We see that S is an additive quantity as we have assumed; that is, S is proportional to N.

Frequently it is more convenient to express S in terms of T and V or T and P. To obtain $S(T,V)$ we substitute $E = \frac{3}{2}NkT$ into (2.132) and obtain

$$\Delta S = \frac{3}{2}Nk\ln\frac{T_2}{T_1} + Nk\ln\frac{V_2}{V_1} \qquad \text{(ideal gas)}. \tag{2.133}$$

Problem 2.24. Applications of (2.133)

(a) Use (2.133) to derive the relation (2.44) between T and V for a quasistatic adiabatic process.

(b) An ideal gas of N particles is confined to a box of chamber V_1 at temperature T. The gas is then allowed to expand freely into a vacuum to fill the entire container of volume V_2. The container is thermally insulated. What is the change in entropy of the gas?

(c) Find $\Delta S(T,P)$ for an ideal classical gas. □

2.20 The Third Law of Thermodynamics

Only differences in the entropy can be calculated using purely thermodynamic relations as we did in Section 2.19. We can define the absolute value of the entropy by using the third law of thermodynamics which states that

$$\lim_{T\to 0} S = 0 \qquad \text{(third law of thermodynamics)}. \tag{2.134}$$

The statistical basis of this law is discussed in Section 4.6. In the context of thermodynamics, the third law can be understood only as a consequence of empirical observations.

The most important consequence of the third law is that all heat capacities must go to zero as the temperature approaches zero. For changes at constant volume, we know that [see (2.91)]

$$S(T_2,V) - S(T_1,V) = \int_{T_1}^{T_2} \frac{C_V(T)}{T}\,dT. \tag{2.135}$$

The condition (2.134) implies that in the limit $T_1 \to 0$, the integral in (2.135) must be finite, and hence we require that $C_V(T) \to 0$ as $T \to 0$. Similarly, we can argue that $C_P \to 0$ as $T \to 0$. Note that these conclusions about the low temperature behavior of C_V and C_P are independent of the nature of the system. Such is the power of thermodynamics. The low temperature behavior of the heat capacity was first established experimentally in 1910–1912.

As we will find in Section 4.6, the third law is a consequence of the fact that the most fundamental description of nature at the microscopic level is quantum mechanical. We have already seen that the heat capacity is a constant for an ideal gas. Hence, the thermal equation of state, $E = \frac{3}{2}NkT$, as well as the pressure equation of state, $PV = NkT$, must cease to be applicable at sufficiently low temperatures.

Example 2.20. Low temperature entropy of an insulating solid

At very low temperature T, the heat capacity C of an insulating solid is proportional to T^3. If we take $C = AT^3$ for a particular solid, what is the entropy of the solid at temperature T?

Solution. As before, the entropy is given by [see (2.91)]

$$S(T) = \int_0^T \frac{C_V(T)}{T} dT, \tag{2.136}$$

where we have used the fact that $S(T = 0) = 0$. We can integrate the right-hand side of (2.136) from $T = 0$ to the desired value of T to find the absolute value of S. The result in this case is $S = AT^3/3$. ♢

2.21 Free Energies

We know that the entropy of an isolated system can never decrease. However, an isolated system is of little experimental interest, and we wish to consider the more typical case where the system of interest is connected to a much larger system, a heat bath, whose properties do not change significantly. In the following we will consider a heat bath whose temperature and pressure are unchanged by interactions with a much smaller system.

If a system is connected to a heat bath, then the entropy of the system may increase or decrease. The only thing we can say for sure is that the entropy of the system plus the heat bath must increase or remain unchanged. Because the entropy is additive, we have[22]

$$S_{\rm composite} = S + S_{\rm bath} \tag{2.137}$$

and

$$\Delta S_{\rm composite} = \Delta S + \Delta S_{\rm bath} \geq 0. \tag{2.138}$$

The properties of the system of interest are denoted by the absence of a subscript. Our goal is to determine if there is a property of the system alone (not the composite system) that is a maximum

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[22] The following discussion is adapted from Mandl, pp. 89–92.

or a minimum. We begin by writing the change $\Delta S_{\rm bath}$ in terms of the properties of the system. Because energy can be transferred between the system and heat bath, we have

$$\Delta S_{\rm bath} = \frac{-Q}{T_{\rm bath}}, \tag{2.139}$$

where Q is the amount of energy transferred to the system by heating, and $-Q$ is the amount of energy transferred to the heat bath. If we use (2.139), we can rewrite (2.138) as

$$\Delta S_{\rm composite} = \Delta S - \frac{Q}{T_{\rm bath}}. \tag{2.140}$$

The application of the first law to the system gives

$$\Delta E = Q + W, \tag{2.141}$$

where ΔE is the change in the energy of the system and W is the work done on it. If the work done on the system is due to the heat bath, then $W = -P_{\rm bath}\Delta V$, where ΔV is the change in volume of the system. Then we can write

$$\Delta S_{\rm composite} = \Delta S - \frac{\Delta E - W}{T_{\rm bath}} = \Delta S - \frac{\Delta E + P_{\rm bath}\Delta V}{T_{\rm bath}} \geq 0. \tag{2.142}$$

A little algebra leads to

$$\Delta E + P_{\rm bath}\Delta V - T_{\rm bath}\Delta S \leq 0. \tag{2.143}$$

This result suggests that we define the *availability* by

$$A = E + P_{\rm bath}V - T_{\rm bath}S, \tag{2.144}$$

so that (2.143) becomes

$$\Delta A = \Delta E + P_{\rm bath}\Delta V - T_{\rm bath}\Delta S \leq 0. \tag{2.145}$$

The availability includes properties of both the system and the heat bath. The significance of the availability will be discussed in the following.

We now look at some typical experimental situations and introduce a quantity that depends only on the properties of the system. First, we assume that its volume and number of particles is fixed, and that its temperature equals the temperature of the heat bath; that is, we set $T_{\rm bath} = T$ and $\Delta V = 0$. In this case we have

$$\Delta A = \Delta E - T\Delta S = \Delta F \leq 0, \tag{2.146}$$

where we have defined the *Helmholtz free energy* as

$$\boxed{F \equiv E - TS}. \tag{2.147}$$

The inequality in (2.146) implies that if a constraint within the system is removed, then the system's Helmholtz free energy will *decrease*. Just as $\Delta S \geq 0$ and $S(E, V, N)$ is a maximum at equilibrium, $\Delta F \leq 0$ and $F(T, V, N)$ is a minimum at equilibrium. Thus, F plays the analogous role for systems at constant T and V that was played by the entropy for an isolated system (constant E and V).

What are the natural variables for F? From our discussion it should be clear that these variables are T, V, and N. The answer can be found by taking the differential of (2.147) and using (2.128). The result is

$$\begin{aligned} dF &= dE - SdT - TdS && (2.148a)\\ &= (TdS - PdV + \mu dN) - SdT - TdS && (2.148b)\\ &= -SdT - PdV + \mu dN. && (2.148c) \end{aligned}$$

We substituted $dE = TdS - PdV + \mu dN$ to go from (2.148a) to (2.148c). From (2.148) we see that $F = F(T, V, N)$ and that S, P, and μ can be obtained by taking appropriate partial derivatives of F. For example,

$$S = -\Big(\frac{\partial F}{\partial T}\Big)_{V,N}, \tag{2.149}$$

$$P = -\Big(\frac{\partial F}{\partial V}\Big)_{T,N}, \tag{2.150}$$

and

$$\mu = \Big(\frac{\partial F}{\partial N}\Big)_{T,V}. \tag{2.151}$$

The Helmholtz free energy is an example of a free energy or *thermodynamic potential*.[23]

We can relax the condition of a fixed volume by requiring that the pressure be specified. In this case mechanical equilibrium requires that the pressure of the system equal the pressure of the bath. This case is common in experiments with fluids where the pressure is fixed at atmospheric pressure. We write $P_{\rm bath} = P$ and express (2.143) as

$$\Delta A = \Delta E + P\Delta V - T\Delta S = \Delta G \leq 0, \tag{2.152}$$

where we have defined the Gibbs free energy as

$$\boxed{G \equiv E - TS + PV = F + PV}. \tag{2.153}$$

The natural variables of G can be found in the same way as we did for F. We find that $G = G(T, P, N)$ and

$$\begin{aligned} dG &= dE - SdT - TdS + PdV + VdP && (2.154a)\\ &= (TdS - PdV + \mu dN) - SdT - TdS + PdV + VdP && (2.154b)\\ &= -SdT + VdP + \mu dN. && (2.154c) \end{aligned}$$

We can use similar reasoning to conclude that G is a minimum at fixed temperature, pressure, and number of particles.

We can also relate G to the chemical potential by noting that G and N are extensive variables (see Section 2.9), but T and P are not. Thus, G must be proportional to N:

$$G = Ng(T, P), \tag{2.155}$$

---

[23] A more formal way of obtaining the various thermodynamic potentials is given in Section 2.24.2.

where $g(T, P)$ is the Gibbs free energy per particle. This function must be the chemical potential because $\partial G/\partial N = g(T, P)$ from (2.155) and $\partial G/\partial N = \mu$ from (2.154). Thus, the chemical potential is the Gibbs free energy per particle:

$$\mu(T, P) = \frac{G}{N} = g(T, P). \tag{2.156}$$

Because g depends only on T and P, we have

$$\begin{aligned} dg = d\mu &= \Big(\frac{\partial g}{\partial P}\Big)_T dP + \Big(\frac{\partial g}{\partial T}\Big)_P dT &(2.157)\\ &= vdP - sdT, &(2.158)\end{aligned}$$

where $v = V/N$ and $s = S/N$. Equation (2.158) is called the *Gibbs-Duhem equation.* The properties of G and the relation (2.158) will be important when we discuss processes involving a change of phase (see Section 7.3).

Another common thermodynamic potential is the *enthalpy* H which we defined in (2.29). This potential is similar to $E(S, V, N)$ except for the requirement of fixed P rather than fixed V.

Problem 2.25. The enthalpy

(a) Given the definition of the enthalpy in (2.29) show that

$$dH = TdS + VdP + \mu dN, \tag{2.159}$$

and

$$T = \Big(\frac{\partial H}{\partial S}\Big)_{P,N}, \tag{2.160}$$

$$V = \Big(\frac{\partial H}{\partial P}\Big)_{S,N}, \tag{2.161}$$

$$\mu = \Big(\frac{\partial H}{\partial N}\Big)_{S,P}. \tag{2.162}$$

(b) Show that H is a minimum for an equilibrium system at fixed entropy. □

Landau potential. A very useful thermodynamic potential is one for which the variables T, V, and μ are specified. This potential has no generally recognized name or symbol, but is sometimes called the *Landau potential* and is usually, but not always, denoted by Ω. Another common name is simply the *grand potential.* We will adopt the notation Ω and refer to Ω as the Landau potential in honor of Lev Landau. The Landau potential is the thermodynamic potential for which the variables T, V, and μ are specified and is given by

$$\boxed{\Omega(T, V, \mu) = F - \mu N}. \tag{2.163}$$

If we take the derivative of Ω and use the fact that $dF = -SdT - PdV + \mu dN$ (see (2.148)), we find that

$$\begin{aligned} d\Omega &= dF - \mu dN - Nd\mu &(2.164a)\\ &= -SdT - PdV - Nd\mu. &(2.164b)\end{aligned}$$

Name	Potential	Differential Form
Internal energy	$E(S,V,N)$	$dE = TdS - PdV + \mu dN$
Entropy	$S(E,V,N)$	$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$
Enthalpy	$H(S,P,N) = E + PV$	$dH = TdS + VdP + \mu dN$
Helmholtz free energy	$F(T,V,N) = E - TS$	$dF = -SdT - PdV + \mu dN$
Gibbs free energy	$G(T,P,N) = F + PV$	$dG = -SdT + VdP + \mu dN$
Landau potential	$\Omega(T,V,\mu) = F - \mu N$	$d\Omega = -SdT - PdV - Nd\mu$

Table 2.2: Summary of the common thermodynamic potentials, their natural variables, and their differential form. From the differential forms we can easily write down various thermodynamic quantities as partial derivatives of the appropriate potential. For example, $N = -(\partial\Omega/\partial\mu)_{T,V}$.

From (2.164b) we have

$$S = -\Big(\frac{\partial\Omega}{\partial T}\Big)_{V,\mu}, \tag{2.165}$$

$$P = -\Big(\frac{\partial\Omega}{\partial V}\Big)_{T,\mu}, \tag{2.166}$$

$$N = -\Big(\frac{\partial\Omega}{\partial \mu}\Big)_{T,V}. \tag{2.167}$$

Because $G = N\mu$, we can write $\Omega = F - G$. Hence, if we use the definition $G = F + PV$, we obtain

$$\Omega(T,V,\mu) = F - \mu N = F - G = -PV. \tag{2.168}$$

The relation (2.168) will be very useful for obtaining the equation of state of various systems (see Section 6.8).

Table 2.2 summarizes the important thermodynamic potentials and their natural variables.

***Useful work and availability**. The free energies that we have introduced are useful for understanding the maximum amount of useful work, $W_{\rm useful}$, that can be done *by* a system when it is connected to a heat bath. The system is not necessarily in thermal or mechanical equilibrium with its surroundings. In addition to the system of interest and its surroundings (the bath), we include a third body, namely, the body on which the system does useful work. The third body is thermally insulated. The total work $W_{\rm by}$ done *by* the system is the work done against its surroundings, $P_{\rm bath}\Delta V$ plus the work done on the body, $W_{\rm useful}$:

$$W_{\rm by} = P_{\rm bath}\Delta V + W_{\rm useful}. \tag{2.169}$$

Because $W_{\rm by}$ is the work done by the system when its volume changes by ΔV, the first term in (2.169) does not contain a negative sign. This term is the work that is necessarily and uselessly performed by the system in changing its volume and thus also the volume of its surroundings. The second term is the useful work done by the system. In (2.143) we replace the work done on the heat bath, $P_{\rm bath}\Delta V$, by the total work done by the system $P_{\rm bath}\Delta V + W_{\rm useful}$ to obtain

$$\Delta E + P_{\rm bath}\Delta V + W_{\rm useful} - T_{\rm bath}\Delta S \leq 0. \tag{2.170}$$

That is, the useful work done is

$$W_{\text{useful}} \leq -(\Delta E + P_{\text{bath}}\Delta V - T_{\text{bath}}\Delta S) = -\Delta A. \tag{2.171}$$

Note that the maximum amount of useful work that can be done by the system is equal to $-\Delta A$. This relation explains the meaning of the terminology *availability* because only $-\Delta A$ is available for useful work. The rest of the work is wasted on the surroundings.

Problem 2.26. Maximum useful work and free energy changes

(a) Show that if the change in volume of the system is zero, $\Delta V = 0$, and the initial and final temperatures are that of the heat bath, then the maximum useful work is $-\Delta F$.

(b) Show that if the initial and final temperature and pressure are that of the bath, then the maximum useful work is $-\Delta G$. ☐

2.22 Thermodynamic Derivatives

All thermodynamic measurements can be expressed in terms of partial derivatives. For example, the pressure P can be expressed as $P = -\partial F/\partial V$. Let us suppose that we make several thermodynamic measurements, for example, C_V, C_P, and κ, the isothermal compressibility. The latter is defined as

$$\kappa = -\frac{1}{V}\Big(\frac{\partial V}{\partial P}\Big)_T \qquad \text{(isothermal compressibility)}. \tag{2.172}$$

Suppose that we wish to know the (isobaric) thermal expansion coefficient α, which is defined as

$$\alpha = \frac{1}{V}\Big(\frac{\partial V}{\partial T}\Big)_P \qquad \text{(thermal expansion coefficient)}. \tag{2.173}$$

(The number of particles N is assumed to be held constant in the above derivatives.) Do we need to make an independent measurement of α or can we determine α by knowing the values of C_V, C_P, and κ? To answer this question and related ones, we first need to know how to manipulate partial derivatives. This aspect of thermodynamics can be confusing when first encountered.

Thermodynamic systems normally have two or more independent variables. For example, we can choose the combination E, V, N or T, P, N. Because there are many choices of combinations of independent variables, it is important to be explicit about which variables are independent and which variables are being held constant in any partial derivative. We suggest that you read Section 2.24.1 to review some of the properties of partial derivatives. The following example illustrates the power of purely thermodynamic arguments based on the manipulation of thermodynamic derivatives.

Example 2.21. Thermodynamics of blackbody radiation

In Section 6.7 we show from first principles some of the basic results of blackbody radiation. In particular, we show that u, the energy per unit volume, is proportional to T^4 [see (6.139a)]. In the following we obtain this result using thermodynamic arguments and two reasonable assumptions. The arguments might be difficult to follow if you are not familiar with blackbody radiation. The point of the example in this context is that the formalism of thermodynamics plus a few assumptions can lead to new results. The following derivation was first given by Boltzmann in 1884.

Solution. The two assumptions are that u depends only on T and the radiation exerts a pressure on the walls of the cavity given by

$$P = \frac{1}{3}u(T). \tag{2.174}$$

Equation (2.174) follows directly from Maxwell's electromagnetic theory and is obtained in Section 6.7 from first principles (see Problem 6.25).

We start from the fundamental thermodynamic relation $dE = TdS - PdV$, and write it as

$$dS = \frac{dE}{T} + \frac{P}{T}dV. \tag{2.175}$$

We let $E = Vu$, substitute $dE = Vdu + udV$ and the relation (2.174) into (2.175), and write

$$dS = \frac{V}{T}du + \frac{u}{T}dV + \frac{1}{3}\frac{u}{T}dV = \frac{V}{T}\frac{du}{dT}dT + \frac{4}{3}\frac{u}{T}dV. \tag{2.176}$$

From (2.176) we have

$$\Big(\frac{\partial S}{\partial V}\Big)_T = \frac{4}{3}\frac{u}{T}, \tag{2.177a}$$

$$\Big(\frac{\partial S}{\partial T}\Big)_V = \frac{V}{T}\frac{du}{dT}. \tag{2.177b}$$

Because the order of the derivatives is irrelevant, $\partial^2 S/\partial V\partial T$ and $\partial^2 S/\partial T\partial V$ are equal. Hence, we obtain

$$\frac{4}{3}\frac{\partial}{\partial T}\Big(\frac{u}{T}\Big) = \frac{\partial}{\partial V}\Big(\frac{V}{T}\Big)\frac{du}{dT}. \tag{2.178}$$

Next we assume that u depends only on T and perform the derivatives in (2.178) to find

$$\frac{4}{3}\Big[\frac{1}{T}\frac{du}{dT} - \frac{u}{T^2}\Big] = \frac{1}{T}\frac{du}{dT}, \tag{2.179}$$

which reduces to

$$\frac{du}{dT} = 4\frac{u}{T}. \tag{2.180}$$

If we assume the form $u(T) = aT^n$ and substitute it in (2.180), we find that this form is a solution for $n = 4$:

$$u(T) = aT^4. \tag{2.181}$$

The constant a in (2.181) cannot be determined by thermodynamic arguments.

We can obtain the entropy by using the first partial derivative in (2.177a). The result is

$$S = \frac{4}{3T}Vu(T) + \text{constant}. \tag{2.182}$$

The constant of integration in (2.182) must be set equal to zero to make S proportional to V. Hence, we conclude that $S = 4aVT^3/3$. ♢

Example 2.21 illustrates the power of thermodynamic arguments and indicates that it would be useful to relate various thermodynamic derivatives to one another. The *Maxwell relations*, which we derive in the following, relate the various thermodynamic derivatives of E, F, G, and H to one another and are useful for eliminating quantities that are difficult to measure in favor of quantities that can be measured directly. We will see that the Maxwell relations can be used to show that the internal energy and enthalpy of an ideal gas depend only on the temperature. We also will answer the question posed in Section 2.22 and relate the coefficient of thermal expansion to other thermodynamic derivatives.

We start with the thermodynamic potential $E(S, V, N)$ and write

$$dE = TdS - PdV + \mu dN. \tag{2.183}$$

In the following we will assume that N is a constant for simplicity. From (2.183) we have that

$$T = \Big(\frac{\partial E}{\partial S}\Big)_V \tag{2.184}$$

and

$$P = -\Big(\frac{\partial E}{\partial V}\Big)_S. \tag{2.185}$$

Because the order of differentiation is irrelevant, we obtain from (2.184) and (2.185)

$$\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V}, \tag{2.186}$$

or

$$\Big(\frac{\partial T}{\partial V}\Big)_S = -\Big(\frac{\partial P}{\partial S}\Big)_V. \tag{2.187}$$

Equation (2.187) is one of the Maxwell relations. The other Maxwell relations are obtained in Problem 2.27.

Problem 2.27. More Maxwell relations

From the differentials of the thermodynamic potentials

$$dF = -SdT - PdV, \tag{2.188}$$
$$dG = -SdT + VdP, \tag{2.189}$$
$$dH = TdS + VdP, \tag{2.190}$$

derive the Maxwell relations

$$\Big(\frac{\partial S}{\partial V}\Big)_T = \Big(\frac{\partial P}{\partial T}\Big)_V, \tag{2.191}$$
$$\Big(\frac{\partial S}{\partial P}\Big)_T = -\Big(\frac{\partial V}{\partial T}\Big)_P, \tag{2.192}$$
$$\Big(\frac{\partial T}{\partial P}\Big)_S = \Big(\frac{\partial V}{\partial S}\Big)_P. \tag{2.193}$$

Also consider a variable number of particles to derive the Maxwell relations

$$\Big(\frac{\partial V}{\partial N}\Big)_P = \Big(\frac{\partial \mu}{\partial P}\Big)_N, \tag{2.194}$$

and

$$\Big(\frac{\partial \mu}{\partial V}\Big)_N = -\Big(\frac{\partial P}{\partial N}\Big)_V. \tag{2.195}$$

□

The Maxwell relations depend on our identification of $(\partial E/\partial S)_V$ with the temperature, a relation that follows from the second law of thermodynamics. The Maxwell relations are not purely mathematical in content, but are different expressions of the second law. In the following, we use these relations to derive some useful relations between various thermodynamic quantities.

Internal energy of an ideal gas. We first show that the internal energy E of an ideal gas is a function only of T given the pressure equation of state, $PV = NkT$. That is, if we consider E as a function of T and V, we want to show that $(\partial E/\partial V)_T = 0$. From the fundamental thermodynamic relation, $dE = TdS - PdV$, we see that $(\partial E/\partial V)_T$ can be expressed as

$$\Big(\frac{\partial E}{\partial V}\Big)_T = T\Big(\frac{\partial S}{\partial V}\Big)_T - P. \tag{2.196}$$

Note the importance of specifying which quantity is being held constant when taking a partial derivative. The quantity $(\partial E/\partial V)_S = -P$ is clearly different from $(\partial E/\partial V)_T$. To show that E is a function of T only, we need to show that the right-hand side of (2.196) is zero. The term involving the entropy in (2.196) can be rewritten using the Maxwell relation (2.191):

$$\Big(\frac{\partial E}{\partial V}\Big)_T = T\Big(\frac{\partial P}{\partial T}\Big)_V - P. \tag{2.197}$$

Because $(\partial P/\partial T)_V = P/T$ for an ideal gas, we see that the right-hand side of (2.197) is zero.

Problem 2.28. Show that the enthalpy of an ideal gas is a function of T only. □

Relation between heat capacities. As we have seen, it is much easier to calculate the heat capacity at constant volume than at constant pressure. However, it is usually easier to measure the heat capacity at constant pressure. For example, most solids expand when heated, and hence it is easier to make measurements at constant pressure. In the following, we derive a thermodynamic relation that relates C_V and C_P. Recall that

$$C_V = \Big(\frac{\partial E}{\partial T}\Big)_V = T\Big(\frac{\partial S}{\partial T}\Big)_V \tag{2.198a}$$

and

$$C_P = \Big(\frac{\partial H}{\partial T}\Big)_P = T\Big(\frac{\partial S}{\partial T}\Big)_P. \tag{2.198b}$$

We consider S as a function of T and P, and write

$$dS = \Big(\frac{\partial S}{\partial T}\Big)_P dT + \Big(\frac{\partial S}{\partial P}\Big)_T dP, \tag{2.199}$$

and take the partial derivative with respect to temperature at constant volume of both sides of (2.199):

$$\Big(\frac{\partial S}{\partial T}\Big)_V = \Big(\frac{\partial S}{\partial T}\Big)_P + \Big(\frac{\partial S}{\partial P}\Big)_T \Big(\frac{\partial P}{\partial T}\Big)_V. \tag{2.200}$$

We then use (2.198) to rewrite (2.200) as

$$\frac{C_V}{T} = \frac{C_P}{T} + \Big(\frac{\partial S}{\partial P}\Big)_T \Big(\frac{\partial P}{\partial T}\Big)_V. \tag{2.201}$$

Because we would like to express $C_P - C_V$ in terms of measurable quantities, we use the Maxwell relation (2.192) to eliminate $(\partial S/\partial P)$ and rewrite (2.201) as

$$C_P - C_V = T\Big(\frac{\partial V}{\partial T}\Big)_P \Big(\frac{\partial P}{\partial T}\Big)_V. \tag{2.202}$$

We next use the identity [see (2.238)]

$$\Big(\frac{\partial V}{\partial T}\Big)_P \Big(\frac{\partial T}{\partial P}\Big)_V \Big(\frac{\partial P}{\partial V}\Big)_T = -1 \tag{2.203}$$

to eliminate $(\partial P/\partial T)_V$ and write

$$C_P - C_V = -T\Big(\frac{\partial P}{\partial V}\Big)_T \Big(\frac{\partial V}{\partial T}\Big)_P^2. \tag{2.204}$$

If we substitute the definitions (2.172) of the isothermal compressibility κ and (2.173) for the thermal expansion coefficient α, we obtain the desired general relation

$$C_P - C_V = V\frac{T}{\kappa}\alpha^2. \tag{2.205}$$

For an ideal gas we have $\kappa = 1/P$ and $\alpha = 1/T$ and (2.205) reduces to [see (2.31)]

$$C_P - C_V = Nk. \tag{2.206}$$

Although we will not derive these conditions here, it is plausible that the heat capacity and compressibility of equilibrium thermodynamic systems must be positive. Given these assumptions, we see from (2.205) that $C_P > C_V$ in general.

2.23 *Applications to Irreversible Processes

Although the thermodynamic quantities of a system can be defined only when the system is in equilibrium, we have found that it is possible to obtain useful results for systems that pass through nonequilibrium states if the initial and final states are in equilibrium. In the following, we will consider some well-known thermodynamic processes.

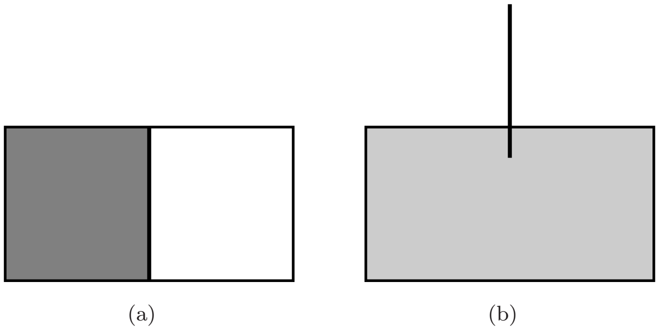

Figure 2.12: (a) A gas is kept in the left half of a box by a partition. The right half is evacuated. (b) The partition is removed and the gas expands irreversibly to fill the entire box.

2.23.1 Joule or free expansion process

In a Joule or free expansion the system expands into a vacuum while the entire system is thermally isolated (see Figure 2.12). The quantity of interest is the temperature change that is produced. Although this process is irreversible, we have learned that it can be treated by thermodynamics. Because $dQ = 0$ and $dW = 0$, the energy is a constant so that $dE(T, V) = 0$. This condition can be written as

$$dE = \Big(\frac{\partial E}{\partial T}\Big)_V dT + \Big(\frac{\partial E}{\partial V}\Big)_T dV = 0. \tag{2.207}$$

Hence, we obtain

$$\begin{aligned}\Big(\frac{\partial T}{\partial V}\Big)_E &= -\frac{(\partial E/\partial V)_T}{(\partial E/\partial T)_V} &(2.208)\\ &= -\frac{1}{C_V}\Big[T\Big(\frac{\partial P}{\partial T}\Big)_V - P\Big]. &(2.209)\end{aligned}$$

Equation (2.209) follows from the definition of C_V and from (2.197). The partial derivative $(\partial T/\partial V)_E$ is known as the Joule coefficient. For a finite change in volume, the total temperature change is found by integrating (2.209):

$$\Delta T = -\int_{V_1}^{V_2} \frac{1}{C_V}\Big[T\Big(\frac{\partial P}{\partial T}\Big)_V - P\Big]dV. \tag{2.210}$$

Because $(\partial P/\partial T)_V = P/T$ for an ideal gas, we conclude that the temperature of an ideal gas is unchanged in a free expansion. If the gas is not dilute, we expect that the intermolecular interactions are important and that the temperature will change in a free expansion.

Problem 2.29. Free expansion of a van der Waals gas

Calculate $(\partial T/\partial V)_E$ for the van der Waals energy equation of state (2.24) and show that a free expansion results in cooling. □

The cooling of a gas during a free expansion can be understood by the following qualitative argument. In a real gas there is an attractive force between the molecules or atoms, which leads to the total potential energy of a dilute gas being negative. As the gas expands, the attractive force becomes weaker, and the total potential energy becomes less negative, that is, it increases. As a result, the kinetic energy must decrease to keep the total energy constant. Because the temperature is proportional to the kinetic energy per particle, the temperature will also decrease. This free expansion process is used in refrigeration.

2.23.2 Joule-Thomson process

The Joule-Thomson (or Joule-Kelvin[24] or porous plug) process is a steady state process in which a gas is forced through a porous plug or expansion valve from a region of high pressure P_1 to a region of lower pressure P_2 [see Figure 2.13]. The gas is thermally isolated from its surroundings. The process is irreversible because the gas is not in equilibrium. We will see that a real gas is either cooled or heated by passing through the plug.

Consider a given amount (for example, one mole) of a gas that occupies a volume V_1 at pressure P_1 on the left-hand side of the valve and a volume V_2 at pressure P_2 when the gas arrives on the right-hand side. The work done on the gas is given by

$$W = -\int_{V_1}^{0} P dV - \int_{0}^{V_2} P dV. \tag{2.211}$$

The pressure on each side of the porous plug is constant, and hence we obtain

$$W = P_1V_1 - P_2V_2. \tag{2.212}$$

Because the process takes place in an isolated tube, there is no energy transfer due to heating, and the change in the internal energy is given by

$$\Delta E = E_2 - E_1 = W = P_1V_1 - P_2V_2. \tag{2.213}$$

Hence, we obtain

$$E_2 + P_2V_2 = E_1 + P_1V_1, \tag{2.214}$$

which can be written as

$$H_2 = H_1. \tag{2.215}$$

That is, the Joule-Thomson process occurs at constant enthalpy. All we can say is that the final enthalpy equals the initial enthalpy; the intermediate states of the gas are nonequilibrium states for which the enthalpy is not defined.

The calculation of the temperature change in the Joule-Thomson effect is similar to our calculation of the Joule effect. Because the process occurs at constant enthalpy, it is useful to write

$$dH(T,P) = \Big(\frac{\partial H}{\partial T}\Big)_P dT + \Big(\frac{\partial H}{\partial P}\Big)_T dP = 0. \tag{2.216}$$

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[24] William Thomson was later awarded a peerage and became Lord Kelvin.

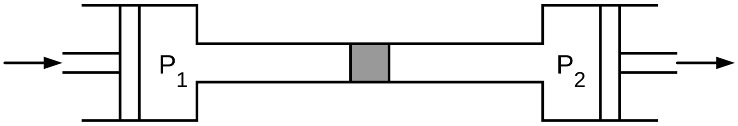

Figure 2.13: Schematic representation of the Joule-Thomson process. The two pistons ensure constant pressures on each side of the porous plug. The porous plug can be made by packing glass wool into a tube. The process can be made continuous by using a pump to return the gas from the region of low pressure to the region of high pressure.

As before, we assume that the number of particles is a constant. From (2.216) we have

$$dT = -\frac{(\partial H/\partial P)_T}{(\partial H/\partial T)_P} dP. \tag{2.217}$$

From the relation $dH = TdS + VdP$ (see (2.159)), we have $(\partial H/\partial P)_T = T(\partial S/\partial P)_T + V$. If we substitute this relation in (2.217), use the Maxwell relation (2.192), and the definition $C_P = (\partial H/\partial T)_P$, we obtain

$$\Big(\frac{\partial T}{\partial P}\Big)_H = \frac{V}{C_P}(T\alpha - 1), \tag{2.218}$$

where the thermal expansion coefficient α is defined by (2.173). Note that the change in pressure dP is negative, that is, the gas goes from a region of high pressure to a region of low pressure. To find the temperature change produced in a finite pressure drop, we integrate (2.218) and find

$$\Delta T = T_2 - T_1 = \int_{P_1}^{P_2} \frac{V}{C_P}\,(T\alpha - 1)\,dP. \tag{2.219}$$

For an ideal gas, $\alpha = 1/T$ and $\Delta T = 0$ as expected.

To understand the nature of the temperature change in a real gas, we calculate α for the van der Waals equation of state (2.12). We write the latter in the form

$$P + a\rho^2 = \frac{\rho kT}{1 - b\rho}, \tag{2.220}$$

and take the derivative with respect to T at constant P:

$$2a\rho\Big(\frac{\partial \rho}{\partial T}\Big)_P = \frac{\rho k}{1 - b\rho} + \Big(\frac{\partial \rho}{\partial T}\Big)_P \frac{kT}{(1 - b\rho)^2}. \tag{2.221}$$

If we express α as

$$\alpha = -\frac{1}{\rho}\Big(\frac{\partial \rho}{\partial T}\Big)_P, \tag{2.222}$$

we can write (2.221) in the form

$$\Big[\frac{kT}{(1 - b\rho)^2} - 2a\rho\Big]\alpha = \frac{k}{(1 - b\rho)}. \tag{2.223}$$

Problem 2.30. Low density limit of the thermal expansion coefficient

For simplicity, consider low densities and show that α in (2.223) is given by

$$\alpha = \frac{k(1-b\rho)}{kT - 2a\rho(1-b\rho)^2}, \tag{2.224a}$$

$$\approx \frac{1}{T}\Big[1 - \rho\Big(b - \frac{2a}{kT}\Big)\Big]. \tag{2.224b}$$

Use the approximation $(1+x)^n \approx 1 + nx$ for small x to obtain (2.224b). Then show that in this approximation

$$T\alpha - 1 = \rho[(2a/kT) - b]. \tag{2.225}$$

$\square$

We can define an inversion temperature $T_{\rm inv}$ at which the derivative $(\partial T/\partial P)_H$ changes sign. From (2.219) and (2.225) we see that $kT_{\rm inv} = 2a/b$ for a low density gas. For $T > T_{\rm inv}$, the gas warms as the pressure falls in the Joule-Thomson expansion; for $T < T_{\rm inv}$, the gas cools as the pressure falls.

For most gases $T_{\rm inv}$ is well above room temperatures. Although the cooling effect is small, the effect can be made cumulative by using the cooled expanded gas in a heat exchanger to precool the incoming gas.

2.24 Supplementary Notes

2.24.1 The mathematics of thermodynamics

Because the notation of thermodynamics is cumbersome, we have tried to simplify it whenever possible. However, one common simplification can lead to confusion.

Consider the functional relations

$$y = f(x) = x^2 \tag{2.226}$$

and

$$x = g(z) = z^{1/2}. \tag{2.227}$$

If we write x in terms of z, we can write y as

$$y = h(z) = f(g(z)) = z. \tag{2.228}$$

We have given the composite function a different symbol h because this function is different from both f and g. But we would soon exhaust the letters of the alphabet, and we frequently write $y = f(z) = z$, even though $f(z)$ is a different function than $f(x)$.

The notation is even more confusing in thermodynamics. Consider, for example, the entropy S as a function of E, V, and N, which we write as $S(E,V,N)$. However, we frequently consider E as a function of T from which we would obtain another functional relation: $S(E(T,V,N),V,N)$. A mathematician would write the latter function with a different symbol, but physicists usually do not. In so doing we confuse the name of a function with that of a variable and use the same

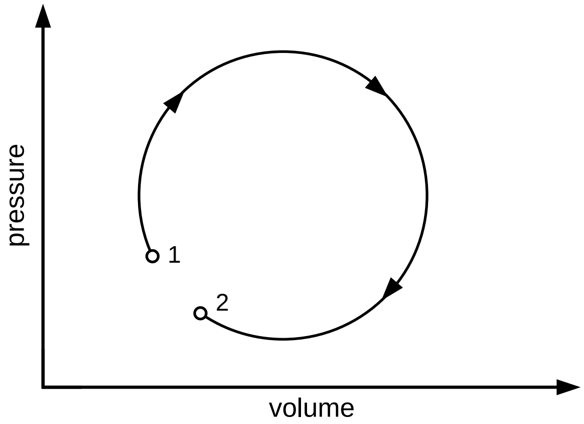

Figure 2.14: The change in internal energy can be made arbitrarily small by making the initial (1) and final (2) states arbitrarily close, but the total work done, which is the area enclosed by the nearly closed curve, is not vanishingly small. Adapted from Bohren and Albrecht.

name (symbol) for the same physical quantity. This sloppiness can cause problems when we take partial derivatives. If we write $\partial S/\partial V$, is E or T to be held fixed? One way to avoid confusion is to write $(\partial S/\partial V)_E$ or $(\partial S/\partial V)_T$, but this notation can become cumbersome.

Another confusing aspect of the mathematics of thermodynamics is the use of differentials. Some authors, including Bohren and Albrecht,[25] have criticized their use. These authors and others argue that the first law should be written as

$$\frac{dE}{dt} = \frac{dQ}{dt} + \frac{dW}{dt}, \tag{2.229}$$

rather than

$$dE = dQ + dW, \tag{2.230}$$

An argument for writing the first law in the form (2.229) is that the first law applies to a process, which must occur over an interval of time. Here, dE/dt represents the rate of energy change, dW/dt is the rate of doing work, and dQ/dt is the rate of heating. In contrast, dE in (2.230) is the infinitesimal change in internal energy, dW is the infinitesimal work done on the system, and dQ is the infinitesimal heat added. However, the meaning of an infinitesimal in this context is not clear. For example, for the process shown in Figure 2.14, the energy difference $E_2 - E_1$ is arbitrarily small and hence could be represented by a differential dE, but the work and heating are not infinitesimal. The use of infinitesimals should not cause confusion if you understand that dy in the context $dy/dx = f(x)$ has a different meaning than in the context $dy = f(x)\,dx$.

Example 2.22. Exact and inexact differentials

Suppose that a system is described by two variables, x and y and $f(x, y) = xy$ (see page 44).[26] Then

$$df = d(xy) = ydx + xdy. \tag{2.231}$$

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[25] See Bohren and Albrecht, pp. 93–99.

[26] This example is taken from Blundell and Blundell [2006], page 105.

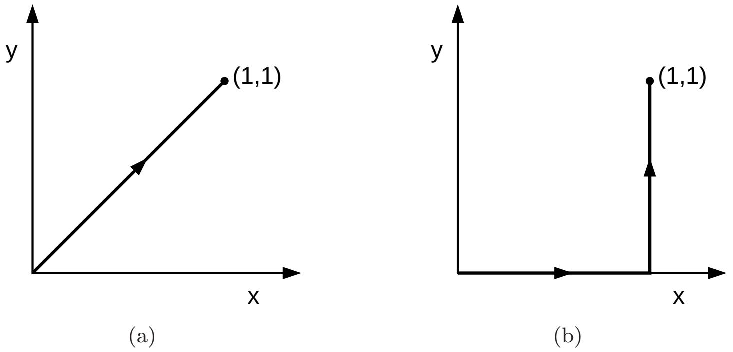

Figure 2.15: Two among many possible paths between the points $(x,\, y) = (0,\, 0)$ and $(1, 1)$.

If $f(x, y)$ changes from $(0, 0)$ to $(1, 1)$, the change in f is given by

$$\Delta f = \int_{0,0}^{1,1} df = xy]_{0,0}^{1,1} - (1 \times 1) - (0 \times 0) = 1. \tag{2.232}$$

This result is independent of the path because df is an exact differential.

Now consider $dg = ydx$. The change in g when (x, y) changes from $(0, 0)$ to $(1, 1)$ along the path shown in Figure 2.15(a) is

$$\Delta g = \int_{0,0}^{1,1} y\, dx = \int_0^1 x\, dx = 1/2. \tag{2.233}$$

Show that when the integral is along the path shown in Figure 2.15(b), the result is $\Delta g = 0$. Hence the value of Δg depends on the path and dg is an inexact differential. Many textbooks write inexact differentials as $\text{đ}g$. ♢

Review of partial derivatives. If z is a function of two independent variables x and y, then the total change in $z(x, y)$ due to changes in x and y can be expressed as

$$dz = \Big(\frac{\partial z}{\partial x}\Big)_y dx + \Big(\frac{\partial z}{\partial y}\Big)_x dy. \tag{2.234}$$

The cross derivatives $\partial^2 z/\partial x\, \partial y$ and $\partial^2 z/\partial y\, \partial x$ are equal, that is, the order of the two derivatives does not matter. We used this property to derive the Maxwell relations in Section 2.22.

The *chain rule* for differentiation holds in the usual way if the *same* variables are held constant in each derivative. For example, we can write

$$\Big(\frac{\partial z}{\partial x}\Big)_y = \Big(\frac{\partial z}{\partial w}\Big)_y \Big(\frac{\partial w}{\partial x}\Big)_y. \tag{2.235}$$

We also can derive a relation whose form is superficially similar to (2.235) when *different* variables are held constant in each term. From (2.234) we set $dz = 0$ and obtain

$$dz = 0 = \Big(\frac{\partial z}{\partial x}\Big)_y dx + \Big(\frac{\partial z}{\partial y}\Big)_x dy. \tag{2.236}$$

We divide both sides of (2.236) by dx:

$$0 = \Big(\frac{\partial z}{\partial x}\Big)_y + \Big(\frac{\partial z}{\partial y}\Big)_x \Big(\frac{\partial y}{\partial x}\Big)_z, \tag{2.237}$$

and rewrite (2.237) as

$$\Big(\frac{\partial z}{\partial x}\Big)_y = -\Big(\frac{\partial z}{\partial y}\Big)_x \Big(\frac{\partial y}{\partial x}\Big)_z. \tag{2.238}$$

Note that (2.238) involves a relation between the three possible partial derivatives which involve x, y, and z.

Problem 2.31. Consider the function

$$z(x, y) = x^2y + 2x^4y^6. \tag{2.239}$$

Calculate $\partial z/\partial x$, $\partial z/\partial y$, $\partial^2 z/\partial x\,\partial y$, and $\partial^2 z/\partial y\,\partial x$ and show that $\partial^2 z/\partial x\,\partial y = \partial^2 z/\partial y\,\partial x$. ☐

2.24.2 Thermodynamic potentials and Legendre transforms

There are many ways of encoding the information in a function. For example Fourier transforms are useful when a function is periodic. In quantum mechanics it is useful to expand a wave function in terms of eigenfunctions. In thermodynamics we usually have more control over certain variables than others. For example, we might prefer to work with the temperature, which is easy to measure and is formally defined as a derivative, rather than the energy or entropy which are more difficult to measure.

Consider a function $f(x)$ of one variable. The *Legendre transform* allows us to replace the independent variable x by the derivative df/dx without sacrificing any of the information in the original relation. In the following we will consider functions of only one variable, but the results can be easily generalized to functions of several variables.

The derivative

$$m(x) \equiv f'(x) \equiv \frac{df(x)}{dx} \tag{2.240}$$

is the slope of $f(x)$ at x. To treat m as the independent variable instead of x, we might be tempted to solve (2.240) for x in terms of m and then simply write f as a function of m. However, this procedure would lead to a loss of some of the mathematical content of the original function $f(x)$. That is, given f as a function of m, we would not be able to reconstruct $f(x)$.

As an example[27] suppose that $f(x) = (1/2)e^{2x}$. Hence $m = e^{2x}$ and $f(m) = m/2$. We now try to reconstruct $f(x)$ from $f(m)$ to determine if we still have the same information. Because $m = f'(x)$, we have $f(m) = f(m(x)) = f'(x)/2$ or $f' = 2f$. The solution of the latter differential equation gives $f(x) = Ae^{2x}$, where A is not specified. So this procedure loses information. The problem is that knowing only the slope does not tell us the value of the intercept at $x = 0$.

The goal of the Legendre transformation is to find the function $g(m)$ such that $g(m)$ contains the same information as the function $f(x)$. In Figure 2.16(a) we show three of the infinite number of curves with the same slope $f'(x)$. Our goal is to replace the information in the set of points

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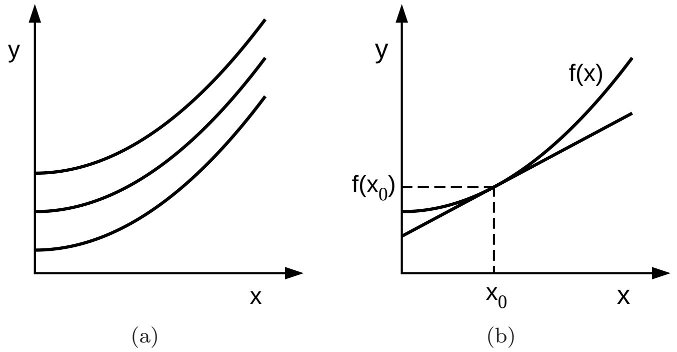
[27] This example is adapted from Chowdhury and Stauffer [2000].



(a) (b)

Figure 2.16: (a) Three of the infinite set of curves with the same values of $f'(x)$ for all x. (b) The curve $f(x)$ and the tangent line at a specific value of $x = x_0$ needed to provide enough information to reproduce $f(x)$.

$\{x, f(x)\}$ by the equivalent information specified by the set $\{m, g(m)\}$. To do so we need to choose the specific curve $f(x)$ shown in Figure 2.16(b). At each point x_0, we can specify a specific curve by giving the value of the $x = 0$ intercept of the tangent line at x_0.

Consider the tangent line that passes through the point $(x_0, f(x_0))$ with slope m and intercept b at $x = 0$. Because the general equation for a straight line is $y = mx + b$, we can write

$$b = y - mx, \tag{2.241a}$$

or

$$g(m(x_0)) = f(x_0) - f'(x_0)x_0. \tag{2.241b}$$

The slope depends on the particular point x_0. The function g for an arbitrary point x is given by

$$g(m(x)) = f(x) - xf'(x) = f(x) - xm. \tag{2.242}$$

The function $g(m)$ is the Legendre transform of $f(x)$.

Our goal is to write g only in terms of the variable m. We now show that the right-hand side of (2.242) depends only on m and not on x. From (2.242) we write

$$dg = df - mdx - xdm. \tag{2.243}$$

Because $df = mdx$ [see (2.240)], we have

$$dg = -xdm. \tag{2.244}$$

Hence, g depends only on m, just as $df = mdx$ indicates that f depends only on x.

To calculate $g(m)$ explicitly we have to eliminate x in (2.242) using $m = f'(x)$. We can solve the latter for x only if there is a one-to-one relation between x and m, which holds if the function $f'(x)$ is monotonic or $f(x)$ is always concave up or always concave down.

Example 2.23. Reconstructing $f(x)$
We again consider $f(x) = \frac{1}{2}e^{2x}$ for which $m(x) = e^{2x}$. Then

$$g = f(x) - xm = \frac{1}{2}e^{2x} - xe^{2x}. \tag{2.245}$$

We next invert the relation $m = e^{2x}$ to solve for x in terms of m: $x = \frac{1}{2}\ln m$. Hence the Legendre transform of $f(x)$ is

$$g(m) = \frac{1}{2}m(1 - \ln m). \tag{2.246}$$

♢

Now suppose that $g(m)$ is given. Can we construct $f(x)$? From (2.244) we have $x = -dg/dm$. From (2.246) we have $x = \frac{1}{2}\ln m$, and hence $m = e^{2x}$ for our example. Hence

$$f = g(m) + xm = \frac{1}{2}m(1 - \ln m) + xm \tag{2.247a}$$

and

$$f(x) = \frac{1}{2}e^{2x}(1 - 2x) + xe^{2x} = \frac{1}{2}e^{2x}, \tag{2.247b}$$

which is the original function.

Problem 2.32. Simple Legendre transforms

(a) Calculate the Legendre transform of $f(x) = x^3$.

(b) Calculate the Legendre transforms of the functions $f(x) = x$ and $f(x) = \sin x$ if they exist. □

Problem 2.33. The Helmholtz free energy as a Legendre transform
Start from the function $E(S, V, N)$ and use the Legendre transform to find the function $F(T, V, N)$. □

Vocabulary

thermodynamics, system, boundary, surroundings, macrostate

insulator, conductor, adiabatic wall, thermal contact

volume V, pressure P, number of particles N, chemical potential μ

thermometer, thermodynamic temperature T (K), Celsius temperature scale (°C), ideal gas temperature scale

W, work done on a system

Q, energy transferred due to a temperature difference only

state function, internal energy E, entropy S

three laws of thermodynamics

intensive and extensive variables

heat capacity C, specific heat c

quasistatic, reversible, irreversible, isothermal, constant volume, adiabatic, quasistatic, and cyclic processes

heat bath, heat source, heat sink, reservoir

Carnot engine, Carnot efficiency, refrigerator, heat pump, efficiency, coefficient of performance

thermal equilibrium, mechanical equilibrium, chemical equilibrium, thermodynamic equilibrium

thermodynamic potential, Helmholtz free energy F, Gibbs free energy G, enthalpy H, Landau potential Ω

ideal gas equation of state, van der Waals equation of state

Boltzmann's constant k, universal gas constant R

Additional Problems

Problem 2.34. Mechanical and thermodynamic equilibrium

Compare the notion of equilibrium in mechanics and thermodynamics. □

Problem 2.35. Meaning of phenomenological

In the text the word phenomenological was used to describe a description of phenomena that is not derived from first principles. In what sense is all of physics phenomenological? □

Problem 2.36. Barometer

Explain how a barometer works to measure pressure. □

Problem 2.37. Is a diamond forever?

Diamond is a metastable form of carbon, which means that it is not in the state with the lowest free energy. That is, diamond is in a local rather than in the global minimum of the free energy. Obviously, the diamond state can stay for a very long time. Is it possible to apply the laws of thermodynamics to diamond? What is the stable form of carbon? □

Problem 2.38. A question of degree

Although you probably learned how to convert between Fahrenheit and Celsius temperatures, you might not remember the details. The fact that 1°C equals $\frac{9}{5}{}^\circ$F is not too difficult to remember, but where does the factor of 32 go? An alternative procedure is to add 40 to the temperature in °C or °F and multiply by $\frac{5}{9}$ if going from °F to °C or by $\frac{9}{5}$ if going from °C to °F. Then subtract 40 from the calculated temperature to obtain the desired conversion. Explain why this procedure works. □

Problem 2.39. Historical development of thermodynamics

Discuss the development of our understanding of thermodynamics and the contributions of people such as Count Rumford (Benjamin Thompson), James Joule, Julius Robert von Mayer, Sadi Carnot, William Thomson (Lord Kelvin), Rudolf Clausius, Anders Celsius, and Gabriel Fahrenheit. Choose two people to discuss and use at least two different sources. □

Problem 2.40. Naming rights

Discuss the meaning of the statement that one of the most important contributions of 19th century thermodynamics was the development of the understanding that heat (and work) are names of *processes* not names of *things*. □

Problem 2.41. Hot and cold

It is common in everyday language to refer to temperatures as "hot" and "cold." Why is this use of language misleading? Does it make sense to say that one body is "twice as hot" as another? Does it matter whether the Celsius or Kelvin temperature scale is used? □

Problem 2.42. Does it make sense to talk about the amount of heat in a room? □

Problem 2.43. Heat as a fluid

(a) In what context can energy transferred by heating be treated as a fluid? Give some examples where this concept of "heat" is used in everyday life. In what context does the concept of "heat" as a fluid break down? Is it possible to isolate "heat" in a bottle or pour it from one object to another?

(b) *Write a short essay based on at least two sources on the history of the "caloric." □

Problem 2.44. Why should we check the pressure in a tire when the tire is cold? □

Problem 2.45. Why do we use the triple point of water to calibrate thermometers? Why not use the melting point or the boiling point? □

Problem 2.46. Money in the bank

In the text we discussed the analogy of the internal energy to the amount of water in a pond. The following analogy due to Dugdale might also be helpful.[28] Suppose that a student has a bank account with a certain amount of money. The student can add to this amount by either depositing or withdrawing cash and by writing or depositing checks from the accounts of others. Does the total amount of money in the student's account distinguish between cash and check transfers? Discuss the analogies to internal energy, work, and heating. □

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[28] See Dugdale, pp. 21–22.

Problem 2.47. Common misconceptions

The following excerpt is taken from a text used by one of the author's children when he was in the sixth grade. The title and the author of the text will remain anonymous. Find the conceptual errors in the text.

A. What is heat?

You have learned that all matter is made up of atoms. Most of these atoms combine to form molecules. These molecules are always moving – they have kinetic energy. *Heat* is the energy of motion (kinetic energy) of the particles that make up any piece of matter.

The amount of heat a material has depends on how many molecules it has and how fast the molecules are moving. The greater the number of molecules and the faster they move, the greater the number of collisions between them. These collisions produce a large amount of heat.

How is heat measured? Scientists measure heat by using a unit called a *calorie*. A calorie is the amount of heat needed to raise the temperature of 1 gram of water 1 degree centigrade (Celsius).

A gram is a unit used for measuring mass. There are about 454 grams in 1 pound.

Scientists use a *small calorie* and a *large Calorie*. The unit used to measure the amount of heat needed to raise the temperature of 1 gram of water 1 degree centigrade is the *small calorie*. The *large calorie* is used to measure units of heat in food. For example, a glass of milk when burned in your body produces about 125 Calories.

Questions:

1. What is heat?
2. What two things does the amount of heat a substance has depend on?
3. What is a calorie?
4. Explain the following: small calorie; large calorie.

B. What is temperature?

The amount of hotness in an object is called its *temperature*. A *thermometer* is used to measure temperature in units called *degrees*. Most thermometers contain a liquid.

C. Expansion and Contraction

Most solids, liquids and gases *expand* when heated and *contract* when cooled. When matter is heated, its molecules move faster. As they move, they collide with their neighbors very rapidly. The collisions force the molecules to spread farther apart. The farther apart they spread, the more the matter expands.

Air, which is a mixture of gases, expands and becomes lighter when its temperature rises. Warm air rises because the cold, heavier air sinks and pushes up the lighter warm air.

What happens when solids or gases are cooled? The molecules slow down and collide less. The molecules move closer together, causing the material to contract. □

Problem 2.48. Why are the terms heat capacity and specific heat poor choices of names? Suggest more appropriate names. Comment on the statement: "The heat capacity of a body is a measure of how much heat the body can hold." □

Problem 2.49. The atmosphere of Mars has a pressure that is only 0.007 times that of Earth and an average temperature of 218 K. What is the volume of 1 mole of the Martian atmosphere? Compare your result with the volume of one mole on Earth. □

Problem 2.50. Gasoline burns in an automobile engine and releases energy at the rate of 160 kW. Energy is lost through the car's radiator at the rate of 51 kW and out the exhaust at 50 kW. An additional 23 kW goes to frictional heating within the car. What fraction of the fuel energy is available for moving the car? □

Problem 2.51. Two moles of an ideal gas at 300 K in a volume of $0.10\,\mathrm{m}^3$ are compressed isothermally by a motor driven piston to a volume of $0.010\,\mathrm{m}^3$. If this process takes places in 120 s, how powerful a motor is needed? □

Problem 2.52. Give an example of a process in which a system is not heated, but its temperature increases. Also give an example of a process in which a system is heated, but its temperature is unchanged. □

Problem 2.53. Expansion of a gas into vacuum

(a) Suppose that a gas expands adiabatically into a vacuum. What is the work done by the gas?

(b) Suppose that the total energy of the gas is given by [see (2.24)]

$$E = \frac{3}{2}NkT - N\frac{N}{V}a, \tag{2.248}$$

where a is a positive constant. Initially the gas occupies a volume V_1 at a temperature T_1. The gas then expands adiabatically into a vacuum so that it occupies a total volume V_2. What is the final temperature of the gas? □

Problem 2.54. Black hole thermodynamics

A black hole is created from the collapse of a massive object into one so dense that nothing can escape beyond a certain radius, including light. The measurable properties of a black hole depend only on its mass, charge, and angular momentum. In this problem we estimate the entropy and temperature of a charge neutral nonrotating black hole.

(a) Because the properties of the black hole depend only on its mass, use dimensional analysis to estimate the radius R of a black hole in terms of its mass M, the gravitational constant G, and the speed of light c. (If you think quantum mechanics is relevant, try including Planck's constant h, but there is no way to obtain a quantity that is a function of M, G, c, and h that has dimensions of length.)

(b) Assume that the entropy is of order Nk, where N is the number of particles in the black hole. The maximum entropy occurs when the particles are photons of wavelength λ of the order of the diameter of the black hole. Take $\lambda = 2R$ and determine the entropy S as a function of M (the total energy is Mc^2 and the energy of a photon is hc/λ). More detailed theoretical arguments give the correct relation

$$S = k\frac{8\pi^2 GM^2}{hc}. \tag{2.249}$$

Your approximate result should have the correct dependence on G, M, h, c, and k. Calculate a numerical value for the entropy for a one solar mass black hole using (2.249). (The solar mass $M_\odot \approx 2 \times 10^{30}\,\mathrm{kg}$.)

(c) Express the entropy in terms of the surface area A of the black hole instead of M. Note that the area is a direct measure of the entropy. Does the entropy increase or decrease when two black holes coalesce into one?

(d) Express S in terms of the total energy E instead of M and determine the temperature for a one solar mass black hole. Use the approximation for R obtained in part (a) to find the temperature in terms of the gravitational field g at the radius R. □

Problem 2.55. Entropy as a state function

(a) Suppose that one mole of a monatomic ideal gas expands in a quasistatic adiabatic process from $P_1 = 1\,\mathrm{Pa}$ and $V_1 = 1\,\mathrm{m}^3$ to $V_2 = 8\,\mathrm{m}^3$. What is the change in the pressure and the entropy of the gas?

(b) What are the initial and final temperatures of the gas?

(c) Consider a process at constant volume that brings the system to the temperature T_2 which you found in part (b). What is the change in entropy of this process?

(d) Next increase the volume to V_2 at constant temperature T_2. What is the change in the entropy in this isothermal process?

(e) Compare the total change in the entropy to the result that you found in part (a). Does the change of the entropy depend on the path between two equilibrium states? □

Problem 2.56. Consider the various processes shown in Figure 2.17 and calculate W, the total work done on the system and Q, the total energy absorbed by heating the system. Assume that the system is an ideal gas. (This problem is adapted from Reif, p. 215.)

(a) The volume is changed quasistatically along the curved path $1 \to 3$ while the gas is kept thermally isolated.

(b) The system is compressed from its original volume of $V_1 = 8\,\mathrm{m}^3$ to its final volume $V_3 = 1\,\mathrm{m}^3$ along the path $1 \to 2$ and $2 \to 3$. The pressure is kept constant at $P_1 = 1\,\mathrm{Pa}$ and the system is cooled to maintain constant pressure. The volume is then kept constant and the system is heated to increase the pressure to $P_2 = 32\,\mathrm{Pa}$.

(c) The pressure is changed at constant volume along the path $1 \to 4$ and then at constant pressure along $4 \to 3$. The two steps of the preceding process are performed in opposite order.

(d) Diagonal path $1 \to 3$. The volume is decreased and the system is heated so that the pressure is proportional to the volume. □

Problem 2.57. More work

Consider a system described by the van der Waals equation of state which expands at constant temperature from volume V_1 to volume V_2. Assume that the density $\rho = N/V \ll 1$ over the range of volumes of interest.

(a) Calculate the work W_{vdw} done on the gas to the lowest relevant order in ρ.

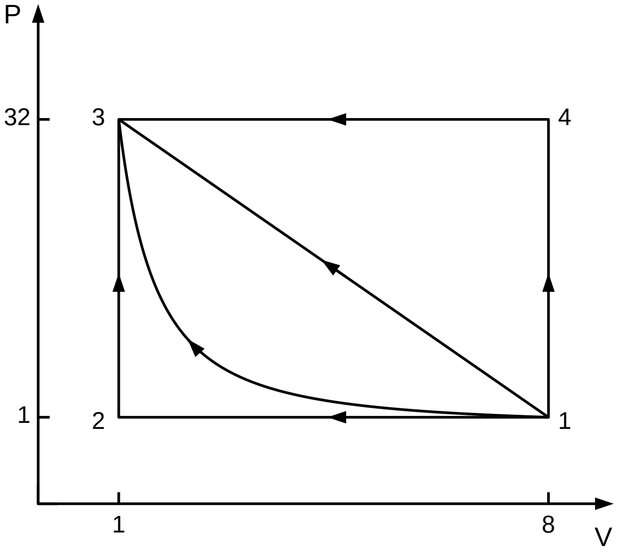

Figure 2.17: Illustration of various thermodynamic processes discussed in Problem 2.56. The units of the pressure P and the volume V are Pa and m^3, respectively.

(b) Calculate the work $W_{\rm ideal}$ done on the gas under the same conditions assuming that the gas is ideal.

(c) Find the difference $W_{\rm vdw} - W_{\rm ideal}$ and discuss the reason why this difference is positive or negative as a function of the temperature. ☐

Problem 2.58. A 0.5 kg copper block at 80°C is dropped into 1 kg of water at 10°C. What is the final temperature? What is the change in entropy of the system? The specific heat of copper is 386 J/(kg K). ☐

Problem 2.59. Carnot efficiencies

(a) Surface temperatures in the tropical oceans are approximately 25°C, while hundreds of meters below the surface the temperature is approximately 5°C. What would be the efficiency of a Carnot engine operating between these temperatures?

(b) What is the efficiency of a Carnot engine operating between the normal freezing and boiling points of water? ☐

Problem 2.60. A small sample of material is taken through a Carnot cycle between a heat source of boiling helium at 1.76 K and a heat sink at an unknown lower temperature. During the process, 7.5 mJ of energy is absorbed by heating from the helium and 0.55 mJ is rejected at the lower temperature. What is the lower temperature? ☐

Problem 2.61. Positive change of the total entropy

(a) In Example 2.16 it was shown that the total entropy change when body A is placed in thermal contact with a heat bath at temperature T_B can be written as

$$\Delta S = C_A f\Big(\frac{T_B}{T_A}\Big), \tag{2.250}$$

where C_A is temperature-independent and T_A is the initial temperature of body A. The function $f(x)$ is given by

$$f(x) = \ln x + \frac{1}{x} - 1, \tag{2.251}$$

where $x = T_B/T_A$. Calculate $f(x = 1)$ and df/dx and show that the total entropy increases when body A is placed in thermal contact with a heat bath at a higher temperature ($x > 1$).

(b) If the total entropy increases in a heating process, does the total entropy decrease in a cooling process? Use similar considerations to show that the total entropy increases in both cases.

(c) Plot $f(x)$ as a function of x and confirm that its minimum value is at $x = 1$ and that $f > 0$ for $x < 1$ and $x > 1$. □

Problem 2.62. Changes in the entropy

Calculate the changes in entropy due to various methods of heating:

(a) One kilogram of water at 0°C is brought into contact with a heat bath at 90°C. What is the change in entropy of the water? What is the change in entropy of the bath? What is the change in entropy of the entire system consisting of both water and heat bath? (The specific heat of water is approximately 4184 J/kg K.)

(b) The water is heated from 0°C to 90°C by first bringing it into contact with a heat bath at 45°C and then with a heat bath at 90°C. What is the change in entropy of the entire system?

(c) Discuss how the water can be heated from 0°C to 90°C without any change in entropy of the entire system. □

Problem 2.63. The Otto cycle

The Otto cycle is an idealized prototype of most present-day internal combustion engines. The idealization assumes that the working substance is air rather than a mixture of gases and vapor whose composition changes during the cycle. For simplicity, we assume that C_V and C_P are constant and that $\gamma = C_P/C_V = 1.4$, the value for air. The more important approximation is that the processes are assumed to be quasistatic. An idealized cycle that represents the six parts of this cycle is known as the air standard Otto cycle and is illustrated in Figure 2.18.

> $5 \rightarrow 1$. *Intake stroke.* The mixture of gasoline and air is drawn into the tube through the intake valve by the movement of the piston. Idealization: A quasistatic isobaric intake of air at pressure P_0 to a volume V_1.
>
> $1 \rightarrow 2$. *Compression stroke.* The intake valve closes and the air-fuel mixture is rapidly compressed in the tube. The compression is nearly adiabatic and the temperature rises. Idealization: A quasistatic adiabatic compression from V_1 to V_2; the temperature rises from T_1 to T_2.

> $2 \to 3$. *Explosion.* The mixture explodes such that the volume remains unchanged and a very high temperature and pressure is reached. Idealization: A quasistatic and constant volume increase of temperature and pressure due to the absorption of energy from a series of heat baths between T_2 and T_3.
>
> $3 \to 4$. *Power stroke.* The hot combustion products expand and do work on the piston. The pressure and temperature decrease considerably. Idealization: A quasistatic adiabatic expansion produces a decrease in temperature.
>
> $4 \to 1$. *Valve exhaust.* At the end of the power stroke the exhaust valve opens and the combustion products are exhausted to the atmosphere. There is a sudden decrease in pressure. Idealization: A quasistatic constant volume decrease in temperature to T_1 and pressure P_0 due to an exchange of energy with a series of heat baths between T_4 and T_1.
>
> $1 \to 5$. *Exhaust stroke.* The piston forces the remaining gases into the atmosphere. The exhaust valve then closes and the intake valve opens for the next intake stroke. Idealization: A quasistatic isobaric expulsion of the air.

Show that the efficiency of the Otto cycle is

$$\eta = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}. \tag{2.252}$$

A compression ratio of about ten can be used without causing knocking. Estimate the theoretical maximum efficiency. In a real engine, the efficiency is about half of this value. ☐

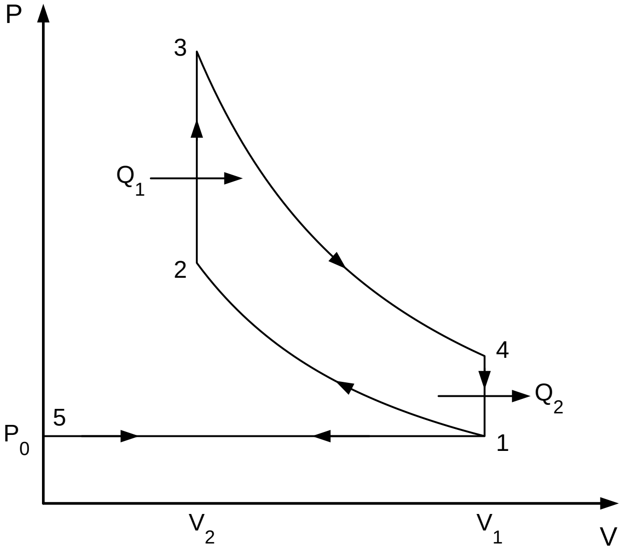

Figure 2.18: The air standard Otto cycle.

Problem 2.64. If S is expressed as a function of T, V or T, P, then it is no longer a thermodynamic potential. That is, the maximum thermodynamic information is contained in S as a function of E and V (for fixed N). Why? ☐

Problem 2.65. The enthalpy as a free energy

Show that the enthalpy $H = E + PV$ is the appropriate free energy if the entropy and number of particles is fixed, but the volume can change. In this case we consider a system connected to a larger body such that the pressure of the system equals that of the large body with the constraint that the larger body and the system do not exchange energy. ☐

Problem 2.66. The Landau potential

Find the Landau potential for the case where the temperature is fixed by a heat bath, the volume is fixed, and particles can move between the systems and the heat bath. You will need to extend the definition of the availability to allow for the number of particles to vary within the system. Use a similar argument about extensive variables to show that the Landau potential equals $-PV$. ☐

Problem 2.67. Joule-Thomson inversion temperature

The inversion temperature for the Joule-Thomson effect is determined by the relation $(\partial T/\partial V)_P = T/V$ [see (2.218)]. In Section 2.23.2 we showed that for low densities and high temperatures (low pressures) the inversion temperature is given by $kT_{\rm inv} = 2a/b$.

(a) Show that at high pressures $T_{\rm inv}$ is given by

$$kT_{\rm inv} = \frac{2a}{9b}\Big[2 \pm \sqrt{1 - 3b^2P/a}\Big]^2. \tag{2.253}$$

(b) Show that as $P \to 0$, $kT_{\rm inv} = 2a/b$.

(c) For $P < a/3b^2$, there are two inversion points between which the derivative $(\partial T/\partial P)_H$ is positive. Outside this temperature interval the derivative is negative. For $P > a/3b^2$ there are no inversion points and $(\partial T/\partial P)_H$ is negative everywhere. Find the pressure dependence of the inversion temperature for the Joule-Thomson effect. ☐

Problem 2.68. More thermodynamic identities

(a) Derive the identities

$$\Big(\frac{\partial C_P}{\partial P}\Big)_T = -T\Big(\frac{\partial^2 V}{\partial T^2}\Big)_P, \tag{2.254a}$$

and

$$\Big(\frac{\partial C_V}{\partial V}\Big)_T = T\Big(\frac{\partial^2 P}{\partial T^2}\Big)_V. \tag{2.254b}$$

(b) Show that

$$\frac{\kappa}{\kappa_S} = \frac{C_P}{C_V}, \tag{2.255}$$

where the isothermal compressibility is given by (2.172) and the adiabatic compressibility κ_S is defined as

$$\kappa_S = -\frac{1}{V}\Big(\frac{\partial V}{\partial P}\Big)_S. \tag{2.256}$$

Use (2.255) and (2.205) to obtain the relation

$$\kappa_T - \kappa_S = \frac{TV}{C_P}\alpha^2. \tag{2.257}$$

□

Suggestions for Further Reading

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The history of thermodynamics and statistical mechanics is fascinating and not one to which we can do justice. We encourage you to read some of the original sources such as the English translation of Sadi Carnot’s paper in *Reflections on the Motive Power of Fire: A Critical Edition with the Surviving Scientific Manuscripts*, edited by Robert Fox, Manchester University Press (1986). Other recommended books are listed in the following.

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Chapter 3

Concepts of Probability

5 October 2010

We introduce the basic concepts of probability and apply them to simple physical systems and everyday life. We discuss the universal nature of the central limit theorem and the Gaussian distribution for the sum of a large number of random variables. Because of the importance of probability in many contexts, our discussion goes beyond what we need for the applications of statistical mechanics that we discuss in later chapters.

3.1 Probability in Everyday Life

One of our goals, which we will consider in Chapter 4 and subsequent chapters, is to relate the behavior of various macroscopic quantities to the underlying microscopic behavior of the individual atoms or other constituents. To do so, we need to introduce some ideas from probability.

We all use ideas of probability in everyday life. For example, every morning many of us decide what to wear based on the probability of rain. We cross streets knowing that the probability of being hit by a car is small. You can make a rough estimate of the probability of being hit by a car. It must be less than one in a thousand, because you have crossed streets thousands of times and hopefully you have not been hit. You might be hit tomorrow, or you might have been hit the first time you tried to cross a street. These comments illustrate that we have some intuitive sense of probability, and because it is a useful concept for survival, we know how to estimate it. As expressed by Laplace (1819), "Probability theory is nothing but common sense reduced to calculation." Another interesting thought is due to Maxwell (1850): "The true logic of this world is the calculus of probabilities." That is, probability is a natural language for describing many real world phenomena.

However, our intuition only takes us so far. Consider airplane travel. Is it safe to fly? Suppose that there is one chance in five million of a plane crashing on a given flight and that there are about 50,000 flights a day. Then every 100 days or so there is a reasonable likelihood of a plane crash somewhere in the world. This estimate is in rough accord with what we know. For a given flight, your chances of crashing are approximately one part in 5×10^6, and if you fly ten times a year for 100 years, it seems that flying is not too much of a risk. Suppose that instead of living

100 years, you could live 50,000 years. In this case you would take 500,000 flights, and it would be much more risky to fly if you wished to live your full 50,000 years. Although this last statement seems reasonable, can you explain why?

Much of the motivation for the mathematical formulation of probability arose from the proficiency of professional gamblers in estimating betting odds and their desire to have more quantitative measures of success. Although games of chance have been played since history has been recorded, the first steps toward a mathematical formulation of games of chance began in the middle of the seventeenth century. Some of the important contributors over the following 150 years include Pascal, Fermat, Descartes, Leibnitz, Newton, Bernoulli, and Laplace, names that are probably familiar to you.

Given the long history of games of chance and the interest in estimating probability in a variety of contexts, it is remarkable that the theory of probability took so long to develop. One reason is that the idea of probability is subtle and is capable of many interpretations. An understanding of probability is elusive due in part to the fact that the probably depends on the status of the information that we have (a fact well known to poker players). Although the rules of probability are defined by simple mathematical rules, an understanding of probability is greatly aided by experience with real data and concrete problems. To test your current understanding of probability, solve Problems 3.1–3.6 before reading the rest of this chapter. Then in Problem 3.7 formulate the laws of probability based on your solutions to these problems.

Problem 3.1. Marbles in a jar

A jar contains two orange, five blue, three red, and four yellow marbles. A marble is drawn at random from the jar. Find the probability that

(a) the marble is orange;

(b) the marble is red;

(c) the marble is orange or blue. □

Problem 3.2. Piggy bank

A piggy bank contains one penny, one nickel, one dime, and one quarter. It is shaken until two coins fall out at random. What is the probability that at least \$0.30 falls out? □

Problem 3.3. Two dice

A person tosses a pair of dice at the same time. Find the probability that

(a) both dice show the same number;

(b) both dice show a number less than 5;

(c) both dice show an even number;

(d) the product of the numbers is 12. □

Problem 3.4. Free throws

A person hits 16 free throws out of 25 attempts. What is the probability that this person will make a free throw on the next attempt? □

Problem 3.5. Toss of a die

Consider an experiment in which a die is tossed 150 times and the number of times each face is observed is counted.[1] The value of A, the number of dots on the face of the die and the number of times that it appeared is shown in Table 3.1.

(a) What is the predicted average value of A assuming a fair die?

(b) What is the average value of A observed in this experiment? □

value of A	frequency
1	23
2	28
3	30
4	21
5	23
6	25

Table 3.1: The number of times face A appeared in 150 tosses (see Problem 3.5).

Problem 3.6. What's in your purse?

A coin is taken at random from a purse that contains one penny, two nickels, four dimes, and three quarters. If x equals the value of the coin, find the average value of x. □

Problem 3.7. Rules of probability

Based on your solutions to Problems 3.1–3.6, state the rules of probability as you understand them at this time. □

The following problems are related to the use of probability in everyday life.

Problem 3.8. Choices

Suppose that you are offered the following choice:

(a) A prize of \$50, or

(b) you flip a (fair) coin and win \$100 if you get a head, but \$0 if you get a tail.

Which choice would you make? Explain your reasoning. Would your choice change if the prize was \$40? □

Problem 3.9. More choices

Suppose that you are offered the following choices:

(a) A prize of \$100 is awarded for each head found in ten flips of a coin, or

---

[1] The earliest known six-sided dice have been found in the Middle East. A die made of baked clay was found in excavations of ancient Mesopotamia. The history of games of chance is discussed by Bennett (1998).

(b) a prize of \$400.

What choice would you make? Explain your reasoning. □

Problem 3.10. Thinking about probability

(a) Suppose that you were to judge an event to be 99.9999% probable. Would you be willing to bet \$999 999 against \$1 that the event would occur? Discuss why probability assessments should be kept separate from decision issues.

(b) In one version of the lottery the player chooses six numbers from 1 through 49. The player wins only if there is an exact match with the numbers that are randomly generated. Suppose that someone gives you a dollar to play the lottery. What sequence of six numbers between 1 and 49 would you choose? Are some choices better than others?

(c) Suppose you toss a coin six times and obtain heads each time. Estimate the probability that you will obtain heads on your seventh toss. Now imagine tossing the coin 60 times, and obtaining heads each time. What do you think would happen on the next toss?

(d) What is the probability that it will rain tomorrow? What is the probability that the Dow Jones industrial average will increase tomorrow?

(e) Give several examples of the use of probability in everyday life. In each case discuss how you would estimate the probability. □

3.2 The Rules of Probability

We now summarize the basic rules and ideas of probability.[2] Suppose that there is an operation or a process that has several distinct possible *outcomes*. The process might be the flip of a coin or the roll of a six-sided die. We call each flip a *trial*. The list of all the possible *events* or *outcomes* is called the *sample space*. We assume that the events are *mutually exclusive*, that is, the occurrence of one event implies that the others cannot happen at the same time. We let n represent the number of events, and label the events by the index i which varies from 1 to n. For now we assume that the sample space is finite and discrete. For example, the flip of a coin results in one of two events, which we refer to as heads and tails and the roll of a die yields one of six possible events.

For each event i, we assign a probability $P(i)$ that satisfies the conditions

$$P(i) \geq 0 \tag{3.1}$$

and

$$\sum_i P(i) = 1. \tag{3.2}$$

$P(i) = 0$ means that the event cannot occur, and $P(i) = 1$ means that the event must occur. The normalization condition (3.2) says that the sum of the probabilities of all possible mutually exclusive outcomes is 1.

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[2] In 1933 the Russian mathematician A. N. Kolmogorov formulated a complete set of axioms for the mathematical definition of probability.

Example 3.1. Sample space of a die

Let x be the number of points on the face of a die. What is the sample space of x?

Solution. The sample space or set of possible events is $x_i = \{1, 2, 3, 4, 5, 6\}$. These six outcomes are mutually exclusive. ♢

The rules of probability will be summarized in (3.3) and (3.5). These abstract rules must be supplemented by an *interpretation* of the term probability. As we will see, there are many different interpretations of probability because any interpretation that satisfies the rules of probability may be regarded as a kind of probability.

A common interpretation of probability is based on *symmetry*. Suppose that we have a two-sided coin that shows heads and tails. There are two possible mutually exclusive outcomes, and if the coin is fair, each outcome is equally likely.[3] If a die with six distinct faces (see Figure 3.1) is perfect, we can use symmetry arguments to argue that each outcome should be counted equally and $P(i) = 1/6$ for each of the six faces. For an actual die, we can estimate the probability of an outcome *a posteriori*, that is, by the observation of the outcome of many throws. As we will see, other kinds of information in addition to symmetry arguments can be used to estimate probabilities.

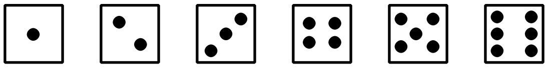

Figure 3.1: The six possible outcomes of the toss of a die.

Suppose that we know that the probability of rolling any face of a die in one throw is equal to 1/6, and we want to find the probability of finding face 3 *or* face 6 in one throw. In this case we wish to know the probability of a trial that is a combination of more elementary operations for which the probabilities are already known. That is, we want to know the probability of the outcome, i *or* j, where i and j are mutually exclusive events. According to the rules of probability, the probability of event i *or* j is given by

$$P(i \text{ or } j) = P(i) + P(j) \qquad \text{(addition rule)}. \tag{3.3}$$

The relation (3.3) is generalizable to more than two events. An important consequence of (3.3) is that if $P(i)$ is the probability of event i, then the probability of event i not occurring is $1 - P(i)$.

Example 3.2. What is the probability of throwing a three or a six with one throw of a die?

Solution. The probability that the face exhibits either 3 or 6 is $\frac{1}{6} + \frac{1}{6} = \frac{1}{3}$. ♢

Example 3.3. What is the probability of *not* throwing a six with one throw of die?

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[3] Is the outcome of a coin toss really random? The outcome of a coin flip is deterministic, but the outcome depends sensitively on the initial conditions, which we don't know precisely. See the references at the end of the chapter.

Solution. The answer is the probability of either 1 or 2 or 3 or 4 or 5. The addition rule gives that the probability $P(\text{not six})$ is

$$P(\text{not six}) = P(1) + P(2) + P(3) + P(4) + P(5) \tag{3.4a}$$

$$= 1 - P(6) = \frac{5}{6}, \tag{3.4b}$$

where the last relation follows from the fact that the sum of the probabilities for all outcomes sums to one. It is useful to take advantage of this property when solving many probability problems. ♢

Another simple rule concerns the probability of the joint occurrence of independent events. These events might be the probability of throwing a 3 on one die *and* the probability of throwing a 4 on a second die. If two events are independent, then the probability of both events occurring is the product of their probabilities

$$P(i \text{ and } j) = P(i)\,P(j) \qquad \text{(multiplication rule)}. \tag{3.5}$$

Events are independent if the occurrence of one event does not affect the probability of the occurrence of the other.

To understand the applicability of (3.5) and the meaning of the independence of events, consider the problem of determining the probability that a person chosen at random is a female over six feet tall. Suppose that we know that the probability of a person to be over six feet tall is $P(6^+) = \frac{1}{10}$, and the probability of being female is $P(\text{female}) = \frac{1}{2}$. We might conclude that the probability of being a tall female is $P(\text{female})P(6^+) = \frac{1}{2} \times \frac{1}{10} = \frac{1}{20}$. This same probability calculation would hold for a tall male. However, this reasoning is incorrect, because the probability of being a tall female differs from the probability of being a tall male. The problem is that the two events – being over six feet tall and being female – are not independent. On the other hand, consider the probability that a person chosen at random is female and was born on September 6. We can reasonably assume equal likelihood of birthdays for all days of the year, and it is correct to conclude that this probability is $\frac{1}{2} \times \frac{1}{365}$ (not counting leap years). Being a woman and being born on September 6 are independent events.

Problem 3.11. Give an example from your solutions to Problems 3.1–3.6 where you used the addition rule or the multiplication rule or both. □

Example 3.4. What is the probability of throwing an even number with one throw of a die?

Solution. We can use the addition rule to find that

$$P(\text{even}) = P(2) + P(4) + P(6) = \frac{1}{6} + \frac{1}{6} + \frac{1}{6} = \frac{1}{2}. \tag{3.6}$$

♢

Example 3.5. What is the probability of the same face appearing on two successive throws of a die?

Solution. We know that the probability of any specific combination of outcomes, for example, (1,1), (2,2), … (6,6) is $\frac{1}{6} \times \frac{1}{6} = \frac{1}{36}$. Hence, by the addition rule

$$P(\text{same face}) = P(1,1) + P(2,2) + \ldots + P(6,6) = 6 \times \frac{1}{36} = \frac{1}{6}. \tag{3.7}$$

♢

Example 3.6. What is the probability that in two throws of a die at least one 6 appears?

Solution. We know that

$$P(6) = \frac{1}{6}, \qquad P(\text{not }6) = \frac{5}{6}. \tag{3.8}$$

There are four possible outcomes $(6, 6)$, $(6, \text{not }6)$, $(\text{not }6, 6)$, and $(\text{not }6, \text{not }6)$ with the respective probabilities

$$P(6, 6) = \frac{1}{6} \times \frac{1}{6} = \frac{1}{36}, \tag{3.9a}$$

$$P(6, \text{not }6) = P(\text{not }6, 6) = \frac{1}{6} \times \frac{5}{6} = \frac{5}{36}, \tag{3.9b}$$

$$P(\text{not }6, \text{not }6) = \frac{5}{6} \times \frac{5}{6} = \frac{25}{36}. \tag{3.9c}$$

All outcomes except the last have at least one 6. Hence, the probability of obtaining at least one 6 is

$$P(\text{at least one }6) = P(6, 6) + P(6, \text{not }6) + P(\text{not }6, 6) \tag{3.10a}$$

$$= \frac{1}{36} + \frac{5}{36} + \frac{5}{36} = \frac{11}{36}. \tag{3.10b}$$

A more direct way of obtaining this result is to use the normalization condition. That is,

$$P(\text{at least one six}) = 1 - P(\text{not }6, \text{not }6) = 1 - \frac{25}{36} = \frac{11}{36}. \tag{3.10c}$$

♢

Example 3.7. What is the probability of obtaining at least one six in four throws of a die?

Solution. We know that, in one throw of a die, there are two outcomes with $P(6) = \frac{1}{6}$ and $P(\text{not }6) = \frac{5}{6}$ as in (3.8). Hence, in four throws of a die there are 16 possible outcomes, only one of which has no 6. We can use the multiplication rule (3.5) to find that

$$P(\text{not }6, \text{not }6, \text{not }6, \text{not }6) = P(\text{not }6)^4 = \Big(\frac{5}{6}\Big)^4, \tag{3.11}$$

and hence

$$P(\text{at least one six}) = 1 - P(\text{not }6, \text{not }6, \text{not }6, \text{not }6) \tag{3.12a}$$

$$= 1 - \Big(\frac{5}{6}\Big)^4 = \frac{671}{1296} \approx 0.517. \tag{3.12b}$$

♢

Frequently we know the probabilities only up to a constant factor. For example, we might know $P(1) = 2P(2)$, but not $P(1)$ or $P(2)$ separately. Suppose we know that $P(i)$ is proportional to $f(i)$, where $f(i)$ is a known function. To obtain the normalized probabilities, we divide each function $f(i)$ by the sum of all the unnormalized probabilities. That is, if $P(i) \propto f(i)$ and $Z = \sum f(i)$, then $P(i) = f(i)/Z$. This procedure is called *normalization*.

Example 3.8. Suppose that in a given class it is three times as likely to receive a C as an A, twice as likely to obtain a B as an A, one-fourth as likely to be assigned a D as an A, and nobody fails the class. What are the probabilities of getting each grade?

Solution. We first assign the unnormalized probability of receiving an A as $f(A) = 1$. Then $f(B) = 2$, $f(C) = 3$, and $f(D) = 0.25$. Then $Z = \sum_i f(i) = 1 + 2 + 3 + 0.25 = 6.25$. Hence, $P(A) = f(A)/Z = 1/6.25 = 0.16$, $P(B) = 2/6.25 = 0.32$, $P(C) = 3/6.25 = 0.48$, and $P(D) = 0.25/6.25 = 0.04$. ♢

The normalization procedure arises again and again in different contexts. We will see that much of the mathematics of statistical mechanics can be formulated in terms of the calculation of normalization constants.

Problem 3.12. Rolling the dice

If a person rolls two dice, what is the probability $P(n)$ of getting the sum n? Plot $P(n)$ as a function of n. □

Problem 3.13. An almost even bet

What is the probability of obtaining at least one double 6 in 24 throws of a pair of dice? □

Problem 3.14. Rolling three dice

Suppose that three dice are thrown at the same time. What is the ratio of the probabilities that the sum of the three faces is 10 compared to 9? □

Problem 3.15. Fallacious reasoning

What is the probability that the total number of spots shown on three dice thrown at the same time is 11? What is the probability that the total is 12? What is the fallacy in the following argument? The number 11 occurs in six ways: (1,4,6), (2,3,6), (1,5,5), (2,4,5), (3,3,5), (3,4,4). The number 12 also occurs in six ways: (1,5,6), (2,4,6), (3,3,6), (2,5,5), (3,4,5), (4,4,4) and hence the two numbers should be equally probable. □

3.3 Mean Values

The specification of the *probability distribution* $P(1)$, $P(2)$, $\ldots, P(n)$ for the n possible values of the variable x constitutes the most complete statistical description of the system. However, in many cases it is more convenient to describe the distribution of the possible values of x in a less detailed way. The most familiar way is to specify the *average* or *mean* value of x, which we will denote as $\overline{x}$. The definition of the mean value of x is

$$\overline{x} \equiv x_1 P(1) + x_2 P(2) + \ldots + x_n P(n) \tag{3.13a}$$

$$= \sum_{i=1}^{n} x_i P(i), \tag{3.13b}$$

where $P(i)$ is the probability of x_i. If $f(x)$ is a function of x, then the mean value of $f(x)$ is given by

$$\overline{f(x)} = \sum_{i=1}^{n} f(x_i) P(i). \tag{3.14}$$

If $f(x)$ and $g(x)$ are any two functions of x, then

$$\overline{f(x)+g(x)} = \sum_{i=1}^{n} [f(x_i)+g(x_i)]P(i) \tag{3.15a}$$

$$= \sum_{i=1}^{n} f(x_i)P(i) + \sum_{i=1}^{n} g(x_i)P(i), \tag{3.15b}$$

or

$$\overline{f(x)+g(x)} = \overline{f(x)} + \overline{g(x)}. \tag{3.15c}$$

Problem 3.16. Show that, if c is a constant, then

$$\overline{cf(x)} = c\overline{f(x)}. \tag{3.16}$$

□

We define the mth *moment* of the probability distribution P as

$$\overline{x^m} \equiv \sum_{i=1}^{n} {x_i}^m P(i), \tag{3.17}$$

where we have let $f(x) = x^m$. The mean of x is the first moment of the probability distribution.

Problem 3.17. Suppose that the variable x takes on the values -2, -1, 0, 1, and 2 with probabilities 1/16, 4/16, 6/16, 4/16, and 1/16, respectively. Calculate the first two moments of x. □

The mean value of x is a measure of the central value of x about which the various values of x_i are distributed. If we measure the deviation of x from its mean, we have

$$\Delta x \equiv x - \overline{x} \tag{3.18}$$

and

$$\overline{\Delta x} = \overline{(x - \overline{x})} = \overline{x} - \overline{x} = 0. \tag{3.19}$$

That is, the average value of the deviation of x from its mean vanishes.

If only one outcome j were possible, we would have $P(i) = 1$ for $i = j$ and zero otherwise; that is, the probability distribution would have zero width. Usually, there is more than one outcome and a measure of the width of the probability distribution is given by

$$\overline{\Delta x^2} \equiv \overline{\big(x - \overline{x}\big)^2}. \tag{3.20}$$

The quantity $\overline{\Delta x^2}$ is known as the *dispersion* or *variance* and its square root is called the *standard deviation*. The use of the square of $x - \overline{x}$ ensures that the contribution of x values that are smaller and larger than $\overline{x}$ contribute to Δx^2 with the same sign. It is easy to see that the larger the spread of values of x about $\overline{x}$, the larger the variance. A useful form for the variance can be found by noting that

$$\overline{\big(x - \overline{x}\big)^2} = \overline{\big(x^2 - 2x\overline{x} + \overline{x}^2\big)} \tag{3.21a}$$

$$= \overline{x^2} - 2\overline{x}\,\overline{x} + \overline{x}^2 \tag{3.21b}$$

$$= \overline{x^2} - \overline{x}^2. \tag{3.21c}$$

throw	probability of success on trial i
1	p
2	qp
3	q^2p
4	q^3p

Table 3.2: Probability of a 6 for the first time on throw i, where $p = 1/6$ is the probability of a 6 on a given throw and $q = 1 - p$ (see Example 3.10).

Because $\overline{\Delta x^2}$ is always nonnegative, it follows that $\overline{x^2} \geq \overline{x}^2$.

The variance is the mean value of $(x - \overline{x})^2$ and represents the square of a width. We will find that it is useful to interpret the width of the probability distribution in terms of the standard deviation σ, which is defined as the square root of the variance. The standard deviation of the probability distribution $P(x)$ is given by

$$\sigma_x = \sqrt{\overline{\Delta x^2}} = \sqrt{\big(\overline{x^2} - \overline{x}^2\big)}. \tag{3.22}$$

Example 3.9. Find the mean value $\overline{x}$, the variance $\overline{\Delta x^2}$, and the standard deviation σ_x for the value of a single throw of a die.

Solution. Because $P(i) = \frac{1}{6}$ for $i = 1, \ldots, 6$, we have that

$$\overline{x} = \frac{1}{6}(1+2+3+4+5+6) = \frac{7}{2} = 3.5, \tag{3.23a}$$

$$\overline{x^2} = \frac{1}{6}(1+4+9+16+25+36) = \frac{46}{3}, \tag{3.23b}$$

$$\overline{\Delta x^2} = \overline{x^2} - \overline{x}^2 = \frac{46}{3} - \frac{49}{4} = \frac{37}{12} \approx 3.08, \tag{3.23c}$$

$$\sigma_x \approx \sqrt{3.08} = 1.76. \tag{3.23d}$$

◊

Example 3.10. On the average, how many times must a die be thrown until a 6 appears?

Solution. Although it might be obvious that the answer is six, it is instructive to confirm this answer directly. Let p be the probability of a 6 on a given throw.

To calculate m, the mean number of throws needed before a 6 appears, we calculate the probability of obtaining a 6 for the first time on the ith throw, multiply this probability by i, and then sum over all i. The first few probabilities are listed in Table 3.2. The resulting sum is

$$m = p + 2pq + 3pq^2 + 4pq^3 + \cdots \tag{3.24a}$$

$$= p(1 + 2q + 3q^2 + \cdots) \tag{3.24b}$$

$$= p\frac{d}{dq}\big(1 + q + q^2 + q^3 + \cdots\big) \tag{3.24c}$$

$$= p\frac{d}{dq}\frac{1}{1-q} = \frac{p}{(1-q)^2} = \frac{1}{p}. \tag{3.24d}$$

Another way to obtain this result is to use the following recursive argument. Because the throws are independent, the mean number of additional throws needed after throwing the die any number of times is still m. If we throw the die once and do not obtain a 6, we will need on average m more throws or a total of $m + 1$. If we throw it twice and do not obtain a 6 on either throw, we will need m more throws or a total of $m + 2$, and so forth. The contribution to the mean due to failing on the first throw and then succeeding sometime later is $q(m + 1)$. The probability of succeeding on the first throw is p and the contribution to the mean is $p(1) = p$. The mean is the sum of these two terms or $m = (1 - p)(m + 1) + p$. The solution for m is $m = 1/p$. ♢

3.4 The Meaning of Probability

How can we assign probabilities to the various events? If event E_1 is more probable than event E_2 $[P(E_1) > P(E_2)]$, we mean that E_1 is more likely to occur than E_2. This statement of our intuitive understanding of probability illustrates that probability is a way of classifying the plausibility of events under conditions of uncertainty. Probability is related to our degree of belief in the occurrence of an event.

This definition of probability is not bound to a single evaluation rule and there are many ways to obtain $P(E_i)$. For example, we could use symmetry considerations as we have done, past frequencies, simulations, theoretical calculations, or, as we will learn in Section 3.4.2, Bayesian inference. Probability assessments depend on who does the evaluation and the status of the information the evaluator has at the moment of the assessment. We always evaluate the conditional probability, that is, the probability of an event E given the information I, $P(E|I)$. Consequently, several people can have simultaneously different degrees of belief about the same event, as is well known to investors in the stock market.

If rational people have access to the same information, they should come to the same conclusion about the probability of an event. The idea of a *coherent bet* forces us to make probability assessments that correspond to our belief in the occurrence of an event. If we consider an event to be 50% probable, then we should be ready to place an even bet on the occurrence of the event or on its opposite. However, if someone wishes to place the bet in one direction but not in the other, it means that this person thinks that the preferred event is more probable than the other. In this case the 50% probability assessment is *incoherent*, and this person's wish does not correspond to his or her belief.

A coherent bet has to be considered *virtual*. For example, a person might judge an event to be 99.9999% probable, but nevertheless refuse to bet \$999999 against \$1, if \$999999 is much more than the person's resources. Nevertheless, the person might be convinced that this bet would be fair if he/she had an infinite budget. Probability assessments should be kept separate from decision issues. Decisions depend not only on the probability of the event, but also on the subjective importance of a given amount of money (see, for example, Problems 3.10 and 3.85).

Our discussion of probability as the degree of belief that an event will occur shows the inadequacy of the frequency definition of probability, which *defines* probability as the ratio of the number of desired outcomes to the total number of possible outcomes. This definition is inadequate because we would have to specify that each outcome has equal probability. Thus we would have to use the term probability in its own definition. If we do an experiment to measure the frequencies of various outcomes, then we need to make an additional assumption that the measured frequencies will be the same in the future as they were in the past. Also we have to make a large number of measurements to ensure accuracy, and we have no way of knowing a priori how many measurements are sufficient. Thus, the definition of probability as a frequency really turns out to be a method for estimating probabilities with some hidden assumptions.

Our definition of probability as a measure of the degree of belief in the occurrence of an outcome implies that probability depends on our prior knowledge, because belief depends on prior knowledge. For example, if we toss a coin and obtain 100 tails in a row, we might use this knowledge as evidence that the coin or toss is biased, and thus estimate that the probability of throwing another tail is very high. However, if a careful physical analysis shows that there is no bias, then we would stick to our estimate of 1/2. The probability assessment depends on what knowledge we bring to the problem. If we have no knowledge other than the possible outcomes, then the best estimate is to assume equal probability for all events. However, this assumption is not a definition, but an example of belief. As an example of the importance of prior knowledge, consider the following problem.

Problem 3.18. A couple with two children

(a) A couple has two children. What is the probability that at least one child is a girl?

(b) Suppose that you know that at least one child is a girl. What is the probability that both children are girls?

(c) Instead suppose that we know that the oldest child is a girl. What is the probability that the youngest is a girl? □

We know that we can estimate probabilities empirically by sampling, that is, by making repeated measurements of the outcome of independent events. Intuitively we believe that if we perform more and more measurements, the calculated average will approach the exact mean of the quantity of interest. This idea is called *the law of large numbers*.

As an example, suppose that we flip a single coin M times and count the number of heads. Our result for the number of heads is shown in Table 3.3. We see that the fraction of heads approaches 1/2 as the number of measurements becomes larger.

Problem 3.19. Multiple tosses of a single coin

Use Program `CoinToss` to simulate multiple tosses of a single coin. What is the correspondence between this simulation of a coin being tossed many times and the actual physical tossing of a coin? If the coin is "fair," what do you think the ratio of the number of heads to the total number of tosses will be? Do you obtain this number after 100 tosses? 10,000 tosses? □

Another way of estimating the probability is to perform a single measurement on many copies or replicas of the system of interest. For example, instead of flipping a single coin 100 times in succession, we collect 100 coins and flip all of them at the same time. The fraction of coins that show heads is an estimate of the probability of that event. The collection of identically prepared systems is called an *ensemble*, and the probability of occurrence of a single event is estimated with respect to this ensemble. The ensemble consists of a large number M of identical systems, that is, systems that satisfy the same known conditions.

tosses	heads	fraction of heads
10	4	0.4
50	29	0.58
100	49	0.49
200	101	0.505
500	235	0.470
1,000	518	0.518
10,000	4997	0.4997
100,000	50021	0.50021
500,000	249946	0.49999
1,000,000	500416	0.50042

Table 3.3: The number and fraction of heads in M tosses of a coin. We did not really toss a coin in the air 10^6 times. Instead we used a computer to generate a sequence of random numbers to simulate the tossing of a coin. Because you might not be familiar with such sequences, imagine a robot that can write the positive integers between 1 and 2^{31} on pieces of paper. The robot places these pieces in a hat, shakes the hat, and then chooses the pieces at random. If the number chosen is less than $\frac{1}{2} \times 2^{31}$, then we say that we found a head. Each piece is placed back in the hat after it is read.

If the system of interest is not changing in time, it is reasonable to assume that an estimate of the probability by either a series of measurements on a single system at different times or similar measurements on many identical systems at the same time would give consistent results.

Note that we have *estimated* various probabilities by a frequency, but have not *defined* probability in terms of a frequency. As emphasized by D'Agostini, past frequency is experimental data. This data happened with certainty so the concept of probability no longer applies. Probability is how much we believe that an event will occur taking into account all available information including past frequencies. Because probability quantifies the degree of belief at a given time, it is not directly measurable. If we make further measurements, they can only influence future assessments of the probability.

3.4.1 Information and uncertainty

Consider two experiments that each have two outcomes E_1 and E_2 with probabilities P_1 and P_2. For example, the experiments could correspond to the toss of a coin. In the first experiment the coin has probabilities $P_1 = P_2 = 1/2$, and in the second experiment (a bent coin) $P_1 = 1/5$ and $P_2 = 4/5$. Intuitively, we would say that the result of the first experiment is more uncertain than the result of the second experiment.

Next consider two additional experiments. In the third experiment there are four outcomes with $P_1 = P_2 = P_3 = P_4 = 1/4$, and in the fourth experiment there are six outcomes with $P_1 = P_2 = P_3 = P_4 = P_5 = P_6 = 1/6$. The fourth experiment is the most uncertain because there are more equally likely outcomes and the second experiment is the least uncertain.

We will now introduce a mathematical measure that is consistent with our intuitive sense of uncertainty. Let us define the uncertainty function $S(P_1, P_2, \ldots, P_i, \ldots)$ where P_i is the probability of event i. We first consider the case where all the probabilities P_i are equal. Then $P_1 = P_2 = \ldots = P_i = 1/\Omega$, where Ω is the total number of outcomes. In this case we have $S = S(1/\Omega, 1/\Omega, \ldots)$ or simply $S(\Omega)$.

It is easy to see that $S(\Omega)$ has to satisfy some simple conditions. For only one outcome, $\Omega = 1$ and there is no uncertainty. Hence we must have

$$S(\Omega = 1) = 0. \tag{3.25}$$

We also have that

$$S(\Omega_1) > S(\Omega_2) \text{ if } \Omega_1 > \Omega_2. \tag{3.26}$$

That is, $S(\Omega)$ is an increasing function of Ω.

We next consider the form of S for multiple events. For example, suppose that we throw a die with Ω_1 outcomes and flip a coin with Ω_2 equally probable outcomes. The total number of outcomes is $\Omega = \Omega_1\Omega_2$. If the result of the die is known, the uncertainty associated with the die is reduced to zero, but there still is uncertainty associated with the toss of the coin. Similarly, we can reduce the uncertainty in the reverse order, but the total uncertainty is still nonzero. These considerations suggest that

$$S(\Omega_1\Omega_2) = S(\Omega_1) + S(\Omega_2). \tag{3.27}$$

It is remarkable that there is an unique functional form that satisfies the three conditions (3.25)–(3.27). We can find this form by writing (3.27) in the form

$$S(xy) = S(x) + S(y), \tag{3.28}$$

and taking the variables x and y to be continuous. (The analysis can be done assuming that x and y are discrete variables, but the analysis is simpler if we assume that x and y are continuous.) Now we take the partial derivative of $S(xy)$ with respect to x and then with respect to y. We let $z = xy$ and obtain

$$\frac{\partial S(z)}{\partial x} = \frac{\partial z}{\partial x}\frac{dS(z)}{dz} = y\frac{dS(z)}{dz}, \tag{3.29a}$$

$$\frac{\partial S(z)}{\partial y} = \frac{\partial z}{\partial y}\frac{dS(z)}{dz} = x\frac{dS(z)}{dz}. \tag{3.29b}$$

From (3.28) we have

$$\frac{\partial S(z)}{\partial x} = \frac{dS(x)}{dx}, \tag{3.30a}$$

$$\frac{\partial S(z)}{\partial y} = \frac{dS(y)}{dy}. \tag{3.30b}$$

By comparing the right-hand side of (3.29) and (3.30), we have

$$\frac{dS}{dx} = y\frac{dS}{dz}, \tag{3.31a}$$

$$\frac{dS}{dy} = x\frac{dS}{dz}. \tag{3.31b}$$

If we multiply (3.31a) by x and (3.31b) by y, we obtain

$$x\frac{dS(x)}{dx} = y\frac{dS(y)}{dy} = z\frac{dS(z)}{dz}. \tag{3.32}$$

Note that the first term in (3.32) depends only on x and the second term depends only on y. Because x and y are independent variables, the three terms in (3.32) must be equal to a constant. Hence we have the desired condition

$$x\frac{dS(x)}{dx} = y\frac{dS(y)}{dy} = A, \tag{3.33}$$

where A is a constant. The differential equation in (3.33) can be integrated to give

$$S(x) = A\ln x + B. \tag{3.34}$$

The integration constant B must be equal to zero to satisfy the condition (3.25). The constant A is arbitrary so we choose $A = 1$. Hence for equal probabilities we have that

$$S(\Omega) = \ln\Omega. \tag{3.35}$$

What about the case where the probabilities for the various events are unequal? We will not derive the result here but only state the result that the general form of the uncertainty S is

$$S = -\sum_i P_i \ln P_i. \tag{3.36}$$

Note that, if all the probabilities are equal, then

$$P_i = \frac{1}{\Omega} \qquad \text{(for all } i\text{)}. \tag{3.37}$$

In this case

$$S = -\sum_i \frac{1}{\Omega}\ln\frac{1}{\Omega} = \Omega\frac{1}{\Omega}\ln\Omega = \ln\Omega, \tag{3.38}$$

because there are Ω equal terms in the sum. Hence (3.36) reduces to (3.35) as required. We also see that, if outcome j is certain, $P_j = 1$ and $P_i = 0$ if $i \neq j$ and $S = -1\ln 1 = 0$. That is, if the outcome is certain, the uncertainty is zero, and there is no missing information.

We have shown that, if the P_i are known, then the uncertainty or missing information S can be calculated. Usually the problem is the other way around, and we want to determine the probabilities. Suppose we flip a perfect coin for which there are two possibilities. We expect that $P_1(\text{heads}) = P_2(\text{tails}) = 1/2$. That is, we would not assign a different probability to each outcome unless we had information to justify it. Intuitively we have adopted the principle of *least bias* or *maximum uncertainty.* Let's reconsider the toss of a coin. In this case S is given by

$$S = -\sum_i P_i \ln P_i = -(P_1 \ln P_1 + P_2 \ln P_2) \tag{3.39a}$$

$$= -\big[P_1 \ln P_1 + (1 - P_1)\ln(1 - P_1)\big], \tag{3.39b}$$

where we have used the fact that $P_1 + P_2 = 1$. We use the principle of maximum uncertainty and set the derivative of S with respect to P_1 equal to zero:[4]

$$\frac{dS}{dP_1} = -[\ln P_1 + 1 - \ln(1 - P_1) - 1] = -\ln\frac{P_1}{1 - P_1} = 0. \tag{3.40}$$

The solution of (3.40) satisfies

$$\frac{P_1}{1 - P_1} = 1, \tag{3.41}$$

which is satisfied by $P_1 = 1/2$. We can check that this solution is a maximum by calculating the second derivative.

$$\frac{\partial^2 S}{\partial P_1^2} = -\Big[\frac{1}{P_1} + \frac{1}{1 - P_1}\Big] = -4, \tag{3.42}$$

which is less than zero, as expected for a maximum.

Problem 3.20. Uncertainty

(a) Consider the toss of a coin for which $P_1 = P_2 = 1/2$ for the two outcomes. What is the uncertainty in this case?

(b) What is the uncertainty for $P_1 = 1/5$ and $P_2 = 4/5$? How does the uncertainty in this case compare to that in part (a)?

(c) On page 118 we discussed four experiments with various outcomes. Compare the uncertainty S of the third and fourth experiments. □

Example 3.11. The toss of a three-sided die yields events E_1, E_2, and E_3 with faces of 1, 2, and 3 points, respectively. As a result of tossing many dice, we learn that the mean number of points is $f = 1.9$, but we do not know the individual probabilities. What are the values of P_1, P_2, and P_3 that maximize the uncertainty consistent with the information that $f = 1.9$?

Solution. We have

$$S = -\big[P_1 \ln P_1 + P_2 \ln P_2 + P_3 \ln P_3\big]. \tag{3.43}$$

We also know that

$$f = 1P_1 + 2P_2 + 3P_3, \tag{3.44}$$

and $P_1 + P_2 + P_3 = 1$. We use the latter condition to eliminate P_3 using $P_3 = 1 - P_1 - P_2$, and rewrite (3.44) as

$$f = P_1 + 2P_2 + 3(1 - P_1 - P_2) = 3 - 2P_1 - P_2. \tag{3.45}$$

We then use (3.45) to eliminate P_2 and P_3 from (3.43) with $P_2 = 3 - f - 2P_1$ and $P_3 = f - 2 + P_1$:

$$S = -[P_1 \ln P_1 + (3 - f - 2P_1)\ln(3 - f - 2P_1) + (f - 2 + P_1)\ln(f - 2 + P_1)]. \tag{3.46}$$

---

[4] We have used the fact that $d(\ln x)/dx = 1/x$.

Because S in (3.46) depends only on P_1, we can differentiate S with respect to P_1 to find its maximum value:

$$\frac{dS}{dP_1} = -\Big[\ln P_1 + 1 - 2\big[\ln(3 - f - 2P_1) + 1\big] + \big[\ln(f - 2 + P_1) + 1\big]\Big] \tag{3.47a}$$

$$= \ln \frac{P_1(f - 2 + P_1)}{(3 - f - 2P_1)^2} = 0. \tag{3.47b}$$

We see that for dS/dP_1 to be equal to zero, the argument of the logarithm must be one. The result is a quadratic equation for P_1 (see Problem 3.21). ♢

Problem 3.21. Fill in the missing steps in Example 3.11 and solve for P_1, P_2, and P_3. ☐

In Section 3.11.1 we maximize the uncertainty for a case for which there are more than three outcomes.

3.4.2 *Bayesian inference

Conditional probabilities are not especially important for the development of equilibrium statistical mechanics, so this section may be omitted for now. Conditional probability and Bayes' theorem are very important for the analysis of data including spam filters for email and image restoration, for example. Bayes' theorem gives us a way of understanding how the probability that a hypothesis is true is affected by new evidence.

Let us define $P(\mathrm{A}|\mathrm{B})$ as the probability of A occurring given that we know that B has occurred. We know that

$$P(\mathrm{A}) = P(\mathrm{A}|\mathrm{B})P(\mathrm{B}) + P(\mathrm{A}|-\mathrm{B})P(-\mathrm{B}), \tag{3.48}$$

where $-$B means that B did not occur. In (3.48) we used the fact that

$$P(\mathrm{A\ and\ B}) = P(\mathrm{A}|\mathrm{B})P(\mathrm{B}) = P(\mathrm{B}|\mathrm{A})P(\mathrm{A}). \tag{3.49}$$

Equation (3.49) means that the probability that A and B occur equals the probability that A occurs given B times the probability that B occurs, which is the same as the probability that B occurs given A times the probability that A occurs. Note that $P(\mathrm{A\ and\ B})$ is the same as $P(\mathrm{B\ and\ A})$, but $P(\mathrm{A}|\mathrm{B})$ does not have the same meaning as $P(\mathrm{B}|\mathrm{A})$.

We can rearrange (3.49) to obtain Bayes' theorem

$$\boxed{P(\mathrm{A}|\mathrm{B}) = \frac{P(\mathrm{B}|\mathrm{A})P(\mathrm{A})}{P(\mathrm{B})}} \qquad \text{(Bayes' theorem).} \tag{3.50}$$

We can generalize (3.50) for multiple possible outcomes A_i for the same B. We rewrite (3.50) as

$$\boxed{P(\mathrm{A}_i|\mathrm{B}) = \frac{P(\mathrm{B}|\mathrm{A}_i)P(\mathrm{A}_i)}{P(\mathrm{B})}} \qquad \text{(multiple outcomes).} \tag{3.51}$$

If all the A_i are mutually exclusive and if at least one of the A_i must occur, then we can also write

$$P(\mathrm{B}) = \sum_i P(\mathrm{B}|\mathrm{A}_i)P(\mathrm{A}_i). \tag{3.52}$$

If we substitute (3.52) for $P(\mathrm{B})$ into (3.51), we obtain

$$P(\mathrm{A}_i|\mathrm{B}) = \frac{P(\mathrm{B}|\mathrm{A}_i)P(\mathrm{A}_i)}{\sum_i P(\mathrm{B}|\mathrm{A}_i)P(\mathrm{A}_i)}. \tag{3.53}$$

Bayes' theorem is very useful for finding the most probable explanation of a given data set. In this context A_i represents the possible explanation and B represents the data. As more data becomes available, the probabilities $P(\mathrm{B}|\mathrm{A}_i)P(\mathrm{A}_i)$ change.

Example 3.12. A chess program has two modes, expert (E) and novice (N). The expert mode beats you 75% of the time and the novice mode beats you 50% of the time. You close your eyes and randomly choose one of the modes and play two games. The computer wins (W) both times. What is the probability that you chose the novice mode?

Solution. The probability of interest is $P(\mathrm{N}|\mathrm{WW})$, which is difficult to calculate directly. Bayes' theorem lets us use the probability $P(\mathrm{WW}|\mathrm{N})$, which is easy to calculate, to determine $P(\mathrm{N}|\mathrm{WW})$. We use (3.50) to write

$$P(\mathrm{N}|\mathrm{WW}) = \frac{P(\mathrm{WW}|\mathrm{N})P(\mathrm{N})}{P(\mathrm{WW})}. \tag{3.54}$$

We know that $P(\mathrm{N}) = 1/2$ and $P(\mathrm{WW}|\mathrm{N}) = (1/2)^2 = 1/4$.

We next have to calculate $P(\mathrm{WW})$. There are two ways that the program could have won the two games: You chose the novice mode and it won twice, or you chose the expert mode and it won twice. Because N and E are mutually exclusive, we have $P(\mathrm{WW}) = P(\mathrm{N\ and\ WW}) + P(\mathrm{E\ and\ WW})$. From (3.49) we have

$$P(\mathrm{WW}) = P(\mathrm{WW}|\mathrm{N})P(\mathrm{N}) + P(\mathrm{WW}|\mathrm{E})P(\mathrm{E}) \tag{3.55a}$$

$$= (1/2 \times 1/2 \times 1/2) + (3/4 \times 3/4 \times 1/2) = \frac{13}{32}. \tag{3.55b}$$

Hence

$$P(\mathrm{N}|\mathrm{WW}) = \frac{P(\mathrm{WW}|\mathrm{N})P(\mathrm{N})}{P(\mathrm{WW})} = \frac{(1/4 \times 1/2)}{\frac{13}{32}} = \frac{4}{13} \approx 0.31. \tag{3.56}$$

Note that the probability of choosing the novice mode has decreased from 50% to about 31% because you have the additional information that the computer won twice and thus you are more likely to have chosen the expert mode. ♢

Example 3.13. Alice plants two types of flowers in her garden: 30% of type A and 70% of type B. Both types yield either red or yellow flowers, with $P(\mathrm{red}|\mathrm{A}) = 0.4$ and $P(\mathrm{red}|\mathrm{B}) = 0.3$.

(a) What is the percentage of red flowers that Alice will obtain?

Solution. We can use the total probability law (3.49) to write

$$P(\mathrm{red}) = P(\mathrm{red}|\mathrm{A})P(\mathrm{A}) + P(\mathrm{red}|\mathrm{B})P(\mathrm{B}) \tag{3.57a}$$

$$= (0.4 \times 0.3) + (0.3 \times 0.7) = 0.33. \tag{3.57b}$$

So Alice will find on average that one of three flowers will be red.

(b) Suppose a red flower is picked at random from Alice's garden. What is the probability of the flower being type A?

Solution. We apply Bayes' theorem (3.53) and obtain

$$P(\text{A}|\text{red}) = \frac{P(\text{red}|\text{A})P(\text{A})}{P(\text{red}|\text{A})P(\text{A}) + P(\text{red}|\text{B})P(\text{B})} \tag{3.58a}$$

$$= \frac{0.4 \times 0.3}{(0.4 \times 0.3) + (0.3 \times 0.7)} = \frac{12}{33} = \frac{4}{11} \approx 0.36. \tag{3.58b}$$

We find that given that the flower is red, its probability of being type A increases to 0.36 because type A has a higher probability than type B of yielding red flowers. ♢

Example 3.14. Do you have a fair coin?

Suppose that there are four coins of the same type in a bag. Three of them are fair, but the fourth is double headed. You choose one coin at random from the bag and toss it five times. It comes up heads each time. What is the probability that you have chosen the double headed coin?

Solution. If the coin were fair, the probability of five heads in a row (5H) would be $(1/2)^5 = 1/32 \approx 0.03$. This probability is small, so you would probably decide that you have not chosen a fair coin. But because you have more information, you can determine a better estimate of the probability.

We have

$$P(\text{5H}) = P(\text{5H}|\text{fair})P(\text{fair}) + P(\text{5H}|\text{not fair})P(\text{not fair}) \tag{3.59a}$$

$$= [(1/2)^5 \times 3/4] + [1 \times 1/4] = 35/128 \approx 0.27. \tag{3.59b}$$

$$P(\text{fair}|\text{5H}) = P(\text{5H}|\text{fair})P(\text{fair})/P(5H) \tag{3.59c}$$

$$= \frac{[(1/2)^5 \times 3/4]}{35/128} = 3/35 = 0.12. \tag{3.59d}$$

Thus the probability that the coin is fair given the five heads in succession is less than the probability 3/4 of picking a fair coin randomly out of the bag. ♢

Problem 3.22. More on choosing a fair coin

Suppose that you have two coins that look and feel identical, but one is double headed and one is fair. The two coins are placed in a box and you choose one at random.

(a) What is the probability that you have chosen the fair coin?

(b) Suppose that you toss the chosen coin twice and obtain heads both times. What is the probability that you have chosen the fair coin? Why is this probability different than in part (a)?

(c) Suppose that you toss the chosen coin four times and obtain four heads. What is the probability that you have chosen the fair coin?

(d) Suppose that there are ten coins in the box with nine fair and one double headed. You toss the chosen coin twice and obtain two heads. What is the probability that you have chosen the fair coin?

(e) Now suppose that the biased coin is not double headed, but has a probability of 0.98 of coming up heads. Also suppose that the probability of choosing the biased coin is 1 in 10^4. What is the probability of choosing the biased coin given that the first toss yields heads? ☐

Example 3.15. Let's Make A Deal

Consider the quandary known as the Let's Make A Deal or Monty Hall problem.[5] In this former television show a contestant is shown three doors. Behind one door is an expensive prize such as a car and behind the other two doors are inexpensive gifts such as a tie. The contestant chooses a door. Suppose the contestant chooses door 1. Then the host opens door 2 containing the tie, knowing that the car is not behind door 2. The contestant now has a choice – stay with the original choice or switch to door 3. What would you do?

Let us use Bayes' theorem (3.53) to determine the best course of action. We want to calculate

$$P(A_1|B) = P(\text{car behind door 1}|\text{door 2 open after door 1 chosen}) \tag{3.60a}$$

and

$$P(A_3|B) = P(\text{car behind door 3}|\text{door 2 open after door 1 chosen}), \tag{3.60b}$$

where A_i denotes the car behind door i. We know that all the $P(A_i)$ equal 1/3, because with no information we assume that the probability that the car is behind each door is the same. Because the host can open door 2 or 3 if the car is behind door 1, but can only open door 2 if the car is behind door 3 we have

$$P(\text{door 2 open after door 1 chosen}|\text{car behind 1}) = \frac{1}{2}, \tag{3.61a}$$

$$P(\text{door 2 open after door 1 chosen}|\text{car behind 2}) = 0, \tag{3.61b}$$

$$P(\text{door 2 open after door 1 chosen}|\text{car behind 3}) = 1. \tag{3.61c}$$

From Bayes' theorem we have

$$P(\text{car behind 1}|\text{door 2 open after door 1 chosen}) = \frac{\frac{1}{2}\times\frac{1}{3}}{(\frac{1}{2}\times\frac{1}{3}) + (0\times\frac{1}{3}) + (1\times\frac{1}{3})} = \frac{1}{3}, \tag{3.62a}$$

$$P(\text{car behind 3}|\text{door 2 open after door 1 chosen}) = \frac{1\times\frac{1}{3}}{(\frac{1}{2}\times\frac{1}{3}) + (0\times\frac{1}{3}) + (1\times\frac{1}{3})} = \frac{2}{3}. \tag{3.62b}$$

The results in (3.62) suggest the contestant has a higher probability of winning the car by switching doors and choosing door 3. The same logic suggests that one should always switch doors independently of which door was originally chosen.

Problem 3.23. Simple considerations

Make a table showing the three possible arrangements of the car and explain in simple terms why switching doubles the chances of winning.

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[5] This question was posed on the TV game show, "Let's Make A Deal," hosted by Monty Hall. See, for example, `www.letsmakeadeal.com/problem.htm>` and `<www.nytimes.com/2008/04/08/science/08monty.html>`.

Problem 3.24. What does the host know?

The point of Bayesian statistics is that it approaches a given data set with a particular model in mind. In the Let's Make A Deal problem the model we have used is that the host knows where the car is.

(a) Suppose that the host doesn't know where the car is, but chooses door 2 at random and there is no car. What is the probability that the car is behind door 1?

(b) Is the probability that you found in part (a) the same as found in Example 3.15? Discuss why the probability that the car is behind door 1 depends on what the host knows. □

Example 3.16. Bayes' theorem and the problem of false positives

Even though you have no symptoms, your doctor wishes to test you for a rare disease that only 1 in 10,000 people of your age contract. The test is 98% accurate, which means that, if you have the disease, 98% of the times the test will come out positive and 2% negative. Also, if you do not have the disease, the test will come out negative 98% of the time and positive 2% of the time. You take the test and it comes out positive. What is the probability that you have the disease? Answer the question before you read the solution using Bayes' theorem.

Solution. Let $P(\mathrm{D})$ represent the probability of having the disease given no other information except the age of the person. In this example $P(\mathrm{D}) = 1/10000 = 0.0001$. The probability of not having the disease is $P(\mathrm{N}) = 1 - P(\mathrm{D}) = 0.9999$. Let $P(+|\mathrm{D}) = 0.98$ represent the probability of testing positive given that you have the disease, and $P(+|\mathrm{N}) = 0.02$ represent the probability of testing positive given that you do not have the disease. We wish to find the probability $P(\mathrm{D}|+)$ that you will test positive for the disease and actually be sick. From Bayes' theorem we have

$$P(\mathrm{D}|+) = \frac{P(+|\mathrm{D})P(\mathrm{D})}{P(+|\mathrm{D})P(\mathrm{D}) + P(+|\mathrm{N})P(\mathrm{N})} \tag{3.63a}$$

$$= \frac{(0.98)(0.0001)}{(0.98)(0.0001) + (0.02)(0.9999)} \tag{3.63b}$$

$$= 0.0047 = 0.47\%. \tag{3.63c}$$

We expect that you will find this result difficult to accept. How can it be that the probability of having the disease is so small given the high reliability of the test? This example, and others like it, shows our lack of intuition about many statistical problems. ♢

Problem 3.25. Testing accuracy

Suppose that a person tests positive for a disease that occurs in 1 in 100, 1 in 1000, 1 in 10,000, or 1 in 100,000 people. Determine in each case how accurate the test must be for the test to give a probability equal to at least 50% of actually having the disease. □

Because of the problem of false positives, some tests might actually reduce your life span and thus are not recommended. Suppose that a certain type of cancer occurs in 1 in 1000 people who are less than 50 years old. The death rate from this cancer is 25% in 10 years. The probability of having cancer if the test is positive is 1 in 20. Because people who test positive become worried, 90% of the patients who test positive have surgery to remove the cancer. As a result of the surgery, 2% die due to complications, and the rest are cured. We have that

$$\begin{aligned} P(\text{death rate due to cancer}) &= P(\text{death}|\text{cancer})P(\text{cancer}) && (3.64\text{a}) \\ &= 0.25 \times 0.001 = 0.00025, && (3.64\text{b}) \end{aligned}$$

$$\begin{aligned} P(\text{death due to test}) &= P(\text{die}|\text{surgery})P(\text{surgery}|\text{positive})P(\text{positive }|\text{cancer}) && (3.64\text{c}) \\ &= 0.02 \times 0.90 \times 0.02 = 0.00036. && (3.64\text{d}) \end{aligned}$$

Hence, the probability of dying from the surgery is greater than dying from the cancer.

Problem 3.26. Three balls in a sack

Imagine that you have a sack of three balls that can be either red or green. There are four hypotheses for the distribution of colors for the balls: (1) all are red, (2) two are red, (3) one is red, and (4) all are green. Initially, you have no information about which hypothesis is correct, and thus you assume that they are equally probable. Suppose that you pick one ball out of the sack and it is green. Use Bayes' theorem to determine the new probabilities for each hypothesis. □

We have emphasized that the definition of probability as a frequency is inadequate. If you are interesting in learning more about Bayesian inference, see in particular the paper by D'Agostini.

3.5 Bernoulli Processes and the Binomial Distribution

Because most physicists spend little time gambling,[6] we will have to develop our intuitive understanding of probability in other ways. Our strategy will be to first consider some physical systems for which we can calculate the probability distribution by analytical methods. Then we will use the computer to generate more data to analyze.

Noninteracting magnetic moments. Consider a system of N noninteracting magnetic dipoles each having a magnetic moment μ and associated spin in an external magnetic field B. The field B is in the up $(+z)$ direction. According to quantum mechanics the component of the magnetic dipole moment along a given axis is limited to certain discrete values. Spin 1/2 implies that a magnetic dipole can either point up (parallel to B) or down (antiparallel to B). We will use the word spin as a shorthand for magnetic dipole. The energy of interaction of a spin with the magnetic field is $E = -\mu B$ if the spin is up and $+\mu B$ if the spin is down (see Figure 3.2). More generally, we can write $E = -s\mu B$, where $s = +1$ (spin up) or $s = -1$ (spin down). As discussed in Section 1.9, page 22, this model is a simplification of a more realistic magnetic system.

We will take p to be the probability that the spin (magnetic moment) is up and q the probability that the spin is down. Because there are no other possible outcomes,we have $p+q = 1$ or $q = 1-p$. If $B = 0$, there is no preferred spatial direction and $p = q = 1/2$. For $B \neq 0$ we do not yet know how to calculate p and for now we will assume that p is given. In Section 4.8 we will learn how to calculate p and q when the system is in equilibrium at temperature T.

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[6] After a Las Vegas hotel hosted a meeting of the American Physical Society (APS) in March 1986, the APS was asked never to return. The Las Vegas newspaper headline read, "Meeting of physicists in town, lowest casino take ever."

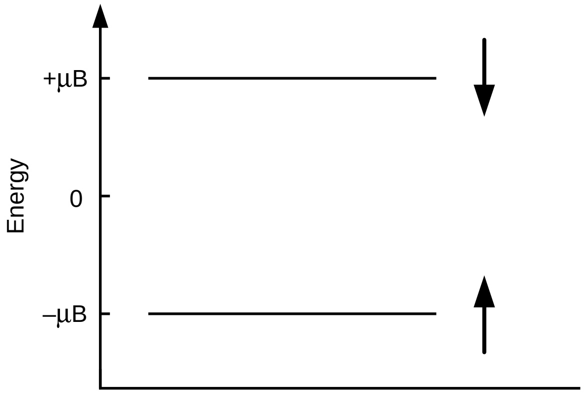

Figure 3.2: The energy of a spin 1/2 magnetic dipole. Note that the state of lowest energy is negative.

We associate with each spin a random variable s_i which has the values ± 1 with probability p and q, respectively. One of the quantities of interest is the magnetization M, which is the net magnetic moment of the system. For a system of N spins the magnetization is given by

$$M = \mu(s_1 + s_2 + \ldots + s_N) = \mu \sum_{i=1}^{N} s_i. \tag{3.65}$$

In the following, we will take $\mu = 1$ for convenience whenever it will not cause confusion.

We will first calculate the mean value of M, then its variance, and finally the probability distribution $P(M)$ that the system has magnetization M. To calculate the mean value of M, we need to take the mean values of both sides of (3.65). We interchange the sum and the average [see (3.15c)] and write

$$\overline{M} = \overline{\Big(\sum_{i=1}^{N} s_i\Big)} = \sum_{i=1}^{N} \overline{s_i}. \tag{3.66}$$

Because the probability that any spin has the value ± 1 is the same for each spin, the mean value of each spin is the same, that is, $\overline{s_1} = \overline{s_2} = \ldots = \overline{s_N} \equiv \overline{s}$. Therefore the sum in (3.66) consists of N equal terms and can be written as

$$\overline{M} = N\overline{s}. \tag{3.67}$$

The meaning of (3.67) is that the mean magnetization is N times the mean magnetization of a single spin. Because $\overline{s} = (1 \times p) + (-1 \times q) = p - q$, we have that

$$\overline{M} = N(p - q). \tag{3.68}$$

To calculate the variance of M, that is, $\overline{(M - \overline{M})^2}$, we write

$$\Delta M = M - \overline{M} = \sum_{i=1}^{N} \Delta s_i, \tag{3.69}$$

where

$$\Delta s_i \equiv s_i - \overline{s}. \tag{3.70}$$

As an example, let us calculate $\overline{(\Delta M)^2}$ for $N = 3$ spins. In this case $(\Delta M)^2$ is given by

$$(\Delta M)^2 = (\Delta s_1 + \Delta s_2 + \Delta s_3)(\Delta s_1 + \Delta s_2 + \Delta s_3) \tag{3.71a}$$

$$= \big[(\Delta s_1)^2 + (\Delta s_2)^2 + (\Delta s_3)^2\big] + 2\big[\Delta s_1 \Delta s_2 + \Delta s_1 \Delta s_3 + \Delta s_2 \Delta s_3\big]. \tag{3.71b}$$

We take the mean value of (3.71b), interchange the order of the sums and averages, and write

$$\overline{(\Delta M)^2} = \big[\overline{(\Delta s_1)^2} + \overline{(\Delta s_2)^2} + \overline{(\Delta s_3)^2}\big] + 2\big[\overline{\Delta s_1 \Delta s_2} + \overline{\Delta s_1 \Delta s_3} + \overline{\Delta s_2 \Delta s_3}\big]. \tag{3.72}$$

The first term in brackets on the right of (3.72) represents the three terms in the sum that are multiplied by themselves. The second term represents all the cross terms arising from different terms in the sum, that is, the products in the second sum refer to different spins. Because different spins are statistically independent (the spins do not interact), we have that

$$\overline{\Delta s_i \, \Delta s_j} = \overline{\Delta s_i} \; \overline{\Delta s_j} = 0 \qquad (i \neq j), \tag{3.73}$$

because $\overline{\Delta s_i} = 0$. That is, each cross term vanishes on the average. Hence (3.73) reduces to a sum of squared terms

$$\overline{(\Delta M)^2} = \big[\overline{(\Delta s_1)^2} + \overline{(\Delta s_2)^2} + \overline{(\Delta s_3)^2}\big]. \tag{3.74}$$

Because each spin is equivalent on the average, each term in (3.74) is equal. Hence, we obtain the desired result

$$\overline{(\Delta M)^2} = 3\overline{(\Delta s)^2}. \tag{3.75}$$

The variance of M is 3 times the variance of a single spin, that is, the variance is additive.

