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Entropy and the Time Evolution of Macroscopic Systems

WALTER T. GRANDY, JR.

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In memory of Edwin T. Jaynes,
who had the courage to challenge established dogma

CONTENTS

The first extension of the maximum entropy principle to nonequilibrium states is made here, with applications to inhomogeneous systems. An initial contact with linear transport processes in simple fluids is also included.

Application to nonequilibrium stationary processes is made at this stage, with a focus on simple fluids.

A careful analysis of time evolution in macroscopic systems is carried out, along with a critique of the standard equation of motion for the density matrix. The practical difference between microscopic and macroscopic equations of motion and the necessary relation to external sources is recognized explicitly.

The concept of thermal driving is introduced, wherein very general external sources going beyond simple mechanical and electrical forces are envisioned, from baseball bats to Bunsen burners. Elements of nonequilibrium thermodynamics are presented.

An interlude in which the previous theoretical developments are applied to the fluid dynamics of simple fluids and the derivation of their macroscopic equations of motion from statistical mechanics.

Finally, the deep questions of the relation of entropy to these topics first raised in Chapter 1 are addressed and resolved satisfactorily.

The story concludes with a discussion of topics of current research interest, with an emphasis on exposing various myths in the folklore.

A mathematical exposition of the equations required to describe small departures from equilibrium.

Microscopic expressions for dissipative currents in simple fluids are exhibited, and the Galilean invariance of statistical mechanics is discussed in some detail.

A brief discussion of how the covariance or correlation functions are analytically continued into the complex plane so as to readily analyze their casual and dissipative properties.

PREFACE

Although the concept of entropy was introduced into thermodynamics more than 140 years ago, broad consensus as to its meaning remains elusive—as evidenced by the continued outpouring of works large and small attempting to capture its essence. My purpose in this book is not just to contribute to this body of work, but to provide a wider exposure to a point of view that presents a deeper and definitive understanding of the concept. In doing so, we are also able to extend the role of entropy to time-dependent physical processes in an unambiguous way, following a path that has only recently become clear.

Over the years the notion of entropy has spread well beyond its original thermal context, of course, and in a number of applications its extension has led to new insights; these include information and communication theory, nonlinear dynamics, and image reconstruction, to name a few. The following material, however, is restricted completely to the role of entropy in thermal physics and its underlying foundation in statistical mechanics. We shall also avoid some attempted redefinitions that often result in violations of elementary logic. Moreover, it is not my intent to produce a "philosophically informed" presentation, whatever that might mean; rather, my sole interest is to present a point of view concerning the application to pure physics.

Potential readers would profit from at least a rudimentary exposure to probability theory, although preferably without hardened views as to its meaning and application. The study of thermodynamics and mathematics at least at the advanced undergraduate level is desirable, and a first introduction to statistical mechanics would be helpful. The present work is not an introduction to any of these subjects, and is not at all a thermodynamics text. It is hoped, however, that the following pages will illuminate the deep nature of entropy as it presides over *all* of thermal physics.

Most of our world and the universe beyond is not, and never has been, in thermal equilibrium. But that state is approximated very well in many, many systems and has proved an enormously useful concept. Nevertheless, there has been a long and continuing effort to extend the definition of entropy to nonequilibrium processes and to develop a corresponding nonequilibrium thermodynamics. While there has been some modest success in these efforts, it seems fair to say that the cumulative results have been rather disappointing. In most cases it is presumed that a nonequilibrium entropy can be defined merely by decreeing that the thermodynamic equilibrium entropy can be written as a function of time, a definition lacking any rational justification. This situation is examined in detail in the following pages and what appears to be a highly satisfactory resolution is presented.

A major reason why entropy has been conceptually controversial is that its underlying meaning transcends its usual application to thermal physics, although that is our interest here. The concept has a deeper origin in probability theory, traces of which are evident in the work of the founders of statistical mechanics, Ludwig Boltzmann and J. Willard Gibbs. The variational algorithm of Gibbs is recognized as central to most of thermal physics, and the later work of Claude Shannon and Edwin Jaynes uncovered its roots in the theory of probability itself as a Principle of Maximum Entropy (PME). There has always been some degree of controversy surrounding the fundamental nature of this principle in physics, as far back as early in the 20th century with the work of Paul and Tatyana Ehrenfest. Much of this "cloud" is due to a lack of appreciation by many theorists of the dominant role of rational inference in science, and a goal of the present work is to overcome this resistance.

Gibbs introduced the phrase "statistical mechanics" as early as 1884 to emphasize the necessity of a statistical point of view in describing macroscopic physical systems in terms of their microscopic constituents, for many macroscopic properties cannot be obtained deductively from the microscopic equations of motion. By means of statistical, or probable inference, one strives to predict physical behavior based only on available macroscopic information, which is pretty much the way science in general operates. We shall adhere strictly to this methodology in the present work, and thereby avoid the temptation to introduce any extraneous presumptions of an "ergodic" or "stochastic" nature. The resulting discussion will therefore be rooted deeply in probability theory.

The first five chapters of the book primarily concern equilibrium systems, and are meant to develop the general viewpoint while laying the foundation for the following chapters. Although many of the results found here will be familiar to some, even those readers will find some new twists and insights. Chapters 6 and 7 extend the entropy principle to nonequilibrium states, while chapters 8 and 9 provide an unambiguous extension of the statistical theory to time-dependent processes. Among the novel features to be found in these later chapters are *derivations* of the Onsager reciprocal relations, as well as the linear constitutive relations for fluids—all of which are traditionally treated phenomenologically. In addition, the theory of linear dynamic response is shown to be a special case of the general thermal driving theory presented here, thereby leading naturally to the associated thermodynamics.

An interlude occurs in Chapter 10, where an application to fluid dynamics is presented by way of illustrating the preceding developments. In Chapter 11 we address the important issues of irreversibility, relaxation, the Second Law, and the approach to equilibrium, all informed by our insistence on a strict grounding in probability theory. The story is concluded in Chapter 12 with a timely discussion of dissipation and entropy production. Several appendices are included containing a number of mathematical details not provided in the main text.

Much of the material in this work arises, in one way or another, from a long and fruitful association with Ed Jaynes—some of it learned from, and other ideas stimulated by, his penetrating insights. He cannot be held accountable, however, for how it all came out.

W.T. Grandy, Jr.
Laramie and Tucson, 2007

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INTRODUCTION

> *Entropy, like force, is an* undefined *object, and if you try to define it, you will suffer the same fate as the force definers of the seventeenth and eighteenth centuries: Either you will get something too special or you will run around in a circle.*
>
> *Clifford Truesdell (1966)*

The notion of entropy from its very conception has carried with it a slight aura of mystery and confusion, even for many accomplished scientists such as Truesdell. In the physical sciences, the concept has generally been restricted to equilibrium thermodynamic systems; although it is now known to play a role in fields such as information theory and nonlinear dynamics, for example, our focus in what follows will be primarily on macroscopic thermal phenomena. Only recently has it been seen how to extend the concept unambiguously to time-dependent phenomena, and to display the broad unifying role of entropy throughout *all* of thermal physics. The purpose here is to explicate the way that this unification occurs, and toward that end it may be useful to begin by recalling how entropy emerged in the development of classical thermodynamics.

1.1 Heat

For millennia mankind had contemplated the nature of heat as its primary source of energy, but without comprehending the concept of energy itself. The impression of a substance flowing from one body to another was almost unavoidable and, despite early observations from thinkers such as Francis Bacon (1620) that heat was some kind of "motion of things," that thought continues to this day to be a convenient crutch for many of us. Bacon's ideas finally received scientific formulation late in the 17th century, first as a theory of heat as *phlogiston*, a substance without color, odor, taste, or weight that was contained in all materials. An alternative version considered it to have negative weight, which would explain the increase in weight of metals when they were heated. This theory remained dominant for almost a century. Eventually the notion of phlogiston was found by experiment to be flawed, primarily through the work of Lavoisier (1783) as he unraveled the mechanism of combustion. He proposed, instead, that heat was a substance he called *caloric*, an imponderable, invisible, and weightless fluid. Caloric differed from phlogiston in that it was not an intrinsic part of matter, but a material substance that can flow to and from bodies. This theory was quite successful in explaining numerous phenomena, such as the expansion of air when heated. Indeed, the theory survived well into the 19th century as more or less the “dark energy” of that period.

Ironically, the idea of heat as caloric was shown to be unsustainable as early as 1797, by Benjamin Thompson (Count Rutherford). By means of boring a cannon barrel he demonstrated that heat generated by friction could not possibly be a substance, but some kind of unconserved motion. Echoing Bacon, thus was born the germ of the idea of kinetic energy. Unfortunately, experimental uncertainties rendered Rumford’s results debatable, and the caloric theory persisted for decades more, supported by distinguished thinkers such as Laplace. Even the later work of Carnot was based on the interpretation of heat as caloric. It would be another 50 years before the work of Mayer, Joule, Helmholtz, and Clausius would establish definitively the nature of heat as a form of energy. The history of heat during this period has been told in great detail by Brush (1976).

In the 21st century it is still common to speak of heat as if it were a “substance” that flows and can be thought of as a fluid;[1] scientifically we still use the phrase “heat capacity” that connotes an amount of something, although we know better. We take note of these foibles only to emphasize that human perception remains a bit “fuzzy” in discussing the concept of heat, difficult to pin down at times. Technically, however, we have no trouble agreeing that heat is not a substance, but a *process* of energy exchange between macroscopic systems and their environments. The energy available for, and involved in, this process is generally referred to as *thermal energy.* But the fact remains that heat is somehow qualitatively different than energy in other forms, such as that associated with work. It was, in fact, this difference between heat and work that led to the idea of internal energy and the First Law of Thermodynamics—and that difference is what concerns us here.

Energy transferred as heat seems to have a certain “randomness,” or lack of organization to it; it takes place through degrees of freedom not carefully controlled. A somewhat fanciful analogy is provided by the “wave” often created by fans at a large sports venue (football, baseball, soccer, etc. stadiums). A substantial section of fans will stand up in unison, sometimes holding up colored placards, and after a short period a similar section adjoining the first will repeat the maneuver as the first section sits down. The continuation of this process presents an impression of a wave propagating around the closed stadium as a well-organized and energetic pulse. This “wave” can continue for as long as the fans’ interest and energy holds up. But one can also imagine the initial section of fans rising as individuals at slightly different times, looking around a bit, and then sitting down at random, all with no cohesion or synchrony—and this can take place throughout the stadium. Every bit as much energy is expended as in the original scenario, yet in some sense does not seem to be as useful, because it is not organized. Of course, the only thing useful about this “wave” would seem

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[1] Momentum and energy, in general, are often spoken of in this way as well, perhaps unavoidably at times.

to be entertainment, not work, but the difference between the two processes does parallel that between heat and work.

The point here is that there exists a sense of something missing when we contemplate heat, some kind of lack of information that is present with work. When a block of wood is moved forcefully across a table, with some downward pressure, the work done on the block goes partly into giving it some kinetic energy, and partly into providing some thermal energy to both block and table; this is verified by increased temperatures. The thought that not all the work went toward kinetic energy conveys a sense of loss, that part of the input energy was degraded to an unorganized form. From a physical point of view this sort of mechanical uncertainty in energy transfer is the essence of heat, and it encompasses its characterization as a form of motion. It is this essence we wish to examine and clarify in what follows, in the course of which we shall find that it is not confined to the notion of heat.

1.2 The emergence of entropy

At the turn of the 19th century the meaning of "heat," though not fully developed, had been clarified considerably, thereby enabling further development of new thermodynamic concepts. One of the most important of those emerged in 1824 when Sadi Carnot had the splendid vision of a *heat engine*, which operates by drawing energy Q_1 in the form of heat from a reservoir[2] in thermal equilibrium at temperature t_1 and delivering an amount of useful work W. For this to operate continuously or cyclically he noted that a cold reservoir at temperature $t_2 < t_1$ was required, into which some heat Q_2 could be deposited. He also had the seminal idea of a *reversible* engine, one that could deliver W back to the engine and heat Q_1 back to the reservoir at t_1. Almost immediately one is led to

> **Carnot's Principle:** No heat engine operating between the same two temperatures can be more efficient than a reversible one.

By efficiency is meant the ratio of work delivered to heat extracted, $e = W/Q \leq 1$.

Unfortunately, Carnot was not able to provide a quantitative expression of his principle, for he had no exact relation linking work and thermal energy; this, of course, was later provided by Joule. It was William Thomson (Lord Kelvin) (1848) who eventually brought attention to Carnot's work, and he reasoned that the efficiency of a reversible engine must have the universal form

$$e_r(t_1, t_2) = 1 - f(t_2)/f(t_1)\,, \tag{1.1}$$

where $f(t)$ is monotonic increasing and the ratio must be the same function for all reversible engines. Thus was discovered the absolute temperature scale $T(t)$,

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[2] Often referred to as a "thermostat" today, a term more commonly associated with a control device, it is presumed so large that its properties are unaffected in the process.

and, in our now common units, (1.1) becomes

$$e_r = 1 - T_2/T_1\,. \tag{1.2}$$

With this advance, Carnot's principle can be stated as follows: the efficiency of a real heat engine must satisfy $e \le e_r$, or

$$e = 1 - Q_2/Q_1 \le 1 - T_2/T_1\,. \tag{1.3}$$

If we now take Q to be algebraic, we can write both Q_1 and Q_2 as positive quantities of thermal energy delivered from reservoirs *to* the engine, and (1.3) takes the suggestive form

$$Q_1/T_1 + Q_2/T_2 \le 0\,, \tag{1.4}$$

with equality if and only if the engine is reversible.

Kelvin also made the generalization to a heat engine that runs cyclically while making contact successively with n reservoirs at temperatures $(T_1, \dots, T_n)$. The total work delivered is $W = \sum_i Q_i$ and Carnot's principle becomes

$$\sum_i Q_i/T_i \le 0\,, \tag{1.5}$$

which Kelvin then employed to develop his thermoelectric equations.

Strangely enough, it was left for Rudolph Clausius (1865) to see that by extending (1.5) to arbitrarily large n the sum goes into a cyclic integral:

$$\oint \frac{dQ}{T} \le 0\,. \tag{1.6}$$

In the limit of a reversible process the equality holds and T becomes the absolute (or Kelvin) temperature of the entire system. But in this latter case, (1.6) is valid for any cycle and the equality is just the condition that the line integral over any part of a cycle is independent of the path. With this realization, and a good deal of further inspiration (*e.g.*, Cropper, 1986), Clausius was led to introduce a new function S of the thermodynamic state of the system, which he called *entropy.* Within an additive constant, S is defined by its difference between two macroscopic equilibrium states,

$$S_a - S_b \equiv \int_b^a \frac{dQ}{T} = \int_b^a C(T)\,\frac{dT}{T}\,, \tag{1.7}$$

where the integrals are over a reversible path (a locus of equilibrium states), and $C(T)$ is a heat capacity. This restriction on the path is necessary because the absolute temperature T is not defined for other than equilibrium states; dQ represents the net thermal energy added to or taken from the system at any point in the process. As a consequence, entropy is defined in classical thermodynamics *only* for states of thermal equilibrium.

But now let us complete the cycle by running the process from a to b along an arbitrary, possibly irreversible path. From (1.6) we find that

$$\int_a^b \frac{dQ}{T} \leq S_b - S_a\,, \tag{1.8}$$

where T is not necessarily the temperature of the system, but that of a reservoir with which the system is temporarily in contact. Keeping in mind the meaning of the Q_i in (1.4), we see that the negative of the left-hand side of (1.8) must be the entropy gained by the reservoirs, so that quite generally Carnot's principle becomes

$$S(\text{final}) \geq S(\text{initial}). \tag{1.9}$$

That is, in the change from one equilibrium state to another along a reversible path, the total entropy of all bodies involved cannot decrease; if it increases, the process is irreversible. The integral in (1.8) thus provides a lower bound for the change in entropy.

Equation (1.9) is Clausius' statement of the Second Law of Thermodynamics. It is a statement of macroscopic phenomenology that cannot be proved solely as a consequence of the microscopic dynamical laws of physics, as already appreciated by Boltzmann (1895): "The Second Law can never be proved mathematically by means of the equations of dynamics alone." Phenomenological changes in entropy are to be found from experimental measurements with calorimeters and thermometers, so that by construction it is a function only of the macroscopic parameters defining the macroscopic state of a system, $S(V, T, N)$, say, where V and N are the system volume and particle number, respectively. It makes no reference to microscopic variables or probabilities, nor can any explicit time dependence be justified in the context of classical thermodynamics.

By the middle of the 19th century Joule had established the mechanical equivalent of heat and the notion of internal energy U had been formulated, allowing Helmholtz (1847) to clarify the law of conservation of energy. Thus emerged a clear statement of the First Law of Thermodynamics: $dU = dW + dQ$, indicating that both heat and work can change the internal energy of the system. Since U is to contain all possible forms of energy, it clearly can change by other means as well. With the work of Clausius the stage was set for completion of the development of classical thermodynamics, for the essential ingredients were now seen to be the entropy and total energy of the macroscopic system. This was expressed rather poetically by Clausius in his famous couplet reflecting the First and Second Laws: "Die Energie der Welt ist constant; Die Entropie der Welt strebt einem Maximum zu."

1.3 Classical thermodynamics

It was Willard Gibbs who completed development of the fundamental theory in 1875, with his monumental work "*On the Equilibrium of Heterogeneous Substances*," hereafter denoted by *HS*. Gibbs interpreted Clausius' observation to be the result of a general variational principle and *defined* the equilibrium state as that for which the variation of S vanishes when energy is held constant, the only other option being that the variation is negative. (He also noted the equivalent variational principle for energy at constant entropy.) The entropy function thus became the central figure in the theory.

It may be of some value to summarize briefly the basic elements in terms of the dominant role played by entropy. A physical system in thermal equilibrium is described by a set of possible equilibrium states that are time independent and, in the simplest cases, reflect the presumed isotropy and homogeneity of that system. The essential role of the theory is to compare two neighboring equilibrium states that the system might occupy under different external constraints.

The systems in question can be classified in various ways. A *closed system* permits interaction with its environment only through exchange of energy, in contrast with an *open system* in which matter can be exchanged as well. An *isolated system* has no interaction of any kind with the external environment, and thus is an idealized but useful construct. It is often valuable to characterize physical systems as *simple* if they have a uniform chemical composition of a single nonvolatile substance possessing uncomplicated properties. A *compound* system is a product or combination of simple systems, but is not a *mixed* or *complex* system such as might be formed of coffee with cream.

To be more precise about the meaning of equilibrium, it is necessary to first define the notion of a *macrostate* of a physical system by specifying or measuring one or several of its relevant properties in terms of a set of macrovariables $\{X_i\}$. These variables are conventionally considered to be either extensive or intensive, according to whether they scale with the size of the system as do volume V and particle number N, or remain the same like temperature and pressure. A particular set of such variables is said to define a *thermodynamic system* corresponding to the physical system under consideration, and in equilibrium these variables are taken as constants of the motion for the total system.

Although a system could, in principle, be described by an enormous number of such properties, there are seldom more than four or five of these variables relevant in a specific experiment, such as pressure, volume, magnetization, and so on. Any particular physical system will possess many possible thermodynamic systems, depending on which macrovariables are being controlled in that experiment, and different sets of variables can be connected by means of Legendre transformations. These variables, along with any constraints such as equations of state, determine the number of macroscopic degrees of freedom characterizing that thermodynamic state. In this sense of choice the definition is somewhat subjective, but no more so than science itself, a human invention whose conclusions we hope are as objective as possible.

That different experimenters may investigate the same physical system by studying its various thermodynamic systems is almost a platitude. For example, if temperature and pressure are varied in one instance, a particular value for the change in entropy will be recorded; if upon reproduction of the experiment an external magnetic field is also varied, then a paramagnetic system would perhaps yield a different value for the entropy change. It is not that we forgot something the first time, but only that we made another subjective choice of what experiment to do the second time around; in both experiments the procedures are completely objective, though the entropies are functions of different variables in the two cases. It cannot be emphasized strongly enough that the experimental entropy is a property of an equilibrium macrostate of a physical system and does *not* refer to anything else about that system. In particular, the thermodynamic entropy does not have a *mechanical* interpretation.

But it may also happen that in the first experiment a varying magnetic field was also present unknown to us, so that the calculated entropy (as outlined below) is in disagreement with the experimental result. One would suspect immediately that there is indeed another unrecognized macrovariable changing throughout the experiment, and so it must either be included in the calculation or shielded in the experiment. Thus, no one thermodynamic system is any more "correct" than any other, but for a given purpose a particular one may be the most useful. Put another way, we do not envision a "complete" set of macrovariables in the sense of a complete set of commuting observables in quantum theory; in principle, one can introduce and control as many macrovariables as one likes.

Gibbs presumed S to be an extensive function of extensive variables, which is often equated to the observation from the definition (1.7) that entropy should be additive; that is, the entropy of a compound system should be the sum of the individual entropies: $S_{12} = S_1 + S_2$. This would seem to make sense, for the heat capacity of two dinner plates held together ought to be twice that of a single plate. The equivalence, however, is a bit more subtle and will require further discussion.

The mathematical properties of entropy required to produce a quantitative formulation of classical thermodynamics can be stated readily for a simple system described by macroscopic variables U, V, N, for which S is presumed to satisfy the following relations (*e.g.*, Tisza, 1966; Callen, 1985):

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)\,, \qquad \lambda \text{ real}\,, \tag{1.10}$$

$$S(U_2, V, N) \geq S(U_1, V, N)\,, \qquad U_2 \geq U_1\,, \tag{1.11}$$

$$S(U_1 + U_2, V_1 + V_2, N_1 + N_2) \geq S(U_1, V_1, N_1) + S(U_2, V_2, N_2)\,, \tag{1.12}$$

where the subscripts refer to different systems forming components of a complex system. Equation (1.10) states that S is homogeneous of degree 1, so that entropy is taken to be an extensive function of extensive variables. This is completely equivalent to Euler's equation for $S(X_1, \ldots)$,

$$S(X_1, \ldots) = \sum_i X_i \frac{\partial S}{\partial X_i}\,, \tag{1.13}$$

with which Gibbs characterized his thermodynamic systems (*HS*), and which also defines the intensive variables as derivatives of S. Thus, U/N and U/V, for example, can be measured anywhere in the homogeneous system and they will yield the same values. We shall find that the notion of extensivity demands much more attention.

Monotonicity is asserted by (1.11), which allows a positive temperature to be defined through $T^{-1} = \partial S/\partial U$. While extensivity is often equated with additivity for two subsystems, Eq.(1.12) extends this to *superadditivity*, reflecting both the essence of the Second Law and the maximal property of entropy at equilibrium. Of great importance is the implication from (1.10) and (1.12) that S is concave over the extensive variables, something to be expected from the maximum property, of course. With $\lambda = \frac{1}{2}$, for example, we have

$$2S\left(\frac{U_1+U_2}{2}, \frac{V_1+V_2}{2}, \frac{N_1+N_2}{2}\right) \geq S(U_1, V_1, N_1) + S(U_2, V_2, N_2)\,, \qquad (1.14)$$

a special case of the general definition of concavity. As Gibbs noted at length, the entropy surface lies below its tangent planes over the entire range of the macrovariables. In turn, concavity implies that S is continuous and possesses both left and right derivatives over the same range, the intensive variables having at most jump discontinuities that suggest possible phase transitions. One can also show that (1.10) and (1.14) imply (1.12), but we hasten to add that (1.12) must refer to a complex system. An excellent discussion of these points in more depth has been given by Wightman (1979).

Equation (1.11) guarantees invertibility of S to obtain $U(S, V, N)$, which is then convex, extensive, and *subadditive*: $U \leq U_1 + U_2$. Thus, U is minimized in equilibrium, and stability conditions for this state can be derived in terms of either S or U.

Clarification of the meaning of both entropy and the Second Law would require a great deal of further effort, as well as much of this exposition; but their utility would soon be evident, as an immediate example illustrates. Consider a container of M moles of a substance in thermal equilibrium, such that there are m moles in the liquid phase and $M - m$ moles in the vapor phase. The container is equipped with a piston and the system is thermally insulated from the surroundings. Let the piston be moved very rapidly to a new position, so that m cannot change much during the motion. The system has a new volume and pressure when the motion halts and we let it return to equilibrium, at which point we wish to know if and by how much the relative portions of liquid and vapor have changed, and to know the final thermodynamic state of the system.

Clearly, the First Law cannot answer these questions, but the Second can: The substance will evaporate further if and only if that leads to an increase in the total entropy of the system. Thus, the Second Law can tell us the direction the process will go, but this alone does not determine the other parameters of the final equilibrium state. A much stronger statement, that the entropy *will* indeed increase to the maximum value allowed by the constraints on the system, results from Gibbs' variational principle, and leads to a quantitative description of that state. The precise details of such a calculation will be developed in the following chapters.

1.4 Is there a Deeper interpretation?

The development of classical thermodynamics was a marvelous achievement, and its many and varied applications led to great technological advances. But the theory was inherently phenomenological, and from a fundamental standpoint many questions begged to be addressed, most particularly with regard to the entropy. For example, what exactly is the meaning of S? Does it have a deeper physical meaning than indicated by its definition via (1.7)? Does it have a broader sweep than its origin in Carnot's heat engines (or in the mind of Clausius)? In addition, one might wonder just *why* entropy should be a maximum in the equilibrium state. Is there an underlying deeper reason for accepting Gibbs' variational principle? What is actually being accomplished by maximizing S subject to given total energy? And what is the logical basis for the Second Law? Since entropy is rarely, if ever, measured directly, there is good reason to pursue these points.

With the emerging acceptance of the particulate view of matter, kinetic theory (and later, statistical mechanics) provided a means to uncover the underlying foundations of thermodynamics in terms of the dynamical behavior of the system's constituent particles. The first to exploit this picture to illuminate the nature of entropy and the Second Law was Ludwig Boltzmann.[3] He seems to have introduced a logarithm into the discussion while constructing a derivation of Maxwell's velocity distribution. He defines a function f to be the distribution of velocities of single particles with mass m, and f_1 to be that for particles with mass m_1, and adopts a hypothesis of 'molecular chaos', or *Stosszahlansatz*, that essentially denies the existence of correlations between distributions of different particles. Through a study of collisions among all particles he then determines conditions for stationarity of the form $ff_1 = f'f_1'$, where f' denotes f as a function of the primed, or postcollision velocity components. He is then able to show that the solution to these equations is Maxwell's distribution.

To derive the above stationarity condition Boltzmann is led to contemplate the sum of all values of $\ln f$ in a volume element $d\omega$ of the single-particle velocity space at a particular time,

$$H \equiv \int f \ln f \, d\omega \,. \tag{1.15}$$

He also derives his famous transport equation, from which he is now able to show that $dH/dt \leq 0$, his equally famous H-theorem (see Chapter 11). If H is interpreted as proportional to the negative of the entropy, S is found to increase

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[3] Most of Boltzmann's work in thermodynamics and statistical mechanics, beginning in 1866, is summarized in his *Vorlesungen über Gästheorie* (1896–1898), which we shall refer to throughout this discussion simply as *Vorlesungen*.

as f evolves to the stationary solution that is Maxwell's equilibrium distribution. Only after the objection by Loschmidt and others that H can increase as well as decrease in time does he realize that (1.15) must be a probability statement, and he "proves" that H decreases *on average.* But in thinking about distributions he was clearly already contemplating probabilities, no doubt influenced by Maxwell who had earlier introduced probability into the kinetic theory (1850).

Boltzmann next turns to elucidating the mathematical meaning of H. He considers an ideal gas and divides the velocity space into equal-size cells, so that the velocity point of a particle present in one cell is equi-probable of being in any other. Alternatively, holding the energy E and total particle number N constant, one can imagine that n_i of the particles have energy ϵ_i, so that

$$N = \sum_i n_i \,, \qquad E = \sum_i n_i \epsilon_i \,. \tag{1.16}$$

Then the total number of possible *microstates* (or "complexions") is the multiplicity

$$w = \frac{N!}{\prod_i (n_i!)} \,, \tag{1.17}$$

so that $f_i \equiv n_i/N$ is thought of as the *frequency* with which a particle is in cell ω_i with energy ϵ_i. The right-hand side of (1.17) is just the multinomial coefficient, and hence the number of ways that a given set $\{n_i\}$ can be realized. So, by maximizing w subject to (1.16) one obtains that set of occupation numbers that can be realized in the greatest number of ways. It is an equivalent procedure to maximize any monotonic increasing function of w, and Stirling's formula[4] for approximating $n!$ for large n suggests $\ln w$. The resulting variational problem is then to maximize

$$\frac{1}{N} \ln w \simeq -\sum_i f_i \ln f_i \,, \tag{1.18}$$

subject to the constraints (1.16). The Maxwell distribution follows immediately, and Boltzmann goes on to show that the *maximum*, now denoted by $N^{-1} \ln W$, is indeed equivalent to (1.15).

At least for an ideal gas, there is a strong suggestion that S may be proportional to $\ln W$. Here he has established this by counting complexions, and in doing so demonstrates that W is actually a multiplicity factor, not a probability; that is, prior to maximization, it counts the total number of microscopic arrangements of the constituents. We mention this because Boltzmann, Planck, and Einstein all thought of W as a probability (*Wahrscheinlichkeit*), although Planck (1913) in his book on radiation is careful to call it a "thermodynamic probability," in contrast to a mathematical probability; he even notes that the former is a factor

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[4] In its simplest form, $\ln N! \sim N \ln N - N, \quad N \gg 1$.

in the latter, as indeed it is. Planck (1901) also supplied the proportionality constant by writing

$$S = k \ln W \,, \tag{1.19}$$

arguably one of the most famous expressions of the 19th century; k is now called Boltzmann's constant. In writing this expression Planck also claimed that it represents an absolute value of entropy, an assertion that will require some modification later. Since it is a maximum, the right-hand side of (1.19) is a measure of that set of microscopic arrangements satisfying the constraints that can be realized in the greatest number of ways; mathematically W is a multiplicity factor.

Having established a mathematical foundation for W, Boltzmann next turned to its physical meaning. In Part II of *Vorlesungen* he developed the classical–mechanical aspects of the theory and introduced his *Ergoden*[5]—this anticipated, and was essentially equivalent, to Gibbs' microcanonical ensemble (see below). We adopt a slightly more modern notation to capture Boltzmann's development, and note that by this time he had moved the discussion into the $6N$-dimensional phase space of particle coordinates and momenta.

Suppose particle number N and volume V are fixed in addition to the total energy E. An element of phase volume for which the energy lies in the range $(E, E + dE)$ is given by $dW = g(E)dE$, where $g(E)$ is the differential phase volume, or density of states, and W has the same meaning as above. For an ideal gas

$$W(E) = \int_R d^3x_1 \cdots d^3x_N \, d^3p_1 \cdots d^3p_N = C_1 V^N E^{\frac{3N}{2}-1} \,, \tag{1.20}$$

and C_1 is independent of E and V. That is, R is such that all coordinates are in a volume V and all momenta are in the range $E < \sum_i p_i^2/2m < E + dE$. But for an ideal gas, $PV = NkT$ and [see Eq.(5–4)]

$$S(T, V, N) = kN \ln V + \frac{3}{2} Nk \ln T + C_2 \,, \tag{1.21}$$

where C_2 is independent of T and V. Comparison of (1.20) and (1.21) immediately establishes (1.19). Thus Boltzmann had shown, at least for the ideal gas, that the left-hand side of (1.19) is the thermodynamic entropy of Clausius, and that the right-hand side is the logarithm of the greatest number of ways in which this state can be realized microscopically; that is, S is a maximum for given E, N, and V.

What a strange relation (1.19) is! It says nothing about heat, yet if S is also given by (1.21) it tells us that the more we heat the system, the more uncertain we are as to its microscopic state, and similarly if we increase the volume. It is just this observation that carries the seeds of a deeper understanding of entropy.

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[5] Despite appearances, this has nothing to do with ergodic notions.

In his paper on critical opalescence Einstein (1910) expressed his views on (1.19), which he referred to as "Boltzmann's Principle." While insisting that (1.19) must be valid, he raised several objections to Boltzmann's interpretation of W itself, the first being to the combinatorial calculation (1.17). Einstein noted that this had only been done for an ideal gas and that it would have to be done in a more complete way for a real system, and in that case probably could not be done at all. This remark is certainly correct in general, for such a calculation of W can only be done properly in very exceptional and simple models. We should point out, however, that the set of exceptional, yet useful, cases is by no means empty, as demonstrated above for the ideal gas and, for example, by Pauling's later calculation of the residual entropy of ice (1935). Nevertheless, one cannot consider (1.19) to be a generally practical way to determine S by counting microstates—as Einstein noted, in classic understatement, one would need a rather complete molecular theory to accomplish that. But despite these shortcomings, Boltzmann's work leading to (1.19) provides us with a great deal of insight into a deep property of the entropy maximum—it simply needs a firmer basis, which will only come much later.

In the above-mentioned 1910 paper, and again at the 1911 Solvay Conference in the discussion following his lecture, Einstein took exception to Boltzmann's definition of probability, primarily because he took that definition to be Eq.(1.17) for W. Rather, he claims that the only cogent definition of probability in this context arises from observing the system for an immensely long period of time θ and determining the fraction τ of the time θ that the system spends in a particular macroscopic state. Then τ/θ represents the probability that the system is in this macrostate. (Incidentally, Boltzmann had earlier employed this kind of definition for probabilities and later abandoned it.) This is, of course, just the temporal frequency with which the system is in this state, if left to itself an infinitely long time.

Once again we see that Einstein's view that W is a probability has led him into this approach, which is certainly no more practical than Boltzmann's as a way to calculate W. But the point that is missed is that it is W's true role as a multiplicity factor that is most important, and which was clearly appreciated by Boltzmann. For Einstein, however, this matter of interpretation became essentially irrelevant in the end, for he eventually inverted (1.19) and asked for the value of W given the entropy, leading to his entire theory of fluctuations. For his purpose W need only be *proportional* to, or a factor in a probability, which it is.

Toward the end of the 19th century, then, Boltzmann had developed considerable theoretical insight into the nature of entropy, albeit through rather simple examples. Gibbs (1902), in his *Elementary Principles of Statistical Mechanics*, hereafter denoted by *SM*, concluded what might be called the classical era of entropy by extending his earlier variational principle and placing Boltzmann's work on more solid ground in the context of Hamiltonian mechanics. In doing this, he made good use of a theorem of Liouville, which we take a moment to discuss briefly here.

Joseph Liouville (1809–1882) was one of the great mathematicians of the 19th century. Motivated by his interest in perturbation theory (according to Lützen, 1990), he discovered and proved an important theorem in the theory of differential equations that he soon extended to systems of first-order equations (Liouville, 1838); he also related the theorem to the Jacobian involving initial values and final solutions. If one applies this theorem to Hamilton's equations in particular, it is a simple matter to arrive at its expression in terms of invariant phase volumes. That is, a manifold of points in phase space at time $t = 0$ with measure M_0 is mapped by the equations of motion into another manifold at time t with measure M_t, and if the system is described completely by a Hamiltonian we find that $M_t = M_0$. An easy way to prove this is by showing that the Jacobian of the transformation from M_0 to M_t is unity. The theorem was forgotten for many years until Maxwell noted some special cases, and in 1871 Boltzmann rediscovered it in the form of conservation of volume in phase space. Subsequently, Maxwell (1879) referred to it as "Boltzmann's theorem"; but when Boltzmann became aware of Liouville's earlier work he renamed it Liouville's theorem (*Vorlesungen*, Secs. 26–29), and the name stuck. Of some importance to the present discussion is that Boltzmann used the theorem to show that W in (1.19) remains unchanged under particle collisions.

Gibbs introduces the notion of an ensemble of $M \gg 1$ identical copies of the physical system, and considers the density D of the points representing these systems in the $6N$-dimensional phase space. In the absence of external influences, Liouville's theorem implies that $dD/dt = 0$ and D is stationary. He is now able to introduce a probability density function in the phase space by writing

$$P(q_1,\ldots,q_N,p_1,\ldots,p_N) \equiv \frac{D}{M} = e^{\eta(q_1,\ldots,q_N,p_1,\ldots,p_N)}\,, \tag{1.22}$$

where $\eta = \log P$ is called the *index of probability of phase*, in which the argument of the logarithm really *is* a probability. Finally, he *defines* the equilibrium state as that for which the average index of probability $\overline{\eta}$ is a minimum, reminiscent of (-)Boltzmann's form in (1.18).

Gibbs never explained just why $\overline{\eta}$ should be a minimum, but the algorithm has led to almost every major success of statistical mechanics for the past 100^+ years.[6] Although his formulation in terms of ensembles provided a powerful calculational tool for studying macroscopic systems in terms of the underlying microscopic dynamics, it was not seen at the time to add much to an understanding of entropy itself, and only much later would it be realized that his method contained a truly deep insight into the concepts of both entropy and probability. Perhaps the key feature of this classical era, from the point of view of the present

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[6] There exists a paper by Gibbs entitled "On the Fundamental Formula of Statistical Mechanics," dated 1884. It is an abstract only, possibly for a talk, but it shows that he had coined the term and was thinking about these ideas long before his book was published. The abstract contains Eq.(19) of his book (*SM*, p.8) and is just Liouville's theorem for the quantity D above (Haas, 1936; p.594).

discussion, is that both Gibbs and Boltzmann had clearly related entropy in one way or another to probabilities.

As the 20th century began, some progress had been made in interpreting entropy, but most of the earlier questions remained; indeed, new ones had emerged. It had been clearly established that S was defined only for equilibrium states and had no time dependence of any kind. But, since it changed when the system moved from one equilibrium state to another, one might think it must be possible to describe S in some way during this process. Why not? After all, the laws of physics principally describe the time evolution of physical quantities. Is S physical in the same sense as E, P, N, and so on? Or is there some innate connection to probability that puts it into a somewhat different class of physical objects? If so, what class and what is the connection? Is S useful for studying few-particle problems? Regardless of these uncertainties, however, one knew and understood how to use entropy in the problems of thermodynamics and progress in practical matters continued apace despite these nagging questions; it would require some entirely different input to move further toward answering them.

2

SOME CLARIFICATION FROM ANOTHER DIRECTION

> *The amount of information obtained in any measurement is always expressed in a* finite *number of bits.*
>
> *Juan G. Roederer (2005)*

In retrospect, it might be suspected that the thermodynamic entropy could somehow be related to information describing a physical system. We have seen that a particular set of macroscopic variables to be controlled in some scenario defines a thermodynamic system, and the entropy is then a function of those variables only; that is, S depends on the specific information provided by these variables.

It has long been understood that physics and the notion of information are intimately related, for data obtained by experiment and observation, sense perceptions, and communication either are or contain information forming the basis of our understanding of nature. For example, the fundamental dynamical laws of physics, generally expressed as equations of motion, are essentially algorithms that process information provided in the form of initial conditions. An exact definition of information itself, however, has proved to be quite difficult, in that it appears to have an ethereal form; it is one of those things that falls into the category of "we know it when we see it." In this respect, we emphasize that information must be distinguished from its representation, or carrier, which we always perceive in some physical manifestation through our senses.

Although an unambiguous clear-cut definition of information remains slippery, like inertia and its measure, mass, the concept becomes useful when it is made measurable. This was first done quantitatively by Ralph Hartley (1928) in a theoretical study of information transmission that extended earlier work of Nyquist (1924). In looking for a measure of information in a message Hartley begins by looking first at the primary symbols that may be used to form the characters conveying the information, such as the dots and dashes of telegraphy; the characters are called secondary symbols. If there are m of the primary symbols that are selected ℓ at a time, than the total number of possible sequences forming secondary symbols is m^ℓ. For example, if there are just two primary symbols represented by 0 and 1, and they can be selected only three at a time, then there are 2^3 possible sequences, or "letters" used to construct a message: $\{111, 101, 110, 011, 001, 010, 100, 000\}$.

Presume that the amount of information H associated with ℓ selections is simply proportional to ℓ,

$$H = K\ell, \tag{2.1}$$

where the constant K depends only on the number m of primary symbols available at each selection. Now consider two systems with differing sets m_1 and m_2, along with respective constants K_1 and K_2. These constants are determined from the condition that whenever the corresponding numbers ℓ_1, ℓ_2 are such that the number of possible sequences is the same for both systems, then the amount of information is the same for both:

$$m_1^{\ell_1} = m_2^{\ell_2} \Longrightarrow H = K_1\ell_1 = K_2\ell_2. \tag{2.2}$$

That is,

$$\frac{K_1}{\log m_1} = \frac{K_2}{\log m_2}. \tag{2.3}$$

But this relation can hold for all values of m only if $K = K_0 \log m$, with K_0 the same for all systems. Since K_0 is arbitrary it can be omitted if the base of the logarithm is made arbitrary, and a particular choice of base will simply determine the unit of information. Substitution of this value of K into (2.1) yields

$$H = \log m^{\ell}, \tag{2.4}$$

and the amount of information associated with ℓ selections is just the logarithm of the number of possible secondary symbol sequences. When $\ell = 1$, the information associated with a single selection is simply the logarithm of the number of primary symbols available, in which case the information content of one selection in our previous example is $\log 2$ and that of any "letter" is $3\log 2$.

Implicit in Hartley's work is the presumption that any secondary symbol, such as one of the eight in our example, is equally likely to arise within a message. From these beginnings the modern theory of communication began to emerge 20 years later with the realization that this was too strong a restriction, noticed almost simultaneously by Norbert Wiener (1948) and Claude Shannon (1948). Wiener's contribution first appears in his book *Cybernetics*, where he introduces as a measure of the information associated with a probability density function $f(x)$ the quantity

$$\int_{-\infty}^{\infty} f(x) \log_2 f(x)\, dx, \tag{2.5}$$

and applies it to a theory of messages in various systems. The similarity of this expression to some encountered in statistical mechanics did not escape Wiener's attention, and he appears to be the first to have associated probabilities with an information source.

At virtually the same time, Shannon realized that the basic problem in sending and receiving messages was a *statistical* one, and he extended Hartley's ideas to situations in which the possible messages were not all equally probable. If messages are composed of an alphabet A with n (secondary) symbols having probabilities of transmission $(p_1, \ldots, p_n)$, the amount of information in a message is defined as[1]

$$H(A) \equiv -K \sum_{i=1}^{n} p_i \log p_i, \qquad \sum_{i}^{n} p_i = 1, \tag{2.6}$$

where K is a positive units-dependent constant. Shannon arrived at this expression through arguments of common sense and consistency, along with requirements of continuity and additivity. A number of different derivations of (2.6) are presented by Jaynes (2003). Because information is often transmitted in strings of *b*inary dig*its* (0s and 1s), it is conventional in communication theory to take the logarithm to the base 2 and measure H in *bits*. Thus, H quantifies the average information per symbol of input, measured in bits. Note that if the symbols are equally probable then, because $\sum_i p_i = 1$, each $p_i = 1/n$ and we regain Hartley's result. If, however, one symbol is transmitted with unit probability, it follows that $H(A) = 0$ and no new information is contained in a message whose content is known in advance. Naturally, one might argue that there is indeed information in this latter event, it is just not useful. But in this theory, it is not the intent of (2.6) to judge usefulness, nor is there any *meaning* to be attributed to a piece of information. This is not the case in our common understanding of the term, of course, but it should be remembered that we are here discussing a theory of communication and not of information itself; discussion of that deeper subject can be found elsewhere (*e.g.*, Roederer, 2005).

Let us elaborate on this point a little further by asking *whose* information is at issue here. It is definitely not that of the sender or receiver of the message, but of the one designing the communication system. The probabilities are to be associated with the information source and refer to alternatives drawn from a finite "alphabet"; they may be based on the frequencies of letters appearing in past samples of similar messages—the frequencies of letters in English text, say. For this reason we often refer to this as *statistical information*, in contrast to what Küppers (1990) calls "pragmatic" information, the kind processed by our brain. It is the latter that presents us with the deeper problem, and is generally what we mean by the term. (For an extended discussion see, e.g., Timpson, 2004.)

Shannon originally thought of naming his measure "uncertainty," because H can also be interpreted as the "amount of uncertainty" or "missing information" represented in the probability distribution $\{p_i\}$. Unfortunately, von Neumann urged him to call it *entropy*, arguing that a similar expression already existed in statistical mechanics, thereby leading to a great deal of confusion in the years to come. Presciently, Shannon refers to H as "the entropy of the set of probabilities $(p_1, \ldots, p_n)$," although they are presumed to be given in any specific problem.

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[1] We follow both Hartley and Shannon in denoting the measure of information by the symbol H, perhaps influenced by, but not to be confused with, Boltzmann's H, even though they are similar in both appearance and meaning.

Of course, there is absolutely no connection to physics at this point[2]—Shannon was laying the mathematical foundations of modern communication theory via the notion of information content. Yet, one was almost compelled to wonder if there might be any relation between theories with such similar mathematical structures, at least on the surface.

2.1 Information and physics

Both Boltzmann and Gibbs had implicitly dealt with definite pieces of information in maximizing certain expressions subject to constraints, for the latter are nothing more than that. In doing so they also created a role for probability in their theories, and explicitly introduced the logarithm into the mathematics. This is the primary reason for going into such detail concerning Hartley's derivation of his measure of information content, Eq.(2.4), for it indicates how naturally this function arises in information theory, as well as in Shannon's measure of uncertainty, Eq.(2.6). Shannon also discusses this at some length at the beginning of his treatise. But an explicit connection between physical entropy and the concept of information has its roots in ideas expressed many years earlier.

In his classic thermodynamics book of 1871 Maxwell introduced his famous "demon" in an attempt to clarify the notions of irreversibility and the Second Law of Thermodynamics. He envisioned "a being whose faculties are so sharpened that he can follow every molecule in its course ...," and inadvertently inaugurated a vast industry in demonology that survives to the present day. The idea was that this demon could divide the volume by means of a partition containing a shutter, and then open and close the shutter so as to accumulate fast molecules on one side and slower ones on the other, thereby violating the Second Law. (He had actually discussed the idea in private communications as early as 1867.) Although an interesting and provocative tool at the time, the work of Boltzmann and Gibbs, and its subsequent development throughout the 20th century, has demonstrated that the very need and rationale for statistical mechanics is the complete lack of the kind of *microscopic* control envisioned for Maxwell's hypothetical demon.[3] Indeed, the conclusion Maxwell drew was that the Second Law was not absolute, but depended on the *absence* of a demon, and therefore must be statistical and apply to macroscopic phenomena.

Nevertheless, the demon and its implications have been, and continue to be, taken seriously, and an extensive literature has accumulated (*e.g.*, Leff and Rex, 1990). And, as might be expected from so much effort, some of the discussion has led to important insights, beginning with Leó Szilárd's famous analysis of

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[2] Nevertheless, such connections were soon attempted, but with little or no logical justification (*e.g.*, Brillouin, 1951, 1956).

[3] Despite these comments, there is a macroscopic device called a Ranque–Hilsch vortex tube whose operation gives one an eerie sense of demons at work (Ranque, 1933; Hilsch, 1947; an extensive review is provided by Cockerill, 1998). More recently, advances in nanotechnology suggest that the kind of microscopic control proposed by Maxwell may yet come to pass, although it remains to be seen what macroscopic implications that may have.

a one-molecule gas in 1929. Briefly, Szilárd (as demon) divides the volume of a cylinder into two parts by means of a partition and makes an observation as to which part the molecule occupies; the partition is now employed as a piston which is allowed to expand under the pressure of the single molecule until the gas fills the entire volume, the temperature being maintained by immersion in a heat bath; if the original partition was into equal parts, we find that the entropy decrease is just $k \log 2$, corresponding to a binary choice, and if the system is run cyclically one can continue to extract energy from it. But Szilárd recognizes that there is a price for this operation in the form of acquiring the needed information to locate the molecule, and thus the entropy decrease is compensated with that represented by this information increase. (Actually, it is the *discarding* of previous information at the end of each cycle that causes the entropy increase.) This is perhaps the first *explicit* relation made between physical entropy and information as we commonly think of it.

At almost the same time, and apparently unaware of Szilárd's work, Gilbert Lewis (1930) provided a very clear and possibly more cogent analysis of exactly what the above scenario is telling us. Suppose, as above, we have a cylinder closed at each end having a middle wall containing a shutter that can be effortlessly opened and closed. Imagine that in this cylinder there is a single molecule each of three different gases, call them A, B, C. Let the entire setup be immersed in a heat bath at temperature T, and presume that our only interest is whether a molecule is in the right or left half of the cylinder. There are then eight possible arrangements or distributions of the three particles, each of which will occur quasi-randomly over and over. The shutter can be closed at any time to trap one of the distributions—say, all three on the right-hand side. If the shutter is now opened, maybe accidentally, there will rather quickly emerge once again the quasi-random sequence of all possible distributions. To return to the state with all three molecules on the right-hand side, we can open and close the shutter repeatedly and in about eight trials we should regain the desired state.

To avoid the appearance of demonology and apparent violations of the Second Law, let us instead invoke the traditional mechanism of moving a piston slowly from the extreme left-hand wall to the center of the cylinder. The work done to overcome the pressure of the molecules is

$$\int_1^2 P\,dV = \int_1^2 \frac{3kT}{V}\,dV = 3kT \log 2, \tag{2.7}$$

and the entropy of the gas decreases by $3k \log 2$. Any particular distribution can be obtained by using a pair of permeable pistons, one on each end. For example, if it is desired to attain a state for which A is on the left, B and C on the right, the left-hand piston is made permeable only to A, the right-hand one permeable only to B and C, and both are moved slowly to the middle. In this and every other case, passing from the unknown to a particular distribution decreases the entropy of the gas by $3k \log 2$.

Note that the act of trapping a distribution does not in itself give rise to a change of entropy. In addition, we see that all of these processes are reversible, in that allowing the pistons to expand under pressure of the gas *increases* its entropy by $3k \log 2$ by regaining the sequence of different distributions. What is not reversible, however, is the act of going from a *known* to an *unknown* distribution, which is the origin of the change of entropy. Hence the loss that occurs in the irreversible process is a *loss of information*, nothing more. This seems to have a subjective flavor, but that is what happens in thermal processes: energy exchanged through macroscopic degrees of freedom we control is called work; some or all of this may be converted to heat, which is energy exchanged through those degrees of freedom over which we have no control, and thus a loss of information. We shall return to a more extensive discussion of irreversibility in Chapter 11.

These unexpected and slightly tenuous connections among entropy, probability, and information would eventually be the keys to grasping at last the true nature of entropy. It was Shannon's work that finally opened the door for the synthesis. At this point, however, the reader is cautioned against making any unwarranted identifications of information-theory quantities with physical entities from thermodynamics, although a number of writers did just that. For example, Shannon's measure (2.6) is quite similar to Boltzmann's expressions (1.15) and (1.18), and Hartley's (2.4) is reminiscent of Boltzmann's representation (1.19). But it is neither wise nor even logical to make those kinds of connections unless those expressions can be shown to stem from common roots. That step requires some additional effort.

3

THE PROBABILITY CONNECTION

> *There is no doubt that in the years to come the study of entropy will become a permanent part of probability theory.*
>
> *A.I. Khinchin (1957)*

Both Boltzmann and Gibbs introduced probabilistic considerations into their work in an essentially *ad hoc* way, although Gibbs did discuss his rationale briefly (*SM*, p.17). To make connections of the kind alluded to earlier, it is necessary first to make a brief digression on some concepts of logic that underlie scientific inquiry. These involve the role of inference in that pursuit, which is a mainstay of creating theories based on observation. And at the heart of that notion is probability theory. (Although we may refer to some physical problems as examples in what follows, nothing in this chapter is explicitly about physics, yet.)

The notions of scientific inference and induction have a long history whose detailed analyses go back at least to the concerns of the Scottish philosopher David Hume (1777). The philosopher Karl Popper (1959), in particular, questioned whether we are rationally justified in reasoning from repeated instances of which we have experience to those of which we have no experience. This boils down to the question: Under what circumstances can induction be justified? As we shall see, the answer depends on the nature of our prior information connecting those instances. A mathematical theory of probability comes into play as the principal tool for quantifying the necessarily inductive methods of scientific reasoning, and one introduces probability in the first place because there is insufficient information or evidence to reason deductively.[1] In a macroscopic system what is obviously missing is knowledge of microscopic trajectories (or states). We must rely therefore on probable inference, which we interpret as a branch of logic, in accordance with the principles espoused almost two centuries ago by Laplace (1812) and explicated further by Pólya (1954).

This interpretation of probability as logic has sometimes been criticized on philosophical grounds of applicability (*e.g.*, Salmon, 1966): "This theory provides no reason for supposing any connection whatever between what is probable and what happens often. It seems to provide no basis for expecting the probable in preference to the improbable." But this misses the point completely. It is not the function of induction or probability to be "right"—it merely tells us what

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[1] The reader will surely not confuse what we mean here by inductive reasoning with the well-known process of mathematical induction, which is an entirely deductive procedure.

predictions are most strongly indicated by present hypotheses and/or information. Given certain evidence, how much weight should be given to alternative propositions?

A more specific response to Prof. Salmon's objection can be formulated in terms of shuffling a deck of cards for a game of bridge. How do we define a "proper" method of shuffling other than to demand it produce all distributions equally? You cannot describe such a method in complete detail, for that would destroy the "randomness," so shuffling must be defined incompletely. One then wonders how to prove that an incompletely defined procedure will produce all distributions with equal frequency. The connection between the probable and what often happens is an experimental one *after the fact*.

There are other interpretations of probability, of course, and the most common and widely held alternative in the scientific context is the so-called frequency interpretation. In this meaning probability is defined in terms of the relative frequencies of occurrence of an attribute in an infinite sequence of events. For example, to say that in tossing an honest coin the probability of getting heads is 1/2 means that, independent of the obvious symmetry, in a potentially infinite sequence of tosses of the coin, the relative frequency with which heads occurs converges to the value 1/2. This would seem to make probability an experimental science, though evidently no such experiment can be carried out.

Two difficulties with this definition are seen immediately. There is no mathematical rule defining the sequence, hence no means for actually discussing its convergence. Hans Reichenbach (1949), a leading proponent of the frequency definition, maintained that there exists an inductive rule for inferring such limits, but this has never been found completely satisfactory. An additional mathematical constraint is that all events in the sequence must be independent; the slightest correlation invalidates not only the process, but also all the limit theorems associated with it. Thus, the theory is limited to a small body of idealized problems.

A further objection centers on the *single* event, which in reality is most often the case of interest—we bet on the outcome of a single horse race, or want a prediction of tomorrow's weather. Only *ad hoc* devices have ever been proposed for addressing this difficulty within the frequency approach.

Despite these objections, frequencies do play a significant role in probability theory; they just are not probabilities, even if they approach them in a limit. For example, frequency data when available are perfectly acceptable for use in constructing probabilities (see below), as well as for verifying them. But a probability is something we assign to represent a state of knowledge, and changes only when that state does. A frequency is a factual property of the real world that can be measured or estimated. We neither measure a probability nor assign a frequency.

All this having been said, the scientific quarrel is not with frequencies *per se*, but with the more insidious idea that probabilities are physically real things, ultimately based on observed frequencies of random variables.

Cramér (1946), for example, takes it as axiomatic that any random variable has a unique frequency distribution. This leads him to believe that the frequency with which a particular face of a tossed die comes up is a physical property of the die, just like its mass or chemical composition. Also, Good (1965) has remarked: "Most of us probably think about a biased coin as if it had a physical probability."

It is highly doubtful that most physicists think like this. Most of us familiar with the laws of mechanics know that the results of tossing a coin depend not only on the physical characteristics of the coin, but also on the way it is tossed; that is, on initial conditions. Anyone in command of those physical laws can build a tossing machine imparting sufficient control to predict the outcome of a toss with 100% accuracy, and hence toss heads or tails at will. Our intuition is that, without control of initial conditions, the probability for heads or tails depends on the physical properties of the coin only to the extent that it is symmetric (or not). Anyone who asserts the existence of a physical probability in an experiment is required also to define precisely the circumstances under which that physical probability can be measured, or else the assertion has no content. As understood long ago by Jevons in 1877, "probability belongs only to the mind." (Jevons, 1958). Laplace had also remarked as early as 1783 that "there is really no such thing as 'chance' in nature, regarded as a cause of events" (Gillispie, 1972).

These points will be continuously emphasized, because the view one adopts toward probability ultimately has a strong bearing on one's interpretation of much of the physical behavior of many-body systems. As we shall see subsequently, a belief in physical probabilities often leads to confusion about the connections between microscopic dynamics and observed macroscopic thermodynamic behavior. For that reason, it will be useful to lay out concisely here at the start the view of probability as logic and summarize the few basic laws governing probabilities.

Following the path from Laplace through Keynes (1921), Jeffreys (1939), and Cox (1946, 1961), we adopt the view that probability is a *relational* concept among two or more propositions. Explicitly, $P(A|I)$ is a real number between 0 (impossibility) and 1 (certainty) expressing the weight to be given to the proposition A based *only* on the hypothesis or information I. Most often—indeed, always—A is one of a number of alternative propositions whose probabilities provide relative estimates of which may be more or less likely than others. The definition has an anthropomorphic flavor, though no more than science itself, in that P depends critically on the nature of the prior information I, and that information may vary among different observers. But given the same I, any construction of $P(A|I)$ must result in the same value, certainly an objective criterion. In this sense, P is a "carrier of information." Thus, our guiding principle is to calculate the probability of things we do not know based only on things we either know or hypothesize for the sake of argument.

According to the consistency axioms put forth by Cox, the algebra of probable inference is a Boolean algebra of propositions. If A asserts the truth of a proposition and $\bar{A}$ its denial, then

$$P(A|I) + P(\bar{A}|I) = 1. \tag{3.1}$$

The product AB asserts the truth of both A and B on the hypothesis I, whereas the logical sum $A + B$ asserts that either A or B or both are true on the same hypothesis. From the axioms one derives the product and sum rules, respectively (*e.g.*, Jaynes, 2003):

$$\begin{aligned} P(AB|I) &= P(A|BI)P(B|I) \\ &= P(B|AI)P(A|I), \end{aligned} \tag{3.2}$$

$$P(A + B|I) = P(A|I) + P(B|I) - P(AB|I). \tag{3.3}$$

Both rules are readily extended to any number of propositions. For example, if a set of alternatives is *exhaustive* in the sense that at least one must be true, then $P(A_1 + \cdots + A_m) = 1$. If, in addition, the propositions are *mutually exclusive*, meaning that only one can be true, then

$$P(A_1 + \cdots + A_m|I) = \sum_{i=1}^{m} P(A_i|I) = 1, \tag{3.4}$$

often realized by normalizing the independent probabilities by their sum.

Consider an exhaustive set of N mutually exclusive alternatives $H = \{H_1, \ldots, H_N\}$, such that I asserts *only* that each is capable of being true. Then Laplace's principle of indifference states that

$$P(H_i|I) = \frac{1}{N}, \qquad 1 \le i \le N, \tag{3.5}$$

which is actually an expression of symmetry. Suppose A is true M times on the set H and false $N - M$ times. Then, with that information I,

$$P(A|I) = \frac{M}{N}, \tag{3.6}$$

known as Bernoulli's principle. These last two expressions constitute basic construction methods for probabilities *when the alternatives satisfy the stated conditions.*

Another such construction principle is contained in the Law of Succession, first stated by Laplace. It applies *only* when the information I states that an event is possible and has occurred n times in the past N trials, *and nothing else.* It is invalid if there is *any* other information available regarding the proposition. In its generalized form, we can consider K alternatives $\{A_1, \cdots, A_K\}$ such that in N trials A_1 has occurred n_1 times, A_2, n_2 times, and so on, such that $\sum_i n_i = N$.

Under the additional stipulation that the same causal mechanism is at work in each trial, the probability for any particular alternative is

$$P(A_i|n_iNK) = \frac{n_i + 1}{N + K}. \tag{3.7}$$

(By summing over i one verifies that we are considering an exhaustive set of mutually exclusive alternatives.) Another, deeper type of construction principle will be introduced below, but we note in passing that Eq.(3.7) suggests exactly how frequency data can be incorporated into a probability distribution if they satisfy the criteria for its validity. In fact, an important piece of insight is captured here if we imagine a die to have been rolled 10 times and "3" comes up in seven of them. How to predict the outcome of the next roll depends very much on the nature of our prior information. If we have examined the die carefully and concluded it is honest, and we believe it is being rolled fairly, then we have little choice but to assign probability 1/6 to all possibilities; but lacking that confidence, we would surely employ (3.7) to state that with probability 1/2 a "3" will come up on the next roll.

It may seem that this issue of probability has been belabored a bit, but it cannot be emphasized enough that it really does matter to us how one views the subject. We shall see quite clearly how that view affects our discussion of many issues arising in statistical mechanics and how it later becomes a crucial factor in the entire formulation of nonequilibrium thermodynamics.

Much of elementary probability theory is contained in the preceding expressions for manipulation and construction of probabilities, and no matter how one chooses to define probability, there is general agreement on these basic equations. A very real difference in viewpoint occurs, however, when we insist that every probability is *conditional*; that is, it is relative to the information or hypothesis I on which it is based. Every P contains a left side and a right side, and P can change whenever *either* side changes. This is evident, for example, in Eq.(3.7) and the example just given. If assets are at risk, only a fool would fail to use such information to recalculate the probabilities. Note carefully, however, that the validity of a given piece of information I is not at issue when calculating P; it is possible that I can be flawed or incomplete, but that is to be judged by the ensuing predictions. The only concern of the basic theory is to produce a P based on that I.

The essence of these observations is captured by the symmetry evident in the product rule (3.2). Since the right-hand sides are equal we can write

$$P(A|BI) = P(A|I)\frac{P(B|AI)}{P(B|I)}. \tag{3.8}$$

This is known as a form of *Bayes' theorem*, though it is a trivial rearrangement of the product rule. An obvious interpretation is that, given the prior probability for A based on I, new information B with prior probability $P(B|I)$

on that same information leads to an updated or posterior probability for A. That is, the probability for A based on both I and B depends not only on the prior probabilities of both A and B, but also on the probability that B is true given that A is true. In applications it is often useful to note that the prior probability $P(B|I)$ can be expanded in terms of any exhaustive set of mutually exclusive propositions $\{H_n\}$ as follows: $P(B|I) = \sum_n P(B|H_nI)P(H_n|I)$, via the product rule.

At one time or another most of us find ourselves pondering one of life's great mysteries: How can two reasonably intelligent people, faced with the same evidence or information about a proposition, reach entirely different conclusions? It would seem that the only possible reason, aside from dishonest motives, is that they come to the question with quite different backgrounds, or prior information. It is that I on the right-hand side of our probabilities that makes all the difference—and makes betting on horse races interesting!

The form (3.8) of Bayes' theorem is very useful conceptually as well as in practice, for it expresses forcefully the strong dependence of a probability on specific evidence or information. It seems difficult to interpret (3.8) at all without an appreciation of the right-hand sides of the probabilities. Of course, for one who believes that a probability is physical, the notion of it changing with new information may not make any sense at all.

Given (3.8), however, how does one actually go about constructing the prior probabilities? At this point we have available for that purpose Bernoulli's principle (3.6) and Laplace's rules (3.5) and (3.7), all of which are valid only under very special conditions. Although these are often quite useful, there is a clear need for a method of incorporating more general forms of information into a prior probability assignment.

