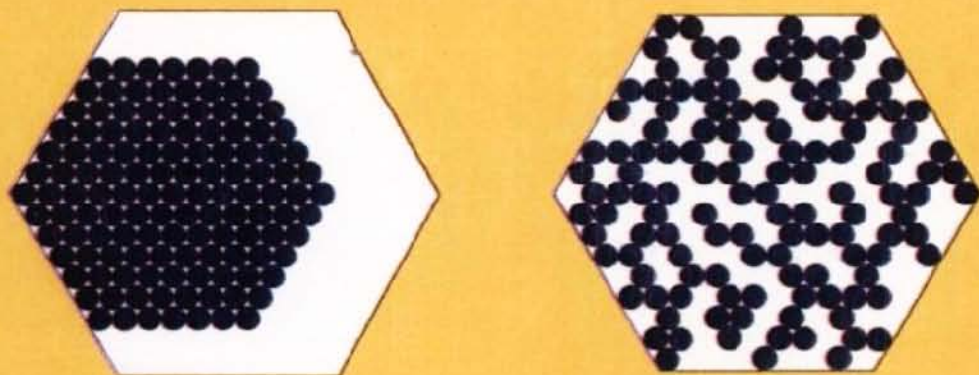


Boris M. Smirnov

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Distributions, Structures, Phenomena,
Kinetics of Atomic Systems



Boris M. Smirnov

Principles of Statistical Physics

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Preface

This book is intended for graduate or advanced students as well as for professionals in physics and chemistry, and covers the fundamental concepts of statistical physics and physical kinetics. These concepts are supported by an examination of contemporary problems for the simplest systems of bound or free atoms. The concepts under consideration relate to a wide range of physical objects: liquids and solids, gases and plasmas, clusters and systems of complex molecules, polymers and amphiphiles. Along with pure substances, two-component systems such as mixtures, solutions, electrolytes, suspensions and gels are considered. A wide spectrum of phenomena are represented, including phase transitions, glassy transitions, nucleation processes, transport phenomena, superfluidity and electrophoresis. The various structures of many-particle systems are analyzed, such as crystal structures of solids and clusters, lamellar structures in solutions, fractal aggregates, and fractal structures, including an aerogel and a fractal fiber.

Different methods of describing some systems and phenomena are compared, allowing one to ascertain various aspects of the problems under consideration. For example, a comparison of statistical and dynamical methods for the analysis of a system of many free atomic particles allows one to understand the basis of statistical physics which deals with the probabilities of a given property for a test particle and the distribution functions of particles of this ensemble. This comparison shows the character of the transition from a dynamical description of individual particles of the ensemble to a statistical description of a random distribution of particles, and the validity of such a randomization in reality.

Starting from the thermodynamic parameters of an ensemble of many particles and the thermodynamic laws in their universal form, we try to supplement this with a microscopic description that does not have such a universal nature. As a result, one can gain a deeper understanding of the nature of objects or phenomena of a given class and determine for them the limits of validity of the simpler method. For example, when analyzing the solid–liquid phase transition, we are guided by condensed rare gases, and the microscopic description of the system as a modified lattice model leads to the conclusion that the phase transition results from excitation of the configuration of these objects and consists in the formation of voids inside the objects. The void concept of configuration excitation allows us to understand the nature of the phase and glassy transitions for condensed rare gases and the difference between the phase definition for bulk systems and clusters. Of course, the elementary configuration excitation has a different nature for other systems, but this analysis shows the problems which must be considered for them.

The book has been developed from a lecture course on statistical physics and the kinetic theory of various atomic systems. Its goal is to present the maximum possible number of concepts from these branches of physics in the simplest way, using simple contemporary problems and a variety of methods. The lecture course depends also on other lecture courses and problems described in detail in the list of books given at the end of this book.

Boris M. Smirnov

1 Introduction

This book covers various aspects of the properties and evolution of systems of many particles which are the objects of statistical physics and physical kinetics. The basic concepts for the description of these systems have existed for more than a century. This book is an addition to existing courses on statistical physics and physical kinetics and includes a new method for studying ensembles of many particles. In describing the various concepts of statistical physics and physical kinetics in this book, we are guided by the simplest systems of many identical atoms – rare and condensed inert gases – although more complex systems are considered for properties which are not typical of inert gases. In addition, the various parameters of rare gases and the phenomena involving them are considered.

In considering ensembles of many identical atomic particles, one can describe the ensemble state on the basis of states of individual particles, accounting for the interactions between them. Then the analysis of the behavior of each particle (or its trajectory in the classical case) that corresponds to a dynamic description of a system of particles may be simplified by using the probability of an individual particle having certain parameters. In this manner we move on to the distribution functions of parameters of individual particles or to a statistical description, and the variation of the distribution function with time characterizes the evolution of this system, which is the basis of physical kinetics. One may expect that this transition to the distribution functions of the parameters of particles will allow us to extract the important information, and therefore this approach both simplifies the analysis and facilitates the removal of minor details from the problem. This is so, but the transition from a dynamic description of a system to a statistical one is not trivial and cannot be grounded in a general form, although it is possible for certain systems. The analysis of this transition allows us to understand more deeply the character of statistical physics, and we use the simplest means and arguments to achieve this goal.

Statistical physics starts from thermodynamics, which deals with average parameters of the ensembles of many particles. The universal laws of thermodynamics and its concepts are the foundations of statistical physics, which is developing by removing some of the assumptions of thermodynamics. Thermodynamics works with equilibrium systems of many particles, whereas statistical physics and physical kinetics consider non-equilibrium and non-stationary particle ensembles.

Based on this pragmatic standpoint and postulating the validity of the statistical description, we try to analyze the properties of a system under consideration in the simplest way. A system of many identical particles permits various structures for these particles and their aggregate states. The structures of systems of bound particles and the competition between different structures will be considered below. In order to understand the nature of the processes and phenomena of statistical physics, we study the simplest or limiting cases. In particular, when considering the problem of the phase transition between aggregate states for clusters and bulk systems, we refer to ensembles of bound atoms with a pair interaction between them,

being guided by condensed rare gases. We restrict ourselves to a two-aggregate approach, where there are only solid or liquid aggregate states of clusters or bulk. The phase transition results from configuration excitation of ensembles of bound atoms, and the elementary excitations in the case of pair interactions between atoms are perturbed vacancies or voids. The void concept allows us to understand the microscopic nature of the phase transition and offers the possibility of analyzing additional aspects of this phenomenon in comparison with thermodynamic ones. As a result, one can connect the phase and glass transitions on the basis of the void concept of configuration excitation for such systems.

The establishment of an equilibrium state of a system of many particles and the evolution of this system result from elementary processes involving individual particles, and the rates of these processes determine the variation of the state of the total system. Then the statistical description of this system is connected to the kinetics of evolution of real systems, and this book contains the theory of equilibria and evolution of some systems. If the equilibrium of the system relates simultaneously to different degrees of freedom, we obtain thermodynamic equilibrium. But the stationary state of real systems may differ from the thermodynamic one in the case of different relaxation times for different degrees of freedom. Then the stationary state of the system is determined by the hierarchy of relaxation times, and a certain hierarchy of relaxation times leads to a corresponding stationary state of the system of many atomic particles. This has real consequences; for instance, if thermodynamic equilibrium were to be reached in our universe it would lead to thermal death of all life, and such a problem was discussed widely in the 19th century. Furthermore, in the case of thermodynamic equilibrium on the Earth's surface, hydrogen and carbon could be found there only in the form of water and carbon dioxide. Under such conditions both living organisms and certain objects or chemical compounds, such as paper, plants or hydrocarbons, could not exist on Earth. These examples show that we are surrounded by non-equilibrium systems in reality, and the character of the establishment of a stationary state for some non-equilibrium systems as well as related phenomena are considered in this book.

If thermodynamic equilibrium is violated, universal thermodynamic laws become invalid. On the other hand, non-equilibrium conditions lead to various states and phenomena, depending on the hierarchy of relaxation times. For example, the parameters of the electron subsystem of a gas-discharge plasma differ from those of a neutral component allowing us to achieve ionization under the action of an external electric field, even in a cold plasma. Next, the properties of fractal structures depend on kinetics of the processes of joining of elemental particles which conserve their individuality in fractal structures. Fractal structures are non-equilibrium ones and can be transformed in compact structures as a result of reconstruction processes. But at low temperatures the restructuring processes last for a long time, and fractal structures are practically stable at relatively low temperatures.

One more example of a non-equilibrium phenomenon is the formation of a glassy state of a system of bound atoms. Let us consider a simple system of particles which can be found in two aggregate states at low and high temperatures: solid and liquid. Usually this transition has an activation character, so that the rate of this transition drops sharply with a decreasing temperature. Therefore rapid cooling of the liquid state up to temperatures below the melting point can lead to the formation of a metastable supercooled state. This is a metastable state, and when perturbed by small fluctuations, the system returns to the initial state. The subsequent cooling of the system to below the freezing point creates a supercooled liquid state

which is unstable, i.e. the system does not return to the initial state after small fluctuations. However, this unstable state has a long lifetime (practically infinite) because of the activation character of the process of decay of this state. In this way, frozen unstable states can be formed at low temperatures. This method of formation of a non-equilibrium state was studied first for glasses, and therefore this unstable state is called the glassy state. Thus the non-equilibrium character of relaxation processes for a system of many atomic particles makes the states and character of evolution of these systems more rich and varied.

In the course of our description, we move from equilibrium systems to non-equilibrium ones, and from stationary systems to non-stationary ones. We start from the general principles of the statistical physics with its application to various objects, and find the connection of statistical physics to adjacent areas of physics, such as thermodynamics and the mechanics of many particles. Elementary processes which lead to equilibria in a system of many particles also determine transport phenomena, and various structures of individual particles may be formed as a result of interactions. All this is a topic of this book. Next, we focus on the phase and glassy transitions in simple systems of bound atoms, and the growth of a new phase as a result of nucleation phenomena.

Contemporary statistical physics and physical kinetics use classical methods, developed a century ago, but new subjects and phenomena arise over time. This book contains a wide spectrum of subjects and phenomena which are analyzed below within the framework of statistical physics. We consider various aspects of these problems concerning the properties, structures and behavior of various objects. Thus we deal with atomic objects and phenomena which are described by the methods of statistical physics and physical kinetics. Such systems, on the one hand, contain a large number of atomic particles, and, on the other hand, thermodynamic equilibrium can be violated in these systems.

Part I
Statistical Physics of Atomic Systems

2 Basic Distributions in Systems of Particles

2.1 The Normal or Gaussian Distribution

Statistical physics deals with systems consisting of a large number of identical elements, and some parameters of the system are the sum of parameters of individual elements. Let us consider two such examples. In the first case the *Brownian motion* of a particle results from its collisions with gaseous atoms, and in the second case we have a system of free particles (atoms), so that the total energy of the system is the sum of the energies of the individual particles, and the momentum of an individual particle varies in a random manner when it collides with other particles. Our task is to find the displacement of the particle position in the first case and the variation of its momentum in the second case after many collisions. Thus our goal in both cases is to find the probability that some variable z has a given value after $n \gg 1$ steps if the distribution for each step is random and the variation of particle parameters after each step is given.

Let the function $f(z, n)$ be the probability that the variable has a given value after n steps, and $\varphi(z_k) dz_k$ is the probability that after the k th step the variable's value ranges from z_k to $z_k + dz_k$. Since the functions $f(z)$, $\varphi(z)$ are the probabilities, they are normalized by the condition:

$$\int_{-\infty}^{\infty} f(z, n) dz = \int_{-\infty}^{\infty} \varphi(z) dz = 1$$

From the definition of the above functions we have:

$$f(z, n) = \int_{-\infty}^{\infty} dz_1 \cdots \int_{-\infty}^{\infty} dz_n \prod_{k=1}^n \varphi(z_k)$$

and

$$z = \sum_{k=1}^n z_k \quad (2.1)$$

Introduce the *characteristic functions*:

$$G(p) = \int_{-\infty}^{\infty} f(z) \exp(-ipz) dz, \quad g(p) = \int_{-\infty}^{\infty} \varphi(z) \exp(-ipz) dz \quad (2.2)$$

The inverse operation yields:

$$f(z) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G(p) \exp(ipz) dp, \quad \varphi(z) = \frac{1}{2\pi} \int_{-\infty}^{\infty} g(p) \exp(ipz) dp$$

Equation (2.2) gives:

$$g(0) = \int_{-\infty}^{\infty} \varphi(z) dz = 1; \quad g'(0) = i \int_{-\infty}^{\infty} z \varphi(z) dz = i \bar{z}_k; \quad g''(0) = -\bar{z}_k^2 \quad (2.3)$$

where $\bar{z}_k$ and $\bar{z}_k^2$ are the mean shift and the mean square shift of the variable after one step. From the formulae (2.1) and (2.3) there follows:

$$G(p) = \int_{-\infty}^{\infty} \exp \left(-ip \sum_{k=1}^n z_k \right) \prod_{k=1}^n \varphi(z_k) dz_k = g^n(p)$$

and hence

$$f(z) = \frac{1}{2\pi} \int_{-\infty}^{\infty} g^n(p) \exp(ipz) dp = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(n \ln g + ipz) dp$$

Since $n \gg 1$, the integral converges at small p . Expanding $\ln g$ in a series over small p , we have

$$\ln g = \ln \left(1 + i \bar{z}_k p - \frac{1}{2} \bar{z}_k^2 p^2 \right) = i \bar{z}_k p - \frac{1}{2} (\bar{z}_k^2 - \bar{z}_k^2) p^2$$

This gives:

$$\begin{aligned} f(z) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dp \exp \left[ip(n \bar{z}_k - z) - \frac{n}{2} (\bar{z}_k^2 - \bar{z}_k^2) p^2 \right] \\ &= \frac{1}{\sqrt{2\pi \Delta^2}} \exp \left[-\frac{(z - \bar{z})^2}{2\Delta^2} \right] \end{aligned} \quad (2.4)$$

where $\bar{z} = n \bar{z}_k$ is the mean shift of the variable after n steps, and $n \Delta^2 = n \left[\bar{z}_k^2 - (\bar{z}_k)^2 \right]$ is the mean square deviation of this quantity. The value Δ for a system of many identical elements is called the *fluctuation* of this quantity. Formula (2.4) is called the *normal distribution* or the *Gaussian distribution*. Formula (2.4) is valid if small p provides the main contribution to the integral (2.3), i.e. $\bar{z}_k p \ll 1$, $\bar{z}_k^2 p^2 \ll 1$. Because this integral is determined by $n \bar{z}_k^2 p^2 \sim 1$, the Gaussian distribution holds true for a large number of steps or elements $n \gg 1$.

2.2 Specifics of Statistical Physics

Statistical physics considers systems containing a large number of elements. Hence average values can be used instead of the distribution for some parameters of these elements. Below we demonstrate this in an example of the distribution of identical particles in a region. In this case we have a closed volume Ω containing a fixed number N of free particles. Our goal is to

find the distribution of a number of particles located in a small part $\Omega_o \ll \Omega$ of this volume. We assume the mean number of these particles $\bar{n} = N\Omega_o/\Omega$ to be large. The probability W_n of finding n particles in a given volume is the product of the probability of locating n particles in this volume $(\Omega_o/\Omega)^n$, the probability of locating the other $N - n$ particles outside this volume $(1 - \Omega_o/\Omega)^{N-n}$, and the number of ways C_N^n to do it, so that this probability is given by the formula

$$W_n = C_N^n \left(\frac{\Omega_o}{\Omega} \right)^n \left(1 - \frac{\Omega_o}{\Omega} \right)^{N-n}$$

This probability satisfies the normalization condition $\sum_n W_n = 1$.

Let us consider the limit $n \gg 1$, $\bar{n} = N\frac{\Omega_o}{\Omega} \gg 1$, $n \ll N$, $n^2 \ll N$. Then we have

$$W_n = \frac{\bar{n}^n}{n!} \exp(-\bar{n}) \quad (2.5)$$

This formula is called the *Poisson formula*.

In the case considered, $n \gg 1$, $\bar{n} \gg 1$, the function W_n has a narrow maximum at $n = \bar{n}$. Using the Stirling formula

$$n! = \frac{1}{\sqrt{2\pi n}} \left(\frac{n}{e} \right)^n, \quad n \gg 1 \quad (2.6)$$

we find that the expansion of W_n near $\bar{n}$ has the form

$$\ln W_n = \ln W_o - \frac{(n - \bar{n})^2}{2\bar{n}} \quad (2.7)$$

where $W_o = (2\pi\bar{n})^{-1/2}$, and the fluctuation of the number of particles in a given volume equals

$$\Delta = \sqrt{n^2 - (\bar{n})^2} = \sqrt{\bar{n}} \ll \bar{n} \quad (2.8)$$

We use this result to demonstrate the general principle of statistical physics. Let us divide the total volume in some cells, so that the average number of particles in the i th cell of the volume Ω_i is equal to $\bar{n}_i = N\frac{\Omega_i}{\Omega}$, where N is the total number of particles in the total volume Ω . Then, ignoring the fluctuations, we deal with the mean numbers $\bar{n}_i$ of particles in the cells, and the distribution of the number of particles in a given cell is concentrated near its average number. One can see that the fluctuations are relatively small, and the above statement is valid if the number of particles in the cells is large enough: $\bar{n}_i \gg 1$.

Note that the distribution of particles in cells, neglecting the fluctuations, can be obtained by two methods. In the first case we make a measurement of the distribution over the cells and find n_i particles in the i th cell. This value coincides with the average value $\bar{n}_i$, with an accuracy up to the size of the fluctuations. In the second case we follow a test particle which is found in a cell i during a time t_i from the total observation time t . Then the number of particles in the i th cell equals Nt_i/t and it coincides with $\bar{n}_i$, again with an accuracy up to the size of the fluctuations. Thus when we operate with average values in statistical physics, in the first approximation we neglect fluctuations.

2.3 Temperature

Let us consider a system of free atoms. Due to collisions between atoms, a certain distribution of atomic energies is established. One can introduce the *temperature* of atoms T for this distribution on the basis of the relationship:

$$\overline{\varepsilon_z} = \frac{1}{2}T \quad (2.9)$$

where $\overline{\varepsilon_z}$ is the average kinetic energy of one atom for its motion in the direction z . Because the three directions are identical, the average kinetic energy of an individual atom $\overline{\varepsilon}$ is equal to

$$\overline{\varepsilon} = \frac{3}{2}T \quad (2.10a)$$

Usually the temperature is expressed in kelvins (K). Often the value $k_B T$ is used in the formulae (2.9) and (2.10) instead of T , where $k_B = 1.38 \cdot 10^{-16}$ erg/K is the Boltzmann constant, the conversion coefficient between erg and K. The use of the *Boltzmann constant* in physical relations is connected to the history of the introduction of temperature, when temperature and energy were considered to be the values of different dimensionalities. Below we accept the *kelvin* as an energetic unit and hence we shall not use the above conversion factor. Table 2.1 shows the connection of this energetic unit to other units.

Table 2.1. Conversion factors between kelvins (K) and other energetic units.

Energy unit	erg	eV	cal/mol	cm ⁻¹	Ry
Conversion factor	$1.3806 \cdot 10^{-16}$	$8.6170 \cdot 10^{-5}$	1.9873	0.69509	$6.3344 \cdot 10^{-6}$

Let us consider an ensemble of n free atoms of a temperature T and find the distribution of this system over the total kinetic energy of atoms. It is given by formula (2.4), where instead of a variable z we use the total kinetic energy of atoms E . Its average value equals

$$\overline{E} = n\overline{\varepsilon} = \frac{3}{2}nT \quad (2.10b)$$

and the mean squared deviation of the total kinetic energy is

$$\Delta^2 = n \left(\overline{\varepsilon^2} - \overline{\varepsilon}^2 \right)$$

where $\overline{\varepsilon}$ and $\overline{\varepsilon^2}$ are the average values of the energy and energy squared for an individual atom. Evidently $\overline{\varepsilon^2} \sim T^2$, and the relative width of the distribution function of the total kinetic energy of the atoms is

$$\delta \sim \frac{\Delta}{\overline{E}} \sim \frac{1}{\sqrt{n}}$$

i.e. this value is small if there are a large number of atoms in the system.

2.4 The Gibbs Principle

An important aspect of statistical physics consists in the analysis of *distribution functions* for particles of an ensemble. In this way we start from the general problem of the energy distribution for weakly interacting particles of a closed system. Let us consider an ensemble of a large number of particles and distribute the particles by states which are described by a set of quantum numbers i . The state of a particle includes its internal quantum numbers, which are the electron shell state for an atom, the vibrational and rotational states for a molecule etc. In addition, we denote the particle state's coordinates $\mathbf{r}$ and momentum $\mathbf{p}$. In reality, we deal with a certain range $\Delta\mathbf{r}$ of particle positions in a space and a range $\Delta\mathbf{p}$ of particle momenta. Hence each value of the index i includes a group of g_i states, which is a large number $g_i \gg 1$.

Our goal is to find the average number of particles found in each group i of states. Let us analyze the peculiarities of a system of free particles. In reality, these particles are free for most of the observation time, but for a short period they interact strongly with surrounding particles or with walls of a vessel where these particles are located. This interaction is of importance because it establishes a certain equilibrium for this system of particles. But, when analyzing the state of an individual particle, we assume it to be free at that time.

Thus we have a gaseous system of many free particles, so that weak interactions of seldom collisions of particles lead to a certain distribution of particles over states depending on the parameters of the system. Taking the total number of particles to be n , we assume that this number does not vary with time. Denote the number of particles in the i th state by n_i . Then the condition of conservation of the total number of particles takes the form:

$$n = \sum_i n_i \quad (2.11)$$

Assuming the system of particles under consideration to be closed (i.e. the system does not exchange by energy with other systems), we require the conservation of the total energy of particles E :

$$E = \sum_i \varepsilon_i n_i \quad (2.12)$$

where ε_i is the energy of a particle in the i th state. In the course of the evolution of the system an individual particle can change its state, but the average number of particles in each state is conserved with some accuracy. Such behavior in a closed system is called *thermodynamic equilibrium*.

Transitions of an individual particle between states result from its collisions with other particles. Apparently, the probability that this particle is found in a given state (as well as the average number of particles in this state) is proportional to the number of ways in which this can happen. This is the *Gibbs principle*, or the principle of homogeneous distribution, which is the basis of statistical physics. Within the framework of this principle, one can assume that the probability of a system of particles being found in a given state is proportional to the number of states which lead to this distribution.

Denote by $P(n_1, n_2, \dots, n_i, \dots)$ the number of ways that n_1 particles are found in the first group of states, n_2 particles are found in the second group of states, n_i particles are found

in the i th group of states, etc. Let us calculate the number of possible ways of obtaining this distribution. Assuming that the location of a particle in a certain group of states does not influence the positions of other particles, the total number of ways for a given distribution of particles over groups of states to occur is given by the product of distributions inside each group, i.e.

$$P(n_1, n_2, \dots, n_i, \dots) = p(n_1)p(n_2) \cdots p(n_i) \cdots \quad (2.13)$$

where $p(n_i)$ is the number of ways to distribute n_i particles inside a given group of states. Let us perform this operation successively.

First, take n_1 particles for the first state from the total number of n particles. There are $C_n^{n_1} = \frac{n!}{(n-n_1)!n_1!}$ ways to do this. Next, select n_2 particles from the remaining $n - n_1$ particles for the second state; this can be done in $C_{n-n_1}^{n_2}$ ways. Continuing this operation, we determine the probability of the considered distribution of particles:

$$P(n_1, n_2, \dots, n_i, \dots) = \frac{n!}{\prod_i (n_i!)} \quad (2.14)$$

where $Const$ is a normalization constant. The basis of this formula is the assumption that the particles are independent, so that the state of one particle does not influence the distribution of the others.

2.5 The Boltzmann Distribution

Let us determine the most probable number of particles $\bar{n}_i$ that are found in a state i for a system of weakly interacting particles. Use the fact that $\bar{n}_i \gg 1$ and the number of ways P of obtaining this distribution as well as its logarithm has a maximum at $n_i = \bar{n}_i$. Introducing $dn_i = n_i - \bar{n}_i$ and assuming $\bar{n}_i \gg dn_i \gg 1$, we expand the value $\ln P$ over dn_i near the maximum of this value. Using the relation $\ln n! = \ln \prod_{m=1}^n m \approx \int_0^n \ln x dx$, we have $d \ln n! / dn = \ln n$.

On the basis of this relation, we obtain from formulae (2.4) and (2.14):

$$\ln P(n_1, n_2, \dots, n_i, \dots) = \ln P(\bar{n}_1, \bar{n}_2, \dots, \bar{n}_i, \dots) - \sum_i \ln \bar{n}_i dn_i - \sum_i \frac{dn_i^2}{2\bar{n}_i}$$

The condition for the maximum of this value gives:

$$\sum_i \ln \bar{n}_i dn_i = 0 \quad (2.15)$$

Alongside this equation, we take into account the relations which follow from equations (2.11) and (2.12):

$$\sum_i dn_i = 0 \quad (2.16)$$

$$\sum_i \varepsilon_i dn_i = 0 \quad (2.17)$$

Equations (2.15) to (2.17) allow us to determine the average number of particles in a given state. Multiplying equation (2.16) by $-\ln C$ and equation (2.17) by $1/T$, where C and T are characteristic parameters of this system, and summing the resultant equations, we have:

$$\sum_i \left(\ln \bar{n}_i - \ln C + \frac{\varepsilon_i}{T} \right) dn_i = 0$$

Because this equation is fulfilled for any dn_i , we require the expression in parentheses to be zero. This leads to the following expression for the most probable number of particles in a given group of states:

$$\bar{n}_i = C \exp \left(-\frac{\varepsilon_i}{T} \right) \quad (2.18)$$

This formula is called the *Boltzmann distribution*. In the course of deducing this formula we assume that the probability of finding a particle in a state i does not depend on the states of other particles. It is valid for certain statistics of particles if the average population of one state is small $\bar{n}_i \ll g_i$. This is the criterion of validity for the Boltzmann distribution.

Let us determine the physical nature of the parameters C and T in equation (2.18), which follows from the additional equations (2.11) and (2.12). From equation (2.11) we have $C \sum_i \exp(-\varepsilon_i/T) = N$, so that the value C is the normalization constant. The energetic parameter T is the temperature of the system. One can see that this definition of the temperature coincides with (2.9).

Let us prove that at large $\bar{n}_i$ the probability of observing a significant deviation from $\bar{n}_i$ is small. According to the above equations this value equals (compare with (2.7) and (2.15)):

$$P(n_1, n_2, \dots, n_i, \dots) = P(\bar{n}_1, \bar{n}_2, \dots, \bar{n}_i, \dots) \exp \left[-\sum_i \frac{(n_i - \bar{n}_i)^2}{2\bar{n}_i} \right] \quad (2.19)$$

In fact, this formula coincides with the Gaussian distribution (2.4). From this it follows that a shift of n_i from the average value $\bar{n}_i$, at which the probability is not so small, is $|n_i - \bar{n}_i| \sim 1/\sqrt{\bar{n}_i}$. Since $\bar{n}_i \gg 1$, the relative shift of a number of particles in one state is small: $|n_i - \bar{n}_i|/\bar{n}_i \sim 1/\sqrt{\bar{n}_i}$. Thus the observed number of particles in a given state differs little from its average value.

On the basis of the above analysis one can formulate the general features of a system of weakly interacting particles when the number of particles is large. Then one can introduce the distribution function of particles over states, which is proportional to the numbers of particles in these states at a given time if we assume that the particles do not interact at that time. This distribution over states is conserved in time with accuracy $\sim 1/\sqrt{\bar{n}_i}$, where $\bar{n}_i$ is the average number of particles in a group of states i . Within the limits of this accuracy, one can define the distribution function in another way. We observe one particle of the system for a long time, when the particle is found in various states. Then the distribution function by states is proportional to the total time during which the particle is found in these states or groups of states. Within the limits of the above accuracy, both definitions of the distribution function are identical. This correspondence between averaging over the phase space of particles and over a long period of observation of one particle is known as the *ergodic theorem*.

2.6 Statistical Weight, Entropy and the Partition Function

In formulae (2.15) and (2.19) the subscript i relates to a group of particle states. Below we consider a general case when i includes a set of degenerate states. Then we introduce the *statistical weight* g_i of a state as a number of degenerate states i . For example, a diatomic molecule in a rotational state with the rotational quantum number J has a statistical weight $g_i = 2J + 1$ that is the number of momentum projections on the molecular axis. Accounting for the statistical weight, formula (2.12) takes the form:

$$\bar{n}_i = C g_i \exp\left(-\frac{\varepsilon_i}{T}\right)$$

where C is the normalization factor. In particular, this formula gives the relation between the number densities of particles in the ground N_o and excited N_i states:

$$N_i = N_o \frac{g_i}{g_o} \exp\left(-\frac{\varepsilon_i}{T}\right) \quad (2.20)$$

where ε_i is the excitation energy, and g_o and g_i are the statistical weights of the ground and excited states.

Let us introduce the *entropy* S_i of a particle which is found in a given group of states:

$$S_i = \ln g_i \quad (2.21)$$

assuming an identical probability for particle location in each of these states. If another particle is found in a state of a group j , the total statistical weight for particle location in these states is $g_{ij} = g_i g_j$, and the total entropy of the system of these particles is $S_{ij} = \ln g_i g_j = S_i + S_j$, i.e. the entropy is the additive function. Generalizing the entropy definition for the case when a particle can be found in several states, we obtain instead of formula (2.21)

$$S = \left\langle \ln \frac{1}{w_i} \right\rangle$$

where w_i is the probability of the particle being located in a given state, and an average is taken over these states. Correspondingly, this formula may be rewritten in the form

$$S = \sum_i w_i \ln \frac{1}{w_i}$$

By transferring to a system consisting of a certain number of particles or subsystems and defining the entropy with an accuracy up to a constant for a given system of particles, one can rewrite this expression for a system of n particles in the form

$$S = - \sum_i n_i \ln n_i \quad (2.22)$$

where n_i is the number of particles located in a given state (or the distribution function of particles over states).

It is convenient to introduce for an ensemble of weakly interacting particles the *partition function* z_i of an individual particle, which corresponds to the location of this particle in the i th state:

$$z_i = g_i \exp\left(-\frac{\varepsilon_i}{T}\right) \quad (2.23a)$$

so that the average number of particles in the i th state is equal to $n_i = nz_i/z$, where $z = \sum z_i$ is the partition function for a given particle. The total partition function of an ensemble of n identical atomic particles is

$$Z = \sum_i Z_i \quad (2.23b)$$

where $Z_i = nz_i$ is the partition function of a given state (or group of states) for an ensemble of n particles.

Various average parameters of a system of many particles can be expressed through the partition function. In particular, the total energy of particles (2.12) equals in the case of the Boltzmann distribution (2.18):

$$E = \sum_i \varepsilon_i n_i = \sum_i \varepsilon_i \frac{Z_i}{Z} = \frac{1}{Z} \sum_i \frac{\partial Z_i}{\partial(-\frac{1}{T})} = T \frac{\partial \ln Z}{\partial \ln T} \quad (2.24)$$

where we use the relation from formula (2.23a)

$$T^2 \frac{\partial Z_i}{\partial T} = \frac{\partial Z_i}{\partial(-\frac{1}{T})} = \varepsilon_i Z_i$$

Considering the thermodynamic equilibrium of an ensemble of n weakly interacting particles with $n \gg 1$ and describing this ensemble by a temperature T , we find that the most likely energies of this ensemble are concentrated in a narrow energy range near E . Composing possible combinations for the distribution of particles over states with nearby total energies $\varepsilon_i \approx E$, we obtain for the total partition function of this particle ensemble

$$Z = \sum_i Z_i = \sum_i g_i \exp\left(-\frac{\varepsilon_i}{T}\right) = \exp\left(-\frac{E}{T}\right) \sum_i g_i = \exp\left(-\frac{E}{T}\right) \Gamma$$

where $\Gamma = \sum_i g_i$ is the total number of ensemble states with this internal energy. By analogy with formula (2.21), one can introduce the *entropy* of this particle ensemble as

$$S = \ln \Gamma \quad (2.25)$$

Then, using formula (2.24), we obtain from this relation the following connection between the entropy and partition function of this particle ensemble:

$$S = \ln Z + \frac{E}{T} = \ln Z + \frac{\partial \ln Z}{\partial \ln T} \quad (2.26)$$

Now let us determine the statistical weight of states of the continuous spectrum. Take into account the fact that the wave function of a free particle with a momentum p_x which is moving along the axis x is equal, up to an arbitrary factor, to $\exp(ip_x x/\hbar)$ if the particle is moving in the positive direction, and to $\exp(-ip_x x/\hbar)$ if the particle is moving in the negative direction ($\hbar = 1.054 \cdot 10^{-27} \text{ erg} \cdot \text{s}$ is the Planck constant h divided by 2π). Let us put the particle into a potential well with infinitely high walls. Then the particle can move freely in the region $0 < x < L$, and the wave function at the walls is zero. Constructing such a wave function that corresponds to a free motion inside the well and is zero at its walls, we have $\psi = C_1 \exp(ip_x x/\hbar) + C_2 \exp(-ip_x x/\hbar)$. From the boundary condition $\psi(0) = 0$ it follows $\psi = C \sin(p_x x/\hbar)$, and from the second boundary condition $\psi(L) = 0$ we have $p_x L/\hbar = \pi k$, where k is an integer. In this way we find the energies of quantum states for a particle moving in a well with infinite rectangular walls.

From this we find that the number of states for a particle with a momentum in the range p_x to $p_x + dp_x$ is equal to $dg = L dp_x/(2\pi\hbar)$ (we take into account two directions of the particle momentum). If the space interval equals dx , the number of particle states is

$$dg = \frac{dp_x dx}{2\pi\hbar} \quad (2.27a)$$

Generalizing this to the three-dimensional case, we obtain for the number of states of a test particle

$$dg = \frac{dp_x dx}{2\pi\hbar} \cdot \frac{dp_y dy}{2\pi\hbar} \cdot \frac{dp_z dz}{2\pi\hbar} = \frac{d\mathbf{p} d\mathbf{r}}{(2\pi\hbar)^3} \quad (2.27b)$$

Here and below we use the notation $d\mathbf{p} = dp_x dp_y dp_z$, $d\mathbf{r} = dx dy dz$. The quantity $d\mathbf{p} d\mathbf{r}$ is called an element of the *phase space*, and the number of states in formulae (2.24) is the *statistical weight of the continuous spectrum* because it is a number of states for an element of the phase space.

Let us return to the method of deducing the Boltzmann formula (2.18). For this goal we divide states into groups such that each group contains a large number of states $g_i \gg 1$. Each group of states corresponds to a particular element of the phase space $d\mathbf{p} d\mathbf{r}/(2\pi\hbar)^3$ of a particle and includes certain internal states. Thus g_i is the statistical weight of a group of states.

Returning to formula (2.24) for the average energy of an ensemble of Boltzmann particles, we find the *heat capacity* of this ensemble of particles as $C = dE/dT$. We assume that the temperature variation has no influence on the energies ε_i of levels of the system. This corresponds to a constant volume of the system under temperature variations. Using formulae (2.23) to (2.24) and accounting for the relation $\partial Z_i/\partial T = \varepsilon_i Z_i/T^2$ for Boltzmann particles, we have for the heat capacity of the system

$$C_V = n \frac{\partial}{\partial T} \left(\frac{\sum_i \varepsilon_i Z_i}{\sum_i Z_i} \right) = \frac{n}{T^2} \left[\frac{\sum_i \varepsilon_i^2 Z_i}{\sum_i Z_i} - \frac{\left(\sum_i \varepsilon_i Z_i \right)^2}{\left(\sum_i Z_i \right)^2} \right] = \frac{n}{T^2} \left[\overline{\varepsilon^2} - (\overline{\varepsilon})^2 \right] \quad (2.28)$$

where the bar means averaging over the ensemble, the energetic parameters of the total system are $\bar{\varepsilon} = \sum_i \varepsilon_i Z_i / Z$, $\overline{\varepsilon^2} = \sum_i \varepsilon_i^2 Z_i / Z$, and the heat capacity is proportional to the number of particles n in the system because the interaction between particles is weak.

2.7 The Maxwell Distribution

Let us consider the velocity distribution of free particles resulting from collisions of these particles which lead to changes in the energy of individual particles. Use the Boltzmann formula (2.18). In the one-dimensional case the particle energy equals $mv_x^2/2$, and the statistical weight of this state is proportional to dv_x , i.e. the number of particles $f(v_x)$ whose velocity is found in the interval from v_x to $v_x + dv_x$ according to formula (2.18) is given by

$$f(v_x) dv_x = C \exp\left(-\frac{mv_x^2}{2T}\right) dv_x$$

where C is the normalization factor. Correspondingly, in the three-dimensional case we have:

$$f(v) d\mathbf{v} = C \exp\left(-\frac{mv^2}{2T}\right) d\mathbf{v}$$

where the vector $\mathbf{v}$ has components v_x, v_y, v_z , $d\mathbf{v} = dv_x dv_y dv_z$, and the kinetic energy of the particle $mv^2/2$ is the sum of the kinetic energies for all the directions of motion. In particular, normalizing the distribution function to the number density of particles N , we have from this, using the normalization condition:

$$f(v) = N \left(\frac{m}{2\pi T}\right)^{3/2} \exp\left(-\frac{mv^2}{2T}\right) \quad (2.29a)$$

Introduce the function $\varphi(v_x) \sim f(v_x)$, which is normalized to unity:

$$\int_{-\infty}^{\infty} \varphi(v_x) dv_x = 1, \quad \varphi(v_x) = \sqrt{\frac{m}{2\pi T}} \exp\left(-\frac{mv_x^2}{2T}\right) \quad (2.29b)$$

Then

$$f(v) = N \varphi(v_x) \varphi(v_y) \varphi(v_z) = N \left(\frac{m}{2\pi T}\right)^{3/2} \exp\left(-\frac{mv^2}{2T}\right)$$

These distribution functions of particles on velocities are called the *Maxwell distributions*. Let us determine the average kinetic energy of particles on the basis of formula (2.29a). We have:

$$\frac{m\overline{v^2}}{2} = \frac{m\overline{v_x^2}}{2} + \frac{m\overline{v_y^2}}{2} + \frac{m\overline{v_z^2}}{2} = \frac{3m\overline{v_x^2}}{2}$$

Next,

$$\begin{aligned} \frac{\overline{mv_x^2}}{2} &= \frac{\int_{-\infty}^{\infty} \frac{mv_x^2}{2} \exp\left(-\frac{mv_x^2}{2T}\right) dv_x}{\int_{-\infty}^{\infty} \exp\left(-\frac{mv_x^2}{2T}\right) dv_x} = -\frac{d \ln \int_{-\infty}^{\infty} \exp\left(-\frac{mv_x^2}{2T}\right) dv_x}{d(-1/T)} \\ &= -\frac{d \ln (aT^{1/2})}{d(-1/T)} = \frac{T}{2} \end{aligned} \quad (2.30)$$

where the constant a does not depend on the temperature. Thus the particle kinetic energy per degree of freedom is equal to $T/2$, and correspondingly the average particle kinetic energy in the three-dimensional space is $\overline{mv^2}/2 = 3T/2$. These relations were used as the definition of the temperature in formulae (2.9) and (2.10). As we have seen, this definition of temperature coincides with that used to deduce the Boltzmann formula (2.18).

Introducing the distribution function $f(\varepsilon)$ on kinetic energies $\varepsilon = mv^2/2$ of free particles, which is normalized by the condition

$$\int_0^{\infty} f(\varepsilon) \varepsilon^{1/2} d\varepsilon = 1 \quad (2.31a)$$

we obtain for this distribution function in the case of the Maxwell distribution of free particles:

$$f(\varepsilon) = \frac{2}{\sqrt{\pi} T^{3/2}} \exp\left(-\frac{\varepsilon}{T}\right) \quad (2.31b)$$

2.8 Mean Parameters of an Ensemble of Free Particles

An ensemble of free particles is the simplest system of particles in which these particles are located in a certain volume, and their interaction is relatively small. Below we determine some average parameters. From the above formulae for the distribution function of free particles we have for the average energy parameters of the ensemble of Maxwell particles:

$$\overline{\varepsilon} = \frac{3T}{2}, \quad \overline{\varepsilon^2} = \frac{15T^2}{4}$$

where n is the number of ensemble particles. Then formula (2.28) gives for the heat capacity of an ensemble of Maxwell particles

$$C_V = \frac{n}{T^2} \left[\overline{\varepsilon^2} - (\overline{\varepsilon})^2 \right] = \frac{3}{2}n$$

On the other hand, we get the same result by introducing the heat capacity of the particle ensemble as

$$C_V = \left(\frac{\partial \overline{E}}{\partial T} \right)_n = \frac{3}{2}n$$

where $\overline{E} = n\overline{\varepsilon} = 3Tn/2$ is the average energy of an ensemble of n free particles.

In addition, we calculate the partition function of an particle ensemble with the Maxwell distribution function of particles on kinetic energies. This system corresponds to an ideal monatomic gas. We have, according to the definition (2.23) of the partition function,

$$Z = \frac{1}{n!} \int \exp\left(-\frac{E}{T}\right) \prod_i \frac{d\mathbf{p}_i d\mathbf{r}_i}{(2\pi\hbar)^3}$$

where n is a number of particles, the total energy of particles equals $E = \sum_i \varepsilon_i$ according to formula (2.12), and the subscript i corresponds to parameters of the i th particle. The factor $1/n!$ accounts for the identical nature of the particles. Using $\varepsilon_i = p_i^2/(2m)$, we have

$$Z = z^n/n!$$

where z is the partition function of an individual particle which equals

$$z = \int \exp\left(-\frac{p^2}{2mT}\right) \cdot \frac{4\pi p^2 dp}{(2\pi\hbar)^3} d\mathbf{r} = \left(\frac{mT}{2\pi\hbar^2}\right)^{3/2} \Omega$$

Here Ω is the system volume. Using the Stirling formula $n! \approx (2\pi n)^{-1/2}(n/e)^n$ for large n , where e is the natural logarithm base, we finally obtain for the partition function of the ensemble of structureless particles

$$Z = \left(\frac{mT}{2\pi\hbar^2}\right)^{\frac{3n}{2}} \left(\frac{e\Omega}{n}\right)^n, \quad \ln Z = n \ln \left[\frac{e}{N} \left(\frac{mT}{2\pi\hbar^2}\right)^{\frac{3}{2}} \right] \quad (2.32)$$

where N is the number density of particles. Note that the value $\ln Z$ is the additive function of individual particles, in this case of a weak interaction between particles.

2.9 Fermi–Dirac and Bose–Einstein Statistics

If we have a system of identical particles, there is an additional interaction between them depending on the type of statistics that these particles obey. *Bose–Einstein statistics* is valid for a system of identical particles with integer-valued spin. Then the total wave function of particles is symmetric with respect to the permutation of any two particles. From this it follows that any number of particles may be found in one state. *Fermi–Dirac statistics* applies to a system of identical particles with half-integral spin. Then the total wave function of particles is antisymmetric with respect to permutation of any two particles, i.e. it equals zero for the same state of two particles. It corresponds to the *Pauli exclusion principle*, so that two particles can not be found in the same state. In particular, electrons obey Fermi–Dirac statistics; at low temperatures the Pauli exclusion principle, which forbids the location of two particles in the same state, determines the behavior of a system of electrons. Hence this principle is the basis of the nature of atomic systems.

As a matter of fact, a certain symmetry of the total wave function of many identical particles means the existence of an interaction between particles called the *exchange interaction*.

In particular, repulsion due to the exchange interaction prohibits electrons from approaching each other. Let us determine the mean number of particles in a state for each symmetry of the wave function of particles as in formula (2.18), which corresponds to noninteracting particles. Write the Boltzmann formula (2.18) for the probability that a particle is found in one state of a group i in the form

$$w_i = \exp\left(\frac{\mu - \varepsilon_i}{T}\right) \quad (2.33)$$

Here w_i is the probability of a state i being occupied by a particle and μ is the *chemical potential* of the distribution, so that the constant in formula (2.18) is equal $C = \exp(\mu/T)$.

Now let us determine the average number of particles for Bose–Einstein statistics, taking w_i of formula (2.33) as the probability that one particle from the ensemble of particles occupies this state. Because Bose–Einstein statistics permits any number of particles to be found in this state, the probability that two particles occupy this state is w_i^2 . The probability of m particles being in this state is w_i^m , so that the average number of particles in this state is

$$\frac{\bar{n}_i}{g_i} = \sum_{m=1}^{\infty} w_i^m = \frac{w_i}{1 - w_i} = \frac{1}{\exp\left(\frac{\varepsilon_i - \mu}{T}\right) - 1} \quad (2.34)$$

Note that we refer the index i to a group of states which number is g_i .

Let us obtain the *Bose–Einstein distribution* (2.34) in other way, similar to that used to deduce the Boltzmann formula (2.18). As before, we divide states of the particle system in groups and use the Gibbs principle together with formula (2.13) which allows one to distribute particles over groups in an independent way. Now let us determine the number of ways $p(n_i)$ of distributing n_i particles over g_i states inside this group of states. We take n_i particles and g_i states as elements of some set and construct sequences from these elements such that the first place occupies a state and other elements are arranged in a random way. Then we consider the number of particles which are found after the corresponding state and before the next one as the number of particles in a given state for this method of distributing particles by states. The number of ways to make different distributions is equal to $(g_i + n_i - 1)!$, and among them are identical ones which can be obtained by permutation of states or particles. Hence the total number of ways to distribute particles by states for Bose–Einstein statistics is

$$p(n_i) = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

Thus, instead of equation (2.15) we get in this case, $g_i \gg 1$, $n_i \gg 1$

$$\sum_i \frac{d \ln p(n_i)}{dn_i} (n_i = \bar{n}_i) dn_i = \sum_i (\ln(g_i + \bar{n}_i) - \ln g_i - \ln \bar{n}_i) dn_i = 0$$

Repeating the operations which were used to deduce formula (2.18) and denoting $C = \exp(-\mu/T)$, we obtain on the basis of this relation the Bose–Einstein formula (2.34) instead of (2.18).

In the case of Fermi–Dirac statistics, we repeat the derivation of the Boltzmann formula (2.18), taking into account the exchange interaction of particles which prohibits the location

of two particles in the same state. Then let us take a group of g_i states with energy ε_i and arrange among them n_i particles. This can be done in

$$p(n_i) = C_{g_i}^{n_i} = \frac{g_i!}{n_i!(g_i - n_i)!}, \quad n_i \leq g_i$$

numbers of ways. Because the total number of ways of arranging particles by states is given by formula (2.13), we have in the case $g_i \gg 1$, $n_i \gg 1$ for Fermi–Dirac statistics

$$\sum_i \frac{d \ln p(n_i)}{dn_i} = \sum_i \ln \frac{n_i}{g_i - n_i}$$

Repeating the operations for deducting formula (2.18), using (2.16) and (2.17), we obtain finally the *Fermi–Dirac distribution*

$$\bar{n}_i = \frac{g_i}{\exp\left(\frac{\varepsilon_i - \mu}{T}\right) + 1} \quad (2.35)$$

where we introduce the chemical potential μ instead of the constant C by analogy with Bose–Einstein statistics. This gives for the average number of particles in one state:

$$\bar{n}_i = \frac{1}{\exp\left(\frac{\varepsilon_i - \mu}{T}\right) + 1} \quad (2.36)$$

In the limit $\bar{n}_i \ll 1$ formulae (2.34) and (2.36) for the population numbers of the Bose–Einstein and Fermi–Dirac statistics transform into the Boltzmann formula (2.18). This limit corresponds to the criterion:

$$\exp\left(\frac{\varepsilon_i - \mu}{T}\right) \gg 1$$

The chemical potential μ in formulae (2.33) to (2.36), as well as the constant C in the Boltzmann formula (2.18), is determined by the normalization condition. In particular, for an ensemble of free particles which obey Bose–Einstein or Fermi–Dirac statistics this condition has the form:

$$N = g \int_0^\infty \frac{4\pi p^2 dp}{(2\pi\hbar)^3} \cdot \left[\exp\left(\frac{\varepsilon_i - \mu}{T}\right) \pm 1 \right]^{-1} \quad (2.37)$$

Here N is the number density of particles; g is the statistical weight of particles depending on their spin S , so that $g = 2S + 1$; the particle energy ε is connected with the momentum p by the relation $\varepsilon = p^2/(2m)$, and the sign $\pm$ depends on the type of statistics. Introducing the parameter $z = \mu/T$, one can rewrite this relation in the form:

$$N = g \frac{(mT)^{3/2}}{\pi^2 \sqrt{2}\hbar^3} \int_0^\infty \frac{\sqrt{x} dx}{\exp(x - z) \pm 1}$$

Thus, in the case when the probability of a particle's location in one state is comparable to one, the distribution of particles by states depends on the statistics of these particles. In the limit, when this probability is small, we have the Boltzmann distribution of particles by states.

2.10 Distribution of Particle Density in External Fields

The Boltzmann formula (2.18) allows us to analyze the distribution function of particles in external fields. As an example of this, consider the distribution of particles in a gravitational field. In this case formula (2.18) gives $N(x) \sim \exp(-U/T)$, where U is the potential energy of the particle in an external field. For the gravitational field we have $U = mgh$, where m is the particle mass, g is the free fall acceleration and h is the altitude above the Earth's surface. Thus formula (2.18) has the form in this case:

$$N(h) = N(0) \exp\left(-\frac{mgh}{T}\right) \quad (2.38)$$

where $N(z)$ is the molecule number density at an altitude z . This distribution is called the *barometric distribution*. For atmospheric air at room temperature we have $mg = 0.11\text{km}^{-1}$, i.e. the atmospheric pressure drops noticeably at altitudes of several kilometers.

Let us consider one more example of field influence on the particle distribution. We consider a quasineutral *plasma*, so that the Coulomb field of a charged particle changes the distribution of the surrounding charged particles. As a result, the Coulomb field of this particle is shielded at some distance from it. For definiteness, let us consider a positively charged plasma particle as a test case and assume that charged particles in the plasma have a charge $\pm e$ (the electron charge). Then in a vacuum the electric potential φ of a test charged particle on a distance r from it is equal to

$$\varphi = \frac{e}{r} \quad (2.39)$$

In the presence of other charged particles in the plasma, the electric potential of a test particle is determined by the Poisson equation

$$\Delta\varphi = 4\pi e(N_- - N_+)$$

Here N_- , N_+ are the number densities of negatively and positively charged plasma particles, which according to formula (2.18) are equal to

$$N_- = N_o \exp\left(\frac{e\varphi}{T}\right), \quad N_+ = N_o \exp\left(-\frac{e\varphi}{T}\right)$$

where N_o is the average number density of charged particles of the plasma and T is the plasma temperature, i.e. the temperature of charged particles. Thus the Poisson equation takes the form:

$$\Delta\varphi = 8\pi e N_o \sinh\left(\frac{e\varphi}{T}\right) \quad (2.40)$$

This equation is valid at large distances from a test particle compared with the average distance between charged particles $N_o^{-1/3}$. At small distances from a test particle, where other charged particles are absent, the right-hand side of the Poisson equation is zero, and the Coulomb electric potential of this particle is given by formula (2.39).

Taking into account that the electric potential of the particle does not depend on angle, we have for distances where $e\varphi \ll T$:

$$\frac{1}{r} \frac{d^2}{dr^2}(r\varphi) = \frac{8\pi N_o e^2}{T} \varphi$$

The solution of this equation, which is transformed into (2.39) at small distances r , has the form:

$$\varphi = \frac{e}{r} \exp\left(-\frac{r}{r_D}\right), \quad r_D = \sqrt{\frac{T}{8\pi N_o e^2}} \quad (2.41)$$

The value r_D is called the *Debye–Hückel radius*. It characterizes a distance of *shielding of electric fields in the plasma* and is one of the basic plasma parameters. By definition, we call an ionized gas a plasma if the Debye–Hückel radius of this system is small compared to its dimension.

This characteristic shielding of the particle field takes place if the shielding distance r_D is large compared with the average distance between charged particles in the plasma $N_o^{-1/3}$. Omitting numerical factors, we obtain this criterion in the form:

$$\frac{e^2 N_o^{1/3}}{T} \ll 1 \quad (2.42)$$

According to this criterion, the typical energy of interaction of charged particles in a plasma or the interaction energy at the average distance between charged particles $e^2 N_o^{1/3}$ is small compared with the thermal energy of particles ($\sim T$). If this criterion is valid, most of the time the charged particles of the plasma are free. This relation is the criterion for an *ideal plasma* that is similar to a gas.

2.11 Fluctuations in a Plasma

We consider an ideal quasineutral plasma that, along with neutral particles, contains electrons and ions of identical charge density (for simplicity, we assume the ion charge to be equal to that of the electron). The mean potential energy of a test charged particle or a typical interaction potential between nearest charged particles is small compared with the typical kinetic energy of this charged particle, which is the definition of an ideal plasma, which in turn is similar to a gas of electrons and ions. The number density of neutral particles of an ideal plasma can exceed that of charged particles, but some properties of this plasma would be determined by charged particles due to the long-range interaction between them. One of the properties of an ideal plasma is the screening of fields in it due to the displacement of charged particles under the action of these fields. A typical distance for this screening is the Debye–Hückel radius (2.41), and the screening results from the displacements of charged particles whose distance from a test charged particle does not exceed the Debye–Hückel radius (2.41). The location of a large number of charged particles in a sphere of the Debye–Hückel radius can also be the definition of an ideal plasma.

Displacements of charged particles in an ideal plasma create a plasma potential that causes an energy change for a charged particle inserted in a plasma through its boundary. Our goal now is to determine the average plasma potential together with the distribution function over the plasma potentials. According to formula (2.41) the potential interaction energy for a test ion with other ion is equal to

$$U = e\varphi = \frac{e^2}{r} \exp\left(-\frac{r}{r_D}\right)$$

so that the mean potential energy of a test ion in an ideal plasma is

$$\begin{aligned} \overline{U} &= \int_0^\infty \frac{e^2}{r} \exp\left(-\frac{r}{r_D}\right) \left[N_o \exp\left(-\frac{e\varphi}{T}\right) - N_o \exp\left(\frac{e\varphi}{T}\right) \right] \cdot 4\pi r^2 dr \\ &= -\frac{e^2}{2r_D}, \quad e\varphi \ll T \end{aligned} \quad (2.43)$$

where we assume the temperatures of electrons and ions to be identical. For an ideal plasma, if the criterion (2.42) is fulfilled the mean potential energy (2.43) of a charged plasma particle is small compared with its thermal energy

$$\overline{U} \ll T$$

Note that this potential energy is identical for positively and negatively charged particles (for ions and electrons).

Using the same method one can find the mean square for the ion or electron potential energy

$$\begin{aligned} \overline{U^2} &= \int_0^\infty \frac{e^4}{r^2} \exp\left(-\frac{2r}{r_D}\right) \left[N_o \exp\left(-\frac{e\varphi}{T}\right) + N_o \exp\left(\frac{e\varphi}{T}\right) \right] \cdot 4\pi r^2 dr \\ &= 4\pi N_o e^4 r_D = \frac{T}{2} \frac{e^2}{r_D}, \quad e\varphi \ll T \end{aligned} \quad (2.44)$$

and

$$\frac{\overline{U^2}}{T^2} \sim \frac{e^2}{r_D T} \ll 1$$

for an ideal plasma. Next,

$$\frac{\overline{U^2}}{(\overline{U})^2} = 16\pi N_o r_D^3 \gg 1$$

according to the definition of an ideal plasma, because many charged particles are located inside a sphere of radius r_D . Therefore we ignore the value $\overline{U}$ in the expression for the

distribution function over the potential energies $f(U)$ of charged particles, and the distribution function in accordance with formula (2.4) has the form

$$f(U)dU = \frac{1}{\sqrt{2\pi\Delta U^2}} \exp\left[-\frac{U^2}{2\Delta U^2}\right] = \frac{dU}{2\pi e^2 \sqrt{2N_o r_D}} \exp\left(-\frac{U^2}{8\pi N_o e^4}\right) \quad (2.45)$$

where $\Delta U = \sqrt{U^2}/2$ is the fluctuation of the potential energy for a charged particle.

Thus the location of a charged particle in an ideal plasma causes the displacement of surrounding particles. In turn this provides shielding of the particle field by plasma particles. Along with this, the surrounding charged particles create random fields near a test charged particle with large fluctuations with respect to the mean particle energy.

We now determine the mean free path of a charged particle (electron or ion) in an ideal plasma as a result of scattering in a random field, allowing for the potential of a plasma field which varies by $\sim \Delta U$ over a distance of $\sim r_D$. Then the particle energy varies by $\sim \Delta U$ over a distance of $\sim r_D$, and since this change has an arbitrary sign, the typical energy of a charged particle $\sim T$ results from $\sim (T/\Delta U)^2$ acts of scattering. From this we estimate the mean free path λ of a charged particles, that is a distance over which the particle energy varies by $\sim T$:

$$\lambda \sim r_D \left(\frac{T}{\Delta U}\right)^2 = \frac{1}{2\pi N_o (e^2/T)^2} \quad (2.46)$$

As is seen, the mean free path of a charged particle in an ideal plasma due to its scattering by plasma non-uniformities is inversely proportional to the mean number density of charged particles and is proportional to the temperature squared.

3 Bose–Einstein Distribution

3.1 Laws of Black Body Radiation

Below we consider systems of particles or quasiparticles which are subject to Bose–Einstein statistics. These systems include photons and the vibrational excitations of molecules and atoms of solids (phonons). We use the general character of interaction of particles or quasiparticles in such systems, so that for most of the period of observation they are free. This allows us to distribute the particles by states. A weak interaction in these systems creates a distribution according to *Bose–Einstein statistics*.

We first consider a system of photons as elementary particles of an electromagnetic field. In the case of so-called *equilibrium radiation* the number of photons of a given frequency is determined by the interaction of this radiation with a gas or with walls. For definiteness, let us take a vessel with walls having a temperature T , so that the radiation field is located inside this vessel. Then interaction between photons of different frequencies proceeds via the absorption and emission of radiation by the walls. The number of photons is not fixed by external conditions, but is determined by the interaction with the walls. This radiation inside the vessel is called *black body radiation*. According to the Boltzmann formula (2.18), the relative probability that n photons of energy $\hbar\omega$ are found in a given state is equal to $\exp(-\hbar\omega n/T)$. Then the mean number of photons $\bar{n}_\omega$ in this state is:

$$\bar{n}_\omega = \frac{\sum_n n \exp(-\frac{\hbar\omega n}{T})}{\sum_n \exp(-\frac{\hbar\omega n}{T})} = \frac{1}{\exp(\frac{\hbar\omega}{T}) - 1} \quad (3.1)$$

This formula is called the *Planck distribution* and corresponds to the *Bose–Einstein distribution* (2.34). Then the *chemical potential* μ is zero, which occurs when the number of particles of the system is not conserved. In this case determination of the distributions of particles by states is based on equations (2.12), (2.15), while equation (2.11) is excluded from consideration. Hence the chemical potential is absent in the expression for the population of states, i.e. $\mu = 0$.

Let us introduce the *spectral radiation density* U_ω as the energy of radiation per unit time, per unit volume, and per unit frequency range. Below we obtain expressions for this quantity. The radiation energy in a frequency range from ω to $\omega + d\omega$ according to the above definition is $\Omega U_\omega d\omega$, where Ω is the vessel volume. On the other hand, this value is $2\hbar\omega n_\omega \Omega d\mathbf{k}/(2\pi)^3$, where the factor 2 accounts for the two polarizations of an electromagnetic wave, $\mathbf{k}$ is the photon wave number, $\Omega d\mathbf{k}/(2\pi)^3$ is the number of states in a given element of the phase space, and n_ω is the number of photons for one state. We take into account that the electromagnetic wave is transverse, i.e. the electric field strength $\mathbf{E}$ of the wave is directed perpendicular to the propagation direction, which is determined by the vector $\mathbf{k}$. Using the dispersion relation

$\omega = ck$ between the frequency ω and wave vector k of the photon (c is the velocity of light), we have from the above relations

$$U_\omega = \frac{\hbar\omega^3}{\pi^2 c^3} n_\omega \quad (3.2)$$

By replacing the Planck distribution (3.1) in formula (3.2), we obtain the *Planck radiation formula* which has the form

$$U_\omega = \frac{\hbar\omega^3}{\pi^2 c^3 [\exp(\hbar\omega/T) - 1]} \quad (3.3)$$

In the classical limiting case $\hbar\omega \ll T$ this formula is transformed into the *Rayleigh–Jeans formula*

$$U_\omega = \frac{\omega^2 T}{\pi^2 c^3}, \quad \hbar\omega \ll T \quad (3.4)$$

Since this formula corresponds to the classical limit, it does not contain the Planck constant. The other limiting case yields the *Wien formula*

$$U_\omega = \frac{\hbar\omega^3}{\pi^2 c^3} \exp\left(-\frac{\hbar\omega}{T}\right), \quad \hbar\omega \gg T \quad (3.5)$$

Let us evaluate the radiation flux emitted by a black body surface on the basis of formula (3.3). It may be defined as the radiation flux coming from a hole in a cavity with opaque walls if this cavity contains the black body radiation. In addition, the black body surface absorbs all the incident radiation. A black body surface emits an isotropic energy flux equal to $cU_\omega d\omega$ per frequency interval $d\omega$, so that the energy flux is

$$\frac{d\Theta}{4\pi} c \int_0^\infty U_\omega d\omega$$

which is emitted in an elementary solid angle $d\Theta = d\varphi d\cos\theta$. Taking the projection of elementary radiation fluxes onto the resultant flux, which is perpendicular to the emitting surface, we obtain for the resultant radiation flux which leaves the emitting surface:

$$J = \int_0^{\pi/2} \int_0^\infty \frac{c}{4\pi} U_\omega d\omega \, 2\pi \cos\theta d\cos\theta = \frac{c}{4} \int_0^\infty U_\omega d\omega = \sigma T^4 \quad (3.6)$$

where θ is the angle between the normal to the surface and the direction of motion of an emitting photon. The constant σ is called the *Stefan–Boltzmann constant*. We use

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^2}{15}$$

and the Stefan–Boltzmann constant equals

$$\sigma = \frac{1}{4\pi^2 c^2 \hbar^3} \int_0^\infty (e^x - 1)^{-1} x^3 dx = \frac{\pi^2}{(60c^2 \hbar^3)} = 5.67 \cdot 10^{-12} \frac{\text{W}}{\text{cm}^2 \text{K}^4}$$

Equation (3.6) is called the *Stefan–Boltzmann law*.

The dependence of the radiation flux (3.6) on parameters may be obtained in the simplest way on the basis of dimensionality considerations. Indeed, the result must depend on the following parameters: T – the radiation temperature; $\hbar$ – the Planck constant; and c – the velocity of light. From these parameters one can make only one combination with the dimensions of flux. This gives $J \sim T^4 \hbar^{-3} c^{-2}$, which coincides with formula (3.6).

We now evaluate the partition function of equilibrium radiation located in a closed vessel of volume V with wall temperature T . We have for the partition function of one oscillation mode of frequency ω

$$Z_\omega = \sum_n \exp\left(-\frac{\hbar\omega n}{T}\right) = \left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right]^{-1}$$

where n is the number of excited vibrations. Because individual oscillations of different modes are independent, the total partition function of the radiation field is the product of the partition functions of individual modes, and the logarithm of the partition function is the sum of the corresponding logarithms. Thus, we have for the logarithm of the total partition function

$$\begin{aligned} \ln Z &= \int \frac{2d\mathbf{r}d\mathbf{k}}{(2\pi)^3} \ln Z_\omega = \frac{V}{2\pi^2 c^3} \int \omega^2 d\omega \ln Z_\omega = \frac{VT^3}{3\pi^2 c^3 \hbar^3} \int_0^\infty x^2 dx \ln \frac{1}{1 - e^x} \\ &= \frac{\pi^2}{45} \frac{VT^3}{c^3 \hbar^3} = \frac{4\sigma T^3 V}{3c} \end{aligned} \quad (3.7)$$

Here $k = \omega/c$ is the photon wave vector, the factor 2 accounts for two polarizations of photons, and σ is the Stefan–Boltzmann constant.

3.2 Spontaneous and Stimulated Emission

Equilibrium radiation can result not only from interaction with the walls of a vessel, but also from processes of absorption and emission of photons by atomic particles. The most efficient process of this kind corresponds to transitions involving discrete states of atoms. These processes are described by the scheme



Assume that the criterion

$$N\sigma_{abs}(\omega)L \gg 1 \quad (3.9)$$

is fulfilled, where N is the number density of atoms, L is a typical size of the system, and $\sigma_{abs}(\omega)$ is the atomic absorption cross section for photons of frequency ω . Equilibrium radiation exists in the system at frequencies for which this criterion is fulfilled, i.e. the equilibrium is supported by processes (3.8). The temperature of this equilibrium radiation coincides in this case with the temperature of atomic excitations.

Let us analyze the equilibrium of an atom with a radiation field in this case. Denote the number of photons in one state of a given group by n_ω . This value increases by one as a result of the transition in the ground (lower) state and decreases by one after absorption of a photon. Because the absorption rate is proportional to the number of photons in the gaseous volume, we write the probability of photon absorption by one atom per unit time in the form:

$$W(i, n_\omega \rightarrow f, n_\omega - 1) = A n_\omega \quad (3.10a)$$

where we denote the lower state by the subscript i and the upper state by the subscript f . Formula (3.9) accounts for the fact that no transitions occur in the absence of photons ($n_\omega = 0$) and only one-photon transitions take place. The value A does not depend on the electromagnetic field strength and is determined only by the parameters of the atomic particle.

The probability per unit time of an atomic transition with emission of a photon can be represented in the form:

$$W(f, n_\omega \rightarrow i, n_\omega + 1) = \frac{1}{\tau} + B n_\omega \quad (3.10b)$$

Here $1/\tau$ is the reciprocal lifetime of the upper state with respect to the radiative transition in the lower state or the rate of *spontaneous emission* of an excited atom which proceeds in the absence of an external field, and the quantity B refers to *stimulated radiation* by an external electromagnetic field. Both values depend only on the properties of the atomic particle. The quantities A and B are known as the *Einstein coefficients*.

The relationship between the parameters $1/\tau$, A and B can be obtained on the basis of the analysis of thermodynamic equilibrium in which are found both atomic particles and photons. Then the relations between the number densities of atomic particles in the excited N_f and ground N_i states are given by the Boltzmann law (2.20):

$$N_f = \frac{g_f}{g_i} N_i \exp\left(-\frac{\hbar\omega}{T}\right)$$

where g_i and g_f are the statistical weights of the ground and excited states, and the photon energy $\hbar\omega$ coincides with the difference between the energies of these states. The mean number of photons in a given state is determined by the Planck distribution (3.1). Under thermodynamic equilibrium, the number of emission transitions per unit time must be equal to the number of absorption transitions per unit time. Using this relation for a unit of volume, we have

$$N_i W(i, \bar{n}_\omega \rightarrow f, \bar{n}_\omega - 1) = N_f W(f, \bar{n}_\omega - 1 \rightarrow i, \bar{n}_\omega)$$

On the basis of formulae (3.10) this relation can be transformed to the following form:

$$N_i A \bar{n}_\omega = N_f (1/\tau + B \bar{n}_\omega) \quad (3.11)$$

Using the above formulae for the relation between the equilibrium number densities of atomic particles and the equilibrium average number of photons in a given state, we obtain for values of the Einstein coefficients $A = g_f/(g_i\tau)$ and $B = 1/\tau$. This leads to the following formulae for the rates of the one-photon processes:

$$W(i, n_\omega \rightarrow f, n_\omega - 1) = \frac{g_f}{g_i\tau} n_\omega, \quad W(f, n_\omega \rightarrow i, n_\omega - 1) = \frac{1}{\tau} + \frac{n_\omega}{\tau} \quad (3.12)$$

Note that the condition of thermodynamic equilibrium requires the presence of stimulated radiation, which is described by the last term and is of fundamental importance.

3.3 Vibrations of Diatomic Nuclei

The Planck formula (3.1) is valid for any system of harmonic oscillators. Below we demonstrate it for the example of *diatomic molecules*. Introduce the interaction potential $U(R)$ between two atoms at a distance R between them; usually this has the form of a potential well with a minimum at a distance $R = R_e$, so that near the minimum the interaction potential has the form

$$U(R) = -D + \frac{\kappa}{2}(R - R_e)^2, \quad \kappa = \frac{\partial^2 U(R)}{\partial R^2} \Big|_{R=R_e} \quad (3.13)$$

and D is the depth of the potential well for pair interaction, so that in the classical case it is the dissociation energy of the diatomic molecule. This interaction potential leads to the Schrödinger equation for the wave function Ψ which describes the relative motion of atoms in the diatomic molecules:

$$-\frac{\hbar^2}{2\mu} \frac{d^2 \Psi}{dx^2} + \frac{\kappa}{2} x^2 \Psi = E \Psi$$

where $x = R - R_e$, $\mu = m/2$ is the reduced mass of nuclei, and m is the mass of one atom. From the solution of this equation we get the spectrum of vibrations of the molecule in the form

$$E = \hbar\omega_o \left(v + \frac{1}{2}\right), \quad \omega_o = \sqrt{\frac{\kappa}{\mu}} = \sqrt{\frac{2\kappa}{m}} \quad (3.14)$$

where v is the so-called *vibrational quantum number* (an integer), and the energy of the vibrational states starts from the bottom of the potential well.

Now let a test molecule be surrounded by atomic particles which establish a certain temperature T for the molecule as a result of collisions. Then according to the Boltzmann formula (2.18), the probability of the molecule being on the v th vibrational level equals

$$P_v = C \exp\left(-\frac{\hbar\omega_o v}{T}\right)$$

From this we find the average number of molecule excitations

$$\bar{v} = \frac{\sum_v v P_v}{\sum_v P_v} = \left[\exp\left(\frac{\hbar\omega_o}{T}\right) - 1 \right]^{-1}$$

which coincides with the Planck formula (3.1). The difference from the case of a radiation field is that here we have oscillators of one frequency, while an electromagnetic field includes oscillators of different frequencies.

3.4 Structures of Solids

The attractive interaction of atoms leads to the formation of condensed systems of these atoms. There are two types of bond inside the system. In the first case, related to metals, the valence electrons of atoms belong to all the atomic nuclei, and the electron subsystem determines for the most part the properties of the system, including the binding of atomic particles. In the second case, interacting atoms conserve their individuality in a condensed system of atoms, or valence electrons can transfer partially to only neighboring atoms, so that interaction in such a system proceeds mostly between the atoms or their ions. Systems in which the interactions between neighboring atoms dominate, as occurs in rare gas solids are systems with a *short-range interaction* between atoms. We will use this system for our demonstration.

We now consider the basic concepts of the crystal structures of atoms, since some processes in such systems are the subject of our discussion below. In solids or crystals (systems of a practically infinite number of atoms) atoms form a *crystal lattice* which is characterized by its translational symmetry. A lattice with such a periodicity is named a *Bravais lattice*, and the coordinates of atoms in the Bravais lattice are given by the relation

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad (3.15)$$

where n_1 , n_2 and n_3 are integers, and the vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ form the basis of this lattice. Denoting as usual the unit vectors along the axes x , y and z as $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$, one can express through these vectors the basis vectors of a given lattice. Table 3.1 contains the expressions for the basis vectors for the simplest crystal lattices.

Let us consider the *close packed structures* whose atoms are bonded with a short-range interaction. Such structures are formed by hard balls of identical size which are located in a box with hard walls. Each internal ball of this structure has 12 nearest neighbors, so that

Table 3.1. The basis vectors for the simplest lattice; a is the lattice constant. Here *fcc* refers to the *face-centered cubic lattice*, *bcc* refers to the *body-centered cubic lattice*, and *hex* relates to the hexagonal lattice.

Lattice	$\mathbf{a}_1/a$	$\mathbf{a}_2/a$	$\mathbf{a}_3/a$
Cubic	$\mathbf{i}$	$\mathbf{j}$	$\mathbf{k}$
<i>fcc</i>	$(\mathbf{j} + \mathbf{k})/2$	$(\mathbf{i} + \mathbf{k})/2$	$(\mathbf{i} + \mathbf{j})/2$
<i>bcc</i>	$(\mathbf{j} + \mathbf{k} - \mathbf{i})/2$	$(\mathbf{i} + \mathbf{k} - \mathbf{j})/2$	$(\mathbf{i} + \mathbf{j} - \mathbf{k})/2$
<i>hex</i>	$\mathbf{i}$	$\mathbf{i}/2 + \mathbf{j}\sqrt{3}/2$	$\mathbf{j}\sqrt{\frac{1}{6}}[1 + (-1)^{n_3}] + \mathbf{k}\sqrt{\frac{2}{3}}$
<i>fcc</i>	$\mathbf{i}$	$\mathbf{i}/2 + \mathbf{j}\sqrt{3}/2$	$\mathbf{j}\sqrt{\frac{1}{3}} + \mathbf{k}\sqrt{\frac{2}{3}}$

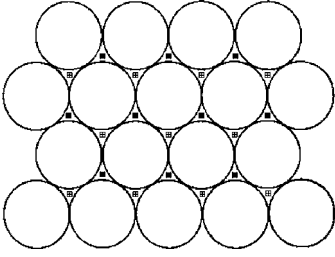


Figure 3.1. Crystal lattices of close packed structures. Circles correspond to positions of atoms-balls of a given layer. Crosses are the positions of atom centers of the previous layer, open squares are the positions of atom centers of the upper layer for the hexagonal structure of the crystal lattice, and filled squares are those for the face-centered cubic lattice.

the *face-centered cubic structure* (fcc) and the *hexagonal structure* are the structures of close packing. In order to show the proximity of these structures, we construct them from balls simultaneously, as shown in Figure 3.1. We first place the balls compactly on a plane, so that each ball touches the 6 nearest ones. Then we construct the second plane of balls by placing the balls in the holes between the balls of the previous layer. The third plane of balls may be constructed in two ways, and then the balls form either the hexagonal or the fcc structure. The projections of balls in the third and first layers coincide for the hexagonal structure and are different for the fcc structure; these structures are represented in Figure 3.2. In Table 3.1 the fcc structure is given for two coordinate systems. The first one reflects the high symmetry of the fcc structure, which along with the periodicity of the lattice is conserved as a result of the following transformations

$$x \longleftrightarrow -x, \quad y \longleftrightarrow -y, \quad z \longleftrightarrow -z, \quad x \longleftrightarrow y \longleftrightarrow z \quad (3.16)$$

Because of the high symmetry of the fcc structure, it occurs more often than the hexagonal one.

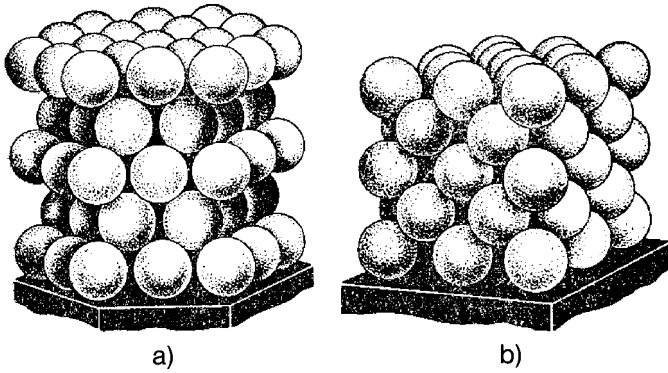


Figure 3.2. Hexagonal (a) and face-centered cubic (b) structures of hard balls.

Let us introduce the *inverse lattice* $\mathbf{K}$ with respect to the Bravais lattice such that the plane wave $\exp(i\mathbf{K}\mathbf{R})$ takes identical values at atom positions, i.e. $\exp(i\mathbf{K}\mathbf{R}) = 1$ or

$$\mathbf{K}\mathbf{R} = 2\pi m \quad (3.17)$$

where m is an integer. Representing the inverse lattice vector in the form

$$\mathbf{K} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3 \quad (3.18)$$

where k_1 , k_2 and k_3 are whole numbers, we have for the basis vectors $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ of the inverse lattice

$$\mathbf{b}_1 = 2\pi \frac{[\mathbf{a}_2 * \mathbf{a}_3]}{\mathbf{a}_1 [\mathbf{a}_2 * \mathbf{a}_3]}, \quad \mathbf{b}_2 = 2\pi \frac{[\mathbf{a}_3 * \mathbf{a}_1]}{\mathbf{a}_2 [\mathbf{a}_3 * \mathbf{a}_1]}, \quad \mathbf{b}_3 = 2\pi \frac{[\mathbf{a}_1 * \mathbf{a}_2]}{\mathbf{a}_3 [\mathbf{a}_1 * \mathbf{a}_2]} \quad (3.19)$$

and we have from the above formulae

$$\mathbf{K} \mathbf{R} = 2\pi(n_1 k_1 + n_2 k_2 + n_3 k_3) \quad (3.20)$$

in accordance with formula (3.17).

Let us construct the *Wigner–Seitz cell* around the origin of the inverse crystal lattice such that all points inside this cell are located closer to a test atom than to other atoms. The Wigner–Seitz cell forms the first *Brillouin zone* of a given lattice. Figure 3.3 represents the Wigner–Seitz cell or the first Brillouin zone for the fcc lattice. This cell forms a regular truncated octahedron whose surface consists of 6 squares and 8 regular hexagons, and the intersection of these figures gives 36 identical edges.

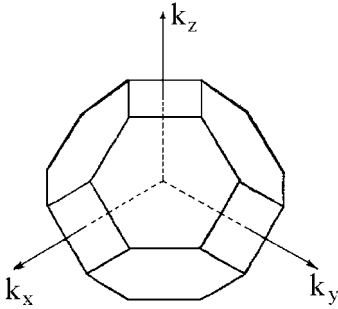


Figure 3.3. The basic Brillouin zone for the face-centered cubic crystal lattice.

In addition to the above notations, the directions of crystal planes are described by the parameters of the vector which is perpendicular to this plane and passes through the origin. These parameters are called the *Miller indices*. For example, if the Miller indices of a given plane are m_1 , m_2 and m_3 , the vector $\mathbf{b} = m_1 \mathbf{i} + m_2 \mathbf{j} + m_3 \mathbf{k}$ is perpendicular to this plane. Moreover, the Miller indices are the minimal whole components of a vector that is perpendicular to a given plane. The Miller indices are denoted as $(m_1 m_2 m_3)$, and the value $\overline{m}_1$ is taken instead of $-m_1$.

If we deal with the surface planes of an elementary crystal cell or with the facets of a small crystalline particle, these planes satisfy a certain symmetry. Let us consider as an example a *truncated octahedron* which has the face-centered cubic structure, so that this structure is characterized by the symmetry (3.16). The surface of this figure consists of 6 squares and 8 hexagons, and the squares are characterized by the Miller indices (100) , (010) , (001) , $(\overline{1}00)$, $(0\overline{1}0)$, $(00\overline{1})$ (where $\overline{1}$ means -1). The sum of these directions is denoted as $\{100\}$, i.e. it is accepted that squares have the directions $\{100\}$. In the same manner, the regular hexagons

of the surface of the truncated octahedron have the direction $\{111\}$. Note that all the planes in each direction are transformed each into other as a result of transformations (3.16) for the face-centered cubic structure.

3.5 Structures of Clusters

We now consider *solid clusters* – crystal systems of a finite number of bound atoms. In contrast to crystals (bulk systems of bound atoms), surface effects are of importance for clusters. We denote by E_n the binding energy of n bound atoms when they form an optimal configuration, and introduce the binding energy of the n th atom as

$$\varepsilon_n \equiv \varepsilon(n) = E_n - E_{n-1} \quad (3.21)$$

Evidently, the maximum binding energy corresponds to the optimal configurations formed by atoms for a given interaction between them. When this configuration relates to a completed geometric figure of atoms, we obtain that the atomic binding energy is larger than that for neighboring numbers of cluster atoms, i.e.

$$\varepsilon(n_m) > \varepsilon(n_m - 1), \quad \varepsilon(n_m) > \varepsilon(n_m + 1) \quad (3.22)$$

Such numbers of cluster atoms are called *magic numbers*.

As an example of a cluster with a magic number of atoms, we consider a cluster of 13 atoms if the interaction of nearest neighbors dominates. The positions of atoms in such a cluster are shown in Figure 3.4 for short-range interaction between atoms. There are two structures of this cluster which can be cut off from the fcc or hexagonal crystals and have 36 bonds between nearest neighbors of such clusters. From Figure 3.4 and formula (3.21) it follows for this and neighboring clusters that $\varepsilon(13) = 5D$ and $\varepsilon(12) = \varepsilon(14) = 4D$, where D is the binding energy per bond. We have from this in accordance with formula (3.22) that $n = 13$ is a magic number for cluster atoms.

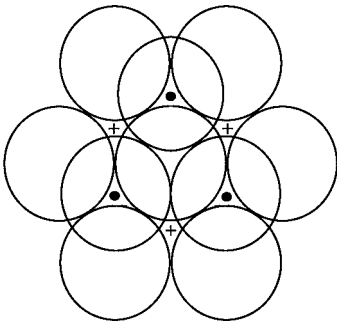


Figure 3.4. Close-packed structures of a cluster consisting of 13 atoms. The basic plane has the direction $\{111\}$ in notations of the Miller indices. If projections of atoms of the upper and lower layers onto the basic plane coincide, the hexahedron is formed as a result of join of centers of nearest surface atoms. This figure belongs to the hexagonal structure. If the above projections are different, the cuboctahedron is formed as a result of join of centers of nearest surface atoms. This figure is an elementary cell of the face-centered cubic lattice.

Let us evaluate the total binding energy E_{fcc} for a *cuboctahedral cluster* of 13 atoms with a pair interaction potential $U(R)$ between atoms. Introducing the distance a between nearest neighbors of this cluster, we have on the basis of Figure 3.4

$$E_{fcc} = -36U(a) - 12U(\sqrt{2}a) - 24U\sqrt{3}a - 6U(2a) \quad (3.23)$$

The Lennard–Jones interaction potential

$$U(R) = D \cdot \left[\left(\frac{R}{R_e} \right)^{12} - 2 \left(\frac{R}{R_e} \right)^6 \right] \quad (3.24)$$

is often used as a model pair interaction potential for atoms. Here R_e is the equilibrium distance between atoms in a diatomic molecule and D is the dissociation energy of the classical molecule. We obtain the total energy of atoms in the cuboctahedral cluster of 13 atoms for this pair interaction potential

$$E_{fcc}(a) = D \cdot \left[76.96 \left(\frac{a}{R_e} \right)^6 - 36.22 \left(\frac{a}{R_e} \right)^{12} \right]$$

From optimization of this expression we have the optimal distance between nearest neighbors $a = 0.990R_e$ and the cluster binding energy $E_{fcc} = 40.88D$.

One can make the same operation for the cluster of 13 atoms of the hexagonal structure (Figure 3.4). The difference between the binding energies for the fcc (cuboctahedral) and *hexagonal cluster* structures results from the interaction of atoms in the lower and upper layers (see Figure 3.4). If we assume the distance between nearest neighbors to be identical for both cases, we express the difference of the atomic binding energies for these structures through the pair interaction potential $U(R)$ of atoms

$$\Delta E = E_{fcc} - E_{hex} = 3U \left(\sqrt{\frac{8}{3}}a \right) + 6U \left(\sqrt{\frac{11}{3}}a \right) - 3U \left(\sqrt{3}a \right) - 6U(2a)$$

where E_{hex} is the binding energy of the hexagonal cluster of 13 atoms. In particular, for the Lennard–Jones interaction potential this formula gives $\Delta E = 0.15D$, i.e. the fcc structure is preferable, but the difference in the binding energies is relatively small ($\approx 0.4\%$), i.e. one can neglect this difference in practice.

Clusters with a pair interaction of atoms also admit the *icosahedral structure*, which is not profitable for bulk systems. Figure 3.5 represents an icosahedral cluster consisting of 13 atoms, and Figure 3.6 gives the *icosahedron* as a geometric figure and the positions of its vertices. In contrast to close packed structures (fcc and hexagonal), the icosahedral structure has no a periodical symmetry and is characterized by two types of distance between nearest neighbors, so that the distance between nearest atoms in the same layer exceeds the distance between nearest atoms in neighboring layers.

Let us consider the icosahedral cluster with the minimal magic number of atoms. Such a cluster consists of 13 atoms (Figure 3.5) and has 12 bonds of length R_1 between the central and surface atoms, and 30 bonds of length R_2 between nearest surface atoms, where

$$R_1 = 0.951R_2$$

In the case of pair interaction between cluster atoms, the total binding energy of atoms in the cluster is

$$E_{ico} = 12U(a) + 30U(1.051a) + 30(1.701a) + 6U(2a)$$

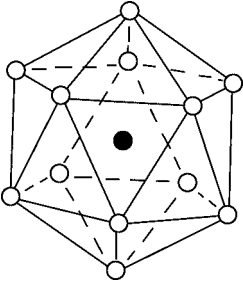


Figure 3.5. The icosahedral cluster consisting of 13 atoms.

In particular, in the case of the Lennard–Jones interaction potential (3.24) between atoms, from optimization of this formula we get $a = 0.964R_e$, $E_{ico} = 44.34D$.

One can see that for a cluster consisting of 13 atoms with the Lennard–Jones interaction potential between atoms the icosahedral cluster structure is preferable to the close-packed structures. The reason is that the number of nearest neighbors is 36 for fcc or hexagonal clusters, and 42 for an icosahedral cluster. Note that each internal atom has 12 nearest neighbors for all these structures. Therefore, because of the two different distances between nearest neighbors for clusters of the icosahedral structure and the identical distances between nearest neighbors for clusters of the close-packed structures, the icosahedral cluster structures are not profitable for large clusters or bulk systems. But for clusters of moderate sizes this structure can compete with the close-packed ones. The presence of the icosahedral structure for clusters of moderate sizes shows that the number of possible structures of clusters exceeds that for bulk systems.

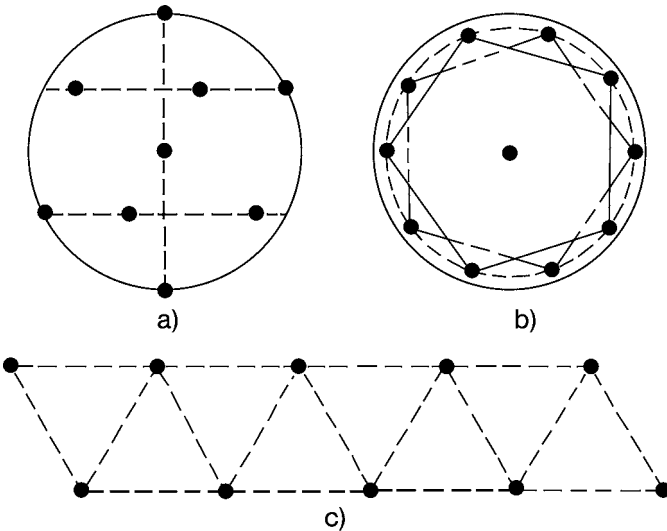


Figure 3.6. The icosahedron as a geometric figure – positions of its center and vertices: (a) side view; (b) top view; (c) developed view of a cylinder in which surface pentagons of the icosahedron are inscribed.

3.6 Vibrations of Nuclei in Crystals

In solids the positions of atoms are characterized by a certain symmetry, i.e. a correlation exists between the positions of the furthest atoms (*long-range order*). At low temperatures the nuclei of a condensed system of atoms move near their equilibrium positions. Evidently, the motion of nuclei has the character of *vibrations*, and the parameters of these vibrations depend on interactions inside the system. This interaction is also responsible for the structure of atoms in the crystal. Below we consider the vibrations of nuclei in the crystal when a pair interaction takes place only between nearest atoms.

At zero temperature the optimal distance between nearest atoms corresponds to the minimum of the pair interaction potential. In addition, it is clear that the frequency ω_o of oscillation of a diatomic molecule with this interaction potential of atoms is the parameter of vibrations for a system of many bound atoms. In the classical limit Newton's equation of relative motion of diatomic atoms has the form

$$\mu \ddot{x} + \kappa x = 0$$

and the solution of this equation $x = C \sin(\omega_o t + \alpha)$, $\omega_o = \sqrt{\kappa/\mu}$ describes the classical vibrations of diatomic nuclei.

Now let us consider classical vibrations of nuclei for a system of many bound atoms. Newton's equation for the vibration of the i th nucleus has the form

$$m \ddot{\mathbf{r}}_i + \kappa \sum_j (\mathbf{R}_{ij} - \mathbf{a}_{ij}) = 0$$

where the vector $\mathbf{R}_{ij}$ is the distance between the i th and j th nuclei, $\mathbf{a}_{ij}$ corresponds to the equilibrium positions of these nuclei, and $\mathbf{r}_i$ is the deviation of the position of the i th atom from its equilibrium position. Assuming these deviations of nuclei to be relatively small and taking x as the direction of the vibrations, we obtain Newton's equations in the form

$$m \ddot{x}_i + \kappa \sum_j X_{ij}^2 (x_i - x_j) = 0$$

Here x_i and x_j are deviations from the equilibrium positions for nuclei i and j , the equilibrium distance between these nuclei is $\mathbf{a} = \mathbf{i}X_{ij} + \mathbf{j}Y_{ij} + \mathbf{k}Z_{ij}$, so that $\mathbf{i}, \mathbf{j}, \mathbf{k}$ are the unit vectors directed along axes x, y, z , and X_{ij}, Y_{ij}, Z_{ij} are projections onto these axes for the vector $\mathbf{a}_{ij}$ which connects nuclei i and j .

We consider the vibrations of nuclei in the form of waves which propagate inside the crystal; such individual waves are termed *phonons*. Taking the parameters of the wave in the form

$$x_i = C \exp(-i\omega t + i\mathbf{k}\mathbf{R})$$

our task is to find the relation between the wave frequency ω and its wave vector $\mathbf{k}$, which is called the *dispersion relation*. Substituting the expression for the wave parameter in Newton's equation, we obtain this relation in the form

$$m\omega^2 = \kappa \sum_j X_{ij}^2 [1 - \exp(i\mathbf{k}\mathbf{R}_{ij})] \quad (3.25)$$

Below we consider long-wave vibrations, so that

$$ka \ll 1 \quad (3.26)$$

This criterion allows one to make the expansion over this small parameter. One can see two types of wave. The *longitudinal wave* propagates in the direction of vibrations of the nuclei, and the dispersion relation (3.25), allowing for the criterion (3.26), has the form

$$\omega^2 = \frac{1}{4a^2} \omega_o^2 k^2 \sum_j X_{ij}^4, \quad \omega_o = \sqrt{\frac{\kappa}{m}} \quad (3.27)$$

Here we assume the crystal to be symmetric, so that terms $\sim ika$ of equation (3.25) are mutually eliminated. Such symmetry takes place for all the examples considered. In the same manner, we have for long *transverse waves*, where the wave vector is directed along axes y and z ,

$$\omega^2 = \frac{1}{4a^2} \omega_o^2 k^2 \sum_j X_{ij}^2 Y_{ij}^2; \quad \omega^2 = \frac{1}{4a^2} \omega_o^2 k^2 \sum_j X_{ij}^2 Z_{ij}^2 \quad (3.28)$$

These dispersion relations for longitudinal and transverse vibrations can be represented in the form

$$\omega = ck \quad (3.29)$$

which is that for photons, and the *speeds of sound* for longitudinal (c_l) and transverse (c_t) acoustic waves are equal to

$$c_l^2 = \frac{1}{4a^2} \omega_o^2 \sum_j X_{ij}^4; \quad c_{1t}^2 = \frac{1}{4a^2} \omega_o^2 \sum_j X_{ij}^2 Y_{ij}^2; \quad c_{2t}^2 = \frac{1}{4a^2} \omega_o^2 \sum_j X_{ij}^2 Z_{ij}^2 \quad (3.30)$$

First we consider the propagation of waves in a crystal when the atoms are arranged in one line. In this case each atom has two nearest neighbors, and $X_{ij} = a$ for nearest neighbors. Hence, formulae (3.30) give

$$c_l = \sqrt{\frac{\kappa}{m}} a = \frac{\omega_o a}{\sqrt{2}}, \quad c_t = 0 \quad (3.31)$$

Another example relates to the *cubic crystal lattice*. Take the frame of reference such that the cube axis z forms an angle θ with the vibration direction, and the direction of vibrations lies in one plane with axes z and x . Then according to formulae (3.27) to (3.29) the speeds of the longitudinal and transverse waves are equal correspondingly to

$$c_l^2 = \omega_o^2 a^2 (\cos^4 \theta + \sin^4 \theta); \quad c_{1t}^2 = 2\omega_o^2 a^2 \sin^2 \theta \cos^2 \theta, \quad c_{2t}^2 = \omega_o^2 a^2 \cos^2 \theta \quad (3.32)$$

From this it follows that the longitudinal speed of sound varies from $\omega_o/\sqrt{2}$ up to $\omega_o/2$, and the transverse speed of sound varies from zero up to $\omega_o/\sqrt{2}$.

Now let us consider a crystal of face-centered structure with a short-range interaction of atoms, i.e. with the interaction of nearest neighbors only. Taking a test atom at the origin of the frame of reference, we find that the centers of its 12 nearest neighbors are located on a sphere of a radius a . First, assume the nearest neighbors of a test atom to be located randomly on this sphere. Then, averaging over positions of these atoms, we get for the longitudinal and transverse speeds of sound, according to formulae (3.30)

$$\begin{aligned} c_l^2 &= 3\omega_o^2 a^2 \int_0^1 \cos^4 \theta d \cos \theta = \frac{3}{5} \omega_o^2 a^2 \\ c_t^2 &= 3\omega_o^2 a^2 \int_0^1 \cos^2 \theta \sin^2 \theta d \cos \theta \int_0^{2\pi} \cos^2 \varphi \frac{d\varphi}{2\pi} = \frac{1}{5} \omega_o^2 a^2 \end{aligned} \quad (3.33)$$

Second, we take a frame of reference such that its axes have the direction $\{100\}$ in the Miller indices notation. Then the coordinates of the 12 nearest neighbors of the test atom are equal to $(0, \pm 1, \pm 1)$, $(\pm 1, 0, \pm 1)$, and $(\pm 1, \pm 1, 0)$, where the coordinates are expressed in units $a/\sqrt{2}$. Taking the x , y and z axes as the directions of the vibrations and the propagation of waves, we obtain for the sound velocity

$$c_l^2 = \frac{1}{2} \omega_o^2 a^2; \quad c_t^2 = \frac{1}{4} \omega_o^2 a^2 \quad (3.34a)$$

Now let us take the frame of reference to be based on the plane $\{111\}$ in the Miller indices notation. Then the positions of the 12 nearest neighbors of a test atom are as shown in Figure 3.4. A test atom is the center of the basis layer and the six nearest neighbors of this layer form a regular hexagon with the test atom as its center. Three atoms of the lower layer and three atoms of the upper layer are located in the hollows of atoms of the basis layer. There are two possibilities for the relative location of atoms in the lower and upper layers. If the projections of these atoms onto the basis plane coincide, all the atoms form the elementary cell of the hexagonal lattice. The geometric figure *hexahedron* is formed as a result by joining the centers of the surface atoms – nearest neighbors. In the other case the projections of the atoms of the lower and upper layers do not coincide, and the atoms form the elementary cell of the face-centered cubic lattice. Then joining the centers of the nearest surface atoms leads to the formation of a different geometric figure – *cuboctahedron*.

Let us take a frame of reference such that a test atom is located at the origin, two axes are located in the basic plane $\{111\}$, and one of these axes passes through an atom. We take the direction of vibrations and the direction of propagation of the wave along these axes. Then according to formulae (3.30) we get for the speeds of sound, depending on the directions of vibration:

$$\frac{c_l^2}{\omega_o^2 a^2} = \frac{5}{8}, \frac{5}{8}, \frac{2}{3}; \quad \frac{c_t^2}{\omega_o^2 a^2} = \frac{5}{24}, \frac{1}{6}, \frac{1}{6} \quad (3.34b)$$

Although the sound velocities depend on the directions of vibration and propagation of waves, these values are concentrated in a narrow range. Let us take the average values of the speeds

of sound and their dispersions on the basis of formulae (3.34). Thus we have

$$c_t^2 = (0.60 \pm 0.07)\omega_o^2 a^2; \quad c_l^2 = (0.20 \pm 0.04)\omega_o^2 a^2 \quad (3.35)$$

Note that in contrast to the cubic structure, the speed of sound of the transverse wave is not zero in any direction of vibration and propagation of the wave because of the larger number of atoms in one cell. Next, the average values of the speeds of sound (3.35) correspond to averaging over the positions of nearest neighbors (3.33). In addition, the speed of sound of the longitudinal wave is higher than that of the transverse one.

3.7 Cluster Oscillations

A bulk system of bound atoms has an infinite number of eigenvibrations. In the cluster case, the number of oscillations is equal to $3n - 5$, where n is the number of cluster atoms. For simplicity, we consider below breathing oscillations for the simplest cluster with completed shells and pairwise atomic interaction, which consists of 13 atoms. The cluster shape does not vary, while the lengths of bonds oscillated in the course of breathing vibrations. Breathing oscillations are characterized by the highest frequency of oscillation.

Assuming a short-range interaction between atoms, we have the following equation for atomic vibration in the cluster:

$$m \ddot{\mathbf{r}}_i + \kappa \sum_j (\mathbf{R}_{ij} - \mathbf{a}_{ij}) = 0$$

where m is the atom mass, κ is the interaction constant, $\mathbf{r}_i$ is the coordinate of the i th cluster atom, $\mathbf{R}_{ij}$ is the distance between the i th and j th atoms, and $\mathbf{a}_{ij}$ is the equilibrium distance between these atoms. Taking $\mathbf{r}_i = \mathbf{a}_i + \delta_i$, where the first term is the equilibrium atom coordinate and the second term is responsible for vibrations, we reduce the above equation to the form

$$m \ddot{\delta}_i + \kappa \sum_j (\delta_i - \delta_j) = 0$$

where the i th and j th atom are nearest neighbors. This set of equations is linear and allows us to find different cluster vibrations. Below we extract from them certain types of vibration.

We first consider for as a demonstration oscillations of diatomic molecules when the vibration equation for the first atom has the form

$$m \ddot{\delta}_1 + \kappa (\delta_1 - \delta_2) = 0$$

and vibrations are directed along the molecule axis. Since the molecule center is motionless during vibrations, we have $\delta_2 = -\delta_1$, and this equation gives the frequency of vibrations

$$\omega_o = \sqrt{\frac{2\kappa}{m}} = \sqrt{\frac{\kappa}{\mu}}$$

where $\mu = m/2$ is the reduced mass of the atoms in the diatomic molecule. This frequency will be used for comparison with oscillation frequencies in clusters.

Let us consider breathing oscillations for a cluster of close-packed structure (face-centered cubic structure or hexagonal structure) with 13 atoms (see Figure 3.4). In the course of such oscillations a cluster conserves its shape, i.e. the distances between nearest neighbors remain identical during this vibration. In this case $\delta_i = \mathbf{n}_i \delta$, where $\mathbf{n}_i$ is the unit vector along the radius vector of a given atom, and δ is the shift in the distance between nearest neighbors from its equilibrium value. Correspondingly, the motion equation for a given surface atom takes the form

$$m \ddot{\delta} + \kappa \delta \sum_j (\mathbf{n}_i - \mathbf{n}_j) = 0$$

where the j th atoms are the nearest neighbors of the i th one. Each surface atom of the cluster under consideration has as nearest neighbors the central atom and four surface atoms, for which $\mathbf{n}_i \mathbf{n}_j = 1/2$, and the resultant force from the nearest neighbors is directed along the bond of this atom with the central one. Hence we have from this equation for the frequency of breathing vibrations of this cluster

$$\omega = \sqrt{\frac{3\kappa}{m}} = \omega_o \sqrt{\frac{3}{2}} = 1.22\omega_o$$

Evidently, since the breathing vibration includes the interaction of all the nearest neighbors, it is characterized by the maximum vibration frequency.

In considering the breathing oscillation of an icosahedral cluster consisting of 13 atoms, we take account of the fact that the cluster has 12 surface atoms as well as clusters of close-packed structure (see Figure 3.5), and there are two lengths of bonds: R , between the surface atom and the central one, and R_o , between two surface atoms. Thus each surface atom partakes in one bond of the length R and five bonds of length R_o . In addition, $R_o = 1.051R$. Since the cluster conserves its symmetric shape during breathing oscillations, the changes in length of the corresponding bonds are connected by the relation

$$\frac{\delta R}{R} = \frac{\delta R_o}{R_o}$$

To determine the frequency of breathing vibrations for this cluster, we use the motion equation for a given surface atom, which has the form

$$m \ddot{\delta} R + \kappa \delta R + \kappa \delta R_o \sum_j \mathbf{n}_i (\mathbf{n}_i - \mathbf{n}_j) = 0$$

where $\mathbf{n}_i$ and $\mathbf{n}_j$ are the radius vectors for a given atom and its nearest neighbors on the cluster surface correspondingly. The sum of forces from nearest neighbors of a given atom is directed along its radius vector. From this we obtain for the frequency of breathing vibrations of this cluster

$$\omega = \sqrt{\frac{\kappa}{m} \left[1 + \frac{5}{2} \left(\frac{R_o}{R} \right)^2 \right]} = 1.37\omega_o \quad (3.36a)$$

since $\mathbf{n}_i(\mathbf{n}_i - \mathbf{n}_j) = R_o/2R$. Since the number of nearest neighbors for the surface atoms of an icosahedral cluster exceeds that for a cluster of close-packed structure, the frequency of breathing vibrations is higher for the icosahedral cluster.

We now consider torsion oscillations of the icosahedral cluster consisting of 13 atoms. We represent this cluster as consisting of a central atom, two pole atoms and two pairs of pentagons, so that the pentagon atoms are located on a circle of a radius $r = 0.851R_o$, and R_o is the distance between the nearest surface atoms (see Figure 3.6). Then if one pentagon is turned with respect to the other, a force arises that tends to return the pentagons to their original positions. Note that in the case of a short-range interaction between atoms, when only nearest neighbors interact, the force acting on a certain pentagon atom results from the two nearest atoms of the other pentagon. The resulting force acting on each atom is directed along a tangent line with respect to a circle in which the pentagon is inscribed. Excluding the rotation of pentagons as a whole around the cluster axis perpendicular to the pentagon planes and passing through their centers, we obtain torsion oscillations in this cluster which are separated from other cluster vibrations and correspond to the turning of pentagons with respect to each other.

As a result of this turning of pentagons, a moment occurs that compels the pentagons to turn back. Nevertheless, in order to use the above formalism, we will consider this problem in terms of atomic displacements. Let the total relative turning of pentagons be $\delta\varphi$, so that the distance between atoms – nearest neighbors, which belong to different pentagons, is

$$R = \sqrt{l^2 + \left[2r \sin\left(\frac{\pi}{10} + \delta\varphi\right)\right]^2} = \sqrt{R_o^2 + 4r^2 \sin^2 \frac{\pi}{5} \cdot \delta\varphi} = R_o + r\delta\varphi$$

where $l = r$ is the distance between pentagons. In order to exclude the simultaneous rotation of pentagons, we take the rotation of the upper pentagon to be $\delta\varphi/2$, and for the lower pentagon to be $-\delta\varphi/2$, in this way using the problem's symmetry. Hence, the shift of a given atom of the upper pentagon is $\delta_i = \mathbf{n}r\delta\varphi/2$, where $\mathbf{n}$ is the unit vector located in the pentagon plane and directed along the tangent to the circle in which this pentagon is inscribed, i.e. this vector is perpendicular to the vector $\mathbf{r}$ that connects a given atom with the pentagon center. Each pentagon atom interacts with two atoms of the other pentagon, giving

$$\sum_j (\delta_i - \delta_j) = \mathbf{k} \cdot 2r \cos \frac{\pi}{5} \cdot \delta\varphi$$

Therefore the equation of motion of a test pentagon atom takes the form

$$m \frac{r}{2} \frac{d^2 \delta\varphi}{dt^2} + 2r\kappa \cos \frac{\pi}{5} \cdot \delta\varphi = 0$$

and the frequency of torsional vibrations is equal to

$$\omega = \sqrt{\frac{4 \cos \frac{\pi}{5} \cdot \kappa}{m}} = 1.27\omega_o \quad (3.36b)$$

A large cluster has many eigenvibrations, and for an icosahedral cluster of 13 atoms, which we have used to demonstrate the general features of cluster vibrations, the number of different

eigenvibrations is 33. Above we have considered two types of cluster vibration which can be separated from the others. In these cases the displacements of atoms during these oscillations create a force on each atom in the direction of these displacements. In other cases several different oscillations may be entangled. As an example, we consider the oscillations of an icosahedral cluster of 13 atoms when the pole atoms move along the axis (see Figure 3.6). One can separate such oscillations into symmetric and asymmetric oscillations with respect to the motion of atoms which have the coordinates z and $-z$. In each of these cases we find that the displacement of the pole atom creates a force acting on the pentagon atoms that on the one hand leads to a simultaneous shift of pentagon atoms in the direction z , and on the other to a shift of pentagon atoms in the radial direction. Thus three vibrations are entangled in this case, so that these vibrations include the motion of pole atoms in the direction z and the motion of pentagon atoms in the same direction and also in radial directions. In these vibrations two regular pentagons are formed by vibrating atoms in the course of vibrations, and these pentagons remain identical but their sizes oscillate. The typical frequency of all the oscillations of this cluster is of the order of ω_o .

3.8 Debye Model

One can consider the normal vibrations of a condensed system of atoms to be individual quasi-particles – phonons. A phonon is an elementary excitation of a system of bound atoms. If the number of such excitations is not large, so that the mutual influence of individual excitations is not essential, one can consider a phonon to be a harmonic vibration with the participation of many atoms. Considering the motion of many atoms as the sum of individual harmonic vibrations, we have a simple form for the description of the excitation of atomic motion in a system of bound atoms. Because of the character of these excitations, phonons are governed by Bose–Einstein statistics.

Let us evaluate the energy which is contained in vibrations of the crystal lattice at low temperatures. The energy per unit volume is equal to

$$E_{ph} = \int \hbar\omega \frac{d\mathbf{k}}{(2\pi)^3} \left[\exp\left(\frac{\hbar\omega}{T}\right) - 1 \right]^{-1}$$

where $\mathbf{k}$ is the wave vector of a phonon and $\hbar\omega$ is the energy of its excitation. Using the dispersion relations for the longitudinal and transverse waves, we obtain at low temperatures

$$E_{ph} = \int \hbar \frac{\omega^3 d\omega}{(2\pi)^3} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \left[\exp\left(\frac{\hbar\omega}{T}\right) - 1 \right]^{-1} = \frac{\pi^2 T^4}{30 \hbar^3} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \quad (3.37a)$$

This formula is similar to the Stefan–Boltzmann formula (3.6), but we also take into account the presence of longitudinal vibrations which are absent in the case of photons. Hence phonons (elementary vibrations of nucleus motion in crystals) are similar to photons (elementary vibrations of the electromagnetic field). From formula (3.37a) we obtain for the *heat capacity* of a crystal at low temperatures

$$C = \frac{\partial E_{ph}}{\partial T} = \frac{2\pi^2 T^3}{15 \hbar^3} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \quad (3.37b)$$

The other limiting case corresponds to high temperatures $\hbar\omega \gg T$, which means the classical limit when each degree of freedom carries the energy T . In this limit the energy per unit volume is equal to

$$E_{ph} = 3NT, \quad E = 3nT \quad (3.38)$$

where N is the number density of crystal atoms, E is the total energy of atoms and n is the total number of atoms. This allows us to represent this energy of phonon excitations as a result of the motion of individual lattice atoms. Since atoms are classical in this limit, one can rewrite formula (3.38) in the form

$$E_{ph} = N(\bar{\varepsilon}_{kin} + \bar{U}), \quad \bar{\varepsilon}_{kin} = \frac{3}{2}T, \quad \bar{U} = \overline{\kappa\Delta^2} = \frac{3}{2}T \quad (3.39)$$

Here $\bar{\varepsilon}_{kin}$ is the average kinetic energy of an individual atom, $\bar{U}$ is its potential energy due to the atom's displacement with respect to its equilibrium position, so that κ is an effective elastic constant according to formula (3.13), and Δ^2 is the square of the displacement. The relationship (3.38) is termed the *Dulong–Petit law*.

Following the *Debye approximation*, we assume that the dispersion relation (3.29) for phonons takes place up to the frequency ω_D , the *Debye frequency*, which is the highest frequency of phonons. We then use the relation for the total number of states per unit volume which is equal to the total classical degrees of freedom for crystal atoms, $3N$ per unit volume

$$3N = \int \frac{d\mathbf{k}}{(2\pi)^3} = \frac{1}{2\pi^2} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \int_0^{\omega_D} \omega^2 d\omega$$

This gives for the Debye frequency

$$\omega_D = \left[\frac{18\pi^2 N}{\left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right)} \right]^{1/3} \quad (3.40)$$

Within the framework of the Debye approximation we find that the energy of crystal excitation, which is connected with the excitation of phonons, depends only on the parameter $\hbar\omega_D/T = \theta_D/T$, where θ_D is the *Debye temperature*. The general expression for the phonon energy has the following form in this approximation

$$\begin{aligned} E_{ph} &= \int \hbar \frac{\omega^3 d\omega}{(2\pi)^3} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \left[\exp\left(\frac{\hbar\omega}{T}\right) - 1 \right]^{-1} \\ &= \frac{1}{2\pi^2} \frac{T^4}{\hbar^3} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \int_0^{\theta_D/T} \frac{x^3 dx}{e^x - 1} \end{aligned} \quad (3.41)$$

In the limiting cases this transforms into formulae (3.37) and (3.39).

Appendix B10 contains the values of the Debye temperatures for solid structures which are obtained at low temperatures along with the parameters of the crystal lattice. Note that

the Debye approximation is a model, and therefore the Debye temperature is determined with a certain accuracy, which is estimated on average as 10%. Because the energy of classical vibrations of lattice atoms is of the order of $M\omega_D^2 a^2$, where M is the atomic mass, and a is the oscillation amplitude, we have that the value $M\omega_D^2 R_e^2$, where R_e is the distance between nearest neighbors, significantly exceeds the binding energy per atom. Table 3.2 contains the ratio of the binding energy per atom ε_{sub} to this value for rare gas solids, and the ratio is small in comparison with one. As is seen from Table 3.2, this ratio satisfies the similarity law.

Table 3.2. The Debye temperatures for solid rare gases.

	Ne	Ar	Kr	Xe	average
θ_D, K	75	92	72	64	
$\omega_D, 10^{12} s^{-1}$	9.8	12	9.4	8.4	
$\varepsilon_{\text{sub}}/(M\omega_D^2 R_e^2), 10^{-4}$	2.1	1.9	1.9	2.2	2.0 ± 0.2

Let us evaluate the partition function Z of the equilibrium phonon gas at low temperatures. By analogy with formula (3.7), we have

$$\ln Z = \frac{\pi^2}{90} \frac{VT^3}{\hbar^3} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right), \quad T \ll \theta_D \quad (3.42)$$

Here we take into account that transverse and longitudinal oscillations occur in the phonon case. From this we obtain that the crystal's specific heat capacity $C = \partial E / \partial T$, where E is the crystal's internal energy, is proportional to T^3 at low temperatures and tends in the classical limit to $3N$, where N is the atom number density, if this value is determined by vibrations of atoms. Figure 3.7 represents this temperature dependence of the crystal heat capacity. In addition, Table 3.3 gives the expressions for some thermodynamic parameters of the Debye crystal in the limiting cases.

Thus, excitation of a crystal lattice can be described as the formation of phonons, and the Debye approximation allows one to determine the bulk parameters of a weakly excited crystal in a simple way.

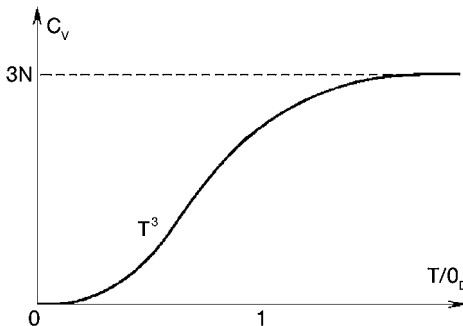


Figure 3.7. The temperature dependence for the crystal heat capacity.

Table 3.3. The limiting expressions for parameters of the Debye crystal.

	$T \ll \theta_D$	$T \gg \theta_D$
$\ln Z$	$-\frac{9}{8}n\frac{\theta_D}{T} + \frac{9\pi^4}{5}n\frac{T^3}{\theta_D^3}$	$3n \ln \frac{T}{\theta_D} + n - \frac{9}{8}\frac{\theta_D}{T}$
C_V	$\frac{4\pi^4}{5}n\left(\frac{T}{\theta_D}\right)^3$	$3n$
E	$\frac{9}{8}n\theta_D + \frac{3\pi^4}{5}n\frac{T^4}{\theta_D^3}$	$3n\left(T + \frac{3}{8}\theta_D\right)$
S	$\frac{12\pi^4}{5}n\left(\frac{T}{\theta_D}\right)^3$	$3n \ln \frac{T}{\theta_D} + 4n$
F	$\frac{9}{8}n\theta_D - \frac{\pi^4}{5}n\frac{T^4}{\theta_D^3}$	$-3n \ln \frac{T}{\theta_D} - nT$

3.9 Distributions in Molecular Gas

Let us consider a gas consisting of diatomic molecules, and find the distribution of molecules on vibrational and rotational levels. The excitation energy of a diatomic molecule has the form

$$E = T_e + \hbar\omega_e \left(v + \frac{1}{2}\right) - \hbar\omega_e x_e \left(v + \frac{1}{2}\right)^2 + B_v J(J+1) \quad (3.43)$$

Here T_e is the electronic excitation energy, so that for the ground electron state of the molecule $T_e = 0$, $\hbar\omega_e$ is the vibrational energy, $\hbar\omega_e x_e$ is the anharmonic vibrational correction, B_v is the rotational constant, and v and J are the vibrational and rotational quantum numbers which are integers; for the ground state $v = J = 0$. Formula (3.43) is the expansion of the excitation energy at low vibrational and rotational excitations.

In the first approximation the *rotational constant* does not depend on the vibrational state and is equal to

$$B = \frac{\hbar^2}{2I} = \frac{\hbar^2}{2\mu R_e^2}$$

where I is the inertial moment of the molecule, μ is the reduced mass of the atoms and R_e is the equilibrium distance between atoms. These parameters for some diatomic molecules are given in Table 3.4. Usually the rotational temperature coincides with the translational one, and we take them to be the gaseous temperature T . According to formula (3.43) the excitation energy of a rotational state with angular momentum J is $BJ(J+1)$, and the statistical weight of this state, i.e. the number of projections of the molecule's angular momentum onto a given direction, equals $2J+1$. Then, assuming $B \ll T$ (as is usually the case) and using the normalization condition $\sum_J N_{vJ} = N_v$, we obtain for the molecule number density at a given vibrational-rotational state and the mean rotational energy ε_{rot} :

$$N_{vJ} = N_v (2J+1) \frac{B}{T} \exp \left[-\frac{BJ(J+1)}{T} \right], \quad \varepsilon_{\text{rot}} = \langle BJ(J+1) \rangle = T \quad (3.44)$$

Correspondingly, we have for the energy and partition function of a gas of diatomic molecules due to the rotational states of diatomic molecules located in a gas in the limit $T \gg B$:

$$E_{\text{rot}} = nT, \quad Z_{\text{rot}} = \frac{T}{B}$$

Table 3.4. Parameters of some homonuclear diatomic molecules in the ground state. (The reduced nuclear mass corresponds to the natural isotope composition of an element and is expressed in atomic mass units, $1.6606 \cdot 10^{-24}$ g).

Dimer	μ , a.u.m.	ω_e , cm^{-1}	$\omega_e x_e$, cm^{-1}	R_e , Å	B , cm^{-1}	D , eV
Ag ₂	53.934	135.8	0.50	2.53	0.049	1.67
Al ₂	13.491	284.2	2.02	2.47	0.205	0.46
Ar ₂	19.97	429.6	1.12	2.103	0.102	3.96
As ₂	37.46	190.9	0.42	2.47	0.028	2.31
Au ₂	98.48	1059	15.7	1.60	1.216	2.8
Ba ₂	5.405	84.1	0.16	4.6	0.009	–
Be ₂	4.506	275.8	12.5	2.45	0.615	0.098
Bi ₂	104.5	173.1	0.376	2.66	0.023	2.08
Br ₂	39.95	325	1.08	2.28	0.082	2.05
C ₂	6.006	1855	13.27	1.24	1.899	5.36
Ca ₂	20.04	64.9	1.087	4.28	0.047	0.13
Cd ₂	56.20	22.5	0.4	5.1	0.011	0.040
Cl ₂	17.73	559.7	2.68	1.99	0.244	2.576
Co ₂	29.47	280	–	2.0	0.14	0.9
Cr ₂	26.00	470	14.1	1.68	0.23	1.66
Cs ₂	66.45	47.02	0.082	4.65	0.013	0.452
Cu ₂	31.77	266.4	1.03	2.21	0.109	1.99
F ₂	9.499	916.6	11.24	1.41	0.89	1.66
Fe ₂	27.92	412	1.4	2.02	0.148	0.9
Ga ₂	34.86	158	1.0	2.76	0.063	1.18
Ge ₂	36.30	259	0.8	2.44	0.078	2.5
H ₂	0.5040	4401	121.3	0.741	60.85	4.478
Hg ₂	100.3	18.5	0.27	3.65	0.013	0.055
I ₂	63.45	214.5	0.615	2.67	0.037	1.542
In ₂	57.41	111	0.8	3.14	0.030	0.83
K ₂	19.55	92.09	0.283	3.92	0.057	0.551
Kr ₂	41.90	24.1	1.34	4.02	0.024	0.018
Li ₂	3.571	351.4	2.59	2.67	0.672	1.05

Table 3.4. (continued)

Dimer	$\mu, a.u.m.$	ω_e, cm^{-1}	$\omega_e x_e, \text{cm}^{-1}$	$R_e, \text{\AA}$	B, cm^{-1}	D, eV
Mg ₂	12.15	51.08	1.623	3.89	0.093	0.053
Mn ₂	27.47	68.1	1.05	2.52	0.097	0.79
Mo ₂	47.97	477	1.51	2.2	0.072	4.1
N ₂	7.003	2359	14.95	1.098	1.998	9.579
Na ₂	11.495	159.1	0.725	3.08	0.155	0.731
Nb ₂	46.45	424.9	0.94	2.1	0.084	5.48
Ne ₂	10.09	31.3	6.48	2.91	0.17	0.037
Ni ₂	29.34	250	1.1	2.3	0.104	1.7
O ₂	8.000	1580	11.98	1.207	1.445	5.12
P ₂	15.49	780.8	2.83	1.89	0.304	–
Pb ₂	103.6	110.2	0.327	2.93	0.019	0.83
Pd ₂	53.21	159	–	2.48	0.051	0.76
Pt ₂	97.54	259.4	0.9	2.34	0.032	0.93
Rb ₂	42.73	57.78	0.139	4.17	0.023	0.495
Rh ₂	51.45	238	–	2.67	0.046	1.5
S ₂	16.03	725.6	2.28	1.89	0.295	4.37
Sb ₂	60.82	269.9	0.58	2.34	0.050	3.09
Sc ₂	22.48	238.9	0.93	2.21	0.153	1.69
Se ₂	39.48	385.3	0.96	2.16	0.89	2.9
Si ₂	14.04	510.9	2.02	2.24	0.239	3.24
Sn ₂	59.34	186.2	0.261	2.75	0.038	2.0
Sr ₂	43.81	39.6	0.45	4.45	0.019	0.13
Te ₂	63.80	249.1	0.537	2.56	0.040	2.7
Ti ₂	23.44	407.9	1.08	1.94	0.187	1.4
Tl ₂	102.2	80	0.5	3.0	0.018	0.001
V ₂	25.47	537.5	3.34	3.78	0.209	2.62
W ₂	91.92	336.8	1.0	–	–	6.9
Xe ₂	65.64	21.12	0.65	4.36	0.013	0.024
Y ₂	44.45	206.5	–	2.8	0.048	1.6
Zn ₂	32.69	25.7	0.60	4.8	0.022	0.034
Zr ₂	45.61	373	–	2.3	0.070	1.5

The excitation energy for polyatomic molecules has a form similar to (3.43), taking into account that a polyatomic molecule has three moments of inertia and different vibrational degrees of freedom. Because of the absence of interactions between these degrees of freedom

at low excitations, the total excitation energy is the sum of the excitation energies for different degrees of freedom. Assuming equilibrium for the subsystem, including vibrational degrees of freedom, we obtain the number density of vibrationally excited molecules with a given type of vibrations according to formula (2.20)

$$N_v = N_0 \exp\left(-\frac{\hbar\omega v}{T_v}\right) \quad (3.45)$$

where N_0 is the number density of molecules in the ground vibrational state and T_v is the vibrational temperature. Since the total number density of molecules is

$$N = \sum_{v=0}^{\infty} N_v = N_0 \sum_{v=0}^{\infty} \exp\left(-\frac{\hbar\omega v}{T_v}\right) = \frac{N_0}{1 - \exp\left(-\frac{\hbar\omega}{T_v}\right)}$$

the number density of excited molecules is equal to

$$N_v = N \cdot \exp\left(-\frac{\hbar\omega v}{T_v}\right) \left[1 - \exp\left(-\frac{\hbar\omega}{T_v}\right)\right] \quad (3.46)$$

The energy and the partition function of a gas consisting of n diatomic molecules are equal to

$$E_{\text{vib}} = \frac{\hbar\omega n}{\exp(\frac{\hbar\omega}{T_v}) - 1}, \quad Z_{\text{vib}} = \frac{n}{1 - \exp(-\frac{\hbar\omega}{T_v})} \quad (3.47)$$

3.10 Bose Condensation

Bose–Einstein statistics allows two or more particles to be in the same state. Hence, if the temperature of a system of Bose particles tends to zero, the particles can move to a state with zero energy. This phenomenon is called *Bose condensation*, and the transition has specific properties. We consider the phenomenon under conditions when the number density of particles in a given volume is conserved, but their temperature decreases. The chemical potential μ of this system of Bose particles is determined by formula (2.40)

$$N = \frac{g \cdot (mT)^{3/2}}{\pi^2 \sqrt{2} \hbar^3} \int_0^{\infty} \sqrt{x} dx \cdot \left[\exp\left(x - \frac{\mu}{T}\right) - 1 \right]^{-1} \quad (3.48)$$

The chemical potential is negative, and the value $|\mu|$ decreases with decreasing temperature. The chemical potential is zero below some temperature T_B , which follows from the relation (3.48) if we take $\mu = 0$:

$$T_B = \frac{3.31 \hbar^2}{m} \cdot \left(\frac{N}{g}\right)^{2/3} \quad (3.49)$$

At lower temperatures some of the atoms go to the state with zero energy. At a fixed temperature in a gas of Bose particles, Bose condensation starts from the number density of atoms

$$N_B = g \cdot \frac{(mT)^{3/2}}{\hbar^3} \quad (3.50)$$

Table 3.5. The condensation temperature T_B (in Kelvin) for some systems of atoms.