We now evaluate $\overline{(\Delta M)^2}$ by finding an explicit expression for $\overline{(\Delta s)^2}$. We have $\overline{s^2} = [1^2 \times p] + [(-1)^2 \times q] = p + q = 1$. Hence,

$$\overline{(\Delta s)^2} = \overline{s^2} - \overline{s}^2 = 1 - (p - q)^2 = 1 - (2p - 1)^2 \tag{3.76a}$$

$$= 1 - 4p^2 + 4p - 1 = 4p(1 - p) = 4pq, \tag{3.76b}$$

and our desired result for $\overline{(\Delta M)^2}$ is

$$\overline{(\Delta M)^2} = 3(4pq). \tag{3.77}$$

Problem 3.27. Variance of N spins

In the text we showed that $\overline{(\Delta M)^2} = 3\overline{(\Delta s)^2}$ for $N = 3$ spins (see [3.75) and (3.77)]. Use similar considerations for N noninteracting spins to show that

$$\overline{(\Delta M)^2} = N(4pq). \tag{3.78}$$

□

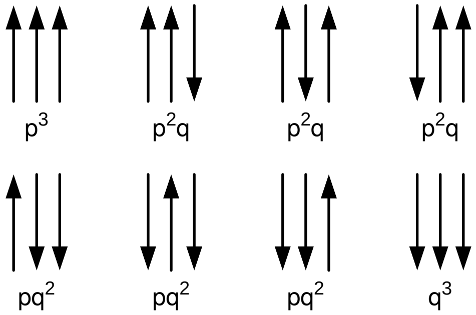

Figure 3.3: An ensemble of $N = 3$ spins. The arrow indicates the direction of a spin. The probability of each member of the ensemble is shown.

Because of the simplicity of a system of noninteracting spins, we can calculate the probability distribution itself and not just the first few moments. As an example, let us consider the statistical properties of a system of $N = 3$ noninteracting spins. Because each spin can be in one of two states, there are $2^{N=3} = 8$ distinct outcomes (see Figure 3.3). Because each spin is independent of the other spins, we can use the multiplication rule (3.5) to calculate the probabilities of each outcome as shown in Figure 3.3. Although each outcome is distinct, several of the microstates have the same number of up spins. The main quantity of interest is the probability $P_N(n)$ that n spins point up out a total of N spins. For example, for $N = 3$ spins, there are three states with $n = 2$, each with probability p^2q so the probability that two spins are up is equal to $3p^2q$. From Figure 3.3 we see that

$$P_3(n = 3) = p^3, \tag{3.79a}$$

$$P_3(n = 2) = 3p^2q, \tag{3.79b}$$

$$P_3(n = 1) = 3pq^2, \tag{3.79c}$$

$$P_3(n = 0) = q^3. \tag{3.79d}$$

Example 3.17. Find the first two moments of $P_3(n)$.

Solution. The first moment $\overline{n}$ of the distribution is given by

$$\overline{n} = (0 \times q^3) + (1 \times 3pq^2) + (2 \times 3p^2q) + (3 \times p^3) \tag{3.80a}$$

$$= 3p\,(q^2 + 2pq + p^2) = 3p\,(q + p)^2 = 3p. \tag{3.80b}$$

Similarly, the second moment $\overline{n^2}$ of the distribution is given by

$$\overline{n^2} = (0 \times q^3) + (1 \times 3pq^2) + (4 \times 3p^2q) + (9 \times p^3) \tag{3.81a}$$

$$= 3p\,(q^2 + 4pq + 3p^2) = 3p(q + 3p)(q + p) \tag{3.81b}$$

$$= 3p\,(q + 3p) = (3p)^2 + 3pq. \tag{3.81c}$$

Hence

$$\overline{(n - \overline{n})^2} = \overline{n^2} - \overline{n}^2 = 3pq. \tag{3.82}$$

◊

The mean magnetization M or the mean number of up spins minus the mean number of down spins is given by $\overline{M} = [\overline{n} - (3 - \overline{n})] = 2\overline{n} - 3 = 6p - 3$, or $\overline{M} = 3(2p - 1) = 3(p - q)$ in agreement with (3.68).

Problem 3.28. Coin flips

The outcome of N coins is identical to N noninteracting spins, if we associate the number of coins with N, the number of heads with n, and the number of tails with $N - n$. For a fair coin the probability p of a head is $p = \frac{1}{2}$ and the probability of a tail is $q = 1 - p = \frac{1}{2}$. What is the probability that in three tosses of a coin, there will be two heads? □

Problem 3.29. One-dimensional random walk

If a drunkard begins at a lamp post and takes N steps of equal length in random directions, how far will the drunkard be from the lamp post?[7] We will consider an idealized example of a random walk for which the steps of the walker are restricted to a line (a one-dimensional random walk). Each step is of equal length a, and at each interval of time, the walker takes either a step to the right with probability p or a step to the left with probability $q = 1 - p$. The direction of each step is independent of the preceding one. Let n be the number of steps to the right, and n' the number of steps to the left. The total number of steps is $N = n + n'$. What is the probability that a random walker in one dimension has taken three steps to the right out of four steps? □

From the above examples and problems, we see that the probability distributions of noninteracting spins, the flip of a coin, and a simple one-dimensional random walk are identical. These examples have two characteristics in common. First, in each trial there are only *two* outcomes, for example, up or down, heads or tails, and right or left. Second, the result of each trial is independent of all previous trials, for example, the drunken sailor has no memory of his or her previous steps. This type of process is called a *Bernoulli* process (after the mathematician Jacob Bernoulli, 1654–1705).

Because of the importance of magnetic systems, we will cast our discussion of Bernoulli processes in terms of noninteracting spins with spin $\frac{1}{2}$. The main quantity of interest is the probability $P_N(n)$ which we now calculate for arbitrary N and n. We know that a particular outcome with n up spins and n' down spins occurs with probability $p^n q^{n'}$. We write the probability $P_N(n)$ as

$$P_N(n) = W_N(n, n')\, p^n q^{n'}, \tag{3.83}$$

where $n' = N - n$ and $W_N(n, n')$ is the number of distinct microstates of N spins with n up spins and n' down spins. From our discussion of $N = 3$ noninteracting spins, we already know the first several values of $W_N(n, n')$.

We can determine the general form of $W_N(n, n')$ by obtaining a recursion relation between W_N and W_{N-1}. A total of n up spins and n' down spins out of N total spins can be found by adding one spin to $N - 1$ spins. The additional spin is either

(1) up if there are already $(n - 1)$ up spins and n' down spins, or

(2) down if there are already n up spins and $(n' - 1)$ down spins.

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[7] The history of the random walk problem is discussed by Montroll and Shlesinger (1984).

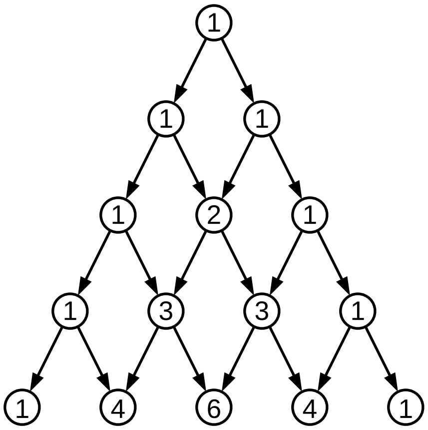

Figure 3.4: The values of the first few coefficients $W_N(n, n')$. Each number is the sum of the two numbers to the left and right above it. This construction is called a Pascal triangle.

Because there are $W_{N-1}(n-1, n')$ ways of reaching the first case and $W_{N-1}(n, n'-1)$ ways of reaching the second case, we obtain the recursion relation

$$W_N(n, n') = W_{N-1}(n-1, n') + W_{N-1}(n, n'-1). \tag{3.84}$$

If we begin with the known values $W_0(0,0) = 1$, $W_1(1,0) = W_1(0,1) = 1$, we can use the recursion relation (3.84) to construct $W_N(n, n')$ for any desired N. For example,

$$W_2(2,0) = W_1(1,0) + W_1(2,-1) = 1 + 0 = 1, \tag{3.85a}$$

$$W_2(1,1) = W_1(0,1) + W_1(1,0) = 1 + 1 = 2, \tag{3.85b}$$

$$W_2(0,2) = W_1(-1,2) + W_1(0,1) = 0 + 1. \tag{3.85c}$$

In Figure 3.4 we show that $W_N(n, n')$ forms a pyramid or (a Pascal) triangle.

It is straightforward to show by induction that the expression

$$W_N(n, n') = \frac{N!}{n!\, n'!} = \frac{N!}{n!(N-n)!} \tag{3.86}$$

satisfies the relation (3.84). Note the convention $0! = 1$. We can combine (3.83) and (3.86) to find the desired result

$$\boxed{P_N(n) = \frac{N!}{n!\,(N-n)!}\, p^n q^{N-n}} \qquad \text{(binomial distribution).} \tag{3.87}$$

The form (3.87) is the *binomial distribution*. Note that for $p = q = 1/2$, $P_N(n)$ reduces to

$$P_N(n) = \frac{N!}{n!\,(N-n)!}\, 2^{-N}. \tag{3.88}$$

The probability $P_N(n)$ is shown in Figure 3.5 for $N = 64$.

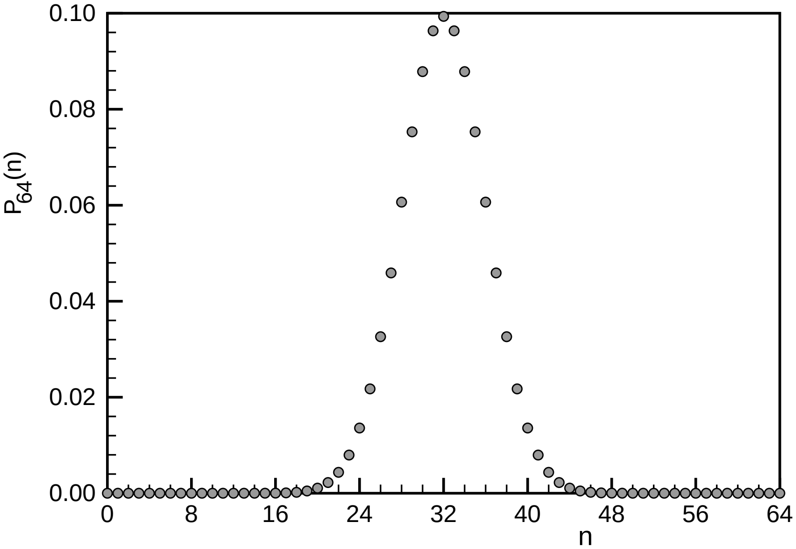

Figure 3.5: The binomial distribution $P_{64}(n)$ for $p = q = 1/2$. What is your visual estimate of the width of the distribution?

Problem 3.30. Binomial distribution

(a) Calculate the probability $P_N(n)$ that n spins are up out of a total of N for $N = 4$ and $N = 16$ and put your results in a table. Calculate the mean values of n and n^2 using your tabulated values of $P_N(n)$. It is possible to do the calculation for general p and q, but choose $p = q = 1/2$ for simplicity. Although it is better to first do the calculation of $P_N(n)$ by hand, you can use Program `Binomial`.

(b) Use Program `Binomial` to plot $P_N(n)$ for larger values of N. Assume that $p = q = 1/2$. Determine the value of n corresponding to the maximum of the probability and visually estimate the width for each value of N. What is your measure of the width? One measure is the value of n at which $P_N(n)$ is equal to half its value at its maximum. What is the qualitative dependence of the width on N? Also compare the relative heights of the maximum of P_N for increasing values of N.

(c) Program `Binomial` also plots $P_N(n)$ versus $n/\overline{n}$. Does the width of $P_N(n)$ appear to become larger or smaller as N is increased?

(d) Plot $\ln P_N(n)$ versus n for $N = 16$. (Choose `Log Axes under` the `Views` menu.) Describe the qualitative dependence of $\ln P_N(n)$ on n. Can $\ln P_N(n)$ be fitted to a parabola of the form $A + B(n - \overline{n})^2$, where A and B are fit parameters? $\square$

Problem 3.31. Asymmetrical distribution

(a) Plot $P_N(n)$ versus n for $N = 16$ and $p = 2/3$. For what value of n is $P_N(n)$ a maximum? How does the width of the distribution compare to what you found in Problem 3.30?

(b) For what values of p and q do you think the width is a maximum for a given N? □

Example 3.18. Show that the expression (3.87) for $P_N(n)$ satisfies the normalization condition (3.2).

Solution. The reason that (3.87) is called the binomial distribution is that its form represents a typical term in the expansion of $(p+q)^N$. By the binomial theorem we have

$$(p+q)^N = \sum_{n=0}^{N} \frac{N!}{n!\,(N-n)!}\, p^n\, q^{N-n}. \tag{3.89}$$

We use (3.87) and write

$$\sum_{n=0}^{N} P_N(n) = \sum_{n=0}^{N} \frac{N!}{n!\,(N-n)!}\, p^n q^{N-n} = (p+q)^N = 1^N = 1, \tag{3.90}$$

where we have used (3.89) and the fact that $p+q=1$. ♢

Mean value. We now find an analytical expression for the dependence of the mean number of up spins $\overline{n}$ on N and p. From the definition (3.13) and (3.87) we have

$$\overline{n} = \sum_{n=0}^{N} n\, P_N(n) = \sum_{n=0}^{N} n\, \frac{N!}{n!\,(N-n)!}\, p^n q^{N-n}. \tag{3.91}$$

We evaluate the sum in (3.91) by using a technique that is useful in a variety of contexts.[8] The technique is based on the fact that

$$p\,\frac{d}{dp} p^n = np^n. \tag{3.92}$$

We use (3.92) to rewrite (3.91) as

$$\overline{n} = \sum_{n=0}^{N} \frac{N!}{n!\,(N-n)!} \big(p\frac{\partial}{\partial p} p^n\big) q^{N-n}. \tag{3.93}$$

We have used a partial derivative in (3.93) to remind us that the derivative operator does not act on q, which we have temporarily assumed to be an independent variable. We interchange the order of summation and differentiation in (3.93) and write

$$\overline{n} = p\frac{\partial}{\partial p}\Big[\sum_{n=0}^{N} \frac{N!}{n!\,(N-n)!}\, p^n q^{N-n}\Big] \tag{3.94a}$$

$$= p\frac{\partial}{\partial p}\,(p+q)^N, \tag{3.94b}$$

Because the operator acts only on p, we have

$$\overline{n} = pN(p+q)^{N-1}. \tag{3.95}$$

---

[8] The integral $\int_0^\infty x^n\, e^{-ax^2}$ for $a>0$ is evaluated in the Appendix using a similar technique.

The result (3.95) is valid for arbitrary p and q, and hence it is applicable for $p+q=1$. Thus our desired result is

$$\overline{n} = pN. \tag{3.96}$$

The nature of the dependence of $\overline{n}$ on N and p should be intuitively clear. Compare the general result (3.96) to the result (3.80b) for $N=3$. What is the dependence of $\overline{n'}$ on N and p?

Relative fluctuations. To determine $\overline{\Delta n^2}$ we need to know $\overline{n^2}$ [see the relation (3.21)]. The average value of n^2 can be calculated in a manner similar to that for $\overline{n}$. We write

$$\begin{aligned}
\overline{n^2} &= \sum_{n=0}^{N} n^2 \frac{N!}{n!\,(N-n)!}\, p^n q^{N-n} && (3.97\text{a})\\
&= \sum_{n=0}^{N} \frac{N!}{n!\,(N-n)!} \Big(p\,\frac{\partial}{\partial p}\Big)^2 p^n q^{N-n} && (3.97\text{b})\\
&= \Big(p\,\frac{\partial}{\partial p}\Big)^2 \sum_{n=0}^{N} \frac{N!}{n!\,(N-n)!}\, p^n q^{N-n} = \Big(p\,\frac{\partial}{\partial p}\Big)^2 (p+q)^N && (3.97\text{c})\\
&= \Big(p\,\frac{\partial}{\partial p}\Big) \big[pN(p+q)^{N-1}\big] && (3.97\text{d})\\
&= p\big[N(p+q)^{N-1} + pN(N-1)(p+q)^{N-2}\big]. && (3.97\text{e})
\end{aligned}$$

Because we are interested in the case $p+q=1$, we have

$$\begin{aligned}
\overline{n^2} &= p\,[N + pN(N-1)] && (3.98\text{a})\\
&= p\,[pN^2 + N(1-p)] = (pN)^2 + p\,(1-p)N && (3.98\text{b})\\
&= \overline{n}^2 + pqN, && (3.98\text{c})
\end{aligned}$$

where we have used (3.96) and substituted $q = 1-p$. Hence, from (3.98c) we find that the variance of n is given by

$${\sigma_n}^2 = \overline{(\Delta n)^2} = \overline{n^2} - \overline{n}^2 = pqN. \tag{3.99}$$

Problem 3.32. Width of the binomial distribution

Compare the calculated values of σ_n from (3.99) with your estimates in Problem 3.30 and to the exact result (3.82) for $N=4$. Explain why σ_n is a measure of the width of $P_N(n)$. ☐

The relative width of the probability distribution of n is given by (3.96) and (3.99)

$$\frac{\sigma_n}{\overline{n}} = \frac{\sqrt{pqN}}{pN} = \Big(\frac{q}{p}\Big)^{1/2} \frac{1}{\sqrt{N}}. \tag{3.100}$$

We see that the relative width goes to zero as $1/\sqrt{N}$.

Frequently we need to evaluate $\ln N!$ for $N \gg 1$. An approximation for $\ln N!$ known as *Stirling's approximation* is[9]

$$\boxed{\ln N! \approx N \ln N - N + \frac{1}{2}\ln(2\pi N)} \qquad \text{(Stirling's approximation).} \tag{3.101}$$

---

[9] It is more accurate to call it the de Moivre-Stirling approximation because de Moivre had already found that $n! \approx c\sqrt{n}n^n/e^n$ for some constant c. Stirling's contribution was to identify the constant c as $\sqrt{2\pi}$.

In some contexts we can neglect the logarithmic term in (3.101) and use the weaker approximation

$$\ln N! \approx N \ln N - N. \tag{3.102}$$

A derivation of Stirling's approximation is given in the Appendix.

Problem 3.33. Range of applicability of Stirling's approximation

(a) What is the largest value of $\ln N!$ that you can calculate exactly using your calculator?

(b) Compare the approximations (3.101) and (3.102) to each other and to the exact value of $\ln N!$ for $N = 5$, 10, 20, and 50. If necessary, compute $\ln N!$ using the relation

$$\ln N! = \sum_{m=1}^{N} \ln m. \tag{3.103}$$

Put your results in a table. What is the percentage error of the two approximations for $N = 50$?

(c) Use Stirling's approximation to show that

$$\frac{d}{dx} \ln x! = \ln x \text{ for } x \gg 1. \tag{3.104}$$

☐

Problem 3.34. Density fluctuations

A container of volume V contains N molecules of a gas. We assume that the gas is dilute so that the position of any one molecule is independent of all other molecules. Although the density is uniform on the average, there are fluctuations in the density. Divide the volume V into two parts V_1 and V_2 with $V = V_1 + V_2$.

(a) What is the probability p that a particular molecule is in the volume V_1?

(b) What is the probability that N_1 molecules are in V_1 and N_2 molecules are in V_2, where $N = N_1 + N_2$?

(c) What is the average number of molecules in each part?

(d) What are the relative fluctuations of the number of molecules in each part? ☐

Problem 3.35. Random walk

Suppose that a random walker takes n steps to the right and n' steps to the left for a total of N steps. Each step is of equal length a and the probability of a step to the right is p. Denote x as the net displacement of a walker after N steps. What is the mean value $\overline{x}$ for an N-step random walk? What is the N dependence of the variance $\overline{(\Delta x)^2}$? ☐

Problem 3.36. Monte Carlo simulation of a one-dimensional random walk

Program `RandomWalk1D` simulates a random walk in one dimension. A walker starts at the origin and takes N steps. At each step the walker goes to the right with probability p or to the left with probability $q = 1 - p$. Each step is the same length and independent of the previous steps. What is the displacement of the walker after N steps? Are some displacements more likely than others?

We can simulate an N-step walk by the following pseudocode:

```
do istep = 1,N
  if (rnd <= p) then
    x = x + 1
  else
    x = x - 1
  end if
end do
```

The function `rnd` generates a random number between zero and one. The quantity x is the net displacement after N steps assuming that the steps are of unit length.

We average over many walkers (trials), where each trial consists of a N step walk and construct a histogram for the number of times that the displacement x is found for a given number of walkers. The probability that the walker is a distance x from the origin after N steps is proportional to the corresponding value of the histogram. This procedure is called *Monte Carlo* sampling.[10]

(a) Is the value of x for one trial of any interest? Why do we have to average over many trials?

(b) Will we obtain the exact result for the probability distribution by doing a Monte Carlo simulation?

(c) Describe the changes of the histogram for larger values of N and $p = 1/2$.

(d) What is the most probable value of x for $p = 1/2$ and $N = 16$ and $N = 32$? What is the approximate width of the distribution? Estimate the width visually. One way to do so is to determine the value of x at which the value of the histogram is one-half of its maximum value. How does the width change as a function of N for fixed p?

(e) Choose $N = 4$ and $p = 1/2$. How does the histogram change, if at all, as the number of walks increases for fixed N? □

The binomial distribution for large N. In Problem 3.30 we found that the binomial distribution has a well-defined maximum and can be approximated by a smooth, continuous function for large N even though only integer values of n are possible. We now find the form of this n dependence.

The first step is to realize that $P_N(n)$ for $N \gg 1$ is a rapidly varying function of n near the maximum of $P_N(n)$ at $\tilde{n} = pN$. For this reason we do not want to approximate $P_N(n)$ directly. Because the logarithm of $P_N(n)$ is a slowly varying function (see Problem 3.30), we expect that the

---

[10] The name "Monte Carlo" was first used by Nicholas Metropolis and Stanislaw Ulam in "The Monte Carlo method," Journal of the American Statistical Association **44** (247), 335–341 (1949).

Taylor series expansion of $\ln P_N(n)$ will converge. Hence, we expand $\ln P_N(n)$ in a Taylor series about the value of $n = \tilde{n}$ at which $\ln P_N(n)$ reaches its maximum value. We have

$$\ln P_N(n) = \ln P_N(n = \tilde{n}) + (n - \tilde{n}) \frac{d \ln P_N(n)}{dn}\Big|_{n=\tilde{n}} + \frac{1}{2}(n - \tilde{n})^2 \frac{d^2 \ln P_N(n)}{d^2 n}\Big|_{n=\tilde{n}} + \cdots . \tag{3.105}$$

Because the expansion (3.105) is about the maximum $n = \tilde{n}$, the first derivative $d \ln P_N(n)/dn\big|_{n=\tilde{n}}$ must be zero and the second derivative $d^2 \ln P_N(n)/dn^2\big|_{n=\tilde{n}}$ must be negative. We assume that the higher terms in (3.105) can be neglected (see Problem 3.76) and adopt the notation

$$\ln A = \ln P_N(n = \tilde{n}) \tag{3.106}$$

and

$$B = -\frac{d^2 \ln P_N(n)}{dn^2}\Big|_{n=\tilde{n}}. \tag{3.107}$$

The approximation (3.105) and the notation in (3.106) and (3.107) allow us to write

$$\ln P_N(n) \approx \ln A - \frac{1}{2} B (n - \tilde{n})^2, \tag{3.108}$$

or

$$P_N(n) \approx A\, e^{-\frac{1}{2} B (n - \tilde{n})^2}. \tag{3.109}$$

We next use Stirling's approximation (3.101) to evaluate the first two derivatives of $\ln P_N(n)$ to find the parameters B and $\tilde{n}$. We first take the logarithm of both sides of (3.87) and obtain

$$\ln P_N(n) = \ln N! - \ln n! - \ln(N - n)! + n \ln p + (N - n) \ln q. \tag{3.110}$$

It is straightforward to use the approximation (3.104) to obtain

$$\frac{d(\ln P_N(n))}{dn} = -\ln n + \ln(N - n) + \ln p - \ln q. \tag{3.111}$$

The most probable value of n is found by finding the value of n that satisfies the condition $d \ln P_N(n)/dn = 0$. We find

$$\frac{N - \tilde{n}}{\tilde{n}} = \frac{q}{p}, \tag{3.112}$$

or $(N - \tilde{n})p = \tilde{n}q$. The relation $p + q = 1$ allows us to write

$$\tilde{n} = pN, \tag{3.113}$$

as expected. Note that $\tilde{n} = \overline{n}$, that is, the value of n for which $P_N(n)$ is a maximum is also the mean value of n.

The second derivative can be found from (3.111). We have

$$\frac{d^2(\ln P_N(n))}{dn^2} = -\frac{1}{n} - \frac{1}{N - n}. \tag{3.114}$$

Hence, the coefficient B defined in (3.107) is given by

$$B = -\frac{d^2 \ln P_N(n)}{dn^2}\Big|_{n=\tilde{n}} = \frac{1}{\tilde{n}} + \frac{1}{N-\tilde{n}} = \frac{1}{Npq}. \tag{3.115}$$

From the relation (3.99) we see that

$$B = \frac{1}{\sigma^2}, \tag{3.116}$$

where σ^2 is the variance of n. In Problem 3.37 you will be asked to show that the coefficient A in (3.107) can be approximated for large N as

$$A = \frac{1}{(2\pi Npq)^{1/2}} = \frac{1}{(2\pi\sigma^2)^{1/2}}. \tag{3.117}$$

We thus find the form of the Gaussian probability distribution

$$\boxed{P_N(n) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(n-\overline{n})^2/2\sigma^2}} \qquad \text{(Gaussian probability distribution).} \tag{3.118}$$

An alternative derivation of the parameters A, $\tilde{n}$, and B is given in Problem 3.72.

Problem 3.37. Calculation of the normalization constant

Derive the form of A in (3.117) using Stirling's approximation (3.101). Note that the weaker form of Stirling's approximation in (3.102) yields the incorrect result that $\ln A = 0$. □

n	$P_{10}(n)$	Gaussian approximation
0	0.000977	0.001700
1	0.009766	0.010285
2	0.043945	0.041707
3	0.117188	0.113372
4	0.205078	0.206577
5	0.246094	0.252313

Table 3.4: Comparison of the exact values of $P_{10}(n)$ with the Gaussian probability distribution (3.118) for $p = q = 1/2$.

From our derivation we see that (3.118) is valid for large values of N and for values of n near $\overline{n}$. The Gaussian approximation is a good approximation even for relatively small values of N for most values of n. A comparison of the Gaussian approximation to the binomial distribution is given in Table 3.4. A discussion of the accuracy of the Gaussian approximation to the binomial distribution is given in Problem 3.76.

The most important feature of the Gaussian probability distribution is that its relative width, $\sigma_n/\overline{n}$, decreases as $N^{-1/2}$. The binomial distribution also shares this feature. The alternate derivation of the Gaussian probability distribution in Problem 3.72 shows why the binomial and Gaussian distributions have the same mean and variance.

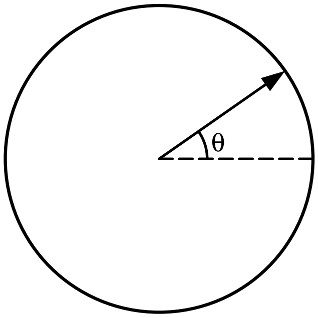

Figure 3.6: The angle θ is an example of a continuous random variable.

3.6 Continuous Probability Distributions

In many cases of physical interest the random variables have continuous values. Examples of continuous variables are the positions of the holes left by darts thrown at a dart board, the position and velocity of a particle described by classical mechanics, and the angle of a compass needle.

As an example, consider a spinner, the equivalent of a wheel of fortune,[11] with an arrow that spins around and stops at some angle at random (see Figure 3.6). In this case the variable θ is a continuous random variable that takes all values in the interval $[0, 2\pi]$. What is the probability that θ has a particular value? Because there are an infinite number of possible values of θ in the interval $[0, 2\pi]$, the probability of obtaining any particular value of θ is zero. Thus, we have to reformulate the question and ask for the probability that the value of θ is between θ and $\theta + \Delta\theta$. In other words, we have to ask for the probability that θ is in a particular angular range $\Delta\theta$ about θ. For example, the probability that θ in Figure 3.6 is between 0 and π is 1/2 and the probability that θ is between 0 and $\pi/2$ is 1/4.

Another example of a continuous random variable is the displacement from the origin of a one-dimensional random walker that steps at random to the right with probability p, but with a step length that is chosen at random between zero and the maximum step length a. The continuous nature of the step length means that the displacement x of the walker is a continuous variable. If we perform a simulation of this random walk, we can record the number of times $H(x)$ that the displacement of the walker from the origin after N steps is in a bin of width Δx between x and $x + \Delta x$. A plot of $H(x)$ as a function of x for the bin width $\Delta x = 0.5$ is shown in Figure 3.7. The histogram $H(x)$ is proportional to the estimated probability that a walker lies in a bin of width Δx a distance x from the origin after N steps. To obtain the probability, we divide $H(x)$ by the total number of walkers N_w.

In practice, the choice of the bin width is a compromise. If Δx is too big, the features of the histogram would be lost. If Δx is too small, many of the bins would be empty for a given number of walkers, and our estimate of the number of walkers in each bin would be less accurate.

Because we expect the number of walkers in a particular bin to be proportional to the width of the bin, we may write $p(x)\Delta x = H(x)/N_w$. The quantity $p(x)$ is called the *probability density.*

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[11] The Wheel of Fortune is an American television game. The name of the show comes from the large spinning wheel that determines the dollar amounts and prizes won by the contestants.

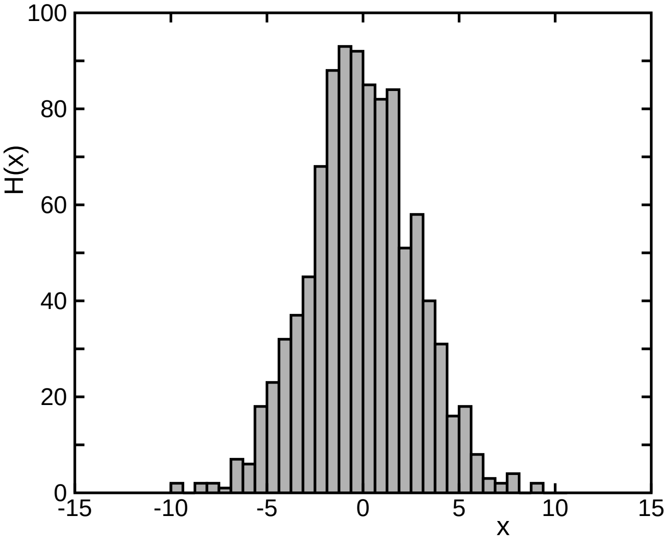

Figure 3.7: Histogram $H(x)$ of the number of times that the displacement of a one-dimensional random walker lies between x and $x + \Delta x$ after $N = 16$ steps (see Problem 3.38). The length of each step is chosen with uniform random probability to be between zero and one. The bin width is $\Delta x = 0.5$. The data were generated with 1000 trials, a relatively small number. The results of this set of trials are the estimates $\overline{x} = -0.045$ and $\overline{x^2} = 4.95$.

In the limit $\Delta x \to 0$, $H(x)$ becomes a continuous function of x, and we can write the probability that the displacement x of the walker is between a and b as (see Figure 3.8)

$$P(a < x < b) = \int_a^b p(x)\, dx. \tag{3.119}$$

Note that the probability density $p(x)$ is nonnegative and has units of one over the dimension of length.

The formal properties of the probability density $p(x)$ can be generalized from the discrete case. For example, the normalization condition is given by

$$\int_{-\infty}^{\infty} p(x)\, dx = 1. \tag{3.120}$$

The mean value of the function $f(x)$ is given by

$$\overline{f} = \int_{-\infty}^{\infty} f(x)\, p(x)\, dx. \tag{3.121}$$

Problem 3.38. Simulation of a one-dimensional random walk with variable step length

Program `RandomWalk1DContinuous` simulates a random walk in one dimension with a variable step length.

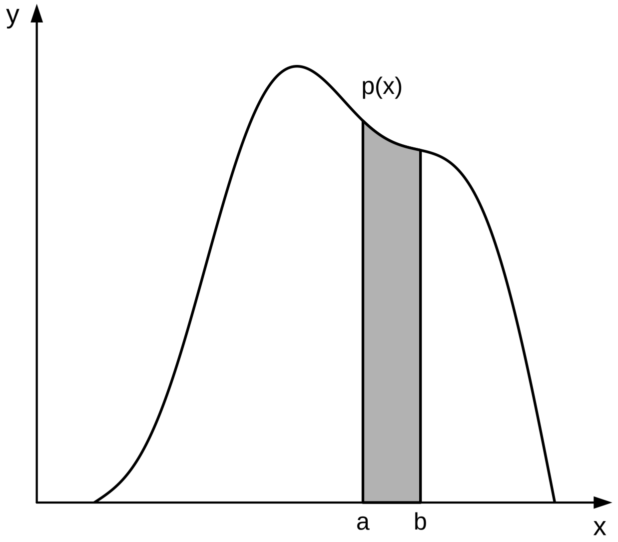

Figure 3.8: The probability that x is between a and b is equal to the shaded area.

(a) The step length is generated at random with a uniform probability between 0 and 1. Calculate the mean displacement and its variance for one step.

(b) Compare your analytical results from part (a) to the results of the simulation for $N = 1$.

(c) How does the variance of the displacement found in the simulation for $N = 16$ depend on the variance of the displacement for $N = 1$ that you calculated in part (a)?

(d) Explore how the histogram changes with the bin width. What is a reasonable choice of the bin width for $N = 100$? □

Problem 3.39. Exponential probability density

The random variable x has the probability density

$$p(x) = \begin{cases} A\,e^{-\lambda x} & (0 \leq x \leq \infty) \\ 0 & (x < 0). \end{cases} \tag{3.122}$$

The exponential probability density plays an important role in statistical mechanics (see (4.79), page 200).

(a) Determine the normalization constant A in terms of λ.

(b) What is the mean value of x? What is the most probable value of x?

(c) What is the mean value of x^2?

(d) Determine the probability for $\lambda = 1$ that a measurement of x yields a value between 1 and 2.

(e) Determine the probability for $\lambda = 1$ that a measurement of x yields a value less than 0.3. ☐

Problem 3.40. Probability density for velocity

Consider the probability density function $p(v_x) = (a/\pi)^{3/2}\, e^{-av_x^2}$ for the velocity of a particle in the x-direction. The probability densities for v_y and v_z have the same form. Each of the three velocity components can range from $-\infty$ to $+\infty$ and a is a constant. This form of the probability density for the velocity will be derived in Section 6.2.2 for a classical system of particles at temperature T.

(a) Show that $p(\mathbf{v})$ is normalized. Use the fact that [see (A.15)]

$$\int_0^\infty e^{-au^2}\, du = \frac{1}{2}\sqrt{\frac{\pi}{a}}. \tag{3.123}$$

Note that this calculation involves doing three similar integrals that can be evaluated separately.

(b) What is the probability that a particle has a velocity between v_x and $v_x + dv_x$, v_y and $v_y + dv_y$, and v_z and $v_z + dv_z$?

(c) What is the probability that $v_x \geq 0$, $v_y \geq 0$, $v_z \geq 0$ simultaneously? ☐

Problem 3.41. Gaussian probability density

(a) Find the first four moments of the Gaussian probability density

$$p(x) = (2\pi)^{-1/2} e^{-x^2/2} \qquad (-\infty < x < \infty). \tag{3.124}$$

(b) Calculate the value of C_4, the fourth-order cumulant, defined by

$$C_4 = \overline{x^4} - 4\overline{x^3}\,\overline{x} - 3\,\overline{x^2}^2 + 12\,\overline{x^2}\,\overline{x}^2 - 6\,\overline{x}^4. \tag{3.125}$$

☐

Problem 3.42. Uniform probability distribution

Consider the probability density given by

$$p(x) = \begin{cases} (2a)^{-1} & (|x| \leq a), \\ 0 & (|x| > a). \end{cases} \tag{3.126}$$

(a) Sketch the dependence of $p(x)$ on x.

(b) Find the first four moments of $p(x)$.

(c) Calculate the value of the fourth-order cumulant C_4 defined in (3.125) for the probability density in (3.126). Compare your result to the corresponding result for C_4 for the Gaussian distribution. ☐

Problem 3.43. Other probability distributions

Not all probability densities have a finite variance as you will find in the following.

(a) Sketch the *Lorentz* or *Cauchy distribution* given by

$$p(x) = \frac{1}{\pi}\frac{\gamma}{(x-a)^2+\gamma^2} \qquad (-\infty < x < \infty). \tag{3.127}$$

Choose $a = 0$ and $\gamma = 1$ and compare the form of $p(x)$ in (3.127) to the Gaussian distribution given by (3.124).

(b) Calculate the first moment of the Lorentz distribution assuming that $a = 0$ and $\gamma = 1$.

(c) Does the second moment exist? □

3.7 The Central Limit Theorem (or Why Thermodynamics Is Possible)

We have discussed how to estimate probabilities empirically by sampling, that is, by making repeated measurements of the outcome of independent random events. Intuitively we believe that if we perform more and more measurements, the calculated average will approach the exact mean of the quantity of interest. This idea is called *the law of large numbers*. However, we can go further and find the form of the probability distribution that a particular measurement differs from the exact mean. The form of this probability distribution is given by the *central limit theorem*. We first illustrate this theorem by considering a simple example.

Suppose that we wish to estimate the probability of obtaining the face with five dots in one throw of a die. The answer of $\frac{1}{6}$ means that if we perform N measurements, five will appear approximately $N/6$ times. What is the meaning of approximately? Let S be the total number of times that a five appears in N measurements. We write

$$S = \sum_{i=1}^{N} s_i, \tag{3.128}$$

where

$$s_i = \begin{cases} 1 & \text{if the } i\text{th throw gives a 5,} \\ 0 & \text{otherwise.} \end{cases} \tag{3.129}$$

The ratio S/N approaches $1/6$ for large N. How does this ratio approach the limit? We can empirically answer this question by repeating the measurement M times. (Each measurement of S consists of N throws of a die.) Because S itself is a random variable, we know that the measured values of S will not be identical. In Figure 3.9 we show the results of $M = 10,000$ measurements of S for $N = 100$ and $N = 800$. We see that the approximate form of the distribution of values of S is a Gaussian. In Problem 3.44 we calculate the absolute and relative width of the distributions.

Problem 3.44. Analysis of Figure 3.9

(a) Estimate the absolute width and the relative width $\Delta S/\overline{S}$ of the distributions shown in Figure 3.9 for $N = 100$ and $N = 800$.

(b) Does the error of any one measurement of S decrease with increasing N as expected?

(c) How would the plot change if the number of measurements M were increased to $M = 100,000$?

□

In Section 3.11.2 we show that in the limit $N \to \infty$, the probability density $p(S)$ is given by

$$\boxed{p(S) = \frac{1}{\sqrt{2\pi\sigma_S^2}}\, e^{-(S-\overline{S})^2/2\sigma_S^2}} \qquad \text{(central limit theorem)}, \tag{3.130}$$

where

$$\overline{S} = N\overline{s}, \tag{3.131}$$

$$\sigma_S^2 = N\sigma^2, \tag{3.132}$$

with $\sigma^2 = \overline{s^2} - \overline{s}^2$. The quantity $p(S)\Delta S$ is the probability that the value of the sum $\sum_{i=1}^{N} s_i$ is between S and $S + \Delta S$. Equation (3.130) is equivalent to the central limit theorem. Note that the Gaussian form in (3.130) holds only for large N and for values of S near its most probable (mean) value. The latter restriction is the reason that the theorem is called the *central* limit theorem; the requirement that N be large is the reason for the term *limit*.

The central limit theorem is one of the most remarkable results of the theory of probability. In its simplest form the theorem states that the probability distribution of the value of the sum of a large number of random variables is approximately a Gaussian. The approximation improves as the number of variables in the sum increases. For the throw of a die we have $\overline{s} = \frac{1}{6}$, $\overline{s^2} = \frac{1}{6}$, and $\sigma^2 = \overline{s^2} - \overline{s}^2 = \frac{1}{6} - \frac{1}{36} = \frac{5}{36}$. For N throws of a die, we have $\overline{S} = N/6$ and $\sigma_S^2 = 5N/36$. We see that in this example the most probable relative error in any one measurement of S decreases as $\sigma_S/\overline{S} = \sqrt{5/N}$.

If we let S represent the displacement of a walker after N steps and let σ^2 equal the mean square displacement of a single step, then the central limit theorem implies that the probability density of the displacement is a Gaussian, which is equivalent to the results that we found for random walks in the limit of large N. Or we can let S represent the magnetization of a system of spins and obtain similar results. The displacement of a random walk after N steps and the magnetization of a system of spins are examples of a *random additive process*. Hence, the probability distribution for random walks, spins, and multiple coin tosses is given by (3.130), and our task reduces to finding expressions for $\overline{s}$ and σ^2 for the particular process of interest.

Problem 3.45. Central limit theorem

Use Program `CentralLimitTheorem` to test the applicability of the central limit theorem.

(a) Assume that the variable s_i is uniformly distributed between 0 and 1. Calculate analytically the mean and standard deviation of s and compare your numerical results with your analytical calculation.

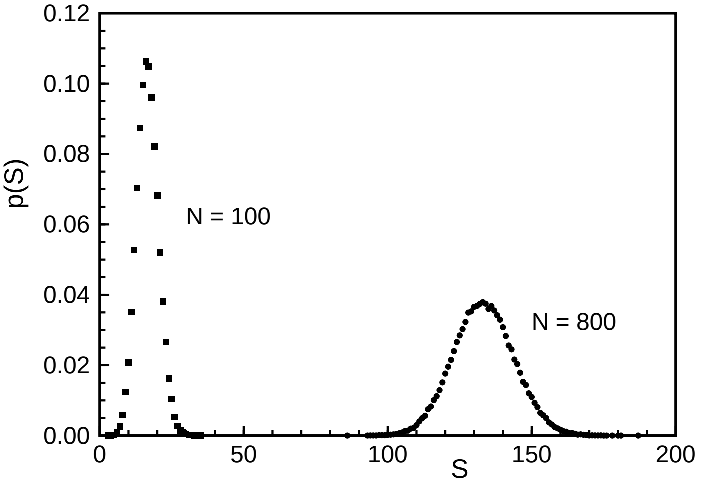

Figure 3.9: The distribution of the measured values of $M = 10,000$ different measurements of the sum S for $N = 100$ and $N = 800$ terms in the sum. The quantity S is the number of times that face 1 appears in N throws of a die. For $N = 100$, the measured values are $\overline{S} = 16.67$, $\overline{S^2} = 291.96$, and $\sigma_S = 3.74$. For $N = 800$, the measured values are $\overline{S} = 133.31$, $\overline{S^2} = 17881.2$, and $\sigma_S = 10.52$. What is the estimated value of the relative width for each case?

(b) Use the default value of $N = 12$, the number of terms in the sum, and describe the qualitative form of $p(S)$, where $p(S)\Delta S$ is the probability that the sum S is between S and $S + \Delta S$. Does the qualitative form of $p(S)$ change as the number of measurements (trials) of S is increased for a given value of N?

(c) What is the approximate width of $p(S)$ for $N = 12$? Describe the changes, if any, of the width of $p(S)$ as N is increased. Increase N by at least a factor of 4. Do your results depend strongly on the number of measurements?

(d) To determine the generality of your results, consider the probability density $f(s) = e^{-s}$ for $s \geq 0$ and answer the same questions as in parts (a)–(c).

(e) Consider the Lorentz distribution $f(s) = (1/\pi)(1/(s^2 + 1))$, where $-\infty \leq s \leq \infty$. What is the mean value and variance of s? Is the form of $p(S)$ consistent with the results that you found in parts (b)–(d)?

(f) Each value of S can be considered to be a measurement. The sample variance $\tilde{\sigma}_S^2$ is a measure of the square of the differences of the result of each measurement and is given by

$$\tilde{\sigma}_S^2 = \frac{1}{N-1} \sum_{i=1}^{N} (S_i - \overline{S})^2. \tag{3.133}$$

The reason for the factor of $N - 1$ rather than N in the definition of $\tilde{\sigma}_S^2$ is that to compute it, we need to use the N values of s to compute the mean of S, and thus, loosely speaking, we have only $N-1$ independent values of s remaining to calculate $\tilde{\sigma}_S^2$. Show that if $N \gg 1$, then $\tilde{\sigma}_S \approx \sigma_S$, where the standard deviation σ_S is given by $\sigma_S^2 = \overline{S^2} - \overline{S}^2$.

(g) The quantity $\tilde{\sigma}_S$ is known as the standard deviation of the means. That is, $\tilde{\sigma}_S$ is a measure of how much variation we expect to find if we make repeated measurements of S. How does the value of $\tilde{\sigma}_S$ compare to your estimated width of the probability density $p(S)$? □

The central limit theorem shows why the Gaussian probability density is ubiquitous in nature. If a random process is related to a sum of a large number of microscopic processes, the sum will be distributed according to the Gaussian distribution *independently* of the nature of the distribution of the microscopic processes.[12]

The central limit theorem implies that macroscopic bodies have well defined macroscopic properties even though their constituent parts are changing rapidly. For example, the particle positions and velocities in a gas or liquid are continuously changing at a rate much faster than a typical measurement time. For this reason we expect that during a measurement of the pressure of a gas or a liquid, there are many collisions with the wall and hence the pressure, which is a sum of the pressure due to the individual particles, has a well defined average. We also expect that the probability that the measured pressure deviates from its average value is proportional to $N^{-1/2}$, where N is the number of particles. Similarly, the vibrations of the molecules in a solid have a time scale much smaller than that of macroscopic measurements, and hence the pressure of a solid also is a well-defined quantity.

Problem 3.46. Random walks and the central limit theorem

Use the central limit theorem to find the probability that a one-dimensional random walker has a displacement between x and $x + dx$. (There is no need to derive the central limit theorem.) □

3.8 *The Poisson Distribution or Should You Fly?

We now return to the question of whether or not it is safe to fly. If the probability of a plane crashing is $p = 10^{-6}$, then $1 - p$ is the probability of surviving a single flight. The probability of surviving N flights is then $P_N = (1-p)^N$. For $N = 1000$, $P_N \approx 0.999$, and for $N = 500,000$, $P_N \approx 0.607$. Thus, our intuition is verified that if we took 1000 flights, we would have only a small chance of crashing.

This type of reasoning is typical when the probability of an individual event is small, but there are very many attempts. Suppose we are interested in the probability of the occurrence of n events out of N attempts given that the probability p of the event for each attempt is very small. The resulting probability is called the *Poisson distribution*, a distribution that is important in the analysis of experimental data. We discuss it here because of its intrinsic interest.

One way to derive the Poisson distribution is to begin with the binomial distribution:

$$P(n) = \frac{N!}{n!\,(N-n)!}\, p^n (1-p)^{N-n}. \tag{3.134}$$

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[12] We will state the central limit theorem more carefully in Section 3.11.2 and note that the theorem holds only if the second moment of the probability distribution of the individual terms in the sum is finite.

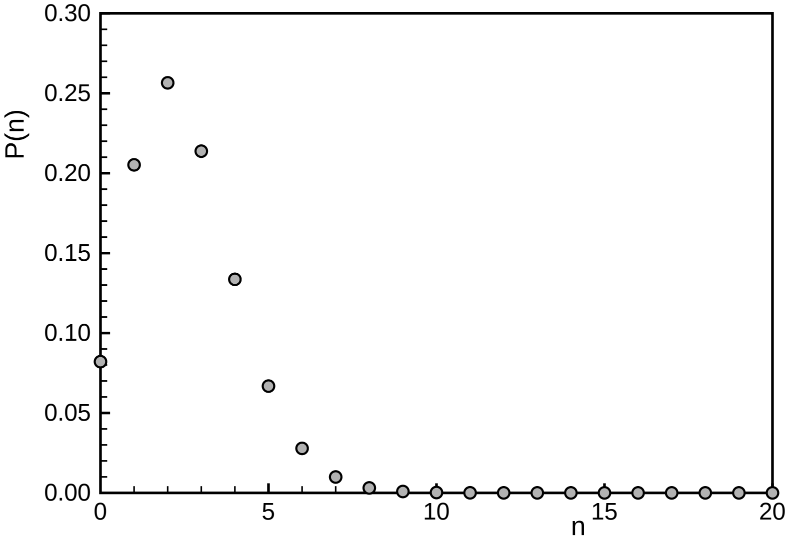

Figure 3.10: Plot of the Poisson probability distribution for $p = 0.0025$ and $N = 1000$.

We will suppress the N dependence of P. We first show that the term $N!/(N-n)!$ can be approximated by N^n in the limit $N \gg n$. We write

$$\begin{aligned}
\frac{N!}{(N-n)!} &= N(N-1)(N-2)\cdots(N-n+1) && (3.135a)\\
&= N^n[1-1/N][1-2/N]\cdots[1-(n-1)/N] && (3.135b)\\
&\approx N^n, && (3.135c)
\end{aligned}$$

where each term in brackets can be replaced by 1 because $N \gg n$. We next write $\ln(1-p)^{(N-n)} = (N-n)\ln(1-p) \approx -(N-n)p \approx -Np$, and hence $q^{N-n} \approx e^{-pN}$. We then combine these approximations to obtain

$$P(n) \approx \frac{1}{n!}N^n\,p^n e^{-pN} = \frac{(Np)^n}{n!}e^{-pN}, \tag{3.136}$$

or

$$\boxed{P(n) = \frac{\overline{n}^n}{n!}e^{-\overline{n}}} \qquad \text{(Poisson distribution)}, \tag{3.137}$$

where $\overline{n} = pN$. The form (3.137) is the Poisson distribution (see Figure 3.10).

Let us apply the Poisson distribution to the airplane survival problem. We want to know the probability of never crashing, that is, $P(n=0)$. The mean $\overline{N} = pN$ equals $10^{-6} \times 1000 = 0.001$ for $N = 1000$ flights and $\overline{N} = 0.5$ for $N = 500,000$ flights. Thus, the survival probability is $P(0) = e^{-\overline{N}} \approx 0.999$ for $N = 1000$ and $P(0) \approx 0.607$ for $N = 500,000$ as we calculated previously. We see that if we fly 500,000 times, we have a much larger probability of dying in a plane crash.

Problem 3.47. Poisson distribution

(a) Show that the Poisson distribution is properly normalized, and calculate the mean and variance of n [see (A.5)]. Because $P(n)$ for $n > N$ is negligibly small, you can sum $P(n)$ from $n = 0$ to $n = \infty$ even though the maximum value of n is N.

(b) Plot the Poisson distribution $P(n)$ as a function of n for $p = 0.01$ and $N = 100$. ☐

3.9 *Traffic Flow and the Exponential Distribution

The Poisson distribution is closely related to the exponential distribution as we will see in the following. Consider a sequence of similar random events which occur at times $t_1, t_2, \ldots$. Examples of such sequences are the times that a Geiger counter registers a decay of a radioactive nucleus and the times of an accident at a busy intersection. Suppose that we determine the sequence over a very long time T that is much greater than any of the intervals $\tau_i = t_i - t_{i-1}$. We also suppose that the mean number of events is λ per unit time so that in the interval τ, the mean number of events is $\lambda\tau$. We also assume that the events occur at random and are independent of each other.

We wish to find the probability $w(\tau)d\tau$ that the interval between events is between τ and $\tau + d\tau$. If an event occurred at $t = 0$, the probability that at least one other event occurs within the interval $[0, \tau]$ is

$$\int_0^\tau w(\tau')\, d\tau'. \tag{3.138}$$

The probability that no event occurs in this interval is

$$1 - \int_0^\tau w(\tau')\, d\tau'. \tag{3.139}$$

Another way of thinking of $w(\tau)$ is that it is the probability that no event occurs in the interval $[0, \tau]$ and then an event occurs within $[\tau,\, \tau + \Delta\tau]$. Thus,

$$\begin{aligned} w(\tau)\Delta\tau &= \text{probability that no event occurs in the interval } [0,\tau] \\ &\qquad \times \text{ probability that an event definitely occurs in the interval } [\tau, \tau + \Delta\tau] \\ &= \Big[1 - \int_0^\tau w(\tau')\, d\tau'\Big]\lambda\Delta\tau. \end{aligned} \tag{3.140}$$

If we cancel $\Delta\tau$ from each side of (3.140) and differentiate both sides with respect to τ, we find

$$\frac{dw}{d\tau} = -\lambda w, \tag{3.141}$$

so that

$$w(\tau) = Ae^{-\lambda\tau}. \tag{3.142}$$

The constant of integration A is determined from the normalization condition:

$$\int_0^\infty w(\tau')\, d\tau' = 1 = A\int_0^\infty e^{-\lambda\tau'}\, d\tau' = A/\lambda. \tag{3.143}$$

Hence, $w(\tau)$ is the exponential function

$$w(\tau) = \lambda e^{-\lambda \tau}. \tag{3.144}$$

These results for the exponential distribution lead naturally to the Poisson distribution. Let us divide the interval $T \gg 1$ into n smaller intervals $\tau = T/n$. What is the probability that 0, 1, 2, 3, ... events occur in the interval τ? We will show that the probability that n events occur in the time interval τ is given by the Poisson distribution:

$$P_n(\tau) = \frac{(\lambda\tau)^n}{n!} e^{-\lambda\tau}, \tag{3.145}$$

where we have set $\overline{n} = \lambda\tau$ in (3.137). We first consider the case $n = 0$. If $n = 0$, the probability that no event occurs in the interval τ is [see (3.140)]

$$P_{n=0}(\tau) = 1 - \int_0^\tau w(\tau')\, d\tau' = 1 - \lambda \int_0^\tau e^{-\lambda\tau'}\, d\tau' = e^{-\lambda\tau}. \tag{3.146}$$

For $n = 1$ there is exactly one event in time interval τ. This event must occur at some time τ'. If it occurs at τ', then no other event can occur in the interval $[\tau', \tau]$ (otherwise n would not equal 1). Thus, we have

$$P_{n=1}(\tau) = \int_0^\tau w(\tau') P_{n=0}(\tau - \tau')\, d\tau' \tag{3.147a}$$

$$= \int_0^\tau \lambda e^{-\lambda\tau'} e^{-\lambda(\tau-\tau')}\, d\tau', \tag{3.147b}$$

where we have used (3.146) with $\tau \to (\tau - \tau')$. Hence,

$$P_{n=1}(\tau) = \int_0^\tau \lambda e^{-\lambda\tau} d\tau' = (\lambda\tau) e^{-\lambda\tau}. \tag{3.148}$$

If n events are to occur in the interval $[0, \tau]$, the first must occur at some time τ' and exactly $(n - 1)$ must occur in the time $(\tau - \tau')$. Hence,

$$P_n(\tau) = \int_0^\tau \lambda e^{-\lambda\tau'} P_{n-1}(\tau - \tau')\, d\tau'. \tag{3.149}$$

Equation (3.149) is a recurrence formula that can be used to derive (3.145) by induction. It is easy to see that (3.145) satisfies (3.149) for $n = 1$. As is usual when solving recursion formulas by induction, we assume that (3.145) is correct for $(n - 1)$. We substitute this result into (3.149) and find

$$P_n(\tau) = \lambda^n e^{-\lambda\tau} \int_0^\tau (\tau - \tau')^{n-1}\, d\tau'/(n-1)! = \frac{(\lambda\tau)^n}{n!} e^{-\lambda\tau}. \tag{3.150}$$

An application of the Poisson distribution is given in Problem 3.48.

*__Problem 3.48.__ Analysis of traffic data

In Table 3.5 we show the number of vehicles passing a marker during a 30 s interval. The observations were made on a single lane of a six-lane divided highway. Assume that the traffic density is so low that passing occurs easily and no platoons of cars develop.

N	frequency
0	1
1	7
2	14
3	25
4	31
5	26
6	27
7	14
8	8
9	3
10	4
11	3
12	1
13	0
14	1
> 15	0

Table 3.5: Observed distribution of vehicles passing a marker on a highway in 30 s intervals, taken from Montroll and Badger (1974), page 98.

(a) Is the distribution of the number of vehicles consistent with the Poisson distribution? If so, what is the value of the parameter λ?

(b) As the traffic density increases, the flow reaches a regime where the vehicles are very close to one another so that they are no longer mutually independent. Make arguments for the form of the probability distribution of the number of vehicles passing a given point in this regime. □

3.10 *Are All Probability Distributions Gaussian?

We have discussed *random additive processes* and found that the probability distribution of their sum is a Gaussian for a sufficiently large number of terms. An example of such a process is a one-dimensional random walk for which the displacement x is the sum of N random steps.

We now discuss *random multiplicative processes*. Examples of such processes include the distributions of incomes, rainfall, and fragment sizes in rock crushing processes.[13] Consider the latter for which we begin with a rock of size w. We strike the rock with a hammer and generate two fragments whose sizes are pw and qw, where $q = 1 - p$. In the next step the possible sizes of the fragments are p^2w, pqw, qpw, and q^2w. What is the distribution of the fragment sizes after N blows of the hammer?

To answer this question consider the value of the product of the binary sequence of N elements in which the numbers x_1 and x_2 appear independently with probabilities p and q, respectively. We write

$$\Pi = x_1 x_1 x_2 x_1 x_2 \ldots \tag{3.151}$$

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[13] The following discussion is based on an article by Redner (1990).

We ask what is $\overline{\Pi}$, the mean value of Π? To calculate $\overline{\Pi}$ we define $P_N(n)$ to be the probability that the product of N independent factors of x_1 and x_2 has the value ${x_1}^n{x_2}^{N-n}$. This probability is given by the number of sequences where x_1 appears n times multiplied by the probability of choosing a specific sequence with x_1 appearing n times. This probability is the familiar binomial distribution:

$$P_N(n) = \frac{N!}{n!\,(N-n)!}p^n q^{N-n}. \tag{3.152}$$

We average over all possible outcomes of the product to obtain its mean value

$$\overline{\Pi} = \sum_{n=0}^{N} P_N(n)\big[{x_1}^n{x_2}^{N-n}\big] = (px_1 + qx_2)^N. \tag{3.153}$$

The most probable event in the product contains Np factors of x_1 and Nq factors of x_2. Hence, the most probable value of the product is

$$\widetilde{\Pi} = ({x_1}^p{x_2}^q)^N. \tag{3.154}$$

To obtain a better feeling for these results we consider some special cases. For $x_1 = 2$, $x_2 = 1/2$, and $p = q = 1/2$ we have $\overline{\Pi} = (1/4)[x_2^2 + 2x_1x_2 + x_2^2] = (1/4)[4 + 2 + 1/4] = 25/16$ for $N = 2$; for general N we have $\overline{\Pi} = (5/4)^N$. In contrast, the most probable value for $N = 2$ is given by $\widetilde{\Pi} = [2^{1/2} \times (1/2)^{1/2}]^2 = 1$; the same result holds for any N. For $p = 1/3$ and $q = 2/3$ and the same values of x_1 and x_2 we find $\overline{\Pi} = 1$ for all N and $\widetilde{\Pi} = [2^{1/3} \times (1/2)^{2/3}]^2 = 2^{-2/3}$ for $N = 2$ and $2^{-N/3}$ for any N. We see that $\widetilde{\Pi} \neq \overline{\Pi}$ for a random multiplicative process. In contrast, the most probable event is a good approximation to the mean value of the sum of a random additive process (and is identical for $p = q$).

The reason for the large discrepancy between $\overline{\Pi}$ and $\widetilde{\Pi}$ is the important role played by rare events. For example, a sequence of N factors of $x_1 = 2$ occurs with a very small probability, but the value of this product is very large in comparison to the most probable value. Hence, this extreme event makes a finite contribution to $\overline{\Pi}$ and a dominant contribution to the higher moments $\overline{\Pi^m}$.

***Problem 3.49.** A simple multiplicative process

(a) Confirm the general result in (3.153) for $N = 4$ by showing explicitly all the possible values of the product.

(b) Consider the case $x_1 = 2$, $x_2 = 1/2$, $p = 1/4$, and $q = 3/4$, and calculate $\overline{\Pi}$ and $\widetilde{\Pi}$.

(c) Show that the mean value of the mth moment $\overline{\Pi^m} = \sum_{n=0}^{N} P(n)\big[x_1)^n x_2^{N-n}\big]^m$ reduces to $(px_1^m)^N$ as $m \to \infty$ (for $x_1 > x_2$). (Hint: Consider the ratio of each term in the sum to the term with x_1^{Nm}.) This result implies that the mth moment is determined solely by the most extreme event for $m \gg 1$.

(d) Explain why a *log-normal* distribution for which $p(\Pi) \sim e^{-(\ln\Pi - \overline{\ln\Pi})^2/2\sigma^2}$ is a reasonable guess for the continuum approximation to the probability of a random multiplicative process for $N \gg 1$. Here $\Pi = x_1^n x_2^{N-n}$. ☐

***Problem 3.50.** Simulation of a multiplicative process

Run Program `MultiplicativeProcess` to simulate the distribution of values of the product ${x_1}^n {x_2}^{N-n}$. Choose $x_1 = 2$, $x_2 = 1/2$, and $p = q = 1/2$. First choose $N = 4$ and estimate $\overline{\Pi}$ and $\widetilde{\Pi}$. Do your estimated values converge more or less uniformly to the analytical values as the number of measurements becomes large? Do a similar simulation for $N = 40$. Compare your results with a similar simulation of a random walk and discuss the importance of extreme events for random multiplicative processes.

3.11 *Supplementary Notes

3.11.1 Method of undetermined multipliers

Suppose that we want to maximize the function $f(x, y) = xy^2$ subject to the constraint that $x^2 + y^2 = 1$. One way would be to substitute $y^2 = 1 - x^2$ and maximize $f(x) = x(1 - x^2)$. This approach works only if f can be reduced to a function of one variable. We first consider this case as a way of introducing the general method of undetermined multipliers.

Our goal is to maximize $f(x, y) = xy^2$ subject to the constraint that $g(x, y) = x^2 + y^2 - 1 = 0$. In the method of undetermined multipliers this problem can be reduced to solving the equation

$$df - \lambda dg = 0, \tag{3.155}$$

where $df = 0$ at the maximum of f, $dg = 0$ because g expresses the constraint, and λ will be chosen so that (3.155) is satisfied. If we substitute $df = y^2 dx + 2xy dy$ and $dg = 2x dx + 2y dy$ in (3.155), we obtain

$$(y^2 - 2\lambda x)dx + 2(xy - \lambda y)dy = 0. \tag{3.156}$$

We choose $\lambda = y^2/2x$ so that the first term is zero at the maximum. Because this term is zero, the second term must also be zero; that is, $x = \lambda = y^2/2x$, so $x = \pm y/\sqrt{2}$. Hence, from the constraint $g(x, y) = 0$, we obtain $x = \sqrt{1/3}$ and $\lambda = 2$.

More generally, we wish to maximize the function $f(x_1, x_2, \ldots, x_N)$ subject to the constraints $g_j(x_1, x_2, \ldots, x_N) = 0$ where $j = 1, 2, \ldots, M$ with $M < N$. The maximum of f is given by

$$df = \sum_{i=1}^{N} \frac{\partial f}{\partial x_i} dx_i = 0, \tag{3.157}$$

and the constraints can be expressed as

$$dg_j = \sum_{i=1}^{N} \frac{\partial g_j}{\partial x_i} dx_i = 0. \tag{3.158}$$

As in our example, we can combine (3.157) and (3.158) and write $df - \sum_{j=1}^{M} \lambda_j dg_j = 0$, or

$$\sum_{i=1}^{N} \Big[\frac{\partial f}{\partial x_i} - \sum_{j=1}^{M} \lambda_j \frac{\partial g_j}{\partial x_i}\Big] dx_i = 0. \tag{3.159}$$

We are free to choose all M values of λ_j such that the first M terms in the square brackets are zero. For the remaining $N-M$ terms, the dx_i can be independently varied because the constraints have been satisfied. Hence, the remaining terms in square brackets must be independently zero, and we are left with $N-M$ equations of the form

$$\frac{\partial f}{\partial x_i} - \sum_{i=1}^{M} \lambda_j \frac{\partial g_j}{\partial x_i} = 0. \tag{3.160}$$

In Example 3.11 we were able to obtain the probabilities by reducing the uncertainty S to a function of a single variable P_1 and then maximizing $S(P_1)$. We now consider a more general problem where there are more outcomes – a loaded die for which there are six outcomes. Suppose that we know that the average number of points on the face of a die is $\overline{n}$. We wish to determine the values of P_1, P_2, …, P_6 that maximize the uncertainty S subject to the constraints

$$\sum_{j=1}^{6} P_j = 1, \tag{3.161}$$

$$\sum_{j=1}^{6} jP_j = \overline{n}. \tag{3.162}$$

For a perfect die $\overline{n} = 3.5$. We take

$$f = S = -\sum_{j=1}^{6} P_j \ln P_j, \tag{3.163a}$$

$$g_1 = \sum_{j=1}^{6} P_j - 1, \tag{3.163b}$$

and

$$g_2 = \sum_{j=1}^{6} jP_j - \overline{n}. \tag{3.163c}$$

We have $\partial f/\partial P_j = -(1 + \ln P_j)$, $\partial g_1/\partial P_j = 1$, and $\partial g_2/\partial P_j = j$, and write (3.160) for $j = 1$ and $j = 2$ as

$$-(1 + \ln P_1) - \alpha - \beta = 0, \tag{3.164a}$$

$$-(1 + \ln P_2) - \alpha - 2\beta = 0, \tag{3.164b}$$

where we have taken α and β (instead of λ_1 and λ_2) as the undetermined Lagrange multipliers. The solution of (3.164) for α and β is

$$\alpha = \ln P_2 - 2\ln P_1 - 1, \tag{3.165a}$$

$$\beta = \ln P_1 - \ln P_2. \tag{3.165b}$$

We solve (3.165b) for $\ln P_2 = \ln P_1 - \beta$ and use (3.165a) to find $\ln P_1 = -1 - \alpha - \beta$. We then use this result to write $\ln P_2$ as $\ln P_2 = -1 - \alpha - 2\beta$. We can independently vary dP_3, …, dP_6

because the two constraints are satisfied by the values of P_1 and P_2. Hence, we have from (3.160) and (3.163) that

$$\ln P_j = -1 - \alpha - j\beta, \tag{3.166}$$

or

$$P_j = e^{-1-\alpha} e^{-\beta j}. \tag{3.167}$$

We eliminate the constant α by the normalization condition (3.161) and write

$$P_j = \frac{e^{-\beta j}}{\sum_j e^{-\beta j}}. \tag{3.168}$$

The constant β is determined by the constraint (3.45):

$$\overline{n} = \frac{e^{-\beta} + 2e^{-2\beta} + 3e^{-3\beta} + 4e^{-4\beta} + 5e^{-5\beta} + 6e^{-6\beta}}{e^{-\beta} + e^{-2\beta} + e^{-3\beta} + e^{-4\beta} + e^{-5\beta} + e^{-6\beta}}. \tag{3.169}$$

Usually, (3.169) must be solved numerically.

The exponential form (3.168) will become very familiar to us [see (4.79)], page 200) and is known as the Boltzmann distribution. In the context of thermal systems the Boltzmann distribution maximizes the uncertainty given the constraints that the probability distribution is normalized and the mean energy is known.

Problem 3.51. Numerical solution of (3.169)

Show that the solution to (3.169) is $\beta = 0$ for $\overline{n} = 7/2$, $\beta = +\infty$ for $\overline{n} = 1$, $\beta = -\infty$ for $\overline{n} = 6$, and $\beta = -0.1746$ for $\overline{n} = 4$. □

3.11.2 Derivation of the central limit theorem

To discuss the derivation of the central limit theorem, it is convenient to introduce the *characteristic function* $\phi(k)$ of the probability density $p(x)$. The main utility of the characteristic function is that it simplifies the analysis of the sums of independent random variables. We define $\phi(k)$ as the Fourier transform of $p(x)$:

$$\phi(k) = \overline{e^{ikx}} = \int_{-\infty}^{\infty} e^{ikx} p(x)\, dx. \tag{3.170}$$

Because $p(x)$ is normalized, it follows that $\phi(k = 0) = 1$. The main property of the Fourier transform that we need is that if $\phi(k)$ is known, we can find $p(x)$ by calculating the inverse Fourier transform:

$$p(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ikx} \phi(k)\, dk. \tag{3.171}$$

Problem 3.52. Characteristic function of a Gaussian

Calculate the characteristic function of the Gaussian probability density. □

One useful property of $\phi(k)$ is that its power series expansion yields the moments of $p(x)$:

$$\phi(k) = \sum_{n=0}^{\infty} \frac{k^n}{n!} \frac{d^n\phi(k)}{dk^n}\Big|_{k=0} \tag{3.172}$$

$$= \overline{e^{ikx}} = \sum_{n=0}^{\infty} \frac{(ik)^n \overline{x^n}}{n!}. \tag{3.173}$$

By comparing coefficients of k^n in (3.172) and (3.173), we see that

$$\overline{x} = -i\frac{d\phi}{dk}\Big|_{k=0}. \tag{3.174}$$

In Problem 3.53 we show that

$$\overline{x^2} - \overline{x}^2 = -\frac{d^2}{dk^2}\ln\phi(k)\Big|_{k=0}, \tag{3.175}$$

and that certain convenient combinations of the moments are related to the power series expansion of the logarithm of the characteristic function.

Problem 3.53. The first few cumulants

The characteristic function generates the *cumulants* C_m defined by

$$\ln\phi(k) = \sum_{n=1}^{\infty} \frac{(ik)^n}{n!} C_n. \tag{3.176}$$

Show that the cumulants are combinations of the moments of x and are given by

$$C_1 = \overline{x}, \tag{3.177a}$$

$$C_2 = \sigma^2 = \overline{x^2} - \overline{x}^2, \tag{3.177b}$$

$$C_3 = \overline{x^3} - 3\,\overline{x^2}\,\overline{x} + 2\,\overline{x}^3, \tag{3.177c}$$

$$C_4 = \overline{x^4} - 4\,\overline{x^3}\,\overline{x} - 3\,\overline{x^2}^2 + 12\,\overline{x^2}\,\overline{x}^2 - 6\,\overline{x}^4. \tag{3.177d}$$

The first few cumulants were calculated for several probability distributions in Problems 3.41(b) and 3.42(c). What is the value of C_4 for the Gaussian distribution? □

Now let us consider the properties of the characteristic function for the sums of independent variables. For example, let $p_1(x)$ be the probability density for the weight x of adult males and let $p_2(y)$ be the probability density for the weight of adult females. If we assume that people marry one another independently of weight, what is the probability density $p(z)$ for the weight z of an adult couple? We have that

$$z = x + y. \tag{3.178}$$

How do the probability densities combine? The answer is given by

$$p(z) = \int p_1(x)p_2(y)\,\delta(z - x - y)\,dx\,dy. \tag{3.179}$$

The integral in (3.179) represents all the possible ways of obtaining the combined weight z as determined by the probability density $p_1(x)p_2(y)$ for the combination of x and y that sums to z. The form (3.179) of the integrand is known as a *convolution.* An important property of a convolution is that its Fourier transform is a simple product. We have

$$\phi_z(k) = \int e^{ikz} p(z)dz \tag{3.180a}$$

$$= \iiint e^{ikz} p_1(x)p_2(y)\delta(z - x - y)dx\,dy\,dz \tag{3.180b}$$

$$= \int e^{ikx} p_1(x)dx \int e^{iky} p_2(y)dy \tag{3.180c}$$

$$= \phi_1(k)\phi_2(k). \tag{3.180d}$$

It is straightforward to generalize this result to a sum of N random variables. We write

$$S = x_1 + x_2 + \ldots + x_N. \tag{3.181}$$

Then

$$\phi_S(k) = \prod_{i=1}^{N} \phi_i(k). \tag{3.182}$$

That is, *the characteristic function of the sum of several independent variables is the product of the individual characteristic functions.* If we take the logarithm of both sides of (3.182), we obtain

$$\ln \phi_S(k) = \sum_{i=1}^{N} \ln \phi_i(k). \tag{3.183}$$

Each side of (3.183) can be expanded as a power series and compared order by order in powers of ik. The result is that when random variables are added, their associated cumulants also add. That is, the nth order cumulants satisfy the relation

$$C_n^S = C_n^1 + C_n^2 + \ldots + C_n^N. \tag{3.184}$$

We conclude that if the random variables x_i are independent (uncorrelated), their cumulants, and in particular, their variances, add. We saw a special case of this result for the variance in (3.75).

If we denote the mean and standard deviation of the weight of an adult male as $\overline{w}$ and σ, respectively, then from (3.177a) and (3.184) we find that the mean weight of N adult males is given by $N\overline{w}$. Similarly from (3.177b) we see that the standard deviation of the weight of N adult males is given by $\sigma_N^2 = N\sigma_w^2$, or $\sigma_N = \sqrt{N}\sigma_w$. Hence, we find the now familiar result that the sum of N random variables scales as N while the standard deviation scales as $\sqrt{N}$.

We are now in a position to derive the central limit theorem. Let x_1, x_2, …, x_N be N mutually independent variables. For simplicity, we assume that each variable has the same probability density $p(x)$. The only condition is that the variance σ_x^2 of the probability density $p(x)$ must be finite. For simplicity, we make the additional assumption that $\overline{x} = 0$, a condition that always can be satisfied by measuring x from its mean. The central limit theorem states that the sum S has the probability density

$$p(S) = \frac{1}{\sqrt{2\pi N{\sigma_x}^2}}\, e^{-S^2/2N{\sigma_x}^2}. \tag{3.185}$$

From (3.177b) we see that $\overline{S^2} = N\sigma_x^2$, and hence the variance of S grows linearly with N. However, the distribution of the values of the arithmetic mean S/N becomes narrower with increasing N:

$$\overline{\Big(\frac{x_1 + x_2 + \ldots x_N}{N}\Big)^2} = \frac{N\sigma_x^2}{N^2} = \frac{\sigma_x^2}{N}. \tag{3.186}$$

From (3.186) we see that it is useful to define a scaled sum

$$z = \frac{1}{\sqrt{N}}(x_1 + x_2 + \ldots + x_N), \tag{3.187}$$

and to write the central limit theorem in the form

$$p(z) = \frac{1}{\sqrt{2\pi\sigma_x^2}}\, e^{-z^2/2\sigma_x^2}. \tag{3.188}$$

To obtain the result (3.188), we write the characteristic function of z as

$$\begin{aligned}
\phi_z(k) = \iiint \cdots \int & e^{ikz}\delta\big(z - \big[\frac{x_1 + x_2 + \ldots + x_N}{N^{1/2}}\big]\big) \\
& \times p(x_1)\, p(x_2) \cdots p(x_N) dz\, dx_1 dx_2 \cdots dx_N && \text{(3.189a)} \\
= \iint \cdots \int & e^{ik(x_1+x_2+\cdots+x_N)/N^{1/2}} p(x_1)\, p(x_2) \ldots p(x_N) dx_1\, dx_2 \cdots dx_N && \text{(3.189b)} \\
= \phi & \Big(\frac{k}{N^{1/2}}\Big)^N. && \text{(3.189c)}
\end{aligned}$$

We next take the logarithm of both sides of (3.189c) and expand the right-hand side in powers of k using (3.176) to find

$$\ln \phi_z(k) = \sum_{m=2}^{\infty} \frac{(ik)^m}{m!} N^{1-m/2} C_m. \tag{3.190}$$

The $m = 1$ term does not contribute in (3.190) because we have assumed that $\overline{x} = 0$. More importantly, note that as $N \to \infty$ the higher-order terms are suppressed so that

$$\ln \phi_z(k) \to -\frac{k^2}{2} C_2, \tag{3.191}$$

or

$$\phi_z(k) \to e^{-k^2\sigma^2/2} + \cdots . \tag{3.192}$$

Because the inverse Fourier transform of a Gaussian is also a Gaussian, we find that

$$p(z) = \frac{1}{\sqrt{2\pi\sigma_x^2}} e^{-z^2/2\sigma_x^2}. \tag{3.193}$$

The leading correction to $\phi(k)$ in (3.193) gives rise to a term of order $N^{-1/2}$, and therefore does not contribute in the limit $N \to \infty$.

The only requirements for the applicability of the central limit theorem are that the various x_i be statistically independent and that the second moment of $p(x)$ exists. It is not necessary that all the x_i have the same distribution. Not all probabilities have a finite second moment as demonstrated by the Lorentz distribution (see Problem 3.43), but the requirements for the central limit theorem are weak and the central limit theorem is widely applicable.

Vocabulary

sample space, events, outcome

uncertainty, principle of least bias or maximum uncertainty

probability distribution $P(i)$ or P_i, probability density $p(x)$

mean value $\overline{f(x)}$, moments, variance $\overline{\Delta x^2}$, standard deviation σ

conditional probability $P(\mathrm{A}|\mathrm{B})$, Bayes' theorem

binomial distribution, Gaussian distribution, Poisson distribution

random walk, random additive processes, central limit theorem

Stirling's approximation

Monte Carlo sampling

Rare or extreme events, random multiplicative processes

cumulants, characteristic function

Additional problems

Problem 3.54. Probability that a site is occupied

In Figure 3.11 we show a square lattice of 16^2 sites each of which is occupied with probability p. Estimate the probability p that a site in the lattice is occupied and explain your reasoning. □

Problem 3.55. Three coins (in a fountain)

Three coins are tossed in succession. Assume that landing heads or tails is equiprobable. Find the probabilities of the following:

(a) the first coin is heads;

(b) exactly two heads have occurred;

(c) not more than two heads have occurred. □

Problem 3.56. A student's fallacious reasoning

A student tries to solve Problem 3.13 by using the following reasoning. The probability of a double 6 is 1/36. Hence the probability of finding at least one double 6 in 24 throws is 24/36. What

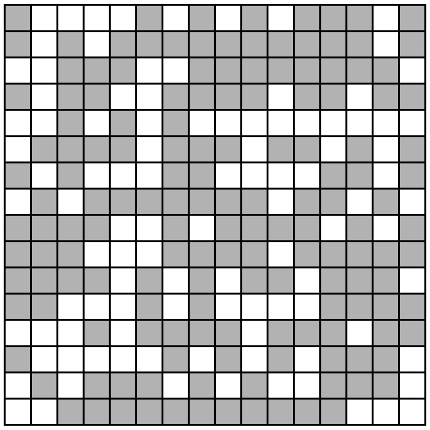

Figure 3.11: Representation of a square lattice of 16×16 sites. The sites are represented by squares. Each site is either occupied (shaded) independently of its neighbors with probability p or is empty (white) with probability $1-p$. These configurations are discussed in the context of percolation in Section 9.3.

is wrong with this reasoning? If you have trouble understanding the error in this reasoning, try solving the problem of finding the probability of at least one double 6 in two throws of a pair of dice. What are the possible outcomes? Is each outcome equally probable? □

Problem 3.57. d'Alembert's fallacious reasoning

(a) What is the probability that heads will appear at least once in two tosses of a single coin? Use the rules of probability to show that the answer is $\frac{3}{4}$.

(b) d'Alembert, a distinguished French mathematician of the eighteenth century, reasoned that there are only three possible outcomes: heads on the first throw, heads on the second throw, and no heads at all. The first two of these three outcomes is favorable. Therefore the probability that heads will appear at least once is $\frac{2}{3}$. What is the fallacy in his reasoning? Even eminent mathematicians (and physicists) have been lead astray by the subtle nature of probability. □

Problem 3.58. Number of fish in a pond

A farmer wants to estimate how many fish are in a pond. The farmer takes out 200 fish and tags them and returns them to the pond. After sufficient time to allow the tagged fish to mix with the others, the farmer removes 250 fish at random and finds that 25 of them are tagged. Estimate the number of fish in the pond. □

Problem 3.59. Estimating the area of a pond

A farmer owns a field that is $10\,\text{m} \times 10\,\text{m}$. In the midst of this field is a pond of unknown area. Suppose that the farmer is able to throw 100 stones at random into the field and finds that 40 of the stones make a splash. How can the farmer use this information to estimate the area of the pond? □

	x_i, y_i		x_i, y_i
1	0.984, 0.246	6	0.637, 0.581
2	0.860, 0.132	7	0.779, 0.218
3	0.316, 0.028	8	0.276, 0.238
4	0.523, 0.542	9	0.081, 0.484
5	0.349, 0.623	10	0.289, 0.032

Table 3.6: A sequence of ten random pairs of numbers (see Problem 3.60).

Problem 3.60. Monte Carlo integration

Consider the ten pairs of numbers (x_i, y_i) given in Table 3.6. The numbers are all in the range $0 < x_i, y_i \leq 1$. Imagine that these numbers were generated by counting the clicks generated by a Geiger counter of radioactive decays, and hence they can be considered to be a part of a sequence of random numbers. Use this sequence to estimate the magnitude of the integral

$$F = \int_0^1 dx\, \sqrt{(1 - x^2)}. \tag{3.194}$$

If you have been successful in estimating the integral in this way, you have found a simple version of a general method known as *Monte Carlo integration.*[14]

(a) Show analytically that the integral in (3.194) is equal to $\pi/4$.

(b) Use Program `MonteCarloEstimation` to estimate the integral (3.194) by Monte Carlo integration. Determine the error (the magnitude of the deviation from the exact answer) for trials of n pairs of points equal to $n = 10^4$, 10^6, and 10^8. Does the error decrease with increasing n on the average?

(c) Estimate the integral using $n = 1000$. Repeat for a total of ten trials using a different random number seed each time. The easiest way to do so is to press the Reset button and then press the Calculate button. The default is for the program to choose a new seed each time based on the clock. Is the magnitude of the variation of your values of the same order as the error between the average value and the exact value? For a large number of trials, the error is estimated from the standard error of the mean, which approximately equals the standard deviation divided by the square root of the number of trials. □

Problem 3.61. Bullseye

A person playing darts hits a bullseye 20% of the time on the average. Why is the probability of b bullseyes in N attempts a binomial distribution? What are the values of p and q? Find the probability that the person hits a bullseye

(a) once in five throws;

(b) twice in ten throws.

---

[14] Monte Carlo methods were first developed to estimate integrals that could not be performed analytically or by the usual numerical methods.

Why are these probabilities not identical? □

Problem 3.62. Family values

There are ten children in a given family. Assuming that a boy is as likely to be born as a girl, find the probability of the family having

(a) five boys and five girls;

(b) three boys and seven girls. □

Problem 3.63. Fathers and sons (and daughters)

What is the probability that five children produced by the same couple will consist of the following (assume that the probabilities of giving birth to a boy and a girl are the same):

(a) three sons and two daughters?

(b) alternating sexes?

(c) alternating sexes starting with a son?

(d) all daughters? □

Problem 3.64. Probability in baseball

A good hitter in major league baseball has a batting average of 300, which means that the hitter will be successful three times out of ten tries on the average. Assume that the batter has four times at bat per game.

(a) What is the probability that he gets no hits in one game?

(b) What is the probability that he will get two hits or less in a three-game series?

(c) What is the probability that he will get five or more hits in a three-game series? Baseball fans might want to think about the significance of "slumps" and "streaks" in baseball. □

Problem 3.65. Playoff winners

(a) In the World Series in baseball and in the playoffs in the National Basketball Association and the National Hockey Association, the winner is determined by the best of seven games. That is, the first team that wins four games wins the series and is the champion. Do a simple statistical calculation assuming that the two teams are evenly matched and show that a seven-game series should occur 31.25% of the time. What is the probability that the series lasts n games? More information can be found at `<www.mste.uiuc.edu/hill/ev/seriesprob.html>` and at `<www.aip.org/isns/reports/2003/080.html>`.

(b) Most teams have better records at home. Assume the two teams are evenly matched and each has a 60% chance of winning at home and a 40% change of winning away. In principle, both teams should have an equal chance of winning a seven game series. Determine which pattern of home games is closer to giving each team a 50% chance of winning. Consider the two common patterns: (1) two home, three away, two home; and (2) two home, two away, one home, one away, one home. ☐

Problem 3.66. Galton board

The Galton board [named after Francis Galton (1822–1911)] is a triangular array of pegs. The rows are numbered $0, 1, \ldots$ from the top row down, such that row n has $n + 1$ pegs. Suppose that a ball is dropped from above the top peg. Each time the ball hits a peg, it bounces to the right with probability p and to the left with probability $1 - p$, independently from peg to peg. Suppose that N balls are dropped successively such that the balls do not encounter one another. How will the balls be distributed at the bottom of the board? Links to applets that simulate the Galton board can be found in the references. ☐

Problem 3.67. The birthday problem

What if somebody offered to bet you that at least two people in your physics class had the same birthday? Would you take the bet?

(a) What are the chances that at least two people in your class have the same birthday? Assume that the number of students is 25.

(b) What are the chances that at least one other person in your class has the same birthday as you? Explain why the chances are less in this case than in part (a). ☐

Problem 3.68. A random walk down Wall Street

Many analysts attempt to select stocks by looking for correlations in the stock market as a whole or for patterns for particular companies. Such an analysis is based on the belief that there are repetitive patterns in stock prices. To understand one reason for the persistence of this belief do the following experiment. Construct a stock chart (a plot of stock price versus time) showing the movements of a hypothetical stock initially selling at \$50 per share. On each successive day the closing stock price is determined by the flip of a coin. If the coin toss is a head, the stock closes 1/2 point (\$0.50) higher than the preceding close. If the toss is a tail, the price is down by 1/2 point. Construct the stock chart for a long enough time to see "cycles" and other "patterns" appear. A sequence of numbers produced in this manner is identical to a random walk, yet the sequence frequently appears to be correlated. The lesson of the charts is that our eyes look for patterns even when none exists. ☐

Problem 3.69. Displacement and number of steps to the right

(a) Suppose that a random walker takes N steps of unit length with probability p of a step to the right. The displacement m of the walker from the origin is given by $m = n - n'$, where n is the number of steps to the right and n' is the number of steps to the left. Show that $\overline{m} = (p - q)N$ and $\sigma_m^2 = \overline{(m - \overline{m})^2} = 4Npq$.

(b) The result (3.78) for $\overline{(\Delta M)^2}$ differs by a factor of four from the result for σ_n^2 in (3.99). Why? ☐

Problem 3.70. Watching a drunkard

A random walker is observed to take a total of N steps, n of which are to the right.

(a) Suppose that a curious observer finds that on ten successive nights the walker takes $N = 20$ steps and that the values of n are given successively by 14, 13, 11, 12, 11, 12, 16, 16, 14, 8. Calculate $\overline{n}$, $\overline{n^2}$, and σ_n. You can use this information to make two estimates of p, the probability of a step to the right. If you obtain different estimates for p, which estimate is likely to be the most accurate?

(b) Suppose that on another ten successive nights the same walker takes $N = 100$ steps and that the values of n are given by 58, 69, 71, 58, 63, 53, 64, 66, 65, 50. Calculate the same quantities as in part (a) and use this information to estimate p. How does the ratio of σ_n to $\overline{n}$ compare for the two values of N? Explain your results.

(c) Calculate $\overline{m}$ and σ_m, where $m = n - n'$ is the net displacement of the walker for parts (a) and (b).

This problem inspired an article by Zia and Schmittmann. □

Problem 3.71. Consider the binomial distribution $P_N(n)$ for $N = 16$ and $p = q = 1/2$.

(a) What is the value of $P_N(n)$ at $n = \overline{n} - \sigma_n$?

(b) What is the value of the product $P_N(n = \overline{n})(2\sigma_n)$? □

Problem 3.72. Alternative derivation of the Gaussian distribution

On page 137 we evaluated the binomial probability $P_N(n)$ using Stirling's approximation to determine the parameters A, B, and $\tilde{n}$ in (3.109). Another way to determine these parameters is to approximate the binomial distribution by a Gaussian and require that the zeroth, first, and second moments of the Gaussian and binomial distribution be equal. We write

$$P(n) = Ae^{-B(n-\tilde{n})^2/2}, \tag{3.195}$$

where A, B, and $\tilde{n}$ are the parameters to be determined. We first require that

$$\int_0^N P(n)\, dn = 1. \tag{3.196}$$

Because $P(n)$ depends on the difference $n - \tilde{n}$, it is convenient to change the variable of integration in (3.196) to $x = n - \tilde{n}$ and write

$$\int_{-Np}^{N(1-p)} P(x)\, dx = 1, \tag{3.197}$$

where

$$P(x) = Ae^{-Bx^2/2}. \tag{3.198}$$

Because we are interested in the limit $N \to \infty$, we can extend the limits in (3.197) to $\pm\infty$:

$$\int_{-\infty}^{\infty} P(x)\, dx = 1. \tag{3.199}$$

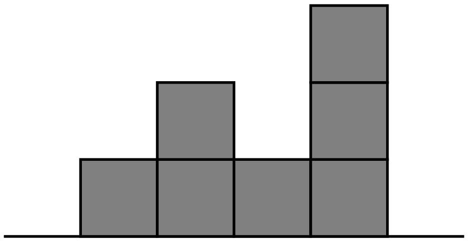

Figure 3.12: Example of a wall as explained in Problem 3.73.

(a) The first moment of the Gaussian distribution is

$$\overline{n} = \int_{-\infty}^{\infty} nP(n)\, dn, \tag{3.200}$$

where $P(n)$ is given by (3.195). Make a change of variables and show that

$$\overline{n} = \int_{-\infty}^{\infty} (x + \tilde{n})P(x)\, dx = \tilde{n}. \tag{3.201}$$

(b) The first moment of the binomial distribution is given by pN according to (3.96). Require the first moments of the binomial and Gaussian distributions to be equal, and determine $\tilde{n}$.

(c) The variance of the binomial distribution is given in (3.99) and is equal to $\overline{(n - \overline{n})^2} = Npq$. The corresponding variance of the Gaussian distribution is given by

$$\overline{(n - \overline{n})^2} = \int_{-\infty}^{\infty} (n - \overline{n})^2\, P(n)\, dn. \tag{3.202}$$

Make the necessary change of variables in (3.202) and do the integrals in (3.199) and (3.202) [see (A.23) and (A.17)] to confirm that the values of B and A are given by (3.115) and (3.117), respectively.

(d) Explain why the third moments of the binomial and Gaussian distribution are not equal. □

Problem 3.73. A simple two-dimensional wall

Consider a two-dimensional "wall" constructed from N squares as shown in Figure 3.12. The base row of the wall must be continuous, but higher rows can have gaps. Each column must be continuous and self-supporting with no overhangs. Determine the total number W_N of different N-site clusters, that is, the number of possible arrangements of N squares consistent with these rules. Assume that the squares are identical. □

Problem 3.74. Heads you win

Two people take turns tossing a coin. The first person to obtain heads is the winner. Find the probabilities of the following events:

(a) The game terminates at the fourth toss;

(b) the first player wins the game;

(c) the second player wins the game. □

***Problem 3.75.** First-passage time

Suppose that a one-dimensional unbiased random walker starts out at the origin $x = 0$ at $t = 0$ and takes unit length steps at regular intervals. As usual the probability of a step to the right is p.

(a) How many steps will it take for the walker to first reach $x = +1$? This quantity, known as the *first-passage time*, is a random variable because it is different for different realizations of the walk. Let P_n be the probability that x first equals $+1$ after n steps. What is P_n for $n = 1$, 3, 5, and 7?

(b) Write a program to simulate a random walker in one dimension and estimate the number of steps needed to first reach $x = +1$. What is your estimate of the probability that the walker will eventually reach $x = +1$ assuming that $p = 1/2$? What is the mean number of steps needed to reach $x = +1$? □

***Problem 3.76.** Range of validity of the Gaussian distribution

How good is the Gaussian distribution as an approximation to the binomial distribution as a function of N? To determine the validity of the Gaussian distribution, consider the next two terms after (3.114) in the power series expansion of $\ln P(n)$:

$$\frac{1}{3!}(n - \tilde{n})^3 C + \frac{1}{4!}(n - \tilde{n})^4 D, \tag{3.203}$$

where $C = d^3 \ln P(n)/d^3 n$ and $D = d^4 \ln P(n)/d^4 n$ evaluated at $n = \tilde{n}$.

(a) Show that $|C| < 1/N^2 p^2 q^2$. What does C equal if $p = q$?

(b) Show that $|D| < 4/N^3 p^3 q^3$.

(c) Show that the results for $|C|$ and $|D|$ imply that the neglect of terms beyond second order in $(n - \tilde{n})$ is justified if $|n - \tilde{n}| \ll Npq$. Explain why stopping at second order is justified if $Npq \gg 1$. □

Problem 3.77. A Lévy flight

A Lévy flight, named after the mathematician Paul Pierre Lévy, is a random walk in which the length ℓ of each step is distributed according to a probability distribution of the form $p(\ell) \propto \ell^{-\mu}$, where $1 < \mu < 3$. Is the form of the probability distribution of the displacement of the walker after N steps a Gaussian? □

Problem 3.78. Balls and boxes

Suppose there are three boxes each with two balls. The first box has two green balls, the second box has one green and one red ball, and the third box has two red balls. Suppose you choose a box at random and find one green ball. What is the probability that the other ball is green? □

Problem 3.79. Telephone numbers

Open a telephone directory to a random page or look at the phone numbers in your cell phone and make a list corresponding to the last digit of the first 100 telephone numbers you see. Find the probability $P(n)$ that the number n appears in your list. Plot $P(n)$ as a function of n and describe its n dependence. Do you expect that $P(n)$ is approximately uniform? □

***Problem 3.80.** Benford's law or looking for number one

Suppose that you constructed a list of the populations of the largest cities in the world, or a list of the house numbers of everybody you know. Other naturally occurring lists include river lengths, mountain heights, radioactive decay half-lives, the size of the files on your computer, and the first digit of each of the numbers that you find in a newspaper. (The first digit of a number such as 0.00123 is 1.) What is the probability $P(n)$ that the *first* digit is n, where $n = 1, \ldots, 9$? Do you think that $P(n)$ will be the same for all n?

It turns out that the form of the probability $P(n)$ is given by

$$P(n) = \log_{10}\Big(1 + \frac{1}{n}\Big). \tag{3.204}$$

The distribution (3.204) is known as *Benford's law* and is named after Frank Benford, a physicist, who independently discovered it in 1938, although it was discovered previously by the astronomer Simon Newcomb in 1881. The distribution (3.204) implies that for certain data sets, the first digit is distributed in a predictable pattern with a higher percentage of the numbers beginning with the digit 1. What are the numerical values of $P(n)$ for the different values of n? Is $P(n)$ normalized?

Accounting data is one of the many types of data that is expected to follow the Benford distribution. It has been found that artificial data sets do not have first digit patterns that follow the Benford distribution. Hence, the more an observed digit pattern deviates from the expected Benford distribution, the more likely the data set is suspect. Tax returns have been checked in this way.

The frequencies of the first digit of 2000 numerical answers to problems given in the back of four physics and mathematics textbooks have been tabulated and found to be distributed in a way consistent with Benford's law. Benford's law is also expected to hold for answers to homework problems.[15] □

***Problem 3.81.** Faking it

Ask several of your friends to flip a coin 100 times and record the results or pretend to flip a coin and fake the results. Can you tell which of your friends faked the results? □

***Problem 3.82.** Zipf's law

Suppose that we analyze a text and count the number of times a given word appears. The word with rank r is the rth word when the words of the text are listed with decreasing frequency. Make a log-log plot of word frequency f versus word rank r. The relation between word rank and word frequency was first stated by George Kingsley Zipf (1902–1950). This relation states that for a given text

$$f \sim \frac{1}{r\ln(1.78R)}, \tag{3.205}$$

---

[15] See Huddle (1997) and Hill (1998).

1	the	15861	11	his	1839
2	of	7239	12	is	1810
3	to	6331	13	he	1700
4	a	5878	14	as	1581
5	and	5614	15	on	1551
6	in	5294	16	by	1467
7	that	2507	17	at	1333
8	for	2228	18	it	1290
9	was	2149	19	from	1228
10	with	1839	20	but	1138

Table 3.7: Ranking of the top 20 words (see Problem 3.82).

where R is the number of different words. Note the inverse power law behavior of the frequency on the rank. The relation (3.205) is known as *Zipf's law.* The top 20 words in an analysis of a 1.6 MB collection of 423 short Time magazine articles (245,412 term occurrences) are given in Table 3.7. Analyze another text and determine if you find a similar relation. □

***Problem 3.83.** Time of response to emails

When you receive an email, how long does it take for you to respond to it? If you keep a record of your received and sent mail, you can analyze the distribution of your response times – the number of hours between receiving an email from someone and replying to it.

It turns out that the time it takes people to reply to emails can be described by a power law; that is, the probability $p(\tau)d\tau$ that the response is between τ and $\tau + d\tau$ is $p(\tau) \sim \tau^{-a}$ with $a \approx 1$. Oliveira and Barabási have shown that the response times of Einstein and Darwin to letters can also be described by a power law, but with an exponent $a \approx 3/2$.[16] This result suggests that there is a universal pattern for human behavior in response to correspondence. What is the implication of a power law response? □

Problem 3.84. Pick any card

Three cards are in a hat. One card is white on both sides, the second is white on one side and red on the other, and the third is red on both sides. The dealer shuffles the cards, takes one out and places it flat on the table. The side showing is red. The dealer now says, "Obviously this card is not the white-white card. It must be either the red-white card or the red-red card. I will bet even money that the other side is red." Is this bet fair? □

***Problem 3.85.** Societal response to rare events

(a) Estimate the probability that an asteroid will impact the Earth and cause major damage. Does it make sense for society to take steps now to guard itself against such an occurrence?

(b) The likelihood of the breakdown of the levees near New Orleans was well known before its occurrence on August 30, 2005. Discuss the various reasons why the decision was made not to strengthen the levees. Relevant issues include the ability of people to think about the

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[16] See Oliveira and Barabási (2005).

probability of rare events, and the large amount of money needed to strengthen the levees to withstand such an event. □

*__Problem 3.86.__ Science and society

Does capital punishment deter murder? Are vegetarians more likely to have daughters? Does it make sense to talk about a "hot hand" in basketball? Are the digits of π random? See `<chance.dartmouth.edu/chancewiki/>` and `<www.dartmouth.edu/~chance/>` to read about interesting issues involving probability and statistics. □

Suggestions for further reading

Vinay Ambegaokar, *Reasoning About Luck*, Cambridge University Press (1996). A book developed for a course for nonscience majors. An excellent introduction to statistical reasoning and its uses in physics.

Ralph Baierlein, *Atoms and Information Theory*, W. H. Freeman (1971). The author derives the Boltzmann distribution using arguments similar to those used to obtain (3.168).

Arieh Ben-Naim, *Entropy Demystified: The Second Law Reduced to Plain Common Sense*, World Scientific (2007).

Deborah J. Bennett, *Randomness*, Harvard University Press (1998).

Peter L. Bernstein, *Against the Gods: The Remarkable Story of Risk*, John Wiley & Sons (1996). The author is a successful investor and an excellent writer. The book includes an excellent summary of the history of probability.

David S. Betts and Roy E. Turner, *Introductory Statistical Mechanics*, Addison-Wesley (1992). Section 3.4 is based in part on Chapter 3 of this text.

Jean-Phillippe Bouchaud and Marc Potters, *Theory of Financial Risks*, Cambridge University Press (2000). This book by two physicists is an example of the application of concepts in probability and statistical mechanics to finance. Although the treatment is at the graduate level and assumes some background in finance, the first several chapters are a good read for students who are interested in the overlap of physics, finance, and economics. Also see J. Doyne Farmer, Martin Shubik, and Eric Smith, "Is economics the next physical science?," Phys. Today **58** (9), 37–42 (2005). A related book on the importance of rare events is by Nassim Nicholas Taleb, *The Black Swan: The Impact of the Highly Improbable*, Random House (2007).

See `<www.compadre.org/stp/>` to download a simulation of the Galton board by Wolfgang Christian and Anne Cox. Other simulations related to statistical and thermal physics are also available at this site.

Giulio D'Agostini, "Teaching statistics in the physics curriculum: Unifying and clarifying role of subjective probability," Am. J. Phys. **67**, 1260–1268 (1999). The author, whose main research interest is in particle physics, discusses subjective probability and Bayes' theorem. Section 3.4 is based in part on this article.

F. N. David, *Games, Gods and Gambling: A History of Probability and Statistical Ideas*, Dover Publications (1998).

Marta C. González, César A. Hidalgo, and Albert-László Barabási, "Understanding individual human mobility patterns," Nature **453**, 779–782 (2008). The authors studied the trajectories of 100,000 cell phone users over a six-month period and found that human trajectories cannot be simply modeled by a Lévy flight or as an ordinary random walk. Similar studies have been done on animal trajectories. The website `<barabasilab.com/>` has many examples of the application of probability to diverse systems of interest in statistical physics.

James R. Huddle, "A note on Benford's law," Math. Comput. Educ. **31**, 66 (1997); T. P. Hill, "The first digit phenomenon," Am. Sci. **86**, 358–363 (1998).

Gene F. Mazenko, *Equilibrium Statistical Mechanics*, John Wiley & Sons (2000). Sections 1.7 and 1.8 of this graduate level text discuss the functional form of the missing information.

Leonard Mlodinow, *The Drunkard's Walk: How Randomness Rules Our Lives*, Vintage Press (2009). A popular book on how the mathematical laws of randomness affect our lives.

Elliott W. Montroll and Michael F. Shlesinger, "On the wonderful world of random walks," in *Studies in Statistical Mechanics*, Vol. XI: Nonequilibrium Phenomena II, edited by J. L. Lebowitz and E. W. Montroll North-Holland (1984). An excellent article on the history of random walks.

Elliott W. Montroll and Wade W. Badger, *Introduction to Quantitative Aspects of Social Phenomena*, Gordon and Breach (1974). The applications of probability that are discussed include traffic flow, income distributions, floods, and the stock market.

João Gama Oliveira and Albert-László Barabási, "Darwin and Einstein correspondence patterns," Nature **437**, 1251 (2005).

Richard Perline, "Zipf's law, the central limit theorem, and the random division of the unit interval," Phys. Rev. E **54**, 220–223 (1996).

The outcome of tossing a coin is not really random. See Ivars Peterson, "Heads or tails?," Science News Online, `<www.sciencenews.org/articles/20040228/mathtrek.asp>` and Erica Klarreich, "Toss out the toss-up: Bias in heads-or-tails," Science News **165** (9), 131 (2004), `<www.sciencenews.org/articles/20040228/fob2.asp>`. Some of the original publications include Joseph Ford, "How random is a coin toss?," Phys. Today **36** (4), 40–47 (1983); Joseph B. Keller, "The probability of heads," Am. Math. Monthly **93**, 191–197 (1986); and Vladimir Z. Vulovic and Richard E. Prange, "Randomness of a true coin toss," Phys. Rev. A **33**, 576–582 (1986).

S. Redner, "Random multiplicative processes: An elementary tutorial," Am. J. Phys. **58**, 267–273 (1990).

Jason Rosenhouse, *The Monty Hall Problem: The Remarkable Story of Math's Most Contentious Brain Teaser*, Oxford University Press (2009).

Charles Ruhla, *The Physics of Chance*, Oxford University Press (1992).

B. Schmittmann and R. K. P. Zia, "'Weather' records: Musings on cold days after a long hot Indian summer," Am. J. Phys. **67**, 1269–1276 (1999). A relatively simple introduction to the statistics of extreme values. Suppose that somebody breaks the record for the 100 m dash. How long do such records typically survive before they are broken?

Kyle Siegrist at the University of Alabama in Huntsville has developed many applets to illustrate concepts in probability and statistics. See `<www.math.uah.edu/stat/>` and follow the link to Bernoulli processes.

J. Torres, S. Fernández, A. Gamero, and A Sola, "How do numbers begin? (The first digit law)," Eur. J. Phys. **28**, L17–L25 (2007).

G. Troll and P. beim Graben, "Zipf's law is not a consequence of the central limit theorem," Phys. Rev. E **57**, 1347–1355 (1998).

Hans Christian von Baeyer, *Information: The New Language of Science*, Harvard University Press (2004). This book raises many profound issues. It is not an easy read even though it is well written.

Charles A. Whitney, *Random Processes in Physical Systems: An Introduction to Probability-Based Computer Simulations*, John Wiley & Sons (1990).

Michael M. Woolfson, *Everyday Probability and Statistics*, Imperial College Press (2008). An interesting book for lay people.

A discussion by Eliezer Yudkowsky of the intuitive basis of Bayesian reasoning can be found at `<yudkowsky.net/bayes/bayes.html>`.

R. K. P. Zia and B. Schmittmann, "Watching a drunkard for 10 nights: A study of distributions of variances," Am. J. Phys. **71**, 859–865 (2003). See Problem 3.70.

Chapter 4

The Methodology of Statistical Mechanics

8 October 2010

We develop the basic methodology of statistical mechanics and provide a microscopic foundation for the concepts of temperature and entropy.

4.1 Introduction

We now will apply the tools and concepts of thermodynamics and probability which we introduced in Chapters 2 and 3 to relate the microscopic and macroscopic descriptions of thermal systems. In so doing we will develop the formalism of *statistical mechanics*. To make explicit the probabilistic assumptions and the type of calculations that are done in statistical mechanics we first discuss an isolated system of noninteracting spins. The main ideas that we will need from Chapter 3 are the rules of probability, the calculation of averages, and the principle of least bias or maximum uncertainty.

Consider an isolated system of $N = 5$ noninteracting spins or magnetic dipoles with magnetic moment μ and spin 1/2 in a magnetic field B. Each spin can be parallel or antiparallel to the magnetic field. The energy of a spin parallel to the magnetic field is $\epsilon = -\mu B$, and the energy of a spin aligned opposite to the field is $\epsilon = +\mu B$. We will consider a specific case for which the total energy of the system is $E = -\mu B$. What is the mean magnetic moment of a given spin in this system? The essential steps needed to answer this question can be summarized as follows.

1. Specify the macrostate and accessible microstates of the system. The macroscopic state or *macrostate* of the system corresponds to the information that we know. In this example we know the total energy E and the number of spins N.

The most complete specification of the system corresponds to the enumeration of the *microstates* or *configurations* of the system. For $N = 5$ there are $2^5 = 32$ microstates specified by the

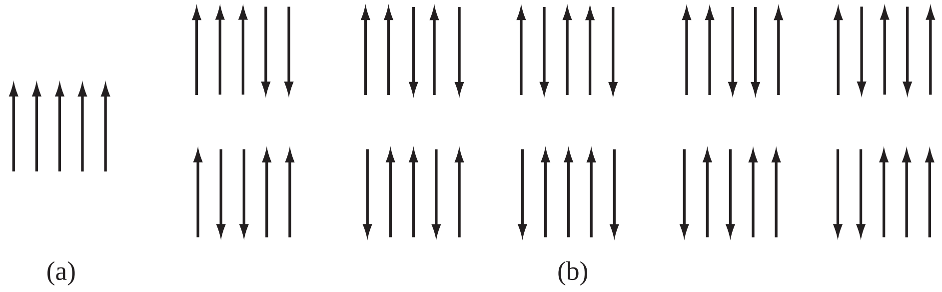

Figure 4.1: (a) Example of an inaccessible microstate corresponding to the macrostate specified by $E = -\mu B$ and $N = 5$. (b) The ten accessible microstates. Spin 1 is the leftmost spin.

orientation of each of the N spins. Not all of the 32 microstates are consistent with the information that $E = -\mu B$. For example, the microstate shown in Figure 4.1(a) is not allowed, that is, such a microstate is inaccessible, because its energy is $E = -5\mu B$. The *accessible* microstates of the system are those that are compatible with the macroscopic conditions. In this example ten of the thirty-two total microstates are accessible (see Figure 4.1(b)).

2. Choose the ensemble. We calculate averages by preparing a collection of identical systems all of which satisfy the macroscopic conditions $E = -\mu B$ and $N = 5$. In this example the ensemble consists of ten systems each of which is in one of the ten accessible microstates.

What can we say about the relative probability of finding the system in one of the ten accessible microstates? Because the system is isolated and each microstate is consistent with the specified macroscopic information, we assume that each microstate in the ensemble is equally likely. This assumption of *equal a priori probabilities* implies that the probability P_s that the system is in microstate s is given by

$$P_s = \frac{1}{\Omega}, \tag{4.1}$$

where Ω represents the number of microstates of energy E. This assumption is equivalent to the principle of least bias or maximum uncertainty that we discussed in Section 3.4.1. For our example we have $\Omega = 10$, and the probability that the system is in any one of its accessible microstates is 1/10. The macroscopic constraints, the microstates consistent with these constraints, and the relative probabilities of the microstates specify the ensemble. Here the constraints are the values of E and N, and the ten accessible microstates are given in Figure 4.1(b) with the probabilities in (4.1).

3. Calculate the mean values and other statistical properties. In this simple example we will calculate the mean value of the orientation of spin 1 [see Figure 4.1(b)]. Because s_1 assumes the value ±1, we have

$$\begin{aligned} \overline{s}_1 &= \sum_{i=1}^{10} P_i s_{1,i} && (4.2\text{a}) \\ &= \frac{1}{10}\big[6(+1) + 4(-1)\big] = \frac{2}{10} = \frac{1}{5}. && (4.2\text{b}) \end{aligned}$$

The sum is over all the accessible microstates and $s_{1,i}$ is the value of spin 1 in the ith member of the ensemble. We see from (4.2b) that the mean value of s_1 is $\overline{s}_1 = 1/5$. The corresponding mean magnetic moment of spin 1 is $\mu\overline{s}_1 = \mu/5$.

Problem 4.1. Simple example

(a) What is the mean value of spin 2 in the above example? Why is its mean value not zero?

(b) What is the probability p that a given spin points up?

(c) What is the probability that if spin 1 is up, then spin 2 also is up? □

There is a more direct way of calculating $\overline{s}_1$ in this case. Because the magnetization of the system is $M = \mu$, three out of the five spins are up. The equivalency of the spins implies that the probability of a spin being up is 3/5. Hence, $\overline{s} = (1)(3/5) + (-1)(2/5) = 1/5$. What is the implicit assumption that we made in the more direct method?

Problem 4.2. Counting microstates

(a) Consider $N = 4$ noninteracting spins with magnetic moment μ that can point either parallel or antiparallel to the magnetic field B. If the total energy $E = -2\mu B$, what are the accessible microstates and the probability that a particular spin is up or down?

(b) Consider $N = 9$ noninteracting spins with total energy $E = -\mu B$. What is the number of up spins, the number of accessible microstates, and the probability that a particular spin is up or down? □

Problem 4.3. Probability of particles moving in the same direction

Consider a one-dimensional ideal gas consisting of $N = 5$ particles each of which has the same speed v, but can move in one of two directions with equal probability. The velocity of each particle is independent. What is the probability that all the particles are moving in the same direction? □

The example that we have just considered is an example of an *isolated system*. In this case the system of spins has fixed values of E, B, and N. An isolated system cannot exchange energy or matter with its surroundings nor do work on another system. The macrostate of an isolated system of particles is specified by E, V, and N (B instead of V for a magnetic system). Isolated systems are conceptually simple because all the accessible microstates have the same probability. We will learn that isolated systems are described by the *microcanonical ensemble* (see Section 4.5).

4.2 A Simple Example of a Thermal Interaction

Now that we have an idea of how we can do probability calculations for an isolated system, we next consider some simple systems that can exchange energy with another system. We will see that for nonisolated systems, the probability of each microstate is not the same.

We know what happens when we place two bodies at different temperatures into thermal contact with one another – energy is transferred from the hotter to the colder body until thermal

microstate	red	white	blue
1	1	1	1
2	2	0	1
3	2	1	0
4	1	0	2
5	1	2	0
6	0	1	2
7	0	2	1
8	3	0	0
9	0	3	0
10	0	0	3

Table 4.1: The ten accessible microstates of a system of $N = 3$ distinguishable particles with total energy $E = 3$. Each particle may have energy 0, 1, 2, ….

equilibrium is reached and the two bodies have the same temperature. We now consider a simple model that illustrates how statistical concepts can help us understand the transfer of energy and the microscopic nature of thermal equilibrium.

Consider a system of N noninteracting distinguishable particles such that the energy of each particle is restricted to integer values, that is, $\epsilon_n = 0,\ 1,\ 2,\ 3,\ \ldots$ We can distinguish the particles by their colors, or we can assume that the particles have the same color, but are fixed on lattice sites. For reasons that we will discuss in Section 6.9, we will refer to this model system as an Einstein solid.[1]

Consider an Einstein solid with $N = 3$ particles (with colors red, white, and blue) in an isolated box and total energy $E = 3$. For these small values of N and E, we can enumerate the accessible microstates by hand. The ten accessible microstates of this system are shown in Table 4.1. Because the energy is specified, the ten accessible microstates are equally probable.

Problem 4.4. An Einstein solid

Consider an Einstein solid composed of N particles with total energy E. The general expression for the number of microstates of this system is

$$\Omega = \frac{(E + N - 1)!}{E!\,(N - 1)!}. \tag{4.3}$$

(a) Verify that (4.3) yields the correct answers for $N = 3$ and $E = 3$.

(b) What is the number of microstates for an Einstein solid with $N = 4$ and $E = 6$?

(c) Suppose that $N = 3$ and $E = 3$ and the particles are labeled red, white, and blue. What is the probability that the red particle has energy equal to one?

(d) Given that the red particle has energy 1, what is the probability that the blue particle has energy 2? □

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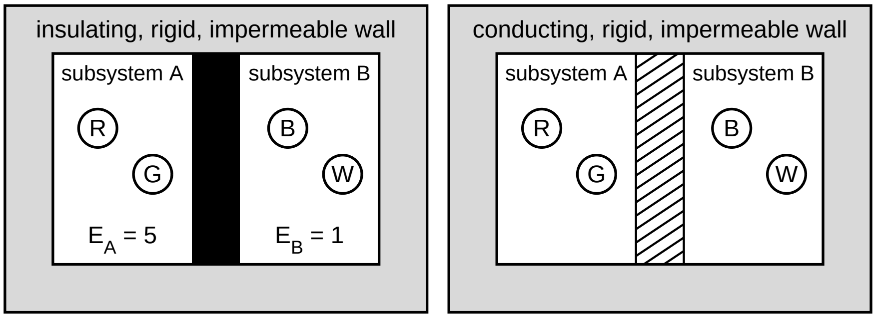
[1] These particles are equivalent to the quanta of the harmonic oscillator, which have energy $E_n = (n + 1/2)\hbar\omega$, where $\hbar = h/2\pi$, and h is Planck's constant. If we measure the energies from the lowest energy state, $\hbar\omega/2$, and choose units such that $\hbar\omega = 1$, we have $\epsilon_n = n$.



(a) (b)

Figure 4.2: An isolated composite system consisting of two subsystems, each with two distinguishable particles. In (a) the wall between the two subsystems is insulating, rigid, and impermeable. In (b) the wall is conducting, rigid, and impermeable. The total energy of the composite system is six.

Now that we know how to enumerate the number of microstates of an Einstein solid, consider an isolated system of $N = 4$ particles that is divided into two *subsystems*. A system consisting of two or more subsystems is called a *composite system*. In this case the latter is surrounded by insulating, rigid, impermeable outer walls so that its energy, volume, and number of particles is fixed. It also is initially separated by a similar partition (see Figure 4.2) so that there can be no change in the energy, number of particles, and the volume of each subsystem. Subsystem A consists of two particles, R (red) and G (green), with $E_A = 5$; subsystem B consists of two particles, B (black) and W (white), with energy $E_B = 1$. The total energy $E_{\rm tot}$ of the isolated composite system consisting of subsystem A plus subsystem B is

$$E_{\rm tot} = E_A + E_B = 5 + 1 = 6. \tag{4.4}$$

The accessible microstates for the isolated composite system are shown in Table 4.2. We see that subsystem A has $\Omega_A = 6$ accessible microstates and subsystem B has $\Omega_B = 2$ accessible microstates. The total number of microstates $\Omega_{\rm tot}$ accessible to the composite system is

$$\Omega_{\rm tot} = \Omega_A \times \Omega_B = 6 \times 2 = 12. \tag{4.5}$$

The partition is an internal constraint that prevents the transfer of energy from one subsystem to another and in this case keeps $E_A = 5$ and $E_B = 1$. (The internal constraint also keeps the volume and number of particles in each subsystem fixed.)

We now consider a simple example of a thermal interaction. Suppose that the insulating, rigid, impermeable partition separating subsystems A and B is changed to a conducting, rigid, impermeable partition (see Figure 4.2). The rigid partition maintains the volumes V_A and V_B, and hence the single-particle energies are not changed. Because the partition is impermeable, the particles cannot penetrate the partition and go from one subsystem to the other. However, energy can be transferred from one subsystem to the other, subject only to the constraint that the total energy of subsystems A and B is constant, that is, $E_{\rm tot} = E_A + E_B = 6$. The microstates of

E_A	accessible microstates of A		E_B	accessible microstates of subsystem B	
5	5,0	0,5	1	1,0	0, 1
	4,1	1,4			
	3,2	2,3			

Table 4.2: The 12 equally probable microstates of the isolated composite system composed of subsystems A and B with $N_A = 2$, $E_A = 5$, $N_B = 2$, and $E_B = 1$. The 12 microstates consist of all combinations of the microstates of A and B.

subsystems A and B are listed in Table 4.3 for all the possible values of E_A and E_B. The total number of microstates $\Omega_{\rm tot}(E_A, E_B)$ accessible to the isolated composite system whose subsystems have energy E_A and E_B is

$$\Omega_{\rm tot}(E_A, E_B) = \Omega_A(E_A)\Omega_B(E_B). \tag{4.6}$$

For example, if $E_A = 4$ and $E_B = 2$, then subsystem A can be in any one of five microstates and subsystem B can be in any of three microstates. These two sets of microstates of subsystems A and B can be combined to give $5 \times 3 = 15$ microstates of the composite system.

The total number of microstates $\Omega_{\rm tot}$ accessible to the composite system can be found by summing $\Omega_A(E_A)\Omega_B(E_B)$ over the possible values of E_A and E_B consistent with the condition that $E_A + E_B = 6$. Hence, $\Omega_{\rm tot}$ can be expressed as

$$\Omega_{\rm tot} = \sum_{E_A} \Omega_A(E_A)\Omega_B(E_{\rm tot} - E_A). \tag{4.7}$$

From Table 4.3 we see that

$$\Omega_{\rm tot} = (7 \times 1) + (6 \times 2) + (5 \times 3) + (4 \times 4) + (3 \times 5) + (2 \times 6) + (1 \times 7) = 84. \tag{4.8}$$

Because the composite system is isolated, its accessible microstates are equally probable, that is, the composite system is equally likely to be in any one of its 84 accessible microstates. Inspection of Table 4.3 shows that the probability that the energy of the composite system is divided such that $E_A = 2$ and $E_B = 4$ is 15/84. Let $P_A(E_A)$ be the probability that subsystem A has energy E_A. We see that $P_A(E_A)$ is given by

$$P_A(E_A) = \frac{\Omega_A(E_A)\Omega_B(E_{\rm tot} - E_A)}{\Omega_{\rm tot}}. \tag{4.9}$$

We show in Table 4.4 the various values of $P_A(E_A)$. Note that $P_A(E_A)$ has a maximum at a nonzero value of E_A. What do you think the form of $P_A(E_A)$ is for very large systems?

The mean energy of subsystem A is found by calculating the ensemble average over the 84 microstates accessible to the composite system. We use the results for $P_A(E_A)$ in Table 4.4 and find that

$$\overline{E}_A = \Big(0 \times \frac{7}{84}\Big) + \Big(1 \times \frac{12}{84}\Big) + \Big(2 \times \frac{15}{84}\Big) + \Big(3 \times \frac{16}{84}\Big) + \Big(4 \times \frac{15}{84}\Big) + \Big(5 \times \frac{12}{84}\Big) + \Big(6 \times \frac{7}{84}\Big) = 3. \tag{4.10}$$

E_A	microstates	$\Omega_A(E_A)$	E_B	microstates	$\Omega_B(E_B)$	$\Omega_A\Omega_B$	$P_A(E_A)$
6	6,0 0,6 5,1 1,5 4,2 2,4 3,3	7	0	0,0	1	7	7/84
5	5,0 0,5 4,1 1,4 3,2 2,3	6	1	1,0 0,1	2	12	12/84
4	4,0 0,4 3,1 1,3 2,2	5	2	2,0 0,2 1,1	3	15	15/84
3	3,0 0,3 2,1 1,2	4	3	3,0 0,3 2,1 1,2	4	16	16/84
2	2,0 0,2 1,1	3	4	4,0 0,4 3,1 1,3 2,2	5	15	15/84
1	1,0 0,1	2	5	5,0 0,5 4,1 1,4 3,2 2,3	6	12	12/84
0	0,0	1	6	6,0 0,6 5,1 1,5 4,2 2,4 3,3	7	7	7/84

Table 4.3: The 84 equally probable microstates accessible to the isolated composite system composed of subsystems A and B after the removal of the internal constraint. The total energy is $E_{\text{tot}} = E_A + E_B = 6$ with $N_A = 2$ and $N_B = 2$. Also shown are the number of accessible microstates in each subsystem and the probability $P_A(E_A)$ that subsystem A has energy E_A.

Problem 4.5. Standard deviation of the energy of subsystem A

Use the results of Table 4.4 to find the standard deviation of the energy of subsystem A. □

Note that the total number of microstates accessible to the isolated composite system increases from 12 to 84 when the internal constraint is removed. From the microscopic point of view, it is clear that the total number of microstates must either remain the same or increase when an internal constraint is removed. Because the number of microstates becomes a very large number for macroscopic systems, it is convenient to work with the logarithm of the number of microstates. We are thus led to define the quantity S by the relation

$$S = k \ln \Omega, \tag{4.11}$$

where k is an arbitrary constant. Note the similarity of the definition (4.11) to the expression for the missing information (3.35). We will later identify the quantity S that we have introduced in (4.11) with the thermodynamic entropy we discussed in Chapter 2.

Although our simple model has only four particles, we can ask questions that are relevant to much larger systems. For example, what is the probability that energy is transferred from one

E_A	$\Omega_A(E_A)$	$\Omega_B(6-E_A)$	$\Omega_A\Omega_B$	$P_A(E_A)$
6	7	1	7	7/84
5	6	2	12	12/84
4	5	3	15	15/84
3	4	4	16	16/84
2	3	5	15	15/84
1	2	6	12	12/84
0	1	7	7	7/84

Table 4.4: The probability $P_A(E_A)$ that subsystem A has energy E_A given that $N_A = N_B = 2$ and $E_{\rm tot} = E_A + E_B = 6$.

subsystem to the other? Given that $E_A = 5$ and $E_B = 1$ initially, we see from Table 4.4 that the probability of subsystem A gaining energy when the internal constraint is removed is 7/84. The probability that its energy remains unchanged is 12/84. In the remaining 65/84 cases, subsystem A loses energy and subsystem B gains energy. Because we know that energy spontaneously flows from a hotter body to a colder body, we can identify subsystem A as initially the hotter body and subsystem B as the cooler body. We will find that as the number of particles in the two subsystems becomes larger (and the energy per particle remains fixed), the probability that energy goes from the hotter to the colder subsystem rapidly increases.

Problem 4.6. Two Einstein solids in thermal contact

Consider two Einstein solids with $N_A = 4$ and $E_A = 10$ and $N_B = 4$ and $E_B = 2$. The two subsystems are thermally isolated from one another. Verify that the number of microstates accessible to subsystem A is 286 and the number of microstates accessible to subsystem B is 10. What is the initial number of accessible microstates for the composite system? Program `EinsteinSolids` determines the number of accessible microstates of an Einstein solid using (4.3) and will help you answer the following questions.

(a) The internal constraint is removed so that the two subsystems may exchange energy. Determine the probability $P_A(E_A)$ that system A has energy E_A. Plot P_A versus E_A and discuss its qualitative energy dependence.

(b) What is the probability that energy is transferred from system A to system B and from system B to system A? What is the probability that energy goes from the hotter to the colder system? How does this probability compare to the probability found from Table 4.3 for a smaller system? Which system was hotter initially?

(c) What is the number of accessible microstates for the composite system after the internal constraint has been relaxed? What is the change in the total entropy of the system (choose units such that $k = 1$)?

(d) Determine the mean energy $\overline{E}_A$, the most probable energy $\tilde{E}_A$, the standard deviations σ_A and σ_B, and the relative fluctuations $\sigma_A/\overline{E}_A$. How does the value of this ratio compare with the value of the ratio calculated in Table 4.3?

(e) The entropy of the composite system when each subsystem is in its most probable macrostate is $\ln\Omega_A(\tilde{E}_A)\Omega_B(E_{\rm tot}-\tilde{E}_A)$. Compare the value of this contribution to the value of the total entropy, $\sum_{E_A}\ln\Omega_A(E_A)\Omega_B(E_{\rm tot}-E_A)$, calculated in part (c)?

(f) *Consider successively larger systems and describe the qualitative behavior of the various quantities. ☐

From the examples and problems we have considered, we conclude that it is plausible to identify thermal equilibrium with the most probable macrostate and the entropy with the logarithm of the number of accessible microstates, We also found that the probability $P(E)$ that a system has energy E is approximately a Gaussian if it can exchange energy with another system. What quantity can we identify with the temperature?

Let's return to the exchange of energy between two simple subsystems and consider the energy dependence of the entropy of each subsystem. Consider an isolated composite system consisting of two subsystems with $N_A = 3$, $N_B = 4$, and total energy $E_{\rm tot} = 10$. The number of microstates for the two subsystems for the various possible values of E_A are summarized in Table 4.5. The most probable macrostate corresponds to $\tilde{E}_A = 4$ and $\tilde{E}_B = 6$. Because of our association of the most probable macrostate with thermal equilibrium, we know that the quantity that is the same for the two subsystems is the temperature. From our considerations in Section 2.13 we tentatively identify the inverse temperature with the derivative of the logarithm of the number of microstates of a system. In columns 5 and 10 of Table 4.5 we show the inverse slope of the entropy $S_A(E_A)$ and $S_B(E_B)$ of subsystems A and B calculated from the central difference approximation for the slopes at E_A and E_B, that is,

$$\frac{1}{T(E)} \approx \frac{[S(E+\Delta E) - S(E-\Delta E)]}{2\Delta E}. \tag{4.12}$$

(We have chosen units such that Boltzmann's constant $k = 1$.) We see from Table 4.5 that the inverse slopes of $S_A(E_A)$ and $S_B(E_B)$ are approximately equal at $E_A = \tilde{E}_A = 4$, corresponding to the value of the most probable energy. (For this small system the entropy of the composite system is not a continuous function of E_A, and thus we do not expect the slopes to be precisely equal.) We conclude that our tentative association of the temperature with the inverse slope of the entropy is plausible.

To obtain more insight into how temperature is related to the slope of the entropy, consider an energy away from equilibrium, say $E_A = 2$. Note that the slope 0.60 of $S_A(E_A = 2)$ in Table 4.5 is larger than the slope 0.30 of $S_B(E_B = 8)$. Hence, if energy is transferred from B to A, the entropy gained by A ($\Delta S = (\partial S/\partial E)\Delta E$) will be greater than the entropy lost by B, and the total entropy would increase as we expect. Because we know that energy is spontaneously transferred from "hot" to "cold," a larger slope must correspond to a lower temperature. This reasoning again suggests that the temperature is associated with the inverse slope of the energy dependence of the entropy.

Problem 4.7. More on two Einstein solids in thermal contact

Program `EntropyEinsteinSolid` computes the entropies of two Einstein solids in thermal contact.

(a) Explore the effect of increasing the values of N_A, N_B, and the total energy $E_{\rm tot}$. Discuss the qualitative dependence of S_A, S_B, and $S_{\rm tot}$ on the energy E_A. In particular, explain why S_A

E_A	$\Omega_A(E_A)$	$\ln\Omega_A(E_A)$	T_A^{-1}	T_A	E_B	$\Omega_B(E_B)$	$\ln\Omega_B(E_B)$	T_B^{-1}	T_B	$\Omega_A\Omega_B$
10	66	4.19	na	na	0	1	0	na	na	66
9	55	4.01	0.19	5.22	1	4	1.39	1.15	0.87	220
8	45	3.81	0.21	4.72	2	10	2.30	0.80	1.24	450
7	36	3.58	0.24	4.20	3	20	3.00	0.63	1.60	720
6	28	3.33	0.27	3.71	4	35	3.56	0.51	1.94	980
5	21	3.05	0.31	3.20	5	56	4.03	0.44	2.28	1176
4	15	2.71	0.37	**2.70**	6	84	4.43	0.38	**2.60**	1260
3	10	2.30	0.46	2.18	7	120	4.79	0.34	2.96	1200
2	6	1.79	0.60	1.66	8	165	5.11	0.30	3.30	990
1	3	1.10	0.90	1.11	9	220	5.39	0.28	3.64	660
0	1	0	na	na	10	286	5.66	na	na	286

Table 4.5: The number of microstates of subsystems A and B for total energy $E_{\rm tot} = E_A + E_B = 10$ and $N_A = 3$ and $N_B = 4$. The number of states was determined using (4.3). There are a total of 8008 microstates. The most probable energy of subsystem A is $\tilde{E}_A = 4$ and the fraction of microstates associated with the most probable macrostate is $1260/8008 \approx 0.157$. This fraction will approach one as the number of particles in the systems become larger.

is an increasing function of E_A and S_B is a decreasing function of E_A. Given this dependence of S_A and S_B on E_A, why does $S_{\rm tot}$ have a maximum at a particular value of E_A?

(b) The values of the magnitudes of the inverse slopes dS_A/dE_A and dS_B/dE_B can be obtained by clicking on the corresponding curves. The values of the magnitudes of the inverse slopes are given in the lower right corner. What is the relation of these slopes to the temperature? Determine the value of E_A at which the slopes are equal. What can you say about the total entropy at this value of E_A? Consider a number of different values for N_A, N_B and $E_{\rm tot}$. Be sure to include a case where $N_A \neq N_B$. ☐

We will formally develop the relations between the number of accessible microstates of an isolated system and various quantities including the entropy and the temperature in Section 4.5.

Boltzmann probability distribution. We next consider the Einstein solid in another physical context. Consider an isolated Einstein solid of six particles with total energy $E_{\rm tot} = 12$. We focus our attention on one of the particles and consider it as subsystem A; subsystem B consists of the other five particles. This example is similar to the ones we have considered, but in this case subsystem A consists of only one particle. The quantity of interest is the mean energy of subsystem A, and the probability P_n that the subsystem is in microstate n with energy ϵ_n. Note that for a system of one particle the symbol n refers to the quantum number of the particle and hence its energy. The number of ways that subsystem A can be in microstate n is one because it consists of only one particle. Thus, for this special subsystem of one particle, there is a one-to-one correspondence between the microstate of the system and the energy of the system.