3.1 The principle of maximum entropy

Following the formal beginning of information theory, E.T. Jaynes noticed during the early 1950s that Shannon's information measure, when restated as

$$S_I(P) = -k\sum_i P_i \ln P_i = -k\langle \ln P\rangle\,, \qquad k = \text{ constant} > 0, \tag{3.9}$$

suggested an application far transcending its original intent and that it could be interpreted as a basic element of probability theory, allowing one to construct prior probabilities from available information (of the "pragmatic" type mentioned earlier). The constant k is again dependent on a choice of units, and in this context the natural logarithm is more appropriate. (The expectation value $\langle\cdots\rangle$ is defined in (3.11) below.) Shannon considered this a measure of the uncertainty one has about the particular events under study, but Jaynes saw that it could also be interpreted as the uncertainty represented by the probability distribution itself, or as a measure of the further information required to achieve certainty.[2] Subsequently, he enunciated a *Principle of Maximum Entropy* (PME), asserting that under a certain class of constraints representing the available information the least biased probability assignment is that which maximizes this *information* entropy subject to those constraints (Jaynes, 1957a). Thus was born a new rule for constructing probabilities in the face of incomplete information. A proof of its uniqueness was supplied much later by Shore and Johnson (1980).

A further comment is necessary at this point concerning the relation between (3.9) and (2.6). Although the former is inspired by the latter, they have entirely different meanings. Shannon's expression defines a measure of the amount of information contained in a message in a way that is independent of its meaning, and the theory provides a quantitative method for analyzing the degradation of that information during transmission, processing, and storage; it is linked to the statistical characteristics of an information source. In contrast, (3.9) defines a functional of probability theory whose variation under common information in the form of constraints provides a distribution containing that information. Indeed, it can be shown that in the case that letter frequencies are known, the probabilities presumed in (2.6) can be readily found from the PME (Jaynes, 2003).

Most writers, when discussing the work of Gibbs, focus primarily on his use of ensembles. While somewhat innovative at the time, this is perhaps the *least* important aspect of his statistical mechanics, for it is the variational principle he adopts for his index of probability η, such that $-\overline{\eta}$ is later identified with the entropy, which is the backbone of the theory. He wrote that his introduction of ensembles was an artifice that "may serve to give precision to notions of probability," and was not necessary. It now seems clear that this is indeed the case, for our understanding of probability theory has evolved to the point that one need focus only on the single system actually under study, as logic requires.

With these new insights into construction of prior probabilities based on given evidence, the structure of the Gibbs algorithm becomes transparent. Although the details have been presented in many places (*e.g.*, Jaynes, 1957a, 2003; Grandy, 1987), we provide a brief recapitulation here for convenient reference. Given an exhaustive set of mutually exclusive alternatives in the form of a set of n propositions $\{x_i\}$, and information interpretable in the form of expectation values of a set of independent functions $\{f_r(x)\}$, $r = 1, \ldots, m < n$, the optimal choice of a probability distribution over $\{x_i\}$ is obtained by maximizing the *information entropy of the probability distribution* (3.9)

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[2] The subscript I indicates that this functional is a feature of probability theory alone and has nothing to do with similarly named objects in other fields, such as thermodynamics; of course, if the context to which it is applied is physical, then it will take on physical meaning.

subject to constraints

$$\sum_{i=1}^{n} P_i = 1\,, \qquad P_i = P(x_i|I) > 0, \tag{3.10}$$

$$I: \quad F_r \equiv \langle f_r(x)\rangle = \sum_{i=1}^{n} P_i f_r(x_i). \tag{3.11}$$

As is well known, the solution to this variational problem is most readily effected by the method of Lagrange multipliers $\{\lambda_r\}, r = 1, \ldots, m < n$, so that the desired probability distribution is given by

$$P_i = \frac{1}{Z} e^{-\lambda\cdot f(x_i)}\,, \qquad Z(\lambda_1, \ldots, \lambda_m) = \sum_i e^{-\lambda\cdot f(x_i)}, \tag{3.12}$$

with the convenient scalar-product notation

$$\lambda \cdot f \equiv \lambda_1 f_1 + \cdots + \lambda_m f_m. \tag{3.13}$$

For historical reasons, the normalization factor Z is called the *partition function*, in terms of which substitution of P_i into (3.10) yields a set of m coupled differential equations formally determining the Lagrange multipliers:

$$F_r = \langle f_r\rangle = -\frac{\partial}{\partial\lambda_r} \ln Z\,, \qquad r = 1, \ldots, m. \tag{3.14}$$

Equation (3.12) is the principal result of the PME, and several features should be emphasized immediately. First, it must be stressed that the expectation values on the left-hand sides of (3.11) and (3.14) are *given numbers* F_r that we have identified in this way so as to incorporate the given information or data mathematically into a probability distribution. Whether we use one notation or the other will depend on which feature of these data we wish to emphasize in a particular discussion. Those data need not be given in the form of expectation values, but the mathematics is particularly neat if they are, and it is a common form. But, whatever the form of the constraints, they must confine the $\langle f_r\rangle$ to some convex set to insure concavity of the entropy. Information in terms of higher moments can be utilized similarly. What we mean by saying that the distribution "contains" the initial information is that such information can again be extracted from the distribution by computing the expectation values (3.11), and the Lagrange multipliers are chosen to do just that through (3.14). Neither $\langle f_r\rangle$ nor λ_r are estimated, but at this point are considered to be exact; the constraints are taken as given numbers, possibly of uncertain precision, and the Lagrange multipliers are parameters that do not exist until S_I is maximized subject to those constraints.

Second, maximizing the *information* entropy S_I over all probability distributions subject to given constraints transforms the context of the discussion into one involving the maximum as a function of the data specific to this application;

it is no longer a functional of probabilities, for they have been "integrated out." To enforce this distinction we shall denote the maximum entropy by S, with no subscript, and recognize that it is now a function only of the measured expectation values or constraint variables. That is, S is the "entropy of the data" (Hobson, 1971), and the impetus provided by information theory is no longer evident. What remains of the notion of information is now only to be found on the right-hand side of $P(A|I)$ in the form of Lagrange multipliers; we are here applying probability theory, *not* information theory.

It is useful to note that not all these data need be specified at once. For example, a distribution can be constructed via the PME based on a datum $\langle f_1 \rangle$; subsequently, further information may emerge in the form $\langle f_2 \rangle$, and the new distribution is obtained by remaximizing S_I subject to both pieces of data. If the new information contradicts the old, there will be no solutions for real λ_2. If the new datum is redundant, in the sense that it is only what would have been predicted with the current information, it will simply drop out of the distribution; otherwise, the new datum and distribution lead to a smaller entropy, since an additional member contracts the class of variations holding the set of constraints constant. This procedure provides a method for incorporating new information into an updated probability estimate, in the spirit of Bayes' theorem (3.8), although they are not the same thing.[3]

Another useful property of the PME that is apparent from (3.12) is that, having obtained this result, it can now be turned around if desired and we could consider the Lagrange multipliers to be the independent variables. From this point of view, (3.14) then provides the *predicted* expectation values.

One further important feature of S is that it is an *absolute* maximum. Let $\{P_i\}$ and $\{Q_i\}$ be two distinct probability distributions satisfying the given constraints, and recall that $x \log x \geq x - 1$ for positive x, with equality if and only if $x = 1$. Then,

$$\sum_i P_i \ln P_i \geq \sum_i P_i \ln Q_i, \tag{3.15}$$

with equality if and only if $P_i = Q_i$ for all i. Choose $\{Q_i\}$ to be the canonical distribution of Eq.(3.12), so that the inequality (3.15) becomes

$$S\{P\} = -k \sum_i P_i \ln P_i \leq k \ln Z + k\lambda \cdot \langle f \rangle. \tag{3.16}$$

In varying $\{P_i\}$ over the class of all possible distributions satisfying the given information, the right-hand side of (3.16) remains fixed and thus provides an upper bound for $S\{P\}$. But this maximum is just that given by (3.9) and (3.12),

$$S = k \ln Z + k\lambda \cdot \langle f \rangle, \tag{3.17}$$

This demonstration was already supplied by Gibbs in *SM* (p.130), and also serves to demonstrate the uniqueness of the Lagrange multipliers with respect to the

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[3] Bayes' theorem processes a conditioning statement about probabilities, whereas the PME processes data into a prior probability.

given data. For, if λ' were also to reproduce $\langle f\rangle$, and $\lambda' \neq \lambda$, then $P_i(\lambda')$ must satisfy (3.16). But the argument with λ and λ' interchanged also leads to (3.16) with the roles of P and Q reversed, and hence a contradiction.

Consider for a moment just a single function f and note that small changes in the problem defined by Eqs.(3.10) and (3.11) can occur through changes in the set of possible values $\{f_i \equiv f(x_i)\}$, as well as from changes δP_i in the assigned probabilities. A small change in the expectation value is then

$$\delta\langle f\rangle = \sum_i P_i \delta f_i + \sum_i f_i \delta P_i, \tag{3.18}$$

and one readily verifies that the corresponding change in the information entropy is

$$\delta S_I = S_I - S_0 = -k \sum_i \delta P_i \ln P_i. \tag{3.19}$$

The first sum on the right-hand side of (3.18) is just $\langle \delta f\rangle$, the expected change in f, so we can rewrite that expression as

$$\delta\langle f\rangle - \langle \delta f\rangle = \delta Q_f, \tag{3.20}$$

where $\delta Q_f \equiv \sum_i f_i \delta P_i$. Also, from (3.19), $\delta S_I = \lambda \delta Q_f$.

Equation (3.20) can be interpreted as a "generalized First Law of Thermodynamics," which is now seen as a special case of a more general rule in probability theory: a small change in any expectation value consists of a small change in the physical quantity ("generalized work") and a small change in the probability distribution ("generalized heat"). Just as with ordinary applications of the First Law, we see that the three ways to generate changes in any scenario are interconnected, and specifying any two determines the third.

A structure for the statistical theory follows from the analytical properties of S and Z. Briefly, the total differential of S is found with the aid of (3.17) to be

$$dS = k\lambda \cdot d\langle f\rangle, \tag{3.21a}$$

so that

$$\frac{\partial S}{\partial \lambda_r} = 0\,, \qquad \frac{\partial S}{\partial \langle f_r\rangle} = k\lambda_r. \tag{3.21b}$$

That is, S is a function only of the measured or specified variables.

The functions $f_r(x)$ can also depend on one or more "external" variables α, say, so that we can consider $f_r(x,\alpha)$ on the set $\{x_i\}$. Then,

$$\frac{\partial \ln Z}{\partial \alpha} = -\lambda \cdot \left\langle \frac{\partial f}{\partial \alpha}\right\rangle, \tag{3.22}$$

and because $\ln Z = \ln Z(\lambda_1, \ldots, \lambda_m, \alpha)$ we have the reciprocity relation

$$\left(\frac{\partial S}{\partial \alpha}\right)_{\{\langle f_r\rangle\}} = K\left(\frac{\partial \ln Z}{\partial \alpha}\right)_{\{\lambda_r\}}, \tag{3.23}$$

indicating which variables are to be held constant under differentiation. When such external variables are present (3.21a) is replaced by

$$\begin{aligned}\frac{1}{k}dS &= \frac{\partial \ln Z}{\partial \alpha}d\alpha + \lambda \cdot d\langle f\rangle \\ &= \lambda \cdot dQ, \end{aligned} \tag{3.24}$$

where

$$dQ_r \equiv d\langle f_r\rangle - \langle df_r\rangle\,, \qquad \langle df_r\rangle \equiv \left\langle \frac{\partial f_r}{\partial \alpha}d\alpha \right\rangle. \tag{3.25}$$

This last expression is a generalized conservation law.

With the use of (3.21b) we can also write (3.17) in the form

$$\frac{1}{k}S = \frac{1}{k}\frac{\partial S}{\partial \langle f\rangle} \cdot \langle f\rangle + \alpha\left(\frac{\ln Z}{\alpha}\right). \tag{3.26}$$

If $(\alpha^{-1}\ln Z)$ is independent of α it can be replaced by $\partial \ln Z/\partial\alpha$, and from (3.23) we can write

$$S = \langle f\rangle \cdot \frac{\partial S}{\partial \langle f\rangle} + \alpha\frac{\partial S}{\partial \alpha}, \tag{3.27}$$

which is just Euler's theorem (1.13). Thus, under the stated condition, S is homogeneous of degree 1 and the maximum entropy is an extensive function of the input data. This result will prove of some value presently.

As always, the sharpness of a probability distribution, and therefore a measure of its predictive power, is provided by the variances and covariances of the fundamental variables. Predicted values are by definition not exact, and may differ from actual values upon measurement. A measure of this is given by the *deviation* of the variable f from its expectation value, $\Delta f \equiv f - \langle f\rangle$. The variance of f is then defined as the expectation value of the square of the deviation, and the covariance of two variables involves the product of their deviations. One readily verifies that the covariance of f_m and f_n is given by

$$\begin{aligned}\langle f_m f_n\rangle - \langle f_m\rangle\langle f_n\rangle &= -\frac{\partial\langle f_m\rangle}{\partial \lambda_n} = -\frac{\partial\langle f_n\rangle}{\partial \lambda_m} \\ &= \frac{\partial^2}{\partial\lambda_m\partial\lambda_n}\ln Z\,, \\ &\equiv K_{mn} = K_{nm}, \end{aligned} \tag{3.28}$$

which reduces to $K_{nn} > 0$, the variance of f_n, when $m = n$. For N degrees of freedom the variance is generally proportional to N^{-1}. Any other function $g(x, \alpha)$ has expectation value $\sum_i P_i g(x_i, \alpha)$, and its covariance with any f_k is

$$\langle f_k g\rangle - \langle f_k\rangle\langle g\rangle = -\frac{\partial\langle g\rangle}{\partial\lambda_k}. \tag{3.29}$$

The covariances K_{mn} will play a significant role in the physical theory to be developed.

From (3.21b) we also have

$$\begin{aligned}\frac{\partial^2 S}{\partial\langle f_m\rangle\partial\langle f_n\rangle} &= \frac{\partial\lambda_m}{\partial\langle f_n\rangle} = \frac{\partial\lambda_n}{\partial\langle f_m\rangle} \\ &\equiv G_{mn} = G_{nm},\end{aligned} \tag{3.30}$$

and because $\langle f_m\rangle$ and $\langle f_n\rangle$ are independent pieces of data one easily shows that G and K are mutually inverse matrices. Equations (3.28) and (3.29) introduce the notion of correlations, as well as provide a measure of the width of the probability distribution.

There is one further feature of the maximum-entropy distribution that will be of interest. In addition to the maximum property of S_I with respect to variations δP_i of the probability distribution, S itself possesses a variational property of some importance. If we vary the entropy in (3.17) with respect to all parameters in the problem, including $\{\lambda_r\}$ and $\{f_r\}$, we obtain an alternative to the derivation of (3.24):

$$\delta S = \lambda\cdot\delta Q = \lambda\cdot\sum_i f(x_i)\delta P_i, \tag{3.31}$$

where δQ_r is given by (3.25). Hence, S is stationary with respect to small changes in the entire problem if the distribution $\{P_i\}$ itself is held constant. The difference in the two types of variational result is meaningful, as is readily seen by examining the second variations. For variations of S_I with respect to distributions $\{P_i\}$, this calculation was effectively carried out in Eq.(3.19). For the case of S, we compute $\delta^2 S$ from (3.27) and retain only first-order variations of the variables. If S is to be a maximum with respect to variation of those constraints, then the desired stability or concavity condition is

$$\delta^2 S \simeq \delta\lambda\cdot\delta\langle f\rangle + \delta\alpha\cdot\delta\left(\frac{\partial S}{\partial\alpha}\right) < 0. \tag{3.32}$$

We return to this presently, but it is the same kind of condition employed by Gibbs [*HS*, Eq.(171)] to establish all his stability conditions in thermodynamics.

The tools developed here are very general and can be applied to a large range of problems in which there is insufficient information with which to effect a completely deductive solution. For example, the PME has successfully been employed in numerous areas of data analysis, image processing, and various fields of physics, including mathematical physics. A number of these applications have been reviewed by Bevensee (1993). In the present work, however, we are most interested to note that these tools of probability theory lend themselves very nicely to the study of macroscopic physical systems in terms of the dynamical behavior of their microscopic constituents. Because the microscopic trajectories and initial conditions are never known for some 10^{23} particles, say, it is necessary to formulate predictions of macroscopic behavior based only on limited and very incomplete macroscopic information. This information can be quite general, of course, but is most useful when formulated so as to be interpreted in terms of expectation values, although it can change rapidly in time and space, say. The simplest example is the case in which such information is fixed and is given in terms of physical constants of the motion. Given the enormous number of degrees of freedom provided by $N \gg 1$ particles, which we consider exclusively in this work, probability distributions and their predictions are extremely sharp. In this way, we are now able to clarify the interrelations between thermodynamic entropy, information, and probability theory.

4

EQUILIBRIUM STATISTICAL MECHANICS AND THERMODYNAMICS

> *Nature does not prepare distributions, factorized or otherwise; she prepares states.*
>
> *E.T. Jaynes (1990)*

The study of a macroscopic system in terms of its microscopic constituents presents an application *par excellence* of the Principle of Maximum Entropy (PME), for one usually has only a few pieces of macroscopic information available with which to make macroscopic predictions of system behavior. Effects of the microscopic dynamical laws can only be studied at the macroscopic level by means of probability theory. We shall formulate such a study in a quantum-mechanical context, not only because that is the proper description of the microscopic physics, but also because the mathematics is much neater and less cluttered than a classical description, although classical examples are quite useful when appropriate.

A system with many degrees of freedom is almost never to be found in a pure quantum-mechanical state, but in a very complicated mixed state.[1] The most efficient way to discuss such states is by means of the density matrix formalism (Landau, 1927; von Neumann, 1927a,b), defined as follows. A density matrix represents a partial state of knowledge of a system. On the basis of that information we conclude that with probability w_1 the system may be in a pure state ψ_1, or in state ψ_2 with probability w_2, and so on. Although the various alternatives ψ_i are not necessarily mutually orthogonal, they can be expanded in terms of a complete orthonormal set $\{u_k\}$:

$$\psi_i(r,t) = \sum_k a_{ik}(t)u_k(r)\,, \tag{4.1}$$

such that $\langle u_k|u_j\rangle = \delta_{kj}$; if ψ_i is normalized, then $\sum_k |a_{ki}|^2 = 1$. The quantum-mechanical expectation value of a Hermitian operator F in state ψ_i is

$$\langle F\rangle_i \equiv \langle\psi_i|F|\psi_i\rangle = \sum_{k,n} a_{ki}a^*_{ni}\langle u_n|F|u_k\rangle\,, \tag{4.2}$$

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[1] It is *not* an entangled state; owing to decoherence, such a state of a macroscopic system would decay almost instantly.

and the expected value of F over all possibilities (in the sense of classical probability theory) is then

$$\langle F\rangle = \sum_i w_i \langle F\rangle_i . \tag{4.3}$$

This last expression can be written more compactly (and generally) in matrix form as

$$\langle F\rangle = \mathrm{Tr}(\rho F)\,, \tag{4.4}$$

where Tr is the matrix trace, and the *density matrix* (or operator) ρ is defined in terms of its matrix elements:

$$\rho_{kn} \equiv \sum_i a_{ki} a^*_{ni} w_i\,. \tag{4.5}$$

The expression (4.4) is commonly known as the *Born rule*, and is derived much more generally by Gleason (1957).

Often it is most useful to define ρ directly in terms of an orthogonal basis $\{|n\rangle\}$; these states are mutually exclusive, thus $\sum_n w_n = 1$. It is also possible that some states $|n\rangle$ are degenerate, so that a number of weights w_n are equal, although all must be less than unity. These remarks lead us to make a more precise definition of a density matrix as a bounded, positive, self-adjoint operator

$$\rho \equiv \sum_n w_n \mathrm{P}_n\,, \tag{4.6}$$

where P_n are projection operators onto a complete set of orthogonal subspaces. Owing to (4.3) and (4.5), $\mathrm{Tr}\rho = 1$. In the orthogonal basis the $\{w_n\}$ are the eigenvalues of ρ and $\{|n\rangle\}$ are its eigenstates, but only up to a choice of orthonormal basis in the subspace of each eigenvalue.

If all the w_n are zero save one—$w_k = 1$, say—then ρ describes a pure state, $\rho = |k\rangle\langle k|$, and in this case $\rho^2 = \rho$. In fact, a necessary and sufficient condition for ρ to describe a pure state is that ρ be *idempotent*, $\rho^2 = \rho$, so that $\mathrm{Tr}\rho^2 = 1$. If ρ describes a mixed state, then $\mathrm{Tr}\rho^2 < 1$.

Because ρ is intimately related to the states ψ_i, which must satisfy the Schrödinger equation, $i\hbar\partial_t\psi_i = H\psi_i$, differentiation in (4.1) implies the equations of motion

$$i\hbar\dot{a}_{ij} = \sum_k a_{ik} H_{jk}\,, \qquad H_{jk} \equiv \langle u_j|H|u_k\rangle\,. \tag{4.7}$$

The superposed dot here denotes a total time derivative, for a_{ij} describes a particular state and depends only on the time. An equation of motion for ρ

follows from direct differentiation in (4.5), after noting that the weights w_i are constants in the equilibrium state:

$$i\hbar\dot{\rho}_{kn} = \sum_q \left(H_{kq}\rho_{qn} - H_{nq}\rho_{kq}\right) , \tag{4.8a}$$

or in operator notation

$$i\hbar\dot{\rho} = [H, \rho] . \tag{4.8b}$$

This last equation is equivalent to unitary transformation by time-evolution operators, $\rho(t) = U(t)\rho_0 U^\dagger(t)$.

The many-body problem is in principle reduced to calculation once the operator ρ describing the initial state of the system is known. In an essential way this operator contains everything we know about the system, both experimentally and theoretically, and new information can only be obtained through further observation. In this respect, it should be noted that ρ contains two different aspects of probability: that inherent in quantum mechanics itself, as well as that associated with incomplete information regarding the initial state of the system; in most cases it is extremely difficult to disentangle the two. This also implies that the expectation value symbol $\langle\cdots\rangle$ refers to both classical and quantum expectation values together. The primary problem of equilibrium statistical mechanics, therefore, is construction of an initial density matrix when only macroscopic information is available and the microscopic state is totally unknown. (Time evolution of ρ will be addressed extensively much later.)

The numbers w_n in (4.6) are not in general specified by the quantum theory itself, but must be determined from whatever information is available in the specification of the problem. Quantum mechanics does not provide in itself any prescription for constructing an initial density matrix from given macroscopic data.

All this begins to sound familiar, and the PME suggests itself as the proper tool for a general determination of ρ. This requires an expression for the entropy of a probability distribution in terms of the density matrix, for which a general form was provided many years ago (von Neumann, 1927b, 1943; Klein, 1931):

$$\begin{aligned} S_I &\equiv -k\mathrm{Tr}(\rho \ln \rho) \\ &= -k\langle \ln \rho \rangle , \end{aligned} \tag{4.9}$$

where k is a units-dependent constant. Because the trace is representation independent, transformation to the diagonal representation confirms that Eq.(4.9) assigns zero information entropy to any pure state, and in that representation this form is seen to be the quantum-mechanical version of Eq.(3.9). Thus, quantum mechanically S_I can be viewed as a measure of "mixedness."

There are a number of properties of S_I that will be quite important in coming applications—here are a few.

Concavity. For the density matrix $\rho = \lambda_1\rho_1 + \lambda_2\rho_2$, where ρ_1, ρ_2 are density matrices and $\lambda_1, \lambda_2 > 0$, $\lambda_1 + \lambda_2 = 1$,

$$S_I(\rho) \geq \lambda_1 S_I(\rho_1) + \lambda_2 S_I(\rho_2)\,. \tag{4.10}$$

This result supports the assertion (1.14) in that context, for example.

Additivity. Let $\mathcal{H}_1$, $\mathcal{H}_2$ be two Hilbert spaces on which are defined density matrices ρ_1, ρ_2, respectively. The information entropy of the density matrix $\rho_1 \otimes \rho_2$ in the direct product space $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$ is then

$$S_I(\rho_1 \otimes \rho_2) = S_I(\rho_1) + S_I(\rho_2)\,, \tag{4.11}$$

which generalizes readily to more than two spaces. It is not surprising that information about a system is the sum of information about its subsystems, but it is not necessarily true that physical entropies add like this. We shall see that such statements can be supported only if the systems are independent.

Subadditivity. This property addresses the situation when the two subsystems are not independent:

$$S_I(\rho) \leq S_I(\rho_1) + S_I(\rho_2) = S_I(\rho_1 \otimes \rho_2)\,, \tag{4.12}$$

with equality if and only if $\rho = \rho_1 \otimes \rho_2$. An example arises when two well-defined subsystems are in equilibrium with each other through interaction. An operator F_1 operating only on the variables of system 1 is represented in the space of the combined system as the direct product $\mathcal{F}_1 \equiv F_1 \otimes \mathbb{1}$, where $\mathbb{1}$ is the unit operator in space 1. The expectation value of $\mathcal{F}_1$ then reduces to a trace involving only the space 1:

$$\langle F_1 \rangle = \mathrm{Tr}(\rho\mathcal{F}_1) = \mathrm{Tr}(\rho_1 F_1)\,, \tag{4.13}$$

where ρ_1 is the projection of ρ in $\mathcal{H}$ onto the subspace $\mathcal{H}_1$, with matrix elements

$$\langle n|\rho_1|k\rangle = \sum_m \langle nm|\rho|km\rangle. \tag{4.14}$$

Similar comments apply to space 2 and operators $\mathcal{F}_2$, F_2, and ρ_2. Clearly the parts of ρ that are summed out in Eq.(4.14) are irrelevant for predicting the expectation value of F_1, even though they contain information about the state of subsystem 2 and correlations between the two. It is equally clear that replacing ρ by the direct product $\rho_1 \otimes \rho_2$, with matrix elements

$$\langle nm|\rho_1 \otimes \rho_2|kl\rangle = \langle n|\rho_1|k\rangle\langle m|\rho_2|l\rangle\,, \tag{4.15}$$

also allows one to calculate expectation values of any operator composed additively of terms operating on subsystem 1 alone, or 2 alone. This process is called *removing correlations* and results in a loss of information as indicated in (4.12).

Proofs of these properties of S_I as defined in (4.9), as well as numerous others, can be found in the review by Wehrl (1978).

Before one can apply the PME to (4.9) it is necessary to specify the exhaustive set of mutually exclusive alternatives, or the logical spectrum, to be considered. This is not a completely trivial exercise, because the probabilities intrinsic to quantum mechanics do not always refer to mutually exclusive propositions. For example, if a system is asserted to be in the state ψ_i, it has probability $|(\phi_j, \psi_i)|^2$ to be in some other state ϕ_j, and this is not necessarily zero unless ϕ_j is orthogonal to ψ_i. But this last observation holds the key. The logical spectrum for the PME is some complete set of orthogonal states, with one *caveat.* Any operator corresponding to an observable of the system will possess an enormously degenerate spectrum, because many different microscopic arrangements can correspond to the same global quantum number. It is actually the set of degenerate subspaces that labels the set of mutually exclusive alternatives. Thus, the logical spectrum for the PME is the complete set of orthogonal subspaces indexed by its spectrum. In terms of projection operators onto these subspaces, the density matrix has the form (4.6), and the eigenvalues of ρ are $\{w_i\}$. The importance of this structure of the logical spectrum will become clearer below.

With these thoughts in mind, application of the PME is now straightforward and proceeds in precisely the same way as in Chapter 3. Suppose the available information about a system is given in the form of expectation values of a number of linear Hermitian operators $F_1, F_2, \ldots, F_m$. At present we shall presume these operators to be constants of the motion, so that their observation defines in a formal way what we mean by a thermal equilibrium state. Possible noncommutativity of the operators presents no difficulties in carrying out the maximization process, and the method of Lagrange multipliers leads to the statistical operator, or density matrix

$$\rho = \frac{1}{Z} e^{-\lambda \cdot F} \,, \tag{4.16}$$

in the notation of (3.13). The partition function is

$$Z(\lambda_1, \ldots, \lambda_m) = \mathrm{Tr} e^{-\lambda \cdot F} \,, \tag{4.17}$$

and the λ_k are determined from a set of coupled differential equations as in (3.14). The formal results are exactly those of Eqs.(3.17) and (3.21)–(3.32), except that the functions are now operators on the Hilbert space, expectation values contain both elements of classical and quantum probabilities as given by (4.4), and determination of the set $\{\lambda_k\}$ effectively determines the eigenvalues $\{w_i\}$ of ρ. To prove that S is an absolute maximum, one follows the argument of (3.15)–(3.17), but based now on the operator identity $\mathrm{Tr}[\rho(\ln \rho - \ln \sigma)] \geq 0$ for two density matrices ρ, σ, a further property proved in Wehrl.

In addition to specifying only constants of the motion in defining a macroscopic equilibrium state, there is usually a tacit presumption of a homogeneous system. The simplest case is that of only a single operator to be considered in (4.16), and the choice of the N-particle Hamiltonian leads to the standard description of a classical thermodynamic system,

$$\rho = \frac{1}{Z} e^{-\beta H_N}\,, \qquad Z(\beta) = \mathrm{Tr} e^{-\beta H_N}\,, \tag{4.18}$$

where the Lagrange multiplier is now denoted by β. Note that there is no consideration of an ensemble of systems here, for attention is focused only on the single system under study, as logic demands (and as also noted earlier by van Kampen, 1962). Equation (4.18) defines the *canonical distribution.*

The expectation value of the Hamiltonian is just the total internal energy of the system, $U = \langle H_N \rangle$, and one is now able to utilize (4.18) in making probabilistic predictions of the same kind for other macroscopic variables that might further describe this system. We consider only a single external variable $\alpha = V$, the system volume, and note from (3.20) that $\langle dH \rangle$ is an element of work dW, which from the definition of pressure is $-PdV$; the pressure can also be identified from (3.22). Equation (3.20) also contains an expression of the First Law, for dQ must be an element of heat. While this law of thermodynamics cannot be derived from more primitive dynamical laws, the expression emerges here as a result of probable inference. Because classically the Kelvin temperature is defined as an integrating factor for heat, Eqs.(3.21) together identify the Lagrange multiplier as $\beta = (kT)^{-1}$, k as Boltzmann's constant in these units, and S as the entropy of Clausius:

$$\frac{1}{k} S(U) = \ln Z + \beta \langle H \rangle\,. \tag{4.19}$$

This expression also defines a Legendre transformation involving the free energy $F \equiv -\beta^{-1} \ln Z$. We also see that if we take $f = U$, $\alpha = V$ in (3.22), this gives us the pressure as $-(\partial F/\partial V)_T$ and leads to one of the goals of statistical mechanics, namely, deriving equations of state. We also see here an example of the freedom noted in Chapter 3 to choose the Lagrange multiplier as the independent variable after maximization; it is usually the temperature that is specified in thermodynamics.

As an aside we leave it to the reader to verify another interesting property of the variational algorithm at work here. While (4.19) reflects the fact that the entropy is a maximum for given energy, it is also true that the energy is a minimum for given entropy, an observation already made by Gibbs in 1875 (*HS*). There exist many other mathematical examples of this type of symmetry.

When contemplated along with the First Law, $dU = dQ + dW$, (4.19) allows us to exhibit the meaning of free energy by asking how much work (or available energy) can be extracted by means of an isothermal interaction with the system: $\delta W = -\delta F = T\delta S - \delta U$. Clearly, the answer will depend on the particular microstate of the system, and hence on how much we know about that state. That information, as we see, is supplied by the entropy, which thus has the additional property of measuring how much energy is "spread out" over uncontrolled degrees of freedom. Put another way, in thermodynamics S expresses the limits on the amount of energy available for work, whereas in statistical mechanics it measures the limits to our knowledge of which microstate the system might occupy; in either case the information deficit is real. When $\log_2$ is employed in Shannon's expression (2.6) for the uncertainty, so that $K = 1$, its relation to entropy is seen to be $S_I = kH \ln 2$. Hence, an increase in uncertainty of 1 bit is equivalent to an increase of $k \ln 2$ in the information entropy.

In this application to classical thermodynamics, (3.27) takes on special significance, for it expresses the entropy as an extensive function of extensive variables, *if the required condition is fulfilled.* In all but the very simplest models direct calculation of $\ln Z$ is not practicable, so one must pursue an indirect course. There may be various ways to establish this condition, but with $\alpha = V$ the standard procedure is to demonstrate it in the infinite volume, or bulk limit $(N, V \to \infty,\ N/V < \infty)$, where it is found to hold for many common Hamiltonians.[2] In some exceptional situations, however, and for some systems, it may not be possible to verify the condition; it may be that the system is not extensive and surface effects are important, or the theory may be describing something other than classical thermodynamics.

If two (nonexceptional) independent systems are brought into thermal contact so that energy can be transferred between them, such that the total energy is conserved, then the entropies are additive as in (4.11). Since the weak interaction Hamiltonian between them is almost never known, there is only one Lagrange multiplier for the total density matrix, and that factors:

$$e^{-\beta(H_1+H_2)} = e^{-\beta H_1} \otimes e^{-\beta H_2}\,, \tag{4.20}$$

as does the partition function, $Z(\beta) = Z_1(\beta)Z_2(\beta)$. This is simply a reflection of the product rule of probability theory, Eq.(3.2). One of these systems could be considered as a thermometer and, because there are no correlations between the two systems, its sole function is to provide the value of β for the other system. Indeed, it is usually β that is taken to be the independent variable and the energy that is predicted.

There is some value in examining the expressions (4.18) in the representation in which H, and hence ρ, is diagonal:

$$p_j = \frac{1}{Z} e^{-\beta E_j}\,, \qquad Z(\beta) = \sum_j e^{-\beta E_j}\,, \tag{4.21}$$

where p_j is an eigenvalue of ρ. The index j here denotes a particular arrangement of microscopic particle states corresponding to a *system* total energy level E_j. But there will be many such arrangements corresponding to a distinct global

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[2] Generally, those for which the 2-body potential has a hard core and falls off faster than r^{-3} for large r. An immediate difficulty is suggested for gravitational interactions.

state E_j, so that in accordance with our restriction on the logical spectrum and ρ in the form (4.6) it is often useful to rewrite (4.21) in the form

$$P_i = \frac{1}{Z} e^{-\beta E_i}\, g_i\,, \qquad Z(\beta) = \sum_i e^{-\beta E_i}\, g_i\,, \tag{4.22}$$

and $Z(\beta)$ is identical in the two cases. The sum is now over all *distinct* global energy levels of the system indexed by i, and the *degeneracy* g_i counts the number of microscopic arrangements of the N particles yielding a total energy E_i. Equations (4.21) and (4.22) are essentially equivalent, for the latter arises from the former by straightforward application of the sum rule for probabilities of mutually exclusive propositions, Eq.(3.3). Thus, P_i is the probability that the system is in *any* state with energy E_i. Also in this representation,

$$U = \langle H \rangle = \sum_i P_i E_i = -\frac{\partial}{\partial \beta} \ln Z(\beta)\,. \tag{4.23}$$

We emphasize, however, that expectation values are still to be computed generally as $\langle A \rangle = \mathrm{Tr}(\rho A)$, and the information entropy is given by $S_I = -k \sum_j p_j \ln p_j$, which must include all possible microscopic states.

A further *caveat*: it should again be remembered that the probability distribution (4.21), or (4.22), is over the energy states of the *system*, which are macroscopic and in principle both measurable and calculable. We are *not* focusing on the microscopic energy states of individual particles in any specific arrangement of particle states; in any event, that is not fruitful. A global system state corresponding to a distinct system energy can be visualized as a macroscopic arrangement of individual particle microstates, or a microstate of the *system*; there may be many such arrangements with this total energy, but they all correspond to the same global state.

Prior to moving on to some generalizations, this might be an opportune moment to address the behavior of thermodynamic entropy near the zero of absolute temperature. In 1906 Nernst noticed that a number of thermodynamic functions approached zero with the temperature, leading him to assert what is generally referred to as the Third Law (or Nernst's theorem): At $T = 0$ K all substances approach the same constant value of the entropy. Sometime later, motivated by a desire to fix the entropy constant, Planck (1927) noted that this universal value could be taken as zero. Nernst later related this statement to another, which can be stated as: No reversible adiabatic process starting at a positive nonzero temperature can bring a system to zero temperature. An extensive analysis of this "law" is not appropriate here, and at any rate can be found elsewhere along with a discussion of applications (*e.g.*, Abriata and Laughlin, 2004), but we can take a moment to indicate how it might come about.

The value of the lowest energy level is arbitrary and usually taken as zero, which we shall do. As $T \to 0$ ($\beta \to \infty$) every term in the partition function $Z(\beta)$ in (4.22) vanishes, with the exception of the ground state. In the limit, the entropy (4.19) then approaches $S(0) = k \ln g_0$. Although by no means proved, it is generally thought that the ground states of all systems are not degenerate, $g_0 = 1$, from which Nernst's theorem follows. In actuality, however, the behavior of matter near absolute zero is somewhat more complicated than this simple calculation would indicate. For example, to speak of thermodynamic entropy the ground state must be an equilibrium state, and hence a maximum with respect to constraints. But $S(0)$ is also supposed to be a minimum! This apparent contradiction can only be resolved by a detailed study of solid-state configurations near $T = 0$ K. In addition, many substances are observed to have a residual entropy, meaning that at temperatures well below their freezing point there exists a constant entropy much larger than that caused by lattice vibrations. The extent of this for water ice has been discussed at some length by Lieb (1967), and clearly such effects must be taken into account when near the ground state.

The canonical distribution (4.18) refers to a single expectation value as input and to a fixed particle number N. But Gibbs saw that his statistical mechanics was readily generalized to include open systems as well as those containing several components, where the number of each component may not be fixed. A formalism emerges that not only accommodates chemical reactions, electromagnetic interactions, and so on, with ease, but also allows for more realistic situations in which the local particle-number density can fluctuate.

Consider a system composed of various species of particle and suppose that, in addition to the total energy, data also are available as to the number of particles of each species in the volume V. Let Greek-letter indices denote the various types of particle, so that the given data include expectation values $\langle N_\alpha \rangle$, $\langle N_\beta \rangle, \ldots$, where N_α is the number operator for α-type particles, and so on. Further presume that the information about the total number of different species is exhaustive, permitting us to write for the total-number operator

$$N = N_\alpha + N_\beta + \cdots = \sum_\alpha N_\alpha \,. \tag{4.24}$$

There could be additional constraints on the system, of course, such as fixed total charge, or other constants of the motion. Or, if α-type particles can transform into or combine with β-type particles, and conversely, then only $\langle N_\alpha + N_\beta \rangle$ will be an observable quantity. Also, if α-type particles are quanta, such as photons, then the lack of particle-number conservation implies that $\langle N_\gamma \rangle$ cannot be fixed. We presume in what follows that none of these additional constraints is operating; were they, however, they would have to be included explicitly.

As in (4.16), maximization of the entropy subject to the constraints

$$\langle H \rangle = \mathrm{Tr}(\rho H) \,, \quad \langle N_\alpha \rangle = \mathrm{Tr}(\rho N_\alpha) \,, \quad \ldots \,, \tag{4.25}$$

yields the density matrix for Gibbs' grand canonical distribution:

$$\rho_G = \frac{1}{Z_\mathrm{G}} \exp\left[-\beta H + \sum_\alpha \lambda_\alpha N_\alpha \right] . \tag{4.26}$$

Because the operator N_α commutes with H, the grand partition function can be written

$$Z_{\mathrm{G}} = \sum_{\substack{N_\alpha=0\\ N_\beta=0\\ \vdots}}^{\infty} \exp\Big(\sum_\alpha \beta\mu_\alpha N_\alpha\Big) \mathrm{Tr}e^{-\beta H\{N_\alpha\}}\,, \tag{4.27}$$

in which N_α, $N_\beta, \ldots$ are now non-negative integers and the dependence of the Hamiltonian on the particle numbers is indicated explicitly. The Lagrange multipliers λ_α have been identified as $\beta\mu_\alpha$, where μ_α is the chemical potential for the αth species, and the equations of thermodynamics are obtained in a manner similar to the above. For a single-component system, and in a representation in which H_N is diagonal,

$$\begin{aligned} Z_{\mathrm{G}} &= \sum_{N=0}^{\infty} e^{\beta\mu N}\, \mathrm{Tr}e^{-\beta H_N} \\ &= \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{i(N)} e^{-\beta E_i(N)}. \end{aligned} \tag{4.28}$$

The equations of thermodynamics are again obtained as suggested in Chapter 3, the maximum entropy in this case being

$$\frac{1}{k}S = \ln Z_{\mathrm{G}} + \beta\langle H\rangle - \beta\mu\langle N\rangle\,. \tag{4.29}$$

This last expression indicates explicitly that the canonical and grand canonical distributions are based on different states of knowledge. As $N \to \infty$, however, they both lead to the same equation of state (Van Hove, 1949); roughly, the fluctuations in N tend to zero in this limit.

Gibbs also considered the rotational distribution obtained when a component J_i of angular momentum is specified as well (*SM*, p. 39); this had been treated earlier by Maxwell (1879), and later in full detail by Heims and Jaynes (1962).

4.1 The meaning of maximum entropy

In keeping with the theme of this exposition, this may be a good point at which to again raise the question as to what is actually happening when the entropy is maximized, both from the physical point of view as well as that of probability theory. Beginning with the latter, we have already seen that maximizing S_I serves to maximize the uncertainty in a probability distribution subject to the available data. A uniform (or flat) distribution indicates that the only information at hand is an awareness of an exhaustive set of alternatives $\{A_i\}$ that are mutually exclusive, implying that $\sum_i P_i = 1$. If there exists other information that can be formulated in terms of expectation values, for example, then the

PME provides the probability distribution that is as uniform as possible in the presence of these data. In turn, this implies that the set $\{P_i\}$ contains all the known information relevant to $\{A_i\}$, *and only that*, so that no unwarranted presumptions are contained in the resulting probabilities. This process might be perceived as subjective, in that the resulting probability depends on the information available; but two observers possessing different information will necessarily obtain different entropies and probability distributions. Given identical information, those observers must construct identical distributions, and in that sense the procedure is information dependent while being observer independent; this point was already made in Chapter 1 in the context of classical thermodynamics.

What is happening under maximization of S_I from a physical standpoint is basically the phenomenon uncovered by Boltzmann and summarized in Eq.(1.19). He calculated the distribution of free particles over the cells in velocity space that could be achieved in the greatest number of ways, by maximizing a multiplicity factor, and observed that the logarithm of this number was essentially the same as the known thermodynamic entropy of the gas. Although he "established" this property of the entropy maximum for an extremely simple model only, the idea is so compelling that one feels it must be true in general. We are now in a position to provide this generalization.

For clarity we will restrict the discussion to the system described by (4.22) and (4.23). Because U is just a number, though of unknown precision, integration in (4.23) yields the identity

$$Z(\beta) = Z(0)e^{-\beta U} \,. \tag{4.30}$$

While formally correct, this identity is useful only if $Z(0)$ is meaningful. In general it is not, for the definition shows that it can be infinite in some cases; for example, for free particles (1.20) implies that $g_i \propto E_i^N$. If, however, the $\sum_i g_i$ is finite, no matter how large, then $Z(0)$ can be meaningful and the identity useful. (Alternatively, we could consider instead $Z(\varepsilon)$ and let $\varepsilon \to 0$ at the end of the calculation.)

Now order the probabilities $\{P_i\}$ so that $P_1 \geq P_2 \geq \cdots$, and define a real number λ such that $0 < \lambda < 1$. Next add the P_i until their sum first equals or exceeds λ,

$$\sum_{i=1}^{n(\lambda)} P_i = \sum_{i=1}^{n(\lambda)} \frac{g_i e^{-\beta E_i}}{Z(\beta)} \gtrsim \lambda \,, \qquad 0 < \lambda < 1 \,, \tag{4.31}$$

which *defines* the number $n(\lambda)$. Corresponding to this total probability is the total degeneracy

$$w_\lambda \equiv \sum_{i=1}^{n(\lambda)} g_i = Z_\lambda(0) \,, \tag{4.32}$$

the meaning of $Z_\lambda(0)$ being obvious. That is, w_λ is the finite dimension of a manifold of degenerate subspaces we shall call the *high-probability manifold* (HPM);

its complement is the low-probability manifold (LPM). As λ is varied, the set $\{P(E_i)\}$ defines a nested sequence of HPMs. Note that small changes in λ will induce large changes in $n(\lambda)$, and hence in w_λ, so that it is prudent to consider logarithms:

$$\begin{aligned}\ln w_\lambda &= \ln Z_\lambda(0) \\ &= \ln Z_\lambda(\beta) + \beta\langle H\rangle_\lambda\,,\end{aligned} \tag{4.33}$$

from the identity (4.30). The replacement of U by the expectation value is sensible because for large N the sums over i have very few terms that are not essentially zero, owing to the very sharp probability distribution; that is, the root-mean-square (rms) fluctuations are $\mathrm{O}(N^{-1/2})$.

These comments lead us to examine the infinite-volume limit in the form of large N,

$$\begin{aligned}\frac{1}{N}\ln W &\equiv \lim_{N\to\infty}\frac{1}{N}\ln w_\lambda \\ &= \lim_{N\to\infty}\frac{1}{N}\left[\ln Z_\lambda(\beta) + \beta\langle H\rangle_\lambda\right],\end{aligned} \tag{4.34}$$

and then ask if the limit exists independent of $n(\lambda)$. It seems clear that for $N \gg 1$ both $Z_\lambda(\beta)$ and $\langle H\rangle_\lambda$ must be essentially independent of the upper limit on the sums, for $g_i e^{-\beta E_i}$ is extraordinarily sharp, and if the limit exists it is surely independent of $n(\lambda)$. But the second line of (4.34) is precisely what is considered in discussion of the infinite-volume limit, and it is proportional to the (finite) maximum entropy per particle (*e.g.*, Ruelle, 1969). Therefore, the left-hand side of (4.34) exists and is the logarithm per particle of the measure of a well-defined HPM, independent of just how we define "high probability." Thus, whenever the limit exists it is also true that the expression (with proper units)

$$S = k\ln W \tag{4.35}$$

is well defined and understood as a measure of the number of microstates compatible with the macroscopic constraint $U = \langle H\rangle$. In other words, existence of the infinite-volume limit is both a necessary and sufficient condition for the validity of what we shall refer to as Boltzmann's theorem. Note that (4.35), in the spirit of Shannon's theory, expresses explicitly the role of entropy as a measure of uncertainty as to the exact microstate of the system, the uncertainty being that of the observer.

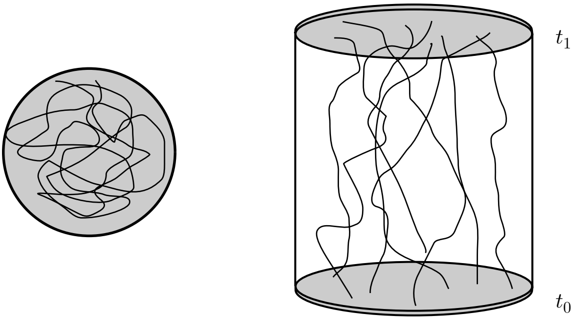
The preceding discussion is really just a sketch of how a rigorous proof might be constructed; it remains a theorem longing for a complete proof. This tentative theorem has the form and content of, and is indeed suggested by, the asymptotic equipartition property of information theory (Shannon and Weaver, 1949; Feinstein, 1958). Indeed, it is plainly true for noninteracting particles, because then the global states are just products of single-particle state vectors and can be considered as ergodic Markov chains, which is the case considered in the information-theory proof.

For reasons to be explained in Chapter 5, the quantities g_i, Z, and W defined in this chapter must undergo further modification if, as usual, the system consists of identical particles. By "identical" here we simply mean that no particle can be distinguished from another by its physical characteristics alone, whether or not the context is classical or quantum.

One sometimes reads that (4.35) applies only to the microcanonical ensemble, and indeed that was just what Boltzmann considered in his *Ergoden*. But the great explanatory power of this expression leads us to jump immediately to its generalization: W is the dimension of the largest set of all microscopic states consistent with *all* the macroscopic constraints on the system. For distributions other than canonical, the procedure is similar. In the grand canonical distribution, for example, $W = W(E, N)$, which can also be realized through the system energy levels $E_i(N)$. Moreover, given an unambiguous definition of time-dependent entropy (to be discussed later), the above construction is valid for $W(t)$, as Boltzmann had envisioned (*Vorlesungen*, p.75). Although W, and therefore the entropy, will change when the values of E and N are changed, the new equilibrium macrostate still refers to the same thermodynamic system. This is one of the beautiful features of the macroscopic equations (thermodynamics), in that one need not repeat the statistical mechanics calculation when the thermodynamic state is changed. Adding additional macroscopic variables to the description, however, means that the problem under study has changed and a new analysis is required.

The multiplicity factor W sheds considerable light on the PME itself. We have noted that the maximum entropy is dependent on a few pieces of macroscopic information in the form of constraints, and in the probabilities that information is now contained in the Lagrange multipliers. Thus, S is said to measure the amount of missing information that would be needed to specify the dynamical state of the system completely. Now we see that W describes the extent of that missing information in terms of the degree of uncertainty remaining as to the exact microstate of the system at any moment—hence, an apparent connection between microscopic and macroscopic information emerges, the *entropy*.

Figure 4.1 provides a schematic description of how (4.35) describes the canonical equilibrium system. The HPM is depicted in Fig. 4.1a as the set of high-probability microstates available to the system, illustrating how the system can move from one microstate to another from moment to moment. (These states, of course, are not contiguous in the phase space.) A clearer picture emerges in Fig. 4.1b as the manifold is expanded along the time axis to illustrate the possible microscopic trajectories, or "world lines" as time unfolds; these lines are loci of microstates within the HPM evolving under the microscopic equations of motion, and thus have equal probabilities. The cross section obtained by a slice through this tube containing these paths in phase-space-time determines the entropy at



(a) (b)

FIG. 4.1. Schematic illustration of (a) the HPM and (b) its time evolution in an equilibrium system. The tube represents the macroscopic history of the equilibrium system under fixed constraints, whereas the trajectories represent all possible high-probability microscopic histories.

any time—in the absence of external interference the cross section, and hence the entropy, remain constant.

It would be difficult to overstate the clarity brought to statistical mechanics by (4.35), particularly as to what is achieved by the Gibbs–Jaynes variational principle. By maximizing S_I one is identifying the macrostate that can be realized not only in the greatest number of ways, but in the overwhelmingly greatest number of ways. To see this, consider a system in a macrostate A_1 with maximum entropy $S_1 = k \ln W_1$ and subject it to a process such that energy, particle number, and/or volume are *increased*; the system then evolves to another macrostate A_2 with $S_2 = k \ln W_2 > S_1$ and $W_2 > W_1$. There is no requirement that A_1 and A_2 be equilibrium states, for (4.35) applies to nonequilibrium states as well; of course, it is conceptually simpler if they are stationary. But just how much greater is W_2 than W_1? The answer is supplied by the ratio

$$\frac{W_1}{W_2} = \exp\left(-\frac{S_2 - S_1}{k}\right) . \tag{4.36}$$

If S_2 and S_1 differ by as little as a nanocalorie at 300 K the right-hand side is $\exp(-10^{12})$, an essentially unfathomable number. When N is on the order of Avogadro's number, the maximum entropy solution is almost a certainty and Boltzmann's insight encompassed in (4.35) and (4.36) tells us why: Gibbs' variational principle predicts that macrostate that can be realized microscopically in the greatest number of ways while agreeing with the macroscopic constraints. As a bonus, (4.36) also provides an explanation for the Second Law, while (4.35) and Liouville's theorem tell us why the entropy cannot change in the absence of external forces. (Quantum mechanically, the role of Liouville's theorem is played by invariance under unitary transformation.) We shall expand further on these issues in Chapter 11.

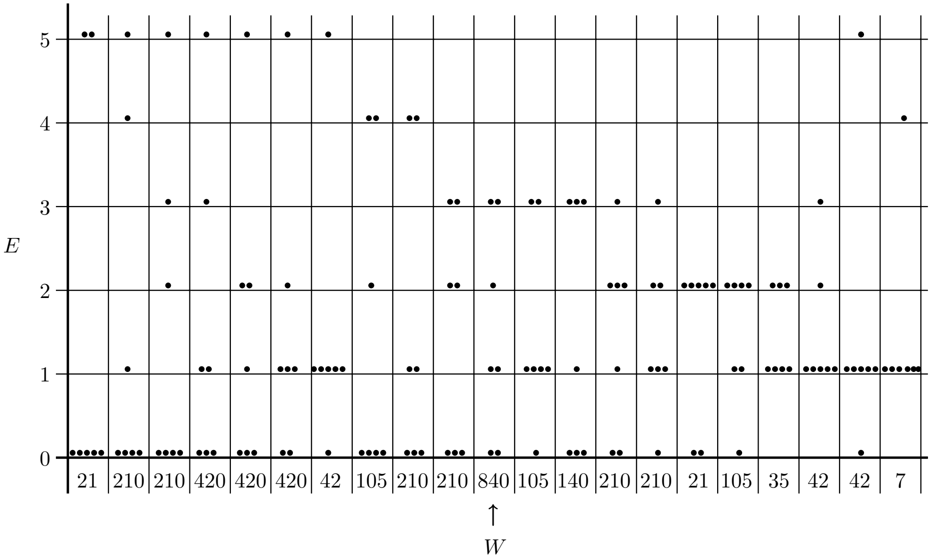


FIG. 4.2. Distribution of microstates for a system of $N = 7$ particles and a total energy $E = 10$ (arbitrary units) that can be spread over 6 evenly spaced energy levels in dimensionless units. There are 21 distinct arrangements of the particles under the energy constraint, but the identical though distinguishable particles can be permuted over these arrangements, giving many ways to populate each arrangement (via the multinomial coefficient). The arrangement achievable in the greatest number of ways is denoted as W.

It cannot be emphasized strongly enough that W is *not* the measure of the set C of all states in the Hilbert space, or in the classical phase space, compatible with the external macroscopic constraints; rather, it is the dimension of the subset of those states that can be realized in *the greatest number of ways*, the HPM. A toy model illustrating this is presented in Fig. 4.2. The limiting process in (4.34) defines a sequence of HPMs for which the entropy has already been maximized, and it is only in the limit that we obtain a final sharply defined HPM. Failure to comprehend this distinction can result in erroneous conclusions about this property of the entropy. For example, it has sometimes been argued that unknown *microscopic* constraints on the particle dynamics may prevent some of the states in C from being realized, possibly restricting the system to some fractal subset of C. One might then suspect that the size of C does not provide a true measure of the entropy of the system. But it is not the size of C that appears in (4.35), but W, the measure of the HPM, and such restrictions are automatically accounted for by the degeneracy factors g_i in (4.32); small values of g_i will be excluded from the sum. In classical language, $g(E)$ is the density-of-states function, whose geometry and topology are governed by the microscopic dynamics, so that only the appropriate contributions end up in W. Indeed, the quantum conditions themselves can be thought of as restricting the phase space to a discrete set of "attractors." Of course, from the macroscopic viewpoint we do not see any of this, and only disagreement with experiment would alert us to the problem: Either some further highly relevant macroscopic constraints have been overlooked, or the model Hamiltonian used in calculating S is inadequate. This was exactly the situation at the dawn of the 20th century with regard to the specific heats of solids.

The picture provided by the preceding discussion illustrates how the probability distribution defines the largest HPM available to the system under the given constraints and assigns essentially the same probability to all states in that manifold. This is the property of *macroscopic uniformity.* In addition, the large number of degrees of freedom of the system causes the HPM to be very sharply defined, implying an extraordinarily sharp distribution and extremely reliable predictions; it is the existence of a complementary LPM that renders the concept of physical fluctuations meaningful.

The existence of macroscopic uniformity is truly remarkable, because there is nothing in the Hamiltonian of either classical or quantum systems that would predict it. Among other things, it implies that the probabilities for each microstate in the HPM are roughly equal, and equal to W^{-1}. With this in mind, (4.35) follows directly from $S = -k\sum_j p_j \ln p_j$ by setting the maximum-entropy solution $p_j = W^{-1}$ for all j and summing only up to W.[3] Like the entropy, W depends only on the constrained macrovariables, and possibly on the time if those variables are changing.

Macroscopic uniformity arises because we deal primarily with experimentally reproducible phenomena (ERP). Given the same initial conditions, it does not seem to matter in many cases where or when we perform similar experiments—the results are reproducible. This notion is expanded and summarized in the principle of Galilean invariance. Thus, statistical mechanics makes its connection with experiment by identifying exactly that manifold of states characterized by ERP. That a phenomenon can be reproduced at all implies that it must be characteristic of the great majority of the states available to the system under the great majority of things done to it during an experiment or natural process, so that not a great deal of information is required in order to ascertain its thermodynamic properties. In Chapter 11 we shall see that a major purpose of the Second Law is to provide a necessary condition for a process to be experimentally reproducible.

To summarize this point, we have found that the physical entropy provides the necessary link between the micro- and macroworld. It is a function only of the

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[3] This is essentially Laplace's principle of insufficient reason, yielding a uniform distribution; many authors adopt it as a fundamental hypothesis of equal *a priori* probabilities, but it is seen here as a *result.* It is not the states in C, but those in the subset W that are equally likely after S_I is maximized.

available macroscopic information about the macroscopic system, but in the form of averages over the underlying microscopic behavior; the Lagrange multipliers play a similar and supporting role. In this sense entropy appears to be a property, not of the physical system, but of the thermodynamic system, or thermodynamic state of the system. That is, there is a certain anthropomorphic quality to the entropy, in that it is very much dependent on the thermodynamic system one chooses to study. These "many faces of entropy" were recognized years ago in a discussion of the same title by Harold Grad (1961). While seemingly innocuous at the moment, these observations will be of critical importance when dynamical processes are considered.

Clearly some kind of quantity like entropy is needed, for it is virtually impossible to apply the fundamental dynamical physical laws to some 10^{23} particles, presuming one could determine their initial conditions at some time. No one has ever succeeded in predicting the crystal lattice directly from Newton's or Schrödinger's equations, for example. There must be some kind of organizing principles at work on this level that, while possibly not readily derived from the lower-level phenomena, nonetheless are ultimately dependent on them. This higher level of behavior is characteristic of *emergent phenomena* (*e.g.*, Ellis, 2005); living matter is an example *par excellence.* In this sense entropy, in its governance of thermodynamics, was one of the earliest emergent variables to be recognized, albeit not widely understood as such for some time. And now we see that it is probability theory that gives rise to this variable that amplifies the microscopic dynamics to the macroscopic level; surprisingly, thermodynamics turns out to be based on a *predictive* theory. It is unlikely that entropy could ever be understood in depth without the probability connection, an assertion that is reinforced as we continue.

At this point in the narrative it may be useful to address a common objection to the preceding discussion. How can we claim that in a physical system entropy is basically a measure of our uncertainty about the microstates occupied by the constituents when we know that it is a physical quantity defined originally by the Clausius expression (1.7), and in that case its changes are measured in the laboratory by means of calorimeters? The question contains its own answer, in that we do not measure S directly; rather, it is the sum of all the changes in thermal energy, dQ, that is found by the calorimeter. But this just brings us back to the nature of heat. Work done on a system is generally considered to be energy transferred through those degrees of freedom over which we have some control, such as by means of mechanical forces. Heat, on the other hand, is energy transferred through degrees of freedom over which we have no control, and thus itself originates in uncertainty. Both concepts, heat and entropy, arise from our attempts to understand the microscopic behavior of large systems from a macroscopic perspective, which is why they are often closely related. Incidentally, the term "thermal energy" here refers to internal motional energy that can be exchanged as heat with the surroundings, or vice versa.

4.2 Fluctuations

Fluctuation phenomena have historically had a large role in statistical physics, from both physical and mathematical perspectives. The idea already arose in (3.28) in connection with variances and covariances, and begins with the notion of the deviation of a quantity from its expected value, as noted there. Indeed, the deviation $\Delta f = f - \langle f\rangle$ is often referred to as the fluctuation of f about its mean value. We shall often employ this generic meaning, so that the covariance $\big\langle (f - \langle f\rangle)(g - \langle g\rangle)\big\rangle$ then appears as the *correlation of fluctuations*; for $g = f$ it is also the expected square of the error. Sometimes what is meant in a discussion is the rms fluctuation, defined as the square-root of the variance divided by the expectation value. Note carefully that these quantities are *statistical* in nature, with no implication that any physical entities they may represent will also fluctuate. But various external factors can certainly induce such fluctuations in the physical variables of a nonisolated system, so that further investigation is indicated.

This last point is of some importance, because the variances of (3.28) now have a thermodynamic interpretation in terms of the system response functions. For example, the heat capacity at constant volume is given by

$$\begin{aligned} C_V = \left(\frac{\partial U}{\partial T}\right)_V &= \frac{\partial^2 \ln Z}{\partial \beta^2} \\ &= \left(kT^2\right)^{-1}\left(\langle H^2\rangle - \langle H\rangle^2\right) \geq 0 \end{aligned} \tag{4.37}$$

This is the first of a number of stability conditions for the equilibrium state.

The derivation of thermodynamics from probability theory cannot be considered complete without establishing the relationship of expectation values to physically measurable values of the associated macroscopic variables, and this also involves fluctuations. Consider any time-dependent classical variable $f(t)$, where it suffices to suppress any other independent variables in this discussion, and consider just the equilibrium system. Given any equilibrium probability distribution for $f(t)$, the best prediction we can make for the variable, in the sense of minimum expected square of the error, is the expectation value

$$\langle f(t)\rangle = \langle f\rangle\,, \tag{4.38}$$

independent of time. The reliability of this prediction is determined, as always, by the variance

$$\begin{aligned} \mathrm{var}[f(t)] &\equiv \langle (f(t) - \langle f\rangle)^2\rangle \\ &= \langle f^2\rangle - \langle f\rangle^2\,, \end{aligned} \tag{4.39}$$

again independent of time. Only if $|\sqrt{\mathrm{var}(f)}/\langle f\rangle| \ll 1$ is the distribution making a sharp prediction, which is to be expected for $N \gg 1$ degrees of freedom.

Now, (4.38) just reflects the value of f predicted by the probability distribution, and is not necessarily the same as the value actually measured for the single physical system being studied. Similarly, (4.39) is only a measure of how well the distribution is predicting that expectation value; it represents the *statistical* fluctuations, and may or may not correspond to possible fluctuations of the physical quantity. Certainly knowledge that the value of f is known only to $\pm 1\%$ does not imply that the physical value actually fluctuates by $\pm 1\%$. This is a point stressed repeatedly by E.T. Jaynes in several different contexts, and we follow his arguments here (*e.g.*, Jaynes, 1979). Nevertheless, the reality of physical fluctuations is not in doubt, as evidenced by the phenomena of Brownian motion, critical opalescence, and spontaneous voltage fluctuations in resistors at constant temperature, so that we might expect a relationship between the two types.

To uncover possible connections of this kind we note that the value measured in the laboratory is not an expectation value, but a time average:

$$\overline{f} \equiv \frac{1}{T}\int_0^T f(t)\,dt\,, \tag{4.40}$$

where the averaging time T will be left unspecified for the moment. The best prediction we can make for this measured value, then, is

$$\langle\overline{f}\rangle = \left\langle \frac{1}{T}\int_0^T f(t)\,dt \right\rangle = \frac{1}{T}\int_0^T \langle f\rangle\,dt\,, \tag{4.41}$$

or in equilibrium,

$$\langle\overline{f}\rangle = \langle f\rangle\,. \tag{4.42}$$

This is a rather general rule of probability theory: An expectation value $\langle f\rangle$ is not equivalent to a time average $\overline{f}$, but it *is* equal to the expectation value of that average.