System	$N = 10^{15} \text{ cm}^{-3}$	$N = 10^{18} \text{ cm}^{-3}$
^4He	$5.5 \cdot 10^{-5}$	$5.5 \cdot 10^{-3}$
^{132}Xe	$1.7 \cdot 10^{-6}$	$1.7 \cdot 10^{-4}$

Table 3.5 gives values T_B for He and Xe.

Considering Bose condensation at temperatures $T < T_B$, one can divide Bose particles into two groups, so that particles of the first group have zero energy and particles of the second group have nonzero energy. Denoting the number density of particles of the first group by N_0 and the number density of particles of the second group by $N_>$, we get, at $T < T_B$

$$N_> = N \cdot \left(\frac{T}{T_B} \right)^{3/2}, \quad N_0 = N - N_> = N \left[1 - \left(\frac{T}{T_B} \right)^{3/2} \right]$$

Let us determine the chemical potential near the temperature of Bose condensation. We have

$$\begin{aligned} N &= g \frac{(mT)^{3/2}}{\pi^2 \sqrt{2} \hbar^3} \int_0^\infty \sqrt{x} dx \cdot \left[\exp \left(x - \frac{\mu}{T} \right) - 1 \right]^{-1} \\ &= N_B(T) + g \frac{(mT)^{3/2}}{\pi^2 \sqrt{2} \hbar^3} \int_0^\infty \sqrt{x} dx \left[\frac{1}{\exp \left(x - \frac{\mu}{T} \right) - 1} - \frac{1}{\exp x - 1} \right] \end{aligned}$$

In the limit of small μ the second integral is determined by small x , so that we obtain, taking into account $\mu < 0$:

$$\int_0^\infty \sqrt{x} dx \cdot \left[\frac{1}{\exp \left(x - \frac{\mu}{T} \right) - 1} - \frac{1}{\exp x - 1} \right] = \int_0^\infty \frac{dx}{\sqrt{x} \cdot \left(x + \frac{|\mu|}{T} \right)} = -\pi \frac{\sqrt{|\mu|}}{T}$$

From this it follows for the chemical potential of Bose particles in this limit

$$\mu = -\frac{2\pi^2 \hbar^6}{g^2 m^3} \cdot [N_B(T) - N]^2 \quad (3.51)$$

3.11 Helium at Low Temperatures

All atoms or molecules except helium form crystals at zero temperature under normal conditions, while helium is found in the liquid state in the absence of an external pressure. This is explained by the weak attraction potential of two helium atoms which has a minimum about

$D \approx 8$ meV at a distance $4.4 \text{ \AA}$. Because $\hbar\omega_D \approx 30$ meV, where ω_D is the Debye frequency, the parameter $\hbar\omega_D/D$, which is proportional to the energy of the zeroth vibrations at the depth of the potential well, is not small enough for crystal formation crystal at zero temperature. Therefore helium crystals can be formed only at high pressures, starting from 25 atm.

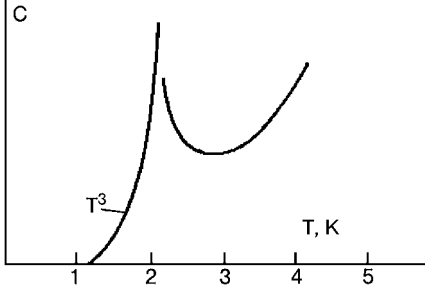


Figure 3.8. The temperature dependence for the helium heat capacity at low temperatures.

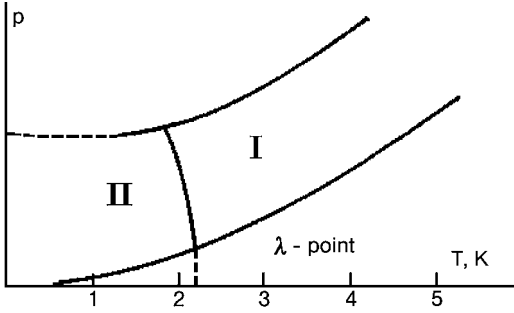


Figure 3.9. Phase diagram for helium at low temperatures.

The other peculiarity of helium at low temperatures is the character of the phase transition. Figure 3.8 gives the helium heat capacity versus its temperature. The phase transition takes place at the temperature $T_\lambda = 2.18$ K, and because the above dependence has the form of a reciprocal letter λ , this phase transition is called the λ -transition, and the transition temperature is called the λ -point. The liquid helium at higher temperatures is called *normal helium* or HeI, while helium at lower temperatures is named HeII. Figure 3.9 gives the phase diagram for helium in this temperature range.

It is clear that such behavior for helium is determined by the spectrum of excitations at low temperatures. The spectrum of excitations in liquid helium is given in Figure 3.10. Long-wave excitations – phonons – are described by the dispersion relation (3.29)

$$\varepsilon = ck$$

where ε is the energy of excitation, k is the wave vector and $c = 2.4 \cdot 10^4$ cm/s is the speed of sound of liquid helium at low temperatures. The quasiparticles whose excitation corresponds to the minimum of the dispersion curve of Figure 3.10 are called *rotons*, and the dispersion relation for them has the form

$$\varepsilon = \Delta + \frac{\hbar^2}{2\mu}(k - k_o)^2 \quad (3.52)$$

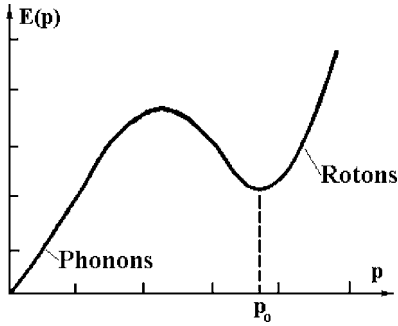


Figure 3.10. Spectrum of excitation of helium at low temperatures.

The parameters of this dispersion relation are $\Delta = 8.65 \text{ K}$, $k_o = 1.92 \text{ \AA}^{-1}$, $\mu = 0.64 \text{ a.u.m.}$ This spectrum of excitation of liquid helium is found on the basis of the inelastic scattering of neutrons.

The existence of the liquid state of helium at low temperatures and the form of excitation spectrum lead to the specific properties of HeII. The principal property is the *superfluidity* of HeII, according to which it flows through a capillary without friction. On the other hand, it has a finite viscosity that follows from experiments with attenuation of torsion oscillations of a cylinder which is located in HeII. This combination of HeII properties seems contradictory, but it is explained within the framework of the *Landau two-liquid model*. According to this model, the normal and ideal components are present simultaneously in HeII. Then the attenuation of torsional oscillations of a cylinder can be explained by its interaction with the normal component of liquid HeII, while superfluidity is a flow of the ideal component of HeII which has zero viscosity. This model is capable of explaining other experimental properties of HeII.

3.12 Superfluidity

Let us analyze the superfluidity phenomenon within the framework of the Landau two-liquid model. Then the superfluid flow is the collective flow of a Bose condensate, and its atoms do not interact due to an exchange interaction potential which is determined by the symmetry of the atomic system. This means that the λ -point is lower than the temperature T_B at which Bose condensation starts. According to formula (3.49) this temperature is $T_B = 3.12 \text{ K}$; if we use the number density of atoms at low temperatures $N_{He} = 2.2 \cdot 10^{22} \text{ cm}^{-3}$ for liquid helium. From this it follows that at the λ -point approximately $2/3$ of the helium atoms form the *Bose condensate*. Note that there is an error in these evaluations because we used the formulae for an ideal gas.

Now let us evaluate the number of atoms which partake in elementary excitations – phonons and rotons. We assume that the number of excitations is equal to the number of atoms which transport these excitations. Therefore, below we calculate the number density of elementary excitations – quasiparticles. Let $\mathbf{P}$ be the momentum per unit volume, and $\mathbf{v}$ be the mean velocity of atoms. Then the number density of atoms N_n of the normal liquid, which creates this motion, satisfies the relation

$$\mathbf{P} = mN_n\mathbf{v}$$

where m is the helium atom's mass. The momentum of the normal liquid is equal to

$$\mathbf{P} = \int \mathbf{p} f(\varepsilon - \mathbf{p}\mathbf{v}) dn$$

where $\mathbf{p}$ is the momentum of a moving atom; $f(\varepsilon)$ is the distribution function of excitations – quasiparticles of energies ε – and we take the excitation energy in a moving system to be $\varepsilon - \mathbf{p}\mathbf{v}$; and dn is a number of quasiparticles per unit volume. In the limit of small velocities $\mathbf{v}$ we have

$$\mathbf{P} = \int \mathbf{p}(\mathbf{p}\mathbf{v}) \frac{df}{d\varepsilon} dn = -\frac{\mathbf{v}}{3} \int p^2 \frac{df}{d\varepsilon} dn,$$

and the number density of atoms of the normal liquid is equal to

$$N_n = -\frac{1}{3m} \int p^2 \frac{df}{d\varepsilon} dn$$

We divide the number density of the normal liquid into two parts, so that the first part, N_{ph} , corresponds to photons and the second, N_{rot} , to rotons, i.e.

$$N_n = N_{ph} + N_{rot} \quad (3.53)$$

To determine N_{ph} we use the dispersion relation for phonons $\omega = ck$ or $\varepsilon = cp$, where c is the speed of sound ($\varepsilon = \hbar\omega$, $p = \hbar k$). Then

$$\frac{df}{d\varepsilon} = \frac{1}{c} \frac{df}{dp}$$

and we have

$$N_{ph} = -\frac{1}{3mc} \int p^2 \frac{df}{d\varepsilon} \frac{4\pi p^2 dp}{(2\pi\hbar)^3} = \frac{4}{3mc} \int p f \frac{4\pi p^2 dp}{(2\pi\hbar)^3} = \frac{4}{3mc^2} E_{ph}$$

where we take the integral by parts, and E_{ph} is the mean phonon energy per unit volume. On the basis of formula (3.37) we have for this value

$$E_{ph} = \frac{2\sigma}{c} T^4 = \frac{\pi^2 T^4}{15\hbar^3 c^3}$$

so that

$$N_{ph} = \frac{\pi^2 T^4}{30m\hbar^3 c^5} \quad (3.54)$$

We calculate the contribution of rotons to the number density of the normal liquid under the condition $T \ll \Delta$. Then the number density of rotons is given by the Boltzmann formula $f = \exp(-\varepsilon/T)$ and $df/d\varepsilon = -f/T$. From this we have, on the basis of the dispersion relation (3.29) and the relation $p = \hbar k$:

$$N_{rot} = \int_0^\infty \frac{p^2}{3mT} \exp\left(-\frac{\varepsilon}{T}\right) \frac{4\pi p^2 dp}{(2\pi\hbar)^3} = \frac{p_o^2}{3mT} \int_0^\infty \exp\left[-\frac{\Delta}{T} - \frac{(p-p_o)^2}{2\mu T}\right] \frac{4\pi p^2 dp}{(2\pi\hbar)^3}$$

or

$$N_{\text{rot}} = \frac{\hbar k_o^4 \sqrt{\mu}}{3\pi m \sqrt{2\pi T}} \exp\left(-\frac{\Delta}{T}\right) \quad (3.55)$$

In particular, from these formulae and the parameters of liquid helium at the temperature $T = 1$ K we have $N_{ph} = 3.9 \cdot 10^{18} \text{ cm}^{-3}$ and $N_{\text{rot}} = 1 \cdot 10^{20} \text{ cm}^{-3}$. From this we find that phonons are essential for helium transport at low temperatures, and near the λ -point rotons provide the main contribution to transport of the liquid. In particular, one can expect at the λ -point

$$N_{\text{rot}} = N \cdot \left(\frac{T_\lambda}{T_B}\right)^3 \quad (3.56)$$

On the basis of the above formulae for an ideal gas and the parameters of liquid helium we have at the λ -point $N_{\text{rot}} = 1.1 \cdot 10^{22} \text{ cm}^{-3}$, while the right-hand side of equation (3.56) gives $7 \cdot 10^{21} \text{ cm}^{-3}$ at the λ -point.

Thus, on the basis of the Landau two-liquid model one can consider the superfluidity of liquid helium as a motion of the Bose condensate. The normal component of liquid helium stops under the action of friction with the walls as a result of the generation of rotons. The ideal component of this liquid – the Bose condensate – moves without friction and is conserved because of the exchange interaction between atoms. This character of superfluidity explains the *thermomechanical effect* in HeII. If part of the liquid helium leaks out of a vessel with HeII through a capillary pipe, the temperature of the residual liquid helium increases. Conversely, if liquid helium is added to HeII in the form of a superfluid flow, the temperature of the initial liquid helium decreases. This thermochemical effect in HeII results from the participation of the Bose condensate in the helium flow.

4 Fermi–Dirac Distribution

4.1 Degenerate Electron Gas

A degenerate Fermi gas can be a model for a metallic plasma and atomic systems. Below we consider an example of such a system – a *degenerate electron gas*, which is a system of electrons at low temperature. The behavior of such a system is governed by the *Pauli exclusion principle* according to which two electrons cannot be located in the same state. At zero temperature electrons have momenta p located in the interval $0 \leq p \leq p_F$, where p_F is the *Fermi momentum*, which can be found from the relation:

$$n = 2 \int_{p \leq p_F} \frac{d\mathbf{p} d\mathbf{r}}{(2\pi\hbar)^3} \quad (4.1)$$

where n is the total number of electrons, the factor 2 accounts for the two directions of electron spin, and $d\mathbf{p}$ and $d\mathbf{r}$ are elements of the electron momentum and plasma volume. Introducing the electron number density $N_e = n / \int d\mathbf{r}$, we obtain the maximum electron momentum p_F , the Fermi momentum, the maximum electron energy (the *Fermi energy* ε_F) for this distribution and the electron velocity v_F on the surface of the Fermi sphere:

$$p_F = (3\pi^2 \hbar^3 N_e)^{1/3}, \quad \varepsilon_F = \frac{p_F^2}{2m_e} = \frac{(3\pi^2 N_e)^{2/3} \hbar^2}{2m_e}, \quad v_F = \frac{p_F}{m_e} \quad (4.2)$$

The distribution of electrons for a degenerate electron gas is given by the Fermi–Dirac formula (2.36) with zero temperature and chemical potential $\mu = \varepsilon_F$.

A degenerate electron gas is characterized by a small parameter

$$\eta = \frac{T}{\varepsilon_F} \quad (4.3)$$

From this it follows that $r_D^2 N_e^{1/3} \ll a_o$, where r_D is the *Debye–Hückel radius* for this electron gas and $a_o = \hbar^2 / (m_e e^2)$ is the Bohr radius. We can see that the degenerate electron gas is a quantum system.

Let us find the total energy per unit volume E_o of a degenerate electron gas at zero temperature

$$E_o = \int_0^{\varepsilon_F} \frac{\varepsilon \cdot 2d\mathbf{p}}{(2\pi\hbar)^3} = \frac{2\sqrt{2}}{5\pi^2} \cdot \frac{m_e^{3/2} \varepsilon_F^{5/2}}{\hbar^3} \quad (4.4)$$

At low temperatures the energy per unit volume is equal to

$$E = \int_0^{\infty} \frac{\varepsilon \cdot 2d\mathbf{p}}{(2\pi\hbar)^3} \cdot \frac{1}{\exp\left(\frac{\varepsilon - \mu}{T}\right) + 1}$$

where $\varepsilon = p^2/(2m_e)$, and in the zeroth approximation the chemical potential for this distribution is $\mu = \varepsilon_F$. We use the fact that the integral

$$E - E_o = \frac{m_e^{3/2} \sqrt{2}}{\pi^2 \hbar^3} \left(\int_0^\infty \varepsilon^{3/2} d\varepsilon \cdot \frac{1}{\exp\left(\frac{\varepsilon - \mu}{T}\right) + 1} - \int_0^{\varepsilon_F} \varepsilon^{3/2} d\varepsilon \right)$$

converges near $\varepsilon = \varepsilon_F$ under the considered criterion $T \ll \varepsilon_F$ ($\mu = \varepsilon_F$). Introducing a new variable $x = (\varepsilon - \mu)/T$, we transform this expression to the form:

$$E - E_o = \frac{m_e^{3/2} \sqrt{2} T^{5/2}}{\pi^2 \hbar^3} \left(\int_0^\infty \left(x + \frac{\mu}{T}\right)^{3/2} dx \frac{1}{1 + \exp x} - \int_{-\frac{\mu}{T}}^0 \left(x + \frac{\mu}{T}\right)^{3/2} dx \frac{\exp x}{1 + \exp x} \right)$$

By changing the variable in the second integral $x \rightarrow -x$ and the lower limit of integration $-\mu/T$ by $-\infty$, we obtain as a result of expansion over a small parameter T/ε_F

$$\begin{aligned} E - E_o &= \frac{m_e^{3/2} \sqrt{2} T^{5/2}}{\pi^2 \hbar^3} \int_0^\infty \frac{dx}{1 + \exp x} \left[\left(\frac{\mu}{T} + x\right)^{3/2} - \left(\frac{\mu}{T} - x\right)^{3/2} \right] \\ &= \frac{3m_e^{3/2} \sqrt{2} T^2 \sqrt{\mu}}{\pi^2 \hbar^3} \int_0^\infty \frac{x dx}{1 + \exp x} = \frac{m_e^{3/2} T^2 \sqrt{\mu}}{\sqrt{2} \hbar^3} \end{aligned}$$

so that ($\mu = \varepsilon_F$)

$$E = E_o \left(1 + \frac{5\pi^2}{4} \frac{T^2}{\varepsilon_F^2} \right) \quad (4.5)$$

From this it follows for the *heat capacity* per unit volume of a degenerate electron gas at low temperatures:

$$C = \frac{dE}{dT} = \frac{5\pi^2}{2} \frac{T}{\varepsilon_F^2} E_o = \frac{m_e^{3/2} T \sqrt{2\varepsilon_F}}{\hbar^3} \quad (4.6)$$

4.2 Plasma of Metals

Let us consider a *metallic plasma* as a degenerate electron gas, taking its positive charge to be distributed uniformly over a space. The Fermi energy is the parameter of a degenerate electron gas, and just this parameter must be used for the analysis of this quantum plasma. Let us introduce the ideality parameter of the quantum plasma as the ratio of the Coulomb interaction of electrons to the Fermi energy:

$$\xi = \frac{e^2}{r_W \varepsilon_F} = \frac{2^{5/3}}{3\pi a_o N_e^{1/3}} = \frac{0.337}{a_o N_e^{1/3}}, \quad r_W = \left(\frac{3}{4\pi N_e} \right)^{1/3} \quad (4.7)$$

where r_W is the *Wigner–Seitz radius* for the electron gas and a_o is the Bohr radius. The ideal degenerate electron gas has a large density compared with the typical atomic value, i.e. $N_e a_o^3 \gg 1$. This means that the closer the properties of a degenerate electron gas are to the properties of a quantum plasma, the larger is the electron number density. In contrast, the role of the Coulomb interaction between charged particles of the plasma decreases with increasing electron number density.

Let us use the model of a degenerate electron gas for electrons of metals. Table 4.1 lists the parameters of real metallic plasmas at room temperature. Metals under consideration contain atoms with one valence electron, and we assume that these electrons of metal atoms form a degenerate electron gas. The parameters of this gas are determined by formula (4.2). It follows from the data in Table 4.1 that the parameter η is small for real single-valent metals, i.e. metallic plasma is a quantum system. But the Coulomb interaction involving electrons and ions of metals is compared to the exchange interaction potential of electrons, which is determined by the Pauli exclusion principle. Thus, a metallic plasma is a quantum one where the potential of the Coulomb interaction of charged particles and the exchange interaction potential of electrons have the same order of magnitude.

Note that the heat capacity of metals is determined by phonons and electrons, so that formula (4.6) determines the contribution to the heat capacity of metals due to electrons, and Table 3.3 gives the contribution to this value due to phonons. As may be seen, at low temperatures the heat capacity of metals is determined by electrons.

Table 4.1. Parameters of single-valent metals at room temperature. These metals consist of atoms with one valence s -electron. Here the structure of the lattice is bcc (body-centered cubic) or fcc (face-centered cubic), a is the lattice constant, ρ is the metal density that determines the number density of electrons N_e , and other parameters are given by formulae (4.2) and (4.3).

Metal	Li	Na	K	Cu	Rb	Ag	Cs	Au
Lattice type	bcc	bcc	bcc	fcc	bcc	fcc	bcc	fcc
a , Å	3.51	4.29	5.34	3.61	5.71	4.09	6.09	4.08
ρ , g/cm ³	0.534	0.97	0.89	8.96	1.53	10.5	1.93	19.3
N_e , 10 ²² cm ⁻³	4.6	2.5	1.4	8.5	11	5.9	8.7	5.9
ε_F , eV	4.7	3.2	2.1	7.1	1.8	5.5	1.6	5.5
v_F , 10 ⁸ cm/s	1.3	1.0	0.86	1.6	0.79	1.4	0.74	1.4
η , 10 ⁻³	5.5	8.2	13	3.7	15	4.6	17	4.6
ξ	1.8	2.2	2.7	1.4	2.9	1.6	3.1	1.6

4.3 Degenerate Electron Gas in a Magnetic Field

If a metal is formed from atoms, valence atomic electrons are transformed into conductivity electrons of the metal, and the cores of these atoms occupy the sites of a crystal lattice. It is convenient to model a system of electrons by a degenerate electron gas which describes some properties of the metal, in particular its heat capacity at low temperatures. Below we consider one more example of metallic properties when a metal is found in an external magnetic field.

The interaction potential of an electron with a magnetic field of strength $\mathbf{H}$ is $-\mu_B \mathbf{n} \mathbf{H}$, where $\mu_B = \frac{e\hbar}{2m_e c} = 9.274 \cdot 10^{-28} \text{ J/G}$ is the electron magnetic moment, which is called the *Bohr magneton*, and $\mathbf{n}$ is the unit vector along the electron spin. Hence, depending on a direction of the electron spin, its energy decreases or increases by the value $\mu_B H$. Let us denote the number density of electrons with spin direction along and opposite to the magnetic field by $N_\uparrow$ and $N_\downarrow$ correspondingly. In the absence of a magnetic field $N_\uparrow = N_\downarrow$ because of the system's symmetry. The Insertion of a magnetic field leads to a redistribution of electrons with a given spin direction, so that the number density of electrons decreases for the spin direction along the magnetic field. The Fermi energy is identical for both spin directions, that is

$$\frac{(3\pi^2 N_\uparrow)^{2/3} \hbar^2}{2m_e} + \mu_B H = \frac{(3\pi^2 N_\downarrow)^{2/3} \hbar^2}{2m_e} - \mu_B H \quad (4.8)$$

Assuming the magnetic field strength to be small compared to a typical atomic value and introducing the quantity $\Delta N = N_\downarrow - N_\uparrow$, we get from the above equation

$$\Delta N = \frac{1}{4\pi} \left(\frac{3N_e}{\pi} \right)^{1/3} \frac{eH}{\hbar c}$$

From this we obtain the *magnetic moment* per unit volume of the degenerate electron gas

$$M = 2\mu_B \Delta N = \alpha H$$

and the *magnetic polarizability* α of the degenerate electron gas is equal to

$$\alpha = \frac{1}{4\pi} \left(\frac{3N}{\pi} \right)^{1/3} \frac{e^2}{m_e c^2} \quad (4.9)$$

4.4 Wigner Crystal

The positive ions of real metals form a certain crystalline lattice at low temperatures and the non-Coulomb interaction of free electrons with ions and bound electrons is of importance for these crystals. Nevertheless, we consider a simplified model of this interaction when the Coulomb interaction of electrons and ions takes place in this system along with the exchange interaction of electrons due to the Pauli exclusion principle. Evidently, if this system forms a certain crystalline lattice, the energy per pair of charged particles (one electron and ion) is equal to

$$\varepsilon = \frac{3p_F^2}{10m_e} - \kappa e^2 N_e^{1/3} \quad (4.10)$$

where the first term is the mean electron kinetic energy, the second term is the mean energy of the Coulomb interaction between charged particles, and the parameter κ depends on the lattice type and accounts for a space distribution of electrons in the crystal. We here take into account the redistribution of charged particles resulting from their interaction, that leads to the attraction character of the mean interaction energy.

Taking $p_F \sim N_e^{1/3}$ and optimizing the expression (4.10) for the reduced energy of the metal plasma, we obtain the optimal parameters of the plasma under consideration

$$a_o N_e^{1/3} = \frac{5\kappa}{3^{5/3}\pi^{4/3}} = 0.174\kappa, \quad \varepsilon_{\min} = -\frac{5}{2 \cdot 3^{5/3}\pi^{4/3}}\kappa^2 \frac{m_e e^4}{\hbar^2} = -\varepsilon_o \kappa^2 \quad (4.11)$$

where $\varepsilon_o = 2.4$ eV. The operation shows that the system under consideration may have a stable configuration of bound ions and electrons ($\varepsilon_{\min} < 0$). The stable distribution of charged particles (the *Wigner crystal*) corresponds to the parameter $\xi = 1.9/\kappa$. We see that the Wigner crystal, as well as real metals, is characterized by the electron number density which is of the order of a typical atomic number density a_o^{-3} .

4.5 The Thomas–Fermi Model of the Atom

If the parameter (4.7) is large for a dense degenerate electron gas, one can determine the potential of the self-consistent field of electrons which influences the behavior of this electron system. Such a situation takes place inside heavy atoms where the electron density is high. The properties of heavy atoms which contain several electron shells can be analyzed on the basis of the *Thomas–Fermi atom model*. We consider this model below as an example of the Fermi–Dirac distribution, and for simplicity we use atomic units $\hbar = m_e = e^2 = 1$. The criterion for the validity of this approximation is

$$pr \gg 1 \quad (4.12)$$

where $p \sim p_F$ is a typical electron momentum and r is the electron–nucleus distance, that is the typical size over which atomic parameters vary significantly. Note that although an atom is a quantum system, its classical description is possible in the region (4.12).

The maximum electron momentum p_F and the potential of the self-consistent field φ are connected by the relation

$$\frac{p_F^2}{2} = e\varphi \quad (4.13)$$

The electric field potential satisfies to the boundary condition $\varphi = 0$ far from the nucleus $r \rightarrow \infty$, where the electron density tends to zero, and hence $p_o \rightarrow 0$. The potential of the self-consistent electron field of an atom satisfies Poisson’s equation

$$\Delta\varphi = 4\pi N \quad (4.14)$$

For convenience we change the sign of this equation compared to that used in electrostatics. Expressing the right-hand side of equation (4.14) in accordance with formulae (4.2) and (4.13), we obtain the equation for the potential φ of the self-consistent field:

$$\Delta\varphi = \frac{8\sqrt{2}}{3\pi}\varphi^{3/2} \quad (4.15)$$

This is the *Thomas–Fermi equation*. It is convenient to use the reduced variables

$$x = 2 \left(\frac{4}{3\pi} \right)^{2/3} Z^{1/3} r = 1.13 Z^{1/3} r; \quad \varphi = \frac{Z}{r} \chi(x) \quad (4.16)$$

Because of the potential of the self-consistent field does not depend on angle variables, we have

$$\Delta\varphi = \frac{1}{r} \frac{d^2}{dr^2} (r\varphi)$$

and the Thomas–Fermi equation (4.15) can be transformed to the form:

$$x^{1/2} \frac{d^2\chi}{dx^2} = \chi^{3/2} \quad (4.17)$$

Since the potential of the self-consistent field coincides with the Coulomb field of the nucleus charge near the nucleus $\varphi = Z/r$, the boundary condition near the center has the form

$$\chi(0) = 1 \quad (4.18a)$$

The other boundary condition results from the absence of the electric charge far from the center

$$\chi(\infty) = 0 \quad (4.18b)$$

The numerical solution of equation (4.17) with the boundary conditions (4.2) is given in Table 4.2. In particular, $\chi'(0) = -1.588$, i.e. the electric potential of the self-consistent field near the center has the form:

$$\varphi(r) = Z/r - 1.794Z^{4/3} \quad (4.19)$$

The second term of this expression is the electric potential which is created by atomic electrons located in the atom center.

Table 4.2. The potential of the self-consistent electric field for the Thomas–Fermi atom model.

x	$\chi(x)$	$-\chi'(x)$	x	$\chi(x)$	$-\chi'(x)$
0	1.000	1.588	2.0	0.243	0.118
0.05	0.935	1.158	2.5	0.193	0.0846
0.1	0.882	0.995	3.0	0.157	0.0625
0.2	0.793	0.794	3.5	0.129	0.0476
0.4	0.660	0.565	4.0	0.108	0.0369
0.6	0.561	0.429	5.0	0.0788	0.0236
0.8	0.485	0.339	6.0	0.0594	0.0159
1.0	0.424	0.274	7.0	0.0461	0.0111
1.5	0.315	0.174	8.0	0.0366	0.0081

The Thomas–Fermi atom model is valid in the region of the atom, where the electron density is high enough to meet the criterion (4.12). Since the size of an atom is of the order of the Bohr radius, i.e. ~ 1 , and the electron number density in the region of the location of the valence electrons is of the order of one, the Thomas–Fermi model is not valid in this region. Hence this model can be used only in the internal region of the atom. The typical size of

this model is $\sim Z^{-1/3}$ according to formula (4.16), which corresponds to the following small parameter of the Thomas–Fermi model

$$Z^{-1/3} \ll 1 \quad (4.20)$$

Fulfillment of this criterion provides the validity of the Thomas–Fermi model for internal electrons.

The Thomas–Fermi model allows one to determine the parameters of a heavy atom, which are given by the internal electrons. In particular, let us find the dependence of the total electron energy of an atom on the atomic charge Z within the framework of the Thomas–Fermi model. The total electron energy is equal to

$$\varepsilon = T + U \quad (4.21)$$

where T is the total kinetic energy of the electrons and U is the potential electron energy, which is the sum of the interaction potentials of electrons with the nucleus and between electrons:

$$U = U_1 + U_2 = - \int \frac{Z}{r} N(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{N(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (4.22)$$

Let us determine the dependence of each of these terms on Z , taking into account the fact that each integral is determined by an atom region $x \sim 1$ ($r \sim Z^{-1/3}$). In this range the typical electron number density is $N \sim Z^2$, a typical electron momentum is $p \sim p_o \sim N^{-1/3} \sim Z^{2/3}$, and a typical volume of this region is $\sim 1/Z$. From this it follows that the electron kinetic energy is

$$T \sim \int \frac{p^2}{m} N d\mathbf{r} \sim Z^{7/3} \quad (4.23a)$$

The energy of interaction of electrons with the nucleus is

$$U_1 \sim \int \frac{Ze^2}{r} N d\mathbf{r} \sim Z^{7/3} \quad (4.23b)$$

The energy of interaction between electrons equals:

$$U_2 = \frac{1}{2} \int \frac{e^2 N(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \sim Z^{7/3} \quad (4.23c)$$

It follows from this that the total binding energy of electrons varies with the nuclear charge as $Z^{7/3}$, i.e. the binding energy per atom is of the order of $Z^{4/3}$. Note that this value is of the order of Z^2 for electrons located near the nucleus, and it does not depend on Z for valence electrons.

4.6 Shell Structure of Atoms

The Pauli exclusion principle influences the behavior of Fermi particles located in external fields. Below we consider the general properties of an atom, which is a system of electrons located in the Coulomb field of an atomic nucleus. Then the Hamiltonian of the atomic electrons has the form

$$\hat{H} = -\frac{1}{2} \sum_i \Delta_i - \sum_i \frac{Z}{r_i} + \sum_{i,k} \frac{1}{|\mathbf{r}_i - \mathbf{r}_k|} \quad (4.24)$$

The first term of the Hamiltonian corresponds to the kinetic energy of the electrons, the second term describes the interaction between the electrons and the nucleus, and the third term takes into account the interaction between electrons. Here $\mathbf{r}_i$ is the coordinate of the i th electron if the origin of the frame of reference is the nucleus and Z is the nuclear charge.

It is convenient to introduce a self-consistent field which accounts for the action of other electrons on a test electron. This operation is similar to using a model where the Hamiltonian (4.24) is changed to another one which has the form

$$\hat{H} = \sum_i \hat{h}_i, \quad \hat{h}_i = -\frac{1}{2} \Delta_i + V(r_i) \quad (4.25)$$

Here $\hat{h}_i$ is the Hamiltonian of an individual electron and $V(r_i)$ is the potential of the self-consistent field which is taken such that the real atomic spectrum would be close to that given by the Hamiltonian (4.24). Because of the atom's symmetry, we assume this potential to be independent of angle.

The Hamiltonian (4.25) allows one to separate variables in the Schrödinger equation $\hat{H}\Psi = E\Psi$, where Ψ is the total wave function of the electrons. It is a combination of products of single-electron wave functions $\psi_i(\mathbf{r}_i)$, which are solutions of single-electron Schrödinger equations:

$$\left[-\frac{1}{2} \Delta_i + V(r_i) \right] \psi_i(\mathbf{r}_i) = \varepsilon_i \psi_i(\mathbf{r}_i) \quad (4.26)$$

where ε_i is the energy of the i th electron. But owing to the Pauli exclusion principle, the total wave function of the electrons is antisymmetric with respect to permutation of any two electrons, i.e. it changes sign as a result of such a permutation. Hence the wave function of the electrons is zero if two electrons with the same spin direction are located at the same point in space. This means that the Pauli exclusion principle creates an exchange interaction between electrons such that the location of two electrons with the same spin at the same point is forbidden. Because of the above symmetry, the total wave function is zero if two electrons are found in the same state, i.e. they have identical spin and space wave functions. This fact is essential for the distribution of electrons by states in an atom.

Let us analyze the electron spectrum for the potential of a self-consistent field $V(r_i)$. Near the nucleus this is the Coulomb field of the nucleus, and the nuclear charge is partially shielded by atomic electrons. Hence the atomic spectrum in this potential is close to that in the Coulomb field. The electron spectrum in the Coulomb field is characterized by the quantum

numbers $nlm\sigma$, where n is the so-called principal quantum number, l is the electron orbital momentum, m is the projection of the electron orbital momentum onto a given direction, and $\sigma = \pm\frac{1}{2}$ is the spin projection. *Quantum numbers* of electrons nlm are integers, so that n, l are positive integers, $n \geq l + 1$, and $-l < m < l$. The maximum binding energy corresponds to the minimum value $n = 1$. In the case of the Coulomb field, electron states are degenerate with respect to quantum numbers $lm\sigma$, i.e. the electron energy does not depend on these quantum numbers. Shielding of the nuclear Coulomb field by atomic electrons removes the degeneracy with respect to l , so that the number of degenerate states for a given nl is equal to $2(2l + 1)$.

4.7 Sequence of Filling of Electron Shells

We now construct an atom on the basis of the above analysis. For this goal we must fill the electron states starting from the lowest one $n = 1, l = 0$. According to the Pauli exclusion principle, only one electron can have a given set of *quantum numbers* $nlm\sigma$. A group of electrons with identical values of quantum numbers nl is called an *electron shell*. Thus, within the framework of a self-consistent field which accounts for the action of the nucleus and other electrons on a sample one, the distribution of electrons in an atom follows these electron shells, so that each shell is characterized by electron quantum numbers nl , i.e. the Pauli exclusion principle leads to the *atomic shell structure*.

Shells with certain quantum numbers nl for an atom in the ground state are realized depending on the nuclear charge Z . In order to demonstrate this connection, we determine the minimum values of Z for a given l within the framework of the Thomas–Fermi atom model. Let us introduce the radial wave function of a valence electron $R(r)$, where r is an electron distance from the nucleus. This wave function satisfies Schrödinger equation, which follows from equation (4.26)

$$\frac{1}{r} \cdot \frac{d^2(rR)}{dr^2} + \left[2\varepsilon - 2\varphi(r) - \frac{l(l+1)}{r^2} \right] R = 0$$

Here ε is the electron energy, $\varphi(r)$ is the potential of the self-consistent field, which is determined according to formula (4.16), l is the electron angular momentum, and $l(l+1)/(2r^2)$ is a centrifugal energy. An electron is bonded at some distance where the relation

$$2\varepsilon - 2\varphi(r) - \frac{l(l+1)}{r^2} > 0 \quad (4.27)$$

holds true. We have for the bound state $\varepsilon < 0$, i.e. $-2r^2\varphi(r) > l(l+1)$. Taking the Thomas–Fermi self-consistent field and using the variables of formulae (4.16), we have:

$$1.77Z^{2/3}x\chi(x) > l(l+1) \quad (4.28)$$

Taking the maximum of the function $x\chi(x)$, which equals 0.486 at $x = 2.1$ (see Table 4.2), we obtain the criterion:

$$0.86Z^{2/3} > l(l+1) \quad (4.29)$$

According to this formula, d -electrons ($l = 2$) occur in the shells of the ground state of atoms starting from $Z = 18$, f -electrons ($l = 3$) can arise at $Z = 52$, and g -electrons ($l = 4$) occur at $Z = 112$. In reality, the first d -electron is observed in the electron shell of the ground atom state at $Z = 21$ (Sc), and the first f -electron arises at $Z = 58$ (Ce). We can see that the above simple analysis gives reasonable estimates.

4.8 The Jellium Model of Metallic Clusters

Let us consider one more example in which electrons form a certain structure due to the Pauli exclusion principle. Below we analyze the structure of large metallic clusters which are systems of bound atoms and are an intermediate object between atoms and bulk metals. Usually clusters have a shell structure, and clusters with filled shells have a heightened stability. Numbers of atoms for such clusters are called *magic numbers*. Clusters with magic numbers of atoms have larger binding energies of surface atoms, ionization potentials, electron affinities etc. than clusters with neighboring numbers of atoms. The structure and magic numbers of clusters depend on the character of the interaction inside them. Below we consider the *jellium model of clusters*, which assumes the charge of positive ions to be distributed uniformly over a cluster space, which is a ball of a certain radius with electrons concentrated inside it. The jellium model describes clusters consisting of alkali metal atoms well.

As a matter of fact, this model resembles plasma models with the uniform distribution of the positive charge over a space similar to that used above for a plasma of metals. Let us use the concept of the *Wigner crystal* for the jellium cluster model. On the one hand, electrons are located in a field of positive charge which has the form of a potential well, and a depth of the order of $e^2 N^{1/3}$, where N is the number density of electrons and ions. On the other hand, the electrons of this degenerate electron gas according to formula (4.2) have a typical kinetic energy of the order of $p_F^2/m_e \sim N^{2/3}$.

From this we find the following form for the typical energy of an electron in accordance with formula (4.10):

$$\varepsilon = aN_e^{2/3} - bN_e^{-1/3} \quad (4.30)$$

where the parameters a , b have the order of a typical atomic value. Optimization of this formula with respect to the cluster radius gives an optimal value for the number density of electrons which is of the order of a typical atomic value. Thus the size of a metallic cluster within the framework of the jellium cluster model is established on the basis of competition of the electrostatic interaction between electrons and ions [the second term of formula (4.30)] and the exchange interaction between electrons due to the Pauli exclusion principle [the first term of formula (4.30)]. This competition leads to a certain cluster size.

Alongside the common properties of a dense plasma at zero temperature, this cluster has specific properties which are determined by its finite size. Indeed, the form of the well which is created by the positive charge of the cluster influences the positions of the electrons, and as a result of the interaction a self-consistent field occurs which determines the quantum numbers of the cluster electrons. Let us consider this problem in its general form. The self-consistent field of the cluster has spherical symmetry, which follows from the problem's symmetry (in reality, it is valid strictly only for clusters with filled electron shells), and the *quantum numbers*

of electrons are the same as for atomic electrons. They are $nlm\sigma$, and in the general case we have $|m| \leq l$, $\sigma = \pm 1/2$. As for the condition $l+1 \leq n$, which occurs for the Coulomb field, this condition is absent in the cluster case. This means that an electron with a certain n can have, in principle, any orbital momentum l . In particular, the sequence of filling of electron shells for clusters of alkali metals is as follows: $1s^2 1p^6 1d^{10} 2s^2 1f^{14} 2p^6 1g^{18} 2d^{10} 1h^{22} 3s^2$. Here we take the usual designations for the quantum numbers nl of the electron shells: the first value is the principal electron quantum number and the second is the electron orbital momentum, so that the values s, p, d, f, g, h correspond to $l = 0, 1, 2, 3, 4, 5$. The superscript indicates the number of electrons in this shell. Thus the magic numbers of this cluster, which correspond to filled electron shells, are 2, 8, 18, 20, 34, 40, 58, 68, 80, 82 etc. Clusters with these numbers of atoms have heightened stability. Thus the Pauli exclusion principle leads to a certain behavior of metallic clusters due to exchange interaction between electrons.

4.9 Shell Structure of Clusters

The atoms or ions of solid clusters in the ground state, where one can ignore nuclear motion, are distributed in accordance with the cluster's symmetry. If atoms occupy the positions which are transformed into each other as a result of symmetry transformations they belong to the same shell. We now move on to consider clusters of the basic symmetry types from this standpoint.

The *face-centered cubic structure* is conserved under the following transformations (3.16)

$$x \longleftrightarrow -x, \quad y \longleftrightarrow -y, \quad z \longleftrightarrow -z, \quad x \longleftrightarrow y \longleftrightarrow z \quad (4.31)$$

The maximum number of atoms of the same shell is equal to the number of symmetry transformations, which is

$$8 \cdot 3! = 48$$

in this case. But the number of atoms of one shell can be less if some transformations do not give new atom positions that occur in any of the following cases of atom positions: $x = 0, y = 0, z = 0, x = y, x = z, y = z$. Excluding the atom position at the origin, we find the minimum number of atoms of one shell as 6.

The *hexagonal lattice* is characterized by symmetry in the cylindrical coordinate system z, ρ, φ

$$z \longleftrightarrow -z, \quad \varphi \longleftrightarrow \varphi + \frac{\pi}{3} \quad (4.32)$$

where k is an integer, and such transformations do not change the completed shell of a hexagonal cluster. The maximum number of transformations in this case, i.e. the maximum number of atoms of one shell is

$$2 \cdot 6 = 12$$

Thus the face-centered cubic structure has a higher symmetry than the hexagonal one. These structures are structures of close packing where each internal atom has 12 nearest neighbors,

and the distances between nearest neighbors are identical in the case of a bulk system or in the case of short-range interactions if only nearest neighbors interact.

Icosahedral symmetry conserves completed cluster shells under rotation by an angle $2\pi/5$ with respect to the six icosahedron symmetry axes which pass through the icosahedron center and two opposite vertices. As a result of this operation, 20 surface icosahedron triangles, formed by joining the nearest icosahedron vertices, are transformed into each other. In addition to this, there is a symmetry for rotation by angle $2\pi/3$ with respect to 10 axes which pass through the centers of opposite triangles and the icosahedron center. From this it follows that the maximum number of atoms of one shell of an icosahedral cluster is 60.

For a magic number n of cluster atoms the atom binding energy $\varepsilon(n)$ is more than $\varepsilon(n+1)$ and $\varepsilon(n-1)$, which correspond to clusters containing one more or one fewer atoms in accordance with formula (3.22). Magic numbers of atoms have clusters with completed shells. In addition, clusters whose atoms form a regular geometrical figure correspond to magic numbers of cluster atoms. Clusters of identical shape form a family in which clusters are characterized by a number of layers. As a demonstration of this, we construct a family of clusters of the *icosahedron* shape. Its basis is the icosahedral cluster of 13 atoms, where one atom is located at the center, and the other 12 atoms are found on the sphere of radius R which is connected to the side length R_2 of the 20 surface triangles by the relation

$$R = \frac{\sqrt{5}}{4 \sin \frac{\pi}{5}} R_2 = 0.951 R_2 \quad (4.33)$$

In order to construct the second cluster of the family of completed icosahedral clusters, we continue with 12 lines joining the surface atoms with the central one at a distance R and placing at these points the vertex atoms of the new cluster. By joining the nearest vertices, we obtain 20 regular triangles with 30 edges. Additional atoms are placed in the middle of these edges. Hence the second cluster of the family of completed icosahedra contains $12 + 30 = 42$ surface atoms, and the total number of atoms in this cluster is 55.

Using this operation to form the m th cluster of this family from the $m-1$ th cluster, we continue by R the lines joining the cluster center and vertices of the previous clusters, placing at these points the 12 vertex atoms of a new cluster shell. Joining the nearest vertices leads to the formation of 20 regular surface triangles with side length mR . We divide each side into m parts and place the edge atoms there. Next, we draw lines parallel to the triangle sides and place atoms at the intersection points. Thus, the new layer contains 12 vertex atoms, $30(m-1)$ edge atoms and $20(m-1)(m-2)/2$ atoms located inside the surface triangles. The total number of atoms in this layer is $10m^2 + 2$, and the total number of atoms n in this icosahedral cluster is

$$n = \frac{10}{3}m^3 + 5m^2 + \frac{11}{3}m + 1 \quad (4.34)$$

Thus one can characterize the construction of a regular cluster by both its filled shells and its layers.

4.10 Clusters with Pair Interaction of Atoms as Fermi Systems

A cluster is a system of a finite number of bound atoms. Below we consider clusters with a pair interaction of atoms, so that an individual atom can be modeled by a ball and occupy a certain place inside the cluster. Clusters with an optimal configuration of atoms form certain geometric figures depending on the character of atom interaction. Then atoms cannot be located at positions occupied by other atoms, and in this respect the cluster as a system of bound atoms is similar to a system of Fermi particles. This analogy is valid if the cluster surface contains many atoms with identical parameters, and the transitions of surface atoms in free positions of the cluster surface determine the parameters of an excited cluster. In contrast to systems of Fermi particles, the binding energy of a surface atom depends on the occupation of positions of its nearest neighbors. Hence the Fermi–Dirac distribution is applicable to cluster configurations with filled or almost filled shells and where the number of transferring atoms is relatively small.

For simplicity, let us analyze large clusters consisting of classical atoms with a short-range interaction when only nearest neighbors partake in interactions in the cluster. Laying aside the problem of competing structures, we consider large clusters of the face-centered cubic structure. Then the distances between nearest neighbors are equal to the equilibrium distance between atoms of the diatomic molecule, and the total binding energy of the cluster atoms at zero temperature is proportional to the number of bonds between nearest neighbors. Hence the optimization of the cluster structure at zero temperature can be made on the basis of the total number of bonds between nearest neighbors.

Within the framework of the *cluster Fermi model*, the distribution function of atoms on shells is given by the Fermi–Dirac formula

$$q_{nk} = \frac{n_k}{1 + \exp\left(\frac{\varepsilon_k - \mu_n}{T}\right)} \quad (4.35)$$

Here q_{nk} is the optimal number of atoms in the k th shell at a given number n of cluster atoms, n_k is the total number of atoms in the k th shell, ε_k is the binding atom energy for this shell and μ_n is the *cluster chemical potential*. From this there follows for the total number of cluster atoms

$$n = \sum_k q_{nk} = \sum_k \frac{n_k}{1 + \exp[(\varepsilon_k - \mu_n)/T]} \quad (4.36)$$

This relation is the equation for the chemical potential μ_n of a cluster consisting of n atoms.

Assume the chemical potential to be a smooth function of a number of cluster atoms $|\mu_{n+1} - \mu_n| \ll \mu_n$, so that $\mu_{n+1} = \mu_n + d\mu_n/dn$. The total cluster energy is

$$E_n = \sum_k \varepsilon_k q_{nk}$$

and the average binding energy $\bar{\varepsilon}_n$ per cluster atom is equal to

$$\bar{\varepsilon}_n = \frac{dE_n}{dn} = \frac{1}{T} \frac{d\mu_n}{dn} \sum_k \varepsilon_k n_k q_{nk} (n_k - q_{nk}) \quad (4.37)$$

From this formula it follows that free and filled shells do not give a contribution to the average binding energy of the cluster atoms.

Let us determine the cluster chemical potential in the *two-shell approximation* if we assume vacancies to be located in two cluster shells or layers only. Then the lower shell is almost filled, and the upper is almost free. Let us denote by l the number of states for the lower shell (layer); the number of states for the upper shell (layer) is denoted by m , the atomic energy of the lower state is ε_l , and the energy of the upper shells is ε_m . Then equation (4.36) for the chemical potential of the Fermi–Dirac distribution has the form:

$$n = \frac{l}{1 + \exp[(\varepsilon_l - \mu)/T]} + \frac{m}{1 + \exp[(\varepsilon_m - \mu)/T]} = l - p + k \quad (4.38)$$

where p is the average number of vacancies in the lower shell and k is the number of atoms in the upper shell. We assume $p, k \ll l, m$, so that

$$p = l \exp\left(\frac{\varepsilon_l - \mu}{T}\right) \left[1 + \exp\left(\frac{\varepsilon_l - \mu}{T}\right)\right]^{-1} = l \exp\left[\frac{\varepsilon_l - \mu}{T}\right], \quad k = m \exp\left[\frac{\mu - \varepsilon_m}{T}\right]$$

From this there follows

$$pk = lm \exp\left(\frac{\varepsilon_l - \varepsilon_m}{T}\right) = lm \exp\left(-\frac{\varepsilon_o}{T}\right) \quad (4.39)$$

where ε_o is the atom excitation energy for transition from the lower shell to the upper. We use as the energy unit the dissociation energy of a diatomic molecule, so that in the case of a short-range interaction of cluster atoms the binding of a surface atom is equal to the number of nearest neighbors for this atom.

The equation for the chemical potential is

$$n - l = m \exp\left(\frac{\mu - \varepsilon_m}{T}\right) - l \exp\left(\frac{\varepsilon_l - \mu}{T}\right) = mX \exp\left(-\frac{\varepsilon_m}{T}\right) - \frac{l}{X} \exp\left(\frac{\varepsilon_l}{T}\right)$$

where $X = \exp\left(\frac{\mu}{T}\right)$. Let us analyze the solution of this equation in the case when the number of cluster atoms corresponds to the number of atoms of the lower shell, i.e. the value $n - l$ is small. Then we have

$$\mu = \frac{\varepsilon_l + \varepsilon_m}{2} + T \ln \frac{l}{m} \quad (4.40)$$

Because of the symmetry of the cluster surfaces we have for the short-range interaction of atoms $\varepsilon_l + \varepsilon_m = -12$, where 12 is the number of nearest neighbors for a close-packed structure (we express the energies in the units of breaking of one bond D). For example, the surface plane $\{111\}$ corresponds to $\varepsilon_l = -9$ and $\varepsilon_m = -3$; the plane $\{100\}$ corresponds to $\varepsilon_l = -8$, $\varepsilon_m = -4$. Thus, at low temperatures we have

$$\mu = -6 + T \ln \frac{l}{m} \quad (4.41)$$

In the general case we recall the two-level approximation assuming the number of excited atoms to be relatively small, so that the excitation of atoms in one shell does not influence the

excitation of atoms in another. Hence, the problem is reduced to the two-shell approximation. Then let us divide surface atoms into two groups. Label the atoms of the cluster surface by the subscript i and the atoms of excited shells by the subscript j . The condition of a small number of excitations means that

$$\exp[(\varepsilon_i - \mu)/T] \ll 1 \quad \text{and} \quad \exp[(\varepsilon_j - \mu)/T] \gg 1$$

Using these conditions for the Fermi–Dirac formula (4.36), we obtain:

$$\Delta n = \sum_i n_i X \exp\left(-\frac{\varepsilon_i}{T}\right) - \sum_j \frac{n_j}{X} \exp\left(\frac{\varepsilon_j}{T}\right)$$

where $\Delta n = n - \sum_j n_j$, $X = \exp(\mu/T)$. This gives for the chemical potential of the cluster:

$$\mu = \frac{\varepsilon_i + \varepsilon_j}{2} + T \ln \left[\frac{\Delta n}{2a} + \sqrt{\left(\frac{\Delta n}{2a}\right)^2 + \frac{b}{a}} \right] \quad (4.42)$$

where $a = \sum_i n_i \exp(-\varepsilon_i/T)$, $b = \sum_j n_j \exp(\varepsilon_j/T)$, and n_i is the total number of feasible excited states. In particular, in the limiting case

$$\Delta n \ll \sqrt{a/b} = 1/X$$

we obtain

$$\mu = -6D + \frac{T}{2} \ln \frac{a}{b} \quad (4.43)$$

This formula is transformed into (4.40) in the two-shell approximation. In this case the numbers of vacancies and excitations are equal to each other and are $\sqrt{ab}$. We see that in this case the cluster is similar to a semiconductor with a small density of free electrons. The atoms of the cluster play the role of electrons in the semiconductor. Such a semiconductor has a Fermi level in the middle of a forbidden zone. Then we have for the cluster chemical potential $\mu = -6D$ with accuracy up to the thermal energy because $\varepsilon_i + \varepsilon_j = -12D$ on average.

It is possible to obtain this result in a simple way by using the symmetry of the problem. Indeed, let us take a unit of a flat surface and assume the surface to be covered fully by atoms at zero temperature. The numbers of vacancies and excitations are the same at a finite temperature, and the system is symmetrical with respect to the replacement of vacancies by excitations. From this it follows that the chemical potential of this surface and the cluster cohesive energy are equal to $-6D$.

4.11 Partition Function of a Weakly Excited Cluster

Let us use the two-level approximation to determine the partition function of an excited cluster in which the lower shell is almost filled and the upper is almost empty. Denoting the number of atoms for filled and free shells by l and m correspondingly, we have for the *cluster partition function* Z_k if the upper shell contains k atoms, and if the lower shell contains p vacancies:

$$Z_k = C_l^{l-p} C_m^k Y^{-k} \quad (4.44)$$

Here l , m are the numbers of atoms in the filled lower and upper shells correspondingly, C_m^k is the number of combinations of k atoms for m states, $Y = \exp(\varepsilon_o/T)$ and ε_o is the excitation energy for atom transition between shells, and the partition function for this distribution equals:

$$Z = \sum_{k=0}^{\min(l,n)} C_l^{m-k} * C_m^k * Y^{-k} \quad (4.45)$$

Formula (4.45) gives the distribution of a cluster of a given size n over the number of atoms k on the upper shell. Here $p = n - k$, so that n is the number of atoms located in the two shells because atoms of internal shells do not take part in the transitions under consideration. The partition function (4.45) has a maximum at $k = k_o$, and we assume $k_o \gg 1$. Denoting $Z_{k_o} = Z_o$, let us represent the distribution function in the form of the Gaussian distribution (2.4):

$$Z_k = Z_o \exp\left(-\frac{(k - k_o)^2}{2\Delta^2}\right) \quad (4.46)$$

From the condition $\int Z_k dk = Z$, where Z is the total partition function (4.46), it follows that $Z_o = Z / (\Delta\sqrt{2\pi})$.

Let us expand $\ln Z_k$ near k_o . From formula (4.45) it follows for $k \ll m$, $p \ll l$:

$$Z_k = \text{Const} \cdot \frac{l^p}{p!} \cdot \frac{m^k}{k!} \cdot Y^{-k}, \quad \ln Z_k = C + p \ln l - \ln p! + k \ln m - \ln k! - k \ln Y$$

Since $n = l - p + k$, for $k \gg 1$ we have $\ln k! = \int_1^k dk' \ln k'$, so that this expansion has the form:

$$\ln Z_k = \ln Z_o - (k - k_o)^2 \left[\frac{1}{2(l + k_o - n)} + \frac{1}{2k_o} \right] = \ln Z_o - \frac{(k - k_o)^2}{2\Delta^2}$$

where k_o satisfies the relation (4.39), so that

$$(l + k_o - n)k_o = \frac{lm}{Y} = lm \exp\left(-\frac{\varepsilon_o}{T}\right), \quad \frac{1}{\Delta^2} = \frac{1}{l + k_o - n} + \frac{1}{k_o} \quad (4.47)$$

and ε_o is the energy of atom transition from the lower shell to the upper. In particular, in the case $n = l$ we have $k_o = \sqrt{lm} \exp[-\varepsilon_o/(2T)] \gg 1$, and the distribution function over the excited states of the cluster has the following form in this case:

$$Z_k = \frac{Z}{\sqrt{\pi k_o}} \exp \left[-\frac{(k - k_o)^2}{k_o} \right] \quad (4.48)$$

The above formulae are valid for $1 \ll k_o \ll l, m$, and are convenient for the analysis of the transition of atoms in a weakly excited cluster.

In order to ascertain the validity of the two-level approximation for real clusters, let us consider clusters of the face-centered cubic structure, which is optimal for large clusters with a short-range interaction. The optimal configuration of atoms for clusters with filled shells or layers, i.e. for clusters with magic numbers of atoms, is a *regular truncated octahedron*, the surface of which consists of 6 squares and 8 regular hexagons. Such figures form a family, and each figure of this family will be characterized by a number m which is the number of internal atoms at each of the 36 edges.

For example, we consider a regular truncated octahedron with $m = 4$, so that the cluster consists of 1289 atoms and has 24 vertex atoms with a binding energy $\varepsilon = 6D$ in the case of short-range interaction of atoms (as before, we express the binding energy of atoms in terms of the numbers of bonds with nearest neighbors), 108 edge atoms with $\varepsilon = 7D$, 54 atoms inside surface squares with $\varepsilon = 8D$, and 296 atoms inside surface hexagons with $\varepsilon = 9D$. Atoms of this cluster can transfer to the surface of its squares (192 positions) where atoms have a binding energy $\varepsilon = 4D$, and to the surface of the regular hexagons (488 positions) where the binding energy is $\varepsilon = 3D$. One can see that the numbers of atoms in identical positions for this cluster structure are large enough to give a temperature range in which the number of transferring atoms is relatively small, and Fermi–Dirac statistics can be valid.

5 Equilibria Between States of Discrete and Continuous Spectra

5.1 The Saha Distribution

In Chapter 2 we consider the distributions of gaseous particles by bound or free states. Now we analyze the specific distributions between the bound and free states of atomic particles. In the case where electrons are such particles, this connection determines the equilibrium between states of continuous and discrete spectra of electrons in a plasma. This equilibrium is maintained by the processes



where e is the electron, A^+ is the ion and A is the atom. We consider a quasineutral plasma in which the electron and ion number densities are equal.

Let us place an ionized gas in a certain volume Ω and denote the number of electrons, ions and atoms in this volume by n_e, n_i, n_a ($n_e = n_i$). The Boltzmann formula (2.20), allowing for the statistical weight of continuous spectrum states, gives for the ratio between free and bound states of electrons:

$$\frac{n_i}{n_a} = \frac{g_e g_i}{g_a} \int \exp \left(-\frac{J + p^2/(2m_e)}{T} \right) \frac{d\mathbf{p} \, d\mathbf{r}}{(2\pi\hbar)^3}$$

Here $g_e = 2, g_i$ and g_a are the statistical weights of electrons, ions and atoms correspondingly with respect to their electronic state, J is the atom ionization potential, and p is the free electron momentum so that $J + p^2/(2m_e)$ is the energy of transition from the ground atom state in a given state of a free electron. We assume atoms to be found only in the ground state.

Integration of this expression over the electron momenta yields:

$$\frac{n_i}{n_a} = \frac{g_e g_i}{g_a} \cdot \left(\frac{m_e T}{2\pi\hbar^2} \right)^{3/2} \cdot \exp \left(-\frac{J}{T} \right) \int d\mathbf{r}$$

Integrating over the volume Ω , we take into account that the exchange of two electrons by their states does not change the state of the electron system. Therefore $\int d\mathbf{r} = \Omega/n_e$, and introducing the number densities of electrons $N_e = n_e/\Omega$, ions $N_i = n_i/\Omega$ and atoms $N_a = n_a/\Omega$, we reduce the obtained expression to the form:

$$\frac{N_e N_i}{N_a} = \frac{g_e g_i}{g_a} \cdot \left(\frac{m_e T}{2\pi\hbar^2} \right)^{3/2} \cdot \exp \left(-\frac{J}{T} \right) \quad (5.2)$$

This formula is named the *Saha distribution*, and the value

$$K(T) = \frac{g_e g_i}{g_a} \cdot \left(\frac{m_e T}{2\pi \hbar^2} \right)^{3/2} \cdot \exp\left(-\frac{J}{T}\right) \quad (5.3)$$

is the *equilibrium constant for the ionization equilibrium* (5.1).

Let us rewrite the Saha distribution in the form of the Boltzmann distribution (2.20):

$$\frac{N_i}{N_a} = \frac{g_c}{g_a} \cdot \exp\left(-\frac{J}{T}\right) \quad (5.4)$$

so that

$$g_c = \frac{g_e g_i}{N_e} \cdot \left(\frac{m_e T}{2\pi \hbar^2} \right)^{3/2} \quad (5.5a)$$

is an effective *statistical weight of continuous spectrum*. For an ideal plasma this statistical weight is large enough because the electron number density N_e is small compared with a typical atomic one. To demonstrate this, we consider as an example a glow-discharge plasma of rare gases, taking its typical parameters $N_e \sim 10^{12} \text{ cm}^{-3}$, $T = 3 \text{ eV}$. Since $g_i = 6$, we have for the statistical weight of a continuous spectrum $g_c \approx 2 \cdot 10^{11}$. The large statistical weight of a continuous spectrum leads to the following conclusion. First, a noticeable ionization takes place at low temperatures $T \ll J$. Second, the probability of an atom excitation is small at these temperatures, i.e. the number density of excited atoms is relatively small. Hence at these temperatures atoms are found in the ground state or are ionized. Correspondingly, the partition function (2.23) of an *ionizing gas* is equal to

$$Z = 1 + g_c \exp\left(-\frac{J}{T}\right) \quad (5.5b)$$

5.2 Heat Capacity of Ionized Gases

Let us consider a buffer gas with a weakly ionized gaseous admixture, so that the ionization potential of the admixture atoms is relatively small, and full ionization of the admixture is possible in the considering temperature range. A buffer gas provides stability for this system, because it allows us to escape the instabilities of a fully ionized plasma. Our goal is to find the heat capacity of this mixture as a function of its temperature. Evidently, this value increases significantly in the range of the ionization transition because of the high statistical weight of the continuous spectrum state in gases.

The specific energy of this system, i.e. the energy per unit volume, is equal to

$$E = \frac{3}{2} T N_o + \frac{3}{2} T (N - N_e) + (J + 3T) N_e \quad (5.6)$$

where N_o is the number density of buffer atoms, N is the initial number density of admixture atoms, T is the mixture temperature, J is the ionization potential of admixture atoms and N_e is the electron number density which is equal to the ion number density because of the plasma's

quasineutrality. We assume the system volume to be constant in the course of its heating. The ratio between the number densities of electrons and atoms for ionization equilibrium in the system is given by the Saha formula (5.2)

$$\frac{N_e^2}{N - N_e} = K(T) \quad (5.7)$$

Here $K(T)$ is the ionization equilibrium constant (5.3). According to formula (5.3) we have $K(T) \sim \exp(-J/T)$, i.e. $dK/dT = KJ/T^2$. N is the number of admixture nuclei, which is conserved in the course of the temperature variation.

We have in the range of the ionization transition for the specific *heat capacity* of an ionizing gas, i.e. the heat capacity per unit volume

$$C_V = \frac{dE}{dT} = \frac{3}{2}N_o + J \frac{dN_e}{dT} = \frac{3}{2}N_o + \frac{J^2 N}{T^2} F\left(\frac{K}{2N}\right) \quad (5.8)$$

$$F(x) = \frac{x}{\sqrt{x^2 + 2x} \cdot (\sqrt{x^2 + 2x} + x + 1)}$$

Here we take into account that the ionization transition proceeds at low temperatures, i.e. $T \ll J$. Hence the contribution of an admixture to the mixture's heat capacity is $(J/T)^2$ more in the range of ionization transition than outside this range. The second term in formula (5.8) has a maximum at $K = 0.8N$. The maximum value of the specific heat capacity of an

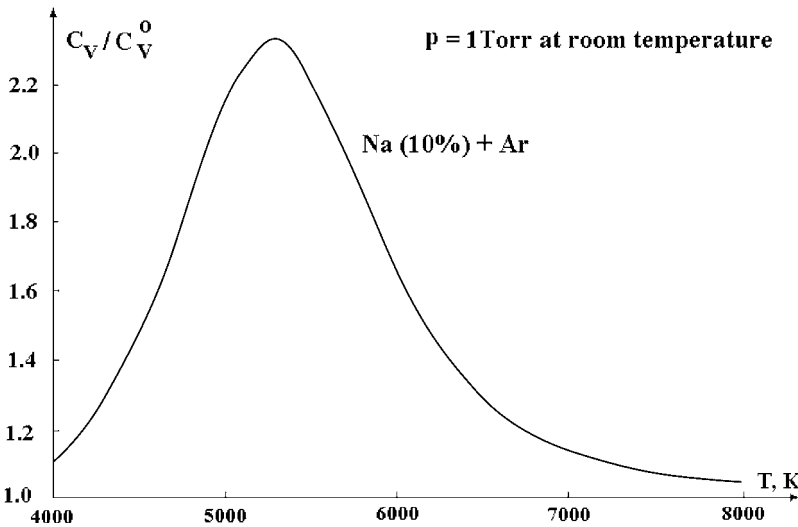


Figure 5.1. The specific heat capacity of the mixture of argon and sodium. At the beginning argon at the pressure 1 Torr is found at room temperature. As it heated, sodium is added to it, so that the sodium concentration is 10% (a number of sodium atoms to a number of argon atoms). The heat capacity corresponds to the temperature range of sodium ionization transition.

ionizing gas is

$$(C_V)_{\max} = \frac{3}{2}N_o + 0.17 \frac{J^2}{T^2} N \quad (5.9)$$

Note that the ionization transition proceeds over a narrow range of temperatures $\Delta T \sim T^2/J$, since owing to the high statistical weight (5.5) of the ionized state the ionization transition takes place at low temperatures $T \ll J$. As a demonstration of this fact, Figure 5.1 gives the temperature dependence of the specific heat capacity of argon at the pressure 1 Torr at room temperature with 10% admixture of sodium in the range of the sodium ionization transition. One can see the bell-shaped form of the temperature dependence of the heat capacity of this mixture because the ionization transition occurs over a narrow temperature range.

5.3 Ionization Equilibrium for Metallic Particles in a Hot Gas

The binding energy of an electron with a metallic surface is called the *work function*. Usually the work function is lower than the ionization potential of the corresponding atom. For example, the ionization potential of a copper atom is equal to 7.73 eV, while the copper work function, the electron binding energy with the copper surface, is 4.40 eV. The corresponding values are equal to 7.58 eV and 4.3 eV for silver, and 3.89 eV and 1.81 eV for cesium. Thus the presence of the metallic particles in a hot vapor affects the ionization equilibrium involving electrons and charged particles. Below we assume that electrons in a hot gas or vapor result from small particles only. Our goal is to determine the equilibrium charge of these particles and the number density of electrons in a hot gas containing free metallic particles.

For simplicity, we assume the particles to be spherical and to have an identical radius r_o . This radius is large enough:

$$r_o \gg e^2/T \quad (5.10)$$

This criterion allows us to consider a particle as a bulk one. The electric potential of a particle varies weakly as a result of the addition of one electron to it. Write the relationship between the number densities of particles n_Z and n_{Z+1} that contain charges Z and $Z+1$ correspondingly. By analogy with the Saha distribution (5.2), we have:

$$\frac{n_Z N_e}{n_{Z+1}} = 2 \left(\frac{m_e T}{2\pi\hbar^2} \right)^{3/2} \cdot \exp \left(-\frac{W_Z}{T} \right) \quad (5.11)$$

where W_Z is the work function for the particle of charge Z , N_e is the electron number density, and the factor 2 accounts for the electrons' statistical weight (two spin projections). The work function of the particle is a sum of the work function of a flat surface W of a given material and the potential energy of the charged particle. Using the electric potential for the particle charge $Z + 1/2$ (the average between Z and $Z + 1$), we have:

$$W_Z = W + \left(Z + \frac{1}{2} \right) \cdot \frac{e^2}{r_o}$$

Substitution of this expression in formula (5.10) transforms it to the form:

$$\frac{n_Z N_e}{n_{Z+1}} = 2 \left(\frac{m_e T}{2\pi\hbar^2} \right)^{3/2} \cdot \exp \left[-\frac{W_Z}{T} - \frac{(Z + 1/2)e^2}{r_o T} \right] \quad (5.12)$$

This formula gives the distribution of charged particles on charges. If the average charge is large, this distribution is sharp. Indeed, introducing n_0 , the number density of neutral particles, we have from formula (5.12)

$$n_Z = n_{Z-1} A \exp \left(-\frac{Z e^2}{r_o T} \right) = n_0 A^Z \exp \left(-\frac{Z^2 e^2}{2 r_o T} \right) \quad (5.13a)$$

where

$$A = \frac{2}{N_e} \left(\frac{m_e T}{2\pi\hbar^2} \right)^{3/2} \exp \left(-\frac{W}{T} \right) \quad (5.13b)$$

If the charges are close to the average one, this relationship can be written in the form of the Gaussian distribution (2.4)

$$n_Z = n_{\bar{Z}} \cdot \exp \left[-\frac{(Z - \bar{Z})^2}{2\Delta Z^2} \right], \quad \Delta Z^2 = \frac{r_o T}{e^2} \quad (5.14)$$

The average charge of particles follows from the relation $\bar{Z} e^2 / (r_o T) = \ln A$, which yields

$$\bar{Z} = \frac{r_o T}{e^2} \ln \left[\frac{2}{N_e} \left(\frac{m_e T}{2\pi\hbar^2} \right)^{3/2} \exp \left(-\frac{W}{T} \right) \right] \quad (5.15)$$

This relation must be combined with the condition of plasma quasineutrality:

$$N_e = \bar{Z} N_p \quad (5.16)$$

where N_p is the total number density of particles. Excluding from these equations the electron number density, we obtain the equation for the average charge of particles in a buffer gas with metallic particles if the electrons result from the ionization of metallic particles only:

$$\bar{Z} = \frac{r_o T}{e^2} \ln \left[\frac{2}{\bar{Z} N_p} \left(\frac{m_e T}{2\pi\hbar^2} \right)^{3/2} \exp \left(-\frac{W}{T} \right) \right] \quad (5.17)$$

We now give an example of metallic particles in a buffer gas in order to demonstrate the reality of the above analysis. Let molybdenum clusters be located in a buffer gas, and the cluster radius be $r_o = 10$ nm, so that the number of atoms per cluster is $n \approx 2 \cdot 10^5$, the gas temperature coincides with the melting point of bulk molybdenum $T_m = 2886$ K, and the molybdenum density in a space is $3 \mu\text{g}/\text{cm}^3$, which corresponds to the average number density of clusters $N_p = 8 \cdot 10^{10} \text{ cm}^{-3}$. Under these conditions the number density of free molybdenum atoms in a space (taking into account the cluster size) is two orders of magnitude lower than the number density of bound molybdenum atoms $\sim 2 \cdot 10^{16} \text{ cm}^{-3}$. Under these

conditions formula (5.17) gives for the average cluster charge $\bar{Z} = 3.7$. This corresponds to the electron number density $N_e = 3 \cdot 10^{11} \text{ cm}^{-3}$ according to formula (5.16) if the electrons result from ionization of hot clusters. The equilibrium number density of electrons is $N_e = 3 \cdot 10^{13} \text{ cm}^{-3}$ if these electrons are formed over a plane molybdenum surface of a given temperature. Therefore the attachment of electrons to metallic clusters does not influence the particle charge, and thus the plasma formed in a hot buffer gas with metallic particles is a specific physical object.

5.4 Thermoemission of Electrons

At high temperatures or large particle sizes the parameter $Ze^2/(r_o T)$ becomes small. Then from formula (5.15) it follows that:

$$N_e = 2 \left(\frac{m_e T}{2\pi\hbar^2} \right)^{3/2} \exp \left(-\frac{W}{T} \right) \quad (5.18)$$

This formula describes the equilibrium density of electrons above a flat surface. In this case the electric potential of the particle is small compared with the typical thermal energy. Therefore the conditions near and far from the particle are identical. Then the average particle charge is determined by formula (5.18), where the number densities of both electrons and particles are known.

Formula (5.18) allows one to find the electron current from a hot surface. Indeed, in the case of equilibrium between electrons and a hot surface, the electron current from the surface is equal to the current toward it. Assuming the probability of electron attachment to the surface at their contact to be one, we obtain for the electron current density to the surface (which is equal to the electron current density from it):

$$i = e \sqrt{\frac{T}{2\pi m_e}} \cdot N_e = \frac{em_e T^2}{2\pi^2 \hbar^3} \exp \left(-\frac{W}{T} \right) \quad (5.19)$$

This formula is known as the *Richardson–Dushman formula* which describes the electron current density emitted by a hot surface. Such an emission is called *thermoemission of electrons*. For the analysis of problems of gaseous discharge it is convenient to rewrite the Richardson–Dushman formula (5.19) for the thermoemission current density in the form:

$$i = A_R T^2 \exp \left(-\frac{W}{T} \right), \quad A_R = \frac{em_e}{2\pi^2 \hbar^3} \quad (5.20)$$

and the *Richardson constant* A_R is equal to $120 \text{ A}/(\text{cm}^2 \text{ K}^2)$ according to formula (5.20). Table 5.1 contains values of this parameter for some metals.

Above we evaluated the emission current from a metallic surface on the basis of its equality to the current emitted and absorbed by a surface. Hence we used the parameters of a surrounding plasma for this aim. Now we find this value from the parameters of *metallic plasma* inside a metal. Analyzing the thermoemission of electrons from this other standpoint, we consider a metallic plasma as a system of degenerate electrons whose distribution of energies is

Table 5.1. The Richardson constant A_R expressed in $\text{A}/(\text{cm}^2\text{K}^2)$.

Metal	Ba	Cs	Cu	Hf	Mo	Nb
A_R	60	160	60	14	51	57

Metal	Pd	Ta	Th	Ti	W	Zr
A_R	60	55	70	60	75	330

given by the Fermi–Dirac formula (2.35). If the electron kinetic energy in the direction of the metal surface exceeds the value $\varepsilon_F + W$, the electron can be released. Then the electron flux from the metallic surface is $\int v_x f(\mathbf{p}) d\mathbf{p}$, where the integral is taken at $m_e v_x^2/2 \geq \varepsilon_F + W$, and v_x is the velocity component towards the surface. From formula (2.37) we have for the number density of electrons in the momentum range from $\mathbf{p}$ up to $\mathbf{p}+d\mathbf{p}$ under the condition $\varepsilon - \mu \gg T$

$$f(\mathbf{p})d\mathbf{p} = \frac{2d\mathbf{p}}{(2\pi\hbar)^3} \exp\left(-\frac{\varepsilon - \mu}{T}\right) \quad (5.21)$$

Using cylindrical coordinates $d\mathbf{p} = 2\pi p_\rho dp_\rho dp_x$, $\varepsilon = \varepsilon_F + p_x^2/(2m_e) + p_\rho^2/(2m_e)$, and $\mu = -\varepsilon_F$, we obtain after integration over p_ρ

$$j = 2\pi m_e T \int v_x \frac{m_e dv_x}{4\pi^3 \hbar^3} \exp\left(-\frac{m_e v_x^2}{2T} + \frac{\mu}{T}\right) = \frac{m_e T^2}{2\pi^2 \hbar^3} \exp\left(-\frac{W}{T}\right) \quad (5.22)$$

Since the electron current density is $i = ej$, this expression coincides with (5.19). Thus, we obtain the same result for the electron thermoemission current from both the equilibrium of a metallic surface with a surrounding plasma and the evaporation of electrons of a metallic plasma which is modeled by a degenerate electron gas.

5.5 Autoelectron and Thermo-autoelectron Emission

Another mechanism for the emission of electrons from a metallic surface is realized in the presence of an electric field and is called *autoelectron emission*. The self-consistent field for electrons in this case is shown in Figure 5.2b, and an electron can be released by passing through a barrier. Let us evaluate the current for a free electron which penetrates the triangular barrier of Figure 5.2b. The wave function Ψ of this electron satisfies the one-dimensional Schrödinger equation

$$-\frac{\hbar^2}{2m_e} \frac{d^2\Psi}{dx^2} + U\Psi = \varepsilon\Psi$$

where ε is the electron energy, $U = 0$ at $x < 0$, and at $x > 0$ we have that $U = W - Fx$, so that W is the surface work function and F is the electric field strength. The electron wave function of a free electron to the left of the barrier has the form

$$\Psi = C \cos kx$$

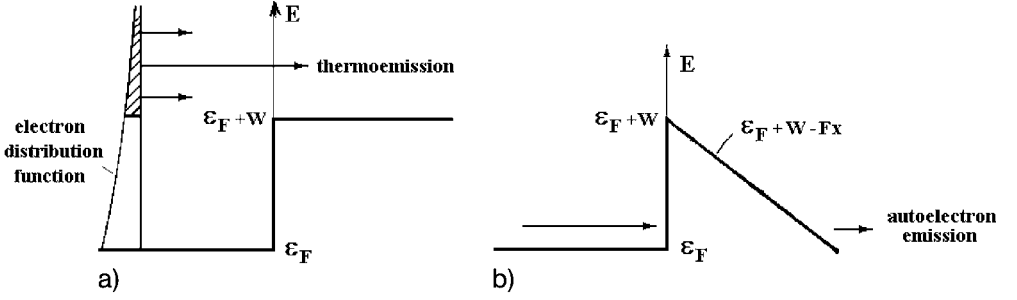


Figure 5.2. The character of thermoemission of electrons (a) and autoelectron emission (b).

where $k = \sqrt{2m_e \varepsilon} / \hbar$ is the electron wave vector. Considering the electric field strength to be relatively small, we use the quasiclassical solution of this equation. Then taking the electron wave function in the form

$$\Psi = C \exp(-S)$$

substituting this in the Schrödinger equation and neglecting the second derivative of S ($(S')^2 \gg S''$), we find for the electron wave function

$$\Psi = C \exp \left[- \int_0^x \sqrt{\frac{2m_e}{\hbar^2} (U - \varepsilon)} dx' \right]$$

From this one can find the electron current density j outside the barrier:

$$j = \frac{\hbar}{2m_e i} (\Psi^* \nabla \Psi - \Psi \nabla \Psi^*)$$

This leads to the *Fowler–Nordheim formula* for autoelectron emission if we neglect the thermal energy of electrons

$$j_{ae} = \frac{e^3 F^2}{16\pi^2 \hbar W} \exp \left(- \frac{4(2m_e)^{1/2} W^{3/2}}{3\hbar e F} \right) \quad (5.23)$$

This formula is valid if the exponent is large, and correspondingly the emission current density is small compared with a typical atomic value.

In fact, the Fowler–Nordheim formula describes the passage of most of the electrons through a barrier (Figure 5.2) whose height is W with respect to the Fermi level, and the passage coefficient is approximately equal to

$$D(W) = \exp \left(- \frac{4(2m_e)^{1/2} W^{3/2}}{3\hbar e F} \right)$$

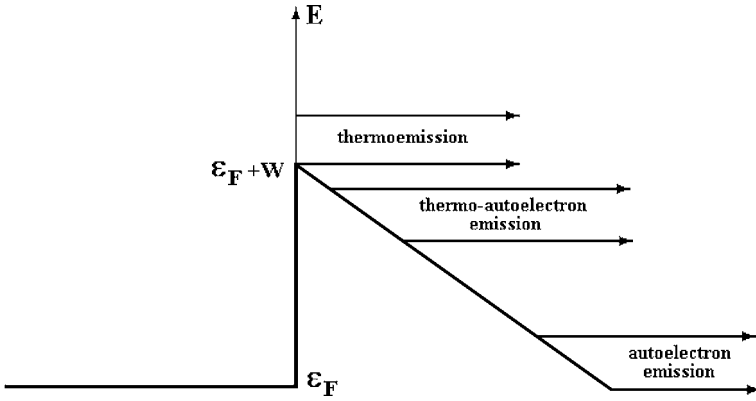


Figure 5.3. Energetic groups of electrons which partake in processes of thermoemission, autoelectron emission and thermo-autoelectron emission.

If an electron has kinetic energy $mv_x^2/2$, the barrier height for it is $W + \varepsilon_F - mv_x^2/2$, and the passage coefficient through this barrier is

$$D\left(W + \varepsilon_F - \frac{mv_x^2}{2}\right) = \exp\left(-\frac{4(2m_e)^{1/2}\left(W + \varepsilon_F - \frac{mv_x^2}{2}\right)^{3/2}}{3\hbar e F}\right)$$

One can divide the released electrons into three groups (Figure 5.3). The first includes fast electrons whose energy exceeds the barrier height, and liberation of these electrons determines the thermoemission of electrons from a metallic surface. Most thermal electrons belong to the second group, and these are released by passing through barrier. The autoelectron emission current (5.23) is due to these electrons. The intermediate character of electron emission is created by fast electrons with a tunnel release (see Figure 5.3). In this type of *thermo-autoelectron emission* the electron current density is given by

$$\begin{aligned} j &= \int v_x f(\mathbf{p}) d\mathbf{p} D\left(W + \varepsilon_F - \frac{mv_x^2}{2}\right) \\ &= \frac{m_e T^2}{2\pi^2 \hbar^3} \int_0^{W/T} dz \exp\left(-z - \frac{4(2m_e)^{1/2}(W - zT)^{3/2}}{3\hbar e F}\right) \end{aligned}$$

where $z = mv_x^2/2T - \varepsilon_F/T$. Under the assumption that a narrow range of z gives the main contribution to this integral (or in the limit $T \rightarrow 0$), we obtain from this formula (5.22). Taking this integral by the pass method, we find the contribution from fast electrons which are liberated by the tunnel transition. Then we have for the pass position z_o

$$z_o = \frac{W}{T} - \frac{\hbar^2 e^2 F^2}{8m_e T^3}$$

and a range near this point determines the thermo-autoelectron emission. We assume that $z_o \gg 1$, i.e. the first term in this formula for z_o is larger than the second one. This gives for the current density of thermo-autoelectron emission of electrons

$$j_{ae} = \frac{m_e^{1/2} e F T}{(2\pi)^{3/2} \hbar^2} \exp\left(-\frac{W}{T} + \frac{\hbar^2 e^2 F^2}{24 m_e T^3}\right) \quad (5.24)$$

This expression is valid if the range Δz which determines this integral is small compared with W/T , which requires fulfilling the following criterion

$$\frac{e F \hbar}{m_e^{1/2}} \ll \sqrt{W T} \quad (5.25)$$

5.6 Dissociative Equilibrium in Molecular Gases

Dissociative equilibrium in molecular gases is similar to ionization equilibrium in atomic gases. The equilibrium between atoms and molecules in a molecular gas is maintained by the processes:



These processes establish an equilibrium between states of discrete and continuous spectra which correspond to bound and free states of atoms. Let us find the relation between the equilibrium number densities of atoms and molecules in this case by analogy with the Saha distribution. On the basis of the Saha formula (5.2) we obtain for the relationship between the number densities of atoms and molecules in the ground state:

$$\frac{N_X N_Y}{N_{XY}(v=0, J=0)} = \frac{g_X g_Y}{g_{XY}} \left(\frac{\mu T}{2\pi \hbar^2}\right)^{3/2} \exp\left(-\frac{D}{T}\right) \quad (5.27)$$

where g_X, g_Y, g_{XY} are the statistical weights of atoms and molecules with respect to their electron state, μ is the reduced mass of atoms X and Y , and D is the dissociation energy of the molecule. We assume the vibrational and translational temperatures to be equal.

In contrast to the ionization equilibrium, in this case molecules are found mostly in excited vibrational–rotational states. Using formulae (3.44) and (3.46) which connect the number density of molecules in the ground state with their total number density, we transform formula (5.27) to the form:

$$\frac{N_X N_Y}{N_{XY}} = K_{\text{dis}}(T) = \frac{g_X g_Y}{g_{XY}} \left(\frac{\mu T}{2\pi \hbar^2}\right)^{3/2} \frac{B}{T} \left[1 - \exp\left(-\frac{\hbar \omega}{T}\right)\right] \exp\left(-\frac{D}{T}\right) \quad (5.28)$$

Here N_{XY} is the total number density of molecules, and K_{dis} is the equilibrium constant for the dissociation equilibrium. Note that rotational momentum is conserved as a result of the dissociation process (5.26). We assume weak vibrational excitation of molecules, which allows us to use the harmonic approximation for vibrations and means that the temperature is

not high. This is fulfilled at temperatures of molecular dissociation because of the high statistical weight of states of continuous spectrum in gases. In particular, by modeling molecules by a classical harmonic oscillator $\hbar\omega \ll T$, we have for the equilibrium constant of dissociation equilibrium

$$K_{\text{dis}} = \frac{g_X g_Y}{g_{XY}} \frac{\mu^{3/2} B \cdot \hbar\omega}{(2\pi)^{3/2} \hbar^3 T^{1/2}} \exp\left(-\frac{D}{T}\right) \quad (5.29)$$

In considering the dissociation equilibrium (5.26) for molecules with identical nuclei, we accept that the number density of nuclei is constant with varying temperature and equals $2N$. Then the ratio of the number densities of atoms N_a and molecules N_m according to formula (5.28) is given by

$$\frac{N_a^2}{N_m} = K(\text{dis}T) \quad (5.30)$$

and $2N = N_a + 2N_m$. In this case N is the initial number density of molecules, and from equation (5.30) it follows that

$$N_a = \sqrt{\frac{K_{\text{dis}}^2}{16} + N K_{\text{dis}}} - \frac{K_{\text{dis}}}{4}$$

where molecules consist of identical atoms. From formula (5.28) for the constant of dissociation equilibrium we have

$$\frac{dK_{\text{dis}}}{dT} = \frac{K_{\text{dis}} D}{T^2}$$

for $D \gg T$. Taking $\hbar\omega \ll T$, we have for the heat capacity per molecule $c_V = 7/2$. Correspondingly, the heat capacity per unit volume under these conditions is equal to

$$C_V = \frac{7}{2}N - \frac{1}{4}N_a + \frac{D}{2} \frac{dN_a}{dT} = \frac{7}{2}N - \frac{1}{4}N_a + \left(\frac{D}{T}\right)^2 N F\left(\frac{K_{\text{dis}}}{8N}\right) \quad (5.31)$$

where the function $F(x)$ is given by formula (5.8). The maximum of the heat capacity at $K_{\text{dis}} = 3.4N$ is equal to

$$(C_V)_{\text{max}} = 3.2N + 0.17 \frac{D^2}{T^2} N \quad (5.32)$$

Figure 5.4 gives the temperature dependence for the specific heat capacity of iodine with a pressure at room temperature of 1 Torr, and formula (5.29) is used for the dissociation equilibrium constant. The maximum contribution of dissociation to the iodine heat capacity exceeds by one order of magnitude the heat capacity due to the molecular heat capacity. From the analysis of the ionization and dissociation transitions we conclude that the heat capacity of the gaseous system increases strongly in the transition range because the breaking of bonds proceeds at low temperatures in comparison with the binding energy for these bonds. Nevertheless, in both cases the heat capacity does not have a strong temperature dependence in the transition range in comparison with the phase transition case.

5.7 Formation of Electron–Positron Pairs in a Radiation Field

The formation of *electron–positron pairs* is an example of equilibrium with variation of a particle number. This equilibrium is established by processes

$$e + e^+ \longleftrightarrow \hbar\omega \quad (5.33)$$

Here $e, e^+, \hbar\omega$ denote an electron, a positron and a photon respectively. We assume this system to be located in a vessel at a given temperature. Then the number densities of electrons and positrons are determined by Fermi–Dirac statistics (2.35) with chemical potential $\mu = 0$, because the numbers of particles are not conserved. The energy of formation of an electron or positron is equal to $c\sqrt{p^2 + m_e^2 c^2}$, where p is the electron or positron momentum and c is the velocity of light. Note that due to the conservation law, the electron and positron formed have opposite directions of momentum and spin. Hence we have identical distributions of electrons and positrons, and below we restrict the analysis to the electron distribution.

According to formula (2.37) we have for the number density of electrons at temperature T

$$N_e = 2 \int_0^\infty \frac{4p^2}{(2\pi\hbar)^3} dp \left[\exp \left(\frac{c\sqrt{p^2 + m_e^2 c^2}}{T} \right) + 1 \right]^{-1} \quad (5.34)$$

We take the chemical potential such that in the limit of large energies this formula is transformed into the Boltzmann formula. As we have seen, formation of pairs is determined by the parameter $T/(m_e c^2)$, where $m_e c^2 = 511$ keV. If this parameter is small, the number density of electrons $N_e \sim \exp(-T/m_e c^2)$ and can be determined on the basis of the Saha formula (5.34).

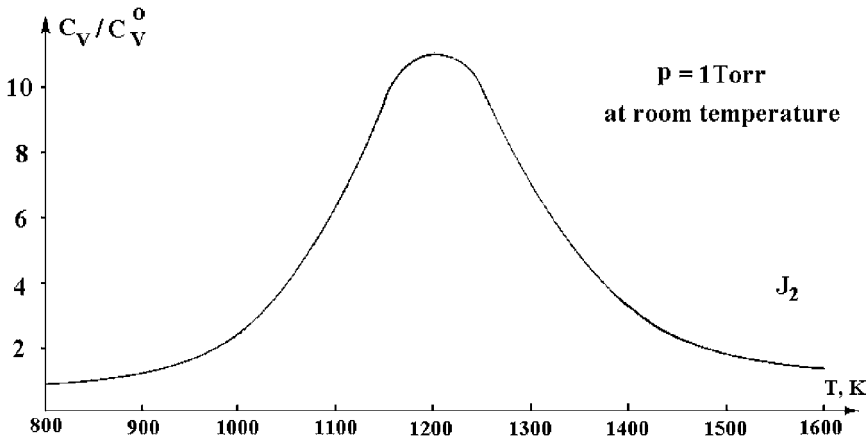


Figure 5.4. The specific heat capacity of iodine J_2 in the range of dissociation transition if the iodine number density corresponds to the pressure 1 Torr at room temperature.

In the other limiting case $T/(m_e c^2) \gg 1$ we have from formula (5.34)

$$N_e = \frac{1}{\pi^2} \left(\frac{T}{\hbar c} \right)^3 \int_0^\infty \frac{x^2 dx}{\exp(x) + 1} = 0.183 \left(\frac{T}{\hbar c} \right)^3$$

The energy of electrons E_e and positrons E_p is equal:

$$E_e = E_p = \frac{1}{\pi^2} \frac{T^4}{(\hbar c)^3} \int_0^\infty \frac{x^3 dx}{\exp(x) + 1} = \frac{7\pi^2}{120} \frac{T^4}{(\hbar c)^3} \quad (5.35)$$

The ratio of the total electron and positron energy to the radiation energy is equal to $7/4$ in this limiting case.

Part II

Equilibrium and Excitation of Atomic Systems

6 Thermodynamic Values and Thermodynamic Equilibria

6.1 Entropy as a Thermodynamic Parameter

In considering a canonical ensemble of atomic particles, we introduce the temperature of this ensemble through the average energy of an individual atomic particle, similar to formulae (2.9) and (2.10) in the case of free particles. At a certain temperature, the total energy of an atomic particle, as well as other parameters of the ensemble of particles, may vary in some range. The *fluctuation* of a value, i.e. the deviation of the current value of a parameter from its average value, is relatively small for a large number of atomic particles. Hence one can simplify the analysis of the particle ensemble by neglecting the fluctuations, and this approach is the basis of thermodynamics. It leads to simple relations between the average parameters of the ensemble and the parameters of external fields in a universal form. The universality in the thermodynamic descriptions of systems of many particles is combined with the phenomenological character of their analysis.

The thermodynamic description of an ensemble of many particles deals with the average parameters of this system when we ignore the deviation of the current value of a parameter of an ensemble of particles from its average value. We take as thermodynamic parameters the particle temperature T , the entropy of the system of particles S , and the total energy of particles E . First we find the connection between these parameters on the basis of the above formulae. The total energy of particles according to formula (2.12) is equal to

$$E = \sum_i \varepsilon_i n_i$$

where n_i is the number of particles located in a state or a group of states i and ε_i is the energy of this state. When dealing with thermodynamic quantities, we change n_i by its average values. In particular, the *entropy* of a particle system equals, according to formula (2.22)

$$S = - \sum_i n_i \ln n_i \quad (6.1)$$

where n_i is the mean number of particles located in a group of states i .

Let us consider a system with the Boltzmann distribution (2.18) of particles by states. Evolution of the system of particles is accompanied by a change in the distribution function of particles by states and leads to a variation in the thermodynamic values of the system. Assuming the temperature of the system to be conserved, we have $d \ln n_i = -\varepsilon_i dn_i / (n_i T)$. Since interaction between particles does not vary $d\varepsilon_i = 0$, and since the total number of

particles of the ensemble is conserved $\sum_i dn_i = 0$, we get

$$\begin{aligned} dS &= \sum_i dn_i \ln n_i = \sum_i dn_i \left(\frac{\varepsilon_i}{T} + \ln C \right) = \frac{1}{T} \sum_i \varepsilon_i dn_i, \quad \text{and} \\ dE &= \sum_i \varepsilon_i dn_i = T dS \end{aligned} \quad (6.2)$$

This relation connects the energy of an ensemble of particles to the entropy of the system.

6.2 First Law of Thermodynamics

Alongside the dependence on internal parameters, the internal energy E of the system of many particles can depend on external fields and the parameters of these fields. Let us take the volume of a system of weakly interacting particles as such a parameter. Then it is necessary to introduce an external field which supports this system volume V . The *mechanical work* dA under the action of the corresponding force $\mathbf{F}$ of an external field which acts on an element of the system surface ds equals

$$dA = \mathbf{F} ds = \left(\frac{\partial E}{\partial V} \right)_S dV = -p ds dx = -p dV$$

where dx is a surface displacement and p is an external *pressure*

$$p = - \left(\frac{\partial E}{\partial V} \right)_S \quad (6.3)$$

Accounting for the dependence of the energy E on two variables, one can write its differential in the form

$$dE = T dS - p dV \quad (6.4)$$

By including the second term in (6.4), compared to (6.2), we account for the interaction of the particle ensemble with external fields. Indeed, the first term of formula (6.4), $dQ = T dS$, is the internal energy of weakly interacting particles or the *heat* resulting from the change of states of the particle ensemble, and the second term of this formula takes into account the interaction of particles with external fields, so that

$$dE = dQ + dA \quad (6.5)$$

where dA is mechanical work under the action of external fields. In particular, formula (6.4) accounts for an external pressure which acts on the ensemble of particles. The work done by an external field in this case is $dA = -p dV$, i.e. the energy is consumed by compression of the system. If the particles are located in a vessel, an external force is transmitted to the system as a result of the reflection of particles from the walls of the vessel.

According to formula (6.5), the energy of the system consists of two parts: the internal energy Q , variations in which are characterized by the release of absorbed heat, and the mechanical work A which is performed by the system. There is in principle the possibility of transitions between these energy types. The relation (6.5) is called the *first law of thermodynamics*. From this it follows that heat and mechanical work are two types of energy which can be transformed each to other.

Let us determine the entropy of an atomic gas which is located at a temperature T in a volume V and contains n atoms. Because the total energy of this system is $E = \frac{3}{2}nT$ and the pressure is equal to $p = nT/V$, we have for the entropy from equation (6.4)

$$dS = \frac{dE}{T} + \frac{p dV}{T} = \frac{3}{2}n \frac{dT}{T} + n \frac{dV}{V} = nd \ln(VT^{3/2})$$

From this it follows that

$$S = n \ln(VT^{3/2}) + \text{const} \quad (6.6)$$

6.3 Joule–Thomson Process

Now let us consider the evolution of a system which is described by thermodynamic parameters. If a quasi-equilibrium state of the system is supported in the course of varying its parameters, the transition between the internal energy or heat Q of the system and its mechanical energy A proceeds in accordance with equation (6.5), and the system can be considered as an equilibrium one at each time. This means that the thermal process of the evolution of the system is represented as a sum of quasistatic processes, so that at each stage of the process the equilibrium inside the system is established and maintained. This requires a slow variation of parameters in the course of the thermal process. For example, if the pressure and volume of a gas vary as a result of the movement of a plunger, the plunger velocity must be small compared with the speed of sound in this gas. Then equilibrium is supported in the system in the course of its evolution. Below we consider some examples of thermal processes.

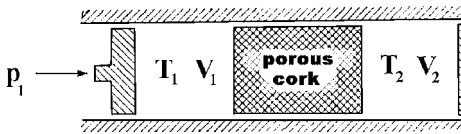


Figure 6.1. Scheme of the Joule-Thomson process.

Let us consider the *Joule–Thomson process* which proceeds with a gas located in a closed volume between two plungers (see Figure 6.1). A porous partition separates this volume into two parts, so that the gas pressures in the first volume p_1 and in the second volume p_2 do not vary in the course of the process when a partition passes from one plunger to another one. The initial gas volume is V_1 , and at the end of the process the gas volume is V_2 . So, at the beginning the right plunger touches the porous partition, while at the end of the process the left volume is zero. The mechanical work that results from a small shift of the plungers is equal to $p_2 dV_2 - p_1 dV_1$, where dV_1 , dV_2 are volume variations. Denoting by E_1 , E_2 the

internal energy of the gas at the beginning and end of the process, we have in the absence of heat exchange between the gas and the vessel

$$E_1 - E_2 = p_2 V_2 - p_1 V_1$$

This means that the gas *enthalpy*

$$H = E + pV \quad (6.7)$$

is conserved during the process.

Introduce the *heat capacity* at constant pressure as

$$C_p = \left(\frac{\partial Q}{\partial T} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (6.8)$$

We have for the Joule–Thomson process

$$dH = 0 = \left(\frac{\partial H}{\partial T} \right)_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp = C_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp$$

This gives for the temperature variation as a result of the Joule–Thomson process

$$\frac{\Delta T}{\Delta p} = \frac{T_2 - T_1}{p_2 - p_1} = -\frac{1}{C_p} \left(\frac{\partial H}{\partial p} \right)_T \quad (6.9)$$

The right-hand side of this equation is named the *Joule–Thomson coefficient*.

The Joule–Thomson process proceeds when a constant pressure is supported in a system of atomic particles. The enthalpy H is the energetic parameter which is conserved when varying the parameters of the system. In the case where a motionless gas as a whole moves with a velocity v , the conservation law has the form

$$H + M \frac{v^2}{2} = \text{const}$$

where M is the mass of the gas element under consideration. In particular, if we reduce this relation to one atom or molecule and take $H = c_p T$, we obtain this relation in the form

$$v^2 = 2c_p \frac{(T_o - T)}{m} \quad (6.10)$$

Here c_p is the heat capacity per atom or molecule, m is its mass, T_o is the initial temperature and v and T are the current parameters.

6.4 Expansion of Gases

If expansion proceeds more slowly than sound propagates, it is a thermodynamic process. The regime of expansion when a gas does not interact with a surrounding system is known as the

adiabatic regime of gas expansion. In this case the gas does not interact with an environment, i.e. $dQ = 0$ or $S = \text{const}$. According to the relation $dS = 0$ and formula (6.6) for the entropy, the *adiabatic expansion* of an atomic gas gives $VT^{3/2} = \text{const}$, or

$$T^{5/2}/p = \text{const}, \quad pV^{5/3} = \text{const} \quad (6.11)$$

We first consider the adiabatic expansion process, where the system does not exchange energy with the surrounding systems. Then the process proceeds fast enough that the system's energy is conserved, but sufficiently slowly that equilibrium is maintained inside the system during the course of its evolution. We introduce the heat capacity of the system as

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V \quad (6.12)$$

so that equations (6.4) and (6.5) can be represented in the form

$$dE = C_V dT - p dV \quad (6.13)$$

In particular, in the case of an atomic gas, using formula (2.28) for the heat capacity, we have that the average internal energy is equal to $\frac{3}{2}nT$, where n is the number of atoms of this gaseous system. In this case we have

$$C_V = \frac{3}{2}n \quad (6.14)$$

From the condition of the adiabatic process we have

$$dE = C_V dT - p dV = 0$$

This equation, along with the equation of the gaseous state $pV = nT$, gives

$$T^{C_V/n} V = \text{const}, \quad T^{C_V/n-1}/p = \text{const} \quad \text{or} \quad pV^{5/3} = \text{const} \quad (6.15)$$

In particular, in the case of an atomic gas, when $C_V = 3n/2$, we have from formula (6.15)

$$T^{3/2}V = \text{const} \quad \text{or} \quad T^{5/2}/p = \text{const}$$

which coincides with formula (6.11) for an ideal gas $p = NT$.

This is a reversible process, so that the entropy does not vary during the process. Now let us consider the isothermal process of gas expansion, where a constant temperature is maintained during the process, and the heat release is taken from an external energy source – a heater. If the initial gas volume is V_o and the final gas volume is $V_f > V_o$, an expanding gas performs the following mechanical work and transmits it to a plunger

$$A = \int_{V_o}^{V_f} p dV = nT \ln \frac{V_f}{V_o}$$

where we account for the state equation for a gas $pV = nT$, and n is the total number of gaseous atoms or molecules. Correspondingly, the heat which is taken from an energy source is equal to

$$Q = A = T\Delta S = nT \ln \frac{V_f}{V_o}$$

and the change in entropy is

$$\Delta S = n \ln \frac{V_f}{V_o}$$

in accordance with formula (6.6). Thus, in this case a gas obtains heat Q , and the gas entropy increases, i.e. this thermal process for the gas is irreversible.

Let us consider the case in which a gas expands in a vacuum or in a region of low pressure. Taking the initial pressure to be p_o , the final pressure to be p_f , and the initial temperature to be T_o , we have from formula (6.15) for the final gaseous temperature T_f

$$T_f = T_o \left(\frac{p_f}{p_o} \right)^{C_V/(C_V-n)}$$

In the case of an atomic gas there follows from this relation

$$T_f = T_o \left(\frac{p_f}{p_o} \right)^3$$

In particular, if a gas expands in the form of a stream, we obtain from this relation and formula (6.10) for the final velocity of the stream

$$v^2 = \frac{2c_p T_o}{m} \left[1 - \left(\frac{p_f}{p_o} \right)^{C_V/(C_V-n)} \right]$$

This gives the drift velocity of a stream of a monatomic gas ($c_p = 5/2$) which expands through a nozzle in a vacuum

$$v = \sqrt{\frac{5T_o}{m}} \tag{6.16}$$

6.5 Carnot Cycle

Let us determined the work resulting from a complete cycle of processes which consists of four stages and returns the system to its initial state. The sequence of these phases is given in Figure 6.2. This circle is called the *Carnot cycle* and it is of importance for engines and energetic systems. The Carnot cycle includes the following four thermodynamic processes (see Figure 6.2):

1. Isothermal expansion of the system at constant temperature T_1 with absorption of heat Q_1 .

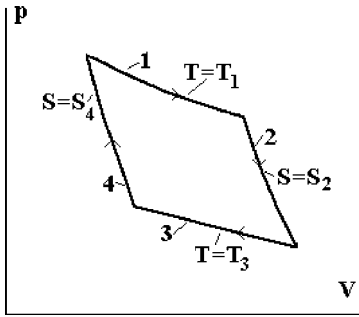


Figure 6.2. The Carnot circle on the $p - V$ diagram: 1,3-isothermal expansion and compression, 2,4-adiabatic expansion and compression.

2. Adiabatic expansion under thermal isolation of the system, so that the entropy S_4 is conserved.
3. Isothermal compression of the system at constant temperature T_3 with release of heat Q_3 .
4. Adiabatic compression under thermal isolation of the system, so that the entropy S_2 is conserved.

As can be seen, the temperature of the system does not vary during stages 1 and 3, while in the course of stages 2 and 4 entropy is conserved.

The Carnot cycle is the simplest cycle of processes which returns the system to its initial state. Mechanical work is consumed during the compression of the system, while during expansion the system creates mechanical work using its internal energy. The diagram of Figure 6.3 allows us to analyze the energy change at each stage, because the mechanical work is $\int p dV$, i.e. it is equal to the area under each curve. Because the system returns to the initial state after each cycle, the energy is taken from external systems or fields. Indeed, the heat $Q_1 = T_1(S_4 - S_2)$ is taken from a heater, and the heat $Q_3 = T_3(S_4 - S_2)$ is transmitted to a refrigerator. Since the total energy of the system is conserved after a cycle, the mechanical work A performed by the system is

$$A = Q_1 - Q_3 = (T_1 - T_3)(S_4 - S_2)$$

From this we get for the *efficiency coefficient* η of this cycle, which is the ratio of the mechanical work performed A to the consumed heat Q_1 :

$$\eta = \frac{A}{Q_1} = \frac{T_1 - T_3}{T_1} = 1 - \frac{T_3}{T_1} \quad (6.17)$$

It can be seen from this that it is impossible to create a perpetual engine.

6.6 Entropy of an Ideal Gas

We now find the connection between variations in the entropy dS and internal energy dE which are given by formula (6.2) at constant temperature and in the absence of external fields. We now generalize this formula taking into account variations of the system levels ε_i under

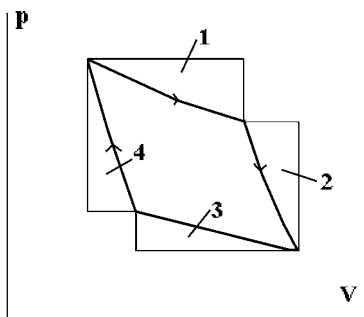


Figure 6.3. The mechanical work on each stage of the Carnot cycle which is $\int p dV$ and corresponds to an area on the $p - V$ diagram for each stage of the Carnot cycle. In the course of expansion, i.e. on stages 1,2 this work is positive, and during compression, i.e. on stages 3,4 the mechanical work is negative.

the action of external fields. The average number of particles found in a given group i of states is $n_i = Z_i/Z$, where Z is the total partition function, and according to formula (2.23) $Z_i = n g_i \exp(-\varepsilon_i/T)$ is the partial partition function of an ensemble of n particles located in a given group of states. Taking variations of the number of particles dn_i in given states with energy $d\varepsilon_i$, we get by analogy with formula (6.2)

$$\begin{aligned} dS &= -d \sum_i n_i \ln n_i = - \sum_i dn_i \ln n_i = \frac{1}{T} \sum_i \varepsilon_i dn_i \\ dE &= \sum_i n_i d\varepsilon_i + \sum_i \varepsilon_i dn_i \\ dZ &= d \sum_i Z_i = - \sum_i Z_i \frac{d\varepsilon_i}{T} = - \frac{Z}{nT} \sum_i n_i d\varepsilon_i \end{aligned}$$

From this it follows that

$$dE = T dS - T \frac{dZ}{Z} \quad (6.18)$$

Formula (6.18) is transformed into (6.2) under the assumption $d\varepsilon_i = 0$, i.e. in the absence of external fields. This leads to formula (2.26) for the entropy of an ensemble of n identical particles

$$S = n \frac{\partial \ln Z}{\partial \ln T} + n \ln Z \quad (6.19)$$

This relation is useful for determining the entropy of a particular system of particles. In particular, we have from this for an ensemble of free atoms on the basis of formula (2.32) for the partition function

$$S = \frac{5}{2}n + n \ln \frac{V}{n} + \frac{3}{2}n \ln \frac{mT}{2\pi\hbar^2} + const \quad (6.20)$$

where m is the atom's mass and V is the volume where these particles are located. This coincides with formula (6.6) for the entropy of a monatomic gas where the dependence on a number of atoms is included in the constant.

6.7 Second Law of Thermodynamics

If a system of particles develops from a certain distribution of particles over states to a random one, the entropy of this system of particles grows. Because the equilibrium state of this system corresponds to a fully randomized distribution of particles under given conditions, the evolution of the system to an equilibrium state is accompanied by a growth in entropy. Since every system tends towards an equilibrium, from this it follows that the entropy of any system increases in the course of its evolution or remains a constant for an equilibrium state of the system. This statement is the *second law of thermodynamics*, and below we will show its validity in the case where two systems of particles with different parameters are joined in a united system.

Let us consider a system which consists of two equilibrium subsystems, so that the first subsystem has a temperature T_1 of particles and contains n_1 particles, and the total internal energy of the particles is E_1 ; for the second subsystem the corresponding parameters are T_2 , n_2 and E_2 . The subsystems are united in one system, so that they interact and exchange energy, leading to the establishment of a uniform temperature. For definiteness we take $T_1 < T_2$, and consider the character of the entropy variation in this process. Because the entropy of a system is the additive function of its parts, we have for the change in total entropy S :

$$dS = dS_1 + dS_2 = dE_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (6.21)$$

We denote by dE_1 and dE_2 variations of the internal energy of the given subsystems and assume that the subsystems are joined via an *adiabatic process*, i.e. the energy variation of the total system is zero: $dE = dE_1 + dE_2 = 0$. Evidently, because of its lower temperature, the first subsystem receives energy from the second subsystem, i.e. $dE_1 > 0$. Then from formula (6.21) it follows that the entropy increases during the process that leads to equilibrium for the total system. This corresponds to the *H-theorem of Boltzmann*.

If a system can be divided into many parts and the temperature T_i is constant for each element, we have

$$dS = \sum_i dS_i = \frac{1}{2} \sum_{i,k} dQ_{ik} \left(\frac{1}{T_k} - \frac{1}{T_i} \right)$$

Here dQ_{ik} is the heat which is transmitted from the i th to the k th element, $dQ_{ik} = -dQ_{ki}$, and the factor $1/2$ accounts for each term being taken in this sum twice. Since heat is transmitted from a hot element to a cold one, we have $dQ_{ik} \geq 0$ if $T_i \geq T_k$. Hence each term in this sum cannot be negative, and

$$dS \geq 0$$

if a system consists of many elements with different parameters. In the case of a reversible evolution of this system $dS = 0$, while for an irreversible process $dS > 0$. The law of increasing entropy as a result of the evolution of a particle ensemble to an equilibrium state is the second law of thermodynamics. This law describes the tendency of the evolution of the system, so that for an equilibrium system $dS/dt = 0$, and if the system tends towards equilibrium, $dS/dt > 0$.

Above we consider the mixing of gases of different temperatures. Now we mix identical gases of identical temperature under the following conditions: the initial gaseous volumes V_1 and V_2 contain an identical number of atoms n , and their mixing results from the breaking of a partition which initially separates the two volumes. The change in entropy as a result of the mixing of the gases is, according to formula (6.20):

$$\Delta S = S(2n, V_1 + V_2) - S(n, V_1) - S(n, V_2) = n \ln \frac{(V_1 + V_2)^2}{4V_1 V_2} \geq 0$$

This case confirms the second law of thermodynamics, so that the entropy increases as a result of establishing equilibrium between the subsystems.

6.8 Thermodynamic Potentials

Relation (6.4) assumes that the system energy depends on variables S and V . One can use any two variables from T , S , p and V as characteristics of the system energy, depending on the conditions of the process. The *free energy* F (or the *Helmholtz free energy*) and its differential are introduced as

$$F = E - TS, \quad dF = -S dT - p dV \quad (6.22)$$

The *enthalpy* H of the system of particles and its differential are equal to

$$H = E + pV, \quad dH = T dS + V dp \quad (6.23)$$

and the *free enthalpy* G (or the *Gibbs free energy*) and its differential are

$$G = E - TS + pV, \quad dG = -S dT + V dp \quad (6.24)$$

The values E , F , H and G are called the *thermodynamic potentials*.

One can express the thermodynamic potentials through the partition function, similar to formula (2.24). In particular, according to formulae (6.18) and (6.19) the free energy F is connected to the partition function by the formula

$$F = -T \ln Z \quad (6.25)$$

Here we choose the constant to be zero, taking into account that at zero temperature $Z = 1$, $S = 0$, because a system of gaseous particles is located in the ground state only. Then on the basis of formulae (6.25) and (2.32) we have the free energy of an atomic gas:

$$F = -nT \ln \left(\left[\frac{V}{n} \left(\frac{mT}{2\pi\hbar^2} \right)^{3/2} \right] + 1 \right) \quad (6.26)$$

A convenient thermodynamic potential from E , F , G and H is used depending on the character of the process. Then we use *Hess's law*, that the difference in values of a thermodynamic potential for final and initial states does not depend on the path of the transition from the initial state to the final state, but depends only on the parameters of these states. In particular,

it is convenient to characterize the formation of a new phase or compounds by the enthalpy difference for the final and ground states. Usually this parameter is the difference between the enthalpies of these states at a pressure of 1 atm and a temperature of 298 K, and is expressed in kcal/mol. This difference is called the standard heat effect of a reaction or the *standard enthalpy* of a new phase.

The above expressions allow one to find the thermodynamic potentials of certain systems of particles, so that the entropy of the system is given by formula (6.19), and its free energy is determined by formula (6.26). Let us use these expressions for a molecular gas consisting of n diatomic molecules, using the distributions of molecules (3.44) and (3.47) for rotational and vibrational levels. Assuming the distribution for each molecule to be independent of the distributions for other molecules, we obtain the following additivity of some thermodynamic parameters $S \sim n$, $\ln Z \sim n$, $E \sim n$ and $F \sim n$. Table 6.1 gives the expressions for these thermodynamic parameters of a gas consisting of n diatomic molecules, where the excitation energy for an individual molecule is given by formula (3.43)

$$\varepsilon(v, J) = BJ(J + 1) + \hbar\omega \left(v + \frac{1}{2} \right) \quad (6.27)$$

Here B is the rotational constant, $\hbar\omega$ is the distance between neighboring vibrational levels, and J and v are the corresponding rotational and vibrational quantum numbers. We consider the classical case for rotations $J \gg 1$ or $T \gg B$, as is realized usually at room temperature. For the general case, we assume that the vibrational temperature T_v differs from the translational and rotational temperature T . Thus the thermodynamic functions under consideration are additive both for a number of molecules and for different degrees of freedom.

Let us now determine the thermodynamic parameters of an equilibrium radiation which is located in some volume V at a temperature T . On the basis of formulae (3.7) and (6.19) we

Table 6.1. Thermodynamic parameters of a gas of diatomic molecules related to the vibrational and rotational degrees of freedom.

	Vibrations	Rotations
Z	$\left[1 - \exp \left(-\frac{\hbar\omega}{T_v} \right) \right]^{-n}$	$\left(\frac{T}{B} \right)^n$
S	$n \left(\frac{\hbar\omega}{T_v \left[\exp \left(\frac{\hbar\omega}{T_v} \right) - 1 \right]} - \ln \left[1 - \exp \left(-\frac{\hbar\omega}{T_v} \right) \right] \right)$	$n \left(1 + \ln \frac{T}{B} \right)$
E	$n \frac{\hbar\omega}{2} \coth \left(\frac{\hbar\omega}{2T_v} \right)$	nT
C_V	$n \left(\frac{\hbar\omega}{2T_v} \right)^2 \left[\sinh \left(\frac{\hbar\omega}{2T_v} \right) \right]^{-2}$	n
F	$n \frac{\hbar\omega}{2} + nT_v \ln \left[1 - \exp \left(-\frac{\hbar\omega}{T_v} \right) \right]$	$-nT \ln \frac{T}{B}$

have

$$F = -T \ln Z = -\frac{4\sigma}{3c} VT^4, \quad S = -\frac{\partial F}{\partial T} = \frac{16\sigma}{3c} VT^3, \quad E = F + TS = \frac{4\sigma}{c} VT^4,$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{4\sigma}{c} VT^4 \quad (6.28)$$

In addition, we have for the total number n of photons when the equilibrium radiation is found in a volume V :

$$n = \int \frac{2d\mathbf{r}d\mathbf{k}}{(2\pi)^3} \left[\exp\left(\frac{\hbar\omega}{T}\right) - 1 \right]^{-1} = \frac{1}{\pi^2} \left(\frac{T}{\hbar c}\right)^3 V \int_0^\infty \frac{x^2 dx}{e^x - 1}$$

The integral is

$$\int_0^\infty \frac{x^2 dx}{e^x - 1} = \sum_{k=0}^\infty \int_0^\infty x^2 dx \exp[-(k+1)x] = \sum_{k=0}^\infty \frac{2}{(k+1)^3} = 2 \sum_{k=1}^\infty \frac{1}{k^3} = 2.404$$

This leads to the state equation for the radiation field

$$n = 0.244 \left(\frac{T}{\hbar c}\right)^3 V$$

Note that thermodynamic parameters can be divided into *intensive values* and *extensive values*. Let us take an ensemble of weakly interacting particles in two equal subsystems separated by a partition. Then the intensive values, such as the temperature and pressure, are identical in each of these subsystems. In contrast, the extensive values, such as the entropy and thermodynamic potentials, for the total system are equal to the sum of the values of the subsystems.

6.9 Heat Capacities

Thermodynamics is based on universal laws and its formalism allows one to obtain the general relations between physical parameters of the system independent of its nature. Below we demonstrate this on an example of *heat capacities* referred to different conditions. The heat capacities of a system of weakly interacting particles are defined according to formulae (6.8) and (6.12)

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V, \quad C_p = \left(\frac{\partial Q}{\partial T}\right)_p$$

and because $dQ = TdS$, we have

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V, \quad C_p = T \left(\frac{\partial S}{\partial T}\right)_p \quad (6.29)$$

Using standard relations for the Jacobian determinant

$$\frac{\partial(x, y)}{\partial(\alpha, \beta)} = \begin{vmatrix} \left(\frac{\partial x}{\partial \alpha}\right)_\beta & \left(\frac{\partial y}{\partial \alpha}\right)_\beta \\ \left(\frac{\partial x}{\partial \beta}\right)_\alpha & \left(\frac{\partial y}{\partial \beta}\right)_\alpha \end{vmatrix}$$

we have for the heat capacity at constant pressure

$$\begin{aligned} C_p &= T \left(\frac{\partial S}{\partial T} \right)_p = T \frac{\partial(S, p)}{\partial(T, p)} = T \frac{\frac{\partial(S, p)}{\partial(T, V)}}{\frac{\partial(T, p)}{\partial(T, V)}} \\ &= \frac{\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial p}{\partial V}\right)_T - \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} = C_V - T \frac{\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} \end{aligned}$$

Next, because

$$\left(\frac{\partial S}{\partial V}\right)_T = - \left[\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T} \right)_V \right]_T = - \left[\frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V} \right)_T \right]_V = \left(\frac{\partial p}{\partial T}\right)_V$$

we have

$$C_p = C_V - T \frac{\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T} \quad (6.30)$$

This formula gives the connection between the heat capacities in a general form. In particular, in the case of an ideal gas consisting of n atomic particles, by substituting in formula (6.30) the equation of gaseous state $pV = nT$ we obtain

$$C_p = C_V + n$$

Note that definition (6.1) for the entropy of a system is valid with accuracy up to a constant. If we take as n_i in this formula the probability of a given state for the system of particles, we obtain at zero temperature $S = 0$ because the system is found in the ground state. This conclusion, that the entropy of a particle ensemble is zero at zero temperature, is called *Nernst's theorem*. From this one can define the constant in the entropy expression. In this limit we have $Z = 1$, so that $F = 0$. Correspondingly, at zero temperature $C_p = C_V$, and all this relates to quantum systems. In the case of a classical ideal gas we have $C_V = \frac{3}{2}n$, $C_p = \frac{5}{2}n$, so that the classical limit at low temperatures does not coincide with the quantum one.

Let us consider a crystal at low temperatures if its heat capacity is determined by excitation of phonons. We use the analogy between a gas of photons and phonons at low temperatures, so that on the basis of formula (6.15) we have $(\partial p / \partial T)_V \sim T^3$. Next, the derivative $(\partial p / \partial V)_T$ tends to a constant at low temperatures, because a shift in the equilibrium distance between neighboring atoms of the crystal is proportional to an external force or to the pressure. Therefore formula (6.30) gives in the limit of low temperatures

$$C_p - C_V \sim T^7 \quad (6.31)$$

This was used in formula (3.37b), where we considered the values C_V and C_p to be identical.

6.10 Equilibrium Conditions

Let us consider an equilibrium system where the equilibrium is violated by a weak perturbation. The *equilibrium criterion* follows from the character of the system's stability and depends on conditions under which the system exists. We have, according to the second law of thermodynamics, that at a fixed energy E of the system its entropy must be maximal in the equilibrium state, i.e. a weak perturbation leads to

$$\frac{dS}{dt} = 0, \quad S = S_{\max}, \quad \text{if } E = \text{const} \quad (6.32)$$

Because of the relation $dS \geq dE/T$, in the case of a perturbation when $S = \text{const}$, we have that the equilibrium corresponds to the minimal energy E of the system. In the case where a weak perturbation corresponds to a fixed temperature, we obtain the relation $dS \geq dE/T$ and $dT = 0$. Then we have for the variation of the free energy:

$$dF = d(E - TS) \leq T dS - d(TS) = -S dT = 0$$

i.e. in this case of equilibrium the free energy must be minimal.

Above we considered a system located in a fixed volume which tends to an equilibrium. Now let us consider a weak perturbation which conserves the temperature and pressure. In this case we have from the variation of the free enthalpy

$$dG = d(E - TS + pV) = dQ - p dV - d(TS) + d(pV) \leq 0 \quad (6.33)$$

where we have used the relations $dS \geq dE/T$, $dT = 0$ and $dp = 0$ for variations in the system. Thus, in the case of fixed temperature and pressure, the equilibrium criterion requires a minimum for the free enthalpy of the system.