The number of accessible microstates of the composite system is shown in Table 4.6 using the relation (4.3). The probability P_n that the subsystem is in microstate n is plotted in Figure 4.3. Note that P_n decreases monotonically with increasing energy. A visual inspection of the energy

microstate n	ϵ_n	$E_{\rm tot} - \epsilon_n$	Ω_B	$P_n(\epsilon_n)$
12	12	0	$4!/(0!\,4!) = 1$	0.00016
11	11	1	$5!/(1!\,4!) = 5$	0.00081
10	10	2	$6!/(2!\,4!) = 15$	0.00242
9	9	3	$7!/(3!\,4!) = 35$	0.00566
8	8	4	$8!/(4!\,4!) = 70$	0.01131
7	7	5	$9!/(5!\,4!) = 126$	0.02036
6	6	6	$10!/(6!\,4!) = 210$	0.03394
5	5	7	$11!/(7!\,4!) = 330$	0.05333
4	4	8	$12!/(8!\,4!) = 495$	0.07999
3	3	9	$13!/(9!\,4!) = 715$	0.11555
2	2	10	$14!/(10!\,4!) = 1001$	0.16176
1	1	11	$15!/(11!\,4!) = 1365$	0.22059
0	0	12	$16!/(12!\,4!) = 1820$	0.29412

Table 4.6: The number of microstates accessible to subsystem A consisting of one particle. Subsystem A is in microstate n with energy $\epsilon_n = n$ and can exchange energy with subsystem B consisting of five particles. The third column is the energy of subsystem B. The total energy of the composite system is $E_{\rm tot} = 12$. The total number of microstates is 6188, and thus $P_n = (1 \times \Omega_B)/6188$.

dependence of P_n in Figure 4.3 indicates that P_n can be approximated by an exponential,

$$P_n \propto e^{-\beta\epsilon_n}, \tag{4.13}$$

where $\epsilon_n = n$ in this example. The plot of $\ln P_n$ versus ϵ_n deviates from an exponential because there is a significant probability that the subsystem has a finite fraction of the total energy for this small composite system. If the number of particles in the composite system is sufficiently large so that the probability of the subsystem having a significant fraction of the total energy is negligible, then the exponential behavior of P_n becomes very well defined. These results are generalized in Section 4.6 where it is shown that the exponential decrease of the probability P_n holds exactly for a system that can exchange energy with a much larger system and that the parameter β is proportional to the inverse temperature of the much larger system. The exponential form of P_n in (4.13) is called the Boltzmann distribution.

Note that the probability P_n is usually not the same as $P(E)$. In (4.13) they are the same because there is only one particle in the subsystem, and thus there is only one way for the subsystem to have energy ϵ_n. If the subsystem has more than one particle, then there are many ways for the particles in the subsystem to share the energy (see Table 4.5). Here $P(E)$ for subsystem A is given by the probability of the subsystem being in a particular microstate with energy E multiplied by the number of microstates $\Omega_A(E)$ with the same energy E. The probability $P(E)$ is proportional to the last column in Table 4.5 and approaches a Gaussian distribution in the limit of a large number of oscillators.

Problem 4.8. More on Einstein solids

Use Program `EinsteinSolids` to count the number of microstates for two Einstein solids that can exchange energy with one another. In this problem we wish to determine the probability $P_A(E_A)$

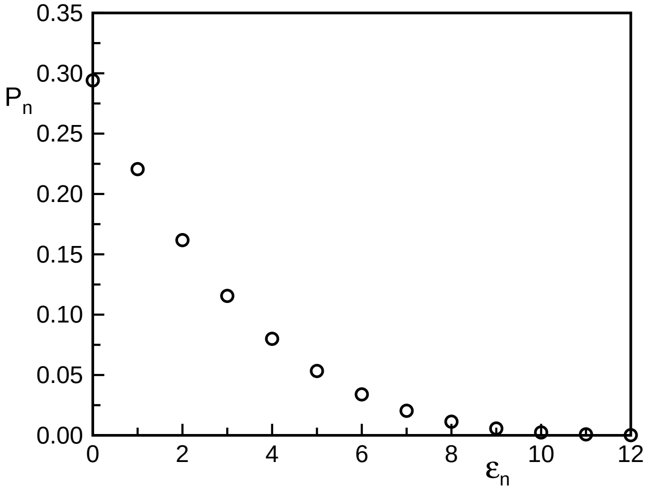


Figure 4.3: The probability P_n for the subsystem to be in microstate n with energy $\epsilon_n = n$. The subsystem can exchange energy with a system of $N = 5$ particles. The total energy of the composite system of six particles is $E_{\rm tot} = 12$. The circles are the values of P_n given in Table 4.6.

that subsystem A has energy E_A given that the total energy is $E = E_A + E_B$, and the total number of particles is N_A and N_B. The initial distribution of the energy in the program is not relevant for this problem.

(a) Choose $E = 200$ and $N_A = N_B = 4$ and estimate the width of $P_A(E_A)$. [Estimate the width at half the maximum value of $P_A(E_A)$.] Repeat for $N_A = N_B = 16$ and $N_A = N_B = 64$. How does the width depend on the number of particles? For example, does the width decrease linearly or by some other power of the number of particles?

(b) Repeat part (a) but with $E = 20$. Do you obtain the same dependence of the width on the number of particles. If not, why not?

(c) Consider $E = 200$, $N_A = 1$, and $N_B = 15$. What is the nature of $P_A(E_A)$? Explain why the curve is a decreasing function of E_A. ☐

Problem 4.9. Qualitative behavior of the probabilities

(a) In Table 4.3 we considered a composite Einstein solid of four particles with two particles in each subsystem. Use the results of Table 4.3 to calculate the probability that subsystem A is in a particular microstate.

Use `EinsteinSolids` Program to help answer the following questions.

(b) The program computes the probability $P_A(E_A)$ that subsystem A has energy E_A. Consider $N_A = 4$, $N_B = 12$ and $E_{\rm tot} = 3$. Run the program and collect the data from the `Data Table` under the `Views` menu.

(c) Determine the probability $P_s(E_s)$ that subsystem A is in a particular microstate by dividing $P_A(E_A)$ by the number of microstates with energy E_A. Plot $P_s(E_s)$.

(d) Explain why the probabilities P_s and $P_A(E_A)$ are not the same. Why is the probability $P_s(E_s)$ a monotonically decreasing function of E_s? What is the qualitative behavior of $P_A(E_A)$? □

Problem 4.10. Rapid increase in the number of states

(a) Consider an Einstein solid of $N = 20$ distinguishable particles. What is the total number of accessible microstates $\Omega(E)$ for $E = 10, 10^2, 10^3, \ldots$? Is $\Omega(E)$ a rapidly increasing function of E for fixed N?

(b) Is Ω a rapidly increasing function of N for fixed E? □

4.3 Counting Microstates

In the examples we have considered so far, we have seen that the most time-consuming task is enumerating (counting) the number of accessible microstates for a system of fixed energy and number of particles. We now discuss how to count the number of accessible microstates for several other systems of interest.

4.3.1 Noninteracting spins

We first reconsider an isolated system of N noninteracting spins with spin 1/2 and magnetic moment μ in an external magnetic field B. Because we can distinguish spins at different lattice sites, a particular microstate or configuration of the system is specified by giving the orientation (up or down) of each of the N spins. We want to find the total number of accessible microstates $\Omega(E, B, N)$ for particular values of E, B, and N.

We know that if n spins are parallel to B and $N - n$ spins are antiparallel to B, the energy of the system is

$$E = n(-\mu B) + (N - n)(\mu B) = -(2n - N)\mu B. \tag{4.14}$$

For a given N and B, n specifies the energy and vice versa. If we solve (4.14) for n, we find

$$n = \frac{N}{2} - \frac{E}{2\mu B}. \tag{4.15}$$

As we found in (3.86), the total number of microstates with energy E is given by the number of ways n spins out of N can be up. This number is given by

$$\Omega(n, N) = \frac{N!}{n!\,(N - n)!}, \tag{4.16}$$

where n is related to E by (4.15). We will apply this result in Example 4.1 on page 197.

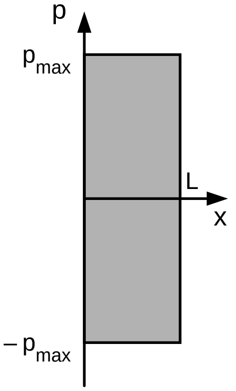


Figure 4.4: The phase space of a single particle of mass m with energy less than or equal to E in a one-dimensional box of length L. The maximum value of the momentum is $p_{\rm max} = \sqrt{2mE}$. Any point within the shaded rectangle corresponds to a microstate with energy less than or equal to E.

4.3.2 A particle in a one-dimensional box

Classical calculation. Consider the microstates of a single classical particle of mass m confined to a one-dimensional box of length L. We know that the microstate of a particle is specified by its position x and momentum p.[2] We say that the microstate (x, p) is a point in *phase space* (see Figure 4.4).

Because the values of the position and momenta of a particle are continuous variables, the number of microstates of the system with energy E is not meaningful and instead we will determine the quantity $g(E)\Delta E$, the number of microstates between E and $E + \Delta E$; the quantity $g(E)$ is the *density of states*. However, it is easier to first calculate $\Gamma(E)$, the number of microstates of the system with energy less than or equal to E (see Table 4.7). The number of microstates between E and $E + \Delta E$, $g(E)\Delta E$, is related to $\Gamma(E)$ by

$$g(E)\Delta E = \Gamma(E + \Delta E) - \Gamma(E) \approx \frac{d\Gamma(E)}{dE}\,\Delta E. \tag{4.17}$$

If the energy of the particle is E and the dimension of the box is L, then the microstates of the particle with energy less than or equal to E are restricted to the rectangle shown in Figure 4.4, where $p_{\rm max} = \sqrt{2mE}$. Because the possible values of x and p are continuous, there are an infinite number of microstates within the rectangle. As we discussed in Section 3.6, we have to group or bin the microstates so that we can count them, and hence we divide the rectangle in Figure 4.4 into bins or cells of area $\Delta x \Delta p$.

The area of the phase space occupied by the trajectory of a particle whose position x is less than or equal to L and whose energy is less than or equal to E is equal to $2p_{\rm max}L$. Hence, the number of cells or microstates equals

$$\Gamma_{\rm cl}(E) = \frac{2p_{\rm max}L}{\Delta x \Delta p} = 2\frac{L}{\Delta x \Delta p}(2mE)^{1/2}. \tag{4.18}$$

---

[2] We could equally well specify the velocity v rather than p, but the momentum p is the appropriate conjugate variable to x in the Hamiltonian formulation of classical mechanics.

$\Omega(E)$	Number of microstates with energy E
$\Gamma(E)$	Number of microstates with energy less than or equal to E
$g(E)\Delta E$	Number of microstates between E and $E+\Delta E$
$g(E)$	Density of states

Table 4.7: Summary of the functions used to count microstates.

In classical physics there is no criterion for choosing the values of Δx and Δp. What is the corresponding density of states?

Quantum calculation. The most fundamental description of matter at the microscopic level is given by quantum mechanics. Although the quantum mechanical description is more abstract, we will find that it makes counting microstates more straightforward (in principle).

As before, we consider a single particle of mass m in a one-dimensional box of length L. According to de Broglie, a particle has wave properties associated with it, and the corresponding standing wave has a node at the boundaries of the box. The standing wave with one antinode can be represented as in Figure 4.5; the corresponding wavelength is given by

$$\lambda = 2L. \tag{4.19}$$

The greater the number of antinodes of the wave, the greater the energy associated with the particle. The possible wavelengths that are consistent with the boundary conditions at $x = 0$ and $x = L$ satisfy

$$\lambda_n = \frac{2L}{n} \qquad (n = 1, 2, 3, \ldots), \tag{4.20}$$

where the index n labels the quantum state of the particle and can be any nonzero, positive integer. From the de Broglie relation,

$$p = \frac{h}{\lambda}, \tag{4.21}$$

and the nonrelativistic relation between the energy E and the momentum p, $E = p^2/2m$, we find that the energy eigenvalues of a particle in a one-dimensional box are given by

$$E_n = \frac{p_n^2}{2m} = \frac{h^2}{2m\,\lambda_n^2} = \frac{n^2h^2}{8mL^2}. \tag{4.22}$$

It is straightforward to count the number of microstates with energy less than or equal to E by solving (4.22) for n:

$$n = \frac{2L}{h}(2mE)^{1/2}. \tag{4.23}$$

Because successive microstates correspond to values of n that differ by 1, the number of states with energy less than or equal to E is given by

$$\Gamma_{\rm qm}(E) = n = \frac{2L}{h}(2mE)^{1/2}. \tag{4.24}$$

Unlike the classical case, the number of states $\Gamma_{\rm qm}(E)$ for a quantum particle in a one-dimensional box has no arbitrary parameters such as Δx and Δp. If we require that the classical

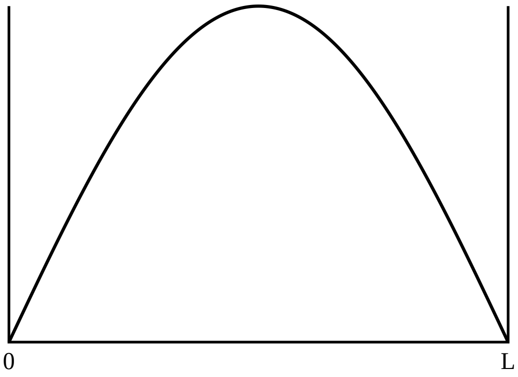


Figure 4.5: Representation of the minimum energy standing wave for a particle in a one-dimensional box. Note that the standing wave equals zero at $x = 0$ and $x = L$.

and quantum enumeration of microstates agree in the semiclassical limit,[3] we see that the number of microstates, $\Gamma_{\rm cl}(E)$ and $\Gamma_{\rm qm}(E)$, agrees for all E if we let $2/(\Delta x \Delta p) = 1/(\pi\hbar)$. This requirement implies that the area $\Delta x \Delta p$ of a cell in phase space is given by

$$\Delta x\, \Delta p = h. \tag{4.25}$$

We see that Planck's constant h can be interpreted as the minimum area of a cell in a two-dimensional phase space. That is, in order for the counting of microstates in a classical system to be consistent with the more fundamental counting of microstates in a quantum system, we cannot specify a microstate of the classical system more precisely than to assign it to a cell of area h in phase space. This fundamental limitation implies that the subdivision of phase space into cells of area less than h is physically meaningless, a result consistent with the Heisenberg uncertainty principle.

It will be convenient to introduce the wave number k by the relation $k = 2\pi/\lambda$. Then we can rewrite the de Broglie relation (4.21) as

$$p = \hbar k. \tag{4.26}$$

For a particle in a one-dimensional box, we can express the condition (4.20) for a standing wave as

$$k = \frac{\pi}{L} n \qquad (n = 1, 2, 3, \ldots). \tag{4.27}$$

Problem 4.11. Suppose that the energy of an electron in a one-dimensional box of length L is $E = 144\,(h^2/8mL^2)$. How many microstates are there with energy less than or equal to this value of E? □

4.3.3 One-dimensional harmonic oscillator

The one-dimensional harmonic oscillator provides another example for which we can straightforwardly count the number of microstates in both the classical and quantum cases. The total energy

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[3] Note that the semiclassical limit is not equivalent to simply letting $\hbar \to 0$.

of the harmonic oscillator is given by

$$E = \frac{p^2}{2m} + \frac{1}{2}\kappa x^2, \tag{4.28}$$

where κ is the spring constant and m is the mass of the particle.

Classical calculation. The part of phase space traversed by the trajectory $x(t), p(t)$ can be determined from (4.28) by dividing both sides by E and substituting $\omega^2 = \kappa/m$:

$$\frac{x(t)^2}{2E/m\omega^2} + \frac{p(t)^2}{2mE} = 1, \tag{4.29}$$

where the total energy E is a constant of the motion. From the form of (4.29) we see that the shape of phase space of a one-dimensional harmonic oscillator is an ellipse,

$$\frac{x^2}{a^2} + \frac{p^2}{b^2} = 1, \tag{4.30}$$

with $a^2 = 2E/(m\omega^2)$ and $b^2 = 2mE$. Hence, the area of phase space with energy less than or equal to E is $\pi ab = 2\pi E/\omega$, and the number of states in this region is

$$\Gamma_{\rm cl}(E) = \frac{\pi ab}{\Delta x\,\Delta p} = \frac{2\pi E}{\omega\,\Delta x\,\Delta p}. \tag{4.31}$$

Quantum calculation. The energy eigenvalues of the harmonic oscillator are given by

$$E_n = \Big(n + \frac{1}{2}\Big)\hbar\omega \qquad (n = 0,\ 1,\ 2,\ \ldots). \tag{4.32}$$

Because n changes by 1, the number of microstates is given by

$$\Gamma_{\rm qm}(E) = n = \frac{E}{\hbar\omega} - \frac{1}{2} \to \frac{E}{\hbar\omega}. \tag{4.33}$$

The constant 1/2 can be neglected in the limit $E \gg \hbar\omega$. We see that $\Gamma_{\rm qm}(E) = \Gamma_{\rm cl}(E)$ for all E, if $2\pi/(\Delta x\,\Delta p) = \hbar$ or $\Delta x\,\Delta p = h$ as before.

4.3.4 One particle in a two-dimensional box

Consider a single particle of mass m in a rectangular box of sides L_x and L_y. The energy of the particle is given by

$$E = \frac{1}{2m}({p_x}^2 + {p_y}^2). \tag{4.34}$$

In two dimensions the wave number becomes a wave vector **k**, which satisfies the one-dimensional condition in each direction [see (4.27)],

$$k_x = \frac{\pi}{L_x} n_x, \qquad k_y = \frac{\pi}{L_y} n_y \qquad (n_x, n_y = 1, 2, 3, \ldots). \tag{4.35}$$

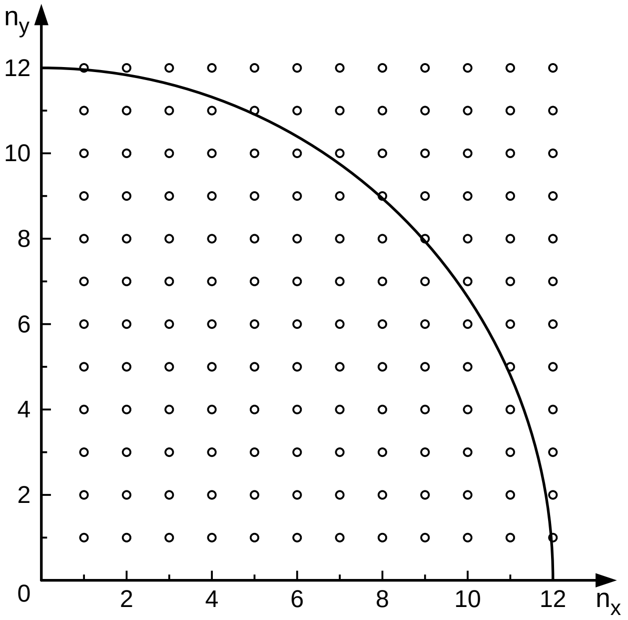

Figure 4.6: The points represent possible values of n_x and n_y. Note that n_x and n_y are integers with $n_x, n_y \geq 1$. Each point represents a single-particle microstate. What is the total number of states for $R \leq 12$? The corresponding number from the asymptotic relation is $\Gamma(E) = \pi\, 12^2/4 \approx 113$.

The corresponding eigenvalues are given by

$$E_{n_x,n_y} = \frac{h^2}{8m}\left[\frac{{n_x}^2}{{L_x}^2} + \frac{{n_y}^2}{{L_y}^2}\right]. \tag{4.36}$$

The states of the particle are labeled by the two integers n_x and n_y with $n_x, n_y \geq 1$. The area associated with each single-particle state in the space defined by the points (n_x, n_y) is 1, as can be seen in Figure 4.6. For simplicity, we assume that $L_x = L_y \equiv L$. The values of (n_x, n_y) for a given E satisfy the condition

$$R^2 = {n_x}^2 + {n_y}^2 = \Big(\frac{2L}{h}\Big)^2 (2mE). \tag{4.37}$$

For large values of n_x and n_y the values of n_x and n_y that correspond to states with energy less than or equal to E lie inside the positive quadrant of a circle of radius R, where

$$R = \frac{2L}{h}(2mE)^{1/2}. \tag{4.38}$$

Hence, the number of states with energy less than or equal to E is given by

$$\Gamma(E) = \frac{1}{4}\pi R^2 = \pi\frac{L^2}{h^2}(2mE). \tag{4.39}$$

Note that $V = L^2$ in this case.

Problem 4.12. Finite-size effects in two dimensions

The expression (4.39) for $\Gamma(E)$ is valid only for large E because the area of a quadrant of a circle overestimates the number of lattice points n_x, n_y inside a circle of radius R. Use Program `IdealGasNumberOfStates` to explore how the relation $\Gamma = \pi R^2/4$ approximates the actual number of microstates. The program computes the number of nonzero, positive integers that satisfy the condition $n_x^2 + n_y^2 \leq R^2$. What is the minimum value of R for which the difference between the asymptotic relation and the exact number is less than 1%? □

4.3.5 One particle in a three-dimensional box

The generalization to three dimensions is straightforward. If we assume that the box is a cube with linear dimension L, we have

$$E = \frac{h^2}{8mL^2}[n_x^2 + n_y^2 + n_z^2]. \tag{4.40}$$

The values of n_x, n_y, and n_z that correspond to microstates with energy less than or equal to E lie inside the positive octant of a sphere of radius R given by

$$R^2 = n_x^2 + n_y^2 + n_z^2 = \Big(\frac{2L}{h}\Big)^2 (2mE). \tag{4.41}$$

Hence

$$\Gamma(E) = \frac{1}{8}\Big(\frac{4}{3}\pi R^3\Big) = \frac{\pi}{6}\Big(\frac{2L}{h}\Big)^3 (2mE)^{3/2} = \frac{4\pi}{3}\frac{V}{h^3}(2mE)^{3/2}, \tag{4.42}$$

where we have let $V = L^3$.

Problem 4.13. Finite-size effects in three dimensions

The expression (4.42) for $\Gamma(E)$ is valid only for large E because the area of an octant of a sphere overestimates the number of lattice points n_x, n_y, n_z. Use Program `IdealGasNumberOfStates` to determine how the relation $\Gamma = \pi R^3/6$ approximates the total number of microstates, as in Problem 4.12. □

Problem 4.14. Estimation of the number of states

Estimate the number of microstates accessible to a gas molecule in a one liter box at room temperature. The mean energy E of a gas molecule such as nitrogen at room temperature can be found from the relation $E = 3kT/2$. Consider an energy interval $\Delta E = 10^{-27}\,$J that is much smaller than E, and calculate the number of microstates $g(E)\Delta E$ accessible to the molecule in the interval between E and $E + \Delta E$. Refer to (4.42) and (4.17). □

4.3.6 Two noninteracting identical particles and the semiclassical limit

Consider two noninteracting particles of mass m of the same species in a one-dimensional box of length L. The total energy is given by

$$E_{n_1,n_2} = \frac{h^2}{8mL^2}\big(n_1^2 + n_2^2\big), \tag{4.43}$$

distinguishable particles		Bose statistics		Fermi statistics	
n_1	n_2	n_1	n_2	n_1	n_2
1	1	1	1		
2	1	2	1	2	1
1	2				
2	2	2	2		
3	1	3	1	3	1
1	3				
3	2	3	2	3	2
2	3				
3	3	3	3		
4	1	4	1	4	1
1	4				
4	2	4	2	4	2
2	4				
4	3	4	3	4	3
3	4				
4	4	4	4		

Table 4.8: The microstates of two identical noninteracting particles of mass m in a one-dimensional box such that each particle can be in one of the four lowest energy states. The rows are ordered by their total energy. If the particles obey Fermi statistics, they cannot be in the same microstate, so $n_1 = 1$, $n_2 = 1$ is not allowed. There is no such restriction for Bose statistics. Because the particles are identical and hence indistinguishable, $n_1 = 1$, $n_2 = 2$ and $n_1 = 2$, $n_2 = 1$ are the same microstate.

where the quantum numbers n_1 and n_2 are positive nonzero integers. To count the microstates correctly, we need to take into account that particles of the same species are *indistinguishable*, one of the fundamental principles of quantum mechanics.

As an example of how to count the microstates of this two-particle system, suppose that each particle can be in one of the four lowest single-particle energy states. The values of n_1 and n_2 that satisfy this constraint are given in Table 4.8. The indistinguishability of the particles means that we cannot assign the quantum numbers n_1 independently of the value of n_2. For example, because the state $(n_1 = 1, n_2 = 2)$ is indistinguishable from the state $(n_1 = 2, n_2 = 1)$, we can include only one of these states.

The assignment of quantum numbers is further complicated by the fact that the particles must obey quantum statistics. We will discuss the nature of quantum statistics in Section 6.3. In brief, particles must obey either Bose or Fermi statistics. If the particles obey Bose statistics, then any number of particles may be in the same single-particle quantum state. In contrast, if the particles obey Fermi statistics, then two particles may not be in the same single-particle quantum state, and hence the states $(n_1, n_2) = (1, 1)$, (2, 2), (3,3), and (4,4) are excluded.

Because the particles are indistinguishable, there are fewer microstates than if the particles were distinguishable, and we might think that enumerating the accessible microstates is easier. However, it is much more difficult because we cannot enumerate the states for each particle individually even though the particles do not interact. For example, if $n_1 = 1$, then $n_2 \neq 1$ for Fermi statistics. However, the counting of microstates can be simplified in the *semiclassical limit*. In this limit the number of single-particle states is much greater than the number of particles. (Obviously, that is not the case in our simple example where each particle is limited to four states.) In the semiclassical limit we do not care if two particles are put in the same single-particle state because there will be many more states where this counting error (for fermions) does not occur. Hence we can assign states to one particle separately without regard to the state of the other particle.

In our example there is a maximum of $4 \times 4 = 16$ possible states because particles 1 and 2 can each be in one of four states. Because the particles are indistinguishable and a state such as $n_1 = 3$, $n_2 = 4$ cannot be distinguished from $n_1 = 4$, $n_2 = 3$, we divide by 2! to approximately correct for overcounting. This correction gives $(4 \times 4)/2! = 8$ states. The actual number for Bose statistics is 10 and Fermi statistics is 6. Dividing by 2! is not a good approximation for such a small system. However, if the number of possible states Γ for each particle is much greater than the number of particles N, then dividing by $N!$ is a very good approximation. To understand the nature of this approximation lets consider the equivalent problem of the number of ways of putting N identical balls into Γ boxes. This number is given by

$$\frac{(N + \Gamma - 1)!}{N!(\Gamma - 1)!}. \tag{4.44}$$

Equation (4.44) is the same expression we used for counting the number of identical quanta of energy that can be distributed among distinct oscillators in the Einstein model. Note that (4.44) counts all the ways of placing the balls into boxes, including putting more than one ball into a box. You can test (4.44) by working out a simple example. In (4.44) the last $\Gamma - 1$ factors in the numerator are canceled by $(\Gamma - 1)!$ in the denominator, and we are left with N more factors, each of which are approximately equal to Γ if $\Gamma \gg N$. Thus, to convert the number of ways of assigning N distinguishable particles (Γ^N) to the number of ways of assigning N indistinguishable particles, we need to divide Γ^N by $N!$. Another way of obtaining this result is to assume that N of the boxes have been filled with one ball each. There is only way to do so if the balls are identical. If the balls are distinguishable, there are N different balls that can occupy box 1, which leaves $N - 1$ different balls that can occupy box 2, $N - 2$ balls that can occupy box 3, and so on, which leads to the factor of $N!$. Because $\Gamma \gg N$, the probability of multiple occupancy of any state is negligible and, thus there is no distinction between Bose and Fermi systems in the semiclassical limit.

4.4 The Number of States of Many Noninteracting Particles: Semiclassical Limit

We now apply these considerations to determine the number of microstates of an ideal classical gas of N particles in a three-dimensional box in the semiclassical limit. (A simpler way to do so that yields the correct E and V dependence is given in Problem 4.15, but the numerical factors are not identical to the result of the more accurate calculation that we discuss here.)

The idea is to first count the microstates assuming that the N particles are distinguishable and then divide by $N!$ to correct for overcounting. We know that for one particle in a three-dimensional box the number of microstates with energy less than or equal to E is given by the volume of the positive part (or octant) of the three-dimensional sphere of radius $R = (2L/h)(2mE)^{1/2}$ [see (4.38)]. For N distinguishable particles in a three-dimensional box, the number of microstates with energy less than or equal to E is given by the volume of the positive part of a $3N$-dimensional hypersphere of radius $R = (2L/h)(2mE)^{1/2}$. In Section 4.14.1 we write the volume $V_n(R)$ of an n-dimensional hypersphere of radius R as

$$V_n(R) = \int_{x_1^2+x_2^2+\cdots+x_n^2<R^2} dx_1\, dx_2\, \cdots dx_n, \tag{4.45}$$

where x_i is the position coordinate in the ith direction. For example, in three dimensions (x_1, x_2, x_3) represents the usual coordinates (x, y, z). The volume $V_n(R)$ is given by (see Section 4.14.1)

$$V_n(R) = \frac{2\pi^{n/2}}{n\Gamma(n/2)} R^n \qquad \text{(integer } n\text{)}, \tag{4.46}$$

where the Gamma function satisfies the relations $\Gamma(n+1) = n\Gamma(n)$, $\Gamma(1/2) = \sqrt{\pi}$. For integer n, $\Gamma(n) = (n-1)!$, and the Gamma function can be interpreted as a generalization of the factorial. The cases $n = 2$ and $n = 3$ yield the expected results, $V_2 = 2\pi R^2/(2\Gamma(1)) = \pi R^2$ because $\Gamma(1) = 1$, and $V_3 = 2\pi^{3/2}R^3/(3\Gamma(3/2)) = 4\pi R^3/3$ because $\Gamma(3/2) = \Gamma(1/2)/2 = \sqrt{\pi}/2$. The volume of the positive part of the n-dimensional sphere of radius R is given by[4]

$$\Gamma_n(R) = \Big(\frac{1}{2}\Big)^n V_n(R). \tag{4.47}$$

We are interested in the case $n = 3N$ and $R = (2mE)^{1/2}(2L/h)$. In this case the volume $\Gamma(E, V, N)$ is given by

$$\begin{aligned}
\Gamma(E,V,N) &= \Big(\frac{1}{2}\Big)^{3N} \frac{2\pi^{3N/2}}{3N(3N/2-1)!} R^{3N} && \text{(4.48a)}\\
&= \Big(\frac{1}{2}\Big)^{3N} \frac{\pi^{3N/2}}{(3N/2)!} R^{3N} && \text{(4.48b)}\\
&= \Big(\frac{1}{2}\Big)^{3N} \Big(\frac{2L}{h}\Big)^{3N} \frac{\pi^{3N/2}}{(3N/2)!} (2mE)^{3N/2} && \text{(4.48c)}\\
&= \Big(\frac{V}{h^3}\Big)^{N} \frac{(2\pi mE)^{3N/2}}{(3N/2)!}. && \text{(4.48d)}
\end{aligned}$$

If we include the factor of $1/N!$ to correct for the overcounting of microstates in the semiclassical limit, we obtain the desired result:

$$\Gamma(E,V,N) = \frac{1}{N!}\Big(\frac{V}{h^3}\Big)^{N} \frac{(2\pi mE)^{3N/2}}{(3N/2)!} \qquad \text{(semiclassical limit)}. \tag{4.49}$$

$\Gamma(E, V, N)$ is the number of states of N noninteracting particles in a three-dimensional box of volume V in the semiclassical limit.

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[4] The volume $\Gamma_n(R)$ should not be confused with the Gamma function $\Gamma(n)$.

A more convenient expression for $\Gamma(E,V,N)$ can be found by using Stirling's approximation (3.101) for $N \gg 1$. We have

$$\begin{aligned}
\ln\Gamma(E,V,N) &= -\ln N! + N\ln\frac{V}{h^3} + \frac{3}{2}N\ln(2\pi mE) - \ln\Big(\frac{3N}{2}\Big)! && \text{(4.50a)}\\
&\approx -N\ln N + N + N\ln V - \frac{3N}{2}\ln h^2 + \frac{3}{2}N\ln(2\pi mE) - \frac{3}{2}N\ln\frac{3N}{2} + \frac{3N}{2} && \text{(4.50b)}\\
&= N\ln\frac{V}{N} + \frac{3}{2}N\ln\frac{4\pi mE}{3Nh^2} + \frac{5}{2}N. && \text{(4.50c)}
\end{aligned}$$

It is frequently convenient to write $\ln\Gamma(E,V,N)$ in terms of $\hbar$ instead of h:

$$\ln\Gamma(E,V,N) = N\ln\frac{V}{N} + \frac{3}{2}N\ln\frac{mE}{3N\pi\hbar^2} + \frac{5}{2}N. \tag{4.51}$$

Problem 4.15. Approximate expression for $\Gamma(E,V,N)$

We can obtain an approximate expression for $\Gamma(E,V,N)$ using simpler physical considerations. We write

$$\Gamma(E,V,N) \approx \frac{1}{N!}\Gamma_1\Big(\frac{E}{N},V\Big)\Gamma_1\Big(\frac{E}{N},V\Big)\cdots\Gamma_1\Big(\frac{E}{N},V\Big) = \frac{1}{N!}\Gamma_1\Big(\frac{E}{N},V\Big)^N, \tag{4.52}$$

where $\Gamma_1(E,V)$ is the number of states of a single particle with energy less than E in a three-dimensional box of volume V. We have assumed that on the average each particle has an energy E/N. Find the form of $\Gamma(E,V,N)$ using the relation (4.42) for Γ_1. How does the dependence on V and E of $\Gamma(E,V,N)$ obtained from this simple argument compare to the V and E dependence of Γ in (4.49). What about the N dependence? □

Problem 4.16. Density of states of an ideal gas

Use (4.51) to calculate the density of states $g(E,V,N)$ and verify that $\Gamma(E,V,N)$ and $g(E,V,N)$ are rapidly increasing functions of E, V, and N. □

4.5 The Microcanonical Ensemble (Fixed E, V, and N)

The macrostate of an isolated system of particles is specified by the energy E, volume V, and number of particles N of the system. All the microstates that are consistent with these conditions are assumed to be equally probable. The collection of systems in the different microstates with the specified values of E, V, and N is called the *microcanonical ensemble*. More precisely, because the energy E is a continuous variable, the energy is specified to be in the range E to $E + \Delta E$, where $\Delta E \ll E$.

In the following we show how the quantities that correspond to the usual thermodynamic quantities, for example, the entropy, temperature, and pressure, are related to the number of microstates. (It might be helpful to review the sections in Chapter 2 on the definitions of the various thermodynamic derivatives and free energies.) We will then use these relations to derive the ideal classical gas equation of state and other well known results using (4.51) for the number of microstates of an ideal gas of N particles in a volume V with energy less than or equal to E in the semiclassical limit.

We first establish the connection between the number of accessible microstates to various thermodynamic quantities by using arguments that are similar to our treatment of the simple models that we considered in Section 4.2. Consider two isolated systems A and B that are separated by an insulating, rigid, and impermeable wall. The macrostate of each system is specified by E_A, V_A, N_A and E_B, V_B, N_B, respectively, and the corresponding number of microstates is $\Omega_A(E_A, V_A, N_A)$ and $\Omega_B(E_B, V_B, N_B)$. Equilibrium in this context means that each accessible microstate is equally represented in the ensemble. The number of microstates of the composite system consisting of the two isolated subsystems A and B is

$$\Omega = \Omega_A(E_A, V_A, N_A)\,\Omega_B(E_B, V_B, N_B). \tag{4.53}$$

We want a definition of the entropy that is a measure of the number of microstates and that is additive for independent systems. We will assume that S is related to Ω by[5]

$$\boxed{S = k \ln \Omega}. \tag{4.54}$$

If we substitute (4.53) in (4.54), we find that $S = S_A + S_B$, and S is an additive function.

Next we modify the wall between A and B so that the wall becomes conducting, but remains rigid and impermeable. We say that we have relaxed the internal constraint of the composite system. The two subsystems are now in thermal contact so that the energies E_A and E_B can vary, subject to the condition that the total energy $E = E_A + E_B$ is fixed; the volumes V_A and V_B and particle numbers N_A and N_B remain unchanged. What happens to the number of accessible microstates after we relax the internal constraint? If subsystem A has energy E_A, it can be in any one of its $\Omega_A(E_A)$ microstates. Similarly, subsystem B can be in any one of its $\Omega_B(E - E_A)$ microstates. Because every possible microstate of A can be combined with every possible microstate of B to give a different microstate of the composite system, it follows that the number of microstates accessible to the composite system when A has energy E_A is the product $\Omega_A(E_A)\Omega_B(E - E_A)$. Hence, the total number of accessible microstates of the composite system is

$$\Omega(E) = \sum_{E_A} \Omega_A(E_A)\Omega_B(E - E_A). \tag{4.55}$$

The probability that system A has energy E_A is given by

$$P_A(E_A) = \frac{\Omega_A(E_A)\Omega_B(E - E_A)}{\Omega(E)}. \tag{4.56}$$

Note that we have implicitly assumed that the interaction between the two systems is weak so that the microstates of each system are unchanged. Because the two systems interact only at the boundary between them, the fraction of particles at the boundary goes to zero in the thermodynamic limit $N, V \to \infty, \rho = N/V =$ constant. That is, the number of particles at the boundary is proportional to the surface area L^2, and the number of particles in the bulk is proportional to the volume $V = L^3$, where L is the linear dimension of the system.

The logarithm of (4.55) does not yield a sum of two functions. However, the dominant contribution to the right-hand side of (4.55) for $N \gg 1$ comes from the term with $E_A = \tilde{E}_A$, where

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[5] Equation (4.54) is a consequence of Boltzmann's work, but was first written in this form by Max Planck. The constant k is known as Boltzmann's constant but was first introduced by Planck.

$\tilde{E}_A$ is the most probable value of E_A. With this approximation we can write

$$\Omega(E) \approx \Omega_A(\tilde{E}_A)\Omega_B(E - \tilde{E}_A). \tag{4.57}$$

The approximation (4.57) better approximates the sum in (4.55) as the thermodynamic limit is approached and allows us to write

$$S = k \ln \Omega = S_A + S_B \tag{4.58}$$

before and after the constraint is removed. We see that one consequence of the proposed relation between S and Ω is that the entropy increases or remains unchanged after an internal constraint is relaxed.

Given the definition (4.54) of S as a function of E, V, and N, it is natural to adopt the thermodynamic definitions of temperature, pressure, and chemical potential:

$$\frac{1}{T} = \Big(\frac{\partial S}{\partial E}\Big)_{V,N}, \tag{4.59}$$

$$\frac{P}{T} = \Big(\frac{\partial S}{\partial V}\Big)_{E,N}, \tag{4.60}$$

$$\frac{\mu}{T} = -\Big(\frac{\partial S}{\partial N}\Big)_{E,V}. \tag{4.61}$$

The definition of the entropy $S = k \ln \Omega$ in (4.54) gives us the desired connection between statistical mechanics and thermodynamics.

How should we generalize the relation of S to the number of microstates for a system in which the energy is a continuous variable? Two possibilities are

$$S = k \ln g(E)\Delta E, \tag{4.62a}$$

$$S = k \ln \Gamma(E). \tag{4.62b}$$

It is easy to show that in the limit $N \to \infty$, the two definitions yield the same result (see Problem 4.18). The reason is that $\Gamma(E)$ and $g(E)$ are such rapidly increasing functions of E that it makes no difference whether we include the microstates with energy less than or equal to E or just the states between E and $E + \Delta E$.

If we use either of the definitions of S given in (4.62) and (4.51), we find that the entropy of an ideal gas in the semiclassical limit for $N \to \infty$ is given by

$$S(E,V,N) = Nk\Big[\ln\frac{V}{N} + \frac{3}{2}\ln\frac{mE}{3N\pi\hbar^2} + \frac{5}{2}\Big]. \tag{4.63}$$

Problem 4.17. Form of the entropy

Compare the form of S given in (4.63) with the form of S determined from thermodynamic considerations in Section 2.19. ☐

Problem 4.18. Equivalent definitions of the entropy

Verify the result (4.63) for the entropy S of an ideal gas using either of the definitions of S given in (4.62). Why can we neglect ΔE compared to E when we use the definition (4.62a)? ☐

We now use the result (4.63) for S to obtain the energy equation of state of an ideal classical gas. From (4.63) we see that

$$\frac{1}{T} = \Big(\frac{\partial S}{\partial E}\Big)_{V,N} = \frac{3}{2}\frac{Nk}{E}, \tag{4.64}$$

and hence we obtain the familiar result

$$E = \frac{3}{2}NkT. \tag{4.65}$$

The pressure equation of state follows from (4.60) and (4.63) and is given by

$$\frac{P}{T} = \Big(\frac{\partial S}{\partial V}\Big)_{E,N} = \frac{Nk}{V}, \tag{4.66}$$

and hence

$$PV = NkT. \tag{4.67}$$

We have finally derived the thermal and mechanical equations of state of an ideal classical gas from first principles! Do the equations of state depend on $\hbar$ and parameters such as m which appear in (4.49)?

Problem 4.19. The Sackur-Tetrode expression for the entropy

Use the relations (4.63) and (4.65) to obtain S as a function of T, V, and N instead of E, V, and N. This relation is known as the *Sackur-Tetrode* equation. ☐

Problem 4.20. The chemical potential of an ideal gas

Use (4.61) and (4.63) to derive the dependence of the chemical potential μ on E, V, and N for an ideal classical gas. Then use (4.65) to determine $\mu(T, V, N)$. We will derive $\mu(T, V, N)$ for the ideal classical gas more simply in Section 6.6. ☐

So far we have used the relation (4.54) between the entropy and the number of accessible states to find the equation of states of an ideal classical gas. In Example 4.1 we apply the same formalism to find the energy equation of state of a system of noninteracting spins.

Example 4.1. Isolated system of N spins

Consider a system of N noninteracting spins and find the dependence of its temperature T on the total energy E. What is the probability that a given spin is up?

Solution. We first have to find the dependence of the entropy S on the energy E of the system. As discussed in Section 4.3.1, the energy E of a system with n spins up out of N in a magnetic field B is

$$E = -(n - n')\mu B = -[n - (N - n)]\mu B = -(2n - N)\mu B, \tag{4.14}$$

where $n' = N - n$ is the number of down spins and μ is the magnetic moment of the spins. From (4.14) we find that the value of n corresponding to a given E is

$$n = \frac{1}{2}\Big(N - \frac{E}{\mu B}\Big). \tag{4.68}$$

The corresponding number of microstates is given by

$$\Omega(n) = \frac{N!}{n!(N-n)!}. \tag{4.16}$$

The thermodynamic temperature T is given by

$$\frac{1}{T} = \Big(\frac{\partial S}{\partial E}\Big)_{B,N} = \frac{dS(n)}{dn}\frac{dn}{dE} = -\frac{1}{2\mu B}\frac{dS}{dn}. \tag{4.69}$$

To calculate dS/dn, we use the approximation (3.104) for large n:

$$\frac{d}{dn}\ln n! = \ln n, \tag{4.70}$$

and find

$$\frac{dS(n)}{dn} = k[-\ln n + \ln(N-n)], \tag{4.71}$$

where $S(n) = k\ln\Omega(n)$ from (4.16). Hence

$$\frac{1}{T} = -k\frac{1}{2\mu B}\ln\frac{N-n}{n}. \tag{4.72}$$

Equation (4.72) yields T as a function of E by eliminating n using (4.68).

The natural variables in the microcanonical ensemble are E, V, and N. Hence, T is a derived quantity and is found as a function of E. As shown in Problem 4.21, we can use (4.14) and (4.72) to express E as a function T. The result is

$$E = -N\mu B\tanh\frac{\mu B}{kT} = -N\mu B\tanh\beta\mu B, \tag{4.73}$$

where $\beta = 1/kT$.

The probability p that a given spin is up is equal to the ratio n/N. If we solve (4.72) for n/N, we find (see Problem 4.21)

$$p = \frac{n}{N} = \frac{1}{1+e^{-2\mu B/kT}} \tag{4.74a}$$

$$= \frac{e^{\mu B/kT}}{e^{\mu B/kT}+e^{-\mu B/kT}} = \frac{e^{\beta\mu B}}{e^{\beta\mu B}+e^{-\beta\mu B}}. \tag{4.74b}$$

We have obtained the result for p that we promised in Section 3.5. ♢

Note we had to consider all N spins even though the spins do not interact with each other. The reason is that the N spins have a definite energy and hence we cannot assign the orientation of each spin independently. We will obtain the result (4.74) by a more straightforward method in Section 4.6.

Problem 4.21. The energy as a function of the temperature

Solve (4.72) for n/N and verify (4.74). Then use (4.14) to solve for E as a function of T and verify (4.73) for a system of N noninteracting spins. ☐

ensemble	macrostate	probability distribution	thermodynamics
microcanonical	E, V, N	$P_s = 1/\Omega$	$S(E, V, N) = k \ln \Omega$
canonical	T, V, N	$P_s = e^{-\beta E_s}/Z$	$F(T, V, N) = -kT \ln Z$
grand canonical	T, V, μ	$P_s = e^{-\beta(E_s - \mu N_s)}/Z_G$	$\Omega_G(T, V, \mu) = -kT \ln Z_G$

Table 4.9: Summary of the three most common ensembles. P_s is the probability that the system is in microstate s.

Although the microcanonical ensemble is conceptually simple, it is almost always not the most practical ensemble. The major problem is that because we must satisfy the constraint that E is specified, we cannot assign energies to each particle individually, even if the particles do not interact. Also because each microstate is equally probable, there are no obvious approximation methods that retain only the most important microstates. Moreover, isolated systems are very difficult to realize experimentally, and the temperature rather than the energy is a more natural independent variable.

Before we discuss the other common ensembles, we summarize their general features in Table 4.9. The internal energy E is fixed in the microcanonical ensemble and the temperature is a derived quantity. In the canonical ensemble the temperature T and hence the mean energy is fixed, but the energy fluctuates. Similarly, the chemical potential and hence the mean number of particles is fixed in the grand canonical ensemble, and the number of particles fluctuates. In all of these ensembles, the volume V is fixed which implies that the pressure fluctuates. We also can choose an ensemble in which the pressure is fixed and the volume fluctuates.

***Problem 4.22.** The Einstein solid in the microcanonical ensemble

Consider a collection of N distinguishable harmonic oscillators with total energy E. The oscillators are distinguishable because they are localized on different lattice sites. In one dimension the energy of each particle is given by $\epsilon_n = (n + \frac{1}{2})\hbar\omega$, where ω is the angular frequency. Hence, the total energy can be written as $E = (Q + \frac{1}{2}N)\hbar\omega$, where Q is the number of quanta. Calculate the dependence of the temperature T on the total energy E in the microcanonical ensemble using the result that the number of accessible microstates in which N distinguishable oscillators can share Q indistinguishable quanta is given by $\Omega = (Q + N - 1)!/Q!(N - 1)!$ [see (4.3)]. Then use this relation to find $E(T)$. This relation is calculated much more simply in the canonical ensemble as shown in Example 4.3. ☐

4.6 The Canonical Ensemble (Fixed T, V, and N)

We now assume that the system of interest can exchange energy with a much larger system known as a *heat bath.* The heat bath is sufficiently large that it is not significantly affected by the smaller system. For example, if we place a glass of cold water into a large room, the temperature of the water will eventually reach the temperature of the air in the room. Because the volume of the glass is small compared to the volume of the room, the cold water does not cool the air appreciably and the air is an example of a heat bath.

The composite system, the system of interest plus the heat bath, is an isolated system. We can characterize the macrostate of the composite system by E, V, N. The accessible microstates of the composite system are equally probable. If the system of interest is in a microstate with energy E_s, then the energy of the heat bath is $E_{\rm b} = E - E_s$. Because the system of interest is much smaller than the heat bath, we know that $E_s \ll E$.[6]

For a given microstate of the system, the heat bath can be in any one of a large number of microstates such that the total energy of the composite system is E. The probability P_s that the system is in microstate s with energy E_s is given by [see (4.53)]

$$P_s = \frac{1 \times \Omega_{\rm b}(E - E_s)}{\sum_s \Omega_{\rm b}(E - E_s)}, \tag{4.75}$$

where $\Omega_{\rm b}(E - E_s)$ is the number of microstates of the heat bath for a given microstate s of the system of interest. As E_s increases, $\Omega_{\rm b}(E - E_s)$, the number of accessible microstates available to the heat bath, decreases. We conclude that P_s is a decreasing function of E_s, because the larger the value of E_s, the less energy is available to the heat bath.

We can simplify the form of P_s by using the fact that $E_s \ll E$. We cannot approximate $\Omega_{\rm b}(E - E_s)$ directly because $\Omega_{\rm b}$ is a rapidly varying function of its argument. For this reason we take the logarithm of (4.75) and write

$$\ln P_s = C + \ln \Omega_{\rm b}(E_{\rm b} = E - E_s), \tag{4.76}$$

where the constant C is related to the denominator of (4.75) and does not depend on E_s. We now expand $\ln \Omega_{\rm b}(E - E_s)$ to leading order in E_s and write

$$\begin{aligned} \ln P_s &\approx C + \ln \Omega_{\rm b}(E) - E_s \Big(\frac{\partial \ln \Omega_{\rm b}(E_{\rm b})}{\partial E_{\rm b}}\Big)_{E_{\rm b}=E} && (4.77\text{a}) \\ &= C + \ln \Omega_{\rm b}(E) - \frac{E_s}{kT}. && (4.77\text{b}) \end{aligned}$$

We have used the relations [from (4.54) and (4.59)]

$$\beta \equiv \frac{1}{kT} = \Big(\frac{\partial \ln \Omega_{\rm b}(E_{\rm b})}{\partial E_{\rm b}}\Big)_{N,V}, \tag{4.78}$$

where T is the temperature of the heat bath. As can be seen from (4.78), β is proportional to the inverse temperature of the heat bath. From (4.77b) we obtain

$$\boxed{P_s = \frac{1}{Z}\, e^{-\beta E_s}} \qquad \text{(Boltzmann distribution).} \tag{4.79}$$

The function Z is found from the normalization condition $\sum_s P_s = 1$ and is given by

$$\boxed{Z = \sum_s e^{-\beta E_s}} \qquad \text{(partition function).} \tag{4.80}$$

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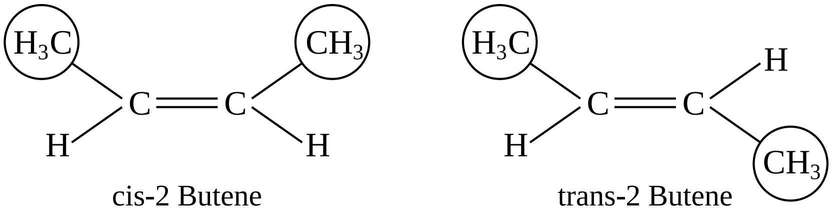
[6] It is not obvious how we should assign the potential energy of interaction of particles at the interface of the system and the heat bath. If the number of particles in the system of interest is large, the number of particles near the interface between the two systems is small in comparison to the number of particles in the bulk so that the potential energy of interaction of particles near the surface can be ignored. Nevertheless, these interactions are essential in order for the system to come into thermal equilibrium with the heat bath.



(a) (b)

Figure 4.7: Butene (C_4H_8) is a colorless gas at room temperature and pressure. It exists in four isomers or structures, two of which are shown. The trans-2 isomer in (b) has lower energy than the cis-2 isomer in (a).

$Z(T, V, N)$ is known as the *partition function*. The symbol Z is from the German *Zustandssumme*, which means "sum over states." The form of P_s in (4.79) applies to a system in equilibrium with a heat bath at temperature T. Note that our derivation of the Boltzmann distribution holds for any system in equilibrium with a heat bath and makes no assumption about the nature of the system and the heat bath.

Problem 4.23. Discuss the relation between the qualitative results that we obtained based on Table 4.6 and the Boltzmann distribution in (4.79). □

Problem 4.24. Relative abundance of two isomers

The hydrocarbon 2-butene, CH_3-CH=CH-CH_3, occurs in two isomers (geometrical structures) called cis and trans. The cis (on this side) isomer of 2-butene has both CH_3 groups on the same side of the C=C double bond. In the trans (across) isomer the CH_3 groups are on opposite sides of the double bond (see Figure 4.7). The energy difference ΔE between the two conformations is approximately $\Delta E/k = 4180\,\mathrm{K}$, with the trans isomer lower than the cis isomer. Determine the relative abundance of the two conformations at $T = 300\,\mathrm{K}$ and $T = 1000\,\mathrm{K}$. □

In the canonical ensemble the temperature T is fixed by the heat bath, and a macrostate is specified by the temperature T, volume V, and the number of particles N. The mean energy of the system is given by

$$\overline{E} = \sum_s P_s E_s = \frac{1}{Z} \sum_s E_s \, e^{-\beta E_s}, \tag{4.81}$$

where we have substituted the Boltzmann form (4.79) for the probability distribution. We use a trick similar to that used in Section 3.5 to obtain a simpler form for $\overline{E}$. First we write

$$\overline{E} = -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_s e^{-\beta E_s}, \tag{4.82}$$

where we have used the fact that $\frac{\partial}{\partial \beta}(e^{-\beta E_s}) = -E_s e^{-\beta E_s}$. Because

$$\frac{\partial Z}{\partial \beta} = -\sum_s E_s e^{-\beta E_s}, \tag{4.83}$$

we can write

$$\boxed{\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln Z}. \tag{4.84}$$

We see that $\overline{E}$ is a function of T for fixed V and N, and can be expressed as a derivative of Z.

In the same spirit we can express C_V, the heat capacity at constant volume, in terms of Z. We have

$$\begin{aligned} C_V &= \frac{\partial \overline{E}}{\partial T} = \frac{d\beta}{dT}\frac{\partial \overline{E}}{\partial \beta} && (4.85) \\ &= \frac{1}{kT^2}\Big[\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2}\Big(\frac{\partial Z}{\partial \beta}\Big)^2\Big], && (4.86) \end{aligned}$$

where $\partial\overline{E}/\partial\beta$ has been calculated from (4.84). Because

$$\overline{E^2} = \frac{1}{Z}\sum_s E_s^2\, e^{-\beta E_s} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}, \tag{4.87}$$

we obtain the relation

$$\boxed{C_V = \frac{1}{kT^2}\Big[\overline{E^2} - \overline{E}^2\Big]}. \tag{4.88}$$

Equation (4.88) relates the equilibrium energy fluctuations to the response of the system to a small change in the energy. Note that we can calculate the variance of the energy, a measure of the magnitude of the energy fluctuations, from the heat capacity. We will later find other examples of the relation of the linear response of an equilibrium system to the equilibrium fluctuations of an associated quantity.[7]

Because the energy is restricted to a very narrow range in the microcanonical ensemble and can range anywhere between zero and infinity in the canonical ensemble, it is not obvious that the two ensembles give the same results for the thermodynamic properties of a system. One way to understand why the thermodynamic properties are independent of the choice of ensemble is to use the relation (4.88) to estimate the range of energies in the canonical ensemble that have a significant probability. Because both E and C_V are extensive quantities, they are both proportional to N. Hence, the N dependence of the relative fluctuations of the energy in the canonical ensemble is given by

$$\frac{\sqrt{\overline{E^2} - \overline{E}^2}}{\overline{E}} = \frac{\sqrt{kT^2 C_V}}{\overline{E}} \sim \frac{N^{1/2}}{N} \sim N^{-1/2}. \tag{4.89}$$

From (4.89) we see that in the limit of large N, the relative fluctuations in the values of E that would be observed in the canonical ensemble are vanishingly small. For this reason the mean energy in the canonical ensemble is a well-defined quantity just as it is in the microcanonical ensemble. However, the fluctuations in the energy are qualitatively different in the two ensembles.

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[7] The relation (4.88) is important conceptually and is useful for simulations at a given temperature (see Section 4.11). However, it is almost always more convenient to *calculate* C_V from its definition in (4.85).

Problem 4.25. Distribution of energy in the canonical ensemble

Given what you have learned so far about the N dependence of the relative energy fluctuations, what is your best guess for the form of the probability that a system in equilibrium with a heat bath at temperature T has energy between E and $E + \Delta E$? The form of the probability distribution of the energy of a system in the canonical ensemble is derived in Section 4.14.2. ☐

Problem 4.26. The Boltzmann probability given by (4.79) is the probability that the system is in a particular microstate with energy E_s. On the basis of what you have learned so far, what do you think is the form of the probability $p(E)\Delta E$ that the system has energy between E and $E + \Delta E$? ☐

In addition to the relation of the mean energy to $\partial \ln Z/\partial\beta$, we can express the mean pressure $\overline{P}$ in terms of $\partial \ln Z/\partial V$. If the system is in microstate s, then a quasistatic change dV in the volume produces the energy change

$$dE_s = \Big(\frac{dE_s}{dV}\Big)_{T,N} dV = -\pi_s\, dV. \tag{4.90}$$

The quantity dE_s in (4.90) is the work done on the system in microstate s to produce the volume change dV. The relation (4.90) defines the pressure $\pi_s = -dE_s/dV$ of the system in microstate s.[8] Hence, the mean pressure of the system is given by

$$\overline{P} = -\sum_s \frac{dE_s}{dV} P_s = \sum_s \pi_s P_s. \tag{4.91}$$

From (4.79), (4.80), and (4.91) we can express the mean pressure as

$$\overline{P} = kT\Big(\frac{\partial \ln Z}{\partial V}\Big)_{T,N}. \tag{4.92}$$

Note that to define the mean pressure we assumed that a small change in the volume does not change the probability distribution P_s of the microstates, but changes only the energy E_s of the microstates. A perturbation of the system will usually induce transitions between the different microstates of the system and hence change the probabilities P_s as well as the energy of the microstates. That is, if the system is initially in microstate s, it will usually not stay in this microstate as the volume is changed. However, if the change occurs sufficiently slowly so that the system can adjust to the change, then the system will remain in microstate s. As discussed in Chapter 2, page 31, such a change is quasistatic.

We can use the relation $\overline{E} = \sum_s P_s E_s$ to write the total change in the energy as

$$d\overline{E} = \sum_s E_s\, dP_s + \sum_s P_s\, dE_s. \tag{4.93}$$

The second term on the right-hand side of (4.93) can be written as

$$\sum_s P_s\, dE_s = \sum_s P_s \frac{dE_s}{dV} dV = -\overline{P} dV. \tag{4.94}$$

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[8] We have written the pressure in microstate s as π_s rather than P_s or p_s to avoid confusion with the probability.

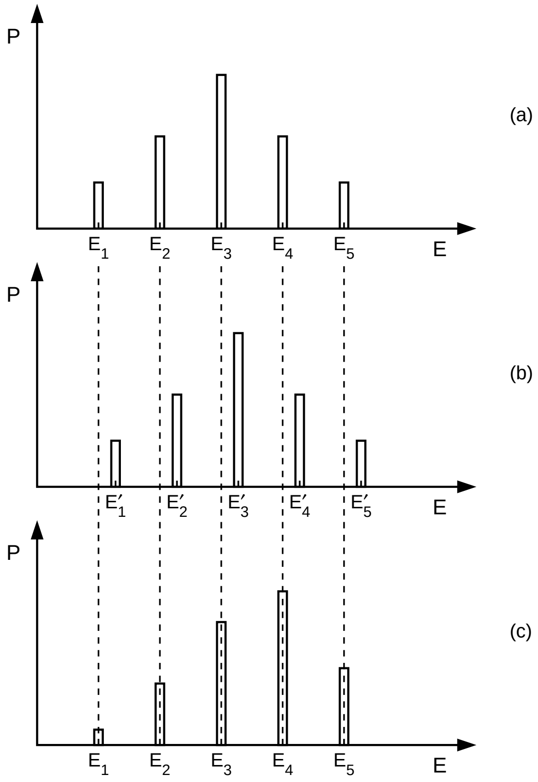

Figure 4.8: (a) Schematic drawing of the eigenstates of a system and their probabilities. (b) The change in the eigenstates of the system when the volume is decreased quasistatically and work is done on the system. No energy is transferred by heating. Note that the probabilities have not changed, and thus the entropy of the system is unchanged. (c) The change in the probabilities of the eigenstates when energy is transferred to the system by heating, and no work is done on the system. In this case the eigenstates are unchanged, but the entropy has increased.

The right-hand side of (4.93) is thus the work done on the system, and we can rewrite (4.93) as

$$d\overline{E} = \sum_s E_s \, dP_s - \overline{P} \, dV. \tag{4.95}$$

If we use the fundamental thermodynamic relation (2.128), $dE = TdS - PdV$ (for fixed N), we can identify the first term in (4.95) with the change in entropy of the system. Hence, we have

$$TdS = \sum_s E_s \, dP_s. \tag{4.96}$$

From (4.96) we see that a change in entropy of the system is related to a change in the probability distribution (see Figure 4.8).

We can use (4.96) to obtain an important expression for the entropy. We rewrite $P_s = e^{-\beta E_s}/Z$

as $E_s = -kT(\ln Z + \ln P_s)$, and substitute this relation for E_s into (4.96):

$$TdS = \sum_s E_s\, dP_s = -kT \sum_s \ln Z\, dP_s - kT \sum_s \ln P_s\, dP_s. \tag{4.97}$$

The first term in (4.97) is zero because the total change in the probability must sum to zero. From (4.97) we write

$$dS = -k \sum_s \ln P_s\, dP_s \tag{4.98a}$$

$$= -k \sum_s d(P_s \ln P_s), \tag{4.98b}$$

where we have again used the fact that $\sum dP_s = 0$. We integrate both sides of (4.98b) to obtain the desired result:

$$\boxed{S = -k \sum_s P_s \ln P_s}. \tag{4.99}$$

We have assumed that the constant of integration is zero [see the discussion after (4.100)]. The quantity defined by (4.11) and (4.99) is known as the *statistical entropy* in contrast to the *thermodynamic entropy* introduced in Chapter 2. Note the similarity of (4.99) to the uncertainty function defined in (3.36).

The relation (4.99) for S is also applicable to the microcanonical ensemble. If there are Ω accessible microstates, then $P_s = 1/\Omega$ for each microstate because each microstate is equally likely. Hence,

$$S = -k \sum_{s=1}^{\Omega} \frac{1}{\Omega} \ln \frac{1}{\Omega} = -k\Omega \frac{1}{\Omega} \ln \frac{1}{\Omega} = k \ln \Omega. \tag{4.100}$$

The constant of integration in going from (4.98b) to (4.99) must be set to zero so that S reduces to its form in the microcanonical ensemble. We see that we can interpret (4.99) as the generalization of its microcanonical form with the appropriate weight for each microstate.

The relation (4.99) is of fundamental importance and shows that the entropy is uniquely determined by the probability distribution P_s of the different microstates. Note that complete predictability (only one accessible microstate) implies the vanishing of the entropy. Also, as the number of accessible microstates increases, the greater the value of S, and hence the higher the degree of unpredictability of the system.

The idea of entropy has come a long way. It was first introduced into thermodynamics as a state function to account for the irreversible behavior of macroscopic systems under certain conditions. The discovery of the connection between this quantity and the probability distribution of the system's microstates was one of the great achievements of Ludwig Boltzmann. It is remarkable that the statistical entropy defined by (4.11) and (4.99) is equivalent to the thermodynamic definition which can be expressed as

$$dS = \frac{dQ}{T}, \tag{4.101}$$

for a quasistatic process. Since then, our understanding of entropy has been extended by Shannon and Jaynes and others to establish a link between thermodynamics and information theory (see

Section 3.4.1). In this context we can say that S is a measure of the lack of information, because the greater the number of microstates that are available to a system in a given macrostate, the less we know about which microstate the system is in.

Although the relation (4.99) is of fundamental importance, we will not use it to calculate the entropy in any of the applications that we consider because it is difficult to calculate the sum. The calculation of the entropy will be discussed in Section 4.7.

The statistical basis of the third law of thermodynamics. We can now see how the third law of thermodynamics (see Section 2.20, page 74) follows from the statistical definition of the entropy. At $T = 0$ the system is in the ground state which we will label by 0. From (4.99) we see that if $P_s = 1$ for microstate 0 and is zero for all other microstates, then $S = 0$. We conclude that $S \to 0$ as $T \to 0$ if the system has a unique ground state. This behavior is what is expected for simple systems.

If there are $g(0)$ microstates with the same ground state energy, then the corresponding (residual) entropy is $S(T = 0) = k \ln g(0)$. In this case the ground state is degenerate.[9] For example, because an electron has spin 1/2, it has two quantum states for each value of its momentum. In practice, there is always a very small, but nonzero magnetic field due to the Earth's magnetic field. Hence, if we could measure the entropy of the ground state of a system of electrons directly, we would find that $S(T = 0) = 0$. However, there are some complex systems for which $g(0) \propto e^N$.[10] We will state the third law of thermodynamics as follows:

> *The entropy of a system at $T = 0$ is a well-defined constant. For any process that brings a system at $T = 0$ from one equilibrium macrostate to another, the change of entropy $\Delta S = 0$.*

Because the entropy can be expressed as $S = \int_0^T (C(T)/T)\, dT$, we conclude that the heat capacity must go to zero as $T \to 0$.

Problem 4.27. Entropy of the ground state of a system of electrons

Explain why the entropy associated with the ground state of a system of N electrons is $kN \ln 2$ in zero magnetic field. ☐

4.7 Connection Between Thermodynamics and Statistical Mechanics in the Canonical Ensemble

Just as $S = k \ln \Omega$ gives the fundamental relation between statistical mechanics and thermodynamics for given values of E, V, and N (see Table 4.9), we now determine the analogous relation in the canonical ensemble where T is fixed rather than E. We have seen that the statistical quantity that enters into the calculation of the mean energy and the mean pressure is not Z, but $\ln Z$ [see (4.84) and (4.92)]. We also learned in Section 2.21 that the Helmholtz free energy $F = E - TS$ is the

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[9] An energy level is said to be degenerate if there are two or more microstates with the same energy.

[10] A simple example of a system with a nontrivial number of ground states is the Ising antiferromagnet on the hexagonal lattice. We will discuss this system in Problem 5.14(d). This system has a nonzero entropy at zero temperature.

thermodynamic potential for the variables T, V, and N. Because this set of variables corresponds to the variables specified by the canonical ensemble, it is natural to look for a connection between $\ln Z$ and F, and we will define the latter as

$$\boxed{F = -kT \ln Z} \quad \text{(statistical mechanics definition of the free energy).} \tag{4.102}$$

We now show that F as defined by (4.102) is equivalent to the thermodynamic definition $F = E - TS$. This equivalence and the relation (4.102) gives the fundamental relation between statistical mechanics and thermodynamics for given values of T, V, and N.

We write the total change in the quantity $\beta F = -\ln Z$ as

$$d(\beta F) = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} d\beta - \frac{1}{Z}\frac{\partial Z}{\partial V}\, dV \tag{4.103a}$$

$$= \overline{E}\, d\beta - \beta \overline{P}\, dV, \tag{4.103b}$$

where we have used (4.84) and (4.91) and the fact that F and Z depend on $T\,(\beta)$ and V. For simplicity, we will ignore the dependence of F and Z on N in this chapter unless otherwise stated. We add and subtract $\beta d\overline{E}$ on the right-hand side of (4.103b) to find

$$d(\beta F) = \overline{E} d\beta + \beta d\overline{E} - \beta d\overline{E} - \beta \overline{P} dV \tag{4.104a}$$

$$= d(\beta \overline{E}) - \beta(d\overline{E} + \overline{P} dV). \tag{4.104b}$$

Hence, we can write

$$d(\beta F - \beta \overline{E}) = -\beta(d\overline{E} + \overline{P} dV). \tag{4.105}$$

From the thermodynamic relation $dE = TdS - \overline{P}dV$ (for fixed N), we can rewrite (4.105) as

$$d(\beta F - \beta \overline{E}) = -\beta(d\overline{E} + \overline{P} dV) = -\beta T dS = -dS/k. \tag{4.106}$$

If we integrate (4.106), we find

$$S/k = \beta(\overline{E} - F) + \text{constant}, \tag{4.107}$$

or

$$F = \overline{E} - TS + \text{constant}. \tag{4.108}$$

If we make the additional assumption that the free energy should equal the internal energy of the system at $T = 0$, we can set the constant in (4.108) equal to zero and obtain

$$F = \overline{E} - TS. \tag{4.109}$$

Equation (4.109) is equivalent to the thermodynamic definition of the Helmholtz free energy with E replaced by $\overline{E}$. In the following, we will often write E instead of $\overline{E}$ because the distinction will be clear from the context.

In Section 2.21 we showed that the Helmholtz free energy F is the natural thermodynamic potential for given values of T, V, and N and that

$$S = -\Big(\frac{\partial F}{\partial T}\Big)_{V,N}, \tag{4.110}$$

$$P = -\Big(\frac{\partial F}{\partial V}\Big)_{T,N}, \tag{4.111}$$

$$\mu = \Big(\frac{\partial F}{\partial N}\Big)_{T,V}. \tag{4.112}$$

These relations still hold with $F = -kT \ln Z$.

We have found that if we start with the statistical mechanical relation $F = -kT \ln Z$ [see (4.102)], we obtain the thermodynamic relation $F = E - TS$ [see (4.109)]. It is instructive to start with the latter and show that it implies that $F = -kT \ln Z$. We substitute $E = -\partial \ln Z/\partial\beta$ and the relation $S = k\beta^2(\partial F/\partial\beta)$ (see (4.110)) and find

$$F = E - TS = -\frac{\partial \ln Z}{\partial \beta} - \beta\Big(\frac{\partial F}{\partial \beta}\Big)_{V,N}. \tag{4.113}$$

We rewrite (4.113) as

$$F + \beta\Big(\frac{\partial F}{\partial \beta}\Big)_{V,N} = \Big(\frac{\partial \beta F}{\partial \beta}\Big)_{V,N} = -\frac{\partial \ln Z}{\partial \beta}. \tag{4.114}$$

If we integrate both sides of (4.114), we find (up to a constant) that

$$F = -kT \ln Z. \tag{4.115}$$

4.8 Simple Applications of the Canonical Ensemble

To gain experience with the canonical ensemble, we first consider some simple examples for which we can do the needed sums over microstates explicitly. In all of these examples, the goal is to calculate the partition function. The usual procedure is to then calculate the free energy using (4.102), the entropy using (4.110), and the mean energy using (4.84). (In these simple examples, the volume of the system will not be relevant, so we will not calculate the pressure.) In principle, we can follow this "recipe" for any physical system, but we will find starting in Chapter 5 that summing over the microstates to evaluate the partition function is usually a formidable task and can be done exactly in only a few cases.

Example 4.2. Two distinguishable particles

Consider a system consisting of two distinguishable particles. Each particle can be in one of two microstates with single-particle energies 0 and Δ. The quantity Δ is called the energy gap. The system is in equilibrium with a heat bath at temperature T. What are the thermodynamic properties of the system?

Solution. The microstates of this two-particle system are $(0,0)$, $(0,\Delta)$, $(\Delta,0)$, and (Δ,Δ). The partition function Z_2 is given by

$$\begin{aligned} Z_2 &= \sum_{s=1}^{4} e^{-\beta E_s} && \text{(4.116a)}\\ &= 1 + 2e^{-\beta\Delta} + e^{-2\beta\Delta} && \text{(4.116b)}\\ &= (1 + e^{-\beta\Delta})^2. && \text{(4.116c)} \end{aligned}$$

We can express Z_2 in terms of Z_1, the partition function for one particle:

$$Z_1 = \sum_{s=1}^{2} e^{-\beta\epsilon_s} = 1 + e^{-\beta\Delta}. \tag{4.117}$$

By comparing the forms of (4.116c) and (4.117), we find that

$$Z_2 = Z_1^2. \tag{4.118}$$

What do you expect the relation is between Z_N, the partition function for N noninteracting distinguishable particles, and Z_1?

Note that if the two particles were indistinguishable, there would be three microstates if the particles were bosons and one microstate if the particles were fermions, and the relation (4.118) would not hold.

Because Z_2 is simply related to Z_1, we can consider the statistical properties of a system consisting of one particle with Z_1 given by (4.117). From (4.79) we find the probability that the system is in each of its two possible microstates is given by

$$P_1 = \frac{1}{Z_1} = \frac{1}{1+e^{-\beta\Delta}}, \tag{4.119a}$$

$$P_2 = \frac{e^{-\beta\Delta}}{Z_1} = \frac{e^{-\beta\Delta}}{1+e^{-\beta\Delta}}. \tag{4.119b}$$

The average energy is given by

$$\overline{e} = \sum_{s=1}^{2} P_s \epsilon_s = \frac{\Delta\, e^{-\beta\Delta}}{1+e^{-\beta\Delta}}. \tag{4.120}$$

We will use a lower case symbol to denote the results for one particle.

Of course, $\overline{e}$ could also be found from the relation $\overline{e} = -\partial \ln Z_1/\partial\beta$. For our example we have

$$Z_1 = 1 + e^{-\beta\Delta}, \tag{4.121}$$

and

$$\frac{\partial Z_1}{\partial \beta} = -\Delta e^{-\beta\Delta}. \tag{4.122}$$

Hence

$$\overline{e} = -\frac{\partial}{\partial\beta} \ln Z_1 = -\frac{1}{Z_1}\frac{\partial Z_1}{\partial\beta} = \frac{\Delta e^{-\beta\Delta}}{1+e^{-\beta\Delta}}, \tag{4.123}$$

in agreement with (4.120). The energy of N noninteracting, distinguishable particles of the same type is given by $\overline{E} = N\overline{e}$.

It is easy to calculate f, the free energy per particle, from the partition function in (4.117). We have

$$f = -kT \ln Z_1 = -kT \ln[1 + e^{-\beta\Delta}]. \tag{4.124}$$

Because we have already calculated f and $\overline{e}$, we can calculate s, the entropy per particle, from the relation $f = e - Ts$, or $s = (e - f)/T$. Alternatively, we can calculate s by taking the temperature derivative of the free energy [see (4.110)]:

$$s = -\Big(\frac{\partial f}{\partial T}\Big)_V = k \ln[1 + e^{-\beta\Delta}] + kT \frac{d\beta}{dT}\frac{\partial}{\partial \beta} \ln[1 + e^{-\beta\Delta}] \tag{4.125a}$$

$$= k \ln[1 + e^{-\beta\Delta}] + kT\Big(\frac{-1}{kT^2}\Big)\frac{-\Delta e^{-\beta\Delta}}{1 + e^{-\beta\Delta}} \tag{4.125b}$$

$$= k \ln[1 + e^{-\beta\Delta}] + \Big(\frac{\Delta}{T}\Big)\frac{e^{-\beta\Delta}}{1 + e^{-\beta\Delta}} \tag{4.125c}$$

$$= k \ln[1 + e^{-\beta\Delta}] + k\frac{\beta\Delta e^{-\beta\Delta}}{1 + e^{-\beta\Delta}}. \tag{4.125d}$$

The behavior of the various thermodynamic properties of this system is explored in Problem 4.47.
◊

Example 4.3. The thermodynamic properties of a single one-dimensional harmonic oscillator in equilibrium with a heat bath at temperature T

Solution. The energy levels of a single harmonic oscillator in one dimension are given by

$$\epsilon_n = \Big(n + \frac{1}{2}\Big)\hbar\omega \qquad (n = 0, 1, 2, \ldots). \tag{4.126}$$

The corresponding partition function is

$$Z_1 = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} = e^{-\beta\hbar\omega/2}\sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} \tag{4.127a}$$

$$= e^{-\beta\hbar\omega/2}(1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \cdots) = e^{-\beta\hbar\omega/2}(1 + x + x^2 + \cdots), \tag{4.127b}$$

where $x = e^{-\beta\hbar\omega}$. The infinite sum in (4.127b) is a geometric series in x and can be summed using the result that $1 + x + x^2 + \ldots = 1/(1 - x)$ (see the Appendix). The result is

$$Z_1 = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}, \tag{4.128}$$

and

$$\ln Z_1 = -\frac{1}{2}\beta\hbar\omega - \ln(1 - e^{-\beta\hbar\omega}). \tag{4.129}$$

◊

Problem 4.28. Thermodynamic properties of a system of harmonic oscillators

(a) Show that for one oscillator

$$f = \frac{1}{2}\hbar\omega + kT\ln(1 - e^{-\beta\hbar\omega}), \tag{4.130}$$

$$s = k\Big[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} - \ln(1 - e^{-\beta\hbar\omega})\Big], \tag{4.131}$$

$$\overline{e} = \hbar\omega\Big[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\Big]. \tag{4.132}$$

Equation (4.132) is Planck's formula for the mean energy of an oscillator at temperature T. The heat capacity is discussed in Problem 4.50.

(b) Given the result (4.132), what is the mean energy of a system of N harmonic oscillators in equilibrium with a heat bath at temperature T?

(c) Compare your answer with the result for the energy of N harmonic oscillators calculated in the microcanonical ensemble in Problem 4.22. Do the two ensembles give identical results? □

Equation (4.80) for Z is a sum over all the microstates of the system. Because the energies of different microstates may be the same, we can group together microstates with the same energy and write (4.80) as

$$Z = \sum_{\text{levels } \ell} \Omega(E_\ell)\, e^{-\beta E_\ell}, \tag{4.133}$$

where $\Omega(E_\ell)$ is the number of microstates with energy E_ℓ. The sum in (4.133) is over all the energy levels of the system, rather than over all the microstates of the system.

Example 4.4. Consider a three-level single-particle system with six microstates with energies 0, ϵ, ϵ, ϵ, 2ϵ, and 2ϵ. What is $\Omega(\epsilon)$ for this system? What is the mean energy of the system if it is in equilibrium with a heat bath at temperature T?

Solution. In this case we have $\Omega(0) = 1$, $\Omega(\epsilon) = 3$, and $\Omega(2\epsilon) = 2$. The partition function is given by [see (4.133)]

$$Z_1 = 1 + 3e^{-\beta\epsilon} + 2e^{-2\beta\epsilon}. \tag{4.134}$$

Hence, the mean energy of a single particle is given by

$$\overline{e} = \epsilon \frac{3e^{-\beta\epsilon} + 4e^{-2\beta\epsilon}}{1 + 3e^{-\beta\epsilon} + 2e^{-2\beta\epsilon}}. \tag{4.135}$$

What is the energy of N such particles? ♢

4.9 An Ideal Thermometer

The temperature of a system is an abstract quantity in part because we don't have a direct way to measure it. Instead, we need to measure some other quantity such as the pressure in a container or the expansion of a metal, and then calibrate these measurements with the temperature by assuming that the measurements change in some known way with temperature. We now discuss a simple thermometer which gives a direct measure of the temperature. This thermometer has only one property, its energy, and can be realized in a computer simulation.

As discussed in Section 2.4 (page 34), an ideal thermometer interacts very weakly with the system of interest, but strongly enough to obtain an accurate measurement. Also, there needs to be a known relation between some property of the thermometer and the temperature.

Consider a system of one particle which we will call a *demon* that can exchange energy with another system (see page 17).[11] Here the demon will play the role of a thermometer, and the other system, which we will call "the system," is much larger and plays the role of a heat bath. We will use the demon to measure the temperature of the heat bath. As long as almost all of the energy resides in the heat bath, the temperature of the heat bath will not change. The demon obeys the following rules or algorithm:

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[11] "Demons" have a rich history in statistical mechanics. See for example, Leff and Rex, [2003].

1. Set up an initial microstate of the system with the desired total energy E and assign an initial energy E_d to the demon. (For convenience the initial demon energy is usually set to zero.)
2. Make a trial change in the microstate. For example, for the Einstein solid, choose a particle at random and randomly increase or decrease its energy by one. For the Ising model, flip a spin chosen at random.
3. Compute the change in energy of the system, ΔE. If $\Delta E \leq 0$, accept the change, and increase the energy of the demon by $|\Delta E|$. If $\Delta E > 0$, accept the change if the demon has enough energy to give to the system, and reduce the demon's energy by ΔE. The only constraint is that the demon's energy must remain greater than a lower bound which we take to be zero. If a trial change is not accepted, the existing microstate is counted in the averages. In either case the total energy E of the system plus the energy E_d of the demon remains constant.
4. Repeat steps 2 and 3 many times.
5. Compute the averages of the quantities of interest once the system and the demon have reached equilibrium.

The demon can trade energy with the system as long as its energy remains greater than its lower bound, which we have chosen to be zero. The demon is a facilitator that allows the particles (or spins) in the system to indirectly trade energy with one another.

In Problems 4.29 and 4.31 we use the demon algorithm to determine the mean energy of the demon and the probability that it is in a particular microstate.

Problem 4.29. The demon and the ideal classical gas

Consider a demon that exchanges energy with an ideal classical gas of N identical particles of mass m in three dimensions. Because the energy of a particle in an ideal gas depends only on its speed, the positions of the particles are irrelevant in this case. The demon chooses a particle at random and changes its velocity in a particular direction by an amount δ chosen at random between $-\delta_m$ and δ_m. The change in energy of the system is $\Delta E = \frac{1}{2}[(v+\delta)^2 - v^2]$; we have chosen units so that $m = 1$. The parameter δ_m is arbitrary. Program `IdealThermometerIdealGas` implements the demon algorithm for an ideal classical gas in d dimensions. For simplicity, the program initially assigns each particle in the gas the same initial velocity $\mathbf{v}$ in the x-direction; $|\mathbf{v}|$ is chosen so that the initial energy of the system is E. The initial demon energy is set equal to zero.

(a) Before you do the simulation, sketch the energy dependence of the probability $p(E_d)\Delta E_d$ that the demon has an energy between E_d and $E_d + \Delta E_d$. Is $p(E_d)$ an increasing or decreasing function of E_d or does it have a maximum at some value of E_d?

(b) Choose $d = 3$ and $N = 40$ and $E = 40$ so that $E/N = 1$. Determine $\overline{E_\mathrm{d}}$, the mean energy of the demon, and $\overline{E}/N$, the mean energy per particle of the system after the demon and the system have reached equilibrium. (Use the `Zero Averages` button.) Then choose other combinations of N and E and determine the relation between $\overline{E_\mathrm{d}}$ and $\overline{E}/N$.

(c) We know that the mean energy of an ideal classical gas in three dimensions is equal to $3NkT/2$ [see (4.65)], where T is the temperature of the system. Use this relation and the values of $\overline{E}/N$ that you found in part (b) to estimate the temperature of the gas. What is the relation of the temperature that you found in this way to $\overline{E_\text{d}}$? (Use units such that $k = 1$.)

(d) Run for a sufficient number of trials so that the form of $p(E_\text{d})$ is well-defined, and verify the exponential form of $p(E_\text{d})$. Compare your results for the temperature that you found in part (c) with the value of $1/\beta$ that you determined from the exponential fit of $p(E_\text{d})$. Then assume that $\beta = 1/kT$ and compare the values of the temperature that you obtained.

(e) We will show in Problem 4.30 that $\overline{E_\text{d}} = kT$ given the exponential form of the probability density $p(E_\text{d})$ that you found in part (d) and the fact that E_d is a continuous variable. How well do your simulation results for $\overline{E_\text{d}}$ agree with this prediction?

(f) How do your results change for an ideal gas in two and three dimensions?

(g) Explain why the form of $p(E_\text{d})$ is given by the Boltzmann distribution. What property (properties) of the demon make it an ideal thermometer?

(h) Compare the initial velocity of the particles in the system to the mean value after equilibrium has been established. What is the form of the distribution of the velocities in equilibrium? □

Problem 4.30. The temperature dependence of the mean demon energy: Continuous case

A demon exchanges energy with an ideal classical gas of N particles in three dimensions (see Problem 4.29). What is the mean energy of the demon?

In this case the demon energy is a continuous variable. Hence, we can analytically determine the relation between the mean demon energy and the temperature:

$$\overline{E_\text{d}} = \frac{\int_0^\infty E_\text{d}\, e^{-\beta E_\text{d}}\, dE_\text{d}}{\int_0^\infty e^{-\beta E_\text{d}}\, dE_\text{d}}. \tag{4.136}$$

(a) Explain why the relation (4.136) for the demon energy is reasonable and determine the temperature dependence of $\overline{E_\text{d}}$.

(b) Would this temperature dependence be different if the gas is in one or two dimensions? Would the temperature dependence change if the particles in the gas interacted with one another? □

Problem 4.31. The demon and the Einstein solid

Consider a demon that exchanges energy with an Einstein solid of N particles. The demon selects a particle at random and randomly changes its energy by ±1 consistent with the constraint that $E_\text{d} \geq 0$. In this case the energy of each particle in the system also must remain nonnegative. Why? If a trial change is not accepted, the existing microstate is counted in all averages. Use Program `IdealThermometerEinsteinSolid` to do the simulations.

(a) Choose $N = 40$ and $E = 200$. What is the mean energy of the demon after equilibrium between the demon and the system has been established? Compare the values of $\overline{E_\text{d}}$ and $\overline{E}/N$. Fix $N = 40$ and change E. How does $\overline{E_\text{d}}$ depend on $\overline{E}/N$?

(b) Compute the probability $P(E_\mathrm{d})$ for various values of E and N. Fit your results to the form $\ln P(E_\mathrm{d}) = -\beta E_\mathrm{d} + \text{constant}$, where β is a parameter. Is β simply related to the mean demon energy?

(c) Explain why the form of $P(E_\mathrm{d})$ is given by the Boltzmann distribution. What property of the demon appears to be universal? □

Problem 4.32. The temperature dependence of the mean demon energy for an Einstein solid

A demon exchanges energy with an Einstein solid of N particles (see Problem 4.31).

(a) Explain why the energy of the demon is restricted to integer values.

(b) Explain why the demon's mean energy is given by

$$\overline{E_\mathrm{d}} = \frac{\sum_{n=0}^{\infty} n e^{-\beta n}}{\sum_{n=0}^{\infty} e^{-\beta n}}. \tag{4.137}$$

(c) Do the sums in (4.137) to determine the temperature dependence of $\overline{E_\mathrm{d}}$. (It is necessary to evaluate only the sum in the denominator of (4.137). The numerator can be determined by an appropriate derivative of the result for the denominator. See Example 4.3.)

(d) Why is the temperature dependence of $\overline{E_\mathrm{d}}$ different for an ideal gas and an Einstein solid?

(e) *In what limit does the temperature dependence become the same? □

4.10 Simulation of the Microcanonical Ensemble

How can we implement the microcanonical ensemble on a computer? One way to do so for a classical system of particles is to use the method of molecular dynamics (see Section 1.4) which is based on the numerical solution of Newton's equations of motion. We first choose initial conditions for the positions and velocities of each particle that are consistent with the desired values of E, V, and N. The numerical solution of Newton's equations generates a trajectory in $6N$-dimensional phase space (for a system in three spatial dimensions). Each point on the trajectory represents a microstate of the microcanonical ensemble with the additional condition that the momentum of the center of mass is fixed. The averages over the phase space trajectory represent a time average.

To do such a simulation we need to be careful to choose a representative initial condition. It could happen that most of the microstates consistent with the desired values of E, V, and N are not easy to reach from a specific microstate, and hence the system might spend a long time in similar nonrepresentative microstates. Because molecular dynamics simulates systems for physical times that are very short (the longest time we can simulate is $\approx 10^{-6}\,\mathrm{s}$), the system might not reach equilibrium within a reasonable amount of computer time if we do not choose the initial microstate properly.

Our assumption that a molecular dynamics simulation generates microstates consistent with the microcanonical ensemble is valid as long as a representative sample of the accessible microstates can be reached during the duration of the simulation. Such a system is said to be *ergodic*.

As we will justify further in Section 6.2.1, we can identify the temperature of a system of interacting classical particles with the kinetic energy per particle using the relation (4.65). (For the ideal gas the total energy is the kinetic energy.) If we were to do a molecular dynamics simulation, we would find that the total energy is approximately constant (it would be a constant if we could numerically solve the equations of motion exactly), and the kinetic energy and hence the temperature fluctuates as is expected for the microcanonical ensemble. The mean temperature of the system becomes well-defined if the system is in equilibrium, the number of particles in the system is sufficiently large, and the simulation is done for a sufficiently long time.

What if we wish to simulate a system at fixed total energy for which Newton's equations of motion is not applicable? For example, there is no dynamics for the Einstein solid in which the particles have only integer values of the energy. Another general way of generating representative microstates is to use a *Monte Carlo* method. As an example, the relevant variables for the Einstein solid are the quantum numbers of each particle such that their sum equals the desired total energy E. Given a set of quantum numbers, how do we generate another set of unbiased quantum numbers with the same energy? Because we want to generate a representative sample of the accessible microstates, we need to make all changes at random. One possibility is to choose two particles at random and make trial changes in their energy by ±1 such that the total energy is unchanged.

A more interesting example is the Ising model in which the spins interact with their nearest neighbors with an energy $+J$ if the spins are parallel and energy $-J$ if the spins are antiparallel (see Section 1.9.3). We will discuss the Ising model in more detail in Chapter 5. Here it is sufficient to understand that the individual spins interact with one another.

The condition that the total energy be fixed makes sampling the accessible microstates of the Ising model difficult. If we choose a spin at random and flip it, the change will frequently change the energy of the system. We can circumvent this difficulty by relaxing the condition that the total energy be fixed by adding to the system of N particles an extra degree of freedom called the demon, as we discussed in Section 4.9. The total energy of the demon plus the original system is fixed. Because the demon is one particle out of $N + 1$, the fluctuations in the energy of the original system are of order $1/N$, which goes to zero as $N \to \infty$. Hence, the demon simulation can be viewed either as a means of illustrating an ideal thermometer by focusing on the demon as a system in the canonical ensemble or as a way of simulating the microcanonical ensemble by focusing on the particles as the system.

4.11 Simulation of the Canonical Ensemble

Suppose that we wish to simulate a system that is in equilibrium with a heat bath at temperature T. One way to do so is to start with an arbitrary microstate of energy E_s and weight it by its relative probability $e^{-\beta E_s}$. For example, we could generate another microstate of an Einstein solid by choosing a particle at random and changing its energy by ±1 at random. If we repeated this process M times, the mean energy of the system could be estimated by

$$\overline{E}(T) = \frac{\sum_{s=1}^{M} E_s e^{-\beta E_s}}{\sum_{s=1}^{M} e^{-\beta E_s}}, \tag{4.138}$$

where E_s is the energy of microstate s and the sum is over the M microstates that have been generated at random. However, this procedure would be very inefficient because the M states would include many high energy states whose weight in averages such as (4.138) would be exponentially small.

One way to make the sampling procedure more efficient is to generate microstates with probabilities proportional to their weight, that is, proportional to $e^{-\beta E_s}$. In this way we would generate microstates with the highest probability. Such a sampling procedure is known as *importance sampling*. The simplest and most common method of importance sampling in statistical mechanics is known as the *Metropolis algorithm*. This algorithm is based on the fact that the ratio of the probability that the system is in microstate j with energy E_j to the probability of being in microstate i with energy E_i is $p_j/p_i = e^{-\beta(E_j - E_i)} = e^{-\beta \Delta E}$, where $\Delta E = E_j - E_i$. We may interpret this ratio as the probability of a transition from microstate i to microstate j. If $\Delta E < 0$, the ratio $e^{-\beta \Delta E}$ is greater than one, and the probability is set to one. The Metropolis algorithm can be summarized as follows:[12]

1. Choose an initial microstate, for example, random initial energies for each particle in an Einstein solid or random positions in a system of particles interacting via the Lennard-Jones potential. Also fix the desired temperature T of the system.
2. Make a trial change in the microstate. For the Einstein solid, choose a particle at random and randomly change its energy by ±1. For a system of interacting particles, change the position of a particle by a small random amount. Compute the change in energy of the system, ΔE, corresponding to this change. If $\Delta E < 0$, then accept the change. If $\Delta E > 0$, accept the change with probability $w = e^{-\beta \Delta E}$. To do so, generate a random number r uniformly distributed in the unit interval. If $r \leq w$, accept the new microstate; otherwise, retain the previous microstate.
3. Repeat step 2 many times.
4. Compute the averages of the quantities of interest after the system has reached equilibrium.

Problem 4.33. Simulation of the Einstein solid in equilibrium with a heat bath

Use the Metropolis algorithm to simulate an Einstein solid of N particles at a temperature T. Program `EinsteinSolidHeatBath` implements the Metropolis algorithm by choosing a particle at random and randomly increasing or decreasing its energy by one unit. If the energy is decreased, the change is accepted. If the energy is increased, the program generates a number r at random in the unit interval and accepts the change if $r \leq e^{-\beta}$, where $\beta = 1/T$. (As usual, we choose units such that Boltzmann's constant $k = 1$.) If a trial change is not accepted, the existing microstate is counted in all averages. This process is repeated many times until the various averages become well-defined.

(a) Choose $N = 20$ and $\beta = 1$. Does the energy of the system eventually reach a well-defined average? If so, vary β and determine $\overline{E}(T)$.

(b) Compare your results to the analytical results found in Example 4.3. □

We will consider many other applications of the Metropolis algorithm in later chapters.

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[12] The Metropolis algorithm is justified in Tobochnik and Gould [2008].

4.12 Grand Canonical Ensemble (Fixed T, V, and μ)

In Section 4.6 we derived the Boltzmann probability distribution for a system in equilibrium with a heat bath at temperature T. We now generalize the heat bath to a reservoir that can exchange particles as well as energy and find the probability distribution for a system in equilibrium with the reservoir at temperature T and chemical potential μ. In this case the role of the reservoir is to fix the chemical potential as well as the temperature. Hence the mean number of particles and the mean energy are determined. This ensemble is known as the *grand canonical ensemble*.

As before, the composite system is isolated with total energy E, total volume V, and total number of particles N. The probability that the (sub)system is in microstate s with energy E_s and N_s particles is given by [see (4.75)]

$$P_s = \frac{1 \times \Omega_{\rm b}(E - E_s, N - N_s)}{\sum_s \Omega_{\rm b}(E - E_s, N - N_s)}. \tag{4.139}$$

The difference between (4.75) and (4.139) is that we have allowed both the energy and the number of particles of the system of interest to vary. As before, we take the logarithm of both sides of (4.139) and exploit the fact that $E_s \ll E$ and $N_s \ll N$. We have

$$\ln P_s \approx \text{constant} - E_s \Big(\frac{\partial \ln \Omega_{\rm b}(E_{\rm b})}{\partial E_{\rm b}}\Big)_{E_{\rm b}=E} - N_s \Big(\frac{\partial \ln \Omega_{\rm b}(N_{\rm b})}{\partial N_{\rm b}}\Big)_{N_{\rm b}=N}, \tag{4.140}$$

where $E_{\rm b} = E - E_s$ and $N_{\rm b} = N - N_s$. If we substitute $\beta = \partial \ln \Omega_{\rm b}/\partial E$ [see (4.78)] and $\beta\mu = -\partial \ln \Omega_{\rm b}/\partial N$ [see (2.120)], we obtain

$$\ln P_s = \text{constant} - \frac{E_s}{kT} + \frac{\mu N_s}{kT}, \tag{4.141}$$

or

$$\boxed{P_s = \frac{1}{Z_G} e^{-\beta(E_s - \mu N_s)}} \qquad \text{(Gibbs distribution)}. \tag{4.142}$$

Equation (4.142) is the Gibbs probability distribution for a variable number of particles. This distribution gives the probability that the system is in microstate s with energy E_s and N_s particles. The *grand partition function* Z_G in (4.142) is found from the normalization condition

$$\sum_s P_s = 1. \tag{4.143}$$

Hence, we obtain

$$\boxed{Z_G = \sum_s e^{-\beta(E_s - \mu N_s)}} \qquad \text{(grand partition function)}. \tag{4.144}$$

In analogy to the relations we found in the canonical ensemble, we expect that there is a simple relation between the Landau potential defined in (2.163) and the grand partition function. Because the derivation of this relation proceeds as in Section 4.6, we simply give the relation

$$\boxed{\Omega = -kT \ln Z_G}. \tag{4.145}$$

Example 4.5. Absorption of atoms on surface sites

Consider a surface with sites that can absorb atoms. Each site can be empty or have at most one absorbed atom. The energy of the site is zero if no atom is present and ϵ if one atom is present. The occupancy of the sites is not correlated. What is the mean number of atoms that are absorbed assuming that the surface is in equilibrium with a reservoir at temperature T and chemical potential μ?

Solution. Because the sites are not correlated, we consider a system of one site. The system has two states with energy 0 and ϵ, and its grand partition function is given by

$$Z_G = 1 + e^{-\beta(\epsilon-\mu)}. \tag{4.146}$$

The probability that one atom is absorbed is

$$p = \frac{e^{-\beta(\epsilon-\mu)}}{Z_G} = \frac{1}{e^{\beta(\epsilon-\mu)}+1}. \tag{4.147}$$

The mean number of atoms absorbed is

$$\overline{n} = 0 \times (1-p) + 1 \times p = \frac{1}{e^{\beta(\epsilon-\mu)}+1}. \tag{4.148}$$

Suppose we know that $\overline{n} = 0.6$ at $T = 3$ (in units such that $k = 1$). What is the chemical potential μ in this case? Choose $\epsilon = 1$ for simplicity.

We solve for μ from (4.148) and find that

$$\mu = \epsilon - kT\ln(\overline{n}^{-1} - 1) = 1 - 3\ln\frac{2}{3} = 1 + 3\ln\frac{3}{2} \approx 2.22. \tag{4.149}$$

◊

4.13 *Entropy is not a Measure of Disorder

Many texts and articles for the scientifically literate refer to entropy as a measure of “disorder” or “randomness.” This interpretation is justified by the relation $S = k\ln\Omega$. The argument is that an increase in the disorder in a system corresponds to an increase in Ω. Sometimes a reference is made to a situation such as the tendency of students’ rooms to become messy. There are two problems with this interpretation – it adds nothing to our understanding of entropy and it is inconsistent with our naive understanding of structural disorder.

We have already discussed the interpretation of the entropy as a measure of the uncertainty or lack of information. Thus, we already have a precise definition of entropy and can describe a student’s messy room as having a high entropy because of our lack of information about the location of a particular paper or article of clothing. We could define disorder as lack of information, but such a definition does not help us to understand entropy any better because it does not provide an independent understanding of disorder.

The other problem with introducing the term disorder to describe entropy is that it can lead to incorrect conclusions. In the following we will describe two examples where the crystalline phase of a given material has a higher entropy than the liquid phase. Yet you would probably agree that a crystal is more ordered than a liquid. So how can a crystal have a higher entropy? The following analogy might be helpful.

Suppose that you are going on a short trip and you need to pack your suitcase with only a few articles.[13] In this case the volume of the suitcase is much greater than the total volume of the articles you wish to pack, and you would probably just randomly threw the articles into the suitcase. Placing the articles in an ordered arrangement would require extra time and the ordered arrangement would probably be lost during your trip. In statistical mechanics terms we say that there are many more ways in which the suitcase can be packed in a disordered arrangement than the ordered one. Hence, we could conclude that the disordered macrostate has a higher entropy than the ordered macrostate. This low density case is consistent with the naive association of entropy and disorder.

Now suppose that you are going on a long trip and you need to pack many articles in the same suitcase, that is, the total volume of the articles to be packed is comparable to the volume of the suitcase. In this high density case you know that randomly throwing the articles into the suitcase won't allow you to shut the suitcase. Such a configuration is incompatible with the volume constraints of the suitcase. If you randomly throw the articles in the suitcase many times, you would find only a few configurations that would allow you to close the suitcase. In contrast, if you pack the articles in a neat and ordered arrangement, the suitcase can be closed. Also there are many such configurations that would satisfy the constraints. We conclude that the number of ordered arrangements of the articles in the suitcase is greater than the number of disordered arrangements. Therefore an ordered arrangement in the high density suitcase has a higher entropy than a structurally disordered state. The association of disorder with entropy is not helpful here.

The suitcase analogy is an example of an *entropy-driven phase transition* from a low to a high density macrostate because energy did not enter into our considerations at all. Another example of a system that exhibits an entropy-driven transition is a system of hard disks. In this seemingly simple model the interaction between two particles is given by

$$u(r) = \begin{cases} \infty & (r < \sigma) \\ 0 & (r \geq \sigma), \end{cases} \tag{4.150}$$

where σ represents the diameter of the hard disks. For this model, only nonoverlapping configurations are allowed and so the potential energy is zero. Hence, the internal energy is solely kinetic and the associated contribution of the energy to the free energy is the ideal gas part which depends only on the temperature and the density. Hence, the difference in the free energy $\Delta F = \Delta E - T\Delta S$ between a hard sphere crystal and a hard sphere fluid at the same density and temperature is equal to $-T\Delta S$.

In the following problem we will do an exploratory simulation of a system of hard disks that suggests that there is a transition from a fluid at low density to a crystal at high density. (We use the term *fluid* when there is no distinction between a gas and a liquid.) That is, at some density ΔF must become negative, which can occur only if $\Delta S = S_{\text{crystal}} - S_{\text{fluid}}$ is positive. We conclude that at high density the entropy of the crystal must be greater than that of a fluid at equal temperature and density for a fluid-solid (freezing) transition to exist.

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[13] This example is due to Laird [1999].

Problem 4.34. Simulation of hard disks

The dynamics of a system of hard disks are straightforward in principle because the particles move in straight lines in between collisions. Program `HardDisksMD` finds when the next two particles are going to collide and moves the particles accordingly.

(a) Run the simulation with the default parameters and record the density and the results for PA/NkT and the temperature. Is the temperature a useful quantity for hard disks? Does it fluctuate during the simulation. If not why not? Does the pressure P fluctuate?

(b) *Compute PA/NkT as a function of density for a fixed number of particles. Is there any evidence of a phase transition where the slope of the pressure with respect to density changes abruptly? □

4.14 Supplementary Notes

4.14.1 The volume of a hypersphere

In the following we derive the expression (4.46) for the volume of a hypersphere of n dimensions. As in (4.45) the volume is given formally by

$$V_n(R) = \int_{x_1^2+x_2^2+\cdots+x_n^2<R^2} dx_1\, dx_2\, \cdots dx_n. \tag{4.151}$$

Because $V_n(R) \propto R^n$ for $n = 2$ and 3, we expect that V_n is proportional to R^n. Hence, we write

$$V_n = C_n R^n, \tag{4.152}$$

where C_n is the unknown constant of proportionality which we wish to find. We rewrite the volume element $dV_n = dx_1\, dx_2\, \cdots dx_n$ as

$$dV_n = dx_1\, dx_2\, \cdots dx_n = S_n(R)\, dR = nC_n R^{n-1} dR, \tag{4.153}$$

where $S_n = nC_n R^{n-1}$ is the surface area of the hypersphere. For example, for $n = 3$ we have $dV_3 = 4\pi R^2\, dR$ and $S_3 = 4\pi R^2$. To find C_n for general n, consider the identity (see the Appendix)

$$I_n = \int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_n\, e^{-(x_1^2+\cdots+x_n^2)} = \Big[\int_{-\infty}^{\infty} dx\, e^{-x^2}\Big]^n = \pi^{n/2}. \tag{4.154}$$

The left-hand side of (4.154) can be written as

$$I_n = \int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_n\, e^{-(x_1^2+\cdots+x_n^2)} = \int_0^{\infty} dR\, S_n(R)\, e^{-R^2} \tag{4.155a}$$

$$= nC_n \int_0^{\infty} dR\, R^{n-1}\, e^{-R^2}. \tag{4.155b}$$

We can relate the integral in (4.155b) to the Gamma function $\Gamma(n)$ defined by the relation

$$\Gamma(n) = \int_0^{\infty} dx\, x^{n-1}\, e^{-x}. \tag{4.156}$$

The relation (4.156) holds for $n > -1$ and whether or not n is an integer. We make the change of variables $u = R^2$ so that

$$I_n = \frac{1}{2} n C_n \int_0^\infty du\, u^{n/2-1}\, e^{-u} = \frac{1}{2} n C_n\, \Gamma(n/2). \tag{4.157}$$

A comparison of (4.157) with (4.154) yields the desired relation

$$C_n = \frac{2\pi^{n/2}}{n\Gamma(\frac{n}{2})} = \frac{\pi^{n/2}}{(n/2)\Gamma(\frac{n}{2})}. \tag{4.158}$$

It follows that

$$V_n(R) = \frac{2\pi^{n/2}}{n\Gamma(\frac{n}{2})} R^n. \tag{4.159}$$

4.14.2 Fluctuations in the canonical ensemble

To gain more insight into the spread of energies that are actually observed in the canonical ensemble, we determine the probability $p(E)\Delta E$ that a system in equilibrium with a heat bath at temperature T has energy E in the range E to $E + \Delta E$. The probability that the system is in any of the microstates with energy E can be written as

$$\frac{\Omega(E) e^{-\beta E}}{\sum\limits_{\text{levels}} \Omega(E) e^{-\beta E}}, \tag{4.160}$$

where $\Omega(E)$ is the number of microstates with energy E. As in (4.133) the sum in the denominator in (4.160) is over the different energy levels of the system. In the thermodynamic limit $N, V \to \infty$, the spacing between consecutive energy levels becomes very small and we can regard E as a continuous variable. We write $p(E)dE$ for the probability that the system in the range E and $E + dE$ and let $g(E)\, dE$ be the number of microstates between E and $E + dE$. (The function $g(E)$ is the density of states and is the same function discussed in Section 4.3.) Hence, we can rewrite (4.160) as

$$p(E)\, dE = \frac{g(E) e^{-\beta E} dE}{\int_0^\infty g(E) e^{-\beta E} dE}. \tag{4.161}$$

As we did on page 137 we can find an approximate form of $p(E)$ by expanding $p(E)$ about $E = \tilde{E}$, the most probable value of E. To do so, we evaluate the derivatives $\partial(\ln p)/\partial E$ and $\partial^2 \ln p/\partial E^2$ using (4.161):

$$\Big(\frac{\partial \ln p}{\partial E}\Big)_{E=\tilde{E}} = \Big(\frac{\partial \ln g}{\partial E}\Big)_{E=\tilde{E}} - \beta = 0, \tag{4.162}$$

and

$$\Big(\frac{\partial^2 \ln p}{\partial E^2}\Big)_{E=\tilde{E}} = \Big(\frac{\partial^2 \ln g}{\partial E^2}\Big)_{E=\tilde{E}}. \tag{4.163}$$

We have

$$\Big(\frac{\partial^2 \ln g}{\partial E^2}\Big)_{E=\tilde{E}} = \frac{\partial}{\partial E}\Big(\frac{\partial \ln g}{\partial E}\Big)_{E=\tilde{E}} = \frac{\partial \beta}{\partial E}. \tag{4.164}$$

Finally, we obtain

$$\frac{\partial \beta}{\partial E} = -\frac{1}{kT^2}\frac{\partial T}{\partial E} = -\frac{1}{kT^2 C_V}. \tag{4.165}$$

We can use these results to expand $\ln p(E)$ about $E = \tilde{E}$ through second order in $(E - \tilde{E})^2$. The result is

$$\ln p(E) = \ln p(\tilde{E}) - \frac{(E-\tilde{E})^2}{2kT^2 C_V} + \cdots, \tag{4.166}$$

or

$$p(E) = p(\tilde{E})e^{-(E-\tilde{E})^2/2kT^2C_V}. \tag{4.167}$$

We see that (4.167) is the standard form of a Gaussian distribution (3.118) with $\overline{E} = \tilde{E}$ and $\sigma_E^2 = kT^2C_V$ as expected.

Vocabulary

composite system, subsystem

equal a priori probabilities

microcanonical ensemble, canonical ensemble, grand canonical ensemble

Boltzmann distribution, Gibbs distribution

entropy S, Helmholtz free energy F, Gibbs free energy G, Landau potential Ω

demon algorithm, Metropolis algorithm

Additional Problems

Problem 4.35. Statistical nature of the Clausius statement of the second law

Discuss the statistical nature of the Clausius statement of the second law that energy cannot go spontaneously from a colder to a hotter body. Under what conditions is the statement applicable? In what sense is this statement incorrect? □

Problem 4.36. Fundamental nature of the second law

Given our discussion of the second law of thermodynamics from both the macroscopic and microscopic points of view, discuss the following quote:

> The law that entropy always increases, the Second Law of Thermodynamics, holds … the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations, then so much the worse for Maxwell's equations.… But if your theory is found to be against the second law of thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation. [Arthur Stanley Eddington, *The Nature of the Physical World*, Cambridge University Press (1932).] □

Problem 4.37. Another two subsystems

Consider an isolated composite system consisting of subsystems A and B that can exchange energy with each other. Subsystem A consists of three noninteracting spins, each having magnetic moment μ. Subsystem B consists of two noninteracting spins each with a magnetic moment 2μ. A magnetic field B is applied to both systems. (This problem is adapted from Reif [1965].)

(a) Suppose that the total energy is $E_{\rm tot} = -3\mu B$. What are the accessible microstates of the composite system? What is the probability $P(M)$ that system A has magnetic moment M?

(b) Suppose that subsystems A and B are initially separated from each other and that the magnetic moment of A is -3μ and the magnetic moment of B is $+4\mu$. The systems are then placed in thermal contact with one another and are allowed to exchange energy. What is the probability $P(M)$ that the magnetic moment of system A has one of its possible values M? What is the mean value of the magnetic moment of system A? □

Problem 4.38. Two magnetic systems in thermal contact

Consider two isolated systems of noninteracting spins with $N_A = 4$ and $N_B = 16$. Their initial energies are $E_A = -2\mu B$ and $E_B = -2\mu B$.

(a) What is the total number of microstates available to the composite system?

(b) If the two systems are now allowed to exchange energy with one another, what is the probability that system A has energy E_A?

(c) What is the mean value of E_A and its relative fluctuations? Calculate the analogous quantities for system B.

(d) What is the most probable macrostate for the composite system? □

***Problem 4.39.** An Einstein solid and a magnetic system

Suppose that system A is an Einstein solid with $N_A = 8$ particles and system B consists of $N_B = 8$ noninteracting spins that can be either up or down. The external magnetic field is such that $\mu B = 1/2$. The magnitude of μB has been chosen so that the changes in the energy of system B and system A are $\Delta E = \pm 1$. The two systems are initially isolated and the initial energies are $E_A = 4$ and $E_B = -1$. What is the initial entropy of the composite system? Remove the internal constraint and allow the two systems to exchange energy. Determine the probability $P_A(E_A)$ that system A has energy E_A, the mean and variance of the energy of each subsystem, the most probable energies $\tilde{E}_A$ and $\tilde{E}_B$, and the probability that energy goes from system A to system B and from system B to system A. Which system is hotter initially? What is the change in the total entropy of the system? □

***Problem 4.40.** Number of states of the one-dimensional Ising model

We can determine the number of microstates $\Omega(E, N)$ of the one-dimensional Ising model for small N by counting on our fingers. For example, it is easy to verify that $\Omega(-2, 2) = 2$, $\Omega(0, 2) = 2$, $\Omega(-3, 3) = 2$, and $\Omega(1, 3) = 6$ for toroidal boundary conditions where the last spin is a neighbor of the first spin. The general expression for $\Omega(E, N)$ for the one-dimensional Ising model for even N in the absence of an external magnetic field is

$$\Omega(E,N) = 2\binom{N}{i} = 2\frac{N!}{i!\,(N-i)!} \qquad (i = 0, 2, 4, \ldots, N), \tag{4.168}$$

where $i = (E+N)/2$ is the number of pairs of nearest neighbor spins pointing in opposite directions. The energy E is measured in units of J so E is an integer.

(a) Verify that (4.168) gives the correct answers for $N = 2$ and 4.

(b) Use the result (4.168) to calculate the free energy for $N = 2$ and 4.

(c) Derive (4.168) by considering the number of ways that i pairs of antiparallel spins can be placed on a lattice. We will discuss the Ising model in more detail in Chapter 5. □

Problem 4.41. Partition function of two independent systems

Show that the partition function Z_{AB} of two independent distinguishable systems A and B both in equilibrium with a heat bath at temperature T equals the product of the partition functions of the separate systems:

$$Z_{AB} = Z_A Z_B. \tag{4.169}$$

□

Problem 4.42. A simple density of states

Suppose that the number of microstates between energy E and $E + \Delta E$ of an isolated system of N particles in a volume V is given by

$$g(E)\Delta E = c(V - bN)^N \Big[E + \frac{N^2 a}{V}\Big]^{3N/2} \Delta E, \tag{4.170}$$

where a, b, and c are constants.

(a) Determine the entropy of the system as a function of E, V, and N.

(b) Determine the temperature T as a function of E, V, and N.

(c) Determine the energy in terms of T, V, and N.

(d) What is the pressure as a function of T and $\rho = N/V$? □

Problem 4.43. Derivation of the ideal classical gas equations of state

Discuss the assumptions that were needed to derive the ideal classical gas equations of state, (4.65) and (4.67). □

Problem 4.44. Qualitative behavior of the density of states

Assume that the density of states $g(E) = E^{3N/2}$ for an ideal classical gas in three dimensions. Plot $g(E), e^{-\beta E}$, and the product $g(E)\, e^{-\beta E}$ versus E for $N = 6$ and $\beta = 1$. What is the qualitative behavior of the three functions? Show that the product $g(E)e^{-\beta E}$ has a maximum at $\tilde{E} = 3N/(2\beta)$. Compare this value to the mean value of E given by

$$\overline{E} = \frac{\int_0^\infty E g(E) e^{-\beta E} dE}{\int_0^\infty g(E) e^{-\beta E} dE}. \tag{4.171}$$

□

Problem 4.45. A simple partition function

The partition function of a hypothetical system is given by

$$\ln Z = aT^4V, \tag{4.172}$$

where a is a constant. Evaluate the mean energy E, the pressure P, and the entropy S. □

Problem 4.46. An analogy for the heat capacity

The following analogy might be useful for understanding the temperature dependence of the heat capacity of a two-state system.

(a) Suppose that you walked into a store with a few dollars in your pocket, and all the items to purchase cost over \$100. Clearly, you wouldn't be able to buy anything. Would your ability to make a purchase change if somebody gave you an extra dollar?

(b) Now assume you walked into the same store after winning the lottery. Would your ability to make a purchase change if somebody gave you an extra dollar?

(c) How much money should you have in your pocket so that an extra dollar would make a difference?

(d) What is the (poor) analogy to the temperature dependence of the heat capacity of a two-state system? □

Problem 4.47. Qualitative temperature dependence of a two-state system

Consider a system of N noninteracting, distinguishable particles each of which can be in single-particle microstates with energy 0 and Δ (see Example 4.2). The system is in equilibrium with a heat bath at temperature T. Answer parts (a)–(c) without doing any explicit calculations.

(a) Sketch the temperature-dependence of the probability that a given particle is in the ground state. Then do the same for the probability that the particle is in the excited state. Discuss the limiting behavior of the probabilities for low and high temperatures. What does high and low temperature mean in this case?

(b) Sketch the T-dependence of the mean energy $E(T)$ and give a simple argument for its behavior.

(c) From your sketch of $E(T)$ sketch the T-dependence of the heat capacity $C(T)$ and describe its qualitative behavior. Give a simple physical argument why C has a maximum and estimate the temperature at which the maximum occurs.

(d) Calculate $C(T)$ explicitly and verify that its behavior is consistent with the qualitative features illustrated in your sketch. The maximum in the heat capacity of a two-state system is sometimes called the Schottky anomaly for historical reasons, but the characterization of this behavior as an anomaly is a misnomer because many systems in nature behave as two-state systems. □

Problem 4.48. Qualitative behavior of the heat capacity for a simple system

Consider a system of N noninteracting, distinguishable particles. Each particle can be in one of three states with energies 0, Δ, and 10Δ. Without doing an explicit calculation, sketch the temperature dependence of the heat capacity. □

Problem 4.49. Mean energy of a two-state system

Consider a system of one particle in equilibrium with a heat bath. The particle has two microstates of energy $\epsilon_1 = 0$ and $\epsilon_2 = \Delta$. Find the probabilities p_1 and p_2 for the mean energy of the system to be 0.2Δ, 0.4Δ, 0.5Δ, 0.6Δ, and Δ, respectively. What are the corresponding temperatures? (Hint: Write the mean energy as $x\Delta$ and express your answers in terms of x.) ☐

Problem 4.50. One-dimensional harmonic oscillators in equilibrium with a heat bath

(a) Calculate the specific heat of the one-dimensional harmonic oscillator as a function of temperature (see Example 4.3).

(b) Plot the T-dependence of the mean energy per particle E/N and the specific heat c. Show that $E \to kT$ at high temperatures for which $kT \gg \hbar\omega$. This result corresponds to the classical limit and will be shown in Section 6.2.1 to be an example of the equipartition theorem. In this limit the energy kT is large in comparison to $\hbar\omega$, the separation between energy levels. Hint: expand the exponential function in (4.132).

(c) Show that at low temperatures for which $\hbar\omega \gg kT$, $E/N = \hbar\omega(\frac{1}{2} + e^{-\beta\hbar\omega})$. What is the value of the heat capacity? Why is the latter so much smaller than it is in the high temperature limit? Why is this behavior different from that of a two-state system?

(d) Verify that $S \to 0$ as $T \to 0$ in agreement with the third law of thermodynamics, and that at high T, $S \to kN\ln(kT/\hbar\omega)$. ☐

Problem 4.51. The compressibility and fluctuations

We have found that the constant volume heat capacity is related to the variance of the energy fluctuations in the canonical ensemble [see (4.88)]. The isothermal compressibility is defined as [see (2.172)]

$$\kappa = -\frac{1}{V}\Big(\frac{\partial V}{\partial P}\Big)_T. \tag{4.173}$$

Explain why κ can be interpreted as a linear response. In analogy to the relation of C_V to energy fluctuations, what type of fluctuations do you think are related to κ at fixed T, P, and N? ☐

Problem 4.52. Consider the system illustrated in Figure 4.9. The system consists of two distinguishable particles, each of which can be in either of two boxes. The system is in thermal equilibrium with a heat bath at temperature T. Assume that the energy of a particle is zero if it is in the left box and r if it is in the right box. There is also a correlation energy term that increases the energy by Δ if the two particles are in the same box.

(a) Enumerate the $2^2 = 4$ microstates and their corresponding energy.

(b) Calculate the partition function Z for arbitrary values of r and Δ and use your result to find the mean energy.

(c) What is the probability that the system is in a particular microstate?

(d) Suppose that $r = 1$ and $\Delta = 15$. Sketch the qualitative behavior of the heat capacity C as a function of T. ☐

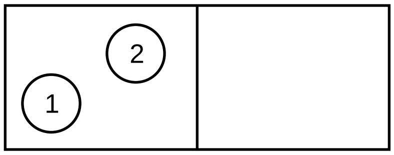

Figure 4.9: The two particles considered in Problem 4.52. The two distinguishable particles can each be in one of the two boxes. The energy of the system depends on which box the particles occupy.

Problem 4.53. Grand partition function of a simple system

Consider a system in equilibrium with a heat bath at temperature T and a particle reservoir at chemical potential μ. The system has a minimum of one particle and a maximum of four distinguishable particles. The particles in the system do not interact and can be in one of two states with energies zero or Δ. Determine the (grand) partition function of the system. ☐

Problem 4.54. Constant pressure ensemble

In the text we derived the form of the probability distribution for a system with fixed T, V, and N (the canonical ensemble) and fixed T, V, and μ (the grand canonical ensemble). What is the form of the probability distribution for an equilibrium system with fixed T, P, and N? This ensemble has no generally accepted name and is not particularly useful for calculations. However, it is useful for doing simulations at a given pressure rather than for a given volume. ☐

Problem 4.55. Alternative derivation of the Boltzmann distribution

Consider a system with a given mean energy $\overline{E}$ and a normalized probability distribution P_s, where P_s is the probability that the system is in microstate s with energy E_s. Show that the Boltzmann distribution maximizes the uncertainty or missing information given the constraints that P_s is normalized and the mean energy is specified (see Section 3.11.1). This derivation does not yield a physical interpretation of the parameter β. How would you determine β in terms of the known constant $\overline{E}$? ☐

Problem 4.56. Demonstration of an entropy-driven transition

The following demonstration illustrates an entropy-driven transition. Get a bag of M&Ms or similar disk-shaped candy. Ball bearings work better, but they are not as tasty. You will also need a flat bottomed glass dish (preferably square) that fits on an overhead projector.

Place the glass dish on the overhead projector and add a few of the candies. Shake the dish gently from side to side to simulate the effects of temperature. You should observe a two-dimensional model of a gas. Gradually add more candies while continuing to shake the dish. As the density is increased further, you will begin to notice clusters of hexagonal crystals.

(a) At what density do large clusters of hexagonal crystals begin to appear?

(b) Do these clusters disappear if you shake the dish faster?

(c) Is energy conserved in this system? Do the particles move if you do not shake the dish?

(d) Compare the behavior of this system (an example of granular matter) to the behavior of a usual gas or liquid. ☐

Suggestions for Further Reading

Joan Adler, "A walk in phase space: Solidification into crystalline and amorphous states," Am. J. Phys. **67**, 1145–1148 (1999). Adler and Laird discuss the demonstration in Problem 4.56.

Ralph Baierlein, *Thermal Physics*, Cambridge University Press, New York (1999).

George B. Benedek and Felix M. H. Villars, *Physics with Illustrative Examples from Medicine and Biology: Statistical Physics*, second edition, Springer (2000).

Carlo Cercignani, *Ludwig Boltzmann: The Man Who Trusted Atoms*, Oxford University Press (1998).

Ruth Chabay and Bruce Sherwood, *Matter & Interactions*, Vol. 1, 3rd ed., John Wiley & Sons (2010). This introductory text discusses the Einstein solid in the same spirit as our text.

Harvey Leff and Andrew F. Rex, editors, *Maxwell's Demon 2: Entropy, Classical and Quantum Information, Computing*, CRC Press (2003).

Brian B. Laird, "Entropy, disorder and freezing," J. Chem. Educ. **76**, 1388–1390 (1999).

Thomas A. Moore and Daniel V. Schroeder, "A different approach to introducing statistical mechanics," Am. J. Phys. **65**, 26–36 (1997).

F. Reif, *Statistical Physics*, Volume 5 of the Berkeley Physics Series, McGraw-Hill (1965).

W. G. V. Rosser, *An Introduction to Statistical Physics*, Ellis Horwood (1982). As far as we know, this book was the first to introduce the Einstein solid in the context of the counting of states and the thermal interaction of simple systems.

Daniel V. Schroeder, *An Introduction to Thermal Physics*, Addison-Wesley (1999).

Jan Tobochnik, Harvey Gould, and Jon Machta, "Understanding the temperature and the chemical potential using computer simulations," Am. J. Phys. **73**(8), 708–716 (2005). This article describes the demon algorithm in detail for use as an ideal thermometer and as an ideal chemical potential meter (see Section 7.2).

Jan Tobochnik and Harvey Gould, "Teaching statistical physics by thinking about models and algorithms," Am. J. Phys. **76**, 353–359 (2008). This article describes why Monte Carlo simulations give the correct thermodynamic averages and discusses ways of simulating systems more efficiently.

Chapter 5

Magnetic Systems

3 June 2011

We apply the general formalism of statistical mechanics developed in Chapter 4 to the Ising model, a model for which the interactions between the magnetic moments are important. We will find that these interactions lead to a wide range of interesting phenomena, including the existence of phase transitions. Computer simulations will be used extensively and a simple, but powerful approximation method known as mean-field theory will be introduced.

5.1 Paramagnetism

The most familiar magnetic system in our everyday experience is probably the magnet on a refrigerator door. This magnet likely consists of iron ions localized on sites of a lattice with conduction electrons that are free to move throughout the crystal. The iron ions each have a magnetic moment and, due to a complicated interaction with each other and with the conduction electrons, they tend to line up with each other. At sufficiently low temperatures, the moments can be aligned by an external magnetic field and produce a net magnetic moment or magnetization which remains even if the magnetic field is removed. Materials that retain a nonzero magnetization in zero magnetic field are called *ferromagnetic*. At high enough temperatures there is enough energy to destroy the magnetization, and the iron is said to be in the *paramagnetic* phase. One of the key goals of this chapter is to understand the transition between the ferromagnetic and paramagnetic phases.

In the simplest model of magnetism the magnetic moment can be in one of two states as discussed in Section 4.3.1. The next level of complexity is to introduce an interaction between neighboring magnetic moments. A model that includes such an interaction is discussed in Section 5.4.

5.2 Noninteracting Magnetic Moments

We first review the behavior of a system of noninteracting magnetic moments with spin 1/2 in equilibrium with a heat bath at temperature T. We discussed this system in Section 4.3.1 and in Example 4.1 using the microcanonical ensemble.

The energy of interaction of a magnetic moment $\boldsymbol{\mu}$ in a magnetic field $\mathbf{B}$ is given by

$$E = -\boldsymbol{\mu}\cdot\mathbf{B} = -\mu_z B, \tag{5.1}$$

where μ_z is the component of the magnetic moment in the direction of the magnetic field $\mathbf{B}$. Because the magnetic moment has spin 1/2, it has two possible orientations. We write $\mu_z = s\mu$, where $s = \pm 1$. The association of the magnetic moment of a particle with its spin is an intrinsic quantum mechanical effect (see Section 5.10.1). We will refer to the magnetic moment or the spin of a particle interchangeably.

What would we like to know about the properties of a system of noninteracting spins? In the absence of an external magnetic field, there is little of interest. The spins point randomly up or down because there is no preferred direction, and the mean internal energy is zero. In contrast, in the presence of an external magnetic field, the net magnetic moment and the energy of the system are nonzero. In the following we will calculate their mean values as a function of the external magnetic field B and the temperature T.

We assume that the spins are fixed on a lattice so that they are *distinguishable* even though the spins are intrinsically quantum mechanical. Hence the only quantum mechanical property of the system is that the spins are restricted to two values. As we will learn, the usual choice for determining the thermal properties of systems defined on a lattice is the canonical ensemble.

Because each spin is independent of the others and distinguishable, we can find the partition function for one spin, Z_1, and use the relation $Z_N = Z_1^N$ to obtain Z_N, the partition function for N spins. (We reached a similar conclusion in Example 4.2.) We can derive this relation between Z_1 and Z_N by writing the energy of the N spins as $E = -\mu B\sum_{i=1}^N s_i$ and expressing the partition function Z_N for the N-spin system as

$$Z_N = \sum_{s_1=\pm1}\sum_{s_2=\pm1}\cdots\sum_{s_N=\pm1} e^{\beta\mu B\Sigma_{i=1}^N s_i} \tag{5.2a}$$

$$= \sum_{s_1=\pm1}\sum_{s_2=\pm1}\cdots\sum_{s_N=\pm1} e^{\beta\mu B s_1}e^{\beta\mu B s_2}\ldots e^{\beta\mu B s_N} \tag{5.2b}$$

$$= \sum_{s_1=\pm1} e^{\beta\mu B s_1}\sum_{s_2=\pm1} e^{\beta\mu B s_2}\cdots\sum_{s_N=\pm1} e^{\beta\mu B s_N} \tag{5.2c}$$

$$= \Big[\sum_{s_1=\pm1} e^{\beta\mu B s_1}\Big]^N = Z_1^N. \tag{5.2d}$$

To find Z_1 we write

$$Z_1 = \sum_{s=\pm1} e^{\beta\mu B s} = e^{\beta\mu B(-1)} + e^{\beta\mu B(+1)} = 2\cosh\beta\mu B. \tag{5.3}$$

Hence, the partition function for N spins is

$$Z_N = (2\cosh\beta\mu B)^N. \tag{5.4}$$

We now use the canonical ensemble formalism that we developed in Section 4.6 to find the thermodynamic properties of the system for a given T and B. The free energy is given by

$$F = -kT\ln Z_N = -NkT\ln Z_1 = -NkT\ln(2\cosh\beta\mu B). \tag{5.5}$$

The mean energy $\overline{E}$ is

$$\overline{E} = -\frac{\partial \ln Z_N}{\partial\beta} = \frac{\partial(\beta F)}{\partial\beta} = -N\mu B\,\tanh\beta\mu B. \tag{5.6}$$

From (5.6) we see that $\overline{E} \to 0$ as $T \to \infty$ ($\beta \to 0$). In the following we will frequently omit the mean value notation when it is clear from the context that an average is implied.

Problem 5.1. Comparison of the results for two ensembles

(a) Compare the result (5.6) for the mean energy $\overline{E}(T)$ of a system of noninteracting spins in the canonical ensemble to the result that you found in Problem 4.21 for $T(E)$ using the microcanonical ensemble.

(b) Why is it much easier to treat a system of noninteracting spins in the canonical ensemble?

(c) What is the probability p that a spin is parallel to the magnetic field B given that the system is in equilibrium with a heat bath at temperature T? Compare your result to the result in (4.74) using the microcanonical ensemble.

(d) What is the relation of the results that we have found for a system of noninteracting spins to the results obtained in Example 4.2? □

The heat capacity C is a measure of the change of the temperature due to the addition of energy at constant magnetic field. The heat capacity at constant magnetic field can be expressed as

$$C = \Big(\frac{\partial E}{\partial T}\Big)_B = -k\beta^2\frac{\partial E}{\partial\beta}. \tag{5.7}$$

(We will write C rather than C_B.) From (5.6) and (5.7) we find that the heat capacity of a system of N noninteracting spins is given by

$$C = kN(\beta\mu B)^2\,\mathrm{sech}^2\,\beta\mu B. \tag{5.8}$$

Note that the heat capacity is always positive, goes to zero at high T, and goes to zero as $T \to 0$, consistent with the third law of thermodynamics.

Magnetization and susceptibility. Two other macroscopic quantities of interest for magnetic systems are the mean magnetization M (in the z direction) given by

$$M = \mu\sum_{i=1}^{N}\overline{s}_i, \tag{5.9}$$

and the isothermal susceptibility χ, which is defined as

$$\chi = \Big(\frac{\partial M}{\partial B}\Big)_T. \tag{5.10}$$

The susceptibility χ is a measure of the change of the magnetization due to the change in the external magnetic field and is another example of a response function.

We will frequently omit the factor of μ in (5.9) so that M becomes the number of spins pointing in a given direction minus the number pointing in the opposite direction. Often it is more convenient to work with the mean magnetization per spin m, an intensive variable, which is defined as

$$m = \frac{1}{N}M. \tag{5.11}$$

As for the discussion of the heat capacity and the specific heat, the meaning of M and m will be clear from the context.