Thus it seems that the predictions of statistical mechanics are clearly related to measured physical values, if the prediction (4.42) is reliable. This again is determined by the variance,

$$\text{var}(\overline{f}) = \frac{1}{T^2}\int_0^T dt\int_0^T dt'\left[\langle f(t)f(t')\rangle - \langle f(t)\rangle\langle f(t')\rangle\right]. \tag{4.43}$$

In equilibrium with time-independent Hamiltonian the expectation values depend only on $t'-t$. With some judicious changes of variable the last expression can then be reduced to a single integral:

$$\text{var}(\overline{f}) = \frac{1}{T^2}\int_0^T (T-\tau)K_{ff}(\tau)\,d\tau\,, \tag{4.44}$$

in terms of the covariance *function*

$$K_{ff}(\tau) \equiv \langle f(0)f(\tau)\rangle - \langle f\rangle^2\,, \tag{4.45}$$

which now appears in the role of a time correlation. If the integrals in (4.44) converge as $T\to\infty$, then the correlations will die off as $1/\sqrt{T}$ and hence $\text{var}(\overline{f})\to 0$

in the limit. When this is true we can assert with some confidence that the expected measurable value equals the expectation value; otherwise, there is no sharp relation between expectation values and time averages. Note, however, that there is no guarantee that the measured value will actually be the same as that in (4.42); only experiment can verify that.

In the same vein, we can ask how the measurable mean-square fluctuations are related to the statistical fluctuations. The time average of the squared deviation from the measured mean is

$$\begin{aligned}(\delta f)^2 &\equiv \frac{1}{T}\int_0^T [f(t) - \overline{f}]^2\, dt \\ &= \overline{f^2} - \overline{f}^2\,, \end{aligned} \tag{4.46}$$

and the expectation value is found to be

$$\langle(\delta f)^2\rangle = \mathrm{var}(f) - \mathrm{var}(\overline{f})\,. \tag{4.47}$$

Hence, measurable fluctuations can be the same as the statistical fluctuations only if the distribution is such, and the averaging time so long, that $|\mathrm{var}(\overline{f})/\mathrm{var}(f)| \ll 1$. Invariably, this is *presumed* to be the case, but we see that verification implies a need to calculate yet another variance $\langle(\delta f)^4\rangle - \langle(\delta f)^2\rangle^2$, which reduces to a 4-fold time average of a 4-point correlation function. Fortunately, we can expect rapid termination of this hierarchy for $N \gg 1$.

There is some importance to asking how physical fluctuations in the system affect the entropy. Because S is a function of the macroscopic input variables (expectation value constraints), $S = S(\langle H\rangle, \langle N\rangle, \ldots)$, we should expect that fluctuations in these variables would lead to corresponding fluctuations in S. The entropy is also a maximum with respect to these data [recall (3.31)], so that it can only fluctuate downward.

With these thoughts in mind, let $S_0 = k \ln W_0$ represent an equilibrium state and envision a fluctuation $S = S_0 + \Delta S$. According to (4.36) the relative probability of a fluctuation in entropy can then be written

$$\frac{W}{W_0} = e^{\Delta S/k} = e^{-|\Delta S|/k}\,. \tag{4.48}$$

Suppose that x is a parameter appearing in S, so that if $S(x)$ fluctuates we can turn things around and ask for the probability of a fluctuation in x. That is, P_x is the probability of x taking a value between $(x_0 + \Delta x)$ and $(x_0 + \Delta x) + dx$:

$$P_x\, dx = Ce^{-|\Delta S(x)|/k}\, dx\,, \tag{4.49}$$

where C is determined by normalization.

Consider first an example of Brownian motion, in which a micron-size particle of mass m is placed in a slightly less dense liquid, so that it must sink to the bottom of the container. What is the probability of thermal fluctuations due to molecular collisions in a small volume around the particle raising it by $\Delta z = z - z_0$? To imagine that these collisions might cancel on average is to make the gambler's error that by wagering a fixed amount at each throw of the dice one cannot lose more than that fixed amount! But we also know that direct conversion of thermal energy to potential energy is a violation of the Second Law. If no work is done, however, a fluctuation in S can arise from a fluctuation in internal energy, or $\Delta S = \Delta U/T = m'g(z - z_0)/T$, where m' is the effective mass due to buoyancy. Hence,

$$P_z\, dz = Ce^{-m'g(z-z_0)/kT}\, dz\,. \tag{4.50}$$

In like manner, we could also estimate the probability for translational or rotational motion, and very quickly be led to a theory of Brownian motion (Einstein, 1905; Smoluchowski, 1908). An enhanced experiment of this type has recently been carried out by Wang, *et al.* (2002) in which violations of the Second Law over periods as long as 2 s are observed in micron-size systems.

As a second example, let x be one of the input expectation values—the number density $n \equiv \langle n \rangle$, say. For small deviations $\Delta n \equiv n - n_0$ we have

$$S = S_0 - \frac{1}{2}\left(\frac{\partial^2 S}{\partial n^2}\right)_{n_0} (n - n_0)^2 + \cdots\,, \tag{4.51}$$

so that

$$\begin{aligned} P_n &= C\exp\left[-\frac{1}{2k}\left(\frac{\partial^2 S}{\partial n^2}\right)_{n_0} (n - n_0)^2\right] \\ &\xrightarrow[\text{ideal gas}]{} C\exp\left[-\tfrac{1}{2}N(n - n_0)^2/n_0^2\right]\,, \end{aligned} \tag{4.52}$$

where for the ideal gas we find $(\partial^2 S/\partial n^2)_{n_0} = 1 + N/n_0^2 \simeq N/n_0^2$. Note that the mean square deviation is

$$\int_0^\infty P_n(\Delta n)^2\, d(\Delta n) = n_0^2/N\,, \tag{4.53}$$

so that the rms fluctuations in n are $\mathrm{O}(N^{-1/2})$, as expected.

In 1 cm^3 of air, the mean deviation in density is about 10^{-10}, but in a cube of edge $\sim 10^{-5}$ cm (the wavelength of light) it is about 6×10^{-3}, which is significant. Therefore, there exist many small volumes of this latter size in a gas for which fluctuations can be substantial, and from which light can scatter. It is upon such arguments that Smoluchowski (1908) and Einstein (1910) based their explanations of critical opalescence and the blue of the sky. But for us the primary lesson of this discussion is that it reinforces explicitly our view of entropy and the Second Law as rooted in probability—the Second Law is continually being violated in very small subvolumes of a system. This realization is far from new, however, for it was noted long ago by Maxwell (1878a):

> Hence the second law of thermodynamics is continually being violated, and that to a considerable extent, in any sufficiently small group of molecules belonging to a real body. As the number of molecules in the group is increased, the deviations from the mean of the whole become smaller and less frequent; and when the number is increased till the group includes a sensible portion of the body, the probability of a measurable variation from the mean occurring in a finite number of years becomes so small that it may be regarded as practically an impossibility.

These observations do not, however, speak to the question of just how small a sub-volume must be for one to be concerned about fluctuations affecting the thermodynamics. It is doubtful there exists any sharp transition in this sense between small and large systems from an experimental viewpoint, but with the increasing interest in nanophysics the description of small fluctuating systems by something akin to thermodynamics is under intense study. For example, it now seems clear that there is a limit to how small a system can be and remain in equilibrium at very low temperatures (Hartmann *et al.*, 2004a,b; Wang *et al.*, 2007).

4.3 A mischaracterization

Although we have made considerable progress in determining the meaning of entropy, perhaps this may be a good time to remark on some of the things it is *not*. For example, it is not a dynamical variable like energy, momentum, coordinates, and so on; nor is it some kind of concrete "stuff." One can certainly write expressions like S/N or S/V as a notational or numerical convenience, for example, but this does *not* imply that entropy can be distributed over particles or units of volume as if it were a density of something. It is not a locally conserved quantity; as Gibbs noted, "In such respects, entropy stands strongly contrasted with energy." Although these are important technical points, which will prove to be more so as we proceed, there is another, more pernicious, perception that is far more widespread and which should be addressed here and now.

In attempting to illustrate the character of entropy one well-known work on statistical mechanics states that "the letters of the alphabet can be arranged in 26! ways, of which only one is the perfectly ordered arrangement ABC ... XYZ, all the rest having varying degrees of disorder. Consequently, an ordered observational state comprises many fewer arrangements than a disordered one, and so if each arrangement contributes roughly the same amount to $[W]$ an ordered state has a much smaller $[W]$, and consequently less entropy, than a disordered one." This sets one to wondering how thermodynamics would appear to another culture that might employ a different standard ordering. In the context of playing cards discussed earlier, there is no such thing as a well-shuffled deck, except with reference to certain familiar sequences. Yet another "learned" assertion: "The second law was originally expressed as a restriction on the possible transformations of heat and work, but it is now seen as being fundamentally a statement about the increase of disorder in the universe."

This order/disorder characterization of entropy is not at all uncommon, as noted already by Maxwell (1878b) in his *Diffusion* article in the *Encyclopedia Britannica*: “Now, confusion, like the correlative term order, is not a property of material things in themselves, but only in relation to the mind which perceives them.”[4] That is, it is a human aesthetic judgment. It is equally human to observe that most things, untended to in the course of events, are prone to decay into a state of disorder relative to some initially perceived order, but to raise this notion to a scientific level requires at the very least provision of some operational means for measuring it directly; we know of none. Those disorderly states result from various interactions with the environment.

Of course, we recognize that there are numerous occasions in which the association of entropy with the notions of order/disorder is sometimes appropriate as a qualitative impression. (Even Boltzmann and Gibbs were not above resorting to this description.) When two unlike perfect gases are mixed, the increase in entropy surely conveys much less an impression of order than before the mixing. The decrease of entropy in moving from the gaseous to the solid state is evidently a move to a more orderly arrangement that has physical meaning. Similarly, the alignment of spins in a magnetic field suggests a degree of order that is absent in zero field; order–disorder transitions in binary alloys provide further examples. Note, however, that in each of these cases there is no ambiguity in assigning the standard physical state against which “disorder” is to be gauged.

Wright (1970) has also discussed this issue and provided some examples for which the connection between entropy and order/disorder is not so readily made. One such is the entropy change in both He and Ar after a change of state from near 0 K to one at 25 °C and 1 atm of pressure. With the known values of constant pressure, heat capacity, and latent heat of transition, these are $\Delta S = 127,\ 154$ (joule $\text{mole}^{-1}\,\text{K}^{-1}$), respectively. It is difficult to see how the heavier slower-moving argon atoms can be meaningfully described as a system more disordered than that of the rapidly moving helium atoms. Other scenarios along these lines have been discussed by Denbigh (1989), and Lambert (2002) has delivered a strong admonition to chemists who continue to use the order/disorder metaphor in their textbooks (an appeal that could be read profitably by some writers of beginning physics texts). Lambert also provides several references illustrating how this misinterpretation has lamentably diffused into the general population.

While these examples might be considered marginal or exceptional, we now turn to one that directly illustrates in no uncertain terms why one cannot take too seriously any simple connection between entropy and order/disorder.

Many years ago, Onsager (1949) considered an isotropic fluid of thin hard rods, which normally can have arbitrary orientations. He argued that at sufficiently high densities, the system could undergo a nematic phase transition to a state of higher entropy, in which the rods have a preferred orientation. The

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[4] By “confusion” Maxwell means something like “random,” as in “the energy of the confused agitation of molecules which we call heat.”

reason this works is that the most efficient way to pack particles like this into a volume is something like end-to-end orientation in parallel sheets. By considerably increasing the free volume, the entropy decrease owing to orientation is more than offset by the increase coming from translational motions. We can see immediately that there is no deeper principle operating here other than maximum entropy: the "ordered" state can be realized in many more ways than can the unoriented state—it takes nothing more than Boltzmann's interpretation of Eq. (4.35), although demonstrating that this can actually happen is another matter.

That other matter was settled just a few years ago by a number of experiments with colloidal suspensions. Adams, *et al.* (1998) have studied mixtures of colloidal rod-like (viruses) and sphere-like (polystyrene latex) particles under conditions in which they have a strictly repulsive hard-particle interaction. By increasing the concentration, and if the free volume is sufficient, like components experience an effective attraction, and phase separation to a state of greater entropy occurs. There is bulk demixing into rod-rich and rod-poor phases in some cases, as well as layers of rods alternating with layers of spheres in others. This type of "geometric" phase transition is often called *depletion attraction* (*e.g.*, Rudhart *et al.*, 1998). Although the origin of the phenomena is sometimes said to lie with "entropic forces"—also, depletion or excluded-volume forces—these are as fictitious as their Coriolis and centrifugal brethren. There are nothing more than phase-space factors at work, although it is the system's preference for a state of maximum entropy that drives the phase transition. But whatever the choice of terminology, we see here a very general example in which a perception of increased order is accompanied by an *increase* in thermodynamic entropy. A similar phenomenon also occurs when packing hard spheres into a box: The state in which the spheres are packed in an FCC lattice is stable and of *higher* entropy than that achieved by random packing (*e.g.*, Chaikin, 2007).

This contrast between perceived order and entropy can also be seen in the reverse sense in binary fluid mixtures (*e.g.*, Andersen and Wheeler, 1978; Walker and Vause, 1987). For various liquids, a mixture can be miscible at high temperature, and then become immiscible at lower temperatures as the two components separate out. In certain mixtures further reduction of the temperature can lead to a second phase change in which the liquids again become miscible, thereby presenting a perception of *decreased* order accompanied by a *decrease* in entropy. It is the onset of hydrogen bonding between unlike molecules that induces this unconventional phase change.

The reader may wonder why we have gone into so much detail in debunking the order/disorder mischaracterization of entropy, particularly since it seems to have such a natural appeal. But that is just the point: It provides an easily comprehensible meaning to the nonscientist that is, and has been, widely abused. This interpretation of "entropy" becomes an apt metaphor for every conceivable human condition that might be called disorderly. Novelists have used it uncritically as a thematic crutch (Pynchon, 1960), social commentators as an agent of social degradation (B. Adams, 1943; H. Adams, 1949; Rifkin and Howard, 1985), and philosophers to analyze postmodernism (McKinney, 1990). This is only a small sample of the misinformation generated by equating entropy with degrees of disorder. Unfortunately, this characterization continues in too many classrooms and texts, just where we would hope to correct it. In later discussions we shall encounter further examples of what entropy is not.

The development at this stage has involved only the simplest of equilibrium thermodynamic systems and, although our insight into the nature of entropy has been expanded somewhat, the scope must be extended considerably if the concept is to achieve its promise. Prior to taking those next steps, however, we pause to address a presumptive property of entropy that has caused a good deal of confusion over the years.

5

THE PRESUMED EXTENSIVITY OF ENTROPY

> *If the particles are regarded as indistinguishable, it seems in accordance with the statistical method to regard the phases as identical.*
>
> *J. Willard Gibbs (1902)*

In classical thermodynamics, it is axiomatic that the entropy is additive for a combination of two independent subsystems, $S = S_1 + S_2$, and thus it is natural to presume that S is extensive. But additivity is not guaranteed in general, as exemplified by any system in which the particles interact under long-range forces (*e.g.*, ionic crystals or spin systems in which the Heisenberg Hamiltonian is not restricted to nearest neighbors): Owing to long-range correlations, $S < S_1 + S_2$, as in (4.12), while the Clausius definition,

$$\Delta S = S_b - S_a = \int_a^b \frac{dQ}{T}, \tag{5.1}$$

remains valid as long as N is constant. In relatively small systems, surface effects may be important so that extensivity is absent.

Many sources, tacitly if not explicitly, equate additivity and extensivity, which can often lead to trouble. A function f of extensive variables $\{Y_i\}$ is extensive if it satisfies the scaling law

$$f(qY_1, qY_2, \ldots) = qf(Y_1, Y_2, \ldots)\,, \qquad 0 < q < \infty. \tag{5.2a}$$

That is, f is homogeneous of degree 1, and a theorem of Euler provides the completely equivalent statement

$$f(Y_1, Y_2, \ldots) = \sum_i Y_i \frac{\partial f}{\partial Y_i}. \tag{5.2b}$$

If we equate f to the entropy S we find the familiar form $TS = E + PV - \mu N + \cdots$, from which thermodynamic stability can be validated. While additivity can readily be shown to imply extensivity, at least for continuous f, the converse is not necessarily true if systems differing in some way are being brought together; for example, even though the two separate systems are extensive, there may be a chemical reaction upon mixing. In any event, the two notions are logically independent.

Compounding the difficulty here is the realization that the terms “intensive” and “extensive” can be ambiguous. As Jaynes (unpublished) has noted, this distinction is sometimes an anthropomorphic one, because it may depend on the particular kind of subdivision we choose to envision. A volume of air may be imagined to consist of a number of smaller contiguous volume elements, so that the pressure is the same in all subsystems, and is therefore intensive, whereas the volume is additive and hence extensive. But we may equally well regard the volume of air as composed of its constituent nitrogen and oxygen subsystems. With this kind of subdivision the volume is the same in all subsystems, while the pressure is the sum of the partial pressures of its constituents; it appears that the roles of "intensive" and "extensive" have been interchanged.

This ambiguity remains even if we consider only spatial subdivisions, such that each subsystem has the same local composition. Consider a stretched rubber band, for example, in which we imagine the rubber band as divided into small subsystems by passing planes through it normal to its axis; the tension is then the same in all subsystems, while the elongation is additive. But if the dividing planes are parallel to the axis, the elongation is the same in all subsystems, while the tension is additive, and the roles of "extensive" and "intensive" are interchanged merely by imagining a different kind of spatial subdivision.

But the issue for entropy goes beyond these matters of choice, as is seen by re-examining the so-called Gibbs "paradox." In his work on the equilibrium of heterogeneous systems, Gibbs briefly discussed the "entropy of mixing" of two ideal gases and, since his statistical mechanics was not yet fully developed, he was discussing only differences in the experimental entropy defined by (5.1). For a monatomic ideal gas with a fixed number of molecules N and equation of state $PV = NkT$, classical thermodynamics tells us that $(\partial S/\partial T)_V = C_V/T$, and $(\partial S/\partial V)_T = (\partial P/\partial T)_V$, so that the entropy difference between two equilibrium states is

$$\begin{aligned} S(T_2, V_2, N) - S(T_1, V_1, N) &= \int_1^2 \left[\left(\frac{\partial S}{\partial V} \right)_T dV + \left(\frac{\partial S}{\partial T} \right)_V dT \right] \\ &= Nk \ln \left(\frac{V_2}{V_1} \right) + \frac{3}{2} Nk \ln \left(\frac{T_2}{T_1} \right) . \end{aligned} \tag{5.3}$$

This expression will be satisfied by any function of the form

$$S(T, V, N) = kN \ln V + \frac{3}{2} Nk \ln T + C, \tag{5.4}$$

up to a constant C, to which we shall return. If we deal only with entropy differences, of course, such constants will not appear in (5.3).

Following Gibbs (*HS*, p.164), we consider two such ideal gases with equal densities $n = N_1/V_1 = N_2/V_2$ at the same constant T and P, separated by a diaphragm in a volume $V = V_1 + V_2$ (Fig. 5.1). The diaphragm is removed and eventually a new equilibrium state of the complex system is reached with $N = N_1 + N_2$ particles in volume $V = V_1 + V_2$, while the temperature, pressure,

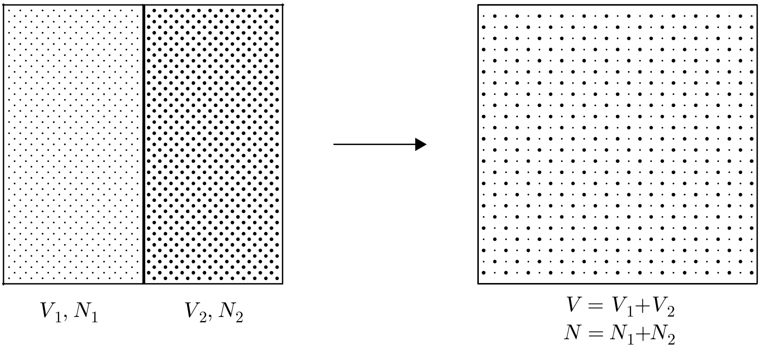

FIG. 5.1. The mixing of two different ideal gases.

and total energy remain unchanged. If the two gases are materially different our expectation that the entropies are additive leads to an entropy difference[1]

$$\begin{aligned}\Delta S \equiv S_f - S_i &= kN_1 \ln \frac{N_1 + N_2}{N_1} + kN_2 \ln \frac{N_1 + N_2}{N_2} \\ &\xrightarrow[N_1=N_2]{} \quad kN \ln 2,\end{aligned} \tag{5.5}$$

in accordance with (1.12). The second line is the case Gibbs considers, and here he notes two important points about this expression: The *entropy of mixing* is independent of the nature of the two gases; but if they are identical this result is not valid and $\Delta S = 0$. This is the origin of the Gibbs "paradox," but he never used that word, for to him it was not a paradox at all.

In the ensuing discussion Gibbs notes that when two unlike gases mix and the entropy increases there is an implication that the gases in principle could be separated again, bringing them back to their original macroscopic states at the expense of making changes in the external environment. This does not mean that each particle would be restored to its original position, however, but only that the initial macrostates would be restored; it would only be required to return each particle originally in V_1 to that volume, and likewise for V_2. Doing so, of course, would be very difficult to carry out by manipulating macroscopic variables alone.

He also sees that the situation for two identical gases is entirely different, and when we say that two identical gases mix with no change in entropy we do *not* mean that molecules originally in V_1 can be restored to V_1 without external changes. One cannot distinguish these two thermodynamic states in any event, for there has been no change in the thermodynamic state of the system. Indeed, restoration occurs by simply reinserting the diaphragm, so that the

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[1] When Gibbs wrote on this, the Boltzmann constant k had not yet been introduced by Planck, so he worked with moles and the gas constant R.

entropy change is zero. He clearly considers mixtures of like and unlike gases to be on "a different footing," indicating that comparing the two situations is not even conceptually possible.

But Gibbs also notes that for different gases there is virtually no limit to the resemblance they might have to one another, differing only in some tiny physical detail, and still lead to an entropy of mixing (5.5), independent of those details. Many writers on this problem have seen its essence to be this persistent discontinuity in ΔS as the physical characteristics of the two gases are continuously made the same. For example, Denbigh and Redhead (1989) have argued that there should be at least *some* diminution in ΔS as these changes occur. Aside from the fact that one simply cannot do this with only macroscopic control, the argument misses the point. The discontinuity here lies with what we mean by "restoring the original state," and for like gases the phrase is meaningless. In one case information is lost upon mixing, but not in the other. Only if S is interpreted as mechanical is this paradoxical.[2]

What Gibbs sees clearly and emphasizes strongly is that S is both macroscopic and statistical in nature. For ideal gases, the equation of state $PV = NkT$ is itself a macroscopic description that is the same for all ideal gases and implies no macroscopic differences for other thermodynamic functions: "In such respects, entropy stands strongly contrasted with energy." Microscopic differences, such as weak interactions among particles, make no contribution at this level, and hence we should not expect to see the entropy of mixing depend on the detailed microscopic characteristics of the gases. Of course, if the constituents of the two unlike gases interact strongly enough with one another to have a macroscopic impact, then the entropy of mixing will not be expected to have the form (5.5) in any event. Finally, by way of further emphasis on the statistical character of S, he notes that there is still a small probability that demixing could occur spontaneously for *either* like or unlike gases; there is no difference between the two cases in this respect. So, for Gibbs the physical situation is completely clear.

But the fact remains that the calculation using the Clausius definition of entropy does not agree with our intuition, and it is not difficult to see why that is. First of all, the definition (5.1) is made for constant N, and in the above mixing scenario N is changed. Second, Gibbs presumes extensivity and therefore additivity in that process, yet (5.1) itself is not necessarily extensive, except in some special cases. Only T and V are varied on the reversible path in (5.3), and hence this equation can only determine the dependence of S on those variables. In fact, if N actually varied on that path then (5.1) would have to contain an additional "entropy convection" term $\int (\mu/T)\, dN$. Ehrenfest and Trkal (1920) had already appreciated these points explicitly and noted that one must really introduce a *reversible* process in which the number of molecules changes; they were properly skeptical about the possibility of doing this.

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[2] In addition, both Gibbs and Planck later understood, and argued explicitly, that chemical differences between two substances cannot be represented by a continuous variable. This was part of the beginnings of quantum mechanics.

In his lectures *circa* 1952 Pauli (1973) seems also to have appreciated this point, for he noted that the entropy of Eq.(5.4) should really be written as

$$S(T,V,N) = k\left[N\ln V + \frac{3}{2}N\ln T\right] + kf(N), \tag{5.6}$$

where $f(N)$ is an arbitrary *function* of N. He observes that if one wishes to make the entropy extensive, then this is an additional condition that must be *imposed* by requiring that S satisfy the scaling law (5.2). Substitution of (5.6) into (5.2a), following Jaynes (1992), yields the functional equation determining $f(N)$:

$$f(qN) = qf(N) - qN\log q. \tag{5.7}$$

Both q and N range over $(0,\infty)$, so the solution for one will also hold for the other when one of them is held fixed. Let $N = 1$ in (5.7) to see the general solution also for $f(N)$,

$$f(N) = Nf(1) - N\ln N, \tag{5.8}$$

which is effectively the Stirling approximation to $\ln(N!)$. The most general extensive entropy function of the Clausius type for the ideal gas thus takes the form

$$S(T,V,N) = Nk\left[\ln\frac{V}{N} + \frac{3}{2}\ln T + f(1)\right]. \tag{5.9}$$

The single arbitrary constant $f(1)$ in this last expression is essentially the chemical constant, but it is not determined by any of the foregoing expressions. The best that can be done by dimensional analysis alone is to rewrite (5.9) as the fully extensive quantity

$$S(T,V,N) = Nk\left[\ln\frac{V}{N} + \frac{3}{2}\ln\left(\frac{mkT}{\xi^2}\right)\right], \tag{5.10}$$

where ξ is an undetermined constant with dimensions of action. Pauli also suggests that any remaining undetermined entropy constant can be evaluated by requiring the entropy of all substances to vanish as $T \to 0$ (Nernst's theorem). Note, however, that N remains a constant in (5.10).

To complement the calculation with the Clausius definition, let us attempt to verify these conclusions quantitatively via the canonical distribution, in which the theoretical maximum entropy that is taken to be equivalent to (5.1) is readily calculated from (4.19),

$$\begin{aligned} S &= k\ln Z + k\beta U \\ &= Nk\ln V + \frac{3}{2}Nk\left[1 - \ln\lambda_T^2\right], \end{aligned} \tag{5.11}$$

where $\lambda_T \equiv \left(2\pi\hbar^2/mkT\right)^{1/2}$ is the *thermal wavelength*, m is the particle mass, and expectation values are implied. Here we have noted that $Z = Z_1^N$, with

$Z_1 = \sum_j e^{-\beta E_j} = V/\lambda_T^3$, and $U = \frac{3}{2}NkT$. This calculation provides the arbitrary constant that was missing in (5.4), which contains Planck's constant and is essentially the chemical potential. When the above mixing scenario is now carried out with (5.11) we find that ΔS is the same as above, Eq.(5.5), but for *both* like and unlike gases, and hence a "paradox," perhaps.

The conventional resolution of this discrepancy begins with the realization that the quantum form of S in (5.11) also is not an extensive quantity. Yet, the Principle of Maximum Entropy (PME) taught us in (3.27) that, under the appropriate conditions on $\ln Z$, S *must* be extensive . Indeed, it can be made so by a further adjustment in (5.11). For reasons to be elucidated presently, we subtract from S a term $k\ln(N!)$ and apply Stirling's formula for large N, which leads to

$$\begin{aligned} S(T,V,N) &= \frac{3}{2}Nk + k\ln\left(\frac{V^N}{\lambda_T^{3N}N!}\right) \\ &= Nk\ln\frac{V}{N} + \frac{3}{2}Nk\left[\frac{5}{3} - \ln\lambda_T^2\right] \\ &= \frac{5}{2}Nk - N\frac{\mu}{T}. \end{aligned} \tag{5.12}$$

This is the Sakur–Tetrode equation, in which S is duly extensive. In the third line we have identified explicitly the chemical potential $\mu = \beta^{-1}\ln(n\lambda_T^3)$, where $n = N/V$ is the particle-number density; note that this term is very similar to the entropy convection term mentioned above. The procedure here is much like that of Pauli applied to the Clausius definition, but now the quantum-mechanical calculation has obtained the chemical potential correctly and it contains $\hbar$. We also note that the factor of 5/2 accounts correctly for the vapor pressure of monatomic solids.

Now when the two gases are mixed and ΔS is calculated using (5.12) we find the expected behavior: $(\Delta S)_{1\neq 2} = kN\ln 2$ and $(\Delta S)_{1=2} = 0$, and the "paradox" is resolved. To see this, notice that for a mixture of different independent gases the factor of $N!$ in (5.12) is replaced by $N_1!N_2!$, rather than $(N_1+N_2)!$. In the case of different gases something has indeed been lost, namely, information.

So, what went wrong in (5.11)? And from where does this term in $\ln(N!)$ originate? The answer must lie with evaluation of the partition function, which we recall from (4.22) is written as a sum over all distinct global energy states,

$$Z(\beta) = \sum_i g_i e^{-\beta E_i}. \tag{5.13}$$

Although g_i counts all possible microstates that have the same total energy E_i, it still necessarily includes even those that differ only by an exchange of identical particles, for the original sum (4.21) was over all *possible* microstates. If $\overline{g}_i$ counts only those microstates with energy E_i that do not differ merely by exchange of particles, then in (5.13) there is an evident factorization $g_i = N!\,\overline{g}_i$. If identical particles are presumed indistinguishable, those $N!$ states should not be counted separately and the partition function should indeed be reduced by that factor; were it not, there would be a serious conflict with the Third Law as well, which has also been noted by Kastler (1983). This is the first indication that the focus should perhaps not be on the indistinguishability of particles, but of states, as already realized by Gibbs in the quotation at the beginning of this chapter. The proper method of extracting this factor of $N!$ in classical statistical mechanics is discussed, for example, by van Kampen (1984), although our conclusions differ from many of his.

Before continuing with this line of thought let us look more closely at the traditional approach that views the origin of $\ln(N!)$ as residing within quantum-statistical mechanics, the notion of indistinguishable *particles*, and the symmetrization postulate for many-body wavefunctions. That is, the state vectors describing two or more bosons must be completely symmetric, and those for fermions must be completely antisymmetric. When N-particle symmetrized state vectors are properly normalized so that the trace of the density matrix is unity, the trace of any other operator A is given by (*e.g.*, Grandy, 1987)

$$\mathrm{Tr}A = \frac{1}{N!} \sum_{\lambda_1 \cdots \lambda_N} \left[\sum_{P'} \varepsilon^{p'} \, P' \langle \lambda_1 \cdots \lambda_N | A | \lambda_1' \cdots \lambda_N' \rangle \right]_{\lambda_i' = \lambda_i} , \tag{5.14}$$

where P' is a permutation operator acting upon the single-particle quantum numbers $\{\lambda_i'\}$, and the sum goes over all such permutations. The quantity ε is $+1$ for bosons and -1 for fermions, and the factor $\varepsilon^{p'}$ is the *signature* of the permutation; that is, since every permutation can be written as a product of transpositions, p' is the number of those in P' and the factor is just ± 1. If one now adopts the view that the limit of classical statistics does not require symmetrization of the many-particle states, then omission of all save the identity permutation in (5.14) yields

$$\big(\mathrm{Tr}A\big)_{\mathrm{B}} = \frac{1}{N!} \sum_{\lambda_1 \cdots \lambda_N} \langle \lambda_1 \cdots \lambda_N | A | \lambda_1 \cdots \lambda_N \rangle . \tag{5.15}$$

The subscript B denotes the *Boltzmann limit*, which we take to be the correct classical limit.[3] Generalization to the multicomponent system in (4.27) is straightforward, the result being a product of factors $(N_\alpha!)^{-1}$. We note that the context in (5.15) may still be quantum mechanical, for it is only the *quantum-statistical* nature of the state vectors that is approximated, while the identical nature of the particles remains. Symmetrization becomes necessary when wavefunctions can overlap; that is, when the thermal de Broglie wavelength exceeds the average interparticle spacing: $n\lambda_T^3 \gtrsim 1$.

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[3] There remains a small error in (5.15) owing to the neglect of all permutations, but it is completely negligible in $\ln Z$ and for large N (Kroemer, 1980; Grandy, 1981).

We note that (5.15) is equivalent to normalizing both sides of (5.13) by $N!$ and writing

$$\frac{Z}{N!} = \sum_i \overline{g}_i e^{\beta E_i}. \tag{5.16}$$

Although the left-hand side of this expression seems to correspond to the way Nature counts its possible states, the sum would be rather difficult to calculate under this constraint. But the left-hand side tells us that we can accomplish this by computing the original Z, in which the sum is to go over *all possible* microstates, and then divide by $N!$. We also see that this correct way to count states must also be extended to the multiplicity factor W, as can be seen from (4.34) in which both sides are proportional in the limit to the maximum entropy per particle. This does not mean that the high-probability manifold of compatible microstates itself does not contain these $N!$ states that differ merely by an exchange of identical particles, but only that its measure does not overcount them. The only way to make sense of such an assertion is to adopt the view that in the discussion of Boltzmann's theorem, (5.16) is to be taken into account and (4.31) should really contain $\overline{g}_i$. Thus, at least tacitly, we must consider W to be normalized by $N!$, so that Boltzmann's entropy expression (4.35) is compatible with (5.12). This in turn means that Planck's comment following (1.19) is not quite correct, for the additional constant $N \ln N - N$ is not insignificant, a conclusion already suggested by (5.8).

Having found a formal origin of this correction term, we can inquire into its possible physical significance. Is there some deep connection between the notion of identical particles and extensivity? Although the answer is not yet completely settled, the question has received a great deal of attention that serves to at least sharpen the issue.

Boltzmann (1897) had established as his first principle of mechanics that a system could consist of identical or similar particles, in the sense that they had equal mass, charge, and so on, but that that they could always be distinguished one from the other. Just how this is to be accomplished in practice is not made clear, but it serves as a very useful artifice in classical mechanics where we employ distinct coordinates (q_i, p_i) for each particle in phase space.

Gibbs subsequently realized that the presumption of distinguishability may be flawed and, in fact, introduced the $N!$ correction in his statistical mechanics book, following a discussion of classical indistinguishability. In *SM* (p.188) he makes "the supposition that phases [*i.e.*, states] are *not* altered by the exchange of places between similar particles." Although Gibbs could not have anticipated the deeper meaning later given to the concept "state of a system," we can detect in his last work the beginnings of a subtle shift of emphasis from particle to state. He distinguishes between "generic" phases that are not altered by permutation of the particles, and "specific" phases that are considered to be different if particles are interchanged. For example, in a single-component system there are $N!$ specific phases comprising a generic phase. The above correction factor then appears when he insists that the entropy must be associated only with generic phases. He also observes that equilibrium with respect to generic phases does not imply equilibrium with respect to specific phases, although the converse is true. This is now obvious, of course, given that the sets over which S_I is varied differ in the two cases. Thus, Gibbs had already anticipated our conclusions above.

While Boltzmann considered particles to be distinguishable, it is clear from his expression (1.17) that interchanging identical particles in a single energy cell did not constitute a different state. But Gibbs has gone one step further, for he effectively observes that exchanging particles *between* cells does not lead to a new state, and that indeed is a precursor of the notion of identical but indistinguishable particles in quantum statistics. This story has been recounted at some length by Pešić (1991), as well as by Kastler (1983).

The above discussion in the final chapter of his book is where Gibbs introduces the grand canonical distribution (GCD), wherein the number of particles in the system can also vary. One might suppose that calculating the entropy with the GCD would serve to resolve the above extensivity issue by itself, and indeed if one pursues this the entropy is found to be given exactly by the third line in (5.12), for free particles. Unfortunately, the same calculation for the two-component system does not lead to the correct resolution of our mixing problem. Gibbs notices this as well, although not explicitly.

In view of the foregoing discussion, this seems a good point to expand on the notions of "identical" and "distinguishable." There should be no difficulty with the former, either classically or quantum mechanically, for it simply means that two particles have all the same fixed physical properties, such as mass, spin, charge, and so on. In classical mechanics we take the additional view that it is always possible to distinguish two such individual particles. In quantum theory this is thought not to be possible if the particles' wavefunctions overlap sufficiently, thereby leading to symmetrized wavefunctions and the Pauli principle. But "distinguish" is basically an active verb requiring someone or something to actually make a distinction, and then the question arises as to who or what is to make that distinction. This becomes rather a sticky situation if we insist that, just because the physicist cannot distinguish between two particles, neither can Nature do so. A more extensive discussion of individuality has been provided by Post (1963).

We can certainly distinguish between an electron here and one on the Moon, but if they are brought into close proximity and described by a two-particle state it becomes difficult, if not impossible, to distinguish that state from one in which the two are interchanged. This suggests that it is not the identical particles that should be considered indistinguishable, but the states. For reasons that are not yet entirely clear, our theories are required to describe the many-particle microstates of Nature in such a way that states differing only in the exchange of two identical particles are one and the same state. This is true in both classical and quantum theories where identical particles are concerned, and independent of whether or not such states need be symmetrized. When wavefunctions overlap, then Nature also requires symmetrized states; deeper reasons for this, as well as for the Pauli principle, remain elusive. Aside from that, the role of the $N!$ factor would seem to be well understood.

The issues of identicality and distinguishability are really independent from the question of extensivity, even though they appear to be related in the present discussion. While extensivity can often be a desirable, even important property of a macroscopic system, its failure surely does not affect those other issues. In systems and processes in which surface effects are important, or in hydrodynamic systems where boundaries play crucial roles, one cannot expect extensivity. Nor can one find that property when particle interactions have a long-range character. Nevertheless, particle identity will persist in any of these systems.

The effect of these musings is to convince us that a proper definition of entropy should at bottom be theoretical, and not based on the incomplete expression of Clausius, Eq.(5.1). As Jaynes (1992) has pointed out in his discussion of this problem, it would be very difficult for any phenomenological theory based on a finite number of observations to provide a complete and general definition of entropy. It is not an empirical question, but a conceptual one. There are different ways one might approach this, and the view expressed here is that we should strive for a statistical theory based soundly on the principles of probability theory, in which S is a function of the macrovariables employed to define the macrostate and satisfies a variational principle: It is the upper bound of $-k\mathrm{Tr}(\rho\log\rho)$ over all density matrices in agreement with those macrovariables. The proper states over which to evaluate the trace are dictated by the Pauli exclusion principle and the symmetrization postulate; these provide additional microscopic conditions on the content of W, as discussed following (4.36). This result will automatically provide all the extra terms needed to analyze any system described by that macrostate, and will agree with both the Clausius and Pauli expressions in those cases where they are appropriate. If processes in which N varies are included in the macroscopic description, as in the GCD, guidance for what should be included in the experimental entropy is immediate; the matter of extensivity takes care of itself.[4] Questions about how to measure entropy changes are addressed by the macroscopic thermodynamic equations themselves.

The mathematical expression of these conclusions is provided by Eq.(3.27) in its application to a thermodynamic system. As noted following (4.19), most effective particle-particle interactions encountered in Nature lead to an extensive entropy in the limit of a very large system. An exception to this result is the gravitational interaction, whose long-range character understandably precludes extensivity (Levy-Leblond, 1969; Hertel and Thirring, 1971); in a system with Coulomb interactions, overall charge neutrality is known to lead to an effective short-range interaction.

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[4] For example, in a photon gas $S(T,V,E)$ is automatically homogeneous of degree 1, presumably because particle number is not conserved.

6

NONEQUILIBRIUM STATES

> *At some point the thought arose (and we confess our ignorance about how it arose and by whom) that it ought to be possible to define an entropy function rigorously for* non*equilibrium states ...*
>
> *E.H. Lieb and J.Yngvason (2003)*

An understanding of entropy at this point has been based strongly on the realization that a probability distribution depends crucially on the information (or hypothesis) that goes into its construction. This is recognized by denoting the probability of an alternative proposition A_i based on prior information I as $P(A_i|I)$. Although the form this information takes has been considered primarily as expectation values, it is certainly possible for I to depend on various parameters and variables. While this has been implicit in our previous work, we now examine it explicitly and confirm the expectations of the above authors.

Although Gibbs was silent as to the rationale for his variational principle, his intent was quite clear: to define and construct a description of the equilibrium state. That is, the Principle of Maximum Entropy (PME) provides a criterion for that state. In the context of the basic probability theory it is also the means for constructing an *initial* probability distribution based on available information, but this aspect is not emphasized in the equilibrium theory. If, for example, in the canonical distribution of (4.16) there is no restriction to constants of the motion, the resulting state described could just as well be one of nonequilibrium based on information at some particular time or place; this is often thought of as a "local equilibrium" distribution (e.g., Mori et al., 1962). Data given only at a single point in space and time, however, can hardly serve to characterize a system whose properties are varying over a space-time region—the resulting density matrix contains no information as to this possibility. The Gibbs variational principle, or PME, is readily applied to information that varies continuously, however, which is then incorporated into a density matrix describing a nonequilibrium state. Given an arbitrary but definite thermokinetic history, we can look for what general behavior of the system can be deduced from only this. That is, based only on past behavior in some spatial region, what can we say about the future elsewhere? The origin of this space-time variation in the data is not addressed at this point. The essential aspects of this construction were first expounded by Jaynes (1963, 1967, 1979).

To illustrate the method of information gathering, consider a system with a fixed time-independent Hamiltonian and suppose the data to be given over a space-time region $R(\boldsymbol{x}, t)$ in the form of an expectation value of a Heisenberg operator $F(\boldsymbol{x}, t)$, which could, for example, be a density or a current. We are reminded that the full equation of motion for such operators, if they are also explicitly time varying, is

$$i\hbar\dot{F} = [F, H] + \partial_t F, \tag{6.1}$$

and the superposed dot will always denote a total time derivative. When the input data vary continuously over R their sum becomes an integral and there is a distinct Lagrange multiplier for each space-time point. Maximization of the entropy subject to the constraint provided by that information leads to a density matrix describing this macrostate:

$$\rho = \frac{1}{Z}\exp\left[-\int_R \lambda(\boldsymbol{x}, t)F(\boldsymbol{x}, t)\, d^3x\, dt\right], \tag{6.2a}$$

where

$$Z[\lambda(\boldsymbol{x}, t)] = \operatorname{Tr}\exp\left[-\int_R \lambda(\boldsymbol{x}, t)F(\boldsymbol{x}, t)\, d^3x\, dt\right] \tag{6.2b}$$

is now the *partition functional.* The Lagrange-multiplier *function* $\lambda(\boldsymbol{x}, t)$ is identified as the solution of the functional differential equation

$$\langle F(\boldsymbol{x}, t)\rangle \equiv \operatorname{Tr}[\rho F(\boldsymbol{x}, t)] = -\frac{\delta}{\delta\lambda(\boldsymbol{x}, t)}\ln Z\,, \qquad (\boldsymbol{x}, t) \in R, \tag{6.3}$$

and is defined only in the region R. Note carefully that the data set denoted by $\langle F(\boldsymbol{x}, t)\rangle$ is a numerical quantity that has been equated to an expectation value to incorporate it into a density matrix. Any other operator $J(\boldsymbol{x}, t)$, including $J = F$, is determined at any other space-time point $(\boldsymbol{x}, t)$ as usual by $\langle J(\boldsymbol{x}, t)\rangle = \operatorname{Tr}\big[\rho J(\boldsymbol{x}, t)\big] = \operatorname{Tr}\big[\rho(t) J(\boldsymbol{x})\big]$. That is, the system with fixed H still evolves unitarily from the initial nonequilibrium state (6.2): $\rho(t) = U(t)\rho U^\dagger(t)$, and for $H \neq H(t)$, $U(t) \to \exp(-itH/\hbar)$. Although ρ may no longer commute with H, its eigenvalues nevertheless remain unchanged.

Inclusion of a number of operators F_ℓ, each with its own information-gathering region R_ℓ and its own Lagrange multiplier function λ_ℓ, is straightforward, and if the data are time independent ρ can describe an inhomogeneous equilibrium system, as discussed later in this chapter. The question is sometimes raised concerning exactly which functions or operators should be included in the description of a macroscopic state, and the short answer is: Include all the relevant information available, for the PME will automatically eliminate that which is redundant or contradictory. A slightly longer answer was provided by Jaynes (1957b) in his second paper introducing information-theoretic ideas into statistical mechanics. He defined a density matrix providing a definite probability assignment for each possible outcome of an experiment as *sufficient* for that experiment. A density matrix that is sufficient for all conceivable experiments on a physical system is called *complete* for that system. Both sufficiency and completeness are defined relative to the initial information, and the existence of complete density matrices presumes that all measurable quantities can be represented by Hermitian operators and that all experimental measurements can be expressed in terms of expectation values. But even if one could, in principle, employ a complete density matrix it would be extremely awkward and inconvenient to do so in practice, for that would require a much larger function space than necessary. If the system is nonmagnetic and there are no magnetic fields present, then there is no point to including those coordinates in a description of the processes of immediate interest, but only those that are sufficient in the present context. The great self-correcting feature of the PME is that if subsequent predictions are not confirmed by experiment, then this is an indication that some relevant constraints have been overlooked or, even better, that new physics has been uncovered.

The form (6.2) illustrates how ρ naturally incorporates (fading) memory effects while placing no restrictions on spatial or temporal scales. But this density matrix is definitely *not* a function of space and time; it merely provides an initial nonequilibrium distribution corresponding to data $\langle F(\boldsymbol{x},t)\rangle$ in R. That is, S_I is maximized subject to constraints at every point in R. If the relevant time interval in R is (t_1,t_2), say, then (6.2) describe the nonequilibrium macroscopic state of the system at $t=t_2$, but in terms of the known history of $\langle F(\boldsymbol{x},t)\rangle$ over that interval. Expectation values of F, or of any other variable C, for $t>t_2$ will depend strongly on that past history—this becomes especially transparent in the linear approximation (below). Lack of any further information outside of R, such as in the future, may render ρ less and less reliable, of course, so near-term predictions would certainly be of primary interest. Nevertheless, (6.2) represent a straightforward extension of the Gibbs variational principle to construction of nonequilibrium states.

The maximum entropy itself is a functional of the initial values $\langle F(\boldsymbol{x},t)\rangle$ in R and follows from substitution of (6.2) into the information entropy:

$$S[\{\langle F\rangle\}] \equiv k\ln Z[\lambda] + k\int_R \lambda(\boldsymbol{x},t)\langle F(\boldsymbol{x},t)\rangle\, d^3x\, dt, \tag{6.4}$$

which also provides an alternative determination of λ,

$$k\lambda(\boldsymbol{x},t) = \frac{\delta S}{\delta\langle F(\boldsymbol{x},t)\rangle}. \tag{6.5}$$

Although S clearly contains all the thermokinetic history of the system provided by $\langle F(\boldsymbol{x},t)\rangle$, it is still just a number; but as a functional of that history it is much richer. If we imagine the evolution of a microstate as a path in “phase space-time,” then there will be a great many such paths compatible with the observed macroscopic trajectory described by $\langle F(\boldsymbol{x},t)\rangle$. As suggested by Fig. 4.1, we can visualize the evolution of the system in terms of a bundle of these possible trajectories, now enclosed in a tube of varying cross section. Because S_I has been maximized throughout R, S is seen to be the measure of that cross section along this tube. Although one can envision taking such a “slice” at any point along the tube, the full history is acquired only at $t = t_2$ where S is given by (6.4). At this point, $S = k \ln W$ is again a measure of all microstates compatible with the available information at $t = t_2$, but these states are now seen to be the endpoints of all those possible microscopic trajectories. It is the tube itself that represents the evolution of the macroscopic system, an observation that eventually leads to a definition of time-dependent entropy in Chapter 9. We begin to see that here, unlike the equilibrium situation, entropy is intimately related to *processes.*[1] Jaynes (1980) has referred to S in this context as the *caliber* of that history, a term we shall not find advantageous to use here.

6.1 The linear approximation

Much, though not all, of the work on macroscopic nonequilibrium phenomena has of necessity centered on small departures from equilibrium, or the linear approximation, so it is of some value to outline that reduction of the present theory. Preliminary to that, however, let us approach this program in a more intuitive way. Suppose the equilibrium distribution to be based on expectation values of two variables, $\langle f\rangle$ and $\langle g\rangle$, with corresponding Lagrange multipliers λ_f, λ_g. We also suppose that no generalized work is being done on the system, so that only "heat-like" sources may operate. A small change from the equilibrium distribution can be characterized by small changes in the Lagrange multipliers, which in turn will induce small variations in the expectation values. Thus,

$$\delta\langle f\rangle = \frac{\partial\langle f\rangle}{\partial\lambda_f}\delta\lambda_f + \frac{\partial\langle f\rangle}{\partial\lambda_g}\delta\lambda_g, \tag{6.6a}$$

$$\delta\langle g\rangle = \frac{\partial\langle g\rangle}{\partial\lambda_f}\delta\lambda_f + \frac{\partial\langle g\rangle}{\partial\lambda_g}\delta\lambda_g. \tag{6.6b}$$

But from (3.28) the negatives of these derivatives are just the covariances of f and g, so (6.6) reduce to the matrix equation

$$\begin{pmatrix}\delta\langle f\rangle\\ \delta\langle g\rangle\end{pmatrix} = -\begin{pmatrix}K_{ff} & K_{fg}\\ K_{gf} & K_{gg}\end{pmatrix}\begin{pmatrix}\delta\lambda_f\\ \delta\lambda_g\end{pmatrix}. \tag{6.7}$$

Substitution of this last result into the concavity condition (3.32) for the entropy maximum yields the inequality $\delta\lambda \cdot K \cdot \delta\lambda > 0$, and K is a symmetric positive-definite matrix. Thus, K in (6.7) can now be inverted to obtain the "forces" $\delta\lambda$. That is, the Lagrange multipliers are uniquely determined by $\langle f\rangle$ and $\langle g\rangle$, as in the fundamental equations (3.14). We also see that, from (3.30), $\delta\langle f\rangle \cdot G \cdot \delta\langle f\rangle > 0$, where G is the matrix inverse of K.

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[1] A similar functional formalism was also developed by Zubarev at about the same time (Zubarev and Kalashnikov, 1970; Zubarev *et al.*, 1996), as an *ad hoc* mechanism that initially appealed to the PME. But the deeper role of the maximum information entropy, as well as the underlying probability theory, seems to have been abandoned, thereby denying the theory a cogent justification and a broader range of applications.

We shall see in Chapter 12 that this small departure from equilibrium corresponds to similar equations obtained in the phenomenological theories of irreversible processes. In that sense, $\delta\langle f\rangle$ corresponds to a "flux" and $\delta\lambda$ to the associated "force," thus characterizing λ as a "potential." Proceeding now to the more formal theory, we envision situations in which the system has been in thermal equilibrium in the remote past and later found to produce a single datum of the form $\langle F(\boldsymbol{x},t)\rangle$. By considering both classes of data we obtain a measure of the departure from equilibrium, expressed by rewriting (6.2) as

$$\begin{aligned} \rho &= \frac{1}{Z}\exp\left[-\beta H - \int_R \lambda(\boldsymbol{x},t)F(\boldsymbol{x},t)\,d^3x\,dt\right]\,, \\ Z[\lambda(\boldsymbol{x},t)] &= \operatorname{Tr}\exp\left[-\beta H - \textstyle\int_R \lambda(\boldsymbol{x},t)F(\boldsymbol{x},t)\,d^3x\,dt\right]. \end{aligned} \tag{6.8}$$

If the integral in the exponentials is small in some sense, representing a small departure from equilibrium, we can employ the perturbation expansion developed in Appendix A. To leading order, the expectation value of some other operator $C(\boldsymbol{x},t)$ is

$$\langle \Delta C(\boldsymbol{x},t)\rangle = -\int_R K^0_{CF}(\boldsymbol{x},t;\boldsymbol{x}',t')\lambda(\boldsymbol{x}',t')\,d^3x'\,dt', \tag{6.9}$$

where $\Delta C = C(\boldsymbol{x},t) - \langle C(\boldsymbol{x})\rangle_0$ is the *deviation* from the equilibrium value, and

$$K^0_{CF}(\boldsymbol{x},t;\boldsymbol{x}',t') = \langle \overline{F(\boldsymbol{x}',t')}C(\boldsymbol{x},t)\rangle_0 - \langle F(\boldsymbol{x}')\rangle_0\langle C(\boldsymbol{x})\rangle_0 \tag{6.10}$$

is called the (linear) *covariance function*; it generalizes the covariances of (3.28), and (6.9) formalizes (6.7). The overbar on F denotes a Kubo transform that arises from the possible noncommutativity of the operators, and which is defined in (A.9); a more useful representation for present purposes is given by

$$\overline{F(\boldsymbol{x},t)} \equiv \int_0^1 e^{-u\ln\rho}\,F(\boldsymbol{x},t)e^{u\ln\rho}\,du. \tag{6.11}$$

Subscripts (and superscripts) 0 indicate that all expectation values on the right-hand sides of (6.9) and (6.10) are to be taken in the equilibrium system described by $\rho_0 = e^{-\beta H}/Z_0$. If C and F are both Hermitian, as is usually presumed, then K^0_{CF} is real, and $K^0_{CC} \geq 0$ if both operators are evaluated at the same space-time point.

The linear prediction (6.9) illustrates explicitly how the expectation value depends on the past history of the system: Correlations of C with F over the entire region R contribute to the integral.

When one proceeds beyond the canonical and grand canonical distributions of Chapter 4, the covariance functions become the fundamental entities of statistical mechanics. From the form of (6.9) it is clear that they govern the linear response of the system to any external disturbance. Because K^0_{CF} is a creature of the equilibrium system, the space-time symmetries of the latter induce a number of useful properties in these functions. The initial equilibrium system is usually presumed to be homogeneous and isotropic, so that the total energy and number operators, as well as the total momentum operator P, commute with one another. This in turn suggests time and space translation invariance, transformations generated, respectively, by the unitary operators

$$U(t) = e^{-iHt/\hbar}, \qquad U(\boldsymbol{x}) = e^{-i\boldsymbol{x}\cdot\boldsymbol{P}/\hbar}, \tag{6.12}$$

and $F(\boldsymbol{x},t) = U^\dagger(\boldsymbol{x})U^\dagger(t)\, F\, U(t)U(\boldsymbol{x})$. Translation invariance, along with (6.11) and cyclic invariance of the trace, provide two further simplifications: The single-operator expectation values are independent of $\boldsymbol{x}$ and t in an initially homogeneous system, and the arguments of K^0_{CF} can now be taken as

$$\boldsymbol{r} \equiv \boldsymbol{x} - \boldsymbol{x}', \qquad \tau \equiv t - t'. \tag{6.13}$$

The operators usually encountered in covariance functions possess definite transformation properties under space inversion (parity) and time reversal (see Appendix B). Under the former, $A(\boldsymbol{r},\tau)$ becomes $P_A A(-\boldsymbol{r},\tau)$, $P_A = \pm 1$; and under the latter, $T_A A(\boldsymbol{r},-\tau)$, $T_A = \pm 1$. Under these transformations

$$\begin{aligned} K^0_{AB}(\boldsymbol{r},\tau) &= P_A P_B K^0_{AB}(-\boldsymbol{r},\tau) = T_A T_B K^0_{AB}(\boldsymbol{r},-\tau) \\ &= P_A P_B T_A T_B K^0_{AB}(-\boldsymbol{r},-\tau) = K^0_{BA}(-\boldsymbol{r},-\tau). \end{aligned} \tag{6.14}$$

For operators having $PT = +1$, we verify the full reciprocity relation

$$K^0_{CF}(\boldsymbol{r},\tau) = K^0_{FC}(\boldsymbol{r},\tau). \tag{6.15}$$

The linear expression (6.9) itself possesses a deeply intuitive interpretation in the pure probability context, which is revealed most clearly by temporarily omitting the spatial variables. In the absence of external driving, the Lagrange multiplier function $\lambda(t)$ is determined formally by (6.3), but one suspects that if we set $C = F$ and restrict t to the region R, then (6.9) becomes a Fredholm integral equation determining $\lambda(t)$ in the only interval in which it is defined. This indeed turns out to be the case, though the demonstration that the two procedures are equivalent requires a little effort (Grandy, 1988). This is, in fact, a very rich result, and to discuss it in slightly more detail, it will be convenient to specify $R(t)$ more definitely, as $[-T, 0]$, say. Thus, the expression

$$\langle F(t)\rangle - \langle F\rangle_0 = -\int_{-T}^{0} K^0_{FF}(t-t')\lambda(t')\,dt' \tag{6.16}$$

is now seen to have several interpretations as t ranges over $(-\infty,\infty)$. When $t > 0$ it gives the predicted future of $F(t)$; with $-T \le t \le 0$ it provides a linear integral equation determining $\lambda(t)$; and when $t < -T$ it yields the retrodicted past of $F(t)$. This last observation underscores the facts that $K^0_{FF}(t)$ is not necessarily a causal function unless required to be so, and that these expressions are based on probable inference; in physical applications the dynamics enters into computation of the covariance function, but does not dictate its interpretation in various time domains. Although physical influences must propagate forward in time, logical inferences about the present can affect our knowledge of the past as well as the future. Retrodiction, of course, is at the heart of fields such as archaeology, cosmology, geology, and paleontology. We emphasize once again that $\langle F(t)\rangle$ for $t > 0$ is simply a prediction based only on information provided in the interval $R(t)$; it is *not* a dynamically evolving quantity for later times. The causal properties of $K^0_{CF}(t)$ are investigated further in Appendix C.

6.2 Simple fluids

The preceding formalism finds a very useful and explicit application in the context of a simple fluid, which will be defined more explicitly presently. A convenient way to formulate this theory is in terms of creation operators $a_i^\dagger$ and annihilation operators a_i for single-particle states i (*e.g.*, Fetter and Walecka, 1971). These operators satisfy commutation relations $[a_i^\dagger, a_j^\dagger] = [a_i, a_j] = 0$, $[a_i, a_j^\dagger] = \delta_{ij}$, where the commutator is defined generally as

$$[A, B] \equiv AB - \varepsilon BA, \tag{6.17}$$

with $\varepsilon = +1\,(-1)$ for bosons (fermions). For time-independent H, time evolution is described by

$$a_i(t) = e^{itH/\hbar}\, a_i e^{-itH/\hbar}, \tag{6.18}$$

and similarly for creation operators. The Hermitian product $N_i \equiv a_i^\dagger a_i$ defines the number operator for the ith state, and has as eigenvalues occupation numbers n_i, which specify the total number of particles in the various single-particle states $|\lambda_i\rangle$. The total-number operator is then

$$N \equiv \sum_i N_i = \sum_i a_i^\dagger a_i, \tag{6.19}$$

and the sum goes over the complete set of single-particle states.

The Hamiltonian generally has the form $H = H_0 + V_1 + V_2$, containing one- and two-body interactions, and has the representation

$$H_0 + V_1 = \sum_{\lambda_i \lambda_k} a_i^\dagger a_k \langle\lambda_i|H_0 + V_1|\lambda_k\rangle, \tag{6.20}$$

$$V_2 = \frac{1}{2} \sum_{\substack{\lambda_i\lambda_j \\ \lambda_k\lambda_\ell}} a_k^\dagger a_\ell^\dagger \langle\lambda_k\lambda_\ell|\hat{V}_2|\lambda_i\lambda_j\rangle a_j a_i. \tag{6.21}$$

The single-particle states $|\lambda_i\rangle$ are usually taken as eigenstates of H_0, so that $\langle\lambda_i|H_0|\lambda_j\rangle = \delta_{ij}\omega_i$ where $\omega_i \equiv p_i^2/2m$ is a free-particle energy for particles of mass m. The remaining matrix elements are, in terms of single-particle wavefunctions ϕ_{λ_i},

$$\langle\lambda_i|V_1|\lambda_j\rangle = \int \phi^*_{\lambda_i}(\boldsymbol{x})V_1(\boldsymbol{x})\phi_{\lambda_k}(\boldsymbol{x})\,d^3x \tag{6.22}$$

$$\langle\lambda_k\lambda_\ell|V_2|\lambda_i\lambda_j\rangle = \int\int \phi^*_{\lambda_k}(\boldsymbol{x}_1)\phi^*_{\lambda_\ell}(\boldsymbol{x}_2)V_2(\boldsymbol{x}_1,\boldsymbol{x}_2)\phi_{\lambda_i}(\boldsymbol{x}_1)\phi_{\lambda_j}(\boldsymbol{x}_2)\,d^3x_1\,d^3x_2. \tag{6.23}$$

Many processes in fluids are most readily described in the coordinate representation, so we introduce field operators as follows:

$$\psi(\boldsymbol{x}) \equiv \sum_i \phi_i(\boldsymbol{x})a_i\,, \qquad \psi^\dagger(\boldsymbol{x}) \equiv \sum_i \phi^*_i(\boldsymbol{x})a^\dagger_i. \tag{6.24}$$

The coefficients are just single-particle wavefunctions normalized to the system volume and belonging to a complete set. The sums range over that complete set and it should be remembered that implicitly the ϕ_i are actually $(2s+1)$-component wavefunctions for particles of spin s, normalized to the system volume. The field operators satisfy the following commutation relations:

$$[\psi(\boldsymbol{x}),\psi(\boldsymbol{x}')] = [\psi^\dagger(\boldsymbol{x}),\psi^\dagger(\boldsymbol{x}')] = 0\,, \quad [\psi(\boldsymbol{x}),\psi^\dagger(\boldsymbol{x}')] = \delta(\boldsymbol{x}-\boldsymbol{x}'). \tag{6.25}$$

One can employ the classical expressions for various quantities in order to deduce their operator forms. For example, from the classical expression for the number density, $n(\mathbf{x}) = \sum_{i=1}^N \delta(\mathbf{x}-\mathbf{x}_i)$, we deduce the following form for the number-density operator:

$$n(\boldsymbol{x}) \equiv \psi^\dagger(\boldsymbol{x})\hat{\psi}(\boldsymbol{x}). \tag{6.26}$$

Time dependence of all field operators follows immediately from (6.24) and (6.18), so that the complete forms of the three locally conserved density operators, number, particle current, and energy, respectively, are

$$n(\boldsymbol{x},t) = \psi^\dagger(\boldsymbol{x},t)\psi(\boldsymbol{x},t)\,, \qquad \boldsymbol{j}(\boldsymbol{x},t) \equiv \frac{i\hbar}{2m}[(\nabla\psi^\dagger)\psi - \psi^\dagger(\nabla\psi)], \tag{6.27}$$

$$h(\boldsymbol{x},t) \equiv \frac{\hbar^2}{2m}(\nabla\psi^\dagger)\cdot(\nabla\psi) + \frac{1}{2}\int V_2(\boldsymbol{x},\boldsymbol{x}')\psi^\dagger(\boldsymbol{x},t)n(\boldsymbol{x}',t)\psi(\boldsymbol{x},t)\,d^3x'. \tag{6.28}$$

The momentum density is just $m\boldsymbol{j}(\boldsymbol{x},t)$. The total number operator N, the Hamiltonian H, and the total momentum operator $\boldsymbol{P}$ are given, respectively, by

$$N \equiv \int \psi^\dagger(\boldsymbol{x},t)\psi(\boldsymbol{x},t)\,d^3x, \quad H = \int h(\boldsymbol{x},t)\,d^3x\,, \quad \boldsymbol{P} \equiv \int m\boldsymbol{j}(\boldsymbol{x},t)\,d^3x. \tag{6.29}$$

These three global operators commute with one another and, according to (6.12), in the absence of external forces they are independent of time. If, along with translation invariance, H is also rotationally invariant, these properties define a simple fluid. All three density operators possess the symmetry $PT = 1$, so that the reciprocity relation (6.15) characterizes this system.