6.11 Chemical Potential

The above relations correspond to systems contained a certain number of particles, and this number does not vary during the process. One can extend these relations to the case where the number of particles n is not conserved in this process by adding the term $-\mu dn$ to the thermodynamic potential, so that we change dE by $dE - \mu dn$, where μ is the *chemical potential*. The same expressions relate to other thermodynamic potentials. From this it follows that

$$\mu = \left(\frac{\partial E}{\partial n} \right)_{S,V} = \left(\frac{\partial F}{\partial n} \right)_{T,V} = \left(\frac{\partial H}{\partial n} \right)_{S,p} = \left(\frac{\partial G}{\partial n} \right)_{T,p} \quad (6.34)$$

Thus the chemical potential can be expressed through different thermodynamic potentials, but it then depends on different variables. In the case of a system of weakly interacting atomic particles, each thermodynamic potential is an additive function of particles. Then the chemical potential of the system is the corresponding thermodynamic potential per particle.

Let us consider an equilibrium system as the sum of two subsystems. Because of the additivity of the thermodynamic potentials, we have

$$G(n_1 + n_2) = G(n_1) + G(n_2)$$

where the system is found under constant temperature and pressure, and n_1 and n_2 are the numbers of particles for each subsystem. Since the total number of particles $n = n_1 + n_2$ is also an additive function and we divide the system into subsystems in an arbitrary way, from this it follows that $G(n) \sim n$. Then we have from (6.24) and (6.34)

$$G(n) = n\mu(p, T) \quad (6.35)$$

i.e. the chemical potential is equal to the thermodynamic potential per particle.

Now let us consider the equilibrium of two subsystems. They can be different components of one phase or different phases of the same component. As happens in reality, we assume the temperature and pressure to be fixed in the system. Then the equilibrium condition (6.33) gives

$$\mu_1(p, T) = \mu_2(p, T) \quad (6.36)$$

where μ_i is the chemical potential of a given component or phase. In particular, on the basis of formulae (6.20) and (6.24) we have for the chemical potential of a monatomic ideal gas

$$\mu(p, T) = \frac{G(p, T)}{n} = \varepsilon_o - \frac{5}{2}T \ln T + T \ln p - \frac{3}{2} \ln \left(\frac{2\pi m}{h^2} \right) \quad (6.37)$$

where we introduce ε_o as the energy of formation of a gas particle.

Let us consider the *ionization equilibrium* (5.1)



The equilibrium condition (6.36) has the form in this case

$$\mu_+ + \mu_e = \mu_a \quad (6.39)$$

where μ_+ , μ_e and μ_a are the chemical potentials of the ion, electron and atom correspondingly. We introduce the energy of ion formation $\varepsilon_o = J$ and the atom ionization potential, and for the electron and atom we take $\varepsilon_o = 0$. Next, let us multiply the expression for the partition function of each partition function by the statistical weight of this particle. Then we get on the basis of formulae (6.36) and (6.37)

$$\frac{p_i p_e}{p_a} = T \frac{g_i g_e}{g_a} \left(\frac{2\pi m T}{h^2} \right)^{3/2} \exp \left(-\frac{J}{T} \right)$$

where p_i , p_e and p_a are the partial pressures of ions, electrons and atoms and g_i , g_e and g_a are their statistical weights. This formula coincides with the Saha formula (5.2). Note that the electron temperature coincides with those for the ions and atoms.

6.12 Chemical Equilibrium

Let us represent the equation of a *chemical equilibrium* between components A_i in the form of the *Donde equation*

$$\sum_i \nu_i A_i = 0 \quad (6.40)$$

where ν_i are whole numbers.

In particular, for the ionization equilibrium we have $\nu_+ = \nu_e = 1$, $\nu_a = -1$. The equilibrium condition (6.36) for the equilibrium (6.38) has the form:

$$\sum_i \nu_i \mu_i(p, T) = 0$$

where μ_i is the chemical potential of the i th component. By analogy with the case of ionization equilibrium, we have the relation between partial pressures of components which partake in the equilibrium under consideration

$$\prod_i p_i^{\nu_i} = K(T) \quad (6.41)$$

where the *equilibrium constant* $K(T)$ of this process equals

$$K(T) = \exp \left(\frac{\sum_i \nu_i \mu_i}{T} \right) \quad (6.42)$$

This relation is named the *active mass law*.

7 Equilibrium State of Atomic Systems

7.1 Criterion of the Gaseous State

The condition of the gaseous state for a system of atomic particles can be formulated in terms of the cross section of particle collisions. A gas is a system of particles with a weak interaction between atomic particles. This means that each particle moves most of the time along straightforward trajectories, i.e. its interaction with the surrounding atomic particles is weak. Only for a relatively small period does a particle interact strongly with another atomic particle, leading to scattering at large angles. This takes place if the *mean free path* of an atomic particle $\lambda = 1/(N\sigma)$ is large compared with the interaction radius $\sqrt{\sigma}$ of this particle with another. Thus the *gaseous state criterion* for a system of atoms has the form

$$N\sigma^{3/2} \ll 1 \quad (7.1)$$

Let us analyze this problem from another standpoint. According to the condition of the gaseous state, the pair interaction potential $U(R)$ of atomic particles at a typical distance between nearest particles $R \sim N^{-1/3}$ is small in comparison with the typical kinetic energy of a particle T , i.e.

$$U(N^{-1/3}) \ll T$$

This means a weak interaction between particles, and

$$U(N^{-1/3}) \ll U(\rho_o) \quad (7.2)$$

where ρ_o is given by the formula $U(\rho_o) \sim T$, and means a strong interaction between colliding particles, so that $\sigma \sim \rho_o^2$ is the cross section of particle scattering for large angles. For a monotonic interaction potential this gives $N^{-1/3} \gg \rho_o$, which leads to formula (7.1).

Let us apply this criterion to a system of charged particles, i.e. to a plasma. Because of the Coulomb interaction between charged particles $|U(R)| = e^2/R$, and the typical cross section of large-angle scattering

$$\sigma \sim \frac{e^4}{T^2}$$

the condition for the gaseous state (7.1) for a plasma is transformed to the criterion of an *ideal plasma*

$$\frac{Ne^6}{T^3} \ll 1 \quad (7.3)$$

where N is the number density of charged particles and T is their temperature. The criterion (7.3) coincides with the criterion (2.42) of an ideal plasma which has another basis. Thus, an ideal plasma is a gas of charged particles.

7.2 Equation of the Gas State

The relation between the bulk parameters of a gas (the pressure p , the temperature T and the number density of particles N) is given by the *equation of state*. Below we derive this equation for an ideal gas. Then one can neglect the collisions between atoms or molecules, but these collisions establish the gaseous pressure. We introduce the *pressure* as the force per unit area of an imaginary surface in the frame of reference where the gas is at rest as a whole. To evaluate this force note that if an element of this surface is perpendicular to the axis x , the flux of particles through this plane with velocities in an interval from v_x up to $v_x + dv_x$ is equal to $dj_x = v_x f dv_x$, where f is the distribution function. Elastic reflection of an atomic particle from this surface leads to the inversion of v_x , i.e. $v_x \rightarrow -v_x$ as a result of the collision of an atomic particle with the surface. Therefore, a reflected particle of mass m transfers to the area a momentum $2mv_x$. The force acting on this area is the change of momentum per unit time. Hence the gaseous pressure, i.e. the force acting per unit area, is equal to

$$p = \int_{v_x > 0} 2mv_x \cdot v_x f dv_x = m \int v_x^2 f dv_x = mN \langle v_x^2 \rangle$$

We take into account that the pressure is identical on the two sides of an imaginary surface.

In the above formula v_x is the velocity component in the frame of reference where the gas is at rest as a whole. Transferring to the initial frame of reference, we have:

$$p = mN \langle (v_x - w_x)^2 \rangle \quad (7.4)$$

where w_x is the component of the mean gas velocity. Because (in the frame of reference where the gas as a whole is at rest) the distribution function is isotropic and the gaseous pressure is the same in all directions:

$$p = mN \langle (v_x - w_x)^2 \rangle = mN \langle (v_y - w_y)^2 \rangle = mN \langle (v_z - w_z)^2 \rangle \quad (7.5)$$

This gives the simple expression for the *pressure tensor* (7.5):

$$P_{\alpha\beta} = p\delta_{\alpha\beta} \quad (7.6)$$

where $\delta_{\alpha\beta}$ is the Kronecker symbol. Since this relationship is also valid for an isotropic liquid, the derived equations describe not only a gas but also a liquid.

The definition of the gas temperature (2.9) expresses it through the mean kinetic energy of particles in the frame of reference where the mean velocity is zero, so that we have

$$\frac{3T}{2} = \frac{m}{2} \langle (\mathbf{v} - \mathbf{w})^2 \rangle$$

Substituting this expression in equation (7.5), we find the following relationship between the pressure and temperature:

$$p = NT \quad (7.7)$$

Equation (7.7) is called the *equation of the gas state*. Taking a gas consisting of n moles of atoms or molecules which are located in a volume V , we rewrite the equation of the gas state in the form

$$pV = nRT \quad (7.8)$$

where R is the so-called *gas constant*, which is equal to

$$R = 82.06 \frac{\text{cm}^3}{\text{mol}} \frac{\text{atm}}{\text{K}} = 8.314 \frac{\text{cm}^3}{\text{mol}} \frac{\text{MPa}}{\text{K}}$$

One can generalize this equation by taking into account the interaction between atoms. The interaction potential of two atoms corresponds to the repulsion at small distances between atoms and attraction at intermediate and large distances. This attraction provides a bound state of a system of many atoms in a condensed system of atoms. We account for these peculiarities by the insertion of two parameters into the equation of state (7.8). Accounting for repulsion at small distances, so that small distances between atoms are not reached, we change in this equation V by $V - nb_W$. In addition, we change p by $p + a_W n^2/V^2$, because the attraction between atoms creates additional pressure. Here we take into account that a volume of a given amount of molecules is proportional to this amount, which is expressed by the value n . From the above consideration we obtain the equation of state for a gas in the form

$$\left(p + \frac{n^2 a_W}{V^2} \right) (V - nb_W) = nRT \quad (7.9)$$

This equation is called the *van der Waals equation*, which is a version of the equation of state that accounts for the interaction between atomic particles. According to the method of derivation, this equation of state accounts for the interaction between atoms or molecules in a gas in an empirical way on the basis of parameters a_W and b_W . Although this equation is derived for a gas, i.e. for a system of weakly interacting atomic particles, it can be used as a model for liquids in which the interaction between atomic particles is not weak. For this reason, this equation is used widely in the analysis of various phenomena involving gases and liquids. We further apply the van der Waals equation to the study of gas–liquid processes and phenomena.

7.3 Virial Theorem

The *virial theorem* of Clapeyron establishes the connection between the mean kinetic energy of a particle and the averaged parameters of its interaction with surrounding particles or fields. We derive it in the classical case, where the equation of motion for the particle is given by the Newton equation

$$m \frac{d^2 \mathbf{r}}{dt^2} = \mathbf{F} \quad (7.10)$$

where $\mathbf{r}$ is the particle coordinate, m is its mass and $\mathbf{F}$ is the force that acts on this particle from other particles of this ensemble or fields.

Let us multiply this equation by x , the particle coordinate along the x -axis, and integrate this over a large time range. We have

$$mx \frac{d^2x}{dt^2} = m \frac{d}{dt} \left(x \frac{dx}{dt} \right) - m \left(\frac{dx}{dt} \right)^2$$

Averaging over a large time τ , we obtain for the second term

$$\frac{1}{\tau} \int_0^\tau m \frac{d}{dt} \left(x \frac{dx}{dt} \right) = \frac{m}{\tau} x \frac{dx}{dt} \Big|_0^\tau$$

and in the limit $\tau \rightarrow \infty$ this term tends to zero. Thus, we get from the above equation

$$m \overline{\left(\frac{dx}{dt} \right)^2} = -\frac{1}{2} \overline{x F_x} = \frac{1}{2} \overline{x \frac{\partial U}{\partial x}} \quad (7.11)$$

where the bar means averaging over time, F_x is the force component, and U is the interaction potential for this particle and others in the presence of external fields. The term on the left-hand side of this equation is the average kinetic energy of the particle, and the right-hand side of this equation is called the *force virial equation*. Equation (7.11) is useful for the analysis of systems of interacting particles.

7.4 The State Equation for an Ensemble of Particles

We now consider an ensemble of particles located in a vessel, with a certain pressure maintained in the vessel. From the virial theorem we have for the particle ensemble

$$\sum_i m \overline{\left(\frac{dx_i}{dt} \right)^2} = -\frac{1}{2} \sum_i \overline{x_i (F_x)_i} - \frac{1}{2} \left[\sum_i \overline{x_i (F_x)_i} \right]_{\text{walls}}$$

where the index i indicates the particle number, a bar means averaging over time, and we divide the force virial for an individual particle into two parts, so that the first relates to other particles of the ensemble, and the second refers to the vessel's walls. Because of equilibrium, one can change the second term on the right-hand side of this equation by the force virial acting from the walls on the particle ensemble. The force from a surface element ds acting on particles of the ensemble is $p ds$, where p is the pressure. Hence, we have

$$\frac{1}{2} \left[\sum_i \overline{x_i (F_x)_i} \right]_{\text{walls}} = \frac{1}{2} \int_S p x ds = \frac{p}{2} \int_V dV = \frac{1}{2} p \Omega$$

where Ω is the volume restricted by the walls and the particle ensemble is located in this volume.

Next, according to the temperature definition, the average kinetic energy of an individual particle for a given direction of motion is

$$\frac{m}{2} \overline{\left(\frac{dx_i}{dt} \right)^2} = \frac{T}{2}$$

and the force virial averaging for a large time range is identical for any particle, that is

$$\sum_i \overline{x_i(F_x)_i} = n \overline{x_i(F_x)_i}$$

where n is the total number of particles in the ensemble under consideration. Thus we finally obtain

$$nT = -n \overline{x_i(F_x)_i} + p\Omega$$

If we introduce a specific volume per atom $V = \Omega/n$, this equation takes the form

$$T = -\overline{x_i(F_x)_i} + pV \quad (7.12)$$

This is the state equation for this particle ensemble. The left-hand side of this equation is the kinetic energy of a particle, the first term on the right-hand side accounts for the force virial which acts on an individual particle from other particles, and the second term takes into account the action of walls. In particular, for a gas, i.e. for a system of weakly interacting particles, one can neglect the virial force, and the state equation takes the form of equation (7.7)

$$T = pV$$

7.5 System of Repulsing Atoms

Let us apply the virial theorem to a system of particles with repulsive interaction. This occurs in dense systems of rare gas atoms under high pressure, so that the mean distance between neighboring atoms is less than the equilibrium distance between atoms in the diatomic molecule, and this leads to a repulsive interaction between neighboring atoms. We will approximate the interaction potential of atoms $U(R)$ over the considered range of distances R between them by the dependence

$$U(R) = \frac{C}{R^k} = U(R_o) \left(\frac{R_o}{R} \right)^k \quad (7.13)$$

where the parameter k is large for real atoms. In particular, Table 7.1 contains the parameters of the pair interaction potential of two identical atoms of rare gases at a distance R_o , where $U(R_o) = 0.3 \text{ eV}$.

In this case the equation (7.12) of state for atoms interacting through the potential (7.13) has the form

$$T = pV - \frac{k}{3} \overline{U}$$

Table 7.1. The parameters of the repulsive interaction potential of two rare gas atoms in accordance with formula (7.13). (The data are taken from V. B. Leonas (1972) *Sov. Phys. Usp.* **15**, 266, 1972)

	Ne	Ar	Kr	Xe
k	7.6	8.1	7.7	5.9
$R_o, \text{\AA}$	2.07	2.85	2.99	3.18

where V is the volume per atom, and $\bar{U}$ is the average interaction potential per atom. Introducing the average number q of nearest neighbors, we have, in the mean field approximation,

$$V = \frac{a^3}{\sqrt{2}} \cdot \frac{12}{q}, \quad \bar{U} = \frac{q}{2} U(a)$$

where a is the distance between nearest neighbors. In the limiting case of a high pressure $pV \gg T$, neglecting the first term on the right-hand side of equation (7.12), we determine from the virial theorem the connection between the pressure p and the distance between nearest neighbors a

$$p = 2\sqrt{2}k \left(\frac{q}{12} \right)^2 \frac{U(a)}{a^3} \quad (7.14)$$

The number of nearest neighbors q is a parameter of this equation, but we will show its validity for a close packed crystal lattice where $q = 12$. Let us draw a plane parallel to a symmetry plane of this lattice, so that the pressure is the force per unit area between atoms located on different sides of the crossing plane. Then the pressure is

$$p = \frac{mf_x}{s} = \frac{mf \cos \theta}{s}$$

where m is the number of nearest neighbors of an atom on test surfaces above and below the separation plane; s is the surface area per atom, and f_x is the projection of the force in the direction perpendicular to the separation plane, so that this force acts between a test atom and its nearest neighbor outside the separation plane; f is this force, and θ is the angle between the line connecting the interacting atoms and the perpendicular to the separation plane. From this we have for the $\{100\}$ separation plane, with $m = 4$, $s = a^2$ and $\cos \theta = 1/\sqrt{2}$,

$$p = \frac{4f(a)}{\sqrt{2}a^2} = \frac{2\sqrt{2}}{a^2} \left| \frac{dU(a)}{da} \right| = \frac{2\sqrt{2}}{a^3} kU(a) \quad (7.15a)$$

If the separation plane has the $\{111\}$ orientation, we have $m = 3$, $s = \sqrt{3}a^2/2$ and $\cos \theta = \sqrt{2/3}$, so that

$$p = \frac{3f(a)}{\frac{\sqrt{3}}{2}a^2} \sqrt{\frac{2}{3}} = \frac{2\sqrt{2}}{a^2} \left| \frac{dU(a)}{da} \right| = \frac{2\sqrt{2}}{a^3} kU(a) \quad (7.15b)$$

We can see that formulae (7.15) are transformed into formula (7.14) in the case $q = 12$. Thus we obtain the state equation for a system of strongly repulsive atoms on the basis of the virial theorem.

7.6 Van der Waals Equation

Figure 7.1 contains a typical *phase diagram* for simple bulk systems which can be found in the solid, liquid and gaseous states. We now analyze the behavior of the *evaporation curve* on this diagram that corresponds to equilibrium between the gaseous and liquid states. The pressure of a gas on this curve is called the *saturated vapor pressure* and increases strongly with increasing temperature. In contrast, the liquid density varies weakly with variation of the temperature. Therefore, at a certain temperature the densities of the liquid and gaseous states become equal. From this there follows the existence of the *critical point*, above which the liquid and gas states are not distinguished.

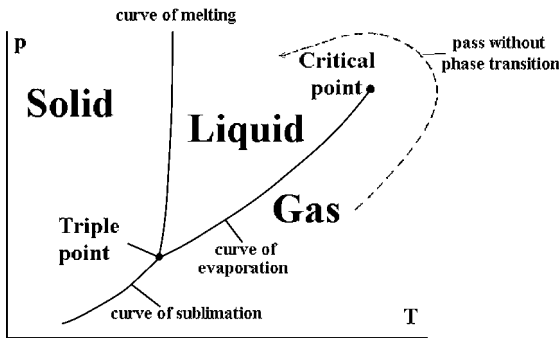


Figure 7.1. The phase diagram of simple atomic systems.

It is convenient to analyze the peculiarities of the transition between the liquid and gaseous states on the basis of the *van der Waals equation* (7.11) that simultaneously describes the gas and liquid states. In analyzing this equation, we take $n = 1$. The parameters of this equation for rare gases are given in Table 7.2. The van der Waals equation is the simplest state equation for a system of interacting particles which takes into account, on the one hand, a finite volume occupied by particles (the parameter b_W) and, on the other hand, an additive pressure due to the attraction of particles (the parameter a_W). This equation is valid strictly when the system of atomic particles under consideration is close to an ideal gas. Table 7.2 contains the parameters of the van der Waals equation for rare gases. Note that in accordance with the concept of this equation, the parameter b_W is the volume per molecule, i.e. this parameter

Table 7.2. The parameters of the van der Waals equation and critical parameters of rare gases.

Gas	Ne	Ar	Kr	Xe	Average
$a_W, 10^5 \text{ MPa}\cdot\text{cm}^6/\text{mol}^2$	0.208	1.35	2.32	4.19	
$b_W, \text{cm}^3/\text{mol}$	16.72	32.01	39.6	51.56	
V_{liq}/b_W	0.97	0.88	0.87	0.83	0.89 ± 0.06
T_{cr}, K	44.4	150.9	209.4	289.7	
$p_{\text{cr}}, \text{MPa}$	2.76	4.90	5.50	5.84	
$V_{\text{cr}}, \text{cm}^3/\text{mol}$	42	75	91	118	
$\rho_{\text{cr}} R_e^3 / (m\sqrt{2})$	0.283	0.302	0.302	0.300	0.297 ± 0.009
$T_{\text{cr}} / (p_{\text{cr}} V_{\text{cr}})$	3.4	3.5	3.2	3.5	3.4 ± 0.1

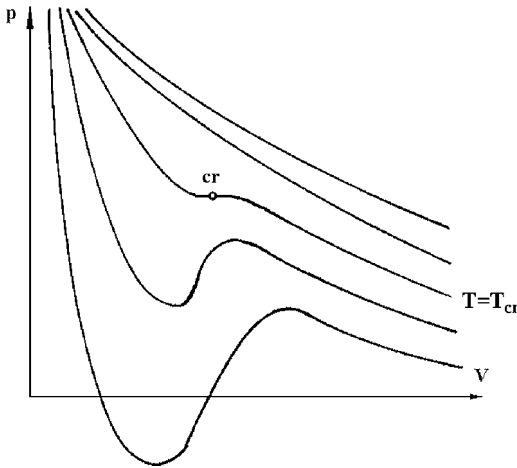


Figure 7.2. Isotherms of the van der Waals equation of state at different temperatures. A temperature increase corresponds to motion up, *cr* means the critical point.

is identical to the volume V_{liq} of the liquid state. The ratio of these parameters is given in Table 7.2 and confirms this statement.

Let us analyze the behavior of *isotherms* for the van der Waals equation, the points along which correspond to states of identical temperature and are represented in Figure 7.2. The solution of this cubic equation at a given temperature can have three roots, but at large temperatures only one root of this equation is real (upper curves of the diagram in Figure 7.2). At low temperatures equation (7.9) can have three real roots at some pressures, so that at these temperatures the function $p(V)$, which is close to a hyperbola at small and large V has a local minimum and maximum at intermediate values of V . Let us analyze in detail an individual isotherm, which is shown separately in Figure 7.3. If we move from large to small volumes V , this corresponds to the transition from the gaseous to the liquid state. The gaseous state can exist up to point *b*, the interval *bf* is not stable, and the curve after point *f* relates to the liquid state. But the interval *fe* corresponds to the metastable state, superheated liquid, and the interval *bc* refers to the other metastable state, supersaturated vapor. The stable state of this system is described by the curve *abfg*, and according to the *Maxwell rule* the line *bdf* separates this curve such that areas of figures *bcd* and *def* are identical, in accordance with the arm rule. Thus, the stable state of the system corresponds to the gas state before point *b*, the liquid state is located after point *f* and the mixture of the liquid and gaseous states refers to the interval *bf*.

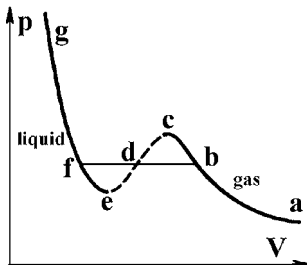


Figure 7.3. An isotherm of the van der Waals equation of state. The stable state corresponds to *abdfg* curve, an interval *bc* respects to supersaturated vapor, and the interval *ef* refers to superheated liquid.

It should be noted that alongside the line $p_{\text{sat}}(T)$, which is the boundary of the stable liquid and gaseous phases, one can construct the *spinodals* $p_l(T)$ and $p_{\text{vap}}(T)$, so that the dependence $p_l(T)$ is the boundary of the superheated liquid, i.e. a liquid metastable state does not exist at $p > p_l(T)$. In an analogous fashion, we have the dependence $p_{\text{vap}}(T)$ as the boundary of the gaseous phase, and a supersaturated vapor cannot exist at lower pressures. The pressure range between $p_l(T)$ and $p_{\text{vap}}(T)$ admits the existence of metastable states of the system under consideration. The positions of spinodals are determined by the equation

$$\left(\frac{\partial p}{\partial V} \right)_T = 0$$

which is the condition for stability loss for the metastable states.

Thus the van der Waals isotherm has a minimum and maximum at temperatures that are not too high. We have for the minimum

$$\left(\frac{\partial p}{\partial V} \right)_T = 0, \quad \left(\frac{\partial^2 p}{\partial V^2} \right)_T > 0$$

and the maximum of some isotherm

$$\left(\frac{\partial p}{\partial V} \right)_T = 0, \quad \left(\frac{\partial^2 p}{\partial V^2} \right)_T < 0$$

As the temperature increases, these extrema are approached, and at the *critical point* they coincide. Therefore the conditions for the critical point are

$$\left(\frac{\partial p}{\partial V} \right)_T = 0, \quad \left(\frac{\partial^2 p}{\partial V^2} \right)_T = 0$$

These relations and the van der Waals equation (7.9) allow one to connect the parameters V_{cr} , p_{cr} and T_{cr} of the critical point with the parameters of the van der Waals equation (we take the gas constant $R = 1$ and $n = 1$):

$$V_{\text{cr}} = 3b_W, \quad p_{\text{cr}} = \frac{a_W}{27b_W^2}, \quad T_{\text{cr}} = \frac{8a_W}{27b_W} \quad (7.16a)$$

One can see that the critical parameters are connected if the system is described by the van der Waals equation of state. Indeed, we have in this case

$$\frac{T_{\text{cr}}}{p_{\text{cr}} V_{\text{cr}}} = \frac{8}{3} \quad (7.16b)$$

Table 7.2 contains the critical parameters of rare gases. The accuracy of the relation (7.16a) testifies to the accuracy of the van der Waals equation for liquids and dense gases.

It is convenient to write the van der Waals equation (7.9) by using dimensionless variables. Indeed, introducing the reduced volume V_* , pressure p_* and temperature T_* on the basis of the relations

$$V_* = \frac{V}{V_{\text{cr}}}, \quad p_* = \frac{p}{p_{\text{cr}}}, \quad T_* = \frac{T}{T_{\text{cr}}} \quad (7.17a)$$

we reduce the van der Waals equation (7.9) to the form:

$$\left(p_* + \frac{3}{V_*^2}\right)(3V_* - 1) = 8T_* \quad (7.17b)$$

In this form the state equation is valid for any gas–liquid systems. In fact, the existence of a general equation of state is analogous to the scaling of various parameters of a system with a pair interaction of atoms when the parameters of condensed systems can be expressed through the parameters of the interaction potential of two atoms.

Within the framework of the van der Waals equation, the combination $T_{\text{cr}}/p_{\text{cr}}V_{\text{cr}}$ is identical for any system and equals $8/3$ according to formula (7.16b). According to the Table 7.2 data, this value is 3.4 ± 0.1 for rare gases. Thus the van der Waals equation is accurate for a gas and its accuracy drops as the atom density increases. But the advantage of the van der Waals equation consists in its simplicity and the possibility of describing simultaneously the gaseous and liquid states. The similarity law is valid for dense rare gases to an accuracy of several per cent, but the van der Waals equation describes the dense rare gases near the critical point with an accuracy of several tens per cent.

7.7 Liquid–Gas Equilibrium

Let us consider the coexistence line between the liquid and gaseous states far from the critical point. We call the gas on the coexistence line the *saturated vapor*, and the pressure on the coexistence line the *saturated vapor pressure*. The curve on the phase diagram that separates the liquid and gaseous states is called the *evaporation curve*, and the interface between the solid and gaseous states is called the *sublimation curve*. Because, on the evaporation curve, the temperature T , pressure p and the chemical potential μ are identical for the liquid and gaseous states, and in accordance with formula (6.36) we have the equation for the coexistence line from the equality $dG_{\text{liq}} = dG_{\text{gas}}$, where G_{liq} and G_{gas} are the Gibbs free energies for the liquid and gaseous states correspondingly

$$\frac{dp}{dT} = \frac{S_{\text{gas}} - S_{\text{liq}}}{V_{\text{gas}} - V_{\text{liq}}} \quad (7.18)$$

Here S_{gas} , S_{liq} are the entropies, and V_{gas} , V_{liq} are the volumes of the gaseous and liquid states. Introducing the latent heat of vapor formation $q = T(S_{\text{gas}} - S_{\text{liq}})$, we obtain the *Clausius–Clapeyron equation*

$$\frac{dp}{dT} = \frac{q}{T\Delta V} \quad (7.19)$$

where $\Delta V = V_{\text{gas}} - V_{\text{liq}}$.

Far from the critical point this equation can be simplified since $V_{\text{gas}} \gg V_{\text{liq}}$. In addition, for an ideal gas we have the state equation (7.8) $pV = RT$, so that the temperature dependence of the saturated vapor pressure has the form

$$p_{\text{sat}} = p_o \exp\left(-\int \frac{q dT}{T^2}\right)$$

where the temperature T and the latent heat q are expressed in the same energetic units. One can assume the latent heat q to be a constant in some range of temperatures, and then

$$p_{\text{sat}} = p_o \exp \left(-\frac{q}{T} \right) \quad (7.20)$$

where q corresponds to this temperature range. As a result, we have for the saturated vapor pressure $p_{\text{sat}}(T)$ over a plane liquid surface in the form

$$p_{\text{sat}}(T) = p_{\text{liq}} \exp \left(-\frac{\varepsilon_{\text{liq}}}{T} \right) \quad (7.21)$$

where p_{liq} is a constant, and the parameter ε_{liq} can be considered as the atomic binding energy for the liquid state of a system of bound atoms in the temperature range under consideration. Table 7.3 gives the parameters of this formula for liquid rare gases near the melting point. Note that the parameters ε_{liq} , p_{liq} can be found by using the parameters of the triple and boiling points, and their values are close to those of Table 7.3. This table gives also the *boiling point* T_b for rare gases, i.e. the temperature at which the saturated vapor pressure is equal to 1 atm. In addition, Table 7.3 contains the evaporation energy per atom at the boiling point ε_{ev} , i.e. the atomic binding energy for the liquid state at the boiling point. As we have seen, this value is close to ε_{liq} , and Table 7.3 gives the ratio of these values.

Table 7.3. The parameters of saturated rare gases over a plane liquid and solid surface near the melting point.

	Ne	Ar	Kr	Xe	Average
ε_{liq} , meV	19.4	69.6	95.6	134	
p_{liq} , MPa	410	1060	1030	1270	
T_b , K	27.05	87.28	120.1	165.1	
ε_{ev} , meV	18.6	68	95	132	
$\varepsilon_{\text{ev}}/\varepsilon_{\text{liq}}$	0.96	0.98	0.99	0.98	0.98 ± 0.01
r_W , Å	2.02	2.40	2.57	2.73	
σ_{tr} , erg/cm ²	5.65	13.55	16.33	18.83	
A_{tr} , meV	18.1	61.4	84.8	111	

Formula (7.20) is valid at small vapor densities when one can neglect the interaction between atomic particles of the gas. This gives the vapor pressure on the line of the liquid–gas equilibrium (the evaporation curve). Formula (7.20) is valid if the saturated vapor pressure is small compared to the typical internal pressure for the liquid, that corresponds to a strong temperature dependence for the saturated vapor pressure. Under such conditions formula (7.20) holds true when the vapor is located in a buffer gas, so that the equilibrium between a liquid and parent vapor proceeds through evaporation and condensation processes on the liquid boundary.

If the saturated vapor pressure exceeds the total gas pressure outside the liquid, it is said to be boiling, and small vapor bubbles are formed inside the liquid. They grow, join and leave

the liquid in the form of a steam. The opposite process concerns the transformation of the vapor to liquid as a result of the formation of small drops inside the vapor. These processes of boiling and condensation proceed effectively in the presence of nuclei of bubble formation or *nuclei of condensation*, such as ions, radicals and active molecules. In a pure substance these processes can be frozen, and then *metastable states* of the substance can be obtained, i.e. a *superheated liquid* or *supersaturated vapor*. These states can exist over a range of parameters for a long time until the above processes convert them to stable states.

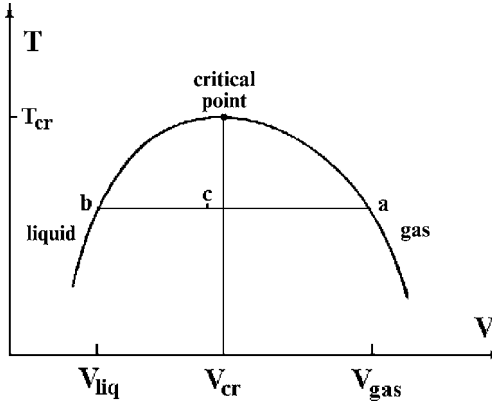


Figure 7.4. A typical T - V phase diagram in the range of existence of liquid and gaseous states.

The peculiarities of the transition between the liquid and gaseous states follow from the analysis of the $T - V$ diagram (Figure 7.4). The left-hand side of the diagram corresponds to the liquid state of the system, and the right-hand side of the diagram relates to the gaseous state. In the intermediate range these phases coexist. Considering the range of coexistence of phases, we introduce the portion of the volume x which is occupied by the gaseous phase at a given point c . Then the vapor volume equals xV_{gas} at a given temperature and the liquid volume is $(1 - x)V_{\text{liq}}$. Because the total volume of the mixture equals V , we obtain

$$V = xV_{\text{gas}} + (1 - x)V_{\text{liq}}$$

From this it follows

$$\frac{x}{1 - x} = \frac{V - V_{\text{liq}}}{V_{\text{gas}} - V} = \frac{bc}{ac} \quad (7.22)$$

This relation is known as the *arm rule*. One can see that the range of stratification of liquid and gaseous phases, which occupies a line on the $p - T$ diagram (Figure 7.1), is transformed into a range on the $V - T$ diagram (Figure 7.4) and $V - p$ diagram. Hence the line between points b and f of an isotherm of Figure 7.3 is transformed into the line ab of the $T(V)$ diagram of Figure 7.4.

At the interface between the liquid and gas phases a force occurs which holds the liquid molecules. This creates the *surface energy*, which is proportional to the area of the interface boundary S , so that the surface energy in this case is equal to

$$E_{\text{sur}} = S\sigma \quad (7.23)$$

where the surface energy per unit area σ is called the *surface tension*. Evidently, under optimal conditions this energy is minimal, which compels a liquid drop to have a spherical shape.

One can consider a liquid drop as a system of n bound atoms, and the energy of this drop can be represented in the form

$$E = -E_n = -\varepsilon_o n + A n^{2/3} \quad (7.24)$$

where E_n is the total binding energy of atoms, ε_o is the binding energy per atom for a bulk system, A is the *specific surface energy*. This formula is an expansion of the drop energy over a small parameter $n^{-1/3}$. Since the drop has a spherical shape, the drop radius is

$$r = r_W n^{1/3} \quad (7.25a)$$

Here r_W is the *Wigner–Seitz* radius, which is given by the formula

$$r_W = \left(\frac{3m}{4\pi\rho} \right)^{1/3} \quad (7.25b)$$

where m is the molecule mass and ρ is the drop density. The parameter r_W characterizes the volume related to one molecule in bulk.

Comparing the expressions (7.23) and (7.24) for the surface energies $4\pi r^2 \sigma = A n^{2/3}$, we obtain the connection between the specific surface energy A and the surface tension σ

$$A = 4\pi r_W^2 \sigma \quad (7.26)$$

Table 7.3 contains the quantities of the Wigner–Seitz radius r_W for liquid rare gases at the triple point, their surface tension σ_{tr} at the triple point, and the corresponding values of the specific surface energy A_{tr} .

7.8 The Equation of the Solid State

The equation (7.7) of the gas state may be obtained in a formal way on the basis of the thermodynamic formalism which accounts for the connection between thermodynamic parameters of this system. Indeed, according to formula (6.22) the pressure is

$$p = \left(\frac{\partial F}{\partial V} \right)_T$$

and the free energy F is given by formulae (6.25) and (6.26) for a system of free particles. Using these formulae, we obtain

$$p = \frac{n}{V} T = NT$$

which coincides with formula (7.7).

In the same way we deduce the state equation of a solid assuming the variation of the solid free energy to be determined by atomic oscillations and using for this the Debye approximation (see Table 3.3). Separating the free energy into two parts

$$F = F_o + F_D$$

so that the first term F_o corresponds to zero temperature, and the second one is due to atomic oscillations, which are considered in the framework of the Debye model, we have the solid state equation

$$p = p_o + \frac{\partial F_D}{\partial V}$$

where the first term on the right-hand side of this equation relates to zero temperature and the second one accounts for the oscillations of atoms. In this way we divide the interaction of atoms of the solid state into two parts, with the second part due to atomic oscillations. Taking the second part of the free energy in the Debye approximation

$$F_D = TF \left(\frac{T}{\theta_D} \right)$$

and assuming the Debye temperature to be dependent on a specific volume V , we obtain

$$p = p_o + \gamma \frac{E(T/\theta_D)}{V}$$

where γ is the *Gruneisen constant*. This accounts for the volume dependence of oscillation frequencies, and if we assume an identical volume dependence for different frequencies, the Gruneisen constant takes the form

$$\gamma = -\frac{d \ln \omega}{d \ln V} \quad (7.27)$$

Thus the expanding Debye approximation allows one to analyze the state equation of a solid under some assumptions for the volume dependencies of frequencies of solid oscillations. We divide interactions into two types, so that the first term of the free energy accounts for the potential interaction inside the solid and corresponds to zero temperature, while the second term results from atomic oscillations or phonons. We assume these degrees of freedom to be independent which may be valid at low excitations.

7.9 Lennard–Jones Crystals and the Character of Interactions in Solid Rare Gases

Being guided by simple systems of interacting atoms, such as rare gases, we will choose a simple real interaction potential of atoms in a condensed system. A typical interaction potential for two atoms is given in Figure 7.5, and atoms with such an interaction potential form a crystal of *close packed structure* at low temperatures, i.e. the solid has the face-centered cubic or hexagonal crystal lattice. We will consider two forms of interaction of atoms in a crystal, and in the second case we use the Lennard–Jones interaction potential for the pair interaction of atoms, in which long-range interactions are of importance for crystal parameters. By comparing the crystal parameters of rare gases with those from models of atomic interaction, we choose the suitable interaction character for real rare gases.

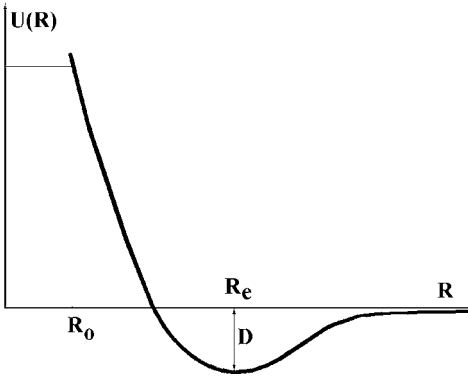


Figure 7.5. A typical interaction potential of two atoms.

In the lattice of the close-packed structure each internal atom has 12 nearest neighbors. Hence, in the absence of a long-range interaction, the distance between nearest neighbors in the crystal lattice a coincides with the equilibrium distance between atoms of a diatomic molecule R_e . Thus we have for the crystal parameters in the case of a short-range interaction of atoms, when only the nearest neighbors of a system interact

$$\varepsilon_{\text{sub}} = 6D, \quad a = R_e \quad (7.28)$$

where ε_{sub} is the binding energy of the crystal per atom at zero temperature, the lattice constant a is the distance between nearest neighbors of the crystal. Note that crystals of rare gases have the face-centered cubic lattice.

Table 7.4. The shell parameters of the face-centered cubic structure; r_k is the shell's distance from a test atom, a is the distance between nearest neighbors, and n_k is the number of atoms in the k th shell.

Shell	r_k^2/a^2	n_k	Shell	r_k^2/a^2	n_k
011	1	12	123	7	48
002	2	6	004	8	6
112	3	24	114	9	24
022	4	12	033	9	12
013	5	24	024	10	24
222	6	8	233	11	24

We now consider the *Lennard–Jones interaction potential* of atoms, which has the form (3.24)

$$U_{LD}(R) = D \cdot \left[\left(\frac{R_e}{R} \right)^{12} - 2 \cdot \left(\frac{R_e}{R} \right)^6 \right] \quad (7.29)$$

where R is the distance between atoms. This interaction potential is popular and includes a long-range part of the interaction. Considering the *Lennard–Jones crystal* whose atoms

interact through the pair interaction potential (7.29), we assume that it has the face-centered cubic structure. To determine the binding energy of atoms of this crystal, we take a test atom as the origin and distribute other atoms over shells, so that the distances of atoms of one shell from the test atom are identical. In addition, the atoms of a certain shell are transformed into each other as a result of transformations (3.16), which conserve this lattice. Table 7.4 gives the parameters of atomic shells for the face-centered cubic structure, and the notation of each shell in Table 7.4 contains the reduced coordinates $x\sqrt{2}/a$, $y\sqrt{2}/a$, $z\sqrt{2}/a$, where $x \leq y \leq z$. The binding energy per atom for a system with a pair interaction of atoms at zero temperature is given by

$$\varepsilon_{\text{sub}} = \frac{1}{2} \sum_k n_k U(r_k) \quad (7.30)$$

where $U(r_k)$ is the interaction potential for an atom of the k th shell with a test atom, and the factor $1/2$ accounts for the fact that each bond relates to two atoms. In the case of the Lennard–Jones crystal we have from formula (7.30) for the specific sublimation energy of the crystal

$$\begin{aligned} \frac{\varepsilon_{\text{sub}}}{D} &= -\frac{C_{12}}{2} \left(\frac{R_e}{a} \right)^{12} + C_6 \left(\frac{R_e}{a} \right)^6, \\ C_{12} &= \sum_k n_k \left(\frac{R_e}{r_k} \right)^{12}, \quad C_6 = \sum_k n_k \left(\frac{R_e}{r_k} \right)^6 \end{aligned} \quad (7.31)$$

Optimizing formula (7.31), we obtain for the equilibrium distance a between nearest neighbors and the specific binding energy ε_{sub}

$$a = R_e \left(\frac{C_{12}}{C_6} \right)^{1/6}, \quad \varepsilon_{\text{sub}} = \frac{C_6^2 D}{2C_{12}} \quad (7.32)$$

Changing the summation in formula (7.31) by integration for $R \geq r_o$ we have the contribution to the constants C_{12} , C_6 from a range where $r_k > r_o$

$$\begin{aligned} \Delta C_{12} &= \sum_{R \geq r_o} \frac{D n_k}{r_k^{12}} = \int_{r_o}^{\infty} \frac{D \sqrt{2}}{a^3} \frac{4\pi r^2 dr}{r^{12}} = \frac{4\pi D \sqrt{2}}{9 r_o^9 a^3}, \\ \Delta C_6 &= \sum_{R \geq r_o} \frac{D n_k}{r_k^6} = \int_{r_o}^{\infty} \frac{D \sqrt{2}}{a^3} \frac{4\pi r^2 dr}{r^6} = \frac{4\pi \sqrt{2} D}{3 r_o^3 a^3} \end{aligned} \quad (7.33)$$

Here we account for the fact that the number density of atoms in a close-packed lattice is $\sqrt{2}/a^3$. Errors in the constants under consideration result from the change from summation to integration in formulae (7.33). Taking $\delta r_o^2 = a^2/2$ according to the data in Table 7.4, we obtain for errors in coefficients

$$\delta C_{12} = \frac{\pi D \sqrt{2}}{a r_o^{11}}, \quad \delta C_6 = \frac{\pi \sqrt{2} D}{a r_o^5} \quad (7.34)$$

Taking r_o^2 between 11 and 12, we get for the face-centered cubic structure of the crystal, on the basis of the data in Table 7.3

$$C_{12} = 12.132, \quad C_6 = 14.45 \pm 0.01 \quad (7.35)$$

If we take into account the next shells, this gives $C_6 = 14.454$. This yields the parameters of the face-centered cubic of the Lennard–Jones crystal

$$a = 0.971R_e, \quad \varepsilon_{\text{sub}} = \frac{C_6^2 D}{2C_{12}} = 8.61D \quad (7.36)$$

and the short-range interaction of atoms gives a contribution of approximately 70% to the energy of the Lennard–Jones crystal with the face-centered cubic structure.

We now compare the parameters of solid rare gases with those according to formulae (7.28) and (7.36). The basic parameters of the pair interaction potential of rare gas atoms are R_e , the equilibrium distance between atoms, and D , the depth of the potential well of the pair interaction potential. These parameters follow from various measurements, such as the differential and total cross sections of elastic scattering of two atoms, the second virial coefficient of rare gases, the diffusion coefficient of atoms in the parent rare gas, the thermal conductivity and viscosity coefficients, spectrum of excitation for dimers of rare gas atoms, and other parameters of solid and liquid rare gases. On the basis of such measurements these parameters are known with an accuracy of some per cent for rare gas atoms.

Comparison of formulae (7.28) and (7.36) for the lattice constant a and the sublimation energy per atom ε_{sub} with the data of Table 7.5 shows a short-range character of interaction for rare gas atoms in solids. Note that the value $\varepsilon_{\text{ev}} + T_{\text{tr}}\Delta s$ corresponds to the sublimation energy of the solid if we neglect the change of the internal energy over the temperature variation from the melting point to the boiling point. Here $\Delta H_{\text{fus}} = T_{\text{tr}}\Delta s$ is the specific fusion energy, so that Δs is the entropy change at melting. Table 7.5 gives the ratio $(\varepsilon_{\text{ev}} + T_{\text{tr}}\Delta s)/\varepsilon_{\text{sub}}$, and its difference from one shows the accuracy of the assumptions used.

Table 7.5. The parameters of the pair interaction potential for rare gas atoms and the reduced parameters of systems consisting of interacting atoms of rare gases.

	Ne	Ar	Kr	Xe	Average
$R_e, \text{\AA}$	3.09	3.76	4.01	4.36	
D, meV	3.64	12.3	17.3	24.4	
$a, \text{\AA}$	3.156	3.755	3.992	4.335	
a/R_e	1.02	1.00	0.99	1.01	1.005 ± 0.013
$\varepsilon_{\text{sub}}, \text{meV}$	22	80	116	164	
$\varepsilon_{\text{sub}}/D$	6.0	6.5	6.7	6.7	6.5 ± 0.3
$(\varepsilon_{\text{ev}} + T_{\text{tr}}\Delta s)/\varepsilon_{\text{sub}}$	1.00	1.00	0.96	0.95	0.98 ± 0.03
$\varepsilon_{\text{sol}}, \text{meV}$	22.5	80.2	112	158	
$\varepsilon_{\text{sol}}/D$	6.2	6.5	6.5	6.5	6.4 ± 0.2
$\varepsilon_{\text{sub}}/\varepsilon_{\text{sol}}$	0.98	1.00	1.04	1.04	1.02 ± 0.03

In addition, Table 7.5 contains the effective binding energy of an atom of solid rare gases ε_{sol} on the *sublimation curve* (Figure 7.1) which separates the solid and gaseous states. The saturated vapor pressure, i.e. the gas pressure on the sublimation curve, follows from the Clausius–Clapeyron formula (7.21) and has the same form as formula (7.21)

$$p_{\text{sat}}(T) = p_{\text{sol}} \exp\left(-\frac{\varepsilon_{\text{sol}}}{T}\right) \quad (7.37)$$

The values ε_{sub} and ε_{sol} characterize the atomic binding energy for the solid state, and their difference also testifies to the accuracy of the assumptions used. The comparison given in Table 7.5 confirms the short-range character of atom interaction in solid rare gases, i.e. the properties of solid rare gases are determined by the interaction between nearest neighbors.

7.10 Equilibrium Between Phases in Rare Gases

Within the framework of thermodynamics, we define a *phase* as a bulk uniform state of a system of free or bound atomic particles, and this system is restricted by a boundary. For the simplest substances we call the phases the gaseous, liquid and solid *aggregate states*. If two phases coexist, they are separated by an interface. Under some conditions, these phases can be found in equilibrium which differs from the chemical one when subsystems are located in the same region of space. Evidently, the equilibrium condition for phases is given by equation (6.36) at the interface. For the simplest systems with three aggregate states we have three coexistence lines, as shown in Figure 7.1. These lines meet at the *triple point*, where three phases can coexist simultaneously. In addition, the coexistence line between the liquid and gaseous states finishes at the *critical point*, and above this point the liquid and gas states are not distinguishable. Therefore one can move from the liquid state to the gaseous one above the critical point as shown by the dotted line on Figure 7.1, and the parameters of the system vary continuously on this line. Note that in the case of solid–liquid transitions the parameters of the system vary by a jump as a result of intersecting the melting line. Below we consider the aggregate states of simple systems and transitions between them within the framework of thermodynamics.

We demonstrate the real character of the phase equilibrium for simple systems with an example of dense and condensed rare gases. Evidently, the main points of the phase curves of Figure 7.1 are the triple point and the critical point. Therefore we consider below the behavior of rare gases at the critical point and near the triple point. Table 7.6 lists the corresponding parameters for rare gases. Here T_{tr} and p_{tr} are the temperature and pressure of rare gases at the triple point, ρ_{sol} and ρ_{liq} are the densities of the solid and liquid states at the triple point, V_{sol} and V_{liq} are the specific volumes for the solid and liquid states at the triple point, and Δs is the entropy change per atom for melting at the triple point. Note that as a result of melting, the specific volume varies according to $\Delta V = V_{\text{liq}} - V_{\text{sol}}$, corresponding to the mechanical work $p_{\text{tr}}\Delta V$. Simultaneously, the specific fusion energy $\Delta H_{\text{fus}} = T_{\text{tr}}\Delta s$ is consumed as a result of melting. It follows from the data of Table 7.6 that the mechanical work near the triple point is relatively small for condensed rare gases. This means that the melting process of condensed rare gases near the triple point can be considered to depend only on one thermodynamic parameter, the entropy s . In addition, the parameter $T_{\text{tr}}/(p_{\text{tr}}V_{\text{sol}})$ for the solid state is large in comparison with that of gases.

Table 7.6. The parameters of dense and condensed rare gases.

	Ne	Ar	Kr	Xe	
T_{tr}, K	24.54	83.78	115.8	161.4	
$p_{\text{tr}}, \text{kPa}$	43.3	68.8	73.1	81.6	
$\rho_{\text{sol}}, \text{g/cm}^3$	1.444	1.623	2.826	3.540	
$\rho_{\text{liq}}, \text{g/cm}^3$	1.247	1.418	2.441	3.076	
$V_{\text{sol}}, \text{cm}^3/\text{mol}$	14.0	24.6	29.6	37.1	
$V_{\text{liq}}, \text{cm}^3/\text{mol}$	16.2	28.2	34.3	42.7	
$T_{\text{tr}}/(p_{\text{tr}} V_{\text{sol}})$	340	400	450	450	410 ± 50
Δs	1.64	1.69	1.70	1.71	1.68 ± 0.03
$p_{\text{tr}} \Delta V / T_{\text{tr}} \Delta s, 10^{-4}$	2.8	2.1	2.1	2.0	2.2 ± 0.4
$a, \text{\AA}$	3.156	3.755	3.992	4.335	—
P, MPa	102	209	235	258	
c	1.600	1.593	1.617	1.589	1.60 ± 0.01

Note the difference between the parameters ε_{sol} and ε_{liq} of the Clausius–Clapeyron formulae which characterize the binding energies of these states per atom, and the parameters ε_{sub} , the specific binding energy in a solid, and ε_{ev} , the energy which is consumed on evaporation of one atom at the boiling point. It follows from Tables 7.2 and 7.4 that ε_{ev} is close to ε_{liq} , and ε_{sub} is close to ε_{sol} . Moreover, according to Table 7.6, the values $\varepsilon_{\text{ev}} + \Delta H_{\text{fus}}$ and ε_{sub} are close (see also Table 7.2), which gives the correspondence between the binding energies of the liquid and solid states.

Solid rare gases have the face-centered cubic lattice. The distance between nearest neighbors a is given in Table 7.6. The crystal density at zero temperature is

$$\rho(0) = \frac{m}{a^3 \sqrt{2}} \quad (7.38)$$

where m is the atomic mass. As the temperature increases, the solid density decreases. The behavior of the melting curve between the solid and liquid states near the triple point is described by the *Simon equation*, which has the form

$$\frac{p - p_{\text{tr}}}{P} = \left(\frac{T}{T_{\text{tr}}} \right)^c - 1 \quad (7.39)$$

where p_{tr} , and T_{tr} are the parameters of the triple point. Table 7.6 contains the parameters of this equation. The data in Table 7.6 testifies the scaling for reduced parameters of condensed rare gases with respect to the pair interaction potential of their atoms.

Thus we divide systems of many atoms or molecules into two groups where the interaction between atomic particles is small or large in comparison with the typical kinetic energy of atomic particles. In gaseous systems the interaction of atomic particles is comparatively small. Hence gaseous systems include systems consisting of free atoms or molecules and an ideal plasma. The mean energy of interaction of an atomic particle with the surrounding particles in gaseous systems is small compared with its kinetic energy. Condensed systems are systems of many bound atomic particles. One can divide condensed systems into solids and liquids.

There is a correlation between the positions of atomic particles in solids, and this correlation relates both to nearest neighbors and non-nearest neighbors. As a result, atomic particles form a crystal lattice, i.e. there is a correlation in the positions of distant atomic particles (so called *long-range order*). We used earlier (Chapter 3) the cubic and face-centered cubic lattices to analyze atomic oscillations in solids. The properties of a crystal lattice determine the character of processes inside it.

8 Thermodynamics of Aggregate States and Phase Transitions

8.1 Scaling for Dense and Condensed Rare Gases

According to the reduced van der Waals equation (7.17), the behavior of various liquids and gases can be described in a similar way in reduced units. Evidently this property can be spread also to the solid state of simple systems. Below we analyze the *similarity law* for rare gases. The properties of a system consisting of rare gas atoms are determined by the interaction between atoms, and because the typical attraction interaction potential of two atoms is small in comparison with typical atomic energies, the interaction of rare gas atoms is pairwise, i.e. one can neglect three-body and many-body interactions of atoms. Considering the scaling problem from the dimensionality standpoint, we take for each rare gas three parameters and construct on the basis of these parameters the values of any dimensionality. One of these parameters is the atomic mass m ; two other parameters are the interaction potential parameters. Figure 7.5 shows a typical interaction potential for two atoms, and we assume the properties of different aggregate states of rare gases to be determined by the attractive part of this interaction potential. Moreover, we assume that the interaction of nearest neighbors plays the main role in dense and condensed rare gases, and hence we use the equilibrium distance between atoms R_e and the depth of the potential well D of the pair interaction potential as two other parameters for the system of units in the *scaling analysis* which are used partially for rare gas systems in the previous chapter. It follows from this that we assume a classical character for atomic interaction and motion in systems of rare gas atoms, so that quantum parameters are not used for this scaling analysis. Table 8.1 gives these three parameters on which the scaling analysis of dense and condensed rare gases is grounded. In addition, Table 8.1 contains the parameters of other dimensionalities which are constructed on the basis of these parameters.

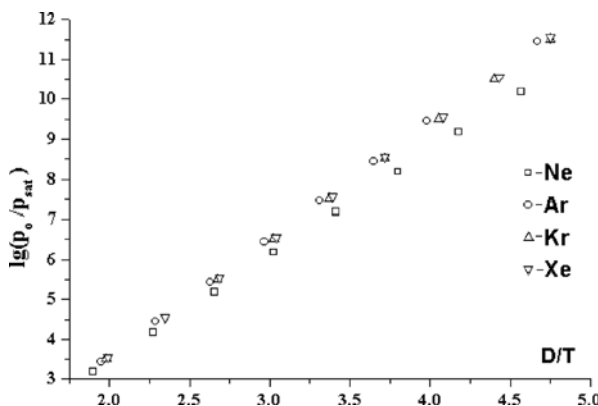
Note that the parameters of the pair interaction potential used follow from various measurements, such as the differential and total cross section of elastic scattering of two atoms, the second virial coefficient of rare gases, the diffusion coefficient of atoms in the parent rare gas, the thermal conductivity and viscosity coefficients, spectra of excitation for dimers of rare gas atoms, and some properties of solid and liquid rare gases. On this basis, the parameters of Table 8.1 for the pair interaction potential of two rare gas atoms are known to an accuracy of several per cent.

Thus this scaling version uses the parameters of the attractive part of the pair interaction potential of atoms, and hence is guided by the *short-range interaction* of atoms, when the interaction between nearest neighbors dominates in a dense or condensed system of atoms. One can construct another scaling version on the basis of a *long-range interaction* of atoms, and comparison of formulae (7.28) and (7.36) with real parameters of solid rare gases confirms a short-range character of atom interaction in this case.

Table 8.1. The parameters of the pair interaction potential for rare gas atoms and the reduced parameters of systems consisting of interacting atoms of rare gases.

	Ne	Ar	Kr	Xe
$R_e, \text{\AA}$	3.09	3.76	4.01	4.36
D, meV	3.64	12.3	17.3	24.4
D, K	42	143	200	278
$m, \text{a.m.u.}$	20.18	39.95	83.80	131.3
$p_o = D/R_e^3, \text{MPa}$	20.2	37.1	43.0	47.1
$V_o = R_e^3, \text{cm}^3/\text{mol}$	17.8	32.0	38.8	49.9
$\rho_o = m\sqrt{2}/R_e^3, \text{g/cm}^3$	1.606	1.764	3.051	3.718
$C_6, \text{a.u.}$	6.3	65	130	270
DR_e^6/C_6	0.84	0.90	0.93	1.04

The reduced parameters of rare gas systems are given in Table 8.2, and from this it follows that the scaling law is valid for dense and condensed rare gases within an accuracy of several per cent. In this table we give the reduced parameters of rare gases near the triple point and on lines of coexistence of phases near the triple point. These parameters are taken from Tables 7.6 and 8.1, where the notations for these values are given. Next, Table 8.3 lists the reduced parameters of the van der Waals equation, critical parameters of rare gases, and also the reduced surface parameters of liquid rare gases.

**Figure 8.1.** The saturated vapor pressure over a solid surface of rare gases. Signs – experimental data, solid curve – formula (7.36).

One can find the atomic binding energies of solid and liquid rare gases in two ways. In the first case this value follows from the total binding energy of bulk rare gases and we define the binding energy per atom by ε_{sub} for solids and ε_{ev} for liquids (see Tables 8.2 and 7.5). In the second case these values are determined by the saturated vapor pressure p_{sat} over solid or liquid surfaces, which according to the *Clausius–Clapeyron equations* (7.21) and (7.37) has

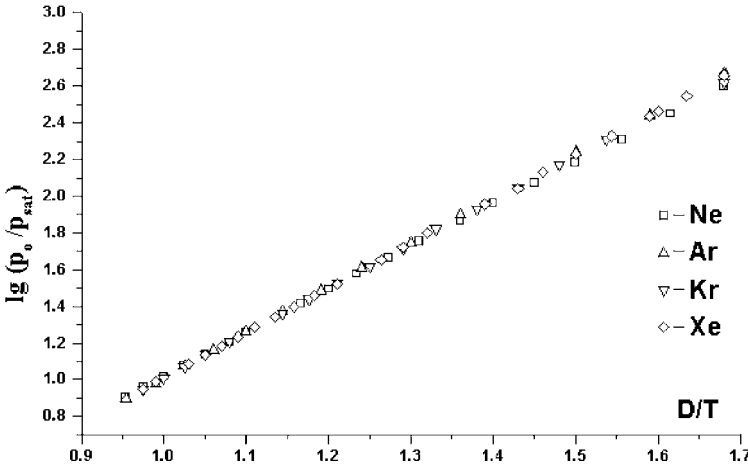


Figure 8.2. The saturated vapor pressure over a liquid surface of rare gases. Signs – experimental data, solid curve – formula (7.21).

the form

$$p_{\text{sat}}(T) = p_{\text{sol}} \exp\left(-\frac{\varepsilon_{\text{sol}}}{T}\right) \quad (8.1)$$

$$p_{\text{sat}}(T) = p_{\text{liq}} \exp\left(-\frac{\varepsilon_{\text{liq}}}{T}\right) \quad (8.2)$$

where p_{sol} and p_{liq} are constants, and the parameters ε_{sol} and ε_{liq} can be considered as the atomic binding energy for solid and liquid systems of bound atoms under consideration. The parameters of this formula for solid and liquid rare gases near the triple point are given in Tables 7.3 and 7.6. Evidently these parameters satisfy the similarity laws, and hence the saturated vapor pressure is submitted to scaling over a wide range of temperatures to a certain accuracy. This is demonstrated in Figures 8.1 and 8.2 for the solid and liquid rare gases.

Along with the parameters of the curves of the solid–gas and liquid–gas phase transitions, which are given by formulae (8.1) and (8.2), Table 8.2 contains the parameters of the melting curve near the triple point. Indeed, according to the Clausius–Clapeyron formula (7.19) we have on the melting curve

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta V} \quad (8.3)$$

where Δs and ΔV are the jumps of the entropy and specific volume as a result of melting, and the reduced values of this derivative are given in Table 8.2. Next, the melting curve intersects the abscissa axis at a temperature T_o near the melting point, so that the value $\Delta T = T_{\text{tr}} - T_o$ is relatively small (see Table 8.2). We give in Table 8.2 also the reduced fusion enthalpy $\Delta H_{\text{fus}} = T_{\text{tr}} \Delta s$.

Let us enumerate the factors which cause an error in the scaling parameters. First, we assume the character of atomic interaction in dense and condensed systems to be independent of

Table 8.2. Reduced parameters of rare gases near the triple point.

	Ne	Ar	Kr	Xe	Average
a/R_e	1.02	1.00	0.99	1.01	1.005 ± 0.013
$\rho(0)/\rho_o$	1.06	1.00	0.99	0.98	1.01 ± 0.04
ρ_{sol}/ρ_o	0.899	0.920	0.926	0.952	0.92 ± 0.02
ρ_{liq}/ρ_o	0.776	0.804	0.800	0.827	0.80 ± 0.02
T_{tr}/D	0.581	0.587	0.578	0.570	0.579 ± 0.007
$p_{\text{tr}}/p_o, 10^{-3}$	2.2	1.9	1.7	1.7	1.9 ± 0.2
V_{liq}/R_e^3	0.912	0.881	0.883	0.856	0.88 ± 0.02
V_{sol}/R_e^3	0.788	0.768	0.762	0.743	0.76 ± 0.02
$\Delta V/R_e^3$	0.124	0.113	0.121	0.113	0.118 ± 0.006
$\varepsilon_{\text{sub}}/D$	6.1	6.5	6.5	6.4	6.4 ± 0.2
Δs	1.64	1.69	1.70	1.71	1.68 ± 0.03
$\Delta H_{\text{fus}}/D$	0.955	0.990	0.980	0.977	0.98 ± 0.02
$p_{\text{tr}}\Delta V/\Delta H_{\text{fus}}, 10^{-4}$	2.8	2.1	2.1	2.0	2.2 ± 0.4
P/p_o	5.14	5.70	5.52	5.52	5.5 ± 0.2
$\varepsilon_{\text{liq}}/D$	5.3	5.7	5.5	5.5	5.5 ± 0.1
$p_{\text{liq}}R_e^3/D$	20	29	24	27	25 ± 4
$\varepsilon_{\text{sol}}/D$	6.2	6.5	6.5	6.5	6.4 ± 0.2
$p_{\text{sol}}R_e^3/D$	89	124	130	104	110 ± 20
$R_e^3 dp/dT$	13.2	15.0	14.0	15.1	14.3 ± 0.9
$(T_{\text{tr}} - T_o)/D, 10^{-4}$	1.7	1.3	1.2	1.1	1.3 ± 0.2

the form of the pair interaction potential of atoms, i.e. it is determined only by the parameters of the potential well in the pair interaction potential. Second, we ignore the contribution of the long-range interaction between atoms to parameters under consideration. Third, we neglect the quantum effects. Fourth, we assume that three-body interactions are not of importance for these systems. Evidently, the degree of validity of these assumptions determines the accuracy of the scaling laws for the rare gas systems. The analysis for dense and condensed rare gases shows that the scaling law holds true to an accuracy of several per cent. The results also allow us to restore the parameters of the pair interaction potential for radon atoms. From the above data and measured thermodynamic parameters of dense and condensed radon it follows for the parameters of the interaction potential of two radon atoms

$$D = 30.2 \pm 0.4 \text{ meV}, \quad R_e = 4.68 \pm 0.04 \text{ \AA}$$

It is essential that there are several different parameters of the same dimensionality, which use allows one to improve the accuracy of the results. Table 8.4 contains the ratios of parameters of identical dimensionality. For the scaling analysis we have used the following parameters of the energy dimensionality: T_{tr} , T_b , T_{cr} , ε_{ev} and ε_{sub} (the notations are given above); the values V_{liq} , V_{cr} and b_W of the volume dimensionality; the values p_{tr} , and p_{cr} of

the pressure dimensionality, as well as the constant a_W of the van der Waals equation. We do not include in this list the values ε_{liq} and ε_{sol} , assuming them to be identical to ε_{ev} , and ε_{sub} , and the values p_{liq} and p_{sol} (formula 8.1), which by definition correspond to the typical atomic number density of atoms and are related to a certain pressure range. The variety of physical parameters under consideration improves the scaling analysis and excludes occasional errors in this analysis.

Table 8.3. The reduced parameters of the van der Waals equation, the reduced boiling point T_b/D , the reduced critical parameters of rare gases, and the reduced surface parameters of liquid rare gases.

	Ne	Ar	Kr	Xe	Average
T_b/D	0.640	0.610	0.601	0.594	0.61 ± 0.02
$a_W/(DR_e^3)$	3.27	3.57	3.59	3.57	3.50 ± 0.15
b_W/R_e^3	0.941	1.000	1.020	1.033	1.00 ± 0.04
T_{cr}/D	1.05	1.06	1.04	1.02	1.04 ± 0.02
$p_{\text{cr}}R_e^3/D$	0.137	0.132	0.128	0.124	0.130 ± 0.006
V_{cr}/R_e^3	2.50	2.34	2.34	2.36	2.38 ± 0.08
$T_{\text{cr}}/(p_{\text{cr}}V_{\text{cr}})$	3.4	3.5	3.2	3.5	3.4 ± 0.1
ρ_{cr}/ρ_o	0.283	0.302	0.302	0.300	0.297 ± 0.009
r_W/R_e	0.654	0.639	0.641	0.627	0.64 ± 0.01
$\sigma_{\text{tr}}R_e^2/D$	0.93	0.97	0.95	0.95	0.94 ± 0.02
A/D	5.0	5.0	4.9	4.5	4.9 ± 0.2

Table 8.4. The ratios of values of identical dimensionality for dense and condensed rare gases.

Ratio	Ne	Ar	Kr	Xe	Average
$\varepsilon_{\text{liq}}/T_{\text{tr}}$	9.2	9.6	9.6	9.6	9.5 ± 0.2
$\varepsilon_{\text{sol}}/T_{\text{tr}}$	10.6	11.2	11.3	11.4	11.1 ± 0.4
$p_{\text{cr}}/p_{\text{tr}}$	64	71	75	72	70 ± 5
$\varepsilon_{\text{sol}}/T_{\text{cr}}$	5.9	6.2	6.2	6.3	6.2 ± 0.2
$\varepsilon_{\text{liq}}/T_{\text{cr}}$	5.1	5.4	5.3	5.4	5.3 ± 0.1
$\varepsilon_{\text{ev}}/T_{\text{cr}}$	4.9	5.2	5.3	5.3	5.2 ± 0.2
$\varepsilon_{\text{ev}}/\varepsilon_{\text{liq}}$	0.96	0.98	0.99	0.98	0.98 ± 0.01
$V_{\text{cr}}/V_{\text{liq}}$	2.74	2.66	2.65	2.76	2.70 ± 0.06
V_{cr}/b	2.51	2.34	2.30	2.29	2.36 ± 0.10
$p_{\text{cr}}/p_{\text{tr}}$	64	71	75	72	70 ± 5
$T_{\text{cr}}R_e^6/C_6$	0.89	0.95	0.97	1.06	0.97 ± 0.07

8.2 Phase Transitions at High Pressures and Temperatures

We considered above the solid–liquid phase transition of a system of bound atoms if bonds are formed due to the attraction of atoms. Moreover, the properties of condensed rare gases are determined mostly by the attraction of neighboring atoms. Under these conditions, the triple point pressure is small in comparison with a typical pressure in this system $p_o = D/R_e^3$ due to the interaction of atoms (see Table 8.2). But if we move along the melting curve with increasing pressure, the role of repulsion in atomic interactions increases. Starting from pressures $p \sim p_o$, one can support the solid–liquid phase transition only by an external pressure, and the repulsion of atoms is of importance in this case. Below we consider the limiting case

$$p \gg p_o \quad (8.4)$$

when the state equation for the system of atoms is determined by the repulsive part of the atom interaction potential.

Assuming the pairwise character of atom interaction, we take for definiteness the interaction potential of two atoms $U(R)$ in the repulsive range of separations R (see Figure 7.5) in accordance with formula (7.13)

$$U(R) = \frac{C}{R^k} = U(R_o) \left(\frac{R_o}{R} \right)^k \quad (8.5)$$

and the parameter k is large for real atoms. In particular, Table 7.1 contains the parameters of the pair interaction potential of two identical atoms of rare gases at a distance R_o , where $U(R_o) = 0.3$ eV.

Basing on the scaling law, it is convenient to introduce the parameter of the length dimensionality, which is equal to

$$d = \left(\frac{C}{T} \right)^{1/k} \quad (8.6)$$

where T is a temperature on the melting line, and introducing the pressure p , the specific volume jump ΔV as a result of melting, and the volume V_{sol} , V_{liq} per atom for the solid and liquid states correspondingly on the melting curve, we obtain the following scaling law on the melting curve

$$p \sim \frac{T}{d^3}, \quad \Delta V \sim V_{\text{sol}} \sim V_{\text{liq}} \sim d^3, \quad N_{\text{sol}} \sim \frac{1}{V} \sim \frac{1}{d^3} \quad (8.7)$$

and the entropy jump $\Delta S \sim 1$. Table 8.5 gives the parameters on the melting curve for a system of atomic particles with the interaction potential (8.5) for different k , and the relation between the pressure p and temperature T on the melting curve gives the state equation for the melting curve. According to these data, the mechanical work during melting $p\Delta V$ is comparable with the melting heat or the fusion enthalpy $\Delta H = T\Delta S$. Moreover, in the limit $k \rightarrow \infty$ the melting becomes a reversible process, so that the fusion energy is compensated by the energy resulted from compression at the phase transition. Note that according to the Table 8.6 data, the mechanical work $p_{\text{tr}}\Delta V_{\text{tr}}$ as a result of melting near the triple point (p_{tr}

is the triple point pressure, and ΔV_{tr} is the volume jump at the triple point) differs from the enthalpy change ΔH_{fus} at melting by almost four orders of magnitude. In the case of a system of repelling particles these values are comparable.

Table 8.5. The parameters of a system of repelling atoms with the interaction potential (8.5) on the melting line.

k	4	6	8	12	∞
pV_{sol}/T	90	38	28	19	11
$V_{sol}\sqrt{2}/d^3$	0.254	0.641	1.030	1.185	1.359
$V_{liq}\sqrt{2}/d^3$	0.255	0.649	1.060	1.230	1.499
$\Delta V/V_{sol}$	0.005	0.013	0.030	0.038	0.103
$p\Delta V/T$	0.45	0.50	0.63	0.72	1.16
ΔS	0.80	0.75	0.84	0.90	1.16

In the limiting case $k \rightarrow \infty$ the interaction of atomic particles is determined by their contact. It is convenient to characterize the state of the system of particles by the *packing density* $\varphi = 4\pi r_o^3 N/3 = \pi d^3 N/6$, where $r_o = d/2$ is the particle radius and N is the number density of particles. This parameter characterizes the volume part which is occupied by particles. For the close packed crystal structure, where each particle-ball touches 12 nearest neighbors, this parameter is equal to $\varphi_{cr} = \pi\sqrt{2}/6 = 0.7405$, and this is the maximum possible value for this parameter. On the melting curve for the solid and liquid states this parameter equals

$$\varphi_{sol} = \frac{\pi d^3}{6V_{sol}} = 0.545, \quad \varphi_{liq} = \frac{\pi d^3}{6V_{liq}} = 0.494 \quad (8.8)$$

as follows from Table 8.5 in the limiting case $k \rightarrow \infty$. Note that each particle has 12 nearest neighbors in the crystal state, while for the fluid state each particle has contacts with 8 nearest neighbors. In addition, the packing density $\varphi = 0.64$ for the solid state in the limit $k \rightarrow \infty$ if the pressure tends to infinity at a given temperature that corresponds to the state equation in the limit of high pressures

$$\frac{pV}{T} = 9.4 \quad (8.9)$$

where V is the volume per atom in this limit for the solid state, and the parameter of the packing density is equal to $\varphi = 0.64$ in this case.

The indicated values for the packing density φ result from computer modeling of a system of spherical particles. We note that at high pressures the particles do not form a crystal for which this parameter is $\varphi_{cr} = 0.74$. Therefore the phase transition whose parameters are given in Table 8.5 is not the order–disorder phase transition, and the dense state which is named in this table as solid is not the crystal state. Additional information follows from simple modeling by filling a container with balls. Figure 8.3 exhibits the packing density as a result of the filling of a container of volume V by steel balls. There are two ways of performing

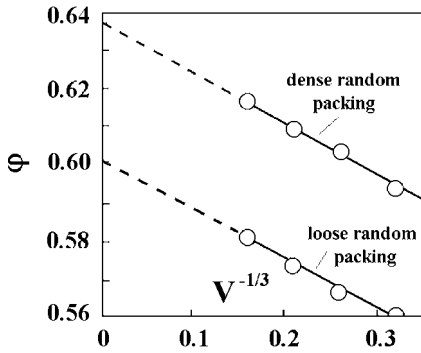


Figure 8.3. The dependence of the packing density on the reciprocal container size (V is the container volume), is this volume is occupied by balls of identical radius for two methods of filling, with shaking and without it (G.D. Scott, *Nature* 188, 908, 1960)

this operation. In the first case balls occupy their initial positions, and the character of such filling is called the *loose random packing* of balls. In the second case the container is shaken, and the balls occupy a more compact configuration. This operation may be improved by the addition of oil in a container, and the distribution of balls is named *dense random packing* or dense random configuration of balls. Evidently, to obtain the values of the packing density for a bulk system it is necessary to take a container volume V very large that allows one to ignore the surface effects. But one can take a container of finite size and extrapolate the packing density to an infinite size of container. This operation is represented in Figure 8.3 and gives for the packing density of a bulk system of balls the values $\varphi = 0.64$ and $\varphi = 0.60$ for the dense random packing and loose random packing states respectively. Of course, the accuracy of this extrapolation is worse than that of computer modeling. Nevertheless, this is added to the results of computer modeling, and it is a principle that the crystal state is not realized in these schemes. Thus from computer modeling, experiments with balls and experiments with dense rare gases, it follows that atomic particles do not form crystals at high pressures when the properties of an atomic system are determined by the repulsion of the atomic particles and the system is maintained by an external pressure.

The packing density φ is connected with the average number q of nearest neighbors, and this connection is given by the relation

$$q = 12 \frac{\varphi}{\varphi_{\text{cr}}} = 16.2\varphi$$

and the number of nearest neighbors for a dense state is $q = 12$ at low pressures $p \ll p_o$, where the system of attracting atoms has the face-centered cubic structure. At high pressures $p \gg p_o$ an average number of nearest neighbors for atoms (the *coordination number*) is approximately 10. This means that a change in the crystalline structure of atoms occurs at $p \sim p_o$. Figure 8.4 gives the melting curve for rare gases in a wide range of pressures, and this curve is constructed on the basis of experimental data. The redistribution of atoms in solid rare gases at $p \sim p_o$ is called the *stacking instability* which results in the formation of elements of hexagonal structure inside the crystal, and at higher pressures the system of atoms consists of clusters of hexagonal structure, i.e. it has a *polycrystalline structure*. Thus, even such a simple system as a pure rare gas has a complex behavior of phase states.

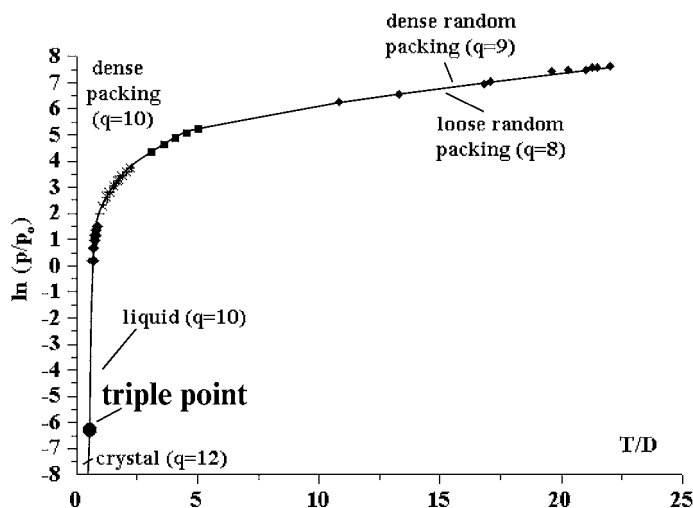


Figure 8.4. The phase diagram for condensed argon in a wide pressure range, signs are experimental data; $p_o = 37$ MPa, $D = 143$ K for argon. Similar diagrams relate to other rare gases.

8.3 Scaling for Molecular Gases

Extending the scaling analysis to molecular systems, we note that the interaction potential of two molecules loses spherical symmetry as it occurs in rare gas atoms. But though the additional parameters of the interaction potential become important, it is necessary to conserve three dimensional parameters as the basis of the scaling analysis. This compels us to use some parameters of molecular interaction averaged over molecule orientations, and this fact decreases the accuracy of the scaling analysis. Because the average over molecule orientations is different for molecules of different structures, it is convenient to divide molecular systems into groups of identical structure and to make the scaling analysis for each group separately. Next, we take the thermodynamic parameters of molecular systems as the dimensional parameters for the scaling analysis instead of the interaction potential parameters, for example, the critical temperature T_{cr} instead of the binding energy D .

As a demonstration, Table 8.6 contains the parameters of dense and condensed systems of tetrafluoride molecules, which are an example of round molecules. The values which are found on the basis of the scaling law are given in parentheses. Although the accuracy of the scaling law in this case is worse than in the case of dense and condensed rare gases, it is estimated to be about 10%, as good as the accuracy of the parameters from which it is obtained. In addition, the ratio of values of identical dimensionality for these molecular systems is close to that for rare gas systems.

One more peculiarity of molecular systems relates to the boiling point, that is defined as the temperature at which the saturated vapor pressure is 1 atm. Hence, the boiling point of different molecular systems corresponds to the identical pressure 1 atm, while the reduced pressures for these systems are different. Therefore the use of the boiling point as a scaling parameter of the system is problematic. In the case of rare gases this scaling is valid because

Table 8.6. The parameters of dense and condensed systems of metal-tetrafluoride and SF_6 molecules.

	MoF ₆	SF ₆	UF ₆	WF ₆	IrF ₆	ReF ₆	Average
T_m , K	291	223	338	276	317	292	
T_{cr} , K	473	319	506	444	(500)	(470)	
ε_{ev} , meV	282	236	394	268	316	293	
ε_{liq} , meV	350	247	442	274	357	364	
ΔH_{fus} , meV	45	52	200	42	87	—	
p_{cr} , MPa	4.75	3.77	4.66	4.34	(8)	(4.6)	
V_{cr} , cm ³ /mol	226	199	250	233	(140)	(240)	
a_W , 10 ⁵ MPa · cm ⁶ /mol ²	(13)	7.86	16.0	13.2	(9)	(14)	
b_W , cm ³ /mol	(100)	88	113	106	(63)	(110)	
ρ_{liq} , g/cm ³	2.6	1.9	4.7	3.4	6.0	3.6	
V_{liq} , cm ³ /mol	81	77	75	88	51	83	
T_{cr}/T_m	1.62	1.43	1.50	1.61	(1.58)	(1.61)	1.54 ± 0.09
$\varepsilon_{ev}/\varepsilon_{liq}$	0.81	0.96	0.89	0.98	0.88	0.80	0.89 ± 0.07
ε_{ev}/T_{cr}	6.9	8.6	9.0	7.0	—	—	8 ± 1
$T_{cr}/(p_{cr}V_{cr})$	3.66	3.53	3.61	3.65	—	—	3.6 ± 0.1
V_{liq}/b_W	—	0.87	0.85	0.83	—	—	0.85 ± 0.02
V_{cr}/b_W	—	2.26	2.21	2.20	—	—	2.22 ± 0.03
V_{cr}/V_{liq}	2.8	2.6	3.3	2.7	—	—	2.8 ± 0.3
$\Delta H_{fus}/\varepsilon_{ev}$	0.16	0.22	0.51	0.16	0.27	—	0.26 ± 0.14

the triple point pressure is significantly less than 1 atm. In the case of molecular gases this relation can be violated. Moreover, in the cases of SF_6 and UF_6 systems the melting point is higher than the boiling point; that is, the boiling relates to the solid phase. Note also the absence of scaling for the fusion energy ΔH_{fus} of these systems, which indicates a different character of melting for these systems.

We consider the systems of tetrafluoride molecules of elements as round molecules, so that these systems must be identical to systems of rare gas atoms. But a comparison of Table 8.6 with Tables 8.3 and 8.4 shows that the identity between these systems is partial. In particular, the ratio $V_{cr}/V_{liq} = 2.70 \pm 0.06$ for rare gas systems corresponds to $V_{cr}/V_{liq} = 2.8 \pm 0.1$ for systems of tetrafluoride molecules, and the combination $T_{cr}/(p_{cr}V_{cr}) = 3.4 \pm 0.1$ for rare gas systems coincides with the value $T_{cr}/(p_{cr}V_{cr}) = 3.6 \pm 0.1$ for systems of tetrafluoride molecules within the limits of accuracy of these values. This means that the expansion of the systems in the course of the transition from the triple point to the critical point is identical for such systems. But the ratio ε_{ev}/T_{cr} is different for inert gases and tetrafluorides, which indicates a different bonding character for these systems. Note that the data used in Table 8.6 have a restricted accuracy, which increases the error in the scaling analysis.

Another example of molecular systems is given in Table 8.7 and relates to halomethanes. Though some of these molecules have a dipole moment, the interaction of dipole momenta of

molecules gives only a small contribution to the energetic parameters of condensed systems, and one can assume that these molecules have a spherical shape. The restoring parameters of molecular systems on the basis of the scaling analysis are given in Table 8.7 in parentheses, and the reduced parameters are close to those of systems of tetrafluoride molecules. Of course, the accuracy for reduced parameters of molecular systems is worse than that for inert gases.

Table 8.7. The parameters of fluorine–chlorine methanes and methane systems.

	CF ₄	CF ₃ Cl	CF ₂ Cl ₂	CFCl ₃	CCl ₄	CH ₄	Average
T_m , K	89.3	(137)	115	(214)	250	90.6	
T_b , K	145	191.7	243.3	296.8	349	111.6	
T_{cr} , K	228	302	385	471.3	556	191	
ε_{liq} , meV	140	163	227	273	348	102	
ε_{ev} , meV	127	(143)	203	(240)	311	85	
p_{cr} , MPa	3.7	3.9	4.1	4.4	4.6	4.60	
p_{liq} , 10 ³ MPa	8	1.6	5.3	3.9	3.9	5.2	
V_{cr} , cm ³ /mol	136	180	217	250	280	99	
V_{liq} , cm ³ /mol	54	—	74	92	97	34	
a_W , 10 ⁵ MPa · cm ⁶ /mol ²	4.0	6.9	10.7	14.7	20.1	2.30	
b_W , cm ³ /mol	63	81	100	111	128	43.0	
T_{cr}/T_m	2.5	—	2.1	—	2.2	2.1	2.2 ± 0.2
T_{cr}/T_b	1.57	1.58	1.58	1.59	1.59	1.71	1.60 ± 0.05
ε_{liq}/T_{cr}	7.1	6.3	6.8	6.7	7.3	6.2	0.67 ± 0.04
$\varepsilon_{ev}/\varepsilon_{liq}$	0.91	—	0.89	—	0.89	0.83	0.88 ± 0.03
V_{cr}/b_W	2.16	2.22	2.17	2.25	2.19	2.30	2.22 ± 0.05
V_{liq}/b_W	0.86	—	0.74	0.83	0.76	0.79	0.80 ± 0.05
$T_{cr}/(p_{cr}V_{cr})$	3.8	3.6	3.6	3.6	3.6	3.5	3.6 ± 0.1

As a result of this analysis, one can formulate the following position for the scaling analysis of molecular systems. When we constructed the scaling laws for rare gases, we based them on two parameters of the pair interaction potential, R_e and D . Because the interaction potential of molecules is anisotropic and depends on the orientation of molecules, a number of these parameters increase, and the validity of the scaling law for molecular systems is problematic. Therefore it is more correct to take some thermodynamic parameters of molecular systems as the basic parameters for the scaling instead of parameters of the pair interaction potential of atoms which are used for rare gas systems. One can find the accuracy of this operation because the number of possible physical parameters of molecular systems is more than three, which is the number of dimensional parameters that are the basis of the dimensionality analysis. Next, we divide molecular systems into groups of identical structures, and analyze the scaling laws inside each separate group. This increases the accuracy of the analysis. In addition, by using the scaling analysis for molecular systems we find the unknown parameters of some systems on the basis of the same parameters of other systems. This is more important than in the case of rare gas systems.

We now consider systems consisting of diatomic molecules which contain identical atoms. These molecules can form gases under certain conditions. We exclude hydrogen from this consideration as a quantum system. Table 8.8 lists the parameters of dense and condensed molecular systems involving diatomic molecules, and the notations for parameters of molecular systems are the same as for dense and condensed rare gases. We note that diatomic molecules form crystal lattices of other structures than the close-packed ones, so that properties of crystals of diatomic molecules differ from those of the close-packed structure. In particular, as follows from Table 8.8, the scaling law for the fusion energy ΔH_{fus} for systems of diatomic molecules is characterized by an accuracy of one order of magnitude worse than that in the case of rare gas systems or for other parameters of Table 8.8. Note that the scaling law for the solid state requires the same crystal structure for the molecular systems under consideration, whereas solids of diatomic molecules of Table 8.8 can have different crystal lattices. Therefore the scaling relations for solid systems of diatomic molecules are characterized by low accuracy, and we use only the parameters of liquid and gaseous molecular systems for this goal, i.e. the parameters of liquids, dense gases and critical parameters.

We note also that the scaling analysis allows us to restore the unknown parameters of molecular systems on the basis of known parameters. The accuracy of this operation for liquid and gaseous systems is about 10%. As for the solid molecular systems, their scaling requires additional analysis and in some cases is not correct to the above accuracy.

8.4 Two-state Approximation for Aggregate States

Usually simple systems of bound atoms have two *aggregate states*, solid and liquid, and we postulate below the existence of two aggregate states for describing the phase transition in a universal way. Analyzing the solid–liquid phase transition in the *two-state approximation*, we join the thermodynamic consideration with the microscopic one. The microscopic consideration is more cumbersome than the thermodynamic one and depends on the nature of bonding in this system. We will be guided by condensed rare gases near the triple point when the solid and liquid states result from an attractive interaction of atoms. Then the external pressure is small in comparison with the typical pressure created by the attraction between atoms, which allows us to neglect mechanical work as a result of the phase transition and other effects induced by the external pressure. This simplifies the problem and exhibits the nature of this phenomenon.

Based on a thermodynamic standpoint, we describe the solid and liquid aggregate states by thermodynamic parameters, and then the solid–liquid phase transition is characterized by the excitation energy ΔE and by a large statistical weight g with respect to the solid state, which determines the entropy $\Delta S = \ln g$ of the liquid state at the phase transition. In this way we return to the thermodynamic description of the system of bound atoms, and the melting point is given by the condition (6.36) if the system is located in a thermostat which maintains a constant temperature in the system. Introducing the partition function of the solid Z_{sol} and liquid Z_{liq} states, we have under these conditions

$$p = \frac{Z_{\text{liq}}}{Z_{\text{sol}}} = \exp\left(\frac{\Delta F}{T}\right) = \exp\left(\Delta S - \frac{\Delta E}{T}\right) \quad (8.10)$$

Table 8.8. The parameters of dense and condensed systems of diatomic molecules.

	F ₂	N ₂	O ₂	Cl ₂	Br ₂	I ₂	Average
T_m , K	53.53	63.29	54.36	172.2	265.9	386.0	
T_b , K	85.03	77.34	90.2	239.1	331.9	457.5	
T_{cr} , K	144.1	126.2	154.6	416.9	588.1	819.1	
ε_{liq} , meV	76	62	78	232	330	468	
ε_{ev} , meV	67.9	57.8	70.6	211	311	432	
ΔH_{fus} , meV	53	7.5	4.6	66	112	158	
ρ_{liq} , g/cm ³	1.52	0.88	1.14	1.51	3.12	(2.7)	
ρ_{sol} , g/cm ³	—	1.03	2.00	2.03	4.05	4.93	
p_{cr} , MPa	5.18	3.39	5.04	7.99	10.3	(12)	
p_{liq} , 10 ³ MPa	3.5	1.1	2.5	9	11	15	
V_{cr} , cm ³ /mol	66	90	73	123	127	155	
a_W , 10 ⁵ MPa · cm ⁶ /mol ²	1.17	1.37	1.38	6.34	9.75	—	
b_W , cm ³ /mol	29.0	38.7	31.9	54.2	59.1	(70)	
T_{cr}/T_m	2.69	2.00	2.84	2.43	2.21	2.12	2.4 ± 0.3
T_{cr}/T_b	1.70	1.63	1.71	1.74	1.77	1.79	1.72 ± 0.06
$T_{cr}/(p_{cr} V_{cr})$	3.5	3.4	3.5	3.5	3.7	—	3.5 ± 0.1
$\varepsilon_{ev}/\varepsilon_{liq}$	0.89	0.93	0.90	0.91	0.94	0.92	0.92 ± 0.02
$\Delta H_{fus}/D$	4.3	0.7	0.35	1.8	2.2	2.2	
ε_{ev}/T_{cr}	5.5	5.3	5.3	5.9	6.1	6.1	5.7 ± 0.4
V_{cr}/b_W	2.28	2.32	2.29	2.27	2.15	—	2.26 ± 0.06

where ΔF , ΔE and ΔS are the changes in the free energy, energy and entropy of the system of n bound atoms as a result of the phase transition, and T is the temperature. By restricting ourselves to a narrow temperature range near the melting point, we neglect the temperature dependence of these values. We assume these parameters of a system of bound atoms to be an additive function of the subsystems constituting this system. Then for a system of n bound atoms we have ($n \gg 1$)

$$\Delta E = n\Delta H_{fus}, \quad \Delta S = n\Delta s_{fus} \quad (8.11)$$

where ΔH_{fus} is the fusion energy per atom, and Δs_{fus} is the entropy jump per atom. The probabilities of the system being found in the solid w_{sol} and liquid w_{liq} states are

$$w_{sol} = \frac{Z_{sol}}{Z} = \frac{1}{1+p}, \quad w_{liq} = \frac{Z_{liq}}{Z} = \frac{p}{1+p},$$

$$p = g \exp\left(-\frac{\Delta E}{T}\right) = \exp\left(-\frac{\Delta F}{T}\right) \quad (8.12)$$

where g is the relative statistical weight of the liquid state $g = \exp \Delta S$. Evidently, the melting point is defined by the relation $w_{\text{liq}}(T_m) = w_{\text{sol}}(T_m)$, or

$$p(T_m) = g \exp \left(-\frac{\Delta E}{T_m} \right) = 1 \quad (8.13)$$

From formulae (8.11) and (8.13) it follows that the melting point does not depend on n

$$T_m = \frac{\Delta H_{\text{fus}}}{\Delta S_{\text{fus}}} \quad (8.14)$$

Of course, the two-state approach is of importance in the case of coexistence of solid and liquid aggregate states that occurs in a system consisting of a finite number of bound atoms in a temperature range near the melting point. *Coexistence of phases* means that for a certain time the system exists in the solid state, and for the rest of the time it is found in the liquid state. In the limit of an infinite number of atoms, the phase transition proceeds by a jump on the temperature scale, and the coexistence of phases is absent for a bulk system.

Excitation of the system under consideration consists of two parts, so that the first relates to vibrations of atoms and the other is connected with the excitation of atomic configurations. The vibrational energy varies weakly during the melting, so that, when analyzing this phenomenon, we are restricted only by the configuration excitation which is responsible for the solid–liquid phase transition. The configuration excitation consists in the formation of *vacancies* or *voids* inside the system of bound atoms, which leads to a variation the number of bonds between atoms – nearest neighbors.

Let us introduce the total energies of atoms $E'_{\text{sol}}(T)$ and $E'_{\text{liq}}(T)$ for the solid and liquid aggregate states of a cluster. Considering a bulk system of atoms as a large cluster whose surface effects are negligible, we assume thermodynamic equilibrium for the motion of cluster atoms that is characterized by a cluster temperature T . In particular, in the case when the thermal energy of a cluster atom significantly exceeds the Debye energy, these values are determined by the Dulong–Petit law (3.38) $E'_{\text{sol}}(T) = E'_{\text{liq}}(T) = 3nT$, where n is the number of cluster atoms. Taking into account the dynamic equilibrium, so that the cluster is found in the solid state during some time intervals and in the liquid state at other times, one can use an appropriately time-weighted average to compute the cluster's mean internal energy. Then the internal energy of the system under consideration is equal to

$$E(T) = E'_{\text{sol}}(T)w_{\text{sol}} + [E'_{\text{liq}}(T) + \Delta E] w_{\text{liq}} = E'_{\text{sol}} + \Delta E \frac{p}{1+p} \quad (8.15)$$

where we take $E'_{\text{sol}} = E'_{\text{liq}}$, i.e. the energy of atomic motion is identical for the solid and liquid states. From this we have for the heat capacity of the system of bound atoms

$$C(T) = \frac{dE}{dT} = C_o(T) + \frac{\Delta E}{(1+p)^2} \frac{dp}{dT} = C_o(T) + \frac{p}{(1+p)^2} \left(\Delta S_m^2 + \Delta S_m \frac{d\Delta S}{dT} \right) \quad (8.16)$$

Here ΔS_m is the entropy jump at the melting point, and the heat capacity $C_o(T) = dE'_{\text{sol}}/dT = dE'_{\text{liq}}/dT$ is determined by atomic oscillations and is characterized by a smooth

temperature dependence, while the temperature dependence of the second term of formula (8.16) due to *configuration excitation* of the cluster is strong. We used above the formula (8.12) for the probability of a cluster being in the liquid cluster state. The heat capacity has a maximum at the melting point T_m , and near this maximum we have, under the assumption that the entropy difference $\Delta S_m = \Delta E/T_m$ does not depend on temperature,

$$C_{\max} = C_o + C_{\max} \exp \left[-\alpha (T - T_m)^2 \right] \quad (8.17a)$$

where

$$C_{\max} = \frac{\Delta E^2}{4T_m^2} = \left(\frac{\Delta S_m}{2} \right)^2, \quad \alpha = \frac{\Delta E^2}{4T_m^4} = \left(\frac{\Delta S_m}{2T_m} \right)^2 \quad (8.17b)$$

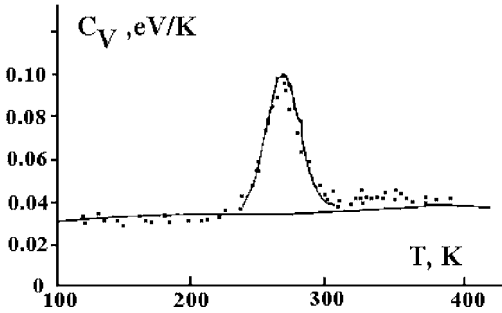


Figure 8.5. The heat capacity of sodium clusters consisting of 139 atoms as a temperature function (M. Schmidt et al. *Phys. Rev. Lett.* 79, 99, 1997).

If we account for a linear temperature dependence for the entropy difference of the liquid and solid state, so that

$$\frac{d\Delta S}{dT} = \frac{\Delta S_m - \Delta S_o}{T_m} \quad (8.18)$$

we obtain from formula (8.16)

$$C(T) = C_o(T) + \Delta S_m (2\Delta S_m - \Delta S_o) \frac{p}{(1+p)^2}, \quad (8.19)$$

$$C_{\max} = \frac{\Delta S_m}{4} (2\Delta S_m - \Delta S_o)$$

where ΔS_m and ΔS_o are the entropy differences at the melting point and zero temperature correspondingly, and $\Delta S_m > \Delta S_o$. These relations are valid under the condition $\Delta E \gg T_m$, or $\Delta S_m \gg 1$. The resonance in the heat capacity refers to a narrow range of temperatures $\Delta T \sim \alpha^{-1/2} \sim T_m/\Delta S_m \ll T_m$. Since the value C_o is proportional to n , the number of cluster atoms, and the fusion energy ΔE is also proportional to n , the influence of the phase transition on the heat capacity grows roughly as $\sim n$. For a bulk system of bound atoms this contribution at its maximum tends to infinity. Indeed, the ratio of the second term of formula (8.17a) to the first one is $\sim n$, and the resonance width is $\sim 1/n$. Hence the temperature dependence of the heat capacity of a large cluster allows us to determine its melting point with high accuracy. As a demonstration, Figure 8.5 contains the temperature dependence for the heat capacity of sodium clusters near the melting point.

8.5 Solid–Solid Cluster Phase Transition

We now consider the phase transition between two solid states of a cluster. This takes place in the case of competition of two structures if at a given number of cluster atoms the cluster ground state refers to a completed structure, and the lowest state of this structure is characterized by its high statistical weight. As an example, one can consider a large cluster of icosahedral structure (see Chapter 3) with a pairwise interaction of atoms with completed shells. The statistical weight of the ground state is of order of one, while a configurationally excited state of the fcc structure has a large statistical weight g . If the excitation energy of the lowest state of the fcc structure is not large, this cluster has an icosahedral structure at zero temperature and changes the structure at low temperatures. We consider this transition on the basis of a model where the transition temperature is below the melting point, and only the ground states of both structures are of importance for the cluster parameters. Then the partition functions for the first structure Z_1 and for the second structure Z_2 have the form

$$Z_1 = 1, \quad Z_2 = g \exp\left(-\frac{\Delta\varepsilon}{T}\right)$$

where g is the ratio of statistical weights, T is the temperature, and $\Delta\varepsilon$ is the energy difference for the ground states of these two structures.

We use an analogy with the solid–liquid transition, so that the probability of the cluster having a certain structure is given by formulae (8.12)

$$w_1 = \frac{1}{1+p}, \quad w_2 = \frac{p}{1+p}, \quad p = g \exp\left(-\frac{\Delta\varepsilon}{T}\right)$$

and the phase transition proceeds at the temperature T_{tr} in accordance with formula (8.13)

$$p(T_{tr}) = g \exp\left(-\frac{\Delta\varepsilon}{T_{tr}}\right) = 1$$

Correspondingly, the heat capacity due to this transition has a resonance form, and in accordance with formula (8.17b) the heat capacity due to configuration excitation is given by

$$C = \left(\frac{\ln g}{2}\right)^2 \exp\left[-\frac{\ln^2 g}{4T_{tr}^2}(T - T_{tr})^2\right] = \frac{\Delta S^2}{4} \exp\left[-\frac{\Delta S^2}{4} \frac{(T - T_{tr})^2}{T_{tr}^2}\right] \quad (8.20)$$

where $\Delta S = n\Delta s \gg 1$ for large clusters $n \gg 1$. As we have seen, a small parameter which determines the narrowness of the transition range is

$$\frac{1}{\Delta S} = \frac{1}{\ln g} \ll 1$$

In spite of the analogy between the nature of the solid–solid and solid–liquid phase transitions in clusters, the entropy change per atom is small compared with that for the solid–solid phase transition and is of the order of one for the solid–liquid transition, which is connected with the nature of these phase transitions. Therefore the entropy change for the solid–solid phase transition is small compared with the cluster entropy due to oscillations of atoms, and the solid–solid phase transition makes only a small contribution to the parameters of solid clusters. For this reason, solid–solid phase transitions in clusters are not essential for solid clusters, in contrast to solid–liquid phase transitions.

8.6 Configuration Excitation of a Large Cluster

Although the phase transition between two solid states has all the peculiarities of *phase transitions of the first order*, it makes only a small contribution to various cluster parameters. The reason lies in the small change of entropy at the phase transition, which results in a small number of atoms taking part in the phase transition. Below we demonstrate the weakness of cluster configuration excitation in an example of a large cluster with a complete atom shell (or an almost complete outermost shell). We assume that the outermost complete cluster shell consists of n atoms, and the next shell is free. There are k positions for atoms on the cluster surface, and the energy of transition of an individual atom from the completed shell to the cluster surface is ε_o . The partition function (2.23) for the configuration state with v atoms located on the cluster surface for $v \ll n, k$ is equal to

$$Z_v = C_n^v C_k^v \exp\left(-\frac{v\varepsilon_o}{T}\right)$$

Since v is relatively small, atoms on the cluster surface do not border each other.

The optimal number of atoms on the cluster surface corresponds to the maximum of the partition function and is

$$v_o = \sqrt{nk} \exp\left(-\frac{\varepsilon_o}{2T}\right) \quad (8.21)$$

The exponent is small for the solid cluster state. For example, for a Lennard–Jones cluster consisting of 923 atoms at the melting point $T_m = 0.44D$, taking $\varepsilon_o = 3D$, we obtain $\exp[-\varepsilon_o/(2T_m)] = 0.03$. From this it follows that the entropy of the optimal configuration excitation on the basis of formula (2.26)

$$\Delta S = \frac{\partial \ln Z_o}{\partial \ln T} + \ln Z_o = \frac{\varepsilon_o v_o}{T} = \frac{\varepsilon_o}{T} \sqrt{nk} \exp\left(-\frac{\varepsilon_o}{2T}\right) \quad (8.22)$$

because the cluster free energy is zero at optimal excitation. Since $\varepsilon_o \gg T$, the entropy per atom for this transition is small compared with the number of cluster atoms. In the case of the solid–liquid phase transition the specific entropy change is comparable to the number of cluster atoms.

One more peculiarity of this configuration excitation is that only one maximum occurs for the partition function of its logarithm, and the free energy $F = -T \ln Z_v$ has one minimum. This means the existence of one aggregate state of this system of bound atoms. We introduce the statistical weight g_v of an excited atom and the excitation energy $\varepsilon_v = \varepsilon_o - \Delta\varepsilon_v$ of atomic transition to the cluster surface, and then the partition function logarithm takes the form

$$\ln Z_v = v \left[2 + 2 \ln \frac{v_o}{v} + \ln X(v) \right], \quad X(v) = g_v \exp\left(\frac{\Delta\varepsilon_v}{T}\right) \quad (8.23)$$

where v_o is given by formula (8.21), and taking $g_v = 1$ and $\Delta\varepsilon_v = 0$, we obtain the above formula for the partition function with one maximum at $v_o \ll n, k$. Evidently, the function $X(v)$ increases by several orders of magnitude at $v \sim n, k \gg v_o$. One can see that if we take $X(v)$ to be a stepwise function in a narrow range of v , so that $\ln Z_v$ decreases at large v , this value accepts the second maximum and the second aggregate state is realized (as occurs in Figure 8.6). Thus, the real behavior of parameters of an elementary configuration excitation can lead to the existence of two aggregate states of a system of bound atoms.

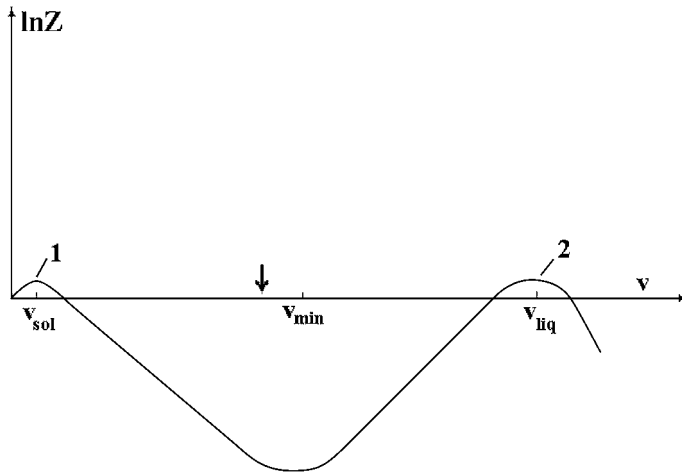


Figure 8.6. The logarithm of the partition function for a system of bound atoms with a pair interaction versus a number of voids. The group of states 1 corresponds to the solid state, the group of states 2 relates to the liquid state, the arrow indicates the beginning of void interaction.

8.7 Lattice Model for Phase Transition

It is convenient to analyze the solid and liquid states within the framework of the *lattice model*. This model places atoms at the sites of a crystal lattice, so that the number of sites exceeds the number of atoms. In addition, only the nearest neighbors of this system form bonds, so that non-nearest neighbors do not interact. A certain distribution of atoms on sites corresponds to a certain number of bonds, and hence to some binding energy. Using this model, one can understand the nature of the phase transition.

Within the framework of this model we divide states of this system into two parts, the order and disorder aggregate states (see Figure 8.7). The transition in the disordered state requires consumption of energy, and we use the average excitation energy of the disordered state. But this state is characterized by a large statistical weight g or entropy S ($g = \ln S$), which makes the transition to the disordered state profitable at some temperatures. Note that since the *order–disorder phase transition* is accompanied by a change of the system's internal energy, it is a phase transition of the first type, and various physical parameters of the system under consideration have a jump as a result of this phase transition.

We consider a version of the lattice model for a system consisting of n bound atoms, if n atoms and v vacancies are located at sites of the crystal lattice. There are two types of space distribution of atoms and vacancies in this system (see Figure 8.7) – the *ordered state*, where vacancies are separated from atoms, and the *disordered state*, where these species are mixed. The ordered state corresponds to the solid state, and the disordered state relates to the liquid state of this system. The mean energy and free energy of the disordered state are given by formulae (8.27) and (8.28) if these parameters are zero for the ordered state. Next, the phase

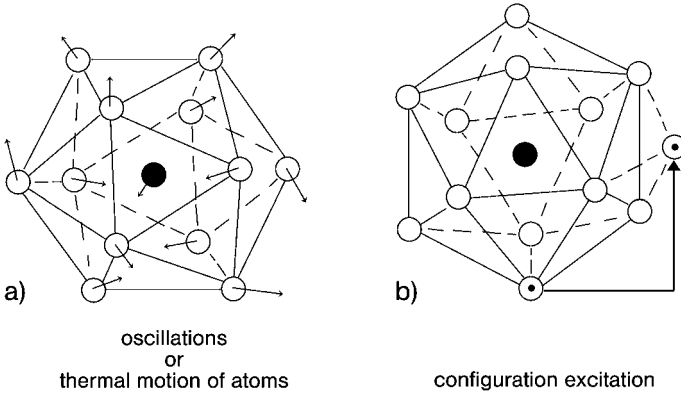


Figure 8.7. Structures of particles of a lattice gas when particles of two types are located in sites of the hexagonal lattice (a) the order state of atoms at zero temperature; (b) a random distribution of atoms at high temperatures.

transition proceeds in a stepwise manner when the free energies for the distributions become identical, i.e. $F_{\text{dis}} = 0$.

We will not exploit this model further because it is approximate for this phase transition, and more detailed use of the model leads to contradictions. Nevertheless, this simple rough model allows one to understand the nature of this phase transition.

8.8 Lattice Model for Liquid State of Bulk Rare Gases

Lacking from the lattice model for describing a pure system of bound atoms is the lattice size which is a model parameter that determines parameters of the disordered state. Now we base the lattice model on that for liquid rare gases and find this parameter from measurements. We introduce as a parameter of the disorder or liquid state of bulk rare gases an average number q of nearest neighbors for internal atoms, and this value is 12 for the solid state. A decrease in the number of nearest neighbors as a result of the solid–liquid phase transition leads to a decrease in the system density from ρ_{sol} for the solid state to ρ_{liq} for the liquid state, which gives for the effective number of nearest neighbors q of the liquid state

$$q = 24 - 12 \frac{\rho_{\text{sol}}}{\rho_{\text{liq}}} \quad (8.24)$$

Next, as a result of this phase transition, the binding energy per atom varies from $\varepsilon_o = \varepsilon_{\text{sub}}$ for the solid state to $q'\varepsilon_o/2$ for the liquid state, where q' is the effective number of nearest neighbors in this case. If the specific fusion energy ΔH_{fus} of this phase transition is determined by variation of the number of nearest neighbors, it is equal to

$$\Delta H_{\text{fus}} = (1 - q'/12)\varepsilon_o$$

and from this we find the effective number of nearest neighbors for the liquid state

$$q' = 12 \left(1 - \frac{\Delta H_{\text{fus}}}{\varepsilon_o} \right) \quad (8.25)$$

Let us introduce the parameter

$$\xi = \frac{\varepsilon_o}{\Delta H_{\text{fus}}} \cdot \frac{\rho_{\text{sol}} - \rho_{\text{liq}}}{\rho_{\text{liq}}} = \frac{\varepsilon_o}{\Delta H_{\text{fus}}} \frac{\Delta V}{V_{\text{sol}}} \quad (8.26)$$

where ΔV is the specific volume jump of melting, and V_{sol} is the volume per atom for the solid state. If the above assumptions are fulfilled and $q = q'$, this parameter must be one. Table 8.9

Table 8.9. Parameters of the structure of liquid rare gases.

	Ne	Ar	Kr	Xe	Average
q	10.10	10.27	10.11	10.19	10.17 ± 0.08
q'	10.07	10.15	10.14	10.19	10.15 ± 0.04
ξ	0.96	0.93	1.02	0.96	0.96 ± 0.04

contains the numbers of nearest neighbors for the liquid state of condensed rare gases q , q' and values of the parameter ξ , which is close to unity. This confirms the used model of the liquid state of rare gases to an accuracy of several per cent. In particular, taking $\xi = 1$, we obtain the connection between the volume per atom V and that for the solid state V_{sol} according to formula (8.24)

$$\frac{V - V_{\text{sol}}}{V_{\text{sol}}} = \frac{\Delta H_{\text{fus}}}{\varepsilon_o} \quad (8.27)$$

8.9 Chemical Equilibria and Phase Transitions

The phase order–disorder transition in a bulk system is a phase transition of the first type, where the internal energy of a bulk system is changed in a stepwise way if the temperature and pressure are constants during this transition. Correspondingly, various parameters of a bulk system as a temperature function have jumps at the phase transition. In contrast to this, the *chemical transformation*, i.e. the transition between two limiting chemical states of a substance, proceeds continuously in some temperature range at constant pressure. The principal difference between the phase transition and chemical transformation is lost for systems consisting of a finite number of atoms – clusters – when the coexistence of phases occurs over some temperature range. This transforms the transition temperature for a bulk system into a temperature range for clusters. Hence from this standpoint the phase transition for clusters is similar to chemical transformations. Nevertheless, there is a major difference between phase transitions and chemical transformations, and we analyze it below.

As an example of chemical transformations, we consider below the ionization equilibrium in gases (see Chapter 5). Using the analogy with the order–disorder phase transition, we

consider two aggregate states of the partially ionized gas: neutral and ionized. Taking a test electron, we introduce the probabilities w_e and w_a that this electron is found in free or bound states, and $w_e + w_a = 1$. The relation between these probabilities is given by the Saha formula (5.5a)

$$\frac{w_e^2}{w_a} = g \exp\left(-\frac{J}{T_e}\right) \quad (8.28)$$

Here J is the atom ionization potential, T_e is the electron temperature, and g is the statistical weight of the continuous spectrum state; the value of g follows from the Saha formula (5.2)

$$g = \frac{1}{N} \frac{g_e g_e}{g_a} \left(\frac{m_e T_e}{2\pi\hbar^2} \right)^{3/2} \quad (8.29)$$

where g_e and g_a are the statistical weights of the electron and atom with respect to their electron states, and N is the total number density of free and bound electrons. Since for an ideal plasma $g \gg 1$, we have for the entropy jump as a result of this chemical transformation $\Delta S = \ln g \gg 1$. This provides a narrow temperature range ΔT for the transition from the ionized state to the neutral state, which is

$$\Delta T \sim \frac{T_*}{\ln g} \quad (8.30)$$

where T_* is the temperature of the ionization transition, defined as $w_e(T_*) = w_a(T_*) = 1/2$.

Let us construct the partial function for the ionized and neutral states. Taking the total number of nuclei in the system to be n and the number of ionized atoms to be m , we determine the probability of this event by the Poisson formula

$$W_{nm} = C_n^m w_e^m w_a^{n-m} = C_n^m w_e^m (1 - w_e)^{n-m}$$

The partition function Z_{nm} of a system with a given number of free and bound electrons is proportional to the value W_{nm} . Note that the formation of m free electrons in this system corresponds to the excitation energy $m(J + 3T_e/2) \approx mJ$. In the case of a large number of free and bound electrons in the system $m \gg 1$, $n \gg 1$, the partition function Z_{nm} as a function of m has a sharp maximum; near the maximum $m = m_o$ it has the form

$$Z_{nm} = Z_o \exp\left[-\alpha (m - m_o)^2\right] \quad (8.31a)$$

and according to the above relations we have

$$m_o = nw_e; \quad \alpha = \frac{1}{2m_o} \cdot \frac{n}{n - m_o} \quad (8.31b)$$

As we have seen, the partition function has a narrow maximum over a range of broken bonds $\Delta m \sim \sqrt{n}$ if $m_o \sim n$, and the relative maximum width $\Delta m/m_o$ tends to zero as $\sim 1/\sqrt{n}$, when the total number of free and bound electrons tends to infinity.

Comparing the partial function of the disordered aggregate state in the case of the order-disorder phase transition with the partial function of the ionized state in the case of ionization

equilibrium, one can see the analogy in their structure. Moreover, in both cases the transition energy is proportional to the number of transferring particles. Above we deal with the total partition function of the disordered aggregate state, which is summed over the number of bonds between particles. Evidently, this partition function is a sharp function of the number of bonds, similar to the partition function of an ionized gas with respect to the number of free electrons. Hence we have an analogy between the disorder aggregate state of a system of interacting atoms and the partition function of an ionized gas, if we set in accordance the number of broken bonds in the first case to the number of ionized atoms in the second case. But in the case of the order–disorder phase transition, there is also the ordered aggregate state, which is characterized by a local maximum at a relatively small number of broken bonds. Thus, in the case of the phase transition, the partition function as a function of excitation energy has two maxima (see Figure 8.6), while in the case of ionized equilibrium only one maximum of the partial function exists. Hence in the case of chemical equilibrium the transition between limiting chemical states proceeds in a continuous way as the temperature varies and the partition function maximum drifts. In the case of the order–disorder phase transition, the transition takes place between two maxima of the partial function and proceeds in a stepwise way as the temperature varies. Thus the phase transitions and chemical transformations have a different nature.

9 Mixtures and Solutions

9.1 Ideal Mixtures

Below we analyze the peculiarities of multicomponent systems from the thermodynamic standpoint. We start from a mixture of ideal gases or several systems consisting of weakly interacting quasiparticles. This mixture is an ideal one if the behavior of each component is the same as in the absence of the other components. Because we neglect the interaction between components, the thermodynamic potentials and the entropy of an ideal mixture are the sum of these values for components of the mixture.

First we connect the free enthalpy of an ideal mixture with the chemical potentials of its components. The free enthalpy of this system is a function of the pressure p and temperature T of the mixture and the number of particles n_i for each component. In addition, the free enthalpy is an additive function, so that an increase in the particle number and volume of the system in λ times leads to the same increase of the free enthalpy, i.e.

$$G(p, T, \lambda n_1, \lambda n_2, \dots, \lambda n_k) = \lambda G(p, T, n_1, n_2, \dots, n_k)$$

From this it follows that

$$G(p, T, n_1, n_2, \dots, n_k) = \sum_i n_i \left(\frac{\partial G}{\partial n_i} \right)_{p, T, n_1, n_2, \dots, n_k} \quad (9.1)$$

Since the chemical potential of each component is

$$\mu_i(p, T) = \left(\frac{\partial G}{\partial n_i} \right)_{p, T, n_1, n_2, \dots, n_k}$$

one can rewrite equation (9.1) for the free enthalpy of an ideal mixture in the form

$$G(p, T, n_1, n_2, \dots, n_k) = \sum_i n_i \mu_i \quad (9.2)$$

From formula (9.2) it follows that

$$dG = \sum_i (n_i d\mu_i + \mu_i dn_i)$$

In addition, the general expression for the free enthalpy has the form

$$dG = \frac{\partial G}{\partial p} dp + \frac{\partial G}{\partial T} dT + \sum_i \frac{\partial G}{\partial n_i} dn_i = -S dT + V dp + \sum_i \mu_i dn_i$$

Comparing these equations, we get

$$\sum_i n_i d\mu_i = -S dT + V dp$$

In particular, if the pressure and temperature are constants, this equation takes the form of the *Gibbs–Duhem relation*

$$\sum_i n_i d\mu_i = 0, \quad dT = 0, \quad dp = 0 \quad (9.3)$$

Let us consider a two-component ideal mixture. Then the relation (9.3) allows one to express the chemical potential of one component through the chemical potential of the other component. Introducing the concentration of each component as $c_1 = n_1/(n_1 + n_2)$ and $c_2 = n_2/(n_1 + n_2)$, where n_1 and n_2 are the numbers of particles of each component, we rewrite the Gibbs–Duhem relation (9.3) in the form

$$c_1 d\mu_1 + c_2 d\mu_2 = 0$$

Because $c_1 + c_2 = 1$, the solution of this equation has the form

$$\mu_2(c) = \mu_2(1) - \int_0^c \frac{c'}{1-c'} \frac{\partial \mu_1(c')}{\partial c'} dc' \quad (9.4)$$

Here $\mu_2(1)$ is the chemical potential of the second component in the absence of the first one. Formula (9.4) is called the *Margules equation*.

9.2 Mixing of Gases

According to formulae (6.20), the entropy of a gas can be represented in the form

$$S = \sum_i n_i \left(s_i^{(o)} - \ln c_i \right) \quad (9.5)$$

where $s_i^{(o)} = \ln n$ is the entropy per particle of the considered component in the absence of others. Correspondingly, the chemical potential of a given component of the mixture is given by the expression

$$\mu_i(p, T, n_1, n_2, \dots, n_k) = \mu_i(p, T) + T \ln c_i \quad (9.6)$$

This formula follows from formula (6.37), taking into account its dependence on the volume.

According to formula (9.5), the mixing of gases leads to an increase in the total entropy. Indeed, let us consider a mixture of two gases, if at the beginning the first gaseous component occupies a volume V_1 and the second gas is located in a volume V_2 such that the pressure and temperature of gases are identical ($n_1/V_1 = n_2/V_2$). Initially these volume are separated by a partition, and the total entropy of the gases is

$$S_o = n_1 \ln V_1 + n_2 \ln V_2 + \text{const}$$

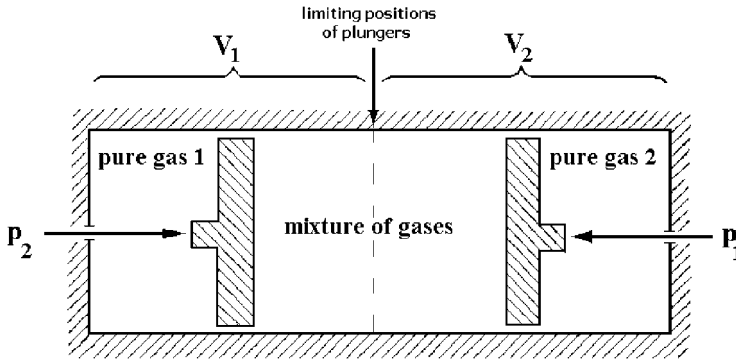


Figure 9.1. Scheme of the van't Hoff vessel. Gas 1 can penetrate through the partition 1, and the partition 2 is transparent for gas 2 only. When plungers move towards each other, gases are separated.

After breaking the partition between gases, the gases are mixed, and their total entropy increases by the value

$$\Delta S = -n_1 \ln \frac{V_1}{V} - n_2 \ln \frac{V_2}{V} = n_1 \ln \frac{1}{c_1} + n_2 \ln \frac{1}{c_2} \quad (9.7)$$

where the total volume $V = V_1 + V_2$. The opposite process, separation of a mixture of two gases, proceeds in a van't Hoff vessel (Figure 9.1). Initially the mixture is located in a vessel, so that the first gas can penetrate through a porous partition 1 and the second gas can penetrate through the porous partition 2. In the course of the motion of the plungers the pressure remains constant in all three regions. At the end of the process, the mixture is separated, so that the first gas is in volume 1 and the second is found in volume 2. The following mechanical work is consumed in the separation of gases

$$A = - \int_V^{V_1} p dV'_1 - \int_V^{V_2} p dV'_2 = -n_1 \ln \frac{V_1}{V} - n_2 \ln \frac{V_2}{V} = T \Delta S \quad (9.8)$$

Above we use the equations of state for ideal gases $pV'_1 = n_1 T$ and $pV'_2 = n_2 T$, where V'_1 and V'_2 are the current volumes of gases during the process, and we take into account that the pressure is constant in the course of the process. One can see that the mechanical work is equal to the heat of mixing of the two gases.

Let us consider the *Gibbs paradox* in connection with the mixing of two gases which are isotopes of the same element. After mixing these gases, the total entropy will increase by the value ΔS , which is given by formula (9.7). Because of the relation (9.8), the temperature and internal energy of the gases do not vary as a result of the mixing process. One can see that the entropy variation is different depending on the isotope masses. If the masses of the isotopes are different, the entropy variation is given by formula (9.7). For identical masses of isotopes, when the atoms of both isotopes are identical, the entropy variation is zero. Hence, if we vary the masses of the isotopes, the difference of the mixture's entropy before and after

mixing varies by a jump from ΔS to zero when the isotope masses are equal. This is the Gibbs paradox. The explanation of the paradox consists in the connection between entropy and information (see Chapter 12). As we take atoms to be identical, the information about the system varies by a jump. Correspondingly, the entropy of this system also varies by the same jump.