We can express M and χ in terms of derivatives of $\ln Z$ by noting that the total energy can be expressed as

$$E = E_0 - MB, \tag{5.12}$$

where E_0 is the energy of interaction of the spins with each other (the energy of the system when $B = 0$) and $-MB$ is the energy of interaction of the spins with the external magnetic field. (For noninteracting spins $E_0 = 0$.) The form of E in (5.12) implies that we can write Z in the form

$$Z = \sum_s e^{-\beta(E_{0,s} - M_s B)}, \tag{5.13}$$

where M_s and $E_{0,s}$ are the values of M and E_0 in microstate s. From (5.13) we have

$$\frac{\partial Z}{\partial B} = \sum_s \beta M_s\, e^{-\beta(E_{0,s} - M_s B)}, \tag{5.14}$$

and hence the mean magnetization is given by

$$M = \frac{1}{Z}\sum_s M_s e^{-\beta(E_{0,s} - M_s B)} \tag{5.15a}$$

$$= \frac{1}{\beta Z}\frac{\partial Z}{\partial B} = kT\frac{\partial \ln Z_N}{\partial B}. \tag{5.15b}$$

If we substitute the relation $F = -kT\ln Z$, we obtain

$$M = -\frac{\partial F}{\partial B}. \tag{5.16}$$

Problem 5.2. Relation of the susceptibility to the magnetization fluctuations

Use considerations similar to that used to derive (5.15b) to show that the isothermal susceptibility can be written as

$$\boxed{\chi = \frac{1}{kT}[\overline{M^2} - \overline{M}^2]}. \tag{5.17}$$

Note the similarity of the form (5.17) with the form (4.88) for the heat capacity C_V. ☐

The relation of the response functions C_V and χ to the equilibrium fluctuations of the energy and magnetization, respectively, are special cases of a general result known as the fluctuation-dissipation theorem.

Example 5.1. Magnetization and susceptibility of a noninteracting system of spins

From (5.5) and (5.16) we find that the mean magnetization of a system of noninteracting spins is

$$M = N\mu \tanh(\beta\mu B). \tag{5.18}$$

The susceptibility can be calculated using (5.10) and (5.18) and is given by

$$\chi = N\mu^2\beta \,\text{sech}^2(\beta\mu B). \tag{5.19}$$

♢

Note that the arguments of the hyperbolic functions in (5.18) and (5.19) must be dimensionless and be proportional to the ratio $\mu B/kT$. Because there are only two energy scales in the system, μB, the energy of interaction of a spin with the magnetic field, and kT, the arguments must depend only on the dimensionless ratio $\mu B/kT$.

For high temperatures $kT \gg \mu B$ ($\beta\mu B \ll 1$), $\text{sech}(\beta\mu B) \to 1$, and the leading behavior of χ is given by

$$\chi \to N\mu^2\beta = \frac{N\mu^2}{kT} \qquad (kT \gg \mu B). \tag{5.20}$$

The result (5.20) is known as the Curie form of the isothermal susceptibility and is commonly observed for magnetic materials at high temperatures.

From (5.18) we see that M is zero at $B = 0$ for all $T > 0$, which implies that the system is paramagnetic. Because a system of noninteracting spins is paramagnetic, such a model is not applicable to materials such as iron which can have a nonzero magnetization even when the magnetic field is zero. Ferromagnetism is due to the interactions between the spins.

Problem 5.3. Thermodynamics of noninteracting spins

(a) Plot the magnetization given by (5.18) and the heat capacity C given in (5.8) as a function of T for a given external magnetic field B. Give a simple argument why C must have a broad maximum somewhere between $T = 0$ and $T = \infty$.

(b) Plot the isothermal susceptibility χ versus T for fixed B and describe its limiting behavior for low temperatures.

(c) Calculate the entropy of a system of N noninteracting spins and discuss its limiting behavior at low ($kT \ll \mu B$) and high temperatures ($kT \gg \mu B$). Does S depend on kT and μB separately? □

Problem 5.4. Adiabatic demagnetization

Consider a solid containing N noninteracting paramagnetic atoms whose magnetic moments can be aligned either parallel or antiparallel to the magnetic field B. The system is in equilibrium with a heat bath at temperature T. The magnetic moment is $\mu = 9.274 \times 10^{-24}$ J/tesla.

(a) If $B = 4$ tesla, at what temperature is 75% of the spins oriented in the $+z$ direction?

(b) Assume that $N = 10^{23}$, $T = 1\,\mathrm{K}$, and B is increased quasistatically from 1 tesla to 10 tesla. What is the magnitude of the energy transfer from the heat bath?

(c) If the system is now thermally isolated at $T = 1\,\mathrm{K}$ and B is quasistatically decreased from 10 tesla to 1 tesla, what is the final temperature of the system? This process is known as *adiabatic demagnetization*. (This problem can be solved without elaborate calculations.) ☐

5.3 Thermodynamics of Magnetism

The fundamental magnetic field is **B**. However, we can usually control only the part of **B** due to currents in wires, and cannot directly control that part of the field due to the magnetic dipoles in a material. Thus, we define a new field **H** by

$$\mathbf{H} = \frac{1}{\mu_0}\mathbf{B} - \frac{\mathbf{M}}{V}, \tag{5.21}$$

where **M** is the magnetization and V is the volume of the system. In this section we use V instead of N to make contact with standard notation in electromagnetism. Our goal in this section is to find the magnetic equivalent of the thermodynamic relation $dW = -PdV$ in terms of **H**, which we can control, and **M**, which we can measure. To gain insight into how to do so we consider a solenoid of length L and n turns per unit length with a magnetic material inside. When a current I flows in the solenoid, there is an emf $\mathcal{E}$ generated in the solenoid wires. The power or rate at which work is done on the magnetic substance is $-\mathcal{E}I$. By Faraday's law we know that

$$\mathcal{E} = -\frac{d\Phi}{dt} = -ALn\frac{dB}{dt}, \tag{5.22}$$

where the cross-sectional area of the solenoid is A, the magnetic flux through each turn is $\Phi = BA$, and there are Ln turns. The work done on the system is

$$dW = -\mathcal{E}Idt = ALnIdB. \tag{5.23}$$

Ampere's law can be used to find that the field H within the ideal solenoid is uniform and is given by

$$H = nI. \tag{5.24}$$

Hence, (5.23) becomes

$$dW = ALHdB = VHdB. \tag{5.25}$$

We use (5.21) to express (5.25) as

$$dW = \mu_0 VHdH + \mu_0 HdM. \tag{5.26}$$

The first term on the right-hand side of (5.26) refers only to the field energy, which would be there even if there were no magnetic material inside the solenoid. Thus, for the purpose of understanding the thermodynamics of the magnetic material, we can neglect the first term and write

$$dW = \mu_0 HdM. \tag{5.27}$$

The form of (5.27) leads us to introduce the magnetic free energy $G(T,M)$, given by

$$dG(T,M) = -SdT + \mu_0 HdM. \tag{5.28}$$

We use the notation G for the free energy as a function of T and M and reserve F for the free energy $F(T,H)$. We define

$$F = G - \mu_0 HM, \tag{5.29}$$

and find

$$\begin{aligned} dF(T,H) &= dG - \mu_0 HdM - \mu_0 MdH && \text{(5.30a)}\\ &= -SdT + \mu_0 HdM - \mu_0 HdM - \mu_0 MdH && \text{(5.30b)}\\ &= -SdT - \mu_0 MdH. && \text{(5.30c)} \end{aligned}$$

Thus, we have

$$\mu_0 M = -\frac{\partial F}{\partial H}. \tag{5.31}$$

The factor of μ_0 is usually incorporated into H, so that we will usually write

$$F(T,H) = G(T,M) - HM, \tag{5.32}$$

as well as $dW = HdM$ and $dG = -SdT + HdM$. Similarly, we will write $dF = -SdT - MdH$, and thus

$$\boxed{M = -\Big(\frac{\partial F}{\partial H}\Big)_T}. \tag{5.33}$$

We also write

$$\boxed{\chi = \Big(\frac{\partial M}{\partial H}\Big)_T}. \tag{5.34}$$

The free energy $F(T,H)$ is frequently more useful because the quantities T and H are the easiest to control experimentally as well as in computer simulations.

5.4 The Ising Model

As we saw in Section 5.1 the absence of interactions between spins implies that the system can only be paramagnetic. The most important and simplest system that exhibits a phase transition is the *Ising model*.[1] The model was proposed by Wilhelm Lenz (1888–1957) in 1920 and was solved exactly for one dimension by his student Ernst Ising[2] (1900–1998) in 1925. Ising was disappointed because the one-dimensional model does not have a phase transition. Lars Onsager (1903–1976) solved the Ising model exactly in 1944 for two dimensions in the absence of an external magnetic field and showed that there was a phase transition in two dimensions.[3]

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[1] Each year hundreds of papers are published that apply the Ising model to problems in fields as diverse as neural networks, protein folding, biological membranes, and social behavior. For this reason the Ising model is sometimes known as the "fruit fly" of statistical mechanics.

[2] A biographical note about Ernst Ising can be found at `<www.bradley.edu/las/phy/personnel/ising.html>`.

[3] The model is sometimes known as the Lenz-Ising model. The history of the Ising model is discussed by Brush (1967).

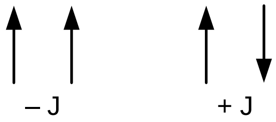

Figure 5.1: Two nearest neighbor spins (in any dimension) have an interaction energy $-J$ if they are parallel and interaction energy $+J$ if they are antiparallel.

In the Ising model the spin at every site is either up (+1) or down (−1). Unless otherwise stated, the interaction is between nearest neighbors only and is given by $-J$ if the spins are parallel and $+J$ if the spins are antiparallel. The total energy can be expressed in the form[4]

$$\boxed{E = -J \sum_{i,j=\mathrm{nn}(i)}^{N} s_i s_j - H \sum_{i=1}^{N} s_i} \qquad \text{(Ising model)}, \tag{5.35}$$

where $s_i = \pm 1$ and J is known as the exchange constant. We will assume that $J > 0$ unless otherwise stated and that the external magnetic field is in the up or positive z direction. In the following we will refer to s as the spin.[5] The first sum in (5.35) is over all pairs of spins that are nearest neighbors. The interaction between two nearest neighbor spins is counted only once. A factor of μ has been incorporated into H, which we will refer to as the magnetic field. In the same spirit the magnetization becomes the net number of positive spins, that is, the number of up spins minus the number of down spins.

Because the number of spins is fixed, we will choose the canonical ensemble and evaluate the partition function. In spite of the apparent simplicity of the Ising model it is possible to obtain exact solutions only in one dimension and in two dimensions in the absence of a magnetic field.[6] In other cases we need to use various approximation methods and computer simulations. There is no general recipe for how to perform the sums and integrals needed to calculate thermodynamic quantities.

5.5 The Ising Chain

In the following we obtain an exact solution of the one-dimensional Ising model and introduce an additional physical quantity of interest.

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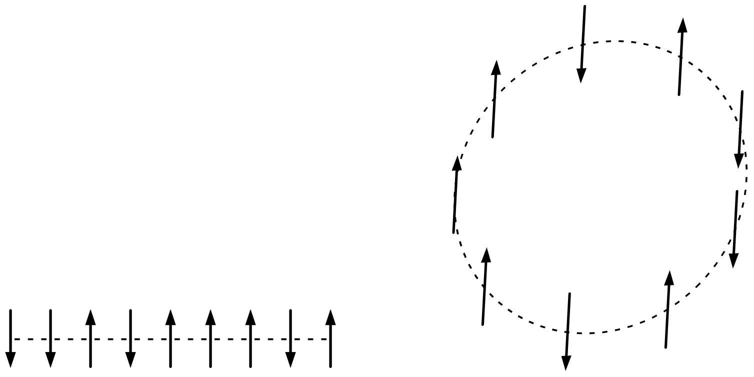
[4] If we interpret the spin as an operator, then the energy is really a Hamiltonian. The distinction is unimportant here.

[5] Because the spin $\hat{S}$ is a quantum mechanical object, we might expect that the commutator of the spin operator with the Hamiltonian is nonzero. However, because the Ising model retains only the component of the spin along the direction of the magnetic field, the commutator of the spin $\hat{S}$ with the Hamiltonian is zero, and we can treat the spins in the Ising model as if they were classical.

[6] It has been shown that the three-dimensional Ising model (and the two-dimensional Ising model with nearest neighbor and next nearest neighbor interactions) is computationally intractable and falls into the same class as other problems such as the traveling salesman problem. See `<www.sandia.gov/LabNews/LN04-21-00/sorin_story.html>` and `<www.siam.org/siamnews/07-00/ising.pdf>`. The Ising model is of interest to computer scientists in part for this reason.



(a) (b)

Figure 5.2: (a) Example of free boundary conditions for $N = 9$ spins. The spins at each end interact with only one spin. In contrast, all the other spins interact with two spins. (b) Example of toroidal boundary conditions. The Nth spin interacts with the first spin so that the chain forms a ring. As a result, all the spins have the same number of neighbors and the chain does not have a surface.

5.5.1 Exact enumeration

As we mentioned, the canonical ensemble is the natural choice for calculating the thermodynamic properties of systems defined on a lattice. Because the spins are interacting, the relation $Z_N = Z_1^N$ is not applicable. The calculation of the partition function Z_N is straightforward in principle. The goal is to enumerate all the microstates of the system and their corresponding energies, calculate Z_N for finite N, and then take the limit $N \to \infty$. The difficulty is that the total number of states, 2^N, is too many for $N \gg 1$. However, for the one-dimensional Ising model (Ising chain) we can calculate Z_N for small N and easily see how to generalize to arbitrary N.

For a finite chain we need to specify the boundary conditions. One possibility is to choose free ends so that the spin at each end has only one neighbor instead of two [see Figure 5.2(a)]. Another choice is toroidal boundary conditions as shown in Figure 5.2(b). This choice implies that the Nth spin is connected to the first spin so that the chain forms a ring. In this case every spin is equivalent, and there is no boundary or surface. The choice of boundary conditions does not matter in the thermodynamic limit, $N \to \infty$.

In the absence of an external magnetic field it is more convenient to choose free boundary conditions when calculating Z directly. (We will choose toroidal boundary conditions when doing simulations.) The energy of the Ising chain in the absence of an external magnetic field with free boundary conditions is given explicitly by

$$E = -J \sum_{i=1}^{N-1} s_i s_{i+1} \qquad \text{(free boundary conditions)}. \tag{5.36}$$

We begin by calculating the partition function for two spins. There are four possible states: both spins up with energy $-J$, both spins down with energy $-J$, and two states with one spin up

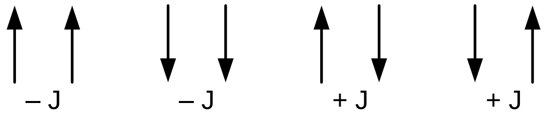


Figure 5.3: The four possible microstates of the $N = 2$ Ising chain.

and one spin down with energy $+J$ (see Figure 5.3). Thus Z_2 is given by

$$Z_2 = 2e^{\beta J} + 2e^{-\beta J} = 4\cosh\beta J. \tag{5.37}$$

In the same way we can enumerate the eight microstates for $N = 3$. We find that

$$\begin{aligned} Z_3 &= 2\,e^{2\beta J} + 4 + 2\,e^{-2\beta J} = 2(e^{\beta J} + e^{-\beta J})^2 && (5.38a)\\ &= (e^{\beta J} + e^{-\beta J})Z_2 = (2\cosh\beta J)Z_2. && (5.38b)\end{aligned}$$

The relation (5.38b) between Z_3 and Z_2 suggests a general relation between Z_N and Z_{N-1}:

$$Z_N = (2\cosh\beta J)Z_{N-1} = 2\big(2\cosh\beta J\big)^{N-1}. \tag{5.39}$$

We can derive the recursion relation (5.39) directly by writing Z_N for the Ising chain in the form

$$Z_N = \sum_{s_1=\pm1}\cdots\sum_{s_N=\pm1} e^{\beta J\sum_{i=1}^{N-1} s_i s_{i+1}}. \tag{5.40}$$

The sum over the two possible states for each spin yields 2^N microstates. To understand the meaning of the sums in (5.40), we write (5.40) for $N = 3$:

$$Z_3 = \sum_{s_1=\pm1}\sum_{s_2=\pm1}\sum_{s_3=\pm1} e^{\beta J s_1 s_2 + \beta J s_2 s_3}. \tag{5.41}$$

The sum over s_3 can be done independently of s_1 and s_2, and we have

$$\begin{aligned} Z_3 &= \sum_{s_1=\pm1}\sum_{s_2=\pm1} e^{\beta J s_1 s_2}\big[e^{\beta J s_2} + e^{-\beta J s_2}\big] && (5.42a)\\ &= \sum_{s_1=\pm1}\sum_{s_2=\pm1} e^{\beta J s_1 s_2} 2\cosh\beta J s_2 = 2\cosh\beta J \sum_{s_1=\pm1}\sum_{s_2=\pm1} e^{\beta J s_1 s_2}. && (5.42b)\end{aligned}$$

We have used the fact that the cosh function is even and hence $\cosh\beta J s_2 = \cosh\beta J$, independently of the sign of s_2. The sum over s_1 and s_2 in (5.42b) is Z_2. Thus Z_3 is given by

$$Z_3 = (2\cosh\beta J)Z_2, \tag{5.43}$$

in agreement with (5.38b).

The analysis of (5.40) for Z_N proceeds similarly. We note that spin s_N occurs only once in the exponential, and we have, independently of the value of s_{N-1},

$$\sum_{s_N=\pm1} e^{\beta J s_{N-1} s_N} = 2\cosh\beta J. \tag{5.44}$$

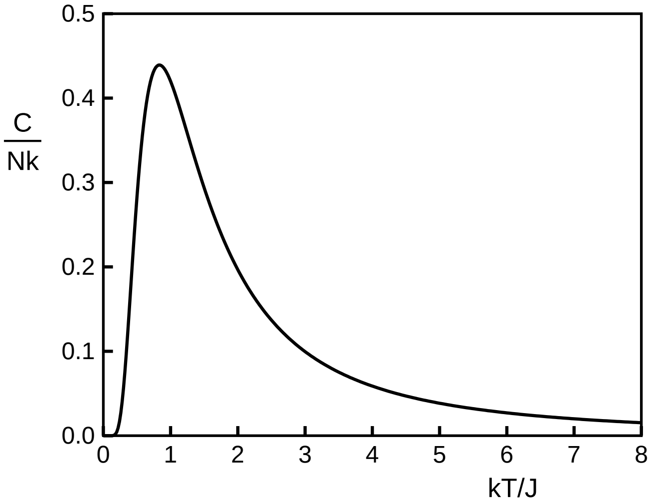


Figure 5.4: The temperature dependence of the specific heat (in units of k) of an Ising chain in the absence of an external magnetic field. At what value of kT/J does C exhibit a maximum?

Hence we can write Z_N as

$$Z_N = (2\cosh\beta J)Z_{N-1}. \tag{5.45}$$

We can continue this process to find

$$\begin{aligned} Z_N &= (2\cosh\beta J)^2 Z_{N-2} && (5.46a)\\ &= (2\cosh\beta J)^3 Z_{N-3} && (5.46b)\\ &\vdots \\ &= (2\cosh\beta J)^{N-1} Z_1 = 2(2\cosh\beta J)^{N-1}, && (5.46c)\end{aligned}$$

where we have used the fact that $Z_1 = \sum_{s_1=\pm1} 1 = 2$. No Boltzmann factor appears in Z_1 because there are no interactions with one spin.

We can use the general result (5.39) for Z_N to find the Helmholtz free energy:

$$F = -kT\ln Z_N = -kT\big[\ln 2 + (N-1)\ln(2\cosh\beta J)\big]. \tag{5.47}$$

In the thermodynamic limit $N \to \infty$, the term proportional to N in (5.47) dominates, and we have the desired result:

$$F = -NkT\ln\big(2\cosh\beta J\big). \tag{5.48}$$

Problem 5.5. Exact enumeration

Enumerate the 2^N microstates for the $N = 4$ Ising chain and find the corresponding contributions to Z_4 for free boundary conditions. Then show that Z_4 and Z_3 satisfy the recursion relation (5.45) for free boundary conditions. ☐

Problem 5.6. Thermodynamics of the Ising chain

(a) What is the ground state of the Ising chain?

(b) What is the entropy S in the limits $T \to 0$ and $T \to \infty$? The answers can be found without doing an explicit calculation.

(c) Use (5.48) for the free energy F to verify the following results for the entropy S, the mean energy $\overline{E}$, and the heat capacity C of the Ising chain:

$$S = Nk\big[\ln(e^{2\beta J} + 1) - \frac{2\beta J}{1 + e^{-2\beta J}}\big], \tag{5.49}$$

$$\overline{E} = -NJ \tanh \beta J, \tag{5.50}$$

$$C = Nk(\beta J)^2 (\operatorname{sech} \beta J)^2. \tag{5.51}$$

Verify that the results in (5.49)–(5.51) reduce to the appropriate behavior for low and high temperatures.

(d) A plot of the T dependence of the heat capacity in the absence of a magnetic field is given in Figure 5.4. Explain why it has a maximum. □

5.5.2 Spin-spin correlation function

We can gain further insight into the properties of the Ising model by calculating the spin-spin correlation function $G(r)$ defined as

$$G(r) = \overline{s_k s_{k+r}} - \overline{s_k}\, \overline{s_{k+r}}. \tag{5.52}$$

Because the average of s_k is independent of the choice of the site k (for toroidal boundary conditions) and equals $m = M/N$, $G(r)$ can be written as

$$G(r) = \overline{s_k s_{k+r}} - m^2. \tag{5.53}$$

The average is over all microstates. Because all lattice sites are equivalent, $G(r)$ is independent of the choice of k and depends only on the separation r (for a given T and H), where r is the separation between the two spins in units of the lattice constant. Note that $G(r = 0) = \overline{m^2} - \overline{m}^2 \propto \chi$ [see (5.17)].

The spin-spin correlation function $G(r)$ is a measure of the degree to which a spin at one site is correlated with a spin at another site. If the spins are not correlated, then $G(r) = 0$. At high temperatures the interaction between spins is unimportant, and hence the spins are randomly oriented in the absence of an external magnetic field. Thus in the limit $kT \gg J$, we expect that $G(r) \to 0$ for any r. For fixed T and H, we expect that, if spin k is up, then the two adjacent spins will have a greater probability of being up than down. For spins further away from spin k, we expect that the probability that spin $k + r$ is up or correlated will decrease. Hence, we expect that $G(r) \to 0$ as $r \to \infty$.

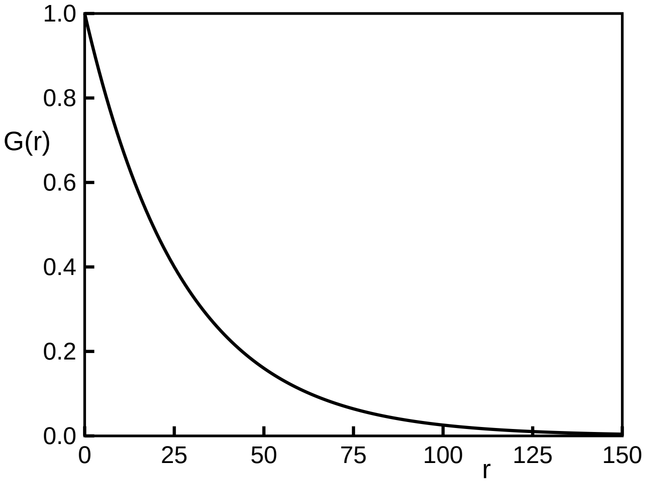


Figure 5.5: Plot of the spin-spin correlation function $G(r)$ as given by (5.54) for the Ising chain for $\beta J = 2$.

Problem 5.7. Calculation of $G(r)$ for three spins

Consider an Ising chain of $N = 3$ spins with free boundary conditions in equilibrium with a heat bath at temperature T and in zero magnetic field. Enumerate the 2^3 microstates and calculate $G(r = 1)$ and $G(r = 2)$ for $k = 1$, the first spin on the left. □

We show in the following that $G(r)$ can be calculated exactly for the Ising chain and is given by

$$G(r) = \big(\tanh \beta J\big)^r. \tag{5.54}$$

A plot of $G(r)$ for $\beta J = 2$ is shown in Figure 5.5. Note that $G(r) \to 0$ for $r \gg 1$ as expected.

We also see from Figure 5.5 that we can associate a length with the decrease of $G(r)$. We will define the *correlation length* ξ by writing $G(r)$ in the form

$$G(r) = e^{-r/\xi} \quad (r \gg 1), \tag{5.55}$$

where

$$\xi = -\frac{1}{\ln(\tanh \beta J)}. \tag{5.56}$$

At low temperatures, $\tanh \beta J \approx 1 - 2e^{-2\beta J}$, and

$$\ln\big(\tanh \beta J\big) \approx -2e^{-2\beta J}. \tag{5.57}$$

Hence

$$\xi = \frac{1}{2}e^{2\beta J} \qquad (\beta J \gg 1). \tag{5.58}$$

The correlation length is a measure of the distance over which the spins are correlated. From (5.58) we see that the correlation length becomes very large for low temperatures ($\beta J \gg 1$).

Problem 5.8. What is the maximum value of $\tanh\beta J$? Show that for finite values of βJ, $G(r)$ given by (5.54) decays with increasing r. ☐

***General calculation of $G(r)$ in one dimension**. To calculate $G(r)$ in the absence of an external magnetic field we assume free boundary conditions. It is useful to generalize the Ising model and assume that the magnitude of each of the nearest neighbor interactions is arbitrary so that the total energy E is given by

$$E = -\sum_{i=1}^{N-1} J_i s_i s_{i+1}, \tag{5.59}$$

where J_i is the interaction energy between spin i and spin $i+1$. At the end of the calculation we will set $J_i = J$. We will find in Section 5.5.4 that $m = 0$ for $T > 0$ for the one-dimensional Ising model. Hence, we can write $G(r) = \overline{s_k s_{k+r}}$. For the form (5.59) of the energy, $\overline{s_k s_{k+r}}$ is given by

$$\overline{s_k s_{k+r}} = \frac{1}{Z_N}\sum_{s_1=\pm1}\cdots\sum_{s_N=\pm1} s_k s_{k+r}\,\exp\Big[\sum_{i=1}^{N-1}\beta J_i s_i s_{i+1}\Big], \tag{5.60}$$

where

$$Z_N = 2\prod_{i=1}^{N-1} 2\cosh\beta J_i. \tag{5.61}$$

The right-hand side of (5.60) is the value of the product of two spins separated by a distance r in a particular microstate times the probability of that microstate.

We now use a trick similar to that used in Section 3.5 and the Appendix to calculate various sums and integrals. If we take the derivative of the exponential in (5.60) with respect to J_k, we bring down a factor of $\beta s_k s_{k+1}$. Hence, the spin-spin correlation function $G(r=1) = \overline{s_k s_{k+1}}$ for the Ising model with $J_i = J$ can be expressed as

$$\begin{aligned}
\overline{s_k s_{k+1}} &= \frac{1}{Z_N}\sum_{s_1=\pm1}\cdots\sum_{s_N=\pm1} s_k s_{k+1}\,\exp\Big[\sum_{i=1}^{N-1}\beta J_i s_i s_{i+1}\Big] &\text{(5.62a)}\\
&= \frac{1}{Z_N}\frac{1}{\beta}\frac{\partial}{\partial J_k}\sum_{s_1=\pm1}\cdots\sum_{s_N=\pm1}\exp\Big[\sum_{i=1}^{N-1}\beta J_i s_i s_{i+1}\Big] &\text{(5.62b)}\\
&= \frac{1}{Z_N}\frac{1}{\beta}\frac{\partial Z_N(J_1,\cdots,J_{N-1})}{\partial J_k}\bigg|_{J_i=J} &\text{(5.62c)}\\
&= \frac{\sinh\beta J}{\cosh\beta J} = \tanh\beta J, &\text{(5.62d)}
\end{aligned}$$

where we have used the form (5.61) for Z_N. To obtain $G(r=2)$, we use the fact that $s_{k+1}^2 = 1$ to write $s_k s_{k+2} = s_k(s_{k+1}s_{k+1})s_{k+2} = (s_k s_{k+1})(s_{k+1}s_{k+2})$. We write

$$\begin{aligned}
G(r=2) &= \frac{1}{Z_N}\sum_{\{s_j\}} s_k s_{k+1} s_{k+1} s_{k+2}\,\exp\Big[\sum_{i=1}^{N-1}\beta J_i s_i s_{i+1}\Big] &\text{(5.63a)}\\
&= \frac{1}{Z_N}\frac{1}{\beta^2}\frac{\partial^2 Z_N(J_1,\cdots,J_{N-1})}{\partial J_k\,\partial J_{k+1}} = [\tanh\beta J]^2. &\text{(5.63b)}
\end{aligned}$$

The method used to obtain $G(r = 1)$ and $G(r = 2)$ can be generalized to arbitrary r. We write

$$G(r) = \frac{1}{Z_N}\frac{1}{\beta^r}\frac{\partial}{\partial J_k}\frac{\partial}{J_{k+1}}\cdots\frac{\partial}{J_{k+r-1}}Z_N, \tag{5.64}$$

and use (5.61) for Z_N to find that

$$G(r) = \tanh\beta J_k \tanh\beta J_{k+1}\cdots\tanh\beta J_{k+r-1} \tag{5.65a}$$

$$= \prod_{k=1}^{r}\tanh\beta J_{k+r-1}. \tag{5.65b}$$

For a uniform interaction, $J_i = J$, and (5.65b) reduces to the result for $G(r)$ in (5.54).

5.5.3 Simulations of the Ising chain

Although we have found an exact solution for the one-dimensional Ising model in the absence of an external magnetic field, we can gain additional physical insight by doing simulations. As we will see, simulations are essential for the Ising model in higher dimensions.

As we discussed in Section 4.11, page 215, the Metropolis algorithm is the simplest and most common Monte Carlo algorithm for a system in equilibrium with a heat bath at temperature T. In the context of the Ising model, the Metropolis algorithm can be implemented as follows:

1. Choose an initial microstate of N spins. The two most common initial states are the ground state with all spins parallel or the $T = \infty$ state where each spin is chosen to be ± 1 at random.
2. Choose a spin at random and make a trial flip. Compute the change in energy of the system, ΔE, corresponding to the flip. The calculation is straightforward because the change in energy is determined by only the nearest neighbor spins. If $\Delta E < 0$, then accept the change. If $\Delta E > 0$, accept the change with probability $p = e^{-\beta\Delta E}$. To do so, generate a random number r uniformly distributed in the unit interval. If $r \leq p$, accept the new microstate; otherwise, retain the previous microstate.
3. Repeat step 2 many times choosing spins at random.
4. Compute averages of the quantities of interest such as E, M, C, and χ after the system has reached equilibrium.

In the following problem we explore some of the qualitative properties of the Ising chain.

Problem 5.9. Computer simulation of the Ising chain

Use Program `Ising1D` to simulate the one-dimensional Ising model. It is convenient to measure the temperature in units such that $J/k = 1$. For example, a temperature of $T = 2$ means that $T = 2J/k$. The "time" is measured in terms of Monte Carlo steps per spin (mcs), where in one Monte Carlo step per spin, N spins are chosen at random for trial changes. (On the average each spin will be chosen equally, but during any finite interval, some spins might be chosen more than others.) Choose $H = 0$. The thermodynamic quantities of interest for the Ising model include the mean energy E, the heat capacity C, and the isothermal susceptibility χ.

(a) Determine the heat capacity C and susceptibility χ for different temperatures, and discuss the qualitative temperature dependence of χ and C. Choose $N \geq 200$.

(b) Why is the mean value of the magnetization of little interest for the one-dimensional Ising model? Why does the simulation usually give $M \neq 0$?

(c) Estimate the mean size of the domains at $T = 1.0$ and $T = 0.5$. By how much does the mean size of the domains increase when T is decreased? Compare your estimates with the correlation length given by (5.56). What is the qualitative temperature dependence of the mean domain size?

(d) Why does the Metropolis algorithm become inefficient at low temperatures? □

5.5.4 *Transfer matrix

So far we have considered the Ising chain only in zero external magnetic field. The solution for nonzero magnetic field requires a different approach. We now apply the *transfer matrix* method to solve for the thermodynamic properties of the Ising chain in nonzero magnetic field. The transfer matrix method is powerful and can be applied to various magnetic systems and to seemingly unrelated quantum mechanical systems. The transfer matrix method also is of historical interest because it led to the exact solution of the two-dimensional Ising model in the absence of a magnetic field. A background in matrix algebra is important for understanding the following discussion.

To apply the transfer matrix method to the one-dimensional Ising model, it is necessary to adopt toroidal boundary conditions so that the chain becomes a ring with $s_{N+1} = s_1$. This boundary condition enables us to write the energy as

$$E = -J\sum_{i=1}^{N} s_i s_{i+1} - \frac{1}{2}H\sum_{i=1}^{N}(s_i + s_{i+1}) \quad \text{(toroidal boundary conditions).} \tag{5.66}$$

The use of toroidal boundary conditions implies that each spin is equivalent.

The transfer matrix $\mathbf{T}$ is defined by its four matrix elements, which are given by

$$T_{s,s'} = e^{\beta[Jss' + \frac{1}{2}H(s+s')]}. \tag{5.67}$$

The explicit form of the matrix elements is

$$T_{++} = e^{\beta(J+H)}, \tag{5.68a}$$

$$T_{--} = e^{\beta(J-H)}, \tag{5.68b}$$

$$T_{-+} = T_{+-} = e^{-\beta J}, \tag{5.68c}$$

or

$$\mathbf{T} = \begin{pmatrix} T_{++} & T_{+-} \\ T_{-+} & T_{--} \end{pmatrix} = \begin{pmatrix} e^{\beta(J+H)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-H)} \end{pmatrix}. \tag{5.69}$$

The definition (5.67) of $\mathbf{T}$ allows us to write Z_N in the form

$$Z_N(T,H) = \sum_{s_1}\sum_{s_2}\cdots\sum_{s_N} T_{s_1,s_2}T_{s_2,s_3}\cdots T_{s_N,s_1}. \tag{5.70}$$

The form of (5.70) is suggestive of the interpretation of $\mathbf{T}$ as a transfer function.

Problem 5.10. Transfer matrix method in zero magnetic field

Show that the partition function for a system of $N = 3$ spins with toroidal boundary conditions can be expressed as the trace (the sum of the diagonal elements) of the product of three matrices:

$$\begin{pmatrix} e^{\beta J} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J} \end{pmatrix} \begin{pmatrix} e^{\beta J} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J} \end{pmatrix} \begin{pmatrix} e^{\beta J} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J} \end{pmatrix}. \tag{5.71}$$

□

The rule for matrix multiplication that we need for the transfer matrix method is

$$(\mathbf{T}^2)_{s_1,s_3} = \sum_{s_2} T_{s_1,s_2} T_{s_2,s_3}, \tag{5.72}$$

or

$$(\mathbf{T})^2 = \begin{pmatrix} T_{++}T_{++} & T_{+-}T_{-+} \\ T_{-+}T_{+-} & T_{--}T_{--} \end{pmatrix}. \tag{5.73}$$

If we multiply N matrices, we obtain

$$(\mathbf{T}^N)_{s_1,s_{N+1}} = \sum_{s_2} \sum_{s_3} \cdots \sum_{s_N} T_{s_1,s_2} T_{s_2,s_3} \cdots T_{s_N,s_{N+1}}. \tag{5.74}$$

This result is very close to the form of Z_N in (5.70). To make it identical, we use toroidal boundary conditions and set $s_{N+1} = s_1$, and sum over s_1:

$$\sum_{s_1} (\mathbf{T}^N)_{s_1,s_1} = \sum_{s_1} \sum_{s_2} \sum_{s_3} \cdots \sum_{s_N} T_{s_1,s_2} T_{s_2,s_3} \cdots T_{s_N,s_1} = Z_N. \tag{5.75}$$

Because $\sum_{s_1} (\mathbf{T}^N)_{s_1,s_1}$ is the definition of the trace (the sum of the diagonal elements) of $(\mathbf{T}^N)$, we have

$$Z_N = \mathrm{Tr}\,(\mathbf{T}^N). \tag{5.76}$$

The fact that Z_N is the trace of the Nth power of a matrix is a consequence of our use of toroidal boundary conditions.

Because the trace of a matrix is independent of the representation of the matrix, the trace in (5.76) may be evaluated by bringing $\mathbf{T}$ into diagonal form:

$$\mathbf{T} = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix}. \tag{5.77}$$

The matrix $\mathbf{T}^N$ is diagonal with the diagonal matrix elements λ_+^N, λ_-^N. In the diagonal representation for $\mathbf{T}$ in (5.77), we have

$$Z_N = \mathrm{Tr}\,(\mathbf{T}^N) = \lambda_+^N + \lambda_-^N, \tag{5.78}$$

where λ_+ and λ_- are the eigenvalues of $\mathbf{T}$.

The eigenvalues $\lambda_\pm$ are given by the solution of the determinant equation

$$\begin{vmatrix} e^{\beta(J+H)} - \lambda & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-H)} - \lambda \end{vmatrix} = 0. \tag{5.79}$$

The roots of (5.79) are

$$\lambda_{\pm} = e^{\beta J} \cosh \beta H \pm \big[e^{-2\beta J} + e^{2\beta J} \sinh^2 \beta H\big]^{1/2}. \tag{5.80}$$

It is easy to show that $\lambda_+ > \lambda_-$ for all β and H, and consequently $(\lambda_-/\lambda_+)^N \to 0$ as $N \to \infty$. In the thermodynamic limit $N \to \infty$ we obtain from (5.78) and (5.80)

$$\lim_{N\to\infty} \frac{1}{N} \ln Z_N(T,H) = \ln \lambda_+ + \ln \Big[1 + \Big(\frac{\lambda_-}{\lambda_+}\Big)^N\Big] = \ln \lambda_+, \tag{5.81}$$

and the free energy per spin is given by

$$f(T,H) = \frac{1}{N} F(T,H) = -kT \ln \big[e^{\beta J} \cosh \beta H + \big(e^{2\beta J} \sinh^2 \beta H + e^{-2\beta J}\big)^{1/2}\big]. \tag{5.82}$$

We can use (5.82) and (5.31) and some algebraic manipulations to find the magnetization per spin m at nonzero T and H:

$$m = -\frac{\partial f}{\partial H} = \frac{\sinh \beta H}{(\sinh^2 \beta H + e^{-4\beta J})^{1/2}}. \tag{5.83}$$

A system is paramagnetic if $m \neq 0$ only when $H \neq 0$, and is ferromagnetic if $m \neq 0$ when $H = 0$. From (5.83) we see that $m = 0$ for $H = 0$ because $\sinh x \approx x$ for small x. Thus for $H = 0$, $\sinh \beta H = 0$ and thus $m = 0$. The one-dimensional Ising model becomes a ferromagnet only at $T = 0$ where $e^{-4\beta J} \to 0$, and thus from (5.83) $|m| \to 1$ at $T = 0$.

Problem 5.11. Isothermal susceptibility of the Ising chain

More insight into the properties of the Ising chain can be found by understanding the temperature dependence of the isothermal susceptibility χ.

(a) Calculate χ using (5.83).

(b) What is the limiting behavior of χ in the limit $T \to 0$ for $H > 0$?

(c) Show that the limiting behavior of the zero-field susceptibility in the limit $T \to 0$ is $\chi \sim e^{2\beta J}$. (The zero-field susceptibility is found by calculating the susceptibility for $H \neq 0$ and then taking the limit $H \to 0$ before other limits such as $T \to 0$ are taken.) Express the limiting behavior in terms of the correlation length ξ. Why does χ diverge as $T \to 0$? □

Because the zero-field susceptibility diverges as $T \to 0$, the fluctuations of the magnetization also diverge in this limit. As we will see in Section 5.6, the divergence of the magnetization fluctuations is one of the characteristics of the critical point of the Ising model. That is, the phase transition from a paramagnet ($m = 0$ for $H = 0$) to a ferromagnet ($m \neq 0$ for $H = 0$) occurs at zero temperature for the one-dimensional Ising model. We will see that the critical point occurs at $T > 0$ for the Ising model in two and higher dimensions.

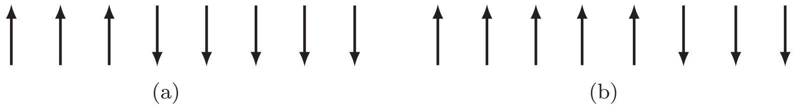


Figure 5.6: A domain wall in one dimension for a system of $N = 8$ spins with free boundary conditions. In (a) the energy of the system is $E = -5J$ ($H = 0$). The energy cost for forming a domain wall is $2J$ (recall that the ground state energy is $-7J$). In (b) the domain wall has moved with no cost in energy.

5.5.5 Absence of a phase transition in one dimension

We found by direct calculations that the one-dimensional Ising model does not have a phase transition for $T > 0$. We now argue that a phase transition in one dimension is impossible if the interaction is short-range, that is, if a given spin interacts with only a finite number of spins.

At $T = 0$ the energy is a minimum with $E = -(N-1)J$ (for free boundary conditions), and the entropy $S = 0$.[7] Consider all the excitations at $T > 0$ obtained by flipping all the spins to the right of some site [see Figure 5.6(a)]. The energy cost of creating such a domain wall is $2J$. Because there are $N - 1$ sites where the domain wall may be placed, the entropy increases by $\Delta S = k \ln(N-1)$. Hence, the free energy cost associated with creating one domain wall is

$$\Delta F = 2J - kT \ln(N-1). \tag{5.84}$$

We see from (5.84) that for $T > 0$ and $N \to \infty$, the creation of a domain wall lowers the free energy. Hence, more domain walls will be created until the spins are completely randomized and the net magnetization is zero. We conclude that $M = 0$ for $T > 0$ in the limit $N \to \infty$.

Problem 5.12. Energy cost of a single domain

Compare the energy of the microstate in Figure 5.6(a) with the energy of the microstate shown in Figure 5.6(b) and discuss why the number of spins in a domain in one dimension can be changed without any energy cost. □

5.6 The Two-Dimensional Ising Model

We first give an argument similar to the one that was given in Section 5.5.5 to suggest the existence of a paramagnetic to ferromagnetism phase transition in the two-dimensional Ising model at a nonzero temperature. We will show that the mean value of the magnetization is nonzero at low, but nonzero temperatures and in zero magnetic field.

The key difference between one and two dimensions is that in the former the existence of one domain wall allows the system to have regions of up and down spins whose size can be changed without any cost of energy. So on the average the number of up and down spins is the same. In two dimensions the existence of one domain does not make the magnetization zero. The regions of

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[7] The ground state for $H = 0$ corresponds to all spins up or all spins down. It is convenient to break this symmetry by assuming that $H = 0^+$ and letting $T \to 0$ before letting $H \to 0^+$.

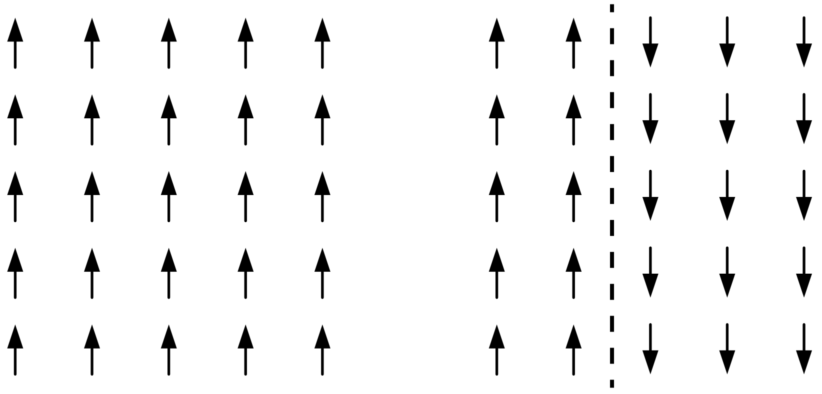

(a) (b)

Figure 5.7: (a) The ground state of a 5×5 Ising model. (b) Example of a domain wall. The energy cost of the domain is $10J$, assuming free boundary conditions.

down spins cannot grow at low temperature because their growth requires longer boundaries and hence more energy.

From Figure 5.7 we see that the energy cost of creating a rectangular domain in two dimensions is given by $2JL$ (for an $L \times L$ lattice with free boundary conditions). Because the domain wall can be at any of the L columns, the entropy is at least order $\ln L$. Hence the free energy cost of creating one domain is $\Delta F \sim 2JL - T \ln L$. hence, we see that $\Delta F > 0$ in the limit $L \to \infty$. Therefore creating one domain increases the free energy and thus most of the spins will remain up, and the magnetization remains positive. Hence $M > 0$ for $T > 0$, and the system is ferromagnetic. This argument suggests why it is possible for the magnetization to be nonzero for $T > 0$. M becomes zero at a critical temperature $T_c > 0$, because there are many other ways of creating domains, thus increasing the entropy and leading to a disordered phase.

5.6.1 Onsager solution

As mentioned, the two-dimensional Ising model was solved exactly in zero magnetic field for a rectangular lattice by Lars Onsager in 1944. Onsager's calculation was the first exact solution that exhibited a phase transition in a model with short-range interactions. Before his calculation, some people believed that statistical mechanics was not capable of yielding a phase transition.

Although Onsager's solution is of much historical interest, the mathematical manipulations are very involved. Moreover, the manipulations are special to the Ising model and cannot be generalized to other systems. For these reasons few workers in statistical mechanics have gone through the Onsager solution in great detail. In the following, we summarize some of the results of the two-dimensional solution for a square lattice.

The critical temperature T_c is given by

$$\sinh \frac{2J}{kT_c} = 1, \tag{5.85}$$

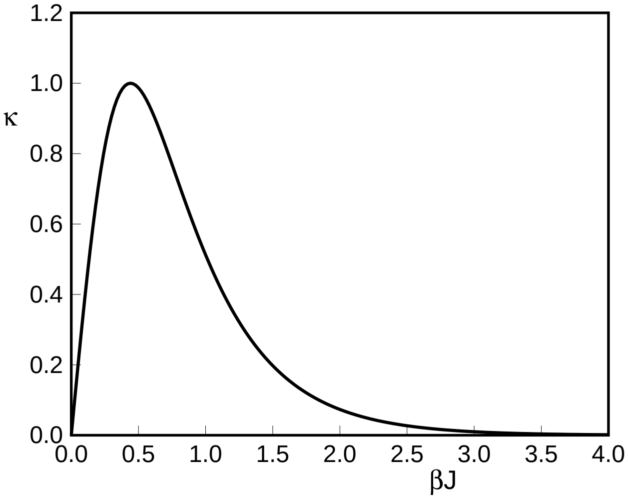


Figure 5.8: Plot of the function κ defined in (5.87) as a function of J/kT.

or

$$\frac{kT_c}{J} = \frac{2}{\ln(1+\sqrt{2})} \approx 2.269. \tag{5.86}$$

It is convenient to express the mean energy in terms of the dimensionless parameter κ defined as

$$\kappa = 2\frac{\sinh 2\beta J}{(\cosh 2\beta J)^2}. \tag{5.87}$$

A plot of the function κ versus βJ is given in Figure 5.8. Note that κ is zero at low and high temperatures and has a maximum of 1 at $T = T_c$.

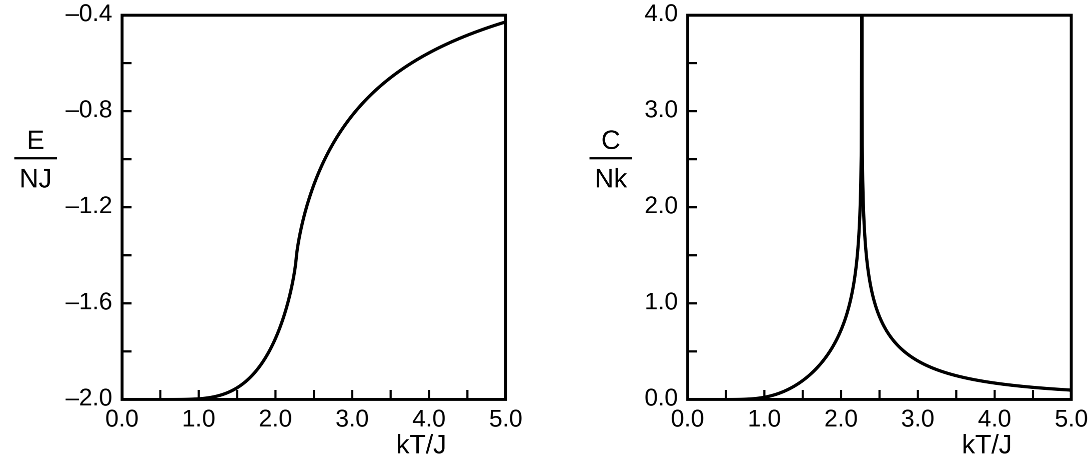
The exact solution for the energy E can be written in the form

$$E = -2NJ\tanh 2\beta J - NJ\frac{\sinh^2 2\beta J - 1}{\sinh 2\beta J\cosh 2\beta J}\Big[\frac{2}{\pi}K_1(\kappa) - 1\Big], \tag{5.88}$$

where

$$K_1(\kappa) = \int_0^{\pi/2} \frac{d\phi}{\sqrt{1-\kappa^2\sin^2\phi}}. \tag{5.89}$$

K_1 is known as the complete elliptic integral of the first kind. The first term in (5.88) is similar to the result (5.50) for the energy of the one-dimensional Ising model with a doubling of the exchange interaction J for two dimensions. The second term in (5.88) vanishes at low and high temperatures (because of the term in brackets) and at $T = T_c$ because of the vanishing of the term $\sinh^2 2\beta J - 1$. The function $K_1(\kappa)$ has a logarithmic singularity at $T = T_c$ at which $\kappa = 1$. Hence, the second term behaves as $(T - T_c)\ln|T - T_c|$ in the vicinity of T_c. We conclude that $E(T)$ is continuous at $T = T_c$ and at all other temperatures [see Figure 5.9(a)].



(a) (b)

Figure 5.9: (a) Temperature dependence of the energy of the Ising model on the square lattice according to (5.88). Note that $E(T)$ is a continuous function of kT/J. (b) Temperature dependence of the specific heat of the Ising model on the square lattice according to (5.90). Note the divergence of the specific heat at the critical temperature.

The heat capacity can be obtained by differentiating $E(T)$ with respect to temperature. It can be shown after some tedious algebra that

$$\begin{aligned} C(T) = Nk\frac{4}{\pi}(\beta J \coth 2\beta J)^2 \Big[&K_1(\kappa) - E_1(\kappa) \\ &- (1 - \tanh^2 2\beta J)\Big(\frac{\pi}{2} + (2\tanh^2 2\beta J - 1)K_1(\kappa)\Big)\Big], \end{aligned} \tag{5.90}$$

where

$$E_1(\kappa) = \int_0^{\pi/2} d\phi\, \sqrt{1 - \kappa^2 \sin^2\phi}. \tag{5.91}$$

E_1 is called the complete elliptic integral of the second kind. A plot of $C(T)$ is given in Figure 5.9(b). The behavior of C near T_c is given by

$$C \approx -Nk\frac{2}{\pi}\Big(\frac{2J}{kT_c}\Big)^2 \ln\Big|1 - \frac{T}{T_c}\Big| + \text{constant} \qquad (T \text{ near } T_c). \tag{5.92}$$

An important property of the Onsager solution is that the heat capacity diverges logarithmically at $T = T_c$:

$$C(T) \sim -\ln|\epsilon|, \tag{5.93}$$

where the reduced temperature difference is given by

$$\epsilon = (T_c - T)/T_c. \tag{5.94}$$

A major test of the approximate treatments that we will develop in Section 5.7 and in Chapter 9 is whether they can yield a heat capacity that diverges as in (5.93).

The power law divergence of $C(T)$ can be written in general as

$$C(T) \sim \epsilon^{-\alpha}, \tag{5.95}$$

Because the divergence of C in (5.93) is logarithmic, which is slower than any power of ϵ, the critical exponent α equals zero for the two-dimensional Ising model.

To know whether the logarithmic divergence of the heat capacity in the Ising model at $T = T_c$ is associated with a phase transition, we need to know if there is a spontaneous magnetization. That is, is there a range of $T > 0$ such that $M \neq 0$ for $H = 0$? (Onsager's solution is limited to zero magnetic field.)

To calculate the spontaneous magnetization we need to calculate the derivative of the free energy with respect to H for nonzero H and then let $H = 0$. In 1952 C. N. Yang calculated the magnetization for $T < T_c$ and the zero-field susceptibility.[8] Yang's exact result for the magnetization per spin can be expressed as

$$m(T) = \begin{cases} \left(1 - [\sinh 2\beta J]^{-4}\right)^{1/8} & (T < T_c), \\ 0 & (T > T_c). \end{cases} \tag{5.96}$$

A plot of m is shown in Figure 5.10. We see that m vanishes near T_c as

$$m \sim \epsilon^{\beta} \qquad (T < T_c), \tag{5.97}$$

where β is a *critical exponent* and should not be confused with the inverse temperature. For the two-dimensional Ising model $\beta = 1/8$.

The magnetization m is an example of an *order parameter*. For the Ising model $m = 0$ for $T > T_c$ (paramagnetic phase), and $m \neq 0$ for $T \leq T_c$ (ferromagnetic phase). The word "order" in the magnetic context is used to denote that below T_c the spins are mostly aligned in the same direction; in contrast, the spins point randomly in both directions for T above T_c.

The behavior of the zero-field susceptibility for T near T_c was found by Yang to be

$$\chi \sim |\epsilon|^{-7/4} \sim |\epsilon|^{-\gamma}, \tag{5.98}$$

where γ is another critical exponent. We see that $\gamma = 7/4$ for the two-dimensional Ising model.

The most important results of the exact solution of the two-dimensional Ising model are that the energy (and the free energy and the entropy) are *continuous* functions for all T, m vanishes continuously at $T = T_c$, the heat capacity diverges logarithmically at $T = T_c^-$, and the zero-field susceptibility and other quantities show power law behavior which can be described by critical exponents. We say that the paramagnetic ↔ ferromagnetic transition in the two-dimensional Ising model is *continuous* because the order parameter m vanishes continuously rather

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[8] C. N. Yang, "The spontaneous magnetization of a two-dimensional Ising model," Phys. Rev. **85**, 808–816 (1952). The result (5.96) was first announced by Onsager at a conference in 1944 but not published. C. N. Yang and T. D. Lee shared the 1957 Nobel Prize in Physics for work on parity violation. See `<nobelprize.org/physics/laureates/1957/>`.

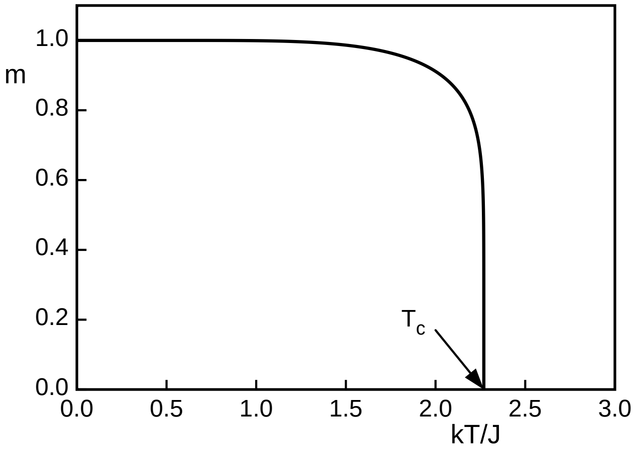

Figure 5.10: The temperature dependence of the spontaneous magnetization $m(T)$ of the two-dimensional Ising model.

than discontinuously. Because the transition occurs only at $T = T_c$ and $H = 0$, the transition occurs at a *critical point*.

So far we have introduced the critical exponents α, β, and γ to describe the behavior of the specific heat, magnetization, and susceptibility near the critical point. We now introduce three more critical exponents: η, ν, and δ (see Table 5.1). The notation $\chi \sim |\epsilon|^{-\gamma}$ means that χ has a singular contribution proportional to $|\epsilon|^{-\gamma}$. The definitions of the critical exponents given in Table 5.1 implicitly assume that the singularities are the same whether the critical point is approached from above or below T_c. The exception is m, which is zero for $T > T_c$.

The critical exponent δ characterizes the dependence of m on the magnetic field at $T = T_c$:

$$|m| \sim |H|^{1/15} \sim |H|^{1/\delta} \qquad (T = T_c). \tag{5.99}$$

We see that $\delta = 15$ for the two-dimensional Ising model.

The behavior of the spin-spin correlation function $G(r)$ for T near T_c and large r is given by

$$G(r) \sim \frac{1}{r^{d-2+\eta}} e^{-r/\xi} \qquad (r \gg 1 \text{ and } |\epsilon| \ll 1), \tag{5.100}$$

where d is the spatial dimension and η is another critical exponent. The correlation length ξ diverges as

$$\xi \sim |\epsilon|^{-\nu}. \tag{5.101}$$

The exact result for the critical exponent ν for the two-dimensional ($d = 2$) Ising model is $\nu = 1$. At $T = T_c$, $G(r)$ decays as a power law for large r:

$$G(r) = \frac{1}{r^{d-2+\eta}} \qquad (T = T_c,\, r \gg 1). \tag{5.102}$$

For the two-dimensional Ising model $\eta = 1/4$. The values of the various critical exponents for the Ising model in two and three dimensions are summarized in Table 5.1.

		values of the exponents		
Quantity	Critical behavior	$d = 2$ (exact)	$d = 3$	mean-field theory
specific heat	$C \sim \epsilon^{-\alpha}$	0 (logarithmic)	0.113	0 (jump)
order parameter	$m \sim \epsilon^{\beta}$	1/8	0.324	1/2
susceptibility	$\chi \sim \epsilon^{-\gamma}$	7/4	1.238	1
equation of state ($\epsilon = 0$)	$m \sim H^{1/\delta}$	15	4.82	3
correlation length	$\xi \sim \epsilon^{-\nu}$	1	0.629	1/2
correlation function $\epsilon = 0$	$G(r) \sim 1/r^{d-2+\eta}$	1/4	0.031	0

Table 5.1: Values of the critical exponents for the Ising model in two and three dimensions. The values of the critical exponents of the Ising model are known exactly in two dimensions and are ratios of integers. The results in three dimensions are not ratios of integers and are approximate. The exponents predicted by mean-field theory are discussed in Sections 5.7, and 9.1, pages 256 and 434.

There is a fundamental difference between the exponential behavior of $G(r)$ for $T \neq T_c$ in (5.100) and the power law behavior of $G(r)$ for $T = T_c$ in (5.102). Systems with correlation functions that decay as a power law are said to be *scale invariant*. That is, power laws look the same on all scales. The replacement $x \to ax$ in the function $f(x) = Ax^{-\eta}$ yields a function that is indistinguishable from $f(x)$ except for a change in the amplitude A by the factor $a^{-\eta}$. In contrast, this invariance does not hold for functions that decay exponentially because making the replacement $x \to ax$ in the function $e^{-x/\xi}$ changes the correlation length ξ by the factor a. The fact that the critical point is scale invariant is the basis for the renormalization group method (see Chapter 9). Scale invariance means that at the critical point there will be domains of spins of the same sign of all sizes.

We stress that the phase transition in the Ising model is the result of the *cooperative* interactions between the spins. Although phase transitions are commonplace, they are remarkable from a microscopic point of view. For example, the behavior of the system changes dramatically with a small change in the temperature even though the interactions between the spins remain unchanged and short-range. The study of phase transitions in relatively simple systems such as the Ising model has helped us begin to understand phenomena as diverse as the distribution of earthquake sizes, the shape of snowflakes, and the transition from a boom economy to a recession.

5.6.2 Computer simulation of the two-dimensional Ising model

The implementation of the Metropolis algorithm for the two-dimensional Ising model proceeds as in one dimension. The only difference is that an individual spin interacts with four nearest neighbors on a square lattice rather than two nearest neighbors in one dimension. Simulations of the Ising model in two dimensions allow us to test approximate theories and determine properties that cannot be calculated analytically. We explore some of the properties of the two-dimensional Ising model in Problem 5.13.

Problem 5.13. Simulation of the two-dimensional Ising model

Use Program `Ising2D` to simulate the Ising model on a square lattice at a given temperature T and external magnetic field H. (Remember that T is given in terms of J/k.) First choose $N = L^2 = 32^2$

and set $H = 0$. For simplicity, the initial orientation of the spins is all spins up.

(a) Choose $T = 10$ and run until equilibrium has been established. Is the orientation of the spins random such that the mean magnetization is approximately equal to zero? What is a typical size of a domain, a region of parallel spins?

(b) Choose a low temperature such as $T = 0.5$. Are the spins still random or do a majority choose a preferred direction? You will notice that $M \approx 0$ for sufficient high T and $M \neq 0$ for sufficiently low T. Hence, there is an intermediate value of T at which M first becomes nonzero.

(c) Start at $T = 4$ and determine the temperature dependence of the magnetization per spin m, the zero-field susceptibility χ, the mean energy E, and the specific heat C. (Note that we have used the same notation for the specific heat and the heat capacity.) Decrease the temperature in intervals of 0.2 until $T \approx 1.6$, equilibrating for at least 1000 mcs before collecting data at each value of T. Describe the qualitative temperature dependence of these quantities. Note that when the simulation is stopped, the mean magnetization and the mean of the absolute value of the magnetization is returned. At low temperatures the magnetization can sometimes flip for small systems so that the value of $\langle |M| \rangle$ is a more accurate representation of the magnetization. For the same reason the susceptibility is given by

$$\chi = \frac{1}{kT}\big[\langle M^2 \rangle - \langle |M| \rangle^2\big], \tag{5.103}$$

rather than by (5.17). A method for estimating the critical exponents is discussed in Problem 5.41.

(d) Set $T = T_c \approx 2.269$ and choose $L \geq 128$. Obtain $\langle M \rangle$ for $H = 0.01$, 0.02, 0.04, 0.08, and 0.16. Make sure you equilibrate the system at each value of H before collecting data. Make a log-log plot of m versus H and estimate the critical exponent δ using (5.99).

(e) Choose $L = 4$ and $T = 2.0$. Does the sign of the magnetization change during the simulation? Choose a larger value of L and observe if the sign of the magnetization changes. Will the sign of M change for $L \gg 1$? Should a theoretical calculation of $\langle M \rangle$ yield $\langle M \rangle \neq 0$ or $\langle M \rangle = 0$ for $T < T_c$? □

***Problem 5.14.** Ising antiferromagnet

So far we have considered the ferromagnetic Ising model for which the energy of interaction between two nearest neighbor spins is $J > 0$. Hence, all spins are parallel in the ground state of the ferromagnetic Ising model. In contrast, if $J < 0$, nearest neighbor spins must be antiparallel to minimize their energy of interaction.

(a) Sketch the ground state of the one-dimensional antiferromagnetic Ising model. Then do the same for the antiferromagnetic Ising model on a square lattice. What is the value of M for the ground state of an Ising antiferromagnet?

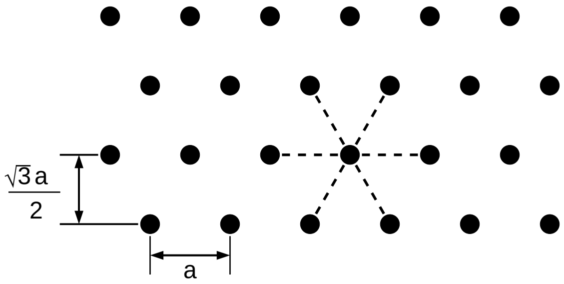

Figure 5.11: Each spin has six nearest neighbors on a hexagonal lattice. This lattice structure is sometimes called a triangular lattice.

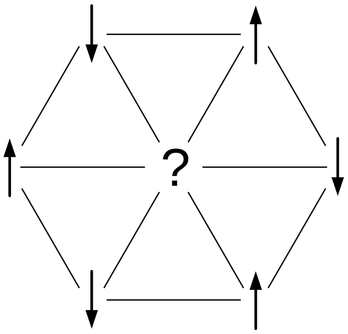

Figure 5.12: The six nearest neighbors of the central spin on a hexagonal lattice are successively antiparallel, corresponding to the lowest energy of interaction for an Ising antiferromagnet. The central spin cannot be antiparallel to all its neighbors and is said to be *frustrated*.

(b) Use Program `IsingAnitferromagnetSquareLattice` to simulate the antiferromagnetic Ising model on a square lattice at various temperatures and describe its qualitative behavior. Does the system have a phase transition at $T > 0$? Does the value of M show evidence of a phase transition?

(c) In addition to the usual thermodynamic quantities the program calculates the *staggered* magnetization and the staggered susceptibility. The staggered magnetization is calculated by considering the square lattice as a checkerboard with black and red sites so that each black site has four red sites as nearest neighbors and vice versa. The staggered magnetization is calculated from $\sum c_i s_i$ where $c_i = +1$ for a black site and $c_i = -1$ for a red site. Describe the behavior of these quantities and compare them to the behavior of M and χ for the ferromagnetic Ising model.

(d) *Consider the Ising antiferromagnetic model on a hexagonal lattice (see Figure 5.11), for which each spin has six nearest neighbors. The ground state in this case is not unique because of *frustration* (see Figure 5.12). Convince yourself that there are multiple ground states. Is the entropy zero or nonzero at $T = 0$?[9] Use Program `IsingAntiferromagnetHexagonalLattice`

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[9] The entropy at zero temperature is $S(T = 0) = 0.3383kN$. See G. H. Wannier, "Antiferromagnetism. The

to simulate the antiferromagnetic Ising model on a hexagonal lattice at various temperatures and describe its qualitative behavior. This system does not have a phase transition for $T > 0$. Are your results consistent with this behavior? ☐

5.7 Mean-Field Theory

Because it is not possible to solve the thermodynamics of the Ising model exactly in three dimensions and the two-dimensional Ising model in the presence of a magnetic field, we need to develop approximate theories. In this section we develop an approximation known as *mean-field* theory. Mean-field theories are relatively easy to treat and usually yield qualitatively correct results, but are not usually quantitatively correct. In Section 5.10.4 we consider a more sophisticated version of mean-field theory for Ising models that yields more accurate values of T_c, and in Section 9.1 we consider a more general formulation of mean-field theory. In Section 8.6 we discuss how to apply similar ideas to gases and liquids.

In its simplest form mean-field theory assumes that each spin interacts with the same effective magnetic field. The effective field is due to the external magnetic field plus the internal field due to all the neighboring spins. That is, spin i "feels" an effective field $H_{\rm eff}$ given by

$$H_{\rm eff} = J\sum_{j=1}^{q} s_j + H, \tag{5.104}$$

where the sum over j in (5.104) is over the q nearest neighbors of i. (Recall that we have incorporated a factor of μ into H so that H in (5.104) has units of energy.) Because the orientation of the neighboring spins depends on the orientation of spin i, $H_{\rm eff}$ fluctuates from its mean value, which is given by

$$\overline{H}_{\rm eff} = J\sum_{j=1}^{q} \overline{s}_j + H = Jqm + H, \tag{5.105}$$

where $\overline{s}_j = m$. In mean-field theory we ignore the deviations of $H_{\rm eff}$ from $\overline{H}_{\rm eff}$ and assume that the field at i is $\overline{H}_{\rm eff}$, independent of the orientation of s_i. This assumption is an approximation because if s_i is up, then its neighbors are more likely to be up. This correlation is ignored in mean-field theory.

The form of the mean effective field in (5.105) is the same throughout the system. The result of this approximation is that the system of N interacting spins has been reduced to a system of one spin interacting with an effective field which depends on all the other spins.

The partition function for one spin in the effective field $\overline{H}_{\rm eff}$ is

$$Z_1 = \sum_{s_1=\pm 1} e^{s_1 \overline{H}_{\rm eff}/kT} = 2\cosh[(Jqm + H)/kT]. \tag{5.106}$$

The free energy per spin is

$$f = -kT\ln Z_1 = -kT\ln\big(2\cosh[(Jqm + H)/kT]\big), \tag{5.107}$$

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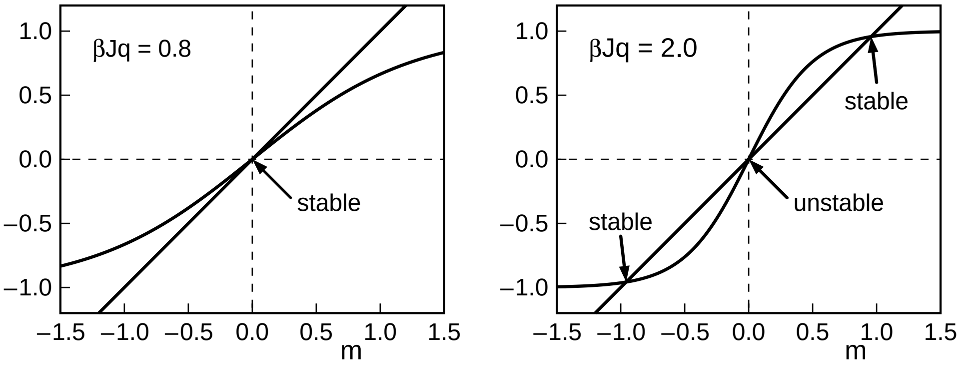
triangular Ising net," Phys. Rev. **79**, 357–364 (1950), erratum, Phys. Rev. B **7**, 5017 (1973).



(a)

(b)

Figure 5.13: Graphical solution of the self-consistent equation (5.108) for $H = 0$. The line $y_1(m) = m$ represents the left-hand side of (5.108), and the function $y_2(m) = \tanh Jqm/kT$ represents the right-hand side. The intersection of y_1 and y_2 gives a possible solution for m. The solution $m = 0$ exists for all T. Stable solutions $m = \pm m_0$ ($m_0 > 0$) exist only for T sufficiently small such that the slope Jq/kT of y_2 near $m = 0$ is greater than 1.

and the magnetization is

$$m = -\frac{\partial f}{\partial H} = \tanh[(Jqm + H)/kT]. \tag{5.108}$$

Equation (5.108) is a *self-consistent* transcendental equation whose solution yields m. The mean-field that influences the mean value of m in turn depends on the mean value of m.

From Figure 5.13 we see that nonzero solutions for m exist for $H = 0$ when $qJ/kT \geq 1$. The critical temperature satisfies the condition that $m \neq 0$ for $T \leq T_c$ and $m = 0$ for $T > T_c$. Thus the critical temperature T_c is given by

$$kT_c = Jq. \tag{5.109}$$

Problem 5.15. Numerical solutions of (5.108)

Use Program `IsingMeanField` to find numerical solutions of (5.108).

(a) Set $H = 0$ and $q = 4$ and determine the value of the mean-field approximation to the critical temperature T_c of the Ising model on a square lattice. Start with $kT/Jq = 10$ and then proceed to lower temperatures. Plot the temperature dependence of m. The equilibrium value of m is the solution with the lowest free energy (see Problem 5.18).

(b) Determine $m(T)$ for the one-dimensional Ising model ($q = 2$) and $H = 0$ and $H = 1$ and compare your values for $m(T)$ with the exact solution in one dimension [see (5.83)]. ☐

For T near T_c the magnetization is small, and we can expand $\tanh Jqm/kT$ ($\tanh x \approx x - x^3/3$ for $x \ll 1$) to find

$$m = Jqm/kT - \frac{1}{3}(Jqm/kT)^3 + \cdots . \tag{5.110}$$

Equation (5.110) has two solutions:

$$m(T > T_c) = 0 \tag{5.111a}$$

and

$$m(T < T_c) = \pm\frac{3^{1/2}}{(Jq/kT)^{3/2}}((Jq/kT) - 1)^{1/2}. \tag{5.111b}$$

The solution $m = 0$ in (5.111a) corresponds to the high temperature paramagnetic state. The solution in (5.111b) corresponds to the low temperature ferromagnetic state ($m \neq 0$). How do we know which solution to choose? The answer can be found by calculating the free energy for both solutions and choosing the solution that gives the smaller free energy (see Problems 5.15 and 5.17).

If we let $Jq = kT_c$ in (5.111b), we can write the spontaneous magnetization (the nonzero magnetization for $T < T_c$) as

$$m(T < T_c) = 3^{1/2}\Big(\frac{T}{T_c}\Big)\Big(\frac{T_c - T}{T_c}\Big)^{1/2}. \tag{5.112}$$

We see from (5.112) that m approaches zero as a power law as T approaches T_c from below. It is convenient to express the temperature dependence of m near the critical temperature in terms of the reduced temperature $\epsilon = (T_c - T)/T_c$ [see (5.94)] and write (5.112) as

$$m(T) \sim \epsilon^{\beta}. \tag{5.113}$$

From (5.112) we see that mean-field theory predicts that $\beta = 1/2$. Compare this prediction to the value of β for the two-dimensional Ising model (see Table 5.1).

We now find the behavior of other important physical properties near T_c. The zero-field isothermal susceptibility (per spin) is given by

$$\chi = \lim_{H\to 0}\frac{\partial m}{\partial H} = \frac{1 - \tanh^2 Jqm/kT}{kT - Jq(1 - \tanh^2 Jqm/kT)} = \frac{1 - m^2}{kT - Jq(1 - m^2)}. \tag{5.114}$$

For $T \gtrsim T_c$ we have $m = 0$ and χ in (5.114) reduces to

$$\chi = \frac{1}{k(T - T_c)} \qquad (T > T_c,\, H = 0), \tag{5.115}$$

where we have used the relation (5.108) with $H = 0$. The result (5.115) for χ is known as the Curie-Weiss law.

For $T \lesssim T_c$ we have from (5.112) that $m^2 \approx 3(T_c - T)/T_c$, $1 - m^2 = (3T - 2T_c)/T_c$, and

$$\chi \approx \frac{1}{k[T - T_c(1 - m^2)]} = \frac{1}{k[T - 3T + 2T_c]} \tag{5.116a}$$

$$= \frac{1}{2k(T_c - T)} \qquad (T \lesssim T_c,\, H = 0). \tag{5.116b}$$

We see that we can characterize the divergence of the zero-field susceptibility as the critical point is approached from either the low or high temperature side by $\chi \sim |\epsilon|^{-\gamma}$ [see (5.98)]. The mean-field prediction for the critical exponent γ is $\gamma = 1$.

The magnetization at T_c as a function of H can be calculated by expanding (5.108) to third order in H with $kT = kT_c = qJ$:

$$m = m + H/kT_c - \frac{1}{3}(m + H/kT_c)^3 + \cdots . \tag{5.117}$$

For $H/kT_c \ll m$ we find

$$m = (3H/kT_c)^{1/3} \propto H^{1/3} \qquad (T = T_c). \tag{5.118}$$

The result (5.118) is consistent with our assumption that $H/kT_c \ll m$. If we use the power law dependence given in (5.99), we see that mean-field theory predicts that the critical exponent δ is $\delta = 3$, which compares poorly with the exact result for the two-dimensional Ising model given by $\delta = 15$.

The easiest way to obtain the energy per spin for $H = 0$ in the mean-field approximation is to write

$$\frac{E}{N} = -\frac{1}{2}Jqm^2, \tag{5.119}$$

which is the average value of the interaction energy divided by 2 to account for double counting. Because $m = 0$ for $T > T_c$, the energy vanishes for all $T > T_c$, and thus the specific heat also vanishes. Below T_c the energy per spin is given by

$$\frac{E}{N} = -\frac{1}{2}Jq\big[\tanh(Jqm/kT)\big]^2. \tag{5.120}$$

Problem 5.16. Behavior of the specific heat near T_c

Use (5.120) and the fact that $m^2 \approx 3(T_c - T)/T_c$ for $T \lesssim T_c$ to show that the specific heat according to mean-field theory is

$$C(T \to T_c^-) = 3k/2. \tag{5.121}$$

Hence, mean-field theory predicts that there is a jump (discontinuity) in the specific heat. ☐

***Problem 5.17.** Improved mean-field theory approximation for the energy

We write s_i and s_j in terms of their deviation from the mean as $s_i = m + \Delta_i$ and $s_j = m + \Delta_j$, and write the product $s_i s_j$ as

$$s_i s_j = (m + \Delta_i)(m + \Delta_j) \tag{5.122a}$$

$$= m^2 + m(\Delta_i + \Delta_j) + \Delta_i \Delta_j. \tag{5.122b}$$

We have ordered the terms in (5.122b) in powers of their deviation from the mean. If we neglect the last term, which is quadratic in the fluctuations from the mean, we obtain

$$s_i s_j \approx m^2 + m(s_i - m) + m(s_j - m) = -m^2 + m(s_i + s_j). \tag{5.123}$$

(a) Show that we can approximate the energy of interaction in the Ising model as

$$-J \sum_{i,j=\mathrm{nn}(i)} s_i s_j = +J \sum_{i,j=\mathrm{nn}(i)} m^2 - Jm \sum_{i,j=\mathrm{nn}(i)} (s_i + s_j) \tag{5.124a}$$

$$= \frac{JqNm^2}{2} - Jqm \sum_{i=1}^{N} s_i. \tag{5.124b}$$

(b) Show that the partition function $Z(T, H, N)$ can be expressed as

$$Z(T,H,N) = e^{-NqJm^2/2kT} \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} e^{(Jqm+H)\sum_i s_i/kT} \tag{5.125a}$$

$$= e^{-NqJm^2/2kT} \Big(\sum_{s=\pm 1} e^{(qJm+H)s/kT} \Big)^N \tag{5.125b}$$

$$= e^{-NqJm^2/2kT} \big[2\cosh(qJm+H)/kT\big]^N. \tag{5.125c}$$

Show that the free energy per spin $f(T,H) = -(kT/N)\ln Z(T,H,N)$ is given by

$$f(T,H) = \frac{1}{2}Jqm^2 - kT\ln\big[2\cosh(qJm+H)/kT\big]. \tag{5.126}$$

□

The expressions for the free energy in (5.107) and (5.126) contain both m and H rather than H only. In this case m represents a parameter. For arbitrary values of m these expressions do not give the equilibrium free energy, which is determined by minimizing f treated as a function of m.

Problem 5.18. Minima of the free energy

(a) To understand the meaning of the various solutions of (5.108), expand the free energy in (5.126) about $m = 0$ with $H = 0$ and show that the form of $f(m)$ near the critical point (small m) is given by

$$f(m) = a + b(1 - \beta qJ)m^2 + cm^4. \tag{5.127}$$

Determine a, b, and c.

(b) If H is nonzero but small, show that there is an additional term $-mH$ in (5.127).

(c) Show that the minimum free energy for $T > T_c$ and $H = 0$ is at $m = 0$, and that $m = \pm m_0$ corresponds to a lower free energy for $T < T_c$.

(d) Use Program `IsingMeanField` to plot $f(m)$ as a function of m for $T > T_c$ and $H = 0$. For what value of m does $f(m)$ have a minimum?

(e) Plot $f(m)$ for $T = 1$ and $H = 0$. Where are the minima of $f(m)$? Do they have the same depth? If so, what is the meaning of this result?

(f) Choose $H = 0.5$ and $T = 1$. Do the two minima have the same depth? The global minimum corresponds to the equilibrium or stable phase. If we quickly "flip" the field and let $H \to -0.5$, the minimum at $m \approx 1$ will become a local minimum. The system will remain in this local minimum for some time before it switches to the global minimum (see Section 5.10.6). □

We now compare the results of mean-field theory near the critical point with the exact results for the one and two-dimensional Ising models. The fact that the mean-field result (5.109) for T_c depends only on q, the number of nearest neighbors, and not the spatial dimension d is one of the inadequacies of the simple version of mean-field theory that we have discussed. The simple mean-field theory even predicts a phase transition in one dimension, which we know is incorrect. In Table 5.2 the mean-field predictions for T_c are compared to the best-known estimates of the

lattice	d	q	T_{mf}/T_c
square	2	4	1.763
hexagonal	2	6	1.648
diamond	3	4	1.479
simple cubic	3	6	1.330
bcc	3	8	1.260
fcc	3	12	1.225

Table 5.2: Comparison of the mean-field predictions for the critical temperature of the Ising model with exact results and the best-known estimates for different spatial dimensions d and lattice symmetries.

critical temperatures for the Ising model for two- and three-dimensional lattices. We see that the mean-field theory predictions for T_c improve as the number of neighbors increases for a given dimension. The inaccuracy of mean-field theory is due to the fact that it ignores correlations between the spins. In Section 5.10.4 we discuss more sophisticated treatments of mean-field theory that include short-range correlations between the spins and yield better estimates of the critical temperature, but not the critical exponents.

Mean-field theory predicts that various thermodynamic properties exhibit power law behavior near T_c, in qualitative agreement with the exact solution of the two-dimensional Ising model and the known properties of the three-dimensional Ising model. This qualitative behavior is characterized by critical exponents. The mean-field predictions for the critical exponents β, γ, and δ are $\beta = 1/2$, $\gamma = 1$, and $\delta = 3$ respectively (see Table 5.1). (The mean-field theory predictions of the other critical exponents are given in Section 9.1.) These values of the critical exponents do not agree with the results of the Onsager solution of the two-dimensional Ising model (see Table 5.1). Also mean-field theory predicts a jump in the specific heat, whereas the Onsager solution predicts a logarithmic divergence. Similar disagreements between the predictions of mean-field theory and the known critical exponents are found in three dimensions, but the discrepancies are not as large.

We also note that the mean-field results for the critical exponents are independent of dimension. In Section 9.1 we discuss a more general version of mean-field theory, which is applicable to a wide variety of systems, and shows why all mean-field theories predict the same values for the critical exponents independent of dimension.

Problem 5.19. Improvement of mean-field theory with dimension

From Table 5.1 we see that the predictions of mean-field theory increase in accuracy with increasing dimension. Why is this trend reasonable? □

Why mean-field theory fails. The main assumption of mean-field theory is that each spin feels the same effective magnetic field due to all the other spins. That is, mean-field theory ignores the fluctuations in the effective field. But if mean-field theory ignores fluctuations, why does the susceptibility diverge near the critical point? (Recall that the susceptibility is a measure of the fluctuations of the magnetization.) Because the fluctuations are ignored in one context, but not another, we see that mean-field theory carries with it the seeds of its own destruction. That is, mean-field theory does not treat the fluctuations consistently. This inconsistency is unimportant if the fluctuations are weak.

Because the fluctuations become more important as the system approaches the critical point, we expect that mean-field theory breaks down for T close to T_c. A criterion for the range of temperatures for which mean-field theory theory is applicable is discussed in Section 9.1, page 434, where it is shown that the fluctuations can be ignored if

$$\xi_0^{-d}|\epsilon|^{(d/2)-2} \ll 1, \tag{5.128}$$

where ξ_0 is the correlation length at $T=0$ and is proportional to the effective range of interaction. The inequality in (5.128) is always satisfied for $d>4$ near the critical point where $\epsilon \ll 1$. That is, mean-field theory yields the correct results for the critical exponents in higher than four dimensions. (In four dimensions the power law behavior is modified by logarithmic factors.) In a conventional superconductor such as tin, $\xi_0 \approx 2300\,\text{Å}$, and the mean-field theory of a superconductor (known as BCS theory) is applicable near the superconducting transition for ϵ as small as 10^{-14}.

5.7.1 *Phase diagram of the Ising model

Nature exhibits two qualitatively different kinds of phase transitions. The more familiar kind, which we observe when ice freezes or water boils, involves a discontinuous change in various thermodynamic quantities such as the energy and the entropy. For example, the density as well as the energy and the entropy change discontinuously when water boils and when ice freezes. This type of phase transition is called a *discontinuous* or *first-order transition*. We will discuss first-order transitions in the context of gases and liquids in Chapter 7.

The other type of phase transition is more subtle. In this case thermodynamic quantities such as the energy and the entropy are continuous, but various derivatives such as the specific heat and the compressibility of a fluid and the susceptibility of a magnetic system show divergent behavior at the phase transition. Such transitions are called *continuous* phase transitions.

We have seen that the Ising model in two dimensions has a continuous phase transition in zero magnetic field such that below the critical temperature T_c there is a nonzero spontaneous magnetization, and above T_c the mean magnetization vanishes as shown by the solid curve in the phase diagram in Figure 5.14. The three-dimensional Ising model has the same qualitative behavior, but the values of the critical temperature and the critical exponents are different.

The behavior of the Ising model is qualitatively different if we apply an external magnetic field H. If $H \neq 0$, the magnetization m is nonzero at all temperatures and has the same sign as H (see Figure 5.15). The same information is shown in a different way in Figure 5.14. Each point in the unshaded region corresponds to an equilibrium value of m for a particular value of T and H.[10]

At a phase transition at least one thermodynamic quantity diverges or has a discontinuity. For example, both the specific heat and the susceptibility diverge at T_c for a ferromagnetic phase

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[10] In a ferromagnetic material such as iron, nickel, and cobalt, the net magnetization frequently vanishes even below T_c. In these materials there are several magnetic domains within which the magnetization is nonzero. These domains are usually oriented at random, leading to zero net magnetization for the entire sample. Such a state is located in the shaded region of Figure 5.14. The randomization of the orientation of the domains occurs when the metal is formed and cooled below T_c and is facilitated by crystal defects. When a piece of iron or similar material is subject to an external magnetic field, the domains align, and the iron becomes "magnetized." When the field is removed the iron remains magnetized. If the iron is subject to external forces such as being banged with a hammer, the domains can be randomized again, and the iron loses its net magnetization. The Ising model is an example of a single-domain ferromagnet.

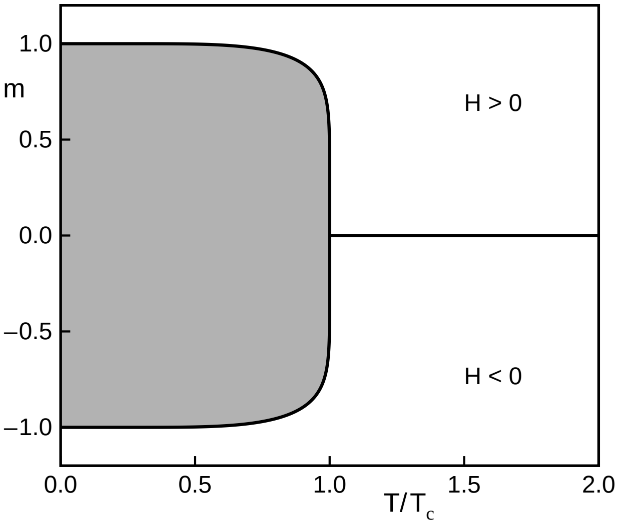

Figure 5.14: Sketch of the phase diagram for an Ising ferromagnet. The bold line represents the magnetization for $H = 0$. Equilibrium magnetization values for $H \neq 0$ are possible at any point in the unshaded region. Points in the shaded region represent nonequilibrium values of m.

transition with $H = 0$. For $H \neq 0$ and $T > T_c$ there is no phase transition as the magnetic field is decreased to zero and then to negative values because no quantity diverges or has a discontinuity. In contrast, for $T < T_c$ there is a transition because as we change the field from $H = 0^+$ to $H = 0^-$ m changes discontinuously from a positive value to a negative value (see Figure 5.15).

Problem 5.20. Ising model in an external magnetic field

Use Program `Ising2D` to simulate the Ising model on a square lattice at a given temperature. Choose $N = L^2 = 32^2$. Run for at least 200 Monte Carlo steps per spin at each value of the field.

(a) Set $H = 0.2$ and $T = 3$ and estimate the approximate value of the magnetization. Then change the field to $H = 0.1$ and continue updating the spins (do not press `New`) so that the simulation is continued from the last microstate. Note the value of the magnetization. Continue this procedure with $H = 0$, then $H = -0.1$ and then $H = -0.2$. Do your values of the magnetization change abruptly as you change the field? Is there any indication of a phase transition as you change H?

(b) Repeat the same procedure as in part (a) at $T = 1.8$ which is below the critical temperature. What happens now? Is there evidence of a sudden change in the magnetization as the direction of the field is changed?

(c) Use Program `Ising2DHysteresis` with $T = 1.8$, the initial magnetic field $H = 1$, $\Delta H = 0.01$, and 10 mcs for each value of H. The program plots the mean magnetization for each value of H, and changes H by ΔH until H reaches $H = -1$, when it changes ΔH to $-\Delta H$. Describe what you obtain and why it occurred. The resulting curve is called a *hysteresis* loop, and is

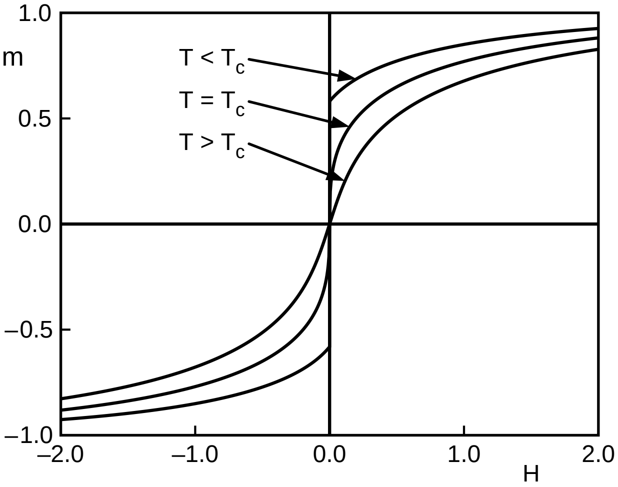

Figure 5.15: The equilibrium values of m as a function of the magnetic field H for $T > T_c$, $T = T_c$, and $T < T_c$. The plot for $T > T_c$ is smooth in contrast to the plot for $T < T_c$ which has a discontinuity at $H = 0$. For $T = T_c$ there is no discontinuity, and the function $m(H)$ has an infinite slope at $H = 0$.

characteristic of discontinuous phase transitions. An example of the data you can obtain in this way is shown in Figure 5.16.

(d) Change the number of mcs per field value to 1 and view the resulting plot for m versus H. Repeat for mcs per field value equal to 100. Explain the differences you see. ☐

5.8 *Simulation of the Density of States

The probability that a system in equilibrium with a heat bath at a temperature T has energy E is given by

$$P(E) = \frac{\Omega(E)}{Z} e^{-\beta E}, \tag{5.129}$$

where $\Omega(E)$ is the number of states with energy E,[11] and the partition function $Z = \sum_E \Omega(E) e^{-\beta E}$. If $\Omega(E)$ is known, we can calculate the mean energy (and other thermodynamic quantities) at any temperature from the relation

$$\overline{E} = \frac{1}{Z} \sum_E E\Omega(E) e^{-\beta E}. \tag{5.130}$$

Hence, the quantity $\Omega(E)$ is of much interest. In the following we discuss an algorithm that directly computes $\Omega(E)$ for the Ising model. In this case the energy is a discrete variable and hence the quantity we wish to compute is the number of spin microstates with the same energy.

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[11] The quantity $\Omega(E)$ is the number of states with energy E for a system such as the Ising model which has discrete values of the energy. It is common to refer to $\Omega(E)$ as the density of states even when the values of E are discrete.

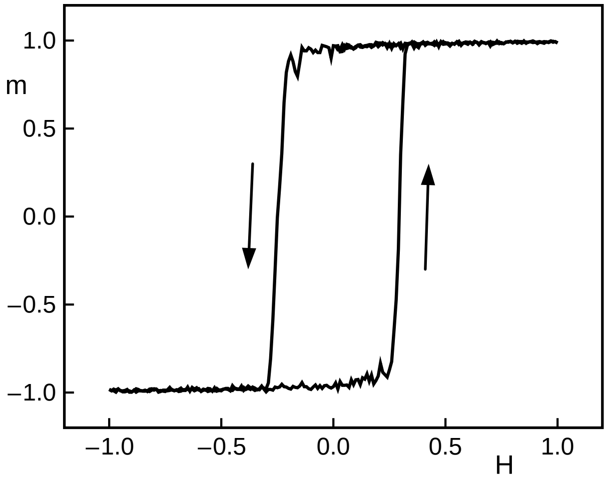

Figure 5.16: Hysteresis curve obtained from the simulation of the two-dimensional Ising model at $T = 1.8$. The field was reduced by $\Delta H = 0.01$ every 10 mcs. The arrows indicate the direction in which the magnetization is changing. Note that starting from saturation at $m = 1$, a "coercive field" of about $H = -0.25$ is needed to reduce the magnetization to zero. The magnetization at zero magnetic field is called the "remnant" magnetization. The equilibrium value of m drops discontinuously from a positive value to a negative value as H decreases from $H = 0^+$ to $H = 0^-$. Hysteresis is a nonequilibrium phenomenon and is a dynamic manifestation of a system that remains in a local minimum for some time before it switches to the global minimum.

Suppose that we were to try to compute $\Omega(E)$ by doing a random walk in energy space by flipping the spins at random and accepting all microstates that we obtain in this way. The histogram of the energy, $H(E)$, the number of visits to each possible energy E of the system, would become proportional to $\Omega(E)$ if the walk visited all possible microstates many times. In practice, it would be impossible to realize such a long random walk given the extremely large number of microstates. For example, an Ising model with $N = 100$ spins has $2^{100} \approx 1.3 \times 10^{30}$ microstates.

An even more important limitation on doing a simple random walk to determine $\Omega(E)$ is that the walk would spend most of its time visiting the same energy values over and over again and would not reach the values of E that are less probable. The idea of the *Wang-Landau* algorithm is to do a random walk in energy space by flipping single spins at random and accepting the changes with a probability that is proportional to the reciprocal of the density of states. In this way energy values that would be visited often using a simple random walk would be visited less often because they have a larger density of states. There is only one problem – we don't know $\Omega(E)$. We will see that the Wang-Landau[12] algorithm estimates $\Omega(E)$ at the same time that it does a random walk.

To implement the algorithm we begin with an arbitrary microstate and a guess for the density of states. The simplest guess is to set $\Omega(E) = 1$ for all possible energies E. The algorithm can be

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[12] We have mentioned the name Landau several times in the text. This Landau is not Lev D. Landau, but David Landau, a well-known physicist at the University of Georgia.

summarized by the follow steps.

1. Choose a spin at random and make a trial flip. Compute the energy before, E_1, and after the flip, E_2, and accept the change with probability
$$p(E_1 \to E_2) = \min(\tilde{\Omega}(E_1)/\tilde{\Omega}(E_2), 1), \tag{5.131}$$
where $\tilde{\Omega}(E)$ is the current estimate of $\Omega(E)$. Equation (5.131) implies that if $\tilde{\Omega}(E_2) \leq \tilde{\Omega}(E_1)$, the state with energy E_2 is always accepted; otherwise, it is accepted with probability $\tilde{\Omega}(E_1)/\tilde{\Omega}(E_2)$. That is, the state with energy E_2 is accepted if a random number r satisfies the condition $r \leq \tilde{\Omega}(E_1)/\tilde{\Omega}(E_2)$. After the trial flip the energy of the system is E_2 if the change is accepted or remains at E_1 if the change is not accepted.

2. To estimate $\Omega(E)$ multiply the current value of $\tilde{\Omega}(E)$ by a modification factor $f > 1$:
$$\tilde{\Omega}(E) = f\tilde{\Omega}(E). \tag{5.132}$$
We also update the existing entry for $H(E)$ in the energy histogram
$$H(E) \to H(E) + 1. \tag{5.133}$$
Because $\tilde{\Omega}(E)$ becomes very large, we must work with the logarithm of the density of states, so that $\ln \tilde{\Omega}(E)$ will fit into double precision numbers. Therefore, each update of the density of states is implemented as $\ln \tilde{\Omega}(E) \to \ln \tilde{\Omega}(E) + \ln f$, and the ratio of the density of states is computed as $\exp[\ln \tilde{\Omega}(E_1) - \ln \tilde{\Omega}(E_2)]$. A reasonable choice of the initial modification factor is $f = f_0 = e \approx 2.71828\ldots$. If f_0 is too small, the random walk will need a very long time to reach all possible energies. Too large a choice of f_0 will lead to large statistical errors.

3. Proceed with the random walk in energy space until an approximately flat histogram $H(E)$ is obtained, that is, until all the possible energy values are visited an approximately equal number of times. Because it is impossible to obtain a perfectly flat histogram, we will say that $H(E)$ is "flat" when $H(E)$ for all possible E is not less than Δ of the average histogram $\overline{H(E)}$; Δ is chosen according to the size and the complexity of the system and the desired accuracy of the density of states. For the two-dimensional Ising model on small lattices, Δ can be chosen to be as high as 0.95, but for large systems the criterion for flatness might never be satisfied if Δ is too close to 1.

4. Once the flatness criterion has been satisfied, reduce the modification factor f using a function such as $f_1 = \sqrt{f_0}$, reset the histogram to $H(E) = 0$ for all values of E, and begin the next iteration of the random walk during which the density of states is modified by f_1 at each trial flip. The density of states is not reset during the simulation. We continue performing the random walk until the histogram $H(E)$ is again flat. We then reduce the modification factor, $f_{i+1} = \sqrt{f_i}$, reset the histogram to $H(E) = 0$ for all values of E, and continue the random walk.

5. The simulation is stopped when f is smaller than a predefined value [such as $f = \exp(10^{-8}) \approx 1.00000001$]. The modification factor acts as a control parameter for the accuracy of the density of states during the simulation and also determines how many Monte Carlo sweeps are necessary for the entire simulation.

The algorithm provides an estimate of the density of states because if the current estimate of $\tilde{\Omega}(E)$ is too low, then the acceptance criterion (5.131) pushes the system to states with lower $\tilde{\Omega}(E)$, thus increasing $\tilde{\Omega}(E)$. If $\tilde{\Omega}(E)$ is too high, the reverse happens. Gradually, the calculation tends to the true value of $\Omega(E)$.

At the end of the simulation, the algorithm provides only a relative density of states. To determine the normalized density of states $\Omega(E)$, we can either use the fact that the total number of states for the Ising model is

$$\sum_E \Omega(E) = 2^N, \tag{5.134}$$

or that the number of ground states (for which $E = -2NJ$) is 2. The latter normalization ensures the accuracy of the density of states at low energies which is important in the calculation of thermodynamic quantities at low temperatures. If we apply (5.134), we cannot guarantee the accuracy of $\Omega(E)$ for energies at or near the ground state, because the rescaling factor is dominated by the maximum density of states. We may use one of these normalization conditions to obtain the absolute density of states and the other normalization condition to check the accuracy of our result.

***Problem 5.21.** Wang-Landau algorithm for the Ising model

Program `IsingDensityOfStates` implements the Wang-Landau algorithm for the Ising model on a square lattice.

(a) Calculate the exact values of $\Omega(E)$ for the 2×2 Ising model. Run the simulation for $L = 2$ and verify that the computed density of states is close to your exact answer.

(b) Choose larger values of L, for example, $L = 16$, and describe the qualitative energy dependence of $\Omega(E)$.

(c) The program also computes the specific heat as a function of temperature using the estimated value of $\tilde{\Omega}(E)$. Describe the qualitative temperature dependence of the specific heat. □

The Potts model. The *Potts model* is a generalization of the Ising model in which each lattice site contains an entity (a spin) that can be in one of q states. If two nearest neighbor sites are in the same state, then the interaction energy is $-K$. The interaction energy is zero if they are in different states. Potts models are useful for describing the absorption of molecules on crystalline surfaces and the behavior of foams, for example, and exhibit a discontinuous or continuous phase transition depending on the value of q.

The Potts model exhibits a phase transition between a high temperature phase where the q states equally populate the sites and a low temperature phase where one of the q states is more common than the others. In two dimensions the transition between these two phases is first-order (see Section 5.7.1) for $q > 4$ and is continuous otherwise. In Problem 5.22 we explore how the Wang-Landau algorithm can provide some insight into the nature of the Potts model and its phase transitions.

***Problem 5.22.** Application of Wang-Landau algorithm to the Potts model

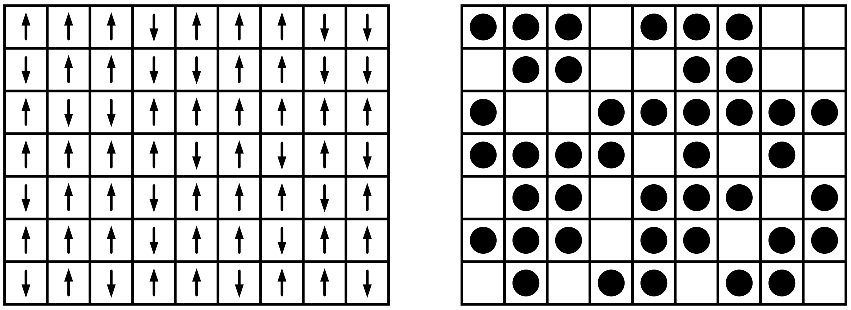
(a) (b)

Figure 5.17: (a) A typical microstate of the Ising model. (b) The same microstate in the lattice gas picture with spin up replaced by a particle and spin down replaced by an empty cell.

(a) What is the relation of the $q = 2$ Potts model to the usual Ising model? In particular, what is the relation of the interaction energy K defined in the Potts model and the interaction energy J defined in the Ising model?

(b) Program `PottsModel` implements the Wang-Landau algorithm for the Potts model on a square lattice. Run the program for $L = 16$ and various values of q and verify that the peak in the heat capacity occurs near the known exact value for the transition temperature given by $T_c = (\ln(1+\sqrt{q}))^{-1}$. You will need more than 100,000 Monte Carlo steps to obtain reliable data.

(c) Choose $q = 2$ and $q = 3$ and observe the energy distribution $P(E) = \Omega e^{-\beta E}$ at $T = T_c$. Do you see one peak or two?

(d) Choose $q = 10$ and observe the energy distribution $P(E)$ at $T = T_c$. You should notice two peaks in this distribution. Discuss why the occurrence of two peaks is appropriate for a first-order transition. ☐

5.9 *Lattice Gas

The Ising model is useful not only because it is the simplest model of magnetism, but also because it can be applied to many other systems. Two common applications are to fluids and to binary alloys. In the fluid model a spin of +1 represents a particle and a spin of −1 represents a void (see Figure 5.17). The hard core repulsion between particles at short distances is modeled by the restriction that there is at most one particle per site. The short-range attractive interaction between particles is modeled by the nearest-neighbor Ising interaction.

Binary alloys are modeled in a similar way with +1 representing one type of atom and −1 representing a second type. The Ising interaction models the tendency of like atoms to be near each other because the attraction between like atoms is stronger than that between unlike atoms in binary alloys. In this section we will focus on the fluid model, which is called the *lattice gas*.

We could proceed by taking the form of the Ising energy given in (5.35) and converting all our previous results in the language of magnetism to the language of fluids. For example, when most spins are up the system is mostly a liquid, and when most spins are down the system is a gas. However, it is useful to change variables so that we can more directly describe the behavior of the system in the language of particles. For this purpose we define a new variable $n_i \equiv (s_i + 1)/2$, so that $n_i = 0$ or 1. The energy function (5.35) becomes

$$E = -J \sum_{i,j=\mathrm{nn}(i)}^{N} (2n_i - 1)(2n_j - 1) - H \sum_{i=1}^{N} (2n_i - 1). \tag{5.135}$$

We expand and rearrange terms and find that on a square lattice

$$E = -4J \sum_{i,j=\mathrm{nn}(i)}^{N} n_i n_j - (2H - 8J) \sum_{i=1}^{N} n_i + N(H - 2J). \tag{5.136}$$

To obtain the factor of 8 in (5.136) note that $\sum_{i,j=\mathrm{nn}(i)}^{N} 2n_i = 4\sum_{i}^{N} 2n_i$, where the factor of 4 arises from the sum over j and is the number of nearest neighbors of i. The sum $\sum_{i,j=\mathrm{nn}(i)}^{N} 2n_j$ gives the same contribution. To avoid double counting we need to divide the sums by a factor of 2.

We define the energy $u_0 \equiv 4J$ and the chemical potential $\mu \equiv 2H - 8J$, and express the energy of the lattice gas as

$$E = -u_0 \sum_{i,j=\mathrm{nn}(i)}^{N} n_i n_j - \mu \sum_{i=1}^{N} n_i + N(H - 2J). \tag{5.137}$$

The constant term $N(H - 2J)$ can be eliminated by redefining the zero of energy.

It is natural to fix the temperature T and external magnetic field H of the Ising model because we can control these quantities experimentally and in simulations. Hence, we usually simulate and calculate the properties of the Ising model in the canonical ensemble. The Metropolis algorithm for simulating the Ising model flips individual spins, which causes the magnetization to fluctuate. Because the magnetization is not conserved, the number of particles in the lattice gas context is not conserved, and hence the same Metropolis algorithm is equivalent to the grand canonical ensemble for a lattice gas. We can modify the Metropolis algorithm to simulate a lattice gas in the canonical ensemble with the number of particles fixed. Instead of flipping individual spins (single spin flip dynamics), we have to interchange two spins. The algorithm proceeds by choosing a pair of nearest neighbor spins at random. If the two spins are parallel, we include the unchanged microstate in various averages. If the two spins are antiparallel, we interchange the two spins and compute the trial change in the energy ΔE as before and accept the trial change with the usual Boltzmann probability. (This algorithm is called spin exchange or Kawasaki dynamics.)

Although the Ising model and the lattice gas are equivalent and all the critical exponents are the same, the interpretation of the phase diagram differs. Suppose that the number of occupied sites equals the number of unoccupied sites. In this case the transition from high to low temperature is continuous. For $T > T_c$ the particles exist in small droplets and the voids exist in small bubbles. In this case the system is neither a liquid or a gas. Below T_c the particles coalesce into a macroscopically large cluster, and the bubbles coalesce into a large region of unoccupied sites.

This change is an example of *phase separation*, and the simultaneous existence of both a gas and liquid is referred to as gas-liquid coexistence.[13] The order parameter of the lattice gas is taken to be $\rho^* \equiv (\rho_L - \rho_G)/\rho_L$, where ρ_L is the particle density of the liquid region and ρ_G is the density of the gas region. Above T_c there is no phase separation (there are no separate liquid and gas regions) and thus $\rho^* = 0$. At $T = 0$, $\rho_L = 1$ and $\rho_G = 0$.[14] The power law behavior of ρ^* as $T \to T_c$ from below T_c is described by the critical exponent β, which has the same value as that for the magnetization in the Ising model. The equality of the critical exponents for the Ising and lattice gas models as well as more realistic models of liquids and gases is an example of *universality* of critical phenomena for qualitatively different systems (see Sections 9.5 and 9.6).

If the number of occupied and unoccupied sites is unequal, then the transition from a fluid to two-phase coexistence as the temperature is lowered is discontinuous. For particle systems it is easier to analyze the transition by varying the pressure rather than the temperature.

As we will discuss in Chapter 7, there is a jump in the density as the pressure is changed along an isotherm in a real fluid. This density change can occur either for a fixed number of particles with a change in the volume or as a change in the number of particles for a fixed volume. We will consider the latter by discussing the lattice gas in the grand canonical ensemble. From (2.168) we know that the thermodynamic potential Ω associated with the grand canonical ensemble is given by $\Omega = -PV$. For the lattice gas the volume V is equal to the number of sites N, a fixed quantity. We know from (4.144) that $\Omega = -kT \ln Z_G$, where Z_G is the grand partition function. The grand partition function for the lattice gas with the energy given by (5.137) is identical to the partition function for the Ising model in a magnetic field with the energy given by (5.35), because the difference is only a change of variables. The free energy for the Ising model in a magnetic field is $F = -kT \ln Z$. Because $Z = Z_G$, we have that $F = \Omega$, and thus we conclude that $-PV$ for the lattice gas equals F for the Ising model. This identification will allow us to understand what happens to the density as we change the pressure along an isotherm. In a lattice gas the density is the number of particles divided by the number of sites or $\rho = \overline{n_i}$. In Ising language ρ is

$$\rho = \frac{1}{2}\overline{(s_i + 1)} = (m + 1)/2, \tag{5.138}$$

where m is the magnetization. Because $-PV = F$, changing the pressure at fixed temperature and volume in the lattice gas corresponds to changing the free energy $F(T, V, H)$ by changing the field H in the Ising model. We know that when H changes from 0^+ to 0^- for $T < T_c$ there is a jump in the magnetization from a positive to a negative value. From (5.138) we see that this jump corresponds to a jump in the density in the lattice gas model, corresponding to a change in the density from a liquid to a gas.

Problem 5.23. Simulation of the two-dimensional lattice gas

(a) What is the value of the critical temperature T_c for the lattice gas in two dimensions (in units of u_0/k)?

(b) Program `LatticeGas` simulates the lattice gas on a square lattice of linear dimension L. The initial state has all the particles at the bottom of the simulation cell. Choose $L = 32$ and set

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[13] If the system were subject to gravity, the liquid region would be at the bottom of a container and the gas would be at the top.

[14] For $T > 0$ the cluster representing the liquid region would have some unoccupied sites and thus $\rho_L < 1$, and the gas region would have some particles so that $\rho_G > 0$.

the gravitational field equal to zero. Do a simulation at $T = 0.4$ with $N = 600$ particles. After a few Monte Carlo steps you should see the bottom region of particles (green sites) develop a few small holes or bubbles and the unoccupied region contain a few isolated particles or small clusters of particles. This system represents a liquid (the predominately green region) in equilibrium with its vapor (the mostly white region). Record the energy. To speed up the simulation set `steps per display` equal to 100.

(c) Increase the temperature in steps of 0.05 until $T = 0.7$. At each temperature run for at least 10,000 mcs to reach equilibrium and then press the `Zero Averages` button. Run for at least 20,000 mcs before recording your estimate of the energy. Describe the visual appearance of the positions of the particle and empty sites at each temperature. At what temperature does the one large liquid region break up into many pieces, such that there is no longer a sharp distinction between the liquid and vapor region? At this temperature there is a single fluid phase. Is there any evidence from your estimates of the energy that a transition from a two-phase to a one-phase system has occurred? Repeat your simulations with $N = 200$.

(d) Repeat part (c) with $N = 512$. In this case the system will pass through a critical point. The change from a one phase to a two-phase system occurs continuously in the thermodynamic limit. Can you detect this change or does the system look similar to the case in part (c)?

(e) If we include a gravitational field, the program removes the periodic boundary conditions in the vertical direction, and thus sites in the top and bottom rows have three neighbors instead of four. The field should help define the liquid and gas regions. Choose $g = 0.01$ and repeat the above simulations. Describe the differences you see.

(f) Simulate a lattice gas of $N = 2048$ particles on a $L = 64$ lattice at $T = 2.0$ with no gravitational field for 5000 mcs. Then change the temperature to $T = 0.2$. This process is called a (temperature) quench, and the resulting behavior is called *spinodal decomposition*. The domains grow very slowly as a function of time. Discuss why it is difficult for the system to reach its equilibrium state for which there is one domain of mostly occupied sites in equilibrium with one domain of mostly unoccupied sites. □

5.10 Supplementary Notes

5.10.1 The Heisenberg model of magnetism

Classical electromagnetic theory tells us that magnetic fields are due to electrical currents and changing electric fields, and that the magnetic fields far from the currents are described by a magnetic dipole. It is natural to assume that magnetic effects in matter are due to microscopic current loops created by the motion of electrons in atoms. However, it was shown by Niels Bohr in his doctoral thesis of 1911 and independently by Johanna H. van Leeuwen in her 1919 doctoral thesis that diamagnetism does not exist in classical physics (see Mattis). Magnetism is a quantum phenomenon.

In the context of magnetism the most obvious new physics due to quantum mechanics is the existence of an intrinsic magnetic moment. The intrinsic magnetic moment is proportional to the intrinsic spin, another quantum mechanical property. We will now derive an approximation for the interaction energy between two magnetic moments. Because the electrons responsible for magnetic behavior are localized near the atoms of a regular lattice in most magnetic materials, we consider the simple case of two localized electrons. Each electron has spin 1/2 and are aligned up or down along the axis specified by the applied magnetic field. The electrons interact with each other and with nearby atoms and are described in part by the spatial wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2)$. This wavefunction must be multiplied by the spin eigenstates to obtain the actual state of the two electron system. We denote the basis for the spin eigenstates as

$$|\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, \tag{5.139}$$

where the arrows correspond to the spin of the electrons. These states are eigenstates of the z-component of the total spin angular momentum[15] $\hat{S}_z$ such that $\hat{S}_z$ operating on any of the states in (5.139) has an eigenvalue equal to the sum of the spins in the z direction. For example, $\hat{S}_z|\uparrow\uparrow\rangle = 1|\uparrow\uparrow\rangle$ and $\hat{S}_z|\uparrow\downarrow\rangle = 0|\uparrow\downarrow\rangle$. Similarly, $\hat{S}_x$ or $\hat{S}_y$ give zero if either operator acts on these eigenstates.

Because electrons are fermions, the basis states in (5.139) are not acceptable because if two electrons are interchanged, the wave function must be antisymmetric. Thus, $\psi(\mathbf{r}_1, \mathbf{r}_2) = +\psi(\mathbf{r}_2, \mathbf{r}_1)$ if the spin state is antisymmetric, and $\psi(\mathbf{r}_1, \mathbf{r}_2) = -\psi(\mathbf{r}_2, \mathbf{r}_1)$ if the spin state is symmetric. The simplest normalized linear combinations of the eigenstates in (5.139) that satisfy this condition are

$$\frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle], \tag{5.140a}$$

$$|\uparrow\uparrow\rangle, \tag{5.140b}$$

$$\frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle], \tag{5.140c}$$

$$|\downarrow\downarrow\rangle. \tag{5.140d}$$

The state in (5.140a) is antisymmetric, because interchanging the two electrons leads to minus the original state. This state has a total spin $S = 0$ and is called the singlet state. The collection of the last three states is called the triplet state and has $S = 1$. If the spins are in the triplet state, then $\psi(\mathbf{r}_1, \mathbf{r}_2) = -\psi(\mathbf{r}_2, \mathbf{r}_1)$. Similarly, if the spins are in the singlet state, then $\psi(\mathbf{r}_1, \mathbf{r}_2) = +\psi(\mathbf{r}_2, \mathbf{r}_1)$. Hence, when $\mathbf{r}_1 = \mathbf{r}_2$, ψ is zero for the triplet state, and thus the electrons stay further apart, and their electrostatic energy is smaller. For the singlet state at $\mathbf{r}_1 = \mathbf{r}_2$, ψ is nonzero, and thus the electrons can be closer to each other, with a larger electrostatic energy. To find a relation between the energy and the spin operators we note that

$$\hat{S} \cdot \hat{S} = (\hat{S}_1 + \hat{S}_2)^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2\,\hat{S}_1 \cdot \hat{S}_2, \tag{5.141}$$

where the operator $\hat{S}$ is the total spin. Because both electrons have spin 1/2, the eigenvalues of $\hat{S}_1^2$ and $\hat{S}_2^2$ are equal and are given by $(1/2)(1 + 1/2) = 3/4$. We see that the eigenvalue S of $\hat{S}$ is zero for the singlet state and is one for the triplet state. Hence, the eigenvalue of $\hat{S}^2$ is $S(S+1) = 0$ for the singlet state and $(1(1+1) = 2$ for the triplet state. Similarly, the eigenvalue S_{12} of $\hat{S}_1 \cdot \hat{S}_2$ equals $-3/4$ for the singlet state and $1/4$ for the triplet state. These considerations allows us to write

$$E = c - JS_{12}, \tag{5.142}$$

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[15] We will denote operators with a caret symbol in this section.

where c is a constant and J is known as the *exchange constant.* If we denote E_{triplet} and E_{singlet} as the triplet energy and the singlet energy, respectively, and let $J = E_{\text{singlet}} - E_{\text{triplet}}$, we can determine c and find

$$E = \frac{1}{4}(E_{\text{singlet}} + 3E_{\text{triplet}}) - JS_{12}. \tag{5.143}$$

You can check (5.143) by showing that when $S_{12} = -3/4$, $E = E_{\text{singlet}}$ and when $S_{12} = 1/4$, $E = E_{\text{triplet}}$. The term in parentheses in (5.143) is a constant and can be omitted by suitably defining the zero of energy. The second term represents a convenient form of the interaction between two spins.

The total energy of the Heisenberg model of magnetism is based on the form (5.143) for the spin-spin interaction and is expressed as

$$\hat{H} = -\sum_{i<j=1}^{N} J_{ij}\,\hat{S}_i \cdot \hat{S}_j - g\mu_0 \mathbf{H}\cdot\sum_{i=1}^{N}\hat{S}_i, \tag{5.144}$$

where $g\mu_0$ is the magnetic moment of the electron. Usually we combine the factors of g and μ_0 into H and write the Heisenberg Hamiltonian as

$$\hat{H} = -\sum_{i<j=1}^{N} J_{ij}\,\hat{S}_i \cdot \hat{S}_j - H\sum_{i=1}^{N}\hat{S}_{z,i} \qquad \text{(Heisenberg model).} \tag{5.145}$$

The form (5.145) of the interaction energy is known as the *Heisenberg model.* The exchange constant J_{ij} can be either positive or negative. Note that $\hat{S}$ as well as the Hamiltonian $\hat{H}$ is an operator, and that the Heisenberg model is quantum mechanical in nature. The distinction between the operator $\hat{H}$ and the magnetic field H will be clear from the context.

The Heisenberg model assumes that we can treat all interactions in terms of pairs of spins. This assumption means that the magnetic ions in the crystal must be sufficiently far apart that the overlap of their wavefunctions is small. We have also neglected any orbital contribution to the total angular momentum. In addition, dipolar interactions can be important and lead to a coupling between the spin degrees of freedom and the relative displacements of the magnetic ions. It is very difficult to obtain the exact Hamiltonian from first principles.

The Heisenberg model is the starting point for most microscopic models of magnetism. We can go to the classical limit $S \to \infty$, consider spins with one, two, or three components, place the spins on lattices of any dimension and any crystal structure, and take J to be positive, negative, random, nearest-neighbor, long-range, and so on. In addition, we can include other interactions such as the interaction of an electron with an ion. The theoretical possibilities are very rich as are the types of magnetic materials of interest experimentally.

5.10.2 Low temperature expansion

The existence of exact analytical solutions for systems with nontrivial interactions is the exception, and we usually must be satisfied with approximate solutions with limited ranges of applicability. If the ground state is known and if we can determine the excitations from the ground state, we can determine the behavior of a system at low temperatures.

Figure 5.18: (a) The ground state of $N = 5$ Ising spins in an external magnetic field H. For toroidal boundary conditions, the ground state energy is $E_0 = -5J - 5H$. (b) The flip of a single spin of $N = 5$ Ising spins. The corresponding energy cost is $4J + 2H$.

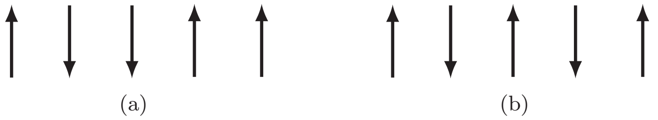

Figure 5.19: Microstates corresponding to two flipped spins of a system of $N = 5$ spins in one dimension. In (a) the flipped spins are nearest neighbors and in (b) the flipped spins are not nearest neighbors.

To understand the nature of this class of approximations we consider the one-dimensional Ising model at low temperatures. We know that the ground state corresponds to all spins completely aligned. When we raise the temperature slightly above $T = 0$, the system can raise its energy by flipping one or more spins. At a given temperature we can consider the excited states corresponding to $1,\ 2, \ldots, f$ flipped spins. These f spins may be connected or may consist of disconnected groups. Each number of flipped spins corresponds to a term in the low temperature expansion of the partition function.

As an example, consider a system of $N = 5$ spins with toroidal boundary conditions. The ground state is shown in Figure 5.18(a). The energy cost of flipping a single spin is $4J + 2H$. A typical microstate with one flipped spin is shown in Figure 5.18(b). (The energy of interaction of the flipped spin with its two neighbors changes from $-2J$ to $+2J$.) Because the flipped spin can be at $N = 5$ different sites, we have

$$Z = [1 + 5\, e^{-\beta(4J+2H)}]e^{-\beta E_0} \qquad (f = 1), \tag{5.146}$$

where $E_0 = -5(J + H)$.

The next higher energy excitation consists of a pair of flipped spins with one type of contribution arising from pairs that are nearest neighbors [see Figure 5.19(a)] and the other type arising from pairs that are not nearest neighbors [see Figure 5.19(b)]. We leave it as an exercise (see Problem 5.24) to determine the corresponding energies and the number of different ways that this type of excitation occurs.

***Problem 5.24.** Low temperature expansion for five spins

(a) Determine the contribution to the partition function corresponding to two flipped spins out of $N = 5$. (Use toroidal boundary conditions.)

(b) Enumerate the 2^5 microstates of the $N = 5$ Ising model in one dimension and classify the microstates corresponding to the energy of the microstate. Then use your results to find the low temperature expansion of Z. Express your result for Z in terms of the variables

$$u = e^{-2J/kT} \tag{5.147a}$$

and

$$w = e^{-2H/kT}. \tag{5.147b}$$

□

***Problem 5.25.** Low temperature behavior of N spins

(a) Generalize your results to N spins in one dimension and calculate Z corresponding to $f = 1$ and $f = 2$ flipped spins. Find the free energy, mean energy, heat capacity, magnetization, and susceptibility, assuming that $u \ll 1$ and $w \ll 1$ [see (5.147)] so that you can use the approximation $\ln(1+\epsilon) \approx \epsilon$.

(b) Generalize the low temperature expansion for the one-dimensional Ising model by expanding in the number of domain walls, and show that the expansion can be summed exactly (see Problem 5.34). (The low temperature expansion of the Ising model can be summed only approximately in higher dimensions using what are known as Padé approximants.) □

5.10.3 High temperature expansion

At high temperatures for which $J/kT \ll 1$, the effects of the interactions between the spins become small, and we can develop a perturbation method based on expanding Z in terms of the small parameter J/kT. For simplicity, we consider the Ising model in zero magnetic field. We write

$$Z_N = \sum_{\{s_i=\pm 1\}} \prod_{i,j=\mathrm{nn}(i)} e^{\beta J s_i s_j}, \tag{5.148}$$

where the sum is over all states of the N spins, and the product is restricted to nearest neighbor pairs of sites $\langle ij \rangle$ in the lattice. We first use the identity

$$e^{\beta J s_i s_j} = \cosh\beta J + s_i s_j \sinh\beta J = (1 + v s_i s_j)\cosh\beta J, \tag{5.149}$$

where

$$v = \tanh\beta J. \tag{5.150}$$

The identity (5.149) can be demonstrated by considering the various cases $s_i, s_j = \pm 1$ (see Problem 5.43). The variable v approaches zero as $T \to \infty$ and will be used as an expansion parameter instead of J/kT for reasons that will become clear. Equation (5.148) can now be written as

$$Z_N = (\cosh\beta J)^p \sum_{\{s_i\}} \prod_{\langle ij \rangle} (1 + v s_i s_j), \tag{5.151}$$

where p is the total number of nearest neighbor pairs in the lattice, that is, the total number of interactions. For a lattice with toroidal boundary conditions

$$p = \frac{1}{2} N q, \tag{5.152}$$

where q is the number of nearest neighbor sites of a given site; $q = 2$ for one dimension and $q = 4$ for a square lattice.

To make this procedure explicit, consider an Ising chain with toroidal boundary conditions for $N = 3$. For this case $p = 3(2)/2 = 3$, and there are three factors in the product in (5.151): $(1+vs_1s_2)(1+vs_2s_3)(1+vs_3s_1)$. We can expand this product in powers of v to obtain the $2^p = 8$ terms in the partition function:

$$\begin{aligned} Z_{N=3} = (\cosh\beta J)^3 \sum_{s_1=-1}^{1}\sum_{s_2=-1}^{1}\sum_{s_3=-1}^{1} \big[1 + v(s_1s_2 + s_2s_3 + s_3s_1) \\ + v^2(s_1s_2s_2s_3 + s_1s_2s_3s_1 + s_2s_3s_3s_1) + v^3 s_1s_2s_2s_3s_3s_1\big]. \end{aligned} \tag{5.153}$$

It is convenient to introduce a one-to-one correspondence between each of the eight terms in the brackets in (5.153) and a diagram. The set of eight diagrams is shown in Figure 5.20. Because v enters into the product in (5.153) as vs_is_j, a diagram of order v^n has n v-bonds. We can use the topology of the diagrams to help us to keep track of the terms in (5.153). The term of order v^0 is $2^{N=3} = 8$. Because $\sum_{s_i=\pm1} s_i = 0$, each of the terms of order v vanishes. Similarly, each of the three terms of order v^2 contains at least one of the spin variables raised to an odd power so that these terms also vanish. For example, $s_1s_2s_2s_3 = s_1s_3$, and both s_1 and s_3 enter to first-order. In general, we have

$$\sum_{s_i=-1}^{1} {s_i}^n = \begin{cases} 2 & n \text{ even}, \\ 0 & n \text{ odd}. \end{cases} \tag{5.154}$$

From (5.154) we see that only terms of order v^0 and v^3 contribute so that

$$Z_{N=3} = \cosh^3\beta J[8 + 8v^3] = 2^3(\cosh^3\beta J + \sinh^3\beta J). \tag{5.155}$$

We can now generalize our analysis to arbitrary N. We have observed that the diagrams that correspond to nonvanishing terms in Z are those that have an even number of bonds from each vertex; these diagrams are called *closed.* A bond from site i corresponds to a product of the form s_is_j. An even number of bonds from site i implies that s_i raised to an even power enters into the sum in (5.151). Hence, only diagrams with an even number of bonds from each vertex yield a nonzero contribution to Z_N.

For the Ising chain only two bonds can come from a given site. Hence, although there are 2^N diagrams for a Ising chain of N spins with toroidal boundary conditions, only the diagrams of order v^0 (with no bonds) and of order v^N contribute to Z_N. We conclude that

$$Z_N = (\cosh\beta J)^N[2^N + 2^N v^N]. \tag{5.156}$$

Problem 5.26. The form of Z_N in (5.156) is not the same as the form of Z_N given in (5.39). Use the fact that $v < 1$ and take the thermodynamic limit $N \to \infty$ to show the equivalence of the two results for Z_N. □

Problem 5.27. High temperature expansion for four spins

Draw the diagrams that correspond to the nonvanishing terms in the high temperature expansion of the partition function for the $N = 4$ Ising chain. □

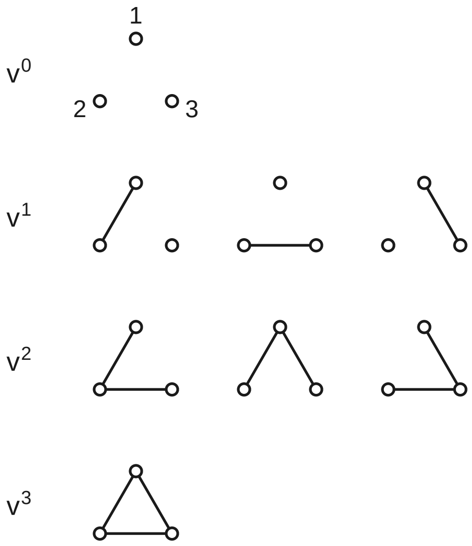

Figure 5.20: The eight diagrams that correspond to the eight terms in the partition function for the $N = 3$ Ising chain. The term $s_i s_j$ is represented by a line between the neighboring sites i and j [see Stanley (1971)].

It is possible to generalize the diagrammatic analysis to higher dimensions. The results of low temperature and high temperature expansions have been used to estimate the values of the various critical exponents (see Domb). An analogous diagrammatic expansion is discussed in Chapter 8 for particle systems.

5.10.4 *Bethe approximation

In Section 5.7 we introduced a simple mean-field theory of the Ising model. In the following we discuss how to improve this approximation.[16]

The idea is that instead of considering a single spin, we consider a group or cluster of spins and the effective field experienced by it. In particular, we will choose the group to be a spin and its q nearest neighbors (see Figure 5.21). The interactions of the nearest neighbors with the central spin are calculated exactly, and the rest of the spins in the system are assumed to act on the nearest neighbors through a self-consistent effective field. The energy of the cluster is

$$H_c = -Js_0 \sum_{j=1}^{q} s_j - Hs_0 - H_{\text{eff}} \sum_{j=1}^{q} s_j \tag{5.157a}$$

$$= -(Js_0 + H_{\text{eff}}) \sum_{j=1}^{q} s_j - Hs_0. \tag{5.157b}$$

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[16] This approach is due to Bethe, who received a Nobel Prize for his work on the theory of stellar nucleosynthesis.

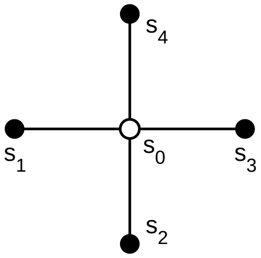

Figure 5.21: The simplest cluster on the square lattice used in the Bethe approximation. The interaction of the central spin with its $q = 4$ nearest neighbors is treated exactly.

For a square lattice $q = 4$. Note that the fluctuating field acting on the nearest neighbor spins $s_1, \ldots, s_q$ has been replaced by the effective field $H_{\rm eff}$.

The cluster partition function Z_c is given by

$$Z_c = \sum_{s_0=\pm 1, s_j=\pm 1} e^{-\beta H_c}. \tag{5.158}$$

We first do the sum over $s_0 = \pm 1$ using (5.157b) and write

$$Z_c = e^{\beta H} \sum_{s_j=\pm 1} e^{\beta(J+H_{\rm eff})(\sum_{j=1}^q s_j)} + e^{-\beta H} \sum_{s_j=\pm 1} e^{\beta(-J+H_{\rm eff})(\sum_{j=1}^q s_j)}. \tag{5.159}$$

For simplicity, we will evaluate the partition function of the cluster for the one-dimensional Ising model for which $q = 2$. Because the two neighboring cluster spins can take the values ↑↑, ↑↓, ↓↑, and ↓↓, the sums in (5.159) yield

$$\begin{aligned} Z_c &= e^{\beta H}\big[e^{2\beta(J+H_{\rm eff})} + 2 + e^{-2\beta(J+H_{\rm eff})}\big] \\ &\quad + e^{-\beta H}\big[e^{2\beta(-J+H_{\rm eff})} + 2 + e^{-2\beta(-J+H_{\rm eff})}\big] \qquad (5.160a) \\ &= 4\big[e^{\beta H}\cosh^2\beta(J+H_{\rm eff}) + e^{-\beta H}\cosh^2\beta(J-H_{\rm eff})\big]. \qquad (5.160b) \end{aligned}$$

The expectation value of the central spin is given by

$$\langle s_0\rangle = \frac{1}{\beta}\frac{\partial \ln Z_c}{\partial H} = \frac{4}{Z_c}\big[e^{\beta H}\cosh^2\beta(J+H_{\rm eff}) - e^{-\beta H}\cosh^2\beta(J-H_{\rm eff})\big]. \tag{5.161}$$

In the following we will set $H = 0$ to find the critical temperature.