The locally conserved densities all have definite equations of motion which are simply the standard Heisenberg equations (6.1). Usually there is no explicit time dependence, so that in the Heisenberg picture

$$\dot{n}(\boldsymbol{x},t) = \frac{i}{\hbar}[H, n(\boldsymbol{x},t)], \tag{6.30a}$$

$$m\dot{\boldsymbol{j}}(\boldsymbol{x},t) = \frac{i}{\hbar}[H, m\boldsymbol{j}(\boldsymbol{x},t)], \tag{6.30b}$$

$$\dot{h}(\boldsymbol{x},t) = \frac{i}{\hbar}[H, h(\boldsymbol{x},t)]. \tag{6.30c}$$

But the left-hand sides of these equations are also involved in statements of the local microscopic conservation laws in the continuum, which usually relate time derivatives of densities to divergences of the corresponding currents. The differential conservation laws are thus obtained by evaluating the commutators on the right-hand sides in the forms

$$\dot{n}(\boldsymbol{x},t) = -\boldsymbol{\nabla}\cdot\boldsymbol{j}(\boldsymbol{x},t), \tag{6.31a}$$

$$m\dot{\boldsymbol{j}}(\boldsymbol{x},t) = -\boldsymbol{\nabla}\cdot\boldsymbol{T}(\boldsymbol{x},t), \tag{6.31b}$$

$$\dot{h}(\boldsymbol{x},t) = -\boldsymbol{\nabla}\cdot\boldsymbol{q}(\boldsymbol{x},t). \tag{6.31c}$$

The superposed dot in these equations denotes a total time derivative, and in the absence of external forces and sources (6.30) are equivalent to unitary transformations.

The current density $\boldsymbol{j}$ is just the usual quantum-mechanical probability current density (6.27), so that (6.31a) is easily verified. Identification of the energy current density $\boldsymbol{q}$ and stress tensor $\boldsymbol{T}$, however, is far from straightforward; in fact, they may not be uniquely defined for arbitrary particle–particle interactions. But if the Hamiltonian is rotationally invariant we can restrict the discussion to spherically symmetric 2-body potentials in a simple fluid, and the dissipative current operators $\boldsymbol{q}$ and $\boldsymbol{T}$ can be identified uniquely by evaluation of the commutators in Eqs.(6.30b,c); the algebra is tedious and the results are exhibited in Appendix B. Thus, the five local microscopic conservation laws (6.31) completely characterize the simple fluid and lead to five long-lived hydrodynamic modes. Local disturbances of these quantities cannot be dissipated locally, but must spread out over the entire system.

The conservative nature of the densities leads to further useful properties of the linear covariance functions. Suppose, for example, that the operator A in K^0_{AB} is one of the above densities d. Then the conservation laws (6.31) provide the identity

$$\frac{d}{dt}K^0_{dB}(\boldsymbol{x},t) = -\nabla\cdot K^0_{\boldsymbol{J}B}(\boldsymbol{x},t), \tag{6.32}$$

where $\boldsymbol{J}$ is the corresponding current density.

Often we are interested in the Fourier-transformed representation, for which we adopt the following notation:

$$K^0_{AB}(\boldsymbol{k},\omega) = \int d^3r\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau}\, K^0_{AB}(\boldsymbol{r},\tau)\,, \tag{6.33a}$$

$$K^0_{AB}(\boldsymbol{r},\tau) = \int \frac{d^3k}{(2\pi)^3} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega\tau}\, K^0_{AB}(\boldsymbol{k},\omega). \tag{6.33b}$$

In applications there is some importance to the value $|\boldsymbol{k}| = 0$ itself, in which case (6.33a) yields the formal expression

$$\lim_{k\to 0} K^0_{AB}(\mathbf{k},\omega) = \int_{-\infty}^{\infty} e^{i\omega\tau}\, d\tau \int K^0_{AB}(\mathbf{r},\tau)\, d^3r, \tag{6.34}$$

exhibiting the volume-integrated covariance function on the right-hand side. This relation will prove quite useful in the context of linear hydrodynamics.

In Appendix C $K^0_{AB}(\boldsymbol{k},\omega)$ is continued into the complex frequency plane and an analysis of its role as a response function is carried out. There it is shown that K^0_{AB} is actually the dissipative part of the physical response of the system and satisfies the relation

$$K^0_{AB}(\boldsymbol{k},\omega) = \frac{1-e^{-\beta\hbar\omega}}{\beta\hbar\omega}\Gamma^0_{AB}(\boldsymbol{k},\omega), \tag{6.35a}$$

where $\Gamma^0_{AB}(\mathbf{k},\omega)$ is the Fourier transform of the ordinary correlation function in the equilibrium system,

$$\begin{aligned}\Gamma^0_{AB}(\mathbf{x},\boldsymbol{x}';t,t') &\equiv \langle \Delta A(\boldsymbol{x},t)\,\Delta B(\boldsymbol{x}',t')\rangle_0 \\ &= \langle B(\boldsymbol{x}',t')A(\boldsymbol{x},t)\rangle_0 - \langle B(\boldsymbol{x}')\rangle_0\langle A(\boldsymbol{x})\rangle_0.\end{aligned} \tag{6.35b}$$

In the limit $\beta\hbar\omega \ll 1$ the covariance function is simply the ordinary correlation function, which also corresponds to omitting Kubo transforms. The first line of (6.35b) demonstrates that Γ^0_{AB}, and therefore K^0_{AB}, is really the *correlation of space-time fluctuations* in the equilibrium system. Both functions arise fundamentally from the covariances and variances of probability theory as indicators of the sharpness of the probability distribution. When space-time dependence is present, however, they also provide additional information on system behavior.

6.3 A transport example

By way of summarizing the essential aspects of this chapter, let us consider a small perturbation to the number density in a simple homogeneous fluid in equilibrium. By this we mean that a disturbance prior to the time of observation t results in a *physical* deviation $\delta n(\boldsymbol{x},t) = n(\boldsymbol{x},t) - \langle n(\boldsymbol{x})\rangle_0$ at points $\boldsymbol{x}$ a short time later. In linear approximation (6.9) yields

$$\langle \delta n(\boldsymbol{x},t)\rangle = -\int_R K^0_{nn}(\boldsymbol{x}-\boldsymbol{x}',t-t')\lambda(\boldsymbol{x}',t')\,d^3x'dt', \tag{6.36}$$

and the associated current density is predicted to be

$$\langle \boldsymbol{j}(\boldsymbol{x},t)\rangle = -\int_R K^0_{\boldsymbol{j}n}(\boldsymbol{x}-\boldsymbol{x}',t-t')\lambda(\boldsymbol{x}',t')\,d^3x'dt'. \tag{6.37}$$

These expectation values can be considered macroscopic densities within a microscopically large, but macroscopically small, volume centered on $\boldsymbol{x}$ at time t, thereby defining a continuum model of the actual discrete system.

As noted earlier in Chapter 3, we can choose the Lagrange multiplier as the independent variable, and here it is useful to choose the form $\lambda(\boldsymbol{x},t) = v(\boldsymbol{x})\dot{w}(t)$. Additionally, the calculation is simplified for this example if R is chosen as some spatial volume and all time prior to t. An integration by parts on the time variable and use of (6.32), followed by a further integration by parts on $\boldsymbol{x}'$, yields for a predicted component of the current

$$\begin{aligned}\langle j_i(\boldsymbol{x},t)\rangle = {}& -w(t)\int v(\boldsymbol{x}')K^0_{j_i n}(\boldsymbol{x}-\boldsymbol{x}',0)\,d^3x' \\ &+\int_{-\infty}^{t} w(t')\,dt'\int K^0_{j_i j_k}(\boldsymbol{x}-\boldsymbol{x}',t-t')\frac{\partial v}{\partial x'_k}\,d^3x'.\end{aligned} \tag{6.38}$$

Similarly,

$$\begin{aligned}\langle \delta n(\boldsymbol{x},t)\rangle = {}& -w(t)\int v(\boldsymbol{x}')K^0_{nn}(\boldsymbol{x}-\boldsymbol{x}',0)\,d^3x' \\ &+\int_{-\infty}^{t} w(t')\,dt'\int K^0_{nj_i}(\boldsymbol{x}-\boldsymbol{x}',t-t')\frac{\partial v}{\partial x'_i}\,d^3x'.\end{aligned} \tag{6.39}$$

Note that there is no suggestion of dynamics here, for ρ contains no information of that kind at this point; t is just some value of our choosing.

The covariance function in the first line of (6.38) vanishes by symmetry, as suggested in connection with (6.14). In view of the discussion following (6.31), a "long-wavelength" approximation corresponding to classical hydrodynamics is appropriate here, meaning that $v(\boldsymbol{x})$ varies so slowly that its derivative is essentially constant over distances for which the correlation functions are appreciable. The derivatives of v can then be brought outside the integrals. Since our attention is focused on a very short time interval after the disturbance, the upper limits of the integrals should be thought of as t^-; that is, particles now at $\boldsymbol{x}$ were a few mean free paths away a few mean free times ago. The covariance function in the second line of (6.39) will also vanish in the final result of interest, as will be explained below, and we now have

$$\langle j_i(\boldsymbol{x},t)\rangle = \frac{\partial v}{\partial x_k}\int_{-\infty}^{t} w(t')\,dt' \int K^0_{j_i j_k}(\boldsymbol{x}-\boldsymbol{x}', t-t')\,d^3x', \tag{6.40a}$$

$$\langle \delta n(\boldsymbol{x},t)\rangle = -w(t)\int v(\boldsymbol{x}')K^0_{nn}(\boldsymbol{x}-\boldsymbol{x}', t)\,d^3x'. \tag{6.40b}$$

After some variable changes in (6.40b) we can take the derivative with respect to $\boldsymbol{x}_k$, so that $\partial v/\partial x_k$ can be extracted from the integral. Elimination of this factor from both expressions in (6.40) results in the relation

$$\langle j_i(\boldsymbol{x},t)\rangle = -D_{ik}(\boldsymbol{x},t)\frac{\partial}{\partial x_k}\langle \delta n(\boldsymbol{x},t)\rangle, \tag{6.41}$$

where

$$D_{ik}(\boldsymbol{x},t) \equiv \frac{\int_{-\infty}^{t} w(t')\,dt' \int K^0_{j_i j_k}(\boldsymbol{x}-\boldsymbol{x}', t-t')\,d^3x'}{w(t)\int K^0_{nn}(\boldsymbol{x}-\boldsymbol{x}', t)\,d^3x'} \tag{6.42}$$

is the *diffusion tensor.*

Equation (6.41) is the general relation between the particle current and the density gradient giving rise to it. Similar expressions for the diffusion tensor appear in the literature, although they usually correspond to a further approximation of quasi-stationarity, in which case $w(t)$ is taken to be slowly varying over the interval $(-\infty, t)$. In that event only values near the upper limit of the time integral matter and the choice $w(t) = e^{\epsilon t}$, $\epsilon > 0$, will serve as well as any. Independent of these choices, the integral in the denominator in (6.42) is generally independent of t.

The only approximations made so far in arriving at (6.41) are the presumption of linearity, and the long-wavelength restriction characteristic of simple fluids. In particular, there are no limitations in temporal or spatial scales, although we do presume the interval $t - t^-$ to be on the order of a mean free time. As a consequence, the result remains a somewhat complicated relation. In application, however, it is almost always the case that a further "short-memory" approximation is made. By this we mean that only very recent information is really relevant to present behavior, so that only values of $t' \sim t$ in (6.42) [and (6.39)] need be considered. (This is tantamount to a presumption of very rapid decay of the time correlations.) If we consider only a one-dimensional model for simplicity, (6.41) reduces to the familiar form

$$\langle j(x,t)\rangle = -D\frac{\partial}{\partial x}\langle n(x,t)\rangle, \tag{6.43}$$

known as *Fick's law of diffusion*, and D is the diffusion coefficient. Although such constitutive equations have long been treated as phenomenological, we now see that they are simply laws of inference based on probability theory, and they arise from merely specifying the possibility of space-time variation in the density matrix. While (6.41) is linear in the density gradient, the full nonlinear relation is just the nonlinear expectation value of the current density—or any higher-order approximation.

The approximate nature of relations like (6.43) was recognized many years ago by Onsager (1931a), who noted that it failed to account for the time needed to accelerate the flow, but that for practical purposes that time-lag could be neglected in all cases that are likely to be studied. This "inertial" problem is resolved, of course, in the general form (6.42).

Finally, if expectation values are taken in (6.31a) and the result combined with (6.43) we obtain the macroscopic equation of motion known as the *diffusion equation*,

$$\frac{d}{dt}\langle n(x,t)\rangle = D\frac{\partial^2}{\partial x^2}\langle n(x,t)\rangle, \tag{6.44}$$

which works because ρ is independent of space-time variables. The "irreversibility" represented here by the first time derivative has often been considered puzzling, and was also noted by Onsager. But one now sees that this is simply an expression of the fact that (6.42) contains only information about the past, and not the future. In this sense, (6.44) provides the best prediction of future values of $\langle n(x,t)\rangle$ that can be made based on knowledge of its past values, when the memory interval is short compared to observation times. Equation (6.44) does not describe any propagating hydrodynamic modes. We shall return to some of these points in later chapters.

6.4 Inhomogeneous systems

A special case of the preceding development arises when the input information varies only spatially, and hence is time independent. This suggests an inhomogeneous physical system that may still be in thermal equilibrium, such as a liquid–vapor equilibrium, or the presence of a uniform gravitational field. The latter had already been studied by Gibbs (*HS*, p.146). Although this does not really come under the umbrella of "nonequilibrium" states, the context is such that it is worthwhile to include it here.

Recall that the information on which the grand canonical distribution of (4.26) was based consisted of the total energy $\langle H\rangle$ and the total particle number $\langle N\rangle$, in terms of the system Hamiltonian and total number operator. Suppose now that, rather than $\langle N\rangle$, the number density $\langle n(\boldsymbol{x})\rangle$ is specified over a spatial region $R(\boldsymbol{x})$ (often taken to be the total system volume V). The density matrix describing this macroscopic equilibrium state is

$$\rho = \frac{1}{Z}\exp\left[-\beta H + \int_R \lambda(\boldsymbol{x}')n(\boldsymbol{x}')\,d^3x'\right], \tag{6.45}$$

which reduces to (4.26) if $n(\boldsymbol{x})$ is in fact constant throughout V, or if only the volume integral of $n(\boldsymbol{x})$ is specified. Once again, neither ρ nor S is an explicit function of $\boldsymbol{x}$. The partition functional is

$$Z[\beta, \lambda(\boldsymbol{x})] = \operatorname{Tr}\exp\left[-\beta H + \int_R \lambda(\boldsymbol{x}')n(\boldsymbol{x}')\, d^3x'\right], \tag{6.46}$$

and the Lagrange multiplier function is formally determined by

$$\langle n(\boldsymbol{x})\rangle = \frac{\delta \ln Z}{\delta\lambda(\boldsymbol{x})}, \qquad \boldsymbol{x} \in R. \tag{6.47}$$

Of course, β is still determined formally by $\langle H\rangle = -\partial \ln Z/\partial\beta$ independent of $\boldsymbol{x}$, although it does not necessarily have the same value it had in the homogeneous state.

The variances and covariances of the general maximum entropy scenario were introduced in Eqs.(3.28) and (3.29) as derivatives of expectation values. Similarly, a functional derivative of the density yields, with the help of the operator identity $\partial_u e^{A(u)} = e^{A(u)}\overline{\partial_u A}$ from Appendix A, the 2-point correlation function

$$\frac{\delta\langle n(\boldsymbol{x}')\rangle}{\delta\lambda(\boldsymbol{x})} = \langle\overline{n(\boldsymbol{x}')}\, n(\boldsymbol{x})\rangle - \langle n(\boldsymbol{x}')\rangle\langle n(\boldsymbol{x})\rangle. \tag{6.48}$$

We recognize immediately the *full* covariance function $K_{nn}(\boldsymbol{x}, \boldsymbol{x}')$; that is, it is not a linear approximation, but contains the complete effect of the system inhomogeneity. Higher-order correlation functions are generated by higher-order derivatives.

Once again we note that this scenario can be turned around at this point and if desired we can as well choose $\lambda(\boldsymbol{x})$ as the independent variable—an external potential $v(\boldsymbol{x})$, say. The formalism now *predicts* the number density in the presence of an external field. For a classical free-particle system, this prediction is carried out to all orders in Appendix A, and with $\lambda(\boldsymbol{x}) = -\beta v(\boldsymbol{x})$ we find that

$$\langle n(\boldsymbol{x})\rangle = n_0 e^{-\beta v(\boldsymbol{x})}, \tag{6.49}$$

where n_0 is the density in the homogeneous equilibrium system. For a uniform gravitational field this is just Boltzmann's barometric formula.

Often the degree of inhomogeneity is small, so that the integral in the exponential in (6.45) can itself be considered a small perturbation to the homogeneous system. Then the linear or first-order approximation to $\langle n(\boldsymbol{x})\rangle$ is

$$\langle n(\boldsymbol{x})\rangle \simeq \langle n(\boldsymbol{x})\rangle_0 + \int_R \lambda(\boldsymbol{x}')K^0_{nn}(\boldsymbol{x}', \boldsymbol{x})\,, d^3x', \tag{6.50}$$

the superscript 0 on the covariance function now indicating that both the density matrix and Kubo transform refer to the homogeneous ($\lambda = 0$) system.

There are some illuminating implications for phase transitions that arise from these observations. Consider a generic fluid isolated from any external influences and for which the internal energy (or temperature) and particle number are specified. The macroscopic equilibrium state of maximum entropy is described by the grand canonical distribution of (4.26),

$$\rho_0 = \frac{1}{Z_0} e^{-\beta(H-\mu N)}, \qquad Z_0 = \operatorname{Tr} e^{-\beta(H-\mu N)}. \tag{6.51}$$

There are additional tacit presumptions underlying this construction, however, the first of which is that H and N are indeed constants of the motion. In addition, the input values $\langle H\rangle$, $\langle N\rangle$ are taken to be time independent and do not change over repeated measurements (except for very small fluctuations). Finally, the system is presumed to be spatially homogeneous, so that measurements made anywhere throughout it yield the same results if we ignore the Earth's weak gravitational field. Homogeneity is almost always a presumption, but such information has not been incorporated *explicitly* into ρ_0.

With external forces excluded we have some confidence that the system is in equilibrium and remains so, but homogeneity logically requires an additional measurement or specification of some sort. On the basis of the given input, (6.51) should be valid for *all* values of β and μ, which can now be treated as independent variables and the expectation values predicted; that is the usual scenario. But if the temperature is lowered considerably and the number density $\langle n(\boldsymbol{x})\rangle$ observed, we may be surprised to find that the system is no longer homogeneous. Nevertheless, (6.51) is still valid in that it still predicts the correct *total* energy and *total* number density N/V; it cannot, however, predict the correct $\langle n(\boldsymbol{x})\rangle$.

If information on homogeneity were to be incorporated explicitly into ρ the density matrix would take the form

$$\rho = \frac{1}{Z} \exp\left[-\int_V \beta(\boldsymbol{x})h(\boldsymbol{x})\, d^3x + \int_V \lambda(\boldsymbol{x})n(\boldsymbol{x})\, d^3x\right], \tag{6.52}$$

in terms of energy and number densities. This does not presume homogeneity, but only states that it has been checked over the entire system. If $\langle h(\boldsymbol{x})\rangle$ and $\langle n(\boldsymbol{x})\rangle$ are found to be essentially constant over V, then the integrated Lagrange multipliers become constants and ρ reduces to ρ_0, Eq.(6.51), where λ is set equal to $\beta\mu$ to introduce the chemical potential explicitly. These observations will attain further significance in Chapter 10.

While this procedure serves to specify uniformity in this system, it cannot address departures from homogeneity when β and/or μ are changed. This is because the description incorporates no information on such a possibility and, indeed, we have been told that the system *is* homogeneous. If changes in these parameters are made that take the system into a 2-phase region of equilibrium, (6.52) will still describe the total system, and the density matrix simply factors as the integrals separate into those over V_1 and V_2:

$$\rho \longrightarrow \frac{1}{Z_1 Z_2} e^{-\beta[H(V_1)-\mu N(V_1)]-\beta[H(V_2)-\mu N(V_2)]} = \rho_1 \otimes \rho_2, \tag{6.53}$$

with $U = U_1 + U_2$, $N = N_1 + N_2$. Of course, there will remain a weak interaction between the two subsystems. This ρ corresponds to a bimodal probability distribution that is rather broad and will exhibit large *statistical* fluctuations; the physical fluctuations in each phase can be expected to be small in phase equilibrium. The real question is: How to *predict* the onset of inhomogeneity, and possibly a transition into two well-defined phases?

In (3.28) we saw that the mean-square statistical fluctuations of energy, say, in the equilibrium system were given by $\langle \Delta H \Delta H \rangle_0 = \partial^2 \ln Z_0 / \partial \beta^2$, which are a measure of the sharpness of the probability distribution. As noted above, these may or may not be the same as the actual physical fluctuations, but for very large systems they are usually numerically equivalent (see Chapter 4). The physical deviations (or fluctuations) that we observe are the quantities of interest here, information about which must be incorporated into the density matrix to study their effect on the system. For simplicity we will monitor only the number density, by including information on the *physical* deviation $\delta n(\boldsymbol{x}) = n(\boldsymbol{x}) - \langle n(\boldsymbol{x}) \rangle_0$ in the construction of ρ. Maximization of the entropy with this additional piece of data yields

$$\rho = \frac{1}{Z} \exp\left[-\beta(H - \mu N) + \int \lambda(\boldsymbol{x}) \delta n(\boldsymbol{x}) \, d^3x \right]. \tag{6.54}$$

Note that the Lagrange multiplier function $\lambda(\boldsymbol{x})$ refers to the deviation, and not the variable itself. For a homogeneous equilibrium system the fluctuations are very small, so that the integral in the exponential is negligible and $\rho \to \rho_0$.

One can now monitor homogeneity by monitoring the fluctuations. Because the integral is small, the linear approximation is entirely appropriate, and in that event

$$\begin{aligned} \langle \delta n(\boldsymbol{x}) \rangle &= \int \lambda(\boldsymbol{x}') K^0_{nn}(\boldsymbol{x} - \boldsymbol{x}') \, d^3x' \\ &= \int \lambda(\boldsymbol{x}') \langle \overline{\delta n(\boldsymbol{x}')} \delta n(\boldsymbol{x}) \rangle_0 \, d^3x'. \end{aligned} \tag{6.55}$$

The correlation function also depends on β and μ, so when these "knobs" are turned the resulting changes in homogeneity, if any, are reflected directly in K^0_{nn}, and the onset of a transition will be indicated by a substantial increase in the magnitude and range of the covariance function, and in the magnitude of the *order parameter* $\langle \delta n \rangle$. The covariance function can be either positive or negative, as can the Lagrange multiplier. While the latter is determined formally by (6.47), one of its properties emerges immediately by integrating (6.55) over the volume. The resulting left-hand side of (6.55) vanishes and the integral of

K^0_{nn} is essentially the isothermal compressibility κ_T. That is, with reference to the grand canonical distribution (6.51), and omission of quantum-commutation effects,

$$\int_V K^0_{nn}(\boldsymbol{r})\,d^3r = V^{-1}\big[\langle N^2\rangle_0 - \langle N\rangle_0^2\big] = \frac{1}{\beta V}\left(\frac{\partial N}{\partial \mu}\right)_{\beta V}$$
$$= \frac{n_0^2}{\beta}\kappa_T, \tag{6.56}$$

where the thermodynamic derivative has been evaluated directly. Thus, the volume integral of $\lambda(\boldsymbol{x})$ must vanish; this makes sense, since the total variation also vanishes.

With these ideas in hand we can construct the beginnings of a theory for the onset of the liquid–gas phase transition. Let $\langle n(\boldsymbol{x})\rangle_0 = n_0$ represent the density in the homogeneous gas phase and consider the approach to the critical point along the critical isochore $n_0 = n_c$, starting with T well above the critical temperature T_c. The immediate problem, according to (6.55), is to study the behavior of K^0_{nn} as the temperature is lowered, but a complete evaluation in the interacting system is virtually impossible. A first approximation is the free-particle limit, which is given by (A.24) in Appendix A. As expected, when quantum-statistical effects are absent there are no correlations of any kind in the ideal gas, and hence no inhomogeneity can be sustained. Thus, the next step would seem to be a perturbation expansion in powers of the interaction. This has been carried out in Grandy (1988), for example, where the leading-order result in the Fourier-transformed representation is found to be

$$K^1_{nn}(\boldsymbol{q}) = K^0_{nn}(\boldsymbol{q})\big[1 - n_0\beta v(\boldsymbol{q})\big]. \tag{6.57}$$

The density n_0 of the homogeneous gas phase is here approximated by that of the ideal gas, and $v(\boldsymbol{q})$ is the Fourier transform of the spherically symmetric 2-body potential,

$$v(\boldsymbol{q}) = \int e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\,V_2(r)\,d^3r = v(-\boldsymbol{q}). \tag{6.58}$$

The free-particle covariance function is just $K^0_{nn}(\boldsymbol{q}) = n_0$. The potential V_2 is usually taken to be the attractive part of the interaction, so that the radial integral in (6.58) has a lower hard-core cutoff at $r = a$, say. The actual form does not really matter much in the critical region.

Equation (6.57) is the beginning of an expansion not only in powers of the interaction, but also in the density. This is clearly not a productive result, for neither $v(\boldsymbol{q})$ nor n_0 should be expected to be particularly small in a neighborhood of the critical point. In addition, the density expansion itself is found to be nonanalytic when applied to transport coefficients (*e.g.*, Dorfman *et al.*, 1994), implying that a re-summation of selected terms in the expansion may be required. The solution found in that case (Kawasaki and Oppenheim, 1965) also suggests itself here, and we examine the summation of the so-called "ring" terms in the expansion. These terms describe microscopic processes in which the same momentum is transferred in successive encounters, and they often lead to divergences in any event if left untreated. The ring approximation to K^0_{nn} has been calculated in Grandy (1988), where it is found that

$$K^r_{nn}(\boldsymbol{q}) = \frac{n_0}{1+\beta n_0 v(\boldsymbol{q})}, \tag{6.59}$$

a first extrapolation to higher densities and stronger interactions that reduces to K^1_{nn} and K^0_{nn} as $v \to 0$.

It has long been known that the intensity of electromagnetic and neutron scattering from fluids near the critical point is proportional to $K_{nn}(\boldsymbol{q})$ and is very strong in the forward direction, corresponding to very small q. An expansion of $v(\boldsymbol{q})$ in a power series is thus suggested, and from (6.58) it is clear that $v'(\boldsymbol{q}) = 0$. Since V_2 is attractive, (6.59) can be approximated as

$$K^r_{nn}(\boldsymbol{q}) \simeq \frac{n_0}{1-\beta n_0 v(0)+\beta n_0 v''(0)q^2}, \tag{6.60}$$

and v'' is positive. To compare this with standard discussions of phase transitions we rewrite it as

$$K^r_{nn}(\boldsymbol{q}) = \frac{\big(\beta v''(0)\big)^{-1}}{\xi^{-2}+q^2}, \tag{6.61}$$

with

$$\xi \equiv \left[\frac{k}{n_0 v''(0)}\big(T-T_c\big)\right]^{-1/2}, \qquad T_c = \frac{n_0 v(0)}{k}. \tag{6.62}$$

Inverse Fourier transformation yields

$$K^r_{nn}(\boldsymbol{r}) = \big(4\pi\beta v''(0)\big)^{-1}\,\frac{e^{-r/\xi}}{r}. \tag{6.63}$$

We see that the *correlation length* ξ behaves like $(T-T_c)^{-\nu}$, where we define a *critical exponent* $\nu = 1/2$. Although K^r_{nn} generally decays exponentially, it falls off like r^{-1} as $T \to T_c$ and the correlations become very long ranged near the critical point. The model thus predicts a phase transition at $T = T_c$ in just the first nontrivial approximation. In further support of this, (6.56) is now replaced by

$$\frac{\kappa_T}{\kappa_T^0} = \frac{\xi^2}{\beta n_0 v''(0)}\int_0^\infty y e^{-y}\,dy \sim \big(T-T_c\big)^{-\gamma}, \tag{6.64}$$

where $\kappa_T^0 = (n_0 kT)^{-1}$ is the ideal-gas value, and $\gamma = 1$ is another critical exponent. Hence, the isothermal compressibility diverges as $T \to T_c$, and we infer a *scaling relation* $\gamma = 2\nu$.

Remarkably, these results agree exactly with the Ornstein–Zernicke theory of this phase transition if their "direct correlation function" is identified with $V_2(r)$ (*e.g.*, Stanley, 1971). As in that theory, the critical exponents do not agree very well with experimental values. Curiously, the model does not yield a satisfactory result in either one or two dimensions, as can be seen by considering an abstraction in D dimensions of the Fourier-transform pair (6.61) and (6.63),

$$G_D(\boldsymbol{r}) = \int \frac{d^D q}{(2\pi)^D} \frac{e^{i\boldsymbol{q}\cdot\boldsymbol{r}}}{a^2+q^2}, \tag{6.65}$$

where $a \equiv \xi^{-1} \to 0$ as $T \to T_c$. Introduction of the integral representation

$$\frac{1}{a^2+q^2} = \int_0^\infty e^{-t(a^2+q^2)}\, dt \tag{6.66}$$

leads to

$$G_D(\boldsymbol{r}) = \begin{cases} \dfrac{1}{4\pi}\dfrac{e^{-ar}}{r}, & D=3 \\ \dfrac{1}{\pi}K_0(ar), & D=2 \\ \dfrac{1}{4a}e^{-ar}, & D=1 \end{cases}, \tag{6.67}$$

where

$$\begin{aligned} K_0(z) \quad &\xrightarrow[z\to 0]{} \quad -\ln z + \text{constant} \\ &\xrightarrow[z\to\infty]{} \quad \left(\frac{\pi}{2z}\right)^{1/2} e^{-z} \end{aligned} \tag{6.68}$$

is the modified Bessel function of the second kind. For $D=3$ we verify (6.63). For finite a, $G_2(\boldsymbol{r})$ eventually decays exponentially but is very large for small r; for any fixed r it diverges logarithmically as $a \to 0$. In one dimension the singularity is even stronger as $T \to T_c$.

While it is quite satisfying that this model does predict a phase transition in three dimensions, it does not provide a satisfactory theory of the liquid–gas transition. Clearly, a much better approximation to the covariance function is required, and possibly the linear nonequilibrium theory is inadequate near the critical point. These issues, and their relation to other theories such as those based on the renormalization group, say, are obviously in need of further investigation.

6.5 Some reflection

The thrust of this chapter has been to extend considerably the role of entropy in thermal processes, away from its usual restriction to homogeneous systems in equilibrium. Although S in (6.5) is not yet an explicit function of space-time variables, it adequately describes a nonequilibrium (or simply inhomogeneous) macroscopic state defined by known information about the system in some space-time interval. This extension still lies within the original probability context of the PME, providing an initial (or prior) distribution based on given data. It provides a purely predictive theory, rather than dynamical; that is, we are not yet able to describe processes themselves. But the preceding discussion illustrates the considerable power of this straightforward extension, and we begin to see how the entropy presides over much of thermal physics.

The full power and extent of the entropy, however, cannot be realized until it is extended to govern time-dependent irreversible processes as well, and that will be the business of the remainder of this work. But we will not be able to address that question until the notion of time-dependent probabilities is put on a firm basis, which we shall defer until Chapter 8. As a preliminary step it will be useful to first extend the results of this chapter to stationary processes, which introduce currents as thermodynamic variables that remain constant in time.

7

STEADY-STATE PROCESSES

> *Consider an irreversible process which, with fixed outside constraints, is passing by itself from the nonstationary to the stationary state. Can we characterize in any sense the resulting distribution of state as the "relatively most probable distribution," and can this be given in terms of the minimum of a function which can be regarded as a generalization of the H-function?*
>
> *P. & T. Ehrenfest (1912)*

By definition, thermal equilibrium is the example *par excellence* of a stationary state, but it does not in itself constitute what we think of as an active process. Rather, one envisions a process involving currents of some kind, usually generated by gradients in associated variables, although independent of time. Such processes are further characterized by time-independent expectation values of operators that exhibit no intrinsic time dependence.

From our work in the preceding chapter one would expect a nonequilibrium steady state to be well described by a density matrix of the general form

$$\rho = \frac{1}{Z} \exp\left[\int_R \lambda(\boldsymbol{x}')F(\boldsymbol{x}')\, d^3x'\right], \tag{7.1}$$

where $F(\boldsymbol{x})$ might be an already-established density gradient or a current density operator depending only on spatial variables. This description is quite satisfactory if F commutes with H and or ρ, but in general it does not. In addition, it does not guarantee that the expectation value of some other operator A will also be time independent, and hence ρ cannot be considered a general stationary-state density matrix. Thus, it is necessary to include some kind of additional constraint in the specification of a nonequilibrium steady state.

The main dynamical feature of the equilibrium state is that it deals only with constants of the motion, among which is the Hamiltonian and the density matrix itself: $[H, \rho] = 0$. These constraints characterize the time-invariant state of an isolated (or closed) system, because the vanishing of the commutator implies that ρ commutes with the time-evolution operator $U(t)$ in (6.12), so that all expectation values are constant in time. The time-invariant state of an open system is also stationary, but H almost certainly will not commute with the operators $F(\boldsymbol{x})$ defining that state, and hence not with ρ. One requires at a minimum that, for time-independent operators A and H,

$$\frac{d}{dt}\langle A\rangle = \frac{d}{dt}\mathrm{Tr}(\rho A) = \frac{1}{i\hbar}\mathrm{Tr}\big([H,\rho]A\big) = 0, \tag{7.2}$$

where we have employed the equation of motion (4.8). Owing to cyclic invariance of the trace, this last requirement is satisfied if either $[\rho, A] = 0$ or $[A, H] = 0$, but this would then have to be verified for every operator A of interest. It would be much more general and efficient to simply *require* ρ to be a constant of the motion for all stationary processes. This procedure had also been employed earlier by Fano (1957), Nakajima (1958), Scalapino (1961), and Kubo, *et al.* (1985).

Derivation of a steady-state density matrix thus proceeds as follows: given an expectation value $\langle F(\boldsymbol{x})\rangle = \mathrm{Tr}(\rho_{st}F)$ over a spatial region R, maximize the entropy subject to this constraint as well as $\mathrm{Tr}\rho_{st} = 1$ and $[\rho_{st}, H] = 0$. Solution of this variational problem is facilitated by defining a variation $\delta\rho = \rho_{st} + \epsilon\eta$, where η represents an arbitrary variation. The stationarity condition requires that $[\delta\rho, H] = 0$, implying that $[\eta, H] = 0$, so that the PME leads to the expression

$$\mathrm{Tr}\big\{\eta[\ln\rho_{st} + \lambda F]\big\} = 0. \tag{7.3}$$

But η is not completely arbitrary, since it must commute with H.

Choose a representation in which H is diagonal, say $|i\rangle = |E\nu\rangle$, where ν denotes all relevant quantum numbers other than the energy. The stationarity condition can then be written

$$\langle E\nu|[H,\eta]|E'\nu'\rangle = (E - E')\langle E\nu|\eta|E'\nu'\rangle = 0. \tag{7.4}$$

Hence, the expectation value of η must vanish for $E' \neq E$, but it remains arbitrary in any degenerate subspace. The condition (7.3) can be written

$$\sum_{i,j}\langle i|\eta|j\rangle\,\langle j|[\ln\rho_{st} + \lambda F]|i\rangle = 0, \tag{7.5}$$

and $\langle i|\eta|j\rangle$ is proportional to δ_{ij}. Therefore, the diagonal elements of the remaining matrix element must vanish, and this can be accomplished by writing the requirement as

$$\langle E\nu|\ln\rho_{st} + \lambda F^d|E'\nu'\rangle = 0, \tag{7.6}$$

where

$$\langle E\nu|F^d|E'\nu'\rangle = \delta_{EE'}\langle E\nu|F|E\nu'\rangle \tag{7.7}$$

is the *diagonal part of the operator* F. The stationarity requirement thus requires that only those parts of the operators commuting with H can appear in the steady-state density matrix, and in place of (7.1) we have

$$\rho_{st} = \frac{1}{Z_{st}} \exp\left[\int_R \lambda(\boldsymbol{x}') F^d(\boldsymbol{x}')\, d^3x'\right]. \tag{7.8}$$

Of course, this density matrix is only useful if we have a convenient expression for the diagonal part of an operator. One way to obtain that is to write the off-diagonal part of F in terms of another operator A,

$$F^d \equiv F - \frac{i}{\hbar}[H, A], \tag{7.9}$$

so that the off-diagonal elements are

$$\langle E\nu|F|E'\nu'\rangle = \frac{i}{\hbar}\langle E\nu|[H, A]|E'\nu'\rangle\,, \qquad E' \neq E. \tag{7.10}$$

Expansion of the commutator then yields

$$\langle E\nu|A|E'\nu'\rangle = \frac{\langle E\nu|F|E'\nu'\rangle}{i(E - E')/\hbar}. \tag{7.11}$$

One readily verifies by insertion into this last equation that A has the representation

$$A = \lim_{\epsilon \to 0} \int_{-\infty}^{0} e^{\epsilon t}\, e^{itH/\hbar}\, F e^{-itH/\hbar}\, dt, \tag{7.12}$$

where the convergence factor $\epsilon \geq 0$ has been introduced to avoid convergence difficulties at the lower limit of integration.

In (7.12) we recognize the Heisenberg operator $F(t)$. Substitution of A into (7.9) and reference to the Heisenberg equation of motion (6.1) then yields the following representations of the diagonal part of an operator:

$$\begin{aligned} F^d &= F - \lim_{\epsilon \to 0^+} \int_{-\infty}^{0} e^{\epsilon t}\, \dot{F}(\boldsymbol{x}, t)\, dt \\ &= \lim_{\epsilon \to 0^+} \epsilon \int_{-\infty}^{0} e^{\epsilon t}\, F(\boldsymbol{x}, t)\, dt \\ &= \lim_{\tau \to \infty} \frac{1}{\tau} \int_{-\tau}^{0} F(\boldsymbol{x}, t)\, dt, \end{aligned} \tag{7.13}$$

The second line follows from an integration by parts; the third is sometimes referred to as Abel's theorem and equates the diagonal part with a time average over the past, which is what we might expect for a stationary process. That is, F^d is that part of F that remains constant under a unitary transformation generated by H.

It must be emphasized that (7.8) describes an already-established steady-state process and does not contain any information on the source of this state, or what is maintaining it. In application of ρ_{st} it will be most convenient to consider the scenario in which the steady state has been created from an earlier equilibrium state, so that information about both is available, thereby facilitating linear approximations. This leads to the form

$$\rho_{st} = \frac{1}{Z_{st}} \exp\left[-\beta H - \int_R \lambda(\boldsymbol{x}) F^d(\boldsymbol{x})\right] d^3x, \tag{7.14}$$

and Z_{st} is again the trace of the exponential. The maximum entropy is

$$\begin{aligned}\frac{1}{k} S_{st} &= \ln Z_{st}[\beta, \lambda(\boldsymbol{x})] + \beta \langle H\rangle_{st} + \int \lambda(\boldsymbol{x}) \langle F^d(\boldsymbol{x})\rangle_{st}\, d^3x \\ &\simeq \frac{1}{k} S_0 - \beta \int \lambda(\boldsymbol{x}) K^0_{HF^d}(\boldsymbol{x})\, d^3x \\ &\quad - \frac{1}{2} \int\int_R \lambda(\boldsymbol{x}) K^0_{F^dF^d}(\boldsymbol{x}-\boldsymbol{x}') \lambda(\boldsymbol{x}')\, d^3x' d^3x, \end{aligned} \tag{7.15}$$

where subscripts st indicate quantities evaluated with ρ_{st}, similarly for subscripts 0 and the equilibrium ρ_0, and the second line is the linear approximation when the steady state departs only slightly from equilibrium. The entropy in this approximation possesses several special properties, beginning with the obvious fact that $S_{st} \neq S_{st}(t)$. Second, although $\langle H\rangle_{st}$ is the total internal energy of the full steady state, β refers to the equilibrium temperature; a constant global temperature may be elusive in this state. Third, if F is odd under time reversal (it is usually a current), then $K^0_{HF^d}(\boldsymbol{x}) = 0$. Finally, by definition $[H, F^d] = 0$, hence $K^0_{AF^d} \to \Gamma^0_{AF^d}$ for all A. It appears that $-S_{st}$ is the function the Ehrenfests were looking for, and its evolution is much like that depicted in Fig. 4.1b.

Having constructed a density matrix describing a steady-state process, we next investigate the stability of that state under small perturbations. Schlögl (1971) has studied stability conditions for the steady state in some depth through consideration of the quantum version of the information gain in changing from a steady-state density matrix ρ'_{st} to another ρ_{st},

$$L(\rho_{st}, \rho'_{st}) = \mathrm{Tr}\big[\rho_{st}\big(\ln \rho_{st} - \ln \rho'_{st}\big)\big], \tag{7.16}$$

which is effectively the entropy change in going from ρ'_{st} to ρ_{st}. He notes that L is a Lyapunov function in that it is positive definite, vanishes only if $\rho_{st} = \rho'_{st}$, and has a positive second-order variation. Pfaffelhuber (1977) demonstrates that the symmetrized version, which is more convenient here,

$$L^*(\rho_{st}, \rho'_{st}) = \frac{1}{2}\mathrm{Tr}\big[\big(\rho_{st} - \rho'_{st}\big)\big(\ln \rho_{st} - \ln \rho'_{st}\big)\big], \tag{7.17}$$

is an equivalent Lyapunov function, and that its first-order variation is given by

$$-\delta L^* = \frac{1}{2}\delta(\Delta\lambda\,\Delta\langle F^d\rangle). \tag{7.18}$$

The notation is that $\Delta\lambda = \lambda - \lambda'$, for example. If δ is taken as a time variation, then Lyapunov's theorem (Lyapunov, 1992) immediately provides a stability condition for the steady state,

$$-\dot{L}^* \geq 0. \tag{7.19}$$

Remarkably, (7.19) closely resembles the Gibbs condition (3.32) for stability of the equilibrium state, but in terms of $-\Delta\dot{S} \geq 0$. The merit of the present approach is that L^* does not depend directly on the entropy and therefore encounters no ambiguities in defining a $\Delta\dot{S}$.

When currents are present the process is intrinsically irreversible, hence entropy is being "produced" somewhere—that is, it is continually changing. But in a steady-state system everything is supposed to be time independent, so that one is now forced to consider what is going on at the system boundaries. Although we shall return to this point in much more detail later, it is clear already that any entropy generated upstream must be removed downstream if the system entropy itself is to remain constant. That constant entropy of the stationary state is then given by (7.15), and any net entropy changes are taking place externally to the system.

7.1 Steady-state transport processes in simple fluids

Consider now a scenario in which the steady state defined by an operator F constitutes a small departure from equilibrium. In linear approximation, another operator C will have expectation value

$$\begin{aligned}\langle\Delta C(\boldsymbol{x})\rangle_{st} = &-\int_R \lambda(\boldsymbol{x}')K^0_{CF}(\boldsymbol{x}-\boldsymbol{x}')\,d^3x' \\ &+ \lim_{\epsilon\to 0^+}\int_V d^3x' \int_{-\infty}^0 e^{\epsilon t}\,\lambda(\boldsymbol{x}')K^0_{C\dot{F}}(\boldsymbol{x}-\boldsymbol{x}',-t)\,dt,\end{aligned} \tag{7.20}$$

where $\Delta C = C - \langle C\rangle_0$, V is the system volume, and we have employed the first line of (7.13) for the diagonal part of an operator. The notation $-t$ in the covariance signifies that the time dependence has been shifted to C in the usual manner for translation invariance of the equilibrium system. More specifically, let $F(\boldsymbol{x})$ be one of the fluid densities $d(\boldsymbol{x})$ and $\boldsymbol{J}$ the corresponding current density, so that the continuity equations (6.31) and the identity (6.32) reduce (7.20) to

$$\begin{aligned}\langle\Delta C(\boldsymbol{x})\rangle_{st} = &-\int_V \lambda(\boldsymbol{x}')K^0_{Cd}(\boldsymbol{x}-\boldsymbol{x}')\,d^3x' \\ &+ \lim_{\epsilon\to 0^+}\int_V d^3x' \int_{-\infty}^0 e^{\epsilon t}\,\nabla'\lambda(\boldsymbol{x}')\cdot K^0_{C\boldsymbol{J}}(\boldsymbol{x}-\boldsymbol{x}',t)\,dt,\end{aligned} \tag{7.21}$$

in which we have dropped a surface term and presumed that the fluctuations are not correlated over the entire volume.[1]

As noted in Chapter 6, classical hydrodynamics corresponds to a long-wavelength approximation, so that $\nabla'\lambda$ can be considered to vary so slowly that it is effectively constant over the range for which $K_{C\boldsymbol{J}}$ is appreciable. With this in mind we can extract the gradient from the integral and write

$$\begin{aligned}\langle \Delta C(\boldsymbol{x})\rangle_{st} \simeq &-\int_V \lambda(\boldsymbol{x}')K^0_{Cd}(\boldsymbol{x}-\boldsymbol{x}')\,d^3x' \\ &+\nabla\lambda\cdot\lim_{\epsilon\to 0^+}\int_v d^3x'\int_{-\infty}^0 e^{\epsilon t}\,K^0_{C\boldsymbol{J}}(\boldsymbol{x}-\boldsymbol{x}',t)\,dt,\end{aligned} \tag{7.22}$$

which is the fundamental equation describing linear transport processes in the steady state. The integration region v is the correlation volume, outside of which the correlations vanish; it is introduced here simply as a reminder that the spatial correlations are presumed not to span the entire volume. We elaborate further on this point in Chapter 10.

At this point we can emulate the diffusion calculation of Chapter 6 by presuming a constant density gradient to exist such that (7.22) leads to

$$\begin{aligned}\langle \Delta n(\boldsymbol{x})\rangle_{st} &= -\int_V \lambda(\boldsymbol{x}')K^0_{nn}(\boldsymbol{x}-\boldsymbol{x}')\,d^3x' \\ &\quad+\nabla\lambda\cdot\int_v d^3x'\int_{-\infty}^0 e^{\epsilon t}\,K^0_{n\boldsymbol{j}}(\boldsymbol{x}-\boldsymbol{x}',t)\,dt \\ &= -\int_V \lambda(\boldsymbol{x}')K_{nn}(\boldsymbol{x}-\boldsymbol{x}')\,d^3x', \end{aligned} \tag{7.23}$$

$$\begin{aligned}\langle \boldsymbol{j}(\boldsymbol{x})\rangle_{st} &= -\int_V \lambda(\boldsymbol{x}')K_{\boldsymbol{j}n}(\boldsymbol{x}-\boldsymbol{x}')\,d^3x' \\ &\quad+\nabla\lambda\cdot\int_v d^3x'\int_{-\infty}^0 e^{\epsilon t}\,K^0_{\boldsymbol{j}\boldsymbol{j}}(\boldsymbol{x}-\boldsymbol{x}',t)\,dt \\ &= \nabla\lambda\cdot\int_v d^3x'\int_{-\infty}^0 e^{\epsilon t}\,K^0_{\boldsymbol{j}\boldsymbol{j}}(\boldsymbol{x}-\boldsymbol{x}',t)\,dt, \end{aligned} \tag{7.24}$$

where the limit $\epsilon\to 0^+$ is understood. We have noted that the first term of the first line in (7.24) vanishes by symmetry, and that the second term in the first line of (7.23) will have the same fate in the situation to be considered below.

Now take the gradient in (7.23), make the long-wavelength approximation, and eliminate $\nabla\lambda$ between this result and (7.24), which leads to the relation

$$\begin{aligned}\langle \boldsymbol{j}(\boldsymbol{x})\rangle_{st} &= -\frac{\int_0^\infty e^{-\epsilon t}\,dt\int_v K^0_{\boldsymbol{j}\boldsymbol{j}}(\boldsymbol{x}-\boldsymbol{x}',t)\,d^3x'}{\int_v K^0_{nn}(\boldsymbol{x}-\boldsymbol{x}')\,d^3x'}\cdot\nabla\langle n(\boldsymbol{x})\rangle_{st} \\ &\equiv -\boldsymbol{D}(\boldsymbol{x})\cdot\nabla\langle n(\boldsymbol{x})\rangle_{st}, \end{aligned} \tag{7.25}$$

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[1] It would be worthwhile for the reader to verify this calculation now, once and for all!

with the proviso that $\epsilon \to 0^+$. Despite the fact that we are considering a steady state here, (7.25) is actually completely equivalent to Eqs.(6.41) and (6.42) if in the latter we make the substitution $w(t) = e^{\epsilon t}$ and make a change of variables in the integral. If the time integral in (7.13) is interpreted as memory, a "short-memory approximation" can also be made in (7.25) and we again obtain Fick's law, (6.43). This is a very useful connection because it is usually simpler conceptually to calculate linear transport coefficients in the steady-state scenario.

As a further example of this approach let us consider thermal conductivity (which need not be restricted to fluids). A steady gradient in energy density is specified in the form of a deviation $\Delta h(\boldsymbol{x}) = h(\boldsymbol{x}) - \langle h \rangle_0$. By a calculation similar to the above, we find for the expected steady-state heat current

$$\langle \boldsymbol{q}(\boldsymbol{x}) \rangle_{st} = \int_v d^3x' \int_0^\infty e^{-\epsilon t}\, \nabla' \lambda(\boldsymbol{x}') \cdot K^0_{\boldsymbol{qq}}(\boldsymbol{x} - \boldsymbol{x}', t)\, dt, \tag{7.26}$$

where the limit $\epsilon \to 0^+$ is understood, and we have not yet invoked the long-wavelength limit. In this case we do not eliminate $\nabla\lambda$, for it contains the gradient of interest. Both dimensionally, and as dictated by the physical scenario, λ must be $\beta(\boldsymbol{x}) = [kT(\boldsymbol{x})]^{-1}$, a space-dependent temperature function. Although such a quantity may be difficult to measure in general, it may be well defined in the steady state. With this substitution the long-wavelength approximation of constant temperature gradient in (7.26) yields

$$\begin{aligned} \langle \boldsymbol{q}(\boldsymbol{x}) \rangle_{st} &\simeq -\nabla T \cdot \int_v d^3x' \int_0^\infty e^{-\epsilon t}\, \frac{K^0_{\boldsymbol{qq}}(\boldsymbol{x} - \boldsymbol{x}', t)}{kT^2(\boldsymbol{x}')}\, dt \\ &\equiv -\boldsymbol{\kappa} \cdot \nabla T(\boldsymbol{x}), \end{aligned} \tag{7.27}$$

in which we identify the thermal conductivity tensor $\boldsymbol{\kappa}$. A short-memory approximation then gives us *Fourier's law of thermal conductivity*, and substitution into (6.31c) yields the heat equation similar to (6.44); these expressions apply to solids as well as fluids.

The same procedure is readily generalized to more complicated processes such as thermal diffusion, thermoelectricity, and so on. For example, in a system of particles each with electric charge e, and in the presence of a static external electric field derived from a potential per unit charge $\phi(\boldsymbol{x})$, the appropriate Lagrange multiplier is no longer the chemical potential μ, but the *electrochemical potential*

$$\psi(\boldsymbol{x}, t) = \mu(\boldsymbol{x}, t) + e\phi(\boldsymbol{x}, t). \tag{7.28}$$

For a steady-state process in the long-wavelength limit and linear approximation, one finds for the electric current $\boldsymbol{j}$ and the heat current $\boldsymbol{q}$ the set of coupled equations

$$\begin{aligned} \langle \boldsymbol{j}(\boldsymbol{x}) \rangle_{st} &= -\frac{1}{ekT} \nabla\psi \cdot \boldsymbol{L}_{\boldsymbol{jj}}(\boldsymbol{x}) + \frac{1}{kT^2} \nabla T \cdot \boldsymbol{L}_{\boldsymbol{jq}}(\boldsymbol{x})\,, \\ \langle \boldsymbol{q}(\boldsymbol{x}) \rangle_{st} &= -\frac{1}{ekT} \nabla\psi \cdot \boldsymbol{L}_{\boldsymbol{qj}}(\boldsymbol{x}) + \frac{1}{kT^2} \nabla T \cdot \boldsymbol{L}_{\boldsymbol{qq}}(\boldsymbol{x}), \end{aligned} \tag{7.29}$$

where the second-rank tensors can be written generically as

$$\boldsymbol{L}_{AB}(\boldsymbol{x}) = \lim_{\epsilon\to 0^+} \int_0^\infty e^{-\epsilon t}\, dt \int_v \langle \overline{B(\boldsymbol{x}')} A(\boldsymbol{x}, t)\rangle_0 \, d^3x'. \tag{7.30}$$

In the short-memory approximation these are the thermoelectric coefficients: $\boldsymbol{L_{jj}}$ is proportional to D and $\boldsymbol{L_{qq}}$ is proportional to $\boldsymbol{\kappa}$, whereas $\boldsymbol{L_{jq}}$ is the Seebeck coefficient and $\boldsymbol{L_{qj}}$ the Peltier coefficient. In an isotropic medium the symmetry properties of the covariance functions imply the Onsager-like reciprocity relation $\boldsymbol{L_{jq}} = \boldsymbol{L_{qj}}$, but this clearly depends strongly on the space-time behavior of the operators involved, as well as on the specific system under study. An in-depth critique of Onsager reciprocity has been provided by Truesdell (1984).

It remains to examine the momentum density in the simple fluid; although the analysis of transport coefficients is readily applied to other systems, the fluid presents a particularly clear model for this exposition. In the steady-state density matrix (7.14), F is taken to be an already-established stationary particle current. In linear approximation and the long-wavelength limit (7.22) is modified to

$$\begin{aligned}\langle \Delta C(\boldsymbol{x})\rangle_{st} = -m \int_V \lambda_i(\boldsymbol{x}') K^0_{Cj^i}(\boldsymbol{x} - \boldsymbol{x}')\, d^3x' \\ + \left(\nabla_k \lambda_i\right) \int_v d^3x' \int_0^\infty e^{-\epsilon t}\, K^0_{CT^{ik}}(\boldsymbol{x} - \boldsymbol{x}', t)\, dt\,,\end{aligned} \tag{7.31}$$

where here and subsequently the limit $\epsilon \to 0^+$ is understood, and sums over repeated indices are implied.

First consider C as the total momentum operator $\boldsymbol{P}$. Then, in the given scenario, we know that $\langle \overline{j_i(\boldsymbol{x}')} P_j(\boldsymbol{x})\rangle_0 = (n_0/\beta)\delta_{ij}$, where n_0 and β are equilibrium values, and $K^0_{\boldsymbol{P}T^{ij}}(\boldsymbol{x} - \boldsymbol{x}', t) = 0$ from the symmetry in the eventual short-memory approximation. Hence (7.31) reduces to

$$\int_V \langle m j_i(\boldsymbol{x})\rangle_{st}\, d^3x = -\frac{n_0 m}{\beta} \int_V \lambda_i(\boldsymbol{x})\, d^3x. \tag{7.32}$$

A convenient notation emerges if we introduce a fluid velocity $v_i(\boldsymbol{x})$ by writing the momentum density as $\langle m j_i(\boldsymbol{x})\rangle_{st} = m n_0 v_i(\boldsymbol{x})$, so that the Lagrange multiplier is identified as $\boldsymbol{\lambda} = -\beta \boldsymbol{v}$.

Now take C in (7.31) to be a component of the energy-momentum tensor. By the usual symmetry arguments,

$$\langle T^{ki}(\boldsymbol{x})\rangle_{st} = \langle T^{ki}\rangle_0 + \nabla_m \lambda_n \int_0^\infty e^{-\epsilon t}\, dt \int_v K^0_{ki,mn}(\boldsymbol{x} - \boldsymbol{x}', t)\, d^3x', \tag{7.33}$$

where the covariance function is that of T^{mn} and T^{ki}, and the equilibrium expectation value $\langle T^{ki}\rangle_0 = P_0 \delta^{ki}$ is the hydrostatic pressure. With the identification of $\boldsymbol{\lambda}$, (7.33) is the general equation defining a fluid; in fact, we can now show that it is a Newtonian fluid.

There are numerous properties of T^{mn} and the covariance functions involving it that are needed at this point; they will simply be stated here and can be verified elsewhere (*e.g.*, Puff and Gillis, 1968). As expected, T^{mn} is symmetric and the space integral in (7.31) can be carried out immediately; the space-integrated covariance function has only a limited number of components in the isotropic equilibrium medium, in that nonzero values can only have indices equal in pairs, such as $\langle T_{12}T_{12}\rangle_0$ and $\langle T_{22}T_{33}\rangle_0$; in addition, the space-integrated tensor itself has the property

$$T_{11} = T_{22} = T_{33} = \tfrac{1}{3}T, \tag{7.34}$$

where T is the tensor trace. If we adopt the notation $v_{i,k} \equiv \partial v_i/\partial x_k$ and the convention that sums are performed over repeated indices, then (7.33) can be rewritten as

$$\langle T_{ki}(\boldsymbol{x})\rangle_{st} = P_0\delta_{ki} - \eta\big(v_{k,i} + v_{i,k} - \tfrac{2}{3}v^{\ell}_{,\ell}\delta_{ki}\big) - \zeta v^{\ell}_{,\ell}\delta_{ki}, \tag{7.35}$$

where we have identified the *shear viscosity*

$$\eta \equiv \beta V \int_0^\infty e^{-\epsilon t}\, K^0_{mn,mn}(t)\, dt\,, \qquad m \neq n, \tag{7.36a}$$

and the *bulk viscosity*

$$\zeta \equiv \frac{\beta V}{9}\int_0^\infty e^{-\epsilon t}\, K^0_{TT}(t)\, dt. \tag{7.36b}$$

In (7.36a) any values of $m \neq n$ can be used, but are generally dictated by the initial current; the indices are *not* summed. Note that both η and ζ are independent of space-time coordinates. Macroscopic equations of motion stemming from the constitutive relation (7.35) will be studied in Chapter 10.

Correlation function expressions of the type developed here have been found by a number of authors over the years and are often known as Green–Kubo coefficients (for a review see Zwanzig, 1965). Although they are usually obtained by somewhat contrived methods, rather than as a straightforward result of probability theory, those results clearly exhibited the right instincts for how the dissipative parameters in the statistical theory should be related to the microscopic physics. Expressions for the linear transport coefficients of hydrodynamics in particular were studied in some detail by Kadanoff and Martin (1963), who derived them by means of linear dynamic response theory; the difficulties with this approach are discussed in Chapters 8 and 9. Further analysis and numerous applications have been provided by Forster (1975).

Because the covariance functions are intrinsically space-time correlation functions, they are intimately related to fluctuations. Consequently, their experimental manifestation is readily observed, particularly in light scattering experiments. For example, in Chapter 4 we saw how both Einstein and Smoluchowski explained critical opalescence in terms of density fluctuations, evidenced by the milky-white appearance of the medium at the liquid–gas phase transition. The blueness of the sky constantly illustrates covariance functions in action.

The simple fluid provides a very useful model for studying many physical systems, and allows us to develop linear constitutive relations from first principles. This is an important step, because these relations have traditionally been considered entirely phenomenological, whereas they are now seen to originate in the laws of inference. Fick's and Fourier's laws, and (7.35) describing a Newtonian fluid have been verified exhaustively, but they all stem from the linear approximation (7.22). One should be aware, however, that there exist materials of some interest that are not adequately described by linear constitutive equations, and require higher-order terms in the perturbation expansion. In the case of non-Newtonian fluids the viscosity coefficients may be space and time dependent, or higher powers of the velocity gradients must be included. Examples of such fluids are ketchup and gravy; a well-known property of the latter is that the viscosity increases with stirring. We shall have occasion to discuss further the effects of nonlinear constitutive relations in Chapter 12.

8

SOURCES AND TIME-DEPENDENT PROCESSES

However beautiful the strategy, you should occasionally look at the results.
Sir Winston Churchill

In classical thermodynamics, entropy and temperature are defined only in equilibrium and, after an arbitrary stimulus, changes are computed only between two such states. Nevertheless, one is inclined to think that these quantities must be changing from instant to instant and place to place during such a process. But how is one to define a time-dependent $S(t)$ for nonequilibrium states if time is not a variable of classical thermodynamics? Do there even exist sensible physical definitions of experimental and theoretical "entropy" analogous to those describing equilibrium states? Other than the possible generalizations $S(t)$ and the density matrix $\rho(t)$, what other key parameters might be essential to a complete description of nonequilibrium? These and other questions have been debated, sometimes heatedly, for over a century without any broad consensus having been reached; we revisit them here.

In Chapter 4 we introduced the density matrix ρ as arguably the most efficient way to study a single macroscopic physical system described completely by a Hamiltonian. For an isolated system with no net external forces, the standard stages in such a study are the following: (i) construct an initial density matrix ρ_0 describing the initial macroscopic state at time t_0; (ii) let the system evolve under its Hamiltonian H, thereby evolving the density matrix ρ by the deterministic microscopic equation of motion

$$i\hbar\dot{\rho} = [H, \rho], \tag{8.1}$$

where the superposed dot denotes a total time derivative; and, (iii) at time t use the time-evolved $\rho(t)$ to predict the expectation value of a system variable C as

$$\langle C(t)\rangle = \mathrm{Tr}[\rho(t)C] = \mathrm{Tr}[\rho_0 C(t)]. \tag{8.2}$$

This last expression illustrates the equivalence of the Schrödinger and Heisenberg pictures, for Eq.(8.1) itself is equivalent to a unitary transformation:

$$\rho(t) = U(t, t_0)\rho_0 U^\dagger(t, t_0), \tag{8.3}$$

where the time-evolution operator $U(t, t_0)$ is determined by

$$i\hbar\frac{dU}{dt} = HU, \tag{8.4}$$

with initial condition $\rho(t_0) = \rho_0$. For the moment we shall consider only the Schrödinger picture in which $\rho(t)$ evolves in time; the density matrix is very definitely *not* a Heisenberg operator. If ρ is stationary, $[H, \rho] = 0$, it is a constant of the motion; and if ρ is a functional only of constants of the motion, the macroscopic state is one of thermodynamic equilibrium, corresponding to maximum entropy, and stage (ii) is solved immediately.

It would appear, at least in principle, that proceeding through these three stages must lead to a complete description of time-varying processes in a macroscopic system in terms of the underlying microscopic dynamics. An exact solution of (8.1) is practicably out of the question for any macroscopic system with a nontrivial Hamiltonian, of course, so that many approximations have been pursued over the years. All such attempts at obtaining macroscopic equations of motion tend to create some sort of irreversibility, but it is difficult to establish whether it is the real thing or simply an artifact of the approximations. In the light of Churchill's admonition, however, we now demonstrate that even *imagining* we could solve (8.1) exactly leads us into serious difficulties.