9.3 The Gibbs Rule for Phases

We now determine the number of independent thermodynamic parameters of a mixture which contains several components in different phases. First we consider a one-component system which can be found in three phases ($r = 3$): gaseous, liquid and solid. The thermodynamic parameters of this system depend on the temperature and pressure. The conditions for equilibrium of the three phases require equality of the chemical potentials of the three phases, giving two equations for the temperature and pressure. Hence we have a certain temperature and pressure at which the three phases coexist. These parameters refer to the *triple point*.

In the general case we introduce the number of *thermodynamic degrees of freedom* f , i.e. the number of variables which can be varied under the equilibrium. In the above case of a one-component system which can be found in three phases, the number of thermodynamic degrees of freedom $f = 0$. In the general case we consider a mixture consisting of p components, and each component can be found in r phases. Let us find the number of thermodynamic degrees of freedom f in this case. We have $p(r - 1)$ equations from the equilibrium conditions which require equality of the chemical potentials for each phase of a given component. Thermodynamic parameters depend on the temperature, pressure and $p - 1$ concentrations of components for each phase, i.e. they depend on $2 + r(p - 1)$ variables. Hence the number of thermodynamic degrees of freedom equals

$$f = 2 + r(p - 1) - p(r - 1) = 2 + p - r \quad (9.9)$$

This relation is called the *Gibbs rule* of phases. This gives the number of independent variables which can describe the equilibrium system under consideration. This rule is useful for the analysis of an equilibrium which includes the different phases of a many-component system. In particular, in the case of a two-component system ($p = 2$) and three phases ($r = 3$) for each component, the number of thermodynamic degrees of freedom is $f = 1$.

9.4 Dilute Solutions

Dilute solutions are characterized by a small concentration of a solute that is dissolved in a solvent. The solute concentration is the ratio of the number of solute molecules to the total number of molecules of the solution. Because solute molecules do not interact with each other in dilute solutions, these solutions are similar to ideal mixtures of gases. In particular, the variation of the solution volume in the course of an increase of the number of solute molecules is proportional to the number of solute molecules. A solute molecule interacts with the surrounding solvent molecules, and this interaction has a short-range character, i.e. a test solute molecule interacts with the nearest solvent molecules only. Hence, electrolytes, where

molecules are ionized, do not relate to dilute solutions even in the limit of low concentrations of solute. On the other hand, one can employ a small solute concentration as a small parameter for the analysis of properties of dilute solutions.

Thus, restricted by the interaction of dissolved molecules with nearest solvent molecules, one can expand the free enthalpy of the solute concentration. Below we consider the case of a two-component dilute solution and represent its free enthalpy in the form

$$G(p, T, c) = G_o(p, T) + G_{\text{int}} = G_o(p, T) + a_2 n_2 + a_{12} \frac{n_1 n_2}{n} \quad (9.10)$$

where $G_o(p, T)$ is the free enthalpy of the solution in the approximation of an ideal mixture, G_{int} accounts for interaction in the solution, n_1 and n_2 are the numbers of solvent and solute molecules respectively, and $n = n_1 + n_2$ is the total number of solution molecules. In the limit $c \rightarrow 0$ interaction between the solvent and solute disappears, so that $G_{\text{int}} \rightarrow 0$. Above we take into account the fact that the free enthalpy is a linear function of the number of molecules.

Let us consider the limit of small solute concentrations $c = n_2/n \ll 1$. Then one can connect the chemical potential of the solvent μ_1 and the solute μ_2 with those of an ideal mixture, which are given by formula (9.6). Accounting for the interaction between components, the solvent chemical potential is determined with an accuracy up to $\sim c^2$, and the chemical potential of the solute is evaluated with an accuracy up to $\sim c$. We have

$$\mu_1 = \mu_1^{(o)} + a_{12}(1-c)^2 + T \ln(1-c) = \mu_1^{(o)} - Tc; \quad \mu_2 = \mu_2^{(o)} + a_2 + a_{12} + T \ln c \quad (9.11)$$

Here $\mu_1^{(o)}$ and $\mu_2^{(o)}$ are the chemical potentials for the pure solvent and free solute, and the parameters a_2 and a_{12} account for the interaction between solute and solvent molecules in the solution. From this it follows for the chemical potential of a solute in dilute solutions

$$\mu_1 = \mu_1^{(o)} - Tc, \quad \mu_2 = \psi_2 + T \ln c \quad (9.12)$$

where $\mu_1^{(o)}$ is the chemical potential of the pure solvent. This formula is analogous to formula (9.6) which gives the chemical potential of an ideal mixture, but here the interaction of a solute molecule with solvent molecules is taken into account.

Let us consider the equilibrium between a dissolved and a free gas and determine the *solubility* of a gas, i.e. the concentration of gas molecules in a solution at a given gas pressure over the solution surface. Taking the gas pressure near the liquid surface of a solvent to be p and the concentration of the dissolved gas to be c , we obtain from the equilibrium condition (6.36) for dissolved and free gases

$$\mu_2 \equiv \psi_2 - T \ln c = \mu_{\text{gas}}(T) \quad (9.13)$$

where we use formula (9.12) for the dissolved gas and μ_{gas} is the chemical potential of the free gas, which is determined according to formula (6.37)

$$\mu_{\text{gas}} = \text{const} - T \ln p$$

where p is the gas pressure. From this we obtain the proportionality between the concentration of a dissolved gas and the pressure of a free gas over the solution surface

$$c \sim p \quad (9.14)$$

This relation is known as the *Henri law* and is valid for dilute solutions.

A general expression for the concentration of a dissolved component, which follows from the equilibrium condition (9.13), has the form

$$c = \exp\left(\frac{\mu_{\text{gas}} - \psi_2}{T}\right)$$

where the chemical potential of solute free molecules μ_{gas} depends on the temperature and gas pressure, while the value ψ_2 depends only on the temperature. Let us compare the solubility of a component for different solvents under identical conditions for the gaseous phase of a solute. We have from this formula

$$\frac{c'}{c} = \exp\left(\frac{\psi_2 - \psi_2'}{T}\right)$$

This means that the ratio of the solubilities of a solute in two solvents does not depend on the solute pressure over solutions. This relation is called the *Nernst law of equidistribution*.

Let us consider the equilibrium between the pure solvent and its dilute solution which are separated by a semi-permeable membrane. The solvent can penetrate this membrane, whereas the solute remains only in the solution. In this case a pressure difference is established between two sides of the membrane, and this difference is called the *osmotic pressure* p_{osm} . It can be found from the equilibrium condition for the solvent for two sides of the membrane

$$\mu_1^{(o)}(p, T) = \mu_1^{(o)}(p + p_{\text{osm}}, T) - cT$$

This gives for the osmotic pressure

$$p_{\text{osm}} = \frac{cT}{\left(\frac{\partial \mu_1^{(o)}}{\partial p}\right)_T} = \frac{cT}{v} \quad (9.15)$$

where v is the volume per molecule of the solvent. This formula is named the *van't Hoff formula* and is analogous to the equation (7.7) of state of an ideal gas.

9.5 Phase Transitions in Dilute Solutions

Below we determine the saturated vapor pressure of a solvent depending on the concentration of a solute. The phase equilibrium for the liquid and gaseous solvents is determined by the relation (6.36)

$$\mu_{\text{liq}}(p, T) = \mu_{\text{gas}}(p, T)$$

where $\mu_{\text{liq}}(p, T)$ and $\mu_{\text{gas}}(p, T)$ are the chemical potentials of the liquid and gaseous solvents. Let us expand the chemical potential for the liquid solvent near the equilibrium for the pure liquid and gaseous solvent

$$\begin{aligned} \mu_{\text{liq}}(p, T, c) &= \mu_{\text{liq}}(p_{\text{sat}}, T_o, 0) + \frac{\partial \mu_{\text{liq}}}{\partial p}(p - p_{\text{sat}}) + \frac{\partial \mu_{\text{liq}}}{\partial T}(T - T_o) - Tc_{\text{liq}} \\ &= \mu_{\text{liq}}(p_{\text{sat}}, T_o) + v_{\text{liq}}\Delta p - s_{\text{liq}}\Delta T - Tc_{\text{liq}} \end{aligned}$$

where v_{liq} and s_{liq} are the volume and entropy per solute molecule, c_{liq} is the solute concentration, $\Delta p = p - p_{\text{sat}}$ and $\Delta T = T - T_o$. Using the same expansion for the gaseous phase, we have the following equation for the equilibrium of the liquid and gaseous phases

$$-\Delta s \Delta T + \Delta v \Delta p = \Delta c \Delta T$$

where $\Delta s = s_{\text{liq}} - s_{\text{gas}}$, $\Delta v = v_{\text{liq}} - v_{\text{gas}}$, $\Delta c = c_{\text{liq}} - c_{\text{gas}}$, and the superscript *gas* refers to the gaseous state. Introducing the heat of transition of a solvent molecule from the gaseous phase to the liquid one $q = T \Delta s$, we rewrite this equation in the form

$$\frac{q \Delta T}{T} + \Delta v \Delta p = T \Delta c \quad (9.16)$$

Note that according to the Gibbs rule (9.9), this phenomenon has $f = 2$ thermodynamic degrees of freedom. This means that from variables $p, T, c_{\text{liq}}, c_{\text{gas}}$ only two variables can be varied arbitrarily. If the solute concentrations c_{liq} and c_{gas} are given, equation (9.16) allows one to determine the variations of the parameters of the phase transition compared with the pure solvent. First we evaluate the shift of the boiling temperature ΔT of a dilute solution compared with the pure solvent. Because the boiling point corresponds to the solvent atmospheric pressure, we have for variation of the boiling temperature according to equation (9.16)

$$\Delta T = \frac{T^2}{q} (c_{\text{gas}} - c_{\text{liq}}) \quad (9.17)$$

In particular, in the case of the total dissolution of a solute in the liquid phase ($c_{\text{gas}} = 0$) this formula gives

$$\Delta T = -\frac{T^2}{q} c_{\text{liq}} \quad (9.18)$$

According to this formula, the boiling point of a dilute solution increases with increasing solute concentration.

Now let us take $T = \text{const}$ and determine the variation of the saturated vapor pressure of a solvent over the liquid surface depending on the solute concentration. We have for the variation of the saturated vapor pressure

$$\Delta p = T \frac{c_{\text{liq}} - c_{\text{gas}}}{v_{\text{liq}} - v_{\text{gas}}}$$

Because the volume per solvent molecule $v_{\text{gas}} \gg v_{\text{liq}}$, this formula takes the form

$$\Delta p = p_{\text{sat}} (c_{\text{gas}} - c_{\text{liq}}) \quad (9.19)$$

where $p_{\text{sat}} = T/v_{\text{gas}}$ is the saturated vapor pressure for the pure solvent at a given temperature. In particular, in the case of the total gas solubility $c_{\text{gas}} = 0$ we have

$$\Delta p = -p_{\text{sat}} c_{\text{liq}} \quad (9.20)$$

From this it follows that the relative decrease in the saturated vapor pressure is proportional to the solute concentration. This relation is named the *Raoult law*.

In the same manner one can analyze the solute's influence on the phase transition between the liquid and solid phases of a solvent in dilute solutions. In particular, the melting point of a dilute solution is lower than that for a pure solvent. To evaluate the shift of the melting point in this case, we will employ the above expansion for the chemical potential of the liquid phase and the same expansion for the solid phase. Then we obtain equation (9.16) in the form

$$-\frac{q\Delta T}{T} + \Delta v \Delta p = T \Delta c \quad (9.21)$$

where q is the specific fusion energy or the heat of melting per molecule, and the differences of the parameters in equation (9.21) refer to the liquid and solid phases. From equation (9.21) we have for a shift in the melting point of a dilute solution by analogy with formula (9.17)

$$\Delta T = \frac{T^2}{q}(c_{\text{sol}} - c_{\text{liq}}) \quad (9.22)$$

In particular, if a solute evaporates as a result of freezing ($c_{\text{sol}} = 0$), this formula gives for a shift of the melting point

$$\Delta T = -\frac{T^2}{q}c_{\text{liq}} \quad (9.23)$$

We see that the melting point of a dilute solution decreases compared with that of the pure solvent.

9.6 Lattice Model for Mixtures

Some properties of solutions and mixtures of atoms or molecules are determined by the interaction between atoms or molecules. If the interaction of nearest neighbors dominates in such systems, the *lattice model* is useful for the analysis of the properties of these systems. Within the framework of this model, we distribute atomic particles of two types over the sites of a crystal lattice, and model in this way an alloy or a mixture of atoms of two types including solutions. We assume a short-range interaction between atomic particles of the system, so that only nearest neighbors interact, and denote the binding energy of two particles of the first type as u , of two particles of the second type as v and of two different particles as w . For definiteness, we take the criterion

$$\varepsilon = \frac{u + v}{2} - w > 0 \quad (9.24)$$

to be fulfilled. Let us denote the number of atomic particles of the first type as n_1 and the number of atomic particles of the second type as n_2 , so that the total number of atomic particles is $n = n_1 + n_2$, and the concentration of atomic particles of the first type $c = n_1/n$ is the parameter of this problem.

We first evaluate the gas entropy within the framework of the lattice gas model in order to demonstrate the possibilities of this model. The entropy of an ideal gas is given by formulae (6.6) and (6.20), and we base our analysis on the entropy definition (2.25), according to which

it is the logarithm of a number of possible states. For a system of n_1 identical particles when they are distributed over n states the entropy is equal to

$$S = \ln \frac{n!}{n_1!n_2!} = n \ln n - n_1 \ln n_1 - n_2 \ln n_2 = n \ln \frac{n}{n - n_1} + n_1 \ln \frac{n - n_1}{n_1} \quad (9.25)$$

We account for $n_1 \gg 1$ and $n \gg 1$. In addition we assume the number of occupied sites in a gas to be relatively small $n_1 \ll n$, and formula (9.25) gives in this case

$$S = n_1 \ln \frac{n}{n_1} \quad (9.26)$$

Taking the total volume of the system $V = nv_o$, where $v_o \sim \lambda^3$, and $\lambda \sim h/\sqrt{mT}$ is the de Broglie wavelength of the atomic particle (m is the particle mass and T is the temperature), we have

$$\frac{n}{n_1} \sim \frac{V}{v_o n_1} \sim \frac{VT^{3/2}m^{3/2}}{\hbar^3 n_1}$$

Substituting this in formula (9.26), we obtain an expression for the gas entropy which differs from that of formula (6.6) by a relatively small value. This confirms the possibilities of the lattice gas model for the analysis of the behavior of a system of interacting particles.

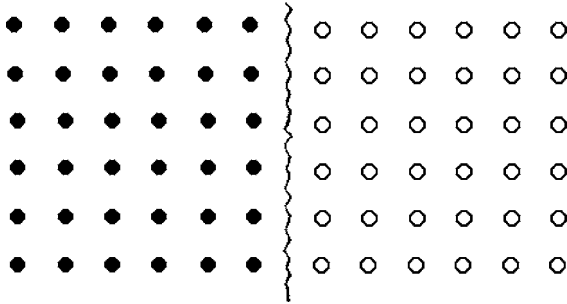


Figure 9.2. The lattice model for the order state of a system of two types of atoms when atoms are located in the sites of a square lattice.

We now analyze the possible states of the system consisting of atomic particles of two types within the framework of the lattice model. One can see that if $\varepsilon > 0$, at low temperatures the system under consideration is separated into two components (see Figure 9.2), and this distribution of atoms we call the *ordered state*. At high temperatures these components may be mixed, and it is the *disordered state* with a random distribution of atomic particles of two sorts. The transition between the ordered to disordered distributions of atomic particles on the sites of a crystal lattice results from the exchange of individual atomic particles. Below we find the possibility of the phase transition between the ordered and disordered states of the system. The disordered state is characterized by a certain excitation energy, with respect to the ordered state, but it has a higher entropy. This model, with the assumptions used about interactions between nearest neighbors is called the *Bragg–Williams approximation*.

We account for the probability c^2 that two nearest atoms of the first type partake in a given bond; this probability is $(1 - c)^2$ for two atoms of the second type, and the probability is $2c(1 - c)$ that two atoms of different types form this bond. If each internal atomic particle has

q nearest neighbors, the total number of bonds in this system equals $qn/2$. Among them we have the number of bonds $qnc^2/2$ between two atoms of the first type, the number of bonds $qn(1-c)^2/2$ between two atoms of the second type and the number of bonds $qnc(1-c)$ between two atoms of different types if atoms are distributed randomly. At zero temperature, when atomic particles of two types are separated, the system energy equals

$$uqnc + vqn(1-c)$$

(since $n \gg 1$, we neglect boundary and surface effects), and if atoms are distributed randomly over the lattice, the average binding energy of atoms is

$$\frac{qn}{2}uc^2 + \frac{qn}{2}v(1-c)^2 + qnwc(1-c)$$

Hence the excitation energy for the disordered state is equal to

$$\Delta E = \varepsilon qnc(1-c)/2, \text{ where } \varepsilon = \frac{u+v}{2} - w \quad (9.27)$$

i.e. only the parameter ε which is defined by formula (9.24) characterizes the excitation of the system of interacting atoms within the framework of this model, and the excitation energy is positive according to the criterion (9.24).

Taking the free energy of the ordered state to be zero $F_{or} = 0$, we determine the free energy for the disordered state. The entropy of the disordered state when atomic particles are distributed randomly is given by formula (9.25)

$$S = \ln \frac{n!}{n_1!n_2!} = -n[c \ln c + (1-c) \ln(1-c)]$$

where we use the Stirling formula and the condition $n_{1,2} \gg 1$. As a result, we have for the free energy $F_{dis}(T)$ of the disordered state

$$F_{dis} = \Delta E - TS = \varepsilon nc(1-c) + Tn[c \ln c + (1-c) \ln(1-c)] \quad (9.28)$$

Thus the lattice model is useful for the analysis of a system of interacting atomic particles of different sorts if the interaction between nearest neighbors determines the properties of the system.

9.7 Stratification of Solutions

We now consider a two-component solution or a mixture of interacting atomic particles of two sorts within the framework of the lattice model. This model allows one to account for the interaction between nearest neighbors and therefore to describe the behavior of solutions where long-range interactions do not dominate. If the criterion (9.24) is valid, i.e. the effective binding energy per molecule ε for the ordered state is positive, the system is found in the ordered state at low temperatures and can transfer to the disordered state at high temperatures. In the case of two-component solutions it is the transition from the *stratification distribution* of molecules into a uniform or random distribution of these molecules. Figure 9.3 gives the

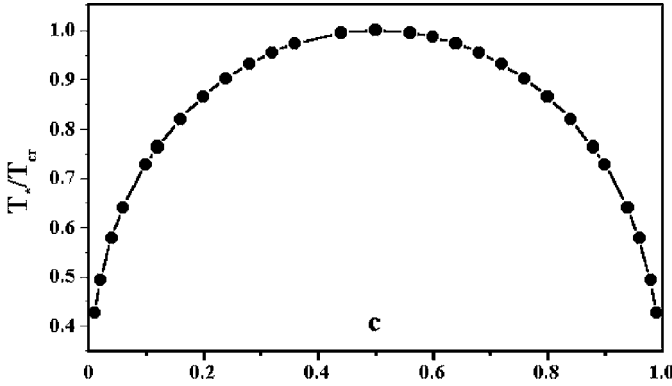


Figure 9.3. Phase diagram of solubility in a two-component solution in accordance with equation (9.31).

phase diagram of the stratification phenomenon, so that below this curve stratification of the solution state takes place, and above the phase curve the solution is uniform. This curve is symmetric with respect to the transformation $c \rightarrow 1 - c$, and the critical temperature of the stratification transition T_{cr} corresponds to the curve top at $c = 1/2$. We now construct the phase curve that separates the stratification distribution of particles from the uniform one.

Evidently, the condition for the phase transition takes the form $\mu_1(c) = \mu_2(c)$ according to the equilibrium condition (6.36), where the index refers to the type of particle. Because of the symmetry of components with respect to the transformation $c \rightarrow 1 - c$, one can represent the equilibrium condition in the form

$$\mu_1(c) = \mu_1(1 - c) \quad (9.29)$$

From formula (9.28) it follows that

$$\begin{aligned} \mu_1(c) &= \frac{\partial F_{dis}}{\partial n_1} = \frac{1}{n} \frac{\partial F_{dis}}{\partial c} = \varepsilon(1 - 2c) + T \ln \frac{c}{1 - c}, \\ \mu_2(c) &= \frac{\partial F_{dis}}{\partial n_2} = \mu_1(1 - c) = -\mu_1(c) \end{aligned} \quad (9.30)$$

and the condition (9.29) gives $\mu_1(c) = 0$, or

$$T_c = \frac{\varepsilon(1 - 2c)}{\ln \frac{1-c}{c}} \quad (9.31)$$

where T_c is the boundary temperature of the uniform distribution, and below this temperature the distribution becomes stratified. The critical temperature T_{cr} , i.e. the maximum boundary temperature, is equal to

$$T_{cr} = T_c(c = 1/2) = \frac{\varepsilon}{2} \quad (9.32)$$

Above the critical temperature T_{cr} this two-component solution is uniform at any concentrations of components. Figure 9.3 represents the phase curve for the phase transition under consideration in accordance with formula (9.31).

Let us return now to dilute solutions when the solute concentration is small. We consider them from the standpoint of the lattice model where the interaction between nearest atomic particles is taken into account. One can see that the expansion of formulae (9.30) for the chemical potential of the solvent and solute leads to formula (9.6) which is derived for an ideal gas. The reason is that an addition to the chemical potential at low concentrations is connected with the entropy term and does not depend on interactions. This fact is the basis of the Henri law (9.14) for the concentration of a dissolved gas, formula (9.18) for the shift in the boiling temperature of a solution in comparison with a pure solvent, the Nernst law of equidistribution for the solubilities of different solutes in a given solvent, the van't Hoff formula (9.15) for the osmotic pressure, and the Raoult law (9.20) for the shift in the saturated vapor pressure over a solution in comparison with that of a pure solvent.

In principle, the stepwise *order–disorder phase transition* is possible for the binary solution under consideration. This jump transition requires the condition that the free energy of the ordered F_{ord} and disordered F_{dis} states would be equal. Since under the calibration using $F_{ord} = 0$ this condition has the form $F_{dis} = 0$, and on the basis of formula (9.28) for the free energy of the disordered state we have for the transition temperature T_{ph}

$$T_{ph} = \varepsilon \cdot \frac{c(1-c)}{c \ln \frac{1}{c} + (1-c) \ln \frac{1}{1-c}} \quad (9.33)$$

One can see that the function $\xi(c) = T_{ph}/T_c$ is less than one over the whole range of concentrations $0 \leq c \leq 1$, so that $\xi(c) \rightarrow 1$, if $c \rightarrow 0$ or $c \rightarrow 1$, and the minimum of this function equals $\xi(1/2) = 1/(2 \ln 2) = 0.72$. Therefore, since $T_c \geq T_{ph}$, we find that the stepwise transition is not realized in this case.

Thus the stratification transition is an order–disorder phase transition of the second type and proceeds in a continuous way as the solution temperature drops. At high temperatures this solution is uniform and the components are mixed. Starting from the temperature T_c , the solution is divided into two parts, and at a given temperature T the dilute concentration is equal to c' , for which the critical temperature is T , and the dilute concentration is $1 - c'$ in the second part. In order to exhibit the peculiarities of this phase transition, we draw in Figure 9.4 the dependence of the specific free energy of a bulk solution on the excitation energy. We take for definiteness the mean solute concentration to be $1/2$, and the ordered state consists of identical parts of solute and solvent, which play the same role in this case. An increase in the concentration of the solute in the solvent, or of the solvent in the solute, leads to an increase in the internal energy, which is given by formula (9.27) in this case. Simultaneously, the free energy in accordance with formula (9.28) decreases. If $T > T_{cr}$, the free energy decreases monotonically with an increase in the excitation energy over the whole range of excitation energy. If $T < T_{cr}$, the free energy has a minimum in the concentration range $0 < c < 1/2$, and if $T = T_{cr}$, the free energy is zero at $c = 1/2$. Thus in the ordered state the solution is separated into two homogeneous parts, so that the solvent dominates in the first part and the solute dominates in the second part.

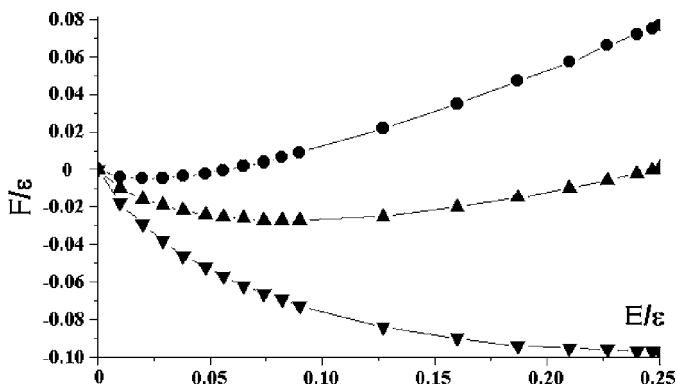


Figure 9.4. The specific free energies of the two-component solution as a function of the excitation energy with respect to a pure solvent, is a certain amount of the solute is dissolved. The lower curve corresponds to the critical temperature $T_{cr} = \varepsilon/2$, the middle curve relates to the temperature $T = 0.36\varepsilon$, if the free energy is zero at the concentration $c = 1/2$, the upper curve corresponds to the temperature $T = 0.25\varepsilon$. The stable state of the solution at each temperature is determined by the minimum of the free energy.

Note that we consider a simple interaction of solution molecules where only the nearest neighbors partake in this interaction and the solution structure is identical for the solvent and solution. Within the framework of this model, two structures of molecules which correspond to the ordered state of the system are formed at low temperatures. Each structure is one of these components with an admixture of the other component which is dissolved in this one. At high temperatures both components are mixed, and the solution becomes uniform. This character of the dissolving processes occurs if the interaction between atoms or molecules of the same component is more profitable energetically than the interaction between atoms or molecules of different components. This corresponds to a simple model for the interaction between components of the solution. In reality, the interaction between components depends on various peculiarities of components that can complicate the solubility diagram.

9.8 Phase Diagrams of Binary Solutions

We now consider a two-component solution if the molecules of both components are bonded in a solution and free in a gas. Figure 9.5 gives an example of the phase diagram in this case, where this diagram has a cigarlike form, so that the upper curve corresponds to boiling of the solvent, and the other one relates to boiling of the solute. Note that in contrast to the phase diagram of a pure component (Figure 7.1), which is constructed in a two-dimensional $p - T$ space, in the case of a binary mixture we deal with the three-dimensional $p - T - c$ space. For simplicity, we restrict the phase diagrams $T - c$ which are projections of the three-dimensional phase diagram in the plane $T - c$.

Let us consider the phase curve which is responsible for the boiling of the solvent, where the concentrations of the solute c_{gas} in the gaseous phase and c_{liq} in the liquid phase are small.

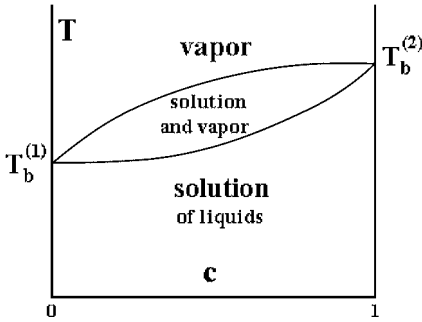


Figure 9.5. The gas-liquid phase diagram for a simple binary solution. $T_b^{(1)}$, $T_b^{(2)}$ are the boiling points for pure components.

Then according to formula (9.17), the solvent's boiling point T expressed through the boiling point in the solute's absence is equal to

$$T - T_b = \frac{T^2}{q}(c_{\text{gas}} - c_{\text{liq}}) \quad (9.34a)$$

In addition, from the solute equilibrium it follows that

$$c_{\text{gas}} = c_{\text{liq}} \exp\left(-\frac{\Delta\varepsilon}{T}\right) \quad (9.34b)$$

where $\Delta\varepsilon = \varepsilon'_{\text{liq}} - \varepsilon_{\text{liq}}$ is the difference in the binding energies for the solute $\varepsilon'_{\text{liq}}$ and solvent ε_{liq} molecules in the solution. Equations (9.34) give the dependence of the solvent boiling point on the solute concentration c_{liq} . In particular, this gives in the limit of small concentrations

$$\frac{dT}{dc_{\text{liq}}} = \frac{T^2}{q} \left[\exp\left(-\frac{\Delta\varepsilon}{T}\right) - 1 \right] \quad (9.35)$$

The phase diagram of Figure 9.5 is the simplest one, where two components do not form a chemical compound and can be dissolved in each other at any concentration. Then among the ranges of liquid and gaseous components of this mixture which correspond to the lowest and upper part of the diagram, the intermediate range exists within the cigar figure with the mixture of the liquid and gaseous phases. This is absent for the pure component under variations of pressure or temperature (Figure 7.1), but occurs on the $V - T$ diagram (Figure 7.4). Note that we have the same form of the phase diagram of the two-component mixture in the range of the solid-liquid phase transition. We also demonstrate in Figure 9.6 the more complex case of a mixture of two components which do not form a chemical compound, but have restricted solubility over some temperature range. If this diagram includes the gaseous and liquid states, along with a range of a mixture of these phases of Figure 9.5, in this case we also have a range of stratification that consists of one-component and two-component layers. At some pressures the $c - T$ ranges of stratification and gaseous-liquid mixture can be separated, as occurs in Figure 9.6. We note that this demonstration relates also to the solid-liquid phase transition.

Chemical transitions can change the phase diagram depending on the character of this transition. We consider below as an example the liquid-gas equilibrium for UO_2 , when along with this compound, UO , UO_3 , O and O_2 can exist under considering conditions. In particular,

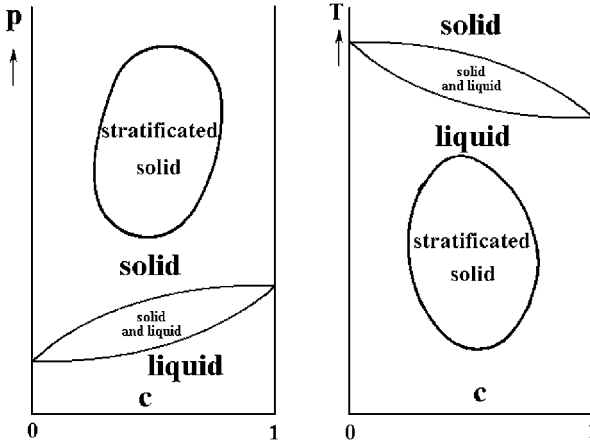


Figure 9.6. The gas-liquid phase diagram for a two-component mixture, if components do not form chemical bonds, but the mutual solubility is limited at some temperatures.

if the liquid and vapor consist of UO_2 , the evaporation curve is denoted by 1 on Figure 9.7a and finishes at the critical point. In reality, the liquid and vapor consist of different chemical compounds and this depends on the evaporation rate. Figure 9.7b gives the ratio between oxygen and uranium atoms in the liquid and vapor, and the maximum oxygen enrichment of the vapor is about 7. It takes place at slow heating when chemical equilibrium is established between the liquid and gaseous phases. Correspondingly, the relative oxygen content in the liquid becomes lower. Depending on the heating rate, the oxygen content is found in region 1 of Figure 9.7b for the vapor and in region 2 for the liquid.

9.9 Thermodynamic Parameters of Plasma

Above we analyzed systems of atomic particles with a short-range interaction between them, where only the nearest neighbors interact. Let us consider a system with a long-range interaction of particles. In a plasma the long-range Coulomb interaction occurs between charged particles, and we consider a weakly ionized gas that contains atoms or molecules of number density N and electrons and positive ions whose average number density is N_o . Although the interaction between charged particles in this system is weak, it is important for some properties of this system. For simplicity, we take the temperature T of all the plasma components to be identical, which gives the internal energy per unit volume of this system if we neglect the interaction between particles of the plasma

$$E' = \frac{3}{2}T(N + 2N_o)$$

so that the specific internal energy of the plasma equals

$$E = \frac{3}{2}T(N + 2N_o) + 2N_o\overline{e\varphi} \quad (9.36)$$

where $\overline{e\varphi}$ is the average energy of interaction between charged particles per particle.

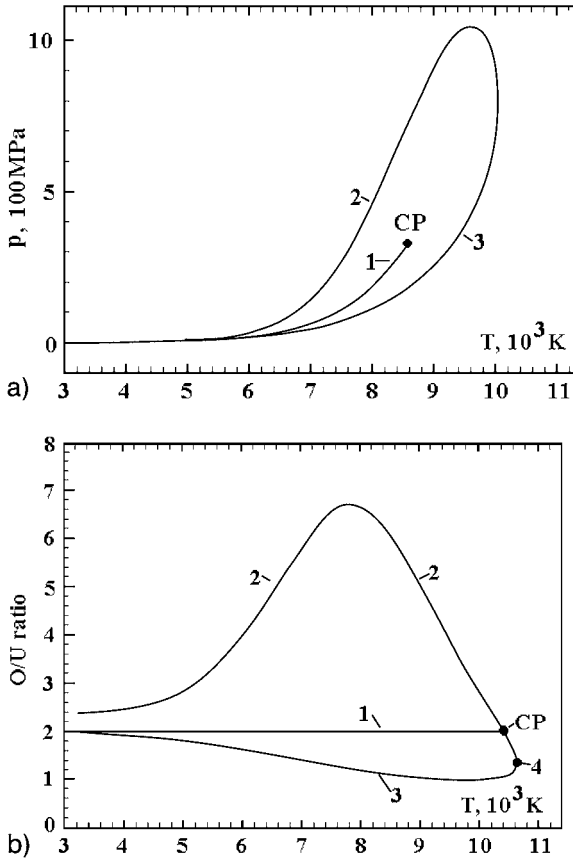


Figure 9.7. Liquid-vapor phase diagrams for UO_2 (I. Iosilevski, G. J. Hyland, C. Ronchi, E. Yakub, *Int. J. Thermophysics* 22, 1253(2001). (a) $p - T$ diagram for UO_2 . (1) the evaporation curve for pure UO_2 , CP - critical point, (2) boiling curve at slow heating, (3) saturation curve at fast heating. (b) The ratio of a number of uranium and oxygen atoms. (1) the evaporation and saturation curve of pure UO_2 at fast heating, CP is the critical point, (2) the boiling curve for vapor at slow heating, (3) the saturation curve of a liquid at fast heating, (4) the point of the maximum temperature on the saturation curve.

We assume the plasma to be an ideal one, i.e. its parameters satisfy the criterion (2.42)

$$\frac{N_o e^6}{T^3} \ll 1 \quad (9.37)$$

In this case fields in the plasma are shielded by charged plasma particles, and the Coulomb long-range interaction of charged particles acts independently of the short-range interaction involving neutral particles. The electric potential of a charged particle is given by formula (2.41) and equals

$$\varphi = \frac{e}{r} \exp\left(-\frac{r}{r_D}\right) \quad (9.38a)$$

where r is the distance from this particle (for definiteness, we assume it to have positive charge), and the *Debye–Hückel radius*

$$r_D = \sqrt{\frac{T}{8\pi N_o e^2}} \quad (9.38b)$$

characterizes the typical distance of screening of the field created by this charge. In the case of an *ideal plasma*, the Debye–Hückel radius is large compared with the typical distance between the nearest charged particles, so that many charged particles partake in the charge shielding.

Our task is to determine the contribution of the interaction between charged particles to the plasma energy. The mechanism of this interaction consists of a shift in the surrounding charged particles under the action of the field of a test charged particle. Then the average interaction energy per charged particle is equal

$$\overline{e\varphi} = \int e\varphi \left[N_o \exp\left(-\frac{e\varphi}{T}\right) - N_o \exp\left(\frac{e\varphi}{T}\right) \right] d\mathbf{r}$$

We account for the Boltzmann distribution of surrounding charged particles in the field of a test particle and assume that many particles take part in the shielding of a charged particle, as occurs in an ideal plasma. For an ideal plasma, large r gives the main contribution to this integral, and the exponent may be expanded over a small parameter ($e\varphi \ll T$). Then we have

$$\overline{e\varphi} = -2N_o \int \frac{(e\varphi)^2}{T} d\mathbf{r} = -\frac{8\pi N_o}{T} \int_0^\infty \frac{e^2}{r^2} \exp\left(-\frac{2r}{r_D}\right) r^2 dr = -\frac{e^2}{2r_D}$$

where we use the formula (9.38a) for the electric potential of a test charged particle and the expression (9.38b) for the Debye–Hückel radius. Substituting this relation in formula (9.36), we get for the internal energy E of an ideal plasma

$$\begin{aligned} E &= E_{\text{id}} + E_{\text{int}}, & E_{\text{id}} &= \left(\frac{3}{2}TN + 3TN_o \right) V, \\ E_{\text{int}} &= -N_o V \frac{e^2}{r_D} = -TN_o V \sqrt{\frac{8\pi N_o e^6}{T^3}} \end{aligned} \quad (9.39)$$

The term due to the interaction of charged particles E_{int} is small compared with the kinetic energy of charged particles of an ideal plasma $3TN_o V$. This corresponds to the criterion (9.37) for an ideal plasma, so that interactions are relatively small. Hence the last term of this formula can be considered as the following term in the expansion of this value over the small parameter (9.37).

Evidently, the same operation may be fulfilled for other thermodynamic parameters of an ideal plasma. We have for the free energy

$$F = F_{\text{id}} + F_{\text{int}} \quad (9.40)$$

and use the relation (6.22) between the internal energy and free energy

$$E = F - +TS = F - T \left(\frac{\partial F}{\partial T} \right)_V$$

Because this relation is valid for each term of the expansion over the small parameter and $E_{\text{int}} \sim F_{\text{int}} \sim T^{-1/2}$, from this it follows

$$F_{\text{int}} = \frac{2}{3} E_{\text{int}} \quad (9.41)$$

Representing the pressure of an ideal plasma in the form

$$p = p_{\text{id}} + p_{\text{int}}$$

we find the additional term from formula (6.22)

$$p_{\text{int}} = - \left(\frac{\partial F_{\text{int}}}{\partial V} \right)_{T,n}$$

where n is the number of charged particles in a given volume. Because $r_D \sim N_o^{-1/2} \sim \sqrt{V}$, we have $F_{\text{int}} \sim V^{-1/2}$, so that

$$p_{\text{int}} = \frac{F_{\text{int}}}{2V} = \frac{E_{\text{int}}}{3V} = -\frac{e^2 N_o}{3r_D} = -\frac{T}{24\pi r_D^3}$$

and the pressure of an ideal plasma has the form

$$p = NT + 2N_o T - \frac{e^2 N_o}{3r_D} = NT + 2N_o T \left(1 - \frac{1}{48\pi N_o r_D^3} \right) \quad (9.42)$$

The correction to the entropy ($S = S_{\text{id}} + S_{\text{int}}$) of an ideal plasma is equal to

$$S_{\text{int}} = \frac{E_{\text{int}} - F_{\text{int}}}{T} = \frac{E_{\text{int}}}{3T} = -\frac{V}{24\pi r_D^3} \quad (9.43)$$

Let us determine the chemical potential of an ideal plasma which has the standard form

$$\mu = \mu_{\text{id}} + \mu_{\text{int}}$$

so that μ_{id} is the chemical potential of an ideal mixture of gases, and the correction μ_{int} takes into account the interaction of charged particles of an ideal plasma. We take this correction from the relation (6.34)

$$\mu_{\text{int}} = - \left(\frac{\partial G_{\text{int}}}{\partial n} \right)_{T,p}$$

where n is the number of charged particles of the plasma. It is necessary to take into account that we start from the parameters of a noninteracting plasma, so that it is located in a volume V and has a pressure p . Because the interaction of charged particles changes the plasma pressure, we have according to formula (6.24) $G_{\text{id}}(p + p_{\text{int}}) = G_{\text{id}}(p) + p_{\text{int}} V$. On the other hand, since $G(p) = F(V) + pV$, $G_{\text{id}}(p) = F_{\text{id}}(V) + pV$ and $F = F_{\text{id}} + F_{\text{int}}$, we have $G(p + p_{\text{int}}) = F(V) + (p + p_{\text{int}})V$. From this it follows $G_{\text{int}}(p + p_{\text{int}}) = F_{\text{int}}(V)$. Thus, we obtain

$$G_{\text{int}}(p = p_{\text{int}}) = F_{\text{int}}(V) = -(n_i + n_e) \frac{e^2}{3r_D} = -\frac{\sqrt{4\pi} e^3}{3\sqrt{V}} (n_i + n_e)^{3/2} \quad (9.44)$$

where n_i and n_e are the numbers of electrons and ions in the plasma. From this one can find corrections due to the interaction of the chemical potential of charged particles of each type.

9.10 Electrolytes

Electrolytes are solutions where some components are partially or fully ionized. Hence these solutions contain charged particles, and the analysis of electrolytes of low concentrations is similar to that of an ideal plasma. The transition from an ideal plasma to a weak electrolyte requires us to take into account the dielectric constant ϵ of a solvent and the charges of positive Z_1 and negative Z_2 ions which are expressed in units of an electron charge and can differ from it. Then the Debye–Hückel radius r_D which is determined by formulae (2.41) and (9.38b) for a plasma of electrolytes has the form

$$r_D = \sqrt{\frac{\epsilon T}{4\pi e^2(N_1 Z_1^2 + N_2 Z_2^2)}} \quad (9.45)$$

where N_1 and N_2 are the number densities of positive and negative ions correspondingly. This formula is transformed into (2.41) in the case of an ideal plasma $\epsilon = 1$, $Z_1 = Z_2 = 1$.

The condition of quasineutrality of an electrolyte plasma is

$$N_1 Z_1 = N_2 Z_2 \quad (9.46)$$

and the ideal plasma condition for each type of ions has the form

$$N_i \left(\frac{Z_i^2 e^2}{\epsilon T} \right)^3 \ll 1 \quad (9.47)$$

where $i = 1$ or $i = 2$.

The *osmotic pressure* due to ions for weak electrolytes equals

$$p_{\text{osm}} = T(N_1 + N_2) - \frac{T}{24\pi r_D^3} \quad (9.48)$$

Let us consider an example in which the salt NaCl is dissolved in water and ions are formed according to the scheme



Take the osmotic pressure of these ions to be 1 atm. Because at room temperature ($T = 293$ K) the dielectric constant of water $\epsilon = 81$, we get for the initial salt density $\rho_{\text{NaCl}} = 1.3$ g/l, which is less by an order of magnitude than the salt content of sea water. The Debye–Hückel radius (9.38b) for this solution equals $r_D = 2.1$ nm, and the correction to the osmotic pressure in formula (9.48) due to the interaction of ions equals -0.06 atm. Thus, the osmotic pressure is determined in this case basically by the presence of atomic particles in the solution, and the interaction of ions makes a small contribution to this value. This effect is of great importance for biological objects, which consist of aqueous solutions. In particular, the osmotic pressure of salts in blood compensates for the internal pressure of blood corpuscles, through which the surface ions of salts cannot penetrate.

10 Phase Transition in Condensed Systems of Atoms

10.1 Peculiarities of the Solid–liquid Phase Transition

In considering the solid–liquid phase transition for a bulk system of bound atoms and their clusters in terms of thermodynamics, we characterize each aggregate state of this system by thermodynamic parameters and use the *two-state approximation* for aggregate states, assuming the existence of two aggregate states for a system of bound atoms, namely the solid and liquid states. Although the thermodynamic description of the aggregate states is universal, it is phenomenological, and we encounter questions connected with the microscopic nature of these states and which include the character of atom interactions. For example, one question is why the phase transition has a stepwise character, while the excitation of a large system is practically continuous. In addition, why for a bulk system do we postulate the existence of two aggregate states, but not one or several? In order to answer these questions, it is necessary to consider the microscopic description of the particle ensemble.

We consider below the case of a pair interaction between atoms. This means that the interaction of a test atom with some other atom does not depend on its interaction with other atoms, which occurs if the interaction potential between atoms is small compared with the typical electron energy. This criterion holds true for clusters of inert gas atoms and clusters of gaseous molecules, i.e. when these molecules are found in a gaseous state under normal conditions. Therefore, considering clusters with a pair interaction between atoms, we will be guided by rare gas clusters. In addition, we assume the behavior of cluster atoms to be classical, and hence helium clusters are not the object of our consideration.

The nature of the order–disorder phase transition for an ensemble of bound atoms follows from the lattice model (see Chapters 8 and 9). Within the framework of this model, atoms are located at the sites of a crystal lattice, and interaction occurs only between nearest neighbors. Then the ordered state is a compact distribution of atoms which leads to the maximum number of bonds between nearest-neighbor atoms, while the disordered state with a random distribution of atoms corresponds to a higher entropy and to the loss of some of the bonds between nearest neighbors compared with the ordered state. The phase transition between these states proceeds by a stepwise change of the binding energy of atoms and the entropy of the optimal distributions of atoms. The order–disorder phase transition models the solid–liquid phase transition for an ensemble of bound atoms, so that the ordered state corresponds to the solid state, and the disordered state corresponds to the liquid state. Since this phase transition leads to a change in the atomic configuration, it results from the configuration excitation of an ensemble of bound atoms.

In considering the *aggregate states* of ensembles of bound atoms with a pair interaction between them, it is convenient to base our analysis on the behavior of the multidimensional potential energy surface of an ensemble of bound atoms. In these terms, the evolution of clusters and bulk systems corresponds to the dynamics of motion along this surface. The pe-

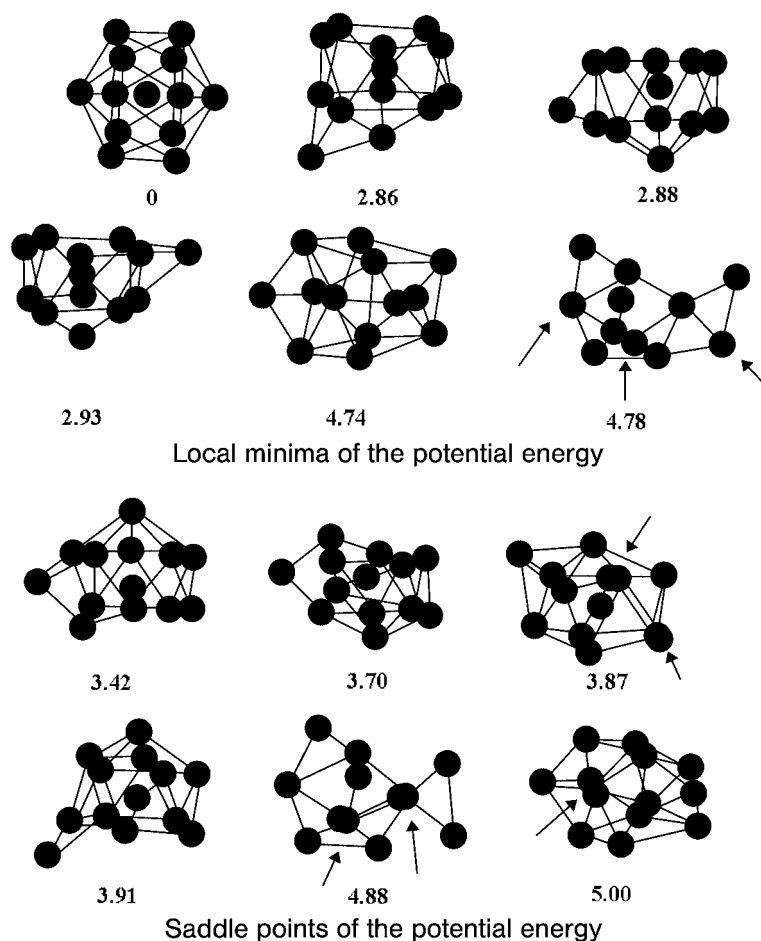


Figure 10.1. Structures of low excited states of the Lennard-Jones cluster consisting of 13 atoms (upper figures) and saddle points for this cluster (lower figure). The values give the excitation energies for local minima and saddle points (D.J. Wales, R.S. Berry. *J. Chem. Phys.* 92, 4283, 1990), relates to zero temperature and are expressed in energies D of breaking of one bond. At nonzero temperature the barrier energies are decreased.

culiarity of the potential energy surface consists of the existence of a large number of local minima at zero temperature depending on the configuration of atoms. Each local minimum corresponds to a certain configurational excitation of a cluster, and neighboring local minima are separated by saddle points of the potential energy, as is demonstrated in Figure 10.1 for the Lennard-Jones cluster of 13 atoms, where the structures of the lowest configuration excitations and configurations of atoms for the lowest saddle points are given. For this reason, cluster evolution at low temperatures results in its location mostly at the local minima of the potential energy surface, and intermediate states are occupied a small part of time. By join-

ing the local minima with nearby energies into aggregate states of this cluster as an ensemble of bound atoms, we simplify the problem and assume that all the time the cluster is found in the aggregate states. This concept assumes the *cluster aggregate state* to be a group of configurationally excited states with nearby excitation energies and allows us to use the thermodynamic parameters to describe the aggregate states. In addition, this character of cluster evolution determines the character of coexistence of the solid and liquid cluster phases such that at any time a cluster is found near the minima of the potential energy which correspond to its aggregate states. In other words, most of the time the cluster is found in the solid or liquid aggregate states, and its location in intermediate states during the transition between aggregate states proceeds during short time intervals.

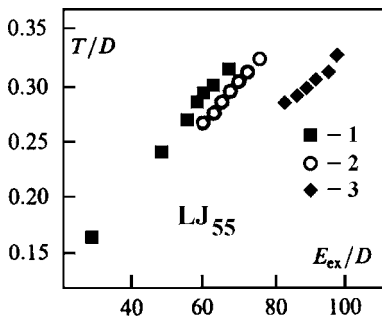


Figure 10.2. Time-averaged caloric curves for the Lennard–Jones cluster consisting of 55 atoms. (1) solid cluster of the icosahedral structure; (2) cluster with the liquid outer shell and solid inner shell; (3) liquid cluster (R.E. Kunz, R.S. Berry. *Phys. Rev. E* 49, 1985 (1994)).

We use here the approach of two aggregate states for clusters (see Chapter 9) where the first aggregate state is the solid one and corresponds to the global minimum of the cluster potential energy. The other aggregate state, the liquid state, is a group of configurationally excited cluster states which corresponds to the minimum of the cluster free energy. This approach does not hold true for all the clusters. In particular, a large cluster with a pair interaction between atoms can be constructed from several atomic shells, and it can have several aggregate states, each of which corresponds to the melting of a certain atomic shell. In particular, the *caloric curve* of Figure 10.2 for the Lennard–Jones cluster of 55 atoms shows three aggregate states, the solid and liquid states, and also the aggregate state of this cluster with a solid core and melted outermost shell. But if the cluster size tends to infinity, there are two configurationally excited states which relate to internal and surface melting, i.e. the approach of two aggregate states holds true. Next, some clusters do not have the liquid state, as occurs for Lennard–Jones clusters consisting of 8 and 14 atoms. But clusters with completed shells have the liquid aggregate state. In these cases configurationally excited states correspond to the transition of several atoms from the outermost atom shell to the cluster surface, and the statistical weight of these configurationally excited states significantly exceeds the statistical weight of the ground state. Therefore realization of such states can be thermodynamically profitable.

Within the framework of the lattice model, *configuration excitation* of the compact or solid state results in the formation of *vacancies* near atoms and leads to the loss of some bonds between nearest-neighbor atoms. In real ensembles of bound atoms vacancies are transformed into *voids* which choose an optimal interaction of neighboring atoms. Then we consider configuration excitation as a result of the formation of a void gas, so that internal voids are formed in very large clusters or bulk systems, and surface voids determine the configuration excitation

of not very large clusters. Although the volume and shape of an individual void vary over time, one can use the average void parameters to describe the configuration excitation in terms of statistical physics. In particular, one can construct the liquid state of a system of bound atoms from the solid one by the creation of a certain number of vacancies which are transformed into voids in the course of relaxation of this system.

Determination of void parameters is a separate problem because these parameters are determined by the simultaneous interaction of many atoms. One can find them based on the parameters of the liquid aggregate state of the system under consideration. In the case of bulk rare gases, the parameters of internal voids follow from the thermodynamic parameters of liquid rare gases; for clusters that are not large and with completed atom shells the parameters of surface voids can follow from the results of computer simulation of clusters by methods of molecular dynamics.

The void concept of configurationally excited states of systems of bound atoms allows us to analyze thermodynamically stable states, such as the solid and liquid aggregate states, and thermodynamically unstable or *glass-like states*. The glass-like states exist due to the specific character of interaction for a system of many bound atoms when local minima of the potential energy surface are separated by barriers. From the standpoint of the void concept, these states contain frozen-in voids, and relaxation of these states results in the diffusion of voids outside, which causes annealing. But because of the barrier character of void diffusion, this process is slowed down at low temperatures, and glass-like states become practically stable in spite of their thermodynamic instability. Hence the void concept allows us to exhibit both the phase and glassy transitions.

We have two types of excitations for a system of bound atoms (see Figure 10.3). The first one corresponds to configuration excitation of atoms and consists in the formation of vacancies or voids inside the system or on its surface. Just this excitation is responsible for the phase transition between aggregate states of this system. The other type of excitation relates to the thermal motion of atoms, which results in the excitation of phonons or cluster oscillations.

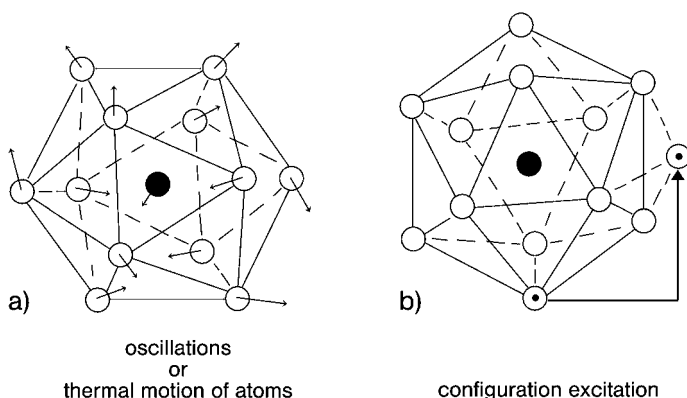


Figure 10.3. Two types of cluster excitations: cluster oscillations due to thermal motion of atoms (a) and configurations excitation (b).

Although we connect the phase transition with configuration excitation, thermal oscillations enforce this phenomenon by a change in the parameters of the phase transition. Indeed, the solid state of these systems is more compact and is characterized by a lower entropy of atom oscillations at a given temperature in comparison with the liquid state, which relates to a more friable distribution of atoms with respect to the solid state. Therefore, along with an entropy jump due to configuration excitation, simultaneously a remarkable entropy jump at the melting point results from the thermal motion of atoms. This indirect influence of the thermal oscillations of atoms on the parameters of the phase transition is of importance and can be important for the existence of the *liquid aggregate state* of this system.

10.2 Configuration Excitation of a Solid

We start from configuration excitation for the solid state of a bulk system of bound atoms with a pair interaction between atoms, where the interaction between nearest neighbors dominates, which is realized for rare gases. Neglecting surface effects for a large system, we take configuration excitation in the form of internal vacancies, assuming thermal and configuration excitations to be separated, and the thermal motion of atoms does not significantly influence its configuration excitation. Therefore, when analyzing the configuration excitation of a system of bound atoms we will not account for the thermal motion of atoms.

We first consider a solid system of atoms with a short-range interaction when atoms form a close-packed crystal lattice (see Figures 3.1 and 3.2) and denote the energy of breaking of one bond by D . Because each bond corresponds to two atoms, and each internal atom of the crystal has 12 nearest neighbors, according to formula (7.28) the binding energy of solid atoms per atom is $6D$. The formation of one vacancy is accompanied by the breaking of 12 bonds and removal of one atom, so that the energy of formation of one vacancy is

$$\varepsilon_v = 6D$$

which is identical to the binding energy per crystal atom.

We now determine the solid parameters for the lattice model. The partition function of an excited crystal consisting of n atoms equals

$$Z = \sum_v Z(v) = \sum_v C_{n+v}^v \exp\left(-\frac{v\varepsilon}{T}\right) \quad (10.1)$$

where n is the number of atoms, v is the number of vacancies, T is the temperature, and the partial partition function is

$$Z(v) = C_{n+v}^v \exp\left(-\frac{v\varepsilon}{T}\right) \quad (10.2)$$

Since $n \gg 1$ and $v \gg 1$, we obtain near the maximum of the partition function assuming $v \ll n$

$$Z(v) = \exp\left[v_{\text{sol}} - \frac{(v - v_{\text{sol}})^2}{2v_{\text{sol}}}\right] \quad (10.3)$$

where the maximum is observed at

$$v_{\text{sol}} = n \exp\left(-\frac{\varepsilon}{T} - 1\right) \quad (10.4)$$

The total partition function of the solid state is

$$Z_{\text{sol}} = \int dv \left(\frac{n}{v}\right)^v \exp\left(-\frac{v\varepsilon}{T}\right) = \int_{v \sim v_{\text{sol}}} Z(v) dv = \sqrt{2\pi v_{\text{sol}}} \exp(v_{\text{sol}}) \quad (10.5)$$

Correspondingly, the energy of configuration excitation is

$$E_{\text{ex}} = \varepsilon v_{\text{sol}} = n\varepsilon \exp\left(-\frac{\varepsilon}{T} - 1\right) \ll n\varepsilon \quad (10.6)$$

Note that the difference

$$\ln Z_{\text{sol}} - \ln Z(v_{\text{sol}}) = \ln \sqrt{2\pi v_{\text{sol}}}$$

is small in comparison with each term in the case $v_{\text{sol}} \gg 1$, which allows one to use the maximum value of the partial partition function instead of the total partition function of the solid state to the above accuracy. We use above that neighboring vacancies do not border each other, i.e. the criterion $v \ll n$ is fulfilled.

From the above analysis of the configuration excitation of a solid state it follows that the number of vacancies formed is relatively small at low temperatures. Therefore individual vacancies do not border each other, and the model used is valid. The existence of a maximum of the partition function (or minimum of the free energy) of this atomic system allows us to connect the aggregate state with elementary excitations of this system. We define the aggregate state as a group of excited states near the maximum of the partial partition function and neglect the possibility of exciting other states, the probabilities of which are negligible. In this way the aggregate state is a group of configurationally excited states.

10.3 Modified Lattice Model for Configuration Excitation of a Bulk System of Bound Atoms

When analyzing the scaling of dense and condensed rare gases in Chapter 8, we convinced ourselves that the properties of these systems are governed by the short-range interaction of atoms. Hence below we develop a *lattice model*, the basis of which is the *short-range interaction* of atoms, for the configuration excitation of a bulk system of bound rare gas atoms. In this case the ordered and disordered states for the lattice model correspond to the solid and liquid aggregate states of a system of bound atoms with a short-range interaction. At the beginning we take a large solid cluster of bound atoms consisting of $n + v$ atoms and allow v atoms to escape, so that the cluster formed consists of n atoms and v vacancies. This cluster relaxes due to atomic interactions, and this relaxation leads to a rapid shrinking of the cluster. A typical relaxation time is of the order of the atomic motion over the distance between nearest atoms, that is $\sim 10^{-12}$ s for real solids at room temperature. The resulting excited state of the

cluster of n atoms contains v voids. We assume the cluster to be very large, which allows us to neglect surface effects, and the voids that form are located inside the cluster.

Thus we characterize the configuration excitation of the system under consideration by the number of voids v inside the system for a given number n of atoms. In fact, this is equivalent to the introduction of the total volume occupied by the system. Although, in contrast to a vacancy, the shape and volume of an individual *void*, an elementary configuration excitation, vary with time, this approach is convenient for the analysis of the statistics of excited states of the system. We use the approach of a mean field, so that individual voids are independent. Each void is characterized by the energy of void formation ε and the statistical weight of a void g , and these parameters depend on the number of voids v in the system for a given number n of atoms. Introducing the statistical weight of an individual void and accounting for the volume and energy of an individual void to be different from that of a vacancy, we generalize the lattice model in this way. Thus, we consider the configuration excitation of the system of bound atoms as a result of the formation of a gas of voids.

The partition function of the system under consideration has the form

$$Z(v) = C_{n+v}^v g^v \exp\left(-\frac{v\varepsilon}{T}\right) \quad (10.7)$$

i.e. the interaction of voids is taken into account by the dependence of the energy of void formation ε on a number of voids. Here C_{n+v}^v is the number of combinations for a given number of voids. We take the energy of formation of an individual void in the form

$$\varepsilon = \varepsilon_o - U\left(\frac{v}{n}\right) \quad (10.8)$$

where U is the effective interaction potential of voids, ε_o is the energy of formation of one vacancy in the crystal, i.e. when $v = 0$ ($\varepsilon_o = 6D$ for a short-range interaction potential). Under the above conditions, we have from the expression (10.7) for the partition function of a gas of voids in the limit $n \gg 1$, $v \gg 1$:

$$\ln Z(v) = v \cdot \left(1 + \ln \frac{ng}{v} - \frac{\varepsilon_o - U}{T}\right) \quad (10.9)$$

In the limit $v/n \rightarrow 0$ we have $g = 1$ and $v = 0$ and the results obtained correspond to the lattice model.

Applying these formulae to the liquid state of a bulk system of atoms with a short-range interaction, we characterize the configurationally excited state of a bulk system of bound atoms by an excitation energy (or number of voids) together with the temperature of atoms, which is a characteristic of their kinetic energy. Because these parameters are assumed to be independent, this system is a nonequilibrium one. The number of voids will vary with time as the system moves towards equilibrium, and the typical time to establishment the equilibrium depends on the system's size because voids move to or from the system boundary as a result of diffusion inside the system. Typical times of observation of this system are small compared with the time to establishment this equilibrium. Next, in order to conserve the system of bound atoms during times of observation, it is necessary to surround it by a gas of atoms at the saturated vapor pressure corresponding to a given temperature of the system. Then processes of atomic attachment and evaporation are equalized, which conserves the number of

bound atoms of the system. In addition, we use the approach of a mean self-consistent field for voids. This allows us to consider configuration excitation as a gas of free voids, but the parameters of an individual void depend on the relative number of voids.

Introducing the energy of formation of one void ε according to formula (10.8), we consider the configuration excitation of a system of bound atoms as the formation of a gas of independent voids. The interaction potential of voids is zero, as well as their derivatives, for the solid state when $v = 0$. An increase in the number of voids v leads to a decrease in the energy of void formation ε , i.e. $U \geq 0$ at any v . Next, formally $\varepsilon \rightarrow 0$ at large v . Below we use the simplest form of the function $U(v/n)$ which accounts for these properties and allows us to construct the liquid state of this system

$$U\left(\frac{v}{n}\right) = \varepsilon_o \left[\exp\left(-\frac{\alpha n}{v}\right) - \exp\left(-k \frac{\alpha n}{v}\right) \right] \quad (10.10)$$

where α and k are the parameters of this quantity. Formula (10.10) is correct for values of v/n that are not large. The void statistical weight equals one at $v = 0$ and increases strongly with increasing v . We take it in the form

$$g = 1 + a \frac{v}{n}, \quad a \gg 1 \quad (10.11)$$

Modifying in this way the lattice model for a bulk model of bound atoms, one can apply this model to systems where interactions between nearest neighbors dominate.

10.4 Liquid State of Rare Gases as a Configurationally Excited State

We now find the parameters of configuration excitation for liquid gases basing on the *modified lattice model* and thermodynamic parameters of the liquid state of rare gases. In addition, we use the similarity or scaling law (Chapter 9) which allows one to express the various parameters of different rare gases through the parameters of the pair interaction potential of atoms. In this way, one can express various parameters of different rare gases through three parameters – m , the atom mass, R_e , the equilibrium distance between atoms in the diatomic molecule, and D , the depth of the potential well for the pair interaction potential of atoms. Analyzing condensed rare gases in these terms, we found that this is the system where the interaction between nearest neighbors dominates. In this case the sublimation energy of the crystal according to formula (7.28) is close to $6D$, because each internal atom has 12 nearest neighbors, and each bond refers to two atoms. In reality, this value is according to Table 8.2 data 6.4 ± 0.2 . Next, the reduced pressure near the triple point is $(1.9 \pm 0.2) \cdot 10^{-3}$, and below we ignore the pressure effects. Hence, one can characterize the excitation of this system by one parameter of configuration excitation, and we take the number of voids formed v as this parameter.

We will find the parameters of an individual void in the liquid state near the triple point on the basis of parameters of real rare gases. Additional information follows from the fact of the existence of one thermodynamically stable configuration state of this system, which is the liquid state. Then the logarithm of the partition function $\ln Z = -F/T$, where F is the free energy, as a function of the number of internal voids must have the form given in Figure 8.6

and is characterized by two maxima. Thus, considering the configuration excitation of a bulk system of n bound atoms as a result of the formation of a gas of v identical voids, we represent formula (10.7) for the partition function of voids in the bulk limit $n \gg 1, v \gg 1$ in the form

$$\ln Z_v = n \ln \left(1 + \frac{v}{n}\right) + v \ln \left(1 + \frac{n}{v}\right) + v \ln g_v - v \frac{\varepsilon_v}{T} = v \left(\Delta S_v - \frac{\varepsilon_v}{T}\right) \quad (10.12)$$

where the entropy variation due to void formation is

$$\Delta S_v = \frac{1}{x} \ln(1+x) + \ln \left(1 + \frac{1}{x}\right) + \ln g_v, \quad x = v/n \quad (10.13)$$

It is convenient to change this expression to

$$\Delta S_v = 1 + \ln \frac{g_v}{x} \quad (10.14)$$

and this change leads to an error below 7% if $x \leq 1/3$, which includes the whole range between solid and liquid states. Then we have for the specific logarithm of the partition function

$$\Phi(x) \equiv \frac{1}{n} \ln Z_v = x \left(1 + \ln \frac{g_v}{x} - \frac{\varepsilon_v}{T}\right) \quad (10.15)$$

This simplification allows us to follow the assumptions used.

From this we get for the solid (crystal) state ($v \ll n, g_v = 1, \varepsilon_v = \varepsilon_{\text{sol}}$)

$$\ln Z_v = v \left(1 + \ln \frac{n}{v} - \frac{\varepsilon_{\text{sol}}}{T}\right)$$

and the minimum condition gives for the number of voids (vacancies) for the solid state in accordance with formula (10.4)

$$\frac{v_{\text{sol}}}{n} = \exp \left(-\frac{\varepsilon_{\text{sol}}}{T}\right)$$

Applying these formulae to the liquid state of rare gases, we use the enthalpy of excitation ΔH_{fus} for the liquid state

$$v\varepsilon_v = n\Delta H_{\text{fus}} \quad (10.16)$$

Now we represent the equations for the above dependence of $\ln Z(v)$, as occurs in Figure 8.6. The position of the minimum of the function $\ln Z(v)$ is given by the equation $d \ln Z(v)/dv = 0$ or

$$\frac{d}{dv}(vU)(v_{\text{min}}) - \varepsilon_o + T \ln \frac{ng(v_{\text{min}})}{v_{\text{min}}} + T \frac{d \ln g(v_{\text{min}})}{d \ln v} = 0 \quad (10.17)$$

where we use equation (10.12) for $\ln Z(v)$ with expression (10.14) for ΔS_v . For the same equation we have, requiring the maximum of this function for the liquid state,

$$\frac{d}{dv}(vU)(v_{\text{liq}}) - \varepsilon_o + T \ln \frac{ng(v_{\text{liq}})}{v_{\text{liq}}} + T \frac{d \ln g(v_{\text{liq}})}{d \ln v} = 0 \quad (10.18)$$

One more relation corresponds to the melting point T_m of the bulk system under consideration. This temperature corresponds to the equality of the free energies for the solid and liquid states. Since we assume the pressure to be zero, this gives $Z_{\text{sol}}(T_m) = Z_{\text{liq}}(T_m)$, and because of the scale of values used, we have $\ln Z_{\text{sol}}(T_m) = v_{\text{sol}}(T_m) = 0$. Thus, this equation takes the form

$$\ln Z(v_{\text{liq}}) = 1 + \ln \frac{ng(v_{\text{liq}})}{v_{\text{liq}}} - \frac{\Delta H_{\text{fus}}}{T_m} \frac{n}{v_{\text{liq}}} = 0 \quad (10.19)$$

where ΔH_{fus} is the enthalpy of the phase transition, and the values of the binding energy per individual void.

Note that at the melting point according to equations (10.18) and (10.19) we have

$$\Phi(x_{\text{liq}}) = \Phi'(x_{\text{liq}}) = 0 \quad (10.20)$$

where $\Phi(x)$ is defined by formula (10.15). Using the dependence (10.11) for the void statistical weight, we obtain from equation (10.20) at the melting point

$$\frac{dU(x_{\text{liq}})}{dx} = 0 \quad (10.21)$$

or

$$\frac{\alpha}{x_{\text{liq}}} = \frac{\ln k}{k-1} \quad (10.22)$$

and we assume $g(v_{\text{liq}}) \gg 1$. Note that according to its physical nature, the function $U(v/n)$ is monotonic, but equation (10.21) shows the absence of the liquid maximum for the monotonic partition function and therefore the function $U(x)$ has a complex form (10.10) that is valid at $v < v_{\text{liq}}$. We obtain one more equation, assuming that the minimum of the function $\ln Z_v$ of Figure 8.6 relates to the void concentration when a test void has one void as a nearest neighbor. This gives $x_{\text{min}} = 1/12$. Neglecting at this point the second term in the expression (10.10) for $U(x)$, and assuming $g(x_{\text{min}}) \gg 1$, or $a \gg 12$, we obtain from the first equation (10.20) $\Phi'(x_{\text{min}}) = 0$

$$(1 + 12\alpha) \exp(-12\alpha) = 1 - \frac{(1 + \ln a)T_m}{\varepsilon_o} \quad (10.23)$$

We give the values of some void parameters in Table 10.1, where $\varepsilon_v = \varepsilon_{\text{sol}} - U$ is the energy consumed for the formation of one void in the liquid state from the initial solid state. We take the energy of void formation on the basis of formula (10.8), the effective interaction potential of voids $U(v/n)$ and the void statistical weight $g(v)$ are given by formulae (10.10) and (10.11) correspondingly. Table 10.1 contains the values a in formula (10.11). In addition, we give in Table 10.1 the volume per void V_{void} for the liquid state that follows from the relation

$$V_{\text{void}} = \frac{n}{v_{\text{liq}}} (V_{\text{sol}} - V_{\text{liq}}) \quad (10.24)$$

where $V_{\text{sol}}, V_{\text{liq}}$ are the volumes per atom for the solid and liquid states correspondingly (see Table 7.6).

Table 10.1. Reduced parameters of voids for bulk liquid rare gases.

	Ne	Ar	Kr	Xe	Average
T_m/D	0.581	0.587	0.578	0.570	0.579 ± 0.007
ε_o/D	6.1	6.5	6.7	6.7	6.5 ± 0.3
$\Delta H_{\text{fus}}/D$	0.955	0.990	0.980	0.977	0.976 ± 0.017
g_{min}	1.9	2.0	2.0	2.0	2.0
g_{max}	1900	3700	4300	4100	3500 ± 1000
n/v_{liq}	3.12	3.13	3.14	3.13	3.13 ± 0.01
$\varepsilon(v_{\text{liq}})/D$	3.00	3.09	3.05	3.05	3.05 ± 0.04
$\Delta S(v_{\text{liq}})/v_{\text{liq}}$	5.16	5.26	5.28	5.35	5.26 ± 0.08
$V_{\text{void}}/V_{\text{sol}}$	0.49	0.46	0.50	0.47	0.48 ± 0.02
$g(v_{\text{liq}})$	55	62	63	68	62 ± 5
a	171	189	193	207	190 ± 15
$g(v_{\text{min}})$	15	17	17	18	17 ± 1
U_{liq}/D	3.1(3.2)	3.4(3.4)	3.6(3.4)	3.6(3.4)	3.4 ± 0.2
$U_{\text{liq}}/\varepsilon_o$	0.51(0.52)	0.52(0.52)	0.54(0.52)	0.54(0.52)	0.52 ± 0.01
$\Delta S(v_{\text{min}})/v_{\text{min}}$	6.19	6.32	6.32	6.38	6.3 ± 0.1
$\frac{1 - T_m \Delta S(v_{\text{min}})}{\varepsilon_o v_{\text{min}}}$	0.41(0.42)	0.43(0.43)	0.44(0.46)	0.44(0.46)	0.44 ± 0.02
α	0.165(0.162)	0.159(0.159)	0.151(0.157)	0.151(0.157)	0.158 ± 0.005
$\alpha n/v_{\text{liq}}$	0.51	0.50	0.48	0.48	0.49 ± 0.02
k	3.26	3.38	3.56	3.58	3.44 ± 0.15

It follows from the data in Table 10.1 that the relative number of voids for the system of bound atoms with a short-range interaction is $v_{\text{liq}} = (0.320 \pm 0.001)n$, and the ratio of the number of voids for the liquid state and at the minimum of the partition function is $v_{\text{liq}}/v_{\text{min}} = 3.85 \pm 0.02$. The energy of formation of one void for the liquid state is approximately half of that for the solid state. Alongside the parameters of the liquid state, on the basis of the results obtained one can analyze the character of relaxation of the excited state of the regular structure to the liquid state by the transformation of vacancies into voids. On the first stage of the excitation process, when the cluster consisting of n atoms and v vacancies is formed, the average number γ of nearest vacancies for a given one is

$$\gamma = \frac{12v}{n+v} = 2.9 \quad (10.25)$$

In addition, during relaxation of the initial excited state, when the liquid state of the system

is formed, the density of atoms varies from ρ_{ex} to ρ_{liq} , and it increases by about 14%. The specific energy released from this relaxation is about $0.48D$ per atom, and is approximately one half of the fusion energy.

10.5 The Role of Thermal Excitation in the Existence of the Liquid State

Note that the solution of equation (10.19) exists at

$$g(v_{\text{liq}}) > g_{\min} = \exp\left(\frac{\Delta H_{\text{fus}}}{T_m} - 1\right) \quad (10.26a)$$

Next, from this equation and the definition of the fusion energy $\Delta H_{\text{fus}} = \varepsilon(v_{\text{liq}})x_{\text{liq}}$ it follows that

$$g(v_{\text{liq}}) = \frac{\Delta H_{\text{fus}}}{\varepsilon_{\text{liq}}} \exp\left(\frac{\varepsilon_{\text{liq}}}{T_m} - 1\right)$$

where $\varepsilon_{\text{liq}} = \varepsilon(v_{\text{liq}})$ is the energy of void formation for the liquid state at the melting point. Because $g(v)$ is a monotonic function of ε_{liq} , and $\varepsilon_{\text{liq}} < \varepsilon_o$, we obtain from this

$$g(v_{\text{liq}}) < g_{\max} = \frac{\Delta H_{\text{fus}}}{\varepsilon_o} \exp\left(\frac{\varepsilon_o}{T_m} - 1\right) \quad (10.26b)$$

and Table 10.1 contains the values of $g_{\min}$ and $g_{\max}$. It is of importance that the liquid state, i.e. a configurationally excited and thermodynamically stable state of a bulk system of bound

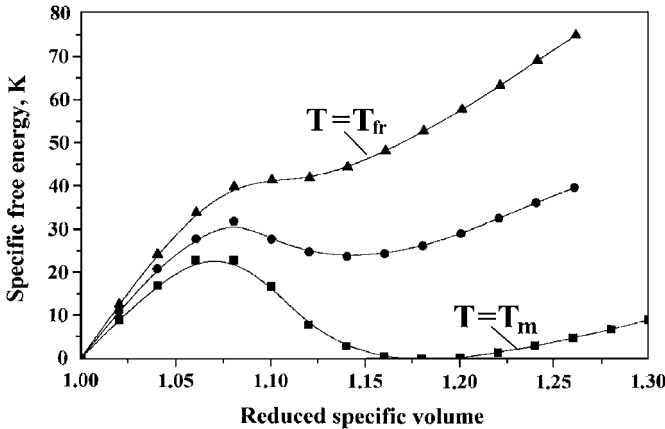


Figure 10.4. The dependence of the specific free energy of condensed rare gases on the reduced volume per one atom. The first minimum in the origin refers to the solid state, the right minimum corresponds to the liquid state, and below the freezing temperature $T = T_{fr}$ the liquid state becomes an unstable one.

atoms, exists only if the void statistical weight is found in a certain range. In particular, if the statistical weight of a void is equal to the statistical weight of a vacancy in the crystal lattice $g = 1$, the liquid state of such a system is absent. Because the void statistical weight is one at zero temperature and increases with the increasing temperature of atomic oscillations, the thermal motion of atoms is of importance for the existence of the liquid state of a system of bound atoms, and this aggregate state is not realized at low temperatures. In contrast, clusters with completed shells have the liquid state because of the high statistical weight of the lowest configurationally excited state. The data of Table 10.1 allow us to determine various parameters of condensed rare gases. In particular, Figure 10.4 contains the specific free energy of bulk rare gases as a function of the reduced excess volume which is proportional to the number of voids. This figure shows the existence of the *freezing point* below which the liquid state is not metastable. Figure 10.5 gives the caloric curves for the solid and liquid states of argon.

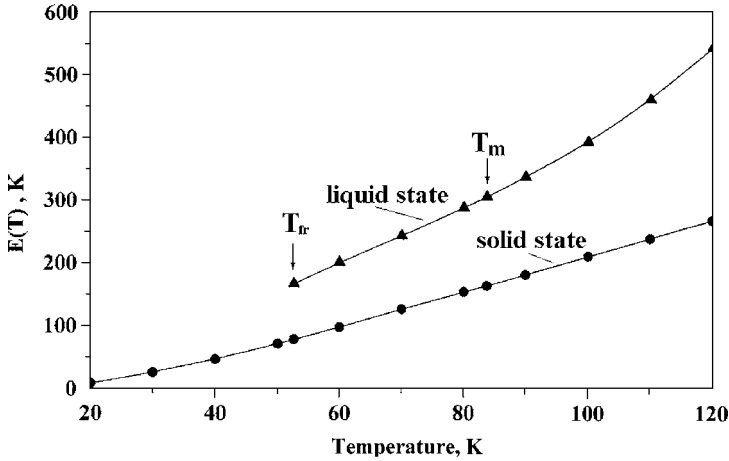


Figure 10.5. Caloric curves for argon – the temperature dependencies for the internal energy of aggregate states. The liquid state finishes at the freezing temperature, and below this temperature it is not metastable state.

We now analyze the results from another standpoint. We represent the entropy of the solid–liquid phase transition as the sum of two parts

$$\Delta S = \Delta S_{conf} + \Delta S_{term} \quad (10.27)$$

so that the first configuration term corresponds to the formation of internal voids, and the second term is related to the thermal motion of atoms. The first term according to formula (10.13) is equal to

$$\Delta S_{conf} = n \ln \left(1 + \frac{v}{n} \right) + v \ln \left(1 + \frac{n}{v} \right)$$

and $\Delta S_{conf}/n = 0.73$ for the above values of void parameters for liquid rare gases. Because the total entropy jump for the phase transition of rare gases is $\Delta S/n = 1.68$, we obtain for

the part due to phonons

$$\Delta S_{term} = 0.95$$

The nature of this term is due to the oscillations of atoms, and this term is 56% of the total entropy. As a result of the phase transition, the specific volume per atom increases, as well as the space volume per atom. This leads to an entropy increase due to atomic motion. If we consider the motion of atoms in the terms of harmonic oscillations, this effect leads to a decrease in the Debye temperature of this system. Let us assume for simplicity that the melting point exceeds the Debye temperature θ_D , so that we use the limiting expression for the entropy of a bulk system of n bound atoms according to the data in Table 3.3, which is equal to

$$S_{osc} = 3n \ln \frac{T}{\theta_D} + 4n \quad (10.28)$$

In this limit, taking $\Delta S_{term} = S_{ocs}$, we find an increase in the Debye temperature as a result of the phase transition by about 40% in the case of validity of the Dulong–Petit law.

Thus, a simple scheme allows us to describe the character of the melting process for a bulk system of atoms with a short-range interaction, i.e. when only nearest neighbors interact. This scheme considers melting as a configuration excitation of the atomic system and models such excitations by means of the formation of voids inside the system. The absence of equilibrium with respect to the number of voids allows us to vary the number of voids continuously, and in this way one can connect the parameters of the solid and liquid states of a system of many bound atoms. Condensed rare gases are real systems with a short-range interaction of atoms, and their thermodynamic parameters for the solid and liquid states at the triple point give the parameters for the microscopic description of the melting process and configuration excitation of the system under consideration. Thus, although thermal and configuration excitations of the system of bound atoms are separated, thermal motion of atoms is of importance for the existence of the liquid aggregate state as a thermodynamically stable state. Indeed, thermal motion gives an additional contribution to the entropy of a configurationally excited, i.e. less compact, state, and in this indirect way thermal motion acts on the parameters of configuration excitation.

10.6 Glassy States and Their Peculiarities

From the standpoint of thermodynamics, a glassy or *vitreous state* is an unstable intermediate state of a system of bound atoms. Figure 10.6 gives the mechanical interpretation of possible states of such a system which was suggested by I. Gutzov, and the *glassy state* in this interpretation is a unstable state. From this interpretation one can see the difference between metastable and unstable states. A small displacement of the system or a small fluctuation leads later to the return of the system to the initial position for the metastable state. In the case of an unstable state, the system does not return to the initial state. Continuing the mechanical interpretation of a glassy state, we consider a particle located in a monotonic potential field (Figure 10.7) where the viscosity of the medium of the particle's location grows as a particle

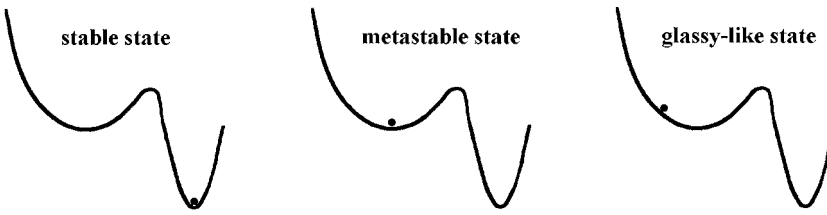


Figure 10.6. The mechanical interpretation for the states of a system according to I. Gutzov: (a) thermodynamically stable state; (b) metastable state; (c) glassy state.

moves down along the potential curve. Then the particle will stop due to the high frictional force, but the stopping point depends on the initial conditions.

In order to understand the nature of glassy states, it is convenient to analyze them for the simplest systems of bound atoms: condensed rare gases. In this case configuration excitation results in the formation of voids inside the system, and from Figure 8.6 it follows that relaxation at any number of voids leads to the transition of the system into the solid or liquid states which correspond to the minimum of the free energy of this system as a function of void number. Then the evolution of the system of bound atoms consists in the diffusion of voids. If the temperature is below the melting point, the liquid state is the metastable state up to the *freezing point* (see Figures 10.4 and 10.5). At temperatures below the freezing point the liquid state does not exist as a metastable one.

The peculiarity of the development of this system consists in the activation character of void motion inside the system. Hence, in rapid cooling of a system of bound atoms, if at the beginning the system is located in the liquid state, one can reach a condition where voids become frozen-in. At low temperatures the rate of void transitions becomes very small, i.e. the lifetime of such unstable states with *frozen voids* becomes very large, practically infinite. Since such transitions were first studied in glasses, the state formed is termed the glassy or vitreous state. But a state with the above properties is typical for various types of systems, in particular, for condensed rare gases and their clusters, the simplest system of bound atoms

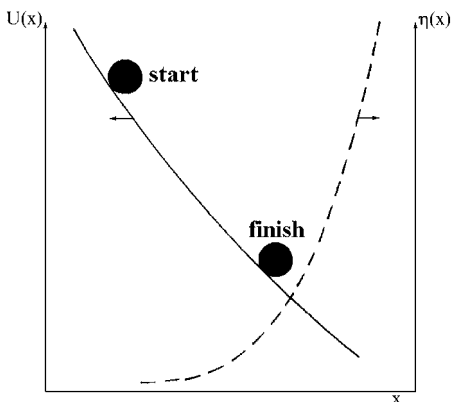


Figure 10.7. The mechanical model of a glassy state. A ball is rolling along an inclined plane in a medium whose viscosity increases sharply with a decreasing altitude. As a result, the ball is stopped due to friction forces, but a stopped point depends on the initial conditions.

where the interaction between nearest neighbors dominates. Below we will be guided by condensed rare gases.

The formation of a glassy state results from the evolution of a system and is connected with the typical time of establishment of an equilibrium state. Therefore, we first consider the character of the transition between aggregate states of the system in the course of variation of its temperature. In particular, in the case of a system of bound atoms with a pair interaction, the establishment of an equilibrium between aggregate states results from the transport of voids. Hence, in the process of establishing equilibrium the system is nonuniform. Nevertheless, for a qualitative analysis we will assume a test region of the system of bound atomic particles to be uniform and introduce the typical times for solid–liquid τ_{sl} and liquid–solid τ_{ls} transitions. According to the *principle of detailed balance*, the connection between these parameters at a given temperature T has the form

$$\frac{1}{\tau_{sl}(T)} = \frac{1}{\tau_{ls}(T)} \cdot \exp\left(\Delta S - \frac{\Delta E}{T}\right) \quad (10.29)$$

where ΔS and ΔE are the changes of entropy and internal energy as a result of the phase transition at a given temperature T .

The balance equations for the evolution of the system as a result of temperature variation have the form

$$\frac{dP_{\text{sol}}}{dt} = -\nu_{sl}P_{\text{sol}} + \nu_{ls}P_{\text{liq}}, \quad \frac{dP_{\text{liq}}}{dt} = \nu_{sl}P_{\text{sol}} - \nu_{ls}P_{\text{liq}} \quad (10.30)$$

where $P_{\text{sol}}(t)$ and $P_{\text{liq}}(t)$ are the probabilities of the system being in the solid and liquid states correspondingly ($P_{\text{sol}} + P_{\text{liq}} = 1$), $\nu_{sl} = 1/\tau_{sl}$ is the rate of transition from the liquid to the solid state, and $\nu_{ls} = 1/\tau_{ls}$ is the rate of the inverse transition. Under small rates of temperature variation dT/dt , the left-hand sides of these equations are relatively small, and the system is in equilibrium at any time

$$P_{\text{sol}}(t) = w_{\text{sol}}[T(t)], \quad P_{\text{liq}}(t) = w_{\text{liq}}[T(t)] \quad (10.31)$$

where the equilibrium probabilities $w_{\text{sol}}(T)$ and $w_{\text{liq}}(T)$ are given by formulae (8.12). In the other limiting case, when a system is cooled rapidly, the probability of transition from the liquid state is small. Then from the set of equations (10.30) it follows for the probability to conserve the liquid state of the system at low temperatures below the melting point T_m

$$P_{\text{liq}} = \exp\left(-\int_T^{T_m} \nu_{ls}(T) \left(\frac{dT}{dt}\right)^{-1} dT\right) \quad (10.32)$$

Because of the activation character of the transition between aggregate states, in accordance with formula (10.29), we have for the rate of transition from the liquid state

$$\nu_{ls}(T) \sim \exp\left(-\frac{\varepsilon_a}{T}\right) \quad (10.33)$$

where ε_a is the activation energy of this transition. The integral (10.32) is valid if $P_{\text{sol}} \ll 1$, and assuming that the integral (10.32) converges near the melting point T_m , we obtain this

formula in the form

$$P_{\text{liq}} = 1 - \frac{T_m^2}{\varepsilon_a \frac{dT}{dt}} \nu_{ls}(T_m)$$

and this formula relates to low temperatures $T < T_m$, when the transition process finishes. Thus, the transition in the solid state is weak, and formula (10.29) holds true if the following criterion for the cooling rate is valid

$$\left| \frac{dT}{dt} \right| \gg \frac{T_m^2}{\varepsilon_a} \nu_{ls}(T_m) \quad (10.34)$$

Note that the rates of the direct and inverse processes are equal at the melting point $\nu_{ls}(T_m) = \nu_{sl}(T_m)$. The criterion (10.34) characterizes the possibility of forming a glassy state on rapid cooling of a system of bound atoms.

We now consider the decay of a glassy state on heating. A glassy state prepared at low temperatures is conserved due to its large lifetime, but heating can lead to a transition into the solid state at the *glassy temperature* T_g . This temperature corresponds to equality of the rates of heating and transition into the solid state, and hence according to the above formulae follows from the relation

$$\frac{dT}{dt} = \frac{T_g^2}{\varepsilon_a} \nu_{ls}(T_g) \quad (10.35)$$

In considering configurationally excited states of condensed matter, we are guided by a system of atoms with a pair interaction between them. Then the liquid state differs from the solid one by voids inside the system. In these terms, a glassy state also contains voids, but in contrast to the liquid state, the concentration of voids can be arbitrary. The transition of this system from the liquid or glassy state into the solid one results in the departure of voids outside the system. When this system of bound atoms in the liquid state is cooled rapidly, voids cannot leave the system and remain partially inside it. Hence the glassy state that forms is close to the liquid state at the melting point. Another method of creating a glassy state under consideration is rapid condensation of a vapor on a target at low temperature. In this way a glassy state is formed, and its heating can lead to formation of the solid state. Because of the presence of voids inside the system, the glassy state, as well as the liquid state, is characterized by an *amorphous structure*, in contrast to the crystal structure of the solid state.

Thus, according to the definition, the glassy state is a thermodynamically unstable state of bound atoms that can be formed by rapid cooling of the system if an infinitely slow cooling leads to the transition of an activation type between two aggregate states of this system. For glasses this transition is accompanied by changing the positions of some radicals, and finally the crystal structure of glass molecules is formed by infinitely slow cooling. One more peculiarity of this transition corresponds to different densities of structures for the initial and final states. Therefore, along with restructuring of molecule positions, voids must be transported to the boundary of this system or vice versa.

Switching to simple bulk systems of bound atoms, such as condensed rare gases, we find that the restructuring of chemical bonds is absent in such systems, but the transport of voids proceeds by analogy with glasses and has the activation character. The glass-like state of such

a system may be prepared by two methods: rapid cooling of the liquid aggregate state or deposition of an atom flux on a substratum at low temperatures below the melting point with the formation of a random distribution of atoms.

One can see by analogy the formation of the glassy state of a system of bound atoms and the general properties of nonequilibrium systems. Indeed, we consider two degrees of freedom for the system of bound atoms, so that the first relates to the thermal motion of atoms, and the second to configuration excitation. If transitions between configurationally excited states take a long time in comparison with typical times of evolution of this system, the coupling between the thermal and configurational degrees of freedom is broken, and the degree of configuration excitation of the system does not depend on its temperature. Then a glassy state of this system may be formed. Thus, configurationally excited states of a bulk system of bound atoms may include both thermodynamically stable or metastable states, i.e. the aggregate states, and thermodynamically unstable states, which at low temperature correspond to glassy or glass-like states.

Part III

Processes and Non-equilibrium Atomic Systems

11 Collision Processes Involving Atomic Particles

11.1 Elementary Collisions of Particles

A weak interaction between atomic particles in a system of free identical particles leads to a certain distribution of particles by states. Acts of strong interaction of particles seldom proceed and therefore only two particles take part in each strong particle interaction. Hence the particle interaction results in processes of *collision of two particles*. Below we analyze the character of collision of two atomic particles and find parameters which describe such a collision. Let us denote the colliding atomic particles by A and B , and first consider a collision of these particles which leads to a change in the internal state of particle A . Denoting the initial state of this particle by the subscript i and the final state by the subscript f , we assume that each collision of particles can result only in a transition between these states, so that a test particle A can finally transfer from a state i in a state f in collisions with particles B . Then the probability $P(t)$ that particle A conserves the initial state up to time t is given by the equation:

$$\frac{dP}{dt} = -\nu_{if} P \quad (11.1)$$

where ν_{if} is the probability of transition per unit time.

Let us use the frame of reference where a test particle A is motionless. The probability of transition per unit time ν_{if} is proportional to the incident flux j of particles B . Hence, the characteristic of the elementary act of particle collisions is the quantity ν_{if}/j which is the *cross section* of the process and does not depend on the number density of particles B . If all the particles B move with identical velocity $\mathbf{v}_B$, their flux is equal to $|\mathbf{v}_A - \mathbf{v}_B| [B]$, where $[B]$ is the number density of particles B , and $\mathbf{v}_A$ is the velocity of particle A . Thus the rate of transition ν_{if} is expressed through the cross section of the transition σ_{if} by the relationship:

$$\nu_{if} = [B] |\mathbf{v}_A - \mathbf{v}_B| \sigma_{if} \quad (11.2)$$

and the cross section σ_{if} can depend on the relative velocity of particles.

If particles A and B are characterized by a certain distribution of velocities, the probability of transition per unit time is

$$\nu_{if} = [B] \langle |\mathbf{v}_A - \mathbf{v}_B| \sigma_{if} \rangle = [B] \langle k_{if} \rangle \quad (11.3)$$

where the angle brackets mean averaging over the relative velocities of particles, and the value $k_{if} = \langle |\mathbf{v}_A - \mathbf{v}_B| \sigma_{if} \rangle$ is called the *rate constant* of the process. This parameter also characterizes the elementary act of collision. The rate constant of the process is useful if the total rate of the process averaging over particle velocities is of interest.

Let us write the *balance equation* for the number density N_i of particles A which are found in a given state i . The balance equation takes into account transitions of particles of this species in other states and has the form

$$\frac{dN_i}{dt} = [B] \sum_f k_{fi} N_f - [B] N_i \sum_f k_{if} \quad (11.4)$$

where k_{if} is the rate constant for transition between states i and f of a particle A resulting from collision with a particle B . The balance equation (11.4) may be extended by the addition of other processes.

Both the rate constant of the process and its cross section can be used as characteristics of the elementary collision event. The physical sense of the cross section can be explained as follows. Take a test particle A passing through a plane including particles B with number per unit area n . As a result of this process, the test particle can transfer from an initial state i to a final state f . Then the probability of this transition is $n\sigma_{if}$, and if $n\sigma_{if} \ll 1$, the value σ_{if} is the effective area around the scattered particle where the transition proceeds.

11.2 Elastic Collisions of Particles

In order to ascertain the character of scattering of two interacting particles, we consider below an elementary process of elastic scattering of two particles in detail. In the case of *elastic collisions* of particles, the internal states of particles do not change but the particles change their velocities. The motion of classical particles is described by the following Newton's equations

$$M_1 \frac{d^2 \mathbf{R}_1}{dt^2} = -\frac{\partial U}{\partial \mathbf{R}_1}, \quad M_2 \frac{d^2 \mathbf{R}_2}{dt^2} = -\frac{\partial U}{\partial \mathbf{R}_2}$$

Here $\mathbf{R}_1$ and $\mathbf{R}_2$ are the coordinates of the corresponding particles, M_1 and M_2 are their masses, and U is the interaction potential of particles, which depends on the relative distance between the particles, i.e. $U = U(\mathbf{R}_1 - \mathbf{R}_2)$. Then $\partial U / \partial \mathbf{R}_j$ is the force acting on this particle due to the other one, and $\partial U / \partial \mathbf{R}_1 = -\partial U / \partial \mathbf{R}_2$.

Let us introduce new variables – the vector of the relative distance between them $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$ and the vector of the center of mass of particles $\mathbf{R}_c = (M_1 \mathbf{R}_1 + M_2 \mathbf{R}_2) / (M_1 + M_2)$. Newton's equations in these variables take the form:

$$(M_1 + M_2) \frac{d^2 \mathbf{R}_c}{dt^2} = 0, \quad \mu \frac{d^2 \mathbf{R}}{dt^2} = -\frac{\partial U}{\partial \mathbf{R}}$$

Here $\mu = M_1 M_2 / (M_1 + M_2)$ is the *reduced mass* of the particles. As we have seen, the center of mass travels with a constant velocity, and scattering is determined by the character of the relative motion of the particles in the center of mass frame. Although the above analysis was made within the framework of classical mechanics, in quantum mechanics the situation is the same. Indeed, in quantum mechanics free motion also takes place for the center of mass of particles in the absence of external fields, and collisions are characterized by the relative motion of particles. Thus, in the absence of external fields the problem of collisions of two

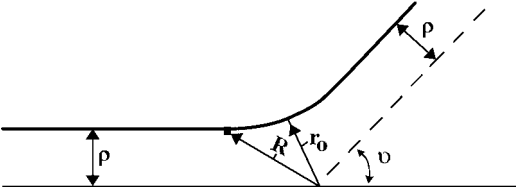


Figure 11.1. The trajectory of relative motion of two colliding particles in the center-of-mass reference frame and collision parameters: ϑ is the scattering angle, ρ is the impact parameter of collision, r_o is the distance of closest approach.

particles is reduced to the problem of the motion of one particle with a reduced mass in a central field. Figure 11.1 indicates the parameters which describe the elastic scattering of classical particles.

If the interaction potential of colliding particles is spherically symmetric, a simple connection between the *impact parameter* ρ and the *distance of closest approach* r_o follows from the conservation of the angular momentum of particles in a central field. The angular momentum is $\mu\rho v$ at large distances between particles and is $\mu v_\tau r_o$ at the distance of closest approach. Here $v = |\mathbf{v}_1 - \mathbf{v}_2|$ is the relative velocity of the particles and v_τ is the tangential component at the distance of closest approach where the normal component of the velocity equals zero, so that the law of energy conservation gives $\mu v_\tau^2/2 = \mu v^2/2 - U(r_o)$. This leads to the following relationship:

$$1 - \frac{\rho^2}{r_o^2} = \frac{U(r_o)}{\varepsilon} \quad (11.5)$$

where $\varepsilon = \mu v^2/2$ is the kinetic energy of particles in the center of mass frame of reference.

We determine the cross section of scattering in the center of mass frame of reference where scattering can be considered as the motion of one particle of the reduced mass μ in the field $U(R)$. Introduce the *differential cross section* of a collision as the ratio of the number of scattering events per unit time and unit solid angle to a flux of incident particles. In the case of a central force field the elementary solid angle is equal to $d\Theta = 2\pi d\cos\vartheta$, and particles are scattered over this angle element from the range of impact parameters from ρ up to $\rho + d\rho$. Because the particle flux is Nv , where N is the number density of particles B , and v is their relative velocity, the number of particles scattered per unit time into a given solid angle is $2\pi\rho d\rho Nv$, so that the differential cross section is equal to

$$d\sigma = 2\pi\rho d\rho \quad (11.6)$$

Elastic scattering of particles determines various gaseous and plasma parameters. Usually the transport parameters of gases are determined by the large-angle scattering of particles. To estimate the typical cross section of scattering at large angles we note that the interaction potential at the distance of closest approach is comparable to the kinetic energy of colliding particles, and this cross section is given by the relation:

$$\sigma = \pi\rho_o^2, \quad \text{where} \quad U(\rho_o) \sim \varepsilon \quad (11.7)$$

Note that the case of Coulomb interaction of charged particles is an exception to the conclusion that the main contribution to the diffusion cross section of scattering (11.8) gives large scattering angles, because in this case the differential cross section has a logarithmic divergence at small angles of scattering. In a plasma, the minimal scattering angles are determined both by Debye–Hückel shielding of charges and by many-body scattering.

11.3 Hard Sphere Model

In the case of a repulsive exchange interaction between atoms, as occurs for atoms with completed electron shells (atoms of rare gases) the repulsive interaction potential increases sharply with decreasing distance between atoms. Then the collision of atoms is described by the *hard sphere model*, which is based on the model interaction potential of atoms having the form

$$U(R) = 0, \quad r > R_o; \quad U(R) = \infty, \quad r < R_o \quad (11.9)$$

where R_o is the interaction radius of particles. The hard sphere model is used widely in the kinetics of neutral gases for scattering of atomic particles.

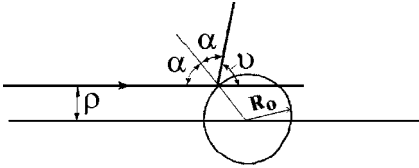


Figure 11.2. Scattering of particles in the center-of-mass reference frame in the case of the hard sphere model.

Let us determine the cross section of scattering within the framework of the hard sphere model. Figure 11.2 gives the dependence of the distance of closest approach on the impact parameter of collision. In this case the scattering is similar to scattering on a hard spherical surface. It follows from Figure 11.2 that the scattering angle is $\vartheta = \pi - 2\alpha$, where $\sin \alpha = \rho/R_o$, i.e. $\rho = R_o \cos(\vartheta/2)$. This gives for the differential cross section, from formula (11.6):

$$d\sigma = 2\pi\rho d\rho = \frac{\pi R_o^2}{2} d\cos\vartheta \quad (11.10a)$$

and we obtain for the diffusion cross section of scattering:

$$\sigma^* = \pi R_o^2 \quad (11.10b)$$

Formula (11.10b) corresponds to a general formula (11.7) that gives an estimate for the cross section of scattering at large angles.

11.4 Cross Section of Capture

Let us consider the case of scattering of attractive atomic particles. In this case the distance of closest approach is less than the impact parameter of collision, which follows from formula (11.5). For simplicity, we approximate the interaction potential by the dependence $U(R) =$

$-C/R^n$. Then if $n > 2$, starting from some impact parameter of collision ρ_c , the distance of closest approach is zero, i.e. the incident particle falls on the center of the target particle. In reality, repulsion between atomic particles takes place at small distances; nevertheless, this character of approach of particles is valid for slow atomic particles.

We determine the impact parameter of capture as the minimum of the dependence $\rho(r_o)$ that follows from formula (11.5)

$$\rho^2 = r_o^2 \left(1 + \frac{C}{r_o^n \varepsilon} \right)$$

From the minimum of this function we find the *capture cross section*

$$\sigma_c = \pi \rho_c^2 = \frac{\pi n}{n-2} \left[\frac{C(n-2)}{2\varepsilon} \right]^{2/n} \quad (11.11)$$

One can see that the dependence of the cross section on parameters is similar to that of formula (11.7) for the cross section of scattering at large angles. In particular, in the case of the polarization interaction of an ion and an atom $U(R) = -\alpha e^2/(2R^4)$, where α is the atom polarizability, and the polarization cross section of ion-atom capture is equal to

$$\sigma_c = 2\pi \sqrt{\frac{\alpha e^2}{\mu v^2}} \quad (11.12)$$

These results are useful for the analysis of scattering of attractive atomic particles.

11.5 Liquid Drop Model

The *liquid drop model* describes *liquid clusters* – systems of finite numbers of bound atoms in the liquid state – and within the framework of this model we assume clusters to have a spherical shape and bulk density. Under these conditions the radius r of the liquid drop which models the cluster under consideration, is connected to the number of cluster atoms n by the relation

$$n = \frac{4\pi\rho}{3m} r^3 = \left(\frac{r}{r_W} \right)^3 \quad (11.13a)$$

where ρ is the density of a bulk liquid, and m is the atomic mass, and the *Wigner-Seitz radius* is

$$r_W = \left(\frac{3m}{4\pi\rho} \right)^{1/3} \quad (11.13b)$$

The liquid drop model corresponds to the hard sphere model for collision processes involving clusters if the cluster radius r is large compared to the typical atomic size a that characterizes the region of action of atomic forces on the cluster surface. In this approximation the cross section of attachment of an atomic particle to a cluster consisting of n atoms is

$$\sigma = \pi r^2 \xi \quad (11.14)$$

where ξ is the probability of atom joining a surface after contact. Correspondingly, the rate constant of such a collision averaged over the velocities of an atomic particle is equal to

$$k_n = \langle v \pi r^2 \xi \rangle = \sqrt{\frac{8T}{\pi m}} \cdot \pi r^2 \xi = k_o n^{2/3} \xi \quad (11.15)$$

where the angle brackets mean an average over velocities v of the colliding atomic particles, m is the mass of the colliding atomic particles, T is the temperature of these atomic particles, and the reduced rate constant is given by

$$k_o = \pi r_W^2 \cdot \sqrt{\frac{8T}{\pi m}} = \pi \cdot \sqrt{\frac{8T}{\pi m}} \cdot \left(\frac{3m}{4\pi\rho} \right)^{2/3} = 1.93 T^{1/2} m^{1/6} \rho^{-2/3} \quad (11.16)$$

Table 11.2 contains the values of the Wigner–Seitz radius (11.14) and the reduced rate constant k_o for metallic clusters in the liquid state at the melting point.

Table 11.2. Parameters of metallic clusters. The Wigner–Seitz radius is defined by formula (11.14), k_o is given by formula (11.16) at the melting point and is expressed in 10^{-11} cm³/s, the saturated vapor pressure is $p_{\text{sat}}(T) = p_o \exp(-\varepsilon_o/T)$, and the parameter p_o is given in 10^5 atm.

Metal	T_m, K	$r_W, \text{\AA}$	k_o	ε_o, eV	p_o	Metal	T_m, K	$r_W, \text{\AA}$	k_o	ε_o, eV	p_o
Li	454	1.75	11	1.61	1.3	Mo	2886	1.60	6.4	6.3	59
Be	1560	1.28	9.8	3.12	23	Rh	3237	1.55	6.2	5.42	7.7
Na	371	2.14	8.4	1.08	0.63	Pd	1828	1.58	4.7	3.67	4.4
Mg	923	1.82	9.3	1.44	1.1	Ag	1235	1.66	4.3	2.87	15
Al	933	1.65	7.3	3.09	11	Cd	594	1.77	3.3	1.06	1.4
K	336	2.65	9.4	0.91	0.37	In	430	1.87	3.1	2.38	0.17
Ca	1115	2.24	12	1.67	0.72	Sn	505	1.89	3.4	3.10	0.24
Sc	1814	1.81	9.5	3.57	8	Sb	904	1.95	4.7	1.5	0.03
Ti	1941	1.67	8.1	4.89	300	Cs	301	3.05	6.4	0.78	0.24
V	2183	1.55	7.2	4.9	46	Ba	1000	2.54	8.0	1.71	0.17
Cr	2180	1.41	5.9	3.79	30	Ta	3290	1.68	5.5	8.1	250
Fe	1812	1.47	5.6	3.83	11	W	3695	1.60	5.2	8.59	230
Co	2750	1.45	6.6	4.10	3.5	Re	3459	1.58	4.9	7.36	63
Ni	1728	1.44	5.1	4.13	47	Os	3100	1.55	4.4	7.94	230
Cu	1358	1.47	4.6	3.40	15	Ir	2819	1.58	4.4	6.44	130
Zn	693	1.58	3.7	1.22	1.6	Pt	2041	1.60	3.8	5.6	170
Ga	303	1.65	2.6	2.76	2.0	Au	1337	1.65	3.2	3.65	12
Ge	1211	1.63	5.0	3.70	15	Hg	334	1.80	1.9	0.62	7.7
Rb	312	2.85	7.1	0.82	0.28	Tl	577	1.93	2.9	1.78	2.0
Sr	1050	2.44	9.4	1.5	0.32	Pb	600	1.97	3.0	1.95	1.0
Zr	2128	1.85	7.6	6.12	52	Bi	544	2.02	3.0	1.92	50
Nb	2750	1.68	7.0	7.35	360	U	1408	1.77	3.5	4.95	5.4

Let us evaluate the rate constant of joining of two clusters within the framework of the liquid drop model for clusters. Then clusters join if they touch each other, and the cross section of the collision process with joining of clusters is

$$\sigma = \pi(r_1 + r_2)^2 \quad (11.17)$$

where r_1 and r_2 are the radii of the colliding clusters. The rate constant of this process is

$$k = \langle v \cdot \pi(r_1 + r_2)^2 \rangle = \sqrt{\frac{8T}{\pi\mu}} \cdot \pi(r_1 + r_2)^2 = k_o \sqrt{\frac{n_1 + n_2}{n_1 n_2}} \cdot (n_1^{1/3} + n_2^{1/3})^2 \quad (11.18)$$

Here v is the relative cluster velocity, μ is the reduced mass of the colliding clusters, the angle brackets mean averaging over cluster velocities, and n_1 and n_2 , are the numbers of cluster atoms; above we have used formula (11.13) for the number of cluster atoms. According to this formula, the rate constant of association of two large neutral clusters with the same order of sizes $n_1 \sim n_2 \sim n$ is of order of $k(n_1, n_2) \sim k_o n^{1/6}$.

11.6 Association of Clusters in Dense Buffer Gas

We now determine the rate constant of the joining of two large clusters in a dense buffer gas within the framework of the liquid drop model. We take clusters to be large in comparison with the mean free path of gaseous atoms in a buffer gas. Then the approach of the clusters results from their diffusion motion. If we fix one cluster, the flux of clusters of the second type toward the surface of a test cluster is given by

$$j = -D \frac{\partial N}{\partial R}$$

where D is the diffusion coefficient of clusters in a buffer gas, R is the distance from the test cluster, and N is the number density of clusters of the second type. Assuming that these clusters are absorbed by a test cluster, we obtain $N = 0$ at $R = r$, where r is the sum of the radii of the associating clusters. Because the attaching clusters disappear on the surface of a test cluster only, we have $J = 4\pi R^2 j = \text{const.}$ From the solution of this equation with the above boundary condition we obtain $N = N_o(1 - r/R)$, where N_o is the number density of attaching clusters far from the absorbing center. From this follows the *Smoluchowski formula* for the number of associating clusters per unit time

$$J = 4\pi D r N_o$$

and the rate constant of this process is given by

$$k_{as} = 4\pi D r \quad (11.19)$$

In this formula D is the diffusion coefficient which is responsible for the approach of the clusters. In particular, according to the nature of the diffusion motion, for the relative distance between clusters we have

$$\overline{\mathbf{R}^2} = \overline{(\mathbf{R}_1 - \mathbf{R}_2)^2} = 6Dt$$

if at the beginning the clusters are located together. Here t is time, $\mathbf{R}_1$ and $\mathbf{R}_2$ are the coordinates of the associating clusters, and a bar means averaging over time. Let us express the diffusion coefficient D of the relative motion of clusters through the diffusion coefficients D_1 and D_2 of these clusters in a buffer gas. By definition, we have $\overline{\mathbf{R}_1^2} = 6D_1t$, $\overline{\mathbf{R}_2^2} = 6D_2t$, so that

$$\overline{\mathbf{R}^2} = \overline{(\mathbf{R}_1 - \mathbf{R}_2)^2} = \overline{\mathbf{R}_1^2} + \overline{\mathbf{R}_2^2} = 6(D_1 + D_2)t$$

We take into account that the motion of the clusters is independent, so that $\overline{\mathbf{R}_1 \mathbf{R}_2} = \overline{\mathbf{R}_1} \cdot \overline{\mathbf{R}_2} = 0$. Thus, for the rate constant of association of two clusters we get

$$k_{as} = 4\pi(D_1 + D_2)(r_1 + r_2)$$

Using the *Stokes formula* for the friction force acting on a spherical cluster in a dense buffer gas or liquid and the Einstein relation between the mobility and diffusion coefficient of a spherical cluster in a dense gas, we obtain for the diffusion coefficient of a large cluster in a dense gas

$$D = \frac{T}{6\pi r \eta}, \quad r \gg \lambda$$

where r is the particle's radius, λ is the mean free path of gaseous atomic particles, and η is the gas viscosity. From this we get for the rate constant of association of two large clusters in a dense buffer gas

$$k_{as} = \frac{2T}{3\eta} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) (r_1 + r_2) = \frac{8T}{3\eta} \left[1 + \frac{(r_1 - r_2)^2}{4r_1 r_2} \right] \quad (11.20)$$

For clusters of similar size the second term in parentheses is small in comparison with the others.

11.7 The Resonant Charge Exchange Process

Alongside the elastic processes of collisions of atomic particles, when the states of particles do not change as a result of collision, the resonant or quasisresonant processes may be significant for the establishment of equilibria in the system of atomic particles. Such collisions are accompanied by a change of the internal states of colliding atomic particles with zero or small variation of the internal energy for these particles. We demonstrate this for the *resonant charge exchange* process, which is an example of resonant processes and is of importance for the transport of atomic ions in a parent gas. Resonant charge exchange proceeds according to the scheme:



where M is an atom, and as a result of this process a valence electron transfers from the field of one ion to the other one. For simplicity, we assume the atom to have one electron state.

According to the symmetry of this problem, the eigenstates of the quasimolecule consisting of the colliding ion and atom can be even or odd depending on whether the corresponding wave functions conserve or change their sign as a result of electron reflection with respect to the symmetry plane. This plane is perpendicular to the axis joining the nuclei and passes through its middle. The eigenenergies of these states ε_g and ε_u depend on the distance R between the nuclei of the colliding atom and ion. At large separations the electron eigenwave functions ψ_g and ψ_u are expressed through the wave functions ψ_1 and ψ_2 corresponding to the location of the valence electron in the field of the first and second atomic cores by the formula

$$\psi_g = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2), \quad \psi_u = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2) \quad (11.22)$$

Because the wave functions ψ_g and ψ_u are the eigenfunctions of the electron Hamiltonian $\hat{H}$, they satisfy the Schrödinger equations:

$$\hat{H}\psi_g = \varepsilon_g\psi_g, \quad \hat{H}\psi_u = \varepsilon_u\psi_u \quad (11.23)$$

We introduce also the exchange interaction potential between an ion and atom on the basis of the formula

$$\Delta(R) = \varepsilon_g(R) - \varepsilon_u(R)$$

In slow collisions when the distance between nuclei R varies slowly in time, one can solve the Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

which describes the evolution of the system of the colliding ion and atom. Then we neglect inelastic transitions between the odd and even states of the quasimolecule consisting of colliding ion and atom. Using the initial condition, such that the electron is located in the field of the first atomic core at the beginning, we have the wave function at $t \rightarrow -\infty$ in the form $\Psi(\mathbf{r}, \mathbf{R}, -\infty) = \psi_1(\mathbf{r})$, where $\mathbf{r}$ is the sum of electron coordinates. Thus, in the absence of inelastic transitions we have for the wave function of the colliding ion and atom

$$\begin{aligned} \Psi(\mathbf{r}, \mathbf{R}, t) = & \frac{1}{\sqrt{2}}\psi_g(\mathbf{r}, \mathbf{R}) \exp \left[-\frac{i}{\hbar} \int_{-\infty}^t \varepsilon_g(t') dt' \right] \\ & + \frac{1}{\sqrt{2}}\psi_u(\mathbf{r}, \mathbf{R}) \exp \left[-\frac{i}{\hbar} \int_{-\infty}^t \varepsilon_u(t') dt' \right] \end{aligned} \quad (11.24)$$

From this we find the probability of resonant charge exchange P_{12} if in the limit $t \rightarrow \infty$ the valence electron is located in the field of the second atomic core

$$\begin{aligned} P_{12} = & |\langle \psi_2(\mathbf{r}) | \Psi(\mathbf{r}, \mathbf{R}, t) \rangle|^2 = \sin^2 \int_{-\infty}^{\infty} \frac{(\varepsilon_g - \varepsilon_u)}{2\hbar} dt \\ = & \sin^2 \int_{-\infty}^{\infty} \frac{\Delta(R)}{2\hbar} dt, \quad \Delta = \varepsilon_g - \varepsilon_u \end{aligned} \quad (11.25)$$

This gives for the cross section of the resonant charge exchange process:

$$\sigma_{\text{res}} = \int_0^{\infty} 2\pi \rho d\rho \sin^2 \int_{-\infty}^{\infty} \frac{\Delta(R)}{2\hbar} dt \quad (11.26)$$

Let us calculate this integral taking into account a strong dependence $\Delta(R)$. For this goal we take the phase of resonant charge exchange

$$\zeta(\rho) = \int_{-\infty}^{\infty} \frac{\Delta(R)}{2\hbar} dt = A\rho^{-n}$$

where ρ is the impact parameter of collision, and $n \gg 1$. We obtain

$$\sigma_{\text{res}} = \int_0^{\infty} 2\pi \rho d\rho \sin^2 \zeta(\rho) = \frac{\pi}{2} (2A)^{2/n} \Gamma\left(1 - \frac{2}{n}\right) \cos \frac{\pi}{n}$$

Writing the result in the form

$$\sigma_{\text{res}} = \frac{\pi R_o^2}{2} f_n$$

where R_o is determined by the relation $\zeta(R_o) = a$, so that the function f_n is equal to

$$f_n = (2a)^{\frac{2}{n}} \Gamma\left(1 - \frac{2}{n}\right) \cos \frac{\pi}{n}$$

It is convenient to take the parameter a such that the second term in the expansion of the function f_n over a small parameter $1/n$ would be zero. This gives $a = e^{-C}/2 = 0.28$, where $C = 0.557$ is the Euler constant. Then the function f_n is given by

$$f_n = \exp\left(-\frac{2C}{n}\right) \Gamma\left(1 - \frac{2}{n}\right) \cos \frac{\pi}{n}$$

and its expansion for large n has the form

$$f_n = 1 - \frac{\pi^2}{6n^2}$$

In reality, the dependence of the exchange interaction ion-atom potential is determined by the overlap of two electron wave functions whose centers are located on different nuclei, so that at large ion-atom distances R this dependence has the form $\Delta \sim \exp(-\gamma R)$, where $\gamma \sim 1/a_o$, and a_o is the Bohr radius. This leads to an exponential dependence $\zeta(\rho) \sim e^{-\gamma\rho}$ at large ρ , and since we approximate the phase of resonant charge exchange $\zeta(\rho)$ as a power function $\zeta(\rho) \sim \rho^{-n}$ of the impact parameter ρ , this corresponds to $n = \gamma\rho \gg 1$. Because of the large value of the cross section of resonant charge exchange, large impact parameters of collisions ρ give the main contribution to the cross section. In such collisions $n = \gamma\rho \gg 1$,

so that the above expansion for $n \gg 1$ holds true, and the expression for the cross section of the resonant charge exchange process can be represented in the form

$$\sigma_{\text{res}} = \frac{\pi R_o^2}{2}, \quad \text{where} \quad \zeta(R_o) = \frac{e^{-C}}{2} = 0.28 \quad (11.27)$$

Appendix B6 contains values of the cross sections of the resonant charge exchange process at the collision energies 0.1, 1 and 10 eV in the laboratory frame of reference where an atom is motionless. It follows from these data that the resonant exchange cross section is large and exceeds the typical gas-kinetic cross section ($\sim 10^{-15} \text{ cm}^2$). In addition, at the collision energy 0.1 eV the parameter $n = \gamma R_o = 12 - 19$ for the cases under consideration for ion-atom collisions when atom and ion are found in the ground states.

Let us determine the dependence of the cross sections of the resonant charge exchange process on the collision velocity. Since $\Delta \sim e^{-\gamma R}$, we have $\zeta(R_o) \sim e^{-\gamma R_o}/v$, where v is the collision velocity. From this it follows that

$$R_o = \frac{1}{\gamma} \ln \frac{v_o}{v}$$

where the parameter $v_o \gg e^2/\hbar$ exceeds a typical atomic value. Thus we obtain the following dependence of the charge exchange cross section on the collision velocity:

$$\sigma_{\text{res}} = \frac{\pi R_o^2}{2} = \frac{\pi}{2\gamma^2} \ln^2 \frac{v_o}{v} \quad (11.28a)$$

In addition, we have from this

$$\alpha = \frac{d \ln \sigma_{\text{res}}(v)}{d \ln v} = -\frac{2}{R_o \gamma} \quad (11.28b)$$

and since $R_o \gamma \gg 1$, the velocity dependence of $\sigma_{\text{res}}(v)$ is weak. The data of Appendix B6 demonstrate a weak dependence $\sigma_{\text{res}}(v)$, so that the increase of the collision velocity by an order of magnitude leads to a decrease in the cross section of approximately a factor of 1.5.