We also want to calculate the expectation value of the spin of the nearest neighbors $\langle s_j\rangle$ for $j = 1, \ldots, q$. Because the system is translationally invariant, we require that $\langle s_0\rangle = \langle s_j\rangle$ and find the effective field $H_{\rm eff}$ by requiring that this condition be satisfied. From (5.159) we see that

$$\langle s_j\rangle = \frac{1}{q}\frac{\partial \ln Z_c}{\partial(\beta H_{\rm eff})}. \tag{5.162}$$

If we substitute (5.160b) for Z_c in (5.162) with $H = 0$, we find

$$\begin{aligned}\langle s_j\rangle = \frac{4}{Z_c}\big[&\sinh\beta(J+H_{\rm eff})\cosh\beta(J+H_{\rm eff}) \\ &- \sinh\beta(J-H_{\rm eff})\cosh\beta(J-H_{\rm eff})\big].\end{aligned} \tag{5.163}$$

The requirement $\langle s_0\rangle = \langle s_j\rangle$ yields the relation

$$\begin{aligned}\cosh^2\beta(J+H_{\rm eff}) - \cosh^2\beta(J-H_{\rm eff}) = {}&\sinh\beta(J+H_{\rm eff})\cosh\beta(J+H_{\rm eff}) \\ &- \sinh\beta(J-H_{\rm eff})\cosh\beta(J-H_{\rm eff}).\end{aligned} \tag{5.164}$$

Equation (5.164) can be simplified by writing $\sinh x = \cosh x - e^{-x}$ with $x = \beta(J \pm H_{\rm eff})$. The result is

$$\frac{\cosh\beta(J+H_{\rm eff})}{\cosh\beta(J-H_{\rm eff})} = e^{2\beta H_{\rm eff}}. \tag{5.165}$$

We can follow a similar procedure to find the generalization of (5.165) to arbitrary q. The result is

$$\frac{\cosh^{q-1}\beta(J+H_{\rm eff})}{\cosh^{q-1}\beta(J-H_{\rm eff})} = e^{2\beta H_{\rm eff}}. \tag{5.166}$$

Equation (5.166) always has the solution $H_{\rm eff} = 0$ corresponding to the high temperature phase. Is there a nonzero solution for $H_{\rm eff}$ for low temperatures? As $H_{\rm eff} \to \infty$, the left-hand side of (5.166) approaches $e^{2\beta J(q-1)}$, a constant independent of $H_{\rm eff}$, and the right-hand side diverges. Therefore, if the slope of the function on the left at $H_{\rm eff} = 0$ is greater than 2β, the two functions must intersect again at finite $H_{\rm eff}$. If we take the derivative of the left-hand side of (5.166) with respect to $H_{\rm eff}$ and set it equal to 2β, we find that the condition for a solution to exist is

$$\coth\beta_c J = q - 1, \tag{5.167}$$

where $\coth x = \cosh x/\sinh x$. Because (5.166) is invariant under $H_{\rm eff} \to -H_{\rm eff}$, there will be two solutions for $T \le T_c$.

On the square lattice ($q = 4$) the condition (5.167) yields $kT_c/J \approx 2.885$ in comparison to the Onsager solution $kT_c/J \approx 2.269$ (see [5.86]) and the result of simple mean-field theory, $kT_c/J = 4$. For the one-dimensional Ising model ($q = 2$), the Bethe approximation predicts $T_c = 0$ in agreement with the exact result. That is, the Bethe approximation does not predict a phase transition in one dimension.

Better results can be found by considering larger clusters. Although such an approach yields more accurate results for T_c, it yields the same mean-field exponents because it depends on the truncation of correlations beyond a certain distance. Hence, this approximation must break down in the vicinity of a critical point where the correlation between spins becomes infinite.

Problem 5.28. The Bethe approximation

(a) Work out the details of the Bethe approximation for the cluster in Figure 5.21 and derive (5.166).

(b) Derive (5.167) for the critical temperature.

(c) Show that $kT_c/J \approx 2.885$ for $q = 4$ and $kT_c/J = 0$ for $q = 2$. □

5.10.5 Fully connected Ising model

We expect that mean-field theory becomes exact for a system in which every spin interacts equally strongly with every other spin in the system because the fluctuations of the effective field go to zero in the limit $N \to \infty$. We will refer to this model as the *fully connected* Ising model.

For such a system the energy is given by (see Problem 5.29)

$$E = \frac{J_N}{2}(N - M^2), \tag{5.168}$$

where M is the magnetization and J_N is the interaction between any two spins. Note that E depends only on M. In Problem 5.29 we also find that the number of states with magnetization M is given by

$$\Omega(M) = \frac{N!}{n!(N-n)!}, \tag{5.169}$$

where n is the number of up spins. As before, $n = N/2 + M/2$ and $N - n = N/2 - M/2$.

Problem 5.29. Energy and density of states of the fully connected Ising model

(a) Show that the energy of a system for which every spin interacts with every other spin is given by (5.168). A straightforward way to proceed is to consider a small system, say $N = 9$, and determine the energy of various microstates. As you do so, you will see how to generalize your results to arbitrary N.

(b) Use similar considerations as in part (a) to find the number of states as in (5.169). □

The energy of interaction J_N of two spins has to scale as $1/N$ so that the total energy of N spins will be proportional to N. We will choose

$$J_N = q\frac{J}{N}. \tag{5.170}$$

The factor of q is included so that we will obtain the usual mean-field result for T_c.

Given the form of the energy in (5.168) and the number of states in (5.169), we can write the partition function as

$$Z_N = \sum_M \frac{N!}{(\frac{N}{2} + \frac{M}{2})!(\frac{N}{2} - \frac{M}{2})!} e^{-\beta J_N (N - M^2)/2} e^{\beta HM}. \tag{5.171}$$

We have included the interaction with an external magnetic field. For $N \gg 1$ we can convert the sum to an integral. We write

$$Z_N = \int_{-\infty}^{\infty} Z(M)\, dM, \tag{5.172}$$

and

$$Z(M) = \frac{N!}{n!(N-n)!} e^{-\beta E} e^{\beta HM}, \tag{5.173}$$

where $n = (M + N)/2$. A plot of $Z(M)$ shows that it is peaked about a particular value of M. So let us do our usual trick of expanding $\ln Z_M$ about its maximum.

We first find the value of M for which $Z(M)$ is a maximum. We write

$$\ln Z(M) = \ln N! - \ln n! - \ln(N - n)! - \beta E + \beta HM. \tag{5.174}$$

We then use the weaker form of Stirling's approximation (3.102), $d(\ln x!)/dx = \ln x$, $dn/dM = 1/2$, and $d(N - n)/dM = -1/2$. The result is

$$\begin{aligned}
\frac{d \ln Z(M)}{dM} &= -\frac{1}{2}\ln n + \frac{1}{2}\ln(N - n) + \beta J_N M + \beta H && \text{(5.175a)}\\
&= -\frac{1}{2}\ln \frac{N}{2}(1 + m) + \frac{1}{2}\ln \frac{N}{2}(1 - m) + q\beta Jm + \beta H && \text{(5.175b)}\\
&= -\frac{1}{2}\ln(1 + m) + \frac{1}{2}\ln(1 - m) + q\beta Jm + \beta H = 0, && \text{(5.175c)}
\end{aligned}$$

where $m = M/N$. We set $d(\ln Z(M))/dM = 0$ to find the value of m that maximizes $Z(M)$. We have

$$\frac{1}{2}\ln\frac{1 - m}{1 + m} = -\beta(qJm + H), \tag{5.176}$$

so that

$$\frac{1 - m}{1 + m} = e^{-2\beta(qJm+H)} \equiv x. \tag{5.177}$$

Finally we solve (5.177) for m in terms of x and obtain $1 - m = x(1 + m)$, $m(-1 - x) = -1 + x$. Hence

$$\begin{aligned}
m = \frac{1 - x}{1 + x} &= \frac{1 - e^{-2\beta(Jqm+H)}}{e^{-2\beta(Jqm+H)} + 1} && \text{(5.178a)}\\
&= \frac{e^{\beta(Jqm+H)} - e^{-\beta(Jqm+H)}}{e^{-\beta(Jqm+H)} + e^{\beta(Jqm+H)}} && \text{(5.178b)}\\
&= \tanh(\beta(Jqm + H). && \text{(5.178c)}
\end{aligned}$$

Note that (5.178c) is identical to the mean-field result in (5.108).[17]

****Problem 5.30.** Fully connected Ising form of Z

(a) Show that $Z(M)$ can be written as a Gaussian and then do the integral over M in (5.172) to find the mean-field form of Z.

(b) Use the form of Z from part (a) to find the mean-field result for the free energy F. Compare your result to (5.126). □

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[17] Mean-field theory corresponds to taking the limit $N \to \infty$ before letting the range of interaction go to infinity. In contrast, the fully connected Ising model corresponds to taking both limits simultaneously. Although the Ising model gives the same results for the partition function as mean-field theory, the fully connected Ising model can yield different results in some other contexts.

5.10.6 Metastability and nucleation

To introduce the concepts of metastability and nucleation we first consider the results of the simulations in Problem 5.31.

Problem 5.31. Simulations of metastability

(a) Use Program `Ising2D` to simulate the Ising model on a square lattice. Choose $L = 64$, $T = 1$, and $H = 0.7$. Run the simulation until the system reaches equilibrium. You will notice that most of the spins are aligned with the magnetic field.

(b) Pause the simulation and let $H = -0.7$; we say that we have "flipped" the field. Continue the simulation after the change of the field and watch spins. Do the spins align themselves with the magnetic field immediately after the flip? Monitor the magnetization of the system as a function of time. Is there an interval of time for which the mean value of m does not change appreciably? At what time does m change sign? What is the equilibrium state of the system after the change of the field?

(c) Keep the temperature fixed at $T = 1$ and decrease the field to $H = 0.6$ and flip the field as in part (b). Does m become negative sooner or later compared to $|H| = 0.7$? Is this time the same each time you do the simulation? (The program uses a different random number seed each time it is run.) □

You probably found that the spins did not immediately flip to align themselves with the magnetic field. Instead most of the spins remained up and the mean values of the magnetization and energy did not change appreciably for many Monte Carlo steps per spin. We say that the system is in a *metastable* state. The reason that the spins do not flip as soon as the field is flipped is that if the field is not too large, it costs energy for a spin to flip because it would likely no longer be parallel with its neighbors. If we wait long enough, we will see isolated "droplets" of spins pointing in the stable (down) direction. If a droplet is too small, it will likely shrink and vanish. In contrast, if the droplet is bigger than a critical size (see Figure 5.22), it will grow and the system will quickly reach its stable equilibrium state. If the droplet has a certain critical size, then it will grow with a probability of 50%. This droplet is called the *nucleating droplet*. The initial decay of the metastable state is called *nucleation*.

Metastable states occur often in nature and in the laboratory. For example, if you take a container of distilled (very pure) water with no dirt, pollen, or other impurities, you can supercool it below the freezing temperature of 0°C. The supercooled water will remain a liquid unless there is a spontaneous density fluctuation. More likely, an external disturbance will create the necessary fluctuation. Search `<youtube.com>` for supercooled water to see some great demonstrations. Metastable states are important in forming crystalline metals from a molten liquid as well as in biological systems and the inflationary scenario of the early universe.

To determine the size of the nucleating droplet consider nucleation at low temperatures so that we can ignore the entropy.[18] A compact droplet (circular in two dimensions and spherical in three dimensions) minimizes the energy cost of creating a droplet of down spins. The energy is

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[18] At higher temperatures we would consider the free energy.

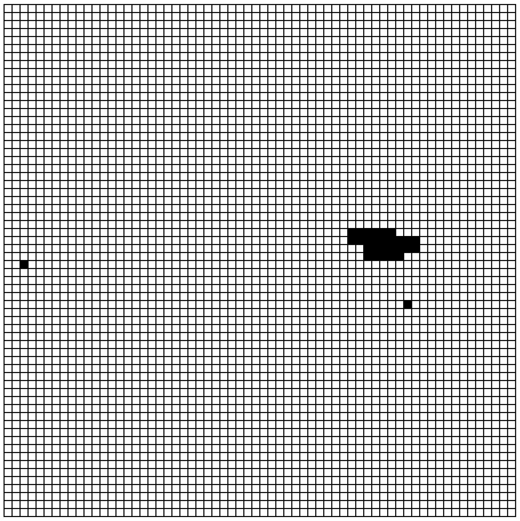

Figure 5.22: Example of a nucleating droplet. The simulation was done for the Ising model on a square lattice with $L = 64$, $T = 1$, and $|H| = 0.7$. The magnetic field was originally up (in the direction of the lighter sites). The nucleating droplet appeared at $t \approx 50\,\mathrm{mcs}$ after the flip of the field and is the largest cluster of down (dark) sites.

decreased by aligning the spins of the droplet with the field. This energy decrease is proportional to the area (volume in three dimensions) of the droplet. Hence,

$$E_{\text{bulk}} = -aHr^d, \tag{5.179}$$

where r is the radius of the droplet, d is the spatial dimension, and a is a constant.

Creating a surface costs energy. The associated energy cost is proportional to the circumference (surface area in three dimensions) of the droplet, and hence

$$E_{\text{surf}} = \sigma r^{d-1}, \tag{5.180}$$

where σ is the energy cost per unit length (per unit area in three dimensions). This quantity is known as the surface tension.

The total energy cost of creating a droplet of radius r is

$$E(r) = -aHr^d + \sigma r^{d-1}. \tag{5.181}$$

The energy cost of the droplet increases as a function of r until a critical radius r_c (see Figure 5.23).

The radius of the nucleating droplet can be obtained by determining the value of r for which $E(r)$ has a maximum:

$$\frac{dE}{dr}\Big|_{r=r_c} = -adHr_c^{d-1} + (d-1)\sigma r_c^{d-2} = 0, \tag{5.182}$$

or

$$-adHr_c + (d-1)\sigma = 0, \tag{5.183}$$

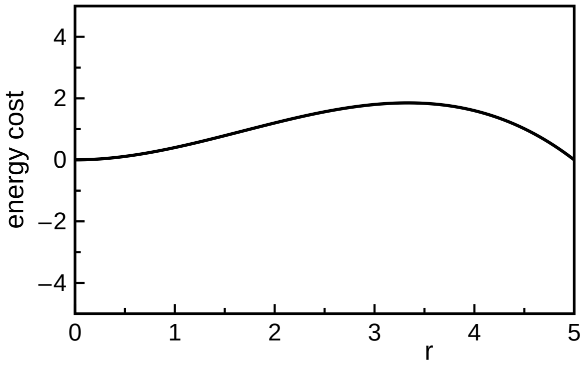

Figure 5.23: The energy cost $E(r)$ of a droplet of radius r from (5.181) for $d = 3$ (with $a = 1$, $\sigma = 0.5$, and $H = 0.1$ chosen for convenience).

and

$$r_c = \frac{(d-1)\sigma}{adH}. \tag{5.184}$$

The energy cost of creating the nucleating droplet is $E_c = b\sigma^d/(aH)^{d-1}$, where b depends on d. The probability of creating the nucleating droplet is proportional to $e^{-\beta E_c}$. The lifetime of the metastable state, that is, the time before the nucleating droplet occurs, is proportional to the inverse of this probability.

Note that we used equilibrium considerations to estimate the radius of the nucleating droplet and the lifetime of the metastable state. This assumption of equilibrium is justified only if the lifetime of the metastable state is long. Hence, we must have $E_c/kT \gg 1$, that is, small fields or low temperatures.

Vocabulary

magnetization m, susceptibility χ

free energies $F(T, H)$, $G(T, M)$

Ising model, exchange constant J, domain wall

spin-spin correlation function $G(r)$, correlation length ξ

order parameter, first-order transition, continuous phase transition, critical point

critical temperature T_c, critical exponents α, β, δ, γ, ν, η

exact enumeration

mean-field theory, Bethe approximation

low and high temperature expansions

hysteresis, metastable state, nucleating droplet

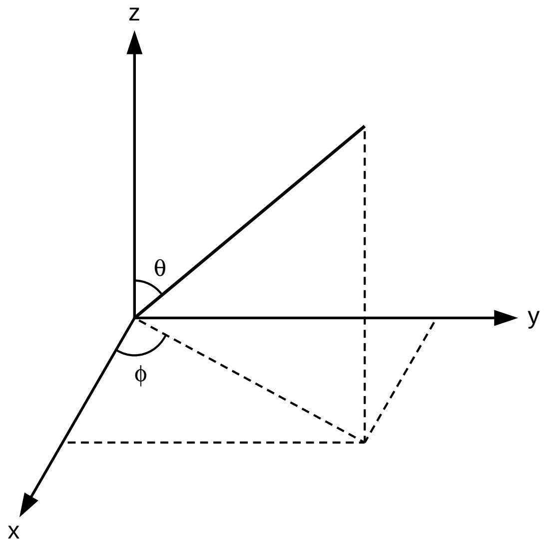

Figure 5.24: The direction of $\boldsymbol{\mu}$ is determined by the angles θ and ϕ of a spherical coordinate system.

Additional Problems

Problem 5.32. Classical paramagnet

The energy of interaction of a classical magnetic dipole with the magnetic field $\mathbf{B}$ is given by $E = -\boldsymbol{\mu}\cdot\mathbf{B}$. In the absence of an external field the dipoles are randomly oriented so that the mean magnetization is zero. The goal of this problem is to find the mean magnetization as a function of B and T. The direction of the magnetization is parallel to $\mathbf{B}$.

The sum over microstates becomes an integral over all directions of $\boldsymbol{\mu}$. The direction of $\boldsymbol{\mu}$ in three dimensions is given by the angles θ and ϕ of a spherical coordinate system as shown in Figure 5.24. The integral is over the solid angle element $d\Omega = \sin\theta d\theta d\phi$. In this coordinate system the energy of the dipole is given by $E = -\mu B\cos\theta$.

(a) Choose spherical coordinates and show that the probability $p(\theta,\phi)d\theta d\phi$ that the dipole is between the angles θ and $\theta + d\theta$ and ϕ and $\phi + d\phi$ is given by

$$p(\theta,\phi)d\theta d\phi = \frac{e^{\beta\mu B\cos\theta}}{Z_1}\sin\theta d\theta d\phi, \tag{5.185}$$

where Z_1 is given by

$$Z_1 = \int_0^{2\pi}\int_0^{\pi} e^{\beta\mu B\cos\theta}\sin\theta\, d\theta\, d\phi. \tag{5.186}$$

(b) How is $\overline{\cos\theta}$ related to Z_1?

(c) Show that the mean magnetization is given by

$$M = N\mu L\big(\beta\mu B\big), \tag{5.187}$$

where the Langevin function $L(x)$ is given by

$$L(x) = \frac{e^x + e^{-x}}{e^x - e^{-x}} - \frac{1}{x} = \coth x - \frac{1}{x}. \tag{5.188}$$

(d) For $|x| < \pi$, $L(x)$ can be expanded as

$$L(x) = \frac{x}{3} - \frac{x^3}{45} + \ldots + \frac{2^{2n}B_{2n}}{(2n)!} + \ldots \qquad (x \ll 1), \tag{5.189}$$

where B_n is the Bernoulli number of order n (see the Appendix). What is M and the susceptibility in the limit of high T?

(e) For large x, $L(x)$ is given by

$$L(x) \approx 1 - \frac{1}{x} + 2e^{-2x} \qquad (x \gg 1). \tag{5.190}$$

What is the behavior of M in the limit of low T?

(f) What is the mean energy and the entropy of a system of N noninteracting magnetic dipoles? Is the behavior of the entropy at low temperatures consistent with the third law of thermodynamics? ☐

Problem 5.33. Arbitrary spin

The magnetic moment of an atom or nucleus is associated with its angular momentum which is quantized. If the angular momentum is J, the magnetic moment along the direction of $\mathbf{B}$ is restricted to $(2J+1)$ orientations. We write the energy of an individual atom as

$$E = -g\mu_0\,\mathbf{J}\cdot\mathbf{B} = -g\mu_0 J_z B. \tag{5.191}$$

The values of μ_0 and g depend on whether we are considering a nucleus, an atom, or an electron. The values of J_z are restricted to $-J$, $-J+1$, $-J+2$, …, $J-1$, J. Hence, the partition function for one atom contains $(2J+1)$ terms:

$$Z_1 = \sum_{m=-J}^{J} e^{-\beta(-g\mu_0 mB)}. \tag{5.192}$$

The summation index m ranges from $-J$ to J in steps of $+1$.

To simplify the notation, we let $\alpha = \beta g\mu_0 B$, and write Z_1 as a finite geometrical series:

$$Z_1 = \sum_{m=-J}^{J} e^{m\alpha} \tag{5.193a}$$

$$= e^{-\alpha J}(1 + e^{\alpha} + e^{2\alpha} + \ldots + e^{2J\alpha}). \tag{5.193b}$$

The sum of a finite geometrical series is given by

$$S_n = \sum_{p=0}^{n} x^p = \frac{x^{n+1} - 1}{x - 1}. \tag{5.194}$$

Given that there are $(2J+1)$ terms in (5.193b), show that

$$Z_1 = e^{-\alpha J} \frac{e^{(2J+1)\alpha} - 1}{e^{\alpha} - 1} = e^{-\alpha J} \frac{[1 - e^{(2J+1)\alpha}]}{1 - e^{\alpha}}. \tag{5.195}$$

Use the above relations to show that

$$M = Ng\mu_0 J B_J(\alpha), \tag{5.196}$$

where the Brillouin function $B_J(\alpha)$ is defined as

$$B_J(\alpha) = \frac{1}{J}\Big[(J+1/2)\coth(J+1/2)\alpha - \frac{1}{2}\coth\alpha/2\Big]. \tag{5.197}$$

What is the limiting behavior of M for high and low T for fixed B? What is the limiting behavior of M for $J = 1/2$ and $J \gg 1$? □

***Problem 5.34.** Density of states

In Problem 4.40 the density of states was given without proof for the one-dimensional Ising model for even N and toroidal boundary conditions:

$$\Omega(E, N) = 2\binom{N}{i} = 2\frac{N!}{i!\,(N-i)!} \qquad (i = 0, 2, 4, \ldots, N), \tag{4.18}$$

with $E = 2\,i - N$. Use this form of Ω and the relation

$$Z_N = \sum_E \Omega(E, N) e^{-\beta E} \tag{5.198}$$

to find the partition function for small values of (even) N. □

Problem 5.35. Sample microstates

The five microstates shown in Figure 5.25 for the Ising chain were generated using the Metropolis algorithm (see Sections 4.11 and 5.5.3) at $\beta J = 2$ using toroidal boundary conditions. On the basis of this limited sample, estimate the mean value of E/J and the magnetization. Calculate the spin-spin correlation function $G(r)$ for $r = 1$, 2, and 3 using the third spin as the origin, and then repeat the calculation using the sixth spin. Remember that the Metropolis algorithm simulates a system in equilibrium with a heat bath at temperature T with the correct weight. Explain why your results are not accurate. □

Problem 5.36. Enumeration of microstates of the two-dimensional Ising model

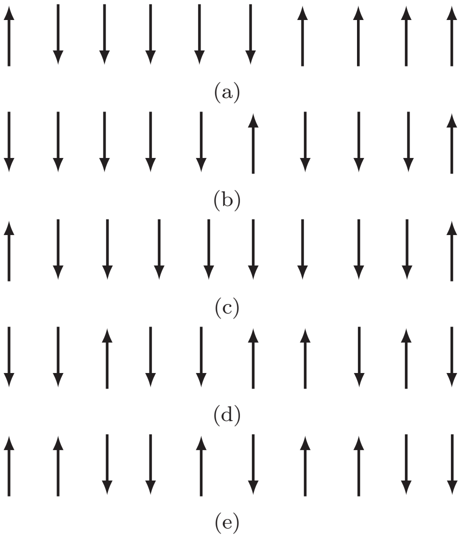

Figure 5.25: Five microstates of the Ising chain with $N = 10$ spins with toroidal boundary conditions generated by the Metropolis algorithm at $\beta J = 2$ and $H = 0$.

(a) Calculate the partition function for the Ising model on a square lattice for $N = 4$ spins in the presence of an external magnetic field H. Assume that the system is in equilibrium with a heat bath at temperature T. Each spin interacts once with each horizontal or vertical nearest neighbor.

(b) Determine $\Omega(E)$, the number of states with energy E, and discuss its dependence on E. Assume that $H = 0$.

(c) The $4^2 = 16$ microstates of the two-dimensional Ising model for $N = 4$ can be grouped into four "ordered" states with energies $\pm J$ and 12 "disordered" states with zero energy. Test the hypothesis that the phase transition occurs when the partition function of the disordered states equals that of the ordered states. What is the resulting value of T_c? This simple reasoning does not work as well for the Ising model in three dimensions. □

Problem 5.37. Form of $P(E)$ for the Ising model

Consider the two-dimensional Ising model in equilibrium with a heat bath at temperature T.

(a) On the basis of general considerations, what is the form of the probability $P(E)\Delta E$ that the system has energy between E and $E + \Delta E$?

(b) Why is this form not applicable at the critical point? □

Problem 5.38. The Ising model and cooperative phenomena

Explore the analogy between the behavior of the Ising model and the behavior of a large group of people. Under what conditions would a group of people act like a collection of individuals, each doing their "own thing?" Under what conditions might they act as a group? What factors could cause a transition from one behavior to the other? The relation of the Ising model to models of economic opinions, urban segregation, and language change is discussed by Stauffer. ☐

Problem 5.39. The demon and the Ising chain

(a) Consider a demon that exchanges energy with the Ising chain by flipping single spins. Show that the possible changes in the energy in zero magnetic field are 0 and $\pm 4J$. Confirm that the possible demon energies are $E_d = 4nJ$, where $n = 0,, 1, 2, \ldots$

(b) Derive an expression for the mean demon energy as a function of the temperature of the system. ☐

***Problem 5.40.** Applications of the transfer matrix method

(a) Consider a one-dimensional Ising-type model with $s_i = 0, \pm 1$. Use the transfer matrix method to calculate the dependence of the energy on T for $H = 0$. The solution requires the differentiation of the root of a cubic equation that you might wish to do numerically.

(b) Use the transfer matrix method to find the thermodynamic properties of the $q = 3$ Potts model in one dimension. ☐

Problem 5.41. Finite-size scaling and critical exponents

Although a finite system cannot exhibit a true phase transition characterized by divergent physical quantities, we expect that if the correlation length $\xi(T)$ is less than the linear dimension L of the system, our simulations will yield results comparable to an infinite system. However, if T is close to T_c, the results of simulations will be limited by finite-size effects. Because we can only simulate finite lattices, it is difficult to obtain estimates for the critical exponents α, β, and γ by using their definitions in (5.95), (5.97), and (5.98) directly.

The effects of finite system size can be made quantitative by the following argument, which is based on the fact that the only important length near the critical point is the correlation length. Consider, for example, the critical behavior of χ. If the correlation length $\xi \gg 1$,[19] but is much less than L, the power law behavior given by (5.98) is expected to hold. However, if ξ is comparable to L, ξ cannot change appreciably and (5.98) is no longer applicable. This qualitative change in the behavior of χ and other physical quantities occurs for

$$\xi \sim L \sim |T - T_c|^{-\nu}. \tag{5.199}$$

We invert (5.199) and write

$$|T - T_c| \sim L^{-1/\nu}. \tag{5.200}$$

Hence, if ξ and L are approximately the same size, we can replace (5.98) by the relation

$$\chi(T = T_c) \sim [L^{-1/\nu}]^{-\gamma} \sim L^{\gamma/\nu}. \tag{5.201}$$

The relation (5.201) between χ and L at $T = T_c$ is consistent with the fact that a phase transition is defined only for infinite systems. We can use the relation (5.201) to determine the ratio γ/ν. This method of analysis is known as *finite size scaling*.

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[19] All lengths are measured in terms of the lattice spacing.

(a) Use Program `Ising2D` to estimate χ at $T = T_c$ for different values of L. Make a log-log plot of χ versus L and use the scaling relation (5.201) to determine the ratio γ/ν. Use the exact result $\nu = 1$ to estimate γ. Then use the same reasoning to determine the exponent β and compare your estimates for β and γ with the exact values given in Table 5.1.

(b) Make a log-log plot of C versus L. If your data for C is sufficiently accurate, you will find that the log-log plot of C versus L is not a straight line but shows curvature. The reason is that the exponent α equals zero for the two-dimensional Ising model, and $C \sim C_0 \ln L$. Is your data for C consistent with this form? The constant C_0 is approximately 0.4995. ☐

Problem 5.42. Low temperature behavior in mean-field theory

(a) Write (5.108) in the form $\beta qJm = \tanh^{-1} m = (1/2)\ln[(1+m)/(1-m)]$ and show that

$$m(T) \approx 1 - 2e^{-\beta qJ} \text{ as } T \to 0. \tag{5.202}$$

(b) Determine the low temperature behavior of χ. Does it approach zero for $T \ll T_c$? ☐

Problem 5.43. Verification of (5.149)

Verify the validity of the identity (5.149) by considering the different possible values of $s_i s_j$ and using the identities $2\cosh x = e^x + e^{-x}$ and $2\sinh x = e^x - e^{-x}$. ☐

***Problem 5.44.** Lifetime of metastable state

In Section 5.10.6 we discussed some of the features of metastable states in the Ising model. Suppose that we flip the magnetic field as in Problem 5.31 and define the lifetime of the metastable state as the number of Monte Carlo steps per spin from the time of the change of the field to the occurrence of the nucleating droplet. Because the system can be treated by equilibrium considerations while it is in a metastable state, the probability of occurrence of the nucleating droplet during any time interval Δt is independent of time. What is the form of the probability $p(t)\Delta t$ that the lifetime of the metastable state is between t and $t + \Delta t$ (see Section 3.9)?

Suggestions for Further Reading

Stephen G. Brush, "History of the Lenz-Ising model," Rev. Mod. Phys. **39**, 883–893 (1967).

Cyril Domb, *The Critical Point*, Taylor & Francis (2996). This graduate level monograph discusses the history of our understanding of phase transitions. Much of the history is accessible to undergraduates.

David L. Goodstein, *States of Matter*, Dover Publications (1985). This book discusses how to apply thermodynamics and statistical mechanics to gases, liquids, and solids, and reviews magnetism in solids.

S. Kobe, "Ernst Ising 1900–1998," Braz. J. Phys. **30** (4), 649–654 (2000). Available online from several web sites.

D. P. Landau, Shan-Ho Tsai, and M. Exler, "A new approach to Monte Carlo simulations in statistical physics: Wang-Landau sampling," Am. J. Phys. 72, 1294–1302 (2004).

B. Liu and M. Gitterman, "The critical temperature of two-dimensional and three-dimensional Ising models," Am. J. Phys. **71**, 806–808 (2003). The authors give a simple argument for the value of the critical temperature of the Ising model which gives the exact result in two dimensions and an approximate result in three dimensions [see Problem 5.36(c)].

F. Mandl, *Statistical Physics*, second edition, John Wiley & Sons (1988). This text has a good discussion of the thermodynamics of magnetism.

Daniel C. Mattis, *The Theory of Magnetism Made Simple*, World Scientific (2006). The Bohr-van Leeuwen theorem is discussed in Section 1.6.

Peter Palffy-Muhoraya, "The single particle potential in mean-field theory," Am. J. Phys. **70**, 433–437 (2002).

M. E. J. Newman and G. T. Barkema, *Monte Carlo Methods in Statistical Physics*, Clarendon Press (1999).

H. Eugene Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Oxford University Press (1971). The discussion of the high temperature expansion in Section 5.10.3 is based in part on this book.

D. Stauffer, "Social applications of two-dimensional Ising models," Am. J. Phys. **76**, 470–473 (2008).

Jan Tobochnik and Harvey Gould, "Teaching statistical physics by thinking about models and algorithms," Am. J. Phys. **76**, 353–359 (2008).

Chapter 6

Many-Particle Systems

2 December 2010

We apply the general formalism of statistical mechanics to systems of many particles and discuss the semiclassical limit of the partition function, the equipartition theorem for classical systems, and the general applicability of the Maxwell velocity distribution. We then consider noninteracting quantum systems and discuss the single particle density of states, the Fermi-Dirac and Bose-Einstein distribution functions, the thermodynamics of ideal Fermi and Bose gases, blackbody radiation, and the specific heat of crystalline solids among other applications.

6.1 The Ideal Gas in the Semiclassical Limit

We first apply the canonical ensemble to an ideal gas in the semiclassical limit. Because the thermodynamic properties of a system are independent of the choice of ensemble, we will find the same thermal and pressure equations of state as we found in Section 4.5. Although we will not obtain any new results, this application will give us more experience in working with the canonical ensemble and again show the subtle nature of the semiclassical limit. In Section 6.6 we will derive the classical equations of state using the grand canonical ensemble without any ad hoc assumptions.

In Sections 4.4 and 4.5 we derived the thermodynamic properties of the ideal classical gas[1] using the microcanonical ensemble. If the gas is in thermal equilibrium with a heat bath at temperature T, it is more natural and convenient to treat the ideal gas in the canonical ensemble. Because the particles are not localized, they cannot be distinguished from each other as were the harmonic oscillators considered in Example 4.3 and the spins in Chapter 5. Hence, we cannot simply focus our attention on one particular particle. The approach we will take here is to treat the particles as distinguishable, and then correct for the error approximately.

As before, we will consider a system of noninteracting particles starting from their fundamental description according to quantum mechanics. If the temperature is sufficiently high, we expect

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[1] The theme music for this section can be found at `<www.classicalgas.com/>`.

that we can treat the particles classically. To do so we cannot simply take the limit $\hbar \to 0$ wherever it appears because the counting of microstates is different in quantum mechanics and classical mechanics. That is, particles of the same type are indistinguishable according to quantum mechanics. So in the following we will consider the *semiclassical* limit, and the particles will remain indistinguishable even in the limit of high temperatures.

To take the semiclassical limit the mean de Broglie wavelength $\overline{\lambda}$ of the particles must be smaller than any other length in the system. For an ideal gas the only two lengths are L, the linear dimension of the system, and the mean distance between particles. Because we are interested in the thermodynamic limit for which $L \gg \overline{\lambda}$, the first condition will always be satisfied. As shown in Problem 6.1, the mean distance between particles in three dimensions is $\rho^{-1/3}$. Hence, the semiclassical limit requires that

$$\overline{\lambda} \ll \rho^{-1/3} \text{ or } \rho\overline{\lambda}^3 \ll 1 \qquad \text{(semiclassical limit)}. \tag{6.1}$$

Problem 6.1. Mean distance between particles

(a) Consider a system of N particles confined to a line of length L. What is the definition of the particle density ρ? The mean distance between particles is L/N. How does this distance depend on ρ?

(b) Consider a system of N particles confined to a square of linear dimension L. How does the mean distance between particles depend on ρ?

(c) Use similar considerations to determine the density dependence of the mean distance between particles in three dimensions. □

To estimate the magnitude of $\overline{\lambda}$ we need to know the typical value of the momentum of a particle. For a nonrelativistic system in the semiclassical limit we know from (4.65) that $\overline{p^2}/2m = 3kT/2$. (We will rederive this result more generally in Section 6.2.1.) Hence $\overline{p^2} \sim mkT$ and $\overline{\lambda} \sim h/\sqrt{\overline{p^2}} \sim h/\sqrt{mkT}$. We will find it is convenient to define the *thermal de Broglie wavelength* λ as

$$\boxed{\lambda \equiv \Big(\frac{h^2}{2\pi mkT}\Big)^{1/2} = \Big(\frac{2\pi\hbar^2}{mkT}\Big)^{1/2}} \qquad \text{(thermal de Broglie wavelength)}. \tag{6.2}$$

This form of λ with the factor of $\sqrt{2\pi}$ will allow us to express the partition function in a convenient form [see (6.11)].

The calculation of the partition function of an ideal gas in the semiclassical limit proceeds as follows. First, we assume that $\lambda \ll \rho^{-1/3}$ so that we can pick out one particle if we make the additional assumption that the particles are distinguishable. (If $\lambda \sim \rho^{-1/3}$, the wavefunctions of the particles overlap.) Because identical particles are intrinsically indistinguishable, we will have to correct for the latter assumption later.

With these considerations in mind we now calculate Z_1, the partition function for one particle, in the semiclassical limit. As we found in (4.40), the energy eigenvalues of a particle in a cube of side L are given by

$$\epsilon_n = \frac{h^2}{8mL^2}({n_x}^2 + {n_y}^2 + {n_z}^2), \tag{6.3}$$

where the subscript n represents the set of quantum numbers n_x, n_y, and n_z, each of which can be any nonzero, positive integer. The corresponding partition function is given by

$$Z_1 = \sum_n e^{-\beta\epsilon_n} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-\beta h^2({n_x}^2+{n_y}^2+{n_z}^2)/8mL^2}. \tag{6.4}$$

Because each sum is independent of the others, we can rewrite (6.4) as

$$Z_1 = \Big[\sum_{n_x=1}^{\infty} e^{-\alpha^2{n_x}^2}\Big]\Big[\sum_{n_y=1}^{\infty} e^{-\alpha^2{n_y}^2}\Big]\Big[\sum_{n_z=1}^{\infty} e^{-\alpha^2{n_z}^2}\Big] = S^3, \tag{6.5}$$

where

$$S = \sum_{n_x=1}^{\infty} e^{-\alpha^2{n_x}^2}. \tag{6.6}$$

and

$$\alpha^2 = \frac{\beta h^2}{8mL^2} = \frac{\pi}{4}\frac{\lambda^2}{L^2}. \tag{6.7}$$

It remains to evaluate the sum over n_x in (6.6). Because the linear dimension L of the container is of macroscopic size, we have $\lambda \ll L$ and α in (6.6) is much less than 1. Hence, because the difference between successive terms in the sum is very small, we can convert the sum in (6.6) to an integral:

$$S = \sum_{n_x=1}^{\infty} e^{-\alpha^2{n_x}^2} = \sum_{n_x=0}^{\infty} e^{-\alpha^2{n_x}^2} - 1 \to \int_0^{\infty} e^{-\alpha^2 n_x^2}\, dn_x - 1. \tag{6.8}$$

We have accounted for the fact that the sum over n_x in (6.6) is from $n_x = 1$ rather than $n_x = 0$. We next make a change of variables and write $u^2 = \alpha^2 n_x^2$. We have that

$$S = \frac{1}{\alpha}\int_0^{\infty} e^{-u^2} du - 1 = L\Big(\frac{2\pi m}{\beta h^2}\Big)^{1/2} - 1. \tag{6.9}$$

The Gaussian integral in (6.9) gives a factor of $\pi^{1/2}/2$ (see the Appendix). Because the first term in (6.9) is order $L/\lambda \gg 1$, we can ignore the second term, and hence we obtain

$$Z_1 = S^3 = V\Big(\frac{2\pi m}{\beta h^2}\Big)^{3/2}. \tag{6.10}$$

The result (6.10) is the partition function associated with the translational motion of one particle in a box. Note that Z_1 can be conveniently expressed as

$$Z_1 = \frac{V}{\lambda^3}. \tag{6.11}$$

It is straightforward to find the mean pressure and energy for one particle in a box. We take the logarithm of both sides of (6.10) and find

$$\ln Z_1 = \ln V - \frac{3}{2}\ln\beta + \frac{3}{2}\ln\frac{2\pi m}{h^2}. \tag{6.12}$$

The mean pressure due to one particle is given by

$$\overline{p} = \frac{1}{\beta}\frac{\partial \ln Z_1}{\partial V}\Big|_{T,N} = \frac{1}{\beta V} = \frac{kT}{V}, \tag{6.13}$$

and the mean energy is

$$\overline{e} = -\frac{\partial \ln Z_1}{\partial \beta}\Big|_{V,N} = \frac{3}{2\beta} = \frac{3}{2}kT. \tag{6.14}$$

The mean energy and pressure of an ideal gas of N particles is N times that of the corresponding quantities for one particle. Hence, we obtain for an ideal classical gas the equations of state

$$\overline{P} = \frac{NkT}{V} \tag{6.15}$$

and

$$\overline{E} = \frac{3}{2}NkT. \tag{6.16}$$

In the following we will usually omit the overbar on mean quantities. The heat capacity at constant volume of an ideal gas of N particles is

$$C_V = \frac{\partial E}{\partial T}\Big|_V = \frac{3}{2}Nk. \tag{6.17}$$

We have derived the mechanical and thermal equations of state for an ideal classical gas for a second time! The derivation of the equations of state is much easier in the canonical ensemble than in the microcanonical ensemble. The reason is that we were able to consider the partition function of one particle because the only constraint is that the temperature is fixed instead of the total energy.

Problem 6.2. Independence of the partition function on the shape of the box

The volume dependence of Z_1 should be independent of the shape of the box. Show that the same result for Z_1 is obtained if the box has linear dimensions L_x, L_y, and L_z with $V = L_xL_yL_z$. □

Problem 6.3. Semiclassical limit of the single particle partition function

We obtained the semiclassical limit of the partition function Z_1 for one particle in a box by writing it as a sum over single particle states and then converting the sum to an integral. Show that the semiclassical partition function Z_1 for a particle in a one-dimensional box can be expressed as

$$Z_1 = \iint \frac{dp\,dx}{h}\, e^{-\beta p^2/2m}. \tag{6.18}$$

The integral over p in (6.18) extends from $-\infty$ to $+\infty$. □

***The entropy of an ideal classical gas of* N *particles*.** Although it is straightforward to calculate the mean energy and pressure of an ideal classical gas by considering the partition function for one particle, the calculation of the entropy is more subtle. To understand the difficulty, consider the calculation of the partition function of an ideal gas of two particles. Because there are no

microstate s	red	blue	E_s
1	ϵ_a	ϵ_a	$2\epsilon_a$
2	ϵ_b	ϵ_b	$2\epsilon_b$
3	ϵ_c	ϵ_c	$2\epsilon_c$
4	ϵ_a	ϵ_b	$\epsilon_a + \epsilon_b$
5	ϵ_b	ϵ_a	$\epsilon_a + \epsilon_b$
6	ϵ_a	ϵ_c	$\epsilon_a + \epsilon_c$
7	ϵ_c	ϵ_a	$\epsilon_a + \epsilon_c$
8	ϵ_b	ϵ_c	$\epsilon_b + \epsilon_c$
9	ϵ_c	ϵ_b	$\epsilon_b + \epsilon_c$

Table 6.1: The nine microstates of a system of two noninteracting distinguishable particles (red and blue). Each particle can be in one of three microstates with energy $\epsilon_a,\ \epsilon_b$, or ϵ_c.

interactions between the particles, we can write the total energy as a sum of the single particle energies $\epsilon_1 + \epsilon_2$, where ϵ_i is the energy of the ith particle. The partition function Z_2 is

$$Z_2 = \sum_{\text{all states}} e^{-\beta(\epsilon_1+\epsilon_2)}. \tag{6.19}$$

The sum over all microstates in (6.19) is over the microstates of the two-particle system. If the two particles were distinguishable, there would be no restriction on the number of particles that could be in any single particle microstate, and we could sum over the possible microstates of each particle separately. Hence, the partition function for a system of two distinguishable particles has the form

$$Z_{2,\,\text{distinguishable}} = Z_1^2. \tag{6.20}$$

It is instructive to show the origin of the relation (6.20) for a specific example. Suppose the two particles are red and blue and are in equilibrium with a heat bath at temperature T. For simplicity, we assume that each particle can be in one of three microstates with energies ϵ_a, ϵ_b, and ϵ_c. The partition function for one particle is given by

$$Z_1 = e^{-\beta\epsilon_a} + e^{-\beta\epsilon_b} + e^{-\beta\epsilon_c}. \tag{6.21}$$

In Table 6.1 we list the $3^2 = 9$ possible microstates of this system of two distinguishable particles. The corresponding partition function is given by

$$\begin{aligned} Z_{2,\,\text{distinguishable}} &= e^{-2\beta\epsilon_a} + e^{-2\beta\epsilon_b} + e^{-2\beta\epsilon_c} \\ &\quad + 2\big[e^{-\beta(\epsilon_a+\epsilon_b)} + e^{-\beta(\epsilon_a+\epsilon_c)} + e^{-\beta(\epsilon_b+\epsilon_c)}\big]. \end{aligned} \tag{6.22}$$

It is easy to see that Z_2 in (6.22) can be factored and expressed as in (6.20).

In contrast, if the two particles are indistinguishable, many of the microstates shown in Table 6.1 cannot be counted as separate microstates. In this case we cannot assign the microstates of the particles independently, and the sum over all microstates in (6.19) cannot be factored as in (6.20). For example, the microstate a, b cannot be distinguished from the microstate b, a.

As discussed in Section 4.3.6, the semiclassical limit assumes that microstates with multiple occupancy such as a, a and b, b can be ignored because there are many more single particle states than there are particles (see Problem 4.14, page 190). (In our simple example, each particle can be in one of only three microstates, and the number of microstates is comparable to the number of particles.) If we assume that the particles are indistinguishable and that microstates with multiple occupancy can be ignored, then Z_2 is given by

$$Z_2 = e^{-\beta(\epsilon_a+\epsilon_b)} + e^{-\beta(\epsilon_a+\epsilon_c)} + e^{-\beta(\epsilon_b+\epsilon_c)} \quad \text{(indistinguishable, no multiple occupancy).} \tag{6.23}$$

We see that if we ignore multiple occupancy there are three microstates for indistinguishable particles and six microstates for distinguishable particles. Hence, in the semiclassical limit we can write $Z_2 = Z_1^2/2!$ where the factor of 2! corrects for overcounting. For three particles (each of which can be in one of three possible microstates) and no multiple occupancy, there would be one microstate of the system for indistinguishable particles and no multiple occupancy, namely, the microstate a, b, c. However, there would be six such microstates for distinguishable particles. Thus if we count microstates assuming that the particles are distinguishable, we would overcount the number of microstates by $N!$, the number of permutations of N particles.

We conclude that if we begin with the fundamental quantum mechanical description of matter, then identical particles are indistinguishable at all temperatures. If we make the assumption that single particle microstates with multiple occupancy can be ignored, we can express the partition function of N noninteracting identical particles as

$$Z_N = \frac{{Z_1}^N}{N!} \qquad \text{(ideal gas, semiclassical limit).} \tag{6.24}$$

We substitute for Z_1 from (6.10) and obtain the partition function of an ideal gas of N particles in the semiclassical limit:

$$Z_N = \frac{V^N}{N!}\Big(\frac{2\pi mkT}{h^2}\Big)^{3N/2}. \tag{6.25}$$

If we take the logarithm of both sides of (6.25) and use Stirling's approximation (3.102), we can write the free energy of an ideal classical gas as

$$F = -kT\ln Z_N = -kTN\Big[\ln\frac{V}{N} + \frac{3}{2}\ln\Big(\frac{2\pi mkT}{h^2}\Big) + 1\Big]. \tag{6.26}$$

In Section 6.6 we will use the grand canonical ensemble to obtain the entropy of an ideal classical gas without any ad hoc assumptions such as assuming that the particles are distinguishable and then correcting for overcounting by including the factor of $N!$. That is, in the grand canonical ensemble we will be able to automatically satisfy the condition that the particles are indistinguishable.

Problem 6.4. Equations of state of an ideal classical gas

Use the result (6.26) to find the pressure equation of state and the mean energy of an ideal gas. Do the equations of state depend on whether the particles are indistinguishable or distinguishable? □

Problem 6.5. Entropy of an ideal classical gas

(a) The entropy can be found from the relations $F = E - TS$ or $S = -\partial F/\partial T$. Show that

$$S(T,V,N) = Nk\Big[\ln\frac{V}{N} + \frac{3}{2}\ln\Big(\frac{2\pi mkT}{h^2}\Big) + \frac{5}{2}\Big]. \tag{6.27}$$

The form of S in (6.27) is known as the *Sackur-Tetrode equation* (see Problem 4.20, page 197). Is this form of S applicable for low temperatures?

(b) Express kT in terms of E and show that $S(E,V,N)$ can be expressed as

$$S(E,V,N) = Nk\Big[\ln\frac{V}{N} + \frac{3}{2}\ln\Big(\frac{4\pi mE}{3Nh^2}\Big) + \frac{5}{2}\Big], \tag{6.28}$$

in agreement with the result (4.63) found using the microcanonical ensemble. ☐

Problem 6.6. The chemical potential of an ideal classical gas

(a) Use the relation $\mu = \partial F/\partial N$ and the result (6.26) to show that the chemical potential of an ideal classical gas is given by

$$\mu = -kT\ln\Big[\frac{V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big]. \tag{6.29}$$

(b) We will see in Chapter 7 that if two systems are placed into contact with different initial chemical potentials, particles will go from the system with higher chemical potential to the system with lower chemical potential. (This behavior is analogous to energy going from high to low temperatures.) Does "high" chemical potential for an ideal classical gas imply "high" or "low" density?

(c) Calculate the entropy and chemical potential of one mole of helium gas at standard temperature and pressure. Take $V = 2.24\times10^{-2}\,\mathrm{m}^3$, $N = 6.02\times10^{23}$, $m = 6.65\times10^{-27}\,\mathrm{kg}$, and $T = 273\,\mathrm{K}$. ☐

Problem 6.7. Entropy as an extensive quantity

(a) Because the entropy is an extensive quantity, we know that if we double the volume and double the number of particles (thus keeping the density constant), the entropy must double. This condition can be written formally as

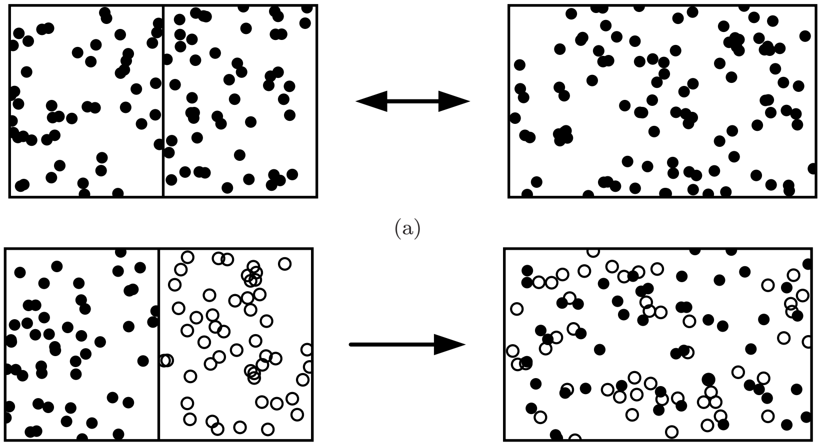
$$S(T,\lambda V,\lambda N) = \lambda S(T,V,N). \tag{6.30}$$

Although this behavior of the entropy is completely general, there is no guarantee that an approximate calculation of S will satisfy this condition. Show that the Sackur-Tetrode form of the entropy of an ideal gas of identical particles, (6.27), satisfies this general condition.

(b) Show that if the $N!$ term were absent from (6.25) for Z_N, S would be given by

$$S = Nk\Big[\ln V + \frac{3}{2}\ln\Big(\frac{2\pi mkT}{h^2}\Big) + \frac{3}{2}\Big]. \tag{6.31}$$

Is this form of S extensive?



(a)

(b)

Figure 6.1: (a) A composite system is prepared such that there are N argon atoms in container A and N argon atoms in container B. The two containers are at the same temperature T and have the same volume V. What is the change of the entropy of the composite system if the partition separating the two containers is removed and the two gases are allowed to mix? (b) A composite system is prepared such that there are N argon atoms in container A and N helium atoms in container B. The other conditions are the same as before. The change in the entropy when the partition is removed is equal to $2Nk\ln 2$.

(c) The fact that (6.31) yields an entropy that is not extensive does *not* indicate that identical particles must be indistinguishable. Instead the problem arises from our identification of S with $\ln Z$ as mentioned in Section 4.6, page 199. Recall that we considered a system with fixed N and made the identification that [see (4.106)]

$$dS/k = d(\ln Z + \beta E). \tag{6.32}$$

It is straightforward to integrate (6.32) and obtain

$$S = k(\ln Z + \beta E) + g(N), \tag{6.33}$$

where $g(N)$ is an arbitrary function only of N. Although we usually set $g(N) = 0$, it is important to remember that $g(N)$ is arbitrary. What must be the form of $g(N)$ in order that the entropy of an ideal classical gas be extensive? □

Entropy of mixing. Consider two containers A and B each of volume V with two identical gases of N argon atoms each at the same temperature T. What is the change of the entropy of the combined system if we remove the partition separating the two containers and allow the two gases to mix [see Figure 6.1)(a)]? Because the argon atoms are identical, nothing has really changed and no information has been lost. Hence, $\Delta S = 0$.

In contrast, suppose that one container is composed of N argon atoms and the other is composed of N helium atoms [see Figure 6.1)(b)]. What is the change of the entropy of the combined system if we remove the partition separating them and allow the two gases to mix? Because argon atoms are distinguishable from helium atoms, we lose information about the system, and therefore we know that the entropy must increase. Alternatively, we know that the entropy must increase because removing the partition between the two containers is an irreversible process. (Reinserting the partition would not separate the two gases.) We conclude that the entropy of mixing is nonzero:

$$\Delta S > 0 \qquad \text{(entropy of mixing)}. \tag{6.34}$$

In the following, we will derive these results for the special case of an ideal classical gas.

Consider two ideal gases at the same temperature T with N_A and N_B particles in containers of volume V_A and V_B, respectively. The gases are initially separated by a partition. We use (6.27) for the entropy and find

$$S_A = N_A k\Big[\ln\frac{V_A}{N_A} + f(T, m_A)\Big], \tag{6.35a}$$

$$S_B = N_B k\Big[\ln\frac{V_B}{N_B} + f(T, m_B)\Big], \tag{6.35b}$$

where the function $f(T, m) = 3/2\ln(2\pi mkT/h^2) + 5/2$, and m_A and m_B are the particle masses in system A and system B, respectively. We then allow the particles to mix so that they fill the entire volume $V = V_A + V_B$. If the particles are identical and have mass m, the total entropy after the removal of the partition is given by

$$S = k(N_A + N_B)\Big[\ln\frac{V_A + V_B}{N_A + N_B} + f(T, m)\Big], \tag{6.36}$$

and the change in the value of S, the *entropy of mixing*, is given by

$$\Delta S = k\Big[(N_A + N_B)\ln\frac{V_A + V_B}{N_A + N_B} - N_A\ln\frac{V_A}{N_A} - N_B\ln\frac{V_B}{N_B}\Big] \qquad \text{(identical gases)}. \tag{6.37}$$

Problem 6.8. Entropy of mixing of identical particles

(a) Use (6.37) to show that $\Delta S = 0$ if the two gases have equal densities before separation. Write $N_A = \rho V_A$ and $N_B = \rho V_B$.

(b) Why is the entropy of mixing nonzero if the two gases initially have different densities even though the particles are identical? □

If the two gases are not identical, the total entropy after mixing is

$$S = k\Big[N_A\ln\frac{V_A + V_B}{N_A} + N_B\ln\frac{V_A + V_B}{N_B} + N_A f(T, m_A) + N_B f(T, m_B)\Big]. \tag{6.38}$$

Then the entropy of mixing becomes

$$\Delta S = k\Big[N_A\ln\frac{V_A + V_B}{N_A} + N_B\ln\frac{V_A + V_B}{N_B} - N_A\ln\frac{V_A}{N_A} - N_B\ln\frac{V_B}{N_B}\Big]. \tag{6.39}$$

For the special case of $N_A = N_B = N$ and $V_A = V_B = V$, we find

$$\Delta S = 2Nk\ln 2. \tag{6.40}$$

Problem 6.9. More on the entropy of mixing

(a) Explain the result (6.40) for nonidentical particles in simple terms.

(b) Consider the special case $N_A = N_B = N$ and $V_A = V_B = V$ and show that if we use the result (6.31) instead of (6.27), the entropy of mixing for identical particles is nonzero. This incorrect result is known as *Gibbs paradox*. Does it imply that classical physics, which assumes that particles of the same type are distinguishable, is incorrect? ☐

6.2 Classical Statistical Mechanics

From our discussions of the ideal gas in the semiclassical limit we found that the approach to the classical limit must be made with care. Planck's constant appears in the expression for the entropy even for the simple case of an ideal gas, and the indistinguishability of the particles is not a classical concept.

If we work entirely within the framework of classical mechanics, we would replace the sum over microstates in the partition function by an integral over phase space, that is,

$$Z_{N,\,\text{classical}} = C_N \int e^{-\beta E(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}\, d\mathbf{r}_1 \ldots d\mathbf{r}_N\, d\mathbf{p}_1 \ldots d\mathbf{p}_N. \tag{6.41}$$

The constant C_N cannot be determined from classical mechanics. From our counting of microstates for a single particle and the harmonic oscillator in Section 4.3 and the arguments for including the factor of $1/N!$ on page 295 we see that we can obtain results consistent with starting from quantum mechanics if we choose the constant C_N to be

$$C_N = \frac{1}{N! h^{3N}}. \tag{6.42}$$

Thus the partition function of a system of N particles in the semiclassical limit can be written as

$$\boxed{Z_{N,\,\text{classical}} = \frac{1}{N!}\int e^{-\beta E(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}\, \frac{d\mathbf{r}_1 \ldots d\mathbf{r}_N\, d\mathbf{p}_1 \ldots d\mathbf{p}_N}{h^{3N}}}. \tag{6.43}$$

We obtained a special case of the form (6.43) in Problem 6.3. In the following three subsections we integrate over phase space as in (6.43) to find some general properties of classical systems of many particles.

6.2.1 The equipartition theorem

We have used the microcanonical and canonical ensembles to show that the energy of an ideal classical gas in three dimensions is given by $E = 3kT/2$. Similarly, we have found that the energy of a one-dimensional harmonic oscillator is given by $E = kT$ in the high temperature limit. These results are special cases of the *equipartition theorem* which can be stated as follows:

> For a classical system in equilibrium with a heat bath at temperature T, the mean value of each contribution to the total energy that is quadratic in a coordinate equals $\frac{1}{2}kT$.

Note that the equipartition theorem holds regardless of the coefficients of the quadratic terms and is valid only for a classical system. If all the contributions to the energy are quadratic, the mean energy is distributed equally to each term (hence the name "equipartition").

To see how to calculate averages according to classical statistical mechanics, we first consider a single particle subject to a potential energy $U(\mathbf{r})$ in equilibrium with a heat bath at temperature T. Classically, the probability of finding the particle in a small volume $d\mathbf{r}$ about $\mathbf{r}$ with a momentum in a small volume $d\mathbf{p}$ about $\mathbf{p}$ is proportional to the Boltzmann factor and the volume $d\mathbf{r}\,d\mathbf{p}$ in phase space:

$$p(\mathbf{r},\mathbf{p})d\mathbf{r}\,d\mathbf{p} = Ae^{-\beta(p^2/2m+U(\mathbf{r}))}d\mathbf{r}\,d\mathbf{p}. \tag{6.44}$$

To normalize the probability and determine the constant A we have to integrate over all the possible values of $\mathbf{r}$ and $\mathbf{p}$.

We next consider a classical system of N particles in the canonical ensemble. The probability density of a particular microstate is proportional to the Boltzmann probability $e^{-\beta E}$, where E is the energy of the microstate. Because a microstate is defined classically by the positions and momenta of every particle, we can express the average of any physical quantity $f(\mathbf{r},\mathbf{p})$ in a classical system as

$$\overline{f} = \frac{\int f(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)\, e^{-\beta E(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}\, d\mathbf{r}_1\ldots d\mathbf{r}_N\, d\mathbf{p}_1\ldots d\mathbf{p}_N}{\int e^{-\beta E(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}\, d\mathbf{r}_1\ldots d\mathbf{r}_N\, d\mathbf{p}_1\ldots d\mathbf{p}_N}. \tag{6.45}$$

Note that the sum over quantum states has been replaced by an integration over phase space. We could divide the numerator and denominator by h^{3N} so that we would obtain the correct number of microstates in the semiclassical limit, but this factor cancels in calculations of average quantities. We have already seen that the mean energy and mean pressure do not depend on whether the factors of h^{3N} and $1/N!$ are included in the partition function.

Suppose that the total energy can be written as a sum of quadratic terms. For example, the kinetic energy of one particle in three dimensions in the nonrelativistic limit can be expressed as $(p_x^2+p_y^2+p_z^2)/2m$. Another example is the one-dimensional harmonic oscillator for which the total energy is $p_x^2/2m + kx^2/2$. For simplicity let's consider a one-dimensional system of two particles, and suppose that the energy of the system can be written as

$$E = \epsilon_1(p_1) + \tilde{E}(x_1,x_2,p_2), \tag{6.46}$$

where $\epsilon_1 = ap_1^2$ with a equal to a constant. We have separated out the quadratic dependence of the energy of particle one on its momentum. We use (6.45) and express the mean value of ϵ_1 as

$$\overline{\epsilon}_1 = \frac{\int_{-\infty}^{\infty} \epsilon_1 \, e^{-\beta E(x_1,x_2,p_1,p_2)} \, dx_1 dx_2 \, dp_1 dp_2}{\int_{-\infty}^{\infty} e^{-\beta E(x_1,x_2,p_1,p_2)} \, dx_1 dx_2 \, dp_1 dp_2} \tag{6.47a}$$

$$= \frac{\int_{-\infty}^{\infty} \epsilon_1 \, e^{-\beta[\epsilon_1 + \tilde{E}(x_1,x_2,p_2)]} \, dx_1 dx_2 \, dp_1 dp_2}{\int_{-\infty}^{\infty} e^{-\beta[\epsilon_1 + \tilde{E}(x_1,x_2,p_2,p_2)]} \, dx_1 dx_2 dp_1 dp_2} \tag{6.47b}$$

$$= \frac{\int_{-\infty}^{\infty} \epsilon_1 \, e^{-\beta \epsilon_1} dp_1 \int e^{-\beta \tilde{E}} \, dx_1 dx_2 \, dp_2}{\int_{-\infty}^{\infty} e^{-\beta \epsilon_1} dp_1 \int e^{-\beta \tilde{E}} \, dx_1 dx_2 \, dp_2}. \tag{6.47c}$$

The integrals over all the coordinates except p_1 cancel, and we have

$$\overline{\epsilon}_1 = \frac{\int_{-\infty}^{\infty} \epsilon_1 \, e^{-\beta \epsilon_1} \, dp_1}{\int_{-\infty}^{\infty} e^{-\beta \epsilon_1} \, dp_1}. \tag{6.48}$$

As we have done in other contexts [see (4.84), page 202] we can write $\overline{\epsilon}_1$ as

$$\overline{\epsilon}_1 = -\frac{\partial}{\partial \beta} \ln \Big(\int_{-\infty}^{\infty} e^{-\beta \epsilon_1} \, dp_1 \Big). \tag{6.49}$$

If we substitute $\epsilon_1 = ap_1^2$, the integral in (6.49) becomes

$$I(\beta) = \int_{-\infty}^{\infty} e^{-\beta \epsilon_1} dp_1 = \int_{-\infty}^{\infty} e^{-\beta a p_1^2} \, dp_1 \tag{6.50a}$$

$$= (\beta a)^{-1/2} \int_{-\infty}^{\infty} e^{-u^2} du, \tag{6.50b}$$

where we have let $u^2 = \beta a p^2$. Note that the integral in (6.50b) is independent of β, and its numerical value is irrelevant. Hence

$$\overline{\epsilon}_1 = -\frac{\partial}{\partial \beta} \ln I(\beta) = \frac{1}{2} kT. \tag{6.51}$$

Equation (6.51) is an example of the equipartition theorem of classical statistical mechanics.

The equipartition theorem is applicable only when the system can be described classically, and is applicable only to each term in the energy that is proportional to a coordinate squared. This coordinate must take on a continuum of values from $-\infty$ to $+\infty$.

Applications of the equipartition theorem. A system of particles in three dimensions has $3N$ quadratic contributions to the kinetic energy, three for each particle. From the equipartition theorem, we know that the mean kinetic energy is $3NkT/2$, independent of the nature of the interactions, if any, between the particles. Hence, the heat capacity at constant volume of an ideal classical monatomic gas is given by $C_V = 3Nk/2$ as we have found previously.

Another application of the equipartition function is to the one-dimensional harmonic oscillator in the classical limit. In this case there are two quadratic contributions to the total energy and hence the mean energy of a one-dimensional classical harmonic oscillator in equilibrium with a heat bath at temperature T is kT. In the harmonic model of a crystal each atom feels a harmonic or spring-like force due to its neighboring atoms (see Section 6.9.1). The N atoms independently perform simple harmonic oscillations about their equilibrium positions. Each atom contributes three quadratic terms to the kinetic energy and three quadratic terms to the potential energy. Hence, in the high temperature limit the energy of a crystal of N atoms is $E = 6NkT/2$, and the heat capacity at constant volume is

$$C_V = 3Nk \qquad \text{(law of Dulong and Petit).} \tag{6.52}$$

The result (6.52) is known as the law of Dulong and Petit. This result was first discovered empirically and is valid only at sufficiently high temperatures. At low temperatures a quantum treatment is necessary and the independence of C_V on T breaks down. The heat capacity of an insulating solid at low temperatures is discussed in Section 6.9.2.

We next consider an ideal gas consisting of diatomic molecules (see Figure 6.5 on page 345). Its pressure equation of state is still given by $PV = NkT$, because the pressure depends only on the translational motion of the center of mass of each molecule. However, its heat capacity differs from that of a ideal monatomic gas because a diatomic molecule has additional energy associated with its vibrational and rotational motion. Hence, we expect that C_V for an ideal diatomic gas to be greater than C_V for an ideal monatomic gas. The temperature dependence of the heat capacity of an ideal diatomic gas is explored in Problem 6.47.

6.2.2 The Maxwell velocity distribution

So far we have used the tools of statistical mechanics to calculate macroscopic quantities of interest in thermodynamics such as the pressure, the temperature, and the heat capacity. We now apply statistical mechanics arguments to gain more detailed information about classical systems of particles by calculating the velocity distribution of the particles.

Consider a classical system of particles in equilibrium with a heat bath at temperature T. We know that the total energy can be written as the sum of two parts: the kinetic energy $K(\mathbf{p}_1, \ldots, \mathbf{p}_N)$ and the potential energy $U(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. The kinetic energy is a quadratic function of the momenta $\mathbf{p}_1, \ldots, \mathbf{p}_N$ (or velocities), and the potential energy is a function of the positions $\mathbf{r}_1, \ldots, \mathbf{r}_N$ of the particles. The total energy is $E = K + U$. The probability density of a microstate of N particles defined by $\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N$ is given in the canonical ensemble by

$$\begin{aligned} p(\mathbf{r}_1, \ldots, \mathbf{r}_N; \mathbf{p}_1, \ldots, \mathbf{p}_N) &= A\, e^{-[K(\mathbf{p}_1,\mathbf{p}_2,\ldots,\mathbf{p}_N)+U(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)]/kT} &\text{(6.53a)}\\ &= A\, e^{-K(\mathbf{p}_1,\mathbf{p}_2,\ldots,\mathbf{p}_N)/kT} e^{-U(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)/kT}, &\text{(6.53b)}\end{aligned}$$

where A is a normalization constant. The probability density p is a product of two factors, one that depends only on the particle positions and the other that depends only on the particle momenta. This factorization implies that the probabilities of the momenta and positions are independent. The probability of the positions of the particles can be written as

$$f(\mathbf{r}_1, \ldots, \mathbf{r}_N)\, d\mathbf{r}_1 \ldots d\mathbf{r}_N = B\, e^{-U(\mathbf{r}_1,\ldots,\mathbf{r}_N)/kT} d\mathbf{r}_1 \ldots d\mathbf{r}_N, \tag{6.54}$$

and the probability of the momenta is given by

$$f(\mathbf{p}_1, \ldots, \mathbf{p}_N)\, d\mathbf{p}_1 \ldots d\mathbf{p}_N = C\, e^{-K(\mathbf{p}_1,\ldots,\mathbf{p}_N)/kT} d\mathbf{p}_1 \ldots d\mathbf{p}_N. \tag{6.55}$$

For notational simplicity, we have denoted the two probability densities by f, even though their meaning is different in (6.54) and (6.55). The constants B and C in (6.54) and (6.55) can be found by requiring that each probability be normalized.

We stress that the probability distribution for the momenta does not depend on the nature of the interaction between the particles and is the same for all classical systems at the same temperature. This statement might seem surprising because it might seem that the velocity distribution should depend on the density of the system. An external potential also does not affect the velocity distribution. These statements do not hold for quantum systems, because in this case the position and momentum operators do not commute. That is, $e^{-\beta(\hat{K}+\hat{U})} \neq e^{-\beta\hat{K}}e^{-\beta\hat{U}}$ for quantum systems, where we have used carets to denote operators in quantum mechanics.

Because the total kinetic energy is a sum of the kinetic energy of each of the particles, the probability density $f(\mathbf{p}_1, \ldots, \mathbf{p}_N)$ is a product of terms that each depend on the momenta of only one particle. This factorization implies that the momentum probabilities of the various particles are independent. These considerations imply that we can write the probability that a particle has momentum $\mathbf{p}$ in the range $d\mathbf{p}$ as

$$f(p_x, p_y, p_z)\, dp_x dp_y dp_z = c\, e^{-(p_x^2+p_y^2+p_z^2)/2mkT} dp_x dp_y dp_z. \tag{6.56}$$

The constant c is given by the normalization condition

$$c\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-(p_x^2+p_y^2+p_z^2)/2mkT} dp_x dp_y dp_z = c\Big[\int_{-\infty}^{\infty} e^{-p^2/2mkT} dp\Big]^3 = 1. \tag{6.57}$$

If we use the fact that $\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = (\pi/\alpha)^{1/2}$ (see the Appendix), we find that $c = (2\pi mkT)^{-3/2}$. Hence the momentum probability distribution can be expressed as

$$f(p_x, p_y, p_z)\, dp_x dp_y dp_z = \frac{1}{(2\pi mkT)^{3/2}}\, e^{-(p_x^2+p_y^2+p_z^2)/2mkT} dp_x dp_y dp_z. \tag{6.58}$$

The corresponding velocity probability distribution is given by

$$f(v_x, v_y, v_z)\, dv_x dv_y dv_z = \Big(\frac{m}{2\pi kT}\Big)^{3/2} e^{-m(v_x^2+v_y^2+v_z^2)/2kT} dv_x dv_y dv_z. \tag{6.59}$$

Equation (6.59) is known as the *Maxwell velocity distribution.* Note that its form is a Gaussian. The probability distribution for the speed is discussed in Section 6.2.3.

Because $f(v_x, v_y, v_z)$ is a product of three independent factors, the probability of the velocity of a particle in a particular direction is independent of the velocity in any other direction. For example, the probability that a particle has a velocity in the x-direction in the range v_x to $v_x + dv_x$ is

$$f(v_x)\, dv_x = \Big(\frac{m}{2\pi kT}\Big)^{1/2} e^{-mv_x^2/2kT} dv_x. \tag{6.60}$$

Many textbooks derive the Maxwell velocity distribution for an ideal classical gas and give the misleading impression that the distribution applies only if the particles are noninteracting. We stress that the Maxwell velocity (and momentum) distribution applies to any classical system regardless of the interactions, if any, between the particles.

Problem 6.10. Is there an upper limit to the velocity?

The upper limit to the velocity of a particle is the velocity of light. Yet the Maxwell velocity distribution imposes no upper limit to the velocity. Does this contradiction lead to difficulties? ☐

Problem 6.11. Simulations of the Maxwell velocity distribution

(a) Program `LJ2DFluidMD` simulates a system of particles interacting via the Lennard-Jones potential (1.1) in two dimensions by solving Newton's equations of motion numerically. The program computes the distribution of velocities in the x-direction among other quantities. Compare the form of the velocity distribution to the form of the Maxwell velocity distribution in (6.60). How does its width depend on the temperature?

(b) Program `IdealThermometerIdealGas` implements the demon algorithm for an ideal classical gas in one dimension (see Section 4.9). All the particles have the same initial velocity. The program computes the distribution of velocities among other quantities. What is the form of the velocity distribution? Give an argument based on the central limit theorem (see Section 3.7) to explain why the distribution has the observed form. Is this form consistent with (6.60)?

6.2.3 The Maxwell speed distribution

We have found that the distribution of velocities in a classical system of particles is a Gaussian and is given by (6.59). To determine the distribution of speeds for a three-dimensional system we need to know the number of microstates between v and $v + \Delta v$. This number is proportional to the volume of a spherical shell of width Δv or $4\pi(v + \Delta v)^3/3 - 4\pi v^3/3 \to 4\pi v^2 \Delta v$ in the limit $\Delta v \to 0$. Hence, the probability that a particle has a speed between v and $v + dv$ is given by

$$f(v)dv = 4\pi A v^2 e^{-mv^2/2kT} dv, \tag{6.61}$$

where A is a normalization constant, which we calculate in Problem 6.12.

Problem 6.12. Maxwell speed distribution

(a) Compare the form of the Maxwell speed distribution (6.61) with the form of the Maxwell velocity distribution (6.59).

(b) Use the normalization condition $\int_0^\infty f(v)dv = 1$ to calculate A and show that

$$f(v)dv = 4\pi v^2 \Big(\frac{m}{2\pi kT}\Big)^{3/2} e^{-mv^2/2kT} dv \qquad \text{(Maxwell speed distribution)}. \tag{6.62}$$

(c) Calculate the mean speed $\overline{v}$, the most probable speed $\tilde{v}$, and the root-mean-square speed $v_{\rm rms}$ and discuss their relative magnitudes.

(d) Make the change of variables $u = v/\sqrt{(2kT/m)}$ and show that

$$f(v)dv = f(u)du = (4/\sqrt{\pi})u^2 e^{-u^2} du, \tag{6.63}$$

where we have again used the same notation for two different, but physically related probability densities. The (dimensionless) speed probability density $f(u)$ is shown in Figure 6.2. ☐

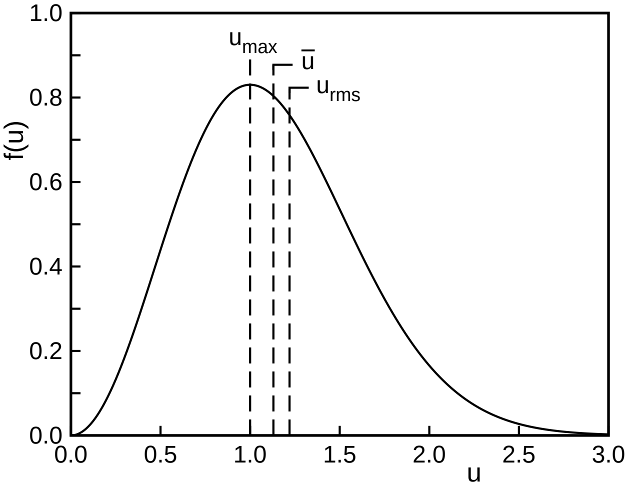


Figure 6.2: The probability density $f(u) = 4/\sqrt{\pi}u^2e^{-u^2}$ that a particle has a dimensionless speed u. Note the difference between the most probable speed $\tilde{u} = 1$, the mean speed $\overline{u} \approx 1.13$, and the root-mean-square speed $u_{\rm rms} \approx 1.22$. The dimensionless speed u is defined by $u \equiv v/(2kT/m)^{1/2}$.

Problem 6.13. Maxwell speed distribution in one or two dimensions

Find the Maxwell speed distribution for particles restricted to one and two dimensions. ☐

6.3 Occupation Numbers and Bose and Fermi Statistics

We now develop the formalism for calculating the thermodynamic properties of ideal gases for which quantum effects are important. We have already noted that the absence of interactions between the particles of an ideal gas enables us to reduce the problem of determining the energy levels of the gas as a whole to determining $\epsilon_{\mathbf{k}}$, the energy levels of a single particle. Because the particles are indistinguishable, we cannot specify the microstate of each particle. Instead a microstate of an ideal gas is specified by the *occupation number* $n_{\mathbf{k}}$, the number of particles in the single particle state $\mathbf{k}$ with energy $\epsilon_{\mathbf{k}}$.[2] If we know the value of the occupation number for each single particle microstate, we can write the total energy of the system in microstate s as

$$E_s = \sum_{\mathbf{k}} n_{\mathbf{k}}\, \epsilon_{\mathbf{k}}. \tag{6.64}$$

The set of $n_{\mathbf{k}}$ completely specifies a microstate of the system.

The partition function for an ideal gas can be expressed in terms of the occupation numbers as

$$Z(V,T,N) = \sum_{\{n_{\mathbf{k}}\}} e^{-\beta \sum_{\mathbf{k}} n_{\mathbf{k}} \epsilon_{\mathbf{k}}}, \tag{6.65}$$

---

[2] The relation of $\mathbf{k}$ to the quantum numbers labeling the single particle microstates is given in (4.35) and in (6.93). In the following we will use $\mathbf{k}$ to label single particle microstates.

where the occupation numbers $n_{\mathbf{k}}$ satisfy the condition

$$N = \sum_{\mathbf{k}} n_{\mathbf{k}}. \tag{6.66}$$

The condition (6.66) is difficult to satisfy in practice, and we will later use the grand canonical ensemble for which the condition of a fixed number of particles is relaxed.

As discussed in Section 4.3.6, one of the fundamental results of relativistic quantum mechanics is that all particles can be classified into two groups. Particles with zero or integral spin such as ^{4}He are *bosons* and have wavefunctions that are symmetric under the exchange of any pair of particles. Particles with half-integral spin such as electrons, protons, and neutrons are *fermions* and have wavefunctions that are antisymmetric under particle exchange. The Bose or Fermi character of composite objects can be found by noting that composite objects that have an even number of fermions are bosons and those containing an odd number of fermions are themselves fermions. For example, an atom of ^{3}He is composed of an odd number of particles: two electrons, two protons, and one neutron each of spin $\frac{1}{2}$. Hence, ^{3}He has half-integral spin, making it a fermion. An atom of ^{4}He has one more neutron so there are an even number of fermions and ^{4}He is a boson.

It is remarkable that all particles fall into one of two mutually exclusive classes with different spin. It is even more remarkable that there is a connection between the spin of a particle and its statistics. Why are particles with half-integral spin fermions and particles with integral spin bosons? The answer lies in the requirements imposed by Lorentz invariance on quantum field theory. This requirement implies that the form of quantum field theory must be the same in all inertial reference frames. Although many physicists believe that the relation between spin and statistics must have a simpler explanation, no such explanation yet exists.[3]

The difference between fermions and bosons is specified by the possible values of $n_{\mathbf{k}}$. For fermions we have

$$n_{\mathbf{k}} = 0 \text{ or } 1 \qquad \text{(fermions)}. \tag{6.67}$$

The restriction (6.67) is a statement of the Pauli exclusion principle for noninteracting particles – two identical fermions cannot be in the same single particle microstate. In contrast, the occupation numbers $n_{\mathbf{k}}$ for identical bosons can take any positive integer value:

$$n_{\mathbf{k}} = 0, 1, 2, \cdots \qquad \text{(bosons)}. \tag{6.68}$$

We will see in the following sections that the nature of the statistics of a many particle system can have a profound effect on its properties.

Example 6.1. Calculate the partition function of an ideal gas of $N = 3$ identical fermions in equilibrium with a heat bath at temperature T. Assume that each particle can be in one of four possible microstates with energies, $\epsilon_1, \epsilon_2, \epsilon_3$, and ϵ_4.

Solution. The possible microstates of the system are summarized in Table 6.2. The spin of the fermions is neglected. Is it possible to reduce this problem to a one-body problem as we did for a noninteracting classical system?

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[3] In spite of its fundamental importance, it is only a slight exaggeration to say that "everyone knows the spin-statistics theorem, but no one understands it." See Duck and Sudarshan (1998).

n_1	n_2	n_3	n_4
0	1	1	1
1	0	1	1
1	1	0	1
1	1	1	0

Table 6.2: The possible states of a three-particle fermion system with four single particle energy microstates (see Example 6.1). The quantity n_1 represents the number of particles in the single particle microstate labeled 1, etc. Note that we have not specified which particle is in a particular microstate.

From Table 6.2 we see that the partition function is given by

$$Z_3 = e^{-\beta(\epsilon_2+\epsilon_3+\epsilon_4)} + e^{-\beta(\epsilon_1+\epsilon_3+\epsilon_4)} + e^{-\beta(\epsilon_1+\epsilon_2+\epsilon_4)} + e^{-\beta(\epsilon_1+\epsilon_2+\epsilon_3)}. \tag{6.69}$$

♢

Problem 6.14. Calculate $\overline{n}_1$, the mean number of fermions in the single particle microstate 1 with energy ϵ_1, for the system in Example 6.1. □

Problem 6.15. Mean energy of a toy model of an ideal Bose gas

(a) Calculate the mean energy of an ideal gas of $N = 2$ identical bosons in equilibrium with a heat bath at temperature T, assuming that each particle can be in one of three microstates with energies 0, Δ, and 2Δ.

(b) Calculate the mean energy for $N = 2$ distinguishable particles assuming that each particle can be in one of three possible microstates.

(c) If $\bar{E}_1$ is the mean energy for one particle and $\bar{E}_2$ is the mean energy for the two-particle system, is $\bar{E}_2 = 2\bar{E}_1$ for either bosons or distinguishable particles? □

6.4 Distribution Functions of Ideal Bose and Fermi Gases

The calculation of the partition function for an ideal gas in the semiclassical limit was done by choosing a single particle as the system. This choice is not possible for an ideal gas at low temperatures where the quantum nature of the particles cannot be ignored. So we need a different strategy. The key idea is that it is possible to distinguish the subset of all particles in a *given single particle microstate* from the particles in all other single particle microstates. For this reason we divide the system of interest into subsystems each of which is the *set of all particles that are in a given single particle microstate*. Because the number of particles in a given microstate varies, we need to use the grand canonical ensemble and assume that each subsystem is coupled to a heat bath and a particle reservoir independently of the other single particle microstates.

Because we have not yet applied the grand canonical ensemble, we review it here. The thermodynamic potential in the grand canonical ensemble is denoted by $\Omega(T, V, \mu)$ and is equal to $-PV$

[see (2.168)]. The relation of thermodynamics to statistical mechanics is given by $\Omega = -kT \ln Z_G$, where the grand partition function Z_G is given by

$$Z_G = \sum_s e^{-\beta(E_s - \mu N_s)}. \tag{6.70}$$

E_s is the energy of microstate s and N_s is the number of particles in microstate s. The goal is to calculate Z_G, then Ω and the pressure equation of state $-PV$ (in terms of T, V, and μ), and then determine S from the relation

$$S = -\Big(\frac{\partial \Omega}{\partial T}\Big)_{V,\mu}, \tag{6.71}$$

and the mean number of particles from the relation

$$\overline{N} = -\Big(\frac{\partial \Omega}{\partial \mu}\Big)_{T,V}. \tag{6.72}$$

The probability of a particular microstate is given by

$$P_s = \frac{1}{Z_G} e^{-\beta(E_s - \mu N_s)} \qquad \text{(Gibbs distribution)}. \tag{6.73}$$

Because we can treat an ideal gas as a collection of independent subsystems where each subsystem is a single particle microstate, Z_G reduces to the product of $Z_{\mathrm{G},\,\mathbf{k}}$ for each subsystem. Thus, the first step is to calculate the grand partition function $Z_{\mathrm{G},\,\mathbf{k}}$ for each subsystem. We write the energy of the $n_{\mathbf{k}}$ particles in the single particle microstate $\mathbf{k}$ as $n_{\mathbf{k}}\,\epsilon_{\mathbf{k}}$ and write $Z_{\mathrm{G},\,\mathbf{k}}$ as

$$Z_{\mathrm{G},\,\mathbf{k}} = \sum_{n_{\mathbf{k}}} e^{-\beta n_{\mathbf{k}}(\epsilon_{\mathbf{k}} - \mu)}, \tag{6.74}$$

where the sum is over the possible values of $n_{\mathbf{k}}$. For fermions this sum is straightforward because $n_{\mathbf{k}} = 0$ and 1 [see (6.67)]. Hence

$$Z_{\mathrm{G},\,\mathbf{k}} = 1 + e^{-\beta(\epsilon_{\mathbf{k}} - \mu)}. \tag{6.75}$$

The corresponding thermodynamic or Landau potential $\Omega_{\mathbf{k}}$ is given by

$$\Omega_{\mathbf{k}} = -kT \ln Z_{\mathrm{G},\,\mathbf{k}} = -kT \ln[1 + e^{-\beta(\epsilon_{\mathbf{k}} - \mu)}]. \tag{6.76}$$

We use the relation $\overline{n}_{\mathbf{k}} = -\partial\Omega_{\mathbf{k}}/\partial\mu$ [see (6.72)] to find the mean number of particles in microstate $\mathbf{k}$. The result is

$$\overline{n}_{\mathbf{k}} = -\frac{\partial \Omega_{\mathbf{k}}}{\partial \mu} = \frac{e^{-\beta(\epsilon_{\mathbf{k}} - \mu)}}{1 + e^{-\beta(\epsilon_{\mathbf{k}} - \mu)}}, \tag{6.77}$$

or

$$\overline{n}_{\mathbf{k}} = \frac{1}{e^{\beta(\epsilon_{\mathbf{k}} - \mu)} + 1} \qquad \text{(Fermi-Dirac distribution)}. \tag{6.78}$$

The result (6.78) for the mean number of particles in single particle microstate $\mathbf{k}$ is known as the *Fermi-Dirac distribution.*

The integer values of $n_{\mathbf{k}}$ are unrestricted for bosons. We write (6.74) as

$$Z_{\mathrm{G},\,\mathbf{k}} = 1 + e^{-\beta(\epsilon_{\mathbf{k}}-\mu)} + e^{-2\beta(\epsilon_{\mathbf{k}}-\mu)} + \cdots = \sum_{n_{\mathbf{k}}=0}^{\infty} \big[e^{-\beta(\epsilon_{\mathbf{k}}-\mu)}\big]^{n_{\mathbf{k}}}. \tag{6.79}$$

The geometric series in (6.79) is convergent for $e^{-\beta(\epsilon_{\mathbf{k}}-\mu)} < 1$. Because this condition must be satisfied for all values of $\epsilon_{\mathbf{k}}$, we require that $e^{\beta\mu} < 1$ or

$$\mu < 0 \qquad\qquad \text{(bosons)}. \tag{6.80}$$

In contrast, the chemical potential may be either positive or negative for fermions. The summation of the geometric series in (6.79) gives

$$Z_{\mathrm{G},\,\mathbf{k}} = \frac{1}{1 - e^{-\beta(\epsilon_{\mathbf{k}}-\mu)}}, \tag{6.81}$$

and hence we obtain

$$\Omega_{\mathbf{k}} = kT \ln\big[1 - e^{-\beta(\epsilon_{\mathbf{k}}-\mu)}\big]. \tag{6.82}$$

The mean number of particles in single particle microstate $\mathbf{k}$ is given by

$$\overline{n}_{\mathbf{k}} = -\frac{\partial \Omega_{\mathbf{k}}}{\partial \mu} = \frac{e^{-\beta(\epsilon_{\mathbf{k}}-\mu)}}{1 - e^{-\beta(\epsilon_{\mathbf{k}}-\mu)}}, \tag{6.83}$$

or

$$\overline{n}_{\mathbf{k}} = \frac{1}{e^{\beta(\epsilon_{\mathbf{k}}-\mu)} - 1} \qquad\qquad \text{(Bose-Einstein distribution)}. \tag{6.84}$$

The form (6.84) is known as the *Bose-Einstein distribution.*

It is frequently convenient to group the Fermi-Dirac and Bose-Einstein distributions together and to write

$$\boxed{\overline{n}_{\mathbf{k}} = \frac{1}{e^{\beta(\epsilon_{\mathbf{k}}-\mu)} \pm 1}. \qquad \begin{cases} + \text{ Fermi-Dirac distribution} \\ - \text{ Bose-Einstein distribution} \end{cases}}. \tag{6.85}$$

The convention is that the upper sign corresponds to Fermi statistics and the lower sign to Bose statistics.

Because the (grand) partition function Z_G is a product, $Z_G = \prod_{\mathbf{k}} Z_{\mathrm{G},\,\mathbf{k}}$, the Landau potential for the ideal gas is given by

$$\Omega(T,V,\mu) = \sum_{\mathbf{k}} \Omega_{\mathbf{k}} = \mp kT \sum_{\mathbf{k}} \ln\big[1 \pm e^{-\beta(\epsilon_{\mathbf{k}}-\mu)}\big]. \tag{6.86}$$

The classical limit. The Fermi-Dirac and Bose-Einstein distributions must reduce to the classical limit under the appropriate conditions. In the classical limit $\overline{n}_{\mathbf{k}} \ll 1$ for all $\mathbf{k}$; that is, the mean number of particles in any single particle microstate must be small. Hence $\epsilon^{\beta(\epsilon_{\mathbf{k}}-\mu)} \gg 1$ and in this limit both the Fermi-Dirac and Bose-Einstein distributions reduce to

$$\overline{n}_{\mathbf{k}} = e^{-\beta(\epsilon_{\mathbf{k}}-\mu)} \qquad \text{(Maxwell-Boltzmann distribution)}. \tag{6.87}$$

This result (6.87) is known as the *Maxwell-Boltzmann distribution.*

6.5 Single Particle Density of States

To find the various thermodynamic quantities we need to calculate various sums. For example, to obtain the mean number of particles in the system we need to sum (6.85) over all single particle states:

$$\overline{N}(T, V, \mu) = \sum_{\mathbf{k}} \overline{n}_{\mathbf{k}} = \sum_{\mathbf{k}} \frac{1}{e^{\beta(\epsilon_{\mathbf{k}} - \mu)} \pm 1}. \tag{6.88}$$

For a given temperature T and volume V, (6.88) is an implicit equation for the chemical potential μ in terms of the mean number of particles. That is, the chemical potential determines the mean number of particles just as the temperature determines the mean energy. Similarly, we can write the mean energy of the system as

$$\overline{E}(T, V, \mu) = \sum_{\mathbf{k}} \overline{n}_{\mathbf{k}}\, \epsilon_{\mathbf{k}}. \tag{6.89}$$

For a macroscopic system the number of particles and the energy are well defined, and we will usually replace $\overline{N}$ and $\overline{E}$ by N and E, respectively.

Because we have described the microscopic states at the most fundamental level, that is, by using quantum mechanics, the macroscopic averages of interest such as (6.88), (6.89), and (6.86) involve sums over the microscopic states. However, because the systems of interest are macroscopic, the volume of the system is so large that the energies of the discrete microstates are very close together and for practical purposes indistinguishable from a continuum. As usual, it is easier to do integrals than to do sums over a very large number of microstates, and hence we will replace the sums in (6.88)–(6.86) by integrals. For example, we will write for an arbitrary function $f(\epsilon)$

$$\sum_{\mathbf{k}} f(\epsilon_{\mathbf{k}}) \to \int_0^\infty f(\epsilon)\, g(\epsilon) d\epsilon, \tag{6.90}$$

where $g(\epsilon)\, d\epsilon$ is the number of single particle microstates between ϵ and $\epsilon + d\epsilon$. The quantity $g(\epsilon)$ is known as the *density of states*, although a better term would be the density of *single* particle microstates.

Although we have calculated the density of states $g(\epsilon)$ for a single particle in a box (see Section 4.3), we review the calculation here to emphasize its generality and the common aspects of the calculation for blackbody radiation, elastic waves in a solid, and electron waves. For convenience, we choose the box to be a cube of linear dimension L and assume that there are standing waves that vanish at the faces of the cube. The condition for a standing wave in one dimension is that the wavelength satisfies the condition

$$\lambda = \frac{2L}{n} \qquad (n = 1,\ 2,\ \ldots), \tag{6.91}$$

where n is a nonzero positive integer. It is useful to define the *wave number* k as

$$k = \frac{2\pi}{\lambda}, \tag{6.92}$$

and write the standing wave condition as $k = n\pi/L$. Because the waves in the x, y, and z directions satisfy similar conditions, we can treat the wave number as a vector whose components satisfy the condition

$$\mathbf{k} = (n_x, n_y, n_z)\frac{\pi}{L}, \tag{6.93}$$

where n_x, n_y, n_z are positive nonzero integers.

Not all values of $\mathbf{k}$ are permissible and each combination of $\{n_x, n_y, n_z\}$ corresponds to a different microstate. In the "number space" defined by the three perpendicular axes labeled by n_x, n_y, and n_z, the possible values of the microstates lie at the centers of cubes of unit edge length. Because the energy of a wave depends only on the magnitude of $\mathbf{k}$, we want to know the number of microstates between k and $k+dk$. As we did in Section 4.3, it is easier to first find $\Gamma(k)$, the number of microstates with wave number less than or equal to k. We know that the volume in n-space of a single particle microstate is 1, and hence the number of single particle microstates in number space that are contained in the positive octant of a sphere of radius n is given by $\Gamma(n) = \frac{1}{8}(4\pi n^3/3)$, where $n^2 = n_x^2 + n_y^2 + n_z^2$. Because $\mathbf{k} = \pi\mathbf{n}/L$, the number of single particle microstates with wave vector less than or equal to k is

$$\Gamma(k) = \frac{1}{8}\frac{4\pi k^3/3}{(\pi/L)^3}. \tag{6.94}$$

If we use the relation

$$g(k)\,dk = \Gamma(k+dk) - \Gamma(k) = \frac{d\Gamma(k)}{dk}\,dk, \tag{6.95}$$

we obtain

$$g(k)\,dk = V\frac{k^2dk}{2\pi^2}, \tag{6.96}$$

where the volume $V = L^3$. Equation (6.96) gives the density of states in k-space between k and $k + dk$.

Although we obtained the result (6.96) for a cube, the result is independent of the shape of the enclosure and the nature of the boundary conditions (see Problem 6.58). That is, if the box is sufficiently large, the surface effects introduced by the box do not affect the physical properties of the system.

Problem 6.16. Single particle density of states in one and two dimensions

Find the form of the density of states in k-space for standing waves in a two-dimensional and in a one-dimensional box. ☐

6.5.1 Photons

The result (6.96) for the density of states in k-space holds for any wave in a three-dimensional enclosure. We next determine the number of states $g(\epsilon)\,d\epsilon$ as a function of the energy ϵ. For simplicity, we adopt the same symbol to represent the density of states in k-space and in ϵ-space because the meaning of g will be clear from the context.

The nature of the dependence of $g(\epsilon)$ on the energy ϵ is determined by the form of the function $\epsilon_{\mathbf{k}}$. For electromagnetic waves of frequency ν we know that $\lambda\nu = c$, $\omega = 2\pi\nu$, and $k = 2\pi/\lambda$. Hence, $\omega = 2\pi c/\lambda$ or

$$\omega = ck. \tag{6.97}$$

The energy ϵ of a photon of frequency ω is

$$\epsilon = \hbar\omega = \hbar ck. \tag{6.98}$$

Because $k = \epsilon/\hbar c$, we find from (6.96) that

$$g(\epsilon)\, d\epsilon = V \frac{\epsilon^2}{2\pi^2\hbar^3c^3}\, d\epsilon. \tag{6.99}$$

The result (6.99) requires one modification. The state of an electromagnetic wave or photon depends not only on its wave vector or momentum, but also on its polarization. There are two mutually perpendicular directions of polarization (right circularly polarized and left circularly polarized) for each electromagnetic wave of wave number $\mathbf{k}$.[4] Thus the number of photon microstates in which the photon has an energy in the range ϵ to $\epsilon + d\epsilon$ is given by

$$g(\epsilon)\, d\epsilon = V \frac{\epsilon^2 d\epsilon}{\pi^2\hbar^3c^3} \qquad \text{(photons)}. \tag{6.100}$$

We will use (6.100) frequently in the following.

6.5.2 Nonrelativistic particles

For a nonrelativistic particle of mass m we know that

$$\epsilon = \frac{p^2}{2m}. \tag{6.101}$$

From the relations $p = h/\lambda$ and $k = 2\pi/\lambda$, we find that the momentum p of a particle is related to its wave vector k by $p = \hbar k$. Hence, the energy can be expressed as

$$\epsilon = \frac{\hbar^2k^2}{2m}, \tag{6.102}$$

and thus

$$d\epsilon = \frac{\hbar^2 k}{m} dk. \tag{6.103}$$

If we use (6.96) and the relations (6.102) and (6.103), we find that the number of microstates in the interval ϵ to $\epsilon + d\epsilon$ is given by

$$g(\epsilon)\, d\epsilon = n_s \frac{V}{4\pi^2\hbar^3}(2m)^{3/2}\, \epsilon^{1/2}\, d\epsilon. \tag{6.104}$$

We have included a factor of n_s, the number of spin states for a given value of k or ϵ. Because electrons have spin 1/2, $n_s = 2$, and we can write (6.104) as

$$g(\epsilon)\, d\epsilon = \frac{V}{2\pi^2\hbar^3}(2m)^{3/2}\, \epsilon^{1/2}\, d\epsilon \qquad \text{(electrons)}. \tag{6.105}$$

It is common to choose units such that $\hbar = 1$, and we will express most of our results in the remainder of this chapter in terms of $\hbar$ instead of h.

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[4] In the language of quantum mechanics we say that the photon has spin 1 and two helicity states. The fact that the photon has spin $S = 1$ and two helicity states rather than $(2S + 1) = 3$ states is a consequence of special relativity for massless particles.

Problem 6.17. Density of states in one and two dimensions

Calculate the density of states $g(\epsilon)$ for a nonrelativistic particle of mass m in in one and two dimensions (see Problem 6.16). Sketch $g(\epsilon)$ on one graph for $d = 1$, 2, and 3 and comment on the different dependence of $g(\epsilon)$ on ϵ for different spatial dimensions. ☐

Problem 6.18. Relativistic particles

Calculate the density of states $g(\epsilon)$ in three dimensions for a relativistic particle of rest mass m for which $\epsilon^2 = p^2c^2 + m^2c^4$. Don't try to simplify your result. ☐

Problem 6.19. Relation between the energy and pressure equations of state for a nonrelativistic ideal gas

The mean energy E is given by

$$\begin{aligned} E &= \int_0^\infty \epsilon \overline{n}(\epsilon)\, g(\epsilon)\, d\epsilon && (6.106a) \\ &= n_s \frac{V}{4\pi^2\hbar^3}(2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2} d\epsilon}{e^{\beta(\epsilon-\mu)} \pm 1}. && (6.106b) \end{aligned}$$

Use (6.86) for the Landau potential and (6.104) for the density of states of nonrelativistic particles in three dimensions to show that Ω can be expressed as

$$\begin{aligned} \Omega &= \mp kT \int_0^\infty g(\epsilon)\, \ln[1 \pm e^{-\beta(\epsilon-\mu)}]\, d\epsilon && (6.107) \\ &= \mp kT \frac{n_s V}{4\pi^2\hbar^3}\,(2m)^{3/2} \int_0^\infty \epsilon^{1/2} \ln[1 \pm e^{-\beta(\epsilon-\mu)}]\, d\epsilon. && (6.108) \end{aligned}$$

Integrate (6.108) by parts with $u = \ln[1 \pm e^{-\beta(\epsilon-\mu)}]$ and $dv = \epsilon^{1/2}\, d\epsilon$ and show that

$$\Omega = -\frac{2}{3} n_s \frac{V}{4\pi^2\hbar^3}(2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2}\, d\epsilon}{e^{\beta(\epsilon-\mu)} \pm 1}. \tag{6.109}$$

The form (6.106b) for E is the same as the general result (6.109) for Ω except for the factor of $-\frac{2}{3}$. Use the relation $\Omega = -PV$ [see (2.168)] to show that

$$PV = \frac{2}{3}E. \tag{6.110}$$

The relation (6.110) is exact and holds for an ideal gas with any statistics at any temperature T, and depends only on the nonrelativistic relation $\epsilon = p^2/2m$. ☐

Problem 6.20. Relation between the energy and pressure equations of state for photons

Use similar considerations as in Problem 6.19 to show that for photons:

$$PV = \frac{1}{3}E. \tag{6.111}$$

Equation (6.111) holds at any temperature and is consistent with Maxwell's equations. Thus, the pressure due to electromagnetic radiation is related to the energy density by $P = u(T)/3$. ☐

6.6 The Equation of State of an Ideal Classical Gas: Application of the Grand Canonical Ensemble

We have already seen how to obtain the equations of state and other thermodynamic quantities for the ideal classical gas in the microcanonical ensemble (fixed E, V, and N) and in the canonical ensemble (fixed T, V, and N). We now discuss how to use the grand canonical ensemble (fixed T, V, and μ) to find the analogous quantities under conditions for which the Maxwell-Boltzmann distribution is applicable. The calculation in the grand canonical ensemble will automatically satisfy the condition that the particles are indistinguishable.

As an example, we first calculate the chemical potential given that the mean number of particles is $\overline{N}$. We use the Maxwell-Boltzmann distribution (6.87) and the density of states (6.104) for particles of mass m and set $n_s = 1$ for simplicity. The result is

$$\overline{N} = \sum_{\mathbf{k}} \overline{n}_{\mathbf{k}} \to \int_0^\infty \overline{n}(\epsilon)\, g(\epsilon)\, d\epsilon \tag{6.112a}$$

$$= \frac{V}{4\pi^2}\Big(\frac{2m}{\hbar^2}\Big)^{3/2} \int_0^\infty e^{-\beta(\epsilon-\mu)}\, \epsilon^{1/2}\, d\epsilon. \tag{6.112b}$$

We make the change of variables $u = \beta\epsilon$ and write (6.112b) as

$$\overline{N} = \frac{V}{4\pi^2}\Big(\frac{2m}{\hbar^2\beta}\Big)^{3/2} e^{\beta\mu} \int_0^\infty e^{-u}\, u^{1/2}\, du. \tag{6.113}$$

The integral in (6.113) can be done analytically (make the change of variables $u = y^2$) and has the value $\pi^{1/2}/2$ (see the Appendix). Hence, the mean number of particles is given by

$$\overline{N}(T, V, \mu) = V\Big(\frac{m}{2\pi\hbar^2\beta}\Big)^{3/2} e^{\beta\mu}. \tag{6.114}$$

Because we cannot easily measure μ, it is of more interest to find the value of μ that yields the desired value of $\overline{N}$. The solution of (6.114) for the chemical potential is

$$\mu = kT \ln\Big[\frac{\overline{N}}{V}\Big(\frac{2\pi\hbar^2\beta}{m}\Big)^{3/2}\Big]. \tag{6.115}$$

What is the difference, if any, between (6.114) and the result (6.29) for μ found in the canonical ensemble?

Problem 6.21. The chemical potential

(a) Estimate the chemical potential of one mole of an ideal monatomic classical gas at standard temperature and pressure and show that $\mu \ll 0$.

(b) Show that $\overline{N}$ can be expressed as [see (6.114)]

$$\overline{N} = \frac{V}{\lambda^3}\, e^{\beta\mu}, \tag{6.116}$$

and hence

$$\mu(T,V) = -kT \ln \frac{1}{\rho\lambda^3}, \tag{6.117}$$

where $\rho = \overline{N}/V$.

(c) In Section 6.1 we argued that the semiclassical limit $\lambda \ll \rho^{-1/3}$ [see (6.1)] implies that $\overline{n}_{\mathbf{k}} \ll 1$; that is, the mean number of particles in any single particle energy state is very small. Use the expression (6.117) for μ and (6.87) for $\overline{n}_{\mathbf{k}}$ to show that the condition $\overline{n}_{\mathbf{k}} \ll 1$ implies that $\lambda \ll \rho^{-1/3}$. ☐

As we saw in Section 2.21, the chemical potential is the change in any of the thermodynamic potentials when a particle is added. It might be expected that $\mu > 0$, because it should cost energy to add a particle. But because the particles do not interact, perhaps $\mu = 0$? So why is $\mu \ll 0$ for an ideal classical gas? The reason is that we have to include the contribution of the entropy. In the canonical ensemble the change in the free energy due to the addition of a particle at constant temperature is $\Delta F = \Delta E - T\Delta S \approx kT - T\Delta S$. The number of places where the additional particle can be located is approximately V/λ^3, and hence $\Delta S \sim k \ln V/\lambda^3$. Because $V/\lambda^3 \gg 1$, $\Delta S \gg \Delta E$, and thus $\Delta F \ll 0$, which implies that $\mu = \Delta F/\Delta N \ll 0$.

The example calculation of $\overline{N}(T,V,\mu)$ leading to (6.114) was not necessary because we can calculate all thermodynamic quantities directly from the Landau potential Ω. We calculate Ω from (6.86) by noting that $e^{\beta\mu} \ll 1$ and approximating the logarithm as $\ln(1 \pm x) \approx \pm x$. We find that

$$\Omega = \mp kT \sum_{\mathbf{k}} \ln\left[1 \pm e^{-\beta(\epsilon_{\mathbf{k}}-\mu)}\right] \tag{6.118a}$$

$$\to -kT \sum_{\mathbf{k}} e^{-\beta(\epsilon_{\mathbf{k}}-\mu)} \qquad \text{(semiclassical limit)}. \tag{6.118b}$$

As expected, the form of Ω in (6.118b) is independent of whether we started with Bose or Fermi statistics.

As usual, we replace the sum over the single particle states by an integral over the density of states and find

$$\Omega = -kT\, e^{\beta\mu} \int_0^\infty g(\epsilon)\, e^{-\beta\epsilon}\, d\epsilon \tag{6.119a}$$

$$= -kT\, \frac{V}{4\pi^2\hbar^3} \Big(\frac{2m}{\beta}\Big)^{3/2} e^{\beta\mu} \int_0^\infty u^{1/2} e^{-u}\, du \tag{6.119b}$$

$$= -\frac{V}{\beta^{5/2}} \Big(\frac{m}{2\pi\hbar^2}\Big)^{3/2} e^{\beta\mu}. \tag{6.119c}$$

If we substitute $\lambda = (2\pi\beta\hbar^2/m)^{1/2}$, we find

$$\Omega = -kT \frac{V}{\lambda^3}\, e^{\beta\mu}. \tag{6.120}$$

From the relation $\Omega = -PV$ [see (2.168)], we obtain

$$P = \frac{kT}{\lambda^3}\, e^{\beta\mu}. \tag{6.121}$$

If we use the thermodynamic relation (6.72), we obtain

$$\overline{N} = -\frac{\partial \Omega}{\partial \mu}\Big|_{V,T} = \frac{V}{\lambda^3}\, e^{\beta\mu}. \tag{6.122}$$

The classical equation of state, $PV = \overline{N}kT$, is obtained by using (6.122) to eliminate μ. The simplest way of finding the energy is to use the relation (6.110).

We can find the entropy $S(T, V, \mu)$ using (6.120) and (6.71):

$$S(T, V, \mu) = -\frac{\partial \Omega}{\partial T}\Big|_{V,\mu} = k\beta^2\, \frac{\partial \Omega}{\partial \beta} \tag{6.123a}$$

$$= Vk\beta^2 \Big[\frac{5}{2\beta^{7/2}} - \frac{\mu}{\beta^{5/2}}\Big]\Big(\frac{m}{2\pi\hbar^2}\Big)^{3/2} e^{\beta\mu}. \tag{6.123b}$$

We eliminate μ from (6.123b) using (6.115) and obtain the Sackur-Tetrode expression for the entropy of an ideal gas:

$$S(T, V, N) = Nk\Big[\frac{5}{2} - \ln\frac{N}{V} - \ln\Big(\frac{2\pi\hbar^2}{mkT}\Big)^{3/2}\Big]. \tag{6.124}$$

We have written N rather than $\overline{N}$ in (6.124). Note that we did not have to introduce any extra factors of $N!$ as we did in Section 6.1, because we already correctly counted the number of microstates.

Problem 6.22. Ideal gas equations of state

Show that $E = (3/2)NkT$ and $PV = NkT$ from the results of this section. □

6.7 Blackbody Radiation

We can regard electromagnetic radiation as equivalent to a system of noninteracting bosons (photons), each of which has an energy $h\nu$, where ν is the frequency of the radiation. If the radiation is in an enclosure, equilibrium will be established and maintained by the interactions of the photons with the atoms of the wall in the enclosure. Because the atoms emit and absorb photons, the total number of photons is not conserved.

If a body in thermal equilibrium emits electromagnetic radiation, this radiation is described as blackbody radiation and the object is said to be a blackbody. This statement does not mean that the body is actually black. The word "black" indicates that the radiation is perfectly absorbed and re-radiated by the object. The frequency spectrum of light radiated by such an idealized body is described by a universal spectrum called the Planck spectrum, which we will derive in the following [see (6.133)]. The nature of the spectrum depends only on the temperature T of the radiation.

We can derive the Planck radiation law using either the canonical or grand canonical ensemble because the photons are continuously absorbed and emitted by the walls of the container and hence their number is not conserved. This lack of a conservation law for the number of particles implies that the chemical potential vanishes. Hence the Bose-Einstein distribution in (6.85) reduces to

$$\overline{n}_{\mathbf{k}} = \frac{1}{e^{\beta\epsilon_{\mathbf{k}}} - 1} \qquad \text{(Planck distribution)} \tag{6.125}$$

for blackbody radiation.

The result (6.125) can be understood by simple considerations. As we have mentioned, equilibrium is established and maintained by the interactions between the photons and the atoms of the wall in the enclosure. The number N of photons in the cavity cannot be imposed externally on the system and is fixed by the temperature T of the walls and the volume V enclosed. Hence, the free energy F for photons cannot depend on N because the latter is not a thermodynamic variable, and we have $\mu = \partial F/\partial N = 0$. If we substitute $\mu = 0$ into the general result (6.84) for the Bose-Einstein distribution, we find that the mean number of photons in single particle state $\mathbf{k}$ is given by

$$\overline{n}_{\mathbf{k}} = \frac{1}{e^{\beta \epsilon_{\mathbf{k}}} - 1}, \tag{6.126}$$

in agreement with (6.125).

To see how (6.126) follows from the canonical ensemble, consider a system in equilibrium with a heat bath at temperature T. Because there is no constraint on the total number of photons, the number of photons in each single particle microstate is independent of the number of photons in all the other single particle microstates. Thus, the partition function is the product of the single particle state partition functions $Z_{\mathbf{k}}(T,V)$ for each state in the same way as the partition function for a collection of noninteracting spins is the product of the partition functions for each spin. We have

$$Z_{\mathbf{k}}(T,V) = \sum_{n_{\mathbf{k}}=0}^{\infty} e^{-\beta n_{\mathbf{k}} \epsilon_{\mathbf{k}}}. \tag{6.127}$$

Because the sum in (6.127) is a geometric series, we obtain

$$Z_{\mathbf{k}}(T,V) = \frac{1}{1 - e^{-\beta \epsilon_{\mathbf{k}}}}. \tag{6.128}$$

In the canonical ensemble the mean number of photons in the single particle microstate $\mathbf{k}$ is given by

$$\overline{n}_{\mathbf{k}} = \frac{\sum_{n_{\mathbf{k}}=0}^{\infty} n_{\mathbf{k}} e^{-\beta n_{\mathbf{k}} \epsilon_{\mathbf{k}}}}{\sum_{n_{\mathbf{k}}=0}^{\infty} e^{-\beta n_{\mathbf{k}} \epsilon_{\mathbf{k}}}} \tag{6.129a}$$

$$= \frac{\partial \ln Z_{\mathbf{k}}}{\partial(-\beta \epsilon_{\mathbf{k}})}. \tag{6.129b}$$

We have from (6.128) and (6.129b)

$$\overline{n}_{\mathbf{k}} = \frac{\partial}{\partial(-\beta \epsilon_{\mathbf{k}})} \Big[-\ln(1 - e^{-\beta \epsilon_{\mathbf{k}}}) \Big] \tag{6.130a}$$

$$= \frac{e^{-\beta \epsilon_{\mathbf{k}}}}{1 - e^{-\beta \epsilon_{\mathbf{k}}}} = \frac{1}{e^{\beta \epsilon_{\mathbf{k}}} - 1}. \tag{6.130b}$$

Planck's theory of blackbody radiation follows from the form of the density of states for photons found in (6.100). The number of photons with energy in the range ϵ to $\epsilon + d\epsilon$ is given by

$$N(\epsilon)\, d\epsilon = \overline{n}(\epsilon) g(\epsilon)\, d\epsilon = \frac{V}{\pi^2 \hbar^3 c^3} \frac{\epsilon^2\, d\epsilon}{e^{\beta\epsilon} - 1}. \tag{6.131}$$

If we substitute $\epsilon = h\nu$ on the right-hand side of (6.131), we find that the number of photons in the frequency range ν to $\nu + d\nu$ is given by

$$N(\nu)\,d\nu = \frac{8\pi V}{c^3}\frac{\nu^2\,d\nu}{e^{\beta h\nu} - 1}. \tag{6.132}$$

The distribution of radiated energy is obtained by multiplying (6.132) by $h\nu$:

$$E(\nu)d\nu = h\nu N(\nu)\,d\nu = \frac{8\pi hV\nu^3}{c^3}\frac{d\nu}{e^{\beta h\nu} - 1}. \tag{6.133}$$

Equation (6.133) gives the energy radiated by a blackbody of volume V in the frequency range between ν and $\nu + d\nu$. The energy per unit volume $u(\nu)$ is given by

$$u(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{\beta h\nu} - 1} \qquad \text{(Planck's radiation law)}. \tag{6.134}$$

We can change variables to $\epsilon = h\nu$ and write the energy density as

$$u(\epsilon) = \frac{8\pi}{(hc)^3}\frac{\epsilon^3}{e^{\epsilon/kT} - 1}. \tag{6.135}$$

The physical system that most closely gives the spectrum of a black body is the spectrum of the cosmic microwave background, which fits the theoretical spectrum of a blackbody better than the best blackbody spectrum that can be made in a laboratory. In contrast, a piece of hot, glowing firewood is not really in thermal equilibrium, and the spectrum of glowing embers is only a crude approximation to the blackbody spectrum. The existence of the cosmic microwave background spectrum and its fit to the blackbody spectrum is compelling evidence that the universe experienced a Big Bang.[5]

Problem 6.23. Wien's displacement law

The maximum of $u(\nu)$ shifts to higher frequencies with increasing temperature. Show that the maximum of u can be found by solving the equation

$$(3 - x)e^x = 3, \tag{6.136}$$

where $x = \beta h\nu_{\rm max}$. Solve (6.136) numerically for x and show that

$$\frac{h\nu_{\rm max}}{kT} = 2.822 \qquad \text{(Wien's displacement law)}. \tag{6.137}$$

□

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[5] The universe is filled with electromagnetic radiation with a distribution of frequencies given by (6.133) with $T \approx 2.725\,$K. This background radiation is a remnant from a time when the universe was composed primarily of electrons and protons at a temperature of about $3000\,$K. This plasma of electrons and protons interacted strongly with the electromagnetic radiation over a wide range of frequencies, so that the matter and radiation reached thermal equilibrium. As the universe expanded, the plasma cooled until it became energetically favorable for electrons and protons to combine to form hydrogen atoms. Atomic hydrogen interacts with radiation only at the frequencies of the hydrogen spectral lines. As a result most of the radiation energy was effectively decoupled from matter so that its temperature is independent of the temperature of the hydrogen atoms. The background radiation is now at about $2.725\,$K because of the expansion of the universe. This expansion causes the radiation to be redshifted. The temperature of the cosmic radiation background will continue to decrease as the universe expands.

Problem 6.24. Derivation of the Rayleigh-Jeans and Wien's laws

(a) Make a change of variables in (6.134) to find the energy emitted by a blackbody at a wavelength between λ and $\lambda + d\lambda$.

(b) Determine the limiting behavior of your result in part (a) for long wavelengths. This limit is called the Rayleigh-Jeans law and is given by

$$u(\lambda)d\lambda = \frac{8\pi kT}{\lambda^4}d\lambda. \tag{6.138}$$

Does this form involve Planck's constant? The result in (6.138) was originally derived from purely classical considerations.

(c) Classical theory predicts what is known as the ultraviolet catastrophe, namely, that an infinite amount of energy is radiated at high frequencies or short wavelengths. Explain how (6.138) would give an infinite result for the total radiated energy, and thus the classical result cannot be correct for all wavelengths.

(d) Determine the limiting behavior of $u(\lambda)$ for short wavelengths. This behavior is known as Wien's law, after Wilhelm Wien who found it by finding a functional form to fit the experimental data. □

Problem 6.25. Thermodynamics of blackbody radiation

Use the various thermodynamic relations to show that

$$E = V\int_0^\infty u(\nu)\,d\nu = \frac{4\sigma}{c}VT^4, \tag{6.139a}$$

$$\Omega = F = -\frac{4\sigma}{3c}VT^4, \tag{6.139b}$$

$$S = \frac{16\sigma}{3c}VT^3, \tag{6.139c}$$

$$P = \frac{4\sigma}{3c}T^4 = \frac{1}{3}\frac{E}{V}, \tag{6.139d}$$

$$G = F + PV = 0. \tag{6.139e}$$

The free energy F in (6.139b) can be calculated from Z starting from (6.128) and using (6.100). The Stefan-Boltzmann constant σ is given by

$$\sigma = \frac{2\pi^5 k^4}{15h^3c^2}. \tag{6.140}$$

The integral

$$\int_0^\infty \frac{x^3\,dx}{e^x - 1} = \frac{\pi^4}{15}. \tag{6.141}$$

is evaluated in the Appendix. □

The relation (6.139a) between the total energy and the temperature is known as the Stefan-Boltzmann law. It was derived based on thermodynamic considerations in Section 2.21.

Problem 6.26. Mean number of photons

Show that the total mean number of photons in an enclosure of volume V is given by

$$N = \frac{V}{\pi^2 c^3}\int_0^\infty \frac{\omega^2 d\omega}{e^{\hbar\omega/kT} - 1} = \frac{V(kT)^3}{\pi^2 c^3 \hbar^3}\int_0^\infty \frac{x^2 dx}{e^x - 1}. \tag{6.142}$$

The integral in (6.142) can be expressed in terms of known functions (see the Appendix). The result is

$$\int_0^\infty \frac{x^2 dx}{e^x - 1} = 2 \times 1.202. \tag{6.143}$$

Hence N depends on T as

$$N = 0.244V\Big(\frac{kT}{\hbar c}\Big)^3. \tag{6.144}$$

□

6.8 The Ideal Fermi Gas

The low temperature properties of metals are dominated by the behavior of the conduction electrons. Given that there are Coulomb interactions between the electrons as well as interactions between the electrons and the positive ions of the lattice, it is remarkable that the *free electron model* in which the electrons are treated as an ideal gas of fermions near zero temperature is an excellent model of the conduction electrons in a metal under most circumstances.[6] In the following, we investigate the properties of an ideal Fermi gas and briefly discuss its applicability as a model of electrons in metals.

As we will see in Problem 6.27, the thermal de Broglie wavelength of the electrons in a typical metal is much larger than the mean interparticle spacing, and hence we must treat the electrons using Fermi statistics. When a system is dominated by quantum mechanical effects, it is said to be *degenerate*.

6.8.1 Ground state properties

We first discuss the noninteracting Fermi gas at $T = 0$. From (6.78) we see that the zero temperature limit ($\beta \to \infty$) of the Fermi-Dirac distribution is

$$\overline{n}(\epsilon) = \begin{cases} 1 & \text{for } \epsilon < \mu, \\ 0 & \text{for } \epsilon > \mu. \end{cases} \tag{6.145}$$

That is, all states whose energies are below the chemical potential are occupied, and all states whose energies are above the chemical potential are unoccupied. The Fermi distribution at $T = 0$ is shown in Figure 6.3.

---

[6] The idea that a system of interacting electrons at low temperatures can be understood as a noninteracting gas of quasiparticles is due to Lev Landau (1908–1968), the same Landau for whom the thermodynamic potential in the grand canonical ensemble is named. Landau worked in many fields including low temperature physics, atomic and nuclear physics, condensed matter physics, and plasma physics. He was awarded the 1962 Nobel Prize for Physics for his work on superfluidity. He was also the coauthor of ten widely used graduate-level textbooks on various areas of theoretical physics.

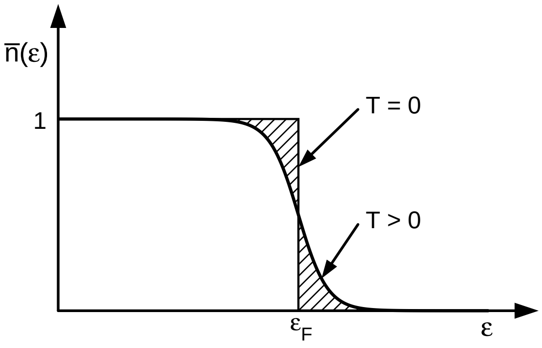

Figure 6.3: The Fermi-Dirac distribution for $T = 0$ and $T \ll T_F$. The form of $\overline{n}(\epsilon)$ for $T > 0$ is based on the assumption that μ is unchanged for $T \ll T_F$. Note that the area under the curve $\overline{n}(\epsilon)$ at $T = 0$ is approximately equal to the area under the curve $\overline{n}(\epsilon)$ for $T \ll T_F$.

The consequences of (6.145) are easy to understand. At $T = 0$, the system is in its *ground state*, and the particles are distributed among the single particle states so that the total energy of the gas is a minimum. Because we may place no more than one particle in each state, we need to construct the ground state of the system by adding a particle into the lowest available energy state until we have placed all the particles. To find the value of $\mu(T = 0)$, we write

$$N = \int_0^\infty \overline{n}(\epsilon) g(\epsilon)\, d\epsilon \underset{T \to 0}{\longrightarrow} \int_0^{\mu(T=0)} g(\epsilon)\, d\epsilon = V \int_0^{\mu(T=0)} \frac{(2m)^{3/2}}{2\pi^2\hbar^3} \epsilon^{1/2}\, d\epsilon. \tag{6.146}$$

We have substituted the electron density of states (6.105) in (6.146). The chemical potential at $T = 0$ is determined by requiring the integral to give the desired number of particles N. Because the value of the chemical potential at $T = 0$ will have special importance, it is common to denote it by ϵ_F:

$$\epsilon_F \equiv \mu(T = 0), \tag{6.147}$$

where ϵ_F, the energy of the highest occupied state, is called the *Fermi energy.*

The integral on the right-hand side of (6.146) gives

$$N = \frac{V}{3\pi^2} \Big(\frac{2m\epsilon_F}{\hbar^2}\Big)^{3/2}. \tag{6.148}$$

From (6.148) we have that

$$\epsilon_F = \frac{\hbar^2}{2m} (3\pi^2 \rho)^{2/3} \qquad \text{(Fermi energy)}, \tag{6.149}$$

where the density $\rho = N/V$. It is convenient to write $\epsilon_F = p_F^2/2m$ where p_F is known as the *Fermi momentum.* It follows that the Fermi momentum p_F is given by

$$p_F = (3\pi^2 \rho)^{1/3} \hbar \qquad \text{(Fermi momentum)}. \tag{6.150}$$

The Fermi momentum can be estimated by using the de Broglie relation $p = h/\overline{\lambda}$ and taking $\overline{\lambda} \sim \rho^{-1/3}$, the mean distance between particles. That is, the particles are "localized" within a distance of order $\rho^{-1/3}$.

At $T = 0$ all the states with momentum smaller than p_F are occupied and all the states above this momentum are unoccupied. The boundary in momentum space between occupied and unoccupied states at $T = 0$ is called the *Fermi surface*. For an ideal Fermi gas in three dimensions the Fermi surface is the surface of a sphere with radius p_F.

We can understand why the chemical potential at $T = 0$ is positive by reasoning similar to that given on page 317 for an ideal classical gas. At $T = 0$ the contribution of $T\Delta S$ to the free energy vanishes, and no particle can be added with energy less than $\mu(T = 0)$. Thus, $\mu(T = 0) > 0$. In contrast, we argued that $\mu(T > 0)$ is much less than zero for an ideal classical gas due to the large change in the entropy when adding (or removing) a particle.

We will find it convenient in the following to introduce a characteristic temperature, the Fermi temperature T_F, by

$$T_F = \epsilon_F/k. \tag{6.151}$$

The values of T_F for typical metals are given in Table 6.3.

A direct consequence of the fact that the density of states in three dimensions is proportional to $\epsilon^{1/2}$ is that the mean energy per particle at $T = 0$ is $3\epsilon_F/5$:

$$\frac{\overline{E}}{N} = \frac{\int_0^{\epsilon_F} \epsilon\, g(\epsilon)\, d\epsilon}{\int_0^{\epsilon_F} g(\epsilon)\, d\epsilon} = \frac{\int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon}{\int_0^{\epsilon_F} \epsilon^{1/2} d\epsilon} \tag{6.152a}$$

$$= \frac{\frac{2}{5}\epsilon_F^{5/2}}{\frac{2}{3}\epsilon_F^{3/2}} = \frac{3}{5}\epsilon_F. \tag{6.152b}$$

The total energy is given by

$$E = \frac{3}{5}N\epsilon_F = \frac{3}{5}N(3\pi^2)^{2/3}\frac{\hbar^2}{2m}\rho^{2/3}. \tag{6.153}$$

The pressure can be immediately found from the general relation $PV = 2E/3$ [see (6.110)] for a nonrelativistic ideal gas at any temperature. Alternatively, the pressure can be found from the relation

$$P = -\frac{\partial F}{\partial V} = \frac{2}{3}\frac{E}{V}, \tag{6.154}$$

because the free energy is equal to the total energy at $T = 0$. The result is that the pressure at $T = 0$ is given by

$$P = \frac{2}{5}\rho\epsilon_F. \tag{6.155}$$

The fact that the pressure is nonzero even at zero temperature is a consequence of the Pauli exclusion principle, which allows only one particle to have zero momentum (two electrons if the spin is considered). All other particles have finite momentum and hence give rise to a nonzero pressure at $T = 0$.

Another way to understand the relation (6.155) is to recall the classical pressure equation of state, $P = \rho kT$, which would predict that the pressure is zero at zero temperature. However, if

element	ϵ_F (eV)	T_F (10^4 K)
Li	4.7	5.5
Na	3.2	3.8
Al	11.7	13.6
Cu	7	8.2
Ag	5.5	6.4

Table 6.3: Values of the Fermi energy and Fermi temperature for several metals at room temperature and atmospheric pressure.

we replace T by the Fermi temperature T_F, then $P \propto \rho k T_F = \rho\epsilon_F$, which is the same as (6.155) except for a numerical factor.

Problem 6.27. Order of magnitude estimates

(a) Verify that the values of ϵ_F given in electon volts (eV) lead to the values of T_F in Table 6.3.

(b) Compare the values of T_F in Table 6.3 to room temperature. What is the value of kT in eV at room temperature?

(c) Given the data in Table 6.3 verify that the electron densities for Li and Cu are $\rho = 4.7 \times 10^{28}\,\mathrm{m}^{-3}$ and $\rho = 8.5 \times 10^{28}\,\mathrm{m}^{-3}$, respectively.

(d) What is the mean distance between the electrons for Li and Cu?

(e) Use the fact that the mass of an electron is 9.1×10^{-31} kg to estimate the de Broglie wavelength corresponding to an electron with energy comparable to the Fermi energy.

(f) Compare your result for the de Broglie wavelength that you found in part (e) to the mean interparticle spacing that you found in part (d). ☐

Problem 6.28. Landau potential at zero temperature

From (6.107) the Landau potential for an ideal Fermi gas at arbitrary T can be expressed as

$$\Omega = -kT \int_0^\infty g(\epsilon)\, \ln[1 + e^{-\beta(\epsilon-\mu)}]\, d\epsilon. \tag{6.156}$$

To obtain the $T = 0$ limit of Ω, we have that $\epsilon < \mu$ in (6.156), $\beta \to \infty$, and hence $\ln[1+e^{-\beta(\epsilon-\mu)}] \to \ln e^{-\beta(\epsilon-\mu)} = -\beta(\epsilon-\mu)$. Hence, show that

$$\Omega = \frac{(2m)^{3/2}V}{2\pi^2\hbar^2} \int_0^{\epsilon_F} d\epsilon\, \epsilon^{1/2}\big(\epsilon - \epsilon_F\big). \tag{6.157}$$

Calculate Ω and determine the pressure at $T = 0$. ☐

Problem 6.29. Show that the limit (6.145) for $\overline{n}(\epsilon)$ at $T = 0$ follows only if $\mu > 0$. ☐

6.8.2 Low temperature properties

One of the greatest successes of the free electron model and Fermi-Dirac statistics is the explanation of the temperature dependence of the heat capacity of a metal. If the electrons behaved as a classical noninteracting gas, we would expect a contribution to the heat capacity equal to $3Nk/2$ as $T \to 0$. Instead, we typically find a very small contribution to the heat capacity which is linear in the temperature, a result that cannot be explained by classical statistical mechanics. Before we derive this result, we first give a qualitative argument for the low temperature dependence of the heat capacity of an ideal Fermi gas.

As we saw in Table 6.3, room temperature is much less than the Fermi temperature of the conduction electrons in a metal, that is, $T \ll T_F$. Hence we should be able to understand the behavior of an ideal Fermi gas at room temperature in terms of its behavior at zero temperature. Because there is only one characteristic energy in the system (the Fermi energy), the criterion for low temperature is that $T \ll T_F$. Hence the conduction electrons in a metal may be treated as if they are effectively near zero temperature even though the metal is at room temperature.

For $0 < T \ll T_F$, the electrons that are within order kT below the Fermi surface have enough energy to occupy the microstates with energies that are order kT above the Fermi energy. In contrast, the electrons that are deep within the Fermi surface do not have enough energy to be excited to microstates above the Fermi energy. Hence, only a small fraction of order T/T_F of the N electrons have a reasonable probability of being excited, and the remainder of the electrons remain unaffected as the temperature is increased from $T = 0$. This reasoning leads us to write the heat capacity of the electrons as $C_V \sim N_{\rm eff}k$, where $N_{\rm eff}$ is the number of electrons that can be excited by exchanging energy with a heat bath. For a classical system, $N_{\rm eff} = N$, but for a Fermi system at $T \ll T_F$, we have that $N_{\rm eff} \sim N(T/T_F)$. Hence, we expect the temperature dependence of the heat capacity to be given by

$$C_V \sim Nk\frac{T}{T_F} \qquad (T \ll T_F). \tag{6.158}$$

From (6.158) we see that the contribution to the heat capacity from the electrons is much smaller than the prediction of the equipartition theorem and is linear in T, as is found empirically. As an example, the measured specific heat of copper for $T < 1\,\mathrm{K}$ is dominated by the contribution of the electrons and is given by $C_V/kN = 0.8 \times 10^{-4}\,T$.