There are two simple applications of our 3-stage scenario that lead us directly to some disturbing questions concerning its general applicability. The first of these involves the response of the system to the presence of a well-defined external field. The *effects* of this field on the system are often claimed to be sensibly described by including an additional term in the Hamiltonian, as in

$$H_t = H_0 - v(t)F, \tag{8.5}$$

where $v(t)$ describes the time-dependent external force and F is a system variable (operator) coupling that force to the medium. A formal solution to (8.1), confirmed by substitution, is given by

$$\rho(t) = \rho_0 + \frac{i}{\hbar}\int_{t_0}^{t} U(t,t')v(t')\big[A, \rho_0\big]U^\dagger(t,t')\,dt', \tag{8.6}$$

and t_0 is the time at which the external force is turned on. The interpretation here is that prior to t_0 the system is in thermal equilibrium, and for $t > t_0$ the density matrix evolves unitarily under the operator $U(t, t')$ determined by (8.4) with Hamiltonian H_t. At any later time the response of the system, described by the departure of expectation values of other operators C from their equilibrium values, is found by substitution of (8.6) into (8.2):

$$\langle C(t)\rangle - \langle C\rangle_0 = \int_{t_0}^{t} \Phi_{CF}(t,t')v(t')\,dt', \tag{8.7}$$

where $\langle\ \rangle_0$ denotes an equilibrium expectation value, and

$$\Phi_{CF}(t,t') \equiv \frac{1}{i\hbar}\langle[F, C(t,t')]\rangle_0 \tag{8.8}$$

is called the *dynamic response functional.* The time dependence of C is given by $C(t, t') = U^\dagger(t, t')C(t')U(t, t')$, which is effectively now a Heisenberg operator.

The time-evolution operator U can be somewhat complicated in general, and most often a linear approximation is employed. Usually H_0 itself is time independent, in which case the leading-order approximation is given by

$$U_0(t,t_0)=\exp\Big[-\frac{i}{\hbar}(t-t_0)H_0\Big], \tag{8.9}$$

as verified by substitution into (8.4). The result is to replace Φ_{FC} in (8.7) with the *linear response function*

$$\phi_{CF}(t-t')=\frac{1}{i\hbar}\langle[F,C(t-t')]\rangle_0, \tag{8.10}$$

and the time dependence is now

$$C(t-t')=e^{i(t-t')H_0/\hbar}\,Fe^{-i(t-t')H_0/\hbar}. \tag{8.11}$$

Although this approximation has been criticized as inappropriately approximating the microscopic dynamics (*e.g.*, van Kampen, 1971), this is really the least of the problems that arise. Unquestionably, the exact time-evolved $\rho(t)$ will predict the correct value of $\langle C(t)\rangle$ at time $t>t_0$, for both the quantum mechanics and associated mathematics are impeccable. But, as noted in (8.3), that time evolution is equivalent to a unitary transformation, under which the eigenvalues of ρ are unchanged. These eigenvalues are the probabilities for the system to be found in any of its possible macrostates under given macroscopic constraints, hence there would seem to be no *macroscopic* change in the system; but there is such a change, obviously, as indicated in (8.7). A further difficulty is that the von Neumann information entropy $S_I=-k\mathrm{Tr}(\rho\ln\rho)$, where k is Boltzmann's constant, is also invariant under unitary transformation, indicating the absence of irreversible behavior during the process despite the possibility of energy having been added to the system throughout the time interval. The external source must be included!

A similar but more general application is the common task of heating a pot of water, on an electric stove, say. To describe this process in complete detail we have to specify the total system Hamiltonian H_0 of the closed system consisting of water, pot, electric burner, and interactions among them:

$$H_0=H_{\text{water}}+H_{\text{pot}}+H_{\text{burner}}+H_{\text{int}}. \tag{8.12}$$

When the burner is turned on, the voltage and current can be enfolded into an external contribution $H_{\text{ext}}(t)$, which leads to a total Hamiltonian $H_{\text{tot}}=H_0+H_{\text{ext}}$ for the heating process. With the water initially in thermal equilibrium with the rest of the system at temperature T_i, we know that the initial density matrix is given by the canonical distribution

$$\rho(0)=\frac{e^{-H_0/kT_i}}{Z}, \qquad Z=\mathrm{Tr}\,e^{-H_0/kT_i}. \tag{8.13}$$

If the burner is turned on for a period $(0,t)$, then the density matrix for the isolated system at time t is obtained by unitary transformation, as above. Upon turning off the switch, one expects the system to relax almost immediately to a final equilibrium state at temperature T_f, and the conventional teaching is that $\rho(t)$ somehow goes over into the final canonical density matrix known to describe thermal equilibrium,

$$\rho(t) \longrightarrow \rho_f = \frac{e^{-H_0/kT_f}}{Z_f}, \qquad Z_f = \operatorname{Tr} e^{-H_0/kT_f}. \tag{8.14}$$

But this cannot happen: Because the eigenvalues of ρ_f and $\rho(t)$ are in general different, the two density matrices are incompatible; the eigenvalues of $\rho(t)$ are just those of $\rho_i = \rho(0)$. Indeed, as in the previous example, the theoretical entropy of the final state is the same as that of the initial state, whereas we are certain that the initial and final *measured* entropies cannot be the same. Where is the irreversibility of this process to be found?

The source of these difficulties is that the Hamiltonian governs only the *microscopic* behavior of the system. While there is little doubt that the $\rho(t)$ evolved under H_{tot} will make correct predictions of macroscopic expectation values, it does so by including only the *local effects* of the external forces, with no reference to either the external sources or the macroscopic constraints; and it is the changes in those constraints that constitute much of the thermodynamics. Time development by unitary transformation alone affects only the basic quantum-mechanical probabilities, but not those of classical probability theory that are determined by the macroscopic constraints. The canonical microscopic equations of motion are ultimately responsible for the changing state of the system, to be sure, but both the impetus for these changes and the observed effects are macroscopic and must be included as such in any realistic analysis.

Recall the discussion in Chapter 3 where we considered small changes in the basic maximum-entropy problem, which can occur from changes in both the basic variables $f_i = f(x_i)$, as well as from changes δP_i in the assigned probabilities. This led to the relation (3.20), $\delta\langle f\rangle - \langle \delta f\rangle = \delta Q_f$, where $\delta Q_f = \sum_i f_i \delta P_i$. The important point for the current discussion is that δQ_f is effectively a *source term*, and it arises only from a change in the probability distribution. From (3.19) it is then clear that any change in the information entropy can only be induced by a δQ. Thus, since a unitary transformation corresponding to the time-evolution equation (8.1) leaves S_I invariant, any complete description of the system evolution must contain some explicit reference to the sources inducing that evolution. A source serves to change the macroscopic constraints on the system, which the microscopic equations alone cannot do, and this can lead to changes in the maximum entropy. In the case of thermal equilibrium, this is simply thermodynamics at work: A small change in $\langle f\rangle$ induced by a source δQ_f results in a new macroscopic state corresponding to a remaximized entropy, a readjustment brought about by the underlying particle dynamics, of course.

With these thoughts in mind, let us note some overall features of entropy and nonequilibrium processes that must be considered in any approach to the problem of generalizing S. Suppose we prepare a system in a nonequilibrium state by applying an external source of some kind that substantially perturbs the equilibrium system, possibly increasing its energy and adding matter to it, for example. This state is defined by imagining the external source to be removed at time $t = t_0$, and at that instant the system is described by a density matrix $\rho(t_0)$. Whether or not we can define a physical entropy at that time, we can certainly compute the maximum information entropy of that nonequilibrium state as $S(t_0) = -k\mathrm{Tr}[\rho(t_0)\ln\rho(t_0)]$. Because the system is now isolated, $\rho(t)$ can only evolve from $\rho(t_0)$ by unitary transformation and S remains constant into the future. What happens next?

At the cutoff $t = t_0$, the entropy $S(t_0)$ refers only to the nonequilibrium state at that time. In the absence of any other external influences we expect the system to relax into a new equilibrium state, for no other reason than it is the one that can be realized in the overwhelmingly greatest number of ways subject to the appropriate macroscopic constraints. The interesting point is that often those constraints are already fixed once the external sources are removed, so that the total energy, particle number, volume, and so on at t_0 are now determined for $t > t_0$. Density inhomogeneities may remain, certainly, which will relax to uniformity over the relaxation period, or to equilibrium distributions in a static external field. The entropy of the final equilibrium state is definitely *not* $S(t_0)$, but it is in principle known well before equilibrium is reached: It is the maximum of the information entropy subject to constraints provided by the values of those thermodynamic variables at $t = t_0$. We may or may not know these values, of course, although a proper theory might predict them; but once the final macrostate is established they can be measured and a new ρ_f calculated by means of the PME, and hence a new entropy predicted for comparison with the experimental form of Clausius. Indeed, in equilibrium the Clausius entropy is an upper bound for S. Thus, in this relaxation mode we may not see a nice, continuous, monotonically increasing entropy function that can be followed into the equilibrium state; but that is not too surprising, given that we know $\rho(t_0)$ cannot evolve unitarily into ρ_f. (More about relaxation in Chapter 11.) There remains a significant dynamical evolution during this relaxation period, but it is primarily on a microscopic level; its macroscopic manifestation is to be found in the relaxation time, and the possible observation of decaying currents. One thing we might compute and measure in this mode is that relaxation time, which does not necessarily have an immediate connection with entropy. (There may, however, exist a "relaxation entropy" associated with the redistribution of energy, say, during the relaxation period.)

Ironically, the equilibrium state described so well by classical thermodynamics is essentially a dead end; it is a *singular limit* in the sense discussed by Berry (2002).[1] Equilibrium is actually a very special, ideal state, for most systems are

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[1] In Berry's words: "Biting into an apple and finding a maggot is unpleasant enough, but finding half a maggot is worse. Discovering one-third of a maggot would be more distressing still: The less you find, the more you may have eaten. Extrapolating to the limit, an encounter with no maggot at all should be the ultimate bad-apple experience. This remorseless logic fails,

not usually in equilibrium, at least not completely. As external influences, and therefore time variations, become smaller, the system still remains in a nonequilibrium state evolving in time. In the limit there is a discontinuous *qualitative* change in the macroscopic system and its description. That is, there is no longer either a macroscopic evolution or a past history,[2] and the main role of the theory is to compare neighboring states of thermal equilibrium without regard for how those states might have been prepared.

It has long been understood, though not widely, that entropy is not a property of a physical system *per se*, but of the thermodynamic system describing it, and the latter is defined by the macroscopic constraints imposed. The above remarks, however, lead us to view entropy more as a property of the macrostate, or of the processes taking place in a system. In the equilibrium state these distinctions are blurred, because the thermodynamic system and the macrostate appear to be one and the same thing and there are no time-dependent macroscopic processes. It will be our goal in the following pages to clarify these comments, as well as to provide an unambiguous definition of time-dependent entropy in nonequilibrium systems, and to understand the possibly very different roles that the entropy concept plays in the two states.

Our problem is that of defining a time-dependent probability *unambiguously.* An understanding that all probabilities are conditional on some kind of information leads to the realization that $P(A_i|I)$ can change in time only if the information I is changing in time, while the propositions A_i are taken as fixed. For example, if the trajectory $y(t)$ of a particle is changing erratically owing to the presence of an unknown time-varying field, the allowed values of y do not change, but information on the current position and some time-dependent effects of that field might permit construction of probabilities for which values of y might be realized at some later time t. In a macroscopic system this type of information $I(t)$ consists of external constraints whose time variation arises from macroscopic sources that drive the system into, and maintain, nonequilibrium states.

8.1 Equation of motion revisited

If we believe that only an external source can produce changing macroscopic constraints and time-varying information $I(t)$, then $\rho(t)$ must evolve in a manner over and above that determined by the Hamiltonian alone. In fact, such an additional evolution is already implied by the density-matrix formalism, as we now demonstrate.

In the equation of motion (8.1) for the density matrix we noted that the superposed dot represented a *total* time derivative. But in many works the

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however, because the limit is singular: A very small maggot fraction ($f \ll 1$) is qualitatively different from no maggot ($f = 0$)."

[2] Requiring the equilibrium system to have no "memory" of its past precludes "mysterious" effects such as those caused by spin echos.

equation is commonly written as

$$i\hbar\partial_t\rho = [H,\rho], \tag{8.15}$$

where H may be time dependent. The standard argument is that the derivative in (8.15) is indeed a partial derivative because this expression is derived directly from the Schrödinger equation, which contains a partial time derivative, although it makes no difference in (8.15) since ρ depends only on t. This comment would not be notable were it not for an additional interpretation made in most writings on statistical mechanics, where ρ describes the entire macroscopic system.

Equation (8.15) is often compared with the Heisenberg equation of motion for an operator $F(t)$ in the Heisenberg picture,

$$\frac{dF}{dt} = \frac{1}{i\hbar}[F,H] + \partial_t F, \tag{8.16}$$

whereupon it is concluded from analogy with Liouville's theorem that $d\rho/dt = 0$ and (8.15) is just the quantum-mechanical version of Liouville's equation in classical statistical mechanics. But there is nothing in quantum mechanics that requires this conclusion, for $\rho(t)$ is not a Heisenberg operator; it is basically a projection operator constructed from state vectors, and in any event (8.15) refers to the Schrödinger picture. Heisenberg operators are analogous to functions of phase in classical mechanics, ρ is not. We shall argue here that the derivative in (8.15) should be considered a total time derivative, as asserted earlier for (8.1); this follows from a more careful derivation of that equation than presented in Chapter 4.

To find an equation of motion for ρ we recall the definition (4.5) of the density matrix in terms of its matrix elements in the orthogonal basis,

$$\rho_{kn} = \sum_i a_{ki}a_{ni}^* w_i\,, \qquad \sum_i w_i = 1, \tag{8.17}$$

where w_i are the weights of the underlying possible states of the system, and the coefficients have equations of motion

$$i\hbar\dot{a}_{ij} = \sum_k a_{ik}H_{jk}\,, \qquad H_{jk} \equiv \langle u_j|H|u_k\rangle. \tag{8.18}$$

The superposed dot here denotes a total time derivative, for a_{ij} describes a particular state and depends only on the time. One thus derives an equation of motion for ρ as in Chapter 4 by direct differentiation in (8.17), but now this step requires a bit more preliminary comment.

Usually the weights w_i are taken to be constants, determined by some means outside the quantum theory itself. In fact, they are classical probabilities and can be determined in principle from the PME under constraints representing information characterizing the macrostate of the system. As noted above, however, if that information is changing in time, as with a nonequilibrium state, then the probabilities will also be time dependent. Hence, quite generally one should consider $w_i = w_i(t)$; if such time dependence is absent we recover the usual situation.

An equation of motion for ρ is now found in a straightforward manner, with the help of (8.17) and (8.18), by computing its total time variation:

$$i\hbar\dot{\rho}_{kn} = \sum_q \big(H_{kq}\rho_{qn} - H_{nq}\rho_{kq}\big) + i\hbar\sum_i \dot{w}_i a_{ki}a^*_{ni}, \tag{8.19}$$

or in operator notation

$$i\hbar\dot{\rho} = [H,\rho] + i\hbar\partial_t\rho. \tag{8.20}$$

The term $i\hbar\partial_t\rho$ is meant to convey only the time variation of the w_i.

Comparison of (8.20) with (8.16) confirms that the former is *not* a Heisenberg equation of motion—the commutators have opposite signs. Indeed, in the Heisenberg picture the only time variation in the density matrix is given by $\partial_t\rho$. If, in fact, the probabilities w_i are constant, as in equilibrium states, then (8.20) verifies (8.15) but with a total time derivative. Otherwise, (8.20) is the general equation of motion for the density matrix, such that the first term on the right-hand side describes the usual unitary time development of an isolated system. The presence of external sources, however, can lead to an explicit time dependence as represented by the second term, and thus the evolution is not completely unitary; classically, Liouville's theorem is not applicable in this case.

Incidentally, although obscure in classical physics, the general thread of this chapter is intrinsic to quantum mechanics. While the Hilbert space is continually being mapped back onto itself, the fundamental structure of the density matrix, such as its eigenvalues, remains unchanged, single-particle systems included. A significant change of state can occur only through an external process, such as a measurement, most often with a macroscopic device.

But even when external sources are explicitly absent, W and S in all real systems will eventually change a bit over time due to "random" weak external interactions with the rest of the universe. Recognition of the necessary role of arbitrary types of external sources suggests that there may exist an easier way to approach the study of nonequilibrium processes like these, other than attempting to solve directly an incredibly complex equation such as (8.20). The first step is an explicit study of the term $i\hbar\partial_t\rho$.

9

THERMAL DRIVING

> *In one respect we have even generalized the entropy principle here, in that we have been able to define the entropy in a gas that is not in a stationary state.*
>
> *Ludwig Boltzmann (1896)*

We seek a description of macroscopic nonequilibrium behavior that is generated by an arbitrary source whose precise details may be unknown. One should be able to infer the presence of such a source from the data, and both the strength and rate of driving of that source should be all that are required for predicting reproducible effects. Given data—expectation values, say—that vary continuously in time, we infer a source at work and expect ρ to be a definite function of time, possibly evolving principally by external means. In the previous chapter we argued that, because all probabilities are conditional on some kind of given information or hypothesis, $P(A_i|I)$ can change in time only if the information I is changing in time, while the propositions $\{A_i\}$ are taken as fixed. With this insight we can see how the Gibbs algorithm might be extended to time-varying macroscopic systems in a straightforward manner.

As in Chapter 6, information gathered in one time interval can certainly be followed by collection in another a short time later, and can continue to be collected in a series of such intervals, but now we imagine the entropy to be remaximized subject to all previous data after each interval. Then let those intervals become shorter and the intervals between them closer together, so that by an obvious limiting procedure they all blend into one continuous interval whose upper endpoint is always the current moment. Thus, there is nothing to prevent us from imagining a situation in which our information or data are continually changing in time. A rationale for envisioning remaximization to occur at every moment, rather than all at once, can be found by again appealing to Boltzmann's expression for the entropy: $S_{\mathrm{B}} = k \ln W$. At any moment W is a measure of the phase volume of all those microstates compatible with the macroscopic constraints that can be realized in the greatest number of ways—and $\ln W$ is the maximum of the information entropy at that instant. As Boltzmann realized, this is a valid representation of the maximized entropy even for a nonstationary state. It is essential to understand that W is a *number* representing the multiplicity of a macrostate that changes only as a result of changing external constraints. It is not a descriptor of which microscopic arrangements are being realized by the system at the moment—there is no way we can ascertain that—but only a measure of how many such states may be compatible with the macrostate defined by those constraints. In principle we could always compute a W for a set of values of the macroscopic constraints without ever carrying out an experiment. Thus, we begin to see how an *evolving* entropy can possibly be related to the time-dependent process.

There may seem to be a problem here for someone who thinks of probabilities as real physical entities, since it might be argued that the system cannot possibly respond fast enough for W to readjust its content instantaneously. But it is not the response of the system that is at issue; only the set of *possible* microstates compatible with the present macroscopic constraints needs to change to readjust W. Those possibilities always exist and need no physical signal to be realized. The physical response throughout the system may well lag the changes in external constraints, but the change in multiplicity is immediate. Only variations in the macroscopic constraints can change W, and those are instantaneous and lead to immediate change in the maximum information entropy S_{B}.

Figure 9.1 depicts a possible history of the macroscopic state of the driven system in phase-space-time as time unfolds from left to right; it is a generalization of Fig. 4.1b. The tube is a bundle of all possible high-probability maximum-entropy trajectories by which the system could have evolved subject to given constraints over a time interval $(0, t)$, and a cross section perpendicular to the time axis is a measure $W(t)$ of the maximum information entropy at that particular time. That is, the trajectories are loci of instantaneous states compatible with $S(t)$ at that time; they each have equal probability of being realized, just as each state in the HPM has equal probability at each t. The tube can expand and contract and explore different regions of phase space as dictated by external forces; it is a history of the high-probability manifold. Unlike the trajectories in Fig. 4.1 that evolve under the microscopic equations of motion, those in Fig. 9.1 are governed by both those and the external forces.

Let us suppose that the system is in thermal equilibrium with time-independent Hamiltonian sometime in the past, and then at $t = 0$ a source is turned on smoothly and specified to run continuously, as described by its effect on the

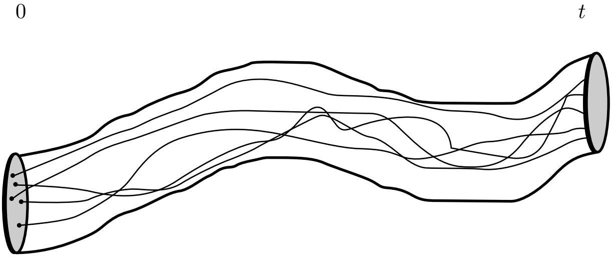

FIG. 9.1. Schematic illustration of the tube in phase-space-time representing the history of a system over a time interval $(0, t)$, containing every high-probability trajectory over which the system could have evolved. A cross section perpendicular to the time axis is a measure of the maximum entropy at that time.

expectation value $\langle F(t)\rangle$. That is, $F(t)$ is given throughout the changing interval $[0,t]$ and is specified to continue to change in a known way until further notice.[1] A variable, and therefore the system itself, is said to be *thermally driven* if no new variables other than those constrained experimentally are needed to characterize the resulting state, and if the Lagrange multipliers corresponding to variables other than those specified remain constant. Those other variables themselves may change, but only as a result of being correlated with those that are driven. Although any complete theory of nonequilibrium must be a continuum field theory, we shall omit spatial dependence explicitly here in the interest of clarity and return to address that point later. For convenience we consider only a single driven operator; multiple operators, both driven and otherwise, are readily included. The Principle Maximum Entropy (PME) then provides the density matrix for thermal driving, which is not constrained to evolve by unitary transformation alone:

$$\begin{aligned} \rho_t &= \frac{1}{Z_t}\exp\left[-\beta H - \int_0^t \lambda(t')F(t')\,dt'\right], \\ Z_t[\beta,\lambda(t)] &= \mathrm{Tr}\,\exp\left[-\beta H - \int_0^t \lambda(t')F(t')\,dt'\right], \end{aligned} \tag{9.1}$$

and the Lagrange multiplier function is *formally* obtained from

$$\langle F(t)\rangle_t = -\frac{\delta}{\delta\lambda(t)}\ln Z_t, \tag{9.2}$$

for t in the driving interval. Reference to the equilibrium state is made explicit not only because it provides a measure of how far the system is removed from equilibrium, but also because it removes all uncertainty as to the previous history of the system prior to introduction of the external source. Clearly, these are not essential features of the construction, and information about the equilibrium system need not be included; it must be, of course, if approximations to the nonequilibrium state are to be made.

A note of caution is in order. When we say that F is "driven" we are *not* asserting that it is the operator itself that is driven, whatever that might mean. Rather, we are monitoring its expectation value, which is changing due to the presence of external forces acting on the system to change the density matrix by changing the external constraints. That is, our information $\langle F\rangle$ is evolving, either actually or by specification.

Since ρ_t can now be considered an explicit function of t, we can employ the operator identity $\partial_x e^{A(x)} = e^{A(x)}\overline{\partial_x A}$ from Appendix A to compute the time derivative:

$$\partial_t\rho_t = \rho_t\lambda(t)\left[\langle F(t)\rangle_t - \overline{F(t)}\right], \tag{9.3}$$

---

[1] The lower limit of the driving interval is chosen as 0 only for convenience.

where the overline denotes a *generalized Kubo transform* as in (6.11),

$$\overline{F(t)} \equiv \int_0^1 e^{-u\ln\rho_t}\, F(t) e^{u\ln\rho_t}\, du. \tag{9.4}$$

The expression (9.3) has the *form* of what is often called a "master equation," but it has an entirely different origin and is exact; it is, in fact, the term $\partial_t\rho$ in the equation of motion (8.20). Because $\lambda(t)$ is defined only on the information-gathering interval $[0,t]$, Eq.(9.3) just specifies the rate at which ρ_t is changing in that interval. Although ρ_t does not evolve by unitary transformation under time-independent H in the Heisenberg picture, in this case it does evolve explicitly, and in the Schrödinger picture this time variation will be in addition to the canonical time evolution. In turn, an unambiguous time dependence for the entropy is implied, as follows.

The theoretical maximum entropy $S_t = -k\mathrm{Tr}[\rho_t \ln\rho_t]$ is obtained explicitly by substitution from (9.1),

$$\frac{1}{k}S_t = \ln Z_t + \beta\langle H\rangle_t + \int_0^t \lambda(t')\langle F(t')\rangle_t\, dt'; \tag{9.5}$$

it is the continuously remaximized information entropy. Equation (9.5) indicates explicitly that $\langle H\,\rangle_t$ changes only as a result of changes in, and correlation with, F. The constraint that H is explicitly not driven implies that $\langle H\,\rangle_t$ changes only as a result of changes in $\langle F(t')\rangle_t$, and the two are no longer independent. Consequently, $\lambda(t)$ cannot be determined directly from S_t by functional differentiation in (9.5); this has important consequences. Other Heisenberg operators will evolve unitarily as usual, but their expectation values will change as determined by ρ_t.

The expectation value of another operator at time t is $\langle C\,\rangle_t = \mathrm{Tr}[\rho_t C]$, and direct differentiation yields, from (9.3),

$$\begin{aligned}\frac{d}{dt}\langle C(t)\rangle_t &= \mathrm{Tr}\big[C(t)\partial_t\rho_t + \rho_t\dot{C}(t)\big]\\ &= \langle\dot{C}(t)\rangle_t - \lambda(t)K^t_{CF}(t,t),\end{aligned} \tag{9.6}$$

where the superposed dot denotes a total time derivative. We have here introduced the *generalized* (*nonlinear*) *covariance function*

$$K^t_{CF}(t',t) \equiv \langle\overline{F(t')}C(t)\rangle_t - \langle F(t')\rangle_t\,\langle C(t)\rangle_t = -\frac{\delta\langle C(t)\rangle_t}{\delta\lambda(t')}, \tag{9.7}$$

which reduces to that of the equilibrium system for $\rho_t \to \rho_0$; that is, subscripts and superscripts t are set to 0. Note that all of the preceding entities are completely nonlinear, in that expectation values, Kubo transforms, and covariance functions are all written in terms of the density matrix ρ_t, which is the meaning of the superscript t on K^t_{CF} as well as the subscripts on expectation values.

Although time-translation invariance is not necessarily a property of the general nonequilibrium system, it is not difficult to show that the reciprocity relation $K^t_{CF}(t',t) = K^t_{FC}(t,t')$ is valid.

Let us introduce a new notation into (9.6), which at first appears to be only a convenience:

$$\sigma_C(t) \equiv \frac{d}{dt}\langle C(t)\rangle_t - \langle \dot{C}(t)\rangle_t = -\lambda(t)K^t_{CF}(t,t). \tag{9.8}$$

For a number of choices of C and F the equal-time covariance function vanishes, but if $C = F$ an illuminating interpretation first noticed by Mitchell (1967) emerges:

$$\begin{aligned}\sigma_F(t) &\equiv \frac{d}{dt}\langle F(t)\rangle_t - \langle \dot{F}(t)\rangle_t \\ &= -\lambda(t)K^t_{FF}(t,t).\end{aligned} \tag{9.9}$$

Owing to the specification of thermal driving, $d\langle F(t)\rangle_t/dt$ is the total time rate of change of $\langle F(t)\rangle_t$ in the system at time t, whereas $\langle \dot{F}(t)\rangle_t$ is the rate of change produced by internal relaxation. Hence, $\sigma_F(t)$ must be the rate at which F is driven or transferred by the external source, and is often what is measured or controlled experimentally. One need know nothing else about the details of the source, because its total effect on the system is expressed by the second equality in (9.9). If the source strength is given, then (9.9) is a nonlinear transcendental equation determining the Lagrange multiplier function $\lambda(t)$.

Note that the first line of (9.9) is once again a conservation law, a time-varying generalization of (3.20) or (3.25); that is, a time-dependent "generalized First Law."

An important reason for eventually including spatial dependence is that we can now *derive* the macroscopic equations of motion. For example, if $F(t)$ is one of the conserved densities $e(\boldsymbol{x},t)$ in a simple fluid and $\boldsymbol{J}(\boldsymbol{x},t)$ the corresponding current density, then the *local* microscopic continuity equation

$$\dot{e}(\boldsymbol{x},t) + \boldsymbol{\nabla}\cdot\boldsymbol{J}(\boldsymbol{x},t) = 0 \tag{9.10}$$

is satisfied irrespective of the state of the system. When this is substituted into the first line of (9.9) we obtain the macroscopic conservation law

$$\frac{d}{dt}\langle e(\boldsymbol{x},t)\rangle_t + \boldsymbol{\nabla}\cdot\langle \boldsymbol{J}(\boldsymbol{x},t)\rangle_t = \sigma_e(\boldsymbol{x},t), \tag{9.11}$$

which is completely nonlinear. Specification of sources therefore provides automatically the thermokinetic equations of motion; for example, if e is the momentum density $m\boldsymbol{j}(\boldsymbol{x},t)$, so that $\boldsymbol{J}$ is the stress tensor T_{ik}, then a series of transformations extracts from (9.11) the Navier–Stokes equations of fluid dynamics (Chapter 10).

9.1 Nonequilibrium thermodynamics

The notion of thermal driving provides a basis for nonequilibrium thermodynamics, which can be developed in much the same way as is done for the equilibrium theory, although the latter can only serve as a guide. As with that case, the operator F can also depend on an external variable α, so that at time t the entropy is $S_t = S_t[\langle H\rangle_t, \langle F(t)\rangle_t; \alpha]$; of course, we could also include a number of other measured variables $\{F_i\}$, though only H and F will be employed here. But now S_t is also a function of time and, from (9.5), its total time derivative is

$$\frac{1}{k}\frac{dS_t}{dt} = \left(\frac{\partial \ln Z_t}{\partial \alpha}\right)\dot{\alpha} + \beta\frac{d\langle H\rangle_t}{dt} - \lambda(t)\int_0^t \lambda(t')K_{FF}^t(t,t')\,dt'. \tag{9.12}$$

Although $\partial_t Z_t$ contributes to $\dot{S}_t$, its contribution is cancelled because

$$\partial_t \ln Z_t = -\lambda(t)\langle F(t)\rangle_t, \tag{9.13}$$

which also provides a novel representation for Z_t upon integration. In principle, then, one can follow the increase (or decrease) of the maximum information entropy in the presence of external sources (or sinks); $\dot{S}_t$ need not be positive.

The most common type of external variable α is the system volume V, so that in the equilibrium theory $(\partial\langle H\rangle/\partial V)dV = -P\,dV$ is an element of work, as indicated by (3.22) and (3.25). This suggests a general interpretation of the first term on the right-hand side of (9.12). As an example, in the present scenario, consider the simple process of an adiabatic free expansion of a gas, wherein only the work term is involved in (9.12). We can now model this by specifying a form for $\alpha = V$; $V(t) = V_0\big(2 - e^{-bt}\big)$, say, would, for b very large, rapidly inflate the volume to double its size over an interval from $t = 0$ to some later time τ. The coefficient of $\dot{\alpha}$ in (9.12) is proportional to the pressure, so that one also needs an equation of state for the gas; but usually the pressure is proportional to V^{-1} and therefore decreases exponentially as well. In the case of an ideal gas, integration of this form for $\dot{S}_t$ over $(0,\tau)$ yields the expected change $S_\tau - S_0 = kN\ln 2$. This result is almost independent of the model as long as $V(\tau) \simeq 2V_0$.

Often $\dot{\alpha} = 0$. In this case we can also explicitly evaluate the term containing the Hamiltonian and rewrite (9.12) as

$$\begin{aligned}\frac{1}{k}\frac{dS_t}{dt} &= -\beta\lambda(t)K_{HF}^t(t,0) - \lambda(t)\int_0^t \lambda(t')K_{FF}^t(t,t')\,dt' \\ &= \gamma_F(t)\sigma_F(t),\end{aligned} \tag{9.14}$$

where we have employed (9.9) and defined a new parameter

$$\gamma_F(t) \equiv \beta\frac{K_{HF}^t(t,0)}{K_{FF}^t(t,t)} + \int_0^t \lambda(t')\frac{K_{FF}^t(t,t')}{K_{FF}^t(t,t)}\,dt'. \tag{9.15}$$

Although this expression for γ at first glance seems only a bookkeeping convenience, it is actually of some physical significance. As noted above, the thermal driving constraint on H prevents $\langle H\rangle_t$ and $\langle F(t)\rangle_t$ from being completely independent; indeed, neither of them is independent of $\langle F(t')\rangle_t$. In turn, and unlike the equilibrium case, $\partial\langle f_m\rangle/\partial\lambda_n$ and $\partial\lambda_n/\partial\langle f_m\rangle$ are no longer the respective elements of a pair of mutually inverse matrices. Thus, $\delta S_t/\delta\langle F(t)\rangle_t$ does not determine $\lambda(t)$; rather, from (9.5),

$$\frac{\delta S_t}{\delta\langle F(t)\rangle_t}=\frac{\delta\langle H\rangle_t}{\delta\lambda(t)}\frac{\delta\lambda(t)}{\delta\langle F(t)\rangle_t}+\int_0^t\lambda(t')\frac{\delta\langle F(t')\rangle_t}{\delta\lambda(t)}\frac{\delta\lambda(t)}{\delta\langle F(t)\rangle_t}\,dt'. \tag{9.16}$$

Owing to interdependencies we can now write $\delta\lambda(t)/\delta\langle F(t)\rangle_t=1/K^t_{FF}(t,t)$, and hence the right-hand side of (9.16) is just $\gamma_F(t)$, which now has the general definition

$$\gamma_F(t)\equiv\left(\frac{\delta S_t}{\delta\langle F(t)\rangle_t}\right)_{\substack{\text{thermal}\\ \text{driving}}}. \tag{9.17}$$

The subscript "thermal driving" reminds us that this derivative is evaluated somewhat differently than in the equilibrium formalism. When the source strength $\sigma_F(t)$ is specified the Lagrange multiplier itself is determined from (9.9).

To interpret γ_F, return to the equilibrium theory and note that a small change in the equilibrium distribution can be characterized by a small change in the Lagrange multiplier, which in turn will induce a small variation in an expectation value: $\delta\langle f\rangle=(\partial\langle f\rangle/\partial\lambda)\delta\lambda=-K_{ff}\delta\lambda$, from (3.28) or (6.6). Hence, $\delta\langle f\rangle$ can be thought of as a "flux" and $-\delta\lambda$ as the "force" driving the system back to equilibrium. We can thus think of λ itself as the "potential" producing this force.

Physically, γ_F is a *transfer potential* in the same sense that λ is thought of as a potential. Just as products of potentials and expectation values appear in the structure of the equilibrium entropy, in thermal driving the entropy production (9.14) is always a sum of products of transfer potentials and source terms measuring the rate of transfer. So, the entropy production is not in general given by products of "fluxes" and "forces," and S_t and $\dot{S}_t$ are not simple generalizations of equilibrium quantities. But the ordinary potentials also play another role in equilibrium: if two systems in contact can exchange energy and particles, then they are in equilibrium if the temperatures and chemical potentials of the two are equal. Similarly, if two systems can exchange quantities F_i under thermal driving, then the conditions for *migrational equilibrium* at time t are

$$\gamma_{F_i}(t)_1=\gamma_{F_i}(t)_2. \tag{9.18}$$

Migrational equilibrium in stationary processes is discussed, for example, by Tykodi (1967).

What is the physical interpretation to be given to S_t? Clearly it refers only to the information encoded in the distribution of (9.1) and cannot refer to the internal entropy of the system. In equilibrium the maximum information entropy is the same as the experimental entropy, but that is not necessarily the case here. For example, if the driving is removed at time $t = t_1$, then S_{t_1} in (9.5) can only provide the entropy of that nonequilibrium state at $t = t_1$; its value will remain the same during subsequent relaxation, owing to unitary time evolution. Although the maximum information (or theoretical) entropy provides a complete description of the system based on all known physical constraints on that system, it cannot describe the ensuing relaxation, for ρ_t contains no new information about that process; it does not "know" the driving constraint has been removed. Nevertheless, S_t does have a definite physical interpretation.

The form of σ_F in (9.9) suggests a natural separation of the rate of change of entropy first suggested by Mitchell (1967). If that expression is substituted into the second line of (9.14) we have

$$\frac{1}{k}\dot{S}_t = \gamma_F(t)\left(\frac{d}{dt}\langle F(t)\rangle_t - \langle \dot{F}(t)\rangle_t\right). \tag{9.19}$$

The first term on the right-hand side of (9.19) must represent the total time rate of change of entropy $\dot{S}_{tot}$ arising from the thermal driving of $F(t)$, whereas the second term is the rate of change of internal entropy $\dot{S}_{int}$ owing to relaxation. Thus, the rate at which the total entropy changes can be written as

$$\dot{S}_{tot}(t) = \dot{S}_t + \dot{S}_{int}(t), \tag{9.20}$$

where the rate of change of the *entropy of transfer* owing to the external source, $\dot{S}_t$, is given by (9.14). This latter quantity is a function only of the driven variable $F(t)$, whereas the internal entropy depends on all variables, driven or not, necessary to describe the nonequilibrium state and its rate is determined by the various relaxation processes taking place in the system. The latter are governed by the basic conservation laws, as well as the material parameters of the system.

The quantity $\dot{S}_{tot}(t)$ is *defined* by the above expression—it arises only as a result of thermal driving, or the presence of a nonequilibrium process. There is no reason to infer the existence of an actual $S_{tot}(t)$ itself for the process.

As seen from (9.12), $\dot{S}_t$ refers only to the information encoded in the maximum-entropy distribution ρ_t. It is a functional only of the driven variable $F(t)$—or, rather, the given information $\langle F(t)\rangle$. It is the rate of change of the maximum information entropy at time t, and is related directly to the source term $\sigma_F(t)$. This emphasizes once again that both system and source must be considered *conjointly* in these processes. In addition, $\dot{S}_t$ is a direct measure of dissipation in the whole owing to the source/sink action, and S_t itself is the entropy of the *process*.

Finally, $\dot{S}_{int}(t)$ is the rate of dissipation within the system owing to relaxation of F internally, and is necessarily non-negative. Although S_{int} itself has no meaning as a time-varying thermodynamic entropy, $\dot{S}_{int}(t)$ is indicative of how S will have changed for the system if it relaxes to equilibrium. But S_{int} is generally very complicated, for it depends on all variables necessary to describe the nonequilibrium state, as well as on the relaxation processes taking place internally. In Chapter 11 we shall come close to identifying a quantity like S_{int} for relaxation processes, but not with a satisfactory general definition.

The *form* of (9.20) has been noted often in phenomenological theories of irreversible thermodynamics (*e.g.*, Onsager, 1931a), although the expression is simply postulated and the quantities within may have slightly different meanings. In particular, Gyarmati (1970) and Ziegler (1983) have developed extensive phenomenological theories of nonequilibrium thermodynamics based on an interpretation of a quantity like $\dot{S}_{int}(t)$. For us, all three quantities in (9.20) have no immediate connection to a measurable thermodynamic entropy, but should be considered as measures of dissipation in the nonequilibrium process and system; this interpretation is examined further in Chapter 12.

In an equilibrium system a major role of S is associated with the Second Law, and this law in its traditional form has little to say about nonequilibrium processes. In these latter processes, however, it is $\dot{S}_t$, rather than S_t itself that plays the major role, as is seen in (9.14)–(9.17). That is, $\dot{S}_t$ governs the transfer process in terms of the rate of driving and the transfer potential, in much the same way that S governs the direction of changes between equilibrium states through dQ/T. In a nonequilibrium process, $\dot{S}_t$ also governs the rate; this is true even in the steady state when one takes into account sources and sinks.

9.2 Linear heating

Further contact with classical thermodynamics emerges from a more specific example, which requires a description in terms of field variables. We shall thus need generalizations of the primary equations of thermal driving to include spatial coordinates:

$$\partial_t \rho_t = \rho_t \int \lambda(\boldsymbol{x}', t) \big[\langle F(\boldsymbol{x}', t) \rangle_t - \overline{F(\boldsymbol{x}', t)} \big] \, d^3x' \,, \tag{9.21}$$

$$\frac{1}{k} S_t = \ln Z_t + \beta \langle H \rangle_t + \int d^3x' \int_0^t dt' \, \lambda(\boldsymbol{x}', t') \langle F(\boldsymbol{x}', t') \rangle_t , \tag{9.22}$$

$$\begin{aligned} \frac{1}{k} \dot{S}_t = & -\beta \int \lambda(\boldsymbol{x}', t) K^t_{HF}(\boldsymbol{x}', t) \, d^3x' \\ & - \int d^3x'' \lambda(\boldsymbol{x}'', t) \int d^3x' \int_0^t dt' \lambda(\boldsymbol{x}'', t') K^t_{FF}(\boldsymbol{x}'', t; \boldsymbol{x}', t'), \end{aligned} \tag{9.23}$$

$$\begin{aligned} \sigma_F(\boldsymbol{x}, t) &= \frac{d}{dt} \langle F(\boldsymbol{x}, t) \rangle_t - \langle \dot{F}(\boldsymbol{x}, t) \rangle_t \\ &= - \int \lambda(\boldsymbol{x}', t) K^t_{FF}(\boldsymbol{x}', t; \boldsymbol{x}, t) \, d^3x' . \end{aligned} \tag{9.24}$$

Note that we have presumed $\dot{\alpha} = 0$, and that a volume integral over the first line of (9.24) returns us to (9.9)

Let the homogeneous system be driven from equilibrium by a thermal source that drives the energy density $h(\boldsymbol{x}, t)$. Again we note that neither the Hamiltonian nor the energy-density *operators* are affected; H remains unchanged and h still evolves unitarily. Rather, it is their expectation values that are explicitly changing in time with the macrostate, and the two operators remain related as in (6.29). This is possibly a subtle point that requires some reflection upon (9.1) and its origin.

In general, the entropy of the process is changing in a somewhat complicated manner, as indicated in (9.12) and (9.23), but in linear approximation we see that

$$\dot{S}_t = k\beta\frac{d}{dt}\langle H\rangle_t = -\beta\int \lambda(\boldsymbol{x}',t)K^0_{Hh}(\boldsymbol{x}',t)\,d^3x'. \tag{9.25}$$

In addition, no work is done on the system in this linear process, so that the conservation law (9.24) reduces to $\sigma_h(\boldsymbol{x},t) = \frac{d}{dt}\langle h(\boldsymbol{x},t)\rangle_t$, and a volume integral yields a time-dependent version of the First Law: $\sigma_h \equiv \dot{Q} = \dot{U}$. The content of (9.25) is then

$$\dot{S}_t = \frac{\dot{Q}}{T}, \tag{9.26}$$

and T remains the temperature of the original equilibrium state; the actual Lagrange multiplier is contained in the second equality in (9.24). These expressions are remarkably like those advocated by Truesdell (1984) in his development of Rational Thermodynamics, and are what one might expect from naïve time differentiation of the corresponding equilibrium expressions. Indeed, such an extrapolation may provide a useful guide to nonequilibrium relations, but in the end only direct derivation from a coherent theory is reliable.

In (9.20) the term $\dot{S}_{int}$ is positive semidefinite, for it corresponds to the increasing internal entropy of relaxation; this is demonstrated explicitly in Chapter 11. Combination with (9.26) then allows one to rewrite (9.20) as an inequality:

$$\dot{S}_{tot} = \frac{\dot{Q}}{T} + \dot{S}_{int} \geq \frac{\dot{Q}}{T}. \tag{9.27}$$

One hesitates to refer to this expression as an extension of the Second Law, for such a designation is fraught with ambiguity; the latter remains a statement about the entropies of two equilibrium states. Instead, it may be more prudent to follow Truesdell in referring to (9.27) as the *Clausius–Planck inequality.*

In linear approximation the heating process is described by

$$\langle h(\boldsymbol{x},t)\rangle_t - \langle h(\boldsymbol{x})\rangle_0 = -\int_V d^3x' \int_0^t dt'\,\lambda(\boldsymbol{x}',t')K^0_{hh}(\boldsymbol{x}-\boldsymbol{x}',t-t'), \tag{9.28}$$

$$\sigma_h(\boldsymbol{x},t) = -\int_V \lambda(\boldsymbol{x}',t)K^0_{hh}(\boldsymbol{x}-\boldsymbol{x}',t=0)\,d^3x'. \tag{9.29}$$

After a well-defined period of driving the source is removed, the system is again isolated, and we expect it to relax to equilibrium; the upper limit of integration in (9.28) is now a constant, say t_1. Presumably this is a reproducible process.

For convenience we take the system volume to be all space and integrate the last two expressions over the entire volume, thereby converting the densities into total Hamiltonians. Owing to spatial uniformity and cyclic invariance the covariance function in (9.28) is then independent of the time (the evolution being unitary after removal of the source), and we shall denote the volume integral of $\sigma_h(\boldsymbol{x},t)$ by $\sigma_h(t)$. Combination of the two equations for $t > t_1$ yields

$$\langle H\rangle_{t_1} - \langle H\rangle_0 = \int_0^{t_1} \sigma_h(t')\,dt'\,, \qquad t > t_1, \tag{9.30a}$$

or

$$\langle H\rangle_{t_1} = \langle H\rangle_0 + \Delta U, \tag{9.30b}$$

which is now a constant. The total internal energy of the new equilibrium state is now known, and the density matrix describing that state can be constructed via the PME.

The last few paragraphs provide a formal description of slowly heating a pot of water on a stove, but in reality much more is going on in that pot than simply increasing the temperature. Experience tells us that the number density is also varying, though N/V is constant (if we ignore evaporation), and a proper treatment ought to include both densities. But thermal driving of $h(\boldsymbol{x},t)$ requires that $n(\boldsymbol{x},t)$ is explicitly *not* driven, changing only as a result of changes in h, through correlations. The proper density matrix describing this model[2] is

$$\begin{aligned}\rho_t = \frac{1}{Z_t}\exp\Bigg[-\beta H - \int d^3x' \int_0^t \Big[\lambda_h(\boldsymbol{x}',t')h(\boldsymbol{x}',t') \\ + \lambda_n(\boldsymbol{x}',t')n(\boldsymbol{x}',t')\Big]\,dt'\Bigg],\end{aligned} \tag{9.31}$$

and the new constraint is expressed by the generalization of (9.8) to the set of linear equations

$$\begin{aligned}\sigma_h(\boldsymbol{x},t) &= -\int \lambda_h(\boldsymbol{x}',t)K^0_{hh}(\boldsymbol{x}-\boldsymbol{x}';t-t)\,d^3x' \\ &\qquad - \int \lambda_n(\boldsymbol{x}',t)K^0_{hn}(\boldsymbol{x}-\boldsymbol{x}';t-t)\,d^3x'\,, \\ 0 &= -\int \lambda_h(\boldsymbol{x}',t)K^0_{nh}(\boldsymbol{x}-\boldsymbol{x}';t-t)\,d^3x' \\ &\qquad - \int \lambda_n(\boldsymbol{x}',t)K^0_{nn}(\boldsymbol{x}-\boldsymbol{x}';t-t)\,d^3x',\end{aligned} \tag{9.32}$$

asserting explicitly that $\sigma_n \equiv 0$.

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[2] This model was presented years ago by Mitchell (1967) as an early example of mode-mode coupling.

In this linear approximation λ_n is determined by λ_h and we can now carry out the spatial Fourier transformations in (9.32). The source strength driving the heating is thus

$$\sigma_h(\boldsymbol{k},t) = -\lambda_h(\boldsymbol{k},t)K^0_{hh}(\boldsymbol{k},0)\left[1-\frac{|K^0_{nh}(\boldsymbol{k},0)|^2}{K^0_{hh}(\boldsymbol{k},0)K^0_{nn}(\boldsymbol{k},0)}\right], \tag{9.33}$$

where the $t = 0$ values in the covariance functions refer to equal times. For Hermitian operators the covariance functions satisfy a Schwarz inequality, so that the ratio in square brackets in this last expression is always less than or equal to unity; hence, for given source strength $\lambda_h(\boldsymbol{k},t)$ is increased by the no-driving constraint on $n(\boldsymbol{x},t)$.

The expression (9.33) is somewhat awkward as it stands, so it is convenient to introduce a new variable, or operator,

$$h'(\boldsymbol{k},t) \equiv h(\boldsymbol{k},t) - \frac{K^0_{nh}(\boldsymbol{k},0)}{K^0_{nn}(\boldsymbol{k},0)}n(\boldsymbol{k},t). \tag{9.34}$$

Some algebra then yields in place of (9.33)

$$\sigma_h(\boldsymbol{k},t) = -\lambda_h(\boldsymbol{k},t)K^0_{h'h'}(\boldsymbol{k},0). \tag{9.35}$$

In the linear case, at least, it is actually h' that is the driven variable under the constraint that n is not driven, and the source term has been renormalized.

With (9.35) the two expectation values of interest are

$$\langle h'(\boldsymbol{k},t)\rangle_t - \langle h'(\boldsymbol{k})\rangle_0 = \int_0^t \sigma_h(\boldsymbol{k},t')\frac{K^0_{h'h'}(\boldsymbol{k},t-t')}{K^0_{h'h'}(\boldsymbol{k},0)}\,dt', \tag{9.36}$$

$$\langle n(\boldsymbol{k},t)\rangle_t - \langle n(\boldsymbol{k})\rangle_0 = \int_0^t \sigma_h(\boldsymbol{k},t')\frac{K^0_{nh'}(\boldsymbol{k},t-t')}{K^0_{h'h'}(\boldsymbol{k},0)}\,dt'. \tag{9.37}$$

Thus, the number density changes only as a consequence of changes in the energy density.

By direct calculation, one verifies that the new covariance functions are given explicitly as

$$\begin{aligned} K^0_{h'h'}(\boldsymbol{k},\tau) &= K^0_{hh}(\boldsymbol{k},\tau) + \left(\frac{K^0_{nh}(\boldsymbol{k},0)}{K^0_{nn}(\boldsymbol{k},0)}\right)^2 K^0_{nn}(\boldsymbol{k},\tau) \\ &\quad - 2\frac{K^0_{nh}(\boldsymbol{k},0)}{K^0_{nn}(\boldsymbol{k},0)}\,K^0_{nn}(\boldsymbol{k},\tau), \end{aligned} \tag{9.38}$$

$$K^0_{nh'}(\boldsymbol{k},\tau) = K^0_{nh}(\boldsymbol{k},\tau) - \frac{K^0_{nh}(\boldsymbol{k},0)}{K^0_{nn}(\boldsymbol{k},0)}\,K^0_{nn}(\boldsymbol{k},\tau)\,. \tag{9.39}$$

With these and the recollection that setting $|\boldsymbol{k}| = 0$ is equivalent to a volume integration, one shows that, if the driving is removed at some time t_1, say, total particle number is conserved in the process, as expected.

The preceding discussion provides a model for carrying out some calculations in nonequilibrium thermodynamics. Undoubtedly one can develop many more applications of this kind along the lines suggested by Truesdell (1984), and in discussions of so-called extended irreversible thermodynamics (*e.g.*, Jou *et al.*, 2001). We shall forego exploring those possibilities here, but before moving on it may be illuminating to examine the case of a particular form of external driving.

9.3 A special case: linear dynamic response

An important feature of the thermal driving mechanism is that the actual details of the thermal driving source are irrelevant, and only the *rates and strengths* at which system variables are driven enter the equations. It should make no difference in many situations whether the driving is thermal or mechanical; we examine the latter context here.

The theory of dynamical response was described briefly in Chapter 8, and the linear version was noted there. The underlying scenario is that a well-defined external field is imposed on a system that has been in thermal equilibrium in the remote past, as described by the Hamiltonian H_0. It is then presumed that the response to this disturbance can be derived by adding a time-dependent term to the Hamiltonian, so that effectively $H = H_0 - Fv(t)$, $t > 0$, where $v(t)$ describes the external field and F is a system operator to which it "couples." But consider the remarks of Lieb and Yngvason (2003):

> That hardly seems like a reasonable way to model a sledgehammer that happens to fall on the system or a gorilla jumping up and down. Most discussions of entropy increase refer to the evolution of systems subject to a dynamical evolution that is usually Hamiltonian (possibly time dependent) or a mixture of Hamiltonian and stochastic evolution. This can hardly even cope with describing a steam engine, much less a random, violent external force.

Some of the difficulties with this approach were sketched earlier, including the observation that $\rho(t)$ in (8.6) can only evolve unitarily. We now see that these problems can be resolved by noting that dynamical response is just a special case of thermal driving.

In what follows spatial variation is not germane to the discussion and for simplicity will be omitted temporarily. Eventual comparison of thermal and dynamical linear response theories requires an identity for the time derivative of the covariance function, which follows from the identity (A.13) or from direct differentiation in (6.10):

$$\begin{aligned}\frac{d}{d\tau}K^0_{CF}(\tau) &= \frac{i}{\beta\hbar}\big\langle[C, F(\tau)]\big\rangle_0 \\ &= -\beta^{-1}\phi_{CF}(\tau),\end{aligned} \tag{9.40}$$

where ϕ_{CF} is the *linear* response function of (8.10). The covariance function evidently contains a good deal more information than does the dynamic response function.

It has also been noted earlier that the maximum-entropy probability distribution can be obtained by specifying *either* $\langle f\rangle$ *or* λ, say. An example of this freedom is illustrated in the canonical distribution (4.18), which could be obtained by specifying either the energy or the temperature; this option was also exercised in the model of spatial inhomogeneity of (6.45). Thus, we return to Eq.(9.1), replacing H with H_0, and let $\lambda(t')$ be the independent variable. In linear approximation (9.9) expresses $\lambda(t)$ directly in terms of the source strength, or driving rate, and dimensional considerations suggest that in the presence of an external field we write this variable in the form

$$\begin{aligned}\lambda(t') &= \beta\frac{d}{dt'}\left[\theta(t-t')v(t')\right]\\ &= \beta\left[-\delta(t-t')v(t')+\theta(t-t')\frac{d}{dt'}v(t')\right],\end{aligned}\tag{9.41}$$

with the condition that $v(0)=0$. The step-function $\theta(t-t')$ is included in (9.41) because λ, and hence v, are defined *only* on the interval $[0,t]$.

Substitution of (9.41) into (9.1) yields the distribution relevant to a well-defined external field,

$$\begin{aligned}\rho_t &= \frac{1}{Z_t}\exp\left[-\beta H_0+\beta\int_0^t\left[\delta(t-t')v(t')-\theta(t-t')\frac{d}{dt'}v(t')\right]F(t')\,dt'\right]\\ &= \frac{1}{Z_t}\exp\left[-\beta H_0+\beta\int_0^t v(t')\dot{F}(t')\,dt'\right],\end{aligned}\tag{9.42}$$

and Z_t, as usual, is the trace of the numerator. Although the exponential contains what appears to be an effective Hamiltonian, we do *not* assert that $\int_0^t v(t')\dot{F}(t')\,dt'$ is an addition to the equilibrium Hamiltonian H_0; there is no rationale of any kind for such an assertion. The Lagrange multiplier function $\lambda(t)$ is a macroscopic quantity, as is its expression as an independent variable in (9.41). Indeed, $v(t)$ may describe the effect of that gorilla! Linear approximation, along with the identity (9.40), yields the departure from equilibrium of the expected value of another operator C at any future time t under driving by the external field:

$$\begin{aligned}\langle C(t)\rangle-\langle C\rangle_0 &= \beta\int_0^t v(t')K^0_{C\dot{F}}(t-t')\,dt'\\ &= \beta\int_0^t v(t')\frac{d}{dt'}K^0_{CF}(t-t')\,dt'\\ &= \int_0^t v(t')\phi_{CF}(t-t')\,dt',\end{aligned}\tag{9.43}$$

which is precisely the result obtained in linear response theory. But now we also have the time-evolved probability distribution (9.42) from which we can develop the associated thermodynamics. Equation (9.43) confirms that, at least linearly, both ρ_t and a unitarily evolved $\rho(t)$ will predict the same expectation values. As suggested following (9.40), however, $\rho(t)$ contains no more macroscopic information than it had to begin with.

As an example of an external source producing a time-varying field, suppose a component of electric polarization $M_i(t)$ is specified, leading to the density matrix

$$\rho_t = \frac{1}{Z_t} \exp\left[-\beta H_0 - \int_0^t \lambda_i(t') M_i(t')\, dt'\right] . \tag{9.44}$$

We presume no spontaneous polarization, so that in linear approximation the expectation of another component at time t is (with no summation over repeated indices)

$$\langle M_j(t)\rangle = -\int_0^t \lambda_i(t') \langle \overline{M_i(t')} M_j(t)\rangle_0 \, dt'. \tag{9.45}$$

Now, with the additional knowledge that (9.45) is the result of turning on an external field, one might be led to think that the Lagrange multiplier is simply a field component, say $E_i(t)$. But (9.41) shows that, even when the *effect* is to add a time-dependent term to the Hamiltonian, the actual source term is somewhat more complicated; only the δ-function term in (9.41) corresponds to that possibility, and the actual source term also describes the rate of change of the field. This again illustrates the earlier observation that the covariance function contains much more information than the dynamic response function.

With (9.41) we can rewrite (9.45) explicitly as

$$\begin{aligned} \langle M_j(t)\rangle =& \beta \langle \overline{M_i(t)} M_j(t)\rangle_0 E_i(t) \\ & - \beta \int_0^t \langle \overline{M_i(t')} M_j(t)\rangle_0 \frac{dE_i(t')}{dt'}\, dt' , \end{aligned} \tag{9.46}$$

which is again the result obtained from the theory of dynamic response. But we have uncovered much more, because now one can do thermodynamics. In the present scenario, we have specified thermal driving of the polarization and incorporated that into a density matrix; additionally, the Lagrange multiplier has been chosen to be the independent variable corresponding to an external field, which allows us to identify the source strength. Thus, from (9.5) we have a definite expression for the time-dependent entropy of the ensuing nonequilibrium state:

$$\begin{aligned} \frac{1}{k} S_t &= \ln Z_t + \beta \langle H\rangle_t - \int_0^t \lambda_i(t') \langle M_i(t')\rangle_t \, dt' , \\ &\simeq \frac{1}{k} S_0 + \beta \int_0^t \lambda_i(t') K^0_{H_0 M_i}(t')\, dt' + \mathrm{O}(\lambda^2), \end{aligned} \tag{9.47}$$

where the second line is the linear approximation and we have identified the entropy of the equilibrium system as $S_0 = k \ln Z_0 + k\beta \langle H_0\rangle_0$. In the case of dynamic response, if one makes the linear approximation to $\rho(t)$ in (8.6) and computes the entropy similarly, it is found that $S(t) - S_0$ vanishes identically, as expected. With (9.40), (9.41), and (9.47), however, the entropy difference can also be written in terms of the linear response function:

$$\frac{1}{k}\big(S_t - S_0\big) \simeq \beta \int_0^t E_i(t')\phi_{H_0 M_i}(t')\,dt', \tag{9.48}$$

once again exhibiting the canonical form $\Delta Q(t)/T$. These remarks strongly suggest that the proper theory of response to a dynamical perturbation is to be found as a special case of thermal driving.

We have now reached a milestone of sorts in the story of entropy, in that the goal of extending the concept in an unambiguous and useful way has been achieved. While variational principles for general nonequilibrium processes have been suggested from time to time, and various candidates have been put forth in special contexts, none have achieved a position on the same level as the equilibrium principle of Gibbs. This is perhaps not too surprising in light of the foregoing discussion, for it would seem now that the Gibbs variational principle has all along been the rule governing *all* thermodynamic states, possibly because it has its roots in a fundamental rule of probability theory: the principle of maximum information entropy. The difficulty has not been our inability to find a compelling definition of physical entropy for nonequilibrium states, so much as a failure to understand the specific role of entropy over the entire spectrum of thermodynamic states. It is only the nature of the constraints that changes, from constants of the motion to steady state to time dependent, while the principle remains the same. This is a satisfying result in that it provides a certain economy of principles.

All this having been said, questions may still linger regarding the physical nature of entropy in the presence of nonequilibrium processes. In equilibrium, the entropy remains a fixed characteristic of that state, and entropy differences between two such states are readily measured, by means of the Clausius definition, say. But in a nonequilibrium process, the entropy is continually changing with the continual change of the state, so that it is actually the rate of change of entropy $\dot{S}_t$ that is the important feature. The maximum information entropy is the only quantity of this sort over which we have any control. In linear heating, for example, this is evident from (9.26) where $\dot{Q}$ is just the rate at which an electric stove element might be transferring energy to a pot of water; it is not necessarily the rate at which energy is being absorbed into the system. If the source is removed and the system allowed to return to equilibrium, the accumulated entropy of that state is determined as usual by the PME subject to the new energy constraint.

The distinction between theoretical entropy in equilibrium scenarios and in nonequilibrium processes cannot be emphasized enough. There is no compelling reason to believe that the classical thermodynamic entropy is a measurable property of nonequilibrium phenomena, a realization that is emerging elsewhere as well (*e.g.*, Gallavotti, 2004). If external forces are removed, it is a mathematical theorem that neither ρ_t nor S_t can evolve into their equilibrium counterparts. That is a singular limit, as discussed earlier, and unless these distinctions are clearly recognized, few real advances can be made in nonequilibrium statistical mechanics.

10

APPLICATION TO FLUID DYNAMICS

> *The bulk relative motion of the fluid can cause only a small change in the statistical properties of the molecular motion when the characteristic time of the bulk motion is long compared with the characteristic time of the molecular motion.*
>
> *G.K. Batchelor (1967)*

The quantum-mechanical density operators describing a simple fluid were defined in Chapter 6 in the context of local fields (wavefunctions). These Heisenberg operators were also shown to satisfy local conservation laws, as in (6.31) and Appendix B. In the case that the Hamiltonian is rotationally invariant we have shown that the conservation laws completely describe a simple fluid in terms of five long-lived hydrodynamic modes.

Expressions for linear transport coefficients in a simple fluid were developed in Chapter 7 in a stationary-state context, where they emerge in the linear constitutive equations for the currents corresponding to the conserved densities. An important feature of these calculations is that the constitutive relations need no longer be considered phenomenological, but are seen to arise from probability theory as laws of inference. In the case of the number density, a time-dependent version of Fick's law was also developed in (6.43), along with the diffusion equation (6.44).

In this chapter we extend the study of simple fluids to dynamic situations as an application of the thermal driving scenario. The first step in this regard is to derive the macroscopic equations of motion for the expectation values of the conserved densities when the system is driven by external sources. The procedure for doing this was discussed in connection with Eq.(9.11), and here we shall consider only the momentum density $p(\boldsymbol{x},t) \equiv m\boldsymbol{j}(\boldsymbol{x},t)$ to be driven. The exact macroscopic equations are then

$$\frac{d}{dt}\langle n(\boldsymbol{x},t)\rangle_t + \nabla_i\langle j^i(\boldsymbol{x},t)\rangle_t = 0, \tag{10.1a}$$

$$m\frac{d}{dt}\langle j^i(\boldsymbol{x},t)\rangle_t + \nabla_k\langle T^{ki}(\boldsymbol{x},t)\rangle_t = \sigma_{j_i}, \tag{10.1b}$$

$$\frac{d}{dt}\langle h(\boldsymbol{x},t)\rangle_t + \nabla_i\langle q^i(\boldsymbol{x},t)\rangle_t = 0. \tag{10.1c}$$

The rate $\sigma_{\boldsymbol{j}}$ that the source drives the momentum density can equally well be written as a force density $n\boldsymbol{f}$, where $\boldsymbol{f}$ is the force per unit mass. As for other driving possibilities, an example would be to drive the number density in an ionized gas, rather than the momentum, and study electron transport. The source in this case would be $\boldsymbol{\sigma}_e = n_e\mu_e\boldsymbol{E}$, where $\boldsymbol{E}$ is a static field and μ_e is the dc electron mobility.

The dissipative currents q^i and T^{ij} are not conserved locally and hence do not satisfy equations of motion associated with conservation laws; usually they are specified by means of linear constitutive equations, as we shall do here. One could construct differential time evolution equations for the macroscopic variables, of course, from the general expression (9.6), but unless these variables are actually driven it is usually much simpler to employ the predicted values as described below.