11.8 The Principle of Detailed Balance for Direct and Inverse Processes

The *principle of detailed balance* establishes the connection between the cross sections of direct and inverse processes. Its basis is such that the time reversal leads to an inverse process. For definiteness, we demonstrate this with an example of the excitation and quenching processes which are described by the scheme



and we will find the connection between the cross sections of the direct and inverse processes. Let us take one particle A and one particle B in a volume Ω , where the particle A can be found only in states i and f . Due to equilibrium, the number of transitions $i \rightarrow f$ per unit time w_{if} is connected by a simple expression with the number of transitions $f \rightarrow i$ per unit time, which

we denote by w_{fi} . Indeed, introducing the interaction operator V which is responsible for these transitions, we have within the framework of the perturbation theory for the transition rates

$$w_{if} = \frac{2\pi}{\hbar} |V_{if}|^2 \frac{dg_f}{d\varepsilon}, \quad w_{fi} = \frac{2\pi}{\hbar} |V_{fi}|^2 \frac{dg_i}{d\varepsilon}$$

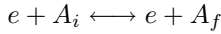
Here $\frac{dg_f}{d\varepsilon}$ and $\frac{dg_i}{d\varepsilon}$ are the statistical weights per unit energy for the corresponding channels of the process. Use the definition of the cross sections of these processes:

$$\sigma_{if} = \frac{w_{if}}{Nv_i} = \Omega \frac{w_{if}}{v_i}, \quad \sigma_{fi} = \frac{w_{fi}}{Nv_f} = \Omega \frac{w_{fi}}{v_f}$$

where $N = 1/\Omega$ is the number density of particles and v_i and v_f are the relative velocities of particles for the corresponding channels. The time reversal gives for the matrix elements of the interaction potential $V_{if} = V_{fi}^*$. This leads to the following relation between the cross sections of the direct and inverse processes:

$$\sigma_{if} v_i \frac{dg_i}{d\varepsilon} = \sigma_{fi} v_f \frac{dg_f}{d\varepsilon} \quad (11.29)$$

Let us use this relation for the inelastic collision of an electron and atom if the collision process proceeds according to the scheme



Then v_i and v_f are the electron velocities for the corresponding channel of the process, and the statistical weight of the corresponding channel is equal to

$$dg_f = \Omega \frac{d\mathbf{p}_f}{(2\pi\hbar)^3} g_f$$

where g_f is the statistical weight of an electronic atom state. Then formula (11.29) takes the form:

$$\sigma_{if} = \sigma_{fi} \frac{v_f^2 g_f}{v_i^2 g_i} \quad (11.30)$$

In particular, near the threshold the *excitation cross section* σ_{ex} has the form ($\sigma_{\text{ex}} = \sigma_{jff}$):

$$\sigma_{\text{ex}} = C \sqrt{E - \Delta\varepsilon}$$

where E is the energy of the incident electron and $\Delta\varepsilon$ is the excitation energy for this transition. Then according to formula (11.30) the cross section of *atom quenching* $\sigma_q = \sigma_{fji}$ resulting from collision with a slow electron of energy $\varepsilon = E - \Delta\varepsilon \ll \Delta\varepsilon$ is equal to

$$\sigma_q = C \frac{g_o \Delta\varepsilon}{g_* \sqrt{E - \Delta\varepsilon}}$$

where we use the notations $j = o$ for the lower state and $f = *$ for the upper state. From this it follows that the rate constant of atom quenching by a slow electron is

$$k_q = v_f \sigma_q = C \frac{g_o \Delta \varepsilon \sqrt{2}}{g_f \sqrt{m_e}} \quad (11.31a)$$

and the rate constant k_{ex} of atom excitation by electron impact is equal to

$$k_{ex} = k_q \frac{g_*}{g_o} \sqrt{\frac{E - \Delta \varepsilon}{\Delta \varepsilon}} = k_q \frac{g_*}{g_o} \sqrt{\frac{\varepsilon}{\Delta \varepsilon}} \quad (11.31b)$$

Thus the quenching rate constant k_q does not depend on the electron energy (m_e is the electron mass) and on the energy distribution function of electrons. Hence it depends only on the parameters of atomic states of the transition. In particular, in the case of quenching of a resonantly excited state when this process is effective, the quenching rate constant within the framework of the perturbation theory is approximately

$$k_q = a \frac{g_o f}{g_* (\Delta \varepsilon)^{3/2}} = \frac{b}{(\Delta \varepsilon)^{7/2} \tau_{*o}}$$

where f is the oscillator strength, τ_{*o} is the radiative lifetime for this transition, and λ is the wavelength of the emitting photon; a and b are numerical coefficients. If the excitation energy $\Delta \varepsilon$ is expressed in eV, and the radiative lifetime is given in ns, the numerical coefficient is $b = 4.3 \cdot 10^{-5} \text{ cm}^3/\text{s}$, if we use experimental data. The accuracy of this formula for quenching of resonantly excited states is about 20%, and Table 11.3 contains the quenching rate constants for some resonantly excited atoms. The rate constant of quenching of atom metastable states by electron impact is lower than those for resonantly excited states because of a more weak coupling between these states during interaction with an electron. This is demonstrated by comparison of the data of Table 11.3 with those of Table 11.4, where these rate constants are given for metastable rare gas atoms.

Let us consider collision processes with a change in the reduced mass of colliding particles as a result of these processes. We first analyze the process of *dissociative recombination* and the inverse process of *associative ionization*



Denoting by σ_{rec} the cross section of dissociative recombination and by σ_{ion} the cross section of associative ionization, we obtain on the basis of formula (11.29)

$$v_e g_e g + \frac{\Omega d \mathbf{p}_e}{(2\pi \hbar)^3} \sigma_{\text{rec}} = v_a g_A g_B \frac{\Omega d \mathbf{p}_a}{(2\pi \hbar)^3} \sigma_{\text{ion}}$$

where the subscripts e , $+$, A , B and a refer respectively to the electron, the molecular ion AB^+ , atoms A and B and to the relative motion of atoms. In addition, the energy conservation in this process yields

$$\frac{m_e v_e^2}{2} = \frac{\mu v_a^2}{2} + \Delta \varepsilon$$

Table 11.3. The parameters of resonantly excited atom states of some atoms and the rate constant of quenching of these states by slow electron impact.

Atom, transition	$\Delta\varepsilon$, eV	λ , nm	f	τ_{*0} , ns	k_q , 10^{-8} cm ³ /s
H($2^1P \rightarrow 1^1S$)	10.20	121.6	0.416	1.60	0.79
He($2^1P \rightarrow 1^1S$)	21.22	58.43	0.276	0.555	0.18
He($2^1P \rightarrow 2^1S$)	0.602	2058	0.376	500	51
He($2^3P \rightarrow 2^3S$)	1.144	1083	0.539	98	27
Li($2^2P \rightarrow 2^2S$)	1.848	670.8	0.74	27	19
Na($3^2P \rightarrow 3^2S$)	2.104	589	0.955	16.3	20
K($4^2P_{1/2} \rightarrow 4^2S_{1/2}$)	1.610	766.9	0.35	26	31
K($4^2P_{3/2} \rightarrow 4^2S_{1/2}$)	1.616	766.5	0.70	25	32
Rb($5^2P_{1/2} \rightarrow 5^2S_{1/2}$)	1.560	794.8	0.32	28	32
Rb($5^2P_{3/2} \rightarrow 5^2S_{1/2}$)	1.589	780.0	0.67	26	33
Cs($6^2P_{1/2} \rightarrow 6^2S_{1/2}$)	1.386	894.4	0.39	30	46
Cs($6^2P_{3/2} \rightarrow 6^2S_{1/2}$)	1.455	852.1	0.81	27	43

Table 11.4. The rate constant of quenching of metastable states of rare gas atoms by slow electron impact.

Atom, transition	$\Delta\varepsilon$, eV	k_q , 10^{-10} cm ³ /s
He($2^3S \rightarrow 1^1S$)	19.82	31
Ne($2^3P_2 \rightarrow 2^1S$)	16.62	2.0
Ar($3^3P_2 \rightarrow 3^2S$)	11.55	4.0
Kr($4^3P_2 \rightarrow 4^2S_0$)	9.915	3.4
Xe($5^2P_2 \rightarrow 5^2S_0$)	8.315	19

The data are taken from: N. B. Kolokolov in: *Chemistry of Plasma*, ed. B. M. Smirnov (Energoatomizdat, Moscow, 1985). v. 12, pp. 56–95.

where μ is the reduced mass of atoms, $\Delta\varepsilon$ is the energy of transition. From this follows the connection between the cross sections of these processes

$$m_e^2 v_e^2 g_{e,g} \sigma_{\text{rec}}(v_e) = \mu^2 v_a^2 g_{A,g} \sigma_{\text{ion}}(v_a) \quad (11.33)$$

where the argument of the cross section indicates a velocity which corresponds to this cross section.

One more example of direct and inverse processes with a change in the reduced mass of the colliding particles relates to the process that proceeds according to the scheme



The direct process is now photoattachment of an electron to an ion or the *photorecombination* process, and the inverse process is *photoionization* of an atom. The relationship (11.31) and

the condition of energy conservation have the following form for these processes

$$v_e g_e g_+ \frac{\Omega d\mathbf{p}_e}{(2\pi\hbar)^3} \cdot \sigma_{\text{rec}} = c g_A \frac{\Omega \cdot 2d\mathbf{k}}{(2\pi)^3} \cdot \sigma_{\text{ion}}, \quad \frac{m_e v_e^2}{2} + J = \hbar\omega$$

Here σ_{rec} and σ_{ion} are the cross sections of photorecombination and photoionization correspondingly, c is the velocity of light, $\mathbf{k}$ is the photon wave vector, 2 is the photon statistical weight (number of polarizations), J is the atom ionization potential, and $\hbar\omega$ is the photon energy; other notations are the same as in the previous case. Using the dispersion relation $\omega = kc$, introducing the electron wave vector $q = m_e v_e / \hbar$, and taking $g_e = 2$ (two spin directions), we get the following relation between the above cross sections

$$\sigma_{\text{rec}} = \frac{g_A}{g_+} \cdot \frac{k^2}{q^2} \cdot \sigma_{\text{ion}} \quad (11.35)$$

Thus the principle of detailed balance gives the relation between the cross sections of direct and inverse processes. Note that the parameters of direct and inverse processes are transformed into each other as a result of time reversal $t \rightarrow -t$.

11.9 Three-body Processes and the Principle of Detailed Balance

As a result of *three-body process*



two colliding atomic particles X and Y form a bound state, and the energy excess is taken by a third atomic particle M . The rate constant of the three-body process γ has dimensionality cm^6/s and allows one to determine the rate of formation of bound states of the colliding atomic particles according to the balance equation

$$\frac{d[XY]}{dt} = \gamma[X][Y][M] \quad (11.37)$$

where $[Z]$ is the number density of atomic particles Z .

The rate constant of the three-body process may be estimated on the basis of the *Thomson theory* which is based on the nature of this process. The formation of a bound state of atomic particles X and Y takes place if a third particle M takes the kinetic energy of the associating particles, i.e. an energy of the order of the thermal energy T of the colliding particles. The association of two atomic particles X and Y can proceed if the attraction potential between atomic particles X and M or Y and M is of the order of the thermal energy or exceeds it. We define a critical radius b by the relation

$$U(b) \sim T$$

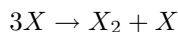
where $U(R)$ is the interaction potential of the atomic particles X and Y . Then the rate of association for a particle X is the rate $v\sigma[Y]$ of its collision with particles Y multiplying by the probability $b^3[M]$ of location of a third atomic particle in the critical region. Here v is a

typical velocity of collision of particles X and Y and σ is the cross section of this collision. Comparing the resulting rate of the association process with that following from the balance equation (11.37), we find for the three-body rate constant which corresponds to the Thomson theory

$$\gamma \sim vb^3\sigma \quad (11.38)$$

Note that we used the classical character of particle motion in deriving this formula.

The formula is simple in the case if the process proceeds in a pure gas according to the scheme



Then $\sigma \sim b^2$, and taking into account the numerical coefficients, the rate constant of the three-body process has the form

$$\gamma = 6\sqrt{\frac{T}{M}}b^5 \quad (11.39)$$

where M is the mass of a particle X . Table 11.5 gives the values of this rate constant for rare gases at the boiling point.

Table 11.5. The rate constant of the three-body process $3X \rightarrow X_2 + X$ for rare gases at the boiling point T_b .

X	Ne	Ar	Kr	Xe
T_b, K	27.0	87.3	120	165
$\gamma(T_b), 10^{-33} \text{ cm}^6/\text{s}$	1.8	6.1	7.1	10

We now consider the *principle of detailed balance* for rates of direct and inverse processes in the case of the three-body process and derive the relation between the rate constants of dissociation and three-body association of particles, so that the direct and inverse processes are described by the scheme (11.36). The balance equation for the number density of components has the form

$$\frac{d[XY]}{dt} = \gamma[X][Y][M] - k_{\text{dis}}[XY][M] \quad (11.40)$$

Here $[Z]$ is the number density of a component Z , γ is the rate constant of the three-body process which is expressed in units cm^6/s and k_{dis} is the rate constant of dissociation of a molecule XY resulting from collision with an atom M . First we assume all the particles to be found in thermodynamic equilibrium, so that the ratio of the number densities of particles is equal to

$$\frac{[X]_o[Y]_o}{[XY]_o} = K_{\text{dis}}(T)$$

where the subscript o means the equilibrium values of the number densities and $K(T)$ is the equilibrium constant for a given system. The equilibrium constant for dissociation equilibrium, if molecules are found in the ground state, is given by formula (5.29). Next, from the balance equation (11.40) it follows that at

$$\frac{[X]_o[Y]_o}{[XY]_o} = \frac{k_{\text{dis}}}{\gamma}$$

Thus from this we have the relation between the rate constants of the direct and inverse processes

$$k_{\text{dis}}(T) = K_{\text{dis}}(T)\gamma(T) \quad (11.41)$$

Note that the equilibrium conditions which we used to derive this relation is only a method, and this relation is valid if one can introduce the same temperature for both the translational motion of atoms and the internal motion in the molecule. The equilibrium between the number density of atoms and molecules may be violated.

11.10 The Principle of Detailed Balance for Processes of Cluster Growth

Another example of a transition with the formation of a bound state of colliding particles is *cluster growth* and the inverse processes which correspond to the scheme



Below we consider the cluster M_n , which is a system of n bound atoms M on the basis of the *liquid drop model*. Within the framework of this model, the cluster is considered as a bulk liquid drop of spherical form, the density of which coincides with the density of the bulk liquid, and the radius r of such a cluster is connected to the number of cluster atoms by formula (11.13). We now consider the equilibrium (11.42) near a flat bulk surface if the process of attachment of vapor atoms to clusters which determines cluster growth is equal to the evaporation of clusters. The attachment flux of atoms to a bulk surface is the product of three factors:

$$j_{\text{at}} = \sqrt{\frac{T}{2\pi m}} \cdot N\xi \quad (11.43)$$

so that the first factor is the average velocity component in the direction perpendicular to the surface, m is the mass of the atom, N is the atom number density and ξ is the probability of an atom joining a surface after contact. The flux of evaporating atoms from a bulk surface is given by the formula:

$$j_{\text{ev}} = C \exp\left(-\frac{\varepsilon_o}{T}\right) \quad (11.44)$$

where ε_o is the binding energy of atoms on the bulk surface (see Table 11.1), parameter C depends weakly on the temperature and is determined by the properties of the surface. If the

atom number density is equal to the number density of saturated vapor N_{sat} at this temperature, the attachment flux becomes equal to the evaporation flux

$$j_{\text{ev}} = j_{\text{at}} = \sqrt{\frac{T}{2\pi m}} N_{\text{sat}}(T) \xi$$

where we take the saturated vapor pressure as $N_{\text{sat}}(T) = N_o \exp(-\varepsilon_o/T)$. Thus we have for the factor C in formula (11.44) for a bulk surface

$$C = \sqrt{\frac{T}{2\pi m}} N_o \xi$$

Within the framework of the liquid drop model for a cluster, the rate constant k_n of atom attachment is given by formula (11.15). To evaluate the rate of cluster evaporation, we assume the cluster surface to be similar to the bulk rate, but the binding energy of cluster surface atoms ε_n differs from the binding energy ε_o of atoms of a bulk surface. Then formula (11.44) for the *evaporation flux of atoms* takes the form

$$\begin{aligned} j_{\text{ev}} &= C \exp\left(-\frac{\varepsilon_n}{T}\right) = \sqrt{\frac{T}{2\pi m}} N_{\text{sat}}(T) \xi \exp\left(-\frac{\varepsilon_n - \varepsilon_o}{T}\right) \\ &= k_n N_{\text{sat}}(T) \exp\left(-\frac{\varepsilon_n - \varepsilon_o}{T}\right) \end{aligned}$$

This gives for the rate of cluster evaporation ν_{n+1} , i.e. for the number of evaporating atoms per unit time

$$\nu_{n+1} = k_n N_{\text{sat}}(T) \exp\left(-\frac{\varepsilon_n - \varepsilon_o}{T}\right) \quad (11.45)$$

Table 11.1 and Appendix B8 contain the values of ε_o at the melting point for the liquid state of metallic clusters.

Relations (11.44) and (11.45) take into account the connection between the direct and inverse processes. We used the fact that the fluxes of attaching and evaporating atoms are identical for a flat surface in a saturated vapor. Note that if the translational temperature T differs from the cluster temperature T_{cl} , which is connected with the vibrations of atoms inside clusters, the last relation takes the form

$$\nu_{n+1} = k_n(T) N_{\text{sat}}(T_{cl}) \exp\left(-\frac{\varepsilon_n - \varepsilon_o}{T_{cl}}\right) \quad (11.46)$$

We here take into account that the translational temperature T relates to free atoms, and the cluster temperature T_{cl} refers to the temperature of bound atoms. Then the atom attachment process is characterized by the temperature T of free atoms, while the evaporation process is connected with the temperature T_{cl} of bound atoms.

12 Kinetic Equation and Collision Integrals

12.1 The Boltzmann Kinetic Equation

We deal in statistical physics with almost closed systems consisting of a large number of particles. These systems interact weakly with their environment, so that the parameters of a closed system are conserved for a long period. A system of many particles can be divided into subsystems. One can consider a subsystem as a closed system for a certain time, which is the shorter the smaller the subsystem is. If we have a gas of free particles, the smallest subsystems are individual particles. Then the subsystem is closed, or the particle is free between two neighboring collisions, a time of the order of λ/v , where v is the typical velocity of particles and $\lambda = (N\sigma)^{-1}$ is its *mean free path* (N is the number density of particles, σ is the cross section of collision of two particles). Because we consider a gas of particles, according to the criterion (11.1) of a gas $\lambda \gg \sigma^{1/2}$, for most of the period of observation a particle does not interact with the surrounding particles, while during short intervals of time it collides with other particles. These collisions lead to an essential change of the particle's state, and because this seldom occurs, only pair interactions of particles determine the evolution of particles in time. Below we derive the *kinetic equation* which describes the behavior of a gaseous system of particles, taking into account pair collisions of particles.

The peculiarity of this description of the evolution of gaseous particles is as follows. First, we account for pair collisions of particles, which in the case of a gas of identical particles X proceed according to the scheme:

$$X(\mathbf{v}_1, J_1) + X(\mathbf{v}_2, J_2) \rightarrow X(\mathbf{v}'_1, J'_1) + X(\mathbf{v}'_2, J'_2) \quad (12.1)$$

Here we describe the particle state by its velocity $\mathbf{v}$ and a set of internal quantum numbers J ; the subscript indicates the particle number. From this it follows that the cross section of particle collision is the parameter which determines the interaction between particles in the system. Being guided by the statistical description of the system, we deal with the average parameters and neglect their fluctuations.

Let us introduce the *distribution function* of particles on parameters $f(\mathbf{v}, J, \mathbf{r}, t)$ to describe the system of particles under consideration, such that $f(\mathbf{v}, J, \mathbf{r}, t)d\mathbf{v}$ is the number of particles per unit volume at point $\mathbf{r}$ at moment t which have a set J of internal quantum numbers and a velocity in the range $\mathbf{v}$ to $\mathbf{v} + d\mathbf{v}$. It follows from the normalization condition that the number density of particles at point $\mathbf{r}$ at moment t is equal to

$$N(\mathbf{r}, t) = \sum_J \int f(\mathbf{v}, J, \mathbf{r}, t)d\mathbf{v} \quad (12.2)$$

The distribution function allows us to analyze the evolution of the system. The *kinetic equation* that describes evolution of the distribution function with time has the form

$$\frac{df}{dt} = I_{\text{col}}(f) \quad (12.3)$$

where $I_{\text{col}}(f)$ is the so-called *collision integral* which takes into account the variation of the number of particles in a given state as a result of pair collisions.

Let us write down the left-hand side of the kinetic equation which describes the motion of particles in an external field in the absence of collisions. We have:

$$\frac{df}{dt} = \frac{f(\mathbf{v} + d\mathbf{v}, \mathbf{J}, \mathbf{r} + d\mathbf{r}, t + dt) - f(\mathbf{v}, J, \mathbf{r}, t)}{dt}$$

In the absence of collisions $d\mathbf{v}/dt = \mathbf{F}/m$, where $\mathbf{F}$ is the force of an external field which acts on one particle, m is the particle mass, and $d\mathbf{r}/dt = \mathbf{v}$. Thus

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \mathbf{v} \frac{\partial f}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m} \frac{\partial f}{\partial \mathbf{v}}$$

and the kinetic equation (12.3) takes the form:

$$\frac{\partial f}{\partial t} + \mathbf{v} \frac{\partial f}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m} \frac{\partial f}{\partial \mathbf{v}} = I_{\text{col}}(f) \quad (12.4)$$

Equation (12.4) is called the *Boltzmann kinetic equation*. It describes the evolution of a gaseous system.

12.2 Collision Integral

The collision integral of the kinetic equation accounts for pair collisions of particles. Because we consider a gas of particles, the typical relaxation time of the distribution function in a gas can be estimated as $\tau \sim (N\sigma v)^{-1}$, where v is a typical collision velocity, N is the number density of particles and σ is the cross section of collision of two particles. On the basis of this value one can suggest a simple approximation for the collision integral:

$$I_{\text{col}}(f) = -\frac{f - f_o}{\tau} \quad (12.5)$$

where f_o is the equilibrium distribution function. This approximation is called the *tau approximation* (τ -approximation). Let us illustrate this approximation with a simple example. Let us disturb an equilibrium state of the system which is described by the distribution function f_o , so that the distribution function at the initial time is $f(0)$. Then the subsequent evolution of the system is described by the equation

$$\frac{df}{dt} = -\frac{f - f_o}{\tau}$$

and its solution has the form:

$$f = f_o + [f(0) - f_o] \exp\left(-\frac{t}{\tau}\right)$$

Thus τ is the *relaxation time* of the system which is of the order of the time between the neighboring collisions of a test particle with other particles. Of course, this time can depend on the collision velocity.

The collision integral accounts for the variation of the distribution function as a result of the pair collisions of atomic particles. We now analyze the collision integral for an atomic gas when it is expressed through the cross section of elastic scattering of atomic particles. Introduce the probability of transition per unit time and unit volume $W(\mathbf{v}_1 J_1, \mathbf{v}_2 J_2 \rightarrow \mathbf{v}'_1 J'_1, \mathbf{v}'_2 J'_2)$ so that $W d\mathbf{v}'_1 d\mathbf{v}'_2$ is the probability per unit time and per unit volume for the collision of two atomic particles with velocities $\mathbf{v}_1$ and $\mathbf{v}_2$, if their final velocities are located in an interval from $\mathbf{v}'_1$ up to $\mathbf{v}'_1 + d\mathbf{v}'_1$ and from $\mathbf{v}'_2$ up to $\mathbf{v}'_2 + d\mathbf{v}'_2$ correspondingly; the internal quantum numbers of atomic particles are changed from J_1 and J_2 to J'_1 and J'_2 . By definition, the collision integral is equal to

$$I_{\text{col}}(f) = \int (f'_1 f'_2 W' - f_1 f_2 W) d\mathbf{v}'_1 d\mathbf{v}'_2 d\mathbf{v}_2 \quad (12.6)$$

where we denote $f_1 = f(\mathbf{v}_1)$ and $W = W(\mathbf{v}_1 J_1, \mathbf{v}_2 J_2 \rightarrow \mathbf{v}'_1 J'_1, \mathbf{v}'_2 J'_2)$, and other values are denoted in the same manner. In addition, we sum in formula (12.6) over the quantum numbers J_2, J'_1, J'_2 . Below, for simplicity, we omit the internal quantum numbers.

Let us use the *principle of detailed balance* which accounts for reversal evolution of a system in the case of time reversal $t \rightarrow -t$. This corresponds to the change $\mathbf{v}_1 \longleftrightarrow \mathbf{v}'_1, \mathbf{v}_2 \longleftrightarrow \mathbf{v}'_2$, so that from this principle it follows that $W = W'$. We use the definition of the cross section of elastic scattering (see Chapter 11) which is the ratio of the number of scattering events per unit time to the flux of incident particles. The differential cross section of elastic scattering is given by

$$d\sigma = \frac{f_1 f_2 W d\mathbf{v}_1 d\mathbf{v}_2 d\mathbf{v}'_1 d\mathbf{v}'_2}{|\mathbf{v}_1 - \mathbf{v}_2| f_1 d\mathbf{v}_1 f_2 d\mathbf{v}_2} = \frac{W d\mathbf{v}'_1 d\mathbf{v}'_2}{|\mathbf{v}_1 - \mathbf{v}_2|}$$

Substitution of this expression in formula (12.6) yields for the collision integral

$$I_{\text{col}}(f) = \int (f'_1 f'_2 - f_1 f_2) |\mathbf{v}_1 - \mathbf{v}_2| d\sigma d\mathbf{v}_2 \quad (12.7)$$

We can see that nine integrations in formula (12.6) are changed into five integrations in formula (12.7). This means that the law of conservation of momentum for colliding particles (three integrations) and the law of conservation of their total energy (one more integration) are taken into account in the expression (12.7). Note that this form of the collision integral is valid not only for the process (12.1) involving identical particles, but also in the case where the evolution of atomic particles is determined by collisions with atomic particles of another type. In particular, the behavior of electrons in a buffer gas is determined by the collisions of electrons with atoms. Then the collision integral has the form

$$I_{\text{col}}(f) = \int (f' \varphi' - f \varphi) |\mathbf{v} - \mathbf{v}_a| d\sigma d\mathbf{v}_a \quad (12.8)$$

where $\mathbf{v}$ and $\mathbf{v}_a$ are the velocities of electrons and atoms, $f = f(\mathbf{v})$ is the distribution function of electrons, and $\varphi = \varphi(\mathbf{v}_a)$ is the distribution function of atoms.

12.3 Equilibrium Gas

Let us consider the equilibrium of an atomic gas when the kinetic equation (12.4) has the form $I_{\text{col}}(f) = 0$. Using formula (12.7) for the collision integral, we conclude that it requires the fulfillment of the relation $f_1 f_2 = f'_1 f'_2$ for any pair of colliding atoms. Rewrite this relation in the form:

$$\ln f(\mathbf{v}_1) + \ln f(\mathbf{v}_2) = \ln f(\mathbf{v}'_1) + \ln f(\mathbf{v}'_2) \quad (12.9)$$

This relation shows that $\ln f(\mathbf{v})$ is the additive function of the integrals of motion. Taking into account the conservation laws for the total momentum and energy of atoms, we obtain the general form of the distribution function:

$$\ln f(\mathbf{v}) = C_1 + C_2 \mathbf{p} + C_3 \varepsilon$$

where $\mathbf{p}$ and ε are the momentum and kinetic energy of the atomic particle, and C_1 , C_2 and C_3 are constants. This gives for the distribution function:

$$f(\mathbf{v}) = A \exp [-\alpha(\mathbf{v} - \mathbf{w})^2] \quad (12.10)$$

We can see that this expression is identical to formula (2.29) for the *Maxwell distribution* function if A is the normalization constant, $\mathbf{w}$ is the average velocity of the distribution, and $\alpha = m/(2T)$, where m is the particle mass and T is the gaseous temperature.

12.4 The Boltzmann *H*-Theorem

The *Boltzmann H-theorem* confirms the principal law in statistical physics that entropy increases if a system tends to equilibrium. Let us introduce the functional

$$H(t) = \int f(\mathbf{v}, t) \ln f(\mathbf{v}, t) d\mathbf{v} ,$$

where $f(\mathbf{v}, t)$ is the distribution function for gaseous particles. Let us prove that in a gas in the absence of external fields we have $dH/dt \leq 0$.

The kinetic equation for the distribution function has the form

$$\frac{\partial f_1}{\partial t} = \int W(\mathbf{v}_1, \mathbf{v}_2 \rightarrow \mathbf{v}'_1, \mathbf{v}'_2) (f'_1 f'_2 - f_1 f_2) d\mathbf{v}'_1 d\mathbf{v}'_2 d\mathbf{v}_2$$

so that

$$\frac{dH}{dt} = \int W(\mathbf{v}_1, \mathbf{v}_2 \rightarrow \mathbf{v}'_1, \mathbf{v}'_2) (f'_1 f'_2 - f_1 f_2) \ln f_1 d\mathbf{v}'_1 d\mathbf{v}'_2 d\mathbf{v}_1 d\mathbf{v}_2 + \frac{d}{dt} \int f_1 d\mathbf{v}_1$$

The second term on the right-hand side of the equation is zero because of the conservation of the total number of particles, and in the first term we use the symmetry of the rate

$W(\mathbf{v}_1, \mathbf{v}_2 \rightarrow \mathbf{v}'_1, \mathbf{v}'_2)$ with respect to the change $\mathbf{v}_1 \longleftrightarrow \mathbf{v}_2$ and $\mathbf{v} \longleftrightarrow \mathbf{v}'_1, \mathbf{v}_2 \longleftrightarrow \mathbf{v}'_2$. This gives

$$\frac{dH}{dt} = \frac{1}{4} \int W(\mathbf{v}_1, \mathbf{v}_2 \rightarrow \mathbf{v}'_1, \mathbf{v}'_2) (f'_1 f'_2 - f_1 f_2) \ln \left(\frac{f_1 f_2}{f'_1 f'_2} \right) d\mathbf{v}'_1 d\mathbf{v}'_2 d\mathbf{v}_1 d\mathbf{v}_2$$

Because $W \geq 0$, the function $(y - x) \ln \frac{x}{y}$ is negative at any positive values of variables x and y , and is zero if $x = y$. From this it follows that:

$$\frac{dH}{dt} \leq 0 \quad (12.11)$$

One can see that $\frac{dH}{dt} = 0$ at $f_1 f_2 = f'_1 f'_2$, that is at the equilibrium conditions (12.9). From the Boltzmann H -theorem (12.11) it follows that the evolution of a gas in the absence of external fields leads to the equilibrium distribution of its particles.

12.5 Entropy and Information

The Boltzmann H -functional is analogous to the *entropy* of the system S , which according to formula (2.22) has the form

$$S = - \sum_i w_i \ln w_i \quad (12.12)$$

where w_i is the probability for the system to be found in i th state. The other entropy definition is given by formula (2.25):

$$S = \ln \Gamma \quad (12.13)$$

where Γ is the effective number of states of a given energy. If a system consists of independent subsystems, the probability of a given state of the system is the product of the probabilities of corresponding states of subsystems. Hence, from formula (12.13) it follows that the entropy of the system is the additive function of the entropies of subsystems

$$S = \sum_k S_k$$

where S_k is the entropy of the k th subsystem.

The entropy of the system is connected with the *information* about this system. Indeed, according to Shannon's definition of information for a given system, it is given by the expression

$$I = - \sum_i w_i \ln w_i \quad (12.14)$$

where w_i is the probability that this system is found in the i th state. This definition coincides with formula (12.12) for the entropy, but there is a significant difference between these

quantities. Indeed, we define the entropy before determining a particular distribution of particles over states, while information is known after obtaining the distribution by states. For example, if we know exactly the distribution of particles by states, the entropy of this system is zero, while information about the system is given by formula (12.14). In contrast, if we know nothing about the state in which the system is located, the system entropy is determined by formula (12.12), which coincides with (12.14), whereas the information is zero. A partial determination of the distribution of a system over states decreases the entropy of the system and increases the information about the system by the same value. Thus, due to the identical definitions (12.12) and (12.14) for entropy and information, we have the following relation between these quantities

$$S + I = 0 \quad (12.15)$$

This means that obtaining some information about a system leads to a corresponding decrease in its entropy.

So, if we have a known distribution of particles by states, the entropy of the system under consideration is zero and the subsequent development of this system leads to an increase in its entropy. As a result of the evolution of this system, we get an equilibrium with a random distribution of particles over states. Hence from this consideration we conclude that a system tends to an equilibrium distribution by states, and the evolution of the system to equilibrium is accompanied by an increase in entropy. Thus the entropy of a system increases when the system tends to equilibrium and is close to a constant when the system is found in equilibrium. This statement corresponds to the *second law of thermodynamics*.

12.6 The Irreversibility of the Evolution of Physical Systems

This conclusion is that the increase in entropy is the definition of the equilibrium state of a system of particles as a random distribution of particles by states. But it contradicts the dynamical description of the evolution of an ensemble of atomic particles when particles are moving along certain trajectories in the classical case or are described by a certain combination of wave packets in the quantum case. This contradiction results from the different character of the distribution function of particles under the statistical and dynamic descriptions. Based on the dynamic description, we know definitely the state of the system, as well as the state of each its particle at a given time, while the framework of statistical physics is based on the probabilities of the location of a test particle by states. Hence the statistical description is based on a random distribution of particles by states, while under dynamic description this state is known definitely on the basis of Newton's or Schrödinger's equations.

Let us consider this contradiction from another standpoint. If the initial state of a system of atomic particles differs significantly from the equilibrium one, the evolution of the system leads to the equilibrium state over a certain time t . But if we stop this system at the moment t and leave it to develop in the reverse direction, the system remains in the equilibrium state at any time, including time t , because according to the H -theorem of Boltzmann the entropy can not decrease. This means that the evolution of this system is irreversible with respect to the time direction under the statistical description, while the laws of classical and quantum mechanics are reversible with respect to this operation. Evidently, the mechanical and statistical

methods are the limiting cases of the description of a system of many particles depending on the degree of randomization of this system. Below we consider a simple example which helps us to analyze the character of the above contradiction and shows under which conditions the laws of statistical physics are working together with the law of increasing entropy.

Let n particles be located in a cubic box of edge L , and these particles reflect elastically from the box walls and scatter elastically in collision with other each. Under these conditions, each particle moves along a certain trajectory, and then the system of particles is subjected to a mechanical description, i.e. time reversal leads to each particle moving along its trajectory in the reverse direction. But if we take into account the oscillations of walls due to their nonzero temperature, this will lead to randomization and to an increase in the entropy of this system in time. We now analyze the character of entropy growth in this case.

Introduce a typical random displacement δr and a velocity change δv which a particle acquires as the result of a single reflection from vibrating walls. Taking v as a typical particle velocity, we find a typical time $t_o = L/v$ between neighboring collisions of a test particle with the walls. Evidently, after k reflections from the walls which last a time $t \approx kt_o$, we have the following random displacement of a particle coordinate Δr and velocity Δv

$$\Delta r^2(t) = \sum_{i=1}^k \delta r_i^2 \sim \delta r^2 k = \delta r^2 \frac{t}{t_o}, \quad \Delta v^2(t) \sim \delta v^2 \frac{t}{t_o}$$

where δr_i^2 is the amplitude squared of the wall displacement during the i th particle collision with the walls. Assuming the collisions of a particle with the walls to be isotropic, we have from this for the entropy of a test particle on the basis of formula (12.13)

$$S_w(t) = \ln \frac{\delta x(t) \Delta y(t) \Delta z(t) \Delta p_x(t) \Delta p_y(t) \Delta p_z(t)}{(2\pi\hbar)^3} \approx 3 \ln \left[\frac{\delta r \delta v}{(2\pi\hbar)^3} \cdot \frac{t}{t_o} \right]$$

or

$$S_w(t) - S(t_o) = 3 \ln \frac{t}{t_o} \quad (12.16a)$$

Note that after total randomization the entropy of a test particle $S_{\max}$ is (the entropy of the total system of particle is this value multiplied by a number of particles)

$$S_{\max} - S(t_o) = 3 \ln \left(\frac{L}{\delta r} \cdot \frac{v}{\delta v} \right) \quad (12.16b)$$

and comparison of the expression with the previous one allows us to find the randomization time as a result of particle reflection from the walls.

Another mechanism of randomization follows from pair collisions of particles. In considering this effect, whose role in randomization was established by Poincaré, we take the trajectory of an individual particle to be constructed from straight segments which turn after each collision. Taking a random displacement of the impact parameter of collision before the first collision to be $\delta \rho$, we obtain for the variation of the scattering angle in the first collision $\delta \theta_1 \sim \delta \rho / \rho_o$, where ρ_o is a typical impact parameter of collision. From this we find the displacement of the impact parameter after the first collision $\Delta \rho_1 \sim \lambda \delta \theta_1 \sim \delta \rho \lambda / \rho_o$,

where λ is the mean free path of a test particle, and the variation of the particle velocity is $\Delta v_1 \sim v \delta \theta_1 \sim \delta \rho / \rho_o$. This leads to the following displacement of the scattering angle in the second collision $\delta \theta_2 \sim \Delta \rho_1 / \rho_o \sim \delta \rho \lambda / \rho_o^2$. From this we find for the displacement of the particle trajectory after the second collision $\Delta \rho_2 \sim \lambda \delta \theta_2 \sim \delta \rho \lambda^2 / \rho_o^2$ and for the velocity deviation after the second collision $\Delta v_2 \sim v \delta \theta_2 \sim \delta \rho \lambda / \rho_o^2$. Continuing this operation, we obtain for the deviations after k collisions

$$\Delta \rho_k \sim \delta \rho \left(\frac{\lambda}{\rho_o} \right)^k, \quad \Delta v_k \sim v \frac{\delta \rho}{\lambda} \left(\frac{\lambda}{\rho_o} \right)^k$$

and since the typical time between neighboring collisions is $\sim \lambda / v$, we find from this for deviations at time t

$$\Delta r(t) \sim \delta \rho \left(\frac{\lambda}{\rho_o} \right)^{vt/\lambda}, \quad \Delta v(t) \sim v \frac{\delta \rho}{\lambda} \left(\frac{\lambda}{\rho_o} \right)^{vt/\lambda}$$

This gives for the entropy growth due to collisions of particles

$$S_{\text{col}}(t) = 3 \frac{vt}{\lambda} \ln \left(\frac{\lambda}{\rho_o} \right) + \text{const} \quad (12.16c)$$

Of course, this formula is valid for $\Delta r \ll \rho_o$. Taking $\Delta \rho \sim \rho_o$, we find an effective number of collisions k which lead to *randomization*, or the corresponding time $t_r = k\lambda / v$

$$k = \frac{\ln \frac{\lambda}{\delta \rho}}{\ln \frac{\lambda}{\rho_o}}, \quad t_r = \frac{\lambda}{v} \frac{\ln \frac{\lambda}{\delta \rho}}{\ln \frac{\lambda}{\rho_o}} \quad (12.17)$$

For example, in the case of atmospheric air we have for the number density of molecules $N \sim 3 \cdot 10^{19} \text{ cm}^{-3}$ and the gas-kinetic cross section $\sigma \sim 3 \cdot 10^{-15} \text{ cm}^2$, so that $\lambda = (N\sigma)^{-1} \sim 10^{-5} \text{ cm}$, $\rho_o = \sqrt{\sigma/\pi} \sim 3 \cdot 10^{-8} \text{ cm}$. Assume the initial displacement of the trajectory to be of the order of the nuclear size $\delta \rho \sim 10^{-13} \text{ cm}$ and neglecting the violation of classical laws over such distances, we obtain from formula (12.16) $k \approx 4$, i.e. several collisions of molecules lead to a random distribution of molecules.

Comparing formulae (12.17) and (12.16c) with the entropy (12.16b) of total randomization, one can see that under the condition

$$\delta v \ll v \cdot \frac{L}{\lambda}$$

collisions lead to randomization when the trajectory of a test particle becomes random. This is named the *Poincaré instability* since A. Poincaré predicted this mechanism of randomization. It follows from formula (12.17) that several collisions and weak random external fields are enough to establishment a random distribution of particles (or “*molecular chaos*” according to Boltzmann) in an almost closed system even for a weak intensity of acoustic waves in this case. Thus, the *irreversibility of statistical physics* results in the randomization of motion inside the system of particles due to a weak external action.

12.7 Irreversibility and the Collapse of Wave Functions

The above analysis shows that the irreversibility in the evolution of a closed system of particles results from a weak interaction with the environment. This interaction leads to randomization in the distribution of atomic particles by states, and the system develops to an equilibrium distribution of particles for an arbitrary direction of time. This is not valid for a completely closed system of classical or quantum atomic particles because of the reversibility of Newton's or Schrödinger's equations. In particular, the evolution of a quantum system of particles is described by the Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$$

where Ψ is the wave function of the system under consideration and $\hat{H}$ is the Hamiltonian of this system. If we apply the conjugation operation and take into account that the Hamiltonian is a self-conjugate operator $\hat{H} = \hat{H}^*$, we obtain $\Psi(t) = C\Psi^*(-t)$, where C is a constant and $|C| = 1$. This relation proves the symmetry in evolution of atomic particles with respect to reversal of time.

But if the ground state of an individual atomic particle of this system is degenerate, the other scenario for development of the system is possible. In this case two atomic particles can form an *Einstein-Podolsky-Rosen pair*, and the subsequent collision of one of these atomic particles with a particle of the system chooses the state of each atomic particle of this pair. Such an action, called the *collapse of wave functions* is similar to an event of measurement and causes the prompt transition of the second atomic particle to a certain state. Because this transition has a random character, this leads to randomization in the distribution of atomic particles by states and leads to the formation of molecular chaos, which is the basis of the Boltzmann kinetic equation.

Below we consider this process for a gas consisting of atoms and a small admixture of their ions. First we analyze the collision of a test ion with its parent atom in a gas of these atoms. The wave function of the colliding atom and its ion according to formula (11.24) is equal to

$$\Psi = \frac{1}{\sqrt{2}} [\psi_1 \cos \zeta(t) + i\psi_2 \sin \zeta(t)] \exp \left(-\frac{i}{\hbar} \int^t \varepsilon dt \right)$$

where the wave functions ψ_1 and ψ_2 correspond to the location of the ion at the first or second nuclei, t is time, $\zeta(t) = \int^t (\varepsilon_g - \varepsilon_u) dt / \hbar$ is the charge exchange phase, and $\varepsilon = (\varepsilon_g + \varepsilon_u)/2$, $\varepsilon_g, \varepsilon_u$ are the energies of the even and odd states for the quasi-molecule consisting of these ions and atom. The value $\varepsilon_g - \varepsilon_u$ drops exponentially with increasing distance between nuclei at large distances. Hence, the transition of the valence electron between fields of two ions finishes at some distance between the nuclei, so that the probability of the first nucleus to belonging to a charged particle after collision equals $\cos^2 \zeta(\infty)$, and the probability of the second nuclei to belong to the charged particle after collision is $\sin^2 \zeta(\infty)$. Let us measure the charge of the first particle, for example, using a mass-spectrometer for this goal. Then this operation automatically chooses the charge of the second particle. Indeed, if the first particle

is charged, the other one is neutral, and vice versa. Such a measurement leads to the *collapse of the wave functions*. The collapse of the wave function chooses only one term in the above formula for the wave function of the quasimolecule.

The measurement operation in the collapse of the wave functions may be changed by the collision of a gas atom with one of these two atomic particles. Because the character of the collision depends on the charge of the colliding atomic particle of the quasimolecule, the collision process chooses its charge and, correspondingly, the charge of the other atomic particle. Therefore each collision of an atom and ion leads to the collapse of their wave functions some time afterwards. Because the process of the collapse of the wave functions has a random character, it causes the evolution of the system of particles to an equilibrium. The collapse of the wave functions is possible for any system of atomic particles with degenerate states of individual particles. For example, in the case of a molecular gas the collapse of the wave functions chooses the projection of the rotational moment of each colliding molecule after the collision of each pair of molecules.

Thus, the collapse of the wave functions of an entangled state of two particles leads to randomization in the distribution of particles by states. This is an additional mechanism of randomization to that under the action of an environment. The establishment of *chaos* due to the collapse of the wave functions is possible if individual particles of the system have degenerate internal states.

12.8 Attractors

The transition from the dynamic description of an ensemble of atomic particles on the basis of Newton's or Schrödinger's equations to the statistical description leads to using the language of probabilities for the particle behavior instead of the determining description of the particle ensemble in the form of trajectories for each particle in the classical case. Then the peculiarities of the mechanical motion of particles are realized in the statistical parameters of the ensemble of particles. We consider this in a simple example. Let us take a particle which moves in a two-dimensional space inside a circle of radius R , reflecting from the circle elastically. Our goal is to determine the probability of finding the particle at a certain point inside the circle through a large time $t \rightarrow \infty$.

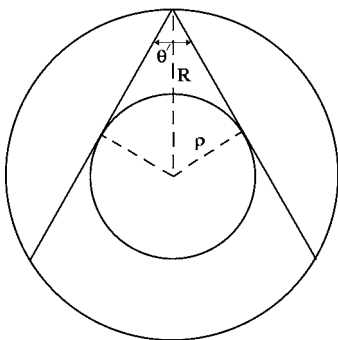


Figure 12.1. Trajectory of motion of a particle between two cylinders.

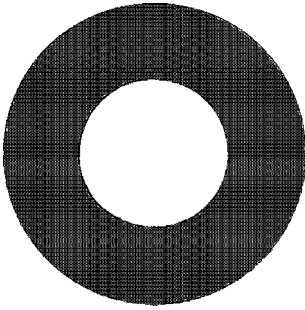


Figure 12.2. A region filled by particle trajectories (attractor).

Evidently, in this case one can construct the particle trajectory. The angle between neighboring segments of the particle trajectory after scattering from the circle equals (see Figure 12.1)

$$\theta = 2 \arcsin \frac{\rho}{R}$$

where ρ is the closest distance of each segment of the particle trajectory from the circle's center, or the impact parameter of the particle with respect to the circle's center. If the value $2\pi/\theta$ is a whole number, the particle moves along the sides of a polygon which is inscribed in the circle and has $2\pi/\theta$ sides. In the general case, the segments of the particle trajectory differ from those during the previous rotation of the particle around the center, and through the time trajectory fill the space between two circles, as is shown in Figure 12.2. This space is called the *attractor* because points in this space attract trajectories of the particle.

One can use this behavior of the particle trajectory in the statistical description of the particle motion by introducing the probability f of a particle being at a given point, so that the probability of a particle's location being in an element of area ds inside the attractor is $f ds$. Because the particle does not interact with the surrounding particles and moves with a constant velocity, the probability is distributed uniformly along each trajectory segment, and the probability under consideration is

$$f = \frac{C}{\sqrt{r^2 - \rho^2}}$$

where r is the distance from the center and C is the normalization constant which follows from the normalization condition $\int f ds = \int f \cdot 2\pi\rho d\rho = 1$. From this it follows that

$$f = \frac{1}{2\pi\sqrt{R^2 - \rho^2}\sqrt{r^2 - \rho^2}}$$

Thus all the points of the particle trajectory are distributed uniformly over angles. Therefore this attractor can be obtained from one trajectory segment by uniform rotation around the circle center. This shows the connection between the dynamical and statistical descriptions of a particle which moves in a finite region of space.

A more complex motion occurs when it becomes unstable. The classical example of this motion relates to the *Lorenz model*, which relates to the convection of a liquid, and this is

described by three nonlinear equations. One can expect a deterministic description of this system. This means that under certain initial parameters the solution of the set of three equations gives certain values of the variables at each time. In reality, for some parameters of these equations an instability occurs, and the evolution of variables over time becomes complex. It is convenient to describe the state of this system at each time as a point in the three-dimensional space of three variables. Then evolution of this system is a movement near two unstable focuses. If the trajectory is captured by one focus, it rotates around it in the form of an increasing spiral. At some amplitudes the trajectory switches to the other focus in the form of an untwisted spiral, and then returns to the first focus. Thus the trajectory described by the state of this system is concentrated in two regions around two focuses and is called a *strange attractor*. It is clear that the behavior of a strange attractor corresponds to the statistical description of this system, even though it results from the solution of the set of three equations. This testifies to the connection between the dynamic and statistical descriptions of simple systems.

12.9 Collision Integral for Electrons in Atomic Gas

The collision of atomic particles is important for the establishment of an equilibrium or evolution of a system of these atomic particles. The influence of collisions of atomic particles on the development of such a system is determined by the collision integral (12.7) of the Boltzmann kinetic equation. We evaluate below the *collision integral* for some systems, and first consider the collision integral resulting from elastic collisions of electrons with atoms of a buffer gas. This allows one to ascertain the character of interaction between the electron and atom subsystems for a weakly ionized gas. The specifics of electron–atom collisions in a gas follow from the small electron mass m_e compared with the atom mass M . Hence if the electron momentum varies strongly as a result of a collision with an atom, the electron energy varies only slightly. Therefore the distribution function of electrons on velocities is close to a symmetrical one for directions of electron motion. If electrons move in a gas in an external electric field, their distribution function can be represented in the form:

$$f(\mathbf{v}) = f_o(v) + v_x f_1(v) \quad (12.18)$$

where the x -axis is directed along an external field.

Assuming the number density of electrons N_e to be small compared with the atom number density N_a , we find that the presence of electrons in a gas does not influence the Maxwell distribution function of atoms $\varphi(v_a)$, and the electron–atom collision integral is a linear function of the distribution function $f(\mathbf{v})$. Thus the electron–atom collision integral I_{ea} has the form:

$$I_{ea}(f) = I_{ea}(f_o) + I_{ea}(v_x f_1) \quad (12.19)$$

First we obtain the expression for the second term of formula (12.19). Using formula (12.8) for the collision integral, we take into account that the atom velocity $\mathbf{v}_a$ does not vary as the result of a collision with an electron and is small compared with its velocity. Then we have

$$I_{ea}(v_x f_1) = \int (\mathbf{v}' - \mathbf{v})_x v d\sigma f_1(v) \varphi(v_a) d\mathbf{v}_a$$

where $\mathbf{v}$ and $\mathbf{v}'$ are the electron velocities before and after collision, $\mathbf{v}_a$ is the atom velocity. Because of the small atom velocity, the character of collision does not depend on $\mathbf{v}_a$, and we integrate over $\int \varphi(\mathbf{v}_a) d\mathbf{v}_a = N_a$, where N_a is the atom number density. Next, we represent the electron velocity after collision as

$$\mathbf{v}' = \mathbf{v} \cos \vartheta + v \mathbf{k} \sin \vartheta$$

where ϑ is the scattering angle and $\mathbf{k}$ is the unit vector of an arbitrary direction in the plane which is perpendicular to the initial electron velocity $\mathbf{v}$. As a result, we obtain $\int (\mathbf{v}' - \mathbf{v})_x d\sigma = -v_x \sigma^*(v)$, where $\sigma^*(v) = \int (1 - \cos \vartheta) d\sigma$ is the diffusion cross section of electron–atom scattering. Thus, we obtain finally

$$I_{ea}(v_x f_1) = -\nu v_x f_1(v) \quad (12.20)$$

where $\nu = N_a v \sigma^*(v)$ is the rate of electron–atom collisions.

To determine $I_{ea}(f_o)$ we account for the fact that the electron energy change after one collision is small compared with its energy. Consider the general group of such processes where the variable z varies in small steps as a result of one act of interaction, i.e. the system's motion is diffusional in nature in the space of this variable z . Introduce the probability $W(z_o, t_o; z, t)$ that the variable has a value z at moment t if at moment t_o it was equal to z_o . The normalization condition of this probability has the form

$$\int W(z_o, t_o; z, t) dz = 1 \quad (12.21a)$$

Apparently, because of the continuous character of evolution of the probability W , it satisfies the continuity equation

$$\frac{\partial W}{\partial t} + \frac{\partial j}{\partial z} = 0 \quad (12.21b)$$

where the flux j can be represented in the linear form:

$$j = AW - B \frac{\partial W}{\partial z} \quad (12.21c)$$

Here the first term relates to the *hydrodynamic flux*, and the second one corresponds to the *diffusion flux*. By definition, the coefficients of this process are equal to

$$A(z, t) = \lim_{\tau \rightarrow 0} \frac{1}{\tau} \int (x - z) W(x, t; z, t + \tau) dx;$$

$$B(z, t) = \lim_{\tau \rightarrow 0} \frac{1}{2\tau} \int (x - z)^2 W(x, t; z, t + \tau) dx$$

The corresponding equation for the probability, the *Fokker–Planck equation*, has the form

$$\frac{\partial W}{\partial t} = -\frac{\partial(AW)}{\partial z} + \frac{\partial^2(BW)}{\partial z^2}$$

This equation can be generalized for the case when the normalization condition instead of (12.21a) has the following form:

$$\int \rho(z)W(z_o, t_o; z, t) dz = 1$$

where $\rho(z)$ is the density of states. The the value W must be changed to ρW in the Fokker-Planck equation, and then it takes the form:

$$\rho \frac{\partial W}{\partial t} = -\frac{\partial(\rho A W)}{\partial z} + \frac{\partial^2(\rho B W)}{\partial z^2}$$

The right-hand side of this equation can be used as the collision integral of the spherical part of the electron distribution function, because it describes the change in the electron energy that occurs in small steps. Let us take instead of $W(z_o, t_o; z, t)$ in the above equation the distribution function f_o , and the electron energy ε instead of the variable z . Then $\rho(\varepsilon) \sim \varepsilon^{1/2}$, and the collision integral takes the form:

$$I_{ea}(f_o) = \frac{1}{\rho(\varepsilon)} \frac{\partial}{\partial \varepsilon} \left[-A \rho f_o + \frac{\partial}{\partial \varepsilon} (B \rho f_o) \right] \quad (12.22)$$

The connection between A and B we find from the condition that if the distribution function coincides with the Maxwell distribution function, the collision integral is zero. This yields:

$$I_{ea}(f_o) = \frac{1}{\rho(\varepsilon)} \frac{\partial}{\partial \varepsilon} \left[\rho(\varepsilon) B(\varepsilon) \left(\frac{\partial f_o}{\partial \varepsilon} + \frac{f_o}{T} \right) \right] \quad (12.23)$$

where T is the gaseous temperature.

By definition, the value $B(\varepsilon)$ equals

$$B(\varepsilon) = \frac{1}{2} \left\langle \int (\varepsilon - \varepsilon')^2 N_a v d\sigma(\varepsilon \rightarrow \varepsilon') \right\rangle \quad (12.24)$$

where the brackets mean averaging over atom energies and $d\sigma$ is the electron-atom cross section which corresponds to a given change in the electron energy. Let us use the conservation of the relative electron-atom velocity as a result of their elastic collision, i.e. $|\mathbf{v} - \mathbf{v}_a| = |\mathbf{v}' - \mathbf{v}_a|$, where $\mathbf{v}$ and $\mathbf{v}'$ are the electron velocities before and after collision, and $\mathbf{v}_a$ is the atom velocity which does not vary in a collision with an electron because the atom's momentum is large in comparison with that of the electron. From this it follows $v^2 - (v')^2 = 2\mathbf{v}_a(\mathbf{v} - \mathbf{v}')$, and formula (12.24) yields:

$$B(\varepsilon) = \frac{m_e^2}{2} \left\langle \frac{v_a^2}{3} \right\rangle \int (\mathbf{v} - \mathbf{v}')^2 N_a v d\sigma = T \frac{m_e^2 v^2}{M} N_a v \sigma^*(v) \quad (12.25)$$

where $\langle v_a^2/3 \rangle = T/M$, T is the gaseous temperature, m_e and M are the electron and atom masses, $|\mathbf{v} - \mathbf{v}'| = 2v \sin(\vartheta/2)$, ϑ is the scattering angle, and $\sigma^*(v) = \int (1 - \cos \vartheta) d\sigma$ is the diffusion cross section of electron-atom scattering. Thus, using $\rho(\varepsilon) \sim \sqrt{\varepsilon}$, we have for the collision integral from the spherical part of the electron distribution function

$$I_{ea}(f_o) = \frac{m_e}{M} \cdot \frac{\partial}{v^2 \partial v} \left[v^3 \nu_{ea} \left(\frac{\partial f_o}{m_e v \partial v} + \frac{f_o}{T} \right) \right] \quad (12.26)$$

where $\nu_{ea} = N_a v \sigma^*(v)$ is the rate of electron–atom collisions. This part of the collision integral describes the energy change in electron–atom collisions.

12.10 The Landau Collision Integral

The equilibrium inside the electron subsystem of a weakly ionized gas results from collisions between electrons. The specifics of electron–electron scattering is such that small scattering angles give the main contribution to the diffusion cross section. This means that the average variation in the electron velocity is small after each collision, and the electron velocity varies in small steps. Then the collision integral, similar to the previous case, has the form of the right-hand side of the three-dimensional Fokker–Planck equation. Such a form of the collision integral is named the *Landau collision integral*. Below we obtain its expression.

Let us start from the general expression (12.6) for the collision integral, which, taking into account the principle of detailed balance for elastic collisions of identical particles $W(\mathbf{v}_1, \mathbf{v}_2 \rightarrow \mathbf{v}'_1, \mathbf{v}'_2) = W(\mathbf{v}'_1, \mathbf{v}'_2 \rightarrow \mathbf{v}_1, \mathbf{v}_2)$ takes the form

$$I_{ee}(f) = - \int [f(\mathbf{v}_1)f(\mathbf{v}_2) - f(\mathbf{v}'_1)f(\mathbf{v}'_2)] W(\mathbf{v}_1, \mathbf{v}_2 \rightarrow \mathbf{v}'_1, \mathbf{v}'_2) d\mathbf{v}'_1 d\mathbf{v}'_2 d\mathbf{v}_2 \quad (12.27)$$

Introducing $\Delta\mathbf{v} = \mathbf{v}'_1 - \mathbf{v}_1$, we have from conservation of the total momentum of electrons as a result of collision $\mathbf{v}'_2 = \mathbf{v}_2 - \Delta\mathbf{v}$. Then one can reduce the number of integrations and transform the collision integral to the following form

$$I_{ee}(f) = - \int [f(\mathbf{v}_1)f(\mathbf{v}_2) - f(\mathbf{v}_1 + \Delta\mathbf{v})f(\mathbf{v}_2 - \Delta\mathbf{v})] W(\mathbf{v}_1, \mathbf{v}_2 \rightarrow \mathbf{v}'_1, \mathbf{v}'_2) d\mathbf{v}'_1 d\mathbf{v}'_2 d\mathbf{v}_2 \quad (12.28)$$

Let us represent the transition probability $W(\mathbf{v}_1, \mathbf{v}_2 \rightarrow \mathbf{v}'_1, \mathbf{v}'_2)$ in the form

$$W = W\left(\frac{\mathbf{v}_1 + \mathbf{v}'_1}{2}, \frac{\mathbf{v}_2 + \mathbf{v}'_2}{2}, \Delta\mathbf{v}\right) = W\left(\mathbf{v}_1 + \frac{\Delta\mathbf{v}}{2}, \mathbf{v}_2 - \frac{\Delta\mathbf{v}}{2}, \Delta\mathbf{v}\right)$$

From the principle of detailed balance it follows that the probability W is an even function of $\Delta\mathbf{v}$, i.e. $W(\Delta\mathbf{v}) = W(-\Delta\mathbf{v})$. Then we obtain in the first order of expansion of the collision integral over the small parameter $\Delta\mathbf{v}$:

$$I_{ee}(f) = - \int \left[f(\mathbf{v}_2) \frac{\partial f(\mathbf{v}_1)}{\partial \mathbf{v}_1} - f(\mathbf{v}_1) \frac{\partial f(\mathbf{v}_2)}{\partial \mathbf{v}_2} \right] \Delta\mathbf{v} W d(\Delta\mathbf{v}) d\mathbf{v}_2$$

Since $W(\mathbf{v}_1 + \Delta\mathbf{v}/2, \mathbf{v}_2 - \Delta\mathbf{v}/2, \Delta\mathbf{v})$ is the even function of $\Delta\mathbf{v}$, this approximation gives zero. In the second-order approximation for $\Delta\mathbf{v}$ we have

$$\begin{aligned} I_{ee}(f) = - \int d\Delta\mathbf{v} d\mathbf{v}_2 W \cdot & \left(\frac{1}{2} \Delta_\alpha \Delta_\beta \frac{\partial^2 f_1}{\partial v_{1\alpha} \partial v_{1\beta}} f_2 \right. \\ & - \Delta_\alpha \Delta_\beta \frac{\partial f_1}{\partial v_{1\alpha}} \frac{\partial f_2}{\partial v_{2\beta}} + \frac{1}{2} \Delta_\alpha \Delta_\beta f_1 \frac{\partial^2 f_2}{\partial v_{2\alpha} \partial v_{2\beta}} \Big) \\ & - \int \Delta\mathbf{v} d\mathbf{v}_2 \frac{1}{2} \Delta_\alpha \left(\frac{\partial W}{\partial v_{1\alpha}} - \frac{\partial W}{\partial v_{2\alpha}} \right) \Delta_\beta \left(\frac{\partial f_1}{\partial v_{1\beta}} f_2 - f_1 \frac{\partial f_2}{\partial v_{2\beta}} \right) \end{aligned}$$

where $f_1 \equiv f(\mathbf{v}_1)$, $f_2 \equiv f(\mathbf{v}_2)$, and $\Delta_\alpha \equiv \Delta v_\alpha$ and there is a summation over twice repeating indices. One can calculate some of terms of the above expression by their integration by parts. We have

$$\begin{aligned} \frac{1}{2} \int d\Delta \mathbf{v} d\mathbf{v}_2 W \cdot \Delta_\alpha \Delta_\beta \frac{\partial f_1}{\partial v_{1\alpha}} \frac{\partial f_2}{\partial v_{2\beta}} + \frac{1}{2} \int d\Delta \mathbf{v} d\mathbf{v}_2 \Delta_\alpha \Delta_\beta \frac{\partial W}{\partial v_{2\alpha}} \frac{\partial f_1}{\partial v_{1\beta}} f_2 \\ = \frac{1}{2} \int d\Delta \mathbf{v} d\mathbf{v}_2 \Delta_\alpha \Delta_\beta \frac{\partial f_1}{\partial v_{1\alpha}} \frac{\partial}{\partial v_{2\beta}} (W f_2) = 0, \end{aligned}$$

$$\begin{aligned} \frac{1}{2} \int d\Delta \mathbf{v} d\mathbf{v}_2 W \cdot \Delta_\alpha \Delta_\beta f_1 \frac{\partial^2 f_2}{\partial v_{2\alpha} \partial v_{2\beta}} + \frac{1}{2} \int d\Delta \mathbf{v} d\mathbf{v}_2 \Delta_\alpha \Delta_\beta \frac{\partial W}{\partial v_{2\alpha}} f_1 \frac{\partial f_2}{\partial v_{2\beta}} \\ = \frac{1}{2} \int d\Delta \mathbf{v} d\mathbf{v}_2 \cdot \Delta_\alpha \Delta_\beta f_1 \frac{\partial}{\partial v_{2\alpha}} \left(W \frac{\partial f_2}{\partial v_{2\beta}} \right) = 0 \end{aligned}$$

since the distribution function is zero at $v_{2\beta} \rightarrow \pm\infty$. After eliminating these terms we obtain:

$$\begin{aligned} I_{ee}(f) = -\frac{1}{2} \int d\Delta \mathbf{v} d\mathbf{v}_2 \Delta_\alpha \Delta_\beta \left(W \frac{\partial^2 f_1}{\partial v_{1\alpha} \partial v_{1\beta}} f_2 - W \frac{\partial f_1}{\partial v_{1\alpha}} \frac{\partial f_2}{\partial v_{2\beta}} \right. \\ \left. + \frac{\partial W}{\partial v_{1\alpha}} \frac{\partial f_1}{\partial v_{1\beta}} f_2 - \frac{\partial W}{\partial v_{2\alpha}} f_1 \frac{\partial f_2}{\partial v_{2\beta}} \right) = -\frac{\partial j_\beta}{\partial v_{1\beta}} \quad (12.29a) \end{aligned}$$

where the flux in the space of electron velocities is equal to

$$j_\beta = \int d\mathbf{v}_2 \left(f_1 \frac{\partial f_2}{\partial v_{2\beta}} - \frac{\partial f_1}{\partial v_{1\beta}} f_2 \right) D_{\alpha\beta}, \quad D_{\alpha\beta} = \frac{1}{2} \int \Delta_\alpha \Delta_\beta W d\Delta \mathbf{v} \quad (12.29b)$$

This symmetric form of the electron–electron collision integral is the Landau collision integral. In fact, we derive in this case the Fokker–Planck equation in the velocity space. Let us evaluate the tensor $D_{\alpha\beta}$. The force acting on a test electron from the other one due to their Coulomb interaction is $\mathbf{F} = e^2 \mathbf{r}/r^3$, where r is the distance between electrons and e is their charge. This gives, for the momentum change of a test electron

$$\Delta \mathbf{p} = \mathbf{n} \int_{-\infty}^{\infty} \frac{e^2 \rho}{r^3} dt = \frac{2e^2}{\rho g} \mathbf{n} \quad (12.30)$$

Here $\mathbf{n}$ is the unit vector along the impact parameter of collision ρ , we use the free motion of electrons $r^2 = \rho^2 + g^2 t^2$, where g is the relative velocity of colliding electrons, and t is time. From this we get for the variation of the velocity of a test electron after collision ($\Delta = \Delta \mathbf{v}$):

$$\Delta_\alpha = \frac{2e^2 \rho_\alpha}{\rho^2 g m_e} \quad (12.31)$$

This gives for the tensor $D_{\alpha\beta}$

$$\begin{aligned} D_{\alpha\beta} &= \frac{1}{2} \int \Delta_\alpha \Delta_\beta W d\Delta \mathbf{v} = \frac{1}{2} \int \Delta_\alpha \Delta_\beta g d\sigma = \frac{2e^4}{m_e^2 g} \int \frac{\rho_\alpha \rho_\beta}{\rho^4} d\sigma \\ &= \frac{4\pi e^4}{m_e^2 g} n_\alpha n_\beta \ln \Lambda \end{aligned} \quad (12.32)$$

Here n_α and n_β are components of the unit vector $\mathbf{n}$ directed along the impact parameter ρ , and the value $\ln \Lambda$ is called the *Coulomb logarithm*. This value is equal to

$$\ln \Lambda = \int_{\rho_<}^{\rho_>} \frac{d\rho}{\rho} \quad (12.33)$$

This integral diverges at both limits. Its divergence at small impact parameters results from ignorance of the trajectory distortion owing to the Coulomb repulsion of electrons, so that this limit follows from the estimate $e^2/\rho_< \sim \varepsilon$, where ε is the typical energy of electrons. The divergence at large impact parameters is a peculiarity of the Coulomb interaction potential. But in a plasma the Coulomb field is shielded according to formula (2.41), so that $\rho_> \sim r_D$, where r_D is the *Debye-Hückel radius* (2.41) of this plasma. We define $\rho_<, \rho_>$ with an accuracy up to a constant factor, and because $\rho_> \gg \rho_<$, it leads to a small error. Thus the Coulomb logarithm is large for an ideal plasma and is equal to

$$\ln \Lambda = \ln \frac{r_D \varepsilon}{e^2} \quad (12.34)$$

From this we have for the *diffusion cross section* of electron-electron collisions in a plasma

$$\sigma^* = \int_0^\infty 2\pi \rho d\rho (1 - \cos \vartheta) = \int_0^\infty 2\pi \rho d\rho \frac{\vartheta^2}{2} = \pi \left(\frac{2e^2}{m_e g^2} \right)^2 \ln \Lambda = \frac{\pi e^4}{\varepsilon^2} \ln \Lambda \quad (12.35)$$

where the scattering angle is equal to $\vartheta = 2e^2/(\rho m_e g^2) = e^2/(\rho \varepsilon)$, and ε is the energy of an incident electron in the laboratory frame of reference, where the other electron is motionless.

To evaluate the tensor $D_{\alpha\beta}$, let us take first the direction of the collision velocity $\mathbf{g}$ along the x -axis, with xy as the plane of motion. Then only Δ_y is not zero, so that only the tensor component D_{yy} is not zero. For this component of the tensor we obtain

$$D_{yy} = \frac{2e^4}{m_e g} \int \frac{1}{\rho^2} 2\pi \rho d\rho = \frac{4\pi e^4}{m_e g} \ln \Lambda$$

where we calculate the integral over impact parameters as above. Taking into account that the direction of the relative velocity of collision is a random value, one can write the expression for the tensor $D_{\alpha\beta}$ in an arbitrary frame of reference. Because this tensor is symmetric with respect to its indices, it can be constructed on the basis of symmetrical tensors $\delta_{\alpha\beta}$ and $g_\alpha g_\beta$. Evidently, it has the form

$$D_{\alpha\beta} = \frac{4\pi e^4}{m_e g^3} g_\alpha g_\beta \ln \Lambda \quad (12.36)$$

Thus the Landau collision integral which accounts for collisions between electrons has the form:

$$I_{ee}(f) = -\frac{\partial j_\beta}{\partial v_{1\beta}}, \quad j_\beta = \int d\mathbf{v}_2 \left(f_1 \frac{\partial f_2}{\partial v_{2\alpha}} - \frac{\partial f_1}{\partial v_{1\alpha}} f_2 \right) D_{\alpha\beta},$$

$$D_{\alpha\beta} = \frac{4\pi e^4}{m_e^2 g^3} g_\alpha g_\beta \ln \Lambda \quad (12.37)$$

This form of the collision integral is analogous to the right-hand side of the Fokker–Planck equation in velocity space.

The Landau collision integral is nonlinear with respect to the electron distribution function. This expression can be simplified for fast electrons whose velocity is large in comparison with the typical electron velocity in a plasma. In this limiting case the tensor $D_{\alpha\beta}$ does not depend on the velocity of slow electrons, i.e.

$$D_{\alpha\beta} = \frac{4\pi e^4}{m_e^2 v^3} v_\alpha v_\beta \ln \Lambda$$

where v is the velocity of a fast electron. In this case according to formula (12.23) the collision integral for fast electrons has the form

$$I_{ee}(f_o) = \frac{1}{m_e v^2} \frac{\partial}{\partial v} \left[v B_{ee}(\varepsilon) \left(\frac{\partial f_o}{m_e v \partial v} + \frac{f_o}{T_e} \right) \right] \quad (12.38)$$

where the energy of a test fast electron is $\varepsilon = m_e v^2/2$, and

$$B(\varepsilon) = \frac{1}{2} \int \frac{(\varepsilon - \varepsilon')^2 N_e v d\sigma(\varepsilon \rightarrow \varepsilon')}{(\varepsilon - \varepsilon')^2 N_e v d\sigma(\varepsilon \rightarrow \varepsilon')} = \frac{N_e}{2} \int \frac{(\varepsilon - \varepsilon')^2 W d\Delta\mathbf{v}}{(\varepsilon - \varepsilon')^2 W d\Delta\mathbf{v}}$$

$$= \frac{N_e}{2} \int \frac{m_e v_\alpha (v_\alpha - v'_\alpha) \cdot m_e v_\beta (v_\beta - v'_\beta) W d\Delta\mathbf{v}}{m_e v_\alpha (v_\alpha - v'_\alpha) \cdot m_e v_\beta (v_\beta - v'_\beta) W d\Delta\mathbf{v}} = \frac{N_e}{2} m_e^2 v_\alpha v_\beta D_{\alpha\beta}$$

Here N_e is the electron number density, ε and ε' are the energies of a fast electron before and after collision, the summation takes place over repeating indices, and averaging is taken over the velocities of a slow electron. We account for the small variation in the velocity of a fast electron as a result of collision, so that $\varepsilon - \varepsilon' = m_e v_\alpha (v_\alpha - v'_\alpha)$. From this we get

$$B_{ee}(\varepsilon) = 2\pi e^4 v N_e \ln \Lambda \quad (12.39)$$

Thus this collision integral is linear with respect to the distribution function of fast electrons and has a simple form.

12.11 Collision Integral for Clusters in Parent Vapor

In the above cases of the collision integral involving electrons, we have based our analysis on a small parameter in the space of electron energies or electron velocities, and therefore the

collision integral has the form of the derivative in the energy or velocity space. Correspondingly, the kinetic equation has the form of the continuity equation in a certain space. We now consider one more example of this type for cluster growth due to processes (11.42) of attachment of atoms to clusters and evaporation of clusters. Then for large clusters, consisting of a large number n of atoms, a small parameter of the theory is $1/n$, and the state of a system of clusters is characterized by the size distribution function f_n of clusters, which is the number density of clusters consisting of n atoms. Assuming the cluster evolution to be determined by attachment and evaporation processes (11.42), we obtain the following kinetic equation for this distribution function

$$\frac{\partial f_n}{\partial t} = Nk_{n-1}f_{n-1} - Nk_nf_n - \nu_nf_n + \nu_{n+1}f_{n+1} \quad (12.40)$$

In fact, the kinetic equation is the balance equation which accounts for transitions between particle states in accordance with the scheme (11.42) of processes. In the stationary case, if equilibrium is supported in a given range of cluster sizes, we have from this equation

$$f_{n+1}\nu_{n+1} = f_nNk_n$$

The relation (11.45) for the rate constants of attachment and evaporation processes transforms this formula to the form

$$\frac{f_{n+1}}{f_n} = s \exp\left(\frac{\varepsilon_{n+1} - \varepsilon_o}{T}\right) \quad (12.41)$$

where this expression accounts for the character of cluster formation in a gas at constant temperature and pressure, and

$$s = \frac{N_{\text{sat}}(T)}{N} \quad (12.42)$$

is the *supersaturation degree* of the vapor. We assume for simplicity the translational and cluster temperatures to be identical.

We now use the *liquid drop model* for clusters (see Chapter 11), and within the framework of this model the total binding energy of cluster atoms E_n with respect to a vacuum according to formula (7.24) is equal to

$$E_n = \varepsilon_o n - An^{2/3}, \quad n \gg 1 \quad (12.43)$$

where ε_o is the bulk binding energy per atom and the second term accounts for the cluster surface energy. From this we have for the atom binding energy of a large cluster $n \gg 1$:

$$\varepsilon_n = \frac{dE_n}{dn} = \varepsilon_o - \frac{2A}{3n^{1/3}} \quad (12.44)$$

Then using the relations (12.41) and (12.44) we obtain:

$$\frac{f_{n+1}}{f_n} = s \exp\left(-\frac{2A}{3n^{1/3}T}\right) \quad (12.45)$$

Condensation of atoms takes place at $S > 1$ if the vapor density exceeds its saturation value for a given temperature. Thus, from formula (12.45) it follows that the cluster number density as a function of their sizes has a minimum at the critical number of cluster atoms n_{cr} , or *critical size*, which according to formula (12.45) has the form:

$$n_{\text{cr}} = \left(\frac{2A}{3T \ln s} \right)^3 \quad (12.46)$$

The concept of critical size means that the probability of cluster growth for large clusters $n > n_{\text{cr}}$ exceeds the probability of evaporation, and such clusters grow, whereas small clusters with $n < n_{\text{cr}}$ evaporate. The critical size concept is the basis of the analysis of the evolution of clusters and small particles in a condensing vapor.

If a cluster is located in a vacuum, its internal energy is equal to the binding energy of cluster atoms (12.43) with a sign change. If the cluster under consideration grows and evaporates in a gas at constant temperature and pressure, we change the cluster internal energy by the free enthalpy. Then if the equilibrium (11.42) is established for clusters of sizes up to n , the equilibrium distribution function f_n according to formula (12.41) is given by

$$f_n = C s^n \exp \left(-\frac{E_n}{T} \right) = C \exp \left(-\frac{G_n}{T} \right) \quad (12.47)$$

where C is the normalization constant and G_n is the free enthalpy.

Because the number of cluster atoms varies as a result of processes (11.42) by one, the right-hand side of the kinetic equation (12.40) for large clusters has the form of the Fokker-Planck equation (12.21)

$$\frac{\partial f_n}{\partial t} = I_{\text{col}}(f_n), \quad I_{\text{col}}(f_n) = -\frac{\partial j_n}{\partial n}, \quad j_n = A_n f_n - B_n \frac{\partial f_n}{\partial n} \quad (12.48)$$

and since for the equilibrium distribution function (12.47) the flux j_n in n -space is zero, we have the following connection between the parameters A_n and B_n for the hydrodynamic and diffusion fluxes

$$A_n = B_n \frac{d \ln f_n}{dn} = \frac{\mu_n}{T} B_n \quad (12.49)$$

Here f_n is the equilibrium size distribution function, and the cluster chemical potential is $\mu_n = dG_n/dn$, where $G_n = E_n - T \ln s$ is the free enthalpy (free Gibbs energy) for the cluster. The hydrodynamic flux parameter A_n follows from equation (12.40) and has the form

$$A_n = N k_n - \nu_{n+1} = k_n N \left[1 - \exp \left(-\frac{\mu_n}{T} \right) \right] \quad (12.50)$$

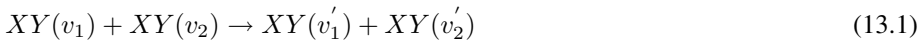
Thus the collision integral for large clusters, whose size in a parent vapor is changed by one as a result of atom attachment and cluster evaporation, is given by the right-hand side of the Fokker-Planck equation (12.21) with parameters of the hydrodynamic and diffusion fluxes in a cluster size space which are given by formulae (12.49) and (12.50).

13 Non-equilibrium Objects and Phenomena

13.1 Non-equilibrium Molecular Gas

Thermodynamic equilibrium in a system is established as a result of the interaction of its elements. In particular, thermodynamic equilibrium in gases results from collisions of its atoms or molecules, and the temperature is the parameter which characterizes the average energy per particle in this system (see Chapter 2). In reality, thermodynamic equilibrium may be violated in a stationary system which has different *degrees of freedom* or can be divided into separate subsystems. In this case a stationary state of this system depends on processes which establish an equilibrium in each subsystem. If processes inside a subsystem are more effective than in other subsystems, one can introduce a temperature for this subsystem or for the corresponding degree of freedom.

As an example of this we consider a molecular gas consisting of diatomic molecules that has translational, rotational and vibrational degrees of freedom. In some cases of gas excitation, in particular, if molecules are inserted in a gas discharge, initially vibrational degrees of freedom are excited, and then the excitation energy is transferred to translational degrees of freedom. This takes place in molecular lasers, and the following processes establish equilibrium in such systems



Here the argument is the vibration number, k is an integer, and the total internal energy of colliding molecules is conserved in the process (13.1) of vibration exchange, i.e.

$$v_1 + v_2 = v'_1 + v'_2 \quad (13.3)$$

The rate constant of the process of *vibrational exchange* (13.1) is significantly stronger than the rate constant of *vibrational relaxation* (13.2). This yields for the vibrational collision integral $I_{\text{vib}} = 0$. This relation establishes an equilibrium on molecule vibrations and leads to the Boltzmann distribution over vibrational levels with the *vibrational temperature* T_v which can differ from the gaseous temperature. The ratio between the vibrational and translational temperatures is determined by the rates of energy transfer to vibrational degrees of freedom and the rate of vibrational relaxation (13.2).

Let us consider an excited molecular gas which is governed by the processes (13.1) and (13.2). If vibrational and translational degrees of freedom are excited or cooled in different ways, these degrees of freedom are characterized by different temperatures. This takes place in gas-discharge molecular lasers, where vibrational degrees of freedom are excited selectively, and in gas-dynamical lasers, where rapid cooling of translational degrees of freedom as

a result of the expansion of a gas takes place. The difference in translational and vibrational temperatures also occurs in shock waves and as a result of jet expansion. Thus it is a widespread case in which a molecular gas is characterized by different vibrational and translational temperatures. The resonant character of exchange by vibrational excitation takes place only for weakly excited molecules. At moderate excitations this does not work because of the molecule's anharmonicity, which leads to a specific vibrational distribution of molecules. Below we analyze such a regime of excitation of a molecular gas.

Let us consider a nonequilibrium gas consisting of diatomic molecules where the translational temperature T differs from the vibrational one T_v . The equilibrium between vibrational states is maintained by resonant exchange transfer of vibrational excitations in collisions of molecules (13.1). Conservation of the total internal energy of molecules in the resonant process (13.1) in the harmonic approximation for vibrations leads to the relation (13.3). The excitation energy of a molecule vibrational level according to formula (3.43) has the form

$$\varepsilon_v = \hbar\omega(v + 1/2) - \hbar\omega x_e(v + 1/2)^2 \quad (13.4)$$

where ω is the harmonic oscillator frequency and x_e is the anharmonicity parameter. The second term of this formula is important for establishing equilibrium in the considering case when the translational and vibrational temperatures are different. Indeed, let us consider the equilibrium (13.1) which leads to the relation between the rate constants

$$f(v_1)f(v_2)k(v_1, v_2 \rightarrow v'_1, v'_2) = f(v'_1)f(v'_2)k(v'_1, v'_2 \rightarrow v_1, v_2) \quad (13.5)$$

where $f(v)$ is the number density of molecules in a given vibrational state, $k(v_1, v_2 \rightarrow v'_1, v'_2)$ is the rate constant of the indicated transition. Because these transitions are governed by the translation temperature, we have from this equilibrium:

$$k(v_1, v_2 \rightarrow v'_1, v'_2) = k(v'_1, v'_2 \rightarrow v_1, v_2) \exp\left(\frac{\Delta\varepsilon}{T}\right) \quad (13.6)$$

where $\Delta\varepsilon = \Delta\varepsilon(v_1) + \Delta\varepsilon(v_2) - \Delta\varepsilon(v'_1) - \Delta\varepsilon(v'_2)$ is the difference in the energies for a given transition, and $\Delta\varepsilon(v) = -\hbar\omega x_e(v + 1/2)^2$. From this it follows for the number density of excited molecules:

$$N(v) = N_0 \exp\left(-\frac{\hbar\omega v}{T_v} + \frac{\hbar\omega x_e v(v + 1)}{T}\right) \quad (13.7)$$

where N_0 is the number density of molecules in the ground vibrational state. This formula is often called the *Treanor distribution*.

Formula (13.7) leads to a nonmonotonic population of vibrational levels as a function of the vibrational quantum number. Assuming the minimum of this function to correspond to large vibrational numbers, we have for the position of the minimum:

$$v_{\min} = \frac{\hbar\omega}{2\hbar\omega x_e} \frac{T}{T_v} = \beta \frac{T}{T_v} \gg 1, \quad \text{where } \beta = \frac{\hbar\omega}{2\hbar\omega x_e} \quad (13.8)$$

and the minimal number density of excited molecules is equal to

$$f(v_{\min}) = f_0 \exp\left(-\frac{\hbar\omega v_{\min}}{2T_v}\right) = f_0 \exp\left[-\frac{(\hbar\omega)^2}{4\hbar\omega x_e} \frac{T}{T_v^2}\right] \quad (13.9)$$

Table 13.1 lists the parameters of some diatomic molecules and the parameter β . Because the vibrational temperature usually exceeds the translational one, the effect under consideration is remarkable at $v \sim 10$.

Thus, this effect of violation of the Boltzmann distribution for vibrationally excited states proceeds due to transitions between vibrational and translational degrees of freedom and becomes effective in collisions involving highly excited molecules. Such transitions mix vibrational and translational degrees of freedom and lead to violation of the Boltzmann distribution with the vibrational temperature for excited states. Note that the model used is not valid for large excitations because the vibrational relaxation processes become effective for such states.

Table 13.1. Parameters of diatomic gaseous molecules: $\hbar\omega_e$ is the molecule vibrational energy, $\hbar\omega_e x_e$ is the molecule anharmonicity, B is the rotational constant, D_o is the dissociation energy, and the parameter β is given by formula (13.8).

Molecule	$\hbar\omega_e, \text{cm}^{-1}$	$\hbar\omega_e x_e, \text{cm}^{-1}$	B, cm^{-1}	D_o, eV	β
Br ₂	325	1.08	0.082	2.05	150
CO	2170	13.3	1.93	11.09	82
Cl ₂	559.7	2.68	0.244	2.58	104
F ₂	916.6	11.2	0.89	1.66	41
H ₂	4401	121	60.8	4.48	18
J ₂	214.5	0.615	0.037	1.54	175
N ₂	2359	14.9	1.998	9.58	79
NO	1904	14.1	1.67	4.39	68
O ₂	1580	12.0	1.445	5.12	66
OH	3738	84.9	18.9	4.39	21

13.2 Violation of the Boltzmann Distribution Due to Radiation

For a gas consisting of atoms and molecules the distribution over some degrees of freedom is determined by the Boltzmann distribution at temperatures that are not low, and this equilibrium is established owing to collisions of these particles. The action of external fields or other factors can violate this distribution. Now we consider such an example when the Boltzmann distribution is violated due to the radiation of excited atoms.

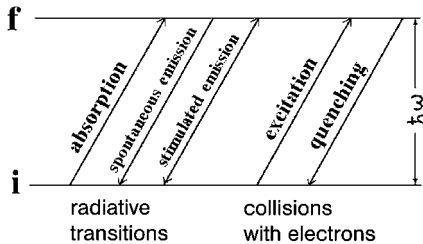


Figure 13.1. The character of transition between the ground and resonantly excited states as a result of electron impact and photon emission.

Inelastic collisions of electrons with atoms establish thermodynamic equilibrium between atoms in the ground and excited states, and as a result of these collisions the number density of atoms N_* in an excited state is given by the Boltzmann formula (2.18)

$$N_* = N_B = \frac{g_*}{g_o} N_o \exp\left(-\frac{\Delta\varepsilon}{T_e}\right) \quad (13.10)$$

where T_e is the electron temperature, N_o is the number density of atoms in the lower or ground state, g_o, g_* are statistical weights of the corresponding states, $\Delta\varepsilon$ is the excitation energy. If the excited state is the resonantly excited one, radiative transitions to the ground state may be of importance and may change the character of the equilibrium. Let us consider the equilibrium of resonantly excited atoms in a plasma which is supported by processes of the Figure 13.1:



These processes lead to the following balance equation for excited atoms

$$\frac{dN_*}{dt} = N_e N_o k_{\text{ex}} - N_e N_* k_q - \frac{N_*}{\tau_r} \quad (13.12)$$

where k_{ex} and k_q are the rate constants for excitation and quenching of an atom by electron impact, τ_r is the radiative lifetime corresponding to the transport of *resonant photons* outside the plasma system. In the stationary case $dN_*/dt = 0$ the number density of excited atoms is equal to

$$N_* = \frac{N_o N_e k_{\text{ex}}}{N_e k_q + \frac{1}{\tau_r}} \quad (13.13)$$

If the radiative time is large $\tau_r \rightarrow \infty$, the solution of the stationary equation (13.12) is transformed into the Boltzmann distribution (13.10). Thus, formula (13.13) can be represented in the form

$$N_* = \frac{N_B}{1 + \frac{1}{N_e k_q \tau_r}} \quad (13.14)$$

where N_B is the number density of excited atoms according to the Boltzmann law (13.10), i.e. it corresponds to thermodynamic equilibrium between excited and nonexcited atomic states. Note that this formula is not only valid for resonantly excited states. One can use τ_r as the lifetime of an excited state with respect to its destruction in any way except for electron collisions, in particular, as a result of collisions with atoms or due to transport to walls.

Formula (13.14) reflects the character of the equilibrium for resonantly excited atoms. Note that thermodynamic equilibrium takes place if the lifetime of excited state under consideration τ in a gaseous system is small compared to a typical time $(N_e k_q)^{-1}$ of atom quenching (not excitation!), i.e. the validity of thermodynamic equilibrium is established by the criterion

$$N_e k_q \tau_r \gg 1 \quad (13.15)$$

If this criterion is valid, the number density of excited atoms is determined by the Boltzmann formula (13.10).

13.3 Processes in Photoresonant Plasma

We now consider one more example of a nonequilibrium plasma in which the stationary state depends on the hierarchy of times of processes in this plasma. This is the *photoresonant plasma* which is formed as a result of the irradiation of a gas or vapor by resonant radiation. The absorption of resonant radiation leads to the formation of resonantly excited atoms, and subsequent processes involving excited atoms lead to the formation of highly excited atoms and to their ionization. Electrons released in the ionization process establish an equilibrium with the excited atoms. As a result, a plasma is formed with nearby temperatures of electrons and excited atoms.

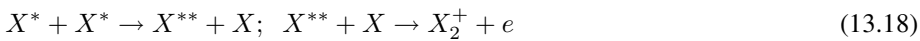
The balance equation for the number density of excited atoms has the following form instead of (13.12)

$$\frac{dN_*}{dt} = G + N_e N_o k_{ex} - N_e N_* k_q - \frac{N_*}{\tau_r} \quad (13.16)$$

where G is the rate of formation of resonantly excited atoms as a result of the absorption of resonant radiation and we assume that the criterion (13.15) holds true. From this it follows that

$$N_* = G\tau_r \quad (13.17)$$

and under the condition (13.15) the electron temperature is close to the temperature of excited atoms, so that $N_o k_{ex} = N_* k_q$. Of course, the rate of excitation G depends on the size of the absorbed region and on the character of broadening of the resonant spectral line, but here we put aside these problems; in addition, τ_r is the effective lifetime of excited atoms accounting for the reabsorption process. In reality τ_r depends on the size of an absorbed region, and this value exceeds the radiative lifetime of an isolated atom if reabsorption processes are of importance. Collisions of excited atoms lead to the subsequent ionization of atoms, for example, according to the scheme



and we denote by k_{ion} an effective rate constant of formation of free electrons from excited atoms, so that the balance equation for electrons can be represented in the form

$$\frac{dN_e}{dt} = k_{ion} N_*^2 \quad (13.19)$$

Since we neglect this channel of quenching of excited atoms in comparison with atom radiation, the following criterion is valid

$$k_{ion} N_* \tau_r \ll 1 \quad (13.20)$$

Along with the processes of formation of the photoresonant plasma, heating of atoms occurs as a result of the elastic collisions of atoms with electrons. We have from the heat balance equation

$$\frac{dT}{dt} \sim \frac{m_e}{M} T_e k_{el} N_e \quad (13.21)$$

where T is the gas temperature, T_e is the electron temperature, M is the atom mass and k_{el} is the elastic rate constant of electron–atom collisions.

Thus we consider a certain regime of existence of a photoresonant plasma, in which a relatively high density of excited atoms is created by an external laser source, and the electron temperature is determined by the number density of excited atoms. In this case the number density of electrons as well as the gas temperature increase with time. This plasma lives for a time τ until an external source of radiation acts on it. We assume that the electron temperature T_e is established due to the first processes of (13.11) and collisions of electrons with atoms in the ground state. Heating of a gas proceeds according to equation (13.21) and does not affect the heat balance of electrons. This leads to the criterion

$$k_q N_* \gg \frac{m_e}{M} k_{el} N_o$$

From this criterion it follows that this regime has a threshold, so that the concentration of excited atoms and, correspondingly, the electron temperature must exceed the threshold value.

Let us consider a particular example to demonstrate the reality of this regime. We take the pumping power such that $N_* \sim 10^{13} \text{ cm}^{-3}$, and we use typical values of the rate constants involving electrons $k_q \sim k_{el} \sim 10^{-7} \text{ cm}^3/\text{s}$, $k_{ion} \sim 10^{-9} \text{ cm}^3/\text{s}$, the radiative lifetime of resonantly excited atoms accounting for photon reabsorption $\tau_r \sim 10^{-6} \text{ s}$, the pulse duration $\tau \sim 10^{-4} \text{ s}$, and the mass ratio $m_e/M \sim 10^{-4}$. From this it follows that $N_e \sim 10^{13} \text{ cm}^{-3}$, $T/T_e \sim 10^{-2}$ and $N_o \ll 10^{17} \text{ cm}^{-3}$. The pumping power is $P \sim \hbar\omega N_*/\tau \sim (1 - 10) \text{ W/cm}^3$ in this case. These estimates confirm the reality of the regime under consideration.

13.4 Equilibrium Establishment for Electrons in an Ideal Plasma

We found above that equilibrium in a gaseous system is established by collisions of its atomic particles, and the type of collisions is determined by the equilibrium. In particular, we know that the equilibrium between the ground and excited atomic states in a plasma results from the quenching of excited states by electron impact. We now consider one more example of plasma equilibrium, in which the electron energy distribution follows from collisions between electrons. Taking a uniform plasma in which the equilibrium in the electron subsystem is established quickly, the electron distribution is characterized by the *electron temperature* T_e . A test electron has an arbitrary energy at a given time, but its energy varies in accordance with the Maxwell distribution function if we observe the electron enough long. We now determine the typical time of change of the electron energy in an ideal uniform plasma.

A test electron interacts with a plasma through collisions with electrons or ions and through the interaction with plasma fields which results from fluctuations and collective degrees of freedom in the plasma. On the basis of formulae (12.38) and (12.39) one can find a typical rate of electron–electron collisions which leads to a significant change in the electron energy. In particular, for a test electron with thermal energy $\sim T_e$ this rate is equal to

$$\frac{1}{\tau_{ee}} \sim N_e v \sigma_{ee} \quad (13.22a)$$

where N_e is the number density of electrons, v is the velocity of a test electron, and the diffusion cross section σ_{ee} of electron–electron collisions is given by formula (12.35). In

the same way one can estimate the rate of change of the electron energy resulting from the interaction with plasma fields. We have from formula (2.46)

$$\frac{1}{\tau_{ee}} \sim \frac{v}{\lambda} \sim N_e v \frac{\pi e^4}{T_e^2} \quad (13.22b)$$

Formulae (13.22a) and (13.22b) differ by the Coulomb logarithm contained in formula (12.35) for the diffusion cross section σ_{ee} of electron–electron collisions. This shows the identity of these formulae and gives a rougher estimate of the plasma fields in formula (2.46). Indeed, fluctuations of plasma fields are determined by the positions of plasma charged particles in a space, and the estimate (2.46) corresponds to strong interactions between charged particles if these interactions lead to scattering over large angles. In reality, the main contribution to the diffusion cross section of charged particles is determined by weak interactions. Therefore, both estimates (13.22a) and (13.22b) relate to the same character of interactions in a plasma, but weak interactions are taken into account in formula (13.22a), while in formula (13.22b) we ignore them.

13.5 Electron Drift in a Gas in an External Electric Field

Equilibria in the degrees of freedom of an atomic system are determined by processes in this system, and the kinetics of these processes is the basis for the equilibrium analysis. Below we consider the equilibrium of electrons in a gas in an external electric field when the distribution function is given by the kinetic equation (12.4)

$$\frac{e\mathbf{E}}{m_e} \frac{\partial f}{\partial \mathbf{v}} = I_{ee}(f) + I_{ea}(f) \quad (13.23)$$

Here f is the electron distribution function, $\mathbf{E}$ is the electron field strength, m_e is the electron mass, I_{ea} is the electron–atom collision integral in accordance with formulae (12.23) and (12.25) and I_{ee} is the Landau collision integral (12.37) for electron–electron collisions. The character of the equilibrium for this system depends on the ratio between I_{ee} and I_{ea} .

Let us consider the limiting case $I_{ee} \gg I_{ea}$, which according to formulae (12.25) and (12.39) corresponds to the criterion

$$N_e \gg \frac{m_e \sigma_{ea}}{M \sigma_{ee}} N \quad (13.24)$$

Here N_e and N are the number densities of electrons and atoms, m_e and M are the masses of electrons and atoms, and σ_{ea} , σ_{ee} are typical cross sections for electron–atom and electron–electron collisions. Because $m_e \ll M$ and $\sigma_{ea} \ll \sigma_{ee}$, this criterion can be valid for a gas with a weak degree of ionization. For example, for an argon plasma the criterion (13.24) has the form $c_e \gg 2 \cdot 10^{-7}$ at the temperature $T_e = 1000$ K, where $c_e = N_e/N_a$ is the electron concentration, and at $T_e = 10^4$ K this criterion is $c_e \gg 5 \cdot 10^{-6}$.

In the limiting case under consideration we have

$$I_{ee}(f) = 0 \quad (13.25)$$

The solution according to equation (12.9) has the form of the Maxwell distribution (2.29a) with the electron temperature, which can differ from the gaseous one. The electron temperature is determined by the character of the energy transfer from an external electric field to a gas. Then the energy transfers first from an external field to the electrons, and later it goes from the electrons to the atoms. One can obtain this conclusion from the kinetic equation (13.25) directly. Let us multiply it by the electron energy $m_e v^2/2$ and integrate over electron velocities. We have

$$\int \frac{m_e v^2}{2} I_{ee} d\mathbf{v} = 0$$

because of the physical nature of the collision integral and conservation the total energy in the electron subsystem. Hence we have the integral relation

$$eEw = \int \frac{m_e v^2}{2} I_{ea} d\mathbf{v} \quad (13.26)$$

where w is the *electron drift velocity*. This is the energy balance equation for electrons, so that the left-hand side of this relationship is the power which one electron obtains from the electric field and the right-hand side is the power transmitted from an electron to atoms as a result of their collisions. From equation (13.26) it follows that ions make a small contribution to the power transmission between an external field and a gas in comparison with electrons, because the electron drift velocity significantly exceeds the ion drift velocity. Thus, the character of the power transmission in a weakly ionized gas from an external electric field to electrons, and from electrons to atoms, does not depend on the criterion (13.24). If this criterion is valid, one can consider electrons as a subsystem for which the criterion (13.24) holds true. If this criterion is violated, we have another character of interaction in the electron–atom system.

The specifics of electron–atom collisions in a gas follow from the small ratio of the electron mass m_e to the mass M of an atom. Even if the electron momentum gains a large change as a result of a collision with an atom, the electron energy varies little. Therefore the velocity distribution of electrons is nearly symmetrical with respect to the directions of electron motion. If the electrons move in a gas in an external electric field, their distribution function according to formula (12.18) can be represented in the form

$$f(\mathbf{v}) = f_o(v) + v_x f_1(v) \quad (13.27)$$

where the x -axis is in the direction of the electric field $\mathbf{E}$.

Assuming the number density of electrons N_e to be small compared with the atom number density N_a , we find that the presence of electrons in a gas does not affect the Maxwell distribution function $\varphi(v_a)$ of the atoms, and the electron–atom collision integral has a linear dependence on the distribution function $f(\mathbf{v})$. Thus, the electron–atom collision integral I_{ea} is given by formula (12.19)

$$I_{ea}(f) = I_{ea}(f_o) + I_{ea}(v_x f_1) \quad (13.28)$$

where the collision integrals $I_{ea}(f_o)$ and $I_{ea}(v_x f_1)$ are given by formulae (12.26) and (12.19).

We now examine the behavior of electrons in an atomic gas subjected to an external electric field. The number density of electrons is relatively small, so that collisions between electrons

are not essential in this process. The nature of the electron behavior is determined both by the character of electron–atom collisions and by the mechanism of energy transfer from an electric field to a gas. We shall treat this problem formally by solving the kinetic equation for the electrons: $(e\mathbf{E}/m_e)\partial f/\partial \mathbf{v} = I_{ea}(f)$. Taking into account the expansion (13.27) for the distribution function and expressions (13.28) and (12.19) for the electron–atom collision integral, we obtain the kinetic equation in the form

$$\frac{eE}{m_e} \left(\frac{v_x}{v} \frac{df_o}{dv} + f_1 + v_x^2 \frac{df_1}{dv} \right) = -\nu v_x f_1 + I_{ea}(f_o) \quad (13.29)$$

To solve this equation we first extract the spherical harmonics of the distribution function. To achieve this, we integrate this equation over $d(\cos\theta)$, where θ is the angle between the vectors $\mathbf{v}$ and $\mathbf{E}$, and multiply this equation by $\cos\theta$ and integrate over angles. Then we obtain the set of equations

$$a \frac{df_o}{dv} = -\nu v f_1, \quad \frac{a}{3v^2} (v^3 f_1) = I_{ea}(f_o) \quad (13.30)$$

where $a = eE/m_e$. The set of equations (13.30) establishes the connection between the spherical and nonspherical parts of the distribution function. This is valid irrespective of the criterion (13.24) for the character of an energy exchange in a weakly ionized gas located in an external electric field. In particular, from this it follows that the *electron drift velocity* in a gas is

$$w_e = \int v_x^2 f_1 d\mathbf{v} = \frac{eE}{3m_e} \left\langle \frac{1}{v^2} \frac{d}{dv} \left(\frac{v^3}{\nu} \right) \right\rangle \quad (13.31)$$

where the averaging is done over the spherical distribution function of the electrons. In particular, if $\nu = \text{const}$, the electron drift velocity w_e and the mean energy $\bar{\varepsilon}$ are given by

$$w_e = \frac{eE}{m_e \nu}, \quad \bar{\varepsilon} = \frac{3}{2}T + \frac{M}{2}w_e^2 \quad (13.32)$$

13.6 Diffusion Coefficient of Electrons in a Gas

The expansion (12.18) and (13.27) for the velocity distribution function of electrons located in a gas is valid if any field acts on electrons. Below we use this expansion to evaluate the diffusion coefficient of electrons in a gas when a field results from a gradient of the electron concentration. This gradient causes an electron flux which tends to equalize the electron concentration at different points that leads to a decrease in the gradient.

Let us determine the electron diffusion coefficient in a weakly ionized gas which is defined by the formula $\mathbf{j}_e = -D_e \nabla N_e$. Then the Boltzmann kinetic equation has the form

$$v_x \nabla f = I_{ea}(f) \quad (13.33)$$

where the electron distribution function in accordance with the expansion (13.27) is $f = f_o(v) + v_x f_1(v)$, and the x -axis is directed along the gradient of the electron number density.

Taking into account $f \sim N_e$, we have $\nabla f = f \cdot \nabla N_e / N_e$. Then we obtain by analogy with the first equation of the set (13.30):

$$v_x f_o \nabla N_e / N_e = -\nu v_x f_1$$

i.e. $f_1 = -f_o \nabla N_e / (\nu N_e)$. Let us calculate the electron flux:

$$\mathbf{j}_e = \int \mathbf{v} f d\mathbf{v} = \int v_x^2 f_1 d\mathbf{v} = -\frac{\nabla N_e}{N_e} \int \frac{v_x^2}{\nu} f_o d\mathbf{v} = -\nabla N_e \left\langle \frac{v_x^2}{\nu} \right\rangle$$

where brackets mean averaging over the electron distribution function f_o . Comparing this formula with the definition of the *electron diffusion coefficient* in a gas

$$\mathbf{j}_e = -D_{\perp} \nabla N_e$$

we obtain the following expression for the transverse diffusion coefficient of electrons:

$$D_{\perp} = \left\langle \frac{v^2}{3\nu} \right\rangle \quad (13.34)$$

Formula (13.34) relates to transverse diffusion because only in this case one can separate corrections to the spherical electron distribution function due to the electric field and due to the gradient of the electron number density.

Let us determine the coefficient of transverse diffusion of electrons in a strong magnetic field if directions of the electric and magnetic fields coincide. This case corresponds to the criterion $\omega_H \gg \nu$, where $\omega_H = eH/(m_e c)$ is the *cyclotron frequency* for electrons. The projection of the electron trajectory on a plane which is perpendicular to the field consists of circles whose centers and radii vary after each collision. The diffusion coefficient according to its definition equal $D_{\perp} = \langle x^2 \rangle / t$, where $\langle x^2 \rangle$ is the square of the displacement for a time t in the direction x perpendicular to the field. We have $x - x_o = r_H \cos \omega_H t$, where x_o is the x -coordinate of the center of the considering electron rotation and $r_H = v_{\rho} / \omega_H$ is the *Larmor radius*, so that v_{ρ} is the electron velocity in the direction perpendicular to the field. From this it follows that $\langle x^2 \rangle = n \langle (x - x_o)^2 \rangle = n v_{\rho}^2 / (2\omega_H^2)$, where n is the number of collisions. Since $t = n/\nu$, where ν is the rate of electron-atom collisions, we obtain:

$$D_{\perp} = \left\langle \frac{v_{\rho}^2 \nu}{2\omega_H^2} \right\rangle = \left\langle \frac{v^2 \nu}{3\omega_H^2} \right\rangle, \quad \omega_H \gg \nu$$

where brackets mean averaging over the electron velocities. Joining this formula with (13.34), we have for the transverse diffusion coefficient of electrons which are located in a gas and are moving perpendicular to electric and magnetic fields

$$D_{\perp} = \frac{1}{3} \left\langle \frac{v^2 \nu}{\omega_H^2 + \nu^2} \right\rangle \quad (13.35)$$

13.7 Distribution Function of Electrons in a Gas in an External Electric Field

The distribution function of electrons when they are located in a gas in an external electric field depends on the validity of the criterion (13.24). If this criterion is fulfilled, the Maxwell distribution function f_o follows from equation (13.25). Using it in the first equation of the set (13.31), we find

$$f_1 = \frac{eE}{\nu T_e} f_o \quad (13.36)$$

and the electron drift velocity equals

$$w_e = \frac{eE}{T} \left\langle \frac{v^2}{\nu} \right\rangle \quad (13.37)$$

The electron temperature T_e is a parameter which can be found from the balance equation (13.26) for the power transmitted from an external field to electrons and from electrons to the atoms of a gas. This equation, using formula (12.26) for the spherical part of the electron-atom collision integral for the electron distribution function, takes the form

$$eEw_e = \int \frac{m_e v^2}{2} I_{ea}(f_o) d\mathbf{v} = \frac{m_e^2}{M} \cdot \left(1 - \frac{T}{T_e}\right) \langle v^2 \nu \rangle \quad (13.38)$$

On the basis of formula (13.37) for the electron drift velocity in a gas, we obtain from this:

$$T_e - T = \frac{Ma^2}{3} \frac{\langle v^2 / \nu \rangle}{\langle v^2 \nu \rangle} \quad (13.39)$$

where $a = eE/m_e$. In particular, in the case $\nu = \text{const}$ we have

$$w_e = \frac{eE}{m_e \nu}, \quad T_e - T = \frac{Mw_e^2}{3} \quad (13.40)$$

Introducing the mean free path $\lambda = (N_a \sigma^*)^{-1}$ in the case $\sigma^*(v) = \text{const}$, we obtain from formulae (13.31) and (13.39)

$$w_e = \frac{2eE}{3m_e} \left\langle \frac{1}{v} \right\rangle = \frac{2\sqrt{2}eE\lambda}{3\sqrt{\pi T_e m_e}} = 0.532 \frac{eE\lambda}{\sqrt{m_e T_e}}, \quad T_e - T = \frac{3\pi Mw_e^2}{32} \quad (13.41)$$

In the limiting case opposed to the criterion (13.24), the solution of the set of equations (13.30) using formula (12.26) for the collision integral gives:

$$f_o(v) = A \exp \left(- \int_0^v \frac{m_e v' dv'}{T + Mu^2/3} \right), \quad f_1(v) = \frac{m_e u f_o}{T + Mu^2/3} \quad (13.42a)$$

where

$$u = \frac{eE}{m_e \nu} = \frac{eE}{m_e N_a v \sigma^*(v)} \quad (13.42b)$$

and the distribution function is normalized by

$$\int_0^{\infty} 4\pi v^2 f_o dv = N_e \quad (13.43)$$

From this it follows the expression for the electron drift velocity in a gas:

$$w = \frac{1}{3} \int_0^{\infty} v^2 f_1 4\pi v^2 dv = \frac{4\pi}{3} \int_0^{\infty} \frac{m_e u f_o}{T + M u^2 / 3} v^4 dv$$

In particular, if $\nu = \text{const}$, from this there follows for the electron drift velocity w_e and the mean energy $\bar{\varepsilon}$

$$w_e = \frac{eE}{m_e \nu}, \quad \bar{\varepsilon} = \frac{3T}{2} + \frac{M w_e^2}{2} \quad (13.44a)$$

and these parameters are given by formula (13.40) in the other limiting case. If $\sigma^*(v) = \text{const}$, the distribution functions (13.42) yield in the limit $\bar{\varepsilon} \gg T$ (here $\lambda = 1/(N_a \sigma^*)$):

$$w_e = 0.857 \left(\frac{m_e}{M} \right)^{1/4} \sqrt{\frac{eE\lambda}{m_e}}, \quad \bar{\varepsilon} = 0.427 eE\lambda \sqrt{\frac{M}{m_e}} = 0.530 M w_e^2 \quad (13.44b)$$

These dependencies differ from those of formula (13.41) for the other limiting cases.

13.8 Atom Excitation by Electrons in a Gas in an Electric Field

Electrons moving in a gas in an external electric field can excite atoms of the gas. Below we evaluate the rate of atom excitation if the typical electron energy is small compared with the excitation energy, and electrons which excite atoms are found in the tail of the energy distribution function of electrons. If an electron is located in a gas in an external electric field, in spite of its relative smallness the nonsymmetric component of the velocity distribution function is of importance, because through it the electron obtains energy from the electric field. We now consider the excitation of gas atoms in collisions with individual electrons located in a gas in an electric field. We assume that collisions with atoms create a strong friction for electrons in an energy space, and the electron energy attains the excitation threshold after many elastic collisions. Then the excitation rate of atoms by electrons is determined by the flux of the excitation energy in the velocity or electron energy space.

To describe this process, we use the expansion (13.27) for a non-stationary distribution function of electrons, and using the standard procedure, as for deriving the set of equations (13.30), we obtain instead this set of equations:

$$\frac{\partial f_o}{\partial t} + \frac{a}{3v^2} \frac{\partial(v f_1)}{\partial v} = I_{ea}(f_o), \quad \frac{\partial f_1}{\partial t} + a \frac{\partial f_o}{\partial v} = -\nu v f_1$$

Assuming the excitation flux to be relatively small, we ignore the non-stationarity overall except for the first term, which corresponds to a small flux in the energy space. As a result, we obtain

$$\frac{\partial f_o}{\partial t} = I_{ea}(f_o) + \frac{a}{3v^2} \frac{d}{dv} \left(\frac{v^2}{\nu} \frac{df_o}{dv} \right)$$

The non-stationarity of the distribution function is due to atom excitation only. Hence, the rate of excitation is

$$\frac{dN_*}{dt} = -\frac{dN_e}{dt} = -\int 4\pi v^2 dv \frac{\partial f_o}{\partial t}$$

where N_* is the number density of excited atoms. On the basis of the collision integral (12.26) for f_o we obtain from this

$$\frac{dN_*}{dt} = 4\pi \frac{m_e}{M} v^3 \nu \left[\left(T + \frac{Ma^2}{3\nu^2} \right) \frac{df_o}{d\varepsilon} + f_o \right]_{|\varepsilon=\Delta\varepsilon}$$

where $\varepsilon = m_e v^2/2$ is the electron energy and $\Delta\varepsilon$ is the energy of atom excitation.

We use the boundary condition $f_o(\Delta\varepsilon) = 0$ for the distribution function which satisfies the following equation under stationary conditions and below the excitation threshold far from it:

$$\left(T + \frac{Ma^2}{3\nu^2} \right) \frac{df_o}{d\varepsilon} + f_o = 0$$

This means fast absorption of electrons above the excitation threshold and gives for the distribution function

$$f_o(\varepsilon) = C [\varphi_o(\varepsilon) - \varphi_o(\Delta\varepsilon)] = C \left[\exp \left(-\int_0^\varepsilon \frac{d\varepsilon'}{T + \frac{Ma^2}{3\nu^2}} \right) - \exp \left(-\int_0^{\Delta\varepsilon} \frac{d\varepsilon'}{T + \frac{Ma^2}{3\nu^2}} \right) \right]$$

and $\varphi_o(\varepsilon)$ is the distribution function if we ignore electron absorption due to the excitation process, so that far from the excitation threshold $\varphi_o(\varepsilon) = f_o(\varepsilon)$. The constant C follows from the normalization condition

$$C = N_e \left[4\pi \int_0^{v_o} v^2 dv \exp \left(-\int_0^\varepsilon \frac{d\varepsilon'}{T + \frac{Ma^2}{3\nu^2}} \right) \right]^{-1}$$

Here N_e is the number density of electrons, and the electron threshold velocity is $v_o = \sqrt{2\Delta\varepsilon/m_e}$. Thus we have for the rate of atom excitation by individual electrons in a gas in an external electric field

$$\frac{dN_*}{dt} = 4\pi v_o^3 \frac{m_e}{M} \nu(v_o) \varphi_o(v_o) = N_e \frac{m_e}{M} \nu(v_o) \cdot \frac{\exp \left(-\int_0^{\Delta\varepsilon} \frac{d\varepsilon'}{T + \frac{Ma^2}{3\nu^2}} \right)}{\int_0^{v_o} \left(\frac{v}{v_o} \right)^2 \frac{dv}{v_o} \exp \left(-\int_0^\varepsilon \frac{d\varepsilon'}{T + \frac{Ma^2}{3\nu^2}} \right)} \quad (13.45)$$

where $\varphi_o(v_o) = \varphi_o(\Delta\varepsilon)$ is the electron distribution function at the excitation threshold if we neglect the excitation process. In the case $\nu(v_o) = \text{const}$ this formula takes the form

$$\frac{dN_*}{dt} = \frac{4}{\sqrt{\pi}} \left(\frac{\Delta\varepsilon}{T + \frac{Ma^2}{3\nu^2}} \right)^{3/2} N_e \frac{m_e}{M} \nu(v_o) \exp \left(-\frac{\Delta\varepsilon}{T + \frac{Ma^2}{3\nu^2}} \right) \quad (13.46)$$

It is of interest to find which part ξ of the power taken by electrons from an external electric field is consumed on atom excitation. We assume that this power is also transformed into the atom thermal energy as a result of elastic collisions between electrons and atoms, and this power per electron is eEw , where w is the electron drift velocity. In the case $\nu = \text{const}$ we have from formula (13.46), neglecting the atom thermal energy ($T \ll Mw^2$)

$$\xi = \frac{x}{1+x}, \quad x = \frac{\Delta\varepsilon \frac{dN_*}{dt}}{eEwN_e} = \frac{4}{3\sqrt{\pi}} \left(\frac{\Delta\varepsilon}{\bar{\varepsilon}} \right)^{5/2} \exp \left(-\frac{\Delta\varepsilon}{\bar{\varepsilon}} \right) \quad (13.47)$$

where $\bar{\varepsilon} = Ma^2/(3\nu^2) = Mw^2/3$ is the average electron energy. Figure 13.2 contains the dependence of the efficiency of atom excitation ξ on the electron energy $\bar{\varepsilon}$ under these conditions.

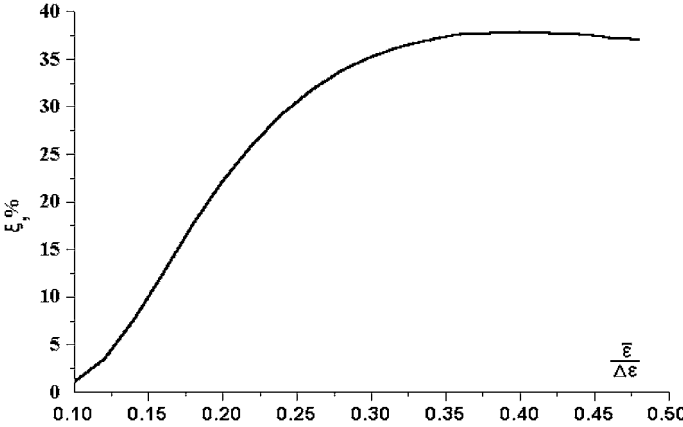


Figure 13.2. The part of an energy which is consumed for atom excitation from the energy obtained from an external electric field by an electron moving in a gas. It is assumed the rate constant of electron-atom elastic scattering to be independent the energy of colliding electron, and a time for a test electron to obtain the energy from zero up to excitation energy is large compared to a time of atom excitation by fast electron in the gas.

The above formulae are based on the assumption that the rate of atom excitation is determined mostly by the diffusion of electrons in an energy space from small energies up to the atom excitation energy. We now consider another limiting case when excitation on the tail of the energy distribution function proceeds slowly and determines the rate of atom excitation by individual electrons, which move in a gas in an external electric field. First we evaluate the distribution function above the excitation threshold in the energy range $\varepsilon \geq \Delta\varepsilon$, including

in the kinetic equation for electrons a term for inelastic electron–atom collisions. We assume that quenching of the excited atom does not proceed by electron impact because of the small number density of electrons. Then the second equation of the set (13.30) takes the form:

$$-\frac{a}{3v^2} \frac{d}{dv} (v^3 f_1) = I_{ea}(f_o) - \nu_{ex} f_o$$

where $\nu_{ex} = N_a k_{ex}$, N_a is the number density of atoms, and k_{ex} is the excitation rate constant of the atom by electron impact. The collision integral I_{ea} takes into account elastic electron–atom collisions. Using the connection (13.31) between f_o and f_1 , we obtain the following equation for f_o :

$$\frac{a}{3v^2} \frac{d}{dv} \left(\frac{v^2}{\nu} \frac{df_o}{dv} \right) + I_{ea}(f_o) - \nu_{ex} f_o = 0$$

Based on the expression (12.23) for the electron–atom collision integral and neglecting the atom kinetic energy ($\sim T$) compared with the electron energy, we have

$$\frac{a}{3v^2} \frac{d}{dv} \left(\frac{v^2}{\nu} \frac{df_o}{dv} \right) + \frac{m_e}{M} \frac{1}{v^2} \frac{d}{dv} (v^3 \nu f_o) - \nu_{ex} f_o = 0 \quad (13.48)$$

We assume the average electron energy $\bar{\varepsilon}$ to be small compared with the atom excitation energy $\Delta\varepsilon$. Then it follows from formula (13.45) that the mean electron energy is $\bar{\varepsilon} \sim Ma^2/\nu^2$. In addition, we assume that atom excitation influences the electron distribution function, i.e.

$$\nu \gg \nu_{ex} \gg \nu \frac{m_e}{M} \frac{\Delta\varepsilon}{\bar{\varepsilon}} \quad (13.49)$$

This allows us to neglect the second term of the kinetic equation (13.48). Let us solve the resultant kinetic equation for the tail of the distribution function on the basis of the quasiclassical method accepting $f_o = A \exp(-S)$, where $S(v)$ is a smooth function, i.e. $(S')^2 \gg S''$. This gives $S' = \sqrt{3\nu_{ex}\nu}/a$, $a = eE/m_e$, and the distribution function for $\varepsilon \gg \bar{\varepsilon}$ has the form:

$$f_o(v) = f_o(v_o) \exp(-S) = f_o(v_o) \exp \left(- \int_{v_o}^v \frac{dv}{a} \sqrt{3\nu_{ex}\nu} \right) \quad (13.50a)$$

where $v_o = \sqrt{2\Delta\varepsilon/m_e}$ and $f_o(v_o)$ is determined by elastic electron–atom collisions. Near the threshold of atom excitation this formula gives:

$$S = \frac{2v_o}{5a} \sqrt{3 \frac{g_*}{g_o} \nu_q \nu_o} \left(\frac{\varepsilon - \Delta\varepsilon}{\Delta\varepsilon} \right)^{5/4} \quad (13.50b)$$

where the rate of elastic electron–atom collisions at the excitation threshold is $\nu_o = \nu(v_o)$, $\nu_q = N_a k_q$, k_q is the rate constant of quenching of the excited atom by electron impact, g_o, g_* are the statistical weights of the ground and excited atom states, $a = eE/m_e$, and we use formula (11.31) for the rate constant of atom excitation by electron impact which connects this rate constant and the rate of quenching of an excited atom by a slow electron.

Using formula (13.50a) for the electron distribution function, we assume that the logarithmic derivative of the distribution function is determined by the excitation process not far from the threshold.

Formulae (13.50) give for the rate of atom excitation by electrons if this process proceeds mostly near the excitation threshold

$$\frac{dN_*}{dt} = \int 4\pi v^2 dv f_o(v_o) e^{-S} \nu_{\text{ex}}(v) = 4.30 a v_o^2 \left(\frac{a}{v_o \nu_o} \right)^{1/5} \left(\frac{\nu_q g_*}{\nu_o g_o} \right)^{2/5} f_o(v_o) \quad (13.51)$$

and the distribution function is normalized by the condition (13.43).

Comparing formulae (13.46) and (13.51) for the rate of atom excitation by individual electrons moving in a gas in an external electric field, one can make a choice between these two limiting case. Indeed, in the case

$$\left(\frac{a}{v_o \nu_o} \right)^{6/5} \left(\frac{\nu_q g_*}{\nu_o g_o} \right)^{2/5} \gg 1 \quad (13.52)$$

the excitation process is restricted by diffusion of electrons in an energy space to the excitation threshold, and the rate of this process is determined by the formulae (13.45) and (13.46). In the other limiting case the excitation rate is determined by formula (13.51). Note that formula (13.51) is valid at low electric field strengths, whereas formula (13.45) holds true at high fields.

13.9 Excitation of Atoms in Plasma

When electrons are located in a plasma, the energy distribution function of electrons drops strongly at the tail due to the excitation of atoms and can be restored owing to collisions between electrons. Analyzing the character of atom excitation in a plasma, we assume for simplicity that the excited states are destroyed as a result of radiation, i.e. quenching by electron impact is absent. We assume the criterion (13.24) to be fulfilled so that we have the Maxwell distribution function of electrons over velocities. In the first limiting case we assume that the Maxwell distribution function is restored at energies $\varepsilon \geq \Delta\varepsilon$ ($\Delta\varepsilon$ is the atom excitation energy) which are responsible for excitation of atoms. Then the rate of atom excitation is equal to

$$\frac{dN_*}{dt} = N_a \int 4\pi v^2 dv \varphi(v) k_{\text{ex}}(v) \quad (13.53)$$

where N_* is the number density of excited atoms, N_a is the number density of atoms in the ground state, $\varphi(v)$ is the Maxwell distribution function of electrons, and k_{ex} is the rate constant of atom excitation by electron impact, which is given by formula (11.31b). Averaging over the Maxwell distribution function of electrons, we have

$$\frac{dN_*}{dt} = N_a N_e \overline{k_{\text{ex}}} = N_a N_e k_q \frac{g_*}{g_o} \exp\left(-\frac{\Delta\varepsilon}{T_e}\right) \quad (13.54)$$

where the average rate constant of atom excitation in the limit $\Delta\varepsilon \gg T_e$ (T_e is the electron temperature) is equal to

$$\bar{k}_{\text{ex}} = \frac{1}{N_e} \int 4\pi v^2 dv \varphi(v) k_{\text{ex}}(v) = \frac{g_*}{g_o} k_q \exp\left(-\frac{\Delta\varepsilon}{T_e}\right) \quad (13.55)$$

Let us consider the other limiting case of excitation of atoms by electrons in a plasma when the criterion (13.24) is valid, but the Maxwell distribution function of electrons is not restored due to electron–electron collisions above the excitation limit because of the absorption of fast electrons as a result of the excitation process. Then the excitation rate is determined by the rate of formation of fast electrons with energy $\varepsilon > \Delta\varepsilon$ as a result of elastic collisions of electrons. On the basis of the kinetic equation (12.4), using the expressions (12.38) and (12.39) for the electron–electron collision integral, we have for the excitation rate per unit volume:

$$\frac{dN_*}{dt} = - \int_{v_o}^{\infty} 4\pi v^2 dv \frac{\partial f}{\partial t} = - \int_{v_o}^{\infty} 4\pi v^2 dv I_{ee}(f_o) = - \frac{4\pi v_o}{m_e} B_{ee}(v_o) \left(\frac{f_o}{T_e} + \frac{df_o}{d\varepsilon} \right)$$

where the distribution function f_o is taken at the excitation energy $\varepsilon = \Delta\varepsilon$. The electron distribution function in this case is the solution of the equation $I_{ee}(f_o) = 0$ under the boundary condition $f_o(v_o) = 0$ which accounts for an effective absorption of electrons above the excitation threshold. Then we have for the distribution function

$$f_o(v) = N_e \left(\frac{m_e}{2\pi T_e} \right)^{3/2} \left[\exp\left(-\frac{\varepsilon}{T_e}\right) - \exp\left(-\frac{\Delta\varepsilon}{T_e}\right) \right], \quad \varepsilon \leq \Delta\varepsilon \quad (13.56)$$

From this it follows that the electron distribution function is the Maxwell distribution far from the excitation threshold, while near the threshold the distribution function tends to zero because of the absorption of electrons due to the excitation of atoms. Using this distribution function and the expression (12.39) for $B_{ee}(v)$, we obtain in this case for the rate of excitation:

$$\frac{dN_*}{dt} = 4\sqrt{2\pi} \cdot \frac{N_e^2 e^4 \Delta\varepsilon \ln \Lambda}{m_e^{1/2} T_e^{5/2}} \exp\left(-\frac{\Delta\varepsilon}{T_e}\right) \quad (13.57)$$

Formula (13.57) is valid for high number densities of electrons when fast establishment of equilibrium takes place for the electron distribution function on velocities. The corresponding criterion has the form:

$$\frac{N_e}{N_a} \gg \frac{k_q}{k_{ee}} \quad (13.58)$$

where the effective rate constant k_{ee} for the Coulomb interaction of electrons follows from comparison of formulae (13.54) and (13.57) and has the form:

$$k_{ee} = 4\sqrt{2\pi} \cdot \frac{g_o}{g_*} \frac{e^4 \Delta\varepsilon \ln \Lambda}{m_e^{1/2} T_e^{5/2}} \quad (13.59)$$

Formula (13.57) is valid under the opposite condition with respect to the criterion (13.58). We can see that the criterion (13.58) is much stronger than (13.24) because $m_e \ll M$. Thus both

considered regimes of atom excitation in a plasma are possible. At relatively small number densities of electrons the distribution function is given by formula (13.56), while the Maxwell distribution function of electrons is valid at high degrees of ionization. Correspondingly, the rate of atom excitation in a plasma varies from that by formula (13.54) to that by formula (13.57) as the electron number density increases.