Our qualitative argument for the low temperature behavior of C_V implicitly assumes that $\mu(T)$ is unchanged for $T \ll T_F$. We can understand why $\mu(T)$ remains unchanged as T is increased slightly from $T = 0$ by the following reasoning. The probability that a single particle state of energy $\epsilon = \mu - \Delta$ is empty is

$$1 - \overline{n}(\epsilon = \mu - \Delta) = 1 - \frac{1}{e^{-\beta\Delta} + 1} = \frac{1}{e^{\beta\Delta} + 1} = \overline{n}(\epsilon = \mu + \Delta). \tag{6.159}$$

We see from (6.159) that, for a given distance Δ from μ, the probability that a particle is lost from a previously occupied single particle state below μ equals the probability that a previously empty single particle state is occupied. This property implies that the area under the step function at $T = 0$ is nearly the same as the area under $\overline{n}(\epsilon)$ for $T \ll T_F$ (see Figure 6.3). That is, $\overline{n}(\epsilon)$ is symmetrical about $\epsilon = \mu$. If we make the additional assumption that the density of states changes very little in the region where $\overline{n}$ departs from a step function, we see that the mean number of particles *lost* from the previously occupied states just balances the mean number *gained* by the previously empty states. Hence, we conclude that for $T \ll T_F$, we still have the correct number of particles without any need to change the value of μ.

Similar reasoning implies that $\mu(T)$ must decrease slightly as T is increased from zero. Suppose that μ were to remain constant as T is increased. Because the density of states is an increasing function of ϵ, the number of electrons with energy $\epsilon > \mu$ would be greater than the number lost with $\epsilon < \mu$. As a result, we would increase the number of electrons by increasing T. To prevent such a nonsensical increase, μ has to decrease slightly. In addition, we know that, because $\mu \ll 0$ for high temperatures where the system behaves like an ideal classical gas, $\mu(T)$ must pass through zero. At what temperature would you estimate that $\mu(T) \approx 0$?

In Problem 6.30 we will determine $\mu(T)$ by evaluating the integral in (6.160) numerically. Then we will evaluate the integral analytically for $T \ll T_F$ and show that $\mu(T) - \mu(T=0) \sim (T/T_F)^2$. Hence, to first order in T/T_F, μ is unchanged.

Problem 6.30. Numerical evaluation of the chemical potential for an ideal Fermi gas

To find the chemical potential for $T > 0$, we need to find the value of μ that yields the desired mean number of particles. We have

$$N = \int_0^\infty \overline{n}(\epsilon) g(\epsilon) d\epsilon = \frac{V(2m)^{3/2}}{2\pi^2\hbar^3} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\beta(\epsilon-\mu)} + 1}, \tag{6.160}$$

where we have used (6.105) for $g(\epsilon)$. It is convenient to let $\epsilon = x\epsilon_F$, $\mu = \mu^*\epsilon_F$, and $T^* = kT/\epsilon_F$, and rewrite (6.160) as

$$\rho = \frac{N}{V} = \frac{(2m)^{3/2}}{2\pi^2\hbar^3} \epsilon_F^{3/2} \int_0^\infty \frac{x^{1/2}\, dx}{e^{(x-\mu^*)/T^*} + 1}, \tag{6.161}$$

or

$$1 = \frac{3}{2} \int_0^\infty \frac{x^{1/2}\, dx}{e^{(x-\mu^*)/T^*} + 1}, \tag{6.162}$$

where we have substituted (6.149) for ϵ_F. To find the dependence of μ^* on T^* and hence μ on T use Program `IdealFermiGasIntegral` to evaluate the integral on the right-hand side of (6.162) numerically.

(a) Start with $T^* = 0.2$ and find μ^* such that (6.162) is satisfied. (Recall that $\mu^* = 1$ at $T^* = 0$.) Does μ^* initially increase or decrease as T is increased from zero? What is the sign of μ^* for $T^* \gg 1$?

(b) At what value of T^* is $\mu^* \approx 0$?

(c) Given the value of $\mu^*(T^*)$, the program computes the numerical value of $E(T)$. Describe its qualitative T dependence and the T dependence of C_V. □

We now derive a quantitative expression for C_V that is applicable for temperatures $T \ll T_F$.[7]

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[7] The following derivation is adapted from Kittel (1996).

The increase $\Delta E = E(T) - E(T = 0)$ in the total energy is given by

$$\Delta E = \int_0^\infty \epsilon\, \overline{n}(\epsilon) g(\epsilon)\, d\epsilon - \int_0^{\epsilon_F} \epsilon\, g(\epsilon)\, d\epsilon, \tag{6.163a}$$

$$= \int_0^{\epsilon_F} \epsilon[\overline{n}(\epsilon) - 1] g(\epsilon)\, d\epsilon + \int_{\epsilon_F}^\infty \epsilon\, \overline{n}(\epsilon) g(\epsilon)\, d\epsilon. \tag{6.163b}$$

We multiply the identity

$$N = \int_0^\infty \overline{n}(\epsilon) g(\epsilon) d\epsilon = \int_0^{\epsilon_F} g(\epsilon)\, d\epsilon \tag{6.164}$$

by ϵ_F and write the integral on the left-hand side as a sum of two contributions to obtain

$$\int_0^{\epsilon_F} \epsilon_F\, \overline{n}(e) g(\epsilon)\, d\epsilon + \int_{\epsilon_F}^\infty \epsilon_F\, \overline{n}(e) g(\epsilon)\, d\epsilon = \int_0^{\epsilon_F} \epsilon_F\, g(\epsilon)\, d\epsilon, \tag{6.165a}$$

or

$$\int_0^{\epsilon_F} \epsilon_F [\overline{n}(\epsilon) - 1] g(\epsilon)\, d\epsilon + \int_{\epsilon_F}^\infty \epsilon_F \overline{n}(\epsilon) g(\epsilon)\, d\epsilon = 0. \tag{6.165b}$$

We can use (6.165b) to rewrite (6.163b) as

$$\Delta E = \int_{\epsilon_F}^\infty (\epsilon - \epsilon_F) \overline{n}(\epsilon) g(\epsilon) d\epsilon + \int_0^{\epsilon_F} (\epsilon_F - \epsilon)[1 - \overline{n}(\epsilon)] g(\epsilon) d\epsilon. \tag{6.166}$$

The heat capacity is found by differentiating ΔE with respect to T. The only temperature dependent quantity in (6.166) is $\overline{n}(\epsilon)$. Hence, we can write C_V as

$$C_V = \int_0^\infty (\epsilon - \epsilon_F) \frac{d\overline{n}(\epsilon)}{dT} g(\epsilon) d\epsilon. \tag{6.167}$$

For $T \ll T_F$, the derivative $d\overline{n}/dT$ is large only for ϵ near ϵ_F. Hence it is a good approximation to evaluate the density of states $g(\epsilon)$ at $\epsilon = \epsilon_F$ and take it outside the integral:

$$C_V = g(\epsilon_F) \int_0^\infty (\epsilon - \epsilon_F) \frac{d\overline{n}}{dT} d\epsilon. \tag{6.168}$$

We can also ignore the temperature dependence of μ in $\overline{n}(\epsilon)$ and replace μ by ϵ_F. With this approximation we have

$$\frac{d\overline{n}}{dT} = \frac{d\overline{n}}{d\beta} \frac{d\beta}{dT} = \frac{1}{kT^2} \frac{(\epsilon - \epsilon_F) e^{\beta(\epsilon - \epsilon_F)}}{[e^{\beta(\epsilon - \epsilon_F)} + 1]^2}. \tag{6.169}$$

We next let $x = (\epsilon - \epsilon_F)/kT$ and use (6.168) and (6.169) to write C_V as

$$C_V = k^2 T g(\epsilon_F) \int_{-\beta\epsilon_F}^\infty \frac{x^2 e^x}{(e^x + 1)^2} dx. \tag{6.170}$$

We can replace the lower limit by $-\infty$ because the factor e^x in the integrand is negligible at $x = -\beta\epsilon_F$ for low temperatures. If we use the integral

$$\int_{-\infty}^\infty \frac{x^2\, e^x}{(e^x + 1)^2} dx = \frac{\pi^2}{3}, \tag{6.171}$$

we can write the heat capacity of an ideal Fermi gas as

$$C_V = \frac{1}{3}\pi^2 g(\epsilon_F) k^2 T. \tag{6.172}$$

It is straightforward to show that

$$g(\epsilon_F) = \frac{3N}{2\epsilon_F} = \frac{3N}{2kT_F}, \tag{6.173}$$

and we arrive at the desired result

$$C_V = \frac{\pi^2}{2} Nk \frac{T}{T_F} \qquad (T \ll T_F). \tag{6.174}$$

A more detailed discussion of the low temperature properties of an ideal Fermi gas is given in Section 6.11.2. For convenience, we summarize the main results here:

$$\Omega = -\frac{2}{3}\frac{2^{1/2} V m^{3/2}}{\pi^2 \hbar^3}\Big[\frac{2}{5}\mu^{5/2} + \frac{\pi^2}{4}(kT)^2 \mu^{1/2}\Big], \tag{6.175}$$

$$\overline{N} = -\frac{\partial \Omega}{\partial \mu} = \frac{V(2m)^{3/2}}{3\pi^2 \hbar^3}\Big[\mu^{3/2} + \frac{\pi^2}{8}(kT)^2 \mu^{-1/2}\Big]. \tag{6.176}$$

The results (6.175) and (6.176) are in the grand canonical ensemble in which the chemical potential is fixed. However, most experiments are done on a sample with a fixed number of electrons, and hence μ must change with T to keep $\overline{N}$ fixed. To find this dependence we rewrite (6.176) as

$$\frac{3\pi^2 \hbar^3 \rho}{(2m)^{3/2}} = \mu^{3/2}\Big[1 + \frac{\pi^2}{8}(kT)^2 \mu^{-2}\Big], \tag{6.177}$$

where $\rho = \overline{N}/V$. If we raise both sides of (6.177) to the 2/3 power and use (6.149), we have

$$\mu = \frac{3^{2/3}\pi^{4/3}\hbar^2 \rho^{2/3}}{2m}\Big[1 + \frac{\pi^2}{8}(kT)^2 \mu^{-2}\Big]^{-2/3} \tag{6.178a}$$

$$= \epsilon_F \Big[1 + \frac{\pi^2}{8}(kT)^2 \mu^{-2}\Big]^{-2/3}. \tag{6.178b}$$

In the limit of $T \to 0$, $\mu = \epsilon_F$ as expected. From (6.178b) we see that the first correction for low temperatures is given by

$$\mu(T) = \epsilon_F \Big[1 - \frac{2}{3}\frac{\pi^2}{8}\frac{(kT)^2}{\mu^2}\Big] = \epsilon_F \Big[1 - \frac{\pi^2}{12}\Big(\frac{T}{T_F}\Big)^2\Big], \tag{6.179}$$

where we have made the expansion $(1+x)^n \approx 1 + nx$ and replaced μ on the right-hand side by $\epsilon_F = kT_F$.

From (6.179) we see that the chemical potential decreases with temperature to keep N fixed, but the decrease is second order in T/T_F (rather than first order), consistent with our earlier qualitative considerations. The explanation for the decrease in $\mu(T)$ is that more particles move from energy states below the Fermi energy to energy states above the Fermi energy as the temperature increases. Because the density of states increases with energy, it is necessary to decrease the chemical potential to keep the number of particles constant. As the temperature becomes larger than the Fermi temperature, the chemical potential changes sign and becomes negative (see Problem 6.30).

Problem 6.31. Low temperature behavior

(a) Fill in the missing steps in (6.163)–(6.174).

(b) Use (6.175) and (6.179) to show that the mean pressure for $T \ll T_F$ is given by

$$P = \frac{2}{5}\rho\epsilon_F\Big[1 + \frac{5\pi^2}{12}\Big(\frac{T}{T_F}\Big)^2 + \ldots\Big]. \tag{6.180}$$

(c) Use the general relation between E and PV to show that

$$E = \frac{3}{5}N\epsilon_F\Big[1 + \frac{5\pi^2}{12}\Big(\frac{T}{T_F}\Big)^2 + \ldots\Big]. \tag{6.181}$$

(d) For completeness, show that the low temperature behavior of the entropy is given by

$$S = \frac{\pi^2}{2}Nk\frac{T}{T_F}. \tag{6.182}$$

We see from (6.174) that the conduction electrons of a metal contribute a linear term to the heat capacity. In Section 6.9 we shall see that the contribution from lattice vibrations contributes a term proportional to T^3 to C_V at low T. Thus, for sufficiently low temperature, the linear term due to the conduction electrons dominates.

Problem 6.32. Effective electron mass

From Table 6.3 we see that $T_F = 8.2\times 10^4\,\mathrm{K}$ for copper. Use (6.174) to find the predicted value of C/NkT for copper. How does this value compare with the experimental value $C/NkT = 8\times 10^{-5}$? It is remarkable that the theoretical prediction agrees so well with the experimental result based on the free electron model. Show that the small discrepancy can be removed by defining an effective mass m^* of the conduction electrons equal to $\approx 1.3\,m_\mathrm{e}$, where m_e is the mass of the electron. What factors might account for the effective mass being greater than m_e? ☐

Problem 6.33. Temperature dependence of the chemical potential in two dimensions

Consider a system of electrons restricted to a surface of area A. Show that the mean number of electrons can be written as

$$\overline{N} = \frac{mA}{\pi\hbar^2}\int_0^\infty \frac{d\epsilon}{e^{\beta(\epsilon-\mu)}+1}. \tag{6.183}$$

The integral in (6.183) can be evaluated in closed form using

$$\int \frac{dx}{1+ae^{bx}} = \frac{1}{b}\ln\frac{e^{bx}}{1+ae^{bx}} + \text{constant}. \tag{6.184}$$

(a) Show that

$$\mu(T) = kT \ln \left[e^{\rho\pi\hbar^2/mkT} - 1 \right], \tag{6.185}$$

where $\rho = \overline{N}/A$.

(b) What is the value of the Fermi energy $\epsilon_F = \mu(T = 0)$? What is the value of μ for $T \gg T_F$?

(c) Plot μ versus T and discuss its qualitative dependence on T. □

6.9 The Heat Capacity of a Crystalline Solid

The free electron model of a metal successfully explains the temperature dependence of the contribution to the heat capacity from the electrons. What about the contribution from the ions? In a crystal each ion is localized about its lattice site and oscillates due to spring-like forces between nearest-neighbor atoms. Classically, we can regard each atom of the solid as having six quadratic contributions to the energy, three of which contribute $\frac{1}{2}kT$ to the mean kinetic energy and three contribute $\frac{1}{2}kT$ to the mean potential energy. Hence, the heat capacity at constant volume of a homogeneous isotropic solid is given by $C_V = 3Nk$, independent of the nature of the solid. This behavior of C_V agrees with experiment remarkably well at high temperatures. (The meaning of high temperature will be defined later in terms of the parameters of the solid.) At low temperatures the classical behavior is an overestimate of the experimentally measured heat capacity for crystalline solids, which is found to be proportional to T^3. To understand this low temperature behavior, we first consider the Einstein model and then the more sophisticated Debye model of a solid.

6.9.1 The Einstein model

The reason why the heat capacity decreases at low temperature is that the oscillations of the crystal must be treated quantum mechanically rather than classically. The simplest model of a solid, proposed by Einstein in 1906, is that each atom behaves like three independent harmonic oscillators each of frequency ω. Because the $3N$ identical oscillators are independent and are associated with distinguishable sites, we need only to find the thermodynamic functions of one of them. The partition function for one oscillator in one dimension is [see (4.129)]

$$Z_1 = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}. \tag{6.186}$$

Other thermodynamic properties of one oscillator are given by

$$f = -kT \ln Z_1 = \frac{\hbar\omega}{2} + kT \ln[1 - e^{-\beta\hbar\omega}], \tag{6.187}$$

$$s = -\frac{\partial f}{\partial T} = -k \ln[1 - e^{-\beta\hbar\omega}] + k\beta\hbar\omega \frac{1}{e^{\beta\hbar\omega} - 1}, \tag{6.188}$$

$$e = f + Ts = (\overline{n} + 1/2)\hbar\omega, \tag{6.189}$$

where

$$\overline{n} = \frac{1}{e^{\beta\hbar\omega} - 1}. \tag{6.190}$$

Note the form of $\overline{n}$, which is identical to the Bose-Einstein distribution with $\mu = 0$. We can think of $\overline{n}$ as the mean number of quanta (phonons). Because the number of phonons is not conserved, $\mu = 0$ in the Bose-Einstein distribution. To obtain extensive quantities such as F, S, and E, we multiply the single particle values by $3N$. For example, the heat capacity of an Einstein solid is given by

$$C_V = \Big(\frac{\partial E}{\partial T}\Big)_V = 3N\Big(\frac{\partial e}{\partial T}\Big)_V = 3Nk(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{[e^{\beta\hbar\omega} - 1]^2}. \tag{6.191}$$

It is convenient to introduce the Einstein temperature

$$kT_E = \hbar\omega, \tag{6.192}$$

and express C_V as

$$C_V = 3Nk\Big(\frac{T_E}{T}\Big)^2 \frac{e^{T_E/T}}{[e^{T_E/T} - 1]^2}. \tag{6.193}$$

The limiting behavior of C_V from (6.191) or (6.193) is

$$C_V \to 3Nk \qquad (T \gg T_E), \tag{6.194a}$$

and

$$C_V \to 3Nk\Big(\frac{\hbar\omega}{kT}\Big)^2 e^{-\hbar\omega/kT} \qquad (T \ll T_E). \tag{6.194b}$$

The calculated heat capacity as $T \to 0$ is consistent with the third law of thermodynamics and is not very different from the heat capacity actually observed for insulating solids. However, it decreases too quickly at low temperatures and does not agree with the observed low temperature behavior $C_V \propto T^3$ satisfied by all insulating solids.

Problem 6.34. Limiting behavior of the heat capacity in the Einstein model

Derive the limiting behavior of C_V given in (6.194). □

6.9.2 Debye theory

The Einstein model is based on the idea that each atom behaves like a harmonic oscillator whose motion is independent of the other atoms. A better approximation was made by Debye (1912), who observed that solids can carry sound waves. Because waves are inherently a collective phenomenon and are not associated with the oscillations of a single atom, it is better to think of a crystalline solid in terms of the collective motion rather than the independent motions of the atoms. The collective or cooperative motion corresponds to the $3N$ normal modes of the system, each with its own frequency.

For each value of the wavevector $\vec{k}$ there are three sound waves in a solid – one longitudinal with velocity c_ℓ and two transverse with velocity c_t. (Note that c_t and c_ℓ are speeds of sound, not light.) The density of states of each mode is determined by the same analysis as for photons. From (6.99) we see that the density of states of the system is given by

$$g(\omega)d\omega = \frac{V\omega^2 d\omega}{2\pi^2}\Big(\frac{2}{c_t^3} + \frac{1}{c_\ell^3}\Big). \tag{6.195}$$

It is convenient to define a mean speed of sound $\overline{c}$ by the relation

$$\frac{3}{\overline{c}^3} = \frac{2}{c_t^3} + \frac{1}{c_\ell^3}, \tag{6.196}$$

so that the density of states can be written as

$$g(\omega)\,d\omega = \frac{3V\omega^2 d\omega}{2\pi^2\overline{c}^3}. \tag{6.197}$$

The total energy is given by

$$E = \int \hbar\omega\,\overline{n}(\omega)g(\omega)\,d\omega, = \frac{3V\hbar}{2\pi^2\overline{c}^3}\int \frac{\omega^3\,d\omega}{e^{\beta\hbar\omega}-1}. \tag{6.198}$$

Equation (6.198) does not take into account the higher frequency modes that do not satisfy the linear relation $\omega = kc$. For reasons that we will discuss shortly, we will use a high frequency cutoff at $\omega = \omega_D$ such that for the frequencies included $\omega \approx kc$. Because the low temperature heat capacity depends only on the low frequency modes, which we have treated correctly using (6.197), it follows that we can obtain a good approximation to the heat capacity by extending the integral in (6.197) to a maximum frequency ω_D which is determined by requiring that the total number of modes be $3N$. That is, we assume that $g(\omega) \propto \omega^2$ for $\omega < \omega_D$ such that

$$3N = \int_0^{\omega_D} g(\omega)\,d\omega. \tag{6.199}$$

If we substitute (6.197) into (6.199), we find that

$$\omega_D = 2\pi\overline{c}\Big(\frac{3\rho}{4\pi}\Big)^{1/3}. \tag{6.200}$$

It is convenient to relate the maximum frequency ω_D to a characteristic temperature, the Debye temperature T_D, by the relation

$$\hbar\omega_D = kT_D. \tag{6.201}$$

The thermal energy can now be expressed as

$$E = \frac{3V\hbar}{2\pi^2 c^3}\int_0^{kT_D/\hbar} \frac{\omega^3\,d\omega}{e^{\beta\hbar\omega}-1} \tag{6.202a}$$

$$= 9NkT\Big(\frac{T}{T_D}\Big)^3 \int_0^{T_D/T} \frac{x^3\,dx}{e^x-1}. \tag{6.202b}$$

In the high temperature limit, $T_D/T \to 0$, and the important contribution to the integral in (6.202) comes from small x. Because the integrand is proportional to x^2 for small x, the integral is proportional to $(T/T_D)^{-3}$, and hence the energy is proportional to T. Thus in the high temperature limit, the heat capacity is independent of the temperature, consistent with the law of Dulong and Petit. In the low temperature limit, $T_D/T \to \infty$, and the integral in (6.202) is independent of temperature. Hence in the limit $T \to 0$, the energy is proportional to T^4 and the heat capacity is proportional to T^3, consistent with experimental results at low temperatures.

Problem 6.35. More on the Einstein and Debye theories

(a) Determine the wavelength λ_D corresponding to ω_D and show that this wavelength is approximately equal to a lattice spacing. This equality provides another justification for a high frequency cutoff because the atoms in a crystal cannot oscillate with a wavelength smaller than a lattice spacing.

(b) Show explicitly that the energy in (6.202) is proportional to T for high temperatures and proportional to T^4 for low temperatures.

(c) Plot the temperature dependence of the mean energy as given by the Einstein and Debye theories on the same graph and compare their predictions.

(d) Derive an expression for the mean energy analogous to (6.202) for one- and two-dimensional crystals. Then find explicit expressions for the high and low temperature dependence of the specific heat on the temperature. □

6.10 The Ideal Bose Gas and Bose Condensation

The historical motivation for discussing the ideal Bose gas is that this idealized system exhibits Bose-Einstein condensation. The original prediction of Bose-Einstein condensation by Satyendra Nath Bose and Albert Einstein in 1924 was considered by some to be a mathematical artifact or even a mistake. In the 1930s Fritz London realized that superfluid liquid helium could be understood in terms of Bose-Einstein condensation. However, the analysis of superfluid liquid helium is complicated by the fact that the helium atoms in a liquid strongly interact with one another. For many years scientists tried to create a Bose condensate in a less complicated system. In 1995 several groups used laser and magnetic traps to create a Bose-Einstein condensate of alkali atoms at approximately $10^{-6}\,$K. In these systems the interaction between the atoms is very weak so that the ideal Bose gas is a good approximation and is no longer only a textbook example.[8]

Although the forms of the Landau potential for the ideal Bose gas and for the ideal Fermi gas differ only superficially [see (6.86)], the two systems behave very differently at low temperatures. The main reason is the difference in the ground states; that is, for a Bose system there is no limit to the number of particles in a single particle state.

The ground state of an ideal Bose gas is easy to construct. We can minimize the total energy by putting all the particles into the single particle state of lowest energy:

$$\epsilon_0 = \frac{\pi^2\hbar^2}{2mL^2}(1^2+1^2+1^2) = \frac{3\pi^2\hbar^2}{2mL^2}. \tag{6.203}$$

The energy of the ground state is given by $N\epsilon_0$. For convenience, we choose the energy scale such that the ground state energy is zero. The behavior of the system cannot depend on the choice of the zero of energy.

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[8] The 2001 Nobel Prize for Physics was awarded to Eric Cornell, Wolfgang Ketterle, and Carl Wieman for achieving Bose-Einstein condensation in dilute gases of alkali atoms and for early fundamental studies of the properties of the condensate.

The behavior of an ideal Bose gas can be understood by considering the temperature dependence of $\overline{N}(T, V, \mu)$:

$$\overline{N} = \sum_{\mathbf{k}} \frac{1}{e^{\beta(\epsilon_{\mathbf{k}}-\mu)} - 1} \to \int_0^\infty \overline{n}(\epsilon) g(\epsilon) d\epsilon \tag{6.204}$$

$$= \frac{V}{4\pi^2\hbar^3}(2m)^{3/2} \int_0^\infty \frac{\epsilon^{1/2}\, d\epsilon}{e^{\beta(\epsilon-\mu)} - 1}. \tag{6.205}$$

For simplicity, we assume that the gas of bosons has zero spin, the same value of the spin as the helium isotope ^{4}He.

To understand the nature of an ideal Bose gas at low temperatures, we assume that the mean density of the system is fixed and consider the effect of lowering the temperature. The correct choice of μ gives the desired value of ρ when substituted into (6.206).

$$\rho = \frac{\overline{N}}{V} = \frac{(2m)^{3/2}}{4\pi^2\hbar^3} \int_0^\infty \frac{\epsilon^{1/2}\, d\epsilon}{e^{\beta(\epsilon-\mu)} - 1}. \tag{6.206}$$

We know that the chemical potential μ of an ideal Bose gas must be negative at all temperatures [see (6.80)]. We also know that for high temperatures, μ reduces to the semiclassical limit given by (6.29), which is large in magnitude and negative. To see how μ must change in (6.206) to keep the density ρ constant as we decrease the temperature, we make the change of variables $\beta\epsilon = x$ and let $\mu \to -|\mu|$:

$$\rho = \frac{(2mkT)^{3/2}}{4\pi^2\hbar^3} \int_0^\infty \frac{x^{1/2}\, dx}{e^{(x+\beta|\mu|)} - 1}. \tag{6.207}$$

As we decrease the temperature, the factor in front of the integral in (6.207) decreases and hence the integral must increase to compensate so that the density remains fixed. Hence $\beta|\mu|$ must become smaller, which implies that $|\mu|$ must become smaller. Because μ is negative for Bose-Einstein statistics, μ becomes less negative. The integral is finite for all values of $\beta|\mu|$ and has its maximum value when $|\mu| = 0$. Thus, there is a minimum value of T such that the right-hand side of (6.207) equals the given value of ρ. We denote this temperature by T_c and determine its value by solving (6.207) with $\mu = 0$:

$$\rho = \frac{(2mkT_c)^{3/2}}{4\pi^2\hbar^3} \int_0^\infty \frac{x^{1/2}\, dx}{e^x - 1}. \tag{6.208}$$

The definite integral in (6.208) can be written in terms of known functions (see the Appendix) and has the value

$$\int_0^\infty \frac{x^{1/2}\, dx}{e^x - 1} = 2.612 \frac{\pi^{1/2}}{2}. \tag{6.209}$$

Hence, we obtain

$$kT_c = \frac{1}{2.612^{2/3}} \frac{2\pi\hbar^2}{m} \rho^{2/3}. \tag{6.210}$$

Problem 6.36. Relation of T_c to the zero-point energy

Express (6.210) in terms of the zero-point energy associated with localizing a particle of mass m in a volume a^3, where $a = \rho^{-1/3}$ is the mean interparticle spacing. □

Problem 6.37. Numerical evaluation of μ for an ideal Bose gas

In this problem we study the behavior of μ as a function of the temperature. Program `IdealBoseGasIntegral` numerically evaluates the integral on the right-hand side of (6.206) for particular values of β and μ. The goal is to find the value of μ for a given value of β that yields the desired value of ρ.

To put (6.206) in a convenient form we introduce dimensionless variables and let $\epsilon = kT_c y$, $T = T_c T^*$, and $\mu = kT_c\mu^*$ and rewrite (6.206) as

$$1 = \frac{2}{2.612\sqrt{\pi}} \int_0^\infty \frac{y^{1/2}dy}{e^{(y-\mu^*)/T^*} - 1}, \tag{6.211a}$$

or

$$1 = 0.432 \int_0^\infty \frac{y^{1/2}dy}{e^{(y-\mu^*)/T^*} - 1}, \tag{6.211b}$$

where we have used (6.210).

(a) Fill in the missing steps and derive (6.211).

(b) The program evaluates the left-hand side of (6.211b). The idea is to find μ^* for a given value of T^* such the left-hand side of (6.211b) equals 1. Begin with $T^* = 10$. First choose $\mu^* = -10$ and find the value of the integral. Do you have to increase or decrease the value of μ^* to make the numerical value of the left-hand side of (6.211b) closer to 1? Change μ^* by trial and error until you find the desired result. You should find that $\mu^* \approx -25.2$.

(c) Next choose $T^* = 5$ and find the value of μ^* so that the left-hand side of (6.211b) equals 1. Does μ^* increase or decrease in magnitude? You can generate a plot of μ^* versus T^* by clicking on the `Plot` button each time you find an approximately correct value of μ. ☐

(d) Discuss the qualitative behavior of μ as a function of T for fixed density.

Problem 6.38. Show that the density ρ_c corresponding to $\mu = 0$ for a given temperature is given by

$$\rho_c = \frac{2.612}{\lambda^3}, \tag{6.212}$$

where λ is given by (6.2). Is it possible for the density to exceed ρ_c for a given temperature? ☐

Problem 6.39. Show that the thermal de Broglie wavelength is comparable to the interparticle spacing at $T = T_c$. What is the implication of this result? ☐

There is no physical reason why we cannot continue lowering the temperature at fixed density (or increasing the density at fixed temperature). Before discussing how we can resolve this difficulty, consider a familiar situation in which an analogous phenomenon occurs. Suppose that we put argon atoms into a container of fixed volume at a given temperature. If the temperature is high enough and the density is low enough, the argon atoms will form a gas and obey the ideal gas equation of state, which we write as $P = NkT/V$. If we now add atoms, we expect that the pressure will increase. However at some density, this dependence will abruptly break down, and P will stop

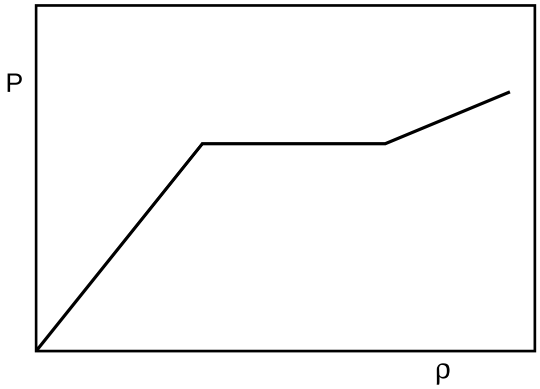

Figure 6.4: Sketch of the dependence of the pressure P on the density N/V at constant temperature for a typical gas and liquid.

changing as indicated in Figure 6.4. We will study this behavior of P in Chapter 7, but you will probably recognize this behavior as a signature of the condensation of the vapor and the existence of a phase transition from gas to liquid. That is, at a certain density for a fixed temperature, droplets of liquid argon will begin to form in the container. As the density is increased further, the liquid droplets will grow, but the pressure will remain constant because most of the extra atoms will go into the denser liquid state.

We can describe the ideal Bose gas in the same terms, that is, in terms of a phase transition. At a special value of T, the chemical potential stops decreasing in magnitude and reaches its limit of $\mu = 0$. Beyond this point, the relation (6.205) is no longer able to keep track of all the particles.

Because the particles cannot appear or disappear when we change the temperature, (6.206) cannot be correct for temperatures $T < T_c$. The origin of the problem lies with the behavior of the three-dimensional density of states $g(\epsilon)$, which is proportional to $\epsilon^{1/2}$ [see (6.104)]. Because of this dependence on ϵ, $g(\epsilon = 0) = 0$, and hence our calculation of $\overline{N}$ has ignored all the particles in the ground state. For the classical and Fermi noninteracting gas, this neglect is of no consequence. In the classical case the mean number of particles in any microstate is much less than one, and in the degenerate Fermi case there are only two electrons in the ground state. However, for the noninteracting Bose gas, the mean number of particles in the ground state is given by

$$\overline{N}_0 = \frac{1}{e^{-\beta\mu} - 1}. \tag{6.213}$$

(Remember that we have set the ground state energy $\epsilon_0 = 0$.) When T is sufficiently small, $\overline{N}_0$ will be very large. Hence, the denominator of (6.213) must be very small, which implies that $e^{-\beta\mu} \approx 1$ and $-\beta\mu$ must be very small. Therefore, we can approximate $e^{-\beta\mu}$ as $1 - \beta\mu$, and $\overline{N}_0$ becomes

$$\overline{N}_0 = -\frac{kT}{\mu} = \frac{kT}{|\mu|} \gg 1. \tag{6.214}$$

The chemical potential must be such that the number of particles in the ground state approaches its maximum value, which is of order N. Hence, if we were to use the integral (6.205) to calculate $\overline{N}$ for $T < T_c$, we would have ignored the particles in the ground state. We have resolved the problem – the missing particles are in the ground state! The phenomenon we have described, *macroscopic occupation of the ground state*, is called *Bose-Einstein condensation*. Macroscopic occupation means that, for $T < T_c$, the ratio $\overline{N}_0/N$ is nonzero in the limit $N \to \infty$.

Now that we know where the missing particles are, we can calculate the thermodynamics of the ideal Bose gas. For $T < T_c$ the chemical potential is zero in the thermodynamic limit, and the mean number of particles *not* in the ground state is given by (6.205):

$$\overline{N}_\epsilon = \frac{V}{4\pi^2\hbar^3}(2m)^{3/2}\int_0^\infty \frac{\epsilon^{1/2}\,d\epsilon}{e^{\beta\epsilon}-1} = N\Big(\frac{T}{T_c}\Big)^{3/2} \qquad (T < T_c), \tag{6.215}$$

where T_c is defined by (6.210). The remaining particles, which we denote as $\overline{N}_0$, are in the ground state. Another way of understanding (6.215) is that, for $T < T_c$, μ must be zero because the number of particles not in the ground state is determined by the temperature. We write $\overline{N} = \overline{N}_0 + \overline{N}_\epsilon$ and

$$\overline{N}_0 = N - \overline{N}_\epsilon = \overline{N}\Big[1 - \Big(\frac{T}{T_c}\Big)^{3/2}\Big] \qquad (T < T_c). \tag{6.216}$$

Because the energy of the gas is determined by the particles with $\epsilon > 0$, we have for $T < T_c$

$$E = \int_0^\infty \frac{\epsilon\, g(\epsilon)\,d\epsilon}{e^{\beta\epsilon}-1} = \frac{V(mkT)^{3/2}\,kT}{2^{1/2}\pi^2\hbar^3}\int_0^\infty \frac{x^{3/2}\,dx}{e^x-1}. \tag{6.217}$$

The definite integral in (6.217) is given in the Appendix:

$$\int_0^\infty \frac{x^{3/2}\,dx}{e^x-1} = 1.341\,\frac{3\pi^{1/2}}{4}. \tag{6.218}$$

If we substitute (6.218) into (6.217), we can write the mean energy as

$$\overline{E} = 3\frac{1.341}{2^{5/2}\pi^{3/2}}\frac{V(mkT)^{3/2}kT}{\hbar^3} = 0.1277\,V\frac{m^{3/2}(kT)^{5/2}}{\hbar^3}. \tag{6.219}$$

Note that $\overline{E} \propto T^{5/2}$ for $T < T_c$. The heat capacity at constant volume is

$$C_V = \frac{\partial\overline{E}}{\partial T} = 3.2V\frac{(mkT)^{3/2}k}{\hbar^3}, \tag{6.220a}$$

or

$$C_V = 1.9\overline{N}_\epsilon k, \tag{6.220b}$$

where we have used (6.215) for $\overline{N}_\epsilon$. Note that the heat capacity has a form similar to an ideal classical gas for which $C_V \propto Nk$.

The pressure of the Bose gas for $T < T_c$ can be obtained from the general relation $PV = 2E/3$ for a nonrelativistic ideal gas. From (6.219) we obtain

$$P = \frac{1.341}{2^{3/2}\pi^{3/2}}\frac{m^{3/2}(kT)^{5/2}}{\hbar^3} = 0.085\frac{m^{3/2}(kT)^{5/2}}{\hbar^3}. \tag{6.221}$$

Note that the pressure is proportional to $T^{5/2}$ and is independent of the density. This independence is a consequence of the fact that the particles in the ground state do not contribute to the pressure.

If additional particles are added to the system at $T < T_c$, the number of particles in the single particle state $\epsilon = 0$ increases, but the pressure does not.

What is remarkable about the phase transition in an ideal Bose gas is that it occurs at all. That is, unlike all other known phase transitions, its occurrence has nothing to do with the interactions between the particles and has everything to do with the nature of the statistics. Depending on which variables are being held constant, the transition in an ideal Bose gas is either first-order or continuous. We postpone a discussion of the nature of first-order and continuous phase transitions until Chapter 9 where we will discuss phase transitions in more detail. It is sufficient to mention here that the order parameter in the ideal Bose gas can be taken to be the fraction of particles in the ground state, and this fraction goes continuously to zero as $T \to T_c$ from below at fixed density.

Another interesting feature of the Bose condensate is that for $T < T_c$, a finite fraction of the atoms are described by the same quantum wavefunction, which gives the condensate many unusual properties. In particular, Bose condensates have been used to produce atomic lasers – laser-like beams in which photons are replaced by atoms – and to study fundamental processes such as superfluidity.

Problem 6.40. Temperature dependence of the pressure

(a) Start from the classical pressure equation of state, $PV = NkT$, replace N by $N_{\rm eff}$ for an ideal Bose gas, and give a qualitative argument why $P \propto T^{5/2}$ at low temperatures.

(b) Show that the ground state contribution to the pressure is given by

$$P_0 = \frac{kT}{V} \ln(\overline{N}_0 + 1). \tag{6.222}$$

Explain why P_0 can be regarded as zero and why the pressure of an Bose gas for $T < T_c$ is independent of the volume. ☐

Problem 6.41. Estimate of the Bose condensation temperature

(a) What is the approximate value of T_c for an ideal Bose gas at a density of $\rho \approx 125\,\text{kg/m}^3$, the density of liquid ^{4}He? Take $m = 6.65 \times 10^{-27}\,\text{kg}$.

(b) The value of T_c for a collection of ^{87}Rb (rubidium) atoms is about 280 nK (2.8×10^{-7} K). What is the mean separation between the atoms? ☐

6.11 Supplementary Notes

6.11.1 Fluctuations in the number of particles

It is convenient to express Z_G in terms of the canonical partition function Z_N for N particles. The sum over all microstates in (6.70) can first be done over all possible microstates s for a fixed number of particles and then over all values of N:

$$Z_G = \sum_{N=1}^{\infty} e^{\beta\mu N} \sum_s e^{-\beta E_s}, \tag{6.223}$$

where E_s is the energy of microstate s with N particles. The latter sum in (6.223) is the canonical partition function for N particles, and we have

$$Z_G = \sum_{N=1}^{\infty} e^{\beta\mu N} Z_N. \tag{6.224}$$

In the following we will derive a relation between the compressibility and the fluctuations of the number of particles. The number of particles fluctuates about the mean number $\overline{N}$, which is given by

$$\overline{N} = kT\frac{\partial \ln Z_G}{\partial \mu} = \frac{1}{Z_G}\sum_N N e^{\beta\mu N} Z_N. \tag{6.225}$$

Because N fluctuates, we need to reinterpret (6.72) as $\overline{N} = -\partial\Omega/\partial\mu$.

Recall from (4.88) that the fluctuations in the energy are related to the heat capacity. In the following we show that the fluctuations in the number of particles are related to the isothermal compressibility κ, which is defined as [see (2.172)]

$$\kappa = -\frac{1}{V}\Big(\frac{\partial V}{\partial P}\Big)_{T,N}. \tag{6.226}$$

The first step in the derivation is given in Problem 6.42.

Problem 6.42. Number fluctuations

Use the Gibbs distribution P_s in (6.73) to show that $\overline{N}$ can be written as

$$\overline{N} = \frac{\sum\limits_s N_s\, e^{-\beta(E_s - \mu N_s)}}{\sum\limits_s e^{-\beta(E_s - \mu N_s)}}. \tag{6.227}$$

Then use (6.227) to show that

$$\Big(\frac{\partial \overline{N}}{\partial \mu}\Big)_{T,V} = \frac{1}{kT}[\overline{N^2} - \overline{N}^2], \tag{6.228}$$

or

$$[\overline{N^2} - \overline{N}^2] = kT\Big(\frac{\partial \overline{N}}{\partial \mu}\Big)_{T,V}, \tag{6.229}$$

where

$$\overline{N^2} = \frac{\sum\limits_s {N_s}^2\, e^{-\beta(E_s - \mu N_s)}}{\sum\limits_s e^{-\beta(E_s - \mu N_s)}}. \tag{6.230}$$

□

In Problem 6.43 we relate the partial derivatives $(\partial\mu/\partial N)_{T,V}$ to $(\partial V/\partial P)_{T,N}$.

Problem 6.43. Another Maxwell relation
Because the Helmholtz free energy $F(T,V,N)$ is extensive, it may be expressed in the form

$$F(T,V,N) = Nf(T,\rho), \tag{6.231}$$

where f is the free energy per particle and is a function of the intensive variables T and ρ.

(a) Show that

$$\mu = f + \rho\Big(\frac{\partial f}{\partial\rho}\Big)_T, \tag{6.232}$$

$$\Big(\frac{\partial\mu}{\partial\rho}\Big)_T = 2\Big(\frac{\partial f}{\partial\rho}\Big)_T + \rho\Big(\frac{\partial^2 f}{\partial\rho^2}\Big)_T, \tag{6.233}$$

and

$$P = \rho^2\Big(\frac{\partial f}{\partial\rho}\Big)_T, \tag{6.234}$$

$$\Big(\frac{\partial P}{\partial\rho}\Big)_T = 2\rho\Big(\frac{\partial f}{\partial\rho}\Big)_T + \rho^2\Big(\frac{\partial^2 f}{\partial\rho^2}\Big)_T = \rho\Big(\frac{\partial\mu}{\partial\rho}\Big)_T. \tag{6.235}$$

Note that (6.235) is an example of a Maxwell relation (see Section 2.22).

(b) Show that

$$\Big(\frac{\partial P}{\partial\rho}\Big)_T = -\frac{V^2}{N}\Big(\frac{\partial P}{\partial V}\Big)_{T,N}, \tag{6.236a}$$

$$\Big(\frac{\partial\mu}{\partial\rho}\Big)_T = V\Big(\frac{\partial\mu}{\partial N}\Big)_{T,V}. \tag{6.236b}$$

(c) Use (6.235) and (6.236) to show that

$$N\Big(\frac{\partial\mu}{\partial N}\Big)_{T,V} = \frac{1}{\rho\kappa}. \tag{6.237}$$

Hence it follows from (6.228) that

$$\kappa = \frac{1}{\rho kT}\frac{(\overline{N^2} - \overline{N}^2)}{\overline{N}}. \tag{6.238}$$

□

Equation (6.238) is another example of the relation of a response function, the compressibility κ, to the mean-square fluctuations of a thermodynamic variable.

From (6.229) we have that

$$\frac{[\overline{N^2} - \overline{N}^2]}{\overline{N}} = \frac{kT}{\overline{N}}\Big(\frac{\partial\overline{N}}{\partial\mu}\Big)_{T,V}. \tag{6.239}$$

Because μ is an intensive quantity, the right-hand side of (6.239) is intensive, that is, independent of $\overline{N}$. Hence the left-hand side of (6.239) must also be independent of $\overline{N}$. This independence implies that the standard deviation is given by $\Delta N = \big[\overline{N^2} - \overline{N}^2\big]^{1/2} \propto \overline{N}^{1/2}$, and therefore the relative fluctuations in the number of particles is

$$\frac{\Delta N}{\overline{N}} \propto \overline{N}^{-1/2} \to 0 \text{ as } \overline{N} \to \infty. \tag{6.240}$$

That is, in the thermodynamic limit, $\overline{N} \to \infty$, $V \to \infty$ with $\rho = \overline{N}/V$ a constant, we can identify the thermodynamic variable N with $\overline{N}$. As in our discussion of the canonical ensemble in Section 4.6, we see that the thermodynamic properties calculated in different ensembles become identical in the thermodynamic limit.

***Problem 6.44.** Number fluctuations in a noninteracting classical gas

(a) Show that the grand partition function of a noninteracting classical gas can be expressed as

$$Z_G = \sum_{N=0}^{\infty} \frac{(zZ_1)^N}{N!} = e^{zZ_1}, \tag{6.241}$$

where the activity $z = e^{\beta\mu}$.

(b) Show that the mean value of N is given by

$$\overline{N} = zZ_1, \tag{6.242}$$

and the probability that there are N particles in the system is given by a Poisson distribution:

$$P_N = \frac{z^N Z_N}{Z_G} = \frac{(zZ_1)^N}{N! Z_G} = \frac{\overline{N}^N}{N!} e^{-\overline{N}}. \tag{6.243}$$

(c) What is the N dependence of the variance, $\overline{(N - \overline{N})^2}$? □

6.11.2 Low temperature expansion of an ideal Fermi gas

We derive the low temperature expansion of the thermodynamic properties of an ideal Fermi gas. For convenience, we first give the formal expressions for the thermodynamic properties of a ideal Fermi gas at temperature T. The mean number of particles is given by

$$\overline{N} = \frac{2^{1/2} V m^{3/2}}{\pi^2 \hbar^3} \int_0^{\infty} \frac{\epsilon^{1/2}\, d\epsilon}{e^{\beta(\epsilon-\mu)} + 1}, \tag{6.244}$$

and the Landau potential Ω is given by [see (6.109)]

$$\Omega = -\frac{2}{3} \frac{2^{1/2} V m^{3/2}}{\pi^2 \hbar^3} \int_0^{\infty} \frac{\epsilon^{3/2}\, d\epsilon}{e^{\beta(\epsilon-\mu)} + 1}. \tag{6.245}$$

The integrals in (6.244) and (6.245) cannot be expressed in terms of familiar functions for all T. However, in the limit $T \ll T_F$ (as is the case for almost all metals), it is sufficient to approximate the integrals. To understand the approximations, we express the integrals (6.244) and (6.245) in the form

$$I = \int_0^\infty \frac{f(\epsilon)\, d\epsilon}{e^{\beta(\epsilon-\mu)}+1}, \tag{6.246}$$

where $f(\epsilon) = \epsilon^{1/2}$ and $e^{3/2}$, respectively.

The expansion procedure is based on the fact that the Fermi-Dirac distribution function $\overline{n}(\epsilon)$ differs from its $T = 0$ form only in a small range of width kT about μ. We let $\epsilon - \mu = kTx$ and write I as

$$\begin{aligned} I &= kT\int_{-\beta\mu}^\infty \frac{f(\mu+kTx)}{e^x+1}\, dx & \text{(6.247a)}\\ &= kT\int_{-\beta\mu}^0 \frac{f(\mu+kTx)}{e^x+1}\, dx + kT\int_0^\infty \frac{f(\mu+kTx)}{e^x+1}\, dx. & \text{(6.247b)}\end{aligned}$$

In the first integrand in (6.247b) we let $x \to -x$ so that

$$I = kT\int_0^{\beta\mu} \frac{f(\mu-kTx)}{e^{-x}+1}\, dx + kT\int_0^\infty \frac{f(\mu+kTx)}{e^x+1}\, dx. \tag{6.247c}$$

We next write $1/(e^{-x}+1) = 1 - 1/(e^x+1)$ in the first integrand in (6.247c) and obtain

$$I = kT\int_0^{\beta\mu} f(\mu-kTx)\, dx - kT\int_0^{\beta\mu} \frac{f(\mu-kTx)}{e^x+1}\, dx + kT\int_0^\infty \frac{f(\mu+kTx)}{e^x+1}\, dx. \tag{6.248}$$

Equation (6.248) is still exact.

Because we are interested in the limit $T \ll T_F$ or $\beta\mu \gg 1$, we can replace the upper limit in the second integral by infinity. Then after making the change of variables, $w = \mu - kTx$, in the first integrand, we find

$$I = \int_0^\mu f(w)\, dw + kT\int_0^\infty \frac{f(\mu+kTx) - f(\mu-kTx)}{e^x+1}\, dx. \tag{6.249}$$

The values of x that contribute to the integrand in the second term in (6.249) are order one, and hence it is reasonable to expand $f(\mu \pm kTx)$ in a power series in kTx and integrate term by term. The result is

$$I = \int_0^\mu f(\epsilon)\, d\epsilon + 2(kT)^2 f'(\mu)\int_0^\infty \frac{xdx}{e^x+1}\, dx + \frac{1}{3}(kT)^4 f'''(\mu)\int_0^\infty \frac{x^3dx}{e^x+1}\, dx + \cdots . \tag{6.250}$$

The definite integrals in (6.250) can be evaluated using analytical methods (see the Appendix). The results are

$$\int_0^\infty \frac{x\, dx}{e^x+1} = \frac{\pi^2}{12}, \tag{6.251}$$

$$\int_0^\infty \frac{x^3\, dx}{e^x+1} = \frac{7\pi^4}{120}. \tag{6.252}$$

If we substitute (6.251) and (6.252) into (6.250), we obtain the desired result

$$I = \int_0^\mu f(\epsilon)\, d\epsilon + \frac{\pi^2}{6}(kT)^2 f'(\mu) + \frac{7\pi^4}{360}(kT)^4 f''' + \cdots . \tag{6.253}$$

Note that although we expanded $f(\mu - kTx)$ in a power series in kTx, the expansion of I in (6.253) is not a power series expansion in $(kT)^2$. Instead (6.253) represents an asymptotic series that is a good approximation to I if only the first several terms are retained.

To find Ω in the limit of low temperatures, we let $f(\epsilon) = \epsilon^{3/2}$ in (6.253). From (6.245) and (6.253) we find that in the limit of low temperatures

$$\Omega = -\frac{2}{3}\frac{2^{1/2}Vm^{3/2}}{\pi^2\hbar^3}\Big[\frac{2}{5}\mu^{5/2} + \frac{\pi^2}{4}(kT)^2\mu^{1/2}\Big], \tag{6.254}$$

$$\overline{N} = -\frac{\partial\Omega}{\partial\mu} = \frac{V(2m)^{3/2}}{3\pi^2\hbar^3}\Big[\mu^{3/2} + \frac{\pi^2}{8}(kT)^2\mu^{-1/2}\Big]. \tag{6.255}$$

A more careful derivation of the low temperature behavior of an ideal Fermi gas has been given by Weinstock (1969).

Vocabulary

thermal de Broglie wavelength, λ

semiclassical limit

equipartition theorem

Maxwell velocity and speed distributions

occupation numbers, spin and statistics, bosons and fermions

Bose-Einstein distribution, Fermi-Dirac distribution, Maxwell-Boltzmann distribution

single particle density of states, $g(\epsilon)$

Fermi energy ϵ_F, Fermi temperature T_F, and Fermi momentum p_F

macroscopic occupation, Bose-Einstein condensation

law of Dulong and Petit, Einstein and Debye theories of a crystalline solid

Additional Problems

Problem 6.45. Explain in simple terms why the mean kinetic energy of a classical particle in equilibrium with a heat bath at temperature T is $\frac{1}{2}kT$ per quadratic contribution to the kinetic energy, independent of the mass of the particle. ☐

Problem 6.46. Heat capacity of a linear rigid rotator

So far we have considered the thermal properties of an ideal monatomic gas consisting of spherically symmetrical, rigid molecules undergoing translational motion, that is, their internal motion was

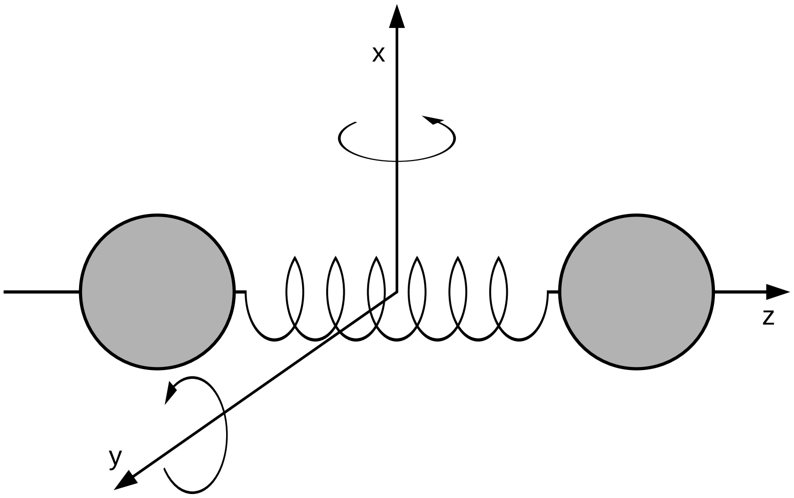

Figure 6.5: A schematic representation of a diatomic molecule.

ignored. Real molecules are neither spherical nor rigid, and rotate about two or three axes and vibrate with many different frequencies. For simplicity, consider a linear rigid rotator consisting of two point masses m_1 and m_2 located a fixed distance r from each other. We first assume that r is fixed and ignore vibrational motion, which is discussed in Problem 6.47. The rotational energy levels are given by

$$\epsilon(j) = j(j+1)\frac{\hbar^2}{2I}, \tag{6.256}$$

where I is the moment of inertia and $j = 0, 1, 2, \ldots$ is the angular momentum quantum number. The degeneracy of each rotational energy level is $(2j + 1)$.

(a) Express the partition function $Z_{\rm rot}$ for one molecule as a sum over energy levels.

(b) The sum that you found in part (a) cannot be evaluated exactly in terms of well-known functions. However, for $T \gg T_{\rm rot} = \hbar^2/(2kI)$, the energy spectrum of the rotational states may be approximated by a continuum and the sum over j can be replaced by an integral. Show that the rotational heat capacity (at constant volume) of an ideal gas of linear rigid rotators is given by $C_{\rm rot} = Nk$ in the high temperature limit $T \gg T_{\rm rot}$. Compare this limiting behavior with the prediction of the equipartition theorem. In this case we say that the linear rigid rotator has two quadratic contributions to the energy. Explain.

(c) The magnitude of $T_{\rm rot}$ for a typical diatomic molecule such as HCl is $T_{\rm rot} \approx 15\,{\rm K}$. Sketch the temperature dependence of $C_{\rm rot}$, including its behavior for $T \ll T_{\rm rot}$ and $T \gg T_{\rm rot}$. ☐

Problem 6.47. Heat capacity of an ideal diatomic gas

In addition to translational and rotational motion, a diatomic molecule can exhibit vibrational motion (see Figure 6.5). It is a good approximation to take the rotational and vibrational motion to be independent and to express the total energy of an ideal diatomic gas as a sum of the translational, rotational, and vibrational contributions. Hence the total heat capacity (at constant volume) of the gas can be written as

$$C = C_{\text{tran}} + C_{\text{rot}} + C_{\text{vib}}. \tag{6.257}$$

The last two terms in (6.257) arise from the internal motion of the molecule. The rotational contribution C_{rot} was discussed in Problem 6.46.

(a) The vibrational motion of a diatomic molecule can be modeled by harmonic oscillations about the minimum of the potential energy of interaction between the two molecules. What is the high temperature limit of C_{vib}?

(b) Let us define a temperature $T_{\text{vib}} = \hbar\omega/k$. The magnitude of T_{vib} for HCl is $T_{\text{vib}} \approx 4227\,\text{K}$, where ω is the vibrational frequency and $\hbar\omega$ is the energy difference between neighboring vibrational energy levels. What do you expect the value of C_{vib} to be at room temperature?

(c) Use the value of T_{rot} given in Problem 6.46 and the value of T_{vib} given in part (b) for HCl to sketch the T dependence of the total heat capacity C in the range $10\,\text{K} \leq T \leq 10,000\,\text{K}$. □

Problem 6.48. Law of atmospheres

Consider an ideal classical gas in equilibrium at temperature T in the presence of an uniform gravitational field. Find the probability $P(z)dz$ that an atom is at a height between z and $z + dz$ above the Earth's surface. How do the density and the pressure depend on z? □

Problem 6.49. Alternative derivation of the Maxwell velocity distribution

The Maxwell velocity distribution can also be derived by making some plausible assumptions. We first assume that the probability density $f(\mathbf{v})$ for one particle is a function only of its speed $|\mathbf{v}|$ or equivalently v^2. We also assume that the velocity distributions of the components v_x, v_y, v_z are independent of each other.

(a) Given these assumptions, explain why we can write

$$f(v_x^2 + v_y^2 + v_z^2) = C f(v_x^2) f(v_y^2) f(v_z^2), \tag{6.258}$$

where C is a constant independent of v_x, v_y, and v_z.

(b) Show that a function that satisfies the condition (6.258) is the exponential function

$$f(v^2) = c\, e^{-\alpha v^2}, \tag{6.259}$$

where c and α are independent of $\mathbf{v}$.

(c) Determine c in terms of α using the normalization condition $1 = \int_{-\infty}^{\infty} f(u)du$ for each component. Why must α be positive?

(d) Use the fact that $\frac{1}{2}kT = \frac{1}{2}m\overline{v_x^2}$ to find the Maxwell velocity distribution in (6.59).

(e) *Show that $f(v^2)$ in part (b) is the only function that satisfies the condition (6.258). □

Problem 6.50. Consequences of the Maxwell velocity distribution

(a) What is the probability that the kinetic energy of a classical nonrelativistic particle is in the range ϵ to $\epsilon + d\epsilon$? What is the most probable kinetic energy? Is it equal to $\frac{1}{2}m\tilde{v}^2$, where $\tilde{v}$ is the most probable speed?

(b) Find the values of $\overline{v}_x, \overline{v_x^2}, \overline{v_x^2 v_y^2}$, and $\overline{v_x v_y^2}$ for a classical system of particles at temperature T. No calculations are necessary. ☐

Problem 6.51. Mean energy of a nonlinear oscillator

Consider a classical one-dimensional nonlinear oscillator whose energy is given by

$$\epsilon = \frac{p^2}{2m} + ax^4, \tag{6.260}$$

where x, p, and m have their usual meanings; the parameter a is a constant.

(a) If the oscillator is in equilibrium with a heat bath at temperature T, calculate its mean kinetic energy, mean potential energy, and mean total energy. (It is not necessary to evaluate any integrals explicitly.)

(b) Consider a classical one-dimensional oscillator whose energy is given by

$$\epsilon = \frac{p^2}{2m} + \frac{1}{2}kx^2 + ax^4. \tag{6.261}$$

In this case the anharmonic contribution ax^4 is very small. What is the leading contribution of this term to the mean potential energy? (Recall that for small u, $e^u \approx 1 + u$.) ☐

Problem 6.52. Granular systems

A system of glass beads or steel balls is an example of a *granular* system. In such a system the beads are macroscopic objects and the collisions between the beads are inelastic. Because the collisions in such a system are inelastic, a gas-like steady state is achieved only by inputting energy, usually by shaking or vibrating the walls of the container. Suppose that the velocities of the particles are measured in a direction perpendicular to the direction of shaking. Do the assumptions we used to derive the Maxwell-Boltzmann velocity distribution apply here?[9] ☐

Problem 6.53. A toy system of two particles

Consider a system consisting of two noninteracting particles in equilibrium with a heat bath at temperature T. Each particle can be in one of three states with energies 0, ϵ_1, and ϵ_2. Find the partition function for the cases described in parts (a)–(c) and then answer parts (d)–(f):

(a) The particles obey Maxwell-Boltzmann statistics and can be considered distinguishable.

(b) The particles obey Fermi-Dirac statistics.

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[9] See for example, the experiments by Daniel L. Blair and Arshad Kudrolli, "Velocity correlations in dense granular gases," Phys. Rev. E **64**, 050301(R) (2001), and the theoretical arguments by J. S. van Zon and F. C. MacKintosh, "Velocity distributions in dissipative granular gases," Phys. Rev. Lett. **93**, 038001 (2004).

(c) The particles obey Bose-Einstein statistics.

(d) Find the probability in each case that the ground state is occupied by one particle.

(e) What is the probability that the ground state is occupied by two particles?

(f) Estimate the probabilities in (d) and (e) for $kT = \epsilon_2 = 2\epsilon_1$. ☐

***Problem 6.54.** Consider a single particle of mass m in a one-dimensional harmonic oscillator potential given by $V(u) = \frac{1}{2}ku^2$. As we found in Example 4.3, the partition function is given by $Z_1 = e^{-x/2}/(1 - e^{-x})$, where $x = \beta\hbar\omega$.

(a) What is the partition function for two noninteracting distinguishable particles in the same potential?

(b) What is the partition function for two noninteracting fermions in the same potential assuming the fermions have no spin?

(c) What is the partition function for two noninteracting bosons in the same potential? Assume the bosons have spin zero.

(d) Calculate the mean energy and entropy in the three cases considered in parts (a)–(c). Plot E and S as a function of T and compare the behavior of E and S in the limiting cases of $T \to 0$ and $T \to \infty$. ☐

Problem 6.55. Neutron stars

A neutron star can be considered to be a collection of noninteracting neutrons, which are spin-1/2 fermions. A typical neutron star has a mass M close to one solar mass, $M_\odot \approx 2 \times 10^{30}$ kg. The mass of a neutron is about $m = 1.67 \times 10^{-27}$ kg. In the following we will estimate the radius R of the neutron star.

(a) Find the energy of a neutron star at $T = 0$ as a function of R, M, and m assuming that the star can be treated as an ideal nonrelativistic Fermi gas.

(b) Assume that the density of the star is uniform and show that its gravitational energy is given by $E_G = -3GM^2/5R$, where the gravitational constant $G = 6.67 \times 10^{-11}\,\mathrm{N\,m^2/kg^2}$. (Hint: from classical mechanics find the gravitational potential energy between an existing sphere of radius r and a shell of volume $4\pi r^2 dr$ coming from infinity to radius r. Then integrate from $r = 0$ to R.)

(c) Assume that gravitational equilibrium occurs when the total energy is minimized and find an expression for the radius R.

(d) Estimate the actual value of R in kilometers. Estimate the mass density and compare it with the density of material on the surface of the Earth such as water.

(e) Determine the Fermi energy and Fermi temperature. A typical internal temperature for a neutron star is $T = 10^8\,\mathrm{K}$. Compare this value with the Fermi temperature and determine if the zero temperature approximation that we have used is applicable.

(f) Compare the rest energy mc^2 of a neutron with the Fermi energy of a neutron star. Is the nonrelativistic approximation valid? □

Problem 6.56. White dwarfs

A white dwarf is a very dense star and can be considered to be a degenerate gas of electrons and an equal number of protons to make it charge neutral. We will also assume that there is one neutron per electron and that the mass of the star is about the same as our Sun. Many of the results of Problem 6.55 can be used here with slight modifications.

(a) Find the mean energy at $T = 0$ as a function of R, M, and m_e, where M is the total mass of the star and m_e is the electron mass.

(b) Assume that the star has a uniform density and show that the gravitational energy of the star is given by $E_G = -3GM^2/5R$.

(c) Assume that gravitational equilibrium occurs when the total energy is minimized and find an expression for the radius R.

(d) Estimate the actual value of R in kilometers. Estimate the mass density and compare it with the density of water on the surface of Earth.

(e) For extremely relativistic electrons the relation between the energy ϵ and momentum p of an electron is given by $\epsilon = cp$, where c is the speed of light. Find the Fermi energy and temperature.

(f) Find the mean energy at $T = 0$ for relativistic electrons in a white dwarf. Add this energy to the gravitational energy. Is there a minimum at a finite value of R? If not, what does this result mean about stability?

(g) Compare the rest energy $m_e c^2$ with the nonrelativistic Fermi energy. Is the nonrelativistic approximation valid? When the rest energy equals the nonrelativistic Fermi energy, we know that the nonrelativistic approximation is not valid. At what value of the total mass does this equality occur? Chandrasekhar obtained a limiting mass of $1.4M_\odot$ by taking into account the more accurate relation $\epsilon = (m_e^2c^4 + c^2p^2)^{1/2}$ and the variation of density within the star. How does your crude estimate compare? □

***Problem 6.57.** Toy systems of fermions

(a) Consider a system of noninteracting (spinless) fermions such that each particle can be a single particle state with energy 0, Δ, and 2Δ. Find an expression for Z_G using (6.224). Determine how the mean number of particles depends on μ for $T = 0$, $kT = \Delta/2$, and $kT = \Delta$.

(b) A system contains N identical noninteracting fermions with $2N$ distinct single particle states. Suppose that $2N/3$ of these states have energy zero, $2N/3$ have energy Δ, and $2N/3$ have energy 2Δ. Show that μ is independent of T. Calculate and sketch the T dependence of the energy and heat capacity. ☐

***Problem 6.58.** Periodic boundary conditions

Assume periodic boundary conditions so that the wavefunction ψ satisfies the condition (in one dimension)

$$\psi(x) = \psi(x + L). \tag{6.262}$$

The form of the one-particle eigenfunction consistent with (6.262) is given by

$$\psi(x) \propto e^{ik_x x}. \tag{6.263}$$

What are the allowed values of k_x? How do they compare with the allowed values of k_x for a particle in a one-dimensional box? Generalize the form (6.263) to a cube and determine the allowed values of $\mathbf{k}$. Find the form of the density of states and show that the same result (6.96) is obtained. ☐

Problem 6.59. Chemical potential of a one-dimensional ideal Fermi gas

Calculate the chemical potential $\mu(T)$ of a one-dimensional ideal Fermi gas at low temperatures $T \ll T_F$. Use the result for $\mu(T)$ found for the two-dimensional case in Problem 6.33 and compare the qualitative behavior of $\mu(T)$ in one, two, and three dimensions. ☐

Problem 6.60. High temperature limit of the ideal Fermi gas

If $T \gg T_F$ at fixed density, quantum effects can be neglected and the thermal properties of an ideal Fermi gas reduce to the ideal classical gas. In the following we will find the first correction to the classical pressure equation of state.

(a) Does the pressure increase or decrease when the temperature is lowered (at constant density)? That is, what is the sign of the first quantum correction to the classical pressure equation of state? The pressure is given by [see (6.109)]

$$P = \frac{(2m)^{3/2}}{3\pi^2\hbar^3} \int_0^\infty \frac{\epsilon^{3/2}\, d\epsilon}{e^{\beta(x-\mu)} + 1}. \tag{6.264}$$

In the high temperature limit, $e^{\beta\mu} \ll 1$, we can make the expansion

$$\frac{1}{e^{\beta(\epsilon-\mu)} + 1} = e^{\beta(\mu-\epsilon)} \frac{1}{1 + e^{-\beta(\epsilon-\mu)}} \tag{6.265a}$$

$$\approx e^{\beta(\mu-\epsilon)} [1 - e^{-\beta(\epsilon-\mu)}]. \tag{6.265b}$$

If we use (6.265b), we obtain

$$e^{\beta\mu} \int_0^\infty x^{3/2} e^{-x} (1 - e^{\beta\mu} e^{-x})\, dx = \frac{3}{4}\pi^{1/2} e^{\beta\mu} \Big[1 - \frac{1}{2^{5/2}} e^{\beta\mu}\Big]. \tag{6.266}$$

Use (6.266) to show that P is given by

$$P = \frac{m^{3/2}(kT)^{5/2}}{2^{1/2}\,\pi^{3/2}\hbar^3}\, e^{\beta\mu} \Big[1 - \frac{1}{2^{5/2}} e^{\beta\mu}\Big]. \tag{6.267}$$

(b) Derive an expression for N similar to (6.267). Eliminate μ and show that the leading order correction to the equation of state is given by

$$PV = NkT\Big[1 + \frac{\pi^{3/2}}{4}\frac{\rho\hbar^3}{(mkT)^{3/2}}\Big] \tag{6.268a}$$

$$= NkT\Big[1 + \frac{1}{2^{7/2}}\rho\lambda^3\Big]. \tag{6.268b}$$

(c) What is the condition for the correction term in (6.268b) to be small? Note that as the temperature is lowered at constant density, the pressure increases. What do you think would be the effect of Bose statistics in this context (see Problem 6.61)? Mullin and Blaylock (2003) have emphasized that it is misleading to interpret the sign of the correction term in (6.268b) in terms of an effective repulsive exchange "force," and stress that the positive sign is a consequence of the symmetrization requirement for same spin fermions. □

Problem 6.61. High temperature limit of ideal Bose gas

If $T \gg T_c$ at fixed density, quantum effects can be neglected and the thermal properties of an ideal Bose gas reduce to those of the ideal classical gas. Does the pressure increase or decrease when the temperature is lowered (at constant density)? That is, what is the first quantum correction to the classical equation of state? The pressure is given by [see (6.109)]

$$P = \frac{2^{1/2}m^{3/2}(kT)^{5/2}}{3\pi^2\hbar^3}\int_0^\infty \frac{x^{3/2}\,dx}{e^{x-\beta\mu}-1}. \tag{6.269}$$

Follow the same procedure as in Problem 6.60 and show that

$$PV = NkT\Big[1 - \frac{\pi^{3/2}}{2}\frac{\rho\hbar^3}{(mkT)^{3/2}}\Big]. \tag{6.270}$$

We see that as the temperature is lowered at constant density, the pressure becomes less than its classical value. □

Problem 6.62. Bose condensation in one and two dimensions?

Does Bose condensation occur for a one and two-dimensional ideal Bose gas? If so, find the transition temperature. If not, explain. □

***Problem 6.63.** Graphene

Graphene is a two-dimensional sheet of carbon, which was first made in the laboratory in 2004 with the help of clear adhesive (Scotch) tape. Graphite, the material used in pencils, consists of many layers of graphene. The gentle stickiness of the tape was used to break apart the many layers of graphite. Among graphene's many interesting properties is that its low temperature behavior can be understood by treating it as a collection of noninteracting excitations which behave as relativistic Dirac fermions and obey the dispersion relation

$$\epsilon_\pm(k) = \pm hvk. \tag{6.271}$$

The spin degeneracy is $g = 2$ and $v \approx 10^6$ m/s.

(a) What is the chemical potential at $T = 0$, assuming that all negative-energy states are occupied and all positive-energy states are empty?

(b) Show that for a system of fermions the probability of finding an occupied state of energy $\mu + \delta$ equals the probability of finding an unoccupied state of energy $\mu - \delta$.

(c) Use the results of parts (a) and (b) to argue that $\mu = 0$ for all T.

(d) Show that the mean energy is given by

$$E(T) - E(0) = 4A \int \frac{\epsilon_+(k)}{e^{\beta\epsilon_+(k)} + 1} d^2k, \tag{6.272}$$

where A is the area of the system.

(e) Calculate the temperature dependence of the heat capacity at low temperatures due to these massless Dirac particles. This problem is adapted from Kardar (2007). ☐

Problem 6.64. Discuss why Bose condensation does not occur in a system of photons corresponding to blackbody radiation. ☐

Problem 6.65. More on the Debye model

(a) Show that if the volume of the crystal is Na^3, where a is the equilibrium distance between atoms, then the Debye wave number, $k_D = \omega_D/\overline{c}$, is about π/a.

(b) Evaluate the integral in (6.202) numerically and plot the heat capacity versus T/T_D over the entire temperature range. ☐

***Problem 6.66.** Bose-Einstein condensation in low-dimensional traps

As you found in Problem 6.62, Bose-Einstein condensation does not occur in ideal one- and two-dimensional systems. However, this result holds only if the system is confined by rigid walls. In the following, we will show that Bose-Einstein condensation can occur if a system is confined by a spatially varying potential. For simplicity, we will treat the system semiclassically.

Let us assume that the confining potential has the form

$$V(r) \sim r^n. \tag{6.273}$$

In this case the region accessible to a particle with energy ϵ has a radius $\ell \sim \epsilon^{1/n}$. Show that the corresponding density of states behaves as

$$g(\epsilon) \sim \ell^d \epsilon^{(1/2)d-1} \sim \epsilon^{d/n} \epsilon^{(1/2)d-1} \sim \epsilon^\alpha, \tag{6.274}$$

where

$$\alpha = \frac{d}{n} + \frac{d}{2} - 1. \tag{6.275}$$

What is the range of values of n for which $T_c > 0$ for $d = 1$ and 2? More information about experiments on Bose-Einstein condensation can be found in the references. ☐

***Problem 6.67.** Number fluctuations in a degenerate ideal Fermi gas

Use the relation (6.228)

$$\overline{(N-\overline{N})^2} = kT\frac{\partial \overline{N}}{\partial \mu} \tag{6.276}$$

to find the number fluctuations in the ideal Fermi gas for fixed T, V, and μ. Show that

$$\overline{(N-\overline{N})^2} = \frac{kT}{2}\frac{V(2m)^{3/2}}{2\pi^2\hbar^3}\int_0^\infty \frac{\epsilon^{-1/2}\,d\epsilon}{e^{\beta(\epsilon-\mu)}+1} \tag{6.277a}$$

$$\to \frac{3\overline{N}T}{2T_F} \qquad (T \ll T_F). \tag{6.277b}$$

Explain why the fluctuations in a degenerate Fermi system are much smaller than in the corresponding classical system. □

Suggestions for further reading

More information about Bose-Einstein condensation can be found at `<jilawww.colorado.edu/bec/>`, `<bec.nist.gov/>`, and `<www.rle.mit.edu/cua_pub/ketterle_group/>`.

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Robert Weinstock, "Heat capacity of an ideal free electron gas: A rigorous derivation," Am. J. Phys. **37**, 1273–1279 (1969).

Chapter 7

The Chemical Potential and Phase Equilibria

7 December 2010

We discuss the nature of the chemical potential by considering some simple models and simulations. We then discuss the role of the chemical potential in understanding phase transitions with a focus on the van der Waals equation of state. We also discuss chemical reactions and the law of mass action.

7.1 Meaning of the chemical potential

Although the chemical potential plays a role analogous to that of temperature and pressure, understanding the nature of the chemical potential is more difficult. We know that, if two systems are at different temperatures and are then placed in thermal contact, there will be a net transfer of energy from one system to the other until the temperatures of the two systems become equal. If there is a movable wall between two systems at different pressures, then the wall will move so as to change the volume of each system to make the pressures equal. Similarly, if two systems are initially at different chemical potentials and are then allowed to exchange particles, there will be a net transfer of particles from the system at the higher chemical potential to the one at the lower chemical potential until the chemical potentials become equal. You are asked to derive this result in Problem 7.1.

Problem 7.1. Chemical equilibrium

Assume that two systems A and B are initially in thermal and mechanical equilibrium, but not in chemical equilibrium, that is, $T_A = T_B$, $P_A = P_B$, but $\mu_A \neq \mu_B$. Use reasoning similar to that used in Section 2.13 to show that particles will be transferred from the system at the higher chemical potential to the system at the lower chemical potential. An easy way to remember the

N_A	$\Omega_A(N_A)$	$\ln\Omega_A(N_A)$	μ_A/kT	N_B	$\Omega_B(N_B)$	$\ln\Omega_B(N_B)$	μ_B/kT	$\Omega_A\Omega_B$
1	1	0	–	9	1287	7.16	–	1287
2	9	2.20	-1.90	8	792	6.68	-0.51	7128
3	45	3.81	-1.45	7	462	6.14	-0.57	20790
4	165	5.11	-1.20	6	252	5.53	-0.65	41580
5	495	6.21	-1.03	5	126	4.84	-0.75	62370
6	1287	7.16	$\mathbf{-0.90}$	4	56	4.03	$\mathbf{-0.90}$	72072
7	3003	8.01	-0.81	3	21	3.05	-1.12	63063
8	6435	8.77	-0.73	2	6	1.79	-1.52	38610
9	12870	9.46	–	1	1	0	–	12870

Table 7.1: The number of states of subsystems A and B such that the composite Einstein solid has a total number of particles $N = N_A + N_B = 10$ with $E_A = 8$ and $E_B = 5$. The number of microstates of each macrostate is determined using (4.3). Neither N_A nor N_B can equal zero, because each subsystem has a nonzero energy and thus each subsystem must have at least one particle. The quantity μ/kT in columns 4 and 8 is determined by computing the ratio $-\Delta \ln \Omega/\Delta N$, with $\Delta N = 1$. The most probable macrostate corresponds to $\tilde{N}_A \approx 6$. The ratio μ/kT is the same (to two decimal places) for both subsystems for this macrostate. The fraction of microstates associated with the most probable macrostate is $72072/319770 \approx 0.23$, where 319770 is the total number of microstates. This fraction will approach 1 as the number of particles and the total energy in the two subsystems become very large.

various thermodynamic relations for μ is to start from the fundamental thermodynamic relation in the form $dE = TdS - PdV + \mu dN$. □

To gain more insight into the nature of the chemical potential we discuss two models for which we can calculate the chemical potential explicitly, the Einstein solid and an ideal gas. In Chapter 4 we considered an Einstein solid consisting of two subsystems each with a fixed number of particles, but with different energies such that the total energy was fixed. We found that the temperatures of the two subsystems are equal for the energy distribution that has the largest number of microstates, and thus is most probable.

We now consider a similar composite Einstein solid consisting of two subsystems each with a variable number of particles such that the total number of particles is fixed, $N = N_A + N_B$. The energies E_A and E_B are fixed in each subsystem. In our example we take $N = N_A + N_B = 10$, $E_A = 8$, and $E_B = 5$. Table 7.1 displays the number of microstates in each subsystem and the total number of microstates in the composite system for the possible values of N_A and N_B. We see that the derivative of $\ln\Omega$ with respect to the number of particles in each subsystem, which equals $-\mu/kT$ [see (2.120), page 72], is almost equal (in our example the derivatives are equal to two decimal places) when the total number of microstates in the composite system is a maximum. We conclude that the quantity that becomes equal in equilibrium for this example is the ratio μ/T. In a more realistic example it would be impossible for particles to move from one system to another without transferring energy as well. In these systems both the temperature and chemical potential would individually become equal at equilibrium.

For the various composite Einstein solids that we considered in Chapter 4 we found that thermal equilibrium is achieved by energy being transferred from the hotter to the cooler subsystem.

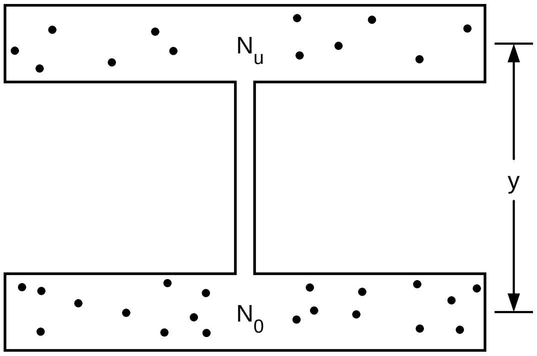

Figure 7.1: A container at height y connected by a tube of negligible volume to a container at height zero.

In the present example chemical equilibrium is reached by a transfer of particles. From Table 7.1 we see that if the two subsystems are initially not in equilibrium, for example, $N_A = 3$, then μ_A/T_A is less (more negative) than μ_B/T_B. Because the system will change to maximize the total entropy, we see that subsystem A will gain particles from subsystem B. Thus, particles will be transfered from a subsystem with the larger (less negative) ratio μ/T to the subsystem with the smaller value of μ/T.

Problem 7.2. Numerical calculation of the chemical potential of the Einstein solid

(a) Use Program `EinsteinSolidChemicalPotential` to consider an isolated Einstein solid consisting of two subsystems. The program counts the number of states using the relation (4.3). The inputs to the program are E_A, E_B, and $N = N_A + N_B$. Imagine that the two subsystems are initially separated by an insulating and impermeable partition, with $N_A = 8$, $N_B = 4$, $E_A = 15$, and $E_B = 30$. What is the initial entropy of the system? The partition is then replaced by one that allows particles but not energy to be transferred between the two subsystems. Construct a table similar to Table 7.1 and show that the ratio μ/T is approximately equal for the most probable macrostate (defined by specific values of N_A and N_B). Is the entropy of this macrostate higher than the initial entropy? Then try other combinations of N, E_A, and E_B. In a more realistic problem particles could not move from one system to another without transferring energy as well.

(b) Why is μ expected to be negative for the Einstein solid?

(c) If the amount of energy is the same in each subsystem of a composite Einstein solid, what would be the equilibrium number of particles in each subsystem? □

We next consider a model consisting of two ideal gases that are in containers at different heights (see Figure 7.1).[1] Because we wish to characterize the containers only by their height, we assume that each container has a very large cross-sectional area and a very small thickness such that the volume of each container is finite. For simplicity, we also assume that both gases are at

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[1] This model is discussed in Baierlein [2001].

the same temperature T and volume V. The energy ϵ_i of the ith particle in either container is given by $\epsilon_i = mv_i^2/2 + mgy_i$, where m is its mass, v_i its speed, and y_i its height, which is either 0 or y. The acceleration due to the gravitational field is denoted by the constant g. We use the subscripts 0 and u to denote the lower and upper container, respectively.

The partition function for each container is a function of its volume, temperature, number of particles, and height. From (6.25) $Z_0(T, V, N_0)$ is given by [see (6.25), page 297]

$$Z_0(T, V, N_0) = \frac{V^{N_0}}{N_0!}\Big(\frac{2\pi mkT}{h^2}\Big)^{3N_0/2}, \tag{7.1}$$

where N_0 is the number of particles in the lower container. Similarly, the partition function Z_u for the upper container can be written as

$$Z_u(T, V, N_u) = \frac{V^{N_u}}{N_u!}\Big(\frac{2\pi mkT}{h^2}\Big)^{3N_u/2} e^{-mgyN_u/kT}, \tag{7.2}$$

where N_u is the number of particles in the upper container. Note the factor of $e^{-mgyN_u/kT}$ in (7.2).

Problem 7.3. Derive the relation (7.2). □

To find the corresponding chemical potentials we use the relations $F = -kT \ln Z$ and $\mu = (\partial F/\partial N)_{T,V}$. Hence the chemical potential μ_0 for the lower container is [see (6.29)]

$$\mu_0 = -kT \ln \Big[\frac{V}{N_0}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big], \tag{7.3}$$

and the chemical potential for the upper container is given by

$$\mu_u = mgy - kT \ln \Big[\frac{V}{N_u}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big]. \tag{7.4}$$

If the two containers have the same number of particles, then the top container has the higher chemical potential as can be seen by comparing (7.3) and (7.4). What will happen if the two containers are connected by a tube of negligible volume so that particles may move from one system to the other? In this case the only quantities that may vary are the number of particles in each container. (We have assumed that they have the same temperature and volume.) Because the number of particles of the composite system $N = N_0 + N_u$ is fixed, there is only one independent variable, which we take to be N_0. This number will change to make the free energy of the composite system a minimum.

To find the total free energy we note that the partition function of the composite system is the product of the partition function for each container because there is no interaction between the particles in the two containers. Hence, we have

$$Z(T, V, N_0) = Z_0(T, V, N_0) Z_u(T, V, N_u). \tag{7.5}$$

We first calculate the total free energy $F = -kT \ln Z$, take the derivative of F with respect to N_0, and set the derivative equal to zero to find the condition for the minimum free energy. The total free energy is [see (6.26), page 297]

$$F = -kTN_0\Big[\ln\frac{V}{N_0} + \frac{3}{2}\ln\Big(\frac{2\pi mkT}{h^2}\Big) + 1\Big] - kTN_u\Big[\ln\frac{V}{N_u} + \frac{3}{2}\ln\Big(\frac{2\pi mkT}{h^2}\Big) + 1 - \frac{mgy}{kT}\Big]. \tag{7.6}$$

We substitute $N_u = N - N_0$, take the derivative of F with respect to N_0, and set the result equal to zero. The result is

$$N_u = N_0 e^{-mgy/kT}. \tag{7.7}$$

The same result would be obtained if we had expressed F in terms of N_u and found $\partial F/\partial N_u$.

Equation (7.7) relates the number of particles in each container at equilibrium and implies that $N_u < N_0$. Thus, if there is initially the same number of particles in each container, particles will be transferred from the higher container to the lower one, that is, from the container at the higher chemical potential to the one at the lower chemical potential.

Problem 7.4. The chemical potential of a simple composite system

(a) Fill in the missing steps and derive (7.7).

(b) Show that $\mu_0 = \mu_u$ when the condition (7.7) is satisfied. Thus the chemical potentials of each part of the composite system are equal at equilibrium. ☐

Equation (7.7) tells us how the number density varies with height assuming that the temperature is independent of height, which is only approximately valid in our atmosphere. (This result was first obtained in Problem 6.48.) We can use similar considerations to show that, if two fluids are separated by a membrane with an electrical potential energy difference $q\Delta V$ between them, then the chemical potential difference between the two fluids will contain a term equal to $q\Delta V$. Here q is the magnitude of the charge of an ion in the fluid and ΔV is the potential difference. The transfer of ions across a cell membrane is due to the creation of a potential difference that produces a difference in the chemical potentials and causes ions to be transferred from a region of higher chemical potential to a region of lower chemical potential.

7.2 Measuring the chemical potential in simulations

7.2.1 The Widom insertion method

Another way of gaining more insight into the meaning of the chemical potential is to think about how we would measure it on a computer. From (2.151) and (4.102) we can write the chemical potential as

$$\mu = \Big(\frac{\partial F}{\partial N}\Big)_{T,V} \approx F_{N+1} - F_N = -kT \ln \frac{Z_{N+1}}{Z_N} \qquad (N \gg 1). \tag{7.8}$$

That is, the chemical potential is the change in the free energy of a system due to the addition of a particle (in the thermodynamic limit). To understand how we can estimate the chemical potential by a Monte Carlo simulation in the canonical ensemble we need to write μ in terms of the appropriate average. The partition function of a N particle system is $Z_N = \sum_s e^{-\beta E_s}$, where E_s is the energy of microstate s with N particles. Similarly, $Z_{N+1} = \sum_{s,r} e^{-\beta E_{s,r}}$, where the sum over r is over all possible coordinates and momenta of the additional particle, and $E_{s,r}$ is the energy when N particles are in the state s, and the additional particle is in state r. We define the quantity $\Delta E_{s,r} \equiv E_{s,r} - E_s$, and rewrite (7.8) as

$$\frac{Z_{N+1}}{Z_N} = \frac{\sum_{s,r} e^{-\beta \Delta E_{s,r}} e^{-\beta E_s}}{\sum_s e^{-\beta E_s}}. \tag{7.9}$$

If we combine (7.8) and (7.9), we find

$$\mu = -kT \ln \Big\langle \sum_r e^{-\beta \Delta E_{s,r}} \Big\rangle, \tag{7.10}$$

where the average is over all N-particle states weighted by the N-particle Boltzmann factor $e^{-\beta E_s} / \sum_s e^{-\beta E_s}$.

For an ideal classical gas there is no interaction between the particles and thus $\Delta E_{s,r}$ does not depend on microstate s. Therefore the sum over s in the numerator of (7.9) cancels the sum over s in the denominator. The sum over r becomes an integral over the position and momentum of the added particle. The integral over the position equals the volume, and hence (7.10) reduces to

$$\mu_{\rm ideal} = -kT \ln \Big[\frac{V}{N} \int e^{-\beta p^2/2m} \, \frac{d^3p}{h^3} \Big]. \tag{7.11}$$

The factor of $1/N$ accounts for the indistinguishability of the particles. Recall that $Z_N \propto 1/N!$ and thus $Z_{N+1}/Z_N \propto N!/(N+1)! = 1/(N+1) \approx 1/N$.

Problem 7.5. Chemical potential of an ideal classical gas

Show that (7.11) leads to the usual ideal classical gas expression for μ given in (6.29). ☐

The energy of the added particle consists of a kinetic energy term and a potential energy term. Because the integral over the momentum degrees of freedom is independent of the interparticle potential for a classical system of particles, a Monte Carlo simulation of a system need consider only the position coordinates. Hence, we need to determine only the change in the potential energy due to an added particle. It is common to write the chemical potential as $\mu = \mu_{\rm ideal} + \mu_{\rm excess}$, where $\mu_{\rm ideal}$ is given in (7.11). From (7.10) we see that the "excess" contribution to the chemical potential can be expressed as

$$\mu_{\rm excess} = -kT \ln \langle e^{-\beta \Delta U} \rangle, \tag{7.12}$$

where ΔU is the change in the potential energy when an imaginary test particle (of the same type) is added at random to a N-particle system.

Equation (7.12) can be used to estimate the chemical potential of gases and liquids. In a standard (Metropolis) Monte Carlo simulation of a system at a given temperature, the microstates of an N particle system are sampled in the usual way with the desired Boltzmann probability. Then a test particle is added periodically at a random position, the quantity $e^{-\beta \Delta U}$ is accumulated, and the particle is removed. The average in (7.12) is the accumulated sum of $e^{-\beta \Delta U}$ divided by the number of times a test particle was added. The addition of the test particle is virtual and it is not actually added.[2] This way of estimating μ is called the *Widom insertion method*.

We can use (7.12) to understand the density dependence of the chemical potential of a fluid. Consider a fluid for which the interaction between particles consists of a strongly repulsive potential at small particle separations and a weakly attractive potential that vanishes at large particle separations. At low densities the test particle will likely land in a region where the interparticle potential is small and negative, and thus the potential energy change due to the added particle

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[2] In principle, the sum over r in (7.10) should be done by adding many test particles in succession at random positions for a given microstate s. Because we sample such a small fraction of all the N-particle microstates, it is sufficient to periodically add only one particle to any particular N-particle microstate generated in the simulation.

will be small and negative ($\Delta U < 0$). In this case the exponential in (7.12) will be greater than 1, and thus the excess chemical potential will be negative. For higher densities an added particle is more likely to land near the potential minimum, and thus ΔU is likely to be more negative. Thus the excess chemical potential will initially decrease as the density is increased. For still higher densities the test particle will likely land on the steeply rising positive part of the potential, and thus ΔU will be large and positive, leading to $-\beta\Delta U < 0$, an exponential less than 1, and thus a positive excess chemical potential. We conclude that there is a minimum in the excess chemical potential as a function of density.

Problem 7.6. The excess chemical potential of a Lennard-Jones fluid

Program `WidomInsertionMethod` implements the Widom insertion method to estimate the chemical potential for a system of particles interacting with the Lennard-Jones potential. Determine the density dependence of the excess chemical potential of a Lennard-Jones fluid. Are your results for $\mu_{\rm excess}$ consistent with our qualitative arguments? □

7.2.2 The chemical demon algorithm

In Sections 1.5 and 4.9 we discussed the demon algorithm and learned that the demon yields a measure of the temperature and that the temperature controls the transfer of energy between two systems. We now generalize the demon algorithm so that the demon carries two sacks, one for energy and one for particles. We will find that the generalized or chemical demon algorithm gives a measure of the chemical potential as well as the temperature, and that the chemical potential controls the transfer of particles between two systems.

We learned in Chapter 4 that, if the demon only exchanges energy with a system, then the probability that the demon has energy E_d is given by the Boltzmann distribution. If the demon can exchange both energy and particles with the system, then the probability $P(E_d, N_d)$ that the demon has energy E_d and N_d particles is given by the Gibbs distribution [see (4.142), page 217]:

$$P(E_d, N_d) = \frac{1}{Z_G} e^{-\beta(E_d - \mu N_d)}, \tag{7.13}$$

where Z_G is the grand canonical partition function. We can think of the demon as a system that exchanges energy and particles with a reservoir at constant T and μ.

To illustrate the nature of the chemical demon, we consider a one-dimensional system of particles. The position and momentum variables of the system are placed in bins of widths Δx and Δp, respectively, so that the phase space of the system is a two-dimensional lattice, with position in one direction and momentum in the other. The chemical demon algorithm can be summarized as follows:

1. Begin with an arbitrary initial configuration of the system with the desired total energy and total number of particles. The N particles of the system are randomly placed on the phase space lattice with no more than one particle on a lattice site. We set $E_d = 0$ and $N_d = 0$ for convenience, where E_d is the energy of the demon and N_d is the number of particles held by the demon.

2. Choose a lattice site (in phase space) at random. If there is a particle there, compute the trial change in energy ΔE that would result if the particle were removed.

3. If $\Delta E < E_d$, accept the move and subtract ΔE from E_d and let $N_d \to N_d + 1$. Otherwise reject the move, but include the unchanged configuration as the new configuration. Go to step 5.
4. If there is no particle at the lattice site and the demon has at least one particle, compute the trial change in energy ΔE needed to add a particle. If $\Delta E < E_d$, accept the addition and subtract ΔE from E_d and let $N_d \to N_d - 1$. Otherwise, retain the unchanged configuration.
5. Repeat steps 2–4 and allow the system to equilibrate before computing averages. Accumulate data for $P(E_d, N_d)$ after each MC step per lattice site.

Note that in this algorithm there is at most one particle at a given lattice site in phase space.

Program `ChemicalDemon` implements this algorithm and computes $P(E_d, N_d)$, the probability that the demon has energy E_d and N_d particles. From (7.13) we see that the slope of $P(E_d, N_d)$ versus E_d for fixed N_d is $-\beta$ and the slope of $P(E_d, N_d)$ versus N_d for fixed E_d is $\beta\mu$.

To see how the chemical demon algorithm can help us to understand the chemical potential, we first consider how the usual demon algorithm with only energy exchanges helps us understand the role of the temperature. Suppose that the demon is able to transfer energy into and out of the system very easily; that is, most of its trial changes are accepted. Under what conditions would the acceptance probability be close to 1? What can we say about the slope of $\ln P(E_d)$ versus E_d? The answer is that the slope would be shallow (and negative) because many demon energies would have nearly the same probability. We can also say that the temperature is high because the demon almost always has sufficient energy to give to the system when necessary. If instead the temperature is low, then a similar argument leads us to expect a steep negative slope for $\ln P(E_d)$ versus E_d. This behavior is independent of the size of the system because the exchange of energy affects only a small part of the system. This independence on the size of system explains why temperature is an intensive quantity.

Now consider the chemical demon and assume that it transfers particles only. From (7.13) we see that the ratio $-\mu/kT$ plays the analogous role for particle transfers as $1/kT$ does for energy. Because $-\mu/kT$ depends on both μ and T, it is more subtle to understand how the chemical potential behaves independently of the temperature. For this reason we assume in the following that the demon has already made a sufficient number of energy transfers so that the demon and the system are in thermal equilibrium.

For simplicity, consider a one-dimensional ideal gas, and let's see what we can infer by thinking about the demon's particle exchanges with the system. We know that the chemical potential is negative, which means that the slope of $\ln P(N_d)$ versus N_d is negative, and the probability of the demon having N_d particles decreases as N_d increases (for a given value of E_d). To understand this behavior consider the occupancy of the sites in two-dimensional phase space. Because the total energy E is fixed, particles will occupy sites with momentum in the range $\pm\sqrt{2mE}$. If the system is dilute, then there will be many empty cells in phase space with near zero momentum. If a particle from one of the higher momentum states is removed by the demon, it will give the demon lots of energy which can be used to return particles to the system at lower momentum sites. It will then be very difficult for the demon to add a particle to a high momentum state. Thus, the probability of the demon having N_d particles will decrease with N_d and the chemical potential must be negative. This argument illustrates how entropy arguments (which depend on the vast number of cells or sites in phase space) are essential for understanding the demon probabilities.

Problem 7.7. The chemical potential of a one-dimensional ideal gas

Program `ChemicalDemon` implements the chemical demon algorithm in which a demon exchanges particles (and energy) with a system of interest.

(a) Assume that the chemical demon exchanges energy and particles with a one-dimensional ideal classical gas. Choose the default parameters $N = 100$, $E = 200$, and $L = 100$, where N is the number of particles, E is the total energy of the system, and L is the length of the box. We use units such that the area of a cell in phase space is $\Delta x \Delta p = 1$. We also choose units such that $m = 1/2$ so that the energy of a particle is given by $\epsilon = p^2$. These choices imply that the momentum and energy are integers. The maximum momentum of a particle is $p_{\max} = \sqrt{E}$. The N particles are initially randomly placed in the cells of the phase space lattice with no more than one particle in a cell such that the desired total energy is obtained. For convenience we set the initial demon energy $E_d = 0$ and particle number $N_d = 0$. Run the simulation and discuss the qualitative features of the positions of the particles in phase space. Where are most of the particles located? Are there particles that have the same position? Run the simulation for different values of E, but the same values for the other parameters. Describe what you see in the phase space plots. Where in phase space are most of the particles located?

(b) Explain why the simulation in part (a) is identical to a simulation of an ideal gas in the semiclassical limit. Show that the chemical potential is given by

$$\mu = -T \ln[(L/N)(\pi T)^{1/2}]. \tag{7.14}$$

(Remember that our choice of units is equivalent to $\Delta x \Delta p = 1$.)

(c) Use the same parameters as in part (a) and run for about 200 Monte Carlo steps per particle (mcs) for equilibration. Then click `Zero Averages` and average over at least 1000 mcs. (You can speed up the simulation by increasing the steps per display to 10 or 100.) After the simulation is stopped, click the `Calculate` button to compute the demon energy and particle number distributions. The plot of $\ln P(E_d, N_d = 1)$ versus E_d should be approximately linear for small E_d. The inverse slope is related to the temperature. The plot of $\ln P(E_d = 1, N_d)$ versus N_d should give a slope equal to μ/T. Compare your Monte Carlo results with the exact result that you found in part (b). ☐

***Problem 7.8.** The effects of interparticle interactions

Consider the effects of including interactions between the particles in a dilute classical gas. If the interaction has a hard core, no two particles can have the same position. This interaction makes it more difficult for the demon to return particles to the system, and we expect the chemical potential to be greater (less negative) than the noninteracting system at the same density.

(a) Use Program `ChemicalDemon` and confirm the effect of including a hard core on the chemical potential of the system.

(b) If we include an attractive interaction between particles that are nearest neighbors in position, the energy of the system will be lowered for some particle additions, thus giving the demon more energy and making it easier for the demon to find places in phase space to add particles. The result is a lowering of the chemical potential compared to the hard core system. Show that this trend is observed in your simulations. ☐

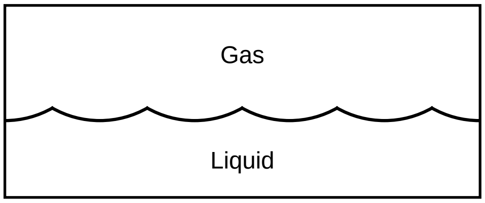

Figure 7.2: Gas-liquid phase separation in the presence of gravity. What would you observe in the absence of gravity? The two phases are in a closed container.

Our discussion suggests that the relative ease of the demon to exchange particles with a system is a measure of the system's chemical potential. We have previously concluded that the temperature is a measure of a system's ability to transfer energy. The chemical potential has an analogous role for the transfer of particles.

7.3 Phase Equilibria

Our considerations so far have been for homogeneous systems consisting of a single species. There are many circumstances for which a system separates into two homogeneous parts. The simplest example is of a closed container filled with the gas and liquid *phases* of the same substance (see Figure 7.2).

The particular phase chosen by a system depends on the pressure and temperature. For example, water is a liquid at room temperature and atmospheric pressure, but if it is cooled below 273.15 K at atmospheric pressure, it will eventually solidify and become ice. And if water is heated above 373.15 K it will vaporize.[3] At each of these temperatures, water undergoes dramatic changes in its properties, and we say that a *phase transition* occurs.

The existence of distinct phases is the result of intermolecular interactions, which are the same in all phases. The interaction of a water molecule, H_2O, with another water molecule is the same whether the molecule is in ice or in vapor. Why is the effect of the interactions so different macroscopically? The answer is the existence of *cooperative effects*, which we discussed briefly in Section 5.6.1 and will discuss in more detail in Chapters 8 and 9.

7.3.1 Equilibrium conditions

In some cases a system exists in only one phase, and in others two phases can coexist. For example, liquid water in equilibrium with its vapor inside a closed container is an example of two-phase coexistence. For simplicity, we will consider the conditions for equilibrium between two phases of a substance consisting of a single type of molecule.

We can understand the coexistence of phases by treating each phase as a subsystem. We know

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[3] If you were to place a thermometer in perfectly pure boiling water, the thermometer would very likely not read 100°C. Superheating is almost inevitable. See Bohren and Albrecht [1998].

that for two systems A and B in thermal equilibrium, their temperatures must be equal:

$$T_A = T_B. \tag{7.15}$$

We also have shown that the pressure of the two phases must be equal in mechanical equilibrium,

$$P_A = P_B, \tag{7.16}$$

because the forces exerted by the two phases on each other at their surface of contact must be equal and opposite.

We will show in the following that, because the number of particles N_A and N_B in each phase can vary, the chemical potentials of the two phases must be equal:

$$\mu_A(T, P) = \mu_B(T, P). \tag{7.17}$$

We have written $\mu(T, P)$ because the temperature and pressure of the two phases are the same.

Because $\mu(T, P) = g(T, P)$ [see (2.156), page 78], where g is the Gibbs free energy per particle, we can also write the equilibrium condition (7.17) as

$$g_A(T, P) = g_B(T, P). \tag{7.18}$$

We now derive the equilibrium condition (7.17) or (7.18). Because T and P are well-defined quantities for a system of two phases, the natural thermodynamic potential is the Gibbs free energy G. Let N_i be the number of particles in phase i and $g_i(T, P)$ be the Gibbs free energy per particle in phase i. Then G can be written as

$$G = N_A g_A + N_B g_B. \tag{7.19}$$

The total number of particles is constant:

$$N = N_A + N_B = \text{constant}. \tag{7.20}$$

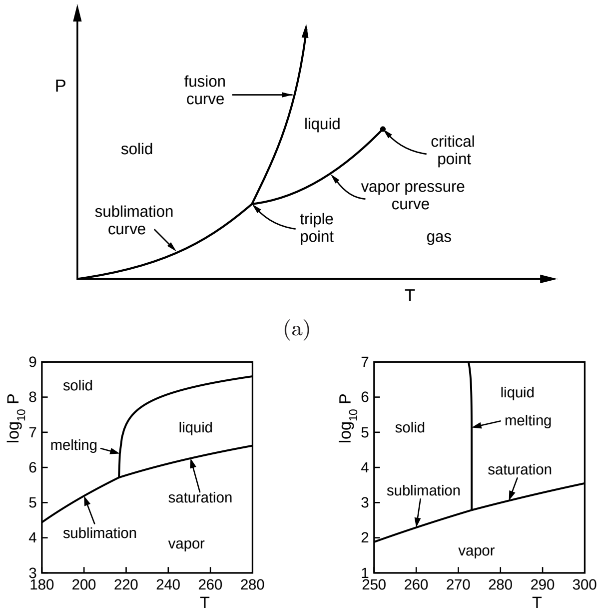
Suppose we let N_A vary. Because G is a minimum in equilibrium (for a given value of T and P), we have

$$dG = 0 = g_A dN_A + g_B dN_B = (g_A - g_B) dN_A, \tag{7.21}$$

where $dN_B = -dN_A$. Hence, we find that a necessary condition for equilibrium is $g_A(T, P) = g_B(T, P)$.

7.3.2 Simple phase diagrams

A typical phase diagram for a simple substance is shown in Figure 7.3(a). The lines represent the phase coexistence curves between the solid and liquid phases, the solid and vapor phases, and the liquid and vapor phases. The condition $g_A = g_B = g_C$ for the coexistence of all three phases leads to a unique temperature and pressure that defines the *triple point*. This unique property of the triple point makes the triple point of water a good choice for a readily reproducible temperature reference point. If we move along the liquid-gas coexistence curve toward higher temperatures, the two phases become more and more alike. At the *critical point*, the liquid-gas coexistence curve



(a)

(b) (c)

Figure 7.3: (a) Sketch of a typical phase diagram of a simple substance. The phase diagram shows the coexistence curves between the solid, liquid, and gas phases. All three phases coexist at the triple point. For temperatures and pressures above the critical point it is not possible to distinguish between a gas and a liquid, and the substance is known as a supercritical fluid. (b) Phase diagram of carbon dioxide with the pressure in pascals and the temperature in kelvin. The logarithm of the pressure is plotted so that the wide range of pressures can be shown. Note the positive slope of the melting curve with pressure. The triple point is at $T_{\rm tp} = 216.6\,{\rm K}$ and $P_{\rm tp} = 5.2 \times 10^5\,{\rm Pa}$. Not shown is the critical point at $T_c = 304.1\,{\rm K}$ and $P_c = 7.38 \times 10^6\,{\rm Pa}$. At atmospheric pressure and room temperature the solid and liquid phases are not stable, and dry ice (solid CO_2) will evaporate directly into a gas. (c) The phase diagram of water. Note the negative slope of the melting curve with pressure. For water $T_{\rm tp} = 273.16\,{\rm K}$, $P_{\rm tp} = 611.66\,{\rm Pa}$, $T_c = 647.31\,{\rm K}$, and $P_c = 22.106 \times 10^6\,{\rm Pa}$. The information for CO_2 and H_2O is from Glasser (2002, 2004).

ends, and there is no longer a distinction between a gas and a liquid. Note that a system can cross the phase boundary from its solid phase directly to its vapor without passing through the liquid phase, a transformation known as *sublimation*. An important commercial process that exploits this transformation is freeze drying.

The condition (7.17) [or (7.18)] for the coexistence of two phases implies that two phases cannot be in equilibrium with each other at all temperatures and pressures. If two phases of a substance coexist, only T or P can be chosen freely, but not both. For example, if liquid water is in equilibrium with its vapor, then the pressure of the water equals the vapor pressure, which is a unique function of the temperature. If the pressure is increased above the vapor pressure, the vapor will condense. If the pressure is decreased below the vapor pressure, the liquid will evaporate.

Suppose that a fraction x of the particles is in phase A and a fraction $1 - x$ of the particles is

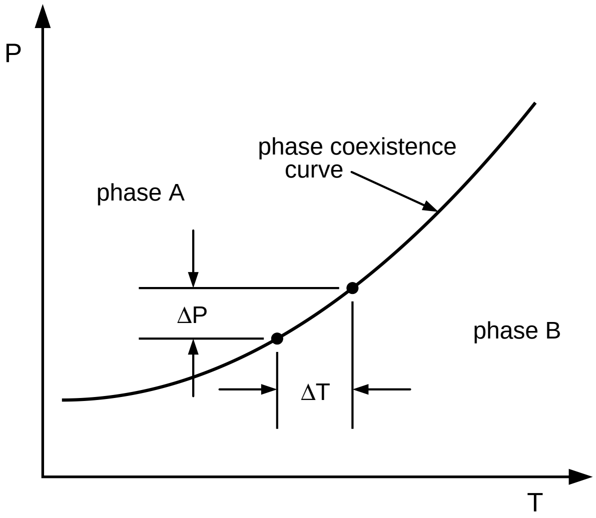


Figure 7.4: Derivation of the Clausius-Clapeyron equation.

in phase B. For values of T and P on the phase boundary where $g_A = g_B$, the Gibbs free energy is equal to $G = xNg_A + (1-x)Ng_B = Ng_A = Ng_B$, which is independent of x. Hence for values of P and V on the phase boundary, the two phases can coexist in equilibrium in any proportion. The locus of points (T, P) such that $g_A = g_B$ is called the *phase coexistence curve*.

The quantity g_i is a well-defined function that is characteristic of the particular phase i. If T and P are such that $g_A < g_B$, then the minimum value of G corresponds to all N particles in phase A, $G = Ng_A$, and this phase is said to be *stable*. If T and P are such that $g_A > g_B$, then the minimum value of G corresponds to all N particles in phase B so that $G = Ng_B$. If, for example, the values of T and P correspond to the stable phase being a gas, then a rapid quench of the temperature to a value such that the liquid phase becomes stable, might lead to the gas phase becoming *metastable*. In this case we say that the gas is *supercooled*. The system will remain in the gas phase for some time until spontaneous density fluctuations drive the system to the stable liquid phase.

7.3.3 Clausius-Clapeyron equation

We now show that the equilibrium condition (7.18) leads to an equation for the slope of the phase coexistence curve. Consider two points on the phase coexistence curve, for example, one point at T, P and a nearby point at $T + \Delta T$ and $P + \Delta P$ (see Figure 7.4). The equilibrium condition (7.18) implies that $g_A(T, P) = g_B(T, P)$ and $g_A(T + \Delta T, P + \Delta P) = g_B(T + \Delta T, P + \Delta P)$. If we write $g_i(T + \Delta T, P + \Delta P) = g_i(T, P) + \Delta g_i$, we have

$$\Delta g_A = \Delta g_B, \tag{7.22}$$

or using (2.154)

$$-s_A \Delta T + v_A \Delta P = -s_B \Delta T + v_B \Delta P, \tag{7.23}$$

where s_i is the entropy per particle and v_i is the volume per particle in phase i. From (7.23) we have

$$\frac{dP}{dT} = \frac{s_B - s_A}{v_B - v_A} = \frac{\Delta s}{\Delta v}. \tag{7.24}$$

Thus, the slope of the coexistence curve at any point on the curve is equal to the ratio of entropy difference to the volume difference as the curve is crossed at that point. For N particles we have $\Delta S = N\Delta s$ and $\Delta V = N\Delta v$, and hence we can express (7.24) as

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}. \tag{7.25}$$

From the relation $(\partial E/\partial V)_T = T(\partial S/\partial V)_T - P$ in (2.196) we can write

$$T\frac{\partial S}{\partial V} = \frac{\partial E}{\partial V} + P. \tag{7.26}$$

At the phase coexistence curve for a given T and P we have

$$T\frac{S_B - S_A}{V_B - V_A} = \frac{E_B - E_A}{V_B - V_A} + P, \tag{7.27}$$

or

$$T(S_B - S_A) = (E_B - E_A) + P(V_B - V_A). \tag{7.28}$$

Because the enthalpy $H = E + PV$, it follows that

$$L \equiv T(S_B - S_A) = H_B - H_A. \tag{7.29}$$

Thus we can write (7.25) as

$$\boxed{\frac{dP}{dT} = \frac{L}{T(V_B - V_A)}} \quad \text{(Clausius-Clapeyron equation).} \tag{7.30}$$

The relation (7.30) is called the *Clausius-Clapeyron equation*. It relates the slope of the phase coexistence curve at the point T, P to the enthalpy change or *latent heat* L,[4] the temperature at the phase boundary, and difference in the volumes of the two phases.

It usually is convenient to work with specific values of L and V, which we denote as ℓ and v, and to write (7.30) as

$$\frac{dP}{dT} = \frac{\ell}{T(v_B - v_A)}. \tag{7.31}$$

The energy ℓ required to melt a given amount of a solid is the *enthalpy of fusion*.[5] The enthalpy of fusion is related to the difference in the enthapies of the liquid and the solid phase and is given by

$$\ell_{\text{fusion}} = h_{\text{liquid}} - h_{\text{solid}} = T(s_{\text{liquid}} - s_{\text{solid}}), \tag{7.32}$$

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[4] The term latent heat is a relic from the time when it was thought that there were two kinds of heat: sensible heat, the kind you can feel, and latent heat, the kind you cannot.

[5] The more common name is *latent heat of fusion*.

where T is the melting temperature at the given pressure. Similarly, the equilibrium of a gas and liquid leads to the enthalpy of vaporization

$$\ell_{\text{vaporization}} = h_{\text{gas}} - h_{\text{liquid}}. \tag{7.33}$$

The enthalpy of sublimation associated with the equilibrium of gas and solid is given by

$$\ell_{\text{sublimation}} = h_{\text{gas}} - h_{\text{solid}}. \tag{7.34}$$

For most substances the slope of the solid-liquid coexistence curve is positive. The Clausius-Clapeyron equation shows that this positive slope is due to the fact that most substances expand on melting and therefore have $\Delta V > 0$. Water is an important exception and contracts when it melts. Hence, for water the slope of the melting curve is negative [see Figure 7.3(c)].

Example 7.1. Pressure dependence of the melting temperature of ice

Solution. Consider the equilibrium between ice and water as an example of the pressure dependence of the melting temperature of ice. The enthalpy of fusion of water at 0°C is

$$\ell_{\text{fusion}} = 3.35 \times 10^5\,\text{J/kg}. \tag{7.35}$$

The specific volumes in the solid and liquid phase are

$$v_{\text{solid}} = 1.09070 \times 10^{-3}\,\text{m}^3/\text{kg}, \tag{7.36a}$$

$$v_{\text{liquid}} = 1.00013 \times 10^{-3}\,\text{m}^3/\text{kg}, \tag{7.36b}$$

so $\Delta v = v_{\text{liquid}} - v_{\text{solid}} = -0.0906 \times 10^{-3}\,\text{m}^3/\text{kg}$. If we substitute these values of ℓ and Δv in (7.31), we find

$$\frac{dP}{dT} = -\frac{3.35 \times 10^5}{273.2 \times (9.06 \times 10^{-5})} = -1.35 \times 10^7\,\text{Pa/K}. \tag{7.37}$$

From (7.37) we see that an increase in pressure of 1.35×10^7 Pa (133 atm) lowers the melting temperature of ice by 1°C. ◊

The lowering of the melting point of ice under pressure is responsible for the motion of glaciers. The deeper parts of a glacier melt under the weight of ice on top allowing the bottom of a glacier to flow. The bottom freezes again when the pressure decreases.

It is sometimes said that ice skaters are able to skate freely because the pressure of the ice skates lowers the melting point of the ice and allows ice skaters to skate on a thin film of water between the blade and the ice. As soon as the pressure is released, the water refreezes. From Example 7.1 we see that if the ice is at −1°C, then the pressure due to the skates must be 135 atm for bulk melting to occur. However, even for extremely narrow skates and a large person, the skates do not exert enough pressure to lead to the melting of ice. For example, assume that the contact area of the blades to be $10^{-4}\,\text{m}^2$ and the mass of the skater to be 100 kg. Then the pressure is given by $P = F/A = mg/A \approx 10^7\,\text{Pa} \approx 100\,\text{atm}$. Because the temperature is frequently less than 0°C during the winter, there must be a mechanism other than pressure-induced melting which is responsible for ice skating. And how do we explain the slide of a hockey puck, which has a large surface area and a small weight? The answer is the existence of surface melting; that is, there is a layer of liquid water on the surface of ice which exists independently of the pressure of an ice skate (see the references).

Example 7.2. Pressure dependence of the boiling point

Because the change in the volume Δv is always positive for the transformation of a liquid to a gas, an increase in the pressure on a liquid always increases the boiling temperature. For water the enthalpy of vaporization is

$$\ell_{\rm vaporization} = 2.257 \times 10^6\,{\rm J/kg}. \tag{7.38}$$

The specific volumes in the liquid and gas phase at $T = 373.15\,{\rm K}$ and $P = 1\,{\rm atm}$ are

$$v_{\rm liquid} = 1.043 \times 10^{-3}\,{\rm m}^3/{\rm kg}, \tag{7.39a}$$

$$v_{\rm gas} = 1.673\,{\rm m}^3/{\rm kg}. \tag{7.39b}$$

Hence from (7.31) we have

$$\frac{dP}{dT} = \frac{2.257 \times 10^6}{373.15 \times 1.672} = 3.62 \times 10^3\,{\rm Pa/K}. \tag{7.40}$$

♢

Example 7.3. Liquid-gas coexistence curve

The Clausius-Clapeyron equation for the vapor pressure curve can be approximated by neglecting the specific volume of the liquid in comparison to the gas, $\Delta v = v_{\rm gas} - v_{\rm liquid} \approx v_{\rm gas}$. From (7.39) we see that for water at its normal boiling point, this approximation introduces an error of less than 0.1%. If we assume that the vapor behaves like an ideal gas, then $v_{\rm gas} = RT/P$ for one mole of the gas. (The gas constant $R = kN_A$, where N_A is Avogadro's number.) With these approximations, (7.31) can be written as

$$\frac{dP}{P} = \ell \frac{dT}{RT^2}, \tag{7.41}$$

where ℓ is the enthalpy of vaporization of one mole. If we also assume that ℓ is approximately temperature independent, we can integrate (7.41) to find

$$\ln P(T) = -\frac{\ell}{RT} + {\rm constant}, \tag{7.42}$$

or

$$P(T) \approx P_0\, e^{-\ell/RT}, \tag{7.43}$$

where P_0 is a constant. ♢

Example 7.4. Liquid-solid coexistence curve

To find an equation for the phase coexistence curve between the liquid and solid phases it is reasonable to assume that the temperature dependence of ℓ and Δv can be neglected. In this approximation we can write (7.31) as

$$dP = \frac{\ell}{\Delta v}\frac{dT}{T}, \tag{7.44}$$

which can be integrated to give

$$P = P_0 + \frac{\ell}{\Delta v} \ln \frac{T}{T_0}, \tag{7.45}$$

where T_0, P_0 is a point on the phase coexistence curve. Because the volume change Δv between the liquid and the solid is small and the entropy change is large, the slope of the coexistence curve in the P-T plane is very steep (see Figure 7.3). ♢

Example 7.5. The triple point of ammonia

In the vicinity of the triple point the liquid-vapor coexistence curve of liquid ammonia is given by $\ln P = 24.38 - 3063/T$, where the pressure is given in pascals and the temperature is in kelvins. The vapor pressure of solid ammonia is $\ln P = 27.92 - 3754/T$. What are the temperature and pressure at the triple point? What are the enthalpies of sublimation and vaporization? What is the enthalpy of fusion at the triple point?

Solution. At the triple point, $P_{\rm solid} = P_{\rm liquid}$ or $24.38 - 3063/T = 27.92 - 3754/T$. The solution is $T = 691/3.54 = 195.2\,$K. The corresponding pressure is $8.7\,$Pa. The relation (7.42), $\ln P = -\ell/RT +$ constant, can be used to find the enthalpy of sublimation and vaporization of ammonia at the triple point. We have $\ell_{\rm sublimation} = 3754R = 3.12 \times 10^4\,$J/mol and $\ell_{\rm vaporization} = 3063R = 2.55 \times 10^4\,$J/mol. The enthalpy of melting satisfies the relation $\ell_{\rm sublimation} = \ell_{\rm vaporization} + \ell_{\rm fusion}$. Hence, $\ell_{\rm fusion} = (3.12 - 2.55) \times 10^4 = 5.74 \times 10^3\,$J/mol. ♢

7.4 The van der Waals Equation of State

7.4.1 Maxwell construction

To gain more insight into the liquid-gas coexistence curve, we explore some of the properties of the van der Waals equation of state, which we repeat here for convenience:

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2} \tag{7.46}$$

$$= \frac{\rho kT}{1 - \rho b} - a\rho^2, \tag{7.47}$$

where the density $\rho = N/V$. It is convenient to rewrite (7.47) in terms of the dimensionless variables

$$\tilde{P} = 27\Big(\frac{b^2}{a}\Big)P, \tag{7.48}$$

$$\tilde{T} = \frac{27}{8}\Big(\frac{b}{a}\Big)kT, \tag{7.49}$$

$$\tilde{\rho} = 3b\rho. \tag{7.50}$$

The reason for the numerical factors will become clear in the following (see Problem 7.10). The van der Waals pressure equation of state (7.47) in terms of these dimensionless variables becomes

$$\tilde{P} = \frac{8\tilde{\rho}\tilde{T}}{3 - \tilde{\rho}} - 3\tilde{\rho}^2, \tag{7.51}$$

Note that the equation of state in terms of the dimensionless variables $\tilde{P}$, $\tilde{T}$, and $\tilde{\rho}$ does not depend explicitly on the material dependent parameters a and b.

Problem 7.9. Dimensionless form of the van der Waals equation of state

Use the definitions (7.48)–(7.50) of $\tilde{P}$, $\tilde{T}$, and $\tilde{\rho}$ to derive (7.51). □

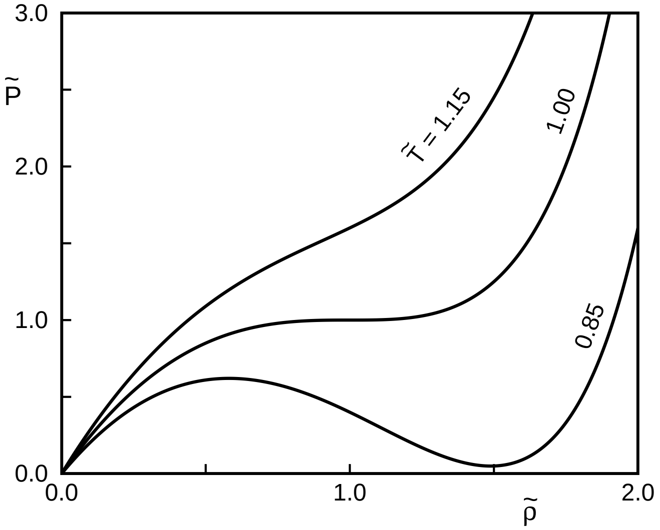

Figure 7.5: Three isotherms for a van der Waals fluid in terms of the dimensionless pressure $\tilde{P}$ and dimensionless density $\tilde{\rho}$ for the dimensionless temperatures $\tilde{T} = 1.15$, 1.0, and 0.85. Note that there is an inflection point at $\tilde{T} = 1$ and $\tilde{\rho} = 1$.

We plot $\tilde{P}$ versus $\tilde{\rho}$ for various temperatures in Figure 7.5. For high temperatures $\tilde{P}$ is a monotonically increasing function of $\tilde{\rho}$ as we would expect. For smaller $\tilde{T}$ there is an inflection point at $\tilde{T} = 1$ and $\tilde{\rho} = 1$. For values of $\tilde{T} \lesssim 1$ we see that $\tilde{P}$ has a local minimum for nonzero $\tilde{\rho}$. This behavior of the van der Waals equation of state is unphysical, and the pressure must be a monotonically increasing function of the density for all temperatures. In other words, a small expansion of the volume of the system should result in a decrease in the pressure. If the opposite happened, the pressure would increase and the volume would continue to increase.

We can make this requirement more precise by considering the isothermal compressibility κ, which is defined as [see (2.172)]

$$\kappa = -\frac{1}{V}\Big(\frac{\partial V}{\partial P}\Big)_{T,N} = \frac{1}{\rho}\Big(\frac{\partial \rho}{\partial P}\Big)_{T,N}. \tag{7.52}$$

Hence, the requirement that $\kappa > 0$ is equivalent to the condition that $(\partial P/\partial\rho)_{T,N} > 0$.[6] From Figure 7.5 we see that this inequality is satisfied for $\tilde{T} > \tilde{T}_c$, where $\tilde{T}_c$ is the temperature corresponding to the inflection point at which

$$\Big(\frac{\partial \tilde{P}}{\partial \tilde{\rho}}\Big)_{\tilde{T}_c,N} = 0, \tag{7.53}$$

$$\Big(\frac{\partial^2 \tilde{P}}{\partial \tilde{\rho}^2}\Big)_{\tilde{T}_c,N} = 0. \tag{7.54}$$

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[6] The inequalities $\kappa > 0$ and $C_V > 0$ can be easily derived in the canonical ensemble [see (6.238) and (4.88)].

Problem 7.10. The critical point of the van der Waals equation of state

(a) Use (7.53) and (7.54) to show that the critical point of the van der Waals equation of state is given by

$$\tilde{P}_c = 1, \tag{7.55a}$$

$$\tilde{T}_c = 1, \tag{7.55b}$$

$$\tilde{\rho}_c = 1. \tag{7.55c}$$

Hence, we can write the dimensionless variables $\tilde{T}$, $\tilde{P}$, and $\tilde{V}$ as $\tilde{T} = T/T_c$, $\tilde{P} = P/P_c$, and $\tilde{V} = V/V_c$. We now see why the various numerical factors were included in the definitions (7.48)–(7.50) of $\tilde{P}$, $\tilde{T}$, and $\tilde{\rho}$.

(b) Show that

$$\frac{V_c}{N} = 3b, \tag{7.56a}$$

$$P_c = \frac{a}{27b^2}, \tag{7.56b}$$

$$kT_c = \frac{8a}{27b}. \tag{7.56c}$$

(c) At what temperature does the compressibility become negative for a given value of the density?

(d) What is the value of the compressibility ratio $P_c/\rho_c kT_c$ according to the van der Waals equation of state? This ratio is close to ≈ 0.29 in a wide variety of systems ranging from Ne to CH_4. □

One of the features of the van der Waals equation of state is that it predicts the *law of corresponding states*, which states that the equations of state of all fluids are identical if they are expressed in terms of dimensionless variables relative to their value at the critical point. This prediction holds only approximately in reality, but it is exact for the van der Waals equation of state; that is, (7.51) is independent of the material parameters a and b.

How can we understand the different nature of the $\tilde{P}$-$\tilde{\rho}$ diagram curves above and below T_c? For temperatures $T > T_c$ there is a unique value of the density for each value of the pressure. Hence a substance at a particular temperature above T_c can pass from a gas to a liquid and vice versa without passing through a phase transition where there would be a large change in some thermodynamic property such as the compressibility.

What happens below T_c? From Figure 7.5 we see that for $\tilde{P} < \tilde{P}_c$, there are three possible values of the density and there is a range of densities for which the system is not thermodynamically stable, that is, $\kappa < 0$. This instability is due to the fact that the van der Waals equation of state for $T < T_c$ is not exact and is not a good approximation of the behavior of $\tilde{P}(\tilde{\rho})$ for a real physical system. We will show in the following that it is possible to interpret the van der Waals phase diagram so that it does give physically reasonable results. In particular, we will find that there is a range of densities for which phase separation occurs and gas and liquid coexist.

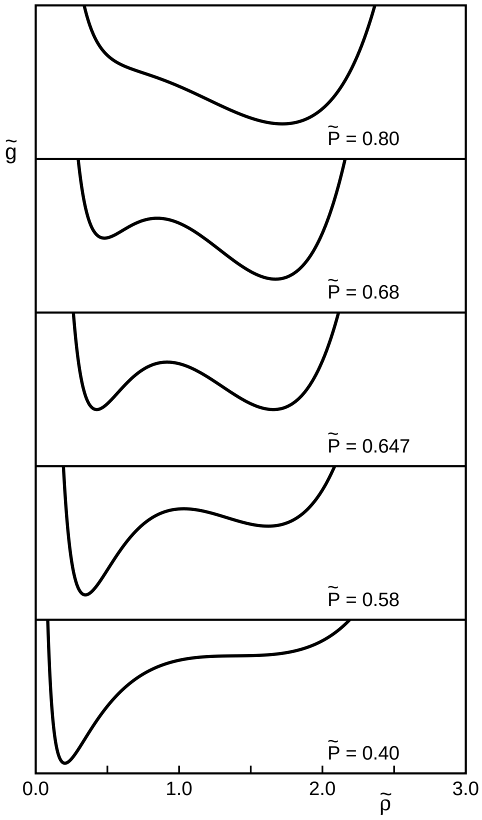

Figure 7.6: Plot of $\tilde{g}(\tilde{\rho})$ in (7.59) at $\tilde{T} = 0.9$ for (a) $\tilde{P} = 0.40$, (b) $\tilde{P} = 0.58$, (c) $\tilde{P} = 0.647$, (d) $\tilde{P} = 0.68$, and (e) $\tilde{P} = 0.80$. As $\tilde{P}$ is increased, the density that gives the minimum value of $\tilde{g}$ changes from the gas phase to the critical point where the two minima are equal, and then to the liquid phase at high density. The local minima correspond to metastable states.

To gain more insight into the nature of the van der Waals equation of state for $\tilde{T} < \tilde{T}_c$, we find the corresponding Gibbs free energy. To do so we first find the Helmholtz free energy F by integrating the relation $P = -(\partial F/\partial V)_T$, with P given by (7.46):

$$F = -NkT \ln(V - Nb) - \frac{aN^2}{V} + NkTw(T), \tag{7.57}$$

where $w(T)$ is an unknown function of T whose form is not needed in the following (see Problem 7.17). Hence, the Gibbs free energy is given by

$$G(T, P) = F + PV = -NkT \ln(V - Nb) - \frac{aN^2}{V} + PV + NkTw(T). \tag{7.58}$$

It is convenient to introduce the dimensionless Gibb's free energy per particle $\tilde{g} = 8G/3NkT_c$ and rewrite (7.58) as

$$\tilde{g} = -3\tilde{\rho} - \frac{8}{3}\tilde{T}\ln\Big(\frac{3}{\tilde{\rho}} - 1\Big) + \tilde{P}/\tilde{\rho}, \tag{7.59}$$

where we have ignored terms that do not depend on $\tilde{\rho}$ or $\tilde{P}$.

The minimum of $\tilde{g}$ for a specific $\tilde{T}$ and $\tilde{P}$ determines the density at equilibrium. Plots of the Gibbs free energy per particle $\tilde{g}(\tilde{\rho})$ as a function of $\tilde{\rho}$ for different values of $\tilde{P}$ and fixed $\tilde{T} = 0.9$ are given in Figure 7.6. We see that for $\tilde{P} = 0.40$, $\tilde{g}$ has one minimum at $\tilde{\rho} \approx 0.20$ corresponding to the gas phase. At $\tilde{P} = 0.58$ there is a local minimum at $\tilde{\rho} \approx 1.66$ corresponding to the metastable liquid phase (a superheated liquid) and a global minimum at $\tilde{\rho} \approx 0.35$ corresponding to the stable gas phase. At $\tilde{P} = 0.647$ the two minima are equal corresponding to the coexistence of the liquid and gas phases. For $\tilde{P} = 0.68$ the global minimum at $\tilde{\rho} \approx 1.67$ corresponds to the liquid phase and the local minimum at $\tilde{\rho} \approx 0.48$ corresponds to the supercooled gas. Finally, for $\tilde{P} = 0.80$, there is only one minimum at $\tilde{\rho} \approx 1.72$, corresponding to the liquid phase.

Another way of understanding the behavior of the system for $\tilde{T} < \tilde{T}_c$ is given in Figure 7.7. Suppose that we prepare the system at the pressure $\tilde{P}_0 = 0.35$ corresponding to the stable gas phase. We then increase the pressure quasistatically, keeping $\tilde{T}$ fixed at $\tilde{T} = 0.9$. At $\tilde{P} \approx 0.42$, $\tilde{g}$ is multivalued, but because $\tilde{g}$ is a minimum for a given value of $\tilde{T}$ and $\tilde{P}$, the system will follow the lower curve until the point C where $\tilde{P} = 0.647$ and the two curves meet. At this value of the pressure the value of $\tilde{g}$ is the same for the gas and liquid phases, and the two phases coexist. As the pressure is increased further the system will follow the lower curve, and the system will be in the liquid phase. However, if we increase the pressure quickly, the system will likely follow the dashed curve and become a metastable gas until $\tilde{P} = 0.724$, the limit of metastability.[7] Similarly, if we start the system in the stable liquid phase and reduce the pressure quickly, the system is likely to follow the dashed curve corresponding to a metastable liquid. The system will remain in a metastable state until a spontaneous density fluctuation takes the system to the state of lower Gibbs free energy.