The nonlinear equations of motion (10.1) are independent of the long-wavelength approximation and are valid arbitrarily far from equilibrium. They represent five equations for the five densities, but it is necessary to employ specific models for $\langle T^{ki}(\boldsymbol{x},t)\rangle$ and $\langle q^i(\boldsymbol{x},t)\rangle$; following Batchelor's recommendation, these are most often taken as the linear approximations to the momentum and heat currents, respectively. For example, under thermal driving the linear approximation (7.33) is replaced by

$$\langle T_{ki}(\boldsymbol{x},t)\rangle_t = \langle T_{ki}\rangle_0 + \int_v d^3x' \int_0^t \nabla_m\lambda_n K^0_{ki,mn}(\boldsymbol{x}-\boldsymbol{x}',t-t')\,dt', \tag{10.2}$$

where summation over repeated indices is implied. The long-wavelength limit is still appropriate and the hydrostatic pressure will eventually be modified. While the Lagrange multiplier is now given by (9.9), it is basically still a velocity, so that one can proceed in the same manner as earlier and find for the dynamic viscosities

$$\eta(t) = \beta V \int_0^t K_{mn,mn}(t-t')\,dt' \qquad m \neq n, \tag{10.3}$$

$$\zeta(t) = \frac{\beta V}{9}\int_0^t K^0_{TT}(t-t')\,dt', \tag{10.4}$$

in the notation employed in (7.36). Usually the short-memory approximations are adequate.

In linear approximation, the solutions to the equations of motion (10.1) are just the linear predictions of the type (9.28). With the notation $\Delta n(\boldsymbol{x},t) = n(\boldsymbol{x},t) - \langle n\rangle_0$, and so on, for the deviations, these are

$$\langle \Delta n(\boldsymbol{x},t)\rangle_t = -\int_v\int_0^t \boldsymbol{\lambda}(\boldsymbol{x}',t')\cdot K^0_{n\boldsymbol{j}}(\boldsymbol{x}-\boldsymbol{x}',t-t')\,d^3x'dt', \tag{10.5a}$$

$$\langle \Delta h(\boldsymbol{x},t)\rangle_t = -\int_v\int_0^t \boldsymbol{\lambda}(\boldsymbol{x}',t')\cdot K^0_{h\boldsymbol{j}}(\boldsymbol{x}-\boldsymbol{x}',t-t')\,d^3x'dt', \tag{10.5b}$$

$$\langle \Delta T_{mn}(\boldsymbol{x},t)\rangle_t = -\int_v\int_0^t \boldsymbol{\lambda}(\boldsymbol{x}',t')\cdot K^0_{T_{mn}\boldsymbol{j}}(\boldsymbol{x}-\boldsymbol{x}',t-t')\,d^3x'dt', \tag{10.5c}$$

$$\langle \Delta \boldsymbol{j}(\boldsymbol{x},t)\rangle_t = -\int_v \int_0^t \boldsymbol{\lambda}(\boldsymbol{x}',t')\cdot K^0_{\boldsymbol{jj}}(\boldsymbol{x}-\boldsymbol{x}',t-t')\,d^3x'dt', \tag{10.5d}$$

$$\langle \Delta \boldsymbol{q}(\boldsymbol{x},t)\rangle_t = -\int_v \int_0^t \boldsymbol{\lambda}(\boldsymbol{x}',t')\cdot K^0_{\boldsymbol{qj}}(\boldsymbol{x}-\boldsymbol{x}',t-t')\,d^3x'dt', \tag{10.5e}$$

and $\boldsymbol{\lambda}$ is obtained from (9.9) in linear approximation. To verify that these are solutions, first take the time derivative of (10.5a),

$$\begin{aligned} -\frac{d}{dt}\langle n(\boldsymbol{x},t)\rangle &= \int_v \boldsymbol{\lambda}(\boldsymbol{x}',t)\cdot K^0_{n\boldsymbol{j}}(\boldsymbol{x}-\boldsymbol{x}',0)\,d^3x' \\ &\qquad + \int_v \int_0^t \boldsymbol{\lambda}(\boldsymbol{x}',t')\cdot K^0_{\dot{n}\boldsymbol{j}}(\boldsymbol{x}-\boldsymbol{x}',t-t')\,d^3x'dt'. \end{aligned} \tag{10.6}$$

Employ the *microscopic* conservation law $\dot{n}+\nabla\cdot\boldsymbol{j}=0$ to write $K^0_{\dot{n}\boldsymbol{j}} = -\nabla\cdot K^0_{\boldsymbol{jj}}$ and note that the first term on the right-hand side of (10.6) vanishes by the symmetry properties (6.14); the result is just what one finds from taking the divergence of (10.5d), thereby verifying (10.1a). A similar calculation verifies (10.1c), but verification of (10.1b) contains a different twist. In the time derivative of (10.5d) the term analogous to the first term on the right-hand side of (10.6) is, from (9.9),

$$\int_v \boldsymbol{\lambda}(\boldsymbol{x}',t)\cdot K^0_{\boldsymbol{jj}}(\boldsymbol{x}-\boldsymbol{x}',0)\,d^3x' = \sigma_{\boldsymbol{j}}(\boldsymbol{x},t). \tag{10.7}$$

Thus, at least in linear approximation, the statistical predictions (10.5) are completely consistent with, and provide the first-order solutions to, the deterministic equations (10.1).

But, having seen how this calculation goes through, one can easily show how it must be true to all orders, and this is demonstrated in Appendix A. Consequently, the exact solutions to the fluid equations of motion are provided by the predicted expectation values of the densities and currents, as they must be. Whether it is more convenient to focus on an approximate solution to the exact equation of motion, or to pursue an exact solution to an approximation to the equation of motion should be dictated by the given scenario. In either case some kind of approximation is always necessary.

10.1 Hydrodynamic fluctuations

The statistical fluctuations are determined, as always, by the correlation of deviations, or covariance functions. In general these are the nonlinear covariances (9.7), or possibly those defined by the steady-state distribution. In any case, they are usually quite difficult to evaluate other than in very approximate models. For the moment, then, attention will be focused on the linear (or equilibrium) covariance functions, not only because they are readily evaluated in the long-wavelength approximation, but also because that and the linear approximation are well controlled; at the end of this chapter we shall discuss some aspects of nonlinear (or nonequilibrium) correlation functions. Thus, in linear hydrodynamics a first approach to fluctuations is a study of K^0_{nn}, $K^0_{\boldsymbol{jj}}$, K^0_{hh}, $K^0_{\boldsymbol{qq}}$, and $K^0_{ki,mn}$, the last referring to the energy-momentum tensors. One should note that these only describe *statistical fluctuations*; whether they can be equated with possible physical fluctuations is another matter and was discussed in Chapter 6.

As discussed in Appendix C, the Fourier-transformed quantity $K^0_{AB}(\boldsymbol{k},\omega)$ is the dissipative part of the physical response of the system, whereas the ordinary (*i.e.*, no Kubo transform) correlation function $\Gamma^0_{AB} \equiv \langle \Delta A \Delta B\rangle_0$, in terms of the deviations defined above, describes the actual fluctuations. The two are related by a fluctuation-dissipation theorem, (6.33a),

$$K^0_{AB}(\boldsymbol{k},\omega) = \frac{1-e^{-\beta\hbar\omega}}{\beta\hbar\omega}\,\Gamma^0_{AB}(\boldsymbol{k},\omega) \quad \xrightarrow[\beta\hbar\omega \ll 1]{} \quad \Gamma^0_{AB}(\boldsymbol{k},\omega). \tag{10.8}$$

The covariances of the densities n, h, and $\boldsymbol{j}$ are obtained in a straightforward manner in the long-wavelength limit and are simple (equilibrium) thermodynamic functions (*e.g.*, Puff and Gillis, 1967; Grandy, 1987). They are

$$\lim_{k\to 0} K^0_{nn}(\boldsymbol{k},\tau) = \frac{n_0^2\kappa_T}{\beta}, \tag{10.9}$$

$$\lim_{k\to 0} K^0_{hh}(\boldsymbol{k},\tau) = \frac{kT^2C_V}{V} + \frac{\kappa_T}{\beta}\left[h_0 + P_0 - \frac{\alpha T}{\kappa_T}\right]^2, \tag{10.10}$$

$$\lim_{k\to 0} K^0_{j_ij_k}(\boldsymbol{k},\tau) = \frac{n_0}{\beta m}\delta_{ik}, \tag{10.11}$$

where κ_T is the isothermal compressibility, α the coefficient of thermal expansion, C_V the constant-volume heat capacity, and subscripts 0 refer to equilibrium quantities. Expressions on the right-hand sides of these last three equations are most readily obtained from familiar thermodynamic derivatives, as suggested in (4.37) and (6.56), but correlations for the dissipative currents require a little more work.

Consider first $K^0_{q_\ell q_m}(\boldsymbol{x}',t';\boldsymbol{x},t) = \big\langle \overline{q_m} q_\ell(\boldsymbol{r},\tau)\big\rangle_0$, which will be abbreviated $K^0_{\ell m}$ temporarily. The space-time Fourier transform is

$$K^0_{\ell m}(\boldsymbol{k},\omega) = \int d^3r\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau}\, K^0_{\ell m}(\boldsymbol{r},\tau). \tag{10.12}$$

Introduce a bit of dispersion into the integral, to insure convergence, by replacing ω with $\omega \pm i\epsilon$, $\epsilon > 0$. The properties (6.14) imply that this covariance function is invariant under time reversal, so that in the limits $k \to 0$, $\omega \to 0$ (10.12) becomes[1]

$$\lim_{\substack{k\to 0\\ \omega\to 0}} K^0_{\ell m}(\boldsymbol{k},\omega) = 2\lim_{\epsilon\to 0}\int d^3r \int_0^{\infty} d\tau\, e^{-|\epsilon|\tau}\, K^0_{\ell m}(\boldsymbol{r},\tau). \tag{10.13}$$

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[1] The limit $\omega \to 0$ eliminates the 3-point-correlation term contributions that are regular in ω.

But this last expression is just the thermal conductivity κ in (7.27), if we note that the factor $T^{-2}(\boldsymbol{x}') \sim T^{-2}(\boldsymbol{x})$ can be extracted from the integral in that expression, as is usual. Symmetry again implies that only the diagonal components contribute here, so the inverse transformation of (10.13) yields in the long-wavelength limit

$$K^0_{q_\ell q_m}(\boldsymbol{r},\tau) \simeq 2\kappa k T^2 \delta(\boldsymbol{r})\delta(\tau)\delta_{\ell m}. \tag{10.14}$$

Similarly, fluctuations in the energy-momentum tensor are described by the covariance function $K^0_{k\ell,mn}(\boldsymbol{r},\tau) = \big\langle \overline{T_{mn}} T_{k\ell}(\boldsymbol{r},\tau)\big\rangle_0 - P_0^2 \delta_{k\ell}\delta_{mn}$. With the definitions (10.3) and (10.4), the above procedure leads to

$$K^0_{k\ell,mn}(\boldsymbol{r},\tau) \simeq 2kT\big[\eta\big(\delta_{km}\delta_{\ell n} + \delta_{kn}\delta_{\ell m}\big) + \big(\zeta - \tfrac{2}{3}\eta\big)\delta_{k\ell}\delta_{mn}\big]\,\delta(\boldsymbol{r})\delta(\tau). \tag{10.15}$$

The long-wavelength expressions (10.14) and (10.15) for fluctuations in the dissipative currents are precisely those found by Landau and Lifshitz (1957) in their study of hydrodynamic fluctuations. Here, however, there is no need to introduce fictitious "random" forces, additional dissipative stresses, or extraneous averaging processes, for these are just the straightforward results expected from probability theory. Hydrodynamic fluctuations of this kind apparently have been observed in convection waves in an isotropic binary mixture of H_2O and ethanol (Quentin and Rehberg, 1995), and they have been applied to the Rayleigh Bénard problem by Schmitz and Cohen (1985).

10.2 Fluid dynamics equations of motion

In fluid mechanics it is customary to reformulate the equations of motion (10.1) in terms of a *fluid velocity* $\boldsymbol{v}$ by introducing a notation $\langle \boldsymbol{j}(\boldsymbol{x},t)\rangle_t = \langle n(\boldsymbol{x},t)\rangle_t \boldsymbol{v}(\boldsymbol{x},t)$. This velocity parameter has the same local interpretation as the expectation values of the densities, and its introduction is motivated partly by Galilean invariance, and partly by the model for the stresses in the driven fluid.

Let us first consider a fluid system in equilibrium to be moving with a constant drift velocity $\boldsymbol{v}$ with respect to the fixed laboratory frame. The views in the two frames are related by a Galilean transformation of the densities and currents that can be carried out by means of a unitary operator $U(\boldsymbol{v}) = \exp[i\boldsymbol{v}\cdot\boldsymbol{G}/\hbar]$, where $\boldsymbol{G}$ is the generator of Galilean transformations. Because the derivation of these relations and the form of $U(\boldsymbol{v})$ is not usually given explicitly in most works on this subject, with some exceptions such as the work by Akhiezer and Peletminskii (1981), we have provided these details in Appendix B. The relevant expectation values in the laboratory frame are

$$\begin{aligned}
\langle n(\boldsymbol{x},t)\rangle &= \langle n(\boldsymbol{x},t)\rangle_{v=0},\\
\langle \boldsymbol{j}(\boldsymbol{x},t)\rangle &= \langle n(\boldsymbol{x},t)\rangle_{v=0}\,\boldsymbol{v},\\
\langle T_{ij}(\boldsymbol{x},t)\rangle &= \langle T_{ij}(\boldsymbol{x},t)\rangle_{v=0} + m\langle n(\boldsymbol{x},t)\rangle_{v=0}\,v_i v_j,\\
\langle h(\boldsymbol{x},t)\rangle &= \langle h(\boldsymbol{x},t)\rangle_{v=0} + \tfrac{1}{2}m\langle n(\boldsymbol{x},t)\rangle_{v=0}\,v^2,\\
\langle q_i(\boldsymbol{x},t)\rangle &= \big[\langle h(\boldsymbol{x},t)\rangle_{v=0} + \tfrac{1}{2}m\langle n(\boldsymbol{x},t)\rangle_{v=0}\,v^2\big]v_i + v^k\langle T_{ki}(\boldsymbol{x},t)\rangle_{v=0}.
\end{aligned} \tag{10.16}$$

The third term in the energy current arises because the operator q_i itself in Appendix B contains a structure similar to that of T_{ij}.

We emphasize that these expressions are just a redescription of the rest-frame system in the laboratory frame, and are of a convective nature. Dissipation cannot arise from unitary transformation alone!

Our underlying interest, however, is with the driven system described by the equations of motion (10.1), in which $\boldsymbol{v}(\boldsymbol{x},t)$ is a dynamical variable. In the laboratory frame (10.16) will then represent the convective effects by means of an instantaneous transformation at each moment, and the appropriate equations for fluid flow result from combining these with (10.1). But preliminary to that it will prove very convenient to adopt a completely macroscopic description in terms of $\boldsymbol{v}(\boldsymbol{x},t)$ and the *mass density* $\rho(\boldsymbol{x},t) \equiv m\langle n(\boldsymbol{x},t)\rangle$, not to be confused with the density matrix.[2] One reason for this is that the subscript notation $v=0$ in (10.16) is no longer appropriate. We shall write e for the total energy density, u for the internal energy density, $\boldsymbol{J}$ for the total energy current, and retain $\boldsymbol{q}$ for the thermal energy current alone. Then, (10.16) become

$$\begin{aligned} m\langle \boldsymbol{j}(\boldsymbol{x},t)\rangle &= \rho\boldsymbol{v}, \\ T_{ij} &= S_{ij} + t_{ij}, \\ e &= u + \tfrac{1}{2}\rho v^2, \\ J_i &= \big(u + \tfrac{1}{2}\rho v^2\big)v_i + v^k S_{ki}, \end{aligned} \tag{10.17}$$

where $t_{ij} \equiv \rho v_i v_j$ is the kinetic energy tensor, and S_{ij} is conventionally called the stress tensor.

Combination of (10.17) with (10.1) yields for the first two equations of motion

$$\partial_t\rho + \partial_i(\rho v^i) = 0, \tag{10.18}$$

$$\partial_t(\rho v^j) + \partial_i(S^{ij} + t^{ij}) = \rho f^j, \tag{10.19}$$

respectively. The energy equation (10.1c), however, requires some further discussion, because only the *total* energy is conserved.

An expression for the kinetic energy density is obtained by taking the scalar product of $\boldsymbol{v}$ with (10.19):

$$\partial_t\big(\tfrac{1}{2}\rho v^2\big) + \partial_i\big(\tfrac{1}{2}\rho v^2 v^i + S^{ij}v_j\big) = S^{ij}\partial_i v_j + \rho f^j v_j. \tag{10.20}$$

The work done by $\boldsymbol{f}$ provides an effective driving force for changes in the energy, so that the conservation equation for the total energy density is

$$\partial_t e + \partial_i\big(ev^i + S^{ij}v_j + q_i\big) = \rho f^j v_j, \tag{10.21}$$

where we have now included in J_i any thermal current $\boldsymbol{q}$ supplied by an external temperature gradient. Subtraction of (10.20) from (10.21), and reference to

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[2] An almost-unavoidable abuse of notation, but the two usually appear in different contexts.

(10.17), gives us the equation of motion for the internal energy density:

$$\partial_t u + \partial_i\big(uv^i + q^i\big) = -S^{ij}\partial_i v_j. \tag{10.22}$$

The right-hand side of this last expression contains the rate of dissipation of mechanical energy due to viscosity—in its effect on the fluid it is equivalent to an irreversible addition of thermal energy to the system.

In summary, the exact equations of motion (10.1) for the driven fluid can be written in the laboratory frame as

$$\partial_t \rho + \partial_i(\rho v_i) = 0, \tag{10.23a}$$

$$\rho\big(\partial_t + v^i\partial_i\big)v^j + \partial_i S^{ij} = \rho f^j, \tag{10.23b}$$

$$\partial_t u + \partial_i(uv^i + q^i) = -S^{ij}\partial_i v_j, \tag{10.23c}$$

where every quantity with the exception of f^j is actually an expectation value in the state described by the density matrix ρ_t. For large macroscopic systems we expect these values to represent sharp predictions but still possess very small deviations from these values.

Often these expressions are written in a form employing the *convective derivative*,

$$\frac{D}{Dt} \equiv \partial_t + \boldsymbol{v}\cdot\nabla. \tag{10.24}$$

For example, (10.23a) would then take the form

$$\frac{D\rho}{Dt} + \rho\nabla\cdot\boldsymbol{v} = 0. \tag{10.25}$$

With the exception of the third term in J_i in (10.17), all of the convective terms could have been included simply by replacing ∂_t with D/Dt in (10.1).

Equations (10.23) constitute a set of five equations in five unknowns, although it remains to specify the functions S^{ij} and q^i. One usually takes these to be the linear approximations to the constitutive equations, even though that would appear to destroy the generality of (10.23). From a practical point of view, however, there is little choice, for even with this approximation the equations are virtually intractable.

Fortunately, experience indicates that, except in extreme circumstances, the small-gradient approximation (10.2) is very good in most situations, in which case the system is called a *Newtonian fluid.* With reference to (7.35), we can extract from (10.2) the following expression for the stress tensor:

$$S_{ij} = P_0\delta_{ij} - \eta\big[v_{i,j} + v_{j,i} - \tfrac{2}{3}\delta_{ij}v^{\ell}{}_{,\ell}\big] - \zeta\delta_{ij}v^{\ell}{}_{,\ell}\,, \tag{10.26}$$

in which we again adopt the notation $v_{j,i} \equiv \partial_i v_j$, so that $\nabla\cdot\boldsymbol{v} = v^{\ell}{}_{,\ell}$. Here we presume η, ζ to be independent of space and time.

The hydrostatic or thermodynamic pressure P_0 is 1/3 the tensor trace of the unperturbed stress tensor, or $\langle T_{ij}\rangle_0 = P_0\delta_{ij}$; that is, only the normal stresses contribute in equilibrium. But in the driven system the fluid pressure is a dynamical variable, owing to compression and expansion of fluid elements. At constant temperature, and for small variations in the density, we can write

$$P - P_0 = \left(\frac{\partial P}{\partial n}\right)_{T,n_0} (n - n_0) + \cdots\,, \tag{10.27}$$

so that the difference is proportional to the inverse compressibility, or elastic modulus. In the current scenario that is precisely the role played by the bulk viscosity ζ, and thus within the current approximation we can identify the dynamic pressure as

$$P(\boldsymbol{x}, t) \simeq P_0 - \zeta {v^\ell}_{,\ell}\,(\boldsymbol{x}, t). \tag{10.28}$$

Hence, (10.26) becomes

$$S_{ij} = P\delta_{ij} - \eta\big[v_{i,j} + v_{j,i} - \tfrac{2}{3}\delta_{ij}{v^\ell}_{,\ell}\big]. \tag{10.29}$$

Note that S_{ij} is symmetric (always), and that the dissipative part has zero tensor trace.[3]

Although η can in principle vary in space and time, the great majority of applications consider it constant. The equations of motion now contain two extra variables: P and a temperature function that will come from $\boldsymbol{q}$, yielding five equations for seven variables. The standard way of treating this problem is to first presume that there are no temperature gradients present, which would not work for problems such as Rayleigh–Bénard convection, of course. Second, in many, if not most, cases of fluid flow the density can be considered uniform and unchanging; that is, the fluid is incompressible. This means that

$$\frac{D\rho}{Dt} = 0, \tag{10.30}$$

and from (10.25) it follows that the velocity is solenoidal: $\nabla \cdot \boldsymbol{v} = 0$. Under these conditions, (10.23c) is irrelevant and (10.23a,b) are closed and completely determine $\boldsymbol{v}$, subject to boundary conditions:

$$\begin{aligned} \frac{D\boldsymbol{v}}{Dt} &= \boldsymbol{f} - \rho^{-1}\nabla P + \nu\nabla^2\boldsymbol{v}, \\ \nabla \cdot \boldsymbol{v} &= 0, \end{aligned} \tag{10.31}$$

where $\nu \equiv \eta/\rho$ is the *kinematic viscosity.* These are generally referred to as the *Navier–Stokes equations*, and if $\nu = 0$ they are the Euler equations for an inviscid fluid.

The convective term in the time derivative in (10.31) introduces a nonlinearity that has long prevented a complete solution in three dimensions, although there

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[3] In general a tensor A_{ij} has a *deviator* $A'_{ij} \equiv A_{ij} - \frac{1}{3}\delta_{ij}A^k_k$ with zero trace. For this reason the nonisotropic part of S_{ij} is often called the *deviatoric stress tensor.*

are special cases in which the nonlinearity vanishes. For example, if the velocity vector has the same direction everywhere and is independent of the coordinate in the flow direction, the convective term vanishes identically. Solutions can also be found in two dimensions. But one of the most important applications of (10.31) is to the study of turbulence in fluid flow, and progress in understanding this phenomenon theoretically has been very limited.

Workers in this field appear to hold the following view: "Those who study turbulence believe that all its important properties are contained in the Navier–Stokes equations for fluid motion." (Falkovich and Sreenivasan, 2006). Although a principal mathematical reason for limited success is the difficulty presented by the nonlinear term in $\boldsymbol{v}$ on the left-hand side of (10.31), one should remain aware of *all* of the approximations leading to these equations; this particular nonlinearity may not be the only roadblock to understanding the phenomena. First, turbulence appears to be very much a state far from equilibrium, and therefore Batchelor's observation at the beginning of this chapter does not necessarily apply for high Reynolds number, (10.32) below. Thus, it is by no means clear that the linear approximation (10.2) leading to the expression (10.29) for the stress tensor tells the whole story; the linearity is in the departure from equilibrium. Unfortunately, higher-order approximations are certain to be virtually impossible to work with. Second, (10.26) is a linear constitutive relation, and as such suffers from certain general restrictions discussed earlier: It is a result of both a long-wavelength and a short-memory approximation.

Given these difficulties, one might entertain the possibility of bypassing the differential equations altogether to focus on the exact predictive solutions to the equations of motion suggested by (10.5) and the subsequent discussion. Even in linear approximation, however, the mathematical difficulties are about as great owing to the complexity of the covariance functions. Nevertheless, it may be possible to illuminate some pieces of the turbulence puzzle by means of the thermal driving scenario.

10.3 The onset of turbulence

We consider a simple fluid undergoing steady-state laminar flow, by which is meant a fluid flowing in smooth parallel layers with no disruption between the layers. Technically, the state of the flow can be described in terms of the dimensionless *Reynolds number*

$$Re \equiv \frac{\ell u}{\nu}, \tag{10.32}$$

where ℓ is a typical dimension of the volume and u an average bulk speed. One can think of Re as a ratio of inertial to viscous forces, so that laminar flow corresponds to small Re. This state is obtained by driving the momentum, and if we start from an equilibrium characterized by the grand canonical distribution the ensuing steady state is described by a density matrix of the form (7.14):

$$\rho_{st} = \frac{1}{Z_{st}} \exp\left[-\beta(H-\mu N) - \int \boldsymbol{\lambda}(\boldsymbol{x}') \cdot \boldsymbol{p}^d(\boldsymbol{x}')\, d^3x'\right], \tag{10.33}$$

where $\boldsymbol{p}^d$ is the diagonal part of the momentum density operator $\boldsymbol{p} = m\boldsymbol{j}$. The flow is then described by streamlines with "average" momentum $\langle \boldsymbol{p}(\boldsymbol{x}) \rangle_{st}$, and the source strength $\sigma_{\boldsymbol{p}}$ is equal to the divergence of the momentum current (from the equation of motion). Both the conditions that $\sigma_{\boldsymbol{p}}$ be constant and $[H, \boldsymbol{p}^d] = 0$ are required for steady-state flow.

At higher Reynolds numbers increased fluctuations away from the steady state can take place and turbulence in the form of seemingly chaotic motion can set in. This state is characterized by high momentum convection and low momentum diffusion. How can we know that the flow is laminar and remains so? Only observation can provide the answer, and that implies that we should monitor the *physical* deviations $\boldsymbol{p} - \langle \boldsymbol{p} \rangle_{st} \equiv \delta \boldsymbol{p}$, as defined in (6.36). In practice one would measure the root-mean-square (rms) deviation, but it is convenient theoretically to consider fluctuations both up and down explicitly.

The physical fluctuations must have a source arising from some sort of perturbation. Such fluctuations will appear to be quasi-random and time dependent, so we can consider them to be 'driven' by the perturbation source and employ the thermal driving mechanism. Thus, we modify (10.33) so that it contains information on possible physical fluctuations by driving the possible deviation of momentum by the perturbation source:

$$\begin{aligned} \rho_t = \frac{1}{Z_t} \exp \bigg[-\beta(H - \mu N) - \int \boldsymbol{\lambda}(\boldsymbol{x}') \cdot \boldsymbol{p}^d(\boldsymbol{x}') \, d^3x' \\ - \int_0^t dt' \int d^3x' \, \boldsymbol{\eta}(\boldsymbol{x}', t') \cdot \delta \boldsymbol{p}(\boldsymbol{x}', t') \bigg] . \end{aligned} \tag{10.34}$$

Just as $\boldsymbol{\lambda}$ is proportional to the constant source strength of the background steady state, we expect $\boldsymbol{\eta}$ to describe the amplitude or strength of the perturbation. The fundamental difference between (10.33) and (10.34) is that ρ_t now includes the possibility that physical fluctuations can occur in the system.

For laminar flow the fluctuation term in (10.34) is very small, so the expectation value of the fluctuation is well described by the linear approximation

$$\langle \delta \boldsymbol{p}(\boldsymbol{x}, t) \rangle = - \int_0^t dt' \int d^3x' \, \boldsymbol{\eta}(\boldsymbol{x}', t') \cdot K^{st}_{\boldsymbol{pp}}(\boldsymbol{x}, t; \boldsymbol{x}', t'), \tag{10.35}$$

where the covariance function here is defined with steady-state expectation values in the laminar-flow distribution ρ_{st}:

$$K^{st}_{AB}(\boldsymbol{x}, t; \boldsymbol{x}', t') = \langle \overline{B(\boldsymbol{x}', t')} A(\boldsymbol{x}, t) \rangle_{st} - \langle B(\boldsymbol{x}', t') \rangle_{st} \langle A(\boldsymbol{x}, t) \rangle_{st}. \tag{10.36}$$

That is, the size of the physical fluctuation is dependent on both the strength of the perturbation and on the space-time correlation of physical deviations over the system volume. It is noted explicitly here that $K^{st}_{\delta\boldsymbol{p}\delta\boldsymbol{p}} = K^{st}_{\boldsymbol{pp}}$, but we stress that (10.35) is *not* what would be obtained by omitting the third term in the exponential in (10.34) and linearizing—(10.35) is a prediction of the physical fluctuation about the laminar stationary-state value with the full density matrix of (10.34), though in linear approximation.

Equation (10.35) indicates how one can monitor the laminar-flow state, which remains laminar as long as this quantity is small. Whereas the nonzero range of the equilibrium function K^0_{AB} is considered very small, on the order of that of the interparticle interactions, the nonequilibrium correlations described by $K^{st}_{\boldsymbol{pp}}$ are known to be of macroscopic range; that is, they decay algebraically rather than exponentially, an assertion that will be substantiated below. Thus, the integrand is nonzero over macroscopic portions of the volume, while according to (10.67) it is proportional to Re, and its ultimate size will be determined by the magnitude of $\boldsymbol{\eta}$, which is the control parameter. It now seems established that the amplitude of the perturbation at which the transition takes place scales something like Re^{-1} (Chapman 2002; Hof *et al.*, 2003), so that as the Reynolds number increases not a great deal of increase in perturbation amplitude is required to produce increasing momentum fluctuations and a "tipping point" for the transition. Large deviations in momentum are the hallmark of turbulent flow.

This pre-turbulence description fits rather nicely with recent discussions of both theoretical and experimental investigations of the onset of turbulence in cylindrical pipes (*e.g.*, Fitzgerald, 2004). Because laminar flow in pipes has been found to be stable against infinitesimal perturbations for very large, if not all, Reynolds numbers, a finite-amplitude perturbation must be necessary for a transition to turbulence.

Given fluctuations in $\boldsymbol{p}$, there should also be fluctuations in T_{mn}, and in linear approximation (relative to the steady state)

$$\langle \delta T_{mn}(\boldsymbol{x},t)\rangle = -\int_0^t dt' \int d^3x'\, K^{st}_{T_{mn}\boldsymbol{p}}(\boldsymbol{x},t;\boldsymbol{x}',t')\cdot\boldsymbol{\eta}(\boldsymbol{x}',t'). \tag{10.37}$$

The time rate of change of $\langle\delta\boldsymbol{p}\rangle$ is

$$\begin{aligned}\frac{d}{dt}\langle\delta\boldsymbol{p}(\boldsymbol{x},t)\rangle = &-\int d^3x'\, K^{st}_{\boldsymbol{pp}}(\boldsymbol{x},t;\boldsymbol{x}',t)\cdot\boldsymbol{\eta}(\boldsymbol{x}',t)\\ &-\int_0^t dt'\, K^{st}_{\dot{\boldsymbol{p}}\boldsymbol{p}}(\boldsymbol{x},t;\boldsymbol{x}',t')\cdot\boldsymbol{\eta}(\boldsymbol{x}',t').\end{aligned} \tag{10.38}$$

Substitution of the *microscopic* local conservation law $\dot{\boldsymbol{p}} = -\nabla\cdot T_{mn}$, integration by parts on $\boldsymbol{x}'$, dropping the surface integral, and comparison with (10.37) yields

$$\frac{d}{dt}\langle\delta\boldsymbol{p}(\boldsymbol{x},t)\rangle + \nabla\cdot\langle\delta T_{mn}(\boldsymbol{x},t)\rangle = -\int d^3x'\, K^{st}_{\boldsymbol{pp}}(\boldsymbol{x},t;\boldsymbol{x}',t)\cdot\boldsymbol{\eta}(\boldsymbol{x}',t), \tag{10.39}$$

the governing equation of motion for the deviation.[4] The formal predictive solution is already given in (10.35), of course, but this expression is still of some

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[4] This is effectively the equation of motion (10.1b), which leads eventually to the Navier–Stokes equations (10.31). That is, the fluctuations are governed by the same laws as the physical variables themselves—something that Onsager (1931a) thought must be true.

theoretical importance. The right-hand side of (10.39) has precisely the form of a source term in the linear thermal driving scenario, (9.24), thereby confirming our interpretation: It is an effective source strength for the physical fluctuations in momentum.

Although (10.35) and (10.39) are of some theoretical significance, it is not clear how important they may be in practice, for $K^{st}_{\boldsymbol{pp}}$ would be difficult to evaluate in any substantial detail. As $\langle\delta\boldsymbol{p}\rangle$ grows the linear approximation loses its validity, and further study of the transition to turbulence requires a nonlinear analysis. There may be experimental guidance available for constructing reasonable models for both $K^{st}_{\boldsymbol{pp}}$ and $\boldsymbol{\eta}(\boldsymbol{x},t)$, but this lies beyond the scope of the present work. At best, (10.35) might serve as an indicator of a pending transition.

10.4 Ultrasonic propagation

We have seen that special cases of thermal driving arise when the rate is zero, describing an equilibrium state, and for dynamical driving in the presence of a well-defined external field. Another occurs when the source σ_F can usefully be replaced by a time-dependent boundary condition. For example, a common experimental arrangement in the study of acoustical phenomena is to drive a quartz plate piezoelectrically so that it generates sound waves along a plane. Thus it is quite realistic to characterize the external source by specifying the particle current on the boundary plane at $z = 0$. The system excited by the sound wave is then described by the density matrix

$$\rho = \frac{1}{Z}\exp\left\{-\beta H + \int dx' \int dy' \int dt'\, \boldsymbol{\lambda}(x',y',t')\cdot \boldsymbol{J}(x',y',0,t')\right\}, \qquad (10.40)$$

and Z is the trace of the exponential.

To keep the model simple the volume is taken to be the entire half-space $z > 0$, and we presume the z-component of current to be specified over the entire xy-plane for all time. Although there are no currents in the equilibrium system, current components at any time in the perturbed system in the right half-space are given by $\langle J_\alpha(x,y,z,t)\rangle = \mathrm{Tr}[\rho\, J_\alpha(x,y,z,t)]$. Restriction to small-amplitude disturbances, corresponding to small departures from equilibrium, implies the linear approximation to be adequate:

$$\langle J_\alpha(x,y,z,t)\rangle = \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dt'\, \lambda(x',y',t') \times K^0_{J_\alpha J_z}(x',y',0,t';x,y,z,t), \qquad (10.41)$$

and consistency requires this expression to reproduce the boundary condition at $z=0$:

$$\begin{aligned}\langle J_z(x,y,0,t)\rangle = \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dt'\, \lambda(x',y',t') \\ \times K^0_{J_zJ_z}(x-x',y-y',0;t-t').\end{aligned} \tag{10.42}$$

We are thus considering low intensities but arbitrary frequencies.

Linearity suggests it is sufficient to consider the disturbance at the boundary to be a monochromatic plane wave. Thus,

$$\langle J_z(x,y,0,t)\rangle = Je^{-i\omega t}, \tag{10.43}$$

where J is a constant amplitude. Substitution of this boundary value into (10.42) allows one to solve the integral equation for $\lambda(x',y',t')$ immediately by Fourier transformation, and the Lagrange multiplier function is determined directly by means of the driving term, as expected. We find that

$$\lambda(x,y,t) = \lambda_\omega\, e^{-i\omega t}, \tag{10.44}$$

with

$$\lambda_\omega^{-1} \equiv J^{-1} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, K^0_{J_zJ_z}(x,y,0,\omega), \tag{10.45}$$

so that λ is independent of spatial variables. Given the form of the covariance function in (10.42), the current in the right half-space will also be independent of x and y:

$$\begin{aligned}\langle J_\alpha(x,y,z,t)\rangle = \lambda_\omega\, e^{-i\omega t} \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dt'\, e^{i\omega t'} \\ \times K^0_{J_\alpha J_z}(x',y',z,t').\end{aligned} \tag{10.46}$$

Define a function

$$\begin{aligned}K^0_{J_\alpha J_z}(z,\omega) &\equiv K^0_{J_\alpha J_z}(0,0,z,\omega) \\ &= \int_{-\infty}^{\infty} \frac{dk_z}{2\pi}\, e^{ik_z z}\, K^0_{J_\alpha J_z}(k_z,\omega),\end{aligned} \tag{10.47}$$

where $K^0_{J_\alpha J_z}(k_z,\omega) \equiv K^0_{J_\alpha J_z}(0,0,k_z,\omega)$. Then (10.41) for the current in the perturbed system can be rewritten as

$$J_\alpha(z,t) \equiv \langle J_\alpha(0,0,z;t)\rangle = J_\alpha(z)e^{-i\omega t}, \tag{10.48}$$

and

$$J_\alpha(z) \equiv \lambda_\omega K^0_{J_\alpha J_z}(z,\omega). \tag{10.49}$$

In the same notation, $\lambda_\omega^{-1} = J^{-1} K^0_{J_z J_z}(0,\omega)$. Thus, the amplitude of the sound wave relative to that of the initial disturbance is

$$\frac{J_\alpha(z)}{J} = \frac{K^0_{J_\alpha J_z}(z,\omega)}{K^0_{J_z J_z}(0,\omega)}. \tag{10.50}$$

So, application of a monochromatic plane wave at the boundary results in a disturbance that propagates through the system harmonically, but with an apparent attenuation along the positive z-axis given by $J_\alpha(z)$. Analysis of the spatial decay depends on the detailed structure of the current–current covariance function, and *only* on that; this remains true if we synthesize a general wave form.

As an example, suppose that

$$K^0_{J_z J_z}(k_z,\omega) = 2\pi g(\omega)\,\delta(k_z - k_0). \tag{10.51a}$$

From(10.50) the z-component of current is then

$$J_z(z) = J\,e^{ik_0 z}, \tag{10.51b}$$

and the initial plane wave propagates with no attenuation.

More interesting is a covariance function of Lorentzian form, such as

$$K^0_{J_z J_z}(k_z,\omega) = \frac{\alpha f(\omega)}{\alpha^2 + (k_z - k_0)^2}. \tag{10.52a}$$

A similar calculation yields

$$J_z(z) = J\,e^{ik_0 z}\,e^{-\alpha|z|}, \tag{10.52b}$$

which exhibits the classical exponential attenuation. Although the Lorentzian form provides at least a sufficient condition for exponential decay of the sound wave, there clearly is no obvious requirement for the attenuation to be exponential in general.

Note that the number density itself could have been predicted in the above discussion, merely by replacing J_α with n. In a similar manner we find that

$$n(z,t) \equiv \langle n(0,0,z;t)\rangle - \langle n\rangle_0 = \lambda_\omega K^0_{nJ_z}(z,\omega)\,e^{-i\omega t}. \tag{10.53}$$

Because the equilibrium system is presumed isotropic, however, the covariance function $K^0_{nJ_z}$ is always directly proportional to the density–density covariance function K^0_{nn}, and therefore

$$K^0_{nJ_z}(z,\omega) = \frac{\omega}{2\pi}\int_{-\infty}^{\infty} \frac{dk_z}{k_z}\,e^{ik_z z}\,K^0_{nn}(k_z,\omega). \tag{10.54}$$

The variation in density, $n(z,t)$, is directly related to the correlated propagation of density fluctuations, and it is precisely this correlation of fluctuations that makes intelligible speech possible.

The preceding model has been adapted by Snow (1967) to an extensive study of free-particle systems. Although there is essentially no propagation in these systems in the classical domain, the quantum systems do exhibit interesting behavior, such as second sound.

10.5 Correlations in nonequilibrium fluids

We conclude this discussion of fluid dynamics with some remarks about correlation functions for simple fluids. Recall the development in Chapter 7 of expressions for linear transport coefficients in these media. In particular, we saw in Eq.(7.25) that the diffusion coefficient was proportional to an integral involving the current–current covariance function,

$$\boldsymbol{D}(\boldsymbol{x}) \propto \lim_{\epsilon\to 0^+} \int_0^\infty e^{-\epsilon t}\, dt \int_v K^0_{\boldsymbol{jj}}(\boldsymbol{x}-\boldsymbol{x}',t)\, d^3x'. \tag{10.55}$$

In arriving at this expression, $\nabla\lambda$ had already been extracted from the integral in a long-wavelength approximation that presumed the gradient to be essentially constant over that range of the volume for which the covariance function was nonzero—this is the correlation volume $v \ll V$. That is, the range over which fluctuations are correlated is taken to be very small, on the order of that of the particle–particle interactions. Were this not the case, the time integral in (10.55) would diverge, as can be seen from the property (6.34) of covariance functions,

$$\lim_{k\to 0} K^0_{AB}(\mathbf{k},\omega) = \int_{-\infty}^{\infty} e^{i\omega\tau}\, d\tau \int K^0_{AB}(\mathbf{r},\tau)\, d^3r. \tag{10.56}$$

If A is one of the locally conserved densities, such as linear momentum $\boldsymbol{p}$, then it can be integrated into the corresponding conserved quantity, such as the total momentum $\boldsymbol{P}$, which commutes with the Hamiltonian. In that event, cyclic invariance of the trace leads to a complete loss of time dependence in $K^0_{\boldsymbol{jj}}$, Eq.(10.55), and hence a divergent integral. That this cannot happen follows from the short range of both the interparticle interactions and the equilibrium correlation function; an example of the latter is given in (A.24). The point is twofold: The integral for $\boldsymbol{D}$ ranges only over v, for which the gradient can be extracted; but the integration of $\boldsymbol{p}$ to $\boldsymbol{P}$ must involve the complete system volume, and this cannot be done while the remaining integral over $V - v$ still contains the gradient. The latter integral vanishes in any event.

The situation well away from equilibrium is quite different, for it is now well known that nonequilibrium space-time correlations in fluids are long ranged; the decay is algebraic rather than exponential, particularly as studied in the steady state (*e.g.*, Dorfman *et al.*, 1994). This can be understood by means of a brief study of the correlation of fluctuations in a nonequilibrium steady state such as that described by the density matrix (10.33). Simple fluids are most often considered in the classical domain, so we shall find it convenient to consider the ordinary correlation function Γ in (6.35), rather than the full covariance function. The expectation value of the product of two physical deviations,

$$\Gamma^{st}_{ab}(\boldsymbol{x},t;\boldsymbol{x}',t') \equiv \mathrm{Tr}\big[\rho_{st}\delta a\, \delta b\big] = \langle \delta b(\boldsymbol{x}',t')\, \delta a(\boldsymbol{x},t)\rangle_{st}, \tag{10.57}$$

can be evaluated in the same way as for any other operator in the linear approximation about the steady state. For simplicity, we will focus explicitly on the density–density correlations and choose $a = b = n$, but the following can be applied to any of the locally conserved densities. Thus, with the aid of (7.20) and (7.21), and the usual integration by parts,

$$\begin{aligned}\Gamma^{st}_{nn} - \Gamma^0_{nn} &\simeq \int_V \lambda_i(\boldsymbol{x}'')\langle \delta n(\boldsymbol{x}',t')\,\delta n(\boldsymbol{x},t)\,p^d_i(\boldsymbol{x}'')\rangle_0\,d^3x'' \\ &= \int_V d^3x'' \int_{-\infty}^0 dt''\,e^{\epsilon t''}\,\nabla_i\lambda_j(\boldsymbol{x}'')\langle \delta n(\boldsymbol{x}',t')\,\delta n(\boldsymbol{x},t)\,T_{ij}(\boldsymbol{x}'',t'')\rangle_0,\end{aligned} \tag{10.58}$$

where the first term from the diagonal part of the operator $\boldsymbol{p}^d$ vanishes by symmetry, and $\lim_{\epsilon\to 0^+}$ is understood. But this limit can be taken immediately, for the subsequent integral turns out to be well behaved.

One can now take the long-wavelength limit and use space-time translation invariance of the equilibrium distribution to rearrange the space and time variables. The x'' integration can also be performed to obtain the space-integrated stress tensor T_{ij}, which in this case will also be independent of time. Then,

$$\Gamma^{st}_{nn} - \Gamma^0_{nn} \simeq \nabla_i\lambda_j \int_0^\infty \langle \delta n(\boldsymbol{x}'+\boldsymbol{r},t''+t')\,\delta n(\boldsymbol{x}',t''+t)\,T_{ij}\rangle_0\,dt'', \tag{10.59}$$

where we have introduced the notation $\boldsymbol{r} \equiv \boldsymbol{x} - \boldsymbol{x}'$. Fourier transformation on $\boldsymbol{x}'$ yields

$$\begin{aligned}\Gamma^{st}_{nn}(\boldsymbol{k};t',t) - \Gamma^0_{nn}(\boldsymbol{k};t',t) &\simeq \nabla_i\lambda_j \\ &\times \int_0^\infty \langle \delta n(-\boldsymbol{k},t''+t')\,\delta n(\boldsymbol{k},t''+t)\,T_{ij}\rangle_0\,dt'',\end{aligned} \tag{10.60}$$

The fluctuations here are about the steady state, $\delta n = n - \langle n\rangle_{st}$, but in steady flow close to equilibrium these are approximated well by $n - \langle n\rangle_0$. In turn, we now approximate δn by $\langle \delta n\rangle_{st} = \big\langle n - \langle n\rangle_0\big\rangle_{st}$, where unit operators are implied as factors. This allows us to determine $\delta n \simeq \langle n\rangle_{st}$ from the macroscopic diffusion equation, and from (11.12) in Chapter 11 we have

$$\langle \delta n(\boldsymbol{x},t)\rangle_{st} = \int \frac{d^3k}{(2\pi)^3} e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\, f(\boldsymbol{k})e^{-Dk^2t}, \tag{10.61}$$

where D is the diffusion constant, and the spectral function $f(\boldsymbol{k})$ is the Fourier transform of the initial value $\langle \delta n(\boldsymbol{x},0)\rangle_{st} \equiv f(\boldsymbol{x})$. Hence,

$$\langle \delta n(\boldsymbol{k},t)\rangle_{st} = f(\boldsymbol{k})e^{-Dk^2t}. \tag{10.62}$$

As a useful model we will adopt the equilibrium fluctuation in the long-wavelength limit and write, from (6.56), $f(\boldsymbol{k}) \simeq (n_0^2\kappa_T/\beta)^{1/2}$, where n_0 is the equilibrium density and κ_T is the isothermal compressibility. Substitution of (10.62) into (10.60) provides the momentum-space correlation function

$$\Gamma^{st}_{nn}(\boldsymbol{k};t',t) \simeq \Gamma^{0}_{nn}(\boldsymbol{k},t-t') + \left(\frac{n_0^2\kappa_T}{\beta}\right)\nabla_i\lambda_j\langle T_{ij}\rangle_0 \times \int_0^\infty e^{-Dk^2(2t''+t+t')}\,dt''. \tag{10.63}$$

Our interest lies with the asymptotic behavior for large r, which corresponds to small k and the long-wavelength limit. We know that Γ^0_{nn} decays exponentially (see below), so that the remaining term contains the long-range component of the correlation function. The Laplace transform is readily evaluated and we have

$$\Gamma^{st}_{nn}(\boldsymbol{k};t',t) \simeq \nabla_i\lambda_j\langle T_{ij}\rangle_0\left(\frac{n_0^2\kappa_T}{2\beta D}\right)\frac{e^{-Dk^2(t+t')}}{k^2}. \tag{10.64}$$

Finally, the inverse Fourier transform gives us

$$\Gamma^{st}_{nn}(\boldsymbol{r};t',t) \simeq \left(\frac{n_0^2\kappa_T}{8\pi\beta D}\nabla_i\lambda_j\langle T_{ij}\rangle_0\right)\frac{1}{r}\,\mathrm{Erf}\left[\tfrac{1}{2}r/\sqrt{D(t+t')}\right]. \tag{10.65}$$

The error function for large argument approaches unity faster than exponentially, so that

$$\Gamma^{st}_{nn}(\boldsymbol{r};t',t) \xrightarrow[r\to\infty]{} \left(\frac{n_0^2\kappa_T}{8\pi\beta D}\nabla_i\lambda_j\langle T_{ij}\rangle_0\right)\frac{1}{r}. \tag{10.66}$$

Physically, the source of these long-range correlations in this model is a coupling of two diffusion modes; mode–mode coupling models have been used extensively in studies of correlation functions in the past (*e.g.*, Dorfmann *et al.*, 1994). In addition, the nonequilibrium nature of Γ^{st}_{nn} is evident from the proportionality to the gradient of a potential.

One immediate piece of physical insight that emerges from (10.66) is associated with the above study of sound propagation, for this behavior of Γ_{nn} is not necessarily restricted to stationary processes. A similar calculation reveals that the long-range nature of the correlation function is also present in a fluid under the influence of an arbitrary sound signal. In connection with the propagation of density fluctuations noted in (10.54), we can now understand why the voice of the speaker at the front of the lecture hall is both received and understood by the listener in the rear.

The momentum correlation function in (10.35) can be analyzed in much the same way. It will suffice to imagine the flow only in the z-direction, say, and consider $\Gamma^{st}_{p_zp_z}$. In this case the diffusion parameter becomes the kinematic viscosity ν, and from the equilibrium fluctuation in the long-wavelength limit we have $f_z(\boldsymbol{k}) \simeq (n_0/\beta m)^{1/2}$. Thus, the long-range portion of the correlation function in this model is

$$\Gamma^{st}_{p_zp_z}(\boldsymbol{r};t',t) \simeq \left(\frac{n_0m}{8\pi\beta\nu}\nabla_i\lambda_j\langle T_{ij}\rangle_0\right)\frac{1}{r}\,\mathrm{Erf}\left[\tfrac{1}{2}r/\sqrt{\nu(t+t')}\right]$$
$$\xrightarrow[r\to\infty]{} \quad \left(\frac{n_0m}{8\pi\beta\nu}\nabla_i\lambda_j\langle T_{ij}\rangle_0\right)\frac{1}{r}. \tag{10.67}$$

Of some interest here is the observation that if we scale the variables to a typical system length and time of flow, and note that $\nabla_i\lambda_j = \beta\nabla_i v_j$ and $\langle T_{ij}\rangle_0$ has dimension mv^2, we find that the right-hand side is just *Re* times something of dimension momentum-density-squared, as it should be.

Although the foregoing calculation validates our analysis of (10.35), there remain some other features asserted about the equilibrium correlation functions that should be discussed as well, such as exponential spatial decay, because they also have a bearing on nonequilibrium problems. Moreover, it now seems to be well established that these correlations in equilibrium simple fluids exhibit an algebraic time decay first uncovered in computer simulations by Alder and Wainwright (1967). This is already evident in (10.65) for the nonequilibrium function, since $\mathrm{Erf}(z) \sim z$ as $z \to 0$.

We can address these points by means of a model much like that above by writing

$$\Gamma^0_{nn}(\boldsymbol{r},\tau) = \langle\delta n(\boldsymbol{x}'+\boldsymbol{r},\tau)\,\delta n(\boldsymbol{x}',0)\rangle_0$$
$$= \int\frac{d^3k}{(2\pi)^3}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\,\langle\delta n(\boldsymbol{k},\tau)\,\delta n(-\boldsymbol{k},0)\rangle_0, \tag{10.68}$$

where $\tau \equiv t-t'$. The approximation (10.62) can be employed once more, along with the choice for $f(\boldsymbol{k})$. A short calculation then leads to

$$\Gamma^0_{nn}(\boldsymbol{r},\tau) \simeq \int\frac{d^3k}{(2\pi)^3}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\,\langle f(-\boldsymbol{k})e^{-Dk^2\tau}f(\boldsymbol{k})\rangle_0$$
$$= \frac{n_0^2\kappa_T}{8\beta(\pi D)^{3/2}}\,\frac{e^{-r^2/4D\tau}}{\tau^{3/2}}$$
$$\xrightarrow[\tau\to 0]{} \quad \frac{n_0^2\kappa_T}{\beta}\,\delta(\boldsymbol{r}). \tag{10.69}$$

We thus verify that Γ^0_{nn} decays exponentially in space and algebraically in time as $\tau^{-3/2}$. In addition, the covariance function is seem to be well behaved as $\tau \to 0$, thereby implying finite expressions for linear transport coefficients of the kind (10.55). The equal-time, or static correlation, functions were essentially given in (10.9)–(10.11) and are thermodynamic functions times $\delta(\boldsymbol{r})$, obtained by use of (10.56). Hence, the third line of (10.69) verifies (10.9).

11

IRREVERSIBILITY, RELAXATION, AND THE APPROACH TO EQUILIBRIUM

> *If we ask what changes in external bodies are necessary to bring the system to its original state, we do not mean a state in which each particle shall occupy more or less the same position as at some previous epoch, but only a state which shall be undistinguishable from the previous one in its sensible properties.*
>
> *J. Willard Gibbs (1875)*

After many intervening chapters we can now return to a number of questions raised at the very beginning of this discussion in connection with the nature of entropy. Specifically, why can S not decrease in isolated systems? Why are most processes irreversible? How and why do macroscopic systems return to equilibrium after being perturbed from that state? Can the Second Law be sensibly extended to encompass nonequilibrium states? And what role, if any, does the maximum information entropy S_t play in clarifying these issues?

There is usually a "cloud of confusion" surrounding questions of this kind, because it is often unclear what definitions different writers have in mind when discussing them. For example, even in these pages we have encountered a number of items called "entropy"—S, S_I, $S_B = k\ln W$, S_t—although we have been very definite about the meaning of each and their relationships to one another. Not only confusion, but error arises when one is not perfectly clear about what is being discussed and simply refers to "entropy," particularly when nonequilibrium processes are involved. We reiterate that the thermodynamic entropy is defined only for equilibrium states, whereas the other quantities mentioned above have definite extensions to nonequilibrium states.[1]

Similarly, and perhaps more disturbing, are the sometimes loose ways of talking about irreversibility and the Second Law. Often it is never made clear what an author is actually discussing in this respect, and it is taken for granted that the concepts need no precise definition. Thus, prior to addressing these issues it is first necessary to discuss exactly what we mean by "irreversibility" and the Second Law of Thermodynamics; we begin with the former.

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[1] We refer here to entropy defined only within the current context and not to those that might be defined as offshoots of Shannon's ideas in information theory, such as algorithmic entropy.

11.1 Irreversibility

As noted in Chapter 1, the notion of *macroscopic reversibility* was first introduced by Carnot in 1824 in his classic work on heat engines. In the sense meant there, a reproducible macroscopic process taking a system from a macrostate A to a macrostate B is reversible if it can be made to proceed in the opposite direction $B \to A$, thereby restoring the original state. Eventually, however, workers such as Clausius, Gibbs, and Planck realized that the reversibility of importance in actual thermal processes is the weaker notion of *Thermodynamic Reversibility*: Even if the process $B \to A$ cannot take place directly, if by any means such as $B \to C \to D \to A$ the original macrostate can be recovered with no external changes, then all entropies are unchanged and the process $A \to B$ is thermodynamically reversible. It would be difficult to state the converse more succinctly than did Planck (1949): "The process of heat conduction cannot be reversed by any means." One can sometimes reverse a few degrees of freedom for a short period, of course, as with spin echoes, but this only reemphasizes the need to interpret equilibrium states as macrostates of *complete* thermal equilibrium (*i.e.*, that retain no memory). When we ask whether a process is reversible or not, the implication almost always is that it takes place between two such states. Note that the "path" of such processes is in the thermodynamic state space, passing through a sequence of macrostates of the system.

The character of macroscopic irreversibility was illustrated nicely in Chapter 5 in the example of Gibbs' "paradox," wherein two unlike gases are mixed and the entropy of the final mixture is seen to be greater than the sum of the two original entropies. There is an additional "entropy of mixing" associated with the irreversible nature of this process. More generally, one can imagine a half-full glass of a priceless wine, say, that a myopic waiter carelessly fills with water so that the wine is mixed irretrievably with the water, but is still contained in the glass; although there is some probability that sometime later the wine could be reconstituted spontaneously within the glass, it is vanishingly small. In both these irreversible processes something is very definitely *lost*—one also speaks of dissipation or degradation. As already noted in Chapter 2, however, a little thought reveals that what is lost is *information* about in which microstate the system may be, and that is the characteristic feature of an irreversible process.

But whose information is lost? Surely the state of the system cannot depend on whether or not we are looking! The essential point is that the initial microstate leading to the reconstructed wine is completely swamped by the overwhelming number of microstates that can be realized in the greatest number of ways. It has been noted earlier that knowing how much control we might be able to exert over a system depends on how well we know its microstate, and that is precisely what the entropy is telling us; that is its thermodynamics function.[2] So the information loss is real.

Our experience is that most macroscopic processes are irreversible. Aside from the obvious cases of significant friction, and so on, why is this? It is a

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[2] This property of entropy has sometimes been considered mysterious (*e.g.*, Caves, 1993).

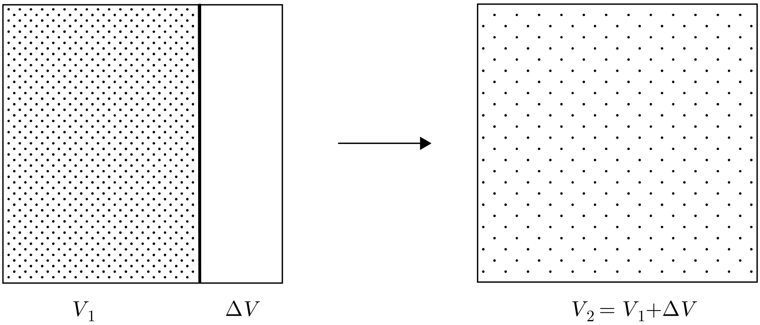

FIG. 11.1. The free expansion of a confined gas into a larger volume.

question to which Boltzmann devoted his life and which he essentially answered correctly; it is best illustrated with a familiar example.

One of the simplest thermodynamic process we can imagine is the free expansion of a confined gas into a larger volume, yet it contains most of the elements essential to a discussion of irreversibility. Initially the gas confined to volume V_1 is considered to be in thermal equilibrium in a macrostate A_1, a state of maximum entropy. This state is defined by energy E_1 (or temperature T_1), and we envision V_1 to be part of a larger volume $V_2 = V_1 + \Delta V$ such that ΔV is initially empty and separated from V_1 by an impermeable membrane. The entire system is isolated adiabatically from its environment (Fig. 11.1).

The membrane is now dissolved, so that the gas expands to fill the volume $V_2 > V_1$, and the system is allowed to return to thermal equilibrium in the macrostate A_2 (see below), perhaps determined when the sound waves generated by the sudden change in volume have died out. We expect this equilibrium state to persist indefinitely and the gas to remain distributed uniformly throughout V_2, as long as the system is isolated.

The tool for verifying these assertions is given by Boltzmann's expression for the maximum entropy, $S_B = k \ln W$, where we recall that W is the measure of a volume in phase space or of a manifold in Hilbert space; it measures the size of the set of N-particle *microstates* compatible with the macroscopic constraints on the system that can be realized in the greatest number of ways. The macrostate A_1 has entropy $S_1 = k \ln W_1$, where W_1 is the size of the set of states C_1 compatible with the constraints defining A_1. After the expansion, the system is in the new macrostate A_2 with entropy $S_2 = k \ln W_2$ and a set of states C_2 compatible with the new volume constraint. If $W_1 = W_2$, the initial and final entropies are equal and the process is macroscopically reversible, whereas if W_2 was smaller than W_1, the process would not be in general reproducible, because there would be possible initial microstates in C_1 that would not map into C_2. If this is a reproducible experiment—in the sense that A_1 can be reproduced, but certainly not any particular microstate in C_1—then it is surely necessary that $W_2 \geq W_1$,

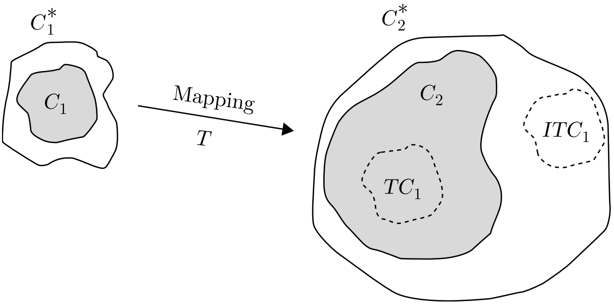

FIG. 11.2. Schematic illustration of the discussion related to the process illustrated in Fig. 11.1. The sets C_i^* are those containing all microstates compatible with their respective constraints, whereas C_i are the respective HPMs of dimension W_i. Dashed lines denote the images of C_1 in C_2^*, one mapped into C_2 and one containing possible time-reversed initial states for an inverse mapping (I) and located in the complement of C_2.

which is the basis of the Second Law and derives from Liouville's theorem. These remarks are illustrated in Fig. 11.2, but just how much larger is the set C_2? This was already answered in (4.36), where we employed Boltzmann's expression to write the ratio of phase volumes as

$$\frac{W_1}{W_2} = \exp\left(-\frac{S_2 - S_1}{k}\right). \tag{11.1}$$

If the difference in entropies is merely a nanocalorie at room temperature, this number is $\sim\exp(-10^{12})$, and the number of microstates compatible with the constraints defining A_1 is vanishingly small compared with those compatible with those defining A_2. Therefore, to have any significant probability of being realized the initial microstates required to regain the macrostate A_1 would have to be contained in the high-probability manifold (HPM) C_2, whose microstates are all compatible with the constraints defining the macrostate A_2; but these requisite initial microstates cannot be realized in many different ways and must therefore lie in the complement of C_2, and according to the argument leading to (4.35) they have very low probability. Moreover, this manifold of requisite initial microstates must have dimension about the same as that of C_1, but from (11.1) this dimension is immeasurably smaller than that of C_2, so that it is even less probable that these initial states could be realized. As understood so clearly by Gibbs and Boltzmann, the time-reversed evolution is not impossible, it is just extremely improbable.

Einstein (1910) had sensed the argument long ago, as have others since then, noting that the system was constantly sampling neighboring states, driven by the particle dynamics. But, because the density of high-probability states is so great, that neighboring state is almost certain to be another state in the HPM. He also appreciated the utility of the form (11.1).

These comments suggest that there is something more to be learned from (11.1). We know that in general, $S/k = \mathrm{O}(N)$, reflecting the usually extensive nature of the entropy. For the type of many-body systems being considered, the likelihood of spontaneous reversal is indeed small. For a very small system, however, the probability may be considerably different from zero and, as amply demonstrated in Chapter 4, the Second Law is readily violated for small N; owing to possible fluctuations, it can also be violated over short time intervals. Figure 11.2 also illustrates how much these remarks depend on the size of the system, for only when $N \gg 1$ is the HPM sharply defined; otherwise, the time-reversed initial states are not so clearly isolated from the high-probability states. These points were illustrated explicitly in Chapter 4, in the discussion of entropy fluctuations. At this point it is difficult to see what more need be said about the origin of thermodynamic irreversibility in *macroscopic* systems; of course, much more has been said!

Over the years many have found it paradoxical that the time-reversal invariant character of the fundamental dynamical laws of microscopic physics could lead to noninvariant macroscopic laws of motion, such as the diffusion equation (6.42). In discussing that equation, we noticed that the evident irreversibility arose because one of its intrinsic components, the constitutive equation, was inferential and depended upon information only about the past and not the future, which was being predicted. Moreover, the microscopic dynamical equations do not stand alone, but must be completed with initial conditions, and that is the crux of the matter: We can only control *macroscopic* initial conditions. In any event, microscopic reversibility and thermodynamic reversibility are two entirely different creatures and are not at all in conflict.