As a demonstration of these results, Table 13.2 contains values of the rate constants (13.59) for rare gas atoms under conditions $T_e = 1$ eV, $\ln \Lambda = 10$, and the boundary ionization degree is given by the relation

$$\left(\frac{N_e}{N_a} \right)_b = \frac{k_q}{k_{ee}}$$

for these parameters. The quenching rate constant for metastable rare gas atoms is taken from Table 11.4.

Table 13.2. The parameters of the criterion (13.58) for metastable rare gas atoms.

Metastable atom	$\Delta\varepsilon$, eV	k_{ee} , 10^{-4} cm ³ /s	$\left(\frac{N_e}{N_a} \right)_b$, 10^{-6}
He(2^3S)	19.82	5.8	5.4
Ne(2^3P_2)	16.62	2.9	0.69
Ar(3^3P_2)	11.55	2.0	2.0
Kr(4^3P_2)	9.915	1.7	2.0
Xe(5^2P_2)	8.315	1.4	13

Note that in the case of large electron densities when the electron distribution function is the Maxwell one, this value, being represented in the form $f = f(v_o) \exp(-S)$, is characterized by the following exponent

$$S = \frac{\varepsilon - \Delta\varepsilon}{T_e} = 3\nu_o^2 \frac{(\varepsilon - \Delta\varepsilon)}{Ma^2} \quad (13.60)$$

Here for simplicity we assume $\nu(v) = \text{const.}$ Because of the criterion (13.55), formula (13.60) gives a smaller decrease of the distribution function with increasing electron energy than that which follows from formula (13.57) which holds true in the limit when collisions between electrons are not significant. Above we assume that the quenching of excited atoms is determined by processes other than electron impact. This corresponds to the opposite criterion with respect to (13.15). We now consider the other case, when quenching of excited atoms is determined by electron–atom collisions, and let us consider the case in which the criterion (13.15) holds true. Then, based on the criterion (13.58), we have that fast electrons are generated and destroyed as a result of inelastic collisions between electrons and atoms. Because of the equilibrium between the atomic states considered, this gives:

$$\nu_{\text{ex}} f_o(v) v^2 dv = \nu_q f_o(v') v'^2$$

Here $v^2 = 2\Delta\varepsilon/m_e + v'^2$, v and v' are the velocities of fast and slow electrons, $\nu_{\text{ex}} = N_a k_{\text{ex}}$ and $\nu_q = N_i k_q$ are the rates of excitation and quenching of atomic states by electron

impact so that N_a and N_i are the number densities of atoms in the ground and excited states correspondingly, and k_{ex} , k_q are the rate constants of the corresponding processes which are connected by the principle of detailed balance (10.29). From this we have:

$$\frac{N_a}{g_o} f_o(v) = \frac{N_*}{g_*} f_o(\sqrt{v^2 - v_o^2}), \quad v > \sqrt{2\Delta\varepsilon/m} \quad (13.61)$$

This relation establishes the connection between the distribution functions of slow and fast electrons. The relation can be written in the form:

$$f_o(v) = \frac{f_o(v_o) f_o(\sqrt{v^2 - v_o^2})}{f_o(0)} \quad (13.62)$$

In particular, for the Maxwell distribution function of slow electrons [$f_o \sim \exp(-\varepsilon/T_e)$] this formula gives:

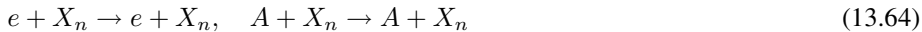
$$f_o(v) = f_o(v_o) \exp\left(\frac{\varepsilon - \Delta\varepsilon}{T_e}\right) \quad (13.63)$$

where T_e is the electron temperature and $\varepsilon = m_e v^2/2$ is the electron energy. Thus inelastic collisions restore the Maxwell distribution function above the threshold of atom excitation.

The above cases of atom excitation in a plasma show that this process depends on the character of establishment of the electron distribution function near the excitation threshold. The result depends both on the rate of restoration of the electron distribution function in electron–electron or electron–atom collisions and on the character of quenching of excited atoms. The competition these processes yields a complicated form of electron distribution function and the effective rate of excitation of atoms in a gas or in a plasma. This excitation has a different form depending on the collision processes which establish the electron distribution function below the excitation threshold and the character of processes for excited atoms.

13.10 Thermal Equilibrium in a Cluster Plasma

One more example relates to a *cluster plasma*, which is a weakly ionized gas with clusters, and clusters determine some properties of this system. Let us assume the criterion (13.24) to be fulfilled, so that this system is characterized by the gaseous T and electron T_e temperatures. The cluster temperature results from the processes



where e , A , and X_n are an electron, an atom of a buffer gas, and a cluster consisting of n atoms. Let us consider a cluster on the basis of the *liquid drop model* (see Section 11.5) according to which a cluster is similar to a liquid drop. Then the cross section of collision of an atom with a cluster is given by formula (11.14) $\sigma = \pi r^2$, where r is the cluster radius determined by formula (11.13) within the framework of the liquid drop model. If a cluster has a positive charge Z , the cross section of the atom–cluster collision is determined by the formula $\sigma_a = \pi \rho^2$, where ρ is the impact parameter in formula (11.5) for collision at which

the distance of closest approach equals the cluster radius. Hence, the cross section of the electron–cluster collision equals

$$\sigma_e = \pi \rho^2(r) = \pi r^2 + \pi r \frac{Ze^2}{\varepsilon} \quad (13.65)$$

where ε is the electron energy.

Now let us determine the *cluster temperature* T_{cl} on the basis of a simple model of collisions such that an atomic particle after collision obtains the cluster thermal energy on average. This means for $T_e > T$ that an atom after the collision event obtains on average the energy $\frac{3}{2}(T_{cl} - T)$ from the cluster, and an electron transfers on average to the cluster the energy $\frac{3}{2}(T_e - T_{cl})$ in one collision. Then the power that the cluster takes from the electrons is

$$\frac{3}{2}(T_e - T_{cl}) \cdot v_e N_e \sigma_e$$

where v_e is the average electron velocity, N_e is the number density of electrons and σ_e is the cross section of electron–cluster collisions. The power which the atoms obtain from the cluster is equal to

$$\frac{3}{2}(T_{cl} - T) \cdot v_a N_a \sigma_a$$

where v_a is the average velocity of atoms, N_a is the number density of atoms and σ_a is the cross section of collisions of atoms with the cluster. The stationary condition, using the above formulae for cross sections averaged over the Maxwell distribution of atoms and electrons, leads to the following expression for the cluster temperature T_{cl}

$$T_{cl} = \frac{T + \zeta T_e}{1 + \zeta} \quad (13.66a)$$

where

$$\zeta = \sqrt{\frac{T_e m_a}{T m_e}} \cdot \left(1 + \frac{Ze^2}{r T_e}\right) \cdot \frac{N_e}{N_a} \quad (13.66b)$$

Thus the cluster temperature lies between the electron and atomic temperatures; this value depends on the parameters of electrons and atoms. This example demonstrates the character of the establishment of a stationary state of a system which is determined by some processes in this non-equilibrium system.

Part IV

Transport Phenomena in Atomic Systems

14 General Principles of Transport Phenomena

14.1 Types of Transport Phenomena

Transport phenomena proceed in nonuniform systems whose parameters are not constant in a space. Then the corresponding fluxes arise and tend to equalize these parameters in the space. As an example, let us consider a uniform buffer gas with an admixture the density of which varies slightly in a space. Let us divide the space into cells, so that the difference between the admixture densities in neighboring cells is small. Then in the first approximation we have the thermodynamic equilibrium in each cell, i.e. the distribution function of admixture atoms is the Maxwell one $\varphi(v)$ in a motionless gas. The second approximation takes into account the density gradient of admixture atoms, and their distribution function takes the form

$$f(\mathbf{v}) = \varphi(v) + v_x f_1(v) \quad (14.1)$$

Here the x -axis is directed along the density gradient, and the second term on the right-hand side of formula (14.1) is responsible for a flux of admixture atoms which tends to equalize the density in the space.

This system state with a flux can be considered as a stationary one if the flux is relatively small. Then the following criterion must be fulfilled for the considered phenomena:

$$\lambda \ll L \quad (14.2)$$

where λ is the *mean free path* of atoms in a gas and L is a typical size of the system or a distance over which a parameter under consideration varies noticeably. If this criterion is fulfilled, we have a stationary state of the system to a first approximation, and transport of particles, heat or momentum occurs in the second approximation corresponding to expansion over small parameters according to criterion (14.2). Below we consider various types of transport phenomena.

The coefficients of proportionality between fluxes and corresponding gradients are called the *kinetic coefficients* or *transport coefficients*. For example, the *diffusion coefficient* D is introduced as the proportionality factor between the particle flux $\mathbf{j}$ and the gradient of the concentration c of a given species

$$\mathbf{j} = -DN\nabla c \quad (14.3)$$

where N is the total number density of atomic particles. If the concentration of a given species is low ($c_k \ll 1$), i.e. this species is an admixture to a buffer gas, the flux of the atomic particles of this species can be written as

$$\mathbf{j} = -D_k \nabla N_k \quad (14.4)$$

where N_k is the number density of atomic particles of a given species. The *thermal conductivity coefficient* κ is defined as the proportionality factor between the heat flux $\mathbf{q}$ and the temperature gradient:

$$\mathbf{q} = -\kappa \nabla T \quad (14.5)$$

The *viscosity coefficient* η is the proportionality factor between the friction force, acting per unit area of a moving gas, and the gradient of the gas average velocity in the direction perpendicular to the surface of a gas element. If the average gas velocity $\mathbf{w}$ is parallel to the x -axis and varies in the z direction, the friction force is proportional to $\partial w_x / \partial z$ and acts on a gaseous element xy . Thus the force F per unit area is equal to

$$F = -\eta \frac{\partial w_x}{\partial z} \quad (14.6)$$

These definitions as well as the previous ones refer to condensed phases also.

Let us estimate the diffusion coefficient of atomic particles in a gas. The diffusion flux equals the difference of the fluxes in the opposite directions. Each of these, to an order of magnitude, equals $N_k v$, where N_k is the number density of atomic particles of a given species, v is a typical velocity. Thus $j \sim \Delta N_k v$, where ΔN_k is the difference of the number densities of atomic particles which partake in this transport. Take into account that atomic particles which reach this point without collisions are located from it on distances of the order of the mean free path $\lambda \sim (N\sigma)^{-1}$, where σ is a typical cross section of elastic collisions of particles and N is the total number density of gas particles. Hence we have $\Delta N_k \sim \lambda \nabla N_k$, and the diffusion flux is $j \sim \lambda v \nabla N_k$. Comparing it with the definition of the diffusion coefficient (14.4), we obtain

$$D \sim v \lambda \sim \frac{1}{N\sigma} \sqrt{\frac{T}{m}} \quad (14.7)$$

Here T is the gas temperature and m is the mass of the particles of a given species, which is assumed to be of the order of the mass of the other gas particles. Note that in this analysis we did not account for the sign of the flux because it is in the opposite direction to that of the number density gradient and tends to equalize the particle number densities at neighboring points. One can conclude the same about the signs of the fluxes and gradients for other transport phenomena. Table 14.1 lists coefficients of self-diffusion for atoms in parent gases at room temperature for the number density of gaseous atoms or molecules $N = 2.689 \cdot 10^{19} \text{ cm}^{-3}$ that correspond to normal conditions ($T = 273 \text{ K}$, $p = 1 \text{ atm}$).

14.2 Diffusion Motion of Particles

The diffusion motion corresponds to the general case where atomic particles neither disappear from or appear in a space. Then we have the following balance equation in a space for the density of atomic particles of a given species N_k :

$$\frac{\partial}{\partial t} \int_V N_k d\mathbf{r} = - \int_S \mathbf{j}_k ds$$

Table 14.1. Coefficients of self-diffusion of atoms in parent gases at room temperature.

Gas	$D, \text{cm}^2/\text{s}$	Gas	$D, \text{cm}^2/\text{s}$	Gas	$D, \text{cm}^2/\text{s}$
He	1.6	H ₂	1.3	H ₂ O	0.28
Ne	0.45	N ₂	0.18	CO ₂	0.096
Ar	0.16	O ₂	0.18	NH ₃	0.25
Kr	0.084	CO	0.18	CH ₄	0.20
Xe	0.048				

Here V is the volume of the cell being considered, S is a surface which restricts this cell, $d\mathbf{r}$ and ds are the volume and surface elements for this cell and $\mathbf{j}_k$ is the flux of atomic particles of a given species through the cell surface. This equation takes into account the balance of particles in a given cell, so that the variation of the particle number density in a cell is determined by the flux of these particles out of or into the cell. This equation is transformed to the form:

$$\int_V \left(\frac{\partial}{\partial t} N_k + \text{div } \mathbf{j}_k \right) d\mathbf{r} = 0 \quad (14.8)$$

and because it is valid for any cell, we have

$$\frac{\partial}{\partial t} N_k + \text{div } \mathbf{j}_k = 0$$

This equation is called the *continuity equation*. In the case of the diffusion motion it has the form

$$\frac{\partial N}{\partial t} = D \Delta N \quad (14.9)$$

It follows from this equation that a typical time for particle transport over a distance of the order of L is $\tau_L \sim L^2/D$. Using the estimate (14.7) for the diffusion coefficient, we have from this $\tau_L \sim \tau_o (L/\lambda)^2$, where $\tau_o \sim \lambda/v$ is a typical time between neighboring collisions of a test atomic particle with a gas particle. Thus the criterion (14.2) leads to $\tau_L \gg \tau_o$ that allows us to consider this process a stationary one.

Bearing in mind the diffusion character of motion of test particles, we introduce the probability $P(\mathbf{r}, t)$ that a test particle is at the point $\mathbf{r}$ at moment t . Assuming this particle to be located at the origin at zero time, we find that this probability is spherically symmetric, and the condition of its normalization has the form

$$\int_0^\infty P(r, t) 4\pi r^2 dr = 1 \quad (14.10)$$

The probability P satisfies the equation (14.9), which in the spherical symmetric case takes the form

$$\frac{\partial P}{\partial t} = \frac{D}{r} \frac{\partial^2}{\partial r^2} (rP)$$

In order to find the average parameters of the diffusion motion, let us multiply this equation by $4\pi r^4 dr$ and integrate the result over dr . The left-hand side of the equation yields

$$\int_0^{\infty} 4\pi r^4 dr \frac{\partial P}{\partial t} = \frac{d}{dt} \int_0^{\infty} r^2 P \cdot 4\pi r^2 dr = \frac{d\overline{r^2}}{dt}$$

where $\overline{r^2}$ is the mean square of the distance from the origin. Integrating twice by parts and using the normalization condition (14.10), we transform the right-hand side of the obtained equation into:

$$D \int_0^{\infty} 4\pi r^4 dr \frac{1}{r} \frac{\partial^2}{\partial r^2} (rW) = -3D \int_0^{\infty} 4\pi r^2 dr \frac{\partial}{\partial r} (rW) = 6D \int_0^{\infty} W 4\pi r^2 dr = 6D$$

The resulting equation is

$$d\overline{r^2} = 6Ddt$$

Since at zero time the particle is located at the origin, the solution of this equation has the form:

$$\overline{r^2} = 6Dt \quad (14.11)$$

Because the motion in different directions is independent and has a random character, from this it follows that

$$\overline{x^2} = \overline{y^2} = \overline{z^2} = 2Dt \quad (14.12)$$

The solution of equation (14.9) can be obtained on the basis of the normal distribution (2.4) which is suitable for this process. Indeed, the diffusion motion consists of random displacements of a particle, and the result of many collisions of this particle with the surrounding ones can use the general concept of the normal distribution. In the spherically symmetric case we have

$$P(\mathbf{r}, t) = w(x, t) w(y, t) w(z, t)$$

and substituting $\Delta = \langle x^2 \rangle = 2Dt$ in formula (2.4), we obtain for each w -function

$$w(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

This yields

$$P(r, t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right) \quad (14.13)$$

14.3 The Einstein Relation

If an atomic particle travels in a vacuum in a field of external forces, it is accelerated. If this particle travels in a gas, collisions with gaseous particles create a frictional force, and the mean velocity of this particle in a gas is established depending on its interaction with external fields. The proportionality coefficient between the particle mean velocity $\mathbf{w}$ and the force $\mathbf{F}$ acting on the particle from an external field is called the particle *mobility*. Thus the definition of the mobility b of a particle gives

$$\mathbf{w} = b\mathbf{F} \quad (14.14)$$

Let us consider the motion of test particles in a buffer gas under the action of an external field if the particles are in thermodynamic equilibrium with the gas. According to the Boltzmann formula (2.18), we have the following distribution for the number density of test particles

$$N = N_o \exp\left(-\frac{U}{T}\right)$$

where U is the potential of an external field, and T is the gaseous temperature. The diffusion flux of the test particles according to formula (14.4) equals $\mathbf{j} = -D\nabla N = -D\mathbf{F}N/T$, where $\mathbf{F} = -\nabla U$ is the force acting on the test particle. Because of the thermodynamic equilibrium, the diffusion flux is compensated by the hydrodynamic flux of the particles $\mathbf{j} = \mathbf{w}N = b\mathbf{F}N$. Equalizing these fluxes, we obtain the following relation between the kinetic coefficients

$$b = \frac{D}{T} \quad (14.15)$$

This relationship is known as the *Einstein relation*. It testifies the identical character of particle collisions which determine the mobility and diffusion coefficient of particles in a gas. The Einstein relation is valid for small fields that do not disturb the thermodynamic equilibrium between the test and gaseous particles. On the basis of formulae (14.15) and (14.7) we have the following estimate of the particle mobility:

$$b \sim \frac{1}{N\sigma\sqrt{mT}} \quad (14.16)$$

14.4 Heat Transport

Heat transport is realized in a similar way to particle transport. The heat flux is defined as

$$\mathbf{q} = \int \mathbf{v} \cdot \frac{mv^2}{2} \cdot f d\mathbf{v} \quad (14.17)$$

where f is the distribution function of particles on velocities, and the relation between the heat flux and the temperature is given by formula (14.5). To estimate the thermal conductivity coefficient we use the same procedure as in the case of the diffusion coefficient. Take the heat

flux through a given point as the difference of these values from both sides, and express the difference of the heat fluxes through the difference in temperatures. Then according to formula (14.17) the heat flux is estimated as $q \sim Nv\Delta T$ because the energies of particles passed to this point from opposite sides are different. Because only particles located at a distance $\sim \lambda$ reach this point without collisions, we have $\Delta T \sim \lambda \nabla T$. Substituting this in the formula for the heat flux and comparing the result with formula (14.5), we obtain the following estimate for the thermal conductivity coefficient:

$$\kappa \sim Nv\lambda \sim \frac{v}{\sigma} \sim \frac{1}{\sigma} \sqrt{\frac{T}{m}} \quad (14.18)$$

As we can see, the thermal conductivity coefficient is independent of the number density of particles. Indeed, an increase in the number density leads to an increase in the number of particles which transfer heat, and to a decrease in the distance of this transport. These two effects are mutually canceled. Table 14.2 gives the thermal conductivity coefficients of gases at a pressure of 1 atm.

Table 14.2. Thermal conductivity coefficients of gases in 10^{-4} W/(cm · K) at 1 atm.

$T, \text{ K}$	100	200	300	400	600	800	1000
H ₂	6.7	13.1	18.3	22.6	30.5	37.8	44.8
He	7.2	11.5	15.1	18.4	25.0	30.4	35.4
CH ₄	—	2.17	3.41	4.88	8.22	—	—
NH ₃	—	1.53	2.47	6.70	6.70	—	—
H ₂ O	—	—	—	2.63	4.59	7.03	9.74
Ne	2.23	3.67	4.89	6.01	7.97	9.71	11.3
CO	0.84	1.72	2.49	3.16	4.40	5.54	6.61
N ₂	0.96	1.83	2.59	3.27	4.46	5.48	6.47
Air	0.95	1.83	2.62	3.28	4.69	5.73	6.67
O ₂	0.92	1.83	2.66	3.30	4.73	5.89	7.10
Ar	0.66	1.26	1.77	2.22	3.07	3.74	4.36
CO ₂	—	0.94	1.66	2.43	4.07	5.51	6.82
Kr	—	0.65	1.00	1.26	1.75	2.21	2.62
Xe	—	0.39	0.58	0.74	1.05	1.35	1.64

Let us derive the heat balance equation of a gas where heat transport occurs due to thermal conductivity. Denote by $\bar{\epsilon}$ the mean energy of a gaseous particle, and for simplicity we consider a one-component gas. Assuming absence of space sources and absorbers of heat, we obtain the heat equation similar to the continuity equation (14.8) for the number density of particles:

$$\frac{\partial}{\partial t}(\bar{\epsilon}N) + \text{div } \mathbf{q} = 0$$

For definiteness, we assume the gas to be located in a fixed volume. Then $\partial\bar{\epsilon}/\partial T = c_V$ is the *heat capacity* per atomic particle, and the above equation takes the form:

$$\frac{\partial T}{\partial t} + \mathbf{w} \cdot \nabla T = \frac{\kappa}{c_V N} \Delta T \quad (14.19)$$

where $\mathbf{w}$ is the mean velocity of atomic particles; we use the continuity equation (14.8) for $\partial N/\partial t$ and the expression (14.5) for the heat flux. For a motionless gas this equation is analogous to the diffusion equation (14.9) and its solution can be obtained by analogy with formula (14.13).

14.5 Thermal Conductivity Due to Internal Degrees of Freedom

An additional channel of heat transport can be connected with the energy transport by internal degrees of freedom. Below we consider this mechanism if atomic particles carry an internal energy in a buffer gas. Then excited particles which travel in a region with a lower temperature transfer their excitation to a gas, and transport of energy proceeds in this way. In contrast, nonexcited particles which pass through a region of higher temperature are excited in this region and take the energy from the gas in this way. The criterion of this mechanism of heat transport is such that the typical distance over which excited and nonexcited particles reach equilibrium is small compared to a typical size of the system.

Let us represent the heat flux as a sum of two terms

$$\mathbf{q} = -\kappa_t \nabla T - \kappa_i \nabla T$$

where κ_t is the thermal conductivity coefficient due to transport of the translation energy of atomic particles, while the second term is due to the transport of energy in the internal degrees of freedom. Hence, the thermal conductivity coefficient is the sum of these two terms:

$$\kappa = \kappa_t + \kappa_i \quad (14.20)$$

and below we analyze the second term.

Let us denote the internal state of the particle by the subscript i . Because of the temperature gradient, the number density of excited particles in a given state is not constant in a space, and their diffusion flux is

$$\mathbf{j}_i = -D_i \nabla N_i = -D_i \frac{\partial N_i}{\partial T} \nabla T$$

This yields the heat flux due to the transport of particles

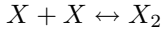
$$\mathbf{q} = \sum_i \varepsilon_i \mathbf{j}_i = - \sum_i \varepsilon_i D_i \frac{\partial N_i}{\partial T} \nabla T$$

where ε_i is the excitation energy of the i th state. Assuming the diffusion coefficient to be independent of particle excitation, we have for the thermal conductivity coefficient due to the internal degrees of freedom

$$\kappa_i = \sum_i \varepsilon_i D_i \frac{\partial N_i}{\partial T} = D \frac{\partial}{\partial T} \sum_i \varepsilon_i N_i = D \frac{\partial}{\partial T} (\bar{\epsilon} N) = D c_V \quad (14.21)$$

where $\bar{\varepsilon} = \sum_i \varepsilon_i N_i / N$ is the mean excitation energy of a particle, $N = \sum_i N_i$ is the total number density of particles, and $c_V = \partial \bar{\varepsilon} / \partial T$ is the heat capacity per particle. Using the estimates (14.7) and (14.18) for the diffusion coefficient and the thermal conductivity coefficient one can conclude that $\kappa_i \sim \kappa_t$ if the excitation energy of particle states is of the order of their thermal energy.

Let us consider the other example of this mechanism of thermal conductivity when it is created in a dissociating gas as a result of the recombination of atoms in a cold region. We have a dissociating gas with a small admixture of diatomic molecules, and there is a thermodynamic equilibrium between atoms and molecules according to the scheme



The number densities of atoms N_a and molecules N_m are connected by the Saha formula (5.28) $N_a^2 / N_m = F(T) \exp(-D/T)$, where D is the dissociation energy of molecules, and $F(T)$ has a weak temperature dependence in comparison with the exponential one. Because $N_a \gg N_m$ and $D \gg T$, we have $\partial N_m / \partial T = (D/T^2) N_m$, and from formula (14.21) it follows for the *heat capacity of a dissociating gas*

$$\kappa_i = D_m N_m \left(\frac{D}{T} \right)^2 \quad (14.22)$$

where D_m is the diffusion coefficient of molecules in an atomic gas. Comparing it with the thermal conductivity coefficient (14.18) due to the translation heat transport, we have

$$\frac{\kappa_i}{\kappa_t} \sim \left(\frac{D}{T} \right)^2 \frac{N_m}{N_a} \quad (14.23)$$

In the regime considered $N_a \gg N_m$, while $D \gg T$. Therefore the ratio (14.23) can be about one at relatively low concentrations of molecules in the gas. Note that the results are valid if the dissociation equilibrium in the gas is re-established over small distances, where small variations in the temperature take place.

14.6 Momentum Transport

The transport of momentum takes place in a moving gas so that the mean velocity of atomic particles varies in the direction perpendicular to the mean velocity. Then the transport of particles leads to the exchange of particle momenta between gas elements with different average velocity. This creates a frictional force which decelerates gaseous elements with a higher velocity and accelerates those having lower velocities. Let us estimate the value of the viscosity coefficient by analogy with this procedure for the diffusion and thermal conductivity coefficients. The force acting per unit gas area as a result of the momentum transport is equal to $F \sim N v m \Delta w_x$, where $N v$ is the particle flux and $m \Delta w_x$ is the difference in the average momenta of atomic particles which are located near a given point at distances from it on the mean free path that the particles can pass without collisions. Therefore particles reach this point from regions which are located at distances from this point which are of the order of the

mean free path λ , and we have $m\Delta w \sim m\lambda\partial w_x/\partial z$. Hence the force acting per unit area equals $F \sim Nvm\lambda\partial w_x/\partial z$. Comparing this with formula (14.6), using $(T/m)^{1/2}$ instead of v and also $(N\sigma)^{-1}$ instead of λ , we obtain the following estimation for the *viscosity coefficient* η

$$\eta \sim \frac{\sqrt{Tm}}{\sigma} \quad (14.24)$$

We can see that the viscosity coefficient is independent of the number density of atomic particles. Similar to the thermal conductivity coefficient, this independence is due to the compensation of two opposite effects occurring with momentum transport. Indeed, the amount of momentum carried is proportional to the number density of particles, while the typical distance of transport is inversely proportional to it. Both effects compensate for each other. Table 14.3 gives the viscosity coefficients of gases.

Table 14.3. Values of viscosity coefficients at a pressure of 1 atm, expressed in 10^{-5} g/(cm · s).

T , K	100	200	300	400	600	800	1000
H ₂	4.21	6.81	8.96	10.8	14.2	17.3	20.1
He	9.77	15.4	19.6	23.8	31.4	38.2	44.5
CH ₄	—	7.75	11.1	14.1	19.3	—	—
H ₂ O	—	—	—	13.2	21.4	29.5	37.6
Ne	14.8	24.1	31.8	38.8	50.6	60.8	70.2
CO	—	12.7	17.7	21.8	28.6	34.3	39.2
N ₂	6.88	12.9	17.8	22.0	29.1	34.9	40.0
Air	7.11	13.2	18.5	23.0	30.6	37.0	42.4
O ₂	7.64	14.8	20.7	25.8	34.4	41.5	47.7
Ar	8.30	16.0	22.7	28.9	38.9	47.4	55.1
CO ₂	—	9.4	14.9	19.4	27.3	33.8	39.5
Kr	—	—	25.6	33.1	45.7	54.7	64.6
Xe	—	—	23.3	30.8	43.6	54.7	64.6

14.7 Thermal Conductivity of Crystals

Let us consider heat transport in solids if it is determined by phonons. Then an increase of the temperature in some region of a solid leads to the generation of phonons in this region in the form of a wave packet. These waves propagate over the whole solid and in this way heat transport proceeds in the solid. Such a consideration is analogous to heat transport in solids and gases. Indeed, heat transport in gases results from the transport of hot atoms in a cold region, and in contrast cold atoms propagate in a hot region. The parameter of this transport is the mean free path for atoms of the gas. In solids phonons carry heat by analogy with atoms in gases. Then one can use formula (14.18) for the thermal conductivity coefficient, changing

the parameters of atomic particles to those of phonons

$$\kappa \sim N_{ph} c \lambda \quad (14.25)$$

Here N_{ph} is the number density of phonons, c is the speed of sound, and λ is the mean free path for phonons in a crystal, which is determined by the phonon–phonon interaction and also by interaction of phonons with other quasiparticles (electrons, dislocations, density fluctuations etc.).

The number density of phonons in the Debye approximation can be determined by analogy with formula (3.41)

$$N_{ph} = \int \frac{d\mathbf{k}}{(2\pi)^3} = \frac{1}{2\pi^2} \frac{T^4}{\hbar^4} \int_0^{T/\theta_D} \frac{x^2 dx}{e^x - 1} \quad (14.26)$$

Note that when considering phonons in the harmonic approximation, we neglect the interaction of phonons with matter where the waves propagate. Introducing the mean free path of phonons λ , we take this interaction into consideration. In these terms, the possibility of introducing phonons requires the criterion

$$\lambda \gg a \quad (14.27)$$

where a is the distance between nearest neighbors of a condensed system.

14.8 Diffusion of Atoms in Condensed Systems

The motion of an atom in a condensed system or matrix is restricted because the positions around a test atom are occupied. Therefore the displacement of a test atom in a matrix proceeds due to voids or vacancies in this matrix. Figure 14.1 represents the possible mechanisms of this process. In the first case an atom transfers to a neighboring vacancy in a crystal, and the surrounding atoms do not in principle take part in this transition. As a result, the vacancy moves in the opposite direction. In the second case many surrounding atoms take part in the

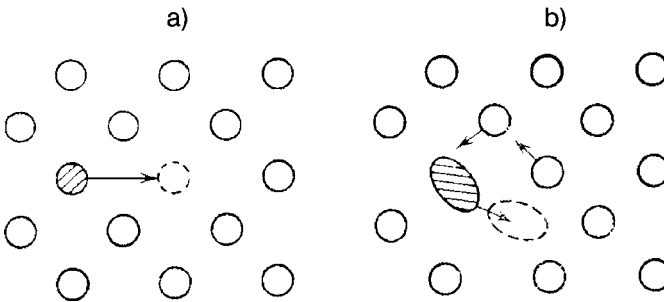


Figure 14.1. The mechanisms of vacancy displacement in a condensed system of atoms: (a) transition of an individual atom; (b) as a result of collective motion of atoms.

displacement of a vacancy or void, i.e. this process has a collective character. In both cases the diffusion process of a vacancy or void has an activation character, so that the rate of this process slows down with a decrease in temperature. Below for simplicity we consider this process for a crystal consisting of atoms with a short-range interaction when the interaction of the nearest atoms gives the main contribution to the crystal parameters.

In this case the *vacancy diffusion* process results in its transition to a free position, and because of the activation character of this process, the diffusion coefficient of a vacancy is estimated as

$$d = d_o \exp\left(-\frac{\varepsilon_a}{T}\right) \quad (14.28)$$

where $d_o \sim \omega_D a^2$, $\omega_D = \Theta_D/\hbar$ is the Debye frequency, a is the lattice constant, T is the current temperature, and ε_a is the *activation energy* for the vacancy displacement to a neighboring lattice site which depends on the relative number of voids or vacancies inside the system.

The activation energy of this process increases with a decrease in the number of voids, and below we consider this transition in the limiting case when atoms form a crystal lattice, and neighboring vacancies do not border each other. We take the face-centered cubic lattice for the solid state of the system of bound atoms. The transition of a vacancy from one site to a neighboring one is analogous to the transition of an atom that borders a vacancy to the vacancy site. For simplicity we fix the other atoms in the sites of the crystal lattice. During the transition to a neighboring site, a test atom must overcome a barrier, and from symmetry considerations the barrier height is the difference in the total interaction potentials of atoms if the test atom is located at a site of the crystal lattice and in between two neighboring vacancies, i.e. we have

$$\varepsilon_a = \sum_i [U(\mathbf{r}_i + \mathbf{a}/2) - U(\mathbf{r}_i)] = \sum_i [U(\mathbf{r}_i + \mathbf{a}/2) - U(\mathbf{r}_i + \mathbf{a})]$$

where $\mathbf{r}_i$ is the coordinate of the i th atom, $U(\mathbf{r}_i)$ is the interaction potential of this and the test atom if the test atom is located at the origin, and a test atom transfers from the origin to the lattice site of coordinate $\mathbf{a}$ ($\mathbf{a}$ is the lattice constant). For a crystal of the face-centered cubic structure this formula takes the form

$$\begin{aligned} \varepsilon_a = & -11U(a) - 2U(\sqrt{2}a) - 4U(\sqrt{3}a) - U(2a) \\ & + 4U\left(\frac{\sqrt{3}}{2}a\right) + 4U\left(\frac{\sqrt{5}}{2}a\right) + 8U\left(\frac{\sqrt{7}}{2}a\right) + 2U\left(\frac{3}{2}a\right) \end{aligned} \quad (14.29)$$

Here we account for the interaction of a transferring atom with nearest neighbors for the initial and final atom positions, and fix the surrounding atoms at their sites.

In particular, for the *Lennard–Jones interaction potential* of atoms (3.24)

$$U(R) = D \left[\left(\frac{R_e}{R}\right)^{12} - 2\left(\frac{R_e}{R}\right)^6 \right]$$

where R_e is the equilibrium distance between atoms for a classical diatomic molecule, and D is the dissociation energy of the molecule. In this case formula (14.29) gives

$$\varepsilon_a = 9.2D \quad (14.30a)$$

In the case of the *Morse interaction potential*

$$U(R) = D (\exp [-2\alpha(R - R_e)] - 2 \exp [-\alpha(R - R_e)])$$

and the Morse parameter $\alpha = 6/R_e$ which gives the identical second derivative of the interaction potential at the equilibrium distance $U''(R_e) = 72/R$ at the values D and R_e , we have

$$\varepsilon_a = 8.2D \quad (14.30b)$$

Note that both interaction potentials are characterized by the identical dissociation energy of the diatomic molecule D and the distance between nearest neighbors of the crystal lattice, i.e. we take for simplicity $a = R_e$. We also take the identical second derivatives of the interaction potential at the equilibrium distance for both cases. These results may be used as the upper limit for the activation energy of the transition under consideration. Evidently, the activation energy of the diffusion process for vacancies or atoms in a crystal is proportional to the sublimation energy ε_{sub} of the crystal per atom.

In fact, we considered above the diffusion of a vacancy in a crystal if the vacancy concentration is small. One can connect the diffusion coefficient of vacancies d_v with the coefficient of *self-diffusion of atoms* d_a . Taking v , the number of voids or vacancies, and n , the number of atoms, and requiring v/n to be constant during this process, we obtain

$$d_v = \frac{n}{v} d_a \quad (14.31)$$

In crystals we have

$$\frac{v}{n} \sim \exp \left(-\frac{\varepsilon_{\text{sub}}}{T} \right)$$

where ε_{sub} is the energy of vacancy formation. Table 14.4 contains the activation energies of self-diffusion of atoms in crystals of rare gases and the ratio $E_a/\varepsilon_{\text{sub}}$. Note that the activation energy E_a of the process of self-diffusion of atoms in crystals is the sum of the activation energy for transport of vacancies ε_a and the energy of vacancy formation ε_{sub} , i.e.

$$E_a = \varepsilon_a + \varepsilon_{\text{sub}}$$

since the rate of atom transport to a neighboring crystal site is proportional to the probability of of vacancy being located at this site. Therefore, according to formulae (14.30) $E_a \approx (2.4 \div 2.5)\varepsilon_{\text{sub}}$, and according to the method of deriving formulae (14.30), it is the upper limit for this value.

In the case of the second mechanism of atom displacement (Figure 14.1b), this process is accompanied by displacements of a large number of ambient atoms. Then the activation

energy E_a of this transition is proportional to $a^2 U''$, where a is the lattice constant and U'' is the second derivative of the pair interaction potential of crystal atoms. By definition of the Debye frequency ω_D , this derivative is $U'' \sim m\omega_D^2$, where m is the atom mass. Hence the activation energy of the diffusion process for atoms in the crystal is proportional to $m\omega_D^2 R_e^2$. The ratio of these values is given in Table 14.4. Thus, according to the data of Table 14.4, both mechanisms may be used for to estimate the activation energy of the diffusion process, and the scaling is valid due to both mechanisms within the limits of accuracy of the experimental data (20–30%).

Table 14.4. The activation energy of the self-diffusion process in solid rare gases.

	E_a , meV (experiment)	E_a/D	$E_a/\varepsilon_{\text{sub}}$	$E_a/m\omega_D^2 R_e^2$
Ne	41 ± 2	11.4 ± 0.5	2.0	0.021
Ar	170 ± 10	13.3 ± 0.7	2.1	0.020
Kr	210 ± 10	12.5 ± 0.5	1.8	0.017
Xe	320 ± 10	13.3 ± 0.4	1.9	0.018
Average		13 ± 1	2.0 ± 0.1	0.019 ± 0.002

In addition, the self-diffusion coefficient in liquid rare gases is determined by formula (14.28), which has the form

$$d = d_o \exp\left(-\frac{E_{\text{liq}}}{T}\right)$$

and because $v \sim n$ for the liquid state, the activation energy are identical for the processes of diffusion of voids and self-diffusion of atoms in the liquid state. Table 14.5 contains the parameters of the above formula for liquid rare gases. Table 14.5 also gives the reduced parameters of self-diffusion of atoms in liquid rare gases, and ω_D is the Debye frequency for solid rare gases, a is the distance between nearest neighbors and ε_{liq} is the binding energy per atom for liquid rare gases near the triple point.

Table 14.5. Parameters of the self-diffusion coefficient of atoms in liquid rare gases. (The data are taken from: L. Bewilogua, L. Gladun and B. Kubsch (1971) *J. Low Temp. Phys.* 4, 299 and J. Naghizadeh and S. A. Rice (1962) *J. Chem. Phys.* 36, 2710.)

	E_{liq} , meV	$d_o, 10^{-3} \text{ cm}^2/\text{s}$	$d_o/(\omega_D a^2)$	E_{liq}/D	$E_{\text{liq}}/\varepsilon_{\text{liq}}$
Ne	10	0.84	0.086	2.7	0.51
Ar	30	1.16	0.068	2.5	0.43
Kr	35	0.48	0.032	2.1	0.37
Xe	52	0.70	0.044	2.2	0.39
Average			0.06 ± 0.02	2.4 ± 0.3	0.42 ± 0.06

14.9 Diffusion of Voids as Elementary Configuration Excitations

Considering the configuration excitation of the liquid aggregate state of rare gases (as well as macroscopic ensembles of bound atoms with a short-range atomic interaction), we introduce an elementary configuration excitation – *void* – that can be defined as a space between the atoms formed from an initially originating vacancy or hole. In this way, one can consider as a mixture of atoms and voids a configurationally excited state of an ensemble of bound atoms where the basic interaction between atoms proceeds between nearest neighbors. This concept is useful for the analysis of various parameters of this system, and we demonstrate it below for determining the diffusion coefficients of voids.

The diffusion of voids is summarized from elementary void jumps, and an individual jump of a void corresponds to a transition from one atomic configuration to a nearby one. From the standpoint of the potential energy surface, such a jump is a transition in the atomic system between neighboring local minima, and therefore this process has an activation character. Hence, the *diffusion coefficient of voids* can be represented in the form

$$D_v = d_v \exp \left(-\frac{E_a}{T} \right) \quad (14.32)$$

where E_a is the activation energy of this process. Because displacements of atoms and voids are mutually connected in this ensemble of bound atoms, the diffusion coefficient of voids D_v can be expressed through the self-diffusion coefficient D_a of atoms by the relation

$$D_v c = -D_a \quad (14.33)$$

This relation takes into account that a displacement of voids is simultaneously the same displacement of atoms in the opposite direction. Below we use this relation for the limiting cases where the atomic system is found in the solid and liquid aggregate states.

Table 14.6 gives the parameters of formula (14.33) for the diffusion coefficient of voids, which are determined on the basis of formula (14.33) and experimental data for the self-diffusion coefficient of atoms in solid and liquid rare gases (see Tables 14.4 and 14.5). Comparison of the activation energies for the diffusion process of voids E_{sol} and E_{liq} with the energies of formation of vacancies ε_o and voids ε_{liq} is made also in Table 14.6 for the solid and liquid aggregate states of rare gases. This comparison shows the correspondence of these values, so that the activation energy of the void diffusion process can be expressed through the energy of vacancy or void formation, whose values are given in Tables 14.4 and 14.5.

Table 14.6. The parameters of diffusion of voids for solid and liquid inert gases.

	E_{sol}/D	$E_{\text{sol}}/\varepsilon_o$	$d_{\text{sol}}, 10^{-4} \text{ cm}^2/\text{s}$	E_{liq}/D	$E_{\text{liq}}/\varepsilon_{\text{liq}}$	$d_{\text{liq}}, 10^{-3} \text{ cm}^2/\text{s}$
Ne	5.3 ± 0.5	0.9 ± 0.1	3	2.7	0.9	2.6
Ar	6.8 ± 0.7	1.0 ± 0.1	3	2.5	0.8	3.6
Kr	5.8 ± 0.5	0.9 ± 0.1	2	2.1	0.7	1.5
Xe	6.6 ± 0.4	1.0 ± 0.1	1	2.2	0.7	2.2

14.10 Void Instability

We consider now the peculiarities of void transport in a system of bound atoms where the degree of configuration excitation varies in space. Since configuration excitation is determined by the void concentration c ($c = v/n$, where n and v are the numbers of atoms and voids in a given system or part of it), a variation of void concentration in a space causes transport of voids. We consider this system as a mixture of atoms and voids, and the void flux that is equalized by the atom flux is equal to

$$j_v = -D_v N \frac{dc}{dx} + w N c \quad (14.34)$$

Here N is the number density of atoms, c is the concentration of voids, D_v is the diffusion coefficient of voids in this system that is connected with the atom diffusion coefficient by the relation (14.33), and w is the drift velocity of voids. On the basis of the chemical potential of atoms $\mu_a(c)$ as a function of void concentration one can describe a thermodynamic state of this system of atoms and voids. According to the definition, the chemical potential $\mu_a(c)$ of atoms is the difference of the free Gibbs energies at a given number of voids and in the absence of voids, and this difference is reduced to one atom. In particular, at equilibrium the void concentration $c \sim \exp(-\mu_a/T)$ and the flux is zero $j_v = 0$. This gives the relation between the drift velocity w and the diffusion coefficient D_v of voids that is analogous to the Einstein relation (14.15) between the mobility and diffusion coefficient of a gas

$$w = \frac{D_v}{T} \frac{d\mu_a(c)}{dc} \quad (14.35)$$

where the gradient of the void concentration is directed along the x -axis.

From this we obtain for the void flux

$$j_v = -D_v N \cdot \left(1 + \frac{c}{T} \frac{d\mu_a}{dc} \right) \frac{dc}{dx}$$

According to the nature of the diffusion flux, it equalizes the densities or concentrations and its direction is opposed to the gradient direction. But this is violated if

$$\frac{d\mu_a}{dc} < -\frac{T}{c} \quad (14.36)$$

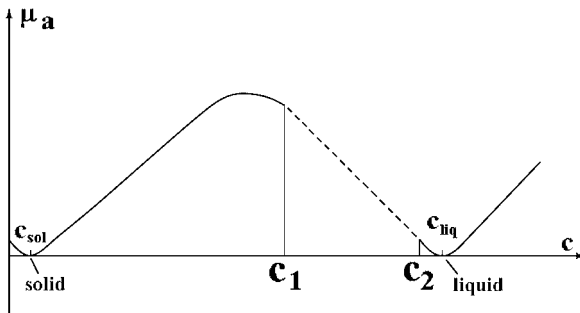


Figure 14.2. The chemical potential of atoms inside a macroscopic ensemble of bound atoms with interaction between nearest neighbors only as a function of the void concentration.

Then a *void instability* occurs. Indeed, under these conditions a randomly arising gradient of void concentration is enforced, and a breaking surface occurs. This instability exists in a system of bound atoms with a pairwise interaction, as follows from Figure 14.2, which is constructed on the basis of Figure 8.6 and gives the dependence of the chemical potential of atoms $\mu_a(c)$ on the void concentration. This value has two minima corresponding to the solid and liquid aggregate states, and at the melting point we take $\mu(0) = \mu(c_{\text{liq}}) = 0$, where c_{liq} is the void concentration for the liquid state. These minima are separated by a barrier, and for inert gases at the triple point the chemical potential maximum is $\mu_a(c_{\text{max}}) = 0.15 \pm 0.01$, and $\mu(c_{\text{max}})/T_m = 0.26 \pm 0.02$, where $c_{\text{max}} = 1/12$ at the melting point $T = T_m$. The void instability occurs in the void concentration range $c_1 < c < c_2$, and Table 14.7 lists values of the boundary concentration for inert gases near the triple point.

Table 14.7. Boundary void concentrations for the void instability.

	Ne	Ar	Kr	Xe
c_1	0.25	0.25	0.25	0.26
c_2	0.31	0.32	0.32	0.31

Thus, the void instability violates the continuous variation of the void concentration from the solid to liquid aggregate state, and if both these states exist in a space they are separated by the breaking surface, and at equilibrium the chemical potentials of atoms are identical from both sides of the breaking surface, in accordance with the equilibrium condition (6.36) of thermodynamics.

14.11 Onsager Symmetry of Transport Coefficients

In considering the transport processes, we presume the equilibrium state of a system to be supported at each space point, which implies the validity of the equilibrium relations between thermodynamic parameters at each point of the system. A small violation of the equilibrium causes fluxes in a space. This leads to an increase in the system entropy and results in energy dissipation under the interaction of fluxes and forces which occurs in this weakly nonequilibrium system.

Let us consider this problem in a formal way. The gradient of a parameter of the system creates a flux j_i and a force F_i which are connected by a linear law because of the weak perturbation

$$j_k = \sum_i \lambda_{ik} F_i \quad (14.37)$$

The interaction of forces and fluxes leads to a release of heat

$$\frac{dQ}{dt} = T \frac{dS}{dt} = \sum_k j_k F_k = \sum_{i,k} \lambda_{ik} F_i F_k \quad (14.38)$$

Here the heat Q and entropy S are taken per unit volume. From this it follows that

$$\lambda_{ik} = T \frac{\partial^2}{\partial F_i \partial F_k} \left(\frac{dS}{dt} \right)$$

and this definition of transport coefficients leads to the *Onsager law* or *reciprocity relation*

$$\lambda_{ik} = \lambda_{ki} \quad (14.39)$$

Now let us return to the simplest fluxes – to the particle flux (14.3), the heat flux (14.5) and the momentum flux (14.6). We construct the generalized fluxes j_i and forces F_i on the basis of the corresponding fluxes and gradients and use as the parameters of the system the gas temperature T , the atom or molecule mass m , and the atom or molecule number density N . Taking into account that a generalized flux has the dimensionality $\text{cm}^{-2} \text{s}^{-1}$ and the generalized force has the dimensionality din=erg/cm , we obtain in the case of the diffusion flux (14.4)

$$\mathbf{j} = -DN\nabla c, \quad \mathbf{F} = -T\nabla c \quad (14.40a)$$

In the case of the heat flux (14.5) we have

$$\mathbf{j} = \frac{\mathbf{q}}{T} = -\frac{\kappa}{T} \nabla T, \quad \mathbf{F} = -\nabla T \quad (14.40b)$$

In the case of the momentum flux (14.6) we get

$$j_x = -\frac{\eta}{\sqrt{mT}} \frac{\partial w_x}{\partial z}, \quad F_x = \sqrt{mT} \frac{\partial w_x}{\partial z} \quad (14.40c)$$

Let us apply the Onsager law to a two-component gaseous system when the concentration c of the second component is small $c \ll 1$. The temperature gradient ∇T is created in this mixture by an external source. As a result of the formation of fluxes in this system, a concentration gradient ∇c occurs that influences the system under consideration. Our goal is to analyze the behavior of this system if gradients are small:

$$\nabla T \ll \frac{T}{\lambda}, \quad \nabla c \ll \frac{c}{\lambda}$$

where λ is the mean free path of admixture atomic particles in the basic gas. Next, the total gaseous pressure p is constant over a space, so that

$$p = NT = \text{const}, \quad \nabla N = -\nabla T \frac{N}{T}$$

where N is the number density of atomic particles of the basic gas and T is the average gaseous temperature. Such a distribution is established quickly with the sound velocity, and transport processes develop under this distribution. Therefore the basic gaseous component is found at equilibrium, i.e. fluxes with the participation of this component do not occur in the transport processes under consideration.

From this it follows that the general form of the flux of admixture atomic particles $\mathbf{j}$ and heat flux $\mathbf{q}$ is:

$$\mathbf{j} = -DN\nabla c - D_T\nabla T, \quad \mathbf{q} = -\kappa_D\nabla c - \kappa\nabla T \quad (14.41)$$

Here D is the diffusion coefficient of the admixture atomic particles in the basic gas, κ is the thermal conductivity coefficient of the basic gas, D_T is the *thermodiffusion coefficient* and κ_D is the *diffusion thermal conductivity coefficient*. In order to reduce the set of equations (14.41) to (14.37), we take the following generalized forces

$$\mathbf{F}_1 = T\nabla c, \quad \mathbf{F}_2 = \nabla T \quad (14.42a)$$

and the following generalized fluxes of quasiparticles:

$$\mathbf{j}_1 = \mathbf{j}, \quad \mathbf{j}_2 = \mathbf{q}/T \quad (14.42b)$$

Then the reciprocity law gives

$$\kappa_D = T^2 D_T \quad (14.43)$$

and equations (14.42) take the form

$$\mathbf{j} = -DN\nabla c - D_T\nabla T, \quad \mathbf{q} = -T^2 D_T\nabla c - \kappa\nabla T \quad (14.44)$$

Thus *cross-fluxes* of the set of equations (14.40) are expressed through one transport coefficient – the thermodiffusion coefficient. The nature of this transport coefficient is connected with the character of the gas thermal conductivity. Heat transport in a gas under the action of a temperature gradient is determined by the motion of atoms or molecules which transfer energy in different directions over distances of the order of the mean free path λ . If fast atoms are more essential in this transport than slow atoms, the transport of particles proceeds in the same direction as the heat, i.e. $D_T > 0$. In the opposite case $D_T < 0$. An estimate of this transport coefficient follows from its definition $D_T \sim j/\nabla T$, where the particle flux $j \sim Nv \sim N\sqrt{T/m}$, and the temperature gradient $\nabla T \sim T/\lambda$. From this it follows that

$$D_T \sim \frac{N\lambda}{\sqrt{Tm}} \quad (14.45)$$

where m is the mass of the admixture particles.

In the equilibrium state of the gaseous system under consideration $\mathbf{j} = 0$ and the temperature gradient ∇T is supported by an external source. Hence, the concentration gradient is supported in this system:

$$\nabla c = -\frac{D_T}{DN}\nabla T$$

From this and equation (14.44) it follows for the heat flux

$$\mathbf{q} = -\kappa_{ef}\nabla T, \quad \kappa_{ef} = \kappa + \frac{D_T^2 T^2}{DN} \quad (14.46)$$

According to this formula, the second term of the expression for the effective thermal conductivity coefficient is positive, i.e. cross-fluxes increase the heat flux in the system under consideration. This term, to an order of magnitude, is equal to

$$\frac{D_T^2 T^2}{DN} \sim N \lambda \sqrt{\frac{T}{m}} \sim \kappa \quad (14.47)$$

i.e. this gives the same contribution to the total thermal conductivity coefficient as the first term of formula (14.46).

15 Transport of Electrons in Gases

15.1 Conductivity of Weakly Ionized Gas

A simple method of the selective action of an external field on the different degrees of freedom of a substance uses gaseous discharges and is based on the interaction between electrons and an electric field. Then energy is transmitted first from the field to the electrons and then it is transmitted in a gas to the atoms through their collisions with electrons. In this case there is a strong action of the electric field on electrons and a weak action on atoms. As a result, atoms have the Maxwell distribution function on velocities, and the electron distribution function on energies can differ significantly from that of atoms.

The electrons of a weakly ionized gas determine the electric properties of the gas, and the gas *conductivity* Σ is defined as the proportionality factor between the electric current density and the electric field strength $\mathbf{E}$ in *Ohm's law*

$$\mathbf{j} = \Sigma \mathbf{E} \quad (15.1)$$

The electric current is the sum of two components – the electron current and the ion current

$$\mathbf{j} = -eN_e \mathbf{w}_e + eN_i \mathbf{w}_i \quad (15.2)$$

where N_e and N_i are the electron and ion number density, and $\mathbf{w}_e$, and $\mathbf{w}_i$ are the electron and ion drift velocities correspondingly. Let us introduce the *mobility of a charged particle* K through its drift velocity $\mathbf{w}$ by the relation

$$\mathbf{w} = K \mathbf{E} \quad (15.3)$$

instead of (14.14). Then we have for the conductivity of a quasineutral ionized gas:

$$\Sigma = e(K_e + K_i) \quad (15.4)$$

where K_e and K_i are the electron and ion mobility. From formula (14.16) we have an estimate of the mobility of a charged particle

$$K \sim \frac{e}{N\sigma\sqrt{\mu T}} \quad (15.5)$$

where N is the number density of gaseous particles, σ is the typical cross section of collision of charged and gaseous atomic particles, and the temperature T characterizes the typical energy of the particles. From this it follows that $K_e \gg K_i$, i.e. electrons give the main contribution to the gas conductivity. Then from formulae (15.4) and (15.5) we have the following estimate of the gas conductivity:

$$\Sigma \sim \frac{N_e e^2}{N\sigma_{ea}\sqrt{m_e T_e}} \quad (15.6)$$

where σ_{ea} is the typical cross section of electron–atom scattering and T_e is the electron temperature.

15.2 Electron Mobility in a Gas

Formula (13.31) allows us to determine the mobility of electrons in a gas

$$K = \frac{e}{3m_e} \left\langle \frac{1}{v^2} \frac{d}{dv} \left(\frac{v^3}{\nu} \right) \right\rangle \quad (15.7)$$

where we use the definition (15.3) for the electron mobility. At low field strengths the electron mobility does not depend on the electric field strength because the electric field weakly perturbs the Maxwell distribution function of electrons. At larger strengths the mobility dependence on the electric field is determined by the velocity dependence for the electron–atom cross section of elastic scattering. In particular, if the rate ν of electron–atom elastic scattering does not depend on the collision velocity, this formula gives

$$K = \frac{e}{m_e \nu} \quad (15.8)$$

If the diffusion cross section of electron–atom scattering σ^* does not depend on the collision velocity, formula (15.7) gives for the electron mobility in a gas in the limit of low strengths

$$K = \frac{2e\lambda}{3m_e} \left\langle \frac{1}{v} \right\rangle = \frac{2}{3} \sqrt{\frac{2}{\pi}} \frac{e\lambda}{\sqrt{m_e T}} = 0.53 \frac{e\lambda}{\sqrt{m_e T}} \quad (15.9)$$

where $\lambda = 1/(N\sigma^*)$ is the mean free path of electrons in a gas (N is the number density of gas atoms and T is the gas temperature).

In the general case the dependence $\nu(v)$ may be complicated. In the case of argon, krypton and xenon the cross section of elastic electron–atom scattering is characterized by the *Ramsauer minimum* at electron energies 0.4–0.6 eV. Then the mobility may be a nonmonotonic function of the electric field strength, as shown in Figure 15.1 for gaseous xenon. Then the mobility has a maximum at a certain electric field strength. Moreover, the *saturation of the electron drift velocity* can be observed over a certain range of strengths, i.e. the electron drift velocity does not depend on the strength in this range. Note that in the case of monotonic dependence of the cross section on the collision velocity the mobility varies monotonically with an increase in the electric field strength. A nonmonotonic strength dependence of the electron mobility, as for xenon according to Figure 15.1, follows from the Ramsauer form of the electron–atom cross section. According to formula (15.8), the electron mobility in a gas is inversely proportional to the number density of gas atoms. For dense and condensed gases when a scattering electron interacts simultaneously with several atoms, this dependence may be another, as demonstrated in Figure 15.2 in the case of xenon.

15.3 Conductivity of Strongly Ionized Plasma

The conductivity of a weakly ionized gas is determined by electron–atom collisions, while in a *strongly ionized plasma* electron–ion collisions prevail over electron–atom collisions. Note that electron–electron collisions do not change the total electron momentum and do

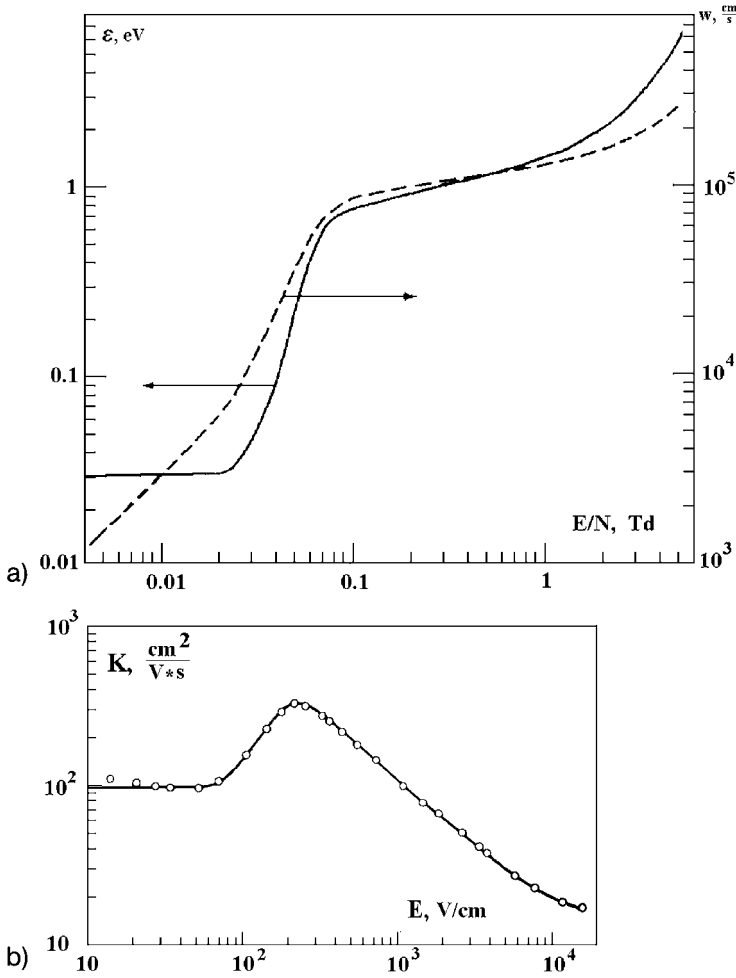


Figure 15.1. The electron drift velocity w and the electron energy ε (a), and the mobility (b) in xenon as a function of the specific electric field strength at the temperature $T = 236K$ and the number density of atoms $N = 3 \cdot 10^{20} \text{ cm}^{-3}$ (S.S.S. Huang, G.R. Freeman. *J. Chem. Phys.* 68, 1355, 1978).

not influence the plasma conductivity. Because of the electron–ion cross section exceeds the electron–atom cross section of elastic scattering, the term a “strongly ionized plasma”, in which electron–ion collisions dominate, can refer to a plasma with a small degree of ionization.

Using formula (13.31) for the drift velocity of electrons, we have on the basis of formula (15.4) for the plasma conductivity

$$\Sigma = \frac{N_e e^2}{3m_e} \left\langle \frac{1}{v^2} \frac{d}{dv} \left(\frac{v^3}{\nu} \right) \right\rangle \quad (15.10)$$

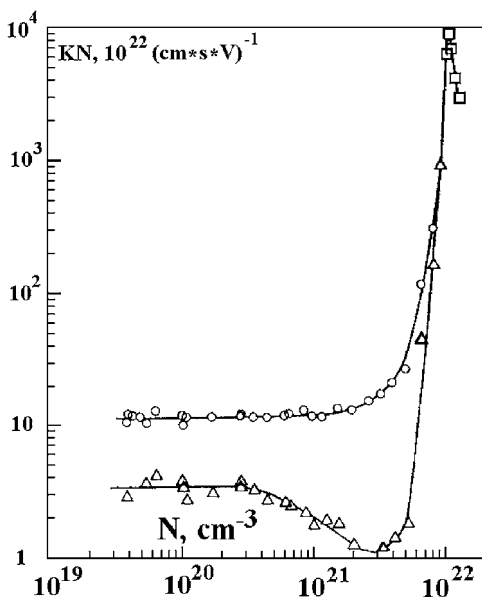


Figure 15.2. The dependence of the value KN on the atom number density for xenon at the temperature $T = 236$ K. Circles refer to the zero-field mobility, triangles relate to the maximum mobility, squares correspond to the electric field strength $E = 30$ V/cm (S.S.S. Huang, G.R. Freeman. *J. Chem. Phys.* 68, 1355(1978)).

where $\nu = N_i v \sigma^*$, and the averaging is made over the electron distribution function.

Because of the plasma quasineutrality $N_e = N_i$, its conductivity does not depend on the electron number density. The diffusion cross section for electron–ion collisions is given by formula (12.35) and has the form $\sigma^* = \pi e^4 \ln \Lambda / \varepsilon^2$, where ε is the electron energy, the *Coulomb logarithm* equals $\ln \Lambda = \ln[e^2 / (r_D T)]$, and r_D is the Debye–Hückel radius. Using the Maxwell distribution function for electrons, we obtain finally the *Spitzer formula* for the plasma conductivity:

$$\Sigma = \frac{2^{5/2} T_e^{3/2}}{\pi^{3/2} m_e^{1/2} e^2 \ln \Lambda} \quad (15.11)$$

15.4 Thermal Diffusion of Electrons in a Gas

In Chapter 14 we considered transport phenomena in gases and plasmas which are caused by gradients in the concentration, temperature and mean flow velocity, and by an external electric field. Along with the fluxes considered, these gradients and fields can create *cross-fluxes*. Below we consider the simplest transport phenomenon of this type, namely, the electron flux under a gradient of the electron temperature. This flux is equal to

$$\mathbf{j} = -D_T \nabla \ln T_e \quad (15.12)$$

This is the definition of the *thermodiffusion coefficient* D_T . We will evaluate this under the condition that the electron number density is high enough that the criterion (13.24) is fulfilled and we can introduce the electron temperature T_e . Then the Boltzmann kinetic equation for electrons has the form (13.25) in the first approximation and in the second approximation it is:

$$\mathbf{v} \nabla f = I_{ea}(f) \quad (15.13)$$

The temperature gradient causes nonsymmetric parts of the electron distribution function to arise, which can be written in the form of the expansions (12.18) and (13.27):

$$f = f_o(v) + v_x f_1(v)$$

where $f_o(v)$ is the Maxwell distribution function of electrons and the x -axis is in the direction of the temperature gradient. Substituting this in equation (15.13) and using formulae (12.20) for the collision integral from the nonsymmetric part of the distribution function, we have

$$v_x \partial f_o / \partial x = -\nu v_x f_1 \quad (15.14)$$

where ν is the rate of electron–atom elastic collisions.

Let us evaluate the electron flux which is created by the nonsymmetric part of the distribution function. Taking into account that the flux is along the x -axis, we have:

$$j_x = \int v_x f_x d\mathbf{v} = \int v_x^2 f_1 d\mathbf{v} = -\frac{1}{3} \int \frac{v^2}{\nu} \frac{\partial f_o}{\partial x} d\mathbf{v} = -\frac{d}{dx} \left[N_e \left\langle \frac{v^2}{3\nu} \right\rangle \right]$$

where brackets mean averaging over the electron velocities. Since the x -dependence occurs due to the gradient of the electron temperature, we obtain from this formula

$$j_x = -\nabla T_e \frac{d}{dT_e} \left[N_e \left\langle \frac{v^2}{3\nu} \right\rangle \right]$$

Comparing this with formula (15.13), we find the following expression for the thermodiffusion coefficient:

$$D_T = T_e \frac{d}{dT_e} \left[N_e \left\langle \frac{v^2}{3\nu} \right\rangle \right] = T_e \frac{d}{dT_e} (N_e D) \quad (15.15)$$

where D is the diffusion coefficient of electrons which is given by formula (13.34).

If the electron pressure $p_e = N_e T_e$ is constant, this formula can be written in the form:

$$D_T = N_e T_e^2 \frac{d(D_e/T_e)}{dT_e} \quad (15.16)$$

In particular, if $\nu = \text{const}$, this formula gives $D_T = 0$. In the case of the power dependence for the rate of electron–atom collisions $\nu \sim v^n$ we obtain

$$D_T = -n N_e D \quad (15.17)$$

This means that the direction of the electron flux with respect to the temperature gradient depends on the sign of n .

15.5 Electron Thermal Conductivity

Because of the small mass of electrons, their transport can give a contribution to the thermal conductivity of a weakly ionized gas. Below we evaluate the coefficient of the *thermal conductivity of electrons*. For this aim let us represent the electron distribution function as

$$f = f_o(v) + (\mathbf{v} \nabla \ln T_e) f_1(v) \quad (15.18)$$

and the kinetic equation (15.13) takes the form:

$$f_o \left(\frac{m_e v^2}{2T_e} - \frac{5}{2} \right) \mathbf{v} \nabla T_e = I_{ea}(f)$$

Here we take into account that the x -dependence of the electron distribution function is due to T_e and the electron pressure $p_e = N_e T_e$ is constant in a space. From this on the basis of formula (12.20), $I_{ea}(v_x f_1) = -\nu v_x f_1$ and we obtain for the nonsymmetric part of the distribution function:

$$f_1 = -\frac{f_o}{\nu} \left(\frac{m_e v^2}{2T_e} - \frac{5}{2} \right)$$

The electron heat flux is equal to

$$\mathbf{q}_e = \int \frac{m_e v^2}{2} v_x f d\mathbf{v} = \int \frac{m_e v^2}{2} v_x^2 \nabla \ln T_e f_1 d\mathbf{v}$$

Introducing the *thermal conductivity coefficient* of electrons by the formula

$$\mathbf{q}_e = -\kappa_e \nabla T_e \quad (15.19)$$

we obtain from this

$$\kappa_e = N_e \left\langle \frac{v^2}{3\nu} \frac{m_e v^2}{2} \left(\frac{m_e v^2}{2} - \frac{5}{2} \right) \right\rangle \quad (15.20)$$

where brackets mean averaging over the electron distribution function.

Assuming $\nu \sim v^n$, i.e. $\nu(v) = \nu_o z^{n/2}$, where $z = m_e v^2 / (2T_e)$, we have from formula (15.20):

$$\kappa_e = \frac{4}{3\sqrt{\pi}} \cdot \frac{T_e N_e}{\nu_o m_e} \left(1 - \frac{n}{2} \right) \Gamma \left(\frac{7-n}{2} \right) \quad (15.21)$$

In particular, if $\nu = \text{const}$, this formula gives

$$\kappa_e = \frac{5T_e N_e}{2\nu_o m_e} \quad (15.22a)$$

If $n = 1$, i.e. $\nu = v/\lambda$ (λ is the mean free path), we have from this formula:

$$\kappa_e = \frac{2}{3\sqrt{\pi}} N_e \lambda \sqrt{\frac{2T_e}{m_e}} \quad (15.22b)$$

In order to determine the contribution of the electron thermal conductivity to the total thermal conductivity coefficient, it is necessary to connect the gradients of the electron T_e and atomic T temperatures. For this let us consider the case when an increase in the electron temperature is determined by an external electric field, and the connection between the electron and atomic temperatures is given by formula (13.39). If $\nu \sim v^n$, this formula gives

$$\nabla T_e = \frac{\nabla T}{1 + n - \frac{nT}{T_e}} \quad (15.23)$$

Below we will consider the case $T_e \gg T$. Then we have for the total thermal conductivity coefficient

$$\kappa = \kappa_a + \kappa_e \frac{\nabla T_e}{\nabla T} = \kappa_a + \frac{\kappa_e}{1 + n} \quad (15.24)$$

where κ_a is the thermal conductivity coefficient of the atomic gas. Using the estimate (14.18) for the atom thermal conductivity coefficient, one can see that the electron thermal conductivity can give a contribution to the total value at low electron number densities $N_e < N_a$ due to the small electron mass and high electron temperature. We assume the criterion (13.24) to be fulfilled that allows us to introduce the *electron temperature*.

The peculiarity of the electron thermal conductivity is such that *cross-fluxes* can be essential in this case. Below we consider the electron thermal conductivity of a weakly ionized gas located in an external electric field, based on the following expressions for fluxes

$$\mathbf{j} = N_e K \mathbf{E} - D_T \nabla \ln T_e, \quad \mathbf{q} = -\kappa_e \nabla T_e + \alpha e \mathbf{E} \quad (15.25)$$

Let us consider the case when the displacement of electrons as a whole does not violate the plasma quasineutrality that corresponds to plasma regions far from electrodes and walls. Then the mobility K in formula (15.25) is the electron mobility, and one can neglect the ion mobility including the ambipolar diffusion. The expression for the electron thermodiffusion coefficient is given by formula (15.16), and formula (15.21) gives the thermal conductivity coefficient. Below we determine the coefficient α in formula (15.25) by the standard method by means of expansions (12.18) and (13.27) of the electron distribution function over the spherical harmonics. Then the first equation of the set (13.30) yields $f_1 = eE f_0 / (\nu T_e)$, and the coefficient α is equal to

$$\alpha = \frac{m_e N_e}{6T_e} \cdot \left\langle \frac{v^4}{\nu} \right\rangle = \frac{4T_e N_e}{3\sqrt{\pi} m_e \nu_o} \Gamma \left(\frac{7}{2} - \frac{n}{2} \right) \quad (15.26)$$

where we take $\nu = \nu_o \left(v / \sqrt{\frac{2T_e}{m_e}} \right)^n$. This gives for $n = 0$

$$\alpha = \frac{5T_e N_e}{2m_e \nu} \quad (15.27a)$$

and for $n = 1$, when $\nu = v/\lambda$, $\lambda = \text{const}$, this formula yields

$$\alpha = \sqrt{\frac{2T_e}{m_e}} \cdot \frac{\lambda}{3\sqrt{\pi}} = \frac{2\lambda N_e}{3v_T} \quad (15.27b)$$

where $v_T = \sqrt{\frac{8T_e}{\pi m_e}}$ is the mean electron velocity.

The relationships (15.27) together with the corresponding expressions for the kinetic coefficients allow us to determine the electron heat flux under different conditions in the plasma. Let us determine the effective thermal conductivity coefficient in the direction perpendicular to an external electric field $\mathbf{E}$. If the plasma is placed into a metallic enclosure, the transverse electric field is absent $E = 0$, and formulae (15.27) coincide with formula (15.19). If the walls are dielectric ones, we have $\mathbf{j} = 0$, which corresponds to the regime of ambipolar diffusion when electrons travel together with ions. On the scale considered this gives $\mathbf{j} = 0$, i.e. the electric field of strength $\mathbf{E} = D_T \nabla \ln T_e / (N_e K)$ arises. Represent the heat flux in the form:

$$\mathbf{q} = -C \kappa_e \nabla T_e \quad (15.28)$$

where the coefficient

$$C = 1 - \frac{\alpha D_T e}{\kappa_e T_e N_e K}$$

Using formula (15.16) for the electron thermodiffusion coefficient and the Einstein relation (14.15), we obtain it in the form $C = 1 + \alpha n / \kappa_e$.

On the basis of formulae (15.12), (15.16) and (15.17), we have:

$$C = \frac{n + 2}{2 - n} \quad (15.29)$$

As we can see, the effective thermal conductivity coefficient for electrons in the two considered cases of metallic and dielectric walls depends on n . For $n = 0$ this value is identical for both cases; for $n = 1$ it is 3 times more in the second case than in the first one.

15.6 The Hall Effect

Let us consider the behavior of electrons in a gas when constant electric and magnetic fields are directed perpendicular each to other. Because an electron has a circular motion in a magnetic field in a plane perpendicular to the magnetic field, the action of electric and magnetic fields creates an electron motion in the direction perpendicular to these fields. The *Hall effect* is connected with the creation of electron currents in the direction which perpendicular to the electric and magnetic fields. In this case the electron distribution function satisfies the kinetic equation

$$(e\mathbf{E} + e[\mathbf{v}\mathbf{H}]) \frac{\partial f}{\partial \mathbf{v}} = I_{ea}(f) \quad (15.30)$$

where $\mathbf{E}$ is the electric field strength and $\mathbf{H}$ is the magnetic field strength, and we take the electric and magnetic field directions along the x - and z -axes correspondingly. One can solve this equation using the same method as we used for electrons in a gas in a constant electric field. Then instead of formulae (12.18) and (13.27) we have for the electron distribution function

$$f(\mathbf{v}) = f_o(v) + v_x f_1(v) + v_y f_2(v) \quad (15.31)$$

and using the expansion over spherical harmonics, we obtain now instead of the first equation of the set (13.30)

$$vf_1 = \frac{av}{(\nu^2 + \omega_H^2)} \frac{df_o}{dv}, \quad vf_2 = \frac{a\omega_H}{(\nu^2 + \omega_H^2)} \frac{df_o}{dv} \quad (15.32)$$

where $a = eE/m_e$ and $\nu = N_a v \sigma_{ea}^*$ is the rate of electron collisions with atoms. These equations lead to the following expressions for components of the electron drift velocity:

$$w_x = \frac{eE}{3m_e} \left\langle \frac{1}{v^2} \frac{d}{dv} \left(\frac{\nu v^2}{\nu^2 + \omega_H^2} \right) \right\rangle, \quad w_y = \frac{eE}{3m_e} \left\langle \frac{1}{v^2} \frac{d}{dv} \left(\frac{\omega_H v^2}{\nu^2 + \omega_H^2} \right) \right\rangle \quad (15.33)$$

In the limit $\omega_H \ll \nu$ the first formula is transformed into (13.31).

In the absence of a magnetic field, the plasma conductivity is a scalar value. The presence of a magnetic field transforms the conductivity of a weakly ionized gas into a tensor, and *Ohm's law* takes the form

$$j_\alpha = \Sigma_{\alpha\beta} E_\beta$$

where j_α is a component of the current density. In the case where the collision rate ν does not depend on the electron velocity, the components of the *conductivity tensor* are given by

$$\Sigma_{xx} = \Sigma_{yy} = \Sigma_o \cdot \frac{1}{1 + \omega_H^2 \tau^2}, \quad \Sigma_{yx} = -\Sigma_{xy} = \Sigma_o \cdot \frac{\omega_H \tau}{1 + \omega_H^2 \tau^2} \quad (15.34)$$

where $\tau = 1/\nu$.

In the limiting case $\omega_H \tau \gg 1$ the total current is directed perpendicular to both the electric and magnetic fields. In this case the plasma conductivity and electric current do not depend on the collision rate because the change in the direction of electron motion is determined by the electron rotation in a magnetic field. We have in this case

$$j_y = ecN_e \frac{E_x}{H} = \frac{E_x}{R_H H} \quad (15.35)$$

where $R_H = 1/(ecN_e)$ is the *Hall constant*.

Let us determine the average electron energy in the case when the criterion (13.24) holds true. The balance equation for the electron energy has the form

$$eEw_x = \int \frac{m_e v^2}{2} I_{ea}(f_o) dv$$

Using formula (15.33) for the electron drift velocity and formula (12.26) for the electron-atom collision integral, we obtain:

$$T_e - T = \frac{Ma^2}{3} \frac{\left\langle \frac{v^2 \nu}{\nu^2 + \omega_H^2} \right\rangle}{\langle v^2 \nu \rangle} \quad (15.36)$$

In particular, if $\nu = \text{const}$, this formula gives

$$T_e - T = \frac{Ma^2}{3(\nu^2 + \omega_H^2)} \quad (15.37)$$

In the limit $\omega_H \gg \nu$ formula (15.36) yields

$$T_e - T = \frac{Ma^2}{3\omega_H^2} = \frac{Mc^2 E^2}{3H^2} \quad (15.38)$$

Let us consider the case when a weakly ionized gas is moving in the transverse magnetic field of strength H with an average velocity u . Then the electric field occurs in the motionless frame of reference of a strength $E' = Hu/c$, where c is the speed of light. This field creates an electric current which is used to obtain electrical energy in *magnetohydrodynamic generators* (MHD). The energy released in a plasma under the action of this electric current corresponds to transformation of the flow energy of a gas into electrical and heat energy. Correspondingly, this process leads to deceleration of the gas flow and a decrease in its average velocity. Along with this, an origin of an electric field causes an increase in the electron temperature which is given by formula (15.38). As we can see, the maximum increase in the electron temperature corresponds to the limit $\omega_H \gg \nu$. In this limit, formula (15.38) yields

$$T_e - T = \frac{Ma^2}{3\omega_H^2} = M \frac{u^2}{3} \quad (15.39)$$

15.7 Deceleration of Fast Electrons in Plasma

Let us analyze the *deceleration of electrons* in an ionized gas or plasma if electron–electron collisions are more effective than electron collisions with neutral particles, i.e. the criterion (13.24) holds true. In particular, it takes place in the course of the deceleration of fast electrons in metals because this process is determined by electron–electron collisions. For this analysis one can use the Landau collision integral (12.38) and (12.39) for a fast test electron. The peculiarity of the deceleration of fast electrons as a result of collisions with slow electrons is due to the strong increase in the Coulomb cross section with an increase in the electron energy. If a fast electron moves in an external electric field, then starting from certain electron velocities an acceleration of the electron in this field will not compensate for electron deceleration in collisions with other electrons. This phenomenon is called the *effect of flying electrons* and will be considered below.

Let us analyze the evolution of a test fast electron whose velocity significantly exceeds the typical energy of plasma electrons. We have the balance equation for the momentum $m_e v_x$ of a test electron when it moves along an electrical field of strength E

$$m_e \frac{dv_x}{dt} = eE - \frac{1}{v_x} \frac{d\varepsilon}{dt}$$

where $d\varepsilon/dt$ is the variation of the electron energy per unit time in collisions with plasma electrons. We take into account that an individual collision leads to scattering at small angles, and an individual act of collision is accompanied by a small energy variation. This value is equal to

$$\frac{d\varepsilon}{dt} = \int N_e v \cdot 2\pi\rho d\rho \cdot \frac{\Delta p^2}{2m_e}$$

Here v is the velocity of a test electron ($v \approx v_x$), N_e is the electron number density, ρ is the impact parameter of collision and Δp is the momentum which is transferred from a test electron to a plasma electron in their collision. According to formula (12.30) we have

$$\Delta p = \frac{2e^2}{\rho v}$$

and we obtain

$$\frac{d\varepsilon}{dt} = N_e \cdot \frac{4\pi e^4}{m_e v} \ln \Lambda$$

where the *Coulomb logarithm* is given by formula (12.34). Finally, we obtain the balance equation for the momentum of a test fast electron which moves along an electric field in a plasma

$$m_e \frac{dv_x}{dt} = eE - N_e \cdot \frac{4\pi e^4}{m_e v^2} \ln \Lambda \quad (15.40)$$

It follows from the balance equation (15.40) that fast electrons are accelerated in the electric field starting from energies

$$\varepsilon \geq \varepsilon_{\text{cr}} = N_e \cdot \frac{2\pi e^4}{eE} \ln \Lambda \quad (15.41)$$

In particular, if the electric field strength E is measured in V/cm, the number density of electrons N_e is measured in 10^{13} cm^{-3} , and the electron energy ε is measured in eV, the criterion (15.41) has the following form if we take $\ln \Lambda = 10$:

$$\varepsilon_{\text{cr}} = 13 \frac{N_e}{E} \quad (15.42)$$

16 Transport of Electrons in Condensed Systems

16.1 Electron Gas of Metals

The above results for the behavior of electrons in an ionized gas can be used partially for the electrons of metals if we change the interaction of electrons with the surrounding atomic particles by an effective mean field. In this *mean field model* the behavior of metal electrons is similar to that of plasma electrons. But in contrast to a weakly ionized gas, because of the high density of electrons in metals they are degenerate at room or low temperatures. Therefore we start from the model of a *degenerate electron gas* (see Chapter 4) for metal electrons. Within the framework of this model, in a space of electron momenta or wave vectors electrons occupy a range inside the *Fermi sphere*. The electron distribution function on energies is given in accordance with formula (2.35)

$$f(\varepsilon) = \text{const} \frac{N_e}{1 + \exp\left(\frac{\varepsilon - \varepsilon_F}{T}\right)} \quad (16.1)$$

where the chemical potential of this distribution or the *Fermi energy* ε_F is given by formula (4.2). This distribution function is normalized by the condition

$$\int f(\varepsilon) \varepsilon^{1/2} d\varepsilon = 1$$

and the small parameter (4.3) T/ε_F relates to this distribution.

Within the framework of this distribution, the electron transport coefficients are determined by the above formulae. Indeed, according to a general scheme, the distribution function of electrons is close to the spherical one, and its expansion over the spherical harmonics is similar to formulae (12.18) and (13.27) if an electron moves in an electric field in a gas. Then the collision integral of the antisymmetric distribution function is given by formula (12.20), which allows one to connect the kinetic coefficients with the spherically symmetric part of the distribution function. In particular, one can use formulae (15.4) and (15.7) for the conductivity of the metallic plasma, which takes the following form under the assumption that the collision rate ν is independent of the electron velocity

$$\Sigma = \frac{N_e e^2 \tau}{m_e} \quad (16.2)$$

where the collision time is $\tau = 1/\nu$. Next, one can repeat the deduction of formula (15.20) for the electron thermal conductivity with the use of the distribution function (16.1) instead of the Maxwell one. This gives for the thermal conductivity coefficient when the collision rate ν does not depend on the electron velocity

$$\kappa = \frac{\pi^2}{3} \frac{N_e \tau T}{m_e} \quad (16.3)$$

In particular, from this the *Wiedemann–Franz law* follows

$$\frac{\kappa e^2}{\Sigma T} = \frac{\pi^2}{3} \quad (16.4)$$

We now apply the results to the simplest metals whose atoms have one valence *s*-electron. Table 4.2 gives the parameters of electrons in the case where they obey Fermi–Dirac statistics. Then the valence electrons of atoms form a degenerate electron gas. We denote by N_o the electron number density of Table 4.1. Another method of finding the number density of electrons is on the basis of formula (15.35) using the metal conductivity and Hall coefficient R_H whose values are given in Table 16.1. In this Table N_e is the electron number density of conducting electrons of metals, which follows from the measured quantities of the Hall coefficient, and the quantities N_e of Table 4.1 are given in parentheses. If the ratio N_e/N_o exceeds one, this means that internal *p*- and *d*-electrons of atoms give a contribution to the metal conductivity. According to the Table 16.1 data we have for the parameter of formula (16.4), averaged over these metals at room temperature, $\kappa e^2/(\Sigma T) = 3.3 \pm 0.2$, while according to the Wiedemann–Franz law (16.4) this ratio is 3.3, and the data of Figure 16.1, which contains the metal parameters, give the same value after averaging over metals. In addition, Table 16.1 contains the average mobility of electrons which follows from formula (15.4)

$$K_e = \frac{\Sigma}{eN_e} = C \frac{\Sigma}{N_e}$$

and if the mobility is measured in $\text{cm}^2/(\text{V} \cdot \text{s})$, the conductivity is given in 10^{16} s^{-1} , and the electron number density is expressed in 10^{22} cm^{-3} , the proportionality coefficient is $C = 6.9$.

Table 16.1. Parameters of single-valent metals at room temperature, so that atoms of these metals have one valence *s*-electron; ρ is the metal density.

Metal	Li	Na	K	Cu	Rb	Ag	Cs	Au
$a, \text{\AA}$	3.51	4.29	5.34	3.61	5.71	4.09	6.09	4.08
$\rho, \text{g/cm}^3$	0.534	0.971	0.862	8.96	1.53	10.5	1.87	19.3
$\Sigma, 10^{16} \text{ s}^{-1}$	9.7	18.9	12.5	53.6	7.0	56.7	4.4	39.6
$\kappa, \text{W}/(\text{cm} \cdot \text{K})$	0.85	1.41	1.02	4.01	0.58	4.29	0.36	3.17
$\kappa e^2/(\Sigma T)$	3.6	3.1	3.4	3.1	3.4	3.1	3.4	3.3
$cR_H, 10^{-4} \frac{\text{cm}^3}{\text{C}}$	−1.7	−2.5	−4.2	−0.55	—	−0.84	−7.8	−0.72
$N_e, 10^{22} \text{ cm}^{-3}$	3.7(4.6)	2.5(2.5)	1.5(1.4)	11(8.5)	(1.1)	7.4(5.9)	0.80(0.87)	8.7(5.9)
$K_e, \text{cm}^2/(\text{V} \cdot \text{s})$	18	52	58	34	44	53	38	32
N_e/N_o	0.79	0.98	1.1	1.3	—	1.3	0.92	1.5
$\tau, 10^{-14} \text{ s}$	1.0	3.0	3.3	1.9	(2.6)	3.0	2.2	1.8
λ/a	38	73	54	82	36	100	26	62
Θ_D, K	370	158	90	310	52	220	54	185
m^*/m_e	1.40	0.98	0.94	1.01	0.87	0.99	0.83	0.99

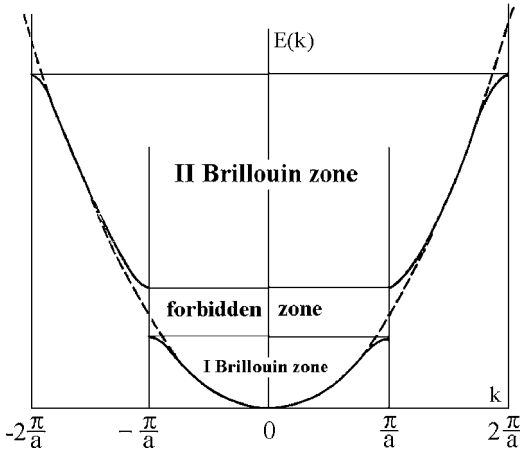


Figure 16.1. The Brillouin zones for a one-dimensional crystal.

Next, we use formula (16.2) for the determination of the typical time τ between neighboring acts of electron scattering in metals, and the values τ for metals under consideration are given in Table 16.1. The mean free path of electrons in metals is defined as $\lambda = v_F \tau$, where v_F is the electron velocity on the surface of the Fermi sphere, and its values are given in Table 4.1. Since the parameter λ/a is large, where a is the lattice constant (see Table 16.1), one can consider electrons of a plasma of these metals to be free for most of the time. Note that the *Debye temperatures* Θ_D of metals under consideration are compared with room temperature (Table 16.1) that allows one to consider lattice atoms as classical ones in processes of electron scattering on these atoms.

16.2 Electrons in a Periodical Field

Above we analyzed the behavior of electrons in a metal plasma changing the interaction of electrons with surrounding lattice by an effective mean field. We now consider the character of electron motion in a periodic field of the crystal lattice. Introducing the self-consistent electric field by which the lattice acts on a test electron, we require the periodicity of the corresponding effective field of the lattice:

$$V(\mathbf{r}) = V(\mathbf{r} + l\mathbf{a}) \quad (16.5)$$

where l is an integer, and $\mathbf{a}$ is the lattice vector which characterizes the lattice symmetry, so that the displacement of the electron coordinate by this value conserves the lattice parameters.

We have the Schrödinger equation for the electron wave function Ψ when the electron moves in the lattice field

$$-\frac{\hbar^2}{2m_e} \Delta \Psi + V(\mathbf{r}) \Psi = \varepsilon \Psi$$

where ε is the electron energy. Accounting for symmetry, it is convenient to represent the electron wave function in the form of the *Bloch functions*

$$\Psi(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} u_{\mathbf{k}}(\mathbf{r}) \exp(i\mathbf{k}\mathbf{r}) \quad (16.6)$$

where Ω is the system volume. The wave function $u_{\mathbf{k}}(\mathbf{r})$ satisfies the relation

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + l\mathbf{a}) \quad (16.7)$$

where l is an integer. The function (16.7) is the solution of the Schrödinger equation

$$\frac{(\hat{\mathbf{p}} + \hbar\mathbf{k})^2}{2m_e} u_{\mathbf{k}}(\mathbf{r}) + V(\mathbf{r})u_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r}), \quad (16.8)$$

where the momentum operator is $\hat{\mathbf{p}} = -i\frac{\hbar}{m_e}\nabla$.

In order to understand the peculiarities of this equation, we consider the case when the perturbation theory is applicable to this equation. We represent equation (16.8) in the form

$$\left[-\frac{\hbar^2}{2m_e} \Delta \Psi + V(\mathbf{r}) \right] u_{\mathbf{k}}(\mathbf{r}) - \left(\frac{i\hbar^2}{m_e} \mathbf{k} \nabla \right) u_{\mathbf{k}}(\mathbf{r}) = \left(\varepsilon_{\mathbf{k}} - \frac{\hbar^2 k^2}{2m_e} \right) u_{\mathbf{k}}(\mathbf{r}) \quad (16.9)$$

Considering the second term of the left-hand side of this equation as a perturbation, we have in the zeroth approximation

$$\left[-\frac{\hbar^2}{2m_e} \Delta \Psi + V(\mathbf{r}) \right] u_{\mathbf{i}}(\mathbf{r}) = \varepsilon_{\mathbf{i}} u_{\mathbf{i}}(\mathbf{r}) \quad (16.10)$$

where $u_{\mathbf{i}}(\mathbf{r})$ is the eigenwave function of this equation, and $\varepsilon_{\mathbf{i}}$ is the eigenenergy of the i th state. One can see that these values do not depend on the wave vector $\mathbf{k}$. In the next order of the perturbation theory, the electron energy is equal to

$$\varepsilon_{\mathbf{k}} = \varepsilon_{\mathbf{o}} + \frac{\hbar^2 k^2}{2m_e} \left[1 + \frac{2}{m_e} \sum \frac{|(p_x)_{oi}|^2}{\varepsilon_{\mathbf{o}} - \varepsilon_{\mathbf{i}}} \right]$$

where the vector $\mathbf{k}$ is directed along the x -axis, the index o corresponds to a given state, and the index i refers to other electron states. One can rewrite this formula in the form

$$\varepsilon_{\mathbf{k}} = \varepsilon_{\mathbf{o}} + \frac{\hbar^2 k^2}{2m_*} \quad (16.11a)$$

where the *electron effective mass* m_* is given by

$$\frac{1}{m_*} = \frac{1}{m_e} \left[1 + \frac{2}{m_e} \sum \frac{|(p_x)_{oi}|^2}{\varepsilon_{\mathbf{o}} - \varepsilon_{\mathbf{i}}} \right] \quad (16.11b)$$

Thus, analyzing the electron behavior inside a metal, one can reduce this problem to the problem of free electrons by the introduction of an electron effective mass which accounts for

the interaction of a test electron with a metal plasma and lattice. This value can depend on the direction of electron motion, i.e. the effective mass is a tensor.

We now use the symmetry of the wave function with respect to the transition

$$\mathbf{k}' = \mathbf{k} + l\mathbf{b} \quad (16.12)$$

where l is a whole number, $\mathbf{b}$ is the vector of an inverse lattice which satisfies the relation

$$\mathbf{a}\mathbf{b} = 2\pi l \quad (16.13)$$

Here l is an integer, and the lattice vector $\mathbf{a}$ is introduced by formula (16.5). We find that the space $\mathbf{k}$ is divided into regions – *Brillouin zones* – in which the electron parameters are repeated. To demonstrate this, we consider a one-dimensional case when atoms are arranged along a line with a distance a between nearest neighbors. Let us divide the range of electron wave vectors k into Brillouin zones, so that the first one corresponds to

$$\frac{\pi}{a} \geq k \geq -\frac{\pi}{a}$$

We consider the interaction of a test electron with the lattice as a perturbation, and according to (16.5) the interaction potential has a *translational symmetry*

$$V(x) = V\left(x + \frac{2\pi}{a}l\right)$$

In the zeroth order approach of perturbation theory, the wave function of a free electron has the form $\sim \exp(ikx)$ for the incident wave and $\sim \exp(-ikx)$ for the reflected wave. Because of the periodicity of the interaction potential only the matrix element between incident and reflected waves from neighboring Brillouin zones is not equal to zero. Indeed, we have

$$\int_{-\infty}^{\infty} V(x) \cos\left(\frac{2\pi}{a}\alpha x\right) dx \sim \delta_{l\alpha}$$

i.e. the matrix element is zero for different states of the same Brillouin zone. This matrix element is not zero for an incident wave $\exp(ikx)$ and reflected wave of the neighboring Brillouin zone $\exp\left[i\left(\frac{2\pi}{a} - k\right)x\right]$. The electron energy in the zero approximation is $\varepsilon(k) = \hbar^2 k^2 / (2m_e)$. Hence if $\varepsilon(\frac{2\pi}{a} - k) - \varepsilon(k) \gg |V|$, where V is a typical interaction potential of the electron with the lattice, the correction to the electron energy in the first order of the perturbation theory contains a large denominator and is relatively small. This means that the strongest interaction takes place near the edge of the Brillouin zone and leads to energy splitting near the edges of Brillouin zones, as shown in Figure 16.1.

Thus, in the one-dimensional case a space of possible electron wave vectors or energies is divided into zones (see Figure 16.1), and each Brillouin zone is characterized by the maximum and minimum electron energies. In this way, the energy range is divided into prohibited and forbidden energy bands. Transition to the three-dimensional case conserves this picture, but makes it more complex. If we distribute electrons over energy levels of this system at low electron temperatures, we obtain the surfaces in a $\mathbf{k}$ -space of the maximum possible energy,

the *Fermi surface*. If this surface does not coincide with the surface of a maximum energy for some Brillouin zone, electrons from the Fermi surface can transfer to excited states at low excitation energies. This corresponds to metals. If the Fermi surface is separated from the energy surface for excited electrons by an energetic gap, we deal with *isolators*, i.e. dielectrics or semiconductors.

16.3 Conductivity of Metals

Above we consider transport phenomena in metals as a result of the motion of free electrons in a mean lattice field and neglect the periodicity of this field. We now take into account the periodical character (16.5) of the field. Accounting for the field periodicity, we transform electrons in metals into quasiparticles which carry a single negative charge and which differ from free electrons by an effective mass. The reduced values of the effective electron mass for metals under consideration are given in Table 16.1. The concept of the effective electron mass allows us to include in our consideration the averaged interaction of electrons inside the lattice in a simple way by renormalization of the electron mass. Hence within the framework of this consideration, at zero temperature an electron moves inside the lattice as a quasiparticle without scattering, which corresponds to infinite metal conductivity. The *metal resistance* is created due to two mechanisms of electron scattering in metals on metal inhomogeneities. The first one relates to electron scattering on dislocations and admixture atoms, and the second one is due to the oscillations of crystal atoms which violate the periodicity in the atomic distribution. The second mechanism of electron scattering disappears at low temperatures and dominates at high temperatures because of the low concentration of admixture atoms and dislocations.

Because of the dependence (16.2) for the metal conductivity, we have for metal the specific resistance $\rho = 1/\Sigma$

$$\rho \sim \frac{1}{\lambda} \sim N\sigma$$

where λ is the mean free path of electrons with respect to its scattering on lattice atoms, N is the number density of lattice atoms and σ is the cross section of electron scattering on a lattice atom. We assume in the above formula that electron scattering on different lattice atoms is independent. Let us take the wave function of an incident electron in the form $\exp[i\mathbf{k}(\mathbf{r} - \mathbf{R})]$, where $\mathbf{k}$ is the electron wave vector, $\mathbf{r}$ is its coordinate and $\mathbf{R}$ is the lattice atom coordinate. Then the scattering amplitude is proportional to the factor $(\mathbf{k} - \mathbf{k}')(\mathbf{R} - \mathbf{R}_o)$, where $\mathbf{k}'$ is the wave vector of the scattering electron and $\mathbf{R}_o$ is the equilibrium position of the lattice atom. Correspondingly, the cross section σ of electron scattering on a lattice atom is proportional to the square Δ^2 of the atom vibration amplitude which according to formula (3.39) is $\Delta^2 \sim T$ for the classical motion of nuclei when the thermal energy T is of the order of or more than the Debye temperature Θ_D . Thus we have

$$\Sigma \sim \Delta^2 \sim \frac{T}{\Theta_D} \quad (16.14)$$

This allows us to represent the temperature dependence of the conductivity or specific resistance of metals. At high temperatures the resistance of metals is determined by electron

scattering on oscillations of lattice atoms, while at low temperatures this scattering becomes small, and electron scattering on dislocations or admixture atoms dominates. Since these mechanisms of the metal resistance do not correlate, one can consider the contribution of these effects to the metal resistance to be independent. This leads to the following form for the total metal conductivity

$$\frac{1}{\Sigma} = \frac{1}{\Sigma_d} + \frac{1}{\Sigma_p} \quad (16.15)$$

where Σ_d is the metal conductivity due to electron scattering on dislocations and admixture atoms, and Σ_p results from the scattering of electrons on lattice oscillations. At low temperatures the first term dominates, while at high temperatures the second term is stronger because of the small concentration of dislocations and admixture atoms. The first term has practically no dependence on temperature, while the contribution of the second one increases with increasing temperature. Therefore, the specific resistance of a metallic object does not depend on the temperature at low temperatures and increases proportional to the temperature at high temperatures. Note that at high temperatures the specific metal conductivity is the same for different samples, while the low-temperature limit of the conductivity depends on the specifics of a given sample.

16.4 Fermi Surface of Metals

Thus, characterizing an electron by the wave vector which describes the motion of the electron inside the lattice as a wave and accounting for the electron interaction with the lattice field and other electrons, we obtain the electron energy in the form

$$\varepsilon = \varepsilon(\mathbf{k}) \quad (16.16)$$

when this electron moves in the lattice field. Then the energy levels with $\varepsilon < \varepsilon_F$ will be occupied. Thus one can characterize this system by the *Fermi surface* in a space of electron wave vectors. This description is similar to that of Chapter 4 for the model of free electrons with the only exchange interaction between electrons being due to the *Pauli exclusion principle*. Then electron occupied a ball in $\mathbf{k}$ -space, which according to formula (4.2) is restricted by a sphere

$$k = k_F = (3\pi^2 N_e)^{1/3}$$

For real metals the Fermi surface

$$\varepsilon(\mathbf{k}) = \varepsilon_F \quad (16.17)$$

becomes more complex. In particular, there is in Figure 16.2 a Fermi surface for coin metals (Cu, Ag, Au). Note that the Fermi surface becomes open, which corresponds to the possibility of an electron transfer between different Brillouin zones in a continuous way.

Open Fermi surfaces are of importance for some fine processes in metals. We demonstrate this with an example of metal conductivity or thermal conductivity at low temperatures, if this is determined by the oscillations of lattice atoms, i.e. the scattering of electrons results from

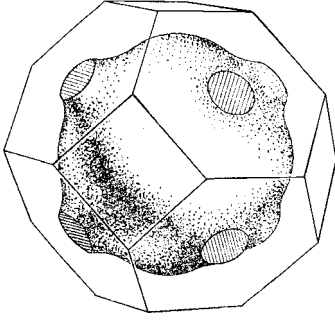


Figure 16.2. Fermi surface of the first Brillouin zone for coin metals (Cu, Ag, Au). Open regions of the Fermi surface corresponds to the direction $\{111\}$.

the absorption or emission of phonons. At low temperatures this can be determined by the process when the wave vectors of the initial and final electron states are $\mathbf{k}$ and $\mathbf{k}'$, and $\mathbf{q}$ is the wave vector of a forming phonon. If the incident and scattering electron are located in the same Brillouin zone, the energy and momentum conservation laws have the form

$$\frac{\hbar^2}{2m_e} (k^2 - (k')^2) = \hbar c_s q \quad (16.18)$$

Since the speed of sound $c_s \sim 1/\sqrt{M}$, where M is the atom mass, and the electron velocity v_F on the Fermi sphere $v_F > e^2/\hbar$, we have $k \approx k'$. Therefore only electrons above the Fermi sphere can take part in this process, and the metal conductivity or its thermal conductivity at low temperatures grow strongly with increasing temperature if these values are determined by the interaction between electrons and lattice oscillations.

At low temperatures a certain contribution to this phenomenon gives the exchange processes (*transfer processes*) when scattering transfers the electron to another Brillouin zone. Then the momentum conservation law takes the form

$$\mathbf{k} = \mathbf{k}' + \mathbf{q} + l\mathbf{b},$$

where $\mathbf{b}$ is the inverse lattice vector, l is an integer and $l = 0$, if the transition proceeds in the limit of the same Brillouin zone. The transfer processes give new possibilities for electron scattering as a result of excitation or quenching of phonons. Then electrons located far from the Fermi surface can take part in this process, i.e. these electrons can be scattered by the crystal lattice. This is of particular importance for open regions of the Fermi surface. In this case the scattering of electrons inside the Fermi surface can be accompanied by the excitation of phonons with low energies.

This analysis shows the importance of the concept of the Fermi surface for the description and analysis of various processes and phenomena in metals. Metallic electrons may be excited in the vicinity of the Fermi surface with a low excitation energy, and this is the definition of metals. In practice, the Fermi surface concept is a modification of the Fermi distribution for a degenerate Fermi gas (see Chapter 4). Moreover, in the case of alkali metals the Fermi surface of the first Brillouin zone does not differ practically from a Fermi sphere for a free dense electron gas. The Fermi surface is a characteristic of metals and determines its properties. As an example, Figure 16.3 exhibits the *de Haas-van Alphen effect* according to which the

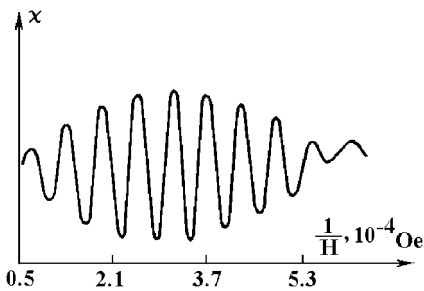


Figure 16.3. The de Haas–van Alphen effect as an oscillation dependence of the magnetic susceptibility on the inverse magnetic field strength for zinc at temperature of 4.2 K.

metal magnetic susceptibility is an oscillation function of the inverse magnetic field strength at low temperatures. The position of the metal Fermi surface determines these oscillations, and in turn the Fermi surface can be restored on the basis of the oscillations of various metal parameters at low temperatures. As an example of such information, Table 16.2 contains the ratio of areas of the open part of the Fermi surface of coin metals (see Figure 16.2) to its total area for the first Brillouin zone. This value results from the analysis of low-frequency oscillations of the magnetic susceptibility as a function of the inverse magnetic field for these metals.

Table 16.2. The ratio of the area of the open Fermi surface S_{op} in the direction $\{111\}$ and to the total area S_{tot} of the Fermi surface projection onto this plane.

Metal	Cu	Ag	Au
$S_{\text{op}}/S_{\text{tot}}$	0.037	0.020	0.034

16.5 Drift of an Excess Electron in Condensed Systems

We now consider the behavior of an *excess electron* that is inserted in a dense system of atoms or molecules, if this electron is injected in this system. In contrast to a gas system, where electron scattering proceeds on individual atoms independently of the positions of other atoms and the electron behavior results at each moment from the interaction with electrons of a single atom, in dense or condensed systems of atoms a test electron interacts simultaneously with electrons of many atoms. Then the system of interacting atoms can be considered as a united electron–atom system in which a test electron is moving. One can consider the energy ε_o of the ground state of an electron in this system as the solution of the Schrödinger equation for the electron wave function ψ_e

$$-\frac{\hbar^2}{2m_e}\Delta\psi_e + V\psi_e = \varepsilon_o\psi_e \tag{16.19}$$

where the potential energy V is created by the interaction of a test electron with the electrons of the surrounding atoms and depends on the positions of their nuclei. When a test electron

moves inside a condensed system, its energy is given by formula (16.11a)

$$\varepsilon_{\mathbf{k}} = \varepsilon_o + \frac{\hbar^2 k^2}{2m_*} \quad (16.20)$$

where m_* is the *electron effective mass* and k is the electron wave vector.

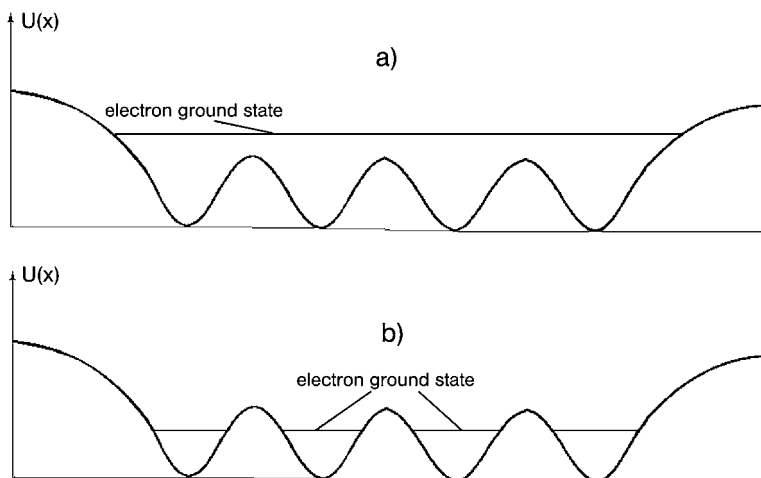


Figure 16.4. Character of motion of an excess slow electron in a condensed system of atoms depending on the position of the ground state electron level; (a) dielectric-type motion; (b) metal-type motion.

Let us introduce an effective energy potential for the motion of a test electron in a condensed system of atoms which can be realized in two ways in accordance with Figure 16.4. In the first case (Figure 16.4a) the electron is locked in a space between two neighboring atoms, and its transition to neighboring positions requires overcoming a barrier and lasts relatively long. This is a *dielectric type of electron drift*. In the second case, a *metallic type of electron drift*, the electron moves almost freely inside the condensed system. We give in Table 16.3 the parameters of liquid inert gases (T is the temperature, N is the number density of atoms) $T_{\max}$, $N_{\max}$ at which the reduced zero-field mobility ($K_{\max}N_{\max}$) is maximal, and also these parameters (T_{tr} , N_{liq} , $K_{\text{tr}}N_{\text{liq}}$) for the liquid state at the triple point. Under these parameters the metallic type of electron mobility is realized. For comparison, we represent the gaseous zero-field reduced mobility $K_{\text{gas}}N$ at room temperature (for gases the value $K_{\text{gas}}N$ does not depend on the number density of atoms). The maximum of the zero-field mobility is strong and narrow. In particular, according to the data of Figure 15.2, the reduced electron mobility in xenon varies by approximately three orders of magnitude in the course of transition from the gaseous state to the liquid one, and depends significantly on the liquid parameters.

Note that the maximum zero-field mobility significantly exceeds not only the gaseous reduced mobility, but also the metallic one. In particular, the reduced zero-field mobility of electrons at room temperature is equal to 2.9 and 3.1 in units $10^{24} (\text{cm} \cdot \text{V} \cdot \text{s})^{-1}$ for copper and silver correspondingly (see Table 16.1). Since electrons of these metals may be considered as a degenerate electron gas (Chapter 4), the typical electron velocity near the Fermi surface

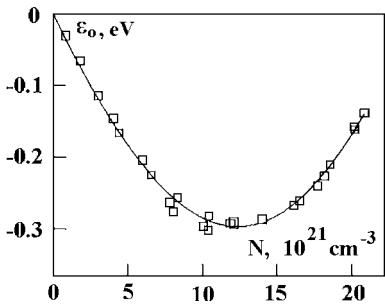


Figure 16.5. The ground state energy of an excess electron in argon with respect to a vacuum depending on the number density of argon atoms (A.K. Al-Omari, K.N. Altmann, R. Reiniger. *J. Chem. Phys.* 105, 1305(1996)).

significantly exceeds the thermal velocity of a free electron. Therefore, although the specific mobilities of an excess electron in condensed inert gases significantly exceed those in metals, the ratios of the electron free mean path to the distance between nearest atoms (or the lattice constant) have the same order of magnitude for both condensed inert gases and metals.

Table 16.3 contains also the minimal value of the electron energy ε_o in the ground state as well the number density of atoms $N_{\min}$ where this minimum is observed. One can see the correlation between the minimal electron potential energy in the ground state and the maximum of the zero-field electron mobility. Figure 16.5 gives the electron energy ε_o of the ground state in condensed argon as a function of the number density of argon atoms. Note that the value ε_o does not characterize the electron behavior inside the system because it is measured with respect to a vacuum, i.e. ε_o is the difference in the electron energies outside and inside this bulk system. In reality, electrons can form a layer on the boundary of bulk argon, and this charged layer equalizes the potentials from both sides of the interface. Note that the behavior of the electron energy ε_o for condensed krypton and xenon is similar to that of Figure 16.5. The above properties relate to heavy inert gases (Ar, Kr, Xe).

Along with the maximum of the zero-field electron mobility, the *saturation of the electron drift velocity* is observed for electron drift in condensed inert gases over some range of electric field strengths, i.e. the electron drift velocity does not depend on the electric field in the range

Table 16.3. Parameters of the zero-field mobility of an excess electron in liquid inert gases.

	Ar	Kr	Xe
$T_{\max}, \text{K}$	155	170	223
$N_{\max}, 10^{22} \text{ cm}^{-3}$	1.2	1.4	1.2
$K_{\max} N_{\max}, 10^{24} (\text{cm} \cdot \text{V} \cdot \text{s})^{-1}$	22	64	72
T_{tr}, K	85	117	163
$N_{\text{liq}}, 10^{22} \text{ cm}^{-3}$	2.1	1.8	1.4
$K_{\text{tr}} N_{\text{liq}}, 10^{24} (\text{cm} \cdot \text{V} \cdot \text{s})^{-1}$	10	29	28
$N_{\min}, 10^{22} \text{ cm}^{-3}$	1.1	1.2	1.1
ε_o, V	-0.3	-0.5	-0.8
$K_{\text{gas}} N, 10^{23} (\text{cm} \cdot \text{V} \cdot \text{s})^{-1}$	12	0.62	0.17

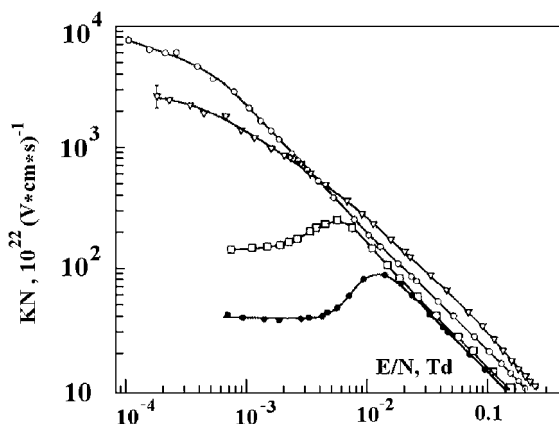


Figure 16.6. The dependence on the reduced electric field strength for the reduced mobility of an excess electron in liquid argon at some temperatures (the temperature T is expressed in Kelvin, the number density N of atoms is given in 10^{22} cm^{-3}): 1 – $T = 288 \text{ K}$, $N = 0.68$; 2 – $T = 278 \text{ K}$, $N = 0.86$; 3 – $T = 216 \text{ K}$, $N = 1.23$; 4 – $T = 163 \text{ K}$, $N = 1.41$ (J.A. Jahnke, L. Meyer, S.A. Rice. *Phys. Rev.* 3A, 734, 1971).

of electric field strengths. This effect is similar to that in gases (see Figure 15.1), which testifies to the identical mechanisms of electron scattering for gaseous and condensed number densities of atoms. At high field strengths electron motion in liquid inert gases resembles that in gases. It follows from Figure 16.6 that the reduced mobility of electrons as a function of the reduced electric field strength at high strengths does not depend strongly on the number density of atoms or the temperature. This is explained by the small cross section of electron scattering on an individual center, which makes this process similar to electron scattering in gases.

One can try to explain the strong maximum in the zero-field reduced mobility of an excess electron in condensed rare gases by the *Ramsauer minimum* in the cross section of electron–atom scattering, which is observed at an electron energy of 0.4–0.6 eV for argon, krypton and xenon atoms. Nevertheless, the Ramsauer effect cannot be used strictly to explain the behavior of an excess electron in condensed rare gases. Indeed, the Ramsauer effect results from the negative electron–atom scattering length that makes the scattering phase for the zeroth electron momentum zero at low electron energies where the electron–atom scattering phase is small for nonzero electron momenta. In spite of the smallness of the cross section at the Ramsauer minimum, this scattering is created at electron–atom distances which are of the order of an atomic size. At these distances an electron interacts with several atoms in condensed rare gases. Therefore the Ramsauer effect cannot act directly on electron drift in condensed gases, and this analogy can be used as a model only.

To understand the nature of a high zero-field electron mobility, we consider the limiting cases. At low number densities of atoms, when they form a gaseous system, electron interaction with a gas takes place only at points where atoms are located. The exchange electron–atom interaction corresponds to attraction, since the electron–atom scattering length is negative for heavy rare gases (Ar, Kr, Xe). In contrast, if the electron penetrates inside

the atom, it leads to repulsion because of the exchange interaction between the electron and atomic core due to the Pauli exclusion principle. Hence the repulsion interaction of an excess electron with an atom ensemble takes place at high pressures. From this it follows that the favorable conditions for drift of a test electron are realized at intermediate atomic densities, when the transition proceeds from attraction to repulsion for an excess electron. These densities correspond to a weak interaction between a test electron and an atomic system on average, which provides high electron mobility. This character of interaction takes place over a narrow range of atomic number densities, and according to its nature this mechanism of high electron mobility differs in principle from that in solids where a high electron mobility is connected with an ordered distribution of atoms in a space.

High electron mobility corresponds to a weak interaction of the electron with the matter where it propagates. Hence on the basis of experimental data, one can construct the *gaseous model* for electron scattering in the range of parameters which lead to high electron mobility. This model assumes that a test electron is scattered on individual centers independently and the cross section of this scattering is small compared to a^2 , where a is the distance between nearest atoms. We use formula (15.9) for the electron mobility at constant cross section σ , whose values as well as the values of the mean free path of electrons $\lambda_{\max} = (N_{\max}\sigma)^{-1}$ are given in Table 16.4 under conditions when the maximum of the electron mobility is attained. One can see that the mean free path $\lambda_{\max}$ is large in comparison with the distance between nearest neighbors $a_{\max}$ under these conditions. In addition, it follows from the data in Table 16.4 that the cross section of electron scattering on an individual center $\sigma = (\lambda_{\max}N_{\max})^{-1}$ is small compared to $\pi a_{\max}^2$. Thus, the gaseous model holds true for electron drift in condensed inert gases in the range of the metallic mobility of an excess electron. This model is valid also at moderate and strong electric field strengths when the electron energy significantly exceeds the typical thermal electron energy. But in spite of the analogy with the Ramsauer effect, the parameters of this model are not connected with the interaction of an electron with individual atoms and can be taken only from experiments.

Along with these data, Table 16.4 contains values of relative volume V_* , where the location of an electron is prohibited because of its repulsion interaction with atom cores due to the Pauli exclusion principle. This prohibition region consists of balls of radius r_* near each nucleus, and the prohibition radius r_* is found from the repulsion exchange interaction of two atoms at the interaction potential value of 0.1 eV.

Table 16.4. Parameters of the gaseous model for electron drift in rare gases.

	Ar	Kr	Xe
$a_{\text{tr}} \text{ \AA}$	4.1	4.3	4.7
$\sigma_{\text{tr}}/\pi a_{\text{tr}}^2$	0.012	0.005	0.005
λ/a_{tr}	65	150	170
$a_{\max} \text{ \AA}$	4.9	4.7	4.9
$\sigma_{\max}/\pi a_{\max}^2$	0.004	0.002	0.002
$\lambda/a_{\max}$	200	450	480
V_*/V_{tr}	0.39	0.38	0.42

16.6 The Tube Character of Electron Drift in Condensed Inert Gases

Thus an excess electron has a high mobility in condensed rare gases in a narrow range of atom number densities at low electric field strengths, and the mobility is less significant at high electric field strengths for the same atom number densities. On the basis of the above results, one can construct the potential energy surface for an excess electron in the following way. The potential energy surface has the form of tubes which pass between atoms – nearest neighbors. These tubes intersect and have bulges in regions with higher distances between atoms. When the energy of a moving electron is small, the tubes of the potential energy surface have a small radius. Then an excess electron that is moving along an individual tube does not transfer to other tubes, so that the electron does not scatter under these conditions. Electron scattering in the course of its motion along a tube is weak due to the variation of the potential energy along a tube, as follows from the data of Table 16.3. An increase in the electric field strength, along with an increase in the electron energy, leads to tube thickening. Correspondingly, this increases the probability of electron transition to a tube of another direction, which corresponds to electron scattering. Hence an increase in electric field strength leads to a decrease of the mean free path of a test electron in condensed rare gases under optimal atomic densities, and the electron mobility decreases significantly in accordance with the data of Figure 16.6. In practice, at high electric field strengths electron scattering proceeds on individual atomic cores, and therefore the character of electron mobility in this case is similar to that in gases.

One can connect the high mobility of an excess electron over some density range of inert gases with the behavior of the potential energy surface where an excess electron propagates. Let us construct this potential energy surface near its minimum, where an electron is attracted. We start from the simplest case when atoms form a crystal lattice, and find electron positions with the minimum potential energy. Evidently, because of the repulsive interaction for an excess electron with atomic interiors, the points of the minimum electron potential are located equidistantly from the nearest nuclei. Hence we draw for the two nearest planes of the crystal lattice the *Voronoi surface*, which separates the action of individual atoms on an electron, so that points inside the Voronoi surface near a given atom are located closer to this atom nucleus than to neighboring ones. The intersections of the Voronoi surface with two considered planes of atoms are shown in Figure 16.7, and they form a net of regular hexagons whose centers are nuclei of the lattice. Evidently, from symmetry considerations, the optimal positions of an excess electron with minimal values of the electron potential energy are located in the middle plane, which is found between the nearest planes of the atoms considered. Intersections of the Voronoi surface with this plane form straightforward lines of three directions, which are solid lines in Figure 16.7.

Evidently, the electron potential energy is minimal on these lines. These lines have the form of the *Delaunay network* or *Delaunay tessellation*. Electron drift inside an inert gas proceeds near these lines. We assume that points of intersection of these lines, i.e. sites of the Delaunay network, are characterized by minima of the electron potential energy, and their values are identical for all the intersection points (signs 4 on Figure 16.7) because of the problem symmetry. Transferring to three-dimensional space, we obtain intersections of six straightforward lines at points whose distance from two nearest neighbors is $a/2$, where a is the distance between nearest neighbors of the lattice.

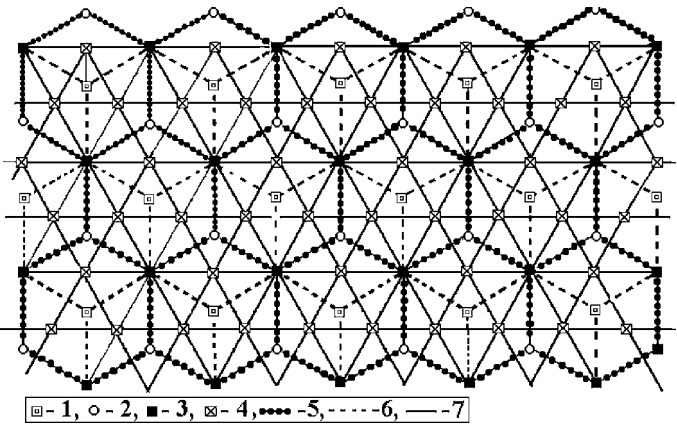


Figure 16.7. The character of the behavior of an excess electron between two planes of the crystal lattice of inert gases. (1) positions of atoms of the first layer, (2) positions of atoms of the second layer, (3) vertices of the hexagons which are intersections of the Voronoi surface with the corresponding layer, (4) positions of the Voronoi surface for an excess electron in the middle plane between these layers with the strongest interaction between the electron and atoms, (5, 6) hexagons – intersections of the Voronoi surface with the corresponding layers, (7) directions of electron current if it is located in the middle plane.

Thus supposing the optimal distance of an excess electron from the nearest nuclei under optimal number densities of atoms is possibly maximal for the minimum electron potential energy, we obtain for the close-packed crystal lattice the optimal electron positions to be located on the Delaunay network which consists of intersecting straight lines. We have two types of lines which alternate, and the period of translation symmetry for the first type of line is a , and for the second type $a/2$. We give in Table 16.5 the distances from six nearest neighbors for points which correspond to the minima of the electron potential energy or are located in the middle between nearest such points which we call as the maxima.