To find the pressure at which phase coexistence occurs at a given temperature we use the fact that $g(P_{\rm gas}, T) = g(P_{\rm liq}, T)$ and $P_{\rm gas} = P_{\rm liq} = P$ on the coexistence curve. Hence, we consider the difference $g(P_{\rm liq}, T) - g(P_{\rm gas}, T)$ and find the pressure P for a given value of T such that the difference is zero. We write

$$g(P_{\rm liq}, T) - g(P_{\rm gas}, T) = \int_{P_{\rm gas}}^{P_{\rm liq}} \Big(\frac{\partial g}{\partial P}\Big)_T dP = \int_{P_{\rm gas}}^{P_{\rm liq}} \frac{dP}{\rho}, \tag{7.60}$$

where we have used the Gibbs-Duhem equation (2.158) at constant temperature,

$$dg = d\mu = \frac{V}{N}dP = \frac{1}{\rho}dP. \tag{7.61}$$

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[7] Above this pressure the system is thermodynamically unstable; that is, the compressibility becomes negative. The pressure at which the system becomes unstable (for a given temperature) is known as the *spinodal*. The spinodal is well defined only for mean-field equations of state such as the van der Waals equation.

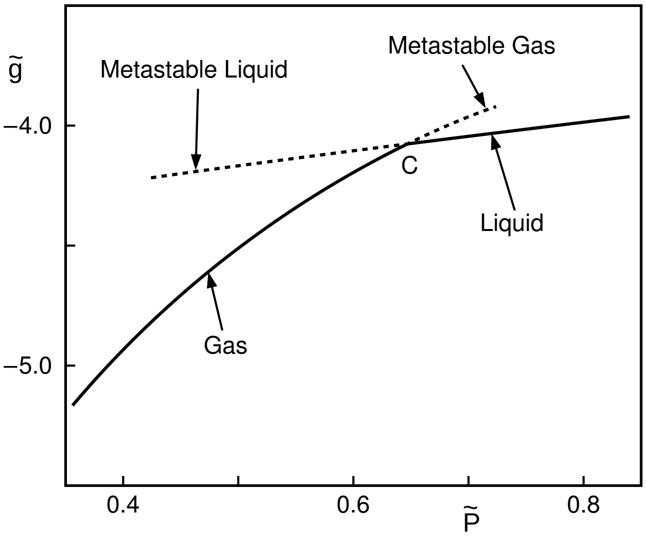

Figure 7.7: Plot of the dimensionless Gibbs free energy per particle $\tilde{g}$ as a function of $\tilde{P}$ at $T = 0.9T_c$ and fixed density. The system is metastable along the dashed curves.

We write the right-hand side of (7.60) as

$$\int_{P_{\rm gas}}^{P_{\rm liq}} \frac{dP}{\rho} = \int_{P_{\rm gas}}^{P_{\rm liq}} \Big[d\Big(\frac{P}{\rho}\Big) - P d\Big(\frac{1}{\rho}\Big)\Big] \tag{7.62a}$$

$$= \frac{P(\rho_{\rm liq}, T)}{\rho_{\rm liq}} - \frac{P(\rho_{\rm gas}, T)}{\rho_{\rm gas}} + \int_{\rho_{\rm gas}}^{\rho_{\rm liq}} \frac{P(\rho)}{\rho^2} d\rho. \tag{7.62b}$$

We substitute (7.62b) into (7.60) and obtain

$$g(\rho_{\rm liq}, T) - g(\rho_{\rm gas}, T) = \frac{P(\rho_{\rm liq}, T)}{\rho_{\rm liq}} - \frac{P(\rho_{\rm gas}, T)}{\rho_{\rm gas}} + \int_{\rho_{\rm gas}}^{\rho_{\rm liq}} \frac{P(\rho)}{\rho^2} d\rho. \tag{7.63}$$

Because $g(\rho_{\rm gas}) = g(\rho_{\rm liq})$ and $P(\rho_{\rm gas}) = P(\rho_{\rm liq}) = P$ on the phase coexistence curve, (7.63) reduces to

$$P\Big[\frac{1}{\rho_{\rm liq}} - \frac{1}{\rho_{\rm gas}}\Big] + \int_{\rho_{\rm gas}}^{\rho_{\rm liq}} \frac{P(\rho)}{\rho^2} d\rho = 0. \tag{7.64}$$

We can alternatively express (7.64) in terms of the volume per particle $v = 1/\rho$:

$$P\big[v_{\rm gas} - v_{\rm liq}\big] - \int_{v_{\rm liq}}^{v_{\rm gas}} P dv = 0. \tag{7.65}$$

The geometrical interpretation of (7.65) can be seen by looking at Figure 7.8. The values of P, $v_{\rm gas}$, and $v_{\rm liq}$ are determined by choosing the shaded areas in Figure 7.8 to have equal areas. This way of interpreting the meaning of the van der Waals equation for $T < T_c$ is known as the

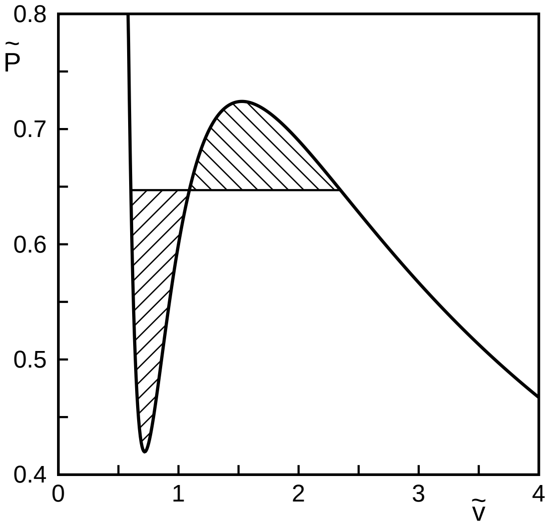

Figure 7.8: Maxwell equal area construction. The pressure $\tilde{P}$ where two phase coexistence begins for $\tilde{T} = 0.9$ is determined so that the areas above and below the horizontal line are equal. In this case $\tilde{P} \approx 0.647$.

Maxwell construction. This construction provides a recipe for finding the equilibrium values of P, $v_{\rm liq}$, and $v_{\rm gas}$ along any isotherm at a temperature $T < T_c$.

****Liquid-gas coexistence curve for the van der Waals equation of state*.** We now use (7.65) to find the values of $\tilde{\rho}_{\rm gas}$ and $\tilde{\rho}_{\rm liq}$ for a given pressure $\tilde{P}$ and temperature $\tilde{T}$ on the coexistence curve. We write (7.51) on the coexistence curve:

$$\tilde{P} = \frac{8\tilde{\rho}_{\rm gas}\tilde{T}}{3 - \tilde{\rho}_{\rm gas}} - 3\tilde{\rho}_{\rm gas}^2 = \frac{8\tilde{\rho}_{\rm liq}\tilde{T}}{3 - \tilde{\rho}_{\rm liq}} - 3\tilde{\rho}_{\rm liq}^2, \tag{7.66}$$

and solve (7.66) for $\tilde{T} < \tilde{T}_c = 1$:

$$\tilde{T} = \frac{1}{8}(3 - \tilde{\rho}_{\rm gas})(3 - \tilde{\rho}_{\rm liq})(\tilde{\rho}_{\rm gas} + \tilde{\rho}_{\rm liq}). \tag{7.67}$$

We substitute $\tilde{T}$ from (7.67) into the right-hand side of (7.66) and find

$$\tilde{P} = \tilde{\rho}_{\rm gas}\tilde{\rho}_{\rm liq}\big[3 - \tilde{\rho}_{\rm gas} - \tilde{\rho}_{\rm liq}\big]. \tag{7.68}$$

We next substitute $\tilde{P}$ from (7.51) into the integral in (7.64) and evaluate the integral:

$$\int_{\tilde{\rho}_{\rm gas}}^{\tilde{\rho}_{\rm liq}} \frac{\tilde{P}(\tilde{\rho})}{\tilde{\rho}^2} d\tilde{\rho} = \int_{\tilde{\rho}_{\rm gas}}^{\tilde{\rho}_{\rm liq}} \frac{1}{\tilde{\rho}^2}\Big[\frac{8\tilde{\rho}\tilde{T}}{3 - \tilde{\rho}} - 3\tilde{\rho}^2\Big] d\tilde{\rho} \tag{7.69a}$$

$$= \Big[\frac{8\tilde{T}}{3} \ln \frac{\tilde{\rho}}{3 - \tilde{\rho}} - 3\tilde{\rho}\Big]_{\tilde{\rho}_{\rm gas}}^{\tilde{\rho}_{\rm liq}} \tag{7.69b}$$

$$= \frac{8\tilde{T}}{3} \ln \left[\frac{\tilde{\rho}_{\rm liq}(3 - \tilde{\rho}_{\rm gas})}{\tilde{\rho}_{\rm gas}(3 - \tilde{\rho}_{\rm liq})}\right] - 3(\tilde{\rho}_{\rm liq} - \tilde{\rho}_{\rm gas}). \tag{7.69c}$$

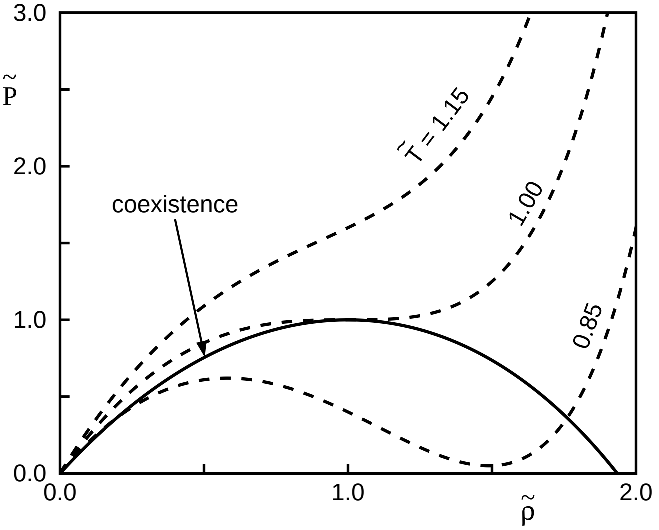

Figure 7.9: The coexistence curve for the van der Waals equation of state as a function of the dimensionless density $\tilde\rho$. Also plotted are three isotherms (dashed lines). For $\tilde T < 1$ the isotherms intersect the coexistence curve (solid line) at two points whose coordinates give the equilibrium values of $\tilde P$, $\tilde\rho_{\rm gas}$, and $\tilde\rho_{\rm liq}$. For $\tilde T = 1$ the isotherm intersects the coexistence curve at one point where $\tilde P = 1$ and $\tilde\rho = \tilde\rho_{\rm gas} = \tilde\rho_{\rm liq} = 1$.

Finally, we substitute $\tilde P$ from (7.68), $\tilde T$ from (7.67), and the integral in (7.69c) into (7.64) and obtain

$$(\tilde\rho_{\rm liq} - \tilde\rho_{\rm gas})(6 - \tilde\rho_{\rm gas} - \tilde\rho_{\rm liq}) = \frac{1}{3}(3 - \tilde\rho_{\rm gas})(3 - \rho_{\rm liq})(\tilde\rho_{\rm gas} + \tilde\rho_{\rm liq}) \ln\left[\frac{\tilde\rho_{\rm liq}(3 - \tilde\rho_{\rm gas})}{\tilde\rho_{\rm gas}(3 - \tilde\rho_{\rm liq})}\right]. \tag{7.70}$$

The final result was obtained by multiplying both sides of the equation by −1, so that both sides are positive. We next use (7.67) for a particular value of $\tilde T$, compute $\tilde\rho_{\rm gas}$ as a function of $\tilde\rho_{\rm liq}$, and find $\tilde\rho_{\rm liq}$ from a numerical solution of (7.70). We can then use this numerical solution in (7.67) to obtain the coexistence curve shown in Figure 7.9.

7.4.2 *The van der Waals critical point

We learned in Chapter 5 that the behavior of the Ising model near a critical point is characterized by power law behavior and critical exponents. In the following we will investigate the nature of the critical point as given by the van der Waals equation of state. We will see that the gas-liquid critical point shows similar behavior and is characterized by mean-field exponents. That is, the van der Waals equation of state is a mean-field equation.

We have already found the values of T_c, P_c, and ρ_c. Suppose that we fix the pressure and the density at their critical point values and lower the temperature starting from above T_c. Then the critical point is where the system must first choose between being a liquid or a gas.

Near the critical point we can write

$$\tilde{\rho}_{\rm liq} = \tilde{\rho}_c + \Delta_{\rm liq} = 1 + \Delta_{\rm liq}, \tag{7.71a}$$

$$\tilde{\rho}_{\rm gas} = \tilde{\rho}_c - \Delta_{\rm gas} = 1 - \Delta_{\rm gas}. \tag{7.71b}$$

We substitute (7.71) into (7.70) and expand each side in powers of $\Delta_{\rm liq}$ and $\Delta_{\rm gas}$. To first order in $\Delta_{\rm liq}$ and $\Delta_{\rm gas}$ we find that $\Delta_{\rm liq} = \Delta_{\rm gas}$. That is, the coexistence curve is symmetrical near the critical point (see Problem 7.11). This symmetry is a special case of the empirical law of "rectilinear diameters," which is exact for the van der Waals equation of state and a good approximation for real systems.

Problem 7.11. Symmetry of the van der Waals coexistence line near the critical point

Consider the van der Waals equation along the coexistence line as given by (7.70). Use (7.71) and show to leading order in $\Delta_{\rm liq}$ and $\Delta_{\rm gas}$ that the coexistence curve is symmetrical, that is, $\Delta_{\rm liq} = \Delta_{\rm gas}$. ☐

Next we find how the difference $\rho_{\rm liq} - \rho_{\rm gas}$ goes to zero as $T \to T_c$ along the coexistence curve. We subtract $\tilde{T}_c = 1$ from both sides of (7.67), expand the right-hand side in powers of $\Delta_{\rm liq}$ and $\Delta_{\rm gas}$, and obtain

$$\tilde{T} - \tilde{T}_c = \frac{1}{8}(3 - \tilde{\rho}_{\rm gas})(3 - \tilde{\rho}_{\rm liq})(\tilde{\rho}_{\rm gas} + \tilde{\rho}_{\rm liq}) - 1 \tag{7.72a}$$

$$= \frac{1}{8}\big[(2 + \Delta_{\rm gas})(2 - \Delta_{\rm liq})(2 + \Delta_{\rm liq} - \Delta_{\rm gas})\big] - 1 \tag{7.72b}$$

$$= \big[2\Delta_{\rm gas}\Delta_{\rm liq} - \Delta_{\rm gas}^2 - 2\Delta_{\rm liq}^2\big]. \tag{7.72c}$$

We then let $\Delta_{\rm liq} = \Delta_{\rm gas} = \Delta$ and write (7.72c) as

$$\tilde{T} - \tilde{T}_c = -\Delta^2 = -\Delta_{\rm liq}^2 = -\Delta_{\rm gas}^2. \tag{7.73}$$

or

$$\tilde{\rho}_{\rm liq} - \tilde{\rho}_c = \tilde{\rho}_c - \tilde{\rho}_{\rm gas} = \big(\tilde{T}_c - \tilde{T}\big)^{1/2}. \tag{7.74}$$

In our discussion of the critical point in the Ising model in Chapter 5, we found that the order parameter m vanishes near T_c from below as $m \propto (T_c - T)^\beta$, where $\beta = 1/2$ in mean-field theory. We can similarly choose the quantity $\tilde{\rho}_{\rm liq} - \tilde{\rho}_c$ as the order parameter of the gas-liquid critical point. Hence, we see from (7.74) that the van der Waals theory predicts $\beta = 1/2$, a manifestation of the mean-field nature of the van der Waals theory.

Just as we considered the divergence of the susceptibility near the Ising critical point, we now consider the temperature dependence of the isothermal compressibility near the gas-liquid critical point. From the definition (7.52) and the van der Waals equation of state in (7.50) we have

$$\kappa = \frac{27b^2}{a}\frac{1}{\tilde{\rho}}\Big(\frac{\partial \tilde{\rho}}{\partial \tilde{P}}\Big)_{T,N}, \tag{7.75}$$

and

$$\frac{\partial \tilde{P}}{\partial \tilde{\rho}} = \frac{24\tilde{T}}{(3 - \tilde{\rho})^2} - 6\tilde{\rho}. \tag{7.76}$$

Note that if we set $\tilde{T} = \tilde{T}_c = 1$ and $\tilde{\rho} = \tilde{\rho}_c = 1$ in (7.76) we find $\partial\tilde{P}/\partial\tilde{\rho} = 0$, and we conclude that the compressibility diverges at the critical point. To see how κ behaves for $\tilde{T}$ near $\tilde{T}_c$ we let $\tilde{\rho} = 1 + \Delta$, and write

$$\frac{\partial\tilde{P}}{\partial\tilde{\rho}} = \frac{24\tilde{T}}{(2-\Delta)^2} - 6(1+\Delta) \approx \frac{3}{4}\Delta^2. \tag{7.77}$$

Hence κ at $\tilde{\rho} = \tilde{\rho}_c = 1$ diverges as

$$\kappa \approx \Delta^{-2} \propto (\tilde{T}_c - \tilde{T})^{-1}, \tag{7.78}$$

where the dependence on $(\tilde{T}_c - \tilde{T})$ is given in (7.74). Note that the (isothermal) compressibility κ and the (zero-field) magnetic susceptibility χ both diverge at the critical point with the exponent $\gamma = 1$, as predicted by the van der Waals equation of state and mean-field theory.

7.5 *Chemical Reactions

Consider a chemical reaction such as the production of water from hydrogen and oxygen,

$$2\mathrm{H}_2 + \mathrm{O}_2 \Leftrightarrow 2\mathrm{H}_2\mathrm{O}. \tag{7.79}$$

The symbol $\Leftrightarrow$ indicates that the reaction can go either way depending on the concentration of each molecular species and the temperature. Equation (7.79) says that it takes two molecules of hydrogen and one molecule of oxygen to make two molecules of water. We rewrite (7.79) in the standard form

$$-2\mathrm{H}_2 - \mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} = 0, \tag{7.80}$$

or more generally

$$\nu_1 N_1 + \nu_2 N_2 + \nu_3 N_3 = 0, \tag{7.81}$$

where N_1 is the number of hydrogen molecules, N_2 is the number of oxygen molecules, and N_3 is the number of water molecules. The *stoichiometric* coefficients are $\nu_1 = -2$, $\nu_2 = -1$, and $\nu_3 = 2$. The (arbitrary) convention is that ν_i is positive for product molecules and negative for reactant molecules.

Imagine we place hydrogen, oxygen, and water in a closed container and allow them to react, perhaps by supplying a spark. Some of the hydrogen and oxygen will be converted to water, such that the number of hydrogen molecules is reduced and becomes twice that of oxygen, and the number of water molecules that is produced will be the same as the reduction of hydrogen molecules. Hence we can write

$$\nu_1 dN_1 + \nu_2 dN_2 + \nu_3 dN_3 = 0. \tag{7.82}$$

We can now determine the equilibrium conditions. We begin with the generalization of (2.154) to many kinds of molecules:

$$dG = -SdT + VdP + \sum_i \mu_i dN_i, \tag{7.83}$$

where μ_i is the chemical potential of molecules of type i. We know that the Gibbs free energy will be a minimum in equilibrium for a given pressure and temperature. The equilibrium condition $dG = 0$ yields (for given values of P and T)

$$0 = \sum_i \nu_i \mu_i. \tag{7.84}$$

The condition for chemical equilibrium for the reaction in (7.80) is

$$2\mu_{\mathrm{H_2}} + \mu_{\mathrm{O_2}} = 2\mu_{\mathrm{H_2O}}. \tag{7.85}$$

If the system is not in chemical equilibrium, then the sum on the right-hand side of (7.84) will not vanish. If the sum is negative, then the reaction proceeds spontaneously toward the products (the molecules on the right-hand side of the reaction equation); if it is positive, the reaction proceeds toward the reactants.

To find the relative concentrations of each type of molecule in equilibrium, we need to know how the chemical potential of each type of molecule depends on its concentration. For simplicity, we assume that the different molecules form a dilute gas which can be approximated as ideal. The reaction takes place in a closed container of volume V at temperature T. For such an idealized system thermodynamic quantities such as the mean energy and pressure are additive. For example, the total pressure is given by $\sum_i P_i$, where P_i is the pressure that would be exerted by the gas of type i if it was in the container all by itself. If we assume that the chemical potential of the ith type depends only on the number of molecules of that type and not on the number of molecules of other types in the container, then the chemical potential for molecules of type i is given by [see (6.115)]

$$\mu_i(T,V,N_i) = -kT \ln \Big[\frac{V}{N_i}\Big(\frac{2\pi m_i kT}{h^2}\Big)^{3/2}\Big] = -kT \ln \Big[\frac{V}{N}\frac{N}{N_i}\Big(\frac{2\pi m_i kT}{h^2}\Big)^{3/2}\Big]. \tag{7.86}$$

If we replace V/N by kT/P and let $n_i = N_i/N$, we can rewrite (7.86) as

$$\mu_i(T,P,n_i) = -kT \ln \Big[\frac{kT}{P}\Big(\frac{2\pi m_i kT}{h^2}\Big)^{3/2}\Big] + kT \ln n_i, \tag{7.87}$$

which we write as

$$\mu_i(T,P,n_i) = \mu_i^{(0)}(T,P) + kT \ln n_i, \tag{7.88}$$

where $\mu_i^{(0)}(T,P)$ is the chemical potential of a pure system consisting of molecules of type i at temperature T and pressure P. The assumption that the chemical potential of the ith type depends only on the fraction of the ith type present, and not on the fractions of the other types, does not hold in general. This assumption is applicable when the types of molecules that are mixed are chemically similar, in dilute solutions that do not involve electrolytes, or in mixtures of gases at low pressures or high temperatures.

We combine (7.84) and (7.88) to obtain

$$\sum_i \mu_i^{(0)}(T,P)\nu_i = -kT \ln K, \tag{7.89}$$

where the equilibrium constant K is defined by

$$K \equiv \prod_i (n_i)^{\nu_i}. \tag{7.90}$$

For example, the equilibrium constant K for the reaction in (7.79) is

$$K = \frac{(n_{\mathrm{H_2O}})^2}{(n_{\mathrm{H_2}})^2 n_{\mathrm{O_2}}}. \tag{7.91}$$

The *law of mass action* states that, if the system is in equilibrium at a given temperature and pressure, then the ratio on the right-hand side of (7.91) is a constant. Given the chemical potentials $\mu_i^{(0)}(T,P)$ we can determine the equilibrium constant and predict the equilibrium concentrations.

How can the law of mass action be used? Consider the same example, but suppose that the concentrations of the various molecules are initially not in equilibrium. The initial reaction ratio is given by

$$Q = \frac{(n^{(i)}_{\mathrm{H_2O}})^2}{(n^{(i)}_{\mathrm{H_2}})^2 n^{(i)}_{\mathrm{O_2}}}, \tag{7.92}$$

where the initial concentrations $n^{(i)}$ are arbitrary. If $Q > K$, then the system will produce more reactants $n_{\mathrm{H_2}}$ and $n_{\mathrm{O_2}}$. If $Q < K$, then the system will produce more product, or water in this case.

We can also find the equilibrium concentration of the reactants and products given the initial arbitrary concentrations of just the reactants. Let x be the final equilibrium concentration of water. Then from (7.91) we have

$$K = \frac{x^2}{(n^{(i)}_{\mathrm{H_2}} - x)^2 (n^{(i)}_{\mathrm{O_2}} - x/2)}, \tag{7.93}$$

where $n^{(i)}_{\mathrm{H_2}} - x$ and $n^{(i)}_{\mathrm{O_2}} - x/2$ are the equilibrium concentrations of the reactants. We can solve (7.93) for x to obtain the equilibrium concentrations of the reactants and products.

To determine how the equilibrium constant depends on T and P we need to know how the chemical potentials of the pure substances change with T and P. We know that the chemical potential is the Gibbs free energy per particle, which is related to the enthalpy by

$$g = \mu = h - Ts, \tag{7.94}$$

where lower case indicates an intensive quantity. From the Gibbs-Duhem equation (2.158) we have that $s = -(\partial\mu/\partial T)_P$, and thus (7.94) becomes

$$\mu = h + T\Big(\frac{\partial \mu}{\partial T}\Big)_P. \tag{7.95}$$

We rearrange terms and divide by T^2 and obtain

$$-\frac{\mu}{T^2} + \frac{1}{T}\Big(\frac{\partial \mu}{\partial T}\Big)_P = -\frac{h}{T^2}, \tag{7.96}$$

which can be rewritten as

$$\frac{\partial}{\partial T}\Big(\frac{\mu}{T}\Big)_P = -\frac{h}{T^2}. \tag{7.97}$$

Check (7.97) by taking derivatives and obtaining (7.96).

If the form for the chemical potential given in (7.88) is applicable, we can divide (7.87) by T, take the temperature derivative, and use (7.97) to find

$$\Big(\frac{\partial \ln K}{\partial T}\Big)_{P,\{n_i\}} = \frac{1}{kT^2}\sum_i \nu_i h_i^{(0)}, \tag{7.98}$$

where $h_i^{(0)}$ is the specific enthalpy of the pure ith substance. Similar calculations lead to

$$\Big(\frac{\partial \ln K}{\partial P}\Big)_{T,\{n_i\}} = -\frac{1}{kT}\sum_i \nu_i v_i^{(0)}, \tag{7.99}$$

which gives the change in K with pressure in terms of the specific volumes $v_i^{(0)}$. If there is sufficient empirical data for the enthalpies and volumes, we can determine K at any temperature and pressure.

If the right-hand side of (7.98) is positive, the reaction is endothermic, which means that the reaction needs energy to produce the products. This energy goes into forming chemical bonds, another form of energy distinct from the kinetic energy of the molecules and the potential energy of interaction between the molecules. If we add energy to the system by heating, (7.98) indicates that $\ln K$ and thus K will increase, which will consume some of the added energy, which in turn will cool the system. Similar reasoning implies that, if the reaction is exothermic (releases energy when producing products), then an increase in the temperature will decrease the amount of the products, thus consuming energy and cooling the system. Cooling an exothermic system results in energy being produced by the reactions so as to oppose the cooling. In either case the system's behavior after a change in temperature is to oppose the change. Analogous behavior occurs for pressure changes. If we increase the pressure and the right-hand side of (7.99) is positive, the reactants will have more volume than the products (ν_i is negative for reactants and positive for products), and K will increase. An increase in K leads to more products, which in turn lowers the volume thus decreasing the pressure. In either case the system opposes the changes. This general rule is called *Le Châtelier's principle* and is analogous to Lenz's law in magnetism.

Problem 7.12. Producing ammonia

Consider the exothermic reaction that produces ammonia:

$$\mathrm{N_2} + 3\mathrm{H_2} \Leftrightarrow 2\mathrm{NH_3}. \tag{7.100}$$

(a) Use Le Châtelier's principle to determine whether an increase in the temperature will lead to an increase or decrease in the amount of ammonia.

(b) Assume that the reactants and products in (7.100) are gases. Use Le Châtelier's principle to determine whether an increase in the pressure will produce more or less ammonia. □

Vocabulary

chemical equilibrium

phase coexistence curve, phase diagram

triple point, critical point

Clausius-Clapeyron equation

enthalpy of fusion, vaporization, and sublimation

metastable state, Maxwell construction

law of mass action

Additional Problems

Problem 7.13. Climb every mountain

Use the result (7.40) to estimate the boiling temperature of water at the height of the highest mountain in your geographical region. ☐

Problem 7.14. Change of boiling temperature

A particular liquid boils at 127°C at a pressure of 1.06×10^5 Pa. Its enthalpy of vaporization is 5000 J/mol. At what temperature will it boil if the pressure is raised to 1.08×10^5 Pa? ☐

Problem 7.15. Approximate height of a hill

A particular liquid boils at a temperature of 105°C at the bottom of a hill and at 95°C at the top of the hill. The enthalpy of vaporization is 1000 J/mol. What is the approximate height of the hill? ☐

***Problem 7.16.** Freezing of ^{4}He

^{4}He exists in liquid form at temperatures below 4.2 K at atmospheric pressure and remains liquid down to zero temperature; helium solidifies only for pressures greater than approximately 25×10^2 Pa. An interesting feature of the liquid-solid coexistence curve is that the melting pressure is reduced slightly from its value at $T = 0$ K by approximately 20 Pa at its minimum at $T = 0.8$ K. We will see that a simple model of the liquid and solid phases of ^{4}He can explain this minimum.

(a) The properties of liquid ^{4}He are dominated by quantized sound waves (known as phonons) which satisfy the dispersion relation $\epsilon = ck$, where c is the speed of sound. Calculate the contribution of these modes to the heat capacity of the liquid at low temperatures.

(b) Calculate the low temperature heat capacity of solid ^{4}He in terms of the longitudinal and transverse sound speeds c_ℓ and c_t.

(c) Use your heat capacity results for the liquid and solid to calculate the entropy difference (per particle) $s_{\rm liquid} - s_{\rm solid}$ assuming a single sound speed $c \approx c_\ell \approx c_t$ and approximately equal volumes per particle $v_{\rm liquid} \approx v_{\rm solid} \approx v$. Which phase has the higher entropy at low temperatures?

(d) Assume a small temperature independent volume difference $\Delta v = v_{\text{liquid}} - v_{\text{solid}}$ and calculate the form of the coexistence curve. To explain the reduction of the melting pressure, which phase must have the higher density? (This problem is adapted from Kardar (2007), p. 209.) □

Problem 7.17. Determination of the function $w(T)$

Because we are interested in the pressure dependence of G for a given temperature, we need not know the function $w(T)$ in (7.57). For completeness determine the form of $w(T)$ from the relation $E = (\partial(\beta F)/\partial\beta)_V$ and the van der Waals energy equation of state [see (2.24)]

$$E = \frac{3}{2}NkT - a\frac{N^2}{V}. \tag{7.101}$$

□

Problem 7.18. Calculation of the critical exponent δ

We can calculate the critical exponent δ predicted by the van der Waals equation of state by taking $T = T_c$ and determining how the order parameter depends on the pressure difference $\tilde{P} - \tilde{P}_c$. From (7.51) we have

$$\tilde{P} - \tilde{P}_c = \frac{8\tilde{\rho}\tilde{T}_c}{3 - \tilde{\rho}} - 3\tilde{\rho}^2 - 1. \tag{7.102}$$

Let $\tilde{\rho} = \tilde{\rho}_c + \Delta = 1 + \Delta$ and $\tilde{T}_c = 1$, and show that

$$\tilde{\rho} - \tilde{\rho}_c \sim \Big[(\tilde{P} - \tilde{P}_c)\Big]^{1/3} \tag{7.103}$$

by placing all the terms in (7.102) over a common denominator. What is the value of δ and how does it compare to the value predicted by mean-field theory? □

Suggestions for Further Reading

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Chapter 8

Classical Gases and Liquids

We discuss approximation techniques for interacting classical particle systems such as dense gases and liquids.

8.1 Introduction

Because there are only a few problems in statistical mechanics that can be solved exactly, we need to find approximate solutions. We introduce several perturbation methods that are applicable when there is a small expansion parameter. Our discussion of interacting classical particle systems will involve some of the same considerations and difficulties that are encountered in quantum field theory (no knowledge of the latter is assumed). For example, we will introduce diagrams that are analogous to Feynman diagrams and find divergences analogous to those found in quantum electrodynamics. We also discuss the spatial correlations between particles due to their interactions and the use of hard spheres as a reference system for understanding the properties of dense fluids.

8.2 Density Expansion

Consider a gas of N identical particles each of mass m at density $\rho = N/V$ and temperature T. We will assume that the total potential energy U is a sum of two-body interactions $u_{ij} = u(|\mathbf{r}_i - \mathbf{r}_j|)$, and write U as

$$U = \sum_{i<j}^{N} u_{ij}. \tag{8.1}$$

The exact form of $u(r)$ for electrically neutral molecules and atoms must be constructed by a first principles quantum mechanical calculation. Such a calculation is very difficult, and for many purposes it is sufficient to choose a simple phenomenological form for $u(r)$. The most important

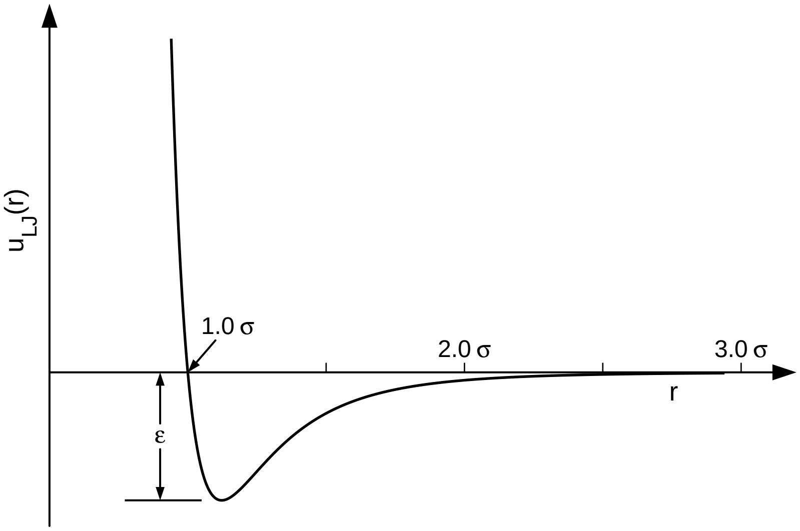

Figure 8.1: Plot of the Lennard-Jones potential $u_{\rm LJ}(r)$, where r is the distance between the particles. The potential is characterized by a length σ and an energy ϵ.

features of $u(r)$ are a strong repulsion for small r and a weak attraction at large r. A common phenomenological form of $u(r)$ is the *Lennard-Jones* or 6-12 potential shown in Figure 8.1:

$$u_{\rm LJ}(r) = 4\epsilon\Big[\Big(\frac{\sigma}{r}\Big)^{12} - \Big(\frac{\sigma}{r}\Big)^{6}\Big]. \tag{8.2}$$

The values of σ and ϵ for argon are $\sigma = 3.4 \times 10^{-10}\,$m and $\epsilon = 1.65 \times 10^{-21}\,$J.

The attractive $1/r^6$ contribution to the Lennard-Jones potential is due to the induced dipole-dipole interaction of two neutral atoms.[1] The resultant attractive interaction is called the *van der Waals* potential. The rapidly increasing repulsive interaction as the separation between atoms is decreased for small r is a consequence of the Pauli exclusion principle. The $1/r^{12}$ form of the repulsive potential in (8.2) is chosen only for convenience.

The existence of many calculations and simulation results for the Lennard-Jones potential encourages us to use it even though there are more accurate forms of the interparticle potential for modeling the interactions in real fluids, proteins, and other complex molecules.

An even simpler form of the interaction between particles is the *hard core* interaction

$$u_{\rm HC}(r) = \begin{cases} \infty & (r < \sigma), \\ 0 & (r > \sigma). \end{cases} \tag{8.3}$$

A system of particles in three dimensions with the interaction (8.3) is called a system of *hard spheres* with σ the diameter of the spheres; the analogous systems in two and one dimensions are

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[1] A simple classical model of this induced dipole-dipole effect is described in Brehm and Mullin (1989), pp. 517–521.

called *hard disks* and *hard rods*. Although this interaction has no attractive part, we will see that it is very useful in understanding the properties of liquids.

Both the hard core interaction and Lennard-Jones potential are short range. The hard core interaction is zero for $r > \sigma$ and the Lennard-Jones potential can often be neglected for $r \gtrsim 2.3\sigma$.[2]

Problem 8.1. The Lennard-Jones potential

(a) Show that the minimum of the Lennard-Jones potential is at $r_{\rm min} = 2^{1/6}\sigma$ and that $u_{\rm LJ}(r_{\rm min}) = -\epsilon$.

(b) Given a potential $u(r)$, the force in the radial direction is given by $= -du(r)/dr$. At what value of r is $-du_{\rm LJ}(r)/dr$ a minimum?

(c) What is the value of $u_{\rm LJ}(r)$ at $r = 2.3\sigma$ compared to its value at its minimum? □

We will consider only classical systems in this chapter and hence assume that the condition $\lambda \ll n^{-1/3}$ is satisfied. The partition function for N identical particles in the semiclassical limit is given by (see Section 6.2)

$$Z_N = \frac{1}{N!\,h^{3N}} \int e^{-\beta(K+U)}\, d\mathbf{p}_1\, d\mathbf{p}_2 \ldots d\mathbf{p}_N\, d\mathbf{r}_1\, d\mathbf{r}_2 \ldots d\mathbf{r}_N, \tag{8.4}$$

where the kinetic energy $K = \sum_i p_i^2/2m$ and the potential energy U is given in (8.1).

Because the potential energy does not depend on the momenta of the particles and the kinetic energy does not depend on the positions of the particles, we can write Z_N in the form

$$\begin{aligned}
Z_N &= \frac{1}{N!\,h^{3N}} \int e^{-\beta K} d\mathbf{p}_1\, d\mathbf{p}_2 \ldots d\mathbf{p}_N \int e^{-\beta U} d\mathbf{r}_1\, d\mathbf{r}_2 \ldots d\mathbf{r}_N &\text{(8.5a)}\\
&= \frac{V^N}{N!\,h^{3N}} \int e^{-\beta K} d\mathbf{p}_1\, d\mathbf{p}_2 \ldots d\mathbf{p}_N\, \frac{1}{V^N} \int e^{-\beta U} d\mathbf{r}_1\, d\mathbf{r}_2 \ldots d\mathbf{r}_N &\text{(8.5b)}\\
&= Z_{\rm ideal} \frac{1}{V^N} \int e^{-\beta U} d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N, &\text{(8.5c)}
\end{aligned}$$

where

$$Z_{\rm ideal} = \frac{1}{N!\,h^{3N}} V^N \int e^{-\beta K} d\mathbf{p}_1\, d\mathbf{p}_2 \ldots d\mathbf{p}_N. \tag{8.6}$$

The factor of V^N in (8.6) is due to the integration over $\mathbf{r}$ with $U = 0$. It is straightforward to do the momentum integrals in (8.6); the result for $Z_{\rm ideal}$ is given in (6.25). The corresponding free energy of an ideal classical gas is $F_{\rm ideal} = -kT \ln Z_{\rm ideal}$ [see (6.26), page 297].

We adopt the notation $\langle \cdots \rangle_0$ to denote an average over the positions of the particles in an ideal gas. That is, each particle in an ideal classical gas has a probability $d\mathbf{r}/V$ of being in the volume $d\mathbf{r}$. We use this notation to rewrite (8.5c) as

$$Z_N = Z_{\rm ideal} \left\langle e^{-\beta U} \right\rangle_0. \tag{8.7}$$

---

[2] Because the Lennard-Jones potential at $r = 2.3\sigma$ is not exactly zero, truncating it at $r = 2.3\sigma$ introduces a discontinuity in the potential. This discontinuity can be avoided by adding a constant to the potential so that $u_{\rm LJ} = 0$ at $r = 2.3\sigma$.

The contribution F_c to the free energy from the correlations between the particles due to their interactions has the form

$$F_c = F - F_{\text{ideal}} = -kT \ln \frac{Z}{Z_{\text{ideal}}} = -kT \ln \left\langle e^{-\beta U} \right\rangle_0. \tag{8.8}$$

We see that the evaluation of the free energy due to the interactions between particles can be reduced to the evaluation of the ensemble average in (8.8).

In general, we cannot calculate F_c exactly for arbitrary densities. We know that the ideal gas equation of state, $PV/NkT = 1$, is a good approximation for a dilute gas for which the intermolecular interactions can be ignored. For this reason we first seek an approximation for F_c for low densities where the interactions between the particles are not too important. If the interactions are short-range, it is plausible that we can obtain an expansion of the pressure and hence F_c in powers of the density. This expansion is known as the density or *virial expansion*[3] and is written as

$$\frac{PV}{NkT} = 1 + \rho\, B_2(T) + \rho^2 B_3(T) + \rho^3 B_4(T) + \cdots . \tag{8.9}$$

The quantities B_n are known as *virial coefficients* and involve the interaction of n particles. The first four virial coefficients are given by the expressions ($B_1 = 1$)

$$B_2(T) = -\frac{1}{2V}\int f_{12}\, d\mathbf{r}_1 d\mathbf{r}_2, \tag{8.10a}$$

$$B_3(T) = -\frac{1}{3V}\int f_{12} f_{13} f_{23}\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3, \tag{8.10b}$$

$$\begin{aligned} B_4(T) = -\frac{1}{8V}\int \big(&3 f_{12} f_{23} f_{34} f_{41} + 6 f_{12} f_{23} f_{34} f_{41} f_{13} \\ &+ f_{12} f_{23} f_{34} f_{41} f_{13} f_{24}\big)\, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4, \end{aligned} \tag{8.10c}$$

where $f_{ij} = f(|\mathbf{r}_i - \mathbf{r}_j|)$, and

$$\boxed{f(r) = e^{-\beta u(r)} - 1}. \tag{8.11}$$

The function $f(r)$ defined in (8.11) is known as the *Mayer f function.*[4] We will give a simple derivation of the second virial coefficient in Section 8.3. The derivation of the third and higher order virial coefficients is much more involved and is given in Section 8.4.3.

Problem 8.2. Density expansion of the free energy

The density expansion of the free energy F_c is usually written as

$$-\beta \frac{F_c}{N} = \sum_{p=1}^{\infty} \frac{b_p \rho^p}{p+1}, \tag{8.12}$$

---

[3] The word *virial* is related to the Latin word for force. Rudolf Clausius named a certain function of the force between particles as “the virial of force.” This name was subsequently applied to the virial expansion because the terms in this expansion are related to the forces between particles.

[4] The f function is named after Joseph Mayer (1904–1983), a chemical physicist who is known for his work in statistical mechanics and the application of statistical mechanics to liquids and dense gases. He was the husband of Maria Goeppert Mayer (1906–1972), who shared the Nobel Prize for physics in 1963. Maria Goeppert Mayer was not able to obtain a tenured faculty position until 1960 because of sexism and nepotism rules. The two of them wrote an influential text on statistical mechanics, J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, John Wiley & Sons (1940).

where the b_p are known as *cluster integrals.* Use the thermodynamic relation $P = -(\partial F/\partial V)_{T,V}$ between the pressure and the free energy to show that B_n and b_{n-1} are related by

$$B_n = -\frac{n-1}{n}\, b_{n-1}. \tag{8.13}$$

□

The density expansion in (8.9) and (8.12) is among the few expansions known in physics that has a nonzero radius of convergence for a wide class of interparticle potentials. Most expansions, such as the low temperature expansion for the ideal Fermi gas, do not converge (see Section 6.11.2).

8.3 The Second Virial Coefficient

We first find the form of the second virial coefficient B_2 by simple considerations. One way is to calculate the partition function for a small number of particles and to determine the effects of including the interactions between particles. For $N = 2$ particles we have

$$\frac{Z_2}{Z_{\rm ideal}} = \frac{1}{V^2}\int e^{-\beta u_{12}}\, d\mathbf{r}_1 d\mathbf{r}_2, \tag{8.14}$$

where $Z_{\rm ideal}$ is the partition function for an ideal gas of two particles. We can simplify the integrals in (8.14) by choosing particle 1 as the origin and specifying the position of particle 2 relative to particle 1.[5] This choice of coordinates gives a factor of V because particle 1 can be anywhere in the box. Hence, we can write (8.14) as

$$\frac{Z_2}{Z_{\rm ideal}} = \frac{1}{V}\int e^{-\beta u(r)} d\mathbf{r}, \tag{8.15}$$

where $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ and $r = |\mathbf{r}|$.

Because we wish to describe a dilute gas, we might consider writing $e^{-\beta u} \approx 1 - \beta u$, thinking that u is small because the particles rarely interact. However, because $u(r) \gg 1$ for sufficiently small r, the integral $\int u(r) d\mathbf{r}$ diverges. That is, the particles rarely interact, but if they do, they interact strongly.

Another difficulty is that the function $e^{-\beta u(r)}$ in the integrand for Z_2 has the undesirable property that it approaches one rather than zero as $r \to \infty$. Because we want to obtain an expansion in the density, we want to write the integrand in (8.15) in terms of a function of r that is significant only if two particles are close to each other. Such a function is the Mayer function $f(r)$ defined in (8.11). Hence we write $e^{-\beta u(r)} = 1 + f(r)$ and express (8.15) as

$$\frac{Z_2}{Z_{\rm ideal}} = \frac{1}{V}\int \big[1 + f(r)\big]\, d\mathbf{r}. \tag{8.16}$$

In Problem 8.3 we show that $f(r) \to 0$ for sufficiently large r for short-range potentials.

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[5] This choice is equivalent to defining the coordinate system $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ and replacing $d\mathbf{r}_1\, d\mathbf{r}_2$ by $d\mathbf{R}\, d\mathbf{r}$. Because the integrand is independent of $\mathbf{R}$, we can do the integral over R and obtain a factor of V.

The first term in the integrand in (8.16) corresponds to no interactions and the second term corresponds to the second virial coefficient B_2 defined in (8.10a). To see this correspondence we choose particle 1 as the origin as before, and rewrite (8.10a) for B_2 as

$$B_2 = -\frac{1}{2}\int f(r)\, d\mathbf{r}. \tag{8.17}$$

If we compare the forms (8.16) and (8.17), we see that we can express $Z_2/Z_{\rm ideal}$ in terms of B_2:

$$\frac{Z_2}{Z_{\rm ideal}} = 1 - \frac{2}{V}B_2. \tag{8.18}$$

We next evaluate $Z_N/Z_{\rm ideal}$ for $N = 3$ particles. We have

$$\frac{Z_3}{Z_{\rm ideal}} = \frac{1}{V^3}\int e^{-\beta\sum u_{ij}}\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3 \tag{8.19a}$$

$$= \frac{1}{V^3}\int \prod_{i<j}(1 + f_{ij})\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3 \tag{8.19b}$$

$$= \frac{1}{V^3}\int \big[(1 + f_{12})(1 + f_{13})(1 + f_{23})\big]\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3 \tag{8.19c}$$

$$= \frac{1}{V^3}\int \big[1 + (f_{12} + f_{13} + f_{23}) + (f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23}) + f_{12}f_{13}f_{23}\big]\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3. \tag{8.19d}$$

If we keep only the first term in (8.19d), we recover the ideal gas result $Z/Z_{\rm ideal} = 1$. It is plausible that only the second sum in (8.19d) involving pairs of particles is important for low densities. Hence, we ignore the remaining terms involving products of two and three products of f. Because the three terms f_{12}, f_{13}, and f_{23} give the same contribution, we have

$$\frac{Z_3}{Z_{\rm ideal}} \approx 1 + \frac{3}{V}\int f(r)\, d\mathbf{r} = 1 - \frac{6}{V}B_2. \tag{8.20}$$

From the form of $Z_2/Z_{\rm ideal}$ and $Z_3/Z_{\rm ideal}$ we can guess the form of $Z_N/Z_{\rm ideal}$ which includes only the second virial coefficient:

$$\frac{Z_N}{Z_{\rm ideal}} \approx 1 - \frac{N(N-1)}{V}B_2. \tag{8.21}$$

Because $N - 1 \approx N$ for $N \gg 1$ and $\rho = N/V$, we have

$$\frac{Z_N}{Z_{\rm ideal}} \approx 1 - N\rho B_2, \tag{8.22}$$

which is the same form that we will now derive for large N. You might wish to skip to the discussion after (8.27).

For arbitrary N we have

$$\frac{Z_N}{Z_{\rm ideal}} = \frac{1}{V^N}\int e^{-\beta\sum u_{ij}}\, d\mathbf{r}_1\, d\mathbf{r}_2 \ldots d\mathbf{r}_N \tag{8.23a}$$

$$= \frac{1}{V^N}\int \prod_{i<j}(1 + f_{ij})\, d\mathbf{r}_1\, d\mathbf{r}_2 \ldots d\mathbf{r}_N. \tag{8.23b}$$

We write

$$\prod_{i<j}(1+f_{ij}) = 1 + \sum_{k<l} f_{kl} + \sum_{k<l,\ m<n} f_{kl}f_{mn} + \cdots\,. \tag{8.24}$$

We keep only the ideal gas contribution and the terms involving pairs of particles and ignore the remaining terms involving products of two or more f's. There are a total of $\frac{1}{2}N(N-1)$ terms in the sum $\sum f_{kl}$, corresponding to the number of ways of choosing pairs of particles. These terms are all equal because they differ only in the way the variables of integration are labeled. Hence, we can express the integral of the second sum in (8.24) as

$$\frac{1}{V^N}\int \sum_{k<l} f_{kl}\, d\mathbf{r}_1 \ldots d\mathbf{r}_N = \frac{1}{V^N}\frac{N(N-1)}{2}\int f(r_{12})\, d\mathbf{r}_1 \ldots d\mathbf{r}_N. \tag{8.25}$$

The integration with respect to $\mathbf{r}_3 \ldots \mathbf{r}_N$ over the volume of the system gives a factor of V^{N-2}.

As before, we can simplify the remaining integration over $\mathbf{r}_1$ and $\mathbf{r}_2$ by choosing particle 1 as the origin and specifying particle 2 relative to particle 1. In this way we obtain an additional factor of V. Hence, we can write the right-hand side of (8.25) as

$$\frac{N(N-1)}{2}\frac{V^{N-2}V}{V^N}\int f(r)\, d\mathbf{r} \to \frac{N^2}{2V}\int f(r)\, d\mathbf{r}, \tag{8.26}$$

where we have again replaced $N-1$ by N. We identify the integral in (8.26) with B_2 and write

$$\frac{Z_N}{Z_{\text{ideal}}} \approx 1 - N\rho B_2, \tag{8.27}$$

as in (8.22).

If the interparticle potential $u(r) \approx 0$ for $r > r_0$, then $f(r)$ differs from zero only for $r < r_0$ and the integral B_2 is bounded and is order r_0^3 in three dimensions (see Problem 8.4). Hence B_2 is independent of V and is an intensive quantity. This well-behaved nature of B_2 implies that the second term in (8.27) is proportional to N and in the limit $N \to \infty$ (for fixed density), this term is larger than the first – not a good start for a perturbation theory.

The reason we have obtained an apparent divergence in the density expansion of Z_N/Z_{ideal} is that we have calculated the wrong quantity. The quantity of physical interest is the free energy F or $\ln Z$, not the partition function Z. Because F is an extensive quantity and is proportional to N, it follows from the relation $F = -kT\ln Z$ that Z_N must depend on the Nth power of an intensive quantity. Hence, we expect the form of the density expansion of Z_N/Z_{ideal} to be

$$\frac{Z_N}{Z_{\text{ideal}}} = \big(1 + a_1\rho + a_2\rho^2 + \ldots\big)^N, \tag{8.28}$$

where a_n are unknown coefficients. Hence we should rewrite (8.27) as

$$\frac{Z_N}{Z_{\text{ideal}}} \approx (1 - \rho B_2)^N, \tag{8.29}$$

so that F is proportional to N and the correct first-order dependence on ρ is obtained. The free energy is given by

$$F = F_{\text{ideal}} - NkT\ln(1-\rho B_2) \approx F_{\text{ideal}} + NkT\rho B_2, \tag{8.30}$$

where we have used the fact that $\ln(1+x) \approx x$ for $x \ll 1$. The corresponding equation of state is given by

$$\frac{PV}{NkT} = 1 + \rho B_2, \tag{8.31}$$

where we have used the relation $P = -(\partial F/\partial V)_{T,N}$.

The second term in (8.31) represents the first-order density correction to the ideal gas equation of state. Because B_2 is order r_0^3, the density expansion for a dilute gas is actually an expansion in powers of the dimensionless quantity ρr_0^3 (see Problem 8.5).

Problem 8.3. Qualitative behavior of the Mayer function

Plot the Mayer function $f(r)$ for the hard core interaction (8.3) and the Lennard-Jones potential (8.2). Does $f(r)$ depend on T for hard spheres? What is the qualitative behavior of $f(r)$ for large r? ☐

Problem 8.4. Second virial coefficient for hard spheres

(a) To calculate B_2 in three dimensions we need to perform the angular integrations in (8.17). Show that, because $u(r)$ depends only on r, B_2 can be written as

$$B_2(T) = -\frac{1}{2}\int f(r)\, d^3r = 2\pi\int_0^\infty \big[1 - e^{-\beta u(r)}\big] r^2 dr. \tag{8.32}$$

(b) Show that $B_2 = 2\pi\sigma^3/3$ for a system of hard spheres of diameter σ.

(c) Determine the form of B_2 for a system of hard disks. ☐

Problem 8.5. Qualitative temperature behavior of $B_2(T)$

Suppose that $u(r)$ has the qualitative behavior shown in Figure 8.1; that is, $u(r)$ is repulsive for small r and weakly attractive for large r. Let r_0 equal the value of r at which $u(r)$ is a minimum (see Problem 8.1) and ϵ equal the value of u at its minimum. We can write (8.32) as

$$B_2(T) = 2\pi\int_0^{r_0} \big[1 - e^{-\beta u(r)}\big] r^2 dr + 2\pi\int_{r_0}^\infty \big[1 - e^{-\beta u(r)}\big] r^2 dr. \tag{8.33}$$

(a) For high temperatures, $kT \gg \epsilon$, we have $u(r)/kT \ll 1$ for $r > r_0$. Explain why the second integral in (8.33) can be neglected in this limit (assuming that the integral $\int_{r_0}^\infty u(r) r^2 dr$ converges) and why the dominant contribution to B_2 is determined by the first integral, for which the integrand is approximately one because $u(r)/kT$ is large and positive for $r < r_0$. Hence for high temperatures show that $B_2(T) \approx b$, where

$$b = 2\pi r_0^3/3. \tag{8.34}$$

We can interpret r_0 as a measure of the effective diameter of the atoms. How is the parameter b related to the "volume" of a particle?

(b) For low temperatures, $kT \ll \epsilon$, the dominant contribution to B_2 is determined by the second term in (8.33). What is the sign of $u(r)$ for $r > r_0$? Show that in this limit $B_2 \approx -a/kT$, where

$$a = -2\pi \int_{r_0}^{\infty} u(r)\, r^2 dr. \tag{8.35}$$

The parameter a is a measure of the strength of the attractive interaction between the particles.

(c) The limits considered in parts (a) and (b) suggest that B_2 can be approximated as

$$B_2 = b - \frac{a}{kT}, \tag{8.36}$$

where b is given by (8.34) and a is given by (8.35). Why does $B_2(T)$ pass through zero at some intermediate temperature? The temperature at which $B_2(T) = 0$ is known at the Boyle temperature. The temperature dependence of B_2 is explored further in Problem 8.30. ☐

Problem 8.6. The second-order virial coefficient for the van der Waals equation

Show that the van der Waals pressure equation of state (2.12) can be expressed as

$$\frac{PV}{NkT} = \frac{1}{1-\rho b} - \frac{a\rho}{kT}. \tag{8.37}$$

Expand the right-hand side of (8.37) in powers of ρ and find the form of B_2 implied by the van der Waals equation of state. ☐

Motivation of the van der Waals equation of state. In Problem 8.5 we found that B_2 can be written in the approximate form (8.36). This form of B_2 allows us to write the equation of state as [see (8.31)]

$$P \approx \frac{NkT}{V}\Big[1 + \rho b - \frac{\rho a}{kT}\Big], \tag{8.38a}$$

or

$$P \approx \rho kT\Big[\frac{1}{1-\rho b} - \frac{\rho a}{kT}\Big] = \frac{\rho kT}{1-\rho b} - \rho^2 a. \tag{8.38b}$$

We have made the approximation that $1+\rho b \approx 1/(1-\rho b)$, which is consistent with our assumption that $\rho b \ll 1$. The equation of state in (8.38b) is the van der Waals equation of state. A more systematic derivation of the van der Waals equation of state is given in Section 8.6.1.

Problem 8.7. Long-range interactions

Assume that $u(r)$ has the form $u(r) \sim r^{-n}$ for large r.

(a) What is the r dependence of $f(r)$ for large r?

(b) What is the condition on n such that the integral in (8.32) for B_2 exists? Consider the r dependence of the integrand of B_2 for large r only.

(c) Why is it plausible that the density expansion (8.8) is not applicable to a system of particles with a long-range interaction proportional to $1/r$ (the Coulomb potential)? ☐

8.4 *Diagrammatic Expansions

In Section 8.3 we found that we had to make some ad hoc assumptions to obtain the form of B_2 from an expansion of Z/Z_{ideal}. To find the form of the higher order virial coefficients more systematically, we will introduce a formalism that allows us to obtain a density expansion of the free energy directly rather than first approximating the partition function. In Section 8.4.2 we first obtain the expansion of the free energy in powers of the inverse temperature β. We find that it is convenient to represent the contributions to the free energy due to the interactions between particles in terms of diagrams. We rearrange this expansion in Section 8.4.3 so that it becomes an expansion in powers of the density ρ.

8.4.1 Cumulants

The form (8.8) for F_c is similar to that frequently encountered in probability theory (see Section 3.11.2, page 155). We define the function $\phi(t)$ as

$$\phi(t) \equiv \langle e^{tx} \rangle, \tag{8.39}$$

where the random variable x occurs according to the probability distribution $p(x)$, that is, the average denoted by $\langle \ldots \rangle$ is over $p(x)$. The function $\phi(t)$ is an example of a *moment generating function* because a power series expansion in t yields

$$\phi(t) = \Big\langle \big[1 + tx + \frac{1}{2!}t^2x^2 + \cdots\big] \Big\rangle \tag{8.40a}$$

$$= 1 + t\langle x \rangle + \frac{t^2}{2!}\langle x^2 \rangle + \cdots \tag{8.40b}$$

$$= \sum_{n=0}^{\infty} \frac{t^n \langle x^n \rangle}{n!}. \tag{8.40c}$$

In the present case the quantity of interest is proportional to $\ln Z$, so we want to consider the series expansion of $\ln \phi$ rather than ϕ. (The correspondence is $t \to -\beta$ and $x \to U$.) The series expansion of $\ln \phi(t)$ can be written in the form

$$\ln \phi = \ln \langle e^{tx} \rangle = \sum_{n=1}^{\infty} \frac{t^n M_n(x)}{n!}, \tag{8.41}$$

where the coefficients M_n are known as *cumulants*. The first four cumulants are

$$M_1 = \langle x \rangle, \tag{8.42a}$$

$$M_2 = \langle x^2 \rangle - \langle x \rangle^2, \tag{8.42b}$$

$$M_3 = \langle x^3 \rangle - 3\langle x^2 \rangle \langle x \rangle + 2\langle x \rangle^3, \tag{8.42c}$$

$$M_4 = \langle x^4 \rangle - 4\langle x^3 \rangle \langle x \rangle - 3\langle x^2 \rangle^2 + 12\langle x^2 \rangle \langle x \rangle^2 - 6\langle x \rangle^4. \tag{8.42d}$$

Problem 8.8. The first four cumulants

Expand $\ln(1+x)$ in a Taylor series [see (**??**)] and obtain the expressions for M_n given in (8.42). $\square$

The advantage of working with cumulants can be seen by considering two independent random variables x and y. Because x and y are statistically independent, we have $\langle xy\rangle = \langle x\rangle\langle y\rangle$, and

$$\ln\big\langle e^{t(x+y)}\big\rangle = \ln\big[\big\langle e^{tx}\big\rangle\big\langle e^{ty}\big\rangle\big] = \ln\big\langle e^{tx}\big\rangle + \ln\big\langle e^{ty}\big\rangle. \tag{8.43}$$

From the relation

$$\ln\big\langle e^{t(x+y)}\big\rangle = \sum_{n=0}^{\infty} \frac{t^n}{n!} M_n(x+y), \tag{8.44}$$

we see that M_n satisfies the additive property:

$$M_n(x+y) = M_n(x) + M_n(y). \tag{8.45}$$

The relation (8.45) implies that all cross terms in M_n involving independent variables vanish, and hence $\ln\phi(x)$ is an extensive or additive quantity.

Example 8.1. Cancellation of cross terms in M_2

Show that the cross terms cancel in M_2.

Solution. We have

$$\begin{aligned}
M_2(x+y) &= \big\langle (x+y)^2\big\rangle - \big\langle (x+y)\big\rangle^2 && (8.46\text{a})\\
&= \big\langle x^2\big\rangle + \cancel{2\langle x\rangle\langle y\rangle} + \big\langle y^2\big\rangle - \big\langle x\big\rangle^2 - \cancel{2\langle x\rangle\langle y\rangle} - \big\langle y\big\rangle^2 && (8.46\text{b})\\
&= \big\langle x^2\big\rangle - \big\langle x\big\rangle^2 + \big\langle y^2\big\rangle - \big\langle y\big\rangle^2 && (8.46\text{c})\\
&= M_2(x) + M_2(y). && (8.46\text{d})
\end{aligned}$$

$\diamondsuit$

Problem 8.9. Cancellation of cross terms in M_3

As an example of the cancellation of cross terms, consider $M_3(x+y)$. From (8.42c) we see that $M_3(x+y)$ is given by

$$M_3(x+y) = \big\langle (x+y)^3\big\rangle - 3\big\langle (x+y)^2\big\rangle\big\langle (x+y)\big\rangle + 2\big\langle (x+y)\big\rangle^3. \tag{8.47}$$

Show explicitly that all cross terms cancel and hence that $M_3(x+y) = M_3(x) + M_3(y)$. $\square$

8.4.2 High temperature expansion

Now that we have discussed the formal properties of the cumulants, we can use these properties to evaluate F_c. According to (8.8) and (8.41) we can write F_c as

$$-\beta F_c = \ln\big\langle e^{-\beta U}\big\rangle_0 = \sum_{n=1}^{\infty} \frac{(-\beta)^n}{n!} M_n. \tag{8.48}$$

The expansion (8.48) in powers of β is known as a *high temperature expansion.* Such an expansion is natural because β is the only parameter that appears explicitly in (8.48). The parameter β actually appears in the dimensionless combination βu_0, where the energy u_0 is a measure of the strength of the interaction. Although we can choose β to be as small as we wish, the interparticle interaction for potentials such as the Lennard-Jones potential is strongly repulsive at short distances (see Figure 8.1), and hence u_0 is not well defined. For this reason a strategy based on expanding in the parameter β is not physically reasonable for an interaction such as the Lennard-Jones potential.

Because of these difficulties, we will first do what we can and then do what we want. Thus we will first determine the high temperature expansion coefficients M_n and assume that the potential is not strongly repulsive for small r. For example, we can choose $u(r)$ to have the form $u(r) = u_0 e^{-r^2/a^2}$ for small r. Then we will find that we can reorder the high temperature expansion to obtain a power series expansion in the density. Because it will be easy to become lost in the details, we emphasize that the main points of this section are the association of diagrams with the various contributions to the cumulants and the fact that only certain kinds of diagrams actually contribute to the free energy.

The first cumulant in the expansion (8.48) is the average of the total potential energy:

$$M_1 = \langle U \rangle = \frac{1}{V^N}\int \sum_{i<j} u_{ij}\, d\mathbf{r}_1\, d\mathbf{r}_2 \ldots d\mathbf{r}_N. \tag{8.49}$$

Because every term in the sum gives the same contribution, we have

$$\begin{aligned} M_1 &= \frac{1}{2}N(N-1)\frac{1}{V^N}\int u_{12}\, d\mathbf{r}_1\, d\mathbf{r}_2 \ldots d\mathbf{r}_N && \text{(8.50a)}\\ &= \frac{1}{2}N(N-1)\frac{1}{V^N}V^{N-2}\int u_{12}\, d\mathbf{r}_1\, d\mathbf{r}_2 && \text{(8.50b)}\\ &= \frac{1}{2}N(N-1)\frac{1}{V^2}\int u_{12}\, d\mathbf{r}_1\, d\mathbf{r}_2. && \text{(8.50c)} \end{aligned}$$

The combinatorial factor $\frac{1}{2}N(N-1)$ is the number of terms in the sum. Because we are interested in the limit $N \to \infty$, we replace $N-1$ by N. We can simplify (8.50c) further by measuring the position of particle 2 from particle 1. We obtain

$$M_1 = \frac{N^2}{2V^2}V\int u(r)\, d\mathbf{r}, \tag{8.51a}$$

or

$$M_1 = \frac{\rho}{2}N\int u(r)\, d\mathbf{r}. \tag{8.51b}$$

Note that M_1 is an extensive quantity as is the free energy; that is, M_1 is proportional to N. Note that the integral in (8.51b) diverges for small r for the Lennard-Jones potential (8.2) and the hard core interaction (8.3), but converges for a Gaussian potential.

We next consider M_2, which is given by

$$M_2 = \langle U^2 \rangle - \langle U \rangle^2, \tag{8.52}$$

where

$$\langle U\rangle = \sum_{i<j}\sum_{j}\langle u_{ij}\rangle \tag{8.53}$$

and

$$\langle U^2\rangle = \sum_{i<j}\sum_{j}\sum_{k<l}\sum_{l}\langle u_{ij}\,u_{kl}\rangle. \tag{8.54}$$

The various terms in (8.54) and (8.53) may be classified according to the number of subscripts in common. As an example, consider a system of $N = 4$ particles. We have

$$U = \sum_{i<j=1}^{N=4} u_{ij} = u_{12} + u_{13} + u_{14} + u_{23} + u_{24} + u_{34} \tag{8.55}$$

and

$$\begin{aligned}U^2 = \big[&u_{12}^2 + u_{13}^2 + u_{14}^2 + u_{23}^2 + u_{24}^2 + u_{34}^2]\\ &+ 2[u_{12}u_{13} + u_{12}u_{14} + u_{12}u_{23} + u_{12}u_{24} + u_{13}u_{14} + u_{13}u_{23}\\ &+ u_{13}u_{34} + u_{14}u_{24} + u_{14}u_{34} + u_{23}u_{24} + u_{23}u_{34} + u_{24}u_{34}]\\ &+ 2[u_{12}u_{34} + u_{13}u_{24} + u_{14}u_{23}\big].\end{aligned} \tag{8.56}$$

An inspection of (8.56) shows that the 36 terms in (8.56) can be grouped into three classes:

1. *No indices in common (disconnected terms).* A typical disconnected term is $\langle u_{12}u_{34}\rangle$. Because the variables $\mathbf{r}_{12}$ and $\mathbf{r}_{34}$ are independent, u_{12} and u_{34} are independent, and we can write

$$\langle u_{12}u_{34}\rangle = \langle u_{12}\rangle\langle u_{34}\rangle. \tag{8.57}$$

From (8.45) we know that every disconnected term such as the one in (8.57) is a cross term that is canceled if all terms in M_2 are included.

2. *One index in common (reducible terms).* An example of a reducible term is $\langle u_{12}u_{23}\rangle$. Such a term also factorizes because of the homogeneity of space. We choose particle 2 as the origin and integrate over $\mathbf{r}_1$ and $\mathbf{r}_3$ and find

$$\langle u_{12}u_{23}\rangle = \frac{1}{V^3}\int u_{12}\,u_{23}\,d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3 \tag{8.58a}$$

$$= \frac{1}{V^2}\int u_{12}\,u_{23}\,d\mathbf{r}_{12}\,d\mathbf{r}_{23} \tag{8.58b}$$

$$= \langle u_{12}\rangle\langle u_{23}\rangle. \tag{8.58c}$$

A factor of V was obtained because particle 2 can be anywhere in the box of volume V. Again we find that the variables $u_{12}u_{23}$ are independent and hence are canceled by other terms in M_2.

3. *Both pairs of indices in common (irreducible terms).* An example of an irreducible term is $\langle u_{12}^2\rangle$. The corresponding contribution to M_2 is [see (8.52)]

$$M_2 = \sum_{i<j=1}^{N}\big[\langle u_{ij}^2\rangle - \langle u_{ij}\rangle^2\big]. \tag{8.59}$$

We can simplify (8.59) by comparing the magnitudes of the two types of terms in the limit $N \to \infty$. We have that

$$\langle u_{ij}^2 \rangle = \frac{1}{V}\int u_{ij}^2 \, d\mathbf{r}_{ij} \propto \frac{1}{V} \propto O\Big(\frac{1}{N}\Big), \tag{8.60a}$$

$$\langle u_{ij} \rangle^2 = \Big(\frac{1}{V}\int u_{ij} \, d\mathbf{r}_{ij}\Big)^2 \propto O\Big(\frac{1}{N^2}\Big). \tag{8.60b}$$

We see that we can ignore the second term in comparison to the first.

These considerations lead us to the desired form of M_2. Because there are $N(N-1)/2$ identical contributions such as (8.60a) to M_2 in (8.59), we obtain

$$M_2 = \frac{N(N-1)}{2V}\int u^2(\mathbf{r}) \, d\mathbf{r} \to \frac{\rho}{2}N\int u^2(\mathbf{r}) \, d\mathbf{r}. \tag{8.61}$$

The most important result of our evaluation of M_1 and M_2 is that the disconnected and reducible contributions do not contribute. The vanishing of the disconnected contributions is essential for M_n and thus for F_c to be an extensive quantity. For example, consider the contribution $\sum_{i<j,k<l} \langle u_{ij}\rangle\langle u_{kl}\rangle$ for $i \neq j \neq k \neq l$. As we saw in (8.60b), each $\langle u_{ij}\rangle$ is order $1/V$. Because each index is different, the number of terms is $\sim N^4$ and hence the order of magnitude of this type of contribution is $N^4/V^2 \sim N^2$. (Recall that $N/V = \rho$ is finite.) Because the presence of the disconnected terms in M_2 would imply that F_c would be proportional to N^2 rather than N, it is necessary that this spurious N dependence cancel exactly. The fact that the disconnected terms do not contribute to F_c was first shown for a classical system of particles by Joseph Mayer in 1937. The corresponding result was not established for a quantum system of particles until 1957.[6]

The reducible terms also vanish but do not lead to a spurious N dependence. As an example, consider the term $\langle u_{ij}u_{jk}u_{kl}\rangle$ with four distinct indices. We can choose relative coordinates and show that $\langle u_{ij}u_{jk}u_{kl}\rangle = \langle u_{ij}\rangle\langle u_{jk}\rangle\langle u_{kl}\rangle$, and hence is canceled for a classical gas. The N dependence of this term is $N^4/V^3 \sim N$. The reducible terms do not cancel for quantum systems.

Problem 8.10. The first two cumulants for a system of four particles

Consider a system of $N = 4$ particles and obtain the explicit form of M_2. Show that the disconnected and reducible contributions cancel. ☐

To simplify the calculation of the higher order cumulants and to understand the difference between the disconnected, reducible, and irreducible terms, it is convenient to introduce a graphical notation that corresponds to the various contributions to M_n. As we have seen, we do not need to consider products of expectation values because they either cancel or are $O(1/N)$ relative to the irreducible terms arising from the first term in M_n. The rules for the calculation of M_n can be stated in graphical terms as follows:

1. For each particle (subscript on u) draw a vertex (a point).

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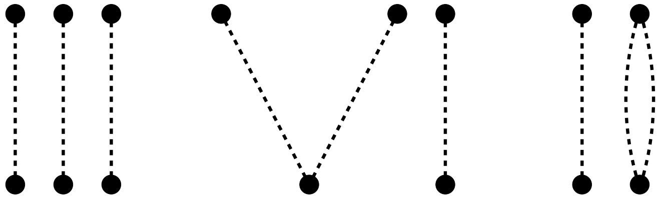
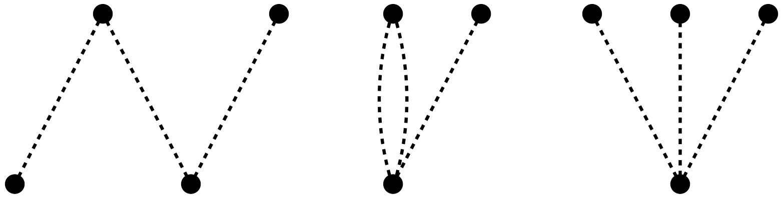
[6] K. A. Brueckner, "Many-body problem for strongly interacting particles. II. Linked cluster expansion," Phys. Rev. **100**, 36–45 (1955); J. Goldstone, "Derivation of Brueckner many-body theory," Proc. Roy. Soc. A **239**, 267–279 (1957). The latter paper uses Feynman diagrams. A more accessible introduction to Feynman diagrams is given by Mattuck [1992].



(a) (b) (c)

Figure 8.2: Examples of disconnected diagrams with three (potential) bonds. The potential (u) bonds are represented by dotted lines and the vertices are represented by filled circles.



(a) (b) (c)

Figure 8.3: Examples of reducible diagrams with three (potential) bonds.

2. Draw a bond (a dotted line) between two vertices. There is a total of n bonds among p vertices, where $2 \leq p \leq n$.
3. If the diagram contains two or more pieces not joined by a bond, then the diagram is *disconnected*. If the diagram can be separated into two disconnected pieces by removing one vertex, then the diagram is *reducible*. The remaining diagrams are *irreducible* and are the only ones that need to be considered.

Examples of various types of disconnected and reducible diagrams are shown in Figs. 8.2–8.4 corresponding to M_3.

It is now straightforward to find the contributions to M_3 corresponding to the two irreducible diagrams shown in Figure 8.4. There are $\frac{1}{2}N(N-1)$ identical contributions of type shown in Figure 8.4(a) and $N(N-1)(N-2)$ of the type shown in Figure 8.4(b). Hence, the form of M_3 in the limit $N \to \infty$ is

$$\frac{M_3}{N} = \frac{\rho}{2}\int u^3(\mathbf{r})\, d\mathbf{r} + \rho^2\int u_{12}\, u_{23}\, u_{31}\, d\mathbf{r}_{12}\, d\mathbf{r}_{23}. \tag{8.62}$$

Problem 8.11. N and V dependence of the diagrams in Figures 8.2–8.4

Verify the N and V dependence of the diagrams in Figures 8.2–8.4 as summarized in Table 8.1. ☐

Problem 8.12. Example of a high temperature expansion

Consider the potential $u(r) = u_0 e^{-\alpha r^2}$, which is finite for small r and goes to zero for large r. For this reason the various integrals for the cumulants are finite and a high temperature expansion is

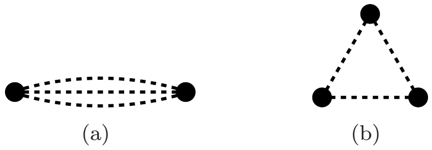

(a) (b)

Figure 8.4: The two irreducible diagrams with three (potential) bonds.

Figure	V dependence	number of terms in the sum	contribution
8.2(a)	V^{-3}	$O(N^6)$	$O(N^3)$
8.2(b)	V^{-3}	$O(N^5)$	$O(N^2)$
8.2(c)	V^{-2}	$O(N^4)$	$O(N^2)$
8.3(a)	V^{-3}	$O(N^4)$	$O(N)$
8.3(b)	V^{-2}	$O(N^3)$	$O(N)$
8.3(c)	V^{-3}	$O(N^4)$	$O(N)$
8.4(a)	V^{-1}	$O(N^2)$	$O(N)$
8.4(b)	V^{-2}	$O(N^3)$	$O(N)$

Table 8.1: Summary of the volume dependence, the number of terms, and the contribution of each of the diagrams in Figures 8.2–8.4.

possible. The high temperature expansion of F_c for this potential is equivalent to expanding in the dimensionless ratio u_0/kT.

(a) Explain why an expansion in powers of u_0/kT is equivalent to grouping the irreducible diagrams according to their number of bonds.

(b) Draw the irreducible diagrams and give the corresponding integrals that contribute to F_c through order $(u_0/kT)^4$. Don't worry about the combinatorial factors.

8.4.3 Density expansion

We saw in Section 8.4.2 that the calculation of M_n can be reduced to enumerating all irreducible diagrams with n bonds and p vertices, where $2 \leq p \leq n$. The expansion (8.48) is a high temperature expansion in powers of u_0/kT; that is, the irreducible diagrams associated with M_n have n bonds. We now show how the high temperature expansion can be reordered so that we obtain an expansion in the density ρ or in the number of vertices p.

Consider an irreducible diagram of n bonds and p vertices. An example is shown in Figure 8.4(a) for $p = 2$ and $n = 3$. The p vertices correspond to p particles and yield a factor of N^p/V^p. One of the integrations can be performed immediately by choosing one of the vertices to be the origin. Hence an irreducible diagram with p vertices contributes a term that is order N^p/V^{p-1}, leading to an order ρ^{p-1} contribution to F_c/N. Hence, a classification of the diagrams according to the number of bonds corresponds to a high temperature expansion, and a classification according to the number of vertices is equivalent to a density expansion. That is, by summing all diagrams with a given number of vertices, the high temperature expansion (8.48) can be converted

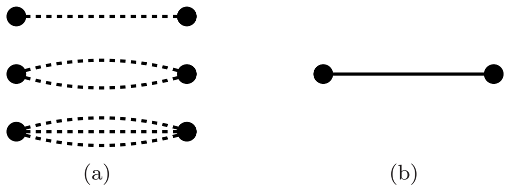


Figure 8.5: (a) The first several irreducible diagrams with two vertices and $n = 1$, 2, and 3 potential bonds (dotted lines). (b) The equivalent diagram with one Mayer f bond (solid line).

to an expansion in the density. The result is traditionally written in the form [see (8.12)]

$$-\beta\frac{F_c}{N} = \sum_{p=1}^{\infty}\frac{b_p\,\rho^p}{p+1}. \tag{8.63}$$

In the following we will find the form of the first few cluster integrals b_p.

We first add the contribution of all the two-vertex diagrams to find b_1 [see Figure 8.5(a)]. From (8.48) we see that a factor of $-\beta$ is associated with each bond. The contribution to $-\beta F_c$ from all two-vertex irreducible diagrams is

$$\sum_{n=1}^{\infty}\frac{(-\beta)^n}{n!}M_n = N\frac{\rho}{2}\sum_{n=1}^{\infty}\frac{(-\beta)^n}{n!}\int u^n(\mathbf{r})\,d\mathbf{r} = N\frac{\rho}{2}\int(e^{-\beta u(\mathbf{r})}-1)\,d\mathbf{r}. \tag{8.64}$$

Because $B_2 = -\frac{1}{2}b_1$ [see (8.13)], we recover the result (8.32) that we found in Section 8.2 by a plausibility argument. Note the appearance of the Mayer f function in (8.64) and that f emerges by summing an infinite number of potential bonds between two particles.

We can now simplify the diagrammatic expansion by replacing the infinite sum of u (potential) bonds between any two particles by f. For example, b_1 corresponds to the single diagram shown in Figure 8.5(b), where the solid line represents the Mayer f function.

To find b_2 we consider the set of all irreducible diagrams with 3 vertices. Some of the diagrams with u bonds are shown in Figure 8.6(a). By considering all the possible combinations of the u bonds, we can sum up all the irreducible diagrams with three vertices with l_{12}, l_{23}, and l_{31} bonds. Instead, we will use our intuition and replace the various combinations of u bonds between two vertices by a single f bond between any two vertices as shown in Figure 8.6(b). The corresponding contribution to b_2 is

$$b_2 = \frac{1}{2!}\int f_{12}f_{23}f_{31}\,d\mathbf{r}_{12}\,d\mathbf{r}_{23}. \tag{8.65}$$

It can be shown that b_p is the sum over all topologically distinct irreducible diagrams among $p+1$ vertices. For example, b_3 corresponds to the four-vertex diagrams shown in Figure 8.7. The corresponding result for b_3 is

$$b_3 = \frac{1}{3!}\int(3f_{12}f_{23}f_{34}f_{41} + 6f_{12}f_{23}f_{34}f_{41}f_{13} + f_{12}f_{23}f_{34}f_{41}f_{13}f_{24})\,d\mathbf{r}_2\,d\mathbf{r}_3\,d\mathbf{r}_4. \tag{8.66}$$

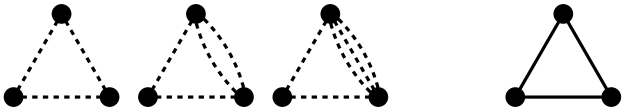

(a) (b)

Figure 8.6: (a) The first several irreducible diagrams with three vertices and various numbers of u bonds (dotted lines). (b) The corresponding diagram with f-bonds (solid lines).

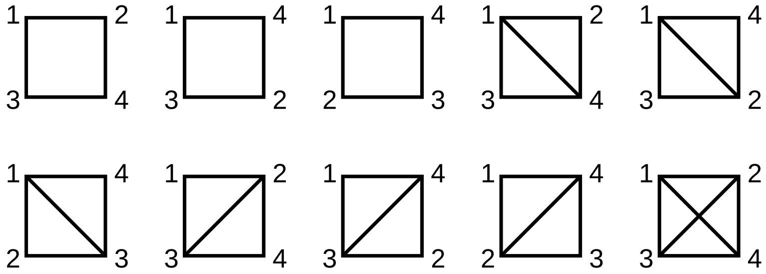


Figure 8.7: The four-vertex diagrams with all the possible different labelings. Note that the bonds are f bonds.

We see that we have converted the original high temperature expansion to a density expansion for the free energy by summing what are known as *ladder diagrams.* These diagrams correspond to all the possible u bonds between any two particles (vertices). The result of this sum is the Mayer f function.

The procedure for finding higher order terms in the density expansion of the free energy is straightforward in principle. To find the contribution of order ρ^{p-1}, we enumerate all the irreducible diagrams with p vertices and various numbers of f bonds. There is only one f bond between any two vertices. The enumeration of the cluster integrals b_p becomes more and more tedious for larger p, and it becomes increasingly difficult to determine the combinatorial factors such as the factors of 3, 6, and 1 in (8.66).

8.4.4 Higher order virial coefficients for hard spheres

The values of the first six virial coefficients (not counting $B_1 = 1$) for hard spheres are given in Table 8.2 in terms of the dimensionless parameter

$$\eta = \pi\rho\sigma^3/6, \tag{8.67}$$

where σ is the diameter of the spheres. The parameter η can be expressed as

$$\eta = \frac{N\dfrac{4\pi}{3}\Big(\dfrac{\sigma}{2}\Big)^3}{V} = \rho\frac{4\pi}{3}\Big(\frac{\sigma}{2}\Big)^3. \tag{8.68}$$

The form of (8.68) shows that η is the fraction of the space occupied by N spheres. For this reason η is called the *packing fraction.* The second virial coefficient B_2 was calculated in Problem 8.4 for hard

virial coefficient	magnitude
ρB_2	$\frac{2}{3}\pi\rho\sigma^3 = 4\eta$
$\rho^2 B_3$	$\frac{5}{18}\pi^2\rho^2\sigma^6 = 10\eta^2$
$\rho^3 B_4$	$18.365\eta^3$
$\rho^4 B_5$	$28.24\eta^4$
$\rho^5 B_6$	$39.5\eta^5$
$\rho^6 B_7$	$56.5\eta^6$

Table 8.2: The values of the first six virial coefficients for hard spheres.

spheres, and the third virial coefficient B_3 is calculated analytically in Section 8.9.1. Boltzmann calculated the fourth-order virial coefficient B_4 in 1899 by considering the excluded volume due to the finite size of the hard spheres. Because formal expressions for the virial coefficients did not exist then, his calculation was based on physical insight and was not confirmed until 1952. Calculations of the hard sphere virial coefficients for $n > 4$ must be done numerically and their values are now known through B_{12}.

Problem 8.13. Density of close packing

Because a system of hard disks and hard spheres cannot overlap, there is a well-defined density of close packing.

(a) The maximum packing density of a system of hard disks corresponds to a hexagonal lattice with each disk touching its six nearest neighbors. Show that in this arrangement $\rho_{\max}\sigma^2 = 2/3^{1/2} \approx 1.1547$ and the corresponding value of η is $\eta_{\max} = \frac{1}{6}\sqrt{3}\pi \approx 0.9069$. This number follows from the ratio of the area of the disk of diameter σ to the area of the circumscribing hexagon whose side equals $\sigma/\sqrt{3}$.[7]

(b) *Show that the maximum packing density of a system of hard spheres is equal to $\rho_{\max} = \sigma^3/\sqrt{2}$, assuming a face centered cubic lattice. What is the corresponding maximum value of η? □

Problem 8.14. Carnahan-Starling equation of state

From the results shown in Table 8.2 we can write the equation of state of a system of hard spheres as

$$\frac{PV}{NkT} = 1 + \sum_{s=1}^{6} C_s \eta^s \tag{8.69a}$$

$$= 1 + 4\eta + 10\eta^2 + 18.365\eta^3 + 28.24\eta^4 + 39.5\eta^5 + 56.5\eta^6. \tag{8.69b}$$

(a) Show that the coefficients C_s can be written in the approximate form $C_s = 3s + s^2$ and that this form of C_s implies that

$$\frac{PV}{NkT} = 1 + \sum_{s=1}^{\infty}(3s + s^2)\eta^s. \tag{8.70}$$

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[7] See for example, C. A. Rogers, *Packing and Covering*, Cambridge University Press (1964), Chapter 1.

(b) Do the sum in (8.70) and show that

$$\frac{PV}{NkT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3}. \tag{8.71}$$

[Hint: start with the infinite sum $\sum_{s=0}^{\infty} \eta^s = (1-\eta)^{-1}$ and take derivatives of both sides with respect to η.] The form (8.71) is known as the Carnahan-Starling equation of state and is a good approximation to the equation of state found by Monte Carlo simulations.

(c) Use the Carnahan-Starling equation of state (8.71) to derive analytical expressions for the entropy S, energy E, and Helmholtz free energy F for a hard sphere fluid. ☐

The virial coefficients for a gas of particles interacting via the Lennard-Jones potential can be calculated numerically (see Problem 8.30 for a calculation of B_2).

8.5 The Radial Distribution Function

Now that we know how to include the interactions between particles to obtain the equation of state of a dilute gas, we consider how these interactions lead to correlations between the particles. We know that if the interactions are neglected, the positions of the particles are uncorrelated, and the probability of finding a particle a distance r away from a particular particle is proportional to the density ρ. In the following, we will introduce the *radial distribution function* $g(r)$ as a measure of the correlations between particles due to their interactions. This function is analogous to the spin-spin correlation function introduced in Section 5.5.2.

Suppose that we choose the origin of our coordinate system at a particular particle (say particle 1). Then the quantity $\rho g(r) d\mathbf{r}$ is defined as the mean number of particles that are within the distance $\mathbf{r}$ and $\mathbf{r} + d\mathbf{r}$ from the origin. That is,

$$\rho g(r) = \text{mean local density a distance } r \text{ from a given particle.} \tag{8.72}$$

If the gas is dilute, we need to consider only the effect of the interactions between particle 1 and any other particle and ignore the effects of all the other particles. Because the energy of interaction between two particles is $u(r)$, the form of $g(r)$ for a dilute gas is given by

$$g(r) = e^{-\beta u(r)} \qquad \text{(dilute gas)}, \tag{8.73}$$

where $e^{-\beta u(r)}$ is the probability that another particle is a distance r away. We will derive the low density limit (8.73) in the following. Note that if $u(r) = 0$, then $g(r) = 1$, and the mean local density equals the mean density ρ.

The radial distribution function $g(r)$ is important because it can be measured experimentally and in simulations, and because the mean energy and mean pressure can be calculated from $g(r)$. We will show that the mean energy is given by

$$E = \frac{3}{2}NkT + \frac{\rho}{2}N\int_0^{\infty} u(r)g(r)\, 4\pi r^2 dr, \tag{8.74}$$

and the mean pressure is given by

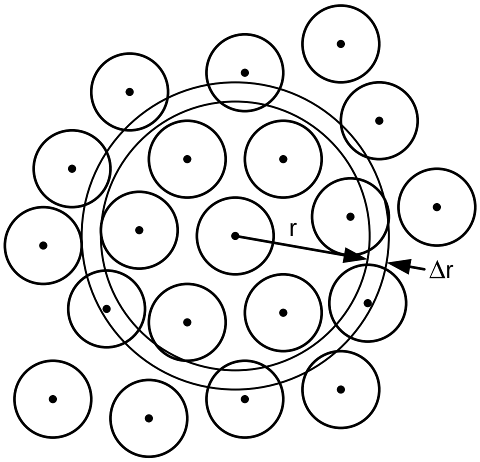

Figure 8.8: The radial distribution function is determined by counting how many particles are within a distance r to $r + \Delta r$ from a given particle.

$$\frac{PV}{NkT} = 1 - \frac{\rho}{6kT} \int_0^\infty r \frac{du(r)}{dr} g(r)\, 4\pi r^2 dr. \tag{8.75}$$

The two terms in (8.74) are the mean kinetic energy and the mean potential energy, respectively. To understand the interpretation of the second term we note that the interaction energy between a particular particle and all other particles between r and $r + dr$ is $u(r)\rho g(r) 4\pi r^2 dr$ (in three dimensions), where $\rho g(r) d\mathbf{r}$ is the local number of particles. The total potential energy is found by integrating over all r and multiplying by $N/2$. The factor of N is included because any of the N particles can be chosen as the particle at the origin; the factor of $1/2$ accounts for the fact that each pair interaction is counted only once.

We can gain more insight into the meaning of the radial distribution function by considering how to compute it for a given configuration of particles in two dimensions. Choose a particle as the origin and draw two concentric circles (spheres in three dimensions), one of radius r and the other of radius $r + \Delta r$ (see Figure 8.8). Count the number of atoms $n(r)$ between r and $r + \Delta r$. Then divide $n(r)$ by the area (volume) $\pi(r + \Delta r)^2 - \pi r^2 \approx 2\pi r \Delta r$ between r and $r + \Delta r$ and the average density of particles. The result is $g(r)$ for one configuration.

$$g(r) = \frac{n(r)}{\rho 2\pi r \Delta r} \qquad \text{(two dimensions).} \tag{8.76}$$

We obtain better statistics by choosing each particle as the origin for a given configuration of particles and by averaging over many configurations.

The qualitative features of $g(r)$ for a system of hard disks are shown in Figure 8.9. We see that $g(r < \sigma) = 0$ because of the presence of the hard core. At large r the other particles are not correlated with the fixed particle at the origin and $g(r) \to 1$ as $r \to \infty$. The properties of $g(r)$ for a system of hard disks at various densities and a Lennard-Jones system of particles at various densities and temperatures are explored in Problem 8.15.

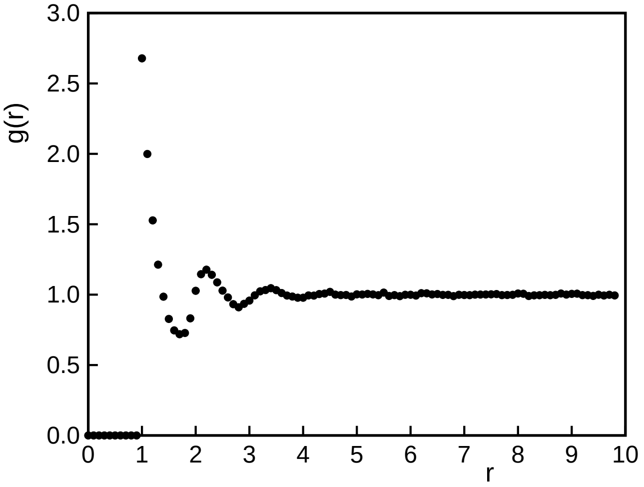

Figure 8.9: Dependence of $g(r)$ on r for a system of $N = 256$ hard disks at a density of $\rho\sigma^2 = 0.64$. What is the meaning of the peaks of $g(r)$?

Problem 8.15. Qualitative behavior of $g(r)$

Use either molecular dynamics (Programs `LJ2DMD` and `HardDisksMD`) or Monte Carlo (Programs `LJ2DMetropolis` and `HardDisksMetropolis`) methods to simulate the static properties of a system of hard disks and particles interacting with the Lennard-Jones potential to determine the behavior of $g(r)$ for various densities and temperatures. We consider two-dimensional systems because they are easier to visualize.

(a) Consider a system of hard disks and describe how $g(r)$ changes with the density ρ. Both the Monte Carlo and molecular dynamics programs use units such that the hard core diameter $\sigma = 1$. Is the temperature of the system relevant?

(b) Consider a system of particles interacting with the Lennard-Jones potential (8.2) at the same densities (and number of particles) as you considered in part (a). How does $g(r)$ for the two systems compare at the same density? How does $g(r)$ change with temperature for a given ρ?

(c) Choose either interaction and describe how $g(r)$ changes as the density is increased. What is the meaning of the peaks in $g(r)$? ☐

****More formal considerations***. To define $g(r)$ more formally[8] we introduce the probability of a configuration of N particles in a volume V in equilibrium with a heat bath at temperature T:

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[8] An alternative way of defining $g(r)$ in terms of the spatial correlations of the density fluctuations is given in Section 8.9.2.

$$P_N(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\, d\mathbf{r}_1\, d\mathbf{r}_2 \ldots d\mathbf{r}_N = \frac{e^{-\beta U} d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N}{\int e^{-\beta U} d\mathbf{r}_1\, d\mathbf{r}_2 \ldots d\mathbf{r}_N} \tag{8.77a}$$

$$= \frac{e^{-\beta U} d\mathbf{r}_1\, d\mathbf{r}_2 \ldots d\mathbf{r}_N}{Q_N}, \tag{8.77b}$$

where U is the total potential energy of the configuration. The quantity $P_N\, d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N$ is the probability that particle 1 is in the range $d\mathbf{r}_1$ about $\mathbf{r}_1$, particle 2 is in the range $d\mathbf{r}_2$ about $\mathbf{r}_2$, etc. Note that the probability density $P_N(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ is properly normalized.

It is convenient to define the *configuration integral* Q_N as

$$Q_N = \int e^{-\beta U}\, d\mathbf{r}_1\, d\mathbf{r}_2 \ldots d\mathbf{r}_N. \tag{8.78}$$

The configuration integral Q_N is related to the partition function Z_N by

$$Q_N = Z_N/(N!\, \lambda^{3N}). \tag{8.79}$$

Q_N is defined so that $Q_N = V^N$ for an ideal gas.

The probability that particle 1 is in the range $d\mathbf{r}_1$ about $\mathbf{r}_1$ and particle 2 is in the range $d\mathbf{r}_2$ about $\mathbf{r}_2$ is obtained by integrating (8.77) over the positions of particles 3 through N:

$$P_2(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_1 d\mathbf{r}_2 = \frac{\int e^{-\beta U} d\mathbf{r}_3 \ldots d\mathbf{r}_N}{Q_N} d\mathbf{r}_1 d\mathbf{r}_2. \tag{8.80}$$

The probability that *any* particle is in the range $d\mathbf{r}_1$ about $\mathbf{r}_1$ and any other particle is in the range $d\mathbf{r}_2$ about $\mathbf{r}_2$ is $N(N-1)P_2\, d\mathbf{r}_1 d\mathbf{r}_2$. The *pair distribution function* $g(\mathbf{r}_1, \mathbf{r}_2)$ is defined as

$$\rho^2 g(\mathbf{r}_1, \mathbf{r}_2) = N(N-1)P_2 = N(N-1)\frac{\int e^{-\beta U} d\mathbf{r}_3 \ldots d\mathbf{r}_N}{Q_N}. \tag{8.81}$$

We use $\rho = N/V$ to write g as

$$g(\mathbf{r}_1, \mathbf{r}_2) = \Big(1 - \frac{1}{N}\Big)\frac{V^2 \int e^{-\beta U} d\mathbf{r}_3 \ldots d\mathbf{r}_N}{Q_N}. \tag{8.82}$$

If the interparticle interaction is spherically symmetric and the system is a fluid (a liquid or a gas), then $g(\mathbf{r}_1, \mathbf{r}_2)$ depends only on the distance $r = |\mathbf{r}_1 - \mathbf{r}_2|$ between particles 1 and 2. We adopt the notation $g(r) = g(r_{12})$ and define the *radial distribution function* $g(r)$ as

$$\boxed{g(r) = \Big(1 - \frac{1}{N}\Big)\frac{V^2 \int e^{-\beta U} d\mathbf{r}_3 \ldots d\mathbf{r}_N}{Q_N}}. \tag{8.83}$$

Note that (8.83) implies that $g(r) = 1 - 1/N$ for an ideal gas. We can ignore the $1/N$ correction in the thermodynamic limit so that $g(r) = 1$. From (8.83) we see that the normalization of $\rho g(r)$ is given by (for $d = 3$)

$$\rho \int g(r) 4\pi r^2 dr = \rho\Big(1 - \frac{1}{N}\Big)V^2 \frac{1}{V} = N - 1 \approx N. \tag{8.84}$$

To determine $g(r)$ for a dilute gas we write $g(r)$ as [see (8.83)]

$$g(r) = \frac{V^2 \int e^{-\beta U} d\mathbf{r}_3 \ldots d\mathbf{r}_N}{Q_N}, \tag{8.85}$$

where we have taken the limit $N \to \infty$. At low densities, we can integrate over particles 3, 4, …, N, assuming that these particles are distant from particles 1 and 2 and also distant from each other. Also, for almost all configurations we can replace U by u_{12} in the numerator. Similarly, the denominator can be approximated by V^N. Hence (8.85) reduces to

$$g(r) \approx \frac{V^2 \, e^{-\beta u_{12}} V^{N-2}}{V^N} = e^{-\beta u(r)}, \tag{8.86}$$

as given in (8.73).

To obtain the relation (8.74) for the mean total energy E in terms of $g(r)$ we write

$$E = \frac{3}{2} NkT + \overline{U}, \tag{8.87}$$

where

$$\overline{U} = \frac{1}{Q_N} \int \cdots \int U e^{-\beta U} \, d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N. \tag{8.88}$$

We assume that U is given by (8.1) and write $\overline{U}$ as

$$\begin{aligned}
\overline{U} &= \frac{N(N-1)}{2} \frac{1}{Q_N} \int e^{-\beta U} u(r_{12}) \, d\mathbf{r}_1 \ldots d\mathbf{r}_N && (8.89a) \\
&= \frac{N(N-1)}{2} \int u(r_{12}) \Big[\frac{\int e^{-\beta U} \, d\mathbf{r}_3 \ldots d\mathbf{r}_N}{Q_N} \Big] d\mathbf{r}_1 d\mathbf{r}_2. && (8.89b)
\end{aligned}$$

From (8.82) we see that the term in brackets is related to $\rho^2 g(\mathbf{r}_1, \mathbf{r}_2)$. Hence we can write $\overline{U}$ as

$$\begin{aligned}
\overline{U} &= \frac{1}{2} \int u(r_{12}) \, \rho^2 g(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_1 d\mathbf{r}_2 = \frac{N^2}{2V} \int u(r) g(r) d\mathbf{r} && (8.90a) \\
&= N \frac{\rho}{2} \int u(r) g(r) \, 4\pi r^2 \, dr. && (8.90b)
\end{aligned}$$

We assumed three dimensions to obtain (8.90b).

The derivation of the relation (8.75) between the mean pressure and $g(r)$ is more involved. We write the pressure in terms of Q_N:

$$P = -\frac{\partial F}{\partial V} = kT \, \frac{\partial \ln Q_N}{\partial V}. \tag{8.91}$$

Recall that $Q_N = V^N$ for an ideal gas. For large V the pressure is independent of the shape of the container. For convenience, we assume that the container is a cube of linear dimension L, and we write Q_N as

$$Q_N = \int_0^L \cdots \int_0^L e^{-\beta U} \, dx_1 \, dy_1 \, dz_1 \ldots dx_N \, dy_N \, dz_N. \tag{8.92}$$

We first change variables so that the limits of integration are independent of L and let $\tilde{x}_i = x_i/L$, etc. This change of variables allows us to take the derivative of Q_N with respect to V. We have

$$Q_N = V^N \int_0^1 \ldots \int_0^1 e^{-\beta U} d\tilde{x}_1\, d\tilde{y}_1\, d\tilde{z}_1 \ldots d\tilde{x}_N\, d\tilde{y}_N\, d\tilde{z}_N, \tag{8.93}$$

where U depends on the separation $\tilde{r}_{ij} = L[(\tilde{x}_i - \tilde{x}_j)^2 + (\tilde{y}_i - \tilde{y}_j)^2 + (\tilde{x}_i - \tilde{z}_j)^2]^{1/2}$. We now take the derivative

$$\begin{aligned}\frac{\partial Q_N}{\partial V} &= NV^{N-1} \int_0^1 \cdots \int_0^1 e^{-\beta U} d\tilde{x}_1 \ldots d\tilde{z}_N \\ &\quad - \frac{V^N}{kT} \int_0^1 \cdots \int_0^1 e^{-\beta U} \frac{\partial U}{\partial V}\, d\tilde{x}_1 \ldots d\tilde{z}_N,\end{aligned} \tag{8.94}$$

where

$$\frac{\partial U}{\partial V} = \sum_{i<j} \frac{du(r_{ij})}{dr_{ij}} \frac{dr_{ij}}{dL} \frac{dL}{dV} = \sum_{i<j} \frac{du(r_{ij})}{dr_{ij}} \frac{r_{ij}}{L} \frac{1}{3L^2}. \tag{8.95}$$

Now that we have differentiated Q_N with respect to V, we transform back to the original variables $x_1, \ldots, z_N$. In the second term of (8.95) we also use the fact that there are $N(N-1)/2$ identical contributions. In this way we obtain

$$\frac{\partial \ln Q_N}{\partial V} = \frac{1}{Q_N} \frac{\partial Q_N}{\partial V} = \frac{N}{V} - \frac{\rho^2}{6VkT} \int r_{12} \frac{du(r_{12})}{dr_{12}} g(r_{12})\, d\mathbf{r}_1\, d\mathbf{r}_2, \tag{8.96}$$

and hence

$$\frac{PV}{NkT} = 1 - \frac{\rho}{6kT} \int_0^\infty r \frac{du(r)}{dr}\, g(r)\, 4\pi r^2 dr. \qquad \text{(virial equation of state)} \tag{8.97}$$

The integrand in (8.97) is related to the virial in classical mechanics and is the mean value of the product $\mathbf{r} \cdot \mathbf{F}$ [cf. Goldstein et al. (2001)].

****Density expansion of $g(r)$***. The density expansion of $g(r)$ is closely related to the density expansion of the free energy. Instead of deriving the relation here, we show only the diagrams corresponding to the first two density contributions. We write

$$g(r) = e^{-\beta u(r)} y(r), \tag{8.98}$$

and

$$y(r) = \sum_{n=0}^{\infty} \rho^n y_n(r), \tag{8.99}$$

with $y_0(r) = 1$. It is convenient to consider the function $y(r)$ defined by (8.98) instead of the function $g(r)$ because $y(r)$ is more slowly varying. The diagrams for $y(r)$ have two fixed points represented by open circles corresponding to particles 1 and 2. The other particles are integrated over the volume of the system. The diagrams for $y_1(r)$ and $y_2(r)$ are shown in Figure 8.10. The corresponding integrals are

$$y_1(r) = \int f(r_{13}) f(r_{23})\, d\mathbf{r}_3, \tag{8.100}$$

and

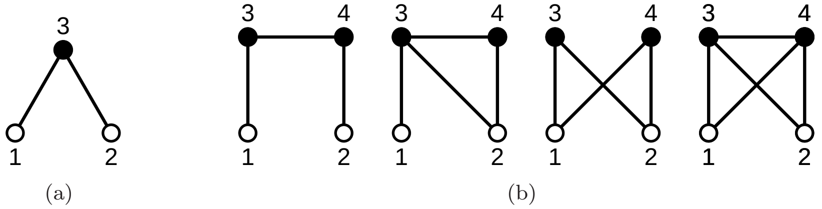

Figure 8.10: The diagrams contributing to (a) $y_1(r)$ and (b) $y_2(r)$. Particles 1 and 2 are represented by open circles and the other particles (filled circles) are integrated over the volume of the system. The bonds correspond to Mayer f functions.

$$\begin{aligned} y_2(r) = \frac{1}{2}\int [2f_{13}f_{34}f_{42} + 4f_{13}f_{34}f_{42}f_{32} + f_{13}f_{42}f_{32}f_{14} \\ + f_{13}f_{34}f_{42}f_{32}f_{14}]\, d\mathbf{r}_3 d\mathbf{r}_4. \end{aligned} \tag{8.101}$$

Note that the diagrams in Figure 8.10 and hence the integrals in (8.100) and (8.101) are closely related to the diagrams for the virial coefficients.

Pressure equation for hard spheres. Because the relation (8.97) involves the derivative of the pair potential $u(r)$, it is not directly applicable to a system of hard spheres. To find the desired relation we write $g(r)$ as in (8.98) and assume that $y(r)$ is a continuous function of r even when $u(r)$ has discontinuities. We substitute this form of $g(r)$ in (8.97) and write

$$\frac{PV}{NkT} = 1 - \frac{2\pi\beta\rho}{3}\int_0^\infty u'(r)e^{-\beta u(r)} y(r)\, r^3 dr \tag{8.102a}$$

$$= 1 + \frac{2\pi\rho}{3}\int_0^\infty \frac{d(e^{-\beta u(r)})}{dr} y(r)\, r^3 dr, \tag{8.102b}$$

where we have used the fact that $d(e^{-\beta u(r)})/dr = -\beta u'(r)e^{-\beta u(r)}$. For hard spheres $e^{-\beta u(r)} = 0$ for $r < \sigma$, $e^{-\beta u(r)} = 1$ for $r > \sigma$ and $d(e^{-\beta u(r)})/dr = \delta(r - \sigma)$. Hence

$$\frac{PV}{NkT} = 1 + \frac{2\pi\rho}{3}\lim_{r\to\sigma^+} r^3 y(r) = 1 + \frac{2\pi\rho}{3}\sigma^3 g(r = \sigma^+). \tag{8.103}$$

We see that the pressure of a hard sphere fluid is determine by the value of $g(r)$ at contact. Note that $g(r)$ goes discontinuously to zero; that is $g(r = \sigma^-) = 0$.

Problem 8.16. Pressure equation for hard disks

Derive the expression analogous to (8.103) for hard disks. □

8.6 Perturbation Theory of Liquids

So far we have discussed several models that can be solved analytically and that add to our understanding of gases and crystalline solids. For example, we have seen that the ideal gas can be used as the starting point for the density expansion of a dilute gas, and the harmonic model is an idealized model of a solid (see Section 6.9, page 331). The development of a microscopic theory of fluids (dense gases and liquids) was hampered for many years by the lack of a convenient small expansion parameter or a simple model.

Simulations of simple liquids have led to the realization that the details of the weak attractive part of the interparticle interaction and the details of the repulsive part of the interaction also are unimportant. As you found in Problem 8.15, the radial distribution function $g(r)$ of a dense fluid does not depend strongly on the temperature, and the radial distribution function $g(r)$ for a system of hard spheres is a good approximation to $g(r)$ for a Lennard-Jones system at the same density. Moreover, we can simulate hard sphere systems relatively easily and obtain essentially exact solutions for $g(r)$ and the equation of state.

The picture of a dense fluid that is suggested by simulations suggests that the repulsive part of the interaction dominates its structure, and the attractive part of the interaction can be treated as a perturbation. In the following we will develop a perturbation theory of liquids in which the unperturbed or reference system is taken to be a system of hard spheres (or disks) rather than an ideal gas. The idea is that the difference between the hard sphere interaction and a more realistic interaction can be used as an effective expansion parameter.

We begin by writing the potential energy as

$$U = U_0 + \tilde{U}, \tag{8.104}$$

where U_0 is the potential energy of the reference system, and $\tilde{U}$ will be treated as a perturbation. The configurational integral Q_N is given by

$$Q_N = \int \cdots \int e^{-\beta(U_0+\tilde{U})}\, d\mathbf{r}_1 \ldots d\mathbf{r}_N. \tag{8.105}$$

We multiply and divide the right-hand side of (8.105) by

$$Q_0 = \int \cdots \int e^{-\beta U_0}\, d\mathbf{r}_1 \ldots d\mathbf{r}_N, \tag{8.106}$$

and write

$$\begin{aligned} Q_N &= \int \cdots \int e^{-\beta U_0}\, d\mathbf{r}_1 \ldots d\mathbf{r}_N \frac{\int \cdots \int e^{-\beta(U_0+\tilde{U})} d\mathbf{r}_1 \ldots d\mathbf{r}_N}{Q_0} && (8.107\text{a}) \\ &= Q_0 \int \cdots \int P_0\, e^{-\beta\tilde{U}}\, d\mathbf{r}_1 \ldots d\mathbf{r}_N, && (8.107\text{b}) \end{aligned}$$

where

$$P_0 = \frac{e^{-\beta U_0}}{Q_0}. \tag{8.108}$$

We see that we can express Q_N in (8.107b) as the average of $\exp(-\beta\tilde{U})$ over the reference system. We write

$$Q_N = Q_0 \langle e^{-\beta\tilde{U}} \rangle_0, \tag{8.109}$$

and

$$-\beta\tilde{F} = \ln \langle e^{-\beta\tilde{U}} \rangle_0 = \sum_{n=1}^{\infty} \frac{(-\beta)^n \tilde{M}_n}{n!}. \tag{8.110}$$

The brackets $\langle \ldots \rangle_0$ denote an average over the microstates of the reference system weighted by the probability P_0. We have written $\tilde{M}$ rather than M to distinguish the cumulants for an arbitrary reference system from the cumulants defined in Section 8.4.2 for the ideal gas reference system. Note the formal similarity between (8.110) and the expression for F_c in (8.8) and the cumulant expansion in (8.48).

Problem 8.17. Ideal gas as a reference system

(a) Compare the forms of (8.109) and (8.110) for an arbitrary reference system to the forms of (8.7) and (8.8), respectively.

(b) Show that if we choose the reference system to be an ideal gas, the expressions (8.109) and (8.110) reduce to (8.7) and (8.8). ☐

We now evaluate the first cumulant $\tilde{M}_1$ in a manner similar to that done to evaluate M_1 in (8.49) for a dilute gas. The leading term in (8.110) is

$$\tilde{M}_1 = \langle \tilde{U} \rangle_0 = \sum_{i<j=1}^{N} \langle \tilde{u}(r_{ij}) \rangle_0 \tag{8.111a}$$

$$= \frac{N(N-1)}{2} \frac{1}{Q_0} \int \cdots \int e^{-\beta U_0}\, \tilde{u}(r_{12})\, d\mathbf{r}_1 \ldots d\mathbf{r}_N. \tag{8.111b}$$

The radial distribution function of the reference system is given by [see (8.81)]

$$\rho^2 g_0(r_{12}) = N(N-1) \frac{\int e^{-\beta U_0}\, d\mathbf{r}_3 \ldots d\mathbf{r}_N}{Q_0}. \tag{8.112}$$

Hence, we can write $\tilde{M}_1$ as

$$\tilde{M}_1 = \frac{\rho^2}{2} \int \tilde{u}(r_{12}) g_0(r_{12})\, d\mathbf{r}_1 d\mathbf{r}_2 \tag{8.113a}$$

$$= \frac{\rho N}{2} \int \tilde{u}(r) g_0(r)\, d\mathbf{r}, \tag{8.113b}$$

and

$$\tilde{F} = \tilde{F}_0 + \frac{\rho N}{2} \int \tilde{u}(r) g_0(r)\, d\mathbf{r}, \tag{8.114}$$

where $\tilde{F}_0$ in (8.114) is the free energy of the reference system. Note that the form of $\tilde{M}_1$ in (8.113b) is similar to the form of M_1 in (8.51b). The difference is that we have included the correlation between the particles due to their interaction.

8.6.1 The van der Waals equation

The idea that the structure of a simple liquid is determined primarily by the repulsive part of the potential is not new and is the basis of the van der Waals equation of state. We now show

how the van der Waals equation of state can be derived from the perturbation theory we have developed by choosing the reference system to be a system of hard spheres and making some simple approximations.

We first assume that g_0 has the simple form

$$g_0(r) = \begin{cases} 0 & (r < \sigma), \\ 1 & (r \geq \sigma). \end{cases} \tag{8.115}$$

This approximate form for $g_0(r)$ gives

$$\tilde{M}_1 = 2\pi\rho N\int_\sigma^\infty \tilde{u}(r)\, r^2 dr = -\rho a N, \tag{8.116}$$

where [see (8.35)]

$$a = -2\pi\int_\sigma^\infty \tilde{u}(r)\, r^2 dr. \tag{8.117}$$

The simplest approximation for $\tilde{F}_0$ is to assume that the effective volume available to a particle in a fluid is smaller than the volume available in an ideal gas. In this spirit we assume that $\tilde{F}_0$ has the same form as it does for an ideal gas (see ((6.26), page 297) with V replaced by $V_{\rm eff}$. We write

$$\frac{\tilde{F}_0}{NkT} = -\Big[\ln\frac{V_{\rm eff}}{N} + \frac{3}{2}\ln\Big(\frac{2\pi mkT}{h^2}\Big) + 1\Big], \tag{8.118}$$

where

$$V_{\rm eff} = V - V_0, \tag{8.119}$$

and

$$V_0 = Nb = \frac{1}{2}N\frac{4\pi\sigma^3}{3}. \tag{8.120}$$

In (8.120) we have accounted for the fact that only half of the volume of a sphere can be assigned to a given particle. The corresponding equation of state with these approximations for $\tilde{M}_1$, $\tilde{F}_0$, and $V_{\rm eff}$ is given by

$$\frac{PV}{NkT} = \frac{1}{1 - b\rho} - \frac{a\rho}{kT}. \tag{8.121}$$

Equation (8.121) is the familiar van der Waals equation of state. The latter gives results that are in qualitative but not quantitative agreement with experiment.

A much more accurate approximation for the equation of state of liquids is known as the Weeks-Chandler-Andersen theory (see the references). In this approach the interparticle potential is separated into a reference part and a perturbative part. One way is to separate the potential into positive and negative contributions. This choice implies that we should separate the Lennard-Jones potential at $r = \sigma$. Another way is to separate the potential at $r = 2^{1/6}\sigma$ so that the force is separated into positive and negative contributions. This choice is the one adopted by the Weeks-Chandler-Andersen theory. The Lennard-Jones potential is expressed as

$$u_{\rm LJ}(r) = u_0(r) + \tilde{u}(r), \tag{8.122}$$

where

$$u_0(r) = \begin{cases} u_{\rm LJ}(r) + \epsilon, & (r < 2^{1/6}\sigma), \\ 0 & (r \geq 2^{1/6}\sigma), \end{cases} \tag{8.123a}$$

$$\tilde{u}(r) = \begin{cases} -\epsilon & (r < 2^{1/6}\sigma), \\ u_{\rm LJ}(r), & (r \geq 2^{1/6}\sigma). \end{cases} \tag{8.123b}$$

We have added and subtracted ϵ to $u_{\rm LJ}(r)$ for $r < 2^{1/6}\sigma$ so that $u_0(r)$ and $\tilde{u}(r)$ are continuous.

Problem 8.18. Qualitative behavior of $\tilde{u}(r)$

Plot the dependence of $\tilde{u}(r)$ on r and confirm that $\tilde{u}(r)$ is a slowly varying function of r. □

Because the reference system in the Weeks-Chandler-Andersen theory is not a system of hard spheres, further approximations are necessary, and the reference system is approximated by hard spheres with a temperature and density dependent diameter. One way to determine the effective diameter is to require that the function $y(r)$ defined in (8.98) be the same for hard spheres and for the repulsive part (8.123a) of the potential. The details will not be given here. What is important to understand is that a successful perturbation theory of dense gases and liquids now exists based on the use of a hard sphere reference system.

8.7 *The Ornstein-Zernike Equation and Integral Equations for $g(r)$

As mentioned in Section 8.5, we can derive a density expansion for the function $y(r)$, which is related to $g(r)$ by (8.98). However, a better approach is to expand a related function that is shorter range. Such a function is the *direct correlation function* $c(r)$.

To define $c(r)$ it is convenient to first define the pair correlation function $h(r)$ by the relation

$$h(r) = g(r) - 1. \tag{8.124}$$

Because $g(r) \to 1$ for $r \gg 1$, $h(r) \to 0$ for sufficiently large r. Also $h(r) = 0$ for an ideal gas. These two properties makes it easier to interpret $h(r)$ rather than $g(r)$ in terms of the correlations between the particles due to their interaction.

We define $c(r)$ by the relation (for a homogeneous and isotropic system):

$$h(r) = c(r) + \rho \int c(|\mathbf{r} - \mathbf{r}'|)\, h(r')\, d\mathbf{r}' \qquad \text{(Ornstein-Zernike equation).} \tag{8.125}$$

The relation (8.125) is known as the *Ornstein-Zernike equation.* Equation (8.125) can be solved recursively by first substituting $h(r) = c(r)$ on the right-hand side and then repeatedly substituting the resultant solution for $h(r)$ on the right-hand side to obtain

$$\begin{aligned} h(r) = c(r) &+ \rho \int c(|\mathbf{r} - \mathbf{r}'|)\, c(r')\, d\mathbf{r}' \\ &+ \rho^2 \iint c(|\mathbf{r} - \mathbf{r}'|)\, c(|\mathbf{r}' - \mathbf{r}''|) c(|\mathbf{r}'' - \mathbf{r}'|)\, d\mathbf{r}' d\mathbf{r}'' + \cdots . \end{aligned} \tag{8.126}$$

The interpretation is that the correlation $h(r)$ between particles 1 and 2 is due to the direct correlation between 1 and 2 and the indirect correlation due to increasing numbers of intermediate particles. This interpretation suggests that the range of $c(r)$ is comparable to the range of the potential $u(r)$, and that $h(r)$ is longer ranged than $u(r)$ due to the effects of the indirect correlations. That is, $c(r)$ usually has a much shorter range than $h(r)$ and hence $g(r)$.[9]

Because the right-hand side of the Ornstein-Zernike equation involves a convolution integral (see (**??**), page **??**), we know that we can find $c(r)$ from $h(r)$ by introducing the Fourier transforms

$$c(k) = \int c(r)\, e^{i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r} \tag{8.127}$$

and

$$h(k) = \int h(r)\, e^{i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r}. \tag{8.128}$$

We take the Fourier transform of both sides of (8.125) and find that

$$h(k) = c(k) + \rho\, c(k)h(k), \tag{8.129}$$

or

$$c(k) = \frac{h(k)}{1 + \rho h(k)}, \tag{8.130}$$

and

$$h(k) = \frac{c(k)}{1 - \rho c(k)}. \tag{8.131}$$

***Problem 8.19.** Properties of $c(r)$

(a) Write $c(r) = c_0(r) + \rho c_1(r) + \ldots$, and show that $c_0(r) = f(r)$ and $c_1(r) = f(r)y_1(r)$, where $y_1(r)$ is given in (8.100).

(b) We know that $g(r) \approx -\beta u(r)$ for $\beta u(r) \ll 1$, as is the case for large r. Show that $c(r) = -\beta u(r)$ for large r. Hence in this limit the range of $c(r)$ is comparable to the range of the potential. ☐

The Ornstein-Zernike equation can be used to obtain several approximate integral equations for $g(r)$ that are applicable to dense fluids. The most useful of these equations for systems with short-range interactions is the *Percus-Yevick* equation. This equation corresponds to ignoring an (infinite) subset of diagrams (and including another subset), but a discussion of these diagrams does not add much physical insight.

One way to motivate the Percus-Yevick equation is to note that the lowest order density contributions to $c(r)$ are $c_0(r) = f(r)y_0(r)$ and $c_1(r) = f(r)y_1(r)$ (see Problem 8.19), where $y_0(r) = 1$. We assume that this relation between $c(r)$ and $y(r)$ holds for all densities:

$$c(r) \approx f(r)y(r) = \big[1 - e^{\beta u(r)}\big] g(r). \tag{8.132}$$

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[9] This assumption does not hold near the critical point.

Equation (8.132) is correct to first order in the density. If we substitute the approximation (8.132) into the Ornstein-Zernike equation (8.125), we obtain the Percus-Yevick equation:

$$y(r) = 1 + \rho\int f(r')y(r')h(|\mathbf{r} - \mathbf{r}'|)\, d\mathbf{r}' \quad \text{(Percus-Yevick equation).} \tag{8.133}$$

We can alternatively express (8.133) as

$$e^{\beta u(r)}g(r) = 1 + \rho\int \big[1 - e^{\beta u(r')}\big]g(r')\big[g(|\mathbf{r} - \mathbf{r}'|) - 1\big]d\mathbf{r}'. \tag{8.134}$$

Equations (8.133) and (8.134) are examples of nonlinear integral equations.

In general, the Percus-Yevick must be solved numerically. However, it can be solved analytically for hard spheres (but not for hard disks). The analytical solution of the Percus-Yevick equation for hard spheres can be expressed as

$$c(r) = \begin{cases} -\dfrac{1}{(1-\eta)^4}\big[(1-2\eta)^2 - 6\eta(1+\frac{1}{2}\eta)^2(r/\sigma) + \frac{1}{2}\eta(1+2\eta)^2(r/\sigma)^2\big] & (r < \sigma), \\ 0, & (r > \sigma). \end{cases} \tag{8.135}$$

Note that the range of $c(r)$ is equal to σ and is much less than the range of $g(r)$.

Given $c(r)$, we can find $g(r)$ by solving the Ornstein-Zernike equation. The derivation is tedious, and we give only the result for $g(r)$ at contact:

$$g(r = \sigma^+) = \frac{1 + \frac{1}{2}\eta}{(1-\eta)^2}. \tag{8.136}$$

We can use (8.136) and (8.103) to obtain the corresponding approximate virial equation of state for hard spheres. The result is

$$\frac{PV}{NkT} = \frac{1 + 2\eta + 3\eta^2}{(1-\eta)^2} \qquad \text{(virial equation of state).} \tag{8.137}$$

An alternative way of calculating the pressure is to use the compressibility relation [see (8.200)]

$$1 + \rho\int [g(r) - 1]\, d\mathbf{r} = \rho kT\kappa, \tag{8.138}$$

which can be expressed as (see Section 8.9.3)

$$\Big(kT\frac{\partial\rho}{\partial P}\Big)^{-1} = 1 - \rho\int c(r)\, d\mathbf{r}. \tag{8.139}$$

If we substitute the Percus-Yevick result (8.135) into (8.139) and integrate, we find

$$\frac{PV}{NkT} = \frac{1 + \eta + \eta^2}{(1-\eta)^3} \qquad \text{(compressibility equation of state).} \tag{8.140}$$

If the Percus-Yevick equation were exact, the two ways of obtaining the equation of state would yield identical results. That is, the Percus-Yevick equation is not thermodynamically consistent.

It is interesting that the Carnahan-Starling equation of state for hard spheres (8.71) can be found by a weighted average of the two approximate equations of state:

$$\frac{PV}{NkT} = \frac{1}{\rho kT}\Big[\frac{1}{3}P_v + \frac{2}{3}P_c\Big], \tag{8.141}$$

where P_v and P_c are given by (8.137) and (8.140), respectively. The Carnahan-Starling equation of state gives better results than either (8.137) or (8.140).

The Percus-Yevick equation gives reasonable results for $g(r)$ and the equation of state for fluid densities. However, it predicts finite pressures for $\eta_{\max} \leq \eta < 1$, even though the maximum packing fraction $\eta_{\max} = \sqrt{2}\pi/6 \approx 0.74$ (see Problem 8.13).

Problem 8.20. Virial equation of state

Use the form of $g(r = \sigma^+)$ given in (8.136) and the relation (8.103) to derive (8.137) for the pressure equation of state as given by the Percus-Yevick equation.

Another simple closure approximation for the Ornstein-Zernike equation can be motivated by the following considerations. Consider a fluid whose particles interact via a pair potential of the form

$$u(r) = \begin{cases} \infty & (r < \sigma), \\ v(r) & (r > \sigma), \end{cases} \tag{8.142}$$

where $v(r)$ is a continuous function of r. Because $u(r) = \infty$ for $r < \sigma$, $g(r) = 0$ for $r < \sigma$. For large r the Percus-Yevick approximation for $c(r)$ reduces to

$$c(r) = -\beta v(r). \tag{8.143}$$

The *mean spherical approximation* is based on the assumption that (8.143) holds not just for large r, but for all r. The mean spherical approximation is

$$c(r) = -\beta v(r) \qquad (r > \sigma), \tag{8.144a}$$

and

$$g(r) = 0 \qquad (r < \sigma), \tag{8.144b}$$

together with the Ornstein-Zernike equation.

The *hypernetted-chain approximation* is another useful integral equation for $g(r)$. It is equivalent to setting

$$c(r) = f(r)y(r) + y(r) - 1 - \ln y(r) \quad \text{(hypernetted-chain equation)}. \tag{8.145}$$

If we analyze the Percus-Yevick and the hypernetted-chain approximations in terms of a diagrammatic expansion (see Problem 8.34), we that the hypernetted-chain approximation includes more diagrams than the Percus-Yevick approximation. However, it turns out that the Percus-Yevick approximation is more accurate for hard spheres and other short-range potentials. In contrast, the hypernetted-chain approximation is more accurate for systems with long-range interactions.

8.8 *One-Component Plasma

We found in Problem 8.7 that the second virial coefficient does not exist if the interparticle potential $u(r)$ decreases less rapidly than $1/r^3$ for large r. For this reason we expect that a density expansion of the free energy and other thermodynamic quantities is not applicable to a gas consisting of charged particles interacting via the Coulomb potential $u(r) \propto 1/r$. We say that the Coulomb potential is long-range because its second moment $\int r^2 u(r) r^2 dr$ diverges for large r. The divergence of the second virial coefficient for the Coulomb potential is symptomatic of the fact that a density expansion is not physically meaningful for a system of particles interacting via a long-range potential.

The simplest model of a system of particles interacting via the Coulomb potential is a gas of mobile electrons moving in a fixed, uniform, positive background. The charge density of the positive background is chosen to make the system overall neutral. Such a system is known as an electron gas or a *one-component plasma* (OCP in the literature).

Problem 8.21. Fourier transform of the Coulomb potential
The interaction potential between two particles of charge q is $u(r) = q^2/r$. Show that the Fourier transform of $u(r)$ is given by

$$u(k) = \frac{4\pi q^2}{k^2}. \tag{8.146}$$

First find the Fourier transform of $\dfrac{1}{r} e^{r/\lambda}$ and then take the limit $\lambda \to \infty$. □

Debye-Hückel theory. Debye and Hückel developed a mean-field theory that includes the interactions between charged particles in a very clever, but approximate way. Consider an electron at $\mathbf{r} = 0$ of charge $-q$. The average electric potential $\phi(\mathbf{r})$ in the neighborhood of $\mathbf{r} = 0$ is given by Poisson's equation:

$$\begin{aligned}\nabla^2 \phi(\mathbf{r}) = -4\pi \big[&(\text{negative point charge at origin}) + (\text{density of positive uniform background}) \\ &+ (\text{density of other electrons})\big].\end{aligned} \tag{8.147a}$$

That is,

$$\nabla^2 \phi(\mathbf{r}) = -4\pi \big[- q\delta(\mathbf{r}) + q\rho - q\rho g(\mathbf{r})\big], \tag{8.147b}$$

where ρ is the mean number density of the electrons and the uniform positive background, and $\rho g(\mathbf{r})$ is the density of the electrons in the vicinity of $\mathbf{r} = 0$. Equation (8.147b) is exact, but we have not specified $g(\mathbf{r})$. The key idea is that $g(\mathbf{r})$ is approximately given by the Boltzmann factor [see (8.73)]

$$g(\mathbf{r}) \approx e^{\beta q \phi(\mathbf{r})}. \tag{8.148}$$

If we combine (8.147b) and (8.148), we obtain the Poisson-Boltzmann equation for $\phi(\mathbf{r})$:

$$\nabla^2 \phi(\mathbf{r}) = -4\pi q \big[- \delta(\mathbf{r}) + \rho - \rho\, e^{q\beta\phi(\mathbf{r})}\big]. \tag{8.149}$$

For $\beta q \phi \ll 1$, we may write $e^{-\beta q \phi(\mathbf{r})} \approx 1 - \beta q \phi(\mathbf{r})$ and obtain the linearized Poisson-Boltzmann equation

$$(\nabla^2 - \kappa_D^2)\phi(r) = 4\pi q\, \delta(r), \tag{8.150}$$

where κ_D^2 is given by

$$\kappa_D^2 = 4\pi\beta\rho q^2. \tag{8.151}$$

The solution of (8.150) can be shown to be (see (9.22), page 438)

$$\phi(r) = -q\frac{e^{-r/\lambda_D}}{r}, \tag{8.152}$$

where $\lambda_D = 1/\kappa_D$. The energy of the other elections in the potential $\phi(r)$ is $u_{\rm eff}(r) = -q\phi(r)$ so that the effective energy of interaction between two electrons is given by

$$u_{\rm eff}(r) = q^2\frac{e^{-r/\lambda_D}}{r}. \tag{8.153}$$

The result (8.153) shows that the electrons collaborate in such a way as to screen the potential of a given electron over a distance λ_D. The quantity λ_D is called the *Debye screening length* and is the radius of the electron cloud which screens the Coulomb potential about any given electron. The screening of the charge of the electrons is another example of a cooperative effect.

Note that to use statistical arguments, it is necessary that many particles have approximately the same potential energy, that is, many particles need to be within the range λ_D of ϕ. This requirement can be written as $\rho\lambda_D^3 \gg 1$. This condition holds in the limit of low density and high temperature.