Nevertheless, it is often suggested that if in the volume V_2 above we reverse all particle velocities, then the Hamiltonian equations will carry out the time-reversed motion and return the system to its original state in V_1. Such an operation can never be done, of course, but it is thought that at some time the system might "stumble" upon the appropriate microscopic initial conditions and carry out just such a spontaneous reversal. Incidentally, this scenario is just one of an infinity of possibilities that could occur in the equilibrium system in V_2. One could envision all the particles congregating in any one of the corners at some time, for example—and any one of these motions is at least a possibility, just as any specific bridge hand is a possibility, but with very low probability.

Kelvin first suggested time symmetry of the microscopic equations as a source of inconsistency, and later Loschmidt (1876) formalized it as a "paradox." But it was Zermelo (1896a,b) who turned it into a reasonable expectation based on Poincaré's recurrence theorem in classical mechanics (Poincaré, 1890): A system having a finite amount of energy and confined to a finite spatial volume will, after a sufficiently long time, return to an arbitrarily small neighborhood of its initial state. Quantization suggests that it might return to that state exactly. It has sometimes been suggested, in fact, that irreversibility is nothing more than the effect of long recurrence times, which may very well be the case. But the proposition lacks content, for relevant recurrence times turn out to be something like $10^{10^{23}}$ years, reemphasizing that the reverse macroscopic processes are not impossible, just very improbable. As Gibbs noted: "The impossibility of an uncompensated decrease of entropy seems to be reduced to an improbability."

Another source of irreversibility proposed in recent years lies with "chaos" in the microscopic equations of motion—that is, nonlinear dynamics exhibiting extreme sensitivity to initial conditions. In such systems the necessary initial conditions for the reversed motions would almost never be achieved; indeed, inaccurate knowledge of initial conditions is exactly the point we have been making. Chaotic motion would certainly be predicted by the system Hamiltonian, which is what we have been using all along, but we still are only able to predict averages over those chaotic motions. Hamilton's equations are deterministic, even when encompassing chaos, but they are neither predictable nor reversible without precise knowledge of initial conditions, and thus bring nothing new to the problem of irreversibility. The irrelevance of chaos to this problem has been discussed at length by Bricmont (1996), notwithstanding the importance of the concept to the study of nonlinear dynamics.

One other possible source of irreversibility we should mention is that of external perturbations, for all real systems are subject to some kind of external perturbation, no matter how small. This idea can be traced back to Émile Borel, who wrote extensively on probability theory in the early part of the 20th century (Borel, 1909, 1914), and he developed a related interest in statistical mechanics and irreversibility. He was critical of some of the ideas of Boltzmann and Gibbs, and in particular objected to the use of Liouville's theorem in relation to the density of phase D. In addition, he was well aware of Poincaré's work on nonlinear dynamics and, owing to a possible exponential divergence of trajectories from one another, argued that any initial phase volume D_0 would later evolve into a region very much different in form to D_0, thereby anticipating the concept of a "mixing" system. Borel also gave a striking example of how small external perturbations could initiate these instabilities. He calculated that a mass of 1 gm displaced through 1 cm at the distance of Sirius would affect the total gravitational field at the Earth's surface only by a factor of 10^{-100}, yet would be enough to change classical molecular trajectories in a box in less than 10^{-6} s!

Undoubtedly, such small external perturbations could affect Poincaré recurrences in real systems, should they last that long, and might in some way affect reversibility. But in general most such effects are insignificant and are averaged over in any event; most models of isolated and closed systems are realistic. Galilean and Lorentz invariances are never exact in the real world either, but in most instances the approximations are excellent. We calculate relaxation times without taking small external influences into account, and the results agree quite well with experiment.

When all is said and done we are led back to our original conclusions. Macroscopic irreversibility is simply a product of very large numbers and multiplicity factors. Attainment of the requisite initial conditions for a massive microscopic reversal in the process illustrated in Fig. 11.1 is so improbable that, in Boltzmann's (probably apocryphal) phrase, "you should live so long." (The folklore also reports that his response to the suggestion that all particle velocities could be reversed was, "go ahead, reverse them!")

11.2 The Second Law

Thermodynamic irreversibility is clearly at the heart of the Second Law of Thermodynamics, and the Clausius statement of the Second Law is only one of several ways to express its implications. A number of negative expressions arose historically along the lines of the impossibility of perpetual motion machines. Representative, and perhaps clearest of these is that due to Kelvin: "It is impossible for heat to flow of itself from a cold reservoir to a hotter one without leaving changes in external bodies." Alternatively, it is not possible to extract heat from a reservoir and perform an equivalent amount of work. The necessary direction of heat flow is seen to be consonant with the result from probable inference, for the equation of heat conduction has the same mathematical form as that for diffusion, and the inferential component, Fourier's law, determines the direction of flow down the temperature gradient. The important point to be grasped here is that the constituent equations are no longer merely phenomenological, but clear mathematical results of the theory; they are not fundamental laws of dynamics, but of inference.

The difficulty with negative statements is that they are not very useful in determining quantitative results, and are not statements of experimental fact. (They do, however, have the positive attribute of being falsifiable by a single incident.) A more positive way to restate Kelvin's assertion is the following: In a process in which heat may flow to or from a system, the total entropy of all bodies involved may increase or remain constant, but will not decrease. In such processes irreversibility is more transparent, for the sets of microstates underlying the initial and final macrostates of the system would not even lie on the same energy surface in phase space.

Of course, the macroscopic state of a system can change without thermal energy transfer, in which case the Second Law can be stated in alternative form: Under an adiabatic change of state the entropy of an isolated system can only remain constant or increase. Rubbing two objects together, for example, is an irreversible adiabatic process, in which the initial and final macrostates also reside on different energy surfaces, but no heat has been transferred. Both statements, in the spirit of Clausius, express only a *tendency*, but in doing so are quite useful in asserting the direction in which a process or potential reaction within the system can go; namely, such that entropy does not decrease. In this sense they are "weak" versions, for today we know that not only will the entropy tend to increase, it will indeed increase to the maximum value allowed by the constraints on the system. This stronger statement is just the Principle of Maximum Entropy (PME), which has been discussed at length in previous chapters. It may, however, also be of interest to demonstrate the weak version explicitly.

Consider a closed system in complete thermal equilibrium at time $t = 0$ and described by a density matrix ρ_0, so that

$$S(0) = S(\rho_0) = -k\mathrm{Tr}(\rho_0 \ln \rho_0) = k \ln W(0), \tag{11.2}$$

where $W(0)$ is the dimension of the HPM $M(0)$, and S is the experimental entropy of an equilibrium state. By "complete" equilibrium we mean that the system has no memory of anything done to it in the past, thereby avoiding any strange effects such as those encountered with spin echoes. Some have argued on philosophical grounds that all matter is correlated to some extent beginning with the creation of the universe (*e.g.*, Price, 1996), which may be correct, but the experimentalist has no choice but to ignore such possible unknown effects, most of which must be vanishingly small in any event.

Now apply some kind of time-dependent perturbation to the system that induces an adiabatic change of state, and then let the system return adiabatically to a new equilibrium state at time t. For example, we can add a time-varying term to the system Hamiltonian, as in (8.5), though with some care. From the macroscopic point of view, the thermodynamic state variables $\{X_1(0), \ldots, X_n(0)\}$ characterizing the initial state are carried into a new set $\{X_1(t), \ldots, X_n(t)\}$ characterizing the final state.[3] In a reproducible experiment beginning with the same macroscopic conditions, the microscopic initial conditions will vary over $M(0)$ but yield the same macroscopic data; the final microstates will vary over $M(t)$ at each repetition of the experiment, yet yield the same macroscopic set $\{X_i(t)\}$. Throughout all repetitions, the initial HPM is mapped unitarily into a new manifold $M(t)$, so that in every case $W(t) = W(0)$. In the context of this example, this invariance is an expression of Liouville's theorem and is exactly what forms the crux of the Second Law.

At the conclusion of the experiment the system is in a new equilibrium state characterized by data $\{X_i(t)\}$ that can be used with the PME to delineate a new HPM $M'(t)$ with dimension $W'(t)$. Since this is an equilibrium state, it must be that the experimental entropy measured at this point has the value $S'(t) = k \ln W'(t)$. Because $M'(t)$ contains all the high-probability states compatible with the new data, regardless of whether or not they also lie in $M(t)$, and if $\{X_i(0)\} \to \{X_i(t)\}$ is to be reproducible, it necessarily follows that $M(t)$ must be contained within $M'(t)$. This is only possible if $W'(t) \geq W(t)$, which then leads to the standard expression of the Second Law:

$$S'(t) = k \ln W'(t) \geq k \ln W(t) = k \ln W(0) = S(0), \tag{11.3}$$

in accord with our view of irreversibility discussed above.

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[3] The notation should not be taken to confer any explicit time dependence on S and W, but only to denote a stage of the experiment.

Recall that we are here considering macrostates that are *experimentally reproducible* by controlling a set of macrovariables $\{X_1, \ldots, X_n\}$ that define the thermodynamic system, and that the entropy is a function *only* of these macroscopic variables: $S_n = S(X_1, \ldots, X_n)$. If a second experimentalist comes along and, unknown to us, manipulates some new variable X_{n+1} outside this set, then he may well bring about a change of state for which S_n decreases spontaneously while S_{n+1} does not. We might thus be deceived into thinking we have observed a spontaneous violation of the Second Law, whereas we are actually considering two different thermodynamic systems that describe the same physical system; unfortunately, this is not an uncommon occurrence. Once again, different states of knowledge can lead to different entropies.

This example evinces some significant insight into the scope of the Second Law, for it is seen to be a statement about the difference in *experimental* entropies between two equilibrium states *of the same thermodynamic system*; it is an expression of macroscopic phenomenology. It does not refer at all to what goes on during the change of state, a point made emphatically by Lieb and Yngvason (1999) in their detailed analysis of classical thermodynamics: "arbitrarily violent processes are allowed to occur in the passage from one equilibrium state to another," as long as they are adiabatic. In particular, the law as stated is not concerned with nonequilibrium processes, or exactly how the ensuing equilibrium is approached; the latter will be investigated presently.

Having noted that, however, is there any possibility of extending the Second Law so as to apply to nonequilibrium states? In general there would not seem to be, for such states can be too arbitrary, such as existing only once ever. But therein lies an opening. If a nonequilibrium state can be reproduced, then our earlier observation that the Second Law comprises a necessary condition on experimentally reproducible processes (ERP) comes into play and Boltzmann's expression, which is valid for nonequilibrium states as well as for equilibrium, allows us to compare entropies for two different such states. With $S = k \ln W$ for a macroscopically reproducible state, it necessarily follows that $W_i \leq W_f$, and hence $S_i \leq S_f$. Of course, the utility of this insight hinges on our ability to calculate, or at least envision, these Ws (or HPMs), and for many processes that becomes problematic—but the set of possibilities is not empty. For example, if a system is driven into a nonequilibrium state and then the external driving removed, it is left momentarily in that state, from which it relaxes to equilibrium. If the process is reproducible then this generalization of the Second Law is valid. This scenario is treated in more detail below, and a quite different application of this perspective to an estimation of the efficiency of animal muscle has been developed by Jaynes (1989).

11.3 Is time asymmetry an issue?

For centuries there has been a great deal of philosophical discussion about the perception of time asymmetry in the universe and in our lives. Indeed, we continue to grapple with the meaning of time, and inevitably run out of it before finding many answers. For physicists at work, however, time is simply a parameter in our fundamental dynamical equations and appears there independent of any direction.

It was noted above that some have found paradox in these observations and wondered how it may be possible to derive the asymmetric world we see around us from these time-symmetric physical laws. We know of no requirement, however, that these two observations be connected, for the initial conditions associated with the one have no relation to those employed by us for the other. Moreover, entropy and the Second Law are essentially epistemological concepts, whereas the fundamental dynamical laws that presumably drive the latter are on an ontological level. We should be well advised to avoid confusing reality with our perception of reality.

In the above discussion of irreversibility and the Second Law, time was never mentioned, for it is not a variable of classical thermodynamics. Yet many have seen in the Second Law an "arrow of time," and hence some explanation of the time asymmetry around us. To bolster this connection, it is often thought to have a cosmological origin, an idea initiated by Boltzmann himself (*Vorlesungen*, p.446). He thought the universe to be in thermal equilibrium, with galaxies as local fluctuations, and for the universe the two directions of time were considered indistinguishable. But, in his view, local observers would find themselves in an improbable low-entropy state from which entropy would increase with their perception of time, and hence a connection between the two.

Our cosmological outlook has changed considerably in a hundred years, but both philosophers (*e.g.*, Price, 1996) and scientists (*e.g.*, Davies, 1975; Penrose, 1989) continue to proffer an explanation for the Second Law in terms of time asymmetry in the universe, or vice versa. In this modern scenario, the universe is thought to have begun in a uniform state of very low entropy, considered so because it would be in opposition to the purely attractive gravitational interaction.

Pondering the mystery of time asymmetry is indeed a worthy pursuit, but we find it quite difficult to relate this apparent feature of the universe to our local observations of irreversibility. It is rather presumptuous to speak of the entropy of a universe about which we still understand so little, and we wonder how one might define thermodynamic entropy for a universe and its major constituents that have never been in equilibrium in their entire existence. Is the Big Bang a reproducible process? On a more prosaic level, we have no idea how to envision, let alone calculate, the entropy of a worm! For these reasons we decline to speculate here on the relation of entropy to the long-term fate of the universe and whether or not it will run down and burn out.

Nevertheless, such speculations continue and would seem to place an unfair and heavy burden on entropy at any rate, which originates in our view as a measure of uncertainty about the specific microstate in which we might expect to find a local thermodynamic system defined by a small number of macroscopic variables. As we have seen, entropy and irreversibility generally have their origins in probability theory, and the application of that to macroscopic physical systems in our world would now appear to be well understood.

The macroscopic equations of motion derived from the time-reversal invariant microscopic laws, and which govern the time evolution of macroscopic systems—the diffusion, heat, and Navier–Stokes equations, for example—do indeed exhibit a time asymmetry; we now understand why this is, and there is no requirement that they be invariant under time reversal. Under these macroscopic laws, densities become uniform and currents die out in isolated systems, phenomena that we next investigate in some detail. It would be more than bizarre to think that this behavior had any intimate relation to the rest of the universe and the human perception of time asymmetry, which may largely be due to the phenomena of consciousness and memory.

11.4 Relaxation and the approach to equilibrium

A desideratum often expressed by writers on this subject is the ability to follow the approach of a many-body system to equilibrium by means of some dynamical equations of motion. For example, given some definite nonequilibrium state, one might like to describe in full detail the relaxation to equilibrium once some external constraints are removed. Among other things, we might obtain in this way an unambiguous determination of relaxation rates. The idea goes back at least to Boltzmann, who offered his famous H-theorem for this purpose; H was defined in (1.15), where the theorem was also mentioned briefly. To describe a general approach to equilibrium from an initial nonequilibrium state he next considered binary collisions in an essential way and employed the basic conservation laws to obtain an equation of motion for the single-particle velocity and position distribution f, the so-called Boltzmann equation. As it happens, careful mathematical derivations of the equation show that it, too, is valid not only under the *Stosszahlansatz* (no correlations), but also only in the limit of vanishing particle size and density (*e.g.*, Lanford, 1975, 1983). Unaware of these stringent constraints, Boltzmann defined the function

$$H(t) \equiv \int f(\boldsymbol{x},\boldsymbol{p},t)\log f(\boldsymbol{x},\boldsymbol{p},t)\,d^3x\,d^3p \tag{11.4}$$

and was able to show that, if f satisfied the Boltzmann equation, then

$$\frac{dH}{dt} \leq 0, \tag{11.5}$$

which is the H-theorem.

As mentioned above, Loschmidt objected that for every motion that makes H increase there must be one that makes it decrease. This led Boltzmann to recognize the underlying probabilistic nature of H and to realize that the H-theorem could only be true on average, which further encouraged him to relate H to the entropy of the system.

A century later Jaynes (1971) demonstrated that the H-theorem, and therefore the Boltzmann equation upon which it is based, cannot generally be valid, even for a dilute gas. In any system with appreciable potential energy of interaction there exists a substantial manifold of initial states such that the approach to equilibrium entails a continuous average *increase* in H. These states are in no way exceptional, nor does the associated anti-H behavior have anything to do with breakdown of the *Stosszahlansatz.* Moreover, there is no inference to be made here concerning failure of the Second Law of Thermodynamics, since H has no relation to the entropy in a real system (*e.g.*, Hill, 1956), particularly one with appreciable potential energy (see Jaynes, 1965).

In his later work Gibbs noted that an arbitrary ensemble distribution, and hence the entropy, remained constant in time owing to Liouville's theorem, and thus could not approach the canonical distribution describing equilibrium. He sought to remedy this by introducing the notion of *coarse graining* (*SM*, pp.144–151), which envisions a coarser partition of the phase space over which to compute the basic probabilities, and he was thus able to demonstrate the approach to equilibrium in the canonical ensemble. But neither a deeper rationale for requiring coarse graining, nor a unique form of the procedure, have ever been demonstrated, and thus the approach cannot be considered fundamental. Indeed, we now know that constancy of S_I under unitary transformation is by no means a difficulty, for it is the maximum of this quantity under external constraints that must be considered. In retrospect we might wonder why both Boltzmann and Gibbs were overly concerned with constructing a time-dependent "entropy" that approached the equilibrium value if the entire concept of entropy at that time referred only to equilibrium in the first place.

Although Boltzmann's description of the approach to equilibrium ultimately failed, we can now better understand why this is so, and also gain some insight into the system's further time development. In the thermally driven system the instantaneous nonequilibrium state is described by the density matrix (9.1), with associated entropy (9.5). The following arguments are made more transparent by adopting a specific physical model, which we will take to be a simple fluid. At $t=0$ the system is presumed to be in a state of complete thermal equilibrium and then driven from that state by driving both the number and energy densities—for example, by heating, stirring, and possibly adding more material to the fixed volume. [Alternatively, one could consider the mode-coupling scenario of (9.31).] The density matrix describing this process is

$$\rho_t = \frac{1}{Z_t} \exp\left[\int_0^t dt' \int_V d^3x \big[-\beta(\boldsymbol{x},t')h(\boldsymbol{x},t') \; + \lambda(\boldsymbol{x},t')n(\boldsymbol{x},t')\big]\right], \tag{11.6}$$

where Z_t is the trace of the exponential, and the plus sign in the argument recognizes the physical interpretation of λ. Note that we have not explicitly included any information about a previous equilibrium state, other than the lower limit on the time integral. The corresponding maximum information entropy of this nonequilibrium process is

$$\frac{1}{k}S_t = \ln Z_t + \int_0^t dt' \int_V d^3x\big[\beta(\boldsymbol{x},t')\langle h(\boldsymbol{x},t')\rangle_t \;-\lambda(\boldsymbol{x},t')\langle n(\boldsymbol{x},t')\rangle_t\big]. \quad (11.7)$$

After some arbitrary driving interval, the external sources are removed at time $t = t_1$ and the system is again isolated. At that time the nonequilibrium state is described by ρ_{t_1} and S_{t_1}, which are now fixed and descriptive of that state only. From (9.20) we note that the total rate of change of entropy for $t > t_1$ is now $\dot{S}_{int}(t)$, so that we expect the system to relax to equilibrium, possibly described in terms of a *relaxation entropy.* In the discussion following (9.18) it seemed that not much could be said about this quantity in general because there was no information available at that point to describe the relaxation. Now, however, it appears that there are indeed two cogent pieces of information that change the situation greatly.

The first definite fact is that the external source has been removed, so that the system is now isolated from further external influences; the second is the set of macroscopic equations of motion derived from the local microscopic conservation laws (6.29). From (10.1) these are

$$\frac{d}{dt}\langle n(\boldsymbol{x},t)\rangle + \nabla_i\langle j^i(\boldsymbol{x},t)\rangle = 0, \quad (11.8a)$$

$$m\frac{d}{dt}\langle j^i(\boldsymbol{x},t)\rangle + \nabla_k\langle T^{ki}(\boldsymbol{x},t)\rangle = 0, \quad (11.8b)$$

$$\frac{d}{dt}\langle h(\boldsymbol{x},t)\rangle + \nabla_i\langle q^i(\boldsymbol{x},t)\rangle = 0, \quad (11.8c)$$

in which any source terms are now set to zero for $t > t_1$. These macroscopic conservation laws determine the subsequent macroscopic behavior of the system, and one can now think of the expectation values as classical densities and currents. (This is a bit more complicated when sources are present, as was evident in Chapter 10.)

The absence of external driving assures us that the *microscopic* time evolution now takes place through unitary transformation, and that the density matrix develops from ρ_{t_1} by means of the equation of motion $i\hbar\dot{\rho} = [H, \rho]$. If the system returns to equilibrium the density matrix $\rho(t)$ evolved in this way will surely predict correctly the equilibrium expectation values of various quantities, but we have already noted the futility of trying to follow this path: $\rho(t_1)$ cannot evolve unitarily to the canonical equilibrium distribution, for its eigenvalues remain unchanged. Moreover, the entropy S_{t_1} is only the maximum information entropy of that arbitrary nonequilibrium state and does not evolve into anything; it merely serves as a benchmark against which to gauge the entropy of the final state. The Second Law is not yet at issue here until we can show that relaxation to a final equilibrium state actually takes place and we have a definite entropy for comparison with earlier quantities.

To tackle this last question we first note that at $t = t_1$ the system is effectively isolated and total system quantities such as E, N, V, and so on, are fixed and define the eventual equilibrium state; indeed, they are essentially the values predicted by ρ_{t_1}, so that eventual state could be constructed right now by means of the PME if we were sure they were the only relevant variables. Additionally, it appears that *something* must be driving the system back toward equilibrium. In the absence of external forces this can only be the particle dynamics pushing the system inexorably toward the equilibrium state, for no other reason than that is the macrostate of maximum entropy corresponding to the overwhelmingly greatest number of microscopic arrangements consistent with those fixed global quantities. One might imagine the existence of "entropic forces" governing the motion, much like the fictitious forces of classical mechanics, such as the Coriolis force, but it is nothing more than the system's preference for a state of maximum entropy at work here. Although the thermal driving constraint has been released, the system at $t = t_1$ is not completely described by those global variables; it is not yet in an equilibrium state, because density gradients and currents continue to exist in the still-inhomogeneous system for $t \geq t_1$, and these will have to smooth out or vanish on the way to equilibrium. A state of thermal equilibrium is defined not only in terms of constants of the motion, but is also presumed to be homogeneous, at least in a single phase; otherwise, we cannot observe a uniform density and chemical potential, or a uniform energy density.

To understand the ensuing process let us consider as an example only the number density, which satisfies (11.8a) and, since there are no external forces for $t > t_1$, over short time intervals the relaxing particle current is found from a constitutive equation, Fick's law: $\langle \boldsymbol{j}(\boldsymbol{x},t)\rangle = -D\,\nabla\langle n(\boldsymbol{x},t)\rangle$, in which it is presumed that D is independent of space-time coordinates. In both the equation of motion and the constitutive equation, one can always replace $\langle n\rangle$ by $\delta n(\boldsymbol{x},t) \equiv \langle n(\boldsymbol{x},t)\rangle - n_0$, where $n_0 = N/V$ is the eventual suspected uniform value of the density fixed at t_1; this replacement allows us to focus appropriately on gradients in the system for $t > t_1$. Combination of the two yields the well-known diffusion equation

$$\partial_t \delta n(\boldsymbol{x},t) = D\,\nabla^2 \delta n(\boldsymbol{x},t), \tag{11.9}$$

which is to be solved subject to knowing the initial value $\delta n(\boldsymbol{x},t_1)$; this value can be taken as that provided by ρ_{t_1}.

But (11.9) cannot be the entire story. First of all, Fick's law arises from both linear and short-memory approximations. While these appear to be valid over a great range of applications, one should nevertheless bear in mind that (11.9) is then itself an approximation. Second, although the total system internal energy is fixed at $t = t_1$, some of that energy remains tied up in the decaying currents and density gradients, and viscous damping is converting some of that energy to heat, as in (10.22). Thus, while the decaying particle current is now induced by the decaying density gradients, that is opposed by friction. Undoubtedly this effect could be derived, with some effort, from a modification of the equation of motion (11.8b) for the current density, but for present purposes it is sufficient to account for it phenomenologically by appending a term $\boldsymbol{a}\langle n(\boldsymbol{x},t)\rangle$ to the right-hand side of Fick's law, where $\boldsymbol{a}$ is a constant with dimensions of velocity. Then, in place of (11.9) we should consider the Fokker–Planck equation

$$\partial_t \delta n(\boldsymbol{x},t) = D\,\nabla^2 \delta n(\boldsymbol{x},t) - \boldsymbol{a}\cdot\nabla[\delta n(\boldsymbol{x},t)], \tag{11.10}$$

with a similar expression for the energy density. In the event that D and a are constants, however, it is well known that a change of variables to $\boldsymbol{y}=\boldsymbol{x}-\boldsymbol{a}t$, $\tau = Dt$ reduces (11.10) to the form (11.9). For the present argument, the differences in the solutions to the two equations are irrelevant, so we will focus on the simpler equation (11.9).

Formal solutions to (11.9) and the corresponding heat equation are well known; we write the generic solution as $u(\boldsymbol{x},t)$ and express the initial value as $u(\boldsymbol{x},0) = f(\boldsymbol{x})$. Two boundary conditions are also required, one of which is already given in the initial condition, the other being that u vanish on the boundaries. Since u represents either $\langle\delta n\rangle$ or $\langle\delta h\rangle$, this requires that the densities become uniform at the boundaries. For a large volume, which we may as well take as all space, a short calculation via separation of variables and Fourier analysis leads to

$$u(\boldsymbol{x},t) = \frac{1}{(2\pi)^3}\int\int f(\boldsymbol{x}')e^{i\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')-Dk^2t}\,d^3x'\,d^3k. \tag{11.11}$$

Either one of the integrals is readily done, yielding the two equivalent forms

$$\begin{aligned} u(\boldsymbol{x},t) &= \frac{1}{(4\pi Dt)^{3/2}}\int f(\boldsymbol{x}')e^{-(\boldsymbol{x}-\boldsymbol{x}')^2/4Dt}\,d^3x' \\ &= \int \frac{d^3k}{(2\pi)^3}e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\,f(\boldsymbol{k})e^{-Dk^2t}, \end{aligned} \tag{11.12}$$

both of which vanish in the limit $t\to\infty$.[4] The first form has the merit of demonstrating that it also vanishes as $|\boldsymbol{x}|\to\infty$, indicating that the densities smooth out at the distant boundaries at any time; in addition, it reproduces the initial condition as $t\to 0$. The second form, however, is a bit more transparent and, depending on the spectral properties of $f(\boldsymbol{k})$, reveals that the dominant wavelengths λ will determine the relaxation time $\tau\sim\lambda^2/D$. Of course, τ will be slightly different for δn and δh, but they should be of the same order of magnitude. Finally, although $u(\boldsymbol{x},t)$ decays monotonically in time, its spatial decay is only contained within a monotonic envelope; that is, because spatial gradients will necessarily change sign throughout the volume during relaxation, $f(\boldsymbol{x}')$ in (11.12) will also oscillate in sign.

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[4] If the Fokker–Planck equation had been employed, the form corresponding to the first line of (11.12) would also have vanished exponentially with t.

Although all external forces have been removed, the above description in terms of decaying gradients and currents has all the earmarks of thermal driving discussed in the previous chapter. But here the "driving" is due to the internal (decaying) gradients. The densities decay into uniform values throughout the system, and hence the currents also vanish as $t \to \infty$.

Now we can see how the maximum entropy must evolve. At any time $t_2 > t_1$ we can consider values $\langle n(\boldsymbol{x}, t_2)\rangle_2$, $\langle h(\boldsymbol{x}, t_2)\rangle_2$ obtained as solutions to (11.9) and its companion for $\langle h\rangle$. The information entropy is then maximized subject to these constraints, so that at this time it is in a state described by

$$\rho(t_2) = \frac{1}{Z(t_2)} \exp\left[-\int_V \beta(\boldsymbol{x}, t_2) h(\boldsymbol{x}, t_2)\, d^3x + \int_V \lambda(\boldsymbol{x}, t_2) n(\boldsymbol{x}, t_2)\, d^3x\right], \tag{11.13}$$

where $Z(t_2)$ is the trace of the exponential, and the Lagrange multipliers are now formally determined from

$$\langle h(\boldsymbol{x}, t_2)\rangle = -\frac{\delta}{\delta\beta(\boldsymbol{x}, t_2)} \ln Z(\beta, \lambda), \qquad \langle n(\boldsymbol{x}, t_2)\rangle = -\frac{\delta}{\delta\lambda(\boldsymbol{x}, t_2)} \ln Z(\beta, \lambda). \tag{11.14}$$

The corresponding entropy $S\big[\rho(t_2)\big]$ is

$$\begin{aligned} \frac{1}{k} S(t_2) = \ln Z(t_2) &+ \int_V \beta(\boldsymbol{x}, t_2) \langle h(\boldsymbol{x}, t_2)\rangle_{t_2}\, d^3x \\ &- \int_V \lambda(\boldsymbol{x}, t_2) \langle n(\boldsymbol{x}, t_2)\rangle_{t_2}\, d^3x. \end{aligned} \tag{11.15}$$

These expressions do not involve functions of the time, but only refer to a single time $t = t_2$.

One can imagine carrying out this procedure in a sequence of as many time steps as desired, and at each step the Lagrange multipliers are determined, so that if this thought process is applied to the entire decay interval it is apparent that they must be evolving as well. The dynamic macroscopic evolution of the system into the final equilibrium state of maximum entropy thus corresponds to the limits

$$\begin{aligned} \langle n(\boldsymbol{x}, t)\rangle &\xrightarrow[t\to\infty]{} n_0 = N/V, \\ \langle h(\boldsymbol{x}, t)\rangle &\xrightarrow[t\to\infty]{} h_0 = E/V, \end{aligned} \tag{11.16}$$

where the expectation values refer to any point in the sequence and the right-hand sides are the constant values noted above. In the limit, the constants (11.16) can be extracted from the integrals in (11.13) and (11.15) to yield the additional constants $\beta \equiv \int \beta(\boldsymbol{x},\infty)\, d^3x$, $\beta\mu \equiv \int \lambda(\boldsymbol{x},\infty)\, d^3x$. At this point we see that the entire description has evolved into that of the grand canonical distribution,

$$\rho_{eq} = \frac{1}{Z_G} e^{-\beta(H-\mu N)}, \tag{11.17}$$

and the maximum entropy in the limit is identical with the physical equilibrium thermodynamic entropy:

$$\frac{1}{k} S_{eq} = \ln Z_G + \beta \langle H \rangle_0 - \beta\mu \langle N \rangle_0. \tag{11.18}$$

This, of course, agrees with the PME applied with the limiting input of (11.16), since those values were already determined at $t = t_1$—it is only in this limit that we can make this identification unambiguously.

It cannot be stressed enough that (11.18) is *not* the limit in any sense of S_{t_1} defined by (11.7); rather, it is the limit of a sequence of maximum-entropy calculations based on data provided by (11.12) at those points, as in (11.15). Nevertheless, this model of the approach to equilibrium does suggest a corresponding model for the time-dependent entropy of internal relaxation $S_{int}(t)$ whose rate of change was introduced in (9.20). One simply adopts the form of (11.15) and imagines the time steps to become increasingly smaller, so that in the limit the relaxation entropy becomes

$$\frac{1}{k} S_{int}(t) = \ln Z(t) + \int_V \beta(\boldsymbol{x},t) \langle h(\boldsymbol{x},t) \rangle\, d^3x - \int_V \lambda(\boldsymbol{x},t) \langle n(\boldsymbol{x},t) \rangle\, d^3x, \tag{11.19}$$

for $t \geq t_1 + \epsilon$. The functions $\langle h(\boldsymbol{x},t) \rangle$ and $\langle n(\boldsymbol{x},t) \rangle$ are given by (11.12), and the Lagrange multipliers are determined from equations of the form (11.14). As $t \to \infty$ we see that $S_{int}(t) \to S_{eq}$, (11.18). This is not at all a rigorous derivation, or even definition, of $S_{int}(t)$, but would appear to capture very nicely the essential physical picture of the relaxation process.

It is of some interest to observe that the final maximum entropy (= thermodynamic entropy) of (11.18) is not less than that of (11.7) at $t = t_1$, which follows from the brief discussion preceding (3.15). The entropy S_{eq} is determined by the global constraints E, N, V, and so on, whereas S_{t_1} is based on the history of $\langle n(\boldsymbol{x},t) \rangle$, $\langle h(\boldsymbol{x},t) \rangle$ over some space-time region. But the values of those global constraints are just those predicted by ρ_{t_1}, so that if they were predicted correctly[5] it follows that S_{t_1} was *a fortiori* maximized with respect to E, N, V, and so on, as well. Hence, since the entropy at $t = t_1$ is maximized with additional constraints, and thus over a more restricted class of variations, we conclude that $S_{t_1} < S_{eq}$. That is, because energy, and possibly matter, have been added to the system $W_{\text{final}} > W_{\text{initial}}$ and the Second Law is verified for

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[5] Independently of whether or not these global variables are *predicted* accurately, their actual values are nevertheless established at $t = t_1$.

this nonequilibrium process. These arguments presume that in all the preceding equations V is the entire system volume.

Finally, it should be noted that we could have begun with a completely arbitrary nonequilibrium state at t_1, as well as with a different type of physical system; the only requirement is a set of macroscopic conservation laws similar to those of (11.8). Other than that, the relaxation process should be very similar to that outlined here.

Because entropy has increased in the above relaxation process, from the initial to the final state, it is often thought that entropy has been "produced" in the process, as if it were a quantity of something. It is as if one were to ask: How much entropy is *in* the system? But our senses continue to suggest that something like this appears to take place in these transitions, at least qualitatively, so we shall complete this study of entropy by examining the idea of entropy production in the following chapter.

12

ENTROPY PRODUCTION AND DISSIPATION RATES

> *The equilibrium condition of thermodynamics S = maximum characterizes the most probable state … In a similar manner, [the principle of the least dissipation of energy] describes the most probable course of an irreversible process.*
>
> *Lars Onsager (1931b)*

Recall that Clausius' definition $dS = dQ/T$ was meant to apply strictly to equilibrium states, or to a path constituting a locus of such states; its original purpose was to compare two nearby equilibrium states. But in heating a pot of water we have the impression that thermal energy is being transferred into the pot continuously like some $\dot{Q}$, and that the temperature must be constantly increasing like $T(t)$. Thus, we might imagine that entropy is increasing at a rate $\dot{S} = \dot{Q}/T$. Whereas a flux of energy is readily imagined, both $\dot{S}$ and $T(t)$ present difficulties, for both S and T have been defined only in equilibrium, and are clearly related to observables only in such states. Somehow, though, one might suppose it possible to describe this process of increasing entropy as it unfolds.

As we have seen, however, this expectation has been frustrated. Although the maximum information entropy can be identified with the experimental thermodynamic entropy in the equilibrium state, S_t cannot be so identified in a nonequilibrium process. Yet this appears to be the only rigorous definition of entropy available to us: $\dot{S}_t$ is just the time rate of change of the maximum information entropy. How is this dilemma to be resolved?

Historically the theoretical notion of the rate of entropy production took shape with Onsager (1931a,b) and his phenomenological development of linear near-equilibrium thermodynamics, in which he generalizes the constitutive relations of Fick, Fourier, Ohm, and so on. As suggested in Chapter 6, this involves "fluxes" J_i and "forces" X_i related linearly as

$$J_i = \sum_k L_{ik} X_k, \tag{12.1}$$

where $L_{ik} = L_{ki}$ are elements of a symmetric matrix of coefficients. We have seen how this symmetry arises trivially in the maximum entropy formalism when space-time symmetries are valid in a particular medium. These quantities are so defined that the rate of entropy production is $\dot{S} = J_i X_i = L_{ik} X_i X_k$, with summation over repeated indices implied.

To even imagine a relation like $\dot{S} = \dot{Q}/T$, however, requires a prescription for some kind of *local equilibrium* over a timescale very small compared with that necessary for the total system to reach equilibrium. If one is inclined to accept this, then it is a short step to postulate existence of a local entropy density as a field variable $s(\boldsymbol{x}, t)$, along with a flow rate or flux $\boldsymbol{J}_s$, and a source strength $\boldsymbol{\sigma}_s(\boldsymbol{x}, t) \geq 0$. These are envisioned to satisfy a local conservation law $\dot{s} + \nabla \cdot \boldsymbol{J}_s = \sigma_s$ of the type describing simple fluids. But from everything we have learned, entropy is not some kind of "stuff" that flows and is locally conserved, so it is not surprising that neither σ_s nor $\dot{S} = \int \sigma_s \, dV$ were defined in any further detail; this remained true in most subsequent discussions of entropy production. (Actually, Onsager eventually seems to have in mind Boltzmann's definition of entropy as $k \ln W$.)

With this framework, Onsager develops a variational principle he calls "least dissipation of energy," in which he distinguishes between $\dot{S}$ and the quadratic dissipation function

$$\Phi(J, J) \equiv \tfrac{1}{2} R_{ik} J_i J_k > 0, \tag{12.2}$$

where R is the matrix inverse of L. That is, if the X_i are specified, the true fluxes J_i maximize the expression

$$\big[\dot{S}(X, J) - \Phi(J, J)\big]. \tag{12.3}$$

Evidently the primary motivation for this principle is that from it he can deduce (12.1) and the reciprocal relations, although he goes on to develop these relations from more general considerations in a following paper.

Of particular interest is the scenario of steady-state flow, for which the conservation laws reduce to $\nabla \cdot \boldsymbol{J} = 0$. In this case the internal entropy production is zero, whereas that due to the process, including sources and sinks, satisfies

$$\dot{S}(J_n) - \Phi(J, J) = \text{maximum}, \tag{12.4}$$

where J_n is the component normal to the boundaries. Onsager shows that for this situation (12.4) is equivalent to $\dot{S}(J_n) = \text{maximum}$. For stationary flow the integral of J_n over the entire boundary must vanish, $\dot{S}(J_n)$ is fixed, and we see that $\Phi(J, J)$ must be a minimum, explaining the name of the principle. In addition, he finds in this situation that necessarily

$$\dot{S}(J_n) = 2\Phi(J, J), \tag{12.5}$$

a result we shall verify by example below.

In summary, the rate of entropy production in the steady state due to the external source/sink is a maximum, but when this is fixed the rate of dissipation is a minimum. It is of some interest to restate this result as follows: When J_n is prescribed, stationary flow is determined by $\nabla \cdot \boldsymbol{J} = 0$ and $\Phi(J, J) = \text{minimum}$. Onsager's analysis was later extended considerably by Onsager and Machlup (1953), and Machlup and Onsager (1953).

A number of years later Prigogine (1947, 1961) developed another "principle" as a condition on steady-state processes, that of *minimum* entropy production.

This is not necessarily in conflict with Onsager—and indeed is readily derived from Onsager's theory—for it envisions additional restrictions on the process, and when this proviso has been ignored the principle has often been misinterpreted. Nevertheless, minimum entropy production has been criticized in the past by both Ziman (1956) and Jaynes (1980), who suggest that a principle of *maximum* entropy production in accord with Onsager might be more in line with our intuition. That is, the system should be trying to get back to the equilibrium state as fast as possible, subject to any constraints preventing that. It is not at all clear why this should be so for a general set of nonequilibrium constraints.

These early works on entropy production principles have led to further developments. Gyarmati (1970) has provided an extensive review of Onsager's theory and incorporated it into a general thermodynamics of continua. He also demonstrates an alternative and equivalent form of Onsager's principle: If the fluxes J_i are specified, then the true forces X_i maximize the expression

$$\big[\dot{S}(X,J) - \Psi(X,X)\big], \tag{12.6}$$

where

$$\Psi(X,X) \equiv \frac{1}{2}L_{ik}X_iX_k > 0 \tag{12.7}$$

is the dissipation function in the force representation. An important aspect of this formulation is its role in showing Prigogine's principle to be a corollary of Onsager's for stationary processes, for the former depends on fixing some fluxes as well as some forces.

Onsager's theory, as well as Gyarmati's extensions, are fundamentally linear, in that they encompass linear constitutive relations and quadratic dissipative functions. It is somewhat remarkable that these early developments parallel so closely the form of our linear approximations in Chapters 6–9, which stem from rigorous nonlinear expressions. Indeed, Ziegler (1968) recognized the incompleteness of the Onsager approach if one wished to study more complicated systems such as plastics, which needed nonlinear constitutive relations to describe them.[1] Eventually these thoughts led to a complete theory of thermomechanics (Ziegler, 1983), in which he developed a "principle of maximal dissipation rate," which is meant to apply to all of nonequilibrium thermodynamics. He claimed this to be equivalent to a principle of *maximum* rate of entropy production, simply by dividing the dissipation rate by the absolute temperature T. While Ziegler's variational principle reduces to that of Onsager in the linear case, there certainly seems to be a conflict over the extremum of the dissipation rate, at least for steady-state processes.

The idea of a maximum rate of entropy production has more recently become popular among scientists studying the global climate (*e.g.*, Ozawa *et al.*, 2003).

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[1] By this time Clifford Truesdell (1984) had been preaching his distrust of linear constitutive relations for years, a point raised earlier in Chapter 6.

Numerous and varied observations appear to suggest that such a maximum principle may be at work in the atmosphere under conditions of turbulent dissipation and nonlinear transport. Although the source of the nonlinearity is not completely clear,[2] Ziegler's maximum principle is to hold in both linear and nonlinear regimes, and so the principle is thought to provide a guide to the determination of the stationary state, should such exist in the atmosphere. If nothing else, this application may provide a good laboratory for testing the feasibility of these ideas.

Prior to analyzing these proposed principles from the statistical mechanics perspective, it may be useful to examine some related examples. Most applications are concerned with the steady state, so we shall focus on these processes. One of the first variational principles of the kind being considered here is due to Kirchhoff (1848) in extending Ohm's law to three dimensions. With an electric field $\boldsymbol{E} = -\nabla\phi$ in a medium of conductivity $\sigma(\boldsymbol{x})$, when the steady state is reached the potential $\phi(\boldsymbol{x})$ must cause no accumulation of charge at any point in the volume: $\nabla \cdot (\sigma\nabla\phi) = 0$, which is just $\nabla \cdot \boldsymbol{J} = 0$. But this is also the Euler–Lagrange equation stemming from the requirement that the rate of Joule heat production in a volume V,

$$\int_V \sigma(\nabla\phi)^2 \, d^3x, \tag{12.8}$$

be stationary with respect to variations $\delta\phi(\boldsymbol{x})$ that vanish on the boundary. The current distributes itself so as to dissipate the least possible heat for given voltages applied on the boundary. Thus, in the stationary state, *minimum* heat production corresponds to the conservation law. Other laws of minimum energy dissipation, or their equivalents, were soon provided by Helmholtz (1859), Rayleigh (1877), and Lorentz (1896) in other areas.

A more explicit and simpler example of Kirchhoff's conservation law has been given by Jaynes (1980). Consider a simple circuit consisting of two plain resistors R_1, R_2 connected in parallel, each in thermal contact with its own heat bath at temperatures T_1, T_2, and let a constant voltage be applied across the terminals. We ask how the current I will be distributed in the circuit after a steady state has been achieved.

On the one hand it is well known that Kirchhoff's rules of charge conservation at the nodes and energy conservation (loop rule), along with the constitutive relations (Ohm's law), provide the answer: The current will distribute itself such that $I_1R_1 = I_2R_2$, and the exact values emerge from the fact that both these voltage drops are equal to V. On the other hand, the rate of entropy production in the resistors is

$$\dot{S} = \left(\frac{R_1}{T_1}\right) I_1^2 + \left(\frac{R_2}{T_2}\right) I_2^2, \tag{12.9}$$

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[2] If the Navier–Stokes equations of motion are considered to describe the atmosphere it should be remembered that they are based on on the *linear* constitutive relation (10.29).

whereas the rate of Joule heat production is

$$\dot{Q} = R_1 I_1^2 + R_2 I_2^2. \tag{12.10}$$

Keeping charge conservation in mind, one finds the entropy production to be a minimum when the current distribution satisfies $R_1 I_1/T_1 = R_2 I_2/T_2$, while minimum heat production requires $I_1 R_1 = I_2 R_2$, which is the correct distribution.

We learn several things from this example, the first of which is that $\dot{S}$ and $\dot{Q}$ are not necessarily equivalent, in accord with Onsager's view in (12.4). Second, when the constitutive relation is given, only the conservation laws are required to solve the steady-state problem, without any additional principles. The generality of this last observation has also been noted by Klein (1960). This is not to deny, however, that an appropriate constitutive relation might be nonlinear and difficult to apply, or even be unknown, in which case a valid principle may well have some practical value. Third, if $T_1 = T_2$ the temperature is not a factor in the problem, $\dot{S} = \dot{Q}/T$, and the role of entropy increase in the environment is of secondary interest at best; the thermal aspect, while in the picture, is in the background. Finally, it is somewhat interesting to note that the extremum problem could be constrained by overall energy (or power) conservation, which then provides a *maximum* and delivers both the current distribution and the loop rule as a result. This is rather deceiving, however, for the constraint already restricts $\dot{Q}$ to a constant contour on that surface; however, the calculation reveals not only the absolute minimum at the origin, but also the maximum VI at the point $(V/R_1, V/R_2)$, and derives the constitutive relation as a bonus. This calculation is readily extended to general linear planar networks, with similar results (*e.g.*, Županović *et al.*, 2004).

A second example, more in line with our overall theme, is provided by the conduction of heat along a thin rod of length L and thermal conductivity κ. Let the rod lie along the x-axis with a high-temperature reservoir T_h at $x = 0$, and a low-temperature reservoir T_c at $x = L$, such that a constant temperature gradient is maintained along the rod. After a steady heat current $q(x)$ is established in the rod, we wish to know the temperature distribution.[3] The basic conservation law in this stationary state is $\nabla \cdot \boldsymbol{q} = 0$, and Fourier's (linear) law of heat conduction tells us that $\boldsymbol{q} = -\kappa \nabla T$. Combination of the two yields the determining equation for the temperature distribution: $\nabla^2 T(x) = 0$, with solution the well-known and well-confirmed linear distribution

$$T(x) = T_h - (T_h - T_c)\frac{x}{L}. \tag{12.11}$$

To understand the role of entropy production here we first note that, by definition, neither internal entropy nor any other state variable is changing during

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[3] One essentially presumes an equilibrium to be established locally in every thin cross section of the rod; that the idea of a temperature distribution is not at all trivial has been discussed at length by Tolman and Fine (1948).

the steady-state process; the system in effect acts merely as a conduit for conducting thermal energy between the reservoirs. The only dissipation or entropy production is that due to the process, much in agreement with our time rate of change of the maximum information entropy $\dot{S}_t$. This degradation of energy is the result of transferring heat from a higher to a lower temperature without extracting any work, and from Fourier's law we find that

$$\dot{S} = \frac{q}{T_c} - \frac{q}{T_h} = -\kappa \nabla T \left(\frac{T_h - T_c}{T_h T_c} \right) . \tag{12.12}$$

With (12.11) this becomes

$$\dot{S} = \frac{\kappa}{L} \frac{(T_h - T_c)^2}{T_h T_c} , \tag{12.13}$$

a well-known result.

From the Onsager point of view the rate of entropy production should be given by

$$\dot{S} = \int \boldsymbol{q} \cdot \nabla \left(\frac{1}{T} \right) d^3x = \int_0^L \frac{\kappa}{T^2(x)} \left[\frac{\partial T(x)}{\partial x} \right]^2 dx, \tag{12.14}$$

and substitution from (12.11) indeed reproduces (12.13). But we are really interested in knowing if there is some kind of extremum principle at work here. The condition for $\dot{S}$ to be an extremum is provided by the Euler–Lagrange equation (*e.g.*, Palffy-Muhory, 2001)

$$T \frac{\partial^2 T}{\partial x^2} = \left(\frac{\partial T}{\partial x} \right)^2 , \tag{12.15}$$

which takes into account the direction of the gradient. One verifies that the correct distribution (12.11) does not satisfy this condition; rather, the relevant solution to (12.15) is

$$T_{ext}(x) = T_h e^{-a(x/L)} , \quad a = \ln(T_h/T_c), \tag{12.16}$$

and to our knowledge this exponential decay has not been observed. Similar conclusions have also been reached by Ross and Vlad (2005) concerning an extremum of $\dot{S}$.[4]

Note that in the entire discussion it is never clear what exactly is meant by S itself, and only $\dot{S}$ has been defined. The amount of thermal energy leaving the high-temperature reservoir is the same as that entering the low-temperature one, and the rates of transfer are the same on either end. But according to (12.12) the

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[4] These same authors also study a general network of elementary chemical reactions obeying ideal mass-action law kinetics and demonstrate that the entropy production rate has an extremum if and only if the system is in equilibrium.

entropy changes in the two are different, and it is that difference that is being produced and represents the degradation of energy in the process.

Hence, the observed temperature distribution in the rod does *not* correspond to any extremum for $\dot{S}$ $\big[$although T_{ext} actually provides an $\dot{S}$ smaller than that of (12.13)$\big]$. Indeed, that distribution simply follows from the linear constitutive relation and the conservation law, and no further principle is required. Below we shall see that (12.14), and hence (12.13), is essentially the dissipation function, and thus describes the rate of degradation of thermal energy; but neither $\dot{S}$ nor Φ is an extremum.

These examples would seem to clarify some aspects of the role of proposed production principles in nonequilibrium processes. Usually a proposition is called a principle because it is something we wish to use but cannot prove—if it were proved it would be a theorem, not a principle. But this always entails the risk that one's principle may turn out to be wrong. Although the above models appear to be counterexamples to any far-reaching statements about the rate of entropy production, one has the feeling that the dissipation rate might provide a useful tool in some situations; a number of these have been reviewed by Bruers (2006).

Theoretically, the conservation laws and constitutive equations, linear or not, should always be enough to determine the steady state. The multitude of situations in which linear constitutive equations are valid is well understood; but there also exist materials in which this is not so, and in these cases the choice of nonlinear relations may not be at all transparent. In Onsager's work there is a suggestion that possibly the need for a constitutive equation could be replaced by some kind of principle of minimum dissipation. But such a solution is problematic, for the dissipative function itself would surely have to be extended beyond the quadratic form as well. Nevertheless, there may yet exist situations where a separate principle, if valid, might prove more tractable than the nonlinear equations of motion.

The real issue here, however, is entropy production. Energy is neither created nor destroyed, and in the end is always conserved. But, as Clausius noted from the beginning, that is not true of the entropy. Entropy is not a concrete entity that is created or destroyed, but only a measure of how much is known about the system's microstate at any one time. It can therefore only increase or decrease as a measure of this information. In most discussions of irreversible thermodynamics neither S nor $\dot{S}$ is clearly defined, although Onsager is definite about the latter; yet they are presumed to be observable in some way. But only the maximum information entropy S_t appears to have a clear and unambiguous definition in nonequilibrium processes, and this cannot be identified as the thermodynamic entropy, except in equilibrium. Skepticism toward identification of a physical internal entropy in nonequilibrium processes has recently been expressed elsewhere as well (*e.g.*, Lieb and Yngvason, 2003; Gallavotti, 2004).

The examples discussed above make it clear that entropy production and the rate of energy dissipation are not necessarily one and the same thing. Since the latter can be given a firm experimental basis, it would seem reasonable to focus on energy degradation and look for possible principles regarding the rate of dissipation, if they indeed exist, and allow entropy to play its certified role as a measure of information uncertainty, or of energy degradation when that is appropriate. This would seem to resonate with Onsager's original principle for stationary states, as well as with Gyarmati's discussion.

12.1 The statistical mechanics formulation

How does this stance fit in with our development of the statistical mechanics of steady-state processes? By way of answering this, suppose a constant current density $\boldsymbol{J}(\boldsymbol{x})$ paired with a locally conserved density $e(\boldsymbol{x})$ in a conservation law to have been established in a system that had previously been in equilibrium with internal energy $U = \langle H \rangle$. The system is described as being in a stationary state by means of the density matrix

$$\rho_{st} = \frac{1}{Z_{st}} \exp\left[-\beta H + \int_R \boldsymbol{\mu}(\boldsymbol{x}) \cdot \boldsymbol{J}(\boldsymbol{x})\, d^3x \right], \tag{12.17}$$

and one could include a number of currents if desired. (The + sign in front of the integral is deliberate.) Information on the Hamiltonian need not be included, but it is needed if we wish to make near-equilibrium approximations. According to Chapter 7, ρ_{st} can be a steady-state density matrix only if $\boldsymbol{J}$ is interpreted as the diagonal part of the current operator, and this implementation requires some care. We shall describe the construction of ρ_{st} at the end of this chapter and find that the variable $\boldsymbol{\mu}(\boldsymbol{x}) = \nabla\lambda(\boldsymbol{x})$, where λ is the Lagrange multiplier associated with the density $e(\boldsymbol{x})$ and plays the role of a "potential" whose gradient is a "force" conjugate to the "flux" $\boldsymbol{J}$; we will use both notations at times.

We shall take the current to be unidirectional, although it will generally span a cross section, and consider the gradient to be in the same direction as $\boldsymbol{J}$. It will also be useful to invoke the freedom of choice inherent in the PME, as done at times earlier, to take the Lagrange multiplier as the independent variable and predict $\boldsymbol{J}$. Thus, given $\nabla\lambda$ the predicted current density is

$$\begin{aligned} \langle J(\boldsymbol{x}) \rangle_{st} &= \mathrm{Tr}\big[\rho_{st} J(\boldsymbol{x})\big] \\ &\simeq \int_R \nabla'\lambda(\boldsymbol{x}') K^0_{JJ}(\boldsymbol{x}-\boldsymbol{x}')\, d^3x', \end{aligned} \tag{12.18}$$

and the second line is the linear approximation, having the Onsager form (12.1); the reciprocity relations are automatic. Whereas the first line of (12.18) represents the complete nonlinear constitutive relation—it is a nonlinear functional of $\nabla\lambda$—the second line provides the familiar linear relation in the long-wavelength limit, first order in the gradient. In this approximation, all expectation values are computed with the density matrix $\rho_0 = e^{-\beta H}/Z_0$ and, according to (12.37) below, ρ_0 is itself amenable to further approximation.

Substitution of ρ_{st} into $S_I = -k\mathrm{Tr}(\rho \ln \rho)$ yields the maximum information entropy of the steady-state process,

$$\frac{1}{k}S_{st} = \ln Z_{st}[\beta, \mu] + \beta\langle H\rangle_{st} - \int_R \mu(\boldsymbol{x})\langle J(\boldsymbol{x})\rangle_{st}\, d^3x. \tag{12.19}$$

This expression is independent of time, as it must be, but $\langle J(\boldsymbol{x})\rangle$ represents a flow and hence indicates some kind of rate of dissipation in the process; in this case the rate is constant.

Now make a linear approximation for both expectation values in (12.19); with the help of (A.18) in Appendix A,

$$\begin{aligned}\frac{1}{k}S_{st} \simeq \frac{1}{k}S_0 - \beta \int_R \nabla'\lambda(\boldsymbol{x}')K^0_{HJ}(\boldsymbol{x}')\, d^3x' \\ - \frac{1}{2}\int\int_R \nabla\lambda(\boldsymbol{x})K^0_{JJ}(\boldsymbol{x}-\boldsymbol{x}')\nabla'\lambda(\boldsymbol{x}')\, d^3x' d^3x.\end{aligned} \tag{12.20}$$

But K^0_{HJ} vanishes by symmetry, so that

$$\begin{aligned}\frac{1}{k}(S_{st} - S_0) &\simeq -\frac{1}{2}\int_R\int_R \nabla\lambda(\boldsymbol{x})K^0_{JJ}(\boldsymbol{x}-\boldsymbol{x}')\nabla'\lambda(\boldsymbol{x}')\, d^3x' d^3x \\ &\equiv -\Psi^0(\nabla\lambda, \nabla\lambda),\end{aligned} \tag{12.21}$$

which has the form of (12.7).

Rather than approximate $\langle J(\boldsymbol{x})\rangle$ in (12.19), we can approximate $\mu(\boldsymbol{x})$ instead, for the entropy can also be expanded in a functional Taylor series. Through leading order,

$$S_{st}[\langle J\rangle] = S_0 - \frac{1}{2}k\int_R\int_R \langle J(\boldsymbol{x})\rangle_{st} G^0_{JJ}(\boldsymbol{x}-\boldsymbol{x}')\langle J(\boldsymbol{x}')\rangle_{st} d^{3x'}\, d^3x + \cdots, \tag{12.22}$$

where

$$G^0_{JJ}(\boldsymbol{x}-\boldsymbol{x}') \equiv \left(\frac{\delta^2 S_{st}}{\delta\langle J(\boldsymbol{x})\rangle_{st}\delta\langle J(\boldsymbol{x}')\rangle_{st}}\right)_0 \tag{12.23}$$

is the functional inverse of $K^0_{JJ}(\boldsymbol{x}-\boldsymbol{x}')$, and according to (12.19) and (12.22)

$$-\mu(\boldsymbol{x}) = \frac{1}{k}\frac{\delta S_{st}}{\delta\langle J\rangle} \simeq -\int_R G^0_{JJ}(\boldsymbol{x}-\boldsymbol{x}')\langle J(\boldsymbol{x}')\rangle_{st}\, d^3x'. \tag{12.24}$$

So, (12.22) can be rewritten as

$$\frac{1}{k}(S_{st} - S_0) \simeq -\Phi^0(J, J), \tag{12.25}$$

where

$$\Phi^0(J,J) \equiv \frac{1}{2}\int_R\int_R \langle J(\boldsymbol{x})\rangle_{st} G^0_{JJ}(\boldsymbol{x}-\boldsymbol{x}')\langle J(\boldsymbol{x}')\rangle_{st}\, d^3x' d^3x \tag{12.26}$$

is the analog of Onsager's dissipation function (12.2). Note that (12.25) is in agreement with Onsager's result (12.5) when we realize that $(S_0 - S_{st})/k = \Phi^0$ is positive definite and that the left-hand side is what Onsager must have meant by $\frac{1}{2}\dot{S}$ in the stationary state.

From (12.24) and (12.26), and from (12.21) and (12.18), we see that

$$\frac{\delta\Phi^0}{\delta\langle J(\boldsymbol{x})\rangle_{st}} = \mu(\boldsymbol{x})\,, \qquad \frac{\delta\Psi^0}{\delta\mu(\boldsymbol{x})} = \langle J(\boldsymbol{x})\rangle_{st}. \tag{12.27}$$

If there are a number of currents one can imagine surfaces S_{st} and Φ^0 in the space of currents, so that the gradient $\boldsymbol{\mu}$ is orthogonal to the contours of constant $\boldsymbol{J}$ along the directions of steepest ascent and descent. Whereas $\boldsymbol{\mu}$ points up the entropy hill toward the maximum, it points downhill toward the minimum on the dissipation surface. A similar description can be given in terms of Ψ^0, $\mu = \nabla\lambda$, and $\langle J\rangle$. The expressions (12.27) are sometimes referred to as "orthogonality conditions" (*e.g.*, Ziegler, 1983), and when the functional derivatives are set to zero they provide the conditions for an extremum. In either case the extremum is a minimum, and just the trivial reduction to the equilibrium system. Note that the second equation in (12.27) is exactly the constitutive equation (12.18).

Both $K^0_{JJ}(\boldsymbol{x}-\boldsymbol{x}')$ and $G^0_{JJ}(\boldsymbol{x}-\boldsymbol{x}')$ exhibit a reciprocity in their indices owing to the different variables in each current; however, this is not the type of reciprocity envisioned in the Onsager definitions (12.2) and (12.7). That arises when we consider a number of currents J_i and their conserved densities, as in (7.29), so that the right-hand side of (12.21), for example, takes the form

$$\Psi^0 = \tfrac{1}{2}\sum_{ik}\int_{R_i}\int_{R_k} \nabla\lambda_i(\boldsymbol{x}) K^0_{J_iJ_k}(\boldsymbol{x}-\boldsymbol{x}')\nabla'\lambda_k(\boldsymbol{x}')\, d^3x' d^3x. \tag{12.28}$$

But the space-time symmetries, when they exist, of the covariance functions lead automatically to the Onsager type reciprocities. Coupled with (12.18), we see that both reciprocity and the constitutive relations (12.1) arise directly from probability theory and the maximum entropy formalism, so that the original point of Onsager's variational principle is rendered moot.

It is satisfying that our general description of the nonequilibrium steady state reduces, in linear approximation, to the same form of irreversible thermodynamics created phenomenologically so many years ago. Now, however, all quantities can be calculated from the fundamental microscopic dynamics of the system, at least in principle. Furthermore, these results confirm our expectation that it is not the production of entropy that is of importance in these processes, but the rate of dissipation itself, which is related only to the constant maximum information entropy. From our experience so far there would seem to be no indication that Φ^0 or Ψ^0 should possess any nontrivial extremum properties, and this is reinforced by applying (12.25) and (12.26) to the thermal conduction problem discussed above.

The covariance function $K^0_{qq}(\boldsymbol{x}-\boldsymbol{x}')$ in (12.21) was evaluated in the hydrodynamic limit in (10.14), and in the present case is

$$K^0_{qq}(\boldsymbol{x}-\boldsymbol{x}') = 2k\kappa T^2(\boldsymbol{x})\delta(\boldsymbol{x}-\boldsymbol{x}'). \tag{12.29}$$

Recall that the Lagrange multiplier for $q(x)$ is that associated with $h(x)$, namely $[kT(x)]^{-1}$. Then,

$$\Psi^0(\nabla\lambda,\nabla\lambda) = \kappa k\int_0^L T^2(x)[\nabla\lambda(x)]^2\,dx = \frac{\kappa}{k}\int_0^L \left[\frac{\partial T(x)}{\partial x}\right]^2\frac{dx}{T^2(x)}, \tag{12.30}$$

in agreement with (12.14) and (12.21). That is, the total rate of entropy production is just that of the maximum information entropy, $\dot{S}_t$, which is constant and proportional to the left-hand side of (12.21); it is a rate of dissipation, or degradation of thermal energy by the process and has nothing to do with entropy production intrinsic to the rod, which is zero by definition.

Having identified the departure of the steady-state entropy from the equilibrium value as the rate of dissipation, we can now return to the full nonlinear form (12.19) to identify the nonlinear version of Ψ, which we note cannot be only the integral on the right-hand side of that equation. As seen in (12.20), the term $\ln Z_{st}[\beta,\mu]$ also makes a contribution. The suggestion, then, is that the complete nonlinear dissipation rate can be written

$$\Psi(\nabla\lambda,\nabla\lambda) = -\Big[\ln Z_{st}[\beta,\mu]-\ln Z_0[\beta]\Big] + \int_R \mu(\boldsymbol{x})\langle J(\boldsymbol{x})\rangle_{st}\,d^3x, \tag{12.31}$$

and a functional derivative analogous to (12.27) yields

$$\frac{\delta\Psi}{\delta\mu(\boldsymbol{x})} = \int_R \mu(\boldsymbol{x}')\frac{\delta\langle J(\boldsymbol{x}')\rangle_{st}}{\delta\mu(\boldsymbol{x})}\,d^3x' = \int_R \mu(\boldsymbol{x}')K_{JJ}(\boldsymbol{x}',\boldsymbol{x})\,d^3x', \tag{12.32}$$

where K_{JJ} is the full nonlinear covariance function. In deriving this nonlinear (in μ) equation we have employed expressions analogous to (6.3), (A.20), and (A.29), with appropriate sign changes.