Table 16.5. Distances between an excess electron located in minima and maxima of the Delaunay network and six nearest nuclei when atoms form the close-packed crystal lattice, and a is the distance between nearest neighbors of this lattice. The number of nuclei with the indicated distance from a given point of the Delaunay network is represented in parentheses.

	Points 4 of Figure 16.7	Between points 4 of Figure 16.7
Lines of the first type	$\frac{a}{2}(2), a\frac{\sqrt{3}}{2}(4)$	$\frac{a}{\sqrt{2}}(6)$
Lines of the second type	$\frac{a}{2}(2), a\frac{\sqrt{3}}{2}(4)$	$\frac{a\sqrt{3}}{4}(1), a\frac{\sqrt{7}}{4}(2), a\frac{\sqrt{11}}{4}(1), a\frac{\sqrt{15}}{4}(2)$

Figure 16.7 shows positions of the Delaunay network that refer to minima of the potential energy for an excess electron. Correspondingly, we obtain three favorable directions of electron propagation which are indicated by solid lines in Figure 16.7. Then a slow electron propagates along these directions inside narrow tubes which surround each line of the De-

launay network. But we use only one direction of the plane [111] for the crystal lattice of close packing (face-centered cubic or hexagonal). The symmetry of the plane [111] admits eight different directions of this plane, and evidently the number of optimal lines for electron propagation coincides with the number of edges of the octahedron figure, all of whose eight facets have the direction [111]. The number of these edges is 12, and evidently there are 12 different straight lines for electron motion.

If a slow electron propagates inside a tube along one of this direction, it is not scattered because of the quantum character of the scattering process. Then an electron possesses the ground state, and its scattering in the course of motion along a given line can proceed for two channels. The first one corresponds to a transition to an excited state that is impossible because of a small electron energy, and the second channel refers to back scattering and is weak. The main contribution to electron scattering gives a transition to another tube located around another line of optimal electron propagation, and this transition can proceed near knots of line intersections. Note that atom oscillations or the motion of atoms do not change this picture because of the adiabatic character of change of the potential energy. When the electron energy increases, the tubes around lines of optimal electron motion are expanded, especially in regions of line intersections. This leads to more intensive electron scattering and respectively to lower electron mobility. Therefore the electron mobility decreases with increasing electron energy.

In the liquid aggregate state the Voronoi surfaces and Delaunay network may be constructed by the above method, but lines of the Delaunay network become distorted in this case. Nevertheless, because of the short order in liquids, the curvature of these lines is not small, and we can take the crystal case as the basis for qualitative consideration. In any case, the number of lines and the character of their intersection is identical in both cases. Supposing that positions on the Delaunay network correspond to the minimal electron potential inside an inert gas, we then obtain that a slow electron is drifting inside this condensed inert gas near lines that form the Delaunay network. Correspondingly, the scattering mechanism due to transition to other tubes of an optimal electron current are identical for the solid and liquid states if this scattering mechanism takes place. One can see that this mechanism of electron scattering differs in principle from electron scattering in metallic crystals where scattering of a free electron is determined by distortions of the crystal lattice.

16.7 Electron Mobility in Condensed Systems

In conclusion, one may note a different character of electron drift in condensed systems of atoms, and in all cases it differs from that in gases where electron drift results from electron scattering on individual atoms. In the case of low electron energies, electron scattering is a collective effect in condensed systems of atoms. In metals, the scattering of valence electrons is determined by the form of the Fermi surface for valence electrons, which is connected with the character of the electron interaction and environment. Taking into account this interaction, one can transform interacting electrons into non-interacting quasiparticles, and the form of the Fermi surface in a space of electron momenta includes this interaction. Then scattering is weak for slow electrons and their mobility is relatively high, because the main contribution to

electron scattering is determined by electrons near the Fermi surface. This also leads to the high conductivity of metals.

The mobility of an excess electron in dielectrics of the crystal structure is also high if the electron–matter interaction makes location of an electron inside the dielectric energetically favorable. This follows from the translation symmetry of the total system, and scattering is determined by the violation of periodic symmetry. If an electron can form a bound state inside a dielectric, the mobility becomes small at low electron energies. An example of this follows from Figure 16.4a, where an electron is locked in an atomic well, and its transition to a neighboring cell has an activation character. In another case of strong electron interaction it forms a negative ion, so that its mobility corresponds to negative ion mobility and hence is small. In particular, it takes place in liquid neon.

In other inert gases (Ar, Kr, Xe) the minimum potential energy for an excess electron corresponds to straight lines in crystals and weakly distorted lines in liquids. The equipotential surfaces in crystals are tubes surrounding lines of minimal potential energy, so that there are 12 directions of straight lines in a crystal, and there are an infinite number of lines of the same direction. A slow excess electron is moving inside a corresponding tube, and its transition to another tube corresponds to electron scattering. Because the probability is small for transition to another tube intersecting this one, the mobility of a slow excess electron is correspondingly high and decreases with increasing electron energy. Thus all the mechanisms of electron scattering inside condensed atomic systems have a collective character.

17 Transport of Ions and Clusters

17.1 Ambipolar Diffusion

The transmission of energy from an external electric field to a weakly ionized motionless gas proceeds through electrons; ions, as slower charged particles make a small contribution to this process. Hence the conductivity and dielectric constant of a weakly ionized gas are determined by electrons, as was considered above. The motion of ions can be essential in a plasma which propagates in a gas as a whole. For example, let us consider an *afterglow plasma* which is created in some space region of a buffer gas and then propagates over a space. This proceeds such that electrons as faster charged particles go forward and pull ions. Then, due to the separation of charges, an electric field occurs that decelerates electrons and accelerates ions. As a result, the plasma moves as a whole with a typical ion velocity.

This self-consistent regime of plasma propagation in a gas is called the *ambipolar diffusion* regime. This relates both to the propagation of an afterglow plasma and to the transport of charged particles to walls in gaseous discharges. Below we analyze this regime of plasma motion in a buffer gas. Then the electric field $\mathbf{E}$ due to separation of charges is of importance for transport of charged particles, so that the electron $\mathbf{j}_e$ and ion $\mathbf{j}_i$ fluxes are given by the expressions

$$\mathbf{j}_e = -D_e \nabla N_e - K_e \mathbf{E} N_e; \quad \mathbf{j}_i = -D_i \nabla N_i + K_i \mathbf{E} N_i \quad (17.1)$$

Here N_e and N_i are the number densities of electrons and ions correspondingly, D_e and D_i are their diffusion coefficients, and K_e and K_i are their mobilities. Because of the electric field acts on electrons and ions in opposite directions, it is included in the flux expressions with different signs. The electric field strength $\mathbf{E}$ is determined by Poisson's equation:

$$\text{div } \mathbf{E} = 4\pi e(N_i - N_e) \quad (17.2)$$

Since a plasma is the converse of quasineutrality during evolution, the charge separation is small

$$\Delta N = |N_i - N_e| \ll N_e \quad (17.3)$$

It is the condition of the ambipolar diffusion regime of plasma propagation which gives $N_e = N_i = N$. Because of the self-consistent character of plasma motion, we have $\mathbf{j}_e = \mathbf{j}_i$. Next, according to formulae (14.7), (15.5), the kinetic coefficients of electrons are large compared with those of ions. In order to satisfy to the above relations, it is necessary to require that the electron flux is zero $j_e = 0$ on the scale of ion values. Indeed, $j_e = j_i$, but $D_e \nabla N_e \gg j_i$, $eEK_e N_e \gg j_i$, i.e. on the scale of electron parameters $\mathbf{j}_e = 0$. From this it follows that

$$\mathbf{E} = -\frac{D_e}{eK_e} \frac{\nabla N}{N} \quad (17.4)$$

and we obtain for the flux of charged particles:

$$\mathbf{j} = \mathbf{j}_i = - \left(D_i + \frac{D_e K_i}{K_e} \right) \nabla N = -D_a \nabla N$$

where D_a is the so-called the *coefficient of ambipolar diffusion*. Thus the plasma evolution has a diffusion character with a self-consistent diffusion coefficient. In particular, in the case of the Maxwell distribution of electrons and ions on velocities we obtain, by using the Einstein relation (14.15):

$$D_a = D_i \left(1 + \frac{T_e}{T_i} \right) \quad (17.5)$$

We can see that in the considered regime a plasma expands with an ion velocity rather than with an electron one.

Let us find the criterion of this regime taking into account the quasineutrality of an expanding plasma, i.e. $\Delta N = |N_i - N_e| \ll N$. From Poisson's equation (17.2) we have $\Delta N \sim E/(4\pi eL)$, where L is a typical size of the plasma. From the equation $\mathbf{j}_e = 0$ on the basis of the set (17.1) and the Einstein relation (14.15) we have $E \sim T/(e^2 L)$, where for simplicity we assume the electron and ion temperatures to be equal. Thus $\Delta N \sim N r_D^2 / L^2$. From this it follows that the criterion of the ambipolar diffusion regime (17.3) coincides with the plasma definition

$$L \gg r_D$$

17.2 Electrophoresis

Let us consider one more phenomenon in a plasma where the transport of ions is of importance. A weakly ionized gas can be used to separate isotopes and elements due to the different currents for different types of charged atomic particles. As an example, we consider *electrophoresis* in a gas discharge plasma. This phenomenon corresponds to the partial separation of components of a gaseous system. Let us place in a cylindrical tube a gas which consists of two components: a buffer gas (for example, helium) and a lightly ionizing admixture (for example, mercury, cadmium, zinc). Ions belong to the admixture because of its small ionization potential, and the number densities of components satisfy the relation:

$$N \gg N_a \gg N_i$$

where N is the number density of atoms of a buffer gas, N_a is the number density of admixture atoms, and N_i is the number density of ions.

Because the ion current relates to ions of the admixture, we have the following balance equation:

$$-D \frac{dN_a}{dx} + w N_i = 0$$

where D is the diffusion coefficient of admixture atoms in a buffer gas, w is the ion drift velocity, the x -axis is directed along the field and discharge tube. Assuming the ion diffusion

coefficient to be $D_i \sim D$, we obtain on the basis of the Einstein relation (14.15) a typical size $L = (d \ln N_a / dx)^{-1}$ which is responsible for the gradient of the admixture number density:

$$L \sim \frac{T}{e E c_i} \quad (17.6)$$

where $c_i = N_i / N_a$ is the degree of ionization of the admixture, T is the temperature of the atoms or ions and E is the electric field strength. So, if a typical size L is small compared with the length of a discharge tube, admixture atoms are collected near the cathode under the action of the electric current in this gaseous discharge.

This phenomenon makes a discharge plasma non-uniform, and the glow of this plasma due to the radiation of excited atoms of the admixture is concentrated near the cathode. The electrophoresis is established for a typical time $\tau \sim L(c_i w)$ after switching on the discharge and influences on discharge parameters. Indeed, in a region near the anode the number density of admixture atoms and ions decreases. This requires an increase in the rate constant of ionization, so that the electric field strength in this region must be increased. Thus electrophoresis can change the parameters of a gas discharge.

17.3 Macroscopic Equation for Ions Moving in Gas

In contrast to transport phenomena in a neutral gas, when the distribution function of atomic particles varies weakly under external fields, the distribution function of charged particles of a weakly ionized gas can vary strongly under the action of external fields. In this case the Maxwell distribution of neutral particles (atoms or molecules) of a gas varies weakly, i.e. the gas conserves the stability of the system. Below we obtain the relation for the ion distribution function when ions are found in a gas in an external electric field.

Let us consider a weakly ionized gas in an external electric field of strength $\mathbf{E}$, so that the kinetic equation for the ion distribution function $f(\mathbf{v})$ over velocities $\mathbf{v}$ has the form

$$\frac{e\mathbf{E}}{m_i} \frac{\partial f(\mathbf{v})}{\partial \mathbf{v}} = I_{ia}(f) \quad (17.7)$$

where $I_{ia}(f)$ is the ion-atom collision integral. Note that in contrast to the criterion (13.24) for electrons, one can neglect ion-ion collisions in comparison with ion-atom ones if $N_i \ll N$ (N_i and N are the ion and atom number densities respectively), i.e. for a weakly ionized gas. This difference with the electron case is due to the differences in their masses.

The ion-atom collision integral is given by formula (12.8) and has the form:

$$I_{ia}(f) = \int (f' \varphi' - f \varphi) |\mathbf{v} - \mathbf{v}_a| d\sigma d\mathbf{v}_a \quad (17.8)$$

Here $f(\mathbf{v})$ is the distribution function of ions, $\varphi(\mathbf{v}_a)$ is the Maxwell distribution function of atoms, $d\sigma$ is the differential cross section of elastic ion-atom collisions, the superscript $'$ characterizes the parameters of atomic particles after scattering. In principle, equation (17.7) with the collision integral (17.8) allows us to determine the ion distribution function. We transform it into a relation which is convenient for the analysis of ion transport.

Let us multiply equation (17.7) by $m\mathbf{v}$ and integrate over $d\mathbf{v}$. We denote by $\mathbf{v}$ and $\mathbf{v}_a$ the initial velocity of the ion and atom correspondingly, m_i and m_a are their masses, and N_i and N_a are their number densities. The resultant equation has the form:

$$e\mathbf{E}N_i = \int m(\mathbf{v}' - \mathbf{v})g d\sigma f(\mathbf{v})\varphi(\mathbf{v}_a)d\mathbf{v}d\mathbf{v}_a \quad (17.9)$$

where $g = |\mathbf{v} - \mathbf{v}_a|$ is the relative velocity of colliding particles, which is conserved as a result of the collision. We use the principle of detailed balance which means the invariance of evolution of the system at time reversal and yields in this case

$$\int \mathbf{v}f'\varphi'd\sigma d\mathbf{v}d\mathbf{v}_a = \int \mathbf{v}'f\varphi d\sigma d\mathbf{v}d\mathbf{v}_a$$

We account for the invariance of the value $d\sigma d\mathbf{v}_1 d\mathbf{v}_2$ with respect to time reversal $t \rightarrow -t$. Equation (17.9) is the balance equation for the force per unit volume, so that the left-hand side of this equation is the specific force acting from the electric field on the ions, and the right-hand side is the friction force which results from the collisions of ions with atoms.

Let us express the ion velocity $\mathbf{v}$ in formula (17.9) through the relative ion-atom velocity $\mathbf{g}$ and the center of mass velocity $\mathbf{V}$ by means of the formula

$$\mathbf{v} = \mathbf{g} + \frac{m_a}{m_i + m_a}\mathbf{V}$$

This gives $m_i(\mathbf{v} - \mathbf{v}') = \mu(\mathbf{g} - \mathbf{g}')$. Write the relative velocity after collision in the form $\mathbf{g}' = \mathbf{g}\cos\vartheta + \mathbf{k}g\sin\vartheta$, where ϑ is the scattering angle, $\mathbf{k}$ is a unit vector directed perpendicular to $\mathbf{g}$. Because of the random distribution of $\mathbf{k}$ in the plane perpendicular to $\mathbf{g}$, the integration over scattering angles gives $\int(\mathbf{g} - \mathbf{g}')d\sigma = \mathbf{g}\sigma^*(g)$, where $\sigma^*(g) = \int(1 - \cos\vartheta)d\sigma$ is the diffusion cross section of ion-atom scattering. Thus equation (17.9) takes the form

$$e\mathbf{E}N_i = \int \mu\mathbf{g}g\sigma^*(g)f(\mathbf{v})\varphi(v_a)d\mathbf{v}d\mathbf{v}_a \quad (17.10)$$

This integral relation for the distribution function $f(\mathbf{v})$ can be a basis for the analysis of the ion behavior in a gas in an external electric field. In particular, in the case of the polarization interaction between the ion and the atom, the diffusion cross section is close to the cross section of polarization capture (11.12) and is inversely proportional to the relative velocity g of collision. Since

$$\int \mathbf{g}f_1f_2d\mathbf{v}_1d\mathbf{v}_2 = (\mathbf{w}_i - \mathbf{w}_a)N_iN_a = \mathbf{w}_iN_iN_a$$

where $\mathbf{w}_i$ is the average ion velocity and $\mathbf{w}_a = 0$ is the average atom velocity, we obtain in this case from equation (13.10)

$$\mathbf{w}_i = \frac{e\mathbf{E}}{\mu N_a k_c} \quad (17.11)$$

where $k_c = 2\pi\sqrt{\alpha e^2/\mu}$ is the rate constant of the polarization capture process, and α is the atom polarizability. Note that this formula is valid at any electric field strengths including large ones when the distribution function of ions differs strongly from the Maxwell one.

17.4 Mobility of Ions

The *mobility of a charged particle* K is defined as the ratio of its drift velocity w to the electric field strength E

$$K = \frac{w}{E} \quad (17.12)$$

and differs from the definition of the mobility of a neutral particle b [formula (14.14)] which is the ratio of the drift velocity to the force acting on a particle from an external field. As can be seen, for electrons and singly charged ions

$$b = \frac{K}{e} \quad (17.13)$$

Correspondingly, the *Einstein relation* (14.15) has the following form for ions:

$$K = \frac{eD}{T} \quad (17.14)$$

where D is the diffusion coefficient of the ion. Using the estimate (14.7) for the particle diffusion coefficient, we obtain the following estimate of the mobility of ions:

$$K \sim \frac{e}{N\sigma\sqrt{\mu T}} \quad (17.15)$$

where μ is the reduced mass of ions and gaseous particles, σ is the cross section of their elastic collision.

17.5 Mobility of Ions in Foreign Gas

Formula (17.15) allows us to estimate the mobility of ions. If ions and gas atoms are of the other type, ion–atom scattering is determined mainly by the polarization interaction between them, and the cross section of their scattering is close to that of polarization capture (formula (11.12)). Then on the basis of formulae (17.11) and (17.12) we obtain for the mobility of ions

$$K = \frac{1}{2\pi N\sqrt{\alpha\mu}} \quad (17.16)$$

where α is the atom polarizability, N is the number density of atoms. Note that elastic scattering in ion–atom collisions increases the effective cross section of ion–atom scattering by 10% compared to the capture cross section. Hence the precise mobility at the polarization ion–atom interaction is about 10% less than that given by formula (17.16).

The ion drift velocity is proportional to the electric field strength E at small E , as given by formula (17.12). If the ion and atom masses are of the same order of magnitude, the criterion that the electric field strength is relatively small takes the following form:

$$eE\lambda \ll T \quad (17.17)$$

where λ is the *mean free path* of ions, and according to this criterion the energy that an ion takes from the electric field during the time between subsequent collisions is small compared with the thermal energy. From the other standpoint, the ion drift velocity is small compared with the typical thermal ion velocity in this case.

17.6 The Chapman–Enskog Method

If the criterion (17.17) is valid, the ion distribution function is close to the Maxwell one. Hence it can be written in the form:

$$f(\mathbf{v}) = \varphi(v) [1 + v_x \psi(v)] \quad (17.18)$$

where $\varphi(v)$ is the Maxwell distribution function of the ion, the electric field is in the direction of the x -axis, and the function $\psi(v)$ can be determined by means of solution of the ion kinetic equation. The general method of evaluation of kinetic coefficients is based on the expansion of the distribution function similar to (17.18). Substitution of this expression in the kinetic equation leads to the integro-differential equation for $\psi(v)$. By representing $\psi(v)$ in the form of the sum of some polynomials of v , one can obtain from this equation the set of equations for the coefficients of these polynomials. The numerical method of determination of these coefficients and the subsequent kinetic coefficients is called the *Chapman–Enskog method*. This numerical method converges well and is therefore used widely for the analysis of transport phenomena. This method is somewhat cumbersome, but it is simplified in the case of ion mobility in a gas because of the collision of different particles. Below we represent the Chapman–Enskog method for the mobility and diffusion of ions in a gas.

In the first approximation of this numerical method (here we restrict ourselves to this approximation) we assume the function ψ in formula (17.18) to be independent of the ion velocity. Then the value of this parameter can be determined on the basis of the integral relation (17.10) for the ion distribution function, and further formula (17.18) yields the ion drift velocity as

$$w = \langle v_x \rangle = \frac{\psi \langle v^2 \rangle}{3} = \psi \frac{T}{m_i}$$

where m_i is the ion mass. In this approximation one can find ψ from the relation (17.10), and then we obtain for the ion mobility

$$K_1 = \frac{3e\sqrt{\pi}}{8N\bar{\sigma}\sqrt{2T}\mu} \quad (17.19)$$

where μ is the reduced ion–atom mass, and the mean cross section $\bar{\sigma}$ corresponds to averaging of the diffusion cross section $\sigma^*(v)$ of ion–atom scattering over the Maxwell distribution function of ions and has the form

$$\bar{\sigma}(T) = \int_0^\infty \sigma^*(x) e^{-x} x^2 dx, \quad x = \frac{\mu g^2}{2T} \quad (17.20)$$

and g is the relative velocity of the ion–atom collision.

The Chapman–Enskog approximation is a general method of calculation of the kinetic coefficients which is based on the expansion over a small numerical parameter for the correction to the Maxwell distribution function of particles if this correction is induced by gradients or fields in an equilibrium gas and is approximated by suitable polynomials. On the basis of the Einstein relation (17.14), one can find the diffusion coefficient of ions from this formula for the ion mobility. In the limiting case $e \rightarrow 0$ we obtain also the diffusion coefficient of

neutral atomic particles due to their elastic collisions. Thus in the first Chapman–Enskog approximation we have for the diffusion coefficient both neutral and charged atomic particles:

$$D_1 = \frac{3\sqrt{\pi T}}{8N\bar{\sigma}\sqrt{2\mu}} \quad (17.21)$$

where the average cross section $\bar{\sigma}$ is given by formula (17.20).

17.7 Mobility of Ions in the Parent Gas

If atomic ions move in their own gas, their mobility can be determined by the resonant charge exchange process (11.21) which proceeds according to the scheme:



The character of ion motion in this case is demonstrated in Figure 17.1 and is known as the *Sena effect*. Then the ion scattering results in charge transfer from one atomic core to the other, and hence the charge exchange cross section characterizes the ion mobility in this case. Indeed, as is seen in the center of mass frame of reference, this process leads to effective ion scattering by the angle $\vartheta = \pi$. Correspondingly, the diffusion cross section in this case is equal to

$$\sigma^* = \int (1 - \cos \vartheta) d\sigma = 2\sigma_{\text{res}} \quad (17.23)$$

where σ_{res} is the cross section of the resonant charge exchange. Then assuming that the resonant transfer cross section σ_{res} does not depend on the collision velocity, we obtain from formula (17.19) at low electric field strengths

$$K_1 = \frac{3e\sqrt{\pi}}{16N\sigma_{\text{res}}\sqrt{Tm}} \quad (17.24)$$

where m is the ion and atom mass.

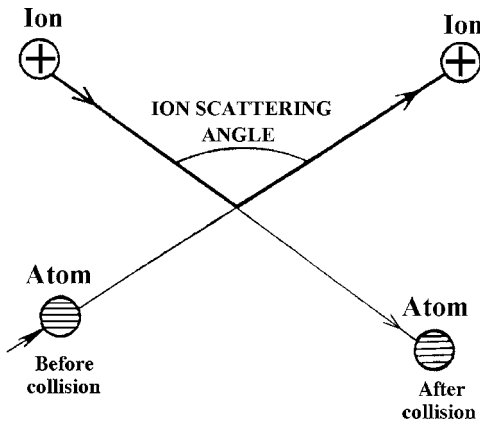


Figure 17.1. The relay character of ion scattering as a result of the charge exchange process (the Sena effect).

According to formula (11.28), the cross section of resonant charge exchange depends weakly on the collision energy, while the cross section of ion–atom elastic scattering varies in inverse proportional to the collision velocity according to formula (11.12). Hence the greater the collision energy, the lower the contribution of elastic ion–atom scattering to the diffusion cross section (17.23). This contribution is the ratio of the diffusion elastic cross section to the charge exchange one. Table 17.1 gives the contribution η of elastic scattering of particles into the mobility of slow ions in the parent gases at room temperature. The value η is the relative decrease of the ion mobility in a parent gas due to elastic ion–atom scattering. In addition, Appendix B7 contains the mobilities and diffusion coefficients for some atomic ions in the parent atomic gases or vapors at the normal atom number density $N = 2.69 \cdot 10^{19} \text{ cm}^{-3}$.

Table 17.1. Decrease η of the ion mobility in the parent gas due to ion–atom elastic scattering for ions in the parent gas at room temperature, and the temperature T_* at which ion–atom elastic scattering decreases the ion mobility in the parent gases by a factor of 1.5.

	He	Ne	Ar	Kr	Xe	Li	Na	K	Rb	Cs
$\eta, \%$	5.8	7.8	11	6.0	9.2	12	8.2	8.9	7.7	7.5
T_*, K	14	19	31	30	27	34	29	27	25	24

The above analysis relates to low electric field strengths E which satisfy the criterion (17.17), and the mean free path in this criterion is $\lambda = (N\sigma_{\text{res}})^{-1}$, where N is the number density of atoms, and σ_{res} is the cross section of the resonant charge exchange process. The left-hand side of the criterion (17.17) is the typical energy obtained by an ion between two subsequent collisions with gaseous atoms, so that the ion drift velocity in the case (17.17) is small compared with the thermal ion velocity. Now we consider the opposite case of large electric fields:

$$eE\lambda \gg T \quad (17.25)$$

when the ion drift velocity exceeds remarkably a thermal velocity of ions and atoms. In this case, because of the weak elastic scattering, the ion velocities in the field direction are greater than those in the other directions. Then we use the character of ion motion in its own gas in a strong electric field such that under the action of an external electric field a test ion accelerates and then stops as a result of the charge exchange process. Further, this process repeats.

The probability $P(t)$ that the ion does not take part in the charge exchange act during time t after the last exchange event satisfies the following equation:

$$\frac{dP}{dt} = -\nu P \quad (17.26)$$

where $\nu = Nv_x\sigma_{\text{res}}$. The solution of this equation is $P(t) = \exp(-\int_0^t \nu dt)$. The motion equation for the ion

$$\frac{mdv_x}{dt} = eE$$

connects the ion velocity component in the field direction v_x with the time t after the last collision

$$v_x = \frac{eEt}{m}$$

so that $P(t)$ is the distribution function of ions on velocities. Assuming the cross section of the resonant charge exchange process σ_{res} to be independent of the collision velocity, we have for the distribution function

$$f(v_x) = C \exp\left(-\frac{mv_x^2}{2eE\lambda}\right), \quad v_x > 0 \quad (17.27)$$

where C is the normalization factor, and the mean free path is equal to $\lambda = 1/(N\sigma_{\text{res}})$. This gives for the ion drift velocity and mean ion energy:

$$w = \langle v_x \rangle = \sqrt{\frac{2eE\lambda}{\pi m}}, \quad \bar{\varepsilon} = \left\langle \frac{mv_x^2}{2} \right\rangle = \frac{eE\lambda}{2} \quad (17.28)$$

As can be seen, in this case the ion drift velocity exceeds remarkably its thermal velocity, and the average ion energy is large compared with its thermal energy T . In addition, if the ion mobility is defined by formula (17.12), it depends on the electric field strength as $E^{-1/2}$.

17.8 Mobility of Ions in Condensed Atomic Systems

If ions are located in a dense or condensed atomic system, their motion is hampered by neighboring atoms, since the mean free path does not exceed the distance between nearest neighbors. Then the displacement of a foreign ion is characterized by a high activation energy, as well as the atom transition in a neighboring position, and the mobility of a foreign ion in a condensed system is small at relatively low temperatures and fields. Another mechanism of transition relates to a parent ion formed by the ionization of an atom of a condensed system, so that the hole moves in a similar way to the resonant charge exchange process, i.e. a bound electron of a neighboring atom transfers in the ion field, and an atom is transformed into a ion. Then formula (17.24), accounting for the activation character of the transition process, gives for the hole mobility

$$K = \frac{3\sqrt{\pi}ea}{8\sqrt{Tm_*}} \exp\left(-\frac{E_a}{T}\right) \quad (17.29)$$

where we change the mean free path $\lambda = 1/(2N\sigma_{\text{res}})$ in formula (17.24) by the distance a between nearest neighbors, m_* is the hole effective mass, and E_a is the *activation energy* of this process. The reason of the barrier character of hole displacement results from the attraction of neighboring atoms to the ion, so that the atomic configuration near the ion differs from the configuration of neutral atoms in this condensed system.

There are two mechanisms for the displacement of an ion in a liquid. In the first case this is determined by an electron transition between two centers, while in the second case a test ion

moves between these two positions. The mobility for the first mechanism is given by formula (17.29), and in the second case the ion diffusion coefficient in a condensed system due to ion displacement is estimated by

$$D = D_o \exp\left(-\frac{E_a}{T}\right), \quad D_o \approx \frac{\overline{v^2}}{3\nu} \approx \frac{\overline{v}a}{3} \quad (17.30)$$

where an average is taken over ion velocities, $\overline{v} = \sqrt{8T/(\pi M)}$ is the average ion velocity and M is the ion mass.

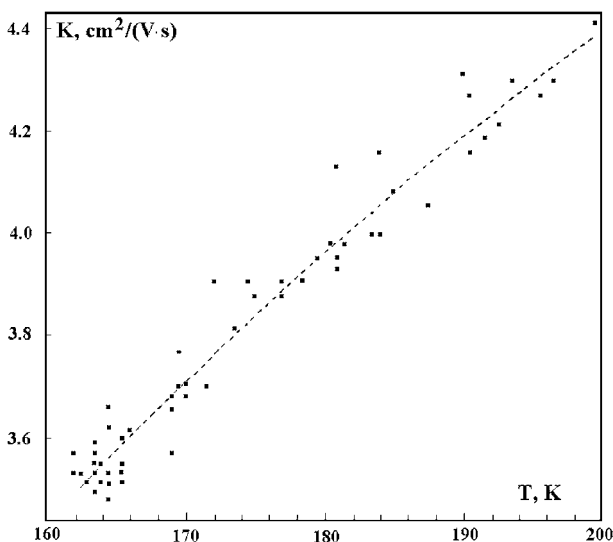


Figure 17.2. The mobility of a positively charged hole in a liquid xenon as a temperature function (O. Hilt, W.F. Schmidt. *Chem. Phys.* 183, 147, 1994).

Figure 17.2 exhibits the hole drift velocity in liquid xenon in weak fields and as a function of temperature. The ion diffusion coefficient D is expressed through its mobility K by the Einstein relation (17.14), which gives

$$D = \frac{KT}{e}$$

and according to the data of Figure 17.2, the ion diffusion coefficient ranges between $3.7 \cdot 10^{-5} \text{ cm}^2/\text{s}$ and $4.4 \cdot 10^{-5} \text{ cm}^2/\text{s}$, if the temperature ranges from 160 K up to 200 K. This corresponds to the activation energy $E_a = 22 \text{ meV}$ in formula (17.29), which is approximately the binding energy per bond for condensed xenon and is less than that for atom transition. Note that because the density of liquid xenon varies during its heating, the above activation energy cannot have the physical sense.

17.9 Diffusion of Small Particles in Gas or Liquid

Formula (17.21) gives the diffusion coefficient for atomic or bulk particles in a gas if the mean free path of gaseous atoms λ is large compared with their size. If a small particle is modeled by a hard sphere, this formula takes the form

$$D = \frac{3\sqrt{T}}{8\sqrt{2\pi m}Nr^2}, \quad \lambda \gg r \quad (17.31)$$

where r is the particle radius. It is clear that this formula is valid if the particle radius is large compared with the radius of action of atomic forces. In particular, if we describe a large cluster or small particle within the framework of the *liquid drop model* (see Chapter 11) and take the cross section of atom scattering on this drop to be equal to its cross section, we have $r = r_W n^{1/3}$, where n is the number of cluster atoms, and r_W is the Wigner–Seitz radius for the liquid of this drop. Then we obtain for the diffusion coefficient D_n of a cluster consisting of n atoms in a buffer gas

$$D_n = \frac{D_o}{n^{2/3}}, \quad \lambda \gg r \quad (17.32a)$$

where according to formula (17.31) in the Chapman–Enskog approximation we have

$$D_o = \frac{3}{8\sqrt{2\pi}r_W^2 N} \sqrt{\frac{T}{m}} \quad (17.32b)$$

Let us consider the other limiting case when a particle radius r significantly exceeds the mean free path of gaseous atoms. The resistance force occurs in this case because a gas stream flows around the particle, so that the relative velocity of atoms of a gas and a particle is zero on the particle surface and is equal to $\mathbf{v}$ far from the particle. Hence, in an intermediate space region near the particle the gas velocity varies from zero to the gas stream velocity. Displacement of gaseous atoms in this region leads to transport of the momentum and creates a friction force. Because this process is connected with the gas viscosity, the friction force is expressed through the gas viscosity coefficient.

According to its definition, the viscosity force F per unit surface is determined by the formula:

$$\frac{F}{S} = \eta \frac{\partial v_\tau}{\partial R}$$

where S is the area of the friction surface, v_τ is the tangential component of the velocity with respect to the stream and R characterizes a typical size of interaction in the normal direction to this stream. From this one can estimate the value of the friction force. Because $S \sim r^2$, $R \sim r$, and $v_\tau \sim v$, the particle velocity, we have an estimate

$$F \sim \eta r v$$

The numerical coefficient which follows from the *Stokes formula* for the friction force, resulting from an accurate solution of this problem, yields for a spherical particle:

$$F = 6\pi\eta r v, \quad \lambda \ll r \quad (17.33)$$

This gives for the particle mobility:

$$K = \mathbf{v}/\mathbf{E} = \frac{e}{6\pi r\eta} \quad (17.34)$$

On the basis of the Einstein relation (17.14), we have from this for the diffusion coefficient of the particle

$$D = \frac{KT}{e} = \frac{T}{6\pi r\eta}, \quad \lambda \ll r \quad (17.35)$$

Note that according to formula (17.34) the diffusion coefficient of a particle does not depend on its material. The only parameter of the particle in the above expression for the diffusion coefficient is its radius.

Let us join formulae (17.32) with formula (17.35) for the other limiting case $\lambda \gg r$. Let us express the viscosity coefficient of a gas through the mean free path of gaseous atoms within the framework of the *hard sphere model* (Chapter 11) based on the assumption that the mean free path does not depend on the atom velocity. Then we get for the particle diffusion coefficient in the gas:

$$D = \frac{T}{6\pi r\eta}(1 + aKn) \quad (17.36)$$

where $a = 3.1$ is the numerical coefficient and $Kn = \lambda/r$ is the *Knudsen number*. In particular, for air at atmospheric pressure and room temperature this formula can be rewritten in the form:

$$D = \frac{D_o}{r} \left(1 + \frac{0.14}{r} \right) \quad (17.37)$$

where $D_o = 1.3 \cdot 10^{-7} \text{ cm}^2/\text{s}$ and the particle radius r is expressed in microns.

17.10 Cluster Instability

Let us use the above results for the analysis of transport processes and distributions in a nonuniform buffer gas with a nucleating admixture. This can be realized in a high-pressure plasma arc. If an atomic metallic vapor is an admixture to a dense buffer gas, this admixture is located in a hot region of the gas discharge in the form of free atoms, while in a cold plasma region clusters are formed. Atoms move from a hot region to a cold one by means of diffusion in a buffer gas and attach there to clusters, whereas one can neglect the diffusion of large clusters because of a small diffusion coefficient. As a result, for a while all the admixture atoms are collected in a cold region of the discharge in the form of clusters. This phenomenon is called *cluster instability* and is observed in a high-pressure plasma arc. We consider below this phenomenon when a metal admixture is found in a hot buffer gas of a high density.

This instability has a threshold character; that is, the number density of metallic atoms must exceed a certain value. We assume the number density of metallic atoms in a cold region N to be equal to the saturated vapor number density N_{sat} , and $N_{\text{sat}} \sim \exp(-\varepsilon_o/T)$, where ε_o

is the atom binding energy. Then the temperature gradient in an arc plasma ∇T creates the gradient of the number density of metallic atoms

$$\nabla N = -\frac{\varepsilon_o}{T^2} N \nabla T \quad (17.38)$$

and this in turn creates the atomic flux from a hot to a cold region

$$j = -D_m \nabla N = D_m N \frac{\varepsilon_o}{T^2} \nabla T \quad (17.39)$$

where D_m is the diffusion coefficient of metallic atoms in a buffer gas. The rate of atom attachment to clusters in a cold region is given by formula (11.15) $k_n = k_o n^{2/3}$. From this we find the depth l of penetration of free atoms in a cold region

$$l = \frac{j}{k_o n^{2/3} N_{cl} N} = \frac{D_m}{k_o N_b} \frac{\varepsilon_o}{T} \frac{\nabla T}{T} n^{1/3} \quad (17.40)$$

Here N_{cl} is the number density of clusters, $N_b = n N_{cl}$ is the total number density of bound atoms in clusters, and n is the average number of cluster atoms. The criterion of the cluster instability is

$$l \ll r_o$$

where r_o is the discharge tube radius. Thus, the cluster instability results from the transport processes of metallic atoms in a buffer gas of a gas discharge, and this instability is realized at a density of metallic atoms that is not too low. It is of importance that the regime under consideration satisfies the criterion

$$N_b \gg N \quad (17.41)$$

where N_b is the number density of bound metallic atoms. This criterion means that most of the metallic atoms are bonded in clusters; that is, the number density of free atoms is small compared to the number density of bound atoms. This condition corresponds to intense nucleation processes in a plasma and provides a collection of metallic atoms in a narrow region of the plasma at the end of the process.

For a numerical estimate we consider argon as a buffer gas at pressure of 1 atm and $T = 3700$ K and tungsten as an admixture. This temperature slightly exceeds the tungsten melting point, and the diffusion coefficient of tungsten atoms in argon under these conditions is $D_m \sim 10$ cm²/s. We take the total number density of bound atoms in a cold region to be $N_b \sim 1 \cdot 10^{16}$ cm⁻³. Note that the number density of free tungsten atoms at this temperature and saturated vapor pressure is $6 \cdot 10^{13}$ cm⁻³, and the equilibrium number density of free tungsten atoms near clusters of an average size $n = 10^3$ is equal to $1 \cdot 10^{14}$ cm⁻³. For this cluster size and laboratory values of the temperature gradient $\nabla T/T \sim 1$ cm⁻¹ we obtain in this case the penetration length $l \sim 0.005$ cm, which is small compared to a typical plasma size.

This transport process, due to the transport of free atoms which are found in equilibrium with clusters, leads to the redistribution of clusters in a space. If the clusters occupy a region

of size Δx , where the formation of clusters is thermodynamically profitable, a remarkable transport of atoms in this region proceeds during a typical time τ , which is estimated by

$$\tau \sim \frac{N_b}{N} \cdot \frac{\Delta x^2}{D_m} \cdot \frac{T}{\varepsilon_o} \cdot \frac{T}{\Delta T} \quad (17.42)$$

where $\Delta T = T_2 - T_1$, so that $\nabla T \approx \Delta T / \Delta x$. Taking $\Delta x \sim 1$ cm for the above example, we find under the above conditions $\tau \sim 1$ s. Thus, for this regime of transport processes, when most of the atoms have become bonded over a period of time and are collected in a cold plasma region, we require that, on the one hand, the saturated vapor pressure at a given temperature is relatively small, so that the criterion (17.41) is fulfilled, and, on the other hand, that compounds of metallic atoms with atoms of other admixtures are not formed at these temperatures.

Part V

Structures of Complex Atomic Systems

18 Peculiarities of Cluster Structures

18.1 Clusters of Close-packed Structure with a Short-range Interaction Between Atoms

By definition, only nearest neighbors interact in clusters with a *short-range interaction* between atoms. At low temperatures a region of location of an individual nucleus may be changed by a point, and for the face-centered cubic (fcc) cluster structure the optimal distance between nearest neighbors a coincides with the equilibrium distance R_e between atoms of the diatomic molecule. The total binding energy of cluster atoms is proportional to the number Q of bonds between nearest neighbors

$$E = QD \quad (18.1)$$

where D is the binding energy per bond.

In the limit of a large number n of cluster atoms, the binding energy of atoms tends to $6nD$ [see formula (7.28)], because each internal atom has 12 nearest neighbors, and each bond relates to two atoms. We introduce the *surface cluster energy* E_{sur} by the relation

$$E = 6nD - E_{\text{sur}} \quad (18.2)$$

Since the surface energy is proportional to the area of the cluster surface, which is proportional to $n^{2/3}$ at large n , it is convenient to introduce the *specific surface energy* A by the formula

$$E_{\text{sur}} = An^{2/3} \quad (18.3)$$

From formulae (18.2) and (18.3) we have

$$A = 6Dn^{1/3} - E/n^{2/3} \quad (18.4)$$

Because $E(n)$ is a stepwise function, the value $A(n)$ is a nonmonotonic function of the number of cluster atoms in the course of filling the cluster shells or layers. The specific surface energy A of a cluster is a characteristic of the cluster structure. The lower this value, the greater the specific binding energy of cluster atoms.

We now construct a fcc solid cluster using the cluster symmetry (3.16) and (4.31) and taking the frame of reference such that the positions of internal cluster atoms are transformed into each other. Then if the coordinates of a test atom are xyz , the coordinates of its nearest neighbors are

$$x, y \pm a/\sqrt{2}, z \pm a/\sqrt{2}; x \pm a/\sqrt{2}, y, z \pm a/\sqrt{2}; x \pm a/\sqrt{2}, y \pm a/\sqrt{2}, z \quad (18.5)$$

where a is the distance between nearest neighbors. It is convenient to introduce the reduced values for atomic coordinates, expressing them in units $a/\sqrt{2}$. Then the coordinates xyz of

each atom are whole numbers. In reduced units the 12 nearest neighbors of a test atom of coordinates xyz have the following coordinates

$$x \pm 1, y \pm 1, z; \quad x \pm 1, y, z \pm 1; \quad x, y \pm 1, z \pm 1 \quad (18.6)$$

We denote a cluster shell by the reduced coordinates of one atom of this shell for which $x \geq y \geq z$ and assemble a solid cluster of the fcc structure from individual atoms, adding a new atom such that it forms the maximum number of bonds with cluster atoms. One can see that the energetically profitable method of *cluster assembling* results from the addition of blocks that are layers or elements of plane facets. *Magic numbers* of clusters correspond to the filling of an individual block. Tables 18.1 and 18.2 give the sequence of filling of cluster layers in these cases and parameters of forming clusters. Figure 18.1 contains the specific surface energy A versus the number of cluster atoms n for optimal cluster configurations.

Note that the scheme of cluster assembling used assumes the cluster to have almost spherical shape in the course of the addition of new atoms. The two schemes for assembling centered and non-centered clusters are different, and for a given number of atoms we choose a scheme which leads to the maximum number of bonds between atoms. Because the cluster energy increases in a stepwise way, any cluster parameters are non-monotonic functions of the number of atoms. This is an important peculiarity of solid clusters. As a demonstration of this fact, Figure 18.1 gives the specific energy of solid clusters of the fcc structure, and points on this figure relate to magic numbers when the corresponding cluster layers are filled.

For the fcc structure of clusters the planes of directions $\{100\}$, $\{110\}$, $\{111\}$ are the symmetry planes. Therefore, if cluster facets have these directions, surface cluster atoms are located on planes, i.e. this cluster has plane boundaries. According to the fcc symmetry of (3.16) and (4.31), there are 6 planes of the direction $\{100\}$, 12 planes of the direction $\{110\}$, and 8 planes of the direction $\{111\}$. Hence, if a cluster forms a geometric figure with facets of directions $\{100\}$, $\{110\}$, $\{111\}$, the surface atoms are located on these facets. Note that a surface atom of a cluster of the fcc structure which is located on a plane of a direction

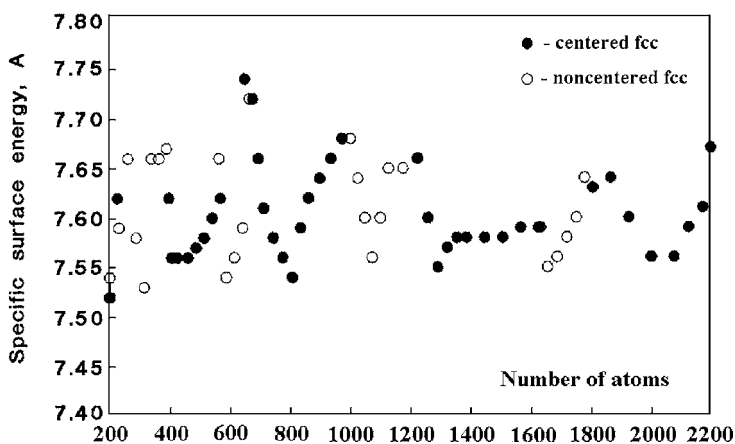


Figure 18.1. The specific surface energy for optimal atom configurations of fcc-clusters. Dark circles correspond to clusters with a central atom and open circles respect to non-centered clusters.

Table 18.1. The order of growth of fcc clusters with a central atom for a short-range interaction of atoms. The values in parentheses indicate the number of nearest neighbors for filling shells, and the *Miller indices* are given for the directions of filling layers.

Filling shells	n	E_{sur}	Filling block
011	2–13	—	—
002(4)	13–19	42–54	—
112(3-5)+022(5)	19–55	54–114	110
013(4)	55–79	114–138	100
222(3)+123(4-6)	79–135	138–210	111
035(5)+004(4)+114(5)+024(6)	135–201	210–258	100
233(3-5)+224(5)+134(5-6)	201–297	258–354	111
015(4-6)+125(5-6)	297–369	354–402	100
044(5)+035(6)	369–405	402–414	110
006(4)+116(5)+026(6)	405–459	414–450	100
334(3-5)+244(5)+235(5-6)+ +145(5-6)+226(5)+136(6)	459–675	450–594	111
055(5)+046(6)	675–711	594–606	110
017(4-6)+127(5-6)+037(6)	711–807	606–654	100
008(4)+118(5)+028(6)	807–861	654–690	100
444(3)+345(4-6)+255(5)+336(5)+ +246(6)+156(5-6)+237(5-6)+147(6)	861–1157	690–858	111
066(5)+057(6)+228(5)+138(6)+048(6)	1157–1289	858–894	110
019(4-6)+129(5-6)+039(6)	1289–1385	894–942	100
455(3-5)+446(5)+356(5-6)+347(5-6)+ 266(5)+257(6)+338(5)+248(6)+ 158(6)+167(5-6)+239(5-6)+149(6)	1385–1865	942–1158	111
077(5)+068(6)+059(6)	1865–1925	1158–1170	110

$\{111\}$ has 9 bonds with other atoms, a surface atom of a plane direction $\{100\}$ has 8 bonds, and a surface atom of a plane direction $\{110\}$ has 7 bonds. Hence the clusters of completed structures with facets of directions $\{111\}$ and $\{100\}$ are more profitable energetically.

Let us construct the *families of clusters* of a completed structure which have the shape of identical geometrical figures and differ in size. We will characterize the size of such figures by the number of layers m of such a figure. The numbers of cluster atoms n for some figures of clusters and their surface energy E_{sur} as a function of the number of figure layers are given in Table 18.3 for some shapes of fcc clusters which are given in Figure 18.2. The specific surface energy of a large cluster of this form $A(\infty)$ characterizes the cluster energetics, and smaller values of this parameter relate to the profitable cluster shape. As follows from the data of Table 18.3, the shape of a *truncated octahedron*, whose surface consists of 6 squares and 8 regular hexagons, is optimal for clusters of the fcc structure.

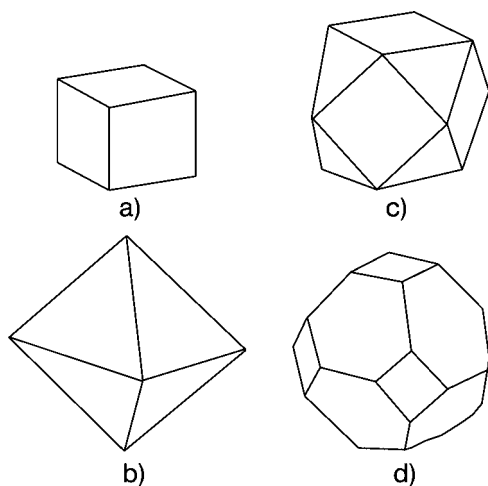


Figure 18.2. Regular fcc structures: (a) cube; (b) cuboctahedron; (c) octahedron; (d) regular truncated octahedron.

Table 18.2. The sequence of growth of fcc clusters without a central atom for a short-range interaction of atoms. The values in parentheses indicate the number of nearest neighbors for a filling shell, and the *Miller indices* are given for the directions of filling layers.

Filling shells	n	E_{sur}	Filling block
001	1–6	—	—
111(3)	6–14	24–48	111
012(3-6)	14–38	48–84	110
003(4)	38–44	84–96	100
122(3-5)+113(5)+023(5-6)	44–116	96–180	110
014(4-6)	116–140	180–204	100
223(3-5)+133(5)+124(5-6)+034(5-6)	140–260	204–312	111
005(4)+115(5)+025(6)	260–314	312–348	100
016(4-6)	314–338	348–372	100
333(3)+234(4-6)+225(5)+ +144(5)+135(6)+126(5-6)	338–538	372–516	111
045(5-6)+036(6)	538–586	516–528	110
007(4)+117(5)+027(6)	586–640	528–564	100
018(4-6)	640–664	564–588	100
344(3-5)+335(5)+245(5-6)+236(5-6)+ +155(5)+146(6)+227(5)+137(6)	664–952	588–756	111
056(5-6)+047(6)	952–1000	756–768	110
128(5-6)+038(6)	1000–1072	768–792	100
009(4)+119(5)+029(6)	1072–1126	792–828	100
445(3-5)+355(4-6)+346(5-6)+256(5-6)+337(5)+ +247(6)+238(5-6)+166(5)+157(6)+148(6)	1126–1510	828–1020	111
067(5-6)+058(6)+229(5)+139(6)+049(6)	1510–1654	1020–1056	110

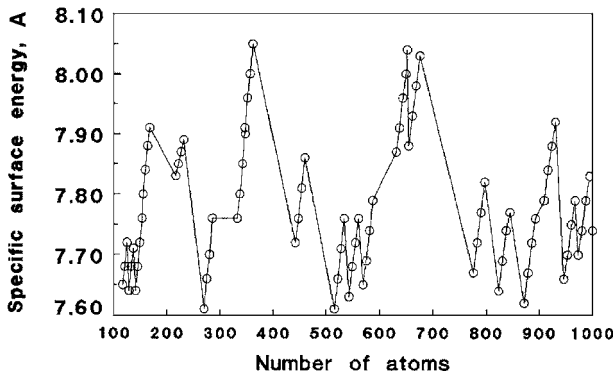


Figure 18.3. The specific surface energy for hexagonal clusters consisting of magic numbers of atoms.

Large clusters of the hexagonal structure cannot compete energetically with large fcc clusters because of their lower symmetry. In reality, the competition between the hexagonal and fcc cluster structures takes place at cluster sizes $n < 100$ when the icosahedral cluster structure is optimal. Hence the hexagonal structure is not important for clusters. We include in Table 18.3 the parameters of a cluster-hexahedron consisting of two hexagonal pyramids whose common base is a regular hexagon. These two pyramids are transformed into each other as a result of reflection with respect to the hexagon plane. In addition to this, Figure 18.3 gives the specific surface energy of hexagonal clusters depending on their size. Values of this figure relate to magic numbers of *hexagonal clusters* which have completed facets.

Table 18.3. Parameters of solid clusters having the shape of the corresponding geometric figure. Here m is a number of layers, n is the number of cluster atoms, E_{sur} is the cluster surface energy, and $A(\infty)$ is the specific surface energy of an infinite cluster.

Figure	n	E_{sur}	$A(\infty)$
Cube	$4m^3 + 6m^2 + 3m + 1$	$24m^2 + 18m + 6$	9.25
Cuboctahedron	$\frac{10}{3}m^3 + 5m^2 + \frac{11}{3}m + 1$	$18m^2 + 18m + 6$	8.07
Octahedron	$\frac{2}{3}m^3 + 2m^2 + \frac{7}{3}m + 1$	$6m^2 + 12m + 6$	7.86
Reg. trunc. oct.*	$16m^3 + 15m^2 + 6m + 1$	$48m^2 + 30m + 6$	7.56
Hexahedron	$4m^3 + 6m^2 + 4m - 7$	$21m^2 + 21m - 12$	8.33

*Regular truncated octahedron

18.2 Energetics of Icosahedral Clusters

In clusters of close-packed structures the distance between any nearest neighbors is identical, whereas there are two distances between nearest neighbors for clusters of the icosahedral structure (see Chapters 3 and 4). Below we consider clusters of the *icosahedral structure* with a short-range interaction between atoms when only nearest neighbors interact. The number of

atoms for the icosahedral cluster is the same as for the cuboctahedral cluster (Table 18.3), so that the number of atoms of the icosahedral cluster with m filled shells is equal to

$$n = \frac{10}{3}m^3 + 5m^2 + \frac{11}{3}m + 1 \quad (18.7)$$

We denote by R the distance between nearest neighbors of neighboring layers and by R_2 the distance between nearest neighbors of the same layer. Each surface atom of a completed icosahedral cluster placed at an icosahedron vertex has one bond of length R and five bonds of length R_2 , each edge atom has two bonds of length R and six bonds of length R_2 , and surface atoms inside triangles have three bonds of length R and six bonds of length R_2 . As a result of summation, we find that addition of the m th icosahedral layer increases the binding energy of the cluster atoms by the value

$$\begin{aligned} \Delta E &= p(\varepsilon_1 + 5\varepsilon_2/2) + q(m-1)(2\varepsilon_1 + 3\varepsilon_2) \\ &\quad + s(m-1)(m-2)(3\varepsilon_1 + 3\varepsilon_2)/2 \\ &= \varepsilon_1(30m^2 - 30m + 12) + \varepsilon_2 \cdot 30m^2 \end{aligned} \quad (18.8a)$$

Here $p = 12$, $q = 30$, $s = 20$ are the numbers of vertices, edges and triangles of the icosahedron correspondingly, $\varepsilon_1 = -U(R)$ and $\varepsilon_2 = -U(R_2)$ are the binding energies of two atoms for distances R and R_2 between them correspondingly, and $U(R)$ is the pair interaction potential of atoms at a distance R between them. We take into account that bonds of the length R_2 connect surface atoms, and such bonds are repeated twice as a result of the addition of a new layer. Thus the total binding energy of the atoms of the icosahedron is given by

$$E = 10m^3(\varepsilon_1 + \varepsilon_2) + 15m^2\varepsilon_2 + m(2\varepsilon_1 + 5\varepsilon_2) \quad (18.8b)$$

Let us transform this formula to the form

$$E = X\varepsilon_1 + Y\varepsilon_2 = -XU(R) - YU(R_2)$$

where X and Y are numbers of the bonds of the first and second type.

$$X = 10m^3 + 2m, \quad Y = 10m^3 + 15m^2 + 5m \quad (18.9)$$

Let us choose the optimal relation between the parameters R , R_2 and R_e , the equilibrium distance between atoms of the diatomic molecule. Optimization of this relation allows one to choose the mean distance between nearest neighbors that leads to the maximum binding energy of the cluster atoms. This operation is simplified because parameters R and R_2 are close to R_e , and formula (18.8b) can be written in the form

$$E = (X + Y)D - \frac{1}{2}U''(R_e) [X(R - R_e)^2 + Y(R_2 - R_e)^2] \quad (18.10)$$

where D is the well depth for the pair interaction potential. Note that the second term is zero if $R = R_2 = R_e$. Optimization of the atom binding energy (18.10) gives

$$X(R - R_e)\frac{\partial R}{\partial R_2} + Y(R_2 - R_e) = 0$$

Since $R = 0.951R_2$, this gives the following expressions for optimal distances:

$$R_2 = R_e \left(1 + \frac{0.047X}{0.904X + Y} \right), \quad R = R_e \left(1 - \frac{0.049Y}{0.904X + Y} \right) \quad (18.11)$$

The optimal binding energy of atoms in an icosahedral cluster is given by

$$E = (X + Y)D - 1.2 \cdot 10^{-3} \frac{XYR_e^2 U''(R_e)}{0.904X + Y} \quad (18.12)$$

Because these values R and R_2 are close, the second term of the total binding energy of formula (18.12) is small compared to the first term. For example, in the case of the truncated Lennard–Jones interaction potential ($U''(R_e) = 72D/R_e^2$), the second term is 2.3% of the first one for large clusters.

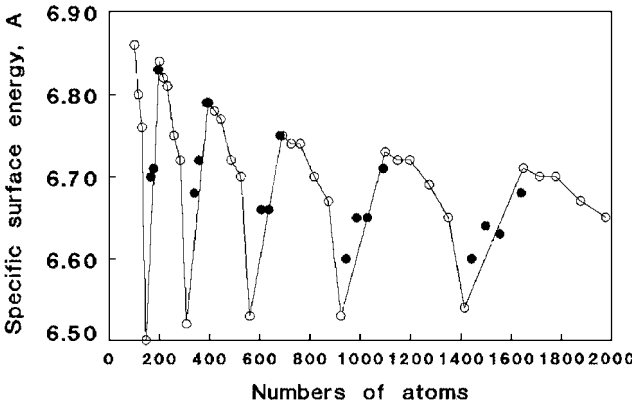


Figure 18.4. The specific surface energy of icosahedral clusters with filled facets.

If we construct the *family of clusters* of the icosahedral structure, so that the number of cluster atoms is given by formula (18.7), the total binding energy of atoms according to formula (18.12) is equal to

$$E = (20m^3 + 15m^2)D - (6.3m^3 + 7.5m^2)R_e^2 U''(R_e) \quad (18.13)$$

The asymptotic form for the binding energy of cluster atoms according to formula (7.24) has the form

$$E = \varepsilon_o n - An^{2/3} \quad (18.14)$$

Reducing this formula (18.13) to this form, we get the parameters of formula (18.14) for the completed icosahedral cluster

$$\varepsilon_o = 6D - 1.89 \cdot 10^{-3} R_e^2 U''(R_e), \quad A = 6.72D - 2.25 \cdot 10^{-3} R_e^2 U''(R_e) \quad (18.15)$$

In particular, for the truncated Lennard–Jones interaction potential ($U''(R_e) = 72D/R_e^2$) we obtain $\varepsilon_o = 5.864D$ and $A = 6.56D$. Note that for the fcc structure we have according

to formula (7.28) $\varepsilon_o = 6D$, and in the limit $n \rightarrow \infty$ the fcc structure of clusters is more preferable than the icosahedral one. The same operation can be done when the last layer of the icosahedral cluster is partially filled. Figure 18.4 shows the dependence on a number of cluster atoms for the specific surface energy of the icosahedral cluster with filling of some surface triangles in the case of the truncated Lennard–Jones interaction potential of atoms, when only nearest neighbors interact.

We now determine the density of the icosahedral structure, taking as a base the m th cluster of the icosahedron family, whose number of atoms is given by formula (18.7), and represent an icosahedron consisting of 20 regular triangular pyramids. The vertex of each pyramid is the icosahedron center, and their bases are surface icosahedron triangles. The volume of this icosahedron cluster is

$$V = 20 \frac{m^3}{6} \cdot \frac{R_2^2 \sqrt{3}}{4} \sqrt{R^2 - \frac{R_2^2}{3}} = 2.536 m^3 R^3 \quad (18.16)$$

In the limit $m \gg 1$ we have from formula (18.9) $X = Y$, i.e., $R = 0.975 R_e$. This gives a cluster density $1.417/R_e^3$, which exceeds the density of the close-packed structure $\sqrt{2}/R_e^3$ by 0.2%. Note that although the mean densities of icosahedral and close-packed structures are practically the same, the close-packed structure is characterized by the isotropic density, while the densities of the icosahedral structure in the radial and transverse directions differ by approximately 5%.

We note above that the maximum number of bonds for an atom located on the fcc surface is equal to 9 and relates to the $\{111\}$ surface. There are 8 such planes according to the symmetry (3.16) and (4.31) of this structure. Atoms located on the icosahedral surface have 9 nearest neighbors also. Thus, 20 surface triangles of the icosahedral cluster are distorted $\{111\}$ planes of the fcc structure.

18.3 Competition of Cluster Structures

In Chapter 3 we showed that the icosahedral structure is the optimal one for a cluster consisting of 13 atoms at zero temperature. In contrast to this, the fcc cluster structure is preferable for large clusters according to formulae (18.2) and (18.15). Hence the transition between optimal structures takes place for intermediate cluster sizes. Moreover, different structures may be mixed for some cluster sizes. For a bulk crystal of a close-packed structure, this phenomenon, which is known as *twinning*, corresponds to the alternation of layers of the fcc and hexagonal structures. Another type of mixing of structures which takes place in the course of filling of icosahedral cluster is given in Figure 18.5. When a low number of facets of a new layer is filled, there are two possibilities for filling of the facet (Figure 18.5), so that in the first case the icosahedral structure is realized, and in the second case it is the fcc structure. The icosahedral structure is more profitable when several facets are filled and they border; in the opposite case the fcc structure of the surface layer is realized.

We demonstrate below competition between the icosahedral and fcc cluster structures on the example of a cluster consisting of 923 atoms. Note that long-range interaction makes a small contribution to the difference of the cluster ground states of the icosahedral and fcc structures. Therefore we restrict ourselves to the short-range interaction of atoms and take

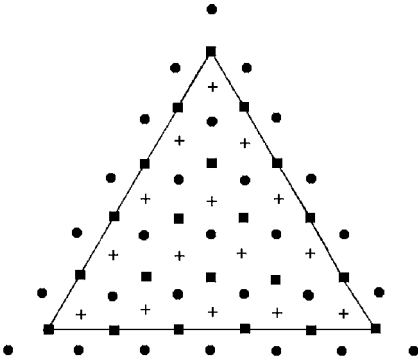


Figure 18.5. Projections of surface atoms of the icosahedral cluster on the plane of a surface triangles. Dark squares respect to positions of atoms of the filled layer and the solid lines join boundary atoms. Dark circles correspond to positions of atoms for the icosahedral structure of the filling layer, and crosses relate to their fcc-structure.

into account the interaction between nearest neighbors. The icosahedral cluster has completed layers for this number of atoms and relates to the icosahedron family with $m = 6$. According to formula (18.9), this cluster has 2172 bonds of length R , 2730 bonds of length R_2 , and the binding energy of atoms of this cluster according to formula (18.12) is equal to

$$E = 4902D - 1.52R_e^2U''(R_e) \quad (18.17)$$

The optimal configuration of the fcc cluster according to the Table 18.1 data can be constructed on the basis of a cluster of 861 atoms. It has the structure of a truncated octahedron and can be obtained from the octahedron of $m = 10$ (see Table 18.3) by cutting off 6 pyramids of the base $m = 2$ near each octahedron vertex. This cluster has 4476 bonds between nearest neighbors, and in order to construct the cluster of 923 atoms it is necessary to place 62 atoms on the surface of this cluster in the optimal way. When we fill one facet of this cluster (the left facet of Figure 18.6), the fcc cluster formed additionally obtains 46 atoms and 252 bonds. In constructing the cluster of 926 atoms, we partially fill another facet with a hexagon consisting of 19 atoms, and the addition of this hexagon increases the number of bonds by 99. Hence the binding energy of the cluster of 926 atoms is 4827. One can transform this cluster into a cluster of 923 atoms by the removal of one site of 3 atoms from one of hexagons. This operation leads to the loss of 17 bonds. If the filling hexagons are located on neighboring facets and border, additional bonds occur between atoms of different hexagons, as shown in Figure 18.6. As a result, we obtain the number of bonds as 4814 for the optimal configuration of atoms for the fcc cluster at zero temperature in comparison with 4902 bonds for the icosahedral structure.

From this one can find the condition for which the icosahedral structure of this cluster of 923 atoms is preferable, so that the binding energy of the icosahedral cluster in the ground state is higher than that of the fcc cluster of this size. This criterion has the form

$$U''(R_e) < \frac{58D}{R_e^2} \quad (18.18)$$

In particular, in the case of the truncated Lennard–Jones interaction potential of atoms, when $U''(R_e) = 72D/R_e^2$, the fcc structure is preferable.

We note the peculiarities of competition between the icosahedral and fcc structures of clusters with a pair interaction of atoms. The difference in the numbers of bonds between

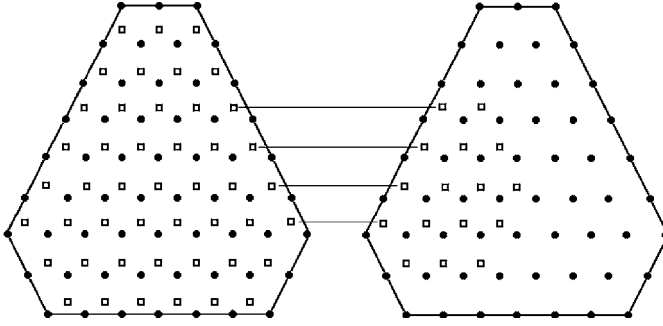


Figure 18.6. Positions of surface atoms for the fcc cluster consisting of 923 atoms. Surface atoms of the core of this cluster, i.e. the cluster of 861 atoms, are shown by dark circles, the positions of a filling on two hexagon facets of the core are drawn by open squares. Fine lines indicate bonds between atoms located on neighboring filling facet. The statistical weight of this state is $8 \cdot 2 \cdot 3 = 48$.

nearest neighbors for competing large clusters is relatively small, and the favorable cluster structure is sensitive to the form of the pair interaction potential of atoms. The competition takes place over a wide range of cluster sizes, and a shift by one of a number of cluster atoms in this range can lead to a change of the favorable structure. The long-range interaction of atoms is not important for this competition at zero temperature. Indeed, the densities of the icosahedral and fcc clusters are close, and hence the contributions of a long-range interaction of atoms to the energy of the icosahedral and fcc clusters are close. Therefore, the total binding energy of cluster atoms is determined mostly by the interaction of nearest neighbors and first non-nearest neighbors.

Alongside the energy of these clusters, their statistical weight g , which is the number of configuration states of this energy, is important. For the icosahedral cluster of 923 atoms we have $g = 1$. We evaluate below the statistical weights for the fcc cluster starting from the total number of states for a cluster resulting from the filling of two facets of the core cluster of 861 atoms by two hexagons. First we evaluate the total number of configuration states of this cluster, which in accordance with the above operation of cluster formation is equal to

$$g = 8 \cdot 7 \cdot (3 \cdot 10 + 3 \cdot 10 + 3 \cdot 13) = 5544 \quad (18.19)$$

The first two factors on the right-hand side of this relation account for the choice of filling facets from 8 facets of the core cluster of 861 atoms in a random way in order to construct the cluster of 926 atoms. Parentheses contain the number of ways of removing a hexagon site, which consists of 3 atoms, in order to transform the cluster of 926 atoms in a given cluster and to distribute the hexagons formed over the chosen facets. Indeed, one can remove a site of 3 atoms from the filling hexagon and move the regular hexagon of 19 atoms to an unfilled facet, and then we find $3 \cdot 10$ ways to do it. By analogy, one can remove one site of the regular hexagon of 19 atoms and place the hexagon of 16 atoms formed in different positions.

We now extract from these configurations of atoms such atom positions when additional bonds occur between the atoms of two facets. Evidently, the optimal atom configuration,

which is given in Figure 18.6, is characterized by the statistical weight

$$g_o = 8 \cdot 2 \cdot 3 = 48 \quad (18.20a)$$

Here 8 is the number ways of choosing a facet which is filled, 2 is the number of ways of choosing a partially filled facet which borders a filled one, and 4 is the number positions of the truncated hexagon of a partially filled facet if the atoms of this hexagon form bonds with atoms of the filled layer of a neighboring facet. In an analogous manner, we find the number of ways of locating a hexagon when atoms of different hexagons form 3, 2 or 1 bonds, and the statistical weights of these states g_1 , g_2 and g_3 are correspondingly equal to

$$g_1 = 8 \cdot 2 \cdot 22 = 354 \quad (18.20b)$$

$$g_2 = 8 \cdot 2 \cdot 10 = 160 \quad (18.20c)$$

and

$$g_3 = 0 \quad (18.20d)$$

From this we find the number of atom positions if atoms of neighboring facets do not form the bonds

$$g_4 = g - g_1 - g_2 - g_3$$

We have

$$g_4 = 4982 \quad (18.20e)$$

Of course, above we account for the portion of configurationally excited cluster states that correspond to the filling of two hexagon facets. Other states may be obtained by transition of one atom from the configuration of Figure 18.6 to a more favorable position. Starting from the optimal atom configuration given in Figure 18.6, we transfer a vertex atom of hexagons on the surface of any of 6 other facets, taking one which is not bonded with the atoms of another hexagon. This operation leads to the loss of 3 bonds, i.e. it corresponds to an excitation energy of $3D$, and gives the statistical weight g_3 of forming states

$$g_3 = 2 \cdot 9 \cdot 6 \cdot 88 + 2 \cdot 10 \cdot 6 \cdot 88 \approx 2 \cdot 10^4 \quad (18.21)$$

Here the first factor in each term is the number of positions of the right hexagon of Figure 18.6 for a given number of vertex atoms of hexagons (the second factor) if these vertex atoms have 6 bonds with nearest neighbors; the third term accounts for the number of free facets, and the last factor is the number of positions of a free facet on which a test atom is located in a hollow between three nearest neighbors. Because the number of vertex hexagon atoms with an excitation energy of $3D$ depends on the position of a small hexagon in Figure 18.6, we divide this sum into two parts. Although there are other atom configurations which lead to this excitation energy, the above value gives the main contribution to the statistical weight of excited states of the excitation energy $3D$.

In the same manner one can find the statistical weight of the lowest excitation state of the icosahedral cluster. The transition of a vertex atom on the cluster surface leads to the minimal excitation energy of $3D$, and the statistical weight of this state is equal to

$$g_3 = (20 \cdot 36 - 5) = 8640 \quad (18.22)$$

Here the first factor is the number of icosahedral vertices, 36 is the number of positions of a test atom on the surface of a surface triangle if an atom is located in a hollow between three surface atoms, 20 is the number of icosahedron surface triangles, and 5 is the number of atom positions on the cluster surface that border the initial position of a test atom. From the analysis of this example one can conclude that for clusters of a completed structure a gap occurs between the ground and first excited state, and this gap corresponds to the breaking of several bonds, whereas for a noncompleted cluster the excitation energy is the energy of breaking of one bond. Next, the statistical weight of lower configurationally excited states for clusters of a noncompleted structure is higher than that for completed clusters.

18.4 Configuration Excitation of Clusters

In considering clusters with a pair interaction of atoms where a short-range interaction of atoms dominates, we showed that at optimal configurations of atoms the distances between nearest neighbors of the cluster are close or equal to the equilibrium distance for the pair interaction potential of atoms. This is fulfilled both for the ground state of the cluster and for *configurationally excited states*. Cluster transitions involving lower excited cluster states occur between two stable configurations of atoms which correspond to local minima of the energy depending on an atom configuration. The local minima are separated by a barrier. Therefore the cluster potential energy in a multidimensional space of atom coordinates has many local minima separated by *saddle points*. This is an important property of clusters with a pair interaction of atoms, and we demonstrate this below with some examples.

We first consider the atom transition between two positions on the surface of the direction $\{111\}$. This surface is filled, and a test atom is located in a hollow between three surface atoms. If we restrict ourselves to short-range interactions between atoms, the binding energy of a test atom is $3D$, where D is the binding energy per bond. When a test atom passes between two neighboring local minima of energy, this transition is called the *edge-bridging transition*, and two bonds are conserved for a test atom with two nearest neighbors in the course of the atom transition. Hence the barrier height is $1D$ in this case. In the case of long-range interaction of atoms, the barrier height decreases. For example, the binding energy of a test atom located in a hollow between three atoms of the surface $\{111\}$ of the crystal with the Lennard–Jones interaction of atoms is $5.1D$, and the binding energy of this atom at the barrier is $4.2D$, so that the barrier height does not vary greatly.

We now consider one more example of cluster configuration excitation that relates to the transition of a vertex atom of the icosahedral cluster of 13 atoms to the cluster surface, as shown in Figure 18.7. At the beginning this cluster has the icosahedron form, and surface atoms then transfer to the cluster surface. The surface of the icosahedral cluster consists of 20 equilateral triangles if the centers of neighboring surface atoms are joined (see Figure 3.5). Evidently, the configuration of the lowest excitation of this cluster corresponds to the transition of some surface atoms in the middle of a surface triangle. One can evaluate the upper boundary

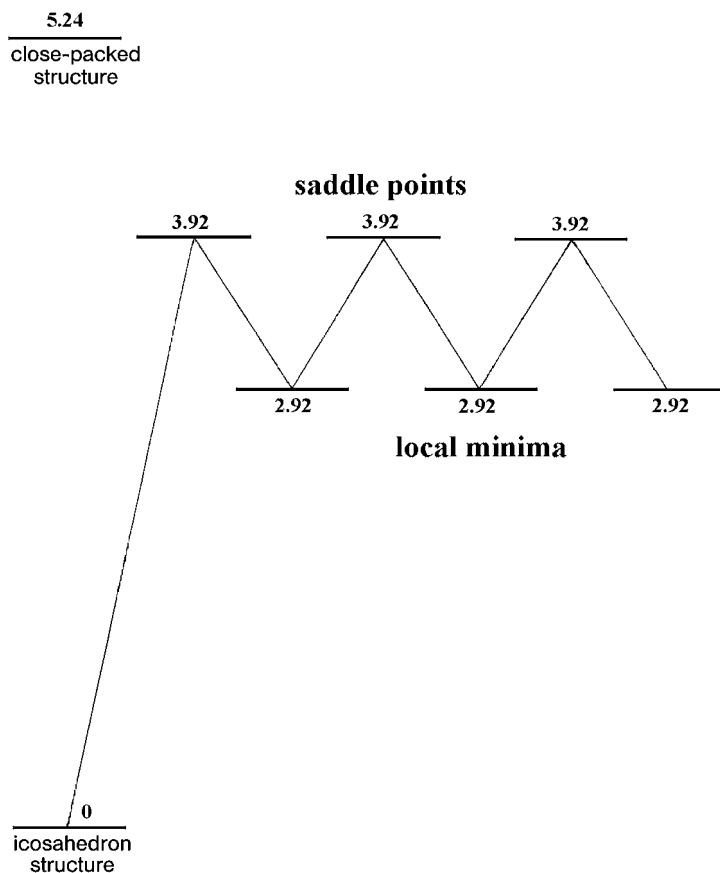


Figure 18.7. The lowest excited states of the cluster consisting of 13 atoms with the truncated Lennard–Jones interaction potential between atoms. The ways of transitions from the ground to excited states through saddle points.

for the excitation energy of this transition, calculating the change in the number of cluster bonds. Indeed, the surface atom has 6 nearest neighbors in the ground state, and the number of bonds is 3 if this atom is found over the middle of a surface triangle. From this it follows that the excitation energy for this configuration is about $3D$, where D is the binding energy per bond. Because the length of bonds between surface atoms differs from those between central and surface atoms for the icosahedral cluster, and since surface atoms are displaced after the removal of the surface atom, the energy of cluster excitation is less than $3D$, but this difference is small. Next, the energy of excitation under consideration is split over three levels depending on the position of the surface triangle over which an exciting atom is found after transition, with respect to the initial position of this atom. Indeed, atom transition is possible in the middle of 15 surface triangles, but due to the five-fold axis of symmetry for the icosahedral cluster, these positions correspond to three different energy levels.

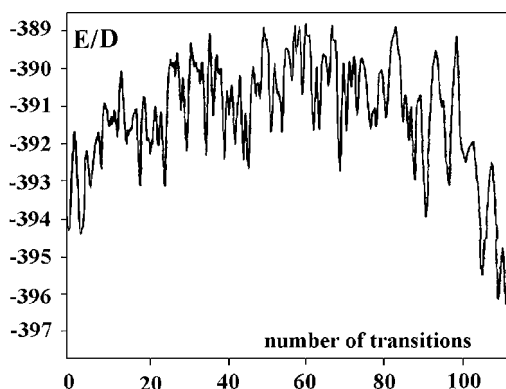


Figure 18.8. The shortest path for the transition between the second lowest electron energy minimum and global minimum for the cluster consisting of 75 atoms with the Lennard–Jones interaction potential (D.J. Wales et al. *Adv. Chem. Phys.* 115, 1 (2000)). This transition proceeds through 65 local minima of the electron energy landscape.

Although we are restricted by the lower excitations of the icosahedral cluster of 13 atoms, this nevertheless exhibits the general character of the behavior of the potential energy of clusters. Figure 18.7 shows the positions of the energy levels and saddle points for the icosahedral cluster with the truncated Lennard–Jones interaction potential between atoms when only nearest neighbors interact. If a surface atom of this icosahedral cluster moves over the cluster surface and finally occupies a position in the neighborhood of the atom which is opposite to this one initially, the transient atom overcomes three barriers to reach such a position. Thus, atoms transfer in clusters along the potential energy surface or the *potential energy landscape*, and this landscape includes many minima and saddle points. As an example, Figure 18.8 gives the optimal path for transition between the lowest and second minima of the potential energy for a cluster consisting of 75 atoms with the Lennard–Jones interaction potential between them. Transition between these minima is accompanied by the passage of the cluster through many local minima and saddle points of the electron energy landscape. These examples demonstrate the general character of transitions in clusters between states of configuration excitation, and these transitions result in the overcoming of barriers which are saddle points of the electron energy landscape. Atoms are locked between the barriers of these saddle points for a long time, and this explains the *short-order* character of atom behavior in bulk liquids.

Above we considered the configuration excitation of clusters at zero temperature. A temperature increase leads to a decrease in the excitation energies and barrier heights. Considering the total kinetic energy of cluster atoms at a given excitation energy, one can observe two groups of states at moderate excitation energies corresponding to the transition of a surface atom on the cluster surface and without this transition. These states relate to the solid and liquid aggregate states. The dynamics of transitions between these states during cluster evolution means *coexistence of phases*, and the cluster lives for part of time in the solid state, while for the rest of the time it is found in the liquid state. Vibrational excitation of a cluster decreases the excitation energy of the liquid state and increases the statistical weight of this aggregate state. In addition, all the configurationally excited states are united in one excited state because of the high rate of transitions between these states at temperatures that are not low. Indeed, due to vibration excitation, the barrier for transition of an excited in neighboring positions on the cluster surface decreases, and this atom can move over the cluster surface more or less freely.

Let us use the truncated Lennard–Jones interaction potential between atoms which corresponds to the interaction between nearest neighbors only. Then according to formula (18.12), the binding energy of atoms of this cluster is equal to $41.24D$ ($X = 12$, $Y = 30$), and to $35.32D$ ($X = 11$, $Y = 25$) for the cluster of 12 atoms, that is the binding energy of a test atom is $5.92D$. An excited atom is located in a hollow between 3 atoms, i.e. it is located above one icosahedron triangle. Evidently, the distance between nearest neighbors is optimal for a test atom, and its binding energy is $2.92D$. There are three types of atom position over icosahedron triangles with respect to the initial position of a test atom, and each type includes five surface triangles. It is necessary for a test atom to overcome a barrier in order to pass to a given position in a hollow in the middle of the corresponding triangle, and in the course of this transition a test atom conserves the bonds with two nearest neighbors, i.e. the binding energy of a test atom at the barrier is approximately $2D$, and the excitation energy for transition to the barrier top is equal to $3.92D$. The subsequent atom transition between neighboring position of energy minima has an activation character.

Note that the number of bonds is 36 for the fcc cluster consisting of 13 atoms, and the excitation energy of the icosahedral cluster for this atom configuration is $5.24D$ in the case of the truncated Lennard–Jones interaction potential between atoms. Figure 18.8 shows the character of transitions between lower states of the cluster of 13 atoms with this interaction potential of atoms. In particular, in order for a test atom to reach a position where its nearest neighbor is the opposite atom with respect to the vacancy, this atom must overcome at least three barriers (Figure 18.7). This form of the cluster energy is typical of any cluster, so that the cluster energy contains many local minima and the transition between them lies through saddle points of the potential energy.

The same positions of cluster levels and atom transitions correspond to other interaction potentials between atoms. For example, the Lennard–Jones cluster of 13 atoms is characterized by the lower excitation energies of $2.86D$, $2.88D$ and $2.93D$, and the excitation energies at the barrier tops $3.42D$, $3.70D$, $3.87D$, and the excitation energy of the close-packed structures is split in $3.54D$ and $3.69D$ for the fcc and hexagonal structures correspondingly. Indeed, let us evaluate the energy of excitation of a cluster saddle point where an exciting atom is located in the middle between the initial and final positions, and the optimal bonds are conserved with two atoms. We assume that the surrounding atoms do not vary their positions during this transition. Under this condition, the saddle point corresponds to a symmetric position of a transferring atom if it conserves two nearest neighbors in the course of the transition. Restricting ourselves to the interaction of nearest neighbors, we obtain in this case for the barrier height

$$\Delta U = -U(R_e) - U(1.687R_e) + 2U(1.437R_e) \quad (18.23)$$

where $U(r)$ is the pair interaction potential of atoms at a distance r , and R_e is the optimal distance between two atoms. In the case of the Lennard–Jones interaction potential of atoms, this formula gives for the barrier height $\Delta U = 0.66D$, whereas in reality it is equal to $0.56D$ for this cluster, in accordance with the above value. The scheme of the lowest excitation energies for local minima and saddle points is similar to that of Figure 18.7. Hence the method used to estimate the energies of the lower excited states and barriers on the basis of the number of breaking bonds is useful. Thus the transition between excited cluster states consists of a

series of transitions between local minima of the cluster energy, overcoming saddle points, and the number of such transitions increases with increasing cluster size. The number of such transitions increases with cluster size.

18.5 Electron Energy Surface of Three Hydrogen Atoms

A pair interaction potential of atoms in a system of bound atoms is correct for a system of weakly interacting atoms, when the interaction of a test atom with another atom does not influence the interaction of a test atom with a third atom. For such a system of bound atoms the potential energy surface for the ground electron state of the system is separated from excited electron states by a large gap at any atom configuration, so that excited electron states are not influenced by its behavior. The electron energy surface of the ground state of this system contains a large number of local minima and saddle points in a multidimensional space of nuclear coordinates, so that transitions between neighboring local minima have an activation character. Such a form of the electron energy determines various properties of this system. In particular, this explains the *short order* for its liquid states according to which the distance between nearest neighbors in liquids is concentrated in a narrow range. But the saddle character of the electron energy surface for a system of bound atoms and correspondingly the activation character of transition between nearest minima is typical for various physical and chemical processes. As an example of such a type, we consider below the system of three interacting hydrogen atoms in the ground state. In spite of the system having three different electron surfaces, the electron surface of the ground electron state contains two local minima, which correspond to H_2+H systems, and these local minima are separated by a barrier. This form of the electron energy determines the character of the process



and as a result of this process an incident atom becomes bound, and an initially bound atom is released. Below we evaluate the electron energy of a system of three hydrogen atoms that allows one to analyze this process. In order to simplify the problem, we neglect the electrostatic interaction of atoms, so that the behavior of the electron energy surface is determined by the exchange interaction of atoms which results from overlapping of the electron wave functions if the electrons belong to different nuclei. In this way we construct the wave function of the system of three hydrogen atoms whose nuclei have an arbitrary configuration, and the eigen-wave functions of the electron Hamiltonian will lead to the determination of electron levels for a given atom configuration.

Evidently, the system consisting of three hydrogen atoms in their ground states has eight electron states in accordance with the total number of combinations of spin projections of isolated atoms, and these states relate to three electron terms. One of these terms is characterized by the total spin $3/2$, and the total electron spin of the other two terms is $1/2$. Thus we have three degenerate electron states for three interacting hydrogen atoms which are found in the ground state.

Using the *Pauli exclusion principle*, we construct the electron wave functions of the system of three interacting hydrogen atoms in the form of the *Slater determinants*

$$\Phi_1 = \frac{1}{\sqrt{6(1 - S_{bc})}} \begin{vmatrix} \psi_a(1)\eta_-(1) & \psi_a(2)\eta_-(2) & \psi_a(3)\eta_-(3) \\ \psi_b(1)\eta_+(1) & \psi_b(2)\eta_+(2) & \psi_b(3)\eta_+(3) \\ \psi_c(1)\eta_+(1) & \psi_c(2)\eta_+(2) & \psi_c(3)\eta_+(3) \end{vmatrix} \quad (18.25a)$$

$$\Phi_2 = \frac{1}{\sqrt{6(1 - S_{ac})}} \begin{vmatrix} \psi_a(1)\eta_+(1) & \psi_a(2)\eta_+(2) & \psi_a(3)\eta_+(3) \\ \psi_b(1)\eta_-(1) & \psi_b(2)\eta_-(2) & \psi_b(3)\eta_-(3) \\ \psi_c(1)\eta_+(1) & \psi_c(2)\eta_+(2) & \psi_c(3)\eta_+(3) \end{vmatrix} \quad (18.25b)$$

$$\Phi_3 = \frac{1}{\sqrt{6(1 - S_{ab})}} \begin{vmatrix} \psi_a(1)\eta_+(1) & \psi_a(2)\eta_+(2) & \psi_a(3)\eta_+(3) \\ \psi_b(1)\eta_+(1) & \psi_b(2)\eta_+(2) & \psi_b(3)\eta_+(3) \\ \psi_c(1)\eta_-(1) & \psi_c(2)\eta_-(2) & \psi_c(3)\eta_-(3) \end{vmatrix} \quad (18.25c)$$

Here $\psi_a(i)$, $\psi_b(i)$ and $\psi_c(i)$ are the normalized space wave functions of the i th electron which is located in the field of nuclei a , b and c respectively, and $\eta_+(i)$ and $\eta_-(i)$ are the spin wave functions of the i th electron if the spin projection is $1/2$ or $-1/2$ onto a given direction. We account for the normalization of the wave functions (18.25), and the overlapping integral is

$$S_{ab} = \langle \psi_a(1)\psi_b(2) | \psi_b(1)\psi_a(2) \rangle = |\langle \psi_a(1) | \psi_b(1) \rangle|^2$$

The basis (18.25) is valid at large distances between nuclei, but in reality this method gives correct values for the exchange interaction of atoms up to atomic distances between nuclei. To determine the positions of electron energy levels for a given configuration of nuclei, we compose the combination of the basis wave functions

$$\Psi = c_1\Phi_1 + c_2\Phi_2 + c_3\Phi_3$$

and require this wave function to be the eigenfunction of the electron Hamiltonian, i.e.

$$\hat{H}\Psi = E\Psi$$

where $E = E(R_{ab}, R_{ac}, R_{bc})$ is the electron energy, and R_{ab} , R_{ac} , R_{bc} are the distances between corresponding nuclei. According to the standard operations of quantum mechanics the electron energy is the solution of the secular equation

$$\begin{bmatrix} E - H_{11} & H_{12} & H_{13} \\ H_{21} & E - H_{22} & H_{23} \\ H_{31} & H_{32} & E - H_{33} \end{bmatrix} = 0 \quad (18.26)$$

where the matrix elements

$$H_{ik} = \frac{\langle \Phi_i | \hat{H} | \Phi_k \rangle}{(\langle \Phi_i | \Phi_i \rangle \langle \Phi_k | \Phi_k \rangle)^{1/2}}$$

are assumed to be real values, since we use real wave functions $\psi_a(i)$. The solution of equation (18.26) yields three electron levels for a given configuration of nuclei.

In order to evaluate the matrix elements of the Hamiltonian, we divide the electron Hamiltonian into two parts:

$$\hat{H} = \hat{h}_{ab}(1, 2) + \hat{h}_c(3) + V \quad (18.27)$$

where

$$\begin{aligned} \hat{h}_{ab}(1, 2) &= -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 - \frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{R_{ab}}, \\ \hat{h}_c(3) &= -\frac{1}{2}\Delta_3 - \frac{1}{r_{3c}}, \\ V &= -\frac{1}{r_{3a}} - \frac{1}{r_{3b}} - \frac{1}{r_{1c}} - \frac{1}{r_{2c}} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_3|} + \frac{1}{|\mathbf{r}_2 - \mathbf{r}_3|} + \frac{1}{R_{ac}} + \frac{1}{R_{bc}} \end{aligned}$$

Here $\mathbf{r}_i$ is the coordinate of the i th electron, r_{ia} is the distance of the i th electron from nucleus a , R_{ab} is the distance between nuclei a and b , the Hamiltonian $\hat{h}_{ab}(1, 2)$ describes the system of two hydrogen atoms with nuclei a and b , and the Hamiltonian $\hat{h}_c(3)$ relates to the hydrogen atom consisting of the third electron and nucleus c ; the operator V accounts for the interaction between these systems. This form is convenient for calculation of the matrix element $\langle \Psi_{ab}(1, 2) \psi_c(3) | \hat{H} | \Psi_{ab}(2, 1) \psi_c(3) \rangle$. In this case the matrix element from the operator V at large distances R between atoms contains an additional small parameter $1/R$ compared with the overlapping integral S between these wave functions.

Separating the Hamiltonian of the three electrons into two-electron and one-electron ones and ignoring the interaction between these systems in the region of electron coordinates which determines the integrals under consideration, we reduce the problem of three electrons to the two-electron problem. The matrix elements of the Hamiltonian in the basis Φ_1, Φ_2, Φ_3 are equal to

$$\begin{aligned} H_{11} &= E_o - \frac{1}{2}\Delta_{bc}, & H_{22} &= E_o - \frac{1}{2}\Delta_{ac}, & H_{33} &= E_o - \frac{1}{2}\Delta_{ab}, \\ H_{12} &= -\frac{1}{2}\Delta_{ab}, & H_{13} &= -\frac{1}{2}\Delta_{ac}, & H_{23} &= -\frac{1}{2}\Delta_{bc} \end{aligned} \quad (18.28)$$

Here

$$\Delta_{ab} = 2 \frac{\langle \Psi_{ab}(1, 2) | \hat{H} | \Psi_{ab}(2, 1) \rangle - \langle \Psi_{ab}(1, 2) | \hat{H} | \Psi_{ab}(1, 2) \rangle \langle \Psi_{ab}(1, 2) | \Psi_{ab}(2, 1) \rangle}{\langle \Psi_{ab}(1, 2) | \Psi_{ab}(1, 2) \rangle} \quad (18.29)$$

is the *exchange interaction potential* for two hydrogen atoms at a distance R_{ab} , E_o is the energy of three hydrogen atoms, accounting for the long-range interaction between them, ε_o is the electron energy of an isolated hydrogen atom, and $\Psi_{ab}(1, 2) = \psi(1a)\psi(2b)$ in this case. Representing the energy of the system of three hydrogen atoms in the form $E = E_o + \varepsilon$, we obtain the following secular equation for the electron energy ε :

$$\begin{vmatrix} \varepsilon - \Delta_{bc} & \Delta_{ab} & \Delta_{ac} \\ \Delta_{ab} & \varepsilon - \Delta_{ac} & \Delta_{bc} \\ \Delta_{ac} & \Delta_{bc} & \varepsilon - \Delta_{ab} \end{vmatrix} = 0 \quad (18.30)$$

This equation is

$$\begin{aligned} & \varepsilon^3 + (\Delta_{ab} + \Delta_{ac} + \Delta_{bc})\varepsilon^2 \\ & + (\Delta_{ab}\Delta_{ac} + \Delta_{ab}\Delta_{bc} + \Delta_{ac}\Delta_{bc} - \Delta_{ab}^2 - \Delta_{ac}^2 - \Delta_{bc}^2)\varepsilon \\ & - \Delta_{ab}^3 - \Delta_{ac}^3 - \Delta_{bc}^3 + 3\Delta_{ab}\Delta_{ac}\Delta_{bc} = 0 \quad (18.31) \end{aligned}$$

Thus we have three electron terms for the system of three hydrogen atoms in the ground states. The total number of states of this system is equal to 8 and corresponds to different projections of the spin of each atom. Two electron terms of the total system relate to the total spin 1/2 of the system (4 electron states), and the third electron term of the total system corresponds to the total electron spin 3/2 and includes 4 electron states. This term can be separated from other two, and the following wave function describes this state:

$$\Phi' = \begin{vmatrix} \psi_a(1)\eta_-(1) & \psi_a(2)\eta_-(2) & \psi_a(3)\eta_-(3) \\ \psi_b(1)\eta_+(1) & \psi_b(2)\eta_+(2) & \psi_b(3)\eta_+(3) \\ \psi_c(1)\eta_+(1) & \psi_c(2)\eta_+(2) & \psi_c(3)\eta_+(3) \end{vmatrix} \quad (18.32)$$

The energy of this state is

$$E_3 = \frac{\langle \Phi' | \hat{H} | \Phi' \rangle}{\langle \Phi' | \Phi' \rangle} = E_o + \frac{1}{2}(\Delta_{ab} + \Delta_{ac} + \Delta_{bc}) \quad (18.33)$$

Here we represent the Hamiltonian in the form (18.27) and neglect the perturbation and also the overlap of the three wave functions. We use the definition (18.29) of the exchange interaction potential Δ_{ab} and assume the validity of the relation $\Psi_{ab}(1, 2) = \psi(1a)\psi(2b)$ in the self-consistent field approximation. Excluding the third electron state from equation (18.31), we find the positions of the two-electron terms for three hydrogen atoms in the ground state if the total spin of the system is 1/2:

$$E_{1,2} = E_o \pm \frac{1}{2} \sqrt{\frac{1}{2}(\Delta_{ab} - \Delta_{ac})^2 + \frac{1}{2}(\Delta_{ab} - \Delta_{bc})^2 + \frac{1}{2}(\Delta_{ac} - \Delta_{bc})^2} \quad (18.34)$$

According to the method used to derive this result, this relates to large separations between any two hydrogen atoms and ignores the long-range interaction between atoms because it is close for different electron terms. This behavior of electron terms is valid at intermediate distances between atoms which are compared with the equilibrium distance between atoms of the hydrogen molecule H_2 , and we use this below.

Let us analyze this formula for the electron energy levels of three hydrogen atoms. This formula accounts for the exchange interaction between atoms, extracting from this the two-electron interaction, and ignores the long-range interaction between atoms. According to this formula, the electron energies depend on the three distances between nuclei: R_{ab} , R_{ac} and R_{bc} . If one atom (c) is removed to infinity, we obtain two terms of the diatomic hydrogen molecule, where the lower energy E_1 corresponds to the singlet molecular term $^1\Sigma_g$, and the two other energies relate to the triplet term $^3\Sigma_u$. So, in this limiting case, depending on the distance R between nuclei, the electron energy is

$$E(R) = 3\varepsilon_o \pm \frac{1}{2}\Delta(R) \quad (18.35)$$

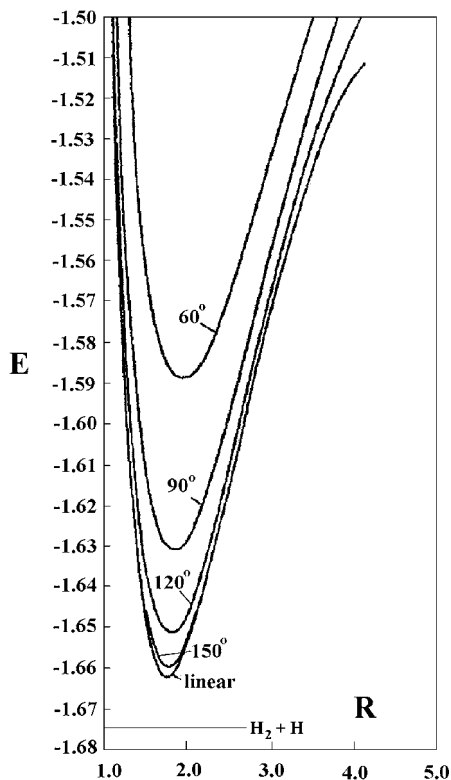


Figure 18.9. The electron energy of the lowest electron term for a system of three interacting hydrogen atoms if they form an isosceles triangle ($ab = bc$) at different angles at the vertex of this triangle (H. Conroy, B.L. Bruner. *J. Chem. Phys.* 47, 921, 1967). Atomic units are used both for the electron energy and for distances.

Note that the splitting of electron levels $\Delta(R_{eq})$ of the hydrogen molecule H_2 at the equilibrium distance R_{eq} is about 6 eV, i.e. it is high compared to the thermal energy. Hence the difference between the electron energies of the two lowest terms is high compared with the thermal energies, and when considering the process (18.24) at thermal energies, we can restrict ourselves to the lowest electron term.

We now consider the behavior of the lowest electron term of the system of three hydrogen atoms in the ground state, starting from the hydrogen molecule when it is located far from the hydrogen atom. Then the energy of this electron state is

$$E_1 = 3\varepsilon_o + \frac{1}{2}\Delta(R_{eq}) - \frac{1}{2}\sqrt{\frac{1}{2}(\Delta_{ab} - \Delta_{ac})^2 + \frac{1}{2}(\Delta_{ab} - \Delta_{bc})^2 + \frac{1}{2}(\Delta_{ac} - \Delta_{bc})^2} \quad (18.36)$$

and taking the system of noninteracting hydrogen molecule ab and hydrogen atom c , i.e. $\Delta_{ab} = \Delta(R_{eq})$, $\Delta_{ac} = \Delta_{bc} = 0$, we obtain according to formula (18.36) $E_1 = 3\varepsilon_o - \frac{1}{2}\Delta(R_{eq})$, which corresponds to the minimum of the electron energy. As the distance between the hydrogen molecule and atom decreases, but $\Delta_{ac}, \Delta_{bc} \ll \Delta(R_{eq})$, we obtain the exchange repulsion between these particles. One can see that the minimal repulsion corresponds to the maximum distance between atoms, i.e. the minimum barrier occurs if the three atoms are

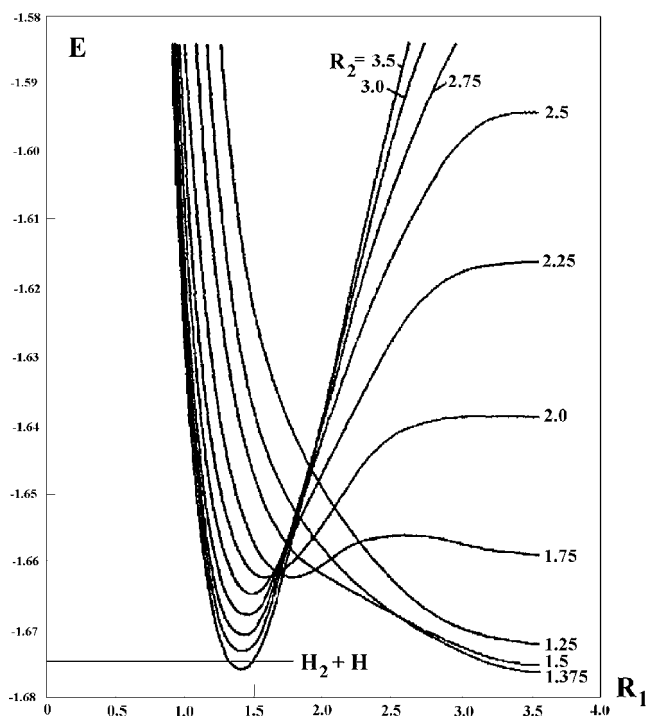


Figure 18.10. The electron energy of the lowest electron term for a system of three interacting hydrogen atoms, if they are located on a line, depending on a distance between the middle and one last atom at different distances between the middle and other last atom (H. Conroy, B.L. Bruner. *J. Chem. Phys.* 47, 921, 1967). Atomic units are used both for the electron energy and for distances.

located on a line. Figure 18.9 gives the electron energy at the barrier top, which corresponds to equal distances between the middle and last atoms according to symmetry consideration. As we can see, the atoms are found on a line, and the distances between the middle and last atoms differ from the equilibrium distance between hydrogen atoms in the hydrogen molecule (Figure 18.10). The minimum barrier height is about 4000 K and significantly exceeds the typical thermal energy of atoms. Therefore the process (18.24) which leads to a change in the configuration of the three hydrogen atoms, has an activation character.

Thus the electron energy surface of the lowest electron term for three hydrogen atoms is separated into parts, where different pairs of hydrogen atoms form a strong bond, and the third hydrogen atom is located far from the diatomic molecule. These configurations correspond to local minima of the energy of three hydrogen atoms, and these minima are separated by barriers. In particular, Figure 18.12 gives lines of identical electron energies for one part of the configuration space for the case in which three hydrogen atoms are located on a line. The saddle points correspond to identical distances between the middle and last atoms, so that the process (18.24) is realized through these atom configurations. This example exhibits shows that local minima and saddle points in a configuration space are a general property of systems

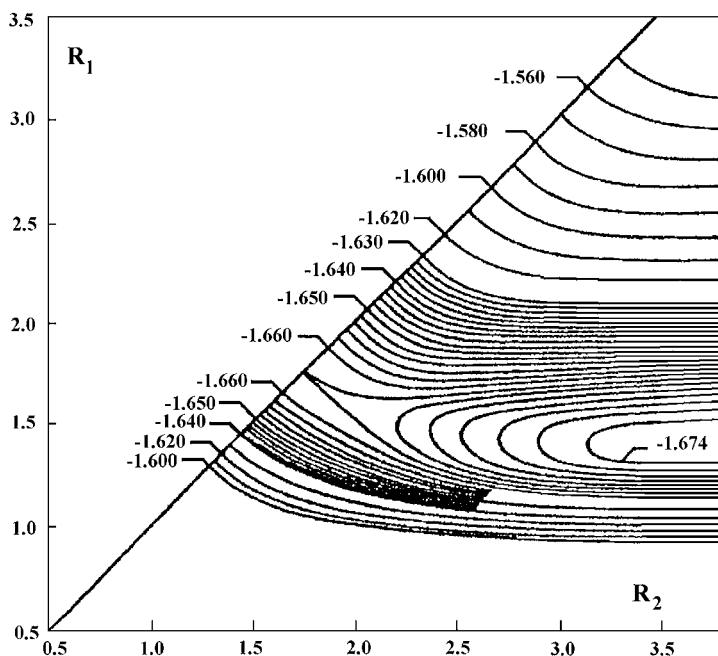


Figure 18.11. Isoenergetic lines of the electron energy surface of a part of the configuration space for a system of three interacting hydrogen atoms if they are located on a line (H. Conroy, B.L. Bruner. *J. Chem. Phys.* 47, 921, 1967). Distances between the middle and last atoms are indicated, and atomic units are used both for the electron energies and for distances.

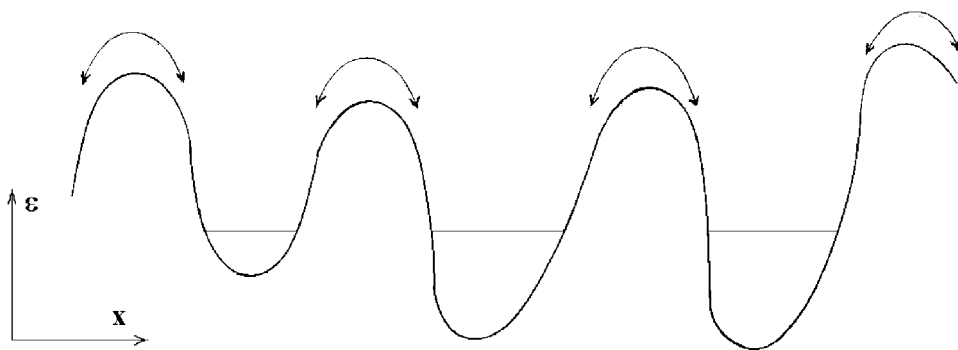


Figure 18.12. The character of evolution of an ensemble of bound atoms. The axis x joins in each case two neighboring local minima of the potential energy surface between which the transition proceeds.

of interacting atoms, and the number of local minima and saddle points increases with the increasing number of interacting atoms. This property is of importance for the evolution of such systems that results from variation of atom configurations.

18.6 Peculiarity of the Potential Energy Surface for Ensembles of Bound Atoms

Above we considered the electron energy surface for three hydrogen atoms in the ground state in order to show the general properties of the ground state electron energy depending on atomic coordinates. It consists of valleys separated by a barrier, and the transition of the system of three interacting hydrogen atoms from one valley to another one has an activation character. The separation of the potential energy surface in such regions is a general property of ensembles of bound atoms when an energetic gap occurs between the ground electron state and the first excited state of this system. In the case of three hydrogen atoms the nature of this effect results from the exchange interaction between atoms, but this form of the potential energy surface also occurs in an ensemble of bound atoms with a pair interaction potential of an usual form, as given in Figure 7.5. In this case, dividing the potential energy surface into regions separated by barriers is a result of the symmetry, and the number of such regions increases with an increase in the number of interacting atoms.

Indeed, let us consider the simplest example of four bound atoms with a pairwise interaction whose basis is the interaction between nearest neighbors. Evidently, the optimal configuration of this system corresponds to a pyramid whose surface consists of three equilateral triangles, and the distance between nearest neighbors corresponds to the equilibrium distance for the pair interaction potential. Then the total binding energy of the atoms is $6D$, where D is the well depth for the pair interaction potential and we account for interaction between nearest neighbors only. There are 8 such atom configurations in a space of atom coordinates because of the symmetry for each atom for reflection with respect to the triangle plane formed by other three atoms. Since for the optimal transition between two such states one can conserve only two bonds of the transferring atom with its nearest neighbors, the barrier height is equal to D for the short-range interaction of atoms. In the case of a 13-atom cluster the number of excited cluster configurations is 180, which follows from Figure 10.3b, and the barrier height is about $1D$, also according to Figures 10.1 and 18.7. Of course, an increase in the number of configurationally excited states with increasing number of cluster atoms is not as sharp for clusters with non-completed atom shells, but this effect is also valid.

This behavior of the potential energy surface for large clusters leads to the specific character of their evolution in a space of atom coordinates. Being located in a given region separated from a neighboring one by an energetic barrier, this ensemble of bound classical atoms is found there for a long time and then passes through a barrier to a neighboring region, as shown in Figure 18.12, which gives the projection of the potential energy surface on the plane with the axis connecting the positions of the potential energy minima for each transition. Thus the evolution of an ensemble of bound atoms consists in the transitions between local minima of the potential energy surface, and the typical time for such transitions is large compared with the typical oscillation time for this atom ensemble. In particular, this character of evolution of a cluster to the global minimum of the potential energy is given in Figure 18.8.

This character of cluster evolution determines the principal properties of clusters and bulk systems of bound atoms. In particular, configurationally excited states of these systems are stable because they belong to the minima of the potential energy surface, and the energy of a

given local minimum characterizes a given configuration excitation. Aggregate states of these ensembles of bound atoms can be composed from corresponding configuration states, and the liquid aggregate state is a group of configurationally excited states with nearby excitation energies. From this the *short order* follows for liquids, which consists in the conservation of the distance between nearest neighbors for the ground and lowest configurationally excited states of the ensemble. Therefore, a glance at an ensemble of bound atoms from the standpoint of the behavior of its potential energy surface allows us to analyze the principal properties of this ensemble.

Thus, the behavior of the potential energy surface of systems of bound atoms depending on atom configurations is their important property. The potential energy surface has a certain number of local minima which are separated by barriers, and the number of these minima increases strongly with an increase in the number of atoms. The transition from the global minimum of the potential energy surface to a local minimum is called configuration excitation and is of importance for aggregate states and phase transitions for ensembles consisting of a large number of bound atoms.

19 Structures of Bonded Large Molecules

19.1 Structures of Atomic and Molecular Systems

A bulk system of interacting atoms and molecules can be found in the gaseous or condensed state depending on the density of atomic particles, their binding energy and the energy or temperature of the system. In turn, condensed states are divided into liquid and solid ones, and solid states are characterized by the *long order* in the location of atomic particles for the solid state, while only a *short order* occurs for the liquid one. This scheme is valid for systems consisting of identical atoms or simple molecules. In spite of the external simplicity of this scheme, the behavior of such substances is quite varied. In particular, the solid state is characterized by a particular crystal lattice, so that an elementary cell of this lattice is repeated in the crystal many times. A bulk solid can be obtained from an elementary cell by multiply reproducing it together with the translation operation. But the number of possible crystal structures which may be constructed by reproduction with translation is equal to 230. This shows the variety of structures of solids.

So the large variety of crystal structures makes solids complex. One substance can have many structures. For example, solid carbon can form three structures – graphite, diamond and fullerite – so that graphite corresponds to the stable state of carbon, and the two other structures relate to its metastable states. A transition is possible between two structures of a solid, as takes place between white and gray tin at room temperature. Note that the metastable states of even simple substances can exist for a long time because of the small rates of the processes of redistribution of atomic particles which lead to an equilibrium. A simple example of this is carbon materials located in the atmosphere, where processes of carbon oxidation last for hundreds years and lead to carbon oxidation.

The number of stable or practically stable states increases as a substance becomes more complex. In particular, a condensed system of atoms of two types can have a disordered state where atoms of different types are mixed and distributed randomly, and the ordered state where these two components are separated. Of course, as the number of components or their complexity increases, this leads to an increase in the number of phase states of the system and complexity of structures of their components. Moreover, new forms of structures occur for complex molecules of a certain form. For example, if these molecules have a rod shape, such as *amphiphilic molecules*, they can align themselves in the same direction, creating in this way lipid layers, films and membranes in liquid solutions. Specific structures are formed if molecules of so called *surface-active substances* surround small particles in solutions. In this way various *suspensions* and *emulsions*, such as inks and paints become stable. These molecules can form thick layers on the surface of liquids and on interfaces. Examples of such layers are the membranes of living cells. If molecules are long, such as polymer molecules, new structures occur, so that known processes and phenomena develop in a new form. Nev-

ertheless, one can establish a bridge with the properties of simple substances, and then new qualitative properties of complex systems can be extracted.

Since metastable forms of substances can be considered as stable in practice, the properties of such substances depend on the method of their preparation. In a system consisting of elemental cells of large size, which are subsequently joined in blocks, external fields can affect the character of growth of such a system and its final structure. Usually, external electric fields promote the joining of these systems under the action of forces induced by the electric field. The larger the systems, the stronger is the influence of the electric field on their joining, which goes in the electric field direction. As a result, *stretched structures* are formed in an electric field, such as *chain aggregates* and *fractal fibers*. We briefly consider below various structures which exist in our environment, their properties and the processes in which they participate.

19.2 Solutions of Amphiphiles

Amphiphiles are molecules which have the shape of rods with polar and nonpolar hydrocarbon endings. The simplest examples of amphiphilic molecules are given in Table 19.1. These molecules can be modeled by rods. We will call a hydrophilic head of such molecules the polar head and a hydrophobic nonpolar ending will be called the hydrocarbon tail. Amphiphilic molecules can be arranged in one direction in solutions to form a liquid crystal, the properties of which are determined by the interaction of amphiphilic molecules with solvent molecules and the interaction between amphiphilic molecules.

Table 19.1. Molecules of simple amphiphiles.

Amphiphilic molecule	Chemical formula
Sodium dezilsulphat	$\text{CH}_3\text{-(CH}_2\text{)}_9\text{-SO}_4\text{Na}$
Chloride dezilammonia	$\text{CH}_3\text{-(CH}_2\text{)}_9\text{-NH}_3\text{Cl}$
Decanol	$\text{CH}_3\text{-(CH}_2\text{)}_9\text{-OH}$
Octilamin	$\text{CH}_3\text{-(CH}_2\text{)}_7\text{-NH}_2$

Let us analyze the possibility of an order–disorder transition in a solution with dissolved amphiphilic molecules. Evidently, the structure of this solution is characterized by the identical direction of molecules. Let us introduce the *director* of this system which corresponds to the average direction of molecules, and label by θ the angle between the direction of a given molecule and the director. One can characterize the degree of regulation in the directions of molecules by the *order parameter* s :

$$s = -\frac{1}{2} + \frac{3}{2} \langle \cos^2 \theta \rangle \quad (19.1)$$

where averaging is taken over the directions of molecules.

Evidently, the *alignment* of molecules is determined by the interaction between them and depends both on the solution temperature and amphiphile concentration. Below we employ

for the analysis of orientation of molecules a simple *Meier model* in which the energy per molecule ε is determined by one parameter U :

$$\varepsilon = U \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) s \quad (19.2)$$

As we can see, the value ε includes the anisotropic part of the interaction energy, so that $\langle \varepsilon \rangle = 0$. Let us take the Boltzmann distribution function f for molecule orientations $f \sim \exp(-\varepsilon/T)$. Then we obtain for the order parameter:

$$s = -\frac{1}{2} + \frac{\frac{3}{2} \int \cos^2 \theta \exp(-\varepsilon/T) d \cos \theta}{\int \exp(-\varepsilon/T) d \cos \theta} = -\frac{1}{2} + \frac{3}{2} \frac{d \ln F(x)}{dx}$$

where $x = 3Us/(2T)$ and $F(x) = \int_0^1 \exp(xz^2) dz$. This gives the following equation for the value x which characterizes the order parameter s :

$$\frac{2}{3} \frac{T}{U} x = -\frac{1}{2} + \frac{3}{2} \frac{d \ln F(x)}{dx}$$

This equation has a trivial solution $x = 0$ that corresponds to the isotropic distribution of molecules and can have two additional solutions. We will find the value of the parameter U/T when a nontrivial solution disappears. The corresponding value x_o relates to the *order-disorder transition* temperature, and at higher temperatures only the isotropic distribution of molecule orientations is possible. At the transition temperature, along with the above equation, the equality of derivatives of the corresponding functions takes place, so that the transition point follows from the equation

$$\frac{2}{3} \frac{T_o}{U} x_o = -\frac{1}{2} + \frac{3}{2} \frac{d \ln F(x)}{dx} \Big|_{x=x_o}, \quad \frac{2}{3} \frac{T_o}{U} = \frac{3}{2} \frac{d^2 \ln F(x)}{dx^2} \Big|_{x=x_o} \quad (19.3)$$

Expecting that the solution of these equations corresponds to $x_o \gg 1$, we use the asymptotic expression of the function $F(x)$ at large x :

$$F(x) \approx \frac{e^x}{2x}, \quad x \gg 1$$

so that equations (19.3) take the form

$$\frac{2}{3} \frac{T_o}{U} x_o = -\frac{1}{2} + \frac{3}{2} \left(1 - \frac{1}{x_o} \right), \quad \frac{2}{3} \frac{T_o}{U} x_o = \frac{3}{2x_o}$$

The solution of this set of equations gives

$$x_o = 3, \quad \frac{T_o}{U} = \frac{1}{4}, \quad s = \frac{1}{2}$$

The accurate solution of the set of equations (19.3) gives slightly shifted values of the parameters

$$x_o = 2.9, \quad \frac{T_o}{U} = 0.22, \quad s = 0.43$$

The temperature T_o characterizes the order–disorder transition for a solution of molecules of cylindrical shape. This is the phase transition of the first type which is accompanied by the following energy consumption per molecule

$$\langle \varepsilon \rangle = 0.18U = 0.84T_o \quad (19.4)$$

Correspondingly, the entropy jump per molecule as a result of this phase transition is

$$\Delta S = \frac{\langle \varepsilon \rangle}{T_o} = 0.84$$

Note that if we consider the phase transition as a transition from the disordered state of freely rotating molecules of a rod shape to the ordered state where each molecule has a certain direction, the entropy jump is $\Delta S = \ln 2 = 0.69$.

This case of amphiphile solutions shows the variety of structures and phase transitions for systems of complex molecules. Continuing the analysis of amphiphile solutions, we note that the ordered state of this solution is a type of *liquid crystal* – a lyotropic liquid crystal. As we have seen, for these objects we mix the concepts of the liquid and solid aggregate states, because the crystal structure of molecules is formed in a liquid. Thus, the complexity of large molecules leads to qualitatively new structures which are determined by the properties of these molecules. Evidently, the formation of a lyotropic liquid crystal is determined by both the solution temperature and amphiphile concentration. There is a critical concentration of amphiphilic molecules for the formation of a lyotropic liquid crystal, and the threshold concentration is lower, the larger the amphiphilic molecule.

19.3 Structures of Amphiphilic Molecules

We find that the isotropic distribution of directions of amphiphilic molecules takes place at small concentrations and high temperatures of molecules in a solution. Then we have a gas of amphiphilic molecules in the solution with a weak interaction between them. A decrease in the temperature or an increase in the concentration of amphiphilic molecules leads to the formation of clusters which include several amphiphilic molecules and are named *micelles*. They can have a different shape depending on the length of amphiphilic molecules and the interaction between them (see Figure 19.1). Small amphiphilic molecules can form spherical micelles, so that in aqueous solutions hydrocarbon endings are directed to the center of the micelle, and hydrophilic heads are located on the sphere surface. Starting from some amphiphile concentrations, this amphiphile solution contains amphiphilic molecules in the form of micelles. Then we obtain a so-called *colloid solution*. A subsequent increase in the amphiphile concentration leads to the formation of the structure of micelles due to the interaction between them. Because interacting micelles are similar to spherical particles, they form the face-centered cubic lattice which is typical for atoms of rare gases and spherical particles with a short-range interaction. Note that in this analysis we were guided by aqueous solutions. According to the *golden rule of chemistry* that similar is dissolved in similar, polar endings are directed to water. In the case of fat liquids as solvents, we have the opposite positions of amphiphilic molecules, so that their hydrocarbon endings are directed to the solvent.

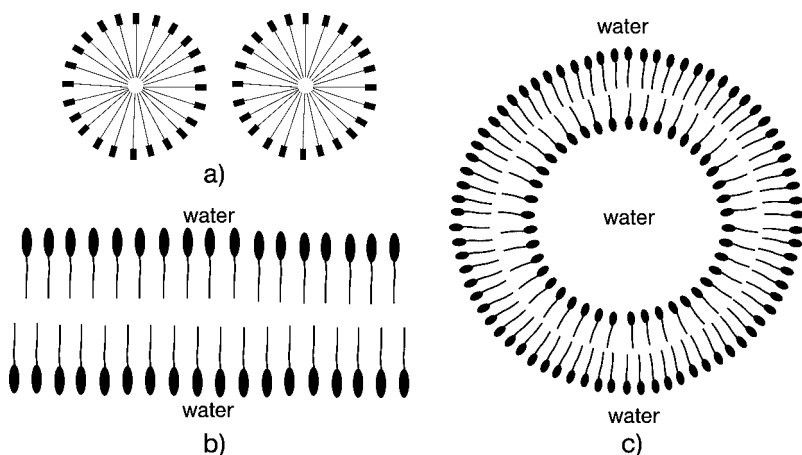


Figure 19.1. Structures of amphiphilic molecules in an aqueous solution. (a) Micelles-bound systems of amphiphilic molecules like to clusters; (b) a double layer of amphiphilic molecules in the solution; (c) a double layer as a membrane which forms a closed film like to a soap bubble or biological membrane.

The interaction of large amphiphilic molecules leads to their alignment, so that cluster-micelles of these molecules form an element of a two-dimensional crystal lattice of the hexagonal structure, i.e. the close-packed structure in a two-dimensional space. As the concentration of amphiphiles increases, micelles join in an infinite layer. As a result, a *lamellar structure* is formed in the solution where amphiphilic molecules form a *double layer*. Each layer has the two-dimensional hexagonal structure of amphiphilic molecules in an identical direction. Usually in lyotropic liquid crystals two layers of amphiphilic molecules are bordered by hydrocarbon hydrophobic tails, so that the projection of a hydrocarbon ending of one layer perpendicular to the molecules' plane is located at the center of the regular triangle formed by the projections of the nearest endings of molecules of the neighboring layer, and polar hydrophilic heads are located on external sides of the double layer. Note that the formation of micelles explains the action of soaps which consist of amphiphilic or similar molecules. Surfaces of micelles consisting of polar heads of molecules split the molecules of fats, and the radicals formed dissolve in water.

At high concentrations of amphiphilic molecules, the double layer is energetically profitable even for amphiphilic molecules which form spherical micelles at small amphiphile concentrations. Lyotropic crystals consist of many double layers of amphiphilic molecules which alternate with the solvent layers. This lamellar structure of solutions of amphiphilic molecules is typical for a wide range of concentrations of amphiphilic molecules. Varying the solute concentration leads to a variation in the thickness of the solvent layer between neighboring double layers of amphiphilic molecules. The lamellar structure of solutions is of importance for life, where water is the solvent.

Due to the specific behavior of amphiphilic molecules on the liquid surface they can form a layer on the surface; these molecules are then called *surfactants* (surface active substances). Let us consider the behavior of amphiphilic molecules on the water surface. Then their polar

heads are pulled into the water, whereas the nonpolar tails are repelled from the water and are found over the surface, as shown in Figure 19.1. By forming a layer on the surface, the amphiphilic molecules change the properties of the water surface and protect the water from evaporation. Note the small amount of amphiphilic molecules in this case because of the small thickness of the amphiphilic layer, which is determined by a length of amphiphilic molecules. Usually these molecules are of length 2–3 nm and the distance between nearest molecules is 0.3–0.6 nm. When this layer of amphiphilic molecules is created at the water–air interface, it is called a *Langmuir monolayer*.

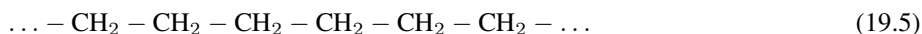
We now consider the role of surfactants (or amphiphiles) in the preservation of suspensions. A *suspension* is a two-component system where small solid particles are located in a liquid. Suspensions, as well as *emulsions*, in which small liquid drops are located in other liquids, are similar to a system of small particles located in a buffer gas. Such a system is unstable with respect to the growth of small particles due to their association, and this phenomenon may be typical for suspensions and emulsions. An additional interaction takes place in polar liquids which can stabilize these systems. In order to analyze this, we consider in detail the formation of gold particles in solutions. This is a classical case of small particles in liquids which has been studied widely, beginning with Michael Faraday.

To produce small particles, it is convenient to use a salt, for example, NaAuCl_4 in tri-sodium lemon acid. Then the gold atoms which result from the decomposition of these molecules join and form small particles in the liquid. Starting from certain sizes, these particles gain a positive charge, so that positive atoms of gold cannot attach to them. Thus the particle size is restricted by the particle charge, which in turn depends on the solution parameters. In this way, one can prepare a solution containing gold particles of a given size which is governed by salting of the solution. Thus the chemical method allows us to create a particle charge which can be abolished, for example, by the addition of pyridine in the case of gold particles. Then gold particles of this solution can be joined.