Problem 8.22. Validity of the Debye-Hückel theory

Show that the condition $\rho\lambda_D^3 \gg 1$ is equivalent to the condition that the mean interaction energy between two charged particles $q^2/(r = \lambda_D)$ be much smaller than the mean kinetic energy. ☐

We now determine the radial distribution function $g(r)$ and the thermodynamic properties of the one-component plasma. From (8.148) we have

$$g(r) = e^{\beta q\phi(r)} \approx 1 - \beta q\phi(r) = 1 - \frac{\beta q^2}{r}e^{-r/\lambda_D}. \tag{8.154}$$

Problem 8.23. Thermodynamic properties of the Debye-Hückel theory

(a) The total energy per particle of the one-component plasma is given by

$$\frac{E}{N} = \frac{3}{2}kT + \frac{\rho}{2}\int [g(r) - 1]\, u(r)\, d\mathbf{r}. \tag{8.155}$$

The factor of $g - 1$ rather than g in the integrand is due to the uniform positive background. Use the approximation (8.154) to show that the mean energy per particle can be expressed as

$$\frac{E}{N} = \frac{3}{2}kT - \frac{1}{2}\frac{q^2}{\lambda_D} = kT\Big[\frac{3}{2} - \frac{1}{2}\frac{q^2}{\lambda_D kT}\Big] = kT\Big[\frac{3}{2} - \frac{\epsilon}{2}\Big], \tag{8.156}$$

where the dimensionless parameter ϵ is defined as

$$\epsilon \equiv \frac{q^2}{\lambda_D kT}. \tag{8.157}$$

(b) Find a expression similar to (8.156) for the mean pressure. ☐

The form of the right-hand side of (8.156) suggests that the Debye-Hückel theory is equivalent to keeping the first term in an expansion in powers of ϵ, in analogy to the expansion in powers of the density for systems with short-range interactions. However, the expansion is more complicated and involves logarithmic terms in ϵ. For example, the next order terms are proportional to ϵ^2 and $\epsilon^2 \ln \epsilon$.

Problem 8.24. The Debye-Hückel approximation of the direct correlation function

Use the form (8.154) to find the corresponding Fourier transform $h(k)$. Then use (8.130) to show that the direct correlation function $c(k)$ in the Debye-Hückel approximation is given by

$$c(k) = -\beta u(k). \tag{8.158}$$

Hence the Debye-Hückel approximation is equivalent to approximating the direct correlation function $c(r)$ by $-\beta u(r)$, the result for $c(r)$ to lowest order in the potential (see Problem 8.19b). ☐

****Diagrammatic expansion***. We derived the density expansion of the free energy by first doing a high temperature expansion (see Section 8.4.2). Although individual terms in this expansion diverge at short separations for systems with a strongly repulsive interaction, we found that the divergence was removed by rearranging the expansion so that all terms of a given density are grouped together and summed.

As we have discussed, an expansion in terms of the density and the interaction of small numbers of particles makes no sense if the interaction is long range. We now discuss how to group individual terms in the high temperature expansion so that the divergence at large separations due to the long-range nature of the Coulomb potential is removed.[10]

Instead of considering the diagrammatic expansion for the free energy, we consider the high temperature expansion for $g(r)$, because the latter is easier to interpret physically. It is convenient to write $g(r)$ in the form

$$g(r) = e^{-\beta\psi(r)}, \tag{8.159}$$

where $\psi(r)$ is the *potential of mean force*. Note that $\psi(r)$ reduces to $u(r)$ in the limit of low densities. Recall that we obtained the low density expansion by first summing all possible potential (u) bonds between two particles. That is, we summed the infinite class of diagrams with the maximum number of bonds for a given number of particles. Because the Coulomb interaction is long-range, it is plausible that we should first sum the infinite class of diagrams corresponding to the maximum number of particles for a given number of bonds. These diagrams are called *ring diagrams*. The first several ring diagrams are shown in Figure 8.11. Because we know that the Coulomb interaction is screened, we expect that we should add up the contributions of all the ring diagrams before we include the contributions of other diagrams.

The contribution of the ring diagrams to $\psi(r)$ is given by

$$\begin{aligned} -\beta\psi(r) \;=\; & -\beta u(r) + \rho \int [-\beta u(r_{13})][-\beta u(r_{32})]\, d\mathbf{r}_3 \\ & + \rho^2 \int [-\beta u(r_{13})][-\beta u(r_{34})][-\beta u(r_{42})]\, d\mathbf{r}_3\, d\mathbf{r}_4 + \ldots, \end{aligned} \tag{8.160}$$

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[10] Important early work was done by J. E. Mayer, "The theory of ionic solutions," J. Chem. Phys. **18**, 1426–1436 (1950).

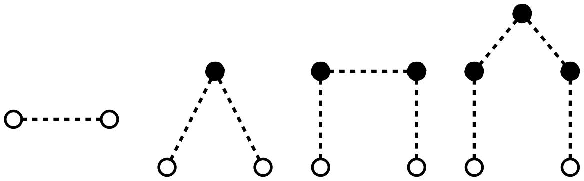

Figure 8.11: The first several ring diagrams for $\psi(r)$. The bonds represent the Coulomb interaction $u(r) = e^2/r$.

where $r = |\mathbf{r}_1 - \mathbf{r}_2|$. The structure of the integrals in (8.160) is the same as the convolution integral discussed in Section 8.9.1. We follow the same procedure and take the spatial Fourier transform of both sides of (8.160). The result can be written as

$$-\beta\psi(k) = -\beta u(k) + \rho[-\beta u(k)]^2 + \rho^2[-\beta u(k)]^3 + \ldots, \tag{8.161}$$

where $u(k)$ is the Fourier transform of $u(r) = e^2/r$ (see Problem 8.146). Because the terms in (8.161) form a geometric series, we obtain

$$-\beta\psi(k) = \frac{-\beta u(k)}{1 + \rho\beta u(k)} = \frac{-\beta 4\pi e^2}{k^2 + \beta\rho 4\pi e^2} \tag{8.162a}$$

$$= -\beta\frac{4\pi e^2}{k^2 + \kappa_D^2}, \tag{8.162b}$$

where κ_D is given by (8.151). Hence

$$\psi(k) = \frac{4\pi e^2}{k^2 + \kappa_D^2} \tag{8.163}$$

and

$$\psi(r) = \frac{\beta e^2}{r}\epsilon^{-\kappa_D r}. \tag{8.164}$$

From (8.164) we see that the effective interaction is the Debye-Hückel screened potential as expected.

8.9 Supplementary Notes

8.9.1 The third virial coefficient for hard spheres

The third virial coefficient B_3 is given by [see (8.10b)]

$$B_3 = -\frac{1}{3V}\int f(|\mathbf{r}_1 - \mathbf{r}_2|)f(|\mathbf{r}_1 - \mathbf{r}_3|)f(|\mathbf{r}_2 - \mathbf{r}_3|)\, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \tag{8.165}$$

B_3 can be calculated for hard spheres by geometrical considerations, but these considerations test one's intuition. An easier way is to take advantage of the fact that (8.165) is an example of a convolution integral (see Section **??**) and can be expressed in terms of the Fourier transform of $f(r)$.

Problem 8.25. Evaluation of B$_3$ for hard spheres

(a) Read Appendix **??** on convolution integrals and show that B_3 in (8.165) can be expressed as

$$B_3 = -\frac{1}{3}\int \frac{d^3k}{(2\pi)^3} f(k)^3, \tag{8.166}$$

where $f(k)$ is the Fourier transform of $f(r)$.

(b) Use (**??**) and the form of $f(r)$ for hard spheres,

$$f(r) = \begin{cases} -1 & (0 < r < \sigma), \\ = 0 & (r > \sigma), \end{cases} \tag{8.167}$$

to show that

$$f(k) = 4\pi\sigma^3 \Big[\frac{\cos k\sigma}{(k\sigma)^2} - \frac{\sin k\sigma}{(k\sigma)^3}\Big]. \tag{8.168}$$

(c) *The integral in (8.166) with (8.168) for $f(k)$ can be evaluated numerically or calculated analytically. Show that the result is

$$B_3 = \frac{5\pi^2}{18}\sigma^6 \qquad \text{(hard spheres).} \tag{8.169}$$

☐

B_4 can also be evaluated analytically for hard spheres, but higher order virial coefficients have to be evaluated by Monte Carlo methods.

8.9.2 Definition of $g(r)$ in terms of the local particle density

Another way of defining $g(r)$ is in terms of the local particle density. Given the properties of the delta function $\delta(x - x_0)$ (see Section **??**), we have that

$$\int_{x_0-\epsilon}^{x_0+\epsilon} \delta(x - x_0)\, dx = 1, \tag{8.170}$$

and the integral over any other values of x gives zero. Hence, the integral of the sum $\sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$ about $\mathbf{r}$ over the volume element $d\mathbf{r}$ gives the number of particles in the volume element. We define the *local particle density*

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i), \tag{8.171}$$

and the single particle density function

$$\rho_1(\mathbf{r}) = \Big\langle \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \Big\rangle, \tag{8.172}$$

where $\big\langle \delta(\mathbf{r} - \mathbf{r}_1) \big\rangle$ is given by

$$\begin{aligned} \big\langle \delta(\mathbf{r} - \mathbf{r}_1) \big\rangle &= \frac{1}{Q_N} \int \delta(\mathbf{r} - \mathbf{r}_1)\, e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}\, d\mathbf{r}_1 \ldots d\mathbf{r}_N & \text{(8.173a)} \\ &= \frac{1}{Q_N} \int e^{-\beta U(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)}\, d\mathbf{r}_2 \ldots d\mathbf{r}_N. & \text{(8.173b)} \end{aligned}$$

Similarly, the two-particle distribution function $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ is defined as

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i \neq j = 1}^{N} \big\langle \delta(\mathbf{r}_1 - \mathbf{r}_i)\delta(\mathbf{r}_2 - \mathbf{r}_j) \big\rangle. \tag{8.174}$$

We can use the same reasoning as in (8.173) to show that ρ_2 as defined in (8.174) can be written as

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \frac{\int e^{-\beta U(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3 \ldots \mathbf{r}_N)}\, d\mathbf{r}_3\, d\mathbf{r}_4 \ldots d\mathbf{r}_N}{\int e^{-\beta U(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3 \ldots \mathbf{r}_N)}\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3\, d\mathbf{r}_4 \ldots d\mathbf{r}_N}. \tag{8.175}$$

If we compare (8.175) and (8.81), we see that we can also express $g(\mathbf{r}_1, \mathbf{r}_2)$ as

$$\rho^2 g(\mathbf{r}_1, \mathbf{r}_2) = \rho_2(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i \neq j} \big\langle \delta(\mathbf{r}_1 - \mathbf{r}_i)\delta(\mathbf{r}_2 - \mathbf{r}_j) \big\rangle. \tag{8.176}$$

Hence, we see that $g(r)$ is related to the spatial correlations of the density fluctuations in the system.

Problem 8.26. One particle distribution function
Use the definition (8.172) and the result (8.173b) to show that $\rho_1(\mathbf{r}) = \rho$ for a homogeneous system. Hint: let $\mathbf{r}_j = \mathbf{r}_1 + \mathbf{x}_j$ for $j \neq 1$. Note that the denominator becomes independent of $\mathbf{r}_1$. ☐

8.9.3 X-ray scattering and the static structure function

The mean distance between particles in a typical fluid or solid is the order of 10^{-10} m. Wavelengths of the order of this distance are available using neutrons or X-rays. To understand how an elastic scattering experiment can probe the static correlations between particles we consider X-ray scattering. A photon of wavelength of 10^{-10} m has an energy of $\hbar\omega = hc/\lambda \approx 10^4$ eV. This energy is very large in comparison to the typical energy of the particles in a liquid which is the order of kT or approximately 0.1 eV at room temperatures. Hence, the collisions of photons with the particles in a liquid and a solid will leave the photon energies almost unchanged and to a good approximation, the scattering can be treated as elastic.

In the following we will show that the scattered intensity $I(\theta)$ of the X-rays is given by

$$I(\theta) \propto N I_0 S(k), \tag{8.177}$$

where the wave vector k is related to the scattering angle θ, and I_0 is the intensity of the incoming beam. The *static structure function* $S(k)$ is defined as

$$\boxed{S(k) = \frac{1}{N}\big\langle \sum_{i,j=1}^{N} e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)}\big\rangle}. \tag{8.178}$$

In the following we will derive (8.177) and show that the radial distribution function $g(r)$ is related to the Fourier transform of $S(k)$.

To obtain (8.177) we assume that the incoming beam is a plane wave of wave vector $\mathbf{q}$. For simplicity we assume that the incident beam is scattered from an atom at the origin. The scattered signal is measured as a function of θ, the angle between the incident and scattered beams (see Figure 8.12). The detector receives a spherical wave of amplitude $f(\theta)/R$, where R is the distance of the detector from the origin. The form factor $f(\theta)$ depends on the detailed physics of the scattering process. Because the scattering is elastic, we have $|\mathbf{q}'| = |\mathbf{q}|$.

The amplitude of the wave scattered by an atom at $\mathbf{r}_i$ has a phase difference of $(\mathbf{q}' - \mathbf{q})\cdot\mathbf{r}_i$ relative to the wave scattered by the atom at the origin. Hence the scattering amplitude from atom i at $\mathbf{r}_i$ is proportional to

$$\frac{f(\theta)}{R} e^{i\mathbf{k}\cdot\mathbf{r}_i}, \tag{8.179}$$

where

$$\mathbf{k} = \mathbf{q}' - \mathbf{q}. \tag{8.180}$$

Because the form factor $f(\theta)$ is the same for all atoms, the total scattering amplitude is the sum

$$A(\theta) = \frac{f(\theta)}{R}\sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i}. \tag{8.181}$$

The detector measures the thermal average of the scattering intensity:

$$I(\theta) = \big\langle |A(\theta)|^2\big\rangle = \frac{|f(\theta)|^2}{R^2}\Big\langle \sum_{i,j} e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)}\Big\rangle = \frac{|f(\theta)|^2}{R^2} N S(\mathbf{k}), \tag{8.182}$$

where the static structure function $S(k)$ is defined in (8.178).

The static structure function $S(k)$ is a measure of the correlations between the positions of the atoms in the liquid. We now show that $S(k)$ is related to the Fourier transform of $g(r)$. We first divide the sum over i and j in (8.178) into self, $i = j$, and distinct, $i \neq j$, contributions. There are N of the former and $N(N-1)$ of the latter. We have

$$S(k) = 1 + \frac{1}{N}N(N-1)\big\langle e^{i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)}\big\rangle \tag{8.183a}$$

$$= 1 + \frac{N(N-1)}{N}\frac{\int e^{i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)}\, e^{-\beta U} d\mathbf{r}_1 \ldots d\mathbf{r}_N}{\int e^{-\beta U}\, d\mathbf{r}_1 \ldots d\mathbf{r}_N}. \tag{8.183b}$$

If we use the definition (8.81) of $g(\mathbf{r}_1, \mathbf{r}_2)$, we can write (8.183b) as

$$S(k) = 1 + \frac{1}{N}\int \rho^2 g(\mathbf{r}_1, \mathbf{r}_2)\, e^{i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)} d\mathbf{r}_1 d\mathbf{r}_2. \tag{8.184}$$

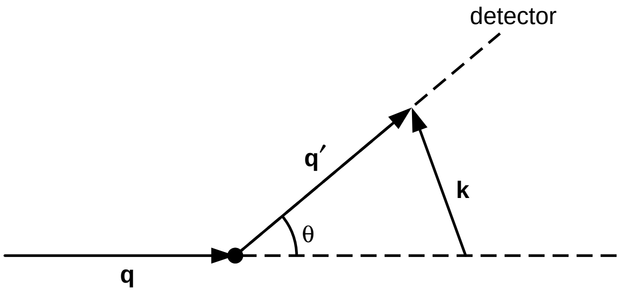

Figure 8.12: The geometry of the elastic scattering of a photon.

For a homogeneous liquid, $g(\mathbf{r}_1, \mathbf{r}_2)$ depends only on $|\mathbf{r}_1 - \mathbf{r}_2|$, and we obtain

$$S(k) = 1 + \rho\int g(r) e^{i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r}. \tag{8.185}$$

It is customary to rewrite (8.185) as

$$S(k) - 1 = \rho\int [g(r) - 1]\, e^{i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r} + \rho\int e^{i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r} \tag{8.186a}$$

$$= \rho\int [g(r) - 1]\, e^{i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r} + \rho(2\pi)^3\delta(\mathbf{k}). \tag{8.186b}$$

The contribution of the $\delta(\mathbf{k})$ term in (8.186b) is unimportant because it is identically zero except when $\mathbf{k} = 0$, that is, for radiation not scattered by the atoms in the fluid. Hence, we can rewrite (8.186b) in the desired form:

$$\boxed{S(k) - 1 = \rho\int [g(r) - 1]\, e^{i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r}}. \tag{8.187}$$

From (8.187) we see that $S(k) - 1$ is the Fourier transform of $g(r) - 1$, and a measurement of the intensity of the elastically scattered radiation yields the Fourier transform of the radial distribution function.

Problem 8.27. Alternative form of $S(k)$

(a) Use the fact that the Fourier transform of the density $\rho(\mathbf{r})$ is

$$\rho_{\mathbf{k}} = \int e^{-i\mathbf{k}\cdot\mathbf{r}} \rho(\mathbf{r})\, d\mathbf{r} = \sum_{i=1}^{N} e^{-i\mathbf{k}\cdot\mathbf{r}_i} \tag{8.188}$$

to show that $S(\mathbf{k})$ can be expressed as

$$S(\mathbf{k}) = \frac{1}{N}\langle \rho_{\mathbf{k}}\rho_{-\mathbf{k}}\rangle. \tag{8.189}$$

(b) Use (8.189) to show that $S(\mathbf{k})$ can be written as

$$S(\mathbf{k}) = \frac{1}{N}\Big\langle \sum_{i=1}^{N}\sum_{j=1}^{N} e^{-i\mathbf{k}\cdot\mathbf{r}_i} e^{i\mathbf{k}\cdot\mathbf{r}_j} \Big\rangle \tag{8.190}$$

$$= \frac{1}{N}\Big\langle \big|\sum_{i=1}^{N} e^{-i\mathbf{k}\cdot\mathbf{r}_i}\big|^2 \Big\rangle. \tag{8.191}$$

□

Compressibility equation. In a scattering experiment the beam samples a subset of the total volume. Because the number of particles in the subset fluctuates, we need to use the grand canonical ensemble to describe the measured values of $S(k)$. The energy and pressure equations (8.74) and (8.97) are identical in both ensembles, but the *compressibility equation* holds only in the grand canonical ensemble because it relates the integral of $g(r) - 1$ and hence $S(k = 0)$ to fluctuations in the density.

In Section 6.11 we derived the relation between the isothermal compressibility and the density (number) fluctuations (see (6.238), page 341):

$$\rho\kappa = \frac{1}{kT}\frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle}. \tag{8.192}$$

We now relate the integral over $g(r)$ to the density fluctuations. In the grand canonical ensemble the probability density of finding n particular particles with positions $\mathbf{r}_1, \ldots, \mathbf{r}_n$ in the range $d\mathbf{r}_1, \ldots, d\mathbf{r}_n$ is given by

$$P_n(\mathbf{r}_1, \ldots, \mathbf{r}_n) = \sum_{N=0}^{\infty} \frac{z^N}{N!\, Z_G} \int e^{-\beta U_N}\, d\mathbf{r}_{n+1} \ldots d\mathbf{r}_N, \tag{8.193}$$

where $z = e^{\beta\mu}$. There are $N(N-1)\ldots(N-n+1) = N!/(N-n)!$ different sets of particles which can correspond to the n particles. Hence, the total probability that any n particles occupy these volume elements is given by

$$P_n(\mathbf{r}_1, \ldots, \mathbf{r}_n) \equiv \rho^n g(\mathbf{r}_1, \ldots, \mathbf{r}_n), \tag{8.194a}$$

$$= \sum_{N=0}^{\infty} \frac{z^N}{N-n)!\, Z_G} \int \cdots \int e^{-\beta U_N}\, d\mathbf{r}_{N+1}, \ldots d\mathbf{r}_N. \tag{8.194b}$$

From the definition of P_1 and P_2, it follows that

$$\int P_1(\mathbf{r}_1)\, d\mathbf{r}_1 = \langle N\rangle \tag{8.195}$$

and

$$\iint P_2(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_1 d\mathbf{r}_2 = \langle N(N-1)\rangle. \tag{8.196}$$

We can use (8.196) and (8.195) to obtain

$$\iint \big[P_2(\mathbf{r}_1, \mathbf{r}_2) - P_1(\mathbf{r}_1)P_1(\mathbf{r}_2)\big]\, d\mathbf{r}_1 d\mathbf{r}_2 = \langle N^2\rangle - \langle N\rangle^2 - \langle N\rangle. \tag{8.197}$$

The left-hand side of (8.197) is equal to $V\rho^2\int[g(r)-1]\,d\mathbf{r}$ for a homogeneous system. Hence we obtain

$$N\rho\int[g(r)-1]\,d\mathbf{r} = \langle N^2\rangle - \langle N\rangle^2 - \langle N\rangle, \tag{8.198}$$

or

$$1+\rho\int[g(r)-1]\,d\mathbf{r} = \frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle}. \tag{8.199}$$

If we use the relation (8.192), we find the desired relation

$$1+\rho\int[g(r)-1]\,d\mathbf{r} = \rho kT\kappa \qquad \text{(compressibility equation)}. \tag{8.200}$$

The relation (8.200), known as the *compressibility equation*, expresses the isothermal compressibility κ as an integral over $g(r)$ and holds only in the grand canonical ensemble. From the relation (8.187) we have

$$S(k=0)-1 = \rho\int[g(r)-1]\,d\mathbf{r}, \tag{8.201}$$

and hence

$$S(k=0) = \rho kT\kappa. \tag{8.202}$$

Problem 8.28. Value of $S(k=0)$ in different ensembles

As mentioned, the condition (8.202) on $S(k=0)$ only applies in the grand canonical ensemble. What is $S(k=0)$ in the canonical ensemble? Why is the value of $S(k=0)$ different in these two ensembles? ☐

Alternative form of the compressibility relation. Finally, we express the compressibility relation (8.138) in terms of $c(r)$ rather than $h(r)=g(r)-1$ by using the Ornstein-Zernike equation (8.125). We write the latter as

$$g(r)-1 = c(r)+\rho\int c(|\mathbf{r}-\mathbf{r}'|)[g(\mathbf{r}')-1]d\mathbf{r}'. \tag{8.203}$$

and multiply both sides by $d\mathbf{r}$ and integrate noting that $\int c(|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r} = \int c(r)\,d\mathbf{r}$. We then rearrange the results to find

$$\int[g(r)-1]\,d\mathbf{r} = \frac{\int c(r)\,d\mathbf{r}}{1-\rho\int c(r)\,d\mathbf{r}}. \tag{8.204}$$

Finally we combine (8.204) with (8.138) to find (8.139).

Vocabulary

density expansion, virial coefficients, cluster integrals

Mayer f function

cumulant, high temperature expansion

disconnected, reducible, and irreducible diagrams

ladder diagrams, ring diagrams

radial distribution function $g(r)$

static structure function $S(k)$

reference theory of liquids

Debye-Hückel theory

Additional Problems

Problem 8.29. Why is the method that we have used to obtain the virial expansion for a classical fluid not applicable to a quantum system? □

Problem 8.30. Temperature dependence of B_2

(a) A simpler potential that captures some of the properties of the Lennard-Jones potential is the square well potential which is defined as

$$u(r) = \begin{cases} \infty & (r < \sigma), \\ -\epsilon & (\sigma < r < \lambda\sigma), \\ 0 & (r > \lambda\sigma), \end{cases} \tag{8.205}$$

where σ is the diameter of the hard core part, $\lambda\sigma$ is the range of the attractive well, and ϵ is the well depth. Show that for this potential the Mayer function $f(r)$ is given by

$$f(r) = \begin{cases} -1 & (r < \sigma), \\ g = e^{\beta\epsilon} - 1 & (r < \lambda\sigma), \\ 0 & (r > \lambda\sigma), \end{cases} \tag{8.206}$$

and

$$B_2(T) = \frac{2\pi\sigma^3}{3}\big[1 - (\lambda^3 - 1)g\big]. \tag{8.207}$$

(b) Make a plot of the temperature dependence of $B_2(T)$ as given by (8.207) and compare it to the approximate temperature dependence given by (8.36).

(c) Program `SecondVirialCoefficient` evaluates the integral over r in (8.32) numerically using a simple numerical method (Simpson's rule) to determine the T dependence of B_2 for the Lennard-Jones potential. Compare the numerical results for the Lennard-Jones potential with the approximate result in (8.36). At what temperature does B_2 vanish? How does this temperature compare with that predicted by (8.36)? □

Problem 8.31. Inversion temperature of argon

In Section 2.23.2, page 86, we discussed the porous plug or Joule-Thomson process in which a gas is forced from a high pressure chamber through a porous plug into a lower pressure chamber. The process occurs at constant enthalpy and the change in temperature of the gas is given by $dT = (\partial T/\partial P)_H\, dP$ for small changes in pressure. Because the change in the pressure is negative, the temperature of the gas decreases when $(\partial T/\partial P)_H$ is positive and increases when $(\partial T/\partial P)_H$ is negative. We know that (see (2.218), page 87)

$$\Big(\frac{\partial T}{\partial P}\Big)_H = \frac{1}{C_P}\Big[T\Big(\frac{\partial V}{\partial T}\Big)_{P,N} - V\Big]. \tag{8.208}$$

For a given pressure find the value of the inversion temperature at which $(\partial T/\partial P)_H = 0$. Assume the approximate equation of state $V = NkT/P + NB_2$ and the approximate form $B_2 = b - a/kT$ with a and b given by their values for the Lennard-Jones potential. Use $\sigma = 3.4\,\text{Å}$ and $\epsilon/k = 120\,\text{K}$ and compare your result with the experimental value of 780 K for argon. ☐

Problem 8.32. Alternative form of B_2

(a) Show that the virial coefficient B_2 given in (8.32) can be written in the form

$$B_2 = -\frac{1}{6kT}\int_0^\infty r\frac{du(r)}{dr}e^{-\beta u(r)}4\pi r^2\,dr. \tag{8.208}$$

(b) Assume that $g(r)$ can be written in the form

$$g(r) = g_0 + \rho g_1(r) + \rho^2 g_2(r) + \cdots. \tag{8.209}$$

Use the virial equation of state (8.97) to obtain

$$\frac{PV}{NkT} = 1 - \frac{\rho}{6kT}\sum_{n=0}^{\infty}\rho^n\int_0^\infty r\frac{du}{dr}g_n(r)\,4\pi r^2\,dr. \tag{8.210}$$

Compare the density expansion (8.9) of PV/NkT with (8.209) and show that

$$B_{n+2} = -\frac{1}{6kT}\int_0^\infty r\frac{du}{dr}g_n(r)4\pi r^2\,dr. \tag{8.211}$$

(c) From the result of part (8.208) show that

$$g_0(r) = e^{-\beta u(r)}. \tag{8.212}$$

(d) Use the relation (8.97) to find the form of B_2 implied by (8.212). ☐

Problem 8.33. Exact equation of state for hard rods

Consider a one-dimensional system of particles confined to a box of length L. The interparticle interaction is given by

$$u(x) = \begin{cases} \infty & (x < \sigma), \\ 0 & (x \geq \sigma). \end{cases} \tag{8.213}$$

This system of hard rods is also known as a Tonks gas.

(a) Evaluate the virial coefficients B_2 and B_3. It is possible to do the integrals analytically.

(b) Note that the form of the interaction (8.213) prevents particles from exchanging places, that is, from changing their order. What is the available "volume" in which the particles can move? Use this consideration to guess the form of the equation of state.

(c) *Calculate the partition function and show that the exact equation of state of a system of hard rods is given by

$$\frac{P}{\rho kT} = \frac{1}{1-\eta}, \tag{8.214}$$

where $\eta = \rho\sigma$ and $\rho = N/L$.

(d) What is the value of the nth virial coefficient that is implied by the form (8.214) of the hard rod equation of state? □

***Problem 8.34.** Virial coefficients implied by the Percus-Yevick approximation

Use the approximate results (8.137) and (8.140) for the Percus-Yevick equation of state for hard spheres to determine the virial coefficients implied by the Percus-Yevick equation. How do these virial coefficients compare with the exact coefficients given in Table 8.2? □

Suggestions for Further Reading

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Chapter 9

Critical Phenomena: Landau Theory and the Renormalization Group Method

26 March 2010

We first discuss a phenomenological mean-field theory of phase transitions due to Landau and introduce the ideas of universality and scaling near critical points. The breakdown of mean-field theory near a critical point leads us to introduce the renormalization group method, which has had a major impact on our understanding of phase transitions, quantum field theory, and turbulence. We introduce the renormalization group method in the context of percolation, a simple geometrical model that exhibits a continuous transition, and then apply renormalization group methods to the Ising model.

9.1 Landau Theory of Phase Transitions

The qualitative features of mean-field theory can be summarized by a simple phenomenological expression for the free energy due to Landau. We will introduce the Landau theory in the context of the Ising model, but the power of the Landau formulation of mean-field theory is that it can be applied to a wide variety of phase transitions ranging from superconductors to liquid crystals and first-order as well as continuous phase transitions.

One of the assumptions of the Landau theory is that a phase transition can be characterized by an *order parameter*, which we take to be the magnetization m. We choose the magnetization as the order parameter because it is zero for $T > T_c$, nonzero for $T \leq T_c$, and its behavior characterizes the nature of the transition.

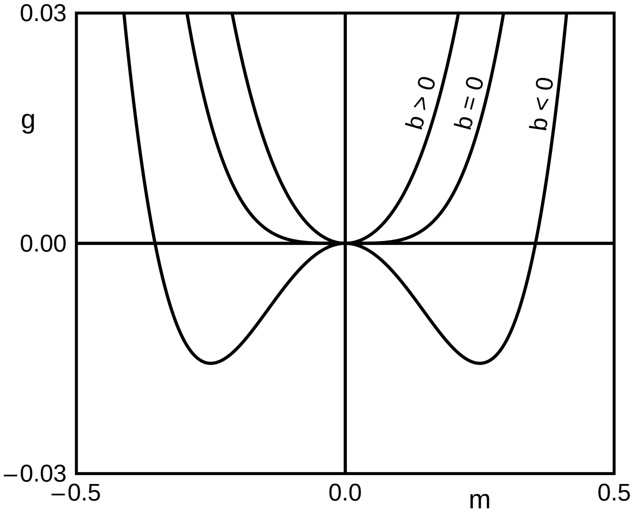

Figure 9.1: The dependence of the Landau form of the free energy density g on the order parameter m for $b = -1$, 0, and 1 with $c = 16$. The minima of g for $b = -1$ are at $m = \pm 0.250$.

Because m is small near the critical point, it is reasonable to assume that the (Gibbs) free energy density g (the free energy per unit volume) can be written in the form

$$g(T, m) = a(T) + \frac{b(T)}{2} m^2 + \frac{c(T)}{4} m^4 - Hm \tag{9.1}$$

for a given value of H. The assumption underlying the form (9.1) is that g can be expanded in a power series in m about $m = 0$ near the critical point. Although the assumption that g is an analytic function of m turns out to be incorrect, Landau theory, like mean-field theory in general, is still a useful tool. Because $g(T, m)$ is symmetrical about $m = 0$ for $H = 0$, there are no odd terms in (9.1). The coefficients b and c are as yet unspecified. We will find that some simple assumptions for the temperature dependence of the coefficients b and c will yield the results of mean-field theory that we found in Section 5.7.

The equilibrium value of m is the value that minimizes the free energy. In Figure 9.1 we show the dependence of g on m for $H = 0$. We see that if $b > 0$ and $c > 0$, then the minimum of g is at $m = 0$, corresponding to the high temperature phase. If $b < 0$ and $c > 0$, then the minimum of g is at $m \neq 0$, corresponding to the low temperature ferromagnetic phase. To find the minimum of g we take the derivative of g with respect to m and write for $H = 0$

$$\frac{\partial g}{\partial m} = bm + cm^3 = 0. \tag{9.2}$$

One obvious solution of (9.2) is $m = 0$, which mimimizes g for $b > 0$ and $c > 0$. The nonzero solution of (9.2) is $m^2 = -b/c$. If we make the simple assumption that $b = b_0(T - T_c)$ and $c > 0$, we find

$$m = \pm\Big(\frac{b_0}{c}\Big)^{1/2} (T_c - T)^{1/2} = \pm\Big(\frac{b_0 T_c}{c}\Big)^{1/2} \epsilon^{1/2} \qquad (T \leq T_c), \tag{9.3}$$

where the dimensionless parameter ϵ is a measure of the deviation from the critical temperature:

$$\epsilon = \frac{|T_c - T|}{T_c}. \tag{9.4}$$

Equation (9.3) predicts that the critical exponent $\beta = 1/2$. Compare this result for β to what we found from the mean-field theory treatment of the Ising model on page 258. How does this value of β compare to the exact value of β for the two-dimensional Ising model?

The behavior of the specific heat C can be found from the relation $C = T\partial s/\partial T$. The entropy density is given by

$$s = -\frac{\partial g}{\partial T} = -a' - \frac{b'}{2}m^2 - \frac{b}{2}(m^2)' - \frac{c}{4}(m^4)', \tag{9.5}$$

where the primes denote the derivative with respect to T, and we have assumed that c is independent of T. From (9.5) and our assumed form for $b(T)$ we have

$$C = T\frac{ds}{dT} = -Ta'' - Tb'(m^2)' - \frac{cT}{4}(m^4)''. \tag{9.6}$$

Because $m = 0$ for $T \geq T_c$, we have $C \to -Ta''$ as $T \to T_c^+$. For $T \to T_c^-$ we have $(m^2)' = -b_0/c$, $b' = b_0$, and $(m^4)'' \to 2(b_0/c)^2$. Hence, we obtain

$$C = \begin{cases} -Ta'' & (T \to T_c^+), \\ -Ta'' + \dfrac{Tb_0^2}{2c}. & (T \to T_c^-). \end{cases} \tag{9.7}$$

We see that Landau theory predicts a jump in the specific heat at the critical point, just as we obtained in our mean-field theory treatment of the Ising model in Section 5.7.

Problem 9.1. Predictions of the Landau theory for the critical exponents γ and δ

(a) Show that the solution of $bm+cm^3-H = 0$ minimizes g for $H \neq 0$, and hence $\chi^{-1} = (b+3cm^2)$. Then show that $\chi^{-1} = b = b_0(T - T_c)$ for $T > T_c$ and $\chi^{-1} = 2b_0(T_c - T)$ for $T < T_c$. Hence Landau theory predicts the same power law form for χ above and below T_c with $\gamma = 1$.

(b) Show that $cm^3 = H$ at the critical point, and hence $\delta = 3$, where δ is defined by $m \sim H^{1/\delta}$. ☐

We can generalize Landau theory to incorporate spatial fluctuations by writing

$$g(\mathbf{r}) = a + \frac{b}{2}m^2(\mathbf{r}) + \frac{c}{4}m^4(\mathbf{r}) + \frac{\lambda}{2}[\nabla m(\mathbf{r})]^2 - m(\mathbf{r})H, \tag{9.8}$$

where the parameter $\lambda > 0$. The gradient term in (9.8) expresses the fact that the free energy is increased by spatial fluctuations in the order parameter. The form of the free energy density in (9.8) is commonly known as the *Landau-Ginzburg* form. The total free energy is given by

$$G = \int g(\mathbf{r})\, d\mathbf{r}, \tag{9.9}$$

and the total magnetization is

$$M = \int m(\mathbf{r})\, d\mathbf{r}. \tag{9.10}$$

We follow the same procedure as before and minimize the total free energy:

$$\delta G = \int \Big[\delta m(\mathbf{r})[b\, m(\mathbf{r}) + c\, m^3(\mathbf{r}) - H] + \lambda \nabla \delta m(\mathbf{r}) \cdot \nabla m(\mathbf{r})\Big]\, d\mathbf{r} = 0. \tag{9.11}$$

The last term in the integrand of (9.11) can be simplified by integrating by parts and requiring that $\delta m(\mathbf{r}) = 0$ at the surface. In this way we obtain

$$b\, m(\mathbf{r}) + c\, m(\mathbf{r})^3 - \lambda \nabla^2 m(\mathbf{r}) = H(\mathbf{r}). \tag{9.12}$$

Equation (9.12) reduces to the usual Landau theory by letting $H(\mathbf{r}) = H$ and $\nabla m(\mathbf{r}) = 0$.

To probe the response of the system we apply a localized magnetic field $H(\mathbf{r}) = H_0 \delta(\mathbf{r})$ and write

$$m(\mathbf{r}) = m_0 + \phi(\mathbf{r}). \tag{9.13}$$

We assume that the spatially varying term $\phi(\mathbf{r})$ is small so that $m(\mathbf{r})^3 \approx m_0^3 + 3m_0^2\phi(\mathbf{r})$. We then substitute (9.13) into (9.12) and obtain

$$\nabla^2 \phi(\mathbf{r}) - \frac{b}{\lambda}\phi(\mathbf{r}) - 3\frac{c}{\lambda} m_0^2\, \phi(\mathbf{r}) - \frac{b}{\lambda} m_0 - \frac{c}{\lambda} m_0^3 = -\frac{H_0}{\lambda}\delta(\mathbf{r}). \tag{9.14}$$

If we substitute $m_0 = 0$ for $T > T_c$ and $m_0^2 = -b/c$ for $T < T_c$ into (9.14), we obtain

$$\nabla^2 \phi - \frac{b}{\lambda}\phi = -\frac{H_0}{\lambda}\delta(\mathbf{r}) \qquad (T > T_c), \tag{9.15a}$$

$$\nabla^2 \phi + 2\frac{b}{\lambda}\phi = -\frac{H_0}{\lambda}\delta(\mathbf{r}). \qquad (T < T_c). \tag{9.15b}$$

Note that $\phi(\mathbf{r})$ in (9.15) satisfies an equation of the same form as we found in the Debye-Hučkel theory (see Section 8.8, page 420).

The easiest way of solving equations of the form

$$\big[\nabla^2 - \xi^{-2}\big]\phi(\mathbf{r}) = -4\pi A \delta(\mathbf{r}) \tag{9.16}$$

is to transform to k-space and write (for three dimensions)

$$\phi(\mathbf{r}) = \int \frac{d^3k}{(2\pi)^3} e^{-i\mathbf{k}\cdot\mathbf{r}} \phi(\mathbf{k}). \tag{9.17}$$

We then write

$$\nabla^2 \phi(\mathbf{r}) = -\int \frac{d^3k}{(2\pi)^3} k^2 e^{-i\mathbf{k}\cdot\mathbf{r}} \phi(\mathbf{k}), \tag{9.18}$$

and the Fourier transform of (9.16) becomes

$$[k^2 + \xi^{-2}]\phi(\mathbf{k}) = 4\pi A, \tag{9.19}$$

or

$$\phi(\mathbf{k}) = \frac{4\pi A}{k^2 + \xi^{-2}}. \tag{9.20}$$

The inverse Fourier transform of (9.20) gives

$$\phi(\mathbf{r}) = \int \frac{d^3k}{(2\pi)^3} \frac{4\pi A}{k^2 + \xi^{-2}} e^{-i\mathbf{k}\cdot\mathbf{r}} = \frac{A}{r} e^{-r/\xi}. \tag{9.21}$$

Hence we see that the solution of (9.15) can be written as

$$\phi(r) = \frac{H_0}{4\pi\lambda} \frac{1}{r} e^{-r/\xi}, \tag{9.22}$$

with

$$\xi(T) = \begin{cases} \Big[\dfrac{\lambda}{b(T)}\Big]^{1/2} & (T > T_c), \\ \Big[\dfrac{-\lambda}{2b(T)}\Big]^{1/2} & (T < T_c). \end{cases} \tag{9.23}$$

Thus, ϕ is a quantitative measure of the response to a small magnetic field applied at a single point. Because $\phi(r)$ is proportional to H, it is an example of a linear response, and its positive sign indicates that the system is paramagnetic. The exponential form for $\phi(r)$ indicates that this response decays rapidly as the distance from the applied field becomes greater than ξ. As we will see, ξ plays another important role as well, namely it can be interpreted as the *correlation length*. Because $b(T) = b_0(T - T_c)$, we see that ξ diverges both above and below T_c as

$$\xi(T) \sim \epsilon^{-\nu}, \tag{9.24}$$

with $\nu = 1/2$.

Problem 9.2. Solution of (9.16)
Work out the steps that were skipped in obtaining the solution (9.21) of (9.16).

The large value of ξ near T_c implies that the fluctuations of the magnetization are correlated over large distances. We can understand how the fluctuations are correlated by calculating the correlation function

$$G(r) = \langle m(r)m(0)\rangle - \langle m\rangle^2. \tag{9.25}$$

[Do not confuse $G(r)$ with the free energy G.] As in Chapter 8 we will write thermal averages as $\langle \ldots \rangle$. We can relate $G(r)$ to the first-order response $\phi(r)$ by the following considerations (see page 232). We write the total energy in the form

$$E = E_0 - \int m(\mathbf{r})H(\mathbf{r})\, d\mathbf{r}, \tag{9.26}$$

where E_0 is the part of the total energy E that is independent of $H(\mathbf{r})$. We have

$$\langle m(\mathbf{r})\rangle = \frac{\sum_s m_s(\mathbf{r})\, e^{-\beta[E_{0,s} - \int m_s(\mathbf{r}')H(\mathbf{r}')\, d\mathbf{r}']}}{\sum_s e^{-\beta[E_{0,s} - \int m_s(\mathbf{r}')H(\mathbf{r}')\, d\mathbf{r}']}}, \tag{9.27}$$

where $E_{0,s}$ and $m_s(\mathbf{r})$ denote the values of E_0 and $m(\mathbf{r})$ in microstate s. We see that

$$\frac{\delta\langle m(\mathbf{r})\rangle}{\delta H(0)} = \beta\big[\langle m(\mathbf{r})m(0)\rangle - \langle m(\mathbf{r})\rangle\langle m(0)\rangle\big] = \beta G(\mathbf{r}). \tag{9.28}$$

Because $m(\mathbf{r}) = m_0 + \phi(\mathbf{r})$, we also have $\delta\langle m(\mathbf{r})\rangle/\delta H(0) = \phi(\mathbf{r})/H_0$ so that from (9.28) we obtain $G(r) = kT\phi(\mathbf{r})/H_0$. We substitute $\phi(\mathbf{r})$ from (9.22) and find that

$$G(r) = \frac{kT}{4\pi\lambda}\frac{1}{r}e^{-r/\xi}. \tag{9.29}$$

From the form of (9.29) we recognize ξ as the correlation length in the neighborhood of T_c, and we see that the fluctuations of the magnetization are correlated over increasingly large distances as the system approaches the critical point.

At $T = T_c$, $\xi = \infty$, and $G(r) \sim 1/r$. For arbitrary spatial dimension d we can write the r dependence of $G(r)$ at $T = T_c$ as

$$G(r) \sim \frac{1}{r^{d-2+\eta}} \qquad (T = T_c), \tag{9.30}$$

where we have introduced another critical exponent η. Landau-Ginzburg theory yields $\eta = 0$ in three dimensions. It can be shown that Landau-Ginzburg theory predicts $\eta = 0$ in all dimensions.

Problem 9.3. Relation of the linear response to the spin-spin correlation function

Derive the relation (9.28) between the linear response $\delta\langle m(\mathbf{r})\rangle/\delta H(0)$ and the spin correlation function $G(r)$. ☐

The existence of long-range correlations of the order parameter is associated with the divergence of the susceptibility χ. As we showed in Chapter 5, χ is related to the fluctuations in M [see (5.17)]:

$$\chi = \frac{1}{NkT}\big[\langle M^2\rangle - \langle M\rangle^2\big] = \frac{1}{NkT}\langle\big[M - \langle M\rangle\big]^2\rangle. \tag{9.31}$$

We write

$$M - \langle M\rangle = \sum_{i=1}^{N}[s_i - \langle s_i\rangle] \tag{9.32}$$

and

$$\chi = \frac{1}{NkT}\sum_{i,j=1}^{N}[\langle s_i s_j\rangle - \langle s_i\rangle\langle s_j\rangle] = \frac{1}{kT}\sum_{j=1}^{N}G_{1j}, \tag{9.33}$$

where $G_{ij} = \langle s_i s_j\rangle - \langle s_i\rangle\langle s_j\rangle$. We have used the definition of G_{ij} and the fact that all sites are equivalent. The generalization of (9.33) to a continuous system is

$$\chi = \frac{1}{kT}\int G(r)\, d\mathbf{r}. \tag{9.34}$$

Problem 9.4. The divergence of the susceptibility and long-range correlations

Show that the relation (9.34) and the form (9.29) of $G(r)$ implies that $\chi \sim |T - T_c|^{-1}$. Hence, the divergence of the susceptibility is associated with the existence of long-range correlations. ☐

Range of validity of mean-field theory. As discussed briefly in Section 5.7, mean-field theory must break down when the system is sufficiently close to a critical point. That is, mean-field theory is applicable only if the fluctuations in the order parameter are much smaller than their mean value. Conversely, if the relative fluctuations are large, mean-field theory must break down. One criterion for the validity of mean-field theory can be expressed as

$$\frac{\int [\langle m(\mathbf{r})m(0)\rangle - \langle m(\mathbf{r})\rangle\langle m(0)\rangle]\, d\mathbf{r}}{\int m^2\, d\mathbf{r}} \ll 1. \tag{9.35}$$

The condition (9.35) is known as the *Ginzburg criterion* and gives a criterion for the self-consistency of mean-field theory. If we substitute $G(r)$ from (9.29) into (9.35) and integrate over a sphere of radius ξ, we find

$$\frac{kT}{4\pi\lambda}\int_0^\xi \frac{e^{-r/\xi}}{r}\, 4\pi r^2 dr = \frac{kT\xi^2}{\lambda}\Big(1 - \frac{2}{e}\Big) \approx \frac{0.264kT\xi^2}{\lambda}. \tag{9.36}$$

Hence, the Ginzburg criterion for the validity of mean-field theory becomes

$$\frac{0.264kT\xi^2}{\lambda} \ll \frac{4\pi}{3}\xi^3 m^2, \tag{9.37}$$

or

$$\frac{0.063kT}{\lambda} \ll \xi m^2 \qquad \text{(Ginzburg criterion)}. \tag{9.38}$$

The numerical factors in (9.36)–(9.38) should not be taken seriously.

Because $\xi \sim |T - T_c|^{-1/2}$ and $m^2 \sim (T - T_c)$, we see that the product ξm^2 approaches zero as $T \to T_c$ and the Ginzburg criterion will not be satisfied for T sufficiently close to T_c. Hence, mean-field theory must break down when the system is sufficiently close to a critical point. However, there exist some systems, for example, conventional superconductivity, for which the correlation length is very large even far from T_c and (9.38) is satisfied in practice for ϵ as small as $\sim 10^{-14}$. For liquid ^{4}He mean-field theory is applicable for $\epsilon \sim 0.3$.[1]

Problem 9.5. The Ginzburg criterion in terms of measurable quantities

The Ginzburg criterion can be expressed in terms of the measurable quantities T_c, ξ_0, the correlation length at $T = 0$, and the jump in the specific heat ΔC at $T = T_c$.

(a) Use (9.23) and the relation $b = b_0(T - T_c)$ to express the correlation length as

$$\xi(T) = \xi_0 \epsilon^{-1/2}, \tag{9.39}$$

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[1] A system such as the Ising model will exhibit mean-field behavior in the limit of infinite range interactions (see Section 5.10.5). If the interaction range is long but finite, the system will exhibit mean-field behavior near but not too near the critical point, and then *cross-over* to non-mean-field behavior close to the critical point. See, for example, Erik Luijten, Henk W. J. Blöte, and Kurt Binder, "Medium-range interactions and crossover to classical critical behavior," Phys. Rev. **54**, 4626–4636 (1996).

where ξ_0 is the correlation length extrapolated to $T = 0$. Show that ξ_0 is given by

$$\xi_0^2 = \frac{\lambda}{2b_0 T_c}. \tag{9.40}$$

Hence we can eliminate the parameter λ in (9.38) in favor of the measurable quantity ξ_0 and the parameter b_0.

(b) Express b_0 in terms of the jump ΔC in the specific heat at T_c by using (9.7) and show that $b_0^2 = (2c/T_c)\Delta C$.

(c) Use the relation (9.3) for $m(T)$ in (9.38) and show that the Ginzburg criterion can be expressed as

$$\frac{0.016\,k}{\Delta C\,\xi_0^3} \ll |\epsilon|^{1/2}. \tag{9.41}$$

Note that if ξ_0 is large as it is for conventional superconductors ($\xi_0 \sim 10^{-7}$ m), then the Ginzburg criterion is satisfied for small values of ϵ. □

Problem 9.6. Generalization of Ginzburg criterion to arbitrary dimension

The general solution for the correlation function $G(r)$ in arbitrary spatial dimension d is not as simple as (9.29), but for $r \gg 1$ has the form

$$G(r) \sim \frac{e^{-r/\xi}}{r^{d-2}}. \tag{9.42}$$

Generalize the Ginzburg criterion (9.35) to arbitrary d and show that it is satisfied if $d\nu - 2\beta > 2\nu$, or

$$d > 2 + 2\beta/\nu. \tag{9.43}$$

Ignore all numerical factors. □

Because mean-field theory yields $\beta = 1/2$ and $\nu = 1/2$, we conclude from Problem 9.6 and the condition (9.43) that the Ising model will exhibit mean-field behavior for T near T_c if $d > d_c = 4$. At $d = d_c$ the *upper critical dimension*, there are logarithmic corrections to the mean-field critical exponents. That is, near the critical point, the exponents predicted by mean-field theory are exact for dimensions greater than four.[2]

9.2 Universality and Scaling Relations

From our simulations of the Ising model and our discussions of mean-field theory near the critical point we have learned that critical phenomena are characterized by power law behavior and critical exponents. This behavior is associated with the divergence of the correlation length as the critical

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[2] It is possible to calculate the critical exponents in less than four dimensions by an expansion in the small parameter $d - 4$ with Landau theory as the zeroth order term. The seminal paper is by Kenneth G. Wilson and Michael E. Fisher, "Critical exponents in 3.99 dimensions," Phys. Rev. Lett. **28**, 240–243 (1972). (A strong background in field theory is needed to understand this paper.)

Fisher	$\gamma = \nu(2 - \eta)$
Rushbrooke	$\alpha + 2\beta + \gamma = 2$
Widom	$\gamma = \beta(\delta - 1)$
Josephson	$\nu d = 2 - \alpha$

Table 9.1: Examples of scaling relations between the critical exponents.

point is approached. We also found an example of universality. That is, mean-field theory predicts that the critical exponents are independent of dimension and are the same for the Ising model and the gas-liquid critical points (see page 378). Because the critical exponents of the Ising model depend on dimension, we know that this statement of universality is too strong. Nonetheless, we will find that some aspects of the universality predicted by mean-field theory are correct.

Aside from the intrinsic importance and occurrence of critical phenomena in nature, an understanding of critical phenomena can serve as an introduction to several important ideas in contemporary physics. These ideas are important in a wide range of areas including condensed matter physics, particle physics, plasma physics, and turbulence. In this section we will discuss two of these ideas – universality and scaling. The renormalization group method, which provides a framework for understanding the origins of both universality and scaling, will be introduced in Sections 9.4–9.6. A discussion of a related method, conformal invariance, is beyond the scope of the text.

To better appreciate the application of universality, recall the nature of the Heisenberg model introduced in Section 5.10.1. In this model each spin has three components S_x, S_y, and S_z, and the order parameter is a three-dimensional vector. We say that the Heisenberg model corresponds to $n = 3$, where n is the number of components of the order parameter. If the spins are restricted to be in a plane, then the model is called the XY (or planar) model and $n = 2$. The now familiar Ising model corresponds to $n = 1$.

The superfluid and (conventional) superconducting phase transitions can be modeled by the XY model near a critical point because the order parameter is described by a quantum mechanical wave function which is characterized by an amplitude and a phase. Thus these systems correspond to $n = 2$. As we discussed in Section 5.9 and Chapter 7, the order parameter of the liquid-gas transition is a scalar and hence $n = 1$.

The assumption of universality is that the behavior of a wide variety of systems near a continuous phase transition depends only on the spatial dimension of the lattice d and the symmetry properties of the order parameter, and does not depend on the details of the interactions. The most common *universality classes* correspond to the scalar, planar, and three-dimensional vector order parameter for which $n = 1$, $n = 2$, and $n = 3$, respectively, and to the spatial dimension d. That is, the critical exponents depend on the combination (n, d). One remarkable implication of universality is that the critical exponents for the gas-liquid critical point are the same as the Ising model, even though these systems seem qualitatively different. That is, the Ising model, which is defined on a lattice, and gases and liquids look the same near their critical points if we consider long length scales. Examples of $n = 2$ are XY ferromagnets (see Problem 9.25), superfluid ^{4}He, and conventional superconductivity. The case $n = 3$ corresponds to the Heisenberg model.

The definitions of the critical exponents are summarized in Table 5.1 (see page 253). We will find in the following that only two of the six critical exponents are independent. The exponents are related by *scaling relations* which are summarized in Table 9.1. The scaling relations are a consequence of the essential physics near the critical point; that is, the correlation length ξ is the only characteristic length of the system.

A simple way to obtain the scaling relations in Table 9.1 is to use dimensional analysis and assume that a quantity that has dimension L^{-p} is proportional to ξ^{-p} near the critical point. Because the quantity βF is dimensionless and proportional to N, we see that $\beta F/V$ has dimensions

$$[\beta f] = L^{-d}. \tag{9.44}$$

Similarly the correlation function $G(r)$ depends on L according to

$$[G(r)] = L^{2-d-\eta}. \tag{9.45}$$

From its definition in (9.25) we see that $G(r)$ has the same dimension as m^2, and hence

$$[m] = L^{(2-d-\eta)/2}. \tag{9.46}$$

If we use the relation (9.31) between χ and the variance of the magnetization, we have

$$[kT\chi] = L^{2-\eta}. \tag{9.47}$$

Finally, because $M = -\partial F/\partial H$ [see (5.16)], we have $[\beta H] \sim [\beta f]/[m] \sim L^{-d}/L^{(2-d-\eta)/2}$, or

$$[H/kT] = L^{(\eta-2-d)/2}. \tag{9.48}$$

Problem 9.7. The scaling relations
We can obtain the scaling relations by replacing L in (9.44)–(9.48) by ξ and letting $\xi \sim \epsilon^{-\nu}$.

(a) Use the relation between the heat capacity and the free energy to show that $2 - \alpha = d\nu$.

(b) Use dimensional analysis to obtain the relations $-\nu(2-d-\eta)/2 = \beta$, $-\nu(2-\eta) = -\gamma$, and $\nu(2+d-\eta)/2 = \beta\delta$. Then do some simple algebra to derive the Rushbrooke and Widom scaling relations in Table 9.1. □

9.3 A Geometrical Phase Transition

Before we consider theoretical techniques more sophisticated than mean-field theory, it is instructive to first introduce a model that is simpler than the Ising model and that also exhibits a continuous phase transition. This simple geometrical model, known as *percolation*, does not involve the temperature or the evaluation of a partition function and is easy to simulate. The questions that are raised by considering the percolation transition will prepare us for a deeper understanding of phase transitions in more complex systems such as the Ising model. Some of the applications of percolation include the flow of oil through porous rock, the behavior of a random resistor network, and the spread of a forest fire.

The simplest percolation model is formulated on a lattice. Assume that every lattice site can be in one of two states, "occupied" or "empty." Each site is occupied independently of its

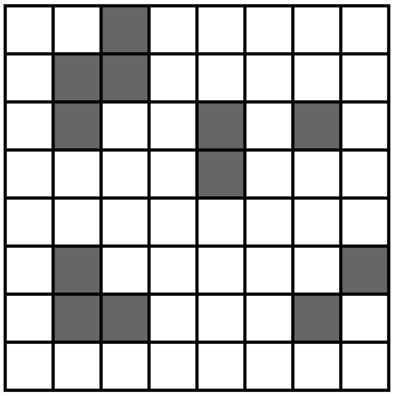

Figure 9.2: Examples of (site) percolation clusters on a square lattice for which each site has four nearest neighbors. Shown are three clusters with one site, one cluster with two sites, one cluster with three sites, and one cluster with four sites.

neighbors with probability p. This model of percolation is called *site* percolation. The nature of percolation is related to the properties of the *clusters* of occupied sites. Two occupied sites belong to the same cluster if they are linked by a path of nearest-neighbor bonds joining occupied sites (see Figure 9.2).

We can use the random number generator on a calculator to generate a random number for each lattice site. A site is occupied if its random number is less than p. Because each site is independent, the order that the sites are visited is irrelevant. If p is small, there are many small clusters [see Figure 9.3(a)]. As p is increased, the size of the clusters increases. If $p \sim 1$, most of the occupied sites form one large cluster that extends from one end of the lattice to the other [see Figure 9.3(c)]. Such a cluster is said to "span" the lattice and is called a *spanning* cluster. What happens for intermediate values of p, for example between $p = 0.5$ and $p = 0.7$ [see Figure 9.3(b)]? It has been shown that in the limit of an infinite lattice there exists a well defined threshold probability p_c such that

For $p \geq p_c$, one spanning cluster or path exists.

For $p \leq p_c$, no spanning cluster exists and all clusters are finite.

The essential characteristic of percolation is *connectedness.* The connectedness of the occupied sites exhibits a qualitative change at $p = p_c$ from a state with no spanning cluster to a state with one spanning cluster. This transition is an example of a continuous *geometrical phase transition.* From our discussions of continuous phase transitions we know that it is convenient to define an order parameter that vanishes for $p < p_c$ and is nonzero for $p \geq p_c$. A convenient choice of the order parameter for percolation is P_∞, the probability that an occupied site is part of the spanning cluster. We can estimate P_∞ for a given configuration on a finite sized lattice from its definition

$$P_\infty = \frac{\text{number of sites in the spanning cluster}}{\text{total number of occupied sites}}. \tag{9.49}$$

To calculate P_∞ we need to average over all possible configurations for a given value of p.

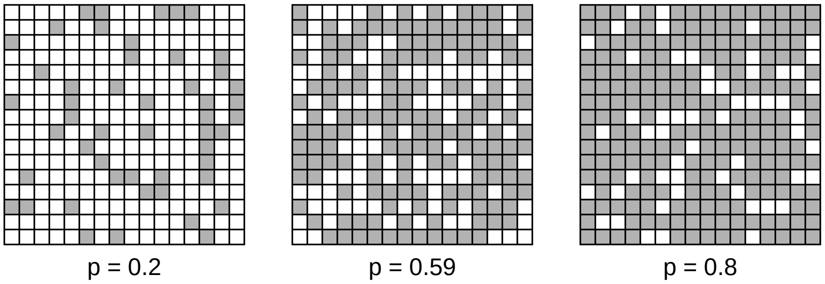

Figure 9.3: Examples of site percolation configurations for $p < p_c$, $p \approx p_c$, and $p > p_c$. The configuration at $p = 0.59$ has a spanning cluster. Find the spanning path for this configuration.

For $p < p_c$ on an infinite lattice there is no spanning cluster and $P_\infty = 0$.[3] At $p = 1$, P_∞ has its maximum value of one because only the spanning cluster exists. These properties suggest that P_∞ is a reasonable choice for the order parameter.

Problem 9.8. Estimation of P_∞

Estimate the value of P_∞ for the configuration shown in Figure 9.3(b). Accurate estimates of P_∞ require averages over many configurations. □

The behavior of P_∞ as a function of p for a finite lattice is shown in Figure 9.4. In the critical region near and above p_c we assume that P_∞ vanishes as

$$P_\infty \sim (p - p_c)^\beta, \tag{9.50}$$

where β denotes the critical exponent for the behavior of the order parameter near the critical point.

Information about the clusters is given by the cluster size distribution $n_s(p)$, which is defined as

$$n_s(p) = \frac{\text{mean number of clusters of size } s}{\text{total number of lattice sites}}. \tag{9.51}$$

For $p \geq p_c$ the spanning cluster is excluded from n_s. To get an idea of how to calculate n_s, we consider $n_s(p)$ for small s on the square lattice. The probability of finding a single isolated occupied site is

$$n_1(p) = p(1 - p)^4, \tag{9.52}$$

because the probability that one site is occupied is p and the probability that all of its four neighboring sites are empty is $(1 - p)^4$. Similarly, $n_2(p)$ is given by

$$n_2(p) = 2p^2(1 - p)^6. \tag{9.53}$$

The factor of 2 in (9.53) is due to the two possible orientations of the two occupied sites.[4]

---

[3] There are configurations that span a lattice for $p < p_c$, such as a column of occupied sites, but these configurations have a low probability of occurring in the limit of an infinite lattice and may be ignored.

[4] It might be thought that there should be a factor of 4 on the right-hand side of (9.53) because each site has four nearest neighbors, and thus there are four ways of choosing two sites. However, because we are averaging over the entire lattice, two of these ways are equivalent.

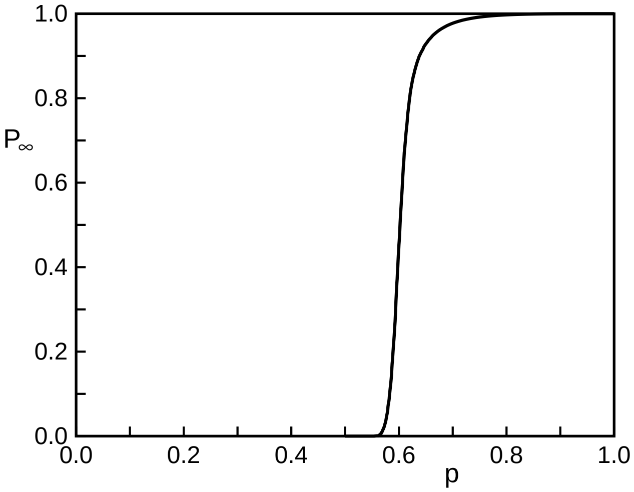

Figure 9.4: Plot of the estimated p dependence of the order parameter P_∞ obtained by averaging over many configurations on a 128×128 square lattice.

At $p = p_c$, n_s scales with s as

$$n_s \sim s^{-\tau}. \tag{9.54}$$

A consequence of the power law relation (9.54) is that clusters of all sizes exist on an infinite lattice for $p = p_c$ (see page 253 for a similar discussion of the Ising critical point).

Many of the properties of interest are related to moments of n_s. Because Nsn_s is the number of occupied sites in clusters of size s, the quantity

$$w_s = \frac{sn_s}{\sum_s sn_s}, \tag{9.55}$$

is the probability that an occupied site chosen at random is part of an s-site cluster. The mean number of occupied sites in a (finite) cluster is defined as

$$S(p) = \sum_s sw_s = \frac{\sum_s s^2 n_s}{\sum_s sn_s}. \tag{9.56}$$

The sum in (9.56) is over the finite clusters. The quantity $S(p)$ behaves near p_c as

$$S(p) \sim (p - p_c)^{-\gamma}. \tag{9.57}$$

We can associate a characteristic length ξ with the clusters. One way is to introduce the radius of gyration R_s of a single cluster of s sites:

$${R_s}^2 = \frac{1}{s} \sum_{i=1}^{s} (\mathbf{r}_i - \overline{\mathbf{r}})^2, \tag{9.58}$$

where

quantity	functional form	exponent	$d = 2$	$d = 3$
order parameter	$P_\infty \sim (p - p_c)^\beta$	β	5/36	0.42
mean size of finite clusters	$S(p) \sim \lvert p - p_c\rvert^{-\gamma}$	γ	43/18	1.82
connectedness length	$\xi(p) = \lvert p - p_c\rvert^{-\nu}$	ν	4/3	0.89
cluster distribution (at $p = p_c$)	$n_s \sim s^{-\tau}$	τ	187/91	2.19

Table 9.2: The critical exponents associated with the percolation transition. The exponents are known exactly in $d = 2$ on the basis of conformal theory arguments and the equivalence of percolation to the q-state Potts model (see page 267) in the limit $q \to 1$. The values of the exponents depend only on the spatial dimension and not on the symmetry of the lattice.

$$\bar{\mathbf{r}} = \frac{1}{s}\sum_{i=1}^{s} \mathbf{r}_i, \tag{9.59}$$

and $\mathbf{r}_i$ is the position of the ith site in the cluster. The statistical weight of the clusters of size s is the probability w_s that a site is a member of a cluster of size s times the number of sites s in the cluster. The *connectedness length* ξ can be defined as a weighted average over the radius of gyration of all finite clusters

$$\xi^2 = \frac{\sum_s s^2 n_s\, {R_s}^2}{\sum_s s^2 n_s}. \tag{9.60}$$

The connectedness length in percolation problems plays the same role as the correlation length in thermal systems. Near p_c we assume that ξ diverges as

$$\xi \sim |p_c - p|^{-\nu}. \tag{9.61}$$

Problem 9.9. Simulation of percolation

Program `Percolation` generates percolation configurations on the square lattice. The program computes $P_\infty(p)$, the fraction of states in the spanning cluster; $S(p)$, the mean number of sites in the finite clusters; $P_{\text{span}}(p)$, the probability of a spanning cluster; and n_s, the number of clusters with s sites for various values of p. The clusters are shown at the default value of $p = 0.5927$, and the largest cluster is shown in red.

(a) Run the program and look at the configurations. A spanning cluster is defined as one that connects the top and bottom of the lattice and the left and right boundaries. How would you describe the structure of the spanning clusters at $p = 0.8$? Are the clusters compact with few holes or ramified and stringy?

(b) Visually inspect the configurations at $p = p_c \approx 0.5927$. How would you describe the spanning clusters at the percolation threshold? Increase the size of the lattice. Do the spanning clusters become less dense? Note that there are clusters of all sizes at $p = p_c$.

(c) Run the program for at least 100 trials and look at the log-log plot of the cluster size distribution n_s versus s at $p = p_c$. Do you see linear behavior for some range of values of s? What functional form does this linear dependence suggest? Choose `Data Table` under the `Views` menu and fit your data to the form $n_s = As^{-\tau}$, where A and τ are fitting parameters. The exact result for τ in $d = 2$ is given in Table 9.2. How does your estimate for τ compare?

lattice	d	q	p_c (site)
linear chain	1	2	1
square	2	4	0.592746
hexagonal	2	6	1/2
simple cubic	3	6	0.3116
bcc	3	8	0.2459
fcc	3	12	0.1992

Table 9.3: Values of the percolation threshold p_c in two and three dimensions for several lattices. The value of p_c depends on the dimension d and the symmetry of the lattice. Errors in the numerical results are in the last digit. The results are from R. M. Ziff and M. E. J. Newman, "Convergence of threshold estimates for two-dimensional percolation," Phys. Rev. E **66**, 016129-1–10 (2002) and Chai-Yu Lin and Chin-Kun Hu, "Universal fnite-size scaling functions for percolation on three-dimensional lattices," Phys. Rev. E **58**, 1521–1527 (1998).

(d) Choose $p = 0.4$ and 0.8 and look at the log-log plots of the cluster size distribution n_s versus s. Is the qualitative behavior of n_s for large s the same as it is at $p = p_c$?

(e) *Choose $L = 128$ and do at least 100 trials (1000 is better) at various values of p near p_c. Copy the data for $S(p)$ and $P_\infty(p)$, and make a log-log plot of $S(p)$ and $P_\infty(p)$ versus $p - p_c$. There should be a region of your plot that is linear, indicating a possible power law. We will estimate the critical exponents β and γ in Problem 9.10. ☐

Problem 9.10. Finite-size scaling

A better way to estimate the values of the critical exponents β and γ than fitting the p dependence of P_∞ and $S(p)$ to their power law forms (9.50) and (9.57) near p_c is to use *finite-size scaling* as we did for the Ising model in Problem 5.41 (see page 289). The underlying assumption of finite-size scaling is that there is only one important length in the system near $p = p_c$, the connectedness length ξ. We write $\xi \sim |p-p_c|^{-\nu}$ and $|p-p_c| \sim \xi^{-1/\nu}$. Hence $P_\infty \sim (p-p_c)^\beta \sim \xi^{-\beta/\nu}$. For a finite system we replace ξ by L and write $P_\infty \sim L^{-\beta/\nu}$. Similar reasoning gives $S \sim L^{\gamma/\nu}$. Use Program `Percolation` to generate configurations at $p = p_c$ for $L = 10$, 20, 40, and 80, and determine the ratios β/ν and γ/ν. Use the exact result $\nu = 4/3$, and compare your results with the exact results for β and γ given in Table 9.2. (Because β is small, your results for β/ν are likely to not be very accurate.) ☐

The values of the percolation threshold p_c depend on the symmetry of the lattice and are summarized in Table 9.3. A summary of the values of the various critical exponents is given in Table 9.2. For two dimensions the exponents are known exactly. For three dimensions no exact results are known, and the exponents have been estimated using various approximate theoretical methods and simulations. The accuracy of the numerical values for the critical exponents is consistent with the assumption of universality, which implies that the exponents are independent of the symmetry of the lattice and depend only on d.

Problem 9.11. Scaling relations for percolation

The critical exponents for percolation satisfy the same scaling relations as do thermal systems. Use the results in Table 9.2 to confirm that $2\beta + \gamma = d\nu$ for percolation. ☐

9.4 Renormalization Group Method for Percolation

Because all length scales are present at the percolation threshold and at the critical point for thermal systems, these systems look the same on any length scale. This property is called *self-similarity*. The mathematical expression of this property for percolation is that n_s behaves as a power law at $p = p_c$, that is, $n_s \sim s^{-\tau}$. In contrast, n_s does not exhibit power law scaling for $p \neq p_c$, and all length scales are not present.

The presence of all length scales makes the usual types of analysis not feasible because all sizes are equally important. For example, we cannot apply perturbation theory which assumes that there is something that can be neglected. The renormalization group method makes a virtue out of necessity and exploits the presence of all length scales. Because the system is self-similar, we can zoom out and expect to see the same picture. In other words, we can study the system at large length scales and find the same power law behavior. Hence, we can ignore the details at small length scales. The renormalization group method averages over smaller length scales and determines how the system is transformed onto itself. We first consider the application of the renormalization group method to percolation to make this procedure more explicit.

The averaging over smaller length scales should be done so that it preserves the essential physics. For percolation the essential physics is connectivity. Consider an $L \times L$ square lattice and divide it into $b \times b$ cells each with b^2 sites. We adopt the rule that a cell is replaced by a single *coarse-grained* occupied site if the cell spans, and is replaced by an unoccupied site if it does not. It is not clear which spanning rule to adopt, for example, vertical spanning, horizontal spanning, vertical and horizontal spanning, and vertical or horizontal spanning. We will adopt horizontal and vertical spanning because it makes enumerating the spanning clusters easier. For very large cells the different spanning rules will yield results for p_c and the critical exponents that converge to the same value.

Program `RGPercolation` implements this spanning rule and shows the original lattice and the lattice found after each coarse-grained transformation. The result of these successive transformations is explored in Problem 9.12.

Problem 9.12. Visual Coarse-Graining

Use Program `RGPercolation` to estimate the value of the percolation threshold. For example, confirm that for $p = 0.4$, the coarse-grained lattices almost always reduce to an unoccupied site. What happens for $p = 0.8$? How can you use the properties of the coarse-grained lattices to estimate p_c? □

Suppose that we make the (drastic) approximation that the occupancy of each cell is independent of all the other cells and is characterized only by the probability p' that a cell is occupied. If the sites are occupied with probability p, then the cells are occupied with probability p', where p' is given by a renormalization transformation of the form

$$p' = R(p). \tag{9.62}$$

$R(p)$ is the total probability that the sites form a spanning path.

In Figure 9.5 we show the five vertically and horizontally spanning configurations for a $b = 2$ cell. The probability p' that the cell and hence the renormalized site is occupied is given by the

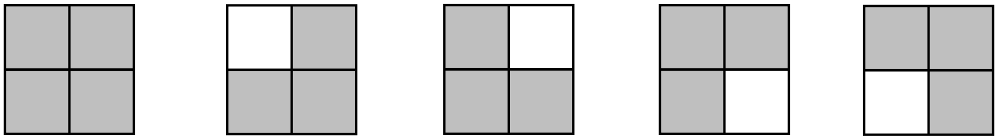

Figure 9.5: The five spanning configurations for a 2×2 cell on a square lattice. We have assumed that a cluster spans a cell only if the cluster connects the top and bottom and the left and right edges of the cell.

sum of the probabilities of all the spanning configurations:

$$p' = R(p) = p^4 + 4p^3(1-p). \tag{9.63}$$

Usually the probability p' that the renormalized site is occupied is different than the occupation probability p of the original sites. For example, suppose that we begin with $p = p_0 = 0.5$. After a single renormalization transformation, the value of p' obtained from (9.63) is $p_1 = R(p_0 = 0.5) = 0.3125$. A second renormalization transformation yields $p_2 = R(p_1) = 0.0934$. It is easy to see that further transformations will drive the system to the *trivial fixed point* $p^* = 0$. Similarly, if we begin with $p = p_0 = 0.8$, we find that successive transformations drive the system to the trivial fixed point $p^* = 1$. This behavior is associated with the fact the connectedness length of the system is finite for $p \neq p_c$ and hence the change of length scale makes the connectedness length smaller after each transformation.

To find the nontrivial fixed point p^* associated with the critical threshold p_c, we need to find the special value of $p = p^*$ such that

$$p^* = R(p^*). \tag{9.64}$$

The solution of the recursion relation (9.63) for p^* yields the two trivial fixed points, $p^* = 0$ and $p^* = 1$, and the nontrivial fixed point $p^* = 0.7676$ which we associate with p_c. This value of p^* for a 2×2 cell should be compared with the best known estimate $p_c \approx 0.5927$ for the square lattice. Note that p^* is an example of an *unstable* fixed point because the iteration of (9.63) for p arbitrarily close but not equal to p^* will drive p to one of the two stable fixed points. The behavior of the successive transformations is summarized by the flow diagram in Figure 9.6. We see that we can associate the unstable fixed point with the percolation threshold p_c.

To calculate the critical exponent ν from the renormalization transformation $R(p)$ we note that all lengths are reduced by a factor of b on the renormalized lattice in comparison to all lengths on the original lattice. Hence ξ', the connectedness length on the renormalized lattice, is related to ξ, the connectedness length on the original lattice, by

$$\xi' = \frac{\xi}{b}. \tag{9.65}$$

Because $\xi(p) = \text{constant}|p - p_c|^{-\nu}$ for $p \sim p_c$ and p_c corresponds to p^*, we have

$$|p' - p^*|^{-\nu} = \frac{1}{b}|p - p^*|^{-\nu}. \tag{9.66}$$

To find the relation between p' and p near p_c we expand $R(p)$ in (9.62) about $p = p^*$ and obtain to first order in $p - p^*$,

$$p' - p^* = R(p) - R(p^*) \approx \lambda\,(p - p^*), \tag{9.67}$$

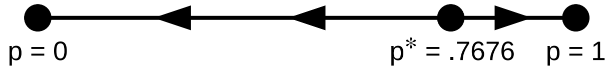

Figure 9.6: The renormalization group flow diagram for percolation on a square lattice corresponding to the recursion relation (9.63).

where

$$\lambda = \frac{dR}{dp}\Big|_{p=p^*}. \tag{9.68}$$

We need to do a little algebra to obtain an explicit expression for ν. We first raise the left and right sides of (9.67) to the $-\nu$ power and write

$$|p' - p^*|^{-\nu} = \lambda^{-\nu}|p - p^*|^{-\nu}. \tag{9.69}$$

We compare (9.66) and (9.69) and obtain

$$\lambda^{-\nu} = b^{-1}. \tag{9.70}$$

Finally, we take the logarithm of both sides of (9.70) and obtain the desired relation for the critical exponent ν:

$$\nu = \frac{\ln b}{\ln \lambda}. \tag{9.71}$$

As an example, we calculate ν for $b = 2$ using (9.63) for $R(p)$. We write $R(p) = p^4 + 4p^3(1-p) = -3p^4 + 4p^3$ and find[5]

$$\lambda = \frac{dR}{dp}\Big|_{p=p^*} = 12p^2(1-p)\Big|_{p=0.7676} = 1.64. \tag{9.72}$$

We then use the relation (9.71) to obtain

$$\nu = \frac{\ln 2}{\ln 1.64} = 1.40. \tag{9.73}$$

The agreement of the result (9.73) with the exact result $\nu = 4/3$ in $d = 2$ is remarkable given the simplicity of our calculation. In comparison, what would we be able to conclude if we were to measure $\xi(p)$ directly on a 2×2 lattice? This agreement is fortuitous because the accuracy of our calculation of ν is not known *a priori*.

What is the nature of the approximations that we have made in calculating ν and p_c? The basic approximation is that the occupancy of each cell is independent of all other cells. This assumption is correct for the original sites, but after one renormalization, we lose some of the original connecting paths and gain connecting paths that were not present in the original lattice. An example of this problem is shown in Figure 9.7. Because this surface effect becomes less important with increasing cell size, one way to improve a renormalization group calculation is to consider larger cells. A better way to obtain more accurate results is discussed in Problem 9.16.

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[5] The fact that $\lambda > 1$ implies that the fixed point is unstable.

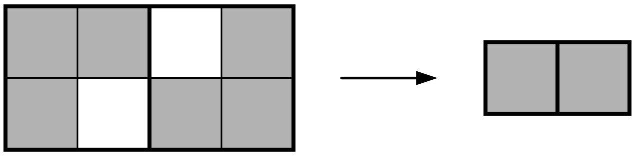

Figure 9.7: Example of an error after one renormalization. The two cells formed by sites on the original lattice on the left are not connected, but the renormalized sites on the right are connected.

Problem 9.13. Vertical spanning rule

Assume that a cell spans if there is a vertically spanning cluster. Choose $b = 2$ and show that $R(p) = 2p^2(1-p)^2 + 4p^3(1-p) + p^4$. Find the corresponding nontrivial fixed point and the exponent ν. □

Problem 9.14. Renormalization transformation on a hexagonal lattice

(a) What are the four spanning configurations for the smallest possible cell ($b = \sqrt{3}$) on a hexagonal lattice? For this geometry the minimum cell contains three sites, at least two of which must be occupied. (See Figure 5.11 for the geometry of a hexagonal lattice.)

(b) Show that the corresponding recursion relation can be expressed as $R(p) = 3p^2 - 2p^3$. Find p^* and ν. The result $p^* = 1/2$ is exact for a hexagonal lattice. □

***Problem 9.15.** Renormalization transformation with $b = 3$

(a) Enumerate all the possible spanning configurations for a $b = 3$ cell on a square lattice. Assume that a cell is occupied if a cluster spans the cell vertically and horizontally. Determine the probability of each configuration and find the renormalization transformation $R(p)$.

(b) Solve for the nontrivial fixed point p^* and the critical exponent ν. One way to determine the fixed point is by trial and error using a calculator or computer. Another straightforward way is to plot the difference $R(p) - p$ versus p and find the value of p at which $R(p) - p$ crosses the horizontal axis.[6] Are your results for p_c and ν closer to their known values than for $b = 2$? □

***Problem 9.16.** Cell to cell renormalization

Instead of renormalizing the set of all spanning 3×3 cells to a single occupied site as in Problem 9.15, it is better to go from cells of linear dimension $b_1 = 3$ to cells of linear dimension $b_2 = 2$. Use the fact that the connectedness lengths of the two lattices are related by $\xi(p_2)/\xi(p_1) = (b_1/b_2)^{-1}$ to derive the relation

$$\nu = \frac{\ln b_1/b_2}{\ln \lambda_1/\lambda_2}, \tag{9.74}$$

---

[6] A more sophisticated way to find the fixed point is to use a numerical method such as the Newton-Raphson method.

where $\lambda_i = dR(p^*, b_i)/dp$ is evaluated at the solution p^* of the fixed point equation, $R_2(b_2, p^*) = R_3(b_1, p^*)$. This "cell-to-cell" transformation yields better results in the limit in which the change in length scale is infinitesimal and is more accurate than considering large cells and renormalizing to a single site. A renormalization transformation with $b_1 = 5$ and $b_2 = 4$ gives results that are close to the exact result $\nu = 4/3$. □

9.5 The Renormalization Group Method and the One-Dimensional Ising Model

In a manner similar to our application of the renormalization group method to percolation, we will average groups of spins and then determine which parameters characterize the renormalized lattice. The result of such a calculation will be the identification of the fixed points. An unstable fixed point corresponds to a critical point. The rate of change of the renormalized parameters near a critical point yields approximate values of the critical exponents.

Although the one-dimensional Ising model does not have a critical point for $T > 0$, the application of the renormalization group method to the one-dimensional Ising model serves as a good introduction to the method (see Maris and Kadanoff).

The energy of the Ising chain with toroidal boundary conditions is [see (5.66)]

$$E = -J\sum_{i=1}^{N} s_i s_{i+1} - \frac{1}{2}H\sum_{i=1}^{N}(s_i + s_{i+1}). \tag{9.75}$$

It is convenient to absorb the factors of β and define the dimensionless parameters $K = \beta J$ and $h = \beta H$. The partition function can be written as

$$Z = \sum_{\{s\}} \exp\Big[\sum_{i=1}^{N}\big(K s_i s_{i+1} + \frac{1}{2}h(s_i + s_{i+1})\big)\Big], \tag{9.76}$$

where the sum is over all possible spin configurations. We first consider $h = 0$.

We have seen that one way to obtain a renormalized lattice is to group sites or spins into cells. Another way to reduce the number of spins is to average or sum over the spins. This method of reducing the degrees of freedom is called *decimation*. For example, for the $d = 1$ Ising model we can write Z as

$$Z(K, N) = \sum_{s_1, s_2, s_3, s_4, \ldots} e^{K(s_1 s_2 + s_2 s_3)} e^{K(s_3 s_4 + s_4 s_5)\cdots}. \tag{9.77}$$

The form of (9.77) suggests that we sum over even spins s_2, s_4, …, and write

$$Z(K, N) = \sum_{s_1, s_3, s_5 \ldots} \big[e^{K(s_1+s_3)} + e^{-K(s_1+s_3)}\big]\big[e^{K(s_3+s_5)} + e^{-K(s_3+s_5)}\big]\cdots. \tag{9.78}$$

We next try to write the partition function in (9.78) in its original form with $N/2$ spins and a different interaction K'. If such a rescaling were possible, we could obtain a recursion relation for K' in terms of K. We require that

$$e^{K(s_1+s_3)} + e^{-K(s_1+s_3)} = A(K)\, e^{K' s_1 s_3}, \tag{9.79}$$

where the function $A(K)$ does not depend on s_1 or s_3. If the relation (9.79) exists, we can write

$$Z(K,N) = \sum_{s_1,s_3,s_5\ldots} A(K)\, e^{K' s_1 s_3} A(K)\, e^{K' s_3 s_5} \ldots \tag{9.80a}$$

$$= [A(K)]^{N/2} Z(K', N/2). \tag{9.80b}$$

In the limit $N \to \infty$ we know that $\ln Z$ is proportional to N, that is,

$$\ln Z = N g(K), \tag{9.81}$$

where $g(K)$ is independent of N. From (9.80b) and (9.81) we obtain

$$\ln Z(K,N) = N g(K) = \frac{N}{2} \ln A(K) + \ln Z(K', N/2) \tag{9.82a}$$

$$= \frac{N}{2} \ln A(K) + \frac{N}{2} g(K'), \tag{9.82b}$$

and

$$g(K') = 2g(K) - \ln A(K). \tag{9.83}$$

We can find the form of $A(K)$ from (9.79). We use the fact that (9.79) holds for all values of s_1 and s_3, and first consider $s_1 = s_3 = 1$ or $s_1 = s_3 = -1$ for which

$$e^{2K} + e^{-2K} = A\, e^{K'}. \tag{9.84}$$

We next consider $s_1 = 1$ and $s_3 = -1$ or $s_1 = -1$ and $s_3 = 1$ and find

$$2 = A\, e^{-K'}. \tag{9.85}$$

From (9.85) we have $A = 2e^{K'}$, and hence from (9.84) we obtain

$$e^{2K} + e^{-2K} = 2e^{2K'}, \tag{9.86}$$

or

$$K' = R(K) = \frac{1}{2} \ln \big[\cosh(2K) \big] \qquad \text{(recursion relation)}. \tag{9.87}$$

From (9.85) and (9.85) we find that $A(K)$ is given by

$$A(K) = 2 \cosh^{1/2}(2K). \tag{9.88}$$

We can use the form of $A(K)$ in (9.88) to rewrite (9.83) as

$$g(K') = 2g(K) - \ln[2 \cosh^{1/2}(2K)]. \tag{9.89}$$

Equations (9.87) and (9.89) are the main results of the renormalization group analysis.

Because $\frac{1}{2} \ln \cosh(2K) \le K$, the successive use of (9.87) leads to smaller values of K (higher temperatures) and hence smaller values of the correlation length. Thus $K = 0$ or $T = \infty$ is a trivial fixed point (see Figure 9.8). This behavior is to be expected because the Ising chain does not have a phase transition at nonzero temperature. For example, suppose we start with $K = 10$ corresponding to a low temperature. The first iteration of (9.87) gives $K' = 9.65$ and further

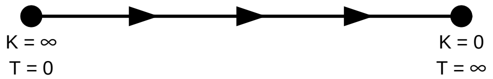

Figure 9.8: The renormalization group flow diagram for the one-dimensional Ising model in zero magnetic field.

iterations lead to $K' = 0$. Because any choice of $K \neq 0$ ultimately renormalizes to $K = 0$, we conclude that every point for $K > 0$ is in the same phase. Only at exactly zero temperature is this statement not true. Hence, there are two fixed points; the one at $T = 0$ ($K = \infty$) is unstable because any perturbation away from $T = 0$ is amplified. The fixed point at $T = \infty$ is stable. The renormalization group flows go from the unstable fixed point to the stable fixed point as shown in Figure 9.8.

Because there is no nontrivial fixed point of (9.87) between $T = 0$ and $T = \infty$, the recursion relation is reversible,[7] and we can follow the transformation backward starting at $K \approx 0$ ($T = \infty$) and going to $K = \infty$ ($T = 0$). The advantage of starting from $T \approx \infty$ is that we can start with the exact solution for $K = 0$ and iterate the recursion relation to higher values of K for which the interaction between the spins becomes increasingly important. To find the recursion relation that works in this direction we solve (9.87) for K in terms of K'. Similarly, we solve (9.89) to find $g(K)$ in terms of $g(K')$. The result is

$$K = \frac{1}{2}\cosh^{-1}(e^{2K'}), \tag{9.90}$$

$$g(K) = \frac{1}{2}\ln 2 + \frac{1}{2}K' + \frac{1}{2}g(K'). \tag{9.91}$$

Suppose we begin with $K' = 0.01$. Because this value of K' is close to zero, the effect of the spin-spin interactions is very small, and we can take $Z(K' = 0.01, N) \approx Z(K' = 0, N) = 2^N$ (all states have equal weight at high temperatures). From (9.81) we have

$$g(K' = 0.01) \approx \ln 2 \approx 0.693147. \tag{9.92}$$

Given $K' = 0.01$, we obtain $K = 0.100334$ from (9.90). The value of $g(K)$ for this value of K is found from (9.91) to be 0.698147. This calculation of $g(K)$ and K is the first step in an iterative procedure that can be repeated indefinitely with K' and $g(K')$ chosen to be the value of K and $g(K)$, respectively, from the previous iteration. The first two iterations are summarized in Table 9.4.

Problem 9.17. Calculation of $g(K)$

(a) Extend the calculation of $g(k)$ in Table 9.4 to larger values of K by doing several more iterations of (9.90) and (9.91). Also calculate the exact value of $\ln Z_N/N$ for the calculated values of K using (5.39) and compare your results to $g(K)$.

---

[7] As we found for percolation and will find for the two-dimensional Ising model in Section 9.6, the usual renormalization transformation does not have an inverse because the number of variables decreases after each renormalization transformation, and the renormalization group is really a *semigroup*. Thus it is more accurate to refer to a renormalization group analysis or to a renormalization group method. However, it is common to refer simply to the renormalization group.

K'	K	$g(K')$	$g(K)$
0.01	0.100334	0.693147	0.698147
0.100334	0.327447	0.698147	0.745814

Table 9.4: The results of the first two iterations of the calculation of $g(K)$ for the one-dimensional Ising model from the recursion relations (9.90) and (9.91). The function $g(K)$ is related to the partition function Z by $\ln Z = Ng$ [see (9.81)].

(b) Because the recursion relations (9.90) and (9.91) are exact, the only source of error is the first value of g. Does the error increase or decrease as the calculation proceeds? □

***Problem 9.18.** The recursion relations for nonzero magnetic field

(a) For nonzero magnetic field show that the function $A(K,h)$ satisfies the relation:

$$2e^{h(s_1+s_3)/2}\cosh[K(s_1+s_3)+h] = A(K,h)\,e^{K's_1s_3+h'(s_1+s_3)/2}. \tag{9.93}$$

(b) Show that the recursion relations for nonzero magnetic field are

$$K' = \frac{1}{4}\ln\frac{\cosh(2K+h)\cosh(2K-h)}{\cosh^2 h}, \tag{9.94a}$$

$$h' = h + \frac{1}{2}\ln\Big[\frac{\cosh(2K+h)}{\cosh(2K-h)}\Big], \tag{9.94b}$$

and

$$\ln A(K,h) = \frac{1}{4}\ln\big[16\cosh(2K+h)\cosh(2K-h)\cosh^2 h\big]. \tag{9.94c}$$

(c) Show that the recursion relations (9.94) have a line of trivial fixed points satisfying $K^* = 0$ and arbitrary h^*, corresponding to the paramagnetic phase, and an unstable ferromagnetic fixed point at $K^* = \infty, h^* = 0$.

(d) Justify the relation

$$Z(K,h,N) = A(K,h)^{N/2}Z(K',h',N/2). \tag{9.95}$$

□

***Problem 9.19.** Transfer matrix method

As shown in Section 5.5.4 the partition function for the N-spin Ising chain can be written as the trace of the Nth power of the transfer matrix $\mathbf{T}$. Another way to reduce the number of degrees of freedom is to describe the system in terms of two-spin cells. We write Z as

$$Z = \mathrm{Tr}\,\mathbf{T}^N = \mathrm{Tr}\,(\mathbf{T}^2)^{N/2} = \mathrm{Tr}\,\mathbf{T}'^{N/2}. \tag{9.96}$$

The transfer matrix for two-spin cells, $\mathbf{T}^2$, can be written as

$$\mathbf{T}^2 = \mathbf{TT} = \begin{pmatrix} e^{2K+2h}+e^{-2K} & e^h+e^{-h} \\ e^{-h}+e^h & e^{2K-2h}+e^{-2K} \end{pmatrix}. \tag{9.97}$$

We require that $\mathbf{T}'$ have the same form as $\mathbf{T}$:

$$\mathbf{T}' = C \begin{pmatrix} e^{K'+h'} & e^{-K'} \\ e^{-K'} & e^{K'-h'} \end{pmatrix}. \tag{9.98}$$

A parameter C must be introduced because matching (9.97) with (9.98) requires matching three matrix elements, which is impossible with only two variables K' and h'.

(a) Show that the three unknowns satisfy the three conditions:

$$Ce^{K'}e^{h'} = e^{2K+2h} + e^{-2K}, \tag{9.99a}$$

$$Ce^{-K'} = e^{h} + e^{-h}, \tag{9.99b}$$

$$Ce^{K'}e^{-h'} = e^{2K-2h} + e^{-2K}. \tag{9.99c}$$

(b) Show that the solution of (9.99) can be written as

$$e^{-2h'} = \frac{e^{2K-2h} + e^{-2K}}{e^{2K+2h} + e^{-2K}}, \tag{9.100a}$$

$$e^{4K'} = \frac{e^{4K} + e^{-2h} + e^{2h} + e^{-4K}}{(e^{h} + e^{-h})^2}, \tag{9.100b}$$

$$C^4 = [e^{4K} + e^{-2h} + e^{2h} + e^{-4K}][e^{h} + e^{-h}]^2. \tag{9.100c}$$

(c) Show that the recursion relations in (9.100) reduce to (9.87) for $h = 0$. For $h \neq 0$ start from some initial state K_0, h_0 and calculate a typical renormalization group trajectory. To what phase (paramagnetic or ferromagnetic) does the fixed point correspond? □

9.6 *The Renormalization Group Method and the Two-Dimensional Ising Model

As pointed out by Wilson,[8] there is no recipe for constructing a renormalization group transformation, and we will consider only one possible approach. In particular, we consider the majority rule transformation developed by Niemeijer and van Leeuwen for the ferromagnetic Ising model on a hexagonal lattice.

The idea of their method is to divide the original lattice with lattice spacing a into cells as we did for percolation in Section 9.4, and replace the original site spins $s_i = \pm 1$ by the renormalized cell spins $\mu_\alpha = \pm 1$. The Latin indices i and j denote the original lattice sites, and the Greek indices α and β denote the renormalized cell spins. As shown in Figure 9.9 we will group the sites of the original hexagonal lattice into cells of three sites each. The cells also form a hexagonal lattice with the lattice constant $a' = \sqrt{3}a$, so that the length rescaling parameter is $b = \sqrt{3}$. We suggest that you focus on the ideas involved in the following calculation rather than the details.

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[8] Ken Wilson was awarded the 1982 Nobel Prize in Physics for developing the renormalization group method for critical phenomena.

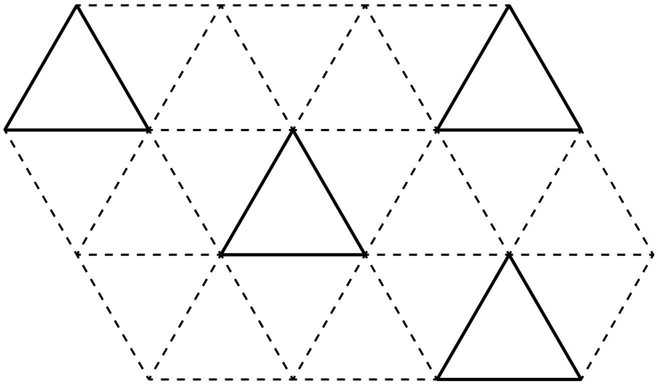

Figure 9.9: Cell spins on a hexagonal lattice. The solid lines indicate intracell interactions; the dotted lines show the intercell interactions.

It is convenient to write the energy of the spins in the form[9]

$$\widetilde{E} = \beta E = -K\sum_{\langle ij\rangle} s_i s_j, \tag{9.101}$$

and the partition function as

$$Z(K) = \sum_{\{s\}} e^{-\widetilde{E}(\{s\})}. \tag{9.102}$$

We have incorporated the factor of β into the energy and have introduced the notation $\widetilde{E} = \beta E$. For simplicity, we will consider $h = 0$ so that there is only one coupling constant $K = \beta J$.

The energy of the renormalized lattice can be written as

$$\widetilde{E}' = \widetilde{E}_0 + \widetilde{V}, \tag{9.103}$$

where $\widetilde{E}_0$ represents the sum of all the interactions between spins within the same cell, and $\widetilde{V}$ is the interaction of spins between different cells. We write

$$\widetilde{E}_0 = -K\sum_{\alpha}\sum_{i,j\subset\alpha} s_i s_j, \tag{9.104}$$

where the sum over α represents the sum over all cells. The spins in cell α satisfy the condition $\mu_\alpha = \mathrm{sgn}(\sum_{i=1}^{3} s_{i,\alpha})$ (the majority rule). The energy of cell α has the form

$$\widetilde{E}_{0,\alpha} = -K(s_{1,\alpha}s_{2,\alpha} + s_{1,\alpha}s_{3,\alpha} + s_{2,\alpha}s_{3,\alpha}). \tag{9.105}$$

We write the interaction $\widetilde{V}$ as

$$\widetilde{V} = -K\sum_{\substack{\alpha,\beta\\ \alpha\neq\beta}}\sum_{i\subset\alpha}\sum_{j\subset\beta} s_i s_j. \tag{9.106}$$

---

[9] More advanced readers will recognize that E should be replaced by the Hamiltonian.

The representation (9.103)–(9.106) is exact.

The replacement of the original site spins by cell spins leads to an energy that does not have the same form as (9.101). That is, the new energy involves interactions between cell spins that are not nearest neighbors. Nevertheless, we will assume that the new energy has the same form:

$$\widetilde{G} + \widetilde{E}' = -K' \sum_{\langle\alpha\beta\rangle} \mu_\alpha \mu_\beta. \tag{9.107}$$

The term $\widetilde{G}$ in (9.107) is independent of the cell spin configurations, and the sum on the right-hand side is over nearest-neighbor cells.

The goal is to obtain a recursion relation

$$K' = R(K) \tag{9.108}$$

and a nontrivial fixed point K^* with

$$\lambda_K = \frac{\partial K'}{\partial K}\bigg|_{K=K^*}, \tag{9.109}$$

and

$$\nu = \frac{\ln \lambda_K}{\ln b}, \tag{9.110}$$

where b is the length rescaling parameter.

In the following we will treat the interactions of the spins within the cells exactly and the interactions between the cells approximately. The renormalized energy is given formally by

$$e^{-\widetilde{G}-\widetilde{E}'} = \sum_{\{s\}} P(\mu, s)\, e^{-(\widetilde{E}_0+\widetilde{V})}. \tag{9.111}$$

The function $P(\mu, s)$ transforms the original three spins to the cell spin and implements the majority rule so that the cell spin equals the sign of the sum of the site spins in the cell. We can write $P(\mu, s)$ for cell spin α as

$$P(\mu_\alpha, s) = \delta\big(\mu_\alpha - \operatorname{sgn}(s_1 + s_2 + s_3)\big). \tag{9.112}$$

It is convenient to treat the noninteracting cells as a reference system (see Section 8.6) and treat the interaction between the cell spins approximately. We can show that[10]

$$e^{-\widetilde{G}} e^{-\widetilde{E}'} = Z_0 \langle e^{-\widetilde{V}} \rangle_0. \tag{9.115}$$

---

[10] We write the average of an arbitrary function $A(s)$ over the noninteracting cells as

$$\langle A \rangle_0 = \frac{\sum_{\{s\}} A(s)\, P(\mu, s)\, e^{-\widetilde{E}_0(s)}}{\sum_{\{s\}} P(\mu, s)\, e^{-\widetilde{E}_0(s)}}. \tag{9.113}$$

We then multiply the top and bottom of (9.111) by $Z_0 = \sum_{\{s'\}} P(\mu, s')\, e^{-\widetilde{E}_0}$, the partition function associated with $\widetilde{E}_0$:

$$e^{-\widetilde{G}} e^{-\widetilde{E}'} = \sum_{\{s\}} P(\mu, s)\, e^{-\widetilde{E}_0} \frac{\sum_{\{s'\}} P(\mu, s')\, e^{-(\widetilde{E}_0+\widetilde{V})}}{\sum_{\{s'\}} P(\mu, s')\, e^{-\widetilde{E}_0}} \tag{9.114a}$$

$$= Z_0 \langle e^{-\widetilde{V}} \rangle_0. \tag{9.114b}$$

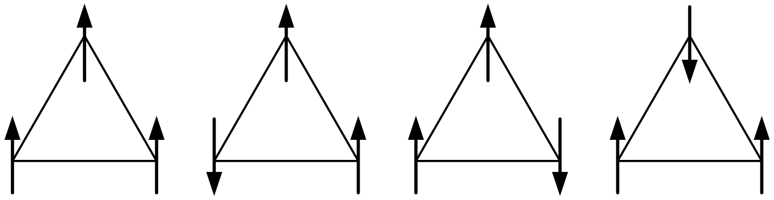

Figure 9.10: The four possible configurations of the three spin cell on a hexagonal lattice such that $\mu = 1$.

where the average is over the original spin variables with respect to $\widetilde{E}_0$, $Z_0 = z(\mu)^{N'}$, $N' = N/b^d$ is the number of cells in the renormalized lattice, and $z(\mu)$ is the sum over the internal spin states of one cell for a given value of μ. The average $\langle e^{-\widetilde{V}}\rangle_0$ is over the noninteracting cells.

We take the logarithm of both sides of (9.115) and obtain

$$\widetilde{G} + \widetilde{E}' = -N' \ln z - \ln\langle e^{-\widetilde{V}}\rangle_0. \tag{9.116}$$

We can identify

$$g = \frac{\widetilde{G}}{N} = \frac{N'}{N} \ln z = \frac{1}{b^d} \ln z \tag{9.117}$$

and

$$\widetilde{E}' = -\ln\langle e^{-\widetilde{V}}\rangle_0. \tag{9.118}$$

Note that (9.118) has the same form as (8.8) and (8.110).

We first calculate z and g and then evaluate the average in (9.118). The sum over the spins in a given cell for $\mu = 1$ can be written as

$$z(\mu = 1) = \sum_{\{s\}} e^{K(s_1 s_2 + s_2 s_3 + s_3 s_1)}. \tag{9.119}$$

The four possible states of the three spins s_1, s_2, s_3 with the restriction that $\mu = 1$ are given in Figure 9.10. Hence,

$$z(\mu = 1) = e^{3K} + 3\, e^{-K}. \tag{9.120}$$

In the absence of a magnetic field the sum for $\mu = -1$ gives the same value for z (see Problem 9.20). From (9.117) and (9.120) we have

$$g(K) = \frac{1}{3} \ln(e^{3K} + 3\, e^{-K}). \tag{9.121}$$

Problem 9.20. Calculation of $z(\mu = -1)$

Calculate $z(\mu = -1)$ and show that $z(\mu)$ is independent of the sign of μ. ☐

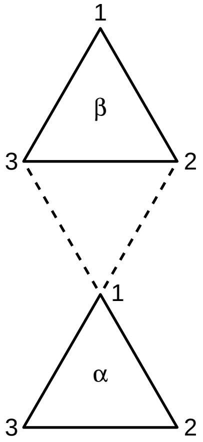

Figure 9.11: The couplings (dotted lines) between nearest-neighbor cell spins $\widetilde{V}_{\alpha\beta}$.

The difficult part of the calculation is the evaluation of the average $\langle e^{-\widetilde{V}}\rangle_0$. We will evaluate it approximately by keeping only the first cumulant (see Section 8.4.1). Because the cumulant expansion is a power series in $K = \beta J$, it is reasonable to assume that the series converges given that $K_c \approx 0.275$ for a hexagonal lattice. We have

$$\ln\langle e^{-\widetilde{V}}\rangle_0 = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} M_n, \tag{9.122}$$

and keep only the first cumulant

$$M_1 = \langle \widetilde{V}\rangle_0. \tag{9.123}$$

The first approximation to the intercell interaction $\widetilde{V}$ can be written as (see Figure 9.11)

$$\widetilde{V}_{\alpha\beta} = -K s_{1,\alpha}[s_{2,\beta} + s_{3,\beta}]. \tag{9.124}$$

Note that $\widetilde{V}$ in (9.124) includes only the interaction of two nearest neighbor cells, and this approximation does not preserve the symmetry of a hexagonal lattice. However, this approximation is consistent with our assumption that the renormalized energy has the same form as the original energy. Because $\widetilde{E}_0$ does not couple different cells, we have

$$\langle \widetilde{V}_{\alpha\beta}\rangle_0 = -2K\langle s_{1,\alpha} s_{2,\beta}\rangle_0 = -2K\langle s_{1,\alpha}\rangle_0 \langle s_{2,\beta}\rangle_0. \tag{9.125}$$

The factor of 2 in (9.125) arises from the fact that $\langle s_{2,\beta}\rangle = \langle s_{3,\beta}\rangle$.

From (9.125) we see that we need to find $\langle s_{1,\alpha}\rangle_0$. Suppose that $\mu_\alpha = 1$. The four states consistent with this condition are shown in Figure 9.10. It is easy to see that

$$\langle s_{1,\alpha}\rangle_0 = \frac{1}{z}\sum_{\{s\}} s_1 e^{K(s_1s_2+s_2s_3+s_3s_1)} \tag{9.126a}$$

$$= \frac{1}{z}\big[+1e^{3K} + 1e^{-K} + 1e^{-K} - 1e^{-K}\big] \tag{9.126b}$$

$$= \frac{1}{z}[e^{3K} + e^{-K}] \qquad (\mu_\alpha = +1). \tag{9.126c}$$

Similarly, we can show that

$$\langle s_{1,\alpha}\rangle_0 = \frac{1}{z}[-e^{3K} - e^{-K}] = -\frac{1}{z}[e^{3K} + e^{-K}] \qquad (\mu_\alpha = -1). \tag{9.126d}$$

Hence, we have

$$\langle s_{1,\alpha}\rangle_0 = \frac{1}{z}[e^{3K} + e^{-K}]\mu_\alpha. \tag{9.127}$$

From (9.125) and (9.127) we have

$$\langle \widetilde{V}_{\alpha\beta}\rangle_0 = -2Kf(K)^2\mu_\alpha\mu_\beta, \tag{9.128}$$

where

$$f(K) = \frac{e^{3K} + e^{-K}}{e^{3K} + 3e^{-K}}. \tag{9.129}$$

Hence,

$$\langle \widetilde{V}\rangle_0 = \sum_{\langle\alpha\beta\rangle}\langle \widetilde{V}_{\alpha\beta}\rangle_0 = -2Kf(K)^2\sum_{\langle\alpha\beta\rangle}\mu_\alpha\mu_\beta \tag{9.130a}$$

$$= -K'\sum_{\langle\alpha\beta\rangle}\mu_\alpha\mu_\beta. \tag{9.130b}$$

Note that $\langle \widetilde{V}\rangle_0$ has the same form as the original nearest neighbor interaction with a renormalized value of the interaction. If we compare (9.128) and (9.130b), we find the recursion relation

$$K' = R(K) = 2Kf(K)^2 \tag{9.131}$$

and

$$\widetilde{E}' = -K'\sum_{\langle\alpha\beta\rangle}\mu_\alpha\mu_\beta. \tag{9.132}$$

Because $f(K=0) = 1/2$ and $f(K=\infty) = 1$, it is easy to see that there are trivial fixed points at $K^* = 0$ and $K^* = \infty$. The nontrivial fixed point occurs at $f(K) = 1/\sqrt{2}$ or at

$$K^* = \frac{1}{4}\ln(2\sqrt{2}+1) \approx 0.3356. \tag{9.133}$$

The exact answer for K_c for a hexagonal lattice is $K_c = \frac{1}{3}\ln 3 = 0.2747$. We also have

$$\lambda_K = \frac{dK'}{dK}\Big|_{K=K^*} = 1.624, \tag{9.134}$$

and hence

$$\nu = \frac{\ln\sqrt{3}}{\ln 1.624} \approx 0.882. \tag{9.135}$$

For comparison, the exact result is $\nu = 1$ (see Table 5.1).

Problem 9.21. Confirm the above results for K^*, λ_K, and ν. ☐

We can extend the renormalization group analysis by considering higher order cumulants. The second order cumulant introduces two new interactions that are not in the original energy. That is, the cell spins interact not only with nearest-neighbor cell spins, but also with second- and third-neighbor cell spins. Hence, for consistency we have to include in our original energy second and third neighbor interactions also. Good results can usually be found by stopping at the second cumulant. More details can be found in the references.

Vocabulary

Landau and Landau-Ginzburg theory
mean-field critical exponents
Ginzburg criterion
scaling relations, universality
percolation, connectivity
cluster, spanning cluster
coarse-graining, renormalization group method
recursion relation

Additional Problems

Problem 9.22. Alternate derivation of Fisher's scaling law

Another way to express the scaling hypothesis is to assume that for $h = 0$, $G(r)$ near $\epsilon = 0$ has the form

$$G(r) \sim \frac{1}{r^{d-2+\eta}} \psi_\pm(r/\xi), \tag{9.136}$$

where $\psi_\pm$ is an unspecified function that depends only on the ratio r/ξ. Use (9.136) and the relation (9.34) to obtain Fisher's scaling law, $\gamma = \nu(2 - \eta)$. ☐

Problem 9.23. Percolation in one dimension

Choose a simple cell for percolation in one dimension and show that $p_c = 1$ and $\nu = 1$ exactly. ☐

***Problem 9.24.** Seven site cell for percolation

We can generalize the triangular cell considered in Problem 9.14 and consider the seven site cell shown in Figure 9.12 and assume that the cell is occupied if the majority of its sites are occupied.

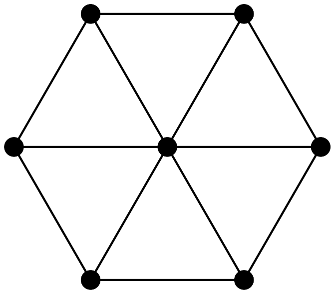

Figure 9.12: The seven site cell considered in Problem 9.24.

(a) Show that the recursion relation is

$$p' = R(p) = 35p^4 - 84p^5 + 70p^6 - 20p^7. \tag{9.137}$$

(b) Show that (9.137) has a nontrivial fixed point at $p^* = 0.5$ and that the connectedness length exponent ν is given by

$$\nu \approx 1.243. \tag{9.138}$$

□

Problem 9.25. Simulations of the two-dimensional XY (planar) model

We briefly mentioned the planar or XY model on page 442. In this model the spins are located on a d-dimensional lattice, but are restricted to point in any direction in the plane. The interaction between two nearest neighbor spins is given by $-J\mathbf{s}_1 \cdot \mathbf{s}_2$, where $\mathbf{s}_1$ and $\mathbf{s}_2$ are two unit spin vectors.

One of the interesting features of the XY model in two dimensions is that the mean magnetization $\langle M \rangle = 0$ for all nonzero temperatures, but there is a phase transition at a nonzero temperature $T_{\rm KT}$ known as the Kosterlitz-Thouless transition. For $T \leq T_{\rm KT}$ the spin-spin correlation $C(r)$ decreases as a power law; for $T > T_{\rm KT}$, $C(r)$ decreases exponentially. The power law decay of $C(r)$ for $T \leq T_{\rm KT}$ implies that every temperature below $T_{\rm KT}$ acts as a critical point.

Program `XYModel` uses the Metropolis algorithm to simulate the XY model in two dimensions. In this case a spin is chosen at random and rotated by a random angle up to a maximum value δ.

(a) Rewrite the interaction $-J\mathbf{s}_i \cdot \mathbf{s}_j$ between nearest neighbor spins i and j in a simpler form by substituting $s_{i,x} = \cos\theta_i$ and $s_{i,y} = \sin\theta_i$, where the phase θ_i is measured from the horizontal axis in the counter-clockwise direction. Show that the result is $-J\cos(\theta_i - \theta_j)$.

(b) An interesting feature of the XY model is the existence of vortices and anti-vortices. A vortex is a region of the lattice where the spins rotate by at least 2π as you trace a closed path. Run the simulation with the default parameters and observe the locations of the vortices. Follow the arrows as they turn around a vortex. A vortex is indicated by a square box. What is the difference between a positive (blue) and negative (red) vortex? Does a vortex ever appear isolated? Count the number of positive vortices and negative vortices. Is the number the same at all times?

(c) Click the `New` button, change the temperature to 0.2, set the initial configuration to random, and run the simulation. You should see quenched-in vortices which don't change with time. Are there an equal number of positive and negative vortices? Are there isolated vortices whose centers are more than a lattice spacing apart?

(d) Click the `New` button and set the initial configuration to ordered and the temperature to 0.2. Also set steps per display to 100 so that the simulation will run much faster. Run the simulation for at least 1000 mcs to equilibrate and 10,000 mcs to collect data, and record your estimates of the energy, specific heat, vorticity, and susceptibility. Repeat for temperatures from 0.3 to 1.5 in steps of 0.1. Plot the energy and specific heat versus the temperature. (The susceptibility diverges for all temperatures below the transition, which occurs near $T = 0.9$. The location of the specific heat peak is different from the transition temperature. The program computes $\chi = (1/NT^2)\langle M^2\rangle$ instead of the usual expression, because $\langle M\rangle = 0$ in the thermodynamic limit.) Is the vorticity (the mean number density of vortices) a smooth function of the temperature?

(e) Look at configurations showing the vortices near the Kosterlitz-Thouless transition at $T_{\rm KT} \approx 0.9$. Is there any evidence that the positive vortices are moving away from the negative vortices? The Kosterlitz-Thouless transition is due to this unbinding of vortex pairs. ☐

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Appendix: Physical Constants and Mathematical Relations

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A.1 Physical Constants and Conversion Factors

constant	symbol	magnitude
Avogadro's number	N_A	6.022×10^{23}
Boltzmann's constant	k	$1.381 \times 10^{-23}\,\mathrm{J/K}$
universal gas constant	R	$8.314\,\mathrm{J/(mol\,K)}$
Planck's constant	h	$6.626 \times 10^{-34}\,\mathrm{J\,s}$
	$\hbar$	$1.055 \times 10^{-34}\,\mathrm{J\,s}$
speed of light	c	$2.998 \times 10^{8}\,\mathrm{m/s}$
electron charge	e	$1.602 \times 10^{-19}\,\mathrm{C}$
electron mass	m_e	$9.109 \times 10^{-31}\,\mathrm{kg}$
proton mass	m_p	$1.672 \times 10^{-27}\,\mathrm{kg}$

Table A.1: Useful physical constants.

newton	$1\,\mathrm{N} \equiv 1\,\mathrm{kg\,m/s^2}$
joule	$1\,\mathrm{J} \equiv 1\,\mathrm{N\,m}$
watt	$1\,\mathrm{W} \equiv 1\,\mathrm{J/s}$
pascal	$1\,\mathrm{Pa} \equiv 1\,\mathrm{N/m^2}$

Table A.2: SI derived units. For information about SI units see <physics.nist.gov/cuu/Units/>.

1 atm	$= 1.013\,\mathrm{bar}$
	$= 1.013 \times 10^{5}\,\mathrm{Pa}$
	$= 760\,\mathrm{mm\,Hg}$
1 cal	$= 4.186\,\mathrm{J}$
1 eV	$= 1.602 \times 10^{-19}\,\mathrm{J}$

Table A.3: Conversion factors.

A.2 Hyperbolic Functions

$$\cosh x = \frac{1}{2}[e^x + e^{-x}]. \tag{A.1}$$

$$\sinh x = \frac{1}{2}[e^x - e^{-x}]. \tag{A.2}$$

$$\tanh x = \frac{\sinh x}{\cosh x} = \frac{e^x - e^{-x}}{e^x + e^{-x}}. \tag{A.3}$$

A.3 Approximations

$$f(x) = f(a) + (x-a)f'(a) + \frac{1}{2!}(x-a)^2 f''(a) + \frac{1}{3!}(x-a)^3 f'''(a) + \cdots . \tag{A.4}$$

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} \approx 1 + x + \frac{x^2}{2!} + \cdots . \tag{A.5}$$

$$\sin x = \sum_{n=0}^{\infty} (-1)^n \frac{x^{2n+1}}{(2n+1)!} \approx x - \frac{x^3}{3!} + \frac{x^5}{5!} + \cdots . \tag{A.6}$$

$$\cos x = \sum_{n=0}^{\infty} (-1)^n \frac{x^{2n}}{(2n)!} \approx 1 - \frac{x^2}{2!} + \frac{x^4}{4!} + \cdots . \tag{A.7}$$

$$(a+x)^p = a^p \left(1 + \frac{x}{a}\right)^p = a^p \sum_{n=0}^{\infty} \binom{p}{n} \left(\frac{x}{a}\right)^n \tag{A.8}$$

$$\approx a^p \left[1 + p\left(\frac{x}{a}\right) + \frac{p(p-1)}{2!}\left(\frac{x}{a}\right)^2 + \cdots\right]. \tag{A.9}$$

$$\frac{1}{1-x} = \sum_{n=1}^{\infty} x^{n-1} \approx 1 + x + x^2 + \cdots . \tag{A.10}$$

$$\ln(1+x) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{x^n}{n} \approx x - \frac{x^2}{2} + \frac{1}{3}x^3 + \cdots . \tag{A.11}$$

$$\tanh x = \sum_{n=1}^{\infty} \frac{2^{2n}(2^{2n}-1)}{(2n)!} B_{2n}\, x^{2n-1} \approx x - \frac{x^3}{3} + \frac{2x^5}{15} + \cdots , \tag{A.12}$$

where B_n are the *Bernoulli numbers* (see Section A.7).

A.4 Euler-Maclaurin Formula

$$\sum_{i=0}^{\infty} f(i) = \int_0^{\infty} f(x)\, dx + \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \frac{1}{720}f'''(0) + \cdots . \tag{A.13}$$

A.5 Gaussian Integrals

$$I_n \equiv \int_{-\infty}^{\infty} x^n e^{-ax^2}\,dx \qquad (n \geq 0,\ a > 0). \tag{A.14}$$

$$I_0 = \Big(\frac{\pi}{a}\Big)^{1/2}. \tag{A.15}$$

$$I_1 = 0. \tag{A.16}$$

$$I_2 = \frac{1}{2}\Big(\frac{\pi}{a^3}\Big)^{1/2}. \tag{A.17}$$

Derivation:

$$I_0 = \int_{-\infty}^{+\infty} e^{-ax^2}\,dx. \tag{A.18}$$

Because x in the integrand of (A.18) is a dummy variable, we may equally well write I_0 as

$$I_0 = \int_{-\infty}^{+\infty} e^{-ay^2}\,dy. \tag{A.19}$$

To convert the integrand to a form we can integrate, we multiply I_0 by itself and write

$$I_0^2 = \int_{-\infty}^{+\infty} e^{-ax^2}\,dx \int_{-\infty}^{+\infty} e^{-ay^2}\,dy = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{-a(x^2+y^2)}\,dx\,dy. \tag{A.20}$$

The double integral in (A.20) extends over the entire x-y plane. We introduce the polar coordinates r and θ, where $r^2 = x^2 + y^2$. The element of area in polar coordinates is $r dr\,d\theta$. Hence, I_0^2 can be rewritten in the form

$$I_0^2 = \int_0^{2\pi}\int_0^{\infty} e^{-ar^2} r dr\,d\theta = 2\pi\int_0^{\infty} e^{-ar^2} r dr. \tag{A.21}$$

We let $z = ar^2$, $dz = 2ardr$, and write

$$I_0^2 = \frac{\pi}{a}\int_0^{\infty} e^{-z}\,dz = \frac{\pi}{a}\Big[-e^{-z}\Big]_0^{\infty} = \frac{\pi}{a}. \tag{A.22}$$

Hence, we obtain the desired result

$$I_0 = \int_{-\infty}^{+\infty} e^{-ax^2}\,dx = \Big(\frac{\pi}{a}\Big)^{1/2}. \tag{A.23}$$

The values of I_n for n odd in (A.15) are zero by symmetry. For odd values of n, we define $\tilde{I}_n$ as

$$\tilde{I}_n = \int_0^{\infty} x^n e^{-ax^2}\,dx \qquad (n \text{ odd}). \tag{A.24}$$

It is straightforward to show that

$$\tilde{I}_1 = \frac{1}{2a}. \tag{A.25}$$

The integrals I_n and $\tilde{I}_n$ for $n > 1$ can be found from the integrals I_0 or $\tilde{I}_1$ using the recursion relation

$$I_n = -\frac{\partial I_{n-2}}{\partial a}. \tag{A.26}$$

A.6 Stirling's Approximation

We first use the definition of $N!$ as

$$N! = 1 \times 2 \times 3 \times \cdots \times N \tag{A.27}$$

to obtain the weaker form of Stirling's approximation

$$\begin{aligned}
\ln N! &= \ln 1 + \ln 2 + \ln 3 + \cdots + \ln N &\text{(A.28a)}\\
&\approx \int_1^N \ln x\, dx = \Big[x \ln x - x\Big]_1^N &\text{(A.28b)}\\
&= N \ln N - N + 1. &\text{(A.28c)}
\end{aligned}$$

For $N \gg 1$ we have $\ln N! \simeq N \ln N - N$.

A more accurate approximation for $N!$ can be found from the integral representation [see (A.36)]:

$$N! = \int_0^\infty x^N e^{-x}\, dx. \tag{A.29}$$

In the integrand, x^N is a rapidly increasing function of x for large N, and e^{-x} is a decreasing function of x. Hence $f(x) = x^N e^{-x}$ exhibits a sharp maximum for some value of x. As usual, it is easier to consider $\ln f(x)$ and find where it has its maximum:

$$\frac{d \ln f(x)}{dx} = \frac{d}{dx}(N \ln x - x) = \frac{N}{x} - 1. \tag{A.30}$$

We next do a Taylor expansion of $\ln f(x)$ about its maximum at $x = N$. We write $x = N + z$, and expand in powers of z:

$$\begin{aligned}
N \ln(N + z) - (N + z) &= N \ln N + N \ln\Big(1 + \frac{z}{N}\Big) - N - z &\text{(A.31a)}\\
&\approx N \ln N + N\Big(\frac{z}{N} - \frac{1}{2}\frac{z^2}{N^2}\Big) - N - z &\text{(A.31b)}\\
&= N \ln N - N - \frac{z^2}{2N}. &\text{(A.31c)}
\end{aligned}$$

Hence,

$$f \approx N^N e^{-N} e^{-Nz^2/2}, \tag{A.32}$$

and thus

$$N! = \int_0^\infty f(x)\, dx \approx N^N e^{-N} \int_{-N}^\infty e^{-Nz^2/2}\, dz. \tag{A.33}$$

Because the integrand is sharply peaked about $z = 0$, we can extend the lower limit of integration to $-\infty$. Hence, we obtain

$$N! \approx N^N e^{-N} \int_{-\infty}^\infty e^{-Nz^2/2}\, dz = N^N e^{-N} (2\pi N)^{1/2}. \tag{A.34}$$

and therefore

$$\ln N! = N \ln N - N + \frac{1}{2}\ln(2\pi N) \quad \text{(Stirling's approximation)}. \tag{A.35}$$

The *Gamma function* is defined as

$$\Gamma(n) = \int_0^\infty x^{n-1}\, e^{-x}\, dx \qquad \text{(Gamma function)}. \tag{A.36}$$

It is easy to show by integrating by parts that

$$\Gamma(n+1) = n\Gamma(n) = n! \qquad \text{(positive integer } n\text{)}. \tag{A.37}$$

Note that $\Gamma(1) = \Gamma(2) = 1$. Hence $\Gamma(n)$ can be interpreted as a generalization of the factorial function.

For half integer arguments, $\Gamma(n/2)$ has the special form

$$\Gamma\Big(\frac{n}{2}\Big) = \frac{(n-2)!!\sqrt{\pi}}{2^{n-1)/2}}, \tag{A.38}$$

where $n!! = n \times (n-2) \times \cdots \times 3 \times 1$ if n is odd and $n!! = n \times (n-2) \times \cdots \times 4 \times 2$ if n is even. We also have $-1!! = 0!! = 1$, $\Gamma(\frac{1}{2}) = \sqrt{\pi}$, and $\Gamma(\frac{3}{2}) = \sqrt{\pi}/2$.

A.7 Bernoulli Numbers

The *Bernoulli numbers* are the coefficients of $x^n/n!$ in the expansion of

$$\frac{x}{e^x - 1} = \sum_{n=0} B_n \frac{x^n}{n!}. \tag{A.39}$$

All the Bernoulli numbers B_n with odd n are zero except for B_1, that is, $B_{2n+1} = 0$ for $n > 0$:

$$B_0 = 1, \quad B_1 = -\frac{1}{2}, \quad B_2 = \frac{1}{6}, \quad B_4 = -\frac{1}{30}, \quad B_6 = \frac{1}{42}, \quad B_8 = -\frac{1}{30}. \tag{A.40}$$

A.8 Probability Distributions

$$P_N(n) = \frac{N!}{n!\,(N-n)!}\, p^n q^{(N-n)} \qquad \text{(binomial distribution)}. \tag{A.41}$$

The binomial distribution is specified by the probability $p = 1 - q$ and N.

$$P(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\overline{x})^2/2\sigma^2} \qquad \text{(Gaussian distribution)}. \tag{A.42}$$

The Gaussian distribution is specified by $\overline{x}$ and $\sigma^2 = \overline{x^2} - \overline{x}^2$:

$$P(n) = \frac{\lambda^n}{n!}\, e^{-\lambda} \qquad \text{(Poisson distribution)}. \tag{A.43}$$

The Poisson distribution is specified only by the parameter $\lambda = \overline{n} = pN$.

A.9 Fourier Transforms

The Fourier transform of the function $f(x)$ is defined as

$$f(k) = \int f(x)\, e^{-ikx}\, dx. \tag{A.44}$$

Similarly, the inverse transform of $f(k)$ is defined as

$$f(x) = \frac{1}{2\pi} \int f(k) e^{ikx}\, dk. \tag{A.45}$$

Note the sign of the exponential in (A.44) and the presence of the factor of $1/2\pi$ in (A.45). Other definitions of the Fourier transform are common, especially in fields other than physics. In three dimensions we have

$$f(k) = \int f(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}}\, d^3r. \tag{A.46}$$

The three integrals in (A.46) can be reduced to a single integral if $f(\mathbf{r})$ depends only on $r = |\mathbf{r}|$ by using spherical coordinates. We write $d\mathbf{r} = dx\, dy\, dz \to r^2 \sin\theta\, dr\, d\theta\, d\phi$ and $\mathbf{k}\cdot\mathbf{r} \to kr\cos\theta$. Hence, we can write

$$f(k) = \int_0^\infty \int_0^\pi \int_0^{2\pi} f(r) e^{-ikr\cos\theta}\, r^2 dr \sin\theta d\theta\, d\phi. \tag{A.47}$$

The integral over ϕ gives 2π. We can do the integral over θ by making the substitution $x = \cos\theta$ and writing $dx = -\sin\theta\, d\theta$:

$$\int_0^\pi e^{-ikr\cos\theta} \sin\theta\, d\theta \to -\int_1^{-1} e^{-ikrx}\, dx = \frac{1}{ikr}\Big[e^{-ikrx}\Big]_{x=1}^{x=-1} \tag{A.48a}$$

$$= \frac{1}{ikr}[e^{ikr} - e^{-ikr}] = \frac{2}{kr}\sin kr, \tag{A.48b}$$

where $[e^{ikr} - e^{-ikr}]/2i = \sin kr$. Hence (A.46) reduces to

$$f(k) = 4\pi \int_0^\infty f(r)\, r \frac{\sin kr}{k}\, dr. \tag{A.49}$$

A.10 The Delta Function

The Kronecker delta δ_{ij} is defined as

$$\delta_{ij} = \begin{cases} 1 & \text{if } i = j, \\ 0 & \text{if } i \neq j, \end{cases} \tag{A.50}$$

where i and j are integers. The Kronecker delta has the property that

$$\sum_{i=-\infty}^{\infty} \delta_{ij} a_i = a_j. \tag{A.51}$$

The *Dirac delta function* $\delta(x)$ can be thought of as a generalization of the Kronecker delta function for continuous variables. Loosely speaking, $\delta(x)$ is zero everywhere except at $x = 0$ where its value is infinitely large such that its integral is 1, that is,

$$\int_{-\infty}^{\infty} \delta(x)\, dx = 1. \tag{A.52}$$

The Dirac delta function has the useful property that

$$\int_{-\infty}^{\infty} f(x)\delta(x)\, dx = f(0), \tag{A.53}$$

or more generally

$$\int_{-\infty}^{\infty} f(x)\delta(x-a)\, dx = f(a). \tag{A.54}$$

Note that the property of the Dirac delta in (A.54) is analogous to (A.51). Another useful property is that

$$\int_{-\infty}^{\infty} \delta(\lambda x)\, dx = \frac{1}{|\lambda|}. \tag{A.55}$$

Despite its name, the Dirac delta function is not really a function and was not first introduced by Dirac.

The Fourier transform can be used to obtain a useful representation of the Dirac delta function. The Fourier transform of $\delta(x)$ is

$$\delta(k) = \int_{-\infty}^{\infty} \delta(x)e^{-ikx}\, dx = 1. \tag{A.56}$$

The inverse transform gives the desired representation:

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ikx}\, dk. \tag{A.57}$$

A.11 Convolution Integrals

A convolution integral expresses the amount of overlap of one function as its argument is shifted from the argument of another function. The form of the convolution integral in one dimension is

$$C(x) = \int_{-\infty}^{\infty} f(x')g(x-x')\, dx'. \tag{A.58}$$

The integral (A.58) can be expressed as a product of two Fourier transforms. To derive this result we use (A.45) to write the right-hand side of (A.58) as

$$C(x) = \frac{1}{(2\pi)^2}\iiint f(k)g(k')e^{ikx'}e^{ik'(x-x')}dk\, dk'\, dx'. \tag{A.59}$$

We first group terms that depend on x' and do the integral over x' using (A.57):

$$\int e^{ix'(k-k')}dx' = 2\pi\delta(k-k'). \tag{A.60}$$

We then use this result to write the right-hand side of (A.59) as

$$C(x) = \frac{1}{2\pi}\iint f(k)g(k')e^{ik'x}\delta(k-k')dk\,dk' \tag{A.61a}$$

$$= \frac{1}{2\pi}\int f(k)g(k)e^{ikx}dk. \tag{A.61b}$$

A.12 Fermi and Bose Integrals

The integrals that commonly occur in the context of the ideal Fermi gas have the form

$$\int_0^\infty \frac{x^n}{e^x+1}dx = \Big(1-\frac{1}{2^n}\Big)\Gamma(n+1)\zeta(n+1), \tag{A.62}$$

where the Riemann zeta function is defined by

$$\zeta(n) = \sum_{k=0}^\infty \frac{1}{(k+1)^n}. \tag{A.63}$$

The values of $\zeta(n)$ that we will use most often are

$$\zeta\Big(\frac{3}{2}\Big) \approx 2.612, \tag{A.64a}$$

$$\zeta(2) = \frac{\pi^2}{6} \approx 1.645, \tag{A.64b}$$

$$\zeta\Big(\frac{5}{2}\Big) \approx 1.341, \tag{A.64c}$$

$$\zeta(3) \approx 1.202, \tag{A.64d}$$

$$\zeta(4) = \frac{\pi^4}{90} \approx 1.082. \tag{A.64e}$$

The integrals that are needed in the context of the ideal Bose gas have the form

$$\int_0^\infty dx\frac{x^n}{e^x-1} = \int_0^\infty dx\frac{x^ne^{-x}}{1-e^{-x}} = \int_0^\infty dx\,x^n\sum_{k=0}^\infty e^{-(k+1)x} \tag{A.65a}$$

$$= \sum_{k=0}^\infty\int_0^\infty dx\,x^ne^{-(k+1)x} = \sum_{k=0}^\infty\frac{1}{(k+1)^{n+1}}\int_0^\infty dy\,y^ne^{-y}. \tag{A.65b}$$

If we use the definition of the Riemann zeta function in (A.62) and the definition of the Gamma function in (A.36), we obtain

$$\int_0^\infty dx\frac{x^n}{e^x} = \zeta(n+1)\Gamma(n+1). \tag{A.66}$$

If n is an integer, than (A.66) reduces to

$$I(n) = n!\zeta(n+1). \tag{A.67}$$

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