Recalling (12.18), one sees that (12.32) reduces to (12.27) in linear approximation. While (12.32) has the look of a nonlinear constitutive relation, it would certainly prove rather difficult in general to use in that capacity. In contrast with both Onsager and Ziegler, these observations do not in themselves seem to support the notion of a *general* extremum principle for dissipation rates in steady-state processes, either linear or nonlinear, near or far from equilibrium. It should be clear that the term "dissipation" is now being considered in a generalized sense, but it inevitably boils down to dissipation or degradation of information.

These considerations are not meant to be limited to stationary processes, of course, and the discussion can be extended to the general thermal driving scenario in which (9.22) and (9.23) play a key role. In fact, the latter provides the full nonlinear relation of the maximum information entropy production to the rate of dissipation for thermal driving:

$$\begin{aligned}\frac{1}{k}\dot{S}_t &= -\beta\int \nabla\lambda(\boldsymbol{x},t)K^t_{HJ}(\boldsymbol{x},t)\,d^3x\\ &\quad -\int_0^t dt'\int_R\int_R \nabla\lambda(\boldsymbol{x},t)K^t_{JJ}(\boldsymbol{x},t;\boldsymbol{x}',t')\nabla'\lambda(\boldsymbol{x}',t')\,d^3x'd^3x\\ &\equiv \beta\frac{d\langle H\rangle_t}{dt}-\Psi(J,J;t),\end{aligned} \tag{12.33}$$

where we have referred to (9.6) for time-independent H, and defined the time-dependent dissipation function. The appearance of the equilibrium parameter $\beta=(kT)^{-1}$ indicates that the internal energy changes only indirectly owing to the driving of J, which in general need not be a current. If the grand canonical distribution had been employed to describe the equilibrium system, for example, a term in $\langle N\rangle$ would have been included. Note that Ψ here is *not* a quadratic approximation, for K^t_{JJ} is a nonlinear functional of the Lagrange multiplier.

We see, however, that if gradients are continually changing with time, then so must the dissipation function, and the notion of an extremum for $\Psi(t)$ must be instantaneous, as it is for S_t. From (9.14) we recall that in the general nonequilibrium process, $\dot{S}_t$ is actually controlled by the driving source and can be positive or negative: $\dot{S}_t=\gamma(t)\sigma(t)$, where $\gamma(t)$ is a transfer potential, and the sign is determined by the external rate $\sigma(t)$. In these circumstances it is not clear whether or not a general extremum principle is useful, or even operative in these general processes.

To illustrate these comments, consider the relatively simple scenario of two volumes containing substances at different temperatures and in thermal contact so that they can exchange energy but no matter. Thermal energy is transferred from the hotter to the cooler body driven by the temperature gradient between them, and one envisions the entropy of the former to be decreasing while that of the latter increases, but not by the same amounts. As in the earlier model of thermal conductivity, the dissipation attached to this irreversible process is associated with the excess entropy production, but whose rate is now continually diminishing with the changing gradient as the temperatures equilibrate. In this situation it is difficult to imagine the possible role of any extremal principle for the rate of entropy production, and the process of heat transfer is described by the conservation law plus constitutive equation in the form of the well-known heat equation.

The one remaining scenario is the relaxation mode, discussed explicitly in Chapter 11. Although there is no specific source contribution $\dot{S}_t$ for this process, there must be some sort of $\dot{S}_{int}(t)$ internally during the relaxation process. For a simple fluid, the rate of dissipation owing to decaying currents is expressed in (10.22). But we have seen in Chapter 11 that this dissipation rate is not readily related to an identifiable entropy production, so that the question of extrema is not easily formulated in this context. In any event, the rate of the entire process is encompassed in the relaxation rate and the conservation laws. Our conclusion is that a "rate of internal entropy production" remains somewhat slippery.

There have been other attempts to derive principles of this sort on the level of statistical mechanics, with mixed results. In particular, Dewar (2003, 2005) has employed the basic maximum entropy formalism employing constraint functions with a very special symmetry to argue for a principle of *maximum* entropy production. The ensuing construction has the merit of focusing only on the maximum information entropy and not some other unspecified "entropy," but the specific nature of the constraints is rather problematic and would seem to severely limit its applicability; the approach also contains other presumptions of a dubious nature concerning the maximum entropy formalism itself. Aside from some spin systems, in the above work these (actually antisymmetric) constraints are meant to provide a basis for employing the PME over sets of microscopic *paths* rather than states, the motivation being to validate not only possible entropy production principles, but also so-called fluctuation theorems (*e.g.*, Evans and Searles, 2002). Inclusion of both forward and backward paths in the logical spectrum is reminiscent of Onsager's "principle of microscopic reversibility." But for possible paths to be well defined, it is necessary to specify both the initial and final macroscopic states, which involves the kind of teleology often attributed to classical action principles.

After all is said and done, the issue with which we began this discussion—the role of additional principles in nonequilibrium thermodynamics—does not appear to be much closer to a definite resolution. In those cases where we are able to apply a principle of minimum (or maximum) rate of energy dissipation, it seems that we already have sufficient tools in the conservation laws and constitutive equations. Although the conservation laws are exact, the constitutive relations are of necessity approximated to some degree, so it may be that the choice of which route to follow very much depends on the details of any specific problem. Rather than focus on some general and improbable principle, it may be more reasonable to search for general conditions or classes of problems for which extremum rate principles might be both valid and productive. A possibly useful project would be to compile a catalog of situations where the choice has proved decisive in reaching a solution, and the atmospheric studies mentioned earlier may be a good place to start. In addition, Martyushev and Seleznev (2006) have recently reviewed a number of other applications that invoke maximum entropy production.

We have already noted above that Kirchhoff's early discovery of a minimum dissipation principle was followed not long after with similar results by Helmholtz, Rayleigh, and Lorentz. In the quote at start of Chapter 7 the Erhrenfests in 1912 had wondered if there might exist a variational principle similar to entropy maximization that would determine the nonequilibrium stationary state. As noted at the end of Chapter 9, numerous writers since have expressed a belief in the existence of a principle characterizing a general nonequilibrium state in the same way that the Gibbs algorithm governs the equilibrium state. In light of the preceding twelve chapters it is not surprising that none have emerged triumphant, for it is now clear that the Gibbs variational principle, because it is grounded in a fundamental rule of probability theory, has all along been the rule governing *all* thermodynamic states—and it provides the macroscopic conservation laws through (9.11), and constitutive relations as in (12.18). At this time there appear to be no compelling reasons, other than in the interest of expediency, to adopt any principles beyond the conservation laws and the thoroughly tested variational principle of Gibbs.

It remains to discuss the construction of (12.17), which proceeds by first considering a stationary deviation of a locally conserved density e from its equilibrium value: $\Delta e(\boldsymbol{x}) \equiv e(\boldsymbol{x}) - e_0$, which need not be small. From Chapter 7, the maximization of the entropy leads to the steady-state density matrix

$$\rho_{st} = \frac{1}{Z_{st}} \exp\left[-\beta H_0 - \int \lambda(\boldsymbol{x}) \Delta e^d(\boldsymbol{x})\, d^3x\right] \tag{12.34}$$

in terms of the diagonal part of e, which is given by (7.13). Thus, the integral in (12.34) can be written as

$$\begin{aligned}\int \lambda(\boldsymbol{x})\Delta e^d(\boldsymbol{x})\, d^3x &= \int \lambda(\boldsymbol{x})\Big[\Delta e(\boldsymbol{x}) - \int_{-\infty}^{0} e^{\epsilon t}\, \dot{e}(\boldsymbol{x},t)\, dt\Big]\, d^3x \\ &= \int \lambda(\boldsymbol{x})\Delta e(\boldsymbol{x})\, d^3x - \int d^3x\, \nabla\lambda(\boldsymbol{x}) \cdot \int_{-\infty}^{0} \boldsymbol{j}(\boldsymbol{x},t) e^{\epsilon t}\, dt,\end{aligned} \tag{12.35}$$

where we have employed the relation $\dot{e} = -\nabla \cdot \boldsymbol{j}$, integrated by parts on x, and dropped the resulting surface integral. The limit $\epsilon \to 0^+$ is understood in the time integral, and the time dependence of $\boldsymbol{j}$ is

$$\boldsymbol{j}(\boldsymbol{x},t) = e^{itH_0/\hbar} \boldsymbol{j}(\boldsymbol{x}) e^{-itH_0/\hbar}. \tag{12.36}$$

If we define

$$H \equiv H_0 + \beta^{-1} \int \lambda(\boldsymbol{x})\Delta e(\boldsymbol{x})\, d^3x\,, \qquad \boldsymbol{J}(\boldsymbol{x}) \equiv \lim_{\epsilon\to 0^+} \int_{-\infty}^{0} e^{\epsilon t}\, \boldsymbol{j}(\boldsymbol{x},t)\, dt, \tag{12.37}$$

then (12.34) reduces to (12.17). Note very carefully that $\boldsymbol{J}$ no longer carries a dimension of t^{-1}, but has dimensions ($e \times$length). The integral in H is dimensionless and not really part of the Hamiltonian; it is placed there only for convenience, and in linear approximation will not contribute to expectation values.

APPENDIX A

PERTURBATION THEORY

A complete perturbation theory for expectation values has been developed by Heims and Jaynes (1962), which we here summarize and generalize slightly. Let ϵ be a small positive number representing a perturbation parameter, and let A and B be arbitrary linear operators on an appropriate space. The unperturbed and perturbed density matrices will be represented, respectively, as

$$\rho_0 = \frac{1}{Z_0} e^A \,, \quad Z_0 = \mathrm{Tr} e^A \,, \quad \langle C \rangle_0 = \mathrm{Tr}(\rho_0 C) \,, \tag{A.1a}$$

$$\rho = \frac{1}{Z} e^{A+\epsilon B} \,, \quad Z = \mathrm{Tr} e^{A+\epsilon B} \,, \quad \langle C \rangle = \mathrm{Tr}(\rho C) \,, \tag{A.1b}$$

In general, the operators A and B will not commute, but the identity (proved below)

$$e^{A+B} = e^A \left[1 + \int_0^1 e^{-xA} \, B e^{x(A+B)} \, dx \right] \tag{A.2}$$

can be applied repeatedly to generate the series

$$e^{A+\epsilon B} = e^A \left[1 + \sum_{n=1}^{\infty} \epsilon^n S_n \right] , \tag{A.3}$$

where

$$S_n \equiv \int_0^1 dx_1 \int_0^{x_1} dx_2 \cdots \int_0^{x_{n-1}} dx_n \, B(x_1) B(x_2) \cdots B(x_n) \,, \tag{A.4}$$

and

$$B(x) \equiv e^{-xA} \, B e^{xA} \,. \tag{A.5}$$

The expectation value of an operator C in the state (A.1b) can be expanded as

$$\begin{aligned} \langle C \rangle - \langle C \rangle_0 &= \sum_{n=1}^{\infty} \frac{\epsilon^n}{n!} \left(\frac{d^n \langle C \rangle}{d\epsilon^n} \right)_{\epsilon=0} \\ &= \sum_{n=1}^{\infty} \epsilon^n [\langle Q_n C \rangle_0 - \langle Q_n \rangle_0 \langle C \rangle_0] \,, \end{aligned} \tag{A.6}$$

where $Q_1 \equiv S_1$ and

$$Q_n \equiv S_n - \sum_{k=1}^{n-1} \langle Q_k \rangle_0 S_{n-k}\,, \qquad n > 1\,. \tag{A.7}$$

Note that all expectation values on the right-hand side of (A.6) are in the state ρ_0.

In the linear, or first-order, approximation Eq.(A.6) yields, when we set $\epsilon = 1$,

$$\langle C \rangle - \langle C \rangle_0 \simeq \int_0^1 dx\, \langle e^{-xA}\, B e^{xA}\, C \rangle_0 - \langle B \rangle_0 \langle C \rangle_0\,. \tag{A.8}$$

It is useful to define the *Kubo transform* of the operator B with respect to A as

$$\overline{B} \equiv \int_0^1 e^{-xA}\, B e^{xA}\, dx\,, \tag{A.9}$$

which arises owing to the possible noncommutativity of A and B. If the transform is defined with respect to the operator A appearing in ρ, as is almost always the case, then $\langle \overline{B} \rangle_0 = \langle B \rangle_0$.

The right-hand side of (A.8) is just the quantum-mechanical covariance of the two operators B and C, and so we find it also useful to define a *covariance function* as

$$K^0_{CB} \equiv \langle \overline{B} C \rangle_0 - \langle B \rangle_0 \langle C \rangle_0\,. \tag{A.10}$$

The superscript 0 on K^0_{CB} indicates that both it and the Kubo transform are calculated with unperturbed quantities.

Two simple identities for K^0_{CB} are immediate. Along with cyclic invariance of the trace, a change of integration variables allows one to prove the reciprocity relation

$$K^0_{CB} = K^0_{BC}\,, \tag{A.11}$$

where it must be remembered that it is always the second subscript that refers to the Kubo transform. In a similar manner, if B has the form

$$B(u) \equiv e^{-uA}\, B(0) e^{uA}\,, \tag{A.12}$$

where u is an arbitrary parameter, then straightforward differentiation yields the very useful relationship

$$\frac{dK^0_{CB}}{du} = \langle [C, B(u)] \rangle_0\,. \tag{A.13}$$

The situation becomes slightly more complicated when the operators of interest are actually Heisenberg operators $F(\boldsymbol{x}, t)$ and functions of both space and time. In this case, the density matrix takes the form

$$\rho = \frac{1}{Z}\exp\left[-\beta H - \int_R \lambda(\boldsymbol{x}',t')F(\boldsymbol{x}',t')\,d^3x'\,dt'\right], \tag{A.14}$$

where H is the Hamiltonian in the homogeneous, time-independent system, and the *partition functional* is

$$Z[\lambda(\boldsymbol{x},t)] \equiv \operatorname{Tr}\exp\left[-\beta H - \int_R \lambda(\boldsymbol{x}',t')F(\boldsymbol{x}',t')\,d^3x'\,dt'\right], \tag{A.15}$$

(Note the sign-convention changes in the exponential functions.) The series expansion (A.6) now involves functional derivatives and can be generated from the operator identity [see (A.40) below]

$$\frac{\partial}{\partial\lambda}e^{A+\lambda B}\bigg|_{\lambda=0} = e^A\,\overline{B}\,. \tag{A.16}$$

One can generate a countably infinite hierarchy of such identities corresponding to derivatives of all orders, and then generalize the results to functional differentiation. As a result, we find that the series (A.6) can be rewritten in the generalized form

$$\begin{aligned}\langle C(\boldsymbol{x},t)\rangle - \langle C(\boldsymbol{x})\rangle_0 = \sum_{n=1}^{\infty}\frac{1}{n!}\int_R d^3x_1'\,dt_1'\cdots\int_R d^3x_n'\,dt_n'\\ \times\lambda(\boldsymbol{x}_1',t_1')\cdots\lambda(\boldsymbol{x}_n',t_n')\left[\frac{\delta^n\langle C(\boldsymbol{x},t)\rangle}{\delta\lambda(\boldsymbol{x}',t')^n}\right]_{\lambda=0}.\end{aligned} \tag{A.17}$$

Often the unperturbed single-operator expectation values are also independent of $\boldsymbol{x}$. Note that the generalization to include a number of operators $F_k(\boldsymbol{x},t)$ is straightforward, and that a similar expansion for $\ln Z$ can be generated:

$$\begin{aligned}\ln Z[\lambda(\boldsymbol{x},t)] = \ln Z_0 - \langle F\rangle_0\int\lambda(\boldsymbol{x},t)\,d^3x\,dt\\ +\frac{1}{2}\int d^3x\,dt\int d^3x'\,dt'\,\lambda(\boldsymbol{x},t)K_{FF}^0(\boldsymbol{x},t;\boldsymbol{x}',t')\lambda(\boldsymbol{x}',t')\\ +\cdots.\end{aligned} \tag{A.18}$$

The linear approximation to $\langle C(\boldsymbol{x},t)\rangle$ now takes the form

$$\langle C(\boldsymbol{x},t)\rangle - \langle C(\boldsymbol{x})\rangle_0 = -\int_R K_{CF}^0(\boldsymbol{x},t;\boldsymbol{x}',t')\lambda(\boldsymbol{x}',t')\,d^3x'\,dt', \tag{A.19a}$$

$$K_{CF}^0(\boldsymbol{x},t;\boldsymbol{x}',t') = \langle\overline{F(\boldsymbol{x}',t')}C(\boldsymbol{x},t)\rangle_0 - \langle F(\boldsymbol{x}')\rangle_0\langle C(\boldsymbol{x})\rangle_0\,. \tag{A.19b}$$

Clearly, higher-order derivatives in (A.17) will generate higher-order correlation functions.

These quantities are also related to the functional derivatives of the logarithm of the partition functional. For example, in the linear theory the covariance function of (A.19) is given by the second functional derivative:

$$K^0_{F_iF_j}(\boldsymbol{x},t;\boldsymbol{x}',t') = \frac{\delta^2}{\delta\lambda_i(\boldsymbol{x},t)\,\delta\lambda_j(\boldsymbol{x}',t')}\ln Z\,, \tag{A.20}$$

where F_i and F_j are two of the Heisenberg operators on which initial data are available.

Alternatively, the near-equilibrium theory is equally well described in terms of the entropy functional $S[F_k(\boldsymbol{x},t)]$, dependent only on the measured or specified values $\langle F_k(\boldsymbol{x},t)\rangle \in R_k(\boldsymbol{x},t)$. The Lagrange multiplier functions are given by the functional derivatives

$$k\lambda_\ell(\boldsymbol{x},t) = \frac{\delta S}{\delta\langle F_\ell(\boldsymbol{x},t)\rangle}\,. \tag{A.21}$$

In a region where S is locally convex, the second functional derivatives then generate a set of space-time functions

$$G_{ij}(\boldsymbol{x},t;\boldsymbol{x}',t') \equiv \frac{\delta^2 S}{\delta\langle F_i(\boldsymbol{x},t)\rangle\,\delta\langle F_j(\boldsymbol{x}',t')\rangle}\,, \tag{A.22}$$

which is essentially the functional inverse of K^0; the acoustic Green function is an example.

The covariance function (A.19b) is generally very difficult to evaluate for interacting particles and one is compelled to explore various approximation schemes. For example, a second perturbation expansion in powers of the interaction can be developed (*e.g.*, Grandy, 1988), but even that becomes unmanageable beyond second order, other than in some exceptional cases. The leading-order, or free-particle quantities are rather easy to evaluate, however, and as an example we consider here the density–density covariance function K^0_{nn} in the Boltzmann, or high-temperature, low-density limit. The calculation is most readily carried out in the Fourier-transformed representation (*e.g.*, Grandy, 1988; Chapter 6), and we find

$$K^0_{nn}(\boldsymbol{k},\omega) = n_0\frac{(2\pi\beta m)^{1/2}}{k}\,e^{-\frac{1}{2}\beta m\omega^2/k^2}\,. \tag{A.23}$$

This is also seen to be a low-frequency limit, corresponding to omission of the Kubo transform. Inverse transformation then yields

$$\begin{aligned} K^0_{nn}(\mathbf{r},\tau)_{\mathrm{B}} &= n_0\left(\frac{\beta m}{2\pi}\right)^{3/2}\frac{1}{|\tau|^3}e^{-\frac{1}{2}\beta m r^2/\tau^2} \\ &\xrightarrow[\tau\to 0^+]{} \quad n_0\delta(\mathbf{r})\,, \end{aligned} \tag{A.24}$$

where n_0 is the density in the homogeneous free-particle system. As expected, in the absence of interactions and quantum-statistical effects, there are no correlations in the ideal fluid.

This last observation leads to another interesting result, for there can be no correlations of any kind in the classical free-particle system, and this should be reflected in all higher-order correlation functions corresponding to the derivatives in (A.17). This can be verified directly for the second-order term from (A.6), the general form of which is also given in Grandy (1988), and for this system we find the expected result

$$\langle n(\boldsymbol{x}')n(\boldsymbol{x}'')n(\boldsymbol{x})\rangle_0 = n_0\delta(\boldsymbol{x}'-\boldsymbol{x})\delta(\boldsymbol{x}''-\boldsymbol{x})\,, \tag{A.25}$$

all other terms in the second derivative being quantum corrections. The pattern is now clear, so that extrapolation to all orders in (A.17) and integration over all spatial variables yields the exponential series. Thus, in the inhomogeneous classical free-particle system

$$\langle n(\boldsymbol{x})\rangle = n_0 e^{\lambda(\boldsymbol{x})}\,. \tag{A.26}$$

A.1 Fluid equations of motion

In the thermal driving scenario ρ_t and Z_t are given by (A.14) and (A.15), respectively, by taking the time interval in the integrals to be $(0,t)$. The source strength, or rate of driving, is given by (9.26) as

$$\sigma_F(\boldsymbol{x},t) = -\int \lambda(\boldsymbol{x}',t)K^t_{FF}(\boldsymbol{x}',t;\boldsymbol{x},t)\,d^3x'\,, \tag{A.27}$$

where

$$\begin{aligned} K^t_{CF}(\boldsymbol{x}',t';\boldsymbol{x},t) &\equiv \langle\overline{F(\boldsymbol{x}',t')}C(\boldsymbol{x},t)\rangle_t - \langle F(\boldsymbol{x}',t')\rangle_t\langle C(\boldsymbol{x},t)\rangle_t \\ &= -\frac{\delta\langle C(\boldsymbol{x},t)\rangle_t}{\delta\lambda(\boldsymbol{x}',t')}\,, \end{aligned} \tag{A.28}$$

and the expectation value of the operator $C(\boldsymbol{x},t)$ can be expressed as the infinite series (A.17).

Owing to the second line of (A.28) we see that

$$\frac{\delta^n\langle C\rangle_t}{\delta\lambda_1\cdots\delta\lambda_n} = -\frac{\delta^{n-1}K^t_{CF}}{\delta\lambda_2\cdots\delta\lambda_n}\,, \qquad n\geq 1\,, \tag{A.29}$$

where it will be convenient to adopt temporarily the notation $\lambda_i = \lambda(\boldsymbol{x}_1,t_1)$, $d\tau_i = d^3x_i\,dt_i$, and let R_i denote the space-time region $(V;0,t)$. After some inspection we find that K^t_{CF} can also be represented as an infinite series:

$$\begin{aligned} K^t_{CF}(\boldsymbol{x}',t';\boldsymbol{x},t) &= K^0_{CF}(\boldsymbol{x}',t';\boldsymbol{x},t) \\ &\quad + \sum_{n=1}^{\infty}\int_{R_1}d\tau_1\cdots\int_{R_n}d\tau_n\,\lambda_1\cdots\lambda_n\frac{1}{n!}\left[\frac{\delta^n K^t_{CF}(\boldsymbol{x}',t';\boldsymbol{x},t)}{\delta\lambda_1\cdots\delta\lambda_n}\right]_{\lambda_i=0}\,. \end{aligned} \tag{A.30}$$

In the case that $\langle C(\boldsymbol{x},t)\rangle_t$ is a fluid density, we can now verify that it satisfies one of the equations of motion (10.1) to all orders in the perturbation series. As an example we shall study the momentum density $\boldsymbol{p} = m\boldsymbol{j}$, which is also the driven variable, and write out the first three terms explicitly, although the first vanishes:

$$\begin{aligned}\frac{d\langle \boldsymbol{p}(\boldsymbol{x},t)\rangle_t}{dt} &\simeq \frac{d}{dt}\int_{R_1} d\tau_1\,\lambda_1 \left[\frac{\delta\langle \boldsymbol{p}(\boldsymbol{x},t)\rangle_t}{\delta\lambda_1}\right]_{\lambda_1=0} \\ &\quad + \frac{d}{dt}\int_{R_1} d\tau_1 \int_{R_2} d\tau_2\,\lambda_1\lambda_2 \frac{1}{2!}\left[\frac{\delta^2\langle \boldsymbol{p}(\boldsymbol{x},t)\rangle_t}{\delta\lambda_1\delta\lambda_2}\right]_{\lambda_{1,2}=0} .\end{aligned} \tag{A.31}$$

Performing the time derivatives leads to five terms, two of which are identical after relabeling dummy variables. This yields

$$\begin{aligned}\frac{d\langle \boldsymbol{p}(\boldsymbol{x},t)\rangle_t}{dt} &= \int d^3x_1\,\lambda(\boldsymbol{x}_1,t)\left[\frac{\delta\langle \boldsymbol{p}(\boldsymbol{x},t)\rangle_t}{\delta\lambda_1}\right]_{\substack{\lambda_1=0\\ t_1=t}} \\ &\quad + \int d^3x_1\,\lambda(\boldsymbol{x}_1,t)\int_{R_2}\lambda_2 d\tau_2 \left[\frac{\delta^2\langle \boldsymbol{p}(\boldsymbol{x},t)\rangle_t}{\delta\lambda_1\delta\lambda_2}\right]_{\substack{\lambda_{1,2}=0\\ t_1=t}} \\ &\quad + \int_{R_1} d\tau_1\,\lambda_1\left[\frac{\delta\langle \dot{\boldsymbol{p}}(\boldsymbol{x},t)\rangle_t}{\delta\lambda_1}\right]_{\lambda_1=0} \\ &\quad + \int_{R_1} d\tau_1 \int_{R_2} d\tau_2\,\lambda_1\lambda_2\frac{1}{2!}\left[\frac{\delta^2\langle \dot{\boldsymbol{p}}(\boldsymbol{x},t)\rangle_t}{\delta\lambda_1\delta\lambda_2}\right]_{\lambda_{1,2}=0} .\end{aligned} \tag{A.32}$$

According to (A.27) and (A.30) the first two terms in (A.32) correspond to the expansion of $\sigma_{\boldsymbol{p}}(\boldsymbol{x},t)$. With the microscopic conservation law $\dot{p}_j = -\nabla_i T_{ij}$, the third and fourth terms correspond to the expansion of $-\nabla_i\langle T_{ij}(\boldsymbol{x},t)\rangle_t$, for ∇_i can be brought outside the expectation value because ρ_t is not a function of spatial coordinates. Hence, by extrapolating to all orders in an obvious way, we have shown directly that

$$\frac{d\langle p_i(\boldsymbol{x},t)\rangle_t}{dt} + \nabla_i\langle T_{ij}(\boldsymbol{x},t)\rangle_t = \sigma_{p_i}(\boldsymbol{x},t)\,, \tag{A.33}$$

and the predicted expectation value is indeed an exact solution of the equation of motion.

A.2 Operator identities

The identity (A.2) for arbitrary linear operators A and B is most easily derived following the method of Karplus and Schwinger (1948). First define a function

$$F(\lambda) \equiv e^{\lambda(A+B)}\,, \tag{A.34}$$

which satisfies the differential equation

$$\frac{dF(\lambda)}{d\lambda} = (A+B)F(\lambda)\,, \qquad F(0) = 1\,. \tag{A.35}$$

Carry out a transformation $F(\lambda) = e^{\lambda A}\,G(\lambda)$, with $G(0) = 1$, for which we develop the differential equation

$$\frac{dG(\lambda)}{d\lambda} = e^{-\lambda A}\,Be^{\lambda A}\,G(\lambda)\,. \tag{A.36}$$

This last equation is now integrated into the integral equation

$$G(\lambda) = 1 + \int_0^\lambda e^{-xA}\,Be^{xA}\,G(x)\,dx\,. \tag{A.37}$$

Finally, transform back from G to F and set $\lambda = 1$ to obtain (A.2).

Many operator identities of this kind were found by both Schwinger and Feynman in their development of quantum electrodynamics. An excellent review of these has been provided by Wilcox (1967), who makes extensive use of the general expression

$$\frac{\partial}{\partial\lambda}e^{-\beta H} = -\int_0^\beta e^{-(\beta-u)H}\,\frac{\partial H}{\partial\lambda}e^{-uH}\,du\,, \tag{A.38}$$

where β and λ are parameters and $H(\lambda)$ is an arbitrary linear operator. This identity is readily proved by showing that both sides of the equation satisfy the first-order differential equation

$$\frac{\partial}{\partial\beta}F(\beta) + HF(\beta) = -e^{-\beta H}\,\frac{\partial H}{\partial\lambda} \tag{A.39}$$

with initial condition $F(0) = 0$.

An example of (A.38) often found useful in the text is given by setting $\beta = 1$ and $H(\lambda) = -C(\lambda)$:

$$\frac{\partial}{\partial\lambda}e^{C} = e^{C}\int_0^1 e^{-uC}\,\frac{\partial C}{\partial\lambda}e^{uC}\,du \equiv e^{C}\,\overline{\partial_\lambda C}\,, \tag{A.40}$$

in terms of the Kubo transform (A.9). This result also provides a proof of (A.16).

APPENDIX B

DISSIPATIVE CURRENTS AND GALILEAN INVARIANCE

The concept of a simple fluid was introduced in Chapter 6, described by a rotationally invariant Hamiltonian and a number of density and current operators. These quantities are defined in terms of the field operators in (6.24) and their commutation relations (6.25), and the Hamiltonian is given by (6.20)–(6.23). We shall consider only $H = H_0 + V_2$ in terms of field operators $\psi^\dagger$ and ψ:

$$H_0 = \int \psi^\dagger(\boldsymbol{x}, t)\Big(-\tfrac{\hbar^2}{2m}\nabla^2\Big)\psi(\boldsymbol{x}, t)\, d^3x\,, \tag{B.1a}$$

$$V_2 = \frac{1}{2}\int \psi^\dagger(\boldsymbol{x}_1, t)\psi^\dagger(\boldsymbol{x}_2, t)V_2(\boldsymbol{x}_1, \boldsymbol{x}_2)\psi(\boldsymbol{x}_1, t)\psi(\boldsymbol{x}_2, t)\, d^3x_1 d^3x_2\,. \tag{B.1b}$$

The locally conserved densities are displayed in (6.27) and (6.28), whereas the associated currents are determined by combining (6.30) and (6.31):

$$\boldsymbol{\nabla}\cdot\boldsymbol{j}(\boldsymbol{x}, t) = \frac{1}{i\hbar}[H, n(\boldsymbol{x}, t)]\,, \tag{B.2a}$$

$$\boldsymbol{\nabla}\cdot\boldsymbol{T}(\boldsymbol{x}, t) = \frac{1}{i\hbar}[H, m\boldsymbol{j}(\boldsymbol{x}, t)]\,, \tag{B.2b}$$

$$\boldsymbol{\nabla}\cdot\boldsymbol{q}(\boldsymbol{x}, t) = \frac{1}{i\hbar}[H, h(\boldsymbol{x}, t)]\,. \tag{B.2c}$$

Hence, identification of the current operators is achieved by evaluating the various commutators.

These evaluations are straightforward, although the algebra is somewhat tedious. The commutation relations (6.25),

$$[\psi(\boldsymbol{x}), \psi(\boldsymbol{x}')] = [\psi^\dagger(\boldsymbol{x}), \psi^\dagger(\boldsymbol{x}')] = 0\,, \quad [\psi(\boldsymbol{x}), \psi^\dagger(\boldsymbol{x}')] = \delta(\boldsymbol{x} - \boldsymbol{x}')\,, \tag{B.3}$$

are used to introduce δ-functions into the calculation while ordering the field operators, and derivatives of δ-functions appear in expressions such as

$$[\psi(\boldsymbol{x}'), \nabla\psi^\dagger(\boldsymbol{x})] = \nabla\delta(\boldsymbol{x} - \boldsymbol{x}') = -[\psi^\dagger(\boldsymbol{x}', \nabla\psi(\boldsymbol{x})]\,. \tag{B.4}$$

In addition, the following identity for noncommuting operators A, B will be required at times:

$$e^{-A}\, Be^{A} = B + \int_0^1 e^{-\lambda A}\,[B, A]e^{\lambda A}\, d\lambda\,, \tag{B.5}$$

which is readily derived from identities already given in Appendix A.

The explicit expression for the particle current density was exhibited in (6.27), and has the same form as the ordinary quantum mechanical probability current density. Evaluation of the commutator in (B.2a) is rather simple, but the reader may want to verify (6.27) directly as an introduction to verification of the dissipative currents. Those calculations are left as an "exercise," as we shall only state the results here. The stress-tensor operator is found to be

$$\begin{aligned} T_{ij}(\boldsymbol{x},t) = {} & -\frac{\hbar^2}{4m}\left[(\nabla_i-\nabla'_i)(\nabla_j-\nabla'_j)\psi^\dagger(\boldsymbol{x}',t)\psi(\boldsymbol{x},t)\right]_{\boldsymbol{x}'=\boldsymbol{x}} \\ & -\frac{1}{8}\int d^3r'\left[\frac{r'_i r'_j}{r'}\frac{dV_2(r')}{dr'}\right]\int_{-1}^{1} d\lambda\,\psi^\dagger\Big(\boldsymbol{x}+\frac{1+\lambda}{2}\boldsymbol{r}',t\Big) \\ & \qquad n\Big(\boldsymbol{x}-\frac{1-\lambda}{2}\boldsymbol{r}',t\Big)\psi\Big(\boldsymbol{x}+\frac{1+\lambda}{2}\boldsymbol{r}',t\Big)\,, \end{aligned} \tag{B.6}$$

and the energy current density operator is

$$\begin{aligned} q_i(\boldsymbol{x},t) = {} & \frac{1}{i\hbar}\left(\frac{\hbar^2}{2m}\right)^2\left[(\nabla_i-\nabla'_i)\nabla'\cdot\nabla\psi^\dagger(\boldsymbol{x}',t)\psi(\boldsymbol{x},t)\right]_{\boldsymbol{x}'=\boldsymbol{x}} \\ & +\frac{1}{2}\int d^3x'\,V_2(|\boldsymbol{x}-\boldsymbol{x}'|)\psi^\dagger(\boldsymbol{x}',t)j_i(\boldsymbol{x},t)\psi(\mathbf{x}',t) \\ & -\frac{1}{4}\int d^3r'\left[\frac{r'_i r'_j}{r'}\frac{dV_2(r')}{dr'}\right]\int_{-1}^{1} d\lambda\,\psi^\dagger\Big(\boldsymbol{x}+\frac{1+\lambda}{2}\boldsymbol{r}',t\Big) \\ & \qquad j_i\Big(\boldsymbol{x}-\frac{1-\lambda}{2}\boldsymbol{r}',t\Big)\psi\Big(\boldsymbol{x}+\frac{1+\lambda}{2}\boldsymbol{r}',t\Big)\,. \end{aligned} \tag{B.7}$$

Note that summation over repeated indices is implied and that it is the possible noncommutativity of the operators that gives rise to the λ-integrals. These expressions for the dissipative current density operators were first derived in this form by Puff and Gillis (1968).[1]

The space-integrated forms of these operators are somewhat simpler, because in that case one can make the replacement

$$\int_{-1}^{1} f(\lambda)\,d\lambda \longrightarrow 2f(1)\,, \tag{B.8}$$

and it is then useful to define

$$T_{ij}(t) \equiv \int T_{ij}(\boldsymbol{x},t)\,d^3x\,, \tag{B.9}$$

$$\boldsymbol{q}(t) \equiv \int \boldsymbol{q}(\boldsymbol{x},t)\,d^3x\,. \tag{B.10}$$

Unlike the situation with $\boldsymbol{P}(t)$ and $N(t)$, these operators are *not* conserved, in that they do not commute with the Hamiltonian. But the space integration does

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[1] We differ from Puff and Gillis in that they find a factor of 1/4 in (B.6) rather than 1/8.

yield the following identities:

$$T_{11}(t) = T_{22}(t) = T_{33}(t) = \frac{1}{3}T^i{}_i(t)\,, \tag{B.11}$$

the last quantity being one-third the tensor trace of $T_{ij}(t)$.

In addition to the symmetry properties discussed earlier, one notes that n, h, and the symmetric tensor T_{ij} are even under time reversal, whereas $\boldsymbol{j}$ and $\boldsymbol{q}$ are odd. These properties, along with the appropriate behavior under Galilean transformations (see below), are sufficient to determine the operators $\boldsymbol{q}$ and T_{ij} *uniquely* for spin-independent interactions. Were the two-body interaction not spherically symmetric, T_{ij} would not be symmetric. In that event the antisymmetric part would be related to an angular-momentum operator, which we shall not consider at this time.

The equilibrium expectation values of the above operators in the canonical distribution are of some interest. If there are no external forces it is easily seen that $\langle n(\boldsymbol{x},t)\rangle_0$ is the total particle number per unit volume, and that $\langle h(\boldsymbol{x},t)\rangle_0$ is the total energy density. The currents $\boldsymbol{j}$ and $\boldsymbol{q}$ vanish in the equilibrium system, but the stress tensor is seen to be

$$\begin{aligned}\langle T_{ij}(\boldsymbol{x},t)\rangle_0 &= \frac{2}{3}\frac{\hbar^2}{2m}\langle(\nabla\psi^\dagger)\cdot(\nabla\psi)\rangle_0\delta_{ij}\\ &\quad -\frac{1}{6}\int d^3r[\boldsymbol{r}\cdot\nabla V_2(r)]\langle\psi^\dagger(\boldsymbol{r})\psi^\dagger(0)\psi(0)\psi(\boldsymbol{r})\rangle_0\,\delta_{ij}\,.\end{aligned} \tag{B.12}$$

The first term on the right-hand side is just 2/3 the average kinetic-energy density, which suggests that Eq.(B.12) is an expression of the virial theorem and that the left-hand side is the equilibrium pressure. Thus,

$$\langle T_{ij}(\boldsymbol{x},t)\rangle_0 = P_0\,\delta_{ij}\,. \tag{B.13}$$

This interpretation depends crucially on rotational invariance of the Hamiltonian, for then the stress tensor has no shear components in equilibrium and the hydrostatic pressure is related to the normal stresses only.

Further insights emerge when the *radial distribution function* is introduced,

$$g(r) \equiv n_0^{-2}\langle\psi^\dagger(\boldsymbol{r})\hat{\psi}^\dagger(0)\psi(0)\psi(\boldsymbol{r})\rangle_0\,. \tag{B.14}$$

The dependence of $g(r)$ only on the magnitude of $\boldsymbol{r}$ is also a consequence of rotational invariance. Define as well

$$\frac{\langle KE\rangle_0}{V} \equiv \frac{\hbar^2}{2m}\int\langle(\nabla\psi^\dagger)\cdot(\nabla\psi)\rangle_0\,d^3r\,. \tag{B.15}$$

The average energy density and pressure in a simple equilibrium fluid can then be written, respectively, as

$$\langle h(\boldsymbol{x},t)\rangle_0 = \frac{\langle KE\rangle_0}{V} + \frac{1}{2}n_0^2 \int V_2(r)g(r)\,d^3r\,, \tag{B.16}$$

$$P_0 = \frac{2}{3}\frac{\langle KE\rangle_0}{V} - \frac{1}{6}n_0^2 \int [\boldsymbol{r}\cdot\nabla V_2(r)]g(r)\,d^3r\,. \tag{B.17}$$

B.1 Galilean invariance

Let $|a\rangle$ be an arbitrary N-particle state vector prepared at time t, and let $|a'\rangle$ be that state vector as observed in a frame moving with constant velocity $\boldsymbol{v}$ with respect to the first. If $\boldsymbol{x}_\alpha$, $\boldsymbol{p}_\alpha$ describe the coordinates and momentum of the αth particle, then expectation values in the two frames are related by the Galilean transformations

$$\begin{aligned} \langle a'|\boldsymbol{x}_\alpha|a'\rangle &\equiv \langle \boldsymbol{x}_\alpha\rangle_{a'} = \langle \boldsymbol{x}_\alpha\rangle_a + \boldsymbol{v}t\,, \\ \langle a'|\boldsymbol{p}_\alpha|a'\rangle &\equiv \langle \boldsymbol{p}_\alpha\rangle_{a'} = \langle \boldsymbol{p}_\alpha\rangle_a + m_\alpha\boldsymbol{v} \end{aligned} \tag{B.18}$$

In the state space such a transformation is represented by a unitary operator $U(\boldsymbol{v})$, such that an infinitesimal transformation $U(\delta\boldsymbol{v})|a\rangle = |a'\rangle$ can be written

$$U(\delta\boldsymbol{v}) = 1 - \frac{i}{\hbar}\delta\boldsymbol{v}\cdot\boldsymbol{G}\,, \qquad \boldsymbol{G}^\dagger = \boldsymbol{G}\,, \tag{B.19}$$

where $\boldsymbol{G}$ is some function of $\boldsymbol{x}_\alpha$, $\boldsymbol{p}_\alpha$. That is, $U^\dagger\boldsymbol{x}_\alpha U = \boldsymbol{x}_\alpha + t\delta\boldsymbol{v}$, $U^\dagger\boldsymbol{p}_\alpha U = \boldsymbol{p}_\alpha + m_\alpha\delta\boldsymbol{v}$, or

$$\begin{aligned} t\delta\boldsymbol{v} &\simeq -\frac{i}{\hbar}[\boldsymbol{x}_\alpha, \delta\boldsymbol{v}\cdot\boldsymbol{G}] = \frac{\partial}{\partial\boldsymbol{p}_\alpha}\delta\boldsymbol{v}\cdot\boldsymbol{G}\,, \\ m_\alpha\delta\boldsymbol{v} &\simeq -\frac{i}{\hbar}[\boldsymbol{p}_\alpha, \delta\boldsymbol{v}\cdot\boldsymbol{G}] = \frac{\partial}{\partial\boldsymbol{x}_\alpha}\delta\boldsymbol{v}\cdot\boldsymbol{G}\,, \end{aligned} \tag{B.20}$$

after evaluating the commutators. But $\delta\boldsymbol{v}$ is arbitrary, which reduces these last expressions to simple differential equations and we find that $\boldsymbol{G} = t\boldsymbol{P} - M\boldsymbol{R}$, where $M \equiv \sum_\alpha m_\alpha$ is the total mass of the system, and $\boldsymbol{R} \equiv M^{-1}\sum_\alpha m_\alpha\boldsymbol{x}_\alpha$ is the center-of-mass operator. Thus, $\boldsymbol{G}$ is the generator of infinitesimal Galilean transformations, and the finite transformation is represented by the unitary operator

$$U(\boldsymbol{v}) = e^{-i\boldsymbol{v}\cdot\boldsymbol{G}/\hbar} = e^{-i\boldsymbol{v}\cdot(t\boldsymbol{P}-M\boldsymbol{R})}\,. \tag{B.21}$$

The complete set of operators corresponding to the 1-parameter subgroups of the Galilean group consists of the unitary operators

$$\begin{aligned} U(\boldsymbol{r}) &= e^{-i\boldsymbol{r}\cdot\boldsymbol{P}/\hbar}\,, \qquad & U(t) &= e^{-itH/\hbar}\,, \\ U(\boldsymbol{n}\theta) &= e^{-i\theta\boldsymbol{n}\cdot\boldsymbol{J}/\hbar}\,, \qquad & U(\boldsymbol{v}) &= e^{-i\boldsymbol{v}\cdot\boldsymbol{G}/\hbar}\,, \end{aligned} \tag{B.22}$$

representing respectively space and time translations, rotations, and Galilean transformations. The subsequent discussion will require knowledge of the various commutation relations among the generators of these subgroups, which can be found in a number of sources (*e.g.*, Jordan, 1969). We exhibit the only nonzero commutators:

$$\begin{aligned} [J_j, J_k] &= i\hbar\varepsilon_{jkm}J_m\,, & [J_j, P_k] &= i\hbar\varepsilon_{jkm}P_m\,, \\ [J_j, G_k] &= i\hbar\varepsilon_{jkm}G_m\,, & [G_j, P_k] &= -i\hbar M\delta_{jk}\,, \end{aligned} \tag{B.23}$$

$$[G_j, H] = -i\hbar P_j$$

where the Levi–Civita symbol ε_{jkm} is ± 1 for an even or odd permutation of $\{jkm\}$, and vanishes if any two are equal. The proper transformation of both operators and density matrix under any of these unitary transformations is

$$F(\alpha) = U^\dagger(\alpha)FU(\alpha)\,, \qquad \rho(\alpha) = U(\alpha)\rho U^\dagger(\alpha)\,. \tag{B.24}$$

To study the effects of Galilean transformations in simple fluids, it is first necessary to find their effect on the field operators, as well as on the total system operators

$$N = \int n(\boldsymbol{x}, t)\, d^3x\,, \quad \boldsymbol{P} = \int m\boldsymbol{j}(\boldsymbol{x}, t)\, d^3x\,, \quad H = \int h(\boldsymbol{x}, t)\, d^3x\,, \tag{B.25a}$$

$$M = m\int n(\boldsymbol{x}, t)\, d^3x\,, \qquad \boldsymbol{R} = \int \boldsymbol{x}n(\boldsymbol{x}, t)\, d^3x\,. \tag{B.25b}$$

In this regard, several operator identities will be found useful: For arbitrary linear operators A and B,

$$e^A Be^{-A} = B + [A, B] + \tfrac{1}{2!}\big[A, [A, B]\big] + \cdots\,; \tag{B.26a}$$

and if both commute with their commutator,

$$e^{A+B} = e^A e^B e^{-\frac{1}{2}[A,B]}\,. \tag{B.26b}$$

Let $\{X_i\}$ be a set of n linear operators whose commutators are linear combinations of these same operators, let $\boldsymbol{X}$ be a vector of these operators, and let Y be another linear combination of them. From the theory of Lie groups we then have the theorem (*e.g.*, Sattinger and Weaver, 1986)

$$e^Y X_j E^{-Y} = \boldsymbol{g}_j\cdot\boldsymbol{X} \Rightarrow e^Y F(X_1, \ldots, X_n)e^{-Y} = F(\boldsymbol{g}_1\cdot\boldsymbol{X}, \ldots, \boldsymbol{g}_n\cdot\boldsymbol{X}). \tag{B.27}$$

From (B.23) and (B.26a) one finds that under a Galilean transformation, the Hamiltonian transforms as

$$e^{i\boldsymbol{v}\cdot\boldsymbol{G}/\hbar}He^{-i\boldsymbol{v}\cdot\boldsymbol{G}/\hbar} = H + \boldsymbol{v}\cdot\boldsymbol{P} + \frac{1}{2}mv^2N\,. \tag{B.28}$$

Similarly, one readily finds from the definitions that

$$\begin{aligned} &[N, \psi(\boldsymbol{x}, t)] = -\psi(\boldsymbol{x}, t)\,, \quad [\boldsymbol{P}, \psi(\boldsymbol{x}, t)] = i\hbar\nabla\psi(\boldsymbol{x}, t)\,, \\ &[m\boldsymbol{R}, \psi(\boldsymbol{x}, t)] = -m\boldsymbol{x}\psi(\boldsymbol{x}, t)\,. \end{aligned} \tag{B.29}$$

Analogous expressions for $\psi^\dagger(\boldsymbol{x})$ follow since N and $\boldsymbol{P}$ are Hermitian.

TABLE B.1. Inversion properties of the field operators for a simple fluid.

Operator	P	T
H	$+$	$+$
$N(t)$	$+$	$+$
$\boldsymbol{P}(t)$	$-$	$-$
$n(\boldsymbol{x},t)$	$+$	$+$
$\boldsymbol{j}(\boldsymbol{x},t)$	$-$	$-$
$h(\boldsymbol{x},t)$	$+$	$+$
$\boldsymbol{q}(\boldsymbol{x},t)$	$-$	$-$
$T_{ij}(\boldsymbol{x},t)$	$+$	$+$

Next consider

$$U^\dagger(\boldsymbol{v})\psi(\boldsymbol{x},t)U(\boldsymbol{v}) = e^{i\boldsymbol{v}\cdot(t\boldsymbol{P}-m\boldsymbol{R})/\hbar}\,\psi(\boldsymbol{x},t)e^{-i\boldsymbol{v}\cdot(t\boldsymbol{P}-m\boldsymbol{R})\hbar}\,, \tag{B.30}$$

where we note that with (B.25b) the generator can now be written $\boldsymbol{G}=\boldsymbol{v}\cdot(t\boldsymbol{P}-m\boldsymbol{R})$. According to (B.23) both $\boldsymbol{P}$ and $\boldsymbol{R}$ commute with their commutator, hence (B.26b) can be used. That commutator is found to be

$$\left[\frac{i}{\hbar}\boldsymbol{v}\cdot\boldsymbol{P}t, -\frac{i}{\hbar}m\boldsymbol{v}\cdot\boldsymbol{R}\right] = -\frac{i}{\hbar}v^2mt\int n(\boldsymbol{x},t)\,d^3x\,. \tag{B.31}$$

Now define

$$\boldsymbol{R}' \equiv \int\left(\boldsymbol{x}-\frac{1}{2}\boldsymbol{v}t\right)n(\boldsymbol{x},t)\,d^3x\,, \tag{B.32}$$

and note that $[\boldsymbol{R}',\psi(\boldsymbol{x},t)] = -(\boldsymbol{x}-\frac{1}{2}\boldsymbol{v}t)\psi(\boldsymbol{x},t)$. Then (B.30) can be written

$$\begin{aligned}U^\dagger(\boldsymbol{v})\psi(\boldsymbol{x},t)U(\boldsymbol{v}) &= e^{it\boldsymbol{v}\cdot\boldsymbol{P}/\hbar}e^{-im\boldsymbol{v}\cdot\boldsymbol{R}'/\hbar}\,\psi(\boldsymbol{x},t)e^{im\boldsymbol{v}\cdot\boldsymbol{R}'/\hbar}e^{-it\boldsymbol{v}\cdot\boldsymbol{P}/\hbar}\\ &= e^{it\boldsymbol{v}\cdot\boldsymbol{P}/\hbar}\,e^{im\boldsymbol{v}\cdot\left(\boldsymbol{x}-\frac{1}{2}\boldsymbol{v}t\right)}\,\psi(\boldsymbol{x},t)e^{-it\boldsymbol{v}\cdot\boldsymbol{P}/\hbar}\,.\end{aligned} \tag{B.33}$$

The remaining transformation is just a translation through $\boldsymbol{v}t$, so that finally

$$U^\dagger(\boldsymbol{v})\psi(\boldsymbol{x},t)U(\boldsymbol{v}) = e^{im\boldsymbol{v}\cdot(\boldsymbol{x}'-\frac{1}{2}\boldsymbol{v}t)}\,\psi(\boldsymbol{x}',t)\,, \tag{B.34}$$

where $\boldsymbol{x}'\equiv\boldsymbol{x}+\boldsymbol{v}t$. Up to a phase factor, this is also the result for the ordinary Schrödinger wavefunction (Levy-Leblond, 1963).

The result (B.34) now enables one to obtain the transformation properties of all quantities describing a simple fluid under the Galilean group, and their space-time inversion properties are exhibited in Table B.1. In particular, we are interested in the Galilean transformation properties of the grand canonical equilibrium distribution

$$\rho_0 = \frac{1}{Z_0} e^{-\beta(H-\mu N)} \qquad Z_0 = \mathrm{Tr} e^{-\beta(H-\mu N)} \,. \tag{B.35}$$

Although the Galilean transformation commutes with N, it does not do so with H. The appropriate transformation for H is given by (B.28); but this equation has the form $U^\dagger H U$, whereas according to (B.24) we actually need $UHU^\dagger$, which can be obtained merely by changing the sign of $\boldsymbol{v}$. From (B.27) the transformed density matrix is therefore

$$\begin{aligned} \rho(\boldsymbol{v}) &= U(\boldsymbol{v}) \rho_0 U^\dagger(\boldsymbol{v}) \\ &= \frac{1}{Z(\boldsymbol{v})} e^{-\beta[H - \boldsymbol{v}\cdot\boldsymbol{P} - (\mu - \frac{1}{2} m v^2) N]} \,. \end{aligned} \tag{B.36}$$

It must be emphasized that this is only a redescription of the system as it undergoes an overall drift velocity, and does not involve any dissipative flow.

Expectation values in the transformed (or laboratory) system are given by

$$\begin{aligned} \langle A \rangle &= \mathrm{Tr}[\rho(\boldsymbol{v}) A] \\ &= \mathrm{Tr}[U(\boldsymbol{v}) \rho_0 U^\dagger(\boldsymbol{v}) A] \\ &= \mathrm{Tr}[\rho_0 U^\dagger(\boldsymbol{v}) A U(\boldsymbol{v})] \,, \end{aligned} \tag{B.37}$$

owing to cyclic invariance of the trace. Thus, rather than evaluate traces with the rather complicated form (B.36), we need only calculate rest-frame ($\boldsymbol{v} = 0$) expectation values of the transformed operators themselves. For example, with (B.34) we see that

$$\begin{aligned} U^\dagger(\boldsymbol{v}) n(\boldsymbol{x}, t) U(\boldsymbol{v}) &= e^{-im\boldsymbol{v}\cdot(\boldsymbol{x}' - \frac{1}{2}\boldsymbol{v}t)} \, \psi^\dagger(\boldsymbol{x}', t) e^{im\boldsymbol{v}\cdot(\boldsymbol{x}' - \frac{1}{2}\boldsymbol{v}t)} \psi(\boldsymbol{x}', t) \\ &= n(\boldsymbol{x}', t) \,, \end{aligned} \tag{B.38}$$

with $\boldsymbol{x}' = \boldsymbol{x} + \boldsymbol{v}t$.

The remaining transformed operators are somewhat more complicated because they contain derivatives; however, these derivatives operate only on the phase factors. For example, one finds that $U^\dagger(\nabla\psi)U = \nabla(U^\dagger \psi U)$, because the gradients of $U^\dagger$ and U cancel. The right-hand side of this expression is then evaluated using (B.34). To (B.38) we can add the following transformed expressions:

$$U^\dagger(\boldsymbol{v}) \boldsymbol{j}(\boldsymbol{x}, t) U(\boldsymbol{v}) = \boldsymbol{j}(\boldsymbol{x}', t) + \boldsymbol{v} n(\boldsymbol{x}', t) \,, \tag{B.39}$$

$$U^\dagger(\boldsymbol{v}) h(\boldsymbol{x}, t) U(\boldsymbol{v}) = h(\boldsymbol{x}', t) + \frac{1}{2} m v^2 n(\boldsymbol{x}', t) + m\boldsymbol{v} \cdot \boldsymbol{j}(\boldsymbol{x}', t) \,, \tag{B.40}$$

$$\begin{aligned} U^\dagger(\boldsymbol{v})T_{ij}(\boldsymbol{x},t)U(\boldsymbol{v}) &= T_{ij}(\boldsymbol{x}',t) + m[v_i j_j(\boldsymbol{x}',t) + v_j j_i(\boldsymbol{x}',t)] \\ &\quad + m v_i v_j n(\boldsymbol{x}',t)\,, \qquad \text{(B.41)} \\ U^\dagger(\boldsymbol{v})q_i(\boldsymbol{x},t)U(\boldsymbol{v}) &= q_i(\boldsymbol{x}',t) + v_i\left[\frac{1}{2}mv^2 n(\boldsymbol{x}',t) + h(\boldsymbol{x}',t) + m\boldsymbol{v}\cdot\boldsymbol{j}(\boldsymbol{x}',t)\right] \\ &\quad + \frac{1}{2}mv^2 j_i(\boldsymbol{x}',t) + v^j T_{ji}(\boldsymbol{x}',t)\,. \qquad \text{(B.42)} \end{aligned}$$

The transformed expectation values are found by substitution of (B.38)–(B.42) into (B.37), noting that there are no currents in the state $\rho_0(\boldsymbol{v}=0)$. One verifies that

$$\begin{aligned} \langle n(\boldsymbol{x},t)\rangle &= \langle n(\boldsymbol{x}',t)\rangle_0\,, \\ \langle \boldsymbol{j}(\boldsymbol{x},t)\rangle &= \boldsymbol{v}\langle n(\boldsymbol{x}',t)\rangle_0\,, \\ \langle h(\boldsymbol{x},t)\rangle &= \langle h(\boldsymbol{x}',t)\rangle_0 + \frac{1}{2}mv^2\langle n(\boldsymbol{x}',t)\rangle_0\,, \qquad \text{(B.43)} \\ \langle T_{ij}(\boldsymbol{x},t)\rangle &= \langle T_{ij}(\boldsymbol{x}',t)\rangle_0 + m v_i v_j\langle n(\boldsymbol{x}',t)\rangle_0\,, \\ \langle q_i(\boldsymbol{x},t)\rangle &= v_i\left[\langle h(\boldsymbol{x}',t)\rangle_0 + \frac{1}{2}mv^2\langle n(\boldsymbol{x}',t)\rangle_0\right] + v^j\langle T_{ij}(\boldsymbol{x}',t)\rangle_0\,, \end{aligned}$$

where subscripts 0 denote expectation values taken with ρ_0, and again $\boldsymbol{x}' = \boldsymbol{x}+\boldsymbol{v}t$. Note that these relations are just what one expects based on a macroscopic hydrodynamic analysis (*e.g.*, Landau and Lifshitz, 1959).

APPENDIX C

ANALYTIC CONTINUATION OF COVARIANCE FUNCTIONS

To study further the properties of the linear covariance function, it is convenient to adopt a scenario similar to that of (6.16) and presume information is to be provided on $\langle F(t)\rangle$ in the infinite past, $-\infty < t \leq 0$. We are interested in the causal situation in which $\langle C(t)\rangle$ is to be predicted for $t > 0$. In linear approximation, the predicted value of the deviation $\Delta C(t)\rangle = C(t) - \langle C\rangle_0$ at $t > 0$ is

$$\begin{aligned}
\langle \Delta C(t)\rangle &= \int_{-\infty}^{0} \lambda(t')K^0_{CF}(t-t')\,dt'\,, \quad t>0 \\
&= \int_{t}^{\infty} \lambda(t-\tau)K^0_{CF}(\tau)\,d\tau \\
&= \int_{0}^{\infty} \theta(\tau-t)\lambda(t-\tau)\theta(\tau)K^0_{CF}(\tau)\,d\tau,
\end{aligned} \tag{C.1}$$

where in the third line we have inserted step functions to indicate explicitly that $\theta(\tau)K^0_{CF}(\tau)$ is a causal function, even though necessarily $\tau > t$. Note that the lower limit of the integral in the third line of (C.1) can be extended to $-\infty$, resulting in a convolution integral. Fourier transformation as in (6.31a) yields

$$\begin{aligned}
\langle \Delta C(\omega)\rangle &= \int_{-\infty}^{0} e^{i\omega t}\,\lambda(t)\,dt \int_{0}^{\infty} e^{i\omega\tau}\,K^0_{CF}(\tau)\,d\tau \\
&= \Lambda(\omega)\;K^0_{CF}(\omega)^+.
\end{aligned} \tag{C.2}$$

Note that $K^0_{CF}(\omega)^+$ is a causal transform, and that $\Lambda(\omega)$ involves $\lambda(t)$ over the only interval on which it is defined. The *full* Fourier transform of $K^0_{CF}(t)$ has the form

$$\int_{-\infty}^{\infty} e^{i\omega t}\,K^0_{CF}(t)\,dt = \int_{0}^{\infty} e^{i\omega t}\,K^0_{CF}(t)\,dt + \int_{-\infty}^{0} e^{i\omega t}\,K^0_{CF}(t)\,dt\,, \tag{C.3a}$$

or

$$K^0_{CF}(\omega) = K^0_{CF}(\omega)^+ + K^0_{CF}(\omega)^-\,. \tag{C.3b}$$

Both $K^0_{CF}(t)$ and $K^0_{CF}(\omega)$ are real, but that is not necessarily true of $K^0_{CF}(\omega)^\pm$.

The form of the causal transform in (C.2) suggests that it may be profitable to study a more general function by continuation into the complex plane. The

Fourier–Laplace transform is defined as

$$\begin{aligned}\widetilde{K}^0_{CF}(z) &\equiv \int_0^\infty e^{izt}\, K^0_{CF}(t)\, dt\,, \quad \mathrm{Im} z > 0 \\ &= \frac{1}{2\pi}\int_{-\infty}^\infty \frac{K^0_{CF}(\omega)}{\omega - z}\, d\omega\,, \quad \mathrm{Im} z \neq 0\,.\end{aligned} \tag{C.4}$$

The function $\widetilde{K}^0_{CF}(z)$ is regular in the upper half-plane and can be continued to the lower half-plane where it is also regular; it has a branch cut along the entire real axis. The real function $K^0_{CF}(\omega)$ is essentially the discontinuity in $\widetilde{K}^0_{CF}(z)$ across the cut.

Equation (C.1) represents the linear response of the system at time t to the behavior of $\langle F(t)\rangle$ in the past, and this is characterized by $\widetilde{K}^0_{CF}(\omega)$. The physical, or causal, response is the boundary value on the real axis as it is approached from above, or from the physical sheet. This can be extracted from (C.4) with the help of the identity,

$$\lim_{\gamma\to 0^+} \frac{1}{x \pm i\gamma} = \mathrm{P}\Big(\frac{1}{x}\Big) \mp i\pi\delta(x)\,, \tag{C.5}$$

where P( ) denotes a principal value. Hence,

$$\lim_{\gamma\to 0^+} \widetilde{K}^0_{CF}(\omega + i\gamma) = \mathrm{P}\int_{-\infty}^\infty \frac{K^0_{CF}(u)}{u-\omega}\,\frac{du}{2\pi} + \frac{i}{2}K^0_{CF}(\omega)\,. \tag{C.6}$$

The *dissipative* part of the response is thus the full Fourier transform:

$$K^0_{CF}(\omega) = 2\mathrm{Im}\widetilde{K}^0_{CF}(\omega + i0^+)\,, \tag{C.7}$$

providing the physical interpretation of the transformed covariance function.

We can now relate the covariance function to the ordinary time correlation function, after developing two further relations. The identity (A.13) can be applied to the time variables to provide the relation

$$\frac{d}{dt'}K^0_{CF}(t-t') = \frac{1}{i\beta\hbar}\langle [F, C(t-t')]\rangle_0\,, \tag{C.8a}$$

and its Fourier transform

$$i\omega K^0_{CF}(\omega) = \frac{1}{i\beta\hbar}\langle [F, C(\omega)]\rangle_0\,. \tag{C.8b}$$

The second relation stems from the identity

$$\int_{-\infty}^\infty \langle C(0)F(t)\rangle_0 e^{i\omega t}\, dt = e^{-\beta\hbar\omega}\int_{-\infty}^\infty \langle F(t)C(0)\rangle_0 e^{i\omega t}\, dt\,, \tag{C.9}$$

for any two Hermitian operators C and F. One proves this by writing out both sides in a representation in which H is diagonal. This identity can now be manipulated into the relation

$$\int_{-\infty}^{\infty} \langle [C(0), F(t)] \rangle_0 e^{i\omega t}\, dt = -\left(1 - e^{-\beta\hbar\omega}\right) \int_{-\infty}^{\infty} \langle F(t) C(0) \rangle_0 e^{i\omega t}\, dt\,. \tag{C.10}$$

With the relations (C.8b) and (C.10), along with the definition (6.35b) of the time correlation function $\Gamma^0_{CF}(\boldsymbol{r}, \tau) = \langle \Delta C(\boldsymbol{r}, \tau)\, \Delta F(0) \rangle_0$, we find for the full transform

$$K^0_{CF}(\boldsymbol{k}, \omega) = \frac{1 - e^{-\beta\hbar\omega}}{\beta\hbar\omega} \Gamma^0_{CF}(\boldsymbol{k}, \omega)\,, \tag{C.11}$$

as advertised in (6.35a). For $\beta\hbar\omega \ll 1$ we see that $K^0_{CF}(\boldsymbol{k}, \omega) \simeq \Gamma^0_{CF}(\boldsymbol{k}, \omega)$, which can only happen if $[F, H] = 0$; that is, when the Kubo transform can be neglected. The possible noncommutativity, of course, is how the Kubo transform arises in the first place.

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