There is another method of conserving small particles in a solution by using amphiphilic molecules (or surfactants). Then amphiphilic molecules are attached to gold particles by hydrocarbon hydrophobic tails, so that their polar heads are directed to the liquid. As a result, a *corona* is formed around the gold particle, as shown in Figure 19.2. In particular, Faraday used this method to stabilize gold particles in water by the addition of gelatine molecules to water, and these molecules form a corona around small gold particles. This method of stabilization of suspensions and emulsions by the addition of some surfactants is used widely in practice. Coronas consisting of surfactants conserve ink, paints, creams, liquid soaps and other suspensions and emulsions.

19.4 Polymers

A *polymer* molecule or macromolecule is a long molecule with repeating *structural groups*. The simplest polymer is polyethylene which is formed from ethylene $\text{CH}_2 = \text{CH}_2$ by the breaking of one bond and the attachment of the same radicals to the free bonds. As a result of such a polymerization process, a long linear molecule is formed with the structure



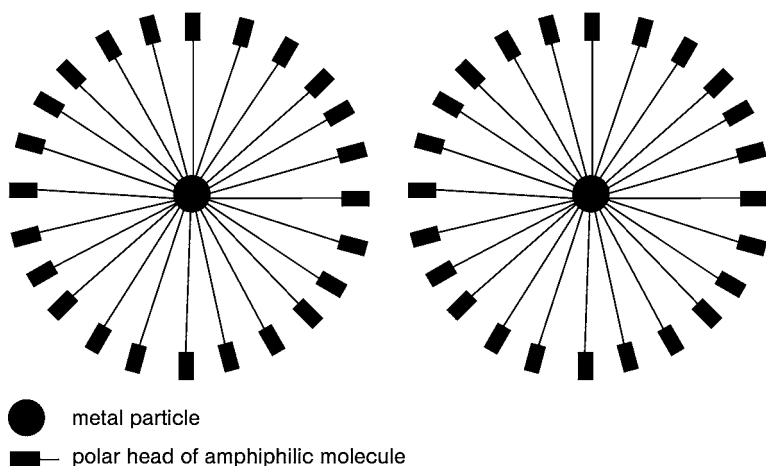


Figure 19.2. The corona structure of a particle in a solution if the particle attracts the tails of amphiphilic molecules.

The polyethylene molecule $(\text{CH}_2)_n$ consisting of n monomer structural groups is the simplest linear polymer molecule.

In the same way, on the basis of the breaking of bonds of simple molecules and the joining of the same elements instead of these bonds, one can obtain other linear polymer molecules. For example, by using the structural group $-\text{CH}_2 - \text{CH} - \text{Cl}-$ instead of $-\text{CH}_2 - \text{CH}_2 -$ in the polyethylene molecule, we obtain polyvinyl chloride. Individual structural groups of this molecule may be changed by other groups. If in the polyethylene case some structural group CH_2 is broken and is transformed to CH , the development of the macromolecule in three directions is possible. Then a linear macromolecule branches at this point and the repetition of branches leads to the formation of a *cross-linked polymer* (see Figure 19.3). Thus

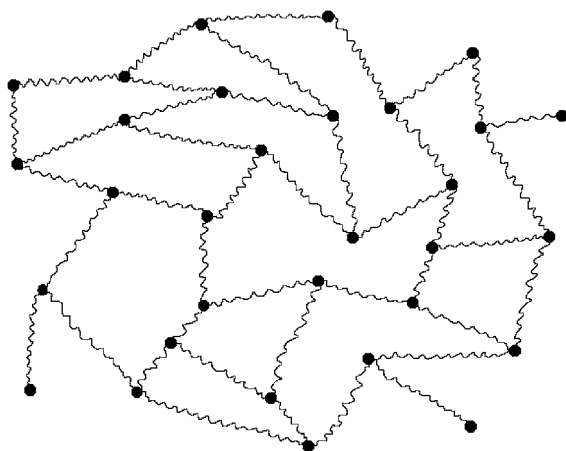


Figure 19.3. Typical cross-linked polymer.

polymer macromolecules can form one-dimensional, two-dimensional and three-dimensional structures.

We now consider the behavior of an individual polymer fiber in either a vacuum or a dilute solution. We assume the polymer fiber to consist of n links, so that a is the length of each link of the polymer fiber, and the angle between nearest links can be arbitrary. Then according to formula (2.4) the probability that the fiber length, i.e. the distance between fiber endings, is equal to r , is given by

$$P(r) = (2\pi\Delta)^{-3/2} \exp\left(-\frac{r^2}{2\Delta^2}\right)$$

where $\Delta = na^2$. Formulae (2.25) and (12.13) give the entropy of distributions which corresponds to the length r of the polymer fiber

$$S = \ln P \approx \frac{r^2}{na^2} + \text{const} \quad (19.6)$$

We determine below the optimal length of the fiber and its dependence on the number n of links. Along with statistics, it is determined by the interaction of links which leads to repulsion when they are located in the vicinity. This gives for the repulsive energy between the links of a polymer fiber consisting of n links

$$U \sim na^3 \cdot \frac{na^3}{r^3} \quad (19.7)$$

and a , the length of one link, is the radius of the action of forces between repulsing links. The first term relates to the fiber volume where interaction may be significant, and the second term is the probability of finding a link per unit volume. We construct the free energy of the polymer fiber

$$F = TS - U$$

and use formulae (19.6) and (19.7) in this expression. Optimization of the free energy gives the *Flory formula* for the optimal length of the polymer fiber

$$r_F \sim n^{3/5} \quad (19.8)$$

This formula corresponds to a low density of polymer fibers located in a space or a solution. In this case the repulsive interaction of the individual elements of a fiber increases with decreasing fiber length, and optimization of the length of a test fiber relates to this interaction. Another limiting case corresponds to a high density (or temperature) of fibers, when the interactions between fibers as well as elements of the same fiber are determined by the density of fibers. Hence this interaction does not affect the fiber length, which is determined by the random directions of neighboring links and is given by the formula

$$\overline{r^2} = na^2 \quad (19.9)$$

According to formula (19.9), the average length of each fiber $a\sqrt{n}$ is small in comparison with its maximum length an . Therefore the action of a stretching force leads to the lengthening of

each fiber, and this determines the elastic properties of a dense system of polymer fibers, in particular the elastic properties of rubbers. Note that this case corresponds to relatively high temperatures. At low temperatures an attractive interaction between the individual links of a polymer fiber dominates, which can change the polymer structure.

19.5 Gels

The lamellar liquid crystal, which is a solution of amphiphilic molecules in water, is an example of a *gel*, which has a solid skeleton and can absorb a large amount of water. In this case water is located in the space between neighboring double layers of amphiphilic molecules, and this lyotropic liquid crystal conserves the lamellar structure over a wide range of solute concentrations. As water penetrates the space between double layers, the bonds inside the double layers are conserved, but the bonds between the double layers are broken. As a result, a gel swells and partially conserves its *skeleton*.

Gels can be formed by different solids with a lamellar structure. Soaps, glues and clays can be gels. Gels are solids of a special structure, so that bonds between some neighboring surfaces of these solids are weaker than inside these surfaces. Small bonds are broken under action of water, which penetrates the space between these surfaces. Then the solid swells, although it partially conserves its lattice or skeleton. This is the main peculiarity of gels.

Usually the basic peculiarity of a gel is its low viscosity, which varies sharply as a result of the sol–gel transition. The structure and properties of gels depend on their nature. In gels consisting of solutions involving amphiphilic molecules, water or a basic liquid is held by a structure of amphiphilic molecules. In the case of polymer solutions, a gel is formed by the sewing of polymer fibers with one another.

Thus a gel consists of a solid skeleton whose molecules are strongly bonded, so that the molecules of the skeleton attract the molecules of a liquid (water), but the binding energy between molecules of the skeleton and liquid is significantly weaker than the binding energy between neighboring molecules of the skeleton. Along with gels whose skeleton consists of amphiphilic molecules, there is another type of gel, the basis of which is a cross-linked polymer molecule. This molecule attracts the molecules of a liquid, and the total system has a *jellium-like structure*.

19.6 Charging of Particles in Suspensions

Suspensions are liquids with solid particles inside them. A simple example of a suspension is milk, where fat particles are found in water. The other example of a suspension is blood – a salt solution of water with blood corpuscles in them. A repulsive interaction between particles in liquids prevents them from coagulating, so that such a system can be stable. The charging of particles in suspensions is of importance for the stability of the suspension. In this case particles are repelled due to the identical charge sign and cannot approach. This effect is essential for polar liquids such as water and is typical of biological objects located both in natural water and in living organisms.

Because the particles of suspension of polar liquids are charged, their charge can influence the behavior of particles in the liquid. In particular, one can cause the coagulation of suspended particles by addition of certain salts or bases to the liquid. Below we determine the particle charge when it is located in a solution. We suppose that the particle charge results from the attachment of solution ions which move towards the particle under the action of its field. On contact with the particle's surface, the ions transfer to the particle their charge. For simplicity, we take the charge of the attaching ions to be equal to that of the electron e . This problem of *charging of a particle* in a liquid is similar to that in a weakly ionized gas, when the particle is charged as a result of attachment of ions to it. Analyzing this problem in the case of the motion of charged ions in a liquid, it is necessary to account for the dielectric constant of the liquid. Below, guided by the charging of small bulk particles in suspensions, we use the formalism for charging processes in an ideal plasma.

Our goal is to determine the ion currents on a particle surface located in a plasma or solution, and the equilibrium ion charge which is established when currents of positive and negative ions on the particle surface are equalized. A particle is assumed to be bulk and spherical, and the motion of ions in a plasma or solution is determined by their diffusion and drift under the action of the electric field of the charged particle. Then the number density of ions is zero on the particle surface and tends to the equilibrium value at large distances from the particle. Taking a particle charge to be Ze , where Z is the particle charge expressed in electron charges, we get for the current of positive ions to the particle at a distance R from it:

$$I_+ = 4\pi R^2 \left(-D_+ \frac{dN}{dR} + K_+ F N \right) e$$

The first term relates to diffusion motion, the second term corresponds to drift motion, N is the number density of ions, D_+ and K_+ are the diffusion coefficient and the mobility of positive ions in a solvent, e is an ion charge which is assumed to be equal to the electron charge, $F = Ze/(\epsilon R^2)$ is the electric field strength created by the particle, ϵ is the solvent dielectric constant. Using the Einstein relationship between the diffusion coefficient and mobility of ions $D_+ = eK_+/T$, where T is the gaseous temperature, we obtain for the current of positive ions on the particle surface

$$I_+ = -4\pi R^2 D_+ e \left(\frac{dN}{dR} - N \frac{Ze^2}{\epsilon T R^2} \right)$$

Assuming that ions do not recombine in a space because of their small density, we have that the ion current does not depend on R . Then one can consider the above relation for the ion current as the equation for the ion number density. Solving this equation with the boundary condition $N(r) = 0$, where r is the particle radius, we obtain:

$$\begin{aligned} N(R) &= \frac{I_+}{4\pi D_+ e} \int_r^R \frac{dR'}{(R')^2} \exp \left(\frac{Ze^2}{\epsilon T R'} - \frac{Ze^2}{\epsilon T R} \right) \\ &= \frac{I_+ T \epsilon}{4\pi D_+ Ze^2} \left[\exp \left(\frac{Ze^2}{\epsilon T r} - \frac{Ze^2}{\epsilon T R} \right) - 1 \right] \end{aligned}$$

Since the ion number density tends to the equilibrium value N_+ in a solution at large R far from the particle, we obtain from this the *Fuks formula* for the ion current to the particle surface

$$I_+ = \frac{4\pi D_+ N_+ Z e^3}{\epsilon T \{\exp[Z e^2 / (\epsilon T r)] - 1\}} \quad (19.10)$$

In the same manner, one can find the current of negative ions towards the particle, which has the form

$$I_- = \frac{4\pi D_- N_- Z e^3}{\epsilon T [1 - \exp[-Z e^2 / (\epsilon T r)]]} \quad (19.11)$$

This formula follows from (19.10) as a result of the change $Z \rightarrow -Z$ and replacing the parameters of positive ions by the parameters of negative ions.

In the stationary case the currents of positive and negative ions (19.10) and (19.11) to the particle surface are identical. Equalizing the currents of ions and taking into account the plasma or solution quasineutrality $N_- = N_+$ on average, we get for the charge of a small particle

$$Z = \frac{\epsilon r T}{e^2} \ln \frac{D_+}{D_-} \quad (19.12)$$

Thus the particle has a negative charge if $D_+ < D_-$, i.e. the mobility of positive ions is lower than that of negative ions or electrons. Note that the formulae are valid under the condition

$$r \gg \lambda, \quad r \gg \frac{e^2}{\epsilon T}, \quad r \gg r_D \quad (19.13)$$

where λ is the mean free path of ions, which is of the order of size of the solvent molecules. The first criterion (19.13) leads to the diffusion character of ion motion; the second criterion allows us to consider the particle charge Z as a continuous value; and owing to the third criterion one can neglect the action of ion fields on their motion near the particle.

19.7 Association in Electric Fields and Chain Aggregates

The rates of processes involving simple atomic particles – electrons, ions, atoms and simple molecules – can be varied under the action of external fields if these fields are of the order of atomic ones. An increase in particle size leads to a strong decrease in the typical fields which are able to vary the rates of processes involving these particles. Therefore moderate fields can influence the rates of processes with the participation of clusters or small particles. In order to show this, we first consider the association of two neutral spherical particles in a uniform electric field as a result of the interaction of induced dipole momenta. The interaction potential of two dipole particles at a large distance $\mathbf{R} = R\mathbf{n}$ ($\mathbf{n}$ is the unit vector along $\mathbf{R}$) between them is equal to

$$U = \frac{[\mathbf{D}_1 \mathbf{D}_2 - 3(\mathbf{D}_1 \mathbf{n})(\mathbf{D}_2 \mathbf{n})]}{R^3} \quad (19.14)$$

Since the dipole momenta of particles $\mathbf{D}_1$ and $\mathbf{D}_2$ are induced by the electric field, they are $\mathbf{D}_1 = \alpha_1 \mathbf{E}$ and $\mathbf{D}_2 = \alpha_2 \mathbf{E}$, where α_1 and α_2 are the particle polarizabilities and $\mathbf{E}$ is the induced electric field strength. Thus the interaction potential of particles is equal to

$$U = -\frac{\alpha_1 \alpha_2 E^2}{R^3} \cdot (3 \cos^2 \theta - 1)$$

where θ is the angle between vectors $\mathbf{R}$ and $\mathbf{E}$. As can be seen, the attraction of particles takes place over a small range of angles $0 < \theta < \arccos(1/\sqrt{3})$, but only this interval is responsible for the association of particles. The normal and tangential components of the force $\mathbf{f}$ between particles owing to the interaction of induced momenta are equal to

$$f_n = \frac{3\alpha_1 \alpha_2 E^2}{R^4} \cdot (3 \cos^2 \theta - 1), \quad f_\tau = \frac{3\alpha_1 \alpha_2 E^2}{R^4} \cdot \sin 2\theta \quad (19.15)$$

For simplicity, we neglect below the tangential force that corresponds to small angles θ . Then the angle θ does not vary during particle collision, and we have for the time of particle approach if initially the distance between them is R

$$\tau = \frac{2\pi\eta R^5 r_{ef}}{5\alpha_1 \alpha_2 E^2 (3 \cos^2 \theta - 1)} \quad (19.16)$$

where η is the gas viscosity, the effective radius of particles is $r_{ef} = (1/r_1 + 1/r_2)^{-1}$, and this expression follows from the equation for the relative motion of particles $f_n = 6\pi\eta r_{ef} dR/dt$.

To determine the average association time, we take a volume around the particle in the center-of-mass frame of reference in such a way that the time of approach at zero angle is the same as for other points of the surface. Then if R_o is the distance from this surface for $\theta = 0$, the corresponding distance for other angles $\cos\theta > 1/\sqrt{3}$ is equal to $R_o(3 \cos^2 \theta - 1)^{1/5}$. This elemental volume equals

$$V = \int_0^{R_o} R^2 dR \int_{1/\sqrt{3}}^1 2\pi d \cos \theta \cdot [(3 \cos^2 \theta - 1)/2]^{3/5} = 0.52 R_o^3$$

Thus, averaging over the initial relative positions of particles, we get

$$\bar{\tau} = \frac{2.8\eta r_{ef}}{\alpha_1 \alpha_2 E^2 N^{5/3}} \quad (19.17)$$

and the effective rate constant of the process is

$$k_{ind} = \frac{1}{N\bar{\tau}} = 0.35 \frac{\alpha_1 \alpha_2 E^2 N^{2/3}}{\eta r_{ef}} \quad (19.18)$$

One can compare the rate constants of association of two neutral spherical particles as a result of the diffusion motion in a buffer gas and due to the interaction of induced dipole

momenta under the action of an external electric field. Taking two identical small metallic particles ($\alpha_1 = \alpha_2 = r^3$), we get from formulae (19.18)

$$\frac{k_{ind}}{k_{dif}} = 0.27 \frac{E^2 N^{2/3} r^5}{T} \quad (19.19)$$

i.e. association in an external electric field due to interaction of induced electric momenta is preferable at high electric field strengths, large sizes and large number densities of particles. In particular, the role of this association mechanism increases with increasing particle size.

Association in an external electric field is of importance for the growth of stretched particles. Such particles are called *chain aggregates*, and some examples of these particles are given in Figure 19.4. In order to show the tendency of stretched particles to grow in an external electric field, we consider below the character of interaction and association of a cylindrical particle of length $2l$ and of radius r with a spherical particle of the same radius in a uniform electric field of strength E . The electric field creates induced dipole momenta of particles D_1 and D_2 , and association of particles results from the interaction of these induced momenta. Assuming $l \gg r$, we take the axis of the cylindrical particle to be directed along the electric field. Supposing particles to be similar to metallic ones, we have for their polarizabilities

$$\alpha_1 = \frac{l^3}{3 \left(\ln \frac{l}{r} - 1.6 \right)}, \quad \alpha_2 = r^3$$

and the induced dipole momenta are $D_1 = \alpha_1 E$ and $D_2 = \alpha_2 E$. In this approximation the induced dipole moment of each element of the cylindrical particle is proportional to its length, independent of its position. Considering large distances between particles compared to their radii, we take a spherical particle as a point, so that the interaction potential between induced

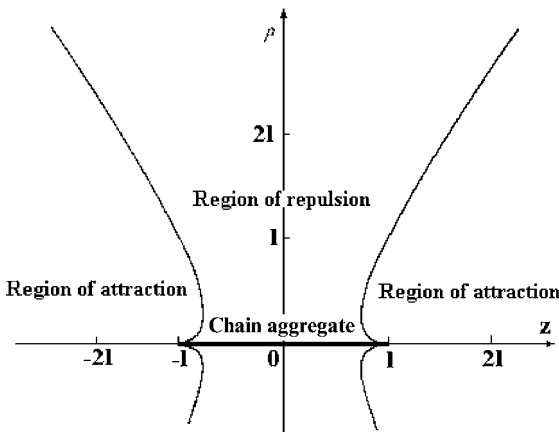


Figure 19.4. Typical chain aggregates resulted from joining of solid particles.

dipoles is given by the following expression:

$$U = \int \frac{d\mathbf{D}_1 \cdot \mathbf{D}_2 - 3(d\mathbf{D}_1 \cdot \mathbf{n})(\mathbf{D}_2 \mathbf{n})}{R^3}$$

$$= \frac{\alpha_1 \alpha_2 E^2}{2l} \int_{-l}^l \frac{dz}{[(z - z_2)^2 + \rho^2]^{3/2}} \left[1 - 3 \frac{(z - z_2)^2}{(z - z_2)^2 + \rho^2} \right]$$

where z is the coordinate along the field for the cylindrical particle, z and ρ are cylindrical coordinates of the spherical particle, and the origin is located at the center of the cylindrical particle. From this expression it follows that the form of the interaction potential due to the interaction of induced dipole momenta is as given in Figure 19.5. A spherical particle is repelled from the trunk of a cylindrical particle and is attracted to its poles.

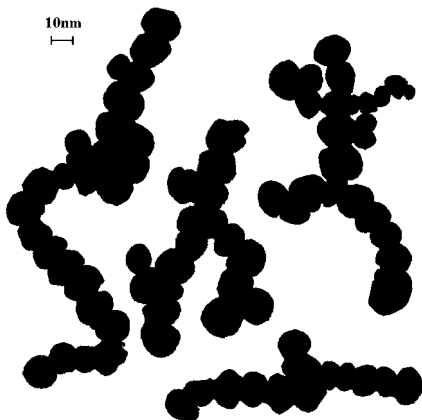


Figure 19.5. The character of interaction of induced dipole momenta for a cylindrical and spherical metallic particles of identical radii in an external electric field.

From the above expression we get in the case when the spherical particle is located at distances $R \gg r$ from the end of the cylindrical particle and near its axis

$$U(R) \sim \frac{D_1 D_2}{l^2 R}$$

In particular, for $R \gg l \gg r$ this formula has the form

$$U(R) = -3 \frac{D_1 D_2}{l^2 R}$$

Neglecting the logarithm terms, we estimate the force of attraction of a spherical particle to a cylindrical one if the approach of the particles is retarded due to the viscosity of a spherical particle in a buffer gas

$$F = 6\pi r v \eta = -3 \frac{D_1 D_2}{l^2 R^2}$$

where $v \sim dR/dt$ is the velocity of particle approach and η is the viscosity coefficient. In this approximation, we get for the typical time of attachment of spherical particles to a cylindrical

one

$$\tau \sim \frac{r\eta R^3 l^2}{D_1 D_2} \sim \frac{\eta R^3}{r^2 l E^2} \sim \frac{\eta}{r^2 l E^2 N} \quad (19.20)$$

where $N \sim R^{-3}$ is the number density of spherical particles. This expression requires the following criterion:

$$N l^3 \gg 1$$

From this we find the effective rate constant of attachment of a spherical particle to a cylindrical one

$$k_{cyl} \sim \frac{r^2 l E^2}{\eta} \quad (19.21)$$

As we can see, this rate constant due to the interaction of induced dipoles does not depend on the number density of spherical particles. We emphasize that the attachment of one spherical particle increases the length of a cylindrical particle by a value of the order of r . Hence a typical time for the growth of a cylindrical particle τ_l , i.e. the typical time over which its length increases significantly, is

$$\tau_l \sim \frac{l}{r} \tau \sim \frac{\eta}{E^2 N r^3} \quad (19.22)$$

Note that this does not depend on the length l of the cylindrical particle. When this particle is located in matter (gas or liquid) of temperature T , the particle axis is directed along an electric field if

$$E^2 \gg \frac{T}{l^3} \quad (19.23)$$

This criterion is fulfilled for a long particle even at low electric field strengths and shows that this mechanism of association starts from a certain length of the forming particle. Another criterion requires that spherical particles subsequently attach to the ends of a cylindrical particle and has the rough form

$$E^2 \gg \frac{T}{l r^2} \quad (19.24)$$

i.e. it is valid for large particles and high electric fields. For example, taking typical parameters of a particle $r \sim 0.1 \mu\text{m}$, $l \sim 10 \mu\text{m}$, we obtain according to this criterion at room temperature $E \gg 200 \text{ V/cm}$, and this cylindrical particle with high conductivity is arranged along the field according to criterion (19.23) at $E \gg 2 \text{ V/cm}$.

From this analysis it follows that long chain aggregates, which result from the association of solid particles due to the interaction of induced dipole momenta, tend to become cylindrical ones with an increase in their length if the forming cylindrical particle conserves high conductivity during its growth. Thus, an external electric field can affect both the rates of association of clusters or small particles and the shape of forming particles. Note that the above estimations relate to the growth of chain aggregates in gases. In reality, a more widespread situation

corresponds to the growth of particles of rod form in a direction perpendicular to the charged surface as a result of the attachment of small particles to this growing particle. Another case relates to the growth of particles in liquids and solutions under the action of an external electric field. Then the dielectric properties of liquids must be taken into account. Thus we obtain that the growth of large particles in an external electric field leads to the formation of chain aggregates (Figure 19.4), a bound system of small particles with shape of a rod.

20 Fractal Systems

20.1 Fractal Dimensionality

Usually we divide atomic systems into gaseous and condensed ones. In gases, the interaction potential of nearest atoms is small compared with their kinetic energy. A system of bound atoms for which the opposite criterion is valid is considered as a condensed state. In turn, condensed states are divided into two aggregate states, solid and liquid, depending on the symmetry of the system and mobility of atoms in it. Usually condensed states respect the continuous structure of atomic matter, so that the properties of this matter are repeated on average on distances of the order of typical atomic sizes. Alongside continuous systems of bound atoms or bound molecules, real physical systems can have a rare *fractal structure*, which we consider below.

We shall focus on structures which result from the joining of small particles located in a gas. Assume that these particles have a simple chemical nature, for example they consist of metallic atoms or molecules of oxides. Then the stable state of the atoms or molecules corresponds to a compact structure. But solid particles may be bonded at their points of contact and form a porous system. Unless such a system is small, it has a fractal structure and is called a *fractal aggregate*. Before considering fractal aggregates we analyze the general properties of fractal systems.

As their name suggests, fractal systems have a dimensionality that differs from the dimensionality of the space in which they exist. Let us demonstrate this with an example of the

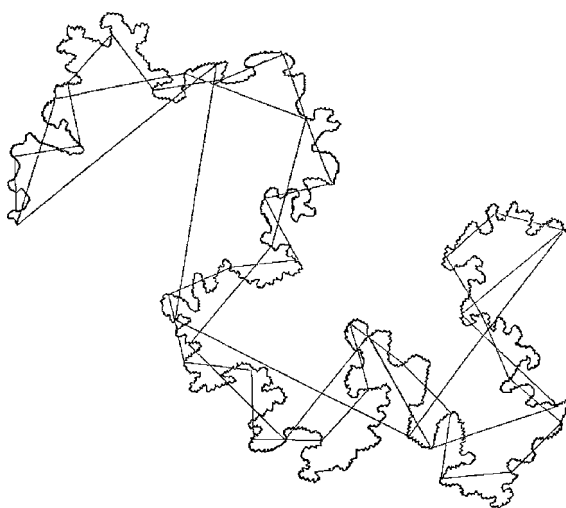


Figure 20.1. Fractal line corresponded to a river or the boundary of a sea, lake or island. The method to measure the curve length is shown when we change this curve by segments of an identical length. The fractal dimensionality of this curve obtained on the basis of this method is equal to 1.43 ± 0.03 .

measurement of the length of a coastline (see Figure 20.1), which could be the perimeter of an island or lake, the length of a river and so on. In order to measure it, we choose a certain scale and join points of the coastline which are separated from each other by this distance. For example, if we measure the lake perimeter by distribute beacons at a distance of 1 km, the distance in kilometers is given by the number of beacons used. In another measurement, we follow the coastline on foot, without departing from the coastline by more than, say, 0.1 m. Expressing the length in numbers of steps and comparing this with the result of the first measurement, one can easily see that the coastline's length in the second case is more than that in the first case. Let us make one more measurement by allowing to an ant to crawl along the coastline without departing from it by more than the width of its body. In this case the length will be greater than in the previous cases.

Evidently, the different results of these measurements are explained by the fact that the more closely we are able to follow the irregular form of the coastline, the smaller the scale that is used. Hence the line length L depends on the scale and can be represented in the form

$$L = a \left(\frac{l}{a} \right)^D \quad (20.1)$$

where a is the scale size and l is the distance between the ends of the line. The value D is called the *fractal dimensionality*. This value for geographical lines on a map is usually 1.3–1.4.

Another example of a fractal line is the trajectory of the *Brownian motion* of a particle. The square of the displacement of a particle after n steps is equal to

$$l^2 = \left(\sum_i \mathbf{r}_i \right)^2 = \sum_{i=1}^n r_i^2 + \sum_{i \neq k} \mathbf{r}_i \mathbf{r}_k$$

where $\mathbf{r}_i$ is the radius vector of the i th displacement. Assuming the directions of the displacements of a particle to be random, we find that the second term on the right-hand side of the above relation is zero. Introducing $a^2 = \overline{r^2}$, we get $l^2 = na^2$. Reducing this formula to (20.1) and accounting for $n = L/a$, we obtain in this case

$$L = a \left(\frac{l}{a} \right)^2 \quad (20.2)$$

i.e. the fractal dimensionality of the trajectory of the Brownian motion is equal to two. Note that this value does not depend on the space dimensionality.

Let us consider one more type of fractal lines, which are called *Koch figures*. In this case we take a segment of a straight line and transform it according to a certain algorithm. By repeating this operation with each segment of the figure several times, we obtain a symmetric fractal line, as shown in Figure 20.2. According to formula (20.2), the fractal dimensionality of the Koch figure is equal to

$$D = \frac{\ln m}{\ln l} \quad (20.3)$$

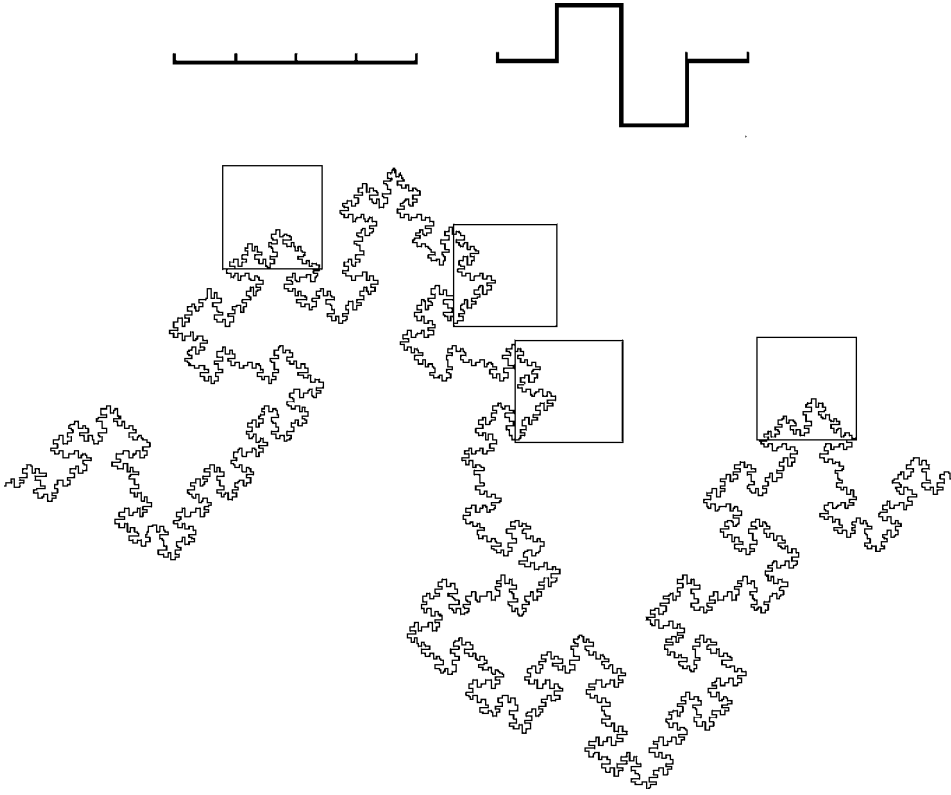


Figure 20.2. The Koch figure: (a) the algorithm of transformation of segments; (b) the Koch figure resulted from four transformation of the segment.

where l is the number of parts into which the elemental segment is divided for each operation, and m is the number of new elements which result from one elemental segment. In particular, in the case of Figure 20.2 the fractal dimensionality of the Koch figure equals $D = \ln 8 / \ln 4 = 1.5$.

It is convenient to consider fractal systems as consisting of a large number of identical elements. For example, an element of the fractal lines in the above examples is an individual segment. In this definition, it is convenient to introduce the *correlation function*

$$C(r) = \frac{1}{n} \sum_i \rho(\mathbf{r}_i) \rho(\mathbf{r}_i + \mathbf{r}) = \frac{\overline{\rho(\mathbf{r}' + \mathbf{r}) \rho(\mathbf{r}')}}{\overline{\rho(\mathbf{r}')}} \quad (20.4)$$

where n is the total number of elements of the fractal system, i is an element number and ρ is the density of elements at this point, so that it is one at a point occupied by elements of the system, and zero at a point not occupied by them; the bar means averaging over the positions of the elements in a volume under consideration. In fact, the correlation function is the mean

density of a fractal system at a distance r from an occupied point. The correlation function does not depend on angles because of the character of averaging.

It is clear that the correlation function drops with increasing distance r from an occupied point. Let us use the approximation

$$C(r) = \frac{const}{r^\alpha} \quad (20.5)$$

where r is significantly larger than the size of an individual element of the structure or a scale size. In this case the fractal dimensionality of a system is introduced as

$$D_\alpha = d - \alpha \quad (20.6)$$

where d is the space dimensionality.

The other definition of the fractal dimensionality of the system relates to its size. Let us introduce the *gyration radius* R of a system of bound particles as its typical size on the basis of the relation

$$R^2 = \frac{1}{2n^2} \sum_{i,j} |\mathbf{r}_i - \mathbf{r}_j|^2 \quad (20.7)$$

where n is the total number of particles or elements of a fractal system, $\mathbf{r}_i$ and $\mathbf{r}_j$ are the coordinates of particles, and the factor 2 in the denominator accounts for each pair being included in this sum twice.

The gyration radius of a fractal system R grows with an increase in the number of elements n that constitute this system. The fractal dimensionality of the fractal system can be introduced on the basis of the relation

$$n \sim R^{D_\beta} \quad (20.8)$$

Note that according to formula (20.5) the number of individual elements n in a sphere of a radius R which cuts off a part of the system is equal to

$$n \sim R^{D_\alpha} \quad (20.9)$$

As we can see, the difference between definitions (20.8) and (20.9) of the fractal dimensionality of a system is such that the first definition relates to parts of the same fractal system, while the second definition deals with fractal systems of the same type and different sizes. Both definitions use the identical concept of fractal systems, though the fractal dimensionalities D_α and D_β can differ slightly for real fractal systems.

One may use not only spherical, but any identical forms of cutting parts of the system to determine the fractal dimensionality. To demonstrate this operation, we consider one more Koch figure (Figure 20.3) which is constructed on the basis of the algorithm indicated in the upper right corner of this figure. Its fractal dimensionality equals $D = \ln 10 / \ln 4 = 1.66$. Let us take a rectangle whose length is equal to the length of the initial straight line segment. The other side of the rectangle is a parameter which is similar to the sphere radius in formula (20.4), and in each case we calculate the number of elements of the Koch figure inside a rectangle.

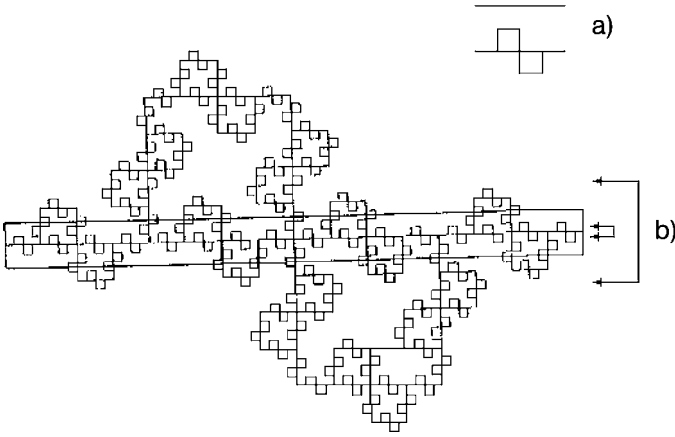


Figure 20.3. The Koch figure resulted from three transformations of the segment on the basis of the algorithm which is indicated in the right upper corner. The method of cutting off parts of the figure is shown.

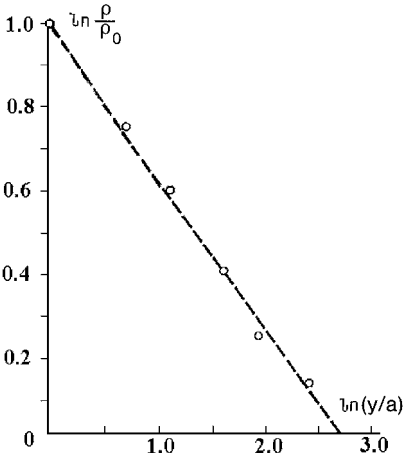


Figure 20.4. The density of pieces of the Koch figure of Fig. 20.2 as a function of the width y of a rectangle, in which is located this cluster piece. The density is expressed in arbitrary units, a is the length of the figure segments. The broken line corresponds to the fractal dimensionality $D = 1.64$ instead its accurate value $D = \ln 10 / \ln 4 = 1.66$.

From this one can find the density of individual segments of the Koch figure inside a rectangle depending on the size of its side. The results of this operation are given in Figure 20.4. The resulting fractal dimensionality is characterized by a certain accuracy with respect to the accurate value. Note that the accuracy of the above operations to determine the fractal dimensionality depends on the number of elements of a fractal system and the number of fractal systems of such a type constructed in an identical way. Correspondingly, the fractal dimensionalities obtained by different methods coincide within a certain accuracy.

20.2 Fractal Aggregates

Let us consider a system of identical spherical solid particles so that the contact of two particles leads to their joining. Evidently, the optimal structure of a system of these bound particles is the structure of close packing which corresponds to the maximum density of particles and provides the maximum number of bonds for neighboring particles. Other structures are metastable with respect to this one. Nevertheless, they can be formed if the binding energy of two particles is enough high. Then the structure of a system of bound particles depends on the way in which the system was formed and the conditions of this process. Rare structures of these particles with fractal properties are called *fractal aggregates*.



Figure 20.5. A typical two-dimensional DLA fractal aggregate.

Below we consider two models of formation of fractal aggregates which are of interest for real systems. In both cases particles are located in a buffer gas and hence have *Brownian motion* within the gas. In the first case free particles attach to particles of a fractal aggregate as a result of their contact, and the fractal aggregate grows in this way. This character of the cluster growth is called *diffusion-limited aggregation* (DLA) and the corresponding model is called the *Witten–Sander model*. A typical cluster of such a type in the two-dimensional space is shown in Figure 20.5. The other character of cluster growth corresponds to the joining of two solid particles in a small cluster, and then small clusters join in clusters of larger sizes, as shown in Figure 20.6. This mechanism of cluster growth is named *cluster–cluster aggregation* (CCA) and usually takes place in reality if fractal aggregates result from nucleation of a vapor, and this process proceeds through the formation of small solid particles. Figure 20.7 demonstrates a typical example of such a structure when gold fractal aggregates are generated in a solution.

The above models reflect the basic mechanisms of assembling fractal aggregates from solid particles in a buffer gas. Table 20.1 gives the fractal dimensionalities of fractal aggregates for two-dimensional ($d = 2$) and three-dimensional ($d = 3$) space if these aggregates are assembled both in a buffer gas (Brownian motion of particles) and in a vacuum (rectilinear motion of particles). These data are based on the assumption that any contact leads to the formation of a bond between the particles. The last case relates to a small sticking probability

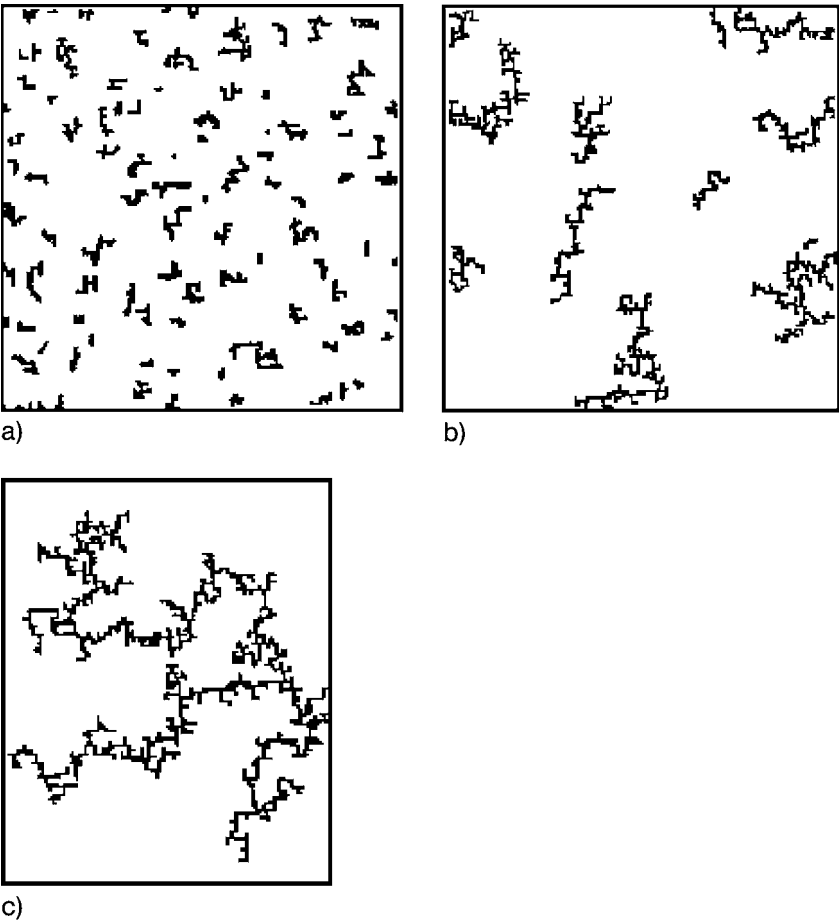


Figure 20.6. The character of growth of the CCA fractal aggregate in time as a result of transformation of individual particles and small clusters in clusters of larger sizes.

Table 20.1. Fractal dimensionalities of clusters resulting from the aggregation of solid particles.

Mechanism of aggregation	$d = 2$	$d = 3$
Rectilinear trajectory, particle–cluster	2	3
Rectilinear trajectory, cluster–cluster	1.54 ± 0.03	1.94 ± 0.08
Brownian motion, particle–cluster	1.68 ± 0.02	2.46 ± 0.05
Brownian motion, cluster–cluster	1.44 ± 0.04	1.77 ± 0.03
Small sticking probability, cluster–cluster	1.55 ± 0.03	2.02 ± 0.06

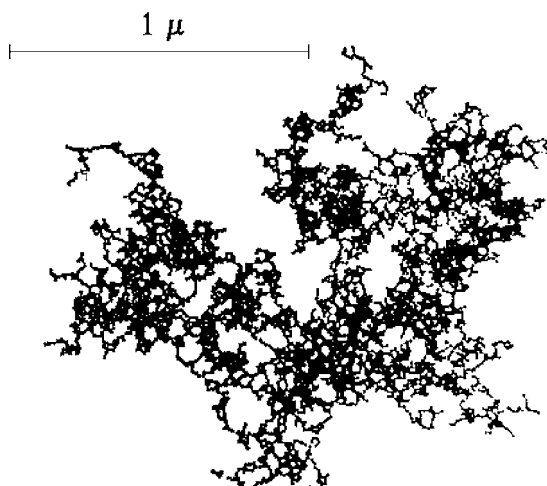


Figure 20.7. The projection of the gold fractal aggregate which is formed in the solution. It is a typical CCA fractal aggregate.

and is characterized by a higher fractal dimensionality for the cluster formed, because in this case particles penetrate inside the aggregate more deeply. For this reason the fractal dimensionality of clusters in the case of a rectilinear trajectory of joining particles is higher than in the case of Brownian motion. Note the large fluctuations of aggregate parameters which lead to an error in their fractal dimensionalities.

The additional parameter of an aggregate is the mean *coordination number*, i.e. the average number of nearest neighbors for aggregate particles. This value for the DLA aggregate resulting from the Brownian motion of particles is equal to 2.20 ± 0.02 in two-dimensional space and 2.25 ± 0.01 for three-dimensional space if the attachment probability is one. Hence, the DLA aggregate consists of arms which grow from a center, and the coordination number characterizes the degree of branching of these arms.

These two models correspond to the basic methods of formation of fractal aggregates which grow as the result of joining of solid particles. We do not deal here with various modifications of these models which account for the details of real processes. Note that the density of these fractal aggregates decreases with increasing size, in accordance with formula (20.5), and therefore large fractal aggregates cannot exist. In reality, the size of a fractal aggregate exceeds the size of the particles which constitute the aggregate by approximately three or four orders of magnitude.

20.3 Fractal Objects Similar to Fractal Aggregates

We consider fractal aggregates as random systems of bound particles which have a latent internal order on average due to the correlation (20.5) between the positions of individual particles. This gives an additional property of the system which is valid in a restricted range of parameters. In particular, for fractal aggregates the relation (20.5) is valid over a range $a \ll r \ll R$, where a is the size of an elemental particle, R is the size of the total system, and r is the distance between particles where the fractal property (20.5) is valid for this system. Evidently

this property can be useful for other systems. Below we consider systems and phenomena which have a fractal nature similar to that of DLA aggregates, analyzing the aggregation process from another standpoint. Let us describe the growth of the DLA aggregate on the basis of the continuity equation for the number density N of nucleating particles, which now has the form (20.9)

$$\frac{\partial N}{\partial t} = D\Delta N$$

In the stationary case this is transformed into the Laplace equation

$$D\Delta N = 0 \quad (20.10a)$$

with the boundary condition

$$v = -a\mathbf{n}\nabla N \quad (20.10b)$$

where a is a numerical coefficient and $\mathbf{n}$ is the unit vector directed perpendicular to the boundary.

Under this boundary condition an instability develops, because the velocity of the boundary is higher for points with larger curvatures. This instability breaks the continuous form of the boundary and leads to the fractal form of the boundary surface. Hence, the description of the growth of DLA aggregates on the basis of equations (20.10) is analogous to the Witten–Sander model when the aggregate is formed from individual particles. But because of the instability of equations (20.10), the supplemented relation can be added to it, which gives the minimal scale of a fractal aggregate. In the case of the Witten–Sander model, this value is given automatically as the particle size. In other problems the supplementary relation may follow from the physical conditions of a system or phenomenon under consideration. Thus, equations (20.10) with supplementary physical conditions are capable of describing fractal systems.

Let us consider other physical systems which are analogous to the DLA aggregate. The phenomenon of *dielectric breakdown* is governed by the Laplace equation $\Delta E = 0$ for the electric field strength in a dielectric medium, and the typical scale is determined by the character of amplification of the electric field at the tip of a charged needle where electrons are gathering. In this case current channels consist of several arms with branching and are similar to the two-dimensional DLA aggregate. The other example is the crystallization of a film on an amorphous surface if this process is determined by the propagation of a thermal wave. To describe this process we have the equation $\Delta T = 0$ instead of (20.10). The crystallization process at some film point leads to an energy release which causes heating of neighboring regions. The size of an inhomogeneity is determined by the thermal connection between the film and substratum. The crystallization process at this point starts when it finishes at a neighboring point, so that the crystallization process at this point is similar to the growth of a DLA aggregate, and the structure of the crystal region is similar to a DLA aggregate in two-dimensional space.

Let us consider a hydrodynamic phenomenon which is similar to DLA aggregation and which proceeds at the boundary of two liquids with different viscosities when a gas or liquid of small viscosity displaces a liquid with a large viscosity (for example, air or water displaces

oil or glycerine). Then the structure of an inserted species in a liquid of higher viscosity has the form of fingers, and this process is called *viscous fingering*. It is described by the equation $\Delta p = 0$, and fingers have a fractal structure. The minimum size of this structure is determined by the viscosity coefficient of the high-viscosity liquid, by the velocity of insertion in this liquid of the low viscosity liquid, and by the liquid–liquid interfacial tension coefficient.

The above examples examine the latent analogy between various physical systems and phenomena. Fractal properties can appear in various random systems and phenomena. For example, in the case of the *turbulent motion* of a gas, the correlation function (20.4) and the specific energy ε which is converted in vortices are connected by the following relation

$$\overline{\varepsilon(\mathbf{r})\varepsilon(\mathbf{r} + \mathbf{r}') } = \overline{\varepsilon^2} \left(\frac{l}{r} \right)^{d-D}$$

This relation is valid at distances in the turbulent liquid $l_d \ll r \ll l$, where l is a typical mixing length, l_d is a typical length for energy dissipation and d is the space dimensionality. In the three-dimensional space the fractal dimensionality of this phenomenon equals $D = 2.5\text{--}2.7$. As follows from the above examples, fractal properties are latent properties of random systems or phenomena which are valid over a finite range of corresponding parameters. Understanding this property is useful for the analysis of such systems and phenomena because the fractal property gives additional information about the system.

20.4 Percolation Clusters

Let us consider a *percolation cluster* which has a fractal structure, but differs from a fractal aggregate in principle. We take a crystal lattice and fill its sites in a particular way, so that the probability p of filling of a site is introduced as a parameter of this system. By joining the neighboring occupied sites we obtain so-called percolation clusters. They are of interest for problems of two kinds. In the first case, one can consider occupied sites of the lattice as pores and study the flow of a liquid or gas through these pores. In the second case, one can consider occupied sites as metallic atoms, while nonfilled sites are dielectric atoms. Assuming that an electric current passes through this system only between neighboring metallic atoms, one can study the propagation of an electric current through this system.

Figure 20.8 gives an example of a system under consideration for the two-dimensional square lattice. Evidently, there is a threshold probability p_c of site occupation at which the largest percolation cluster connects opposite sides of the lattice. This critical value is called the *percolation threshold*. It is equal to $p_c = 0.593$ for the two-dimensional square lattice and to $p_c = 0.5$ for the two-dimensional triangular lattice. Percolation processes start if the density of occupied sites exceeds the percolation threshold.

Let us introduce the cluster mass M as the number of knots joined in this cluster, which is an analog of cluster elements in formula (20.8). Below we consider the fractal properties of percolation clusters near the percolation threshold. The mass of the largest cluster M_o as a function of a lattice size L is determined by the relation

$$M_o \sim L^D \tag{20.11}$$

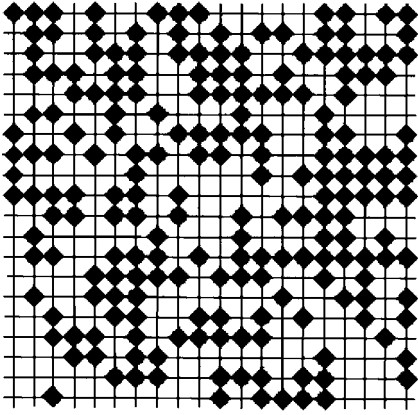


Figure 20.8. The percolation cluster on the square net where one half of sites is occupied. The percolation threshold is higher and equals 0.593.

where D is the fractal dimensionality, which equals $D = 1.89$ for the two-dimensional square lattice and $D = 91/48 = 1.90$ for the two-dimensional triangular lattice. Note that the lattice size L is of the order of the gyration radius for largest clusters in this case. From formula (20.11) there follows for clusters of mass M and gyration radius R (formula (20.7)) the following relation

$$M \sim R^D \quad (20.12)$$

We obtain this relation restricted to the size R of the lattice, so that a cluster of this size will be the largest one for new boundaries of the lattice. Formula (20.12) is similar to formula (20.8). From this there follows the analogy of the percolation cluster with other fractal systems.

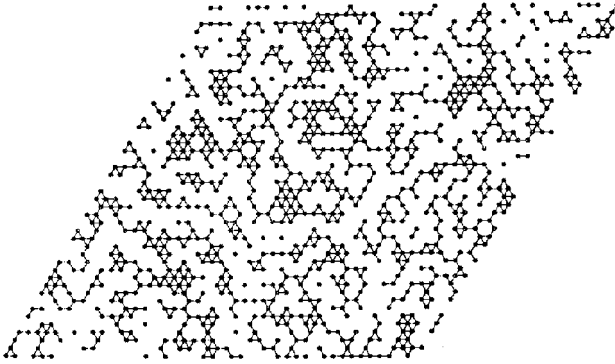


Figure 20.9. The percolation cluster on the triangle net at the percolation threshold when one half of sites is occupied.

For simplicity, we restrict ourselves to studying the triangular lattice (Figure 20.9). Let us make the *renormalization transformation* of the triangular lattice, as shown in Figure 20.10. As a result, the number of sites of a new lattice decreases by a factor of 3. The extracted triangles are transformed into the sites of a new lattice, and we consider this site to be occupied if three or two vertices of the primary triangle are occupied. Then the density of occupied sites of a new lattice is equal to

$$p' = p^3 + 3p^2(1 - p) \quad (20.13)$$

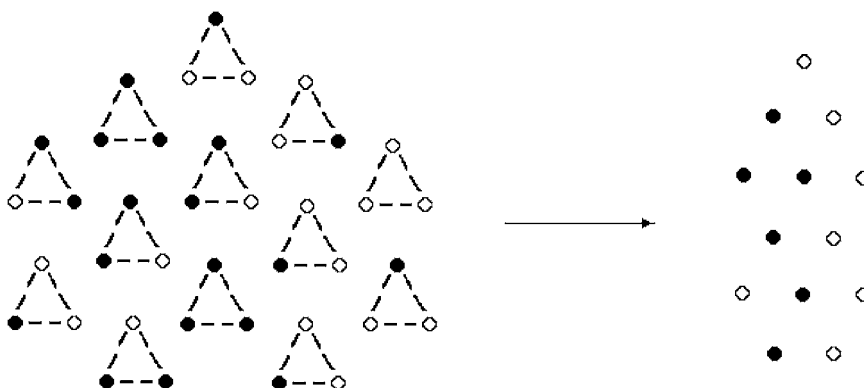


Figure 20.10. The character of transformation of a percolation cluster on the triangle net. A number of sites of a new lattice resulted from one operation of the cluster transformation decreases in 3 times, so that a triangle of three sites is transformed in one site. This site is occupied if the incident triangle contains three or two occupied sites, and it is free if a number of occupied sites is one or zero.

and the first term on the right-hand side of this relation corresponds to the filling of three vertices, and the second one corresponds to the occupation of two vertices. One can see that if $p < p_c$, the density of occupied sites in a new lattice decreases, while if $p > p_c$, the density of occupied sites increases. Thus the critical density, i.e. the threshold percolation density, is determined by the equation

$$p_c = p_c^3 + 3p_c^2(1 - p_c) \quad (20.14)$$

The solution of this equation gives the threshold percolation density $p_c = 0.5$. Thus the method of transformation of a percolation cluster located in a triangular lattice allows us to determine the percolation threshold.

Assume that the size of the primary triangle lattice varies by a factor s as a result of some renormalization transformations. Evidently, we have in this case

$$M_o(L) = C(s)M_o(L/s)$$

where L is the gyration radius of clusters or the lattice size for largest clusters before renormalization, and $C(s)$ is a function of scale change. One can see that the relation (20.11) is valid if we take $C(s) = s^D$. Thus we have the following scaling relation for percolation clusters of maximum size in the limit of large L

$$M_o(L) = s^D M_o\left(\frac{L}{s}\right) \quad (20.15)$$

One can rewrite this relation in the form

$$M(R) = s^D M\left(\frac{R}{s}\right) \quad (20.16)$$

where the argument is the gyration radius for clusters of a given mass. Note that according to formula (20.11) the mass of the largest clusters is $M \sim L^D$, where L is a lattice size, while the total mass of clusters for this lattice (or the total number of lattice occupied sites) is $\sim L^2$. From this it follows that large clusters give a small contribution to the total mass of occupied sites.

Let us determine the size distribution function for large percolation clusters. Denoting by $f_M dM$ the probability that a given site of the lattice belongs to clusters with a mass that ranges from M up to $M + dM$, we take the mass dependence of the size distribution function in the form

$$f_M \sim M^{-\tau} \quad (20.17)$$

Next, we make the renormalization transformation of the two-dimensional triangular lattice near the percolation threshold $L' = L/s$. Then a cluster of mass M is transformed into a cluster of mass M' , and because the concentration of occupied sites does not vary at the percolation threshold, we have $M' = M/s^D$. Since the scale varies by a factor of s , we obtain

$$f_M = f_{M'}/s^2$$

Comparing this with the relation that follows from (20.17)

$$\frac{f_M}{f_{M'}} = \left(\frac{M'}{M} \right)^\tau = s^{-D\tau}$$

we get

$$\tau = \frac{2}{D} \quad (20.18)$$

In the case of the two-dimensional triangular lattice we have $\tau = 1.055$.

Let us introduce the average connection length

$$\zeta^2 = \langle R^2 \rangle \quad (20.19)$$

where R is the gyration radius of a cluster, and an average is made over all the clusters of the lattice. Evidently, for an infinite lattice we have at $0 < p_c - p \ll p_c$ the following dependence

$$\zeta(p) \sim |p_c - p|^{-\nu} \quad (20.20)$$

with some value of the power, and the value ζ^2 tends to infinity when $p \rightarrow p_c$. If we change the scale by a factor of s , the variation of this value is $\zeta' = \zeta(p') = \zeta(p)/s$. Equation (20.13) for p' gives in this case $p_c - p' = \frac{3}{2}(p_c - p)$ if the scale varies by a factor of $\sqrt{3}$, and

$$p_c - p' = \left(\frac{3}{2} \right)^\lambda (p_c - p)$$

if the scale varies by a factor of λ , so that $\lambda = \ln(3/2)/\ln\sqrt{3}$. From this and the relation $\zeta(p') = \zeta(p)/s$ we get for the power in the expansion of the connection length

$$\nu = \ln\sqrt{3}/\ln(3/2) = 1.355 \quad (20.21)$$

Thus the property of self-similarity of percolation clusters allows us to analyze their asymptotic properties.

Now let us determine the dependence $\zeta^2(L)$ by the use of formula (20.19)

$$\zeta^2 = \frac{\int R^2 f_M dM}{\int f_M dM} \sim \int R^2 f_M dM$$

On the basis of formula (20.17) we have

$$f_M = M^{-\tau} F\left(\frac{M}{L^D}\right)$$

where $F(x)$ is a universal function. Using formula (20.12), we get

$$\zeta^2 \sim L^{2D}$$

We use that the main contribution to this integral follows from large cluster sizes $R \sim L$, while smaller cluster sizes $R \ll L$ determine the normalization condition $\int f_M dM = p_c$.

This analysis shows that the percolation cluster is a typical fractal system which has general fractal properties in accord with relations (20.8) and (20.9). On the other hand, the percolation cluster requires another analysis compared with fractal aggregates because of their different nature, and other physical properties of this system are of interest. Hence various fractal systems must be analyzed separately in connection with phenomena involving these systems. The fractal property gives additional information for each system, but does not unify these systems as physical objects.

20.5 Aerogel

Let us consider the formation of CCA aggregates from particles located in a buffer gas. This process proceeds in accord with Figure 20.6. As clusters grow their density increases, and if the aggregates formed are stable enough, the process finishes when the density of particles in the aggregates becomes equal to their initial density in a gas. At this density, surface particles of neighboring aggregates form bonds, and as a result, a large system of bound particles is formed which occupies the whole volume. This system is called an *aerogel*, and its structure is given in Figure 20.11.

Though aerogels are usually produced in a liquid phase, this consideration allows us to understand general aerogel properties. At small distances an aerogel has fractal properties (20.4) and (20.5), i.e. there is a correlation in the positions of particles that constitute it. For large distances an aerogel is uniform. The distance of transition between these positions is called the *correlation length*. For example, in the case of CCA aggregates the correlation length R_c follows from the relation

$$N \cdot \frac{4\pi R_c^3}{3} = \left(\frac{R_c}{a}\right)^D$$

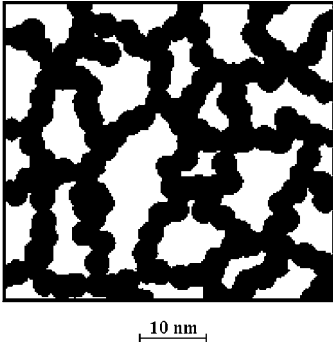


Figure 20.11. Aerogel.

The left- and right-hand sides of this relation are the number of particles in an aggregate of critical size. Here N is the number density of particles in a gas and a is the particle radius. This gives for the correlation length of an aerogel

$$R_c = \left(\frac{3}{4\pi N} \right)^{1/(3-D)} a^{-D/(3-D)} \quad (20.22)$$

In particular, for an aerogel which is formed from CCA aggregates this quantity is equal to ($D = 1.8$)

$$R_c = 0.3 \frac{a}{(Na^3)^{0.83}} \quad (20.23)$$

Aerogels are produced in liquids under supercritical conditions that allow one to remove molecules which are absorbed by the pores of a forming aerogel. The best-known aerogel material is SiO_2 , though aerogels of other ceramics and other materials can be produced in a similar way. Ceramics which consist of oxide molecules are characterized by the highest binding energies between molecules, so that contact between oxide particles provides the maximum bonding between particles. In fact, aerogels are porous substances, and pores occupy almost all the volume of aerogels. The density of an aerogel can vary over a wide range, with a limit at the density of air. The fractal dimensionality at close distances in aerogels ranges from 2.1–2.3. An aerogel is an example of a porous bulk system which is characterized by fractal properties.

20.6 Fractal Fiber

A *fractal fiber* (Figure 20.12) is another example of a bulk system with fractal properties. An aerogel is a uniform system at large distances, whereas the anisotropy structure of a fractal fiber results from its formation in an external field. Indeed, let us consider the character of the growth of a cluster consisting of fractal aggregates when it proceeds in a uniform electric field and is determined by the interaction of induced dipole momenta of fractal aggregates. Modeling fractal aggregates by a spherical metallic particles, we obtain the process of the growth of fractal systems to be similar to that for solid metallic particles in an external electric field, as considered in Section 19.7.

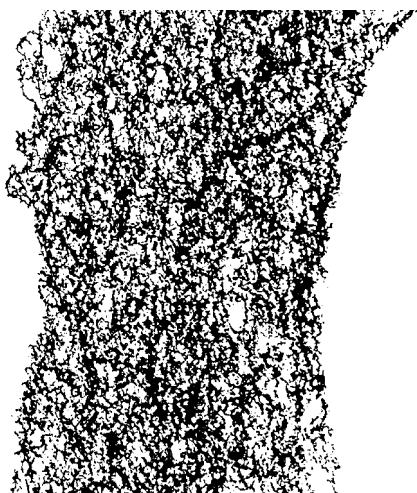


Figure 20.12. Fractal fiber.

Indeed, modeling a fractal aggregate by a spherical metallic particle, we get its polarizability $\alpha \approx R^3$, where R is the aggregate radius. We start from the association of fractal aggregates, when in accordance with formula (19.18), the effective rate constant of joining of two spherical fractal aggregates is equal to

$$k_{ind} \sim \frac{\alpha_1 \alpha_2 E^2 N^{2/3}}{\eta R} \sim \frac{R^5 E^2 N^{2/3}}{\eta} \quad (20.24)$$

where $\alpha_1 \sim \alpha_2 \sim R^3$ are the polarizabilities of the joining aggregates, E is the electric field strength, N is the number density of aggregates, and η is the viscosity coefficient of a buffer gas in which the process proceeds. Considering the aggregates as metallic particles, we have the following definition of the effective rate constant of the process under consideration:

$$\frac{dn}{dt} = k_{ind} N n$$

where n is the average number of elemental fractal aggregates constituted a forming cluster. We have $N \sim N_o/n$, where N_o is the total number density of elemental aggregates in the cluster. From formula (20.24) it follows

$$\frac{dn}{dt} \sim \frac{R^5 E^2 N_o^{2/3}}{\eta} \sim \frac{a^5 E^2 N_o^{2/3} n^{5/D-2/3}}{\eta} \quad (20.25)$$

where a is the typical radius of an elemental particle and D is the fractal dimensionality of aggregates.

Comparing the rate (20.25) with the rate of cluster–cluster aggregation in the absence of electric fields, we obtain for the ratio of typical times of these processes

$$\frac{\tau_{CCA}}{\tau_{ind}} \sim \frac{E^2}{T} N_o^{2/3} a^5 n^{5/D-2/3} \quad (20.26)$$

where τ_{el} is a typical time of aggregation resulting from the interaction of induced dipole momenta and τ_{CCA} is the typical time of diffusion-limited aggregation in the absence of electric fields. As we have seen, the aggregate growth due to the interaction of induced dipole momenta is essential for large aggregates. In particular, taking the fractal dimensionality of an aggregate to be $D = 1.7\text{--}1.8$, we have the criterion that the mechanism of aggregation due to the interaction of induced dipole momenta determines the rate of aggregate growth

$$E \gg \frac{T^{1/2}}{N_o^{1/3} a^{5/2} n^{1.1}} \quad (20.27)$$

Finally, the joining of fractal aggregates as a result of the interaction of induced dipole momenta under the action of an electric field leads to the formation of a fractal fiber which resembles a cylindrical particle with the axis directed along the electric field (Figure 19.5). For example, real fractal fibers of metallic oxides have a diameter about $50\text{ }\mu\text{m}$ (Figure 20.12) and length up to several centimeters. A typical time for the growth of a fractal fiber is given by formula (19.22)

$$\tau_l \sim \frac{\eta}{R^3 E^2 N}$$

Note one more peculiarity of the growth of a fractal fiber compared with a continuous cylindrical particle. We assume that the conductivity of a former fiber is high enough that the electric potential of its surface is constant over the whole fiber when it is located in an external electric field. But the bonding between fractal aggregates inside a fractal fiber proceeds over time, so that this growth scenario can be valid only for a slow process.

Part VI

Nucleation Phenomena

21 Character of Nucleation in Gases and Plasma

21.1 Peculiarities of Condensation of Supersaturated Vapor

We consider the *phase states* of bulk matter as a uniform distribution of its elements in a space, and the phase transition consists in the transformation of one uniform distribution to another. But conserving the uniformity of a bulk material does not allow the phase transition to occur in a continuous way. As a demonstration of this, we take the liquid–solid phase transition for a large system with a pair interaction of atoms, where the partition function as a function of the number of elementary excitations is given in Figure 8.6. Hence below the melting point the free energy as a function of the number of elementary configuration excitations – *voids* is given in Figure 21.1. One can see the impossibility of a transition to a solid minimum step by step as a result of the departure of voids. Therefore another way in which such a transition may be realized is when *nuclei of a new phase* – small crystals – are formed at some points of the systems, and then excess voids leave the system. Hence the formation and growth of a new phase, the *nucleation process*, proceeds through the formation and growth of nuclei of the new phase.

Thus the phase transition proceeds through the growth of a new phase inside an old one in some space regions. This relates to various phase transitions, including the separation of some components in a solution, the formation of islands of a new phase on a surface, the growth of a solid phase inside a liquid or liquid clusters in a solid, etc. All these processes of the growth of a new phase have common features. For definiteness, we focus below on the phase transition between gaseous and condensed phases, and the parameter describing an equilibrium between these phases is the *saturated vapor pressure*. As the vapor pressure exceeds the saturated vapor pressure, the vapor state becomes unstable and a vapor excess can transfer into a condensed phase. Let us consider a saturated vapor which is located in a space restricted by walls. If the walls are moisten by a vapor, vapor atoms attach to the walls and form a thin film. Then the vapor excess is transformed into a condensed phase as a result of attachment to this film, so that this film covers the walls. As a result, the vapor pressure tends to the saturated vapor pressure, and the remaining vapor transfers to the wall film.

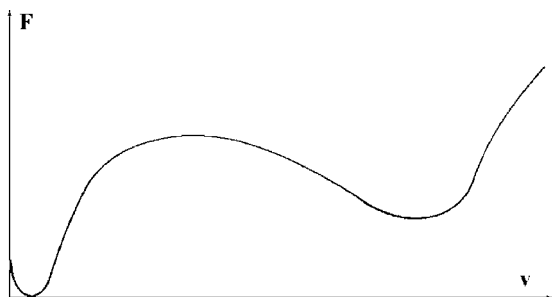


Figure 21.1. The free energy of a bulk system of bound atoms with two aggregate states (solid and liquid) at a temperature where the excited aggregate state is metastable. Then if the system remains uniform, after a small change of a number of elementary configuration excitations the system returns in the metastable state.

If the walls are not moisten by a vapor, and vapor atoms do not form a thin film on the walls, the transition of a supersaturated vapor in a stable state results in the formation of clusters, drops or small particles in a space, and subsequently a condensed phase grows on these centers, which are called *nuclei of condensation*. The growth of a new phase proceeds in this case according to the scheme



where M is an atom, and this process establishes the equilibrium between clusters of neighboring sizes.

We consider below the equilibrium of a bulk liquid drop that is located in a parent vapor with a *supersaturation degree* in accordance with formula (12.42)

$$s = \frac{p}{p_{\text{sat}}(T)} = \frac{N}{N_{\text{sat}}(T)} \quad (21.2)$$

and this value is large in a supersaturated vapor. Here p is the gas pressure, N is the number density of condensing atoms, $p_{\text{sat}}(T)$ is the saturated vapor pressure at a given temperature T , and $N_{\text{sat}}(T)$ is the number density of atoms at the saturated vapor pressure. According to formula (7.21) the saturated vapor pressure is

$$p_{\text{sat}}(T) = p_{\text{liq}} \exp\left(-\frac{\varepsilon_o}{T}\right) \quad (21.3)$$

The equilibrium of this drop with the surrounding vapor is determined by the equality of the chemical potentials of the drop μ and the surrounding parent vapor, and we determine the free enthalpy $G = \mu n$ of the drop consisting of n atoms, because this value characterizes the equilibrium under consideration. We represent the free enthalpy of a bulk drop to be the sum of two terms which account for the space and surface energies

$$G = n(\varepsilon_g - \varepsilon_o) + 4\pi r^2 \sigma \quad (21.4)$$

where the drop radius is $r = r_W n^{1/3}$, r_W is the Wigner–Seitz radius, ε_o is the binding energy of internal atoms of the particle, ε_g is an atom's energy in the surrounding gas, and σ is the surface tension. Here we take the free enthalpy of the gas to be zero. Below we find the equilibrium conditions for the system of a drop and its vapor at given temperature and pressure.

Substituting in formula (21.4) the binding energy of internal atoms ε_o from formulae (7.24) and (7.26) and introducing in this formula the radius of a drop of spherical shape, we obtain for the free enthalpy of the drop as a function of its radius

$$G = 4\pi r^2 \sigma - \frac{r^3}{r_W^3} (T \ln s + \text{const})$$

Using the fact that the equilibrium condition $G = 0$ for a plane surface has the form $s = 1$ according to the definition of the saturated vapor pressure, we neglect in the limit $r \rightarrow \infty$ the surface tension of the drop. This gives $\text{const} = 0$, and the drop free enthalpy has the form

$$G = 4\pi r^2 \sigma - \frac{r^3}{r_W^3} T \ln s \quad (21.5)$$

It is convenient to express the free enthalpy for a given gas pressure through the temperature T_* at which a current gas pressure coincides with the saturated vapor pressure, i.e.

$$p = p_{\text{liq}} \exp\left(-\frac{\varepsilon_o}{T_*}\right)$$

We have

$$G = 4\pi r^2 \sigma - \frac{r^3}{r_W^3} \varepsilon_o \left(\frac{T}{T_*} - 1 \right) \quad (21.6)$$

This formula allows us to analyze the character of nucleation through the formation and growth of liquid drops in a pure vapor. The probability of formation of a drop of a given radius r is $\sim \exp[-G(r)/T]$, and the nucleation process has a barrier character, so that the barrier top corresponds to the *critical radius* of a drop r_{cr} at which the free enthalpy has the maximum $dG(r_{\text{cr}})/dr = 0$, and the critical radius is equal to

$$r_{\text{cr}} = \frac{8\pi\sigma r_W^3}{3T \ln s} = \frac{8\pi\sigma r_W^3}{3\varepsilon_o} \cdot \frac{T_*}{T - T_*} \quad (21.7)$$

The critical radius is the principal parameter of the nucleation process. Atom attachment is profitable for $r > r_{\text{cr}}$, and drops of such sizes grow freely. In contrast, if the drop radius is below the critical one, the probability of drop evaporation exceeds the probability of atom attachment. The free enthalpy of a drop of critical radius is

$$G(r_{\text{cr}}) = \frac{4\pi\sigma r_{\text{cr}}^2}{3} = \frac{1}{2} \left(\frac{r_{\text{cr}}}{r_W} \right)^2 T \ln s = \frac{1}{2} \left(\frac{8\pi\sigma r_W^2}{3\varepsilon_o} \right)^2 \cdot \left(\frac{T_*}{T - T_*} \right)^2 \quad (21.8)$$

which characterizes the energy of formation of a drop of critical radius. Since the probability of this event is $\sim \exp[-G(r_{\text{cr}})/T]$, the nucleation process proceeds for long enough in a pure gas, i.e. a vapor can be found for some time in a supersaturated state. In addition, formula (21.6) may be represented in the form

$$G(r) = 4\pi\sigma \left(r^2 - \frac{2r^3}{3r_{\text{cr}}} \right); \quad \frac{dG(r_{\text{cr}})}{dr} = 0, \quad \frac{d^2G(r_{\text{cr}})}{dr^2} = -16\pi\sigma r_{\text{cr}} \quad (21.9)$$

If we change in formula (21.5) the drop radius r by a number n of its atoms according to formula (7.25a), $n = r^3/r_W^3$, we obtain for the free enthalpy of a drop or liquid cluster

$$G_n = An^{2/3} - nT \ln s = -E_n + \varepsilon_o n - nT \ln s \quad (21.10)$$

where $A = 4\pi r_W^2 \sigma$ is the specific surface energy of the drop in accordance with formula (7.26), the total binding energy E_n of drop atoms is determined by formula (7.24), and ε_o is the binding energy per atom for the bulk system. From this we find also the chemical potential of a drop consisting of n atoms and having a radius r :

$$\mu_n = G_{n+1} - G_n = \frac{dG_n}{dn} = \frac{8\pi}{3} \sigma r_W^3 \left(\frac{1}{r} - \frac{1}{r_{\text{cr}}} \right) \quad (21.11)$$

One can see that the chemical potential is zero at the critical size because the free enthalpy has a maximum there, and near the critical size we have

$$\mu_n = \frac{8\pi\sigma r_W^3}{3r_{cr}^2}(r_{cr} - r) = \frac{8\pi\sigma r_W^6}{9r_{cr}^4}(n_{cr} - n) \quad (21.12)$$

We now rewrite the principle of detailed balance (11.46), which connects the rate of cluster evaporation $\nu_{n+1}(T)$ and the rate constant of atom attachment k_n to a cluster of n atoms on the basis of the free enthalpy quantities. We have from formulae (7.24) and (21.10)

$$\varepsilon_n - \varepsilon_o = E_{n+1} - E_n - \varepsilon_o = G_{n+1} - G_n - T \ln s = \mu_n - T \ln s$$

where G_n is the free enthalpy of this liquid cluster and μ_n is its chemical potential. In these terms, the relation (11.46) takes the form in accordance with formula (12.50)

$$\nu_{n+1}(T) = Nk_n \exp\left(\frac{\mu_n}{T}\right) \quad (21.13)$$

In this form the principle of detailed balance accounts for the behavior of matter in which free atoms and a test cluster are located, and G_n is the energy of cluster formation in this matter.

21.2 Nuclei of Condensation

In considering the nucleation process in a pure supersaturated vapor, we found that this process slows down because of the barrier character of formation of growing drops. The reason for this is a decrease in the mean binding energy of drop atoms in comparison with the binding energy of internal atoms because of the surface energy. This effect does not occur in the presence of an additional interaction for attaching atoms, when ions, radicals or active molecules are centers for growth of a condensed phase. These centers are *nuclei of condensation*. In particular, if chemically active molecules are added to a growing drop, attachment of atoms to this drop is analogous to the formation of a thin film on moistened walls. From the standpoint of the critical radius concept, in these cases the critical drop radius is zero. Below we demonstrate this tendency for a bulk charged particle.

Taking a particle charge to be e , we evaluate the part of the free enthalpy of a particle ΔG that corresponds to the particle's charge. We have

$$\Delta G = \int_0^\infty \frac{\epsilon E^2}{8\pi} d\mathbf{R}$$

Here $\mathbf{R}$ is the coordinate of a point in the frame of reference where the origin is located at the particle's center and is the point of ion location, E is the electric field strength, and ϵ is the dielectric constant of matter, which we assume to be one outside the particle and to be a constant inside it. Then the electric field strength is equal to $e/(\epsilon R^2)$ inside the particle at a distance R from its center and e/R^2 outside the particle. From this it follows for this part of the free enthalpy of the particle

$$\Delta G = \frac{e^2}{R} \left(1 - \frac{1}{\epsilon}\right) + const$$

where *const* does not depend on the particle's radius. Taking this term into account, we obtain for the free enthalpy of the particle instead of (21.5)

$$G = 4\pi r^2 \sigma - \frac{r^3}{r_W^3} T \ln s + \frac{e^2}{2r} \left(1 - \frac{1}{\epsilon}\right) + \text{const}$$

The equilibrium condition, corresponding to the maximum of the free enthalpy, has the form $dG/dr = 0$ and leads to the following equation for the critical radius:

$$8\pi r_{\text{cr}}^2 \sigma - 3 \frac{r_{\text{cr}}^2}{r_W^3} T \ln s - \frac{e^2}{2r_{\text{cr}}} \left(1 - \frac{1}{\epsilon}\right) = 0 \quad (21.14)$$

Rewrite equation (21.1) in the form

$$\ln s = \frac{8\pi \sigma r_W^3}{3T r_{\text{cr}}} \left[1 - \frac{e^2}{16\pi r_{\text{cr}}^3 \sigma} \left(1 - \frac{1}{\epsilon}\right)\right] \quad (21.15)$$

This formula corresponds to (21.7) at $e = 0$ and has the maximum at the critical radius

$$r_{\text{max}} = \left[\frac{e^2}{4\pi \sigma} \left(1 - \frac{1}{\epsilon}\right) \right]^{1/4}$$

when the supersaturation degree s_{max} is equal to

$$\ln s_{\text{max}} = \frac{8\pi \sigma r_W^3}{3T r_{\text{max}}} \quad (21.16)$$

One can see that if $\ln s$ exceeds this value, equation (21.15) for $\ln s$ has no solution, and a particle of any size grows.

21.3 Instability of Uniform Nucleating Vapor

In the course of condensation of a pure gas or vapor through the formation and growth of clusters, a uniform mixture is formed consisting of a condensing supersaturated vapor and clusters of different sizes. Analyzing the evolution of this system, we show below that it is unstable. Introduce the distribution function f_n of clusters as the number density of n clusters and denote by N the number density of free atoms. Considering the process of cluster growth and evaporation according to the scheme (21.1), we obtain the kinetic equation (12.40) for the size distribution function of clusters

$$\frac{\partial f_n}{\partial t} = N k_{n-1} f_{n-1} - N k_n f_n - \nu_n f_n + \nu_{n+1} f_{n+1} \quad (21.17)$$

where k_n is the rate constant of atom attachment to a cluster consisting of n atoms which is given by the relation (11.15) for $n \gg 1$:

$$k_n = k_o \xi n^{2/3}$$

and the frequency of atom evaporation for a cluster of n atoms ν_n are connected with the rate k_{n-1} of atom attachment to a cluster of $n - 1$ atoms by the principle of detailed balance (21.13). From this we have formula (12.47) for the size distribution function of clusters under equilibrium conditions

$$f_n = C \exp\left(-\frac{G_n}{T}\right) \quad (21.18)$$

Here we use formula (21.10) which connects the cluster energy E_n with the cluster free enthalpy G_n , and C is the normalization factor. The free enthalpy has a maximum at the critical cluster size, and the equilibrium distribution function has a minimum at the critical cluster size.

If we assume that the criterion

$$An_{\text{cr}}^{2/3} \gg T \quad (21.19)$$

holds true, the normalization criterion for the total number density N_b of bound atoms $\int n f_n dn = N_b$ is determined by small sizes $n \ll n_{\text{cr}}$, and the formula for drops or liquid clusters under thermodynamic equilibrium takes the form

$$f_n = C \exp\left(-\frac{G_n}{T}\right), \quad C = \frac{1}{3} N_b \left(\frac{A}{T}\right)^3 \quad (21.20)$$

Based on the continuous size dependence (21.10) for the free enthalpy of a surface atom, we obtain an analog for the size distribution function of liquid clusters or liquid drops. The critical cluster size at which the size distribution function of liquid clusters has a minimum, as it is shown in Figure 21.2a, corresponding to the critical radius of a bulk liquid drop. The equilibrium distribution function for clusters of small sizes falls with increasing size, confirming the barrier character of the condensation process. In contrast, at large sizes the equilibrium distribution function grows with increasing cluster size, so that the normalization condition is violated for large clusters and the distribution of clusters is non-stationary due to the growth of large clusters. If the growth of large clusters is important, it leads to a decrease in the number density of small clusters and free atoms.

In contrast to liquid clusters, solid clusters are characterized by a nonmonotonic size dependence of their parameters. In particular, the binding energy of atoms ε_n has local maxima at *magic numbers* of clusters which correspond to completed cluster structures. Let us analyze the behavior of the distribution function of clusters f_n near the magic number n , when $\varepsilon_n > \varepsilon_{n\pm 1}$, assuming the thermodynamic equilibrium between clusters of neighboring sizes to be established. Taking $\varepsilon_n - \varepsilon_{n+1} \gg T$ and $\varepsilon_n - \varepsilon_{n-1} \gg T$, we get from the expression (20.20) $f_n/f_{n-1} \gg f_{n+1}/f_n$, i.e. $f_n \gg \sqrt{f_{n-1}f_{n+1}}$. By analogy we have $f_{n-1} \ll \sqrt{f_n f_{n-2}}$. Next, assuming $|\varepsilon_{n+1} - \varepsilon_{n+2}| \sim T$, we have $f_{n+1}^2 \sim f_n f_{n+2}$, i.e. $f_{n+2} \ll f_{n+1}^{3/2}/f_{n-1}^{1/2}$. From the symmetry considerations we have $f_{n-1} \sim f_{n+1}$, which gives $f_n \gg f_{n\pm 1} > f_{n\pm 2}$. Thus the size distribution function of clusters f_n has a maximum at the magic numbers of cluster atoms and decreases near this maximum (see Figure 21.2b).

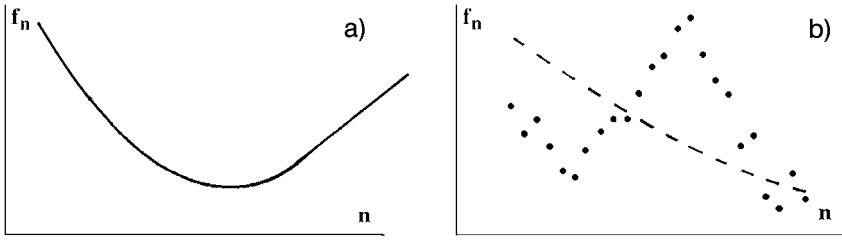


Figure 21.2. The size distribution function f_n of liquid clusters (a) and solid clusters (b) near a magic number of cluster atoms. n_{cr} is the critical number of cluster atoms, n_{mag} is a magic number of cluster atoms. A dotted curve in (b) respects to a bulk particle, closed circles account for a nonmonotonic dependence of the cluster cohesive energy on a number of atoms.

Such a dependence determines the character of evolution of clusters in the course of *growth of solid clusters*. We now consider the evolution of a supersaturated vapor when the system develops from the gaseous phase to condensed one due to the cluster growth process. If the cluster size is $n - 1$, the atom attachment process is more profitable for this cluster. If its size is $n + 1$, the evaporation process is favorable. In both cases the tendency is to form a cluster with a completed structure which corresponds to magic numbers of atoms. Therefore, in the course of cluster growth the cluster size is stopped at magic sizes. Thus there is a notable difference between the growth of a small particle or liquid cluster, in which this growth proceeds almost continuously, and that of a solid cluster, which in the course of its growth is stuck fast at magic numbers, so that the transition between neighboring magic numbers proceeds relatively slowly. As a result, in the case of solid clusters a free jet expansion gives a narrow size distribution function of clusters in a beam, with the maximum near a magic number of atoms, while this distribution function is wide for liquid clusters.

21.4 Classical Theory of Growth of Liquid Drops in Supersaturated Vapor

We now consider the growth of liquid drops in a supersaturated vapor in the first stage of this process when it does not influence the number density of free atoms. In this case, for small drops, including drops of the critical radius, there is a thermodynamic equilibrium between drops of different sizes. For large drops this is violated, and the number density of free atoms decreases in time as a result of atom attachment to large drops. Hence a flux occurs in a space of drop sizes, and this flux, depending on the drop size, is constant up to large sizes. We start from a size $l \sim 1$, where the size distribution function f_n coincides with the equilibrium one that is given by formula (21.20), and the size distribution function f_n is zero at large sizes. Therefore we take the almost equilibrium size distribution function f_n up to a size $m \gg n_{cr}$,

and $f_{m+1} = 0$. This corresponds to the equation set

$$\begin{aligned} f_l N k_l - f_{l+1} \nu_{l+1} &= J, \\ f_{l+1} N k_{l+1} - f_{l+2} \nu_{l+2} &= J, \\ f_{l+2} N k_{l+2} - f_{l+3} \nu_{l+3} &= J, \\ &\dots \\ f_{m-1} N k_{m-1} - f_m \nu_m &= J, \\ f_m N k_m &= J \end{aligned}$$

Here J is the flux of attaching atoms, and using the principle of detailed balance (21.13), we reduce this set of equations to the form

$$\begin{aligned} f_m &= \frac{J}{N k_m} \\ f_{m-1} &= f_m \exp\left(\frac{G_m - G_{m-1}}{T}\right) + \frac{J}{N k_{m-1}} \\ &\dots \\ f_{l+1} &= f_{l+2} \exp\left(\frac{G_{l+2} - G_{l+1}}{T}\right) + \frac{J}{N k_{l+1}} \\ f_l &= f_{l+1} \exp\left(\frac{G_{l+1} - G_l}{T}\right) + \frac{J}{N k_l} \\ &\dots \end{aligned}$$

In the limit $J \rightarrow 0$ one can obtain from this the expression (21.18) for the equilibrium distribution function. Subsequently solving this set of equations, we obtain for the flux of attaching atoms

$$J = \frac{f_l N}{\sum_{p=l}^m \frac{1}{k_p} \exp\left(\frac{G_p - G_l}{T}\right)} = \frac{CN}{\sum_{p=l}^m \frac{1}{k_p} \exp\left(\frac{G_p}{T}\right)}$$

We use the above formula (21.18) for the equilibrium size distribution function f_l , and the normalization constant C is given by formula (21.20). Changing summation in this formula into integration, we obtain

$$J = \frac{CN}{\int_l^m \frac{dp}{k_p} \exp\left(\frac{G_p}{T}\right)}$$

We use that the integral in this formula converges at sizes near the critical one and depends weakly on the lower limit l and upper limit m . Taking m to be large, one can represent the above formula in the form

$$J = \frac{CN}{\int_0^{\infty} \frac{dp}{k_p} \exp\left(\frac{G_p}{T}\right)} \quad (21.21)$$

Because the main contribution to the integral (21.21) gives drop sizes near the critical size, we obtain from this

$$J = Nk(n_{\text{cr}})CT \exp\left(-\frac{G(n_{\text{cr}})}{T}\right) = Nk(n_{\text{cr}})f(n_{\text{cr}})\Gamma$$

$$\text{where } \Gamma = \left[-\frac{1}{2\pi T} \frac{\partial^2 G_n}{\partial n^2} \Big|_{n=n_{\text{cr}}}\right]^{1/2} \quad (21.22)$$

Here $f(n_{\text{cr}})$ is the equilibrium size distribution function of drops, and Γ is called the *Zeldovich parameter*. From formula (21.9) it follows that

$$\Gamma = (8\pi\sigma r_{\text{cr}})^{1/2} r_W \quad (21.23)$$

Formulae (21.22) and (21.20) give the flux of bonding atoms in a supersaturated vapor until the number density of drops is small and does not influence the number density of free atoms. Then drops of small sizes, including the critical one, are found under thermodynamic equilibrium with each other. One can represent the flux of attaching atoms in the form

$$J = \left(\frac{8T}{\pi m}\right)^{1/2} \pi r_W^2 N^2 \frac{2\sigma^{1/2} r_W^3}{3r_{\text{cr}}^2} \exp\left[-\frac{1}{2T} \left(\frac{8\pi\sigma r_W^2}{3\varepsilon_o}\right)^2 \cdot \left(\frac{T_*}{T - T_*}\right)^2\right] \quad (21.24)$$

where T_* is the temperature at which the current vapor pressure is equal to the saturated vapor pressure.

One can determine the flux in a space of cluster sizes on the basis of the Fokker–Planck equation (12.48)

$$J = j_n = A_n f_n - B_n \frac{\partial f_n}{\partial n}$$

On the basis of formula (21.20) for the equilibrium distribution function of liquid clusters, formula (21.10) for the free enthalpy G_n , and the principle of detailed balance (21.13) we have formula (12.50) for the coefficients of the collision integral (12.48) in the case of cluster growth as a result of processes (21.1)

$$A_n = B_n \frac{d \ln f_n}{dn} = -\frac{\mu_n}{T} B_n; \quad A_n = Nk_n - \nu_{n+1} = Nk_n \left[1 - \exp\left(-\frac{\mu_n}{T}\right)\right] \quad (21.25)$$

and these relations hold true for large clusters $n \gg 1$.

We consider the relation for the cluster flux j_n in a space of cluster sizes as an equation for the distribution function f_n which coincides with the equilibrium one (21.18) at relatively small n and tends to zero at large cluster sizes. Using the relation (21.25) between parameters of this equation, one can rewrite it in the form

$$J = -B_n \exp\left(\frac{G_n}{T}\right) \frac{d}{dn} \left[f_n \exp\left(-\frac{G_n}{T}\right)\right]$$

The solution of this equation is

$$f_n = -J \exp\left(-\frac{G_n}{T}\right) \left[\int \frac{dn}{B_n} \exp\left(\frac{G_n}{T}\right) + const \right]$$

and using the boundary condition $f_n \rightarrow 0$ if $n \rightarrow \infty$, we have from this

$$f_n = J \exp\left(-\frac{G_n}{T}\right) \int_n^\infty \frac{dn}{B_n} \exp\left(\frac{G_n}{T}\right)$$

At cluster sizes n which are small compared to the critical size we have from this

$$J = C \left[N \int_0^\infty \frac{dn}{B_n} \exp\left(\frac{G_n}{T}\right) \right]^{-1}$$

where C is the normalization factor in formula (21.20).

We use the expressions (21.25) for the value B_n near the critical size, where $\mu_n \rightarrow 0$

$$B_n = \frac{T}{\mu_n} A_n = \frac{T}{\mu_n} N k_n \left[1 - \exp\left(-\frac{\mu_n}{T}\right) \right] = N k_n$$

This gives for the flux of attaching atoms

$$J = \frac{CN}{\int_0^\infty \frac{dn}{k_n} \exp\left(\frac{G_n}{T}\right)} \quad (21.26)$$

which coincides with that of formula (21.21). Hence both methods give the identical result.

Thus the rate of nucleation of a supersaturated vapor consisting of free atoms as a result of the atom attachment processes (21.1) is determined by cluster growth in a range of cluster sizes near the critical size. We note the character of cluster growth in this case. Most of the atoms are free, and the equilibrium between liquid clusters and free atoms results from attachment and evaporation processes. The rates of attachment and evaporation of atoms are approximately equal, and this equality establishes thermodynamic equilibrium between liquid clusters of different sizes. Since the difference between these rates is relatively small, the cluster growth process does not violate thermodynamic equilibrium for clusters of different sizes.

21.5 Nucleation at Strong Supersaturation

The concept of the critical radius is correct if the critical radius r_{cr} greatly exceeds the size of an atom. This means that a growing cluster contains many atoms; it can be considered as a bulk particle, and therefore one can assume its parameters to be continuous functions of a number of cluster atoms. In this case, within the framework of the classical theory of

nucleation, we have that the rate of attachment of new atoms to the cluster surface and the rate of atom evaporation from the cluster surface are almost equal, and the total rate of cluster growth is small compared to each of these rates. This is achieved at levels of supersaturation that are not high.

In the other limiting case of strong supersaturation the critical radius tends to zero according to formula (21.7), which allows us to ignore the evaporation processes, and restrict ourselves to attachment processes only. Then the size of an individual cluster, if growth proceeds in a gas and starts from $t = 0$, is described by the balance equation

$$\frac{dn}{dt} = k_n N = k_o n^{2/3} N \quad (21.27)$$

where N is the number density of free atoms, the attachment rate constant k_n is given by formula (11.15) if the cluster is described by the liquid drop model, the sticking probability of an atom to the cluster surface is one, and the reduced rate constant k_o is given by formula (11.16). If the nucleation process proceeds in condensed matter, the attachment of atoms can be determined by the diffusion of free atoms in this matter. In contrast to the gaseous case, when the number density of free atoms is uniform near the cluster, due to the diffusion character of motion the distribution of atoms near the cluster becomes nonuniform.

Indeed, the flux of attaching atoms at the surface of a bulk spherical cluster is described by the diffusion equation

$$\mathbf{j} = -DN_a \nabla c$$

where N_a is the total number density of atoms in a space, D is the diffusion coefficient of admixture atoms in condensed matter and c is the concentration of these atoms. Considering this equation as the equation for the atom concentration in a space, and solving this equation under the boundary condition $c(r) = 0$ (r is the cluster radius), we obtain from this equation

$$c(R) = c_o \left(1 - \frac{r}{R}\right)$$

Here R is the distance from the cluster center, $c_o = N/N_a$ is the concentration of admixture atoms far from the cluster, and N is their number density far from the cluster. Note that the equilibrium concentration of admixture atoms is less significant in comparison with c_o , i.e. the state with joining admixture atoms is thermodynamically profitable. From this formula we have for the rate of cluster growth in this case

$$J = 4\pi R^2 j = 4\pi R^2 DN_a \left| \frac{dc}{dR} \right| = 4\pi DNR \quad (21.28)$$

This is the *Smoluchowski formula* (11.19).

The criterion of the diffusion character of the nucleation process has the form

$$D \ll v_T R \quad (21.29)$$

where v_T is the typical thermal velocity of atoms. In particular, if this process proceeds in a gas, and according to formula (14.7) we have $D \sim v_T \lambda$, where λ is the mean free path of atoms, the diffusion character of atom attachment to a cluster occurs if

$$\lambda \gg r \quad (21.30)$$

21.6 Nucleation under Solid–Liquid Phase Transition

Aggregate and glassy states of a bulk system of free or bound atoms correspond to a uniform distribution of atoms in a space. But the phase transition between these states proceeds through the formation of growing nuclei of a new phase inside an old one, and the space distribution of atoms is not uniform in the course of growth of a new phase. We now analyze the liquid–solid phase transition from the standpoint of the growth of clusters of a new phase. Using the analogy with nucleation in a gaseous phase, we have for the free enthalpy of the solid spherical bulk cluster located in a liquid on the basis of formula (21.4)

$$G = -n\Delta\varepsilon + Tn \ln s + 4\pi r^2 \Delta\sigma + \text{const}$$

where n is a number of cluster atoms, r is its radius, $\Delta\varepsilon$ is the difference of the atom binding energy for the solid and liquid states, s is the analog of supersaturation (21.3) ($\ln s = \varepsilon_o/T - \varepsilon_o/T_m$, where T is a current temperature, T_m is the melting point for bulk), $\Delta\sigma > 0$ is the positive part of the difference of the surface tensions for the solid and liquid aggregate states. From this, accounting for $n = r^3/r_W^3$ and taking $G(r)/r^3 \rightarrow 0$, if $T = T_m$ for a bulk cluster, we obtain

$$G(r) = -\frac{r^3}{r_W^3}(T_m - T) \ln s + 4\pi r^2 \Delta\sigma = -\frac{r^3}{r_W^3} \varepsilon_o \frac{T_m - T}{T_m} + 4\pi r^2 \Delta\sigma \quad (21.31)$$

From this we find the critical radius r_{cr} at which $dG(r)/dr = 0$

$$r_{\text{cr}} = \frac{8\pi \Delta\sigma r_W^3}{3\varepsilon_o} \frac{T_m}{T_m - T} \quad (21.32)$$

Correspondingly, the cluster free enthalpy at the critical size is equal to (this value for the liquid phase is zero)

$$G(r_{\text{cr}}) = \frac{1}{2} \left(\frac{8\pi \Delta\sigma r_W^2}{3\varepsilon_o} \right)^3 \cdot \left(\frac{T_m}{T - T_m} \right)^2, \quad T < T_m \quad (21.33)$$

The same expression we have for a liquid cluster that is formed inside the solid cluster, but in this case $T_m < T$.

Let us consider simple solids and liquids consisting of atoms with pairwise atomic interactions, so that the liquid aggregate state differs from the solid one by the presence of a void gas inside the liquid. Then one can use the analogy with gaseous systems, considering the nucleation process as a result of void transport inside the system. According to the criterion (14.36), the space distribution of voids cannot vary in a continuous way from the solid phase to the liquid one. The void instability creates a *breaking surface* in a space that separates the solid and liquid phases. Under thermodynamic equilibrium according to the relation (6.36) the chemical potentials are equal on both sides of the breaking surface, i.e. $\mu_a(0) = \mu_a(c_{\text{liq}})$, and this equilibrium is conserved in time. But if this equality is not fulfilled, the breaking surface moves such that the volume of the favorable phase increases.

For definiteness, we first consider the growth of a solid phase in a bulk liquid assuming the solid nucleus to be a spherical particle of radius r_o . Since $\Delta\mu_a \equiv \mu_a(c_{\text{liq}}) - \mu_a(0) > 0$,

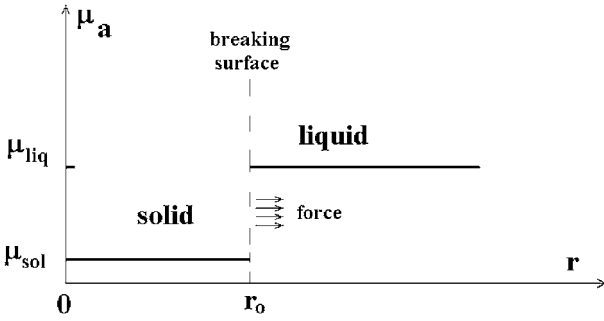


Figure 21.3. The character of growth of a solid nucleus in a liquid for a system of bound atoms with a pairwise interaction. A force due to the difference of the atom chemical potentials from two sides of the breaking sphere acts on voids in the liquid and compels them to move outside the breaking sphere. As a result, the solid nucleus is growing.

this radius increases with time. Indeed, according to Figure 21.3, a force $F(r)$ acts on voids of the liquid phase, where r is the distance from the nucleus center, and

$$\Delta\mu_a = \int_{r_o}^{\infty} F(r) dr \quad (21.34)$$

On the other hand, this force cause a void flux outside, and this leads to nucleus growth. Using the expression (14.35), which connects the void drift velocity w with their diffusion coefficients, and requiring the total void flux at a distance r from the nucleus center to be independent of r , we find on the basis of formula (21.34)

$$F(r) = \Delta\mu_a \frac{r_o}{r^2}$$

and this gives for the void drift velocity at a distance r from the center:

$$w(r) = \Delta\mu_a \frac{r_o}{r^2} \frac{D_{\text{liq}}}{T c_{\text{liq}}} \quad (21.35)$$

where D_{liq} is the self-diffusion coefficient of atoms for the liquid aggregate state and c_{liq} is the void concentration for the liquid state. From this we find the total void flux outside at a distance r from the nucleus center

$$J = 4\pi r^2 w N c_{\text{liq}} = 4\pi r_o N \frac{D_{\text{liq}}}{T} \Delta\mu_a \quad (21.36)$$

where N is the number density of atoms. Since the void flux is connected with nucleus growth, we obtain from this for the rate of nucleus growth

$$\frac{dr_o}{dt} = \frac{D_{\text{liq}}}{r_o} \frac{\Delta\mu_a}{T c_{\text{liq}}} \quad (21.37)$$

Let us evaluate the rate of nucleus growth in the case when the temperature T is close to the melting point T_m . Then we have $\mu_{\text{liq}} - \mu_{\text{sol}} = (T_m - T)s$, where s is the transition entropy per atom, and formula (21.37) gives

$$\frac{dr_o^2}{dt} = \delta_{\text{sol}} \frac{(T_m - T)}{T} \exp \left[-\alpha_{\text{sol}} \frac{(T_m - T)}{D} \right],$$

$$\delta_{\text{sol}} = \frac{1}{2} D_{\text{liq}}(T_m)s, \quad \alpha_{\text{sol}} = \frac{E_{\text{liq}}D}{T_m^2} \quad (21.38)$$

Table 21.1 contains the parameters δ_{sol} , α_{sol} of this formula for rare gases, and the values $D_{\text{liq}}(T_m)$ are taken from Table 14.5.

Table 21.1. The parameters of growth of a solid nucleus in liquid inert gases.

	c_{liq}	c_{cr}	$\delta_{\text{sol}}, 10^{-5} \text{ cm}^2/\text{s}$	α_{sol}	$\delta_{\text{liq}}, 10^{-8} \text{ cm}^2/\text{s}$	α_{liq}
Ne	0.31	0.25	8.2	8.0	$10 \cdot 10^{\pm 0.4}$	16 ± 2
Ar	0.32	0.25	17	7.2	$1 \cdot 10^{\pm 0.5}$	20 ± 2
Kr	0.32	0.26	14	6.3	$3 \cdot 10^{\pm 0.4}$	17 ± 2
Xe	0.31	0.25	17	6.8	$0.4 \cdot 10^{\pm 0.3}$	20 ± 1

In analogous matter we will consider the growth of a liquid nucleus inside a solid, and then formula (21.38) is transformed to the form

$$\frac{dr_o^2}{dt} = \delta_{\text{liq}} \frac{(T_m - T)}{T} \exp \left[-\alpha_{\text{liq}} \frac{(T_m - T)}{D} \right],$$

$$\delta_{\text{liq}} = \frac{1}{2} D_{\text{sol}}(T_m)s, \quad \alpha_{\text{liq}} = \frac{E_{\text{sol}}D}{T_m^2} \quad (21.39)$$

The parameters δ_{liq} and α_{liq} of this formula are given in Table 21.1, where the values $D_{\text{sol}}(T_m)$ are taken from Table 14.4.

Although we did not analyze critical phenomena, they can be taken into account by including surface terms in $\Delta\mu_a$. Formulae (21.38) and (21.39) do not take this into account, and hence they hold true if the current nucleus radius significantly exceeds the critical one.

Thus for a bulk system of bound atoms one can consider the liquid aggregate state as a two-component system consisting of bound atoms and voids inside the system. Transition between the solid and liquid states by continuous variation of the void concentration is impossible because of the character of void transport. This leads to the existence of the breaking surface that separates two phases and causes void transport outside the nucleus. As a result the nucleus grows, and the rate of growth is expressed through the coefficient of self-diffusion of atoms in this system. The analysis fulfilled shows an analogy for different nucleation processes with the formation and growth of a new phase.

22 Processes of Cluster Growth

22.1 Mechanisms of Cluster Growth in Gases

We base the following on the scheme (21.1) above of cluster growth (Figure 22.1a), so that the transformation of a gas in clusters results from atom attachment to clusters and the evaporation of cluster atoms. If the rate of atom attachment exceeds the rate of atom evaporation for a certain group of clusters, the number of free atoms decreases over time due to these clusters, and the number of bound atoms increases. Another mechanism (Figure 22.1b) of cluster growth corresponds to the scheme



This is the *coagulation* process, and since the surface area of a forming cluster exceeds the total surface area of colliding clusters, the temperature of the bound atoms increases as a result of this process. Note that the coagulation process takes place for neutral clusters. If clusters are located in a plasma or weakly ionized gas, they obtain a charge, and the repulsive Coulomb interaction of two colliding clusters promotes their approach and joining. Hence the coagulation process is usually forbidden for charged clusters.

Let us return to the scheme (21.1) of cluster growth. At a certain stage of this process, when the growth of large clusters influences the number density of small clusters and free

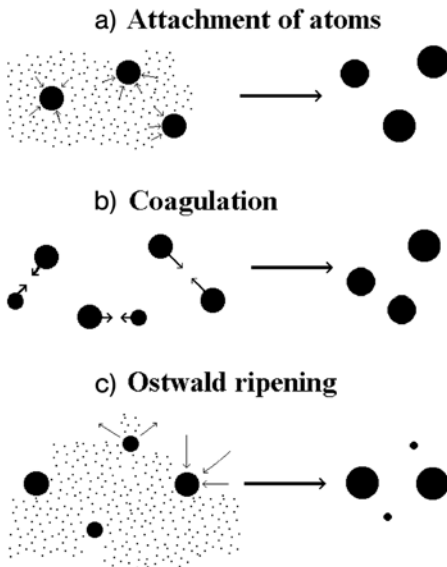


Figure 22.1. Mechanisms of cluster growth. (a) Attachment of atoms to a cluster; (b) Coagulation of clusters; (c) Coalescence or Ostwald ripening of clusters – evaporation of small clusters and growth of large clusters, i.e. transition of atoms from small clusters to large ones through an equilibrium vapor.

atoms, a new equilibrium type is realized. The same character of processes takes place if clusters are inserted in a buffer gas, where they evaporate atoms, and the equilibrium between free and bound atoms is established. This equilibrium leads to equality between the number of attaching and evaporating atoms per unit time, which gives a certain number of free and bound atoms. But because large clusters grow and small clusters evaporate under this equilibrium, the size distribution function of clusters varies with time, so that the average cluster size increases with time. Thus clusters grow through an equilibrium with the parent atomic vapor. This mechanism (Figure 22.1c) of cluster growth is called *Ostwald ripening* or the *coalescence* process.

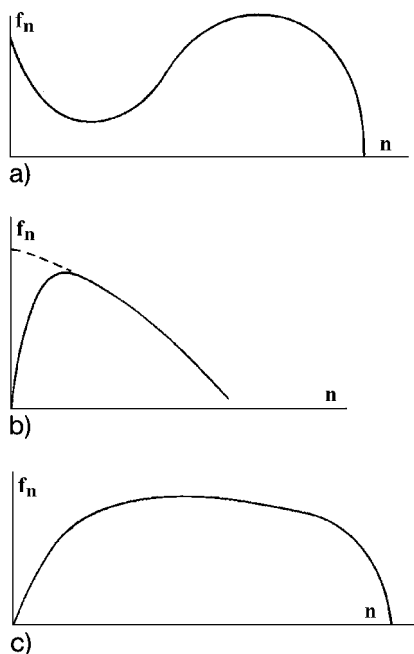


Figure 22.2. A typical form of the size distribution function for different mechanisms of cluster growth: (a) atom attachment (21.1) to clusters in a gas or vapor of free atoms; (b) coagulation (22.1); (c) coalescence or Ostwald ripening.

We have different forms of the size distribution function of clusters for these three mechanisms of cluster growth, as shown in Figure 22.2. When cluster growth is determined by atom attachment to clusters, and the atom attachment process does not affect the number density of free atoms, the size distribution function of clusters has the form of Figure 22.1a. The distribution function has a minimum at the critical cluster size and tends to zero for very large cluster sizes. When the average cluster size significantly exceeds the critical cluster size, the balance equation for the cluster size growth has the form

$$\frac{dn}{dt} = k_n N = k_o n^{2/3} N$$

and gives for a typical cluster size

$$n \sim (k_o N t)^3 \gg 1$$

where t is a typical time for cluster growth. Because during this time the total number density of bound atoms N_b remains small compared to the number density N of free atoms, i.e. $N_b \ll N$, this is valid during restricted times

$$t \ll \frac{1}{k_o N} \left(\frac{N}{N_{cl}} \right)^{1/3} \quad (22.2a)$$

where $N_{cl} \sim N_b/n$ is the number density of clusters. On the other hand, in this consideration a typical cluster size n is large compared with the critical size n_{cr} , which gives

$$t \gg \frac{n_{cr}^{1/3}}{k_o N} \quad (22.2b)$$

During this time the distribution function has the form of Figure 22.2a.

In the case of cluster coagulation the size distribution function of clusters f_n drops with increasing size for sizes which give the main contribution to the total number of bound atoms. The function f_n may tend to zero or to a constant in the limit of small sizes, depending on the character of the size dependence for joining of two small clusters. The distribution function f_n for this mechanism of cluster growth is given in Figure 22.2b. In the case of the coalescence mechanism of cluster growth, the distribution function has a maximum at the critical size, as shown in Figure 22.2c, and drops in both directions. The rates of cluster growth of this mechanism depend strongly on the temperature.

22.2 Kinetics of Cluster Coagulation

The transition from a gaseous state to a condensed one starts from the formation of nuclei of condensation in a supersaturated gas, i.e. clusters consisting of gas atoms. When the nucleation process develops according to the scheme (21.1), bulk clusters grow if their size increases to the critical size, which in turn drops with increasing supersaturation degree of the nucleating gas. Therefore the effective cluster growth proceeds at high supersaturation levels that occur if a gas or vapor expands in a vacuum or is inserted in a plasma. Below we consider the character of cluster growth at high degrees of gas supersaturation.

In considering the cluster growth process, we will be guided by a real case in which joining atoms, specifically metallic atoms, are an admixture to a buffer gas. Then the metallic atoms expand together with the buffer gas atoms under free jet expansion, and a plasma is formed on the same basis as a buffer gas in which cluster growth proceeds in a plasma. The presence of a buffer gas does not influence the basic processes of cluster growth, but it creates stability in the total system. Because of the high degree of supersaturation for a nucleating vapor, the total rate of atom evaporation from the cluster surface is small in comparison with the total rate of attachment of atoms to clusters, and we ignore the evaporation process in a basic range of cluster sizes. We first consider the coagulation process within the framework of the liquid drop model for clusters, when the rate constant of joining of two colliding clusters is given by formula (11.18). We keep the scheme (22.1) for cluster growth. Then the evolution of the size distribution function f_n , which is the number density of clusters consisting of n atoms,

follows the *Smoluchowski equation*

$$\frac{\partial f_n}{\partial t} = -f_n \int k(n, l) f_l dl + \frac{1}{2} \int k(n-l, l) f_{n-l} f_l dl \quad (22.3)$$

Here $k(n, l)$ is the rate constant of the process (22.1), the factor $1/2$ accounts for the fact that collisions of clusters consisting of $n-m$ and m atoms are present in the equation twice, and the distribution function is normalized as $\int f_n dn = N_{cl}$, where N_{cl} is the number density of clusters. In addition, the total number density N_b of bound atoms is $N_b = \int n f_n dn$.

Let us multiply the Smoluchowski equation (22.3) by n and integrate it over dn . We obtain

$$\begin{aligned} \frac{d}{dt} \int_0^\infty n f_n dn &= \frac{dN_b}{dt} \\ &= - \int_0^\infty n f_n dn \int_0^\infty k(n, l) f_l dl + \frac{1}{2} \int_0^\infty n dn \int_0^n f_{n-l} f_l k(n-l, l) dl = 0 \end{aligned}$$

if we change in the second term $n-l \rightarrow n$. Thus, the conservation of the total number of bound atoms over time is taken into account within the framework of the Smoluchowski equation. Let us introduce the average cluster size $\bar{n}$ as

$$\bar{n} = \frac{N_b}{N_{cl}} \quad (22.4)$$

and the evolution of the average size of clusters is given by the equation

$$\frac{d\bar{n}}{dt} = -\frac{N_b}{N_{cl}^2} \frac{dN_{cl}}{dt} = -\frac{N_b}{N_{cl}^2} \int_0^\infty \frac{\partial f_n}{\partial t} dn = \frac{N_b}{2N_{cl}^2} \int_0^\infty f_n dn \int_0^\infty k(n, m) f_m dm \quad (22.5)$$

Let us consider the evolution of joining clusters of large sizes in comparison with the mean free path of atoms in a gas or liquid, where growing clusters are located. Then according to formulae (11.18) and (11.20) the rate constant of joining of two clusters does not depend or depends weakly on their size in two limiting cases of cluster sizes, and taking $k(n, l) = k_{as}$, we obtain from equation (22.5) in this case

$$\bar{n} = \frac{1}{2} N_b k_{as} t \quad (22.6)$$

if initially the mean particle size is relatively small. Next, the Smoluchowski equation may be reduced to the form

$$\frac{\partial f_n}{\partial \tau} = -f_n \int_0^\infty f_l dl + \frac{1}{2} \int_0^n f_{n-l} f_l dl \quad (22.7)$$

where the reduced time is $\tau = N_b k_{as} t$. One can show that the solution of this equation has the form

$$f_n = \frac{4N_b}{\tau^2} \exp\left(-\frac{2n}{\tau}\right) \quad (22.8)$$

where the distribution function is normalized by the condition $N_b = \int_0^\infty n f_n dn$. In particular, the solution (22.8) gives for the average cluster size formula (22.6) $\bar{n} = \tau/2$.

Let us consider *coagulation* of clusters or small particles in an expanding gas, so that $N_b \sim \exp(-t/\tau_{\text{ex}})$, where τ_{ex} is the expansion time. The same time dependence relates to the size distribution function f_n . We account for this in the balance equation by an additional factor $\exp(-t/\tau_{\text{ex}})$, so that this equation takes the form

$$\frac{d\bar{n}}{dt} = \frac{N_b}{2N_{cl}^2} \int_0^\infty f_n dn \int_0^\infty k(n, l) f_l dl \cdot \exp\left(-\frac{t}{\tau_{\text{ex}}}\right) \quad (22.9)$$

where N_b and N_{cl} are the initial values. For large clusters or particles, when the rate constant of particle association does not depend on size, this equation has the form

$$\frac{d\bar{n}}{dt} = \frac{1}{2} N_b k_{as} \exp\left(-\frac{t}{\tau_{\text{ex}}}\right)$$

In the limit of small t the solution of this equation is given by formula (22.6), and in the limit of large times $t \gg \tau_{\text{ex}}$ the average particle size is

$$\bar{n} = \frac{1}{2} N_b k_{as} \tau_{\text{ex}} \quad (22.10)$$

Note that in this regime the cluster growth finishes when their number density drops significantly due to expansion.

In the case of coagulation of clusters or particles of small sizes, when the rate constant of coagulation is given by formula (11.18), we use equation (22.5) for the average cluster size, and the time dependence for the total number density of bound atoms is $N_b \sim \exp(-t/\tau_{\text{ex}})$. Because of the weak size dependence of the rate constant of cluster joining, we neglect this dependence in equation (22.5), so that the size distribution function has the form of formula (22.8)

$$f_n = \frac{N_b}{\bar{n}^2} \exp\left(-\frac{n}{\bar{n}}\right)$$

Then equation (22.5) is simplified to the form

$$\begin{aligned} \frac{d\bar{n}}{dt} &= N_b k_o \bar{n}^{1/6} I \exp\left(-\frac{t}{\tau_{\text{ex}}}\right) \\ I &= \frac{1}{2} \int_0^\infty \int_0^\infty (x^{1/3} + y^{1/3})^2 \sqrt{\frac{x+y}{xy}} \exp(-x-y) dx dy = 3.5 \end{aligned}$$

From this there follows for the average cluster size

$$\bar{n} = \left(\frac{5I}{6} N_b k_o \tau_{\text{ex}}\right)^{1.2} = 3.6 \cdot (N_b k_o \tau_{\text{ex}})^{1.2} \quad (22.11)$$

Note that N_b is the total number density of bound atoms at the beginning of this process. The above analysis requires large sizes of forming clusters $\bar{n} \gg 1$. Evidently it is valid if

$$k_o N_b \tau_{\text{ex}} \gg 1 \quad (22.12)$$

22.3 The Coalescence Stage of Cluster Growth

We now consider the *coalescence* stage of cluster growth (Figure 22.1c), which results in an interaction between clusters and atoms which are found in equilibrium with the clusters. The clusters are locked in a space due to their low mobility, and the evolution of cluster sizes is determined by the processes of atom attachment to clusters and the evaporation of atoms from the cluster surface. If clusters are grains in solid solutions or islands on a solid surface, the atoms exist separately, being found in equilibrium with clusters. Another case of this cluster growth process relates to an equilibrium of charged metallic clusters with their atoms in a dense weakly ionized buffer gas, because the coagulation process is prohibited in this case. Under these conditions, the most of the atoms are located in grains, islands or clusters, and the typical time for the coalescence process is relatively large. We first consider the size evolution of an individual cluster assuming it to have a spherical shape in a three-dimensional space.

The evolution of an individual cluster size is determined by processes of atom evaporation, atom attachment and their diffusion near the cluster, where according to formula (14.3) the atomic flux j to the cluster surface has the form

$$j = -DN \frac{dc}{dr}$$

Here r is the atom's distance from the cluster center, D is the atom diffusion coefficient in a medium around the cluster, N is the number density of free atoms and c is the concentration of free atoms. Denoting the atom concentration far from the cluster $c(\infty)$ by c_∞ and the atom concentration near the cluster surface $c(r_o) = c_o$, we obtain from the above equation

$$c(r) = c_\infty + (c_o - c_\infty) \frac{r_o}{r} \quad (22.13)$$

This gives the atom flux to the cluster surface

$$j = DN \cdot \frac{c_\infty - c_o}{r_o} \quad (22.14)$$

We take the sign in this formula such that the flux is directed towards the cluster when the atom concentration far from the cluster exceeds that near the cluster surface.

The flux of attaching atoms to the cluster surface is

$$j_{\text{at}} = v_T N c_o \quad (22.15)$$

Here v_T is the thermal atom velocity near the cluster surface, and in the case of free atoms this value is

$$v_T = \sqrt{\frac{T}{2\pi m_a}}$$

where T is the temperature and m_a is the atom mass. Adding the flux of evaporating atoms and defining the critical atom concentration c_{cr} such that at this concentration the total atom flux is zero, we get for the total atom flux to the cluster surface

$$j = v_T N (c_o - c_{cr}) \quad (22.16)$$

From a comparison of formulae (22.14) and (22.15) it follows

$$c_o = \frac{c_{cr} + \alpha c_\infty}{1 + \alpha}, \quad \alpha = \frac{D}{v_T r_o}, \quad j = \frac{DN}{r_o} \cdot \frac{c_\infty - c_{cr}}{1 + \alpha} \quad (22.17)$$

It follows from formulae (22.17) that the concentration of atoms near the cluster surface varies around the critical concentration at a given cluster size. The parameter $\alpha \sim \lambda/r_o$, where λ is the mean free path of free atoms, is small for the growth of grains in solid solutions and islands on a solid surface. Correspondingly, the rate of cluster growth is limited by the small value of the diffusion coefficient. In the other limiting case, when charged clusters are grown in a dense buffer gas, the diffusion process is fast and does not influence the rate of cluster growth. In this case the atom concentration near the cluster coincides with that far from the cluster $c_o \approx c_\infty$, and the rate of cluster growth does not depend on the diffusion coefficient D of atoms.

22.4 Growth of Grains in a Solid Solution

We now consider the case of coalescence involving the *growth of grains* in a solid solution when the diffusion coefficient of atoms in a solution is relatively small. Indeed, according to formula (14.28), the diffusion coefficient of atoms in a solution is estimated as

$$D \sim v_T a \exp\left(-\frac{E_a}{T}\right)$$

where v_T is the typical thermal velocity of atoms, a is of the order of atomic size, and the activation energy of the diffusion process E_a significantly exceeds the thermal energy $\sim T$. For large grains $r_o \gg a$ the parameter α in formula (22.17) is small. This means that the diffusion process restricts the rate of the growth process of grains, and the total rate of attaching (or evaporating) atoms for an individual grain according to formula (22.17) is equal to

$$J = 4\pi r_o^2 j = 4\pi r_o DN \cdot [c_\infty - c_{cr}(r_o)] \quad (22.18)$$

Note that $c_{cr}(r_o)$ is the critical concentration of atoms in the solution for a given grain size. At this concentration, the rates of attaching and evaporating atoms are equal for grains of a given size. In addition, we introduce the critical grain size r_{cr} , so that $c_\infty = c_{cr}(r_{cr})$, i.e. at this grain size the rates of evaporation and attachment are equal for a given atom concentration c_∞ far from the grains. In addition, the mean distance between neighboring grains significantly exceeds the typical grain size.

Let us introduce the reduced grain size $u = r_o/r_{cr}$ and the size distribution function $f(u)$ for grains that is normalized by the condition

$$\int f(u) du = N_{cl}, \quad \int n(u) f(u) du = N_b \quad (22.19)$$

where N_{cl} is the number density of grains that decreases in time, $n(u)$ is the number of atoms constituting a grain of size u , and N_b is the number density of bound atoms in grains, which is conserved over time. If we take $N = N_b$, in this case the concentration of “free atoms” is relatively small $c_\infty \ll 1$. For this reason, and because the diffusion coefficient of atoms is small, the time to establish an equilibrium between “free atoms” and grains is small compared with the typical time of variation of grain sizes. This allows us to consider the character of grain growth as a stationary process. Next, the total rate of attachment and evaporation of atoms is zero because of the problem stationarity, i.e.

$$4\pi r_o D N_b \cdot \int [c_\infty - c_{cr}(u)] f(u) du = 0 \quad (22.20)$$

This is the equilibrium condition between grains and “free atoms”, and this formula determines the equilibrium concentration $c_\infty = c_{cr}(1)$ of atoms with respect to the total number density of these atoms in a solution. In reality, this integral can be divided in two parts

$$\begin{aligned} \left(\frac{dN}{dt} \right)_{ev} &= 4\pi r_o D N_b \cdot \int_0^1 [c_\infty - c_{cr}(u)] f(u) du \\ \left(\frac{dN}{dt} \right)_{at} &= 4\pi r_o D N_b \cdot \int_1^\infty [c_\infty - c_{cr}(u)] f(u) du \end{aligned} \quad (22.21a)$$

so that the first value relates to atoms evaporating from small grains, and the second one describes the rate of attaching atoms to large grains, and according to formula (22.20) we have the equilibrium condition

$$\left(\frac{dN}{dt} \right)_{ev} + \left(\frac{dN}{dt} \right)_{at} = 0 \quad (22.21b)$$

After some time, an asymptotic regime is established in which the form of the size distribution function of grains expressed in reduced variables does not vary with time (it is given in Figure 22.3). This distribution function means that although grains are grown, and the number of grains decreases, the form of the distribution function is conserved. One more peculiarity of this distribution function is the existence of a so called “locked point”, so that at higher sizes the distribution function is zero. In addition, in the first approximation the asymptotic distribution function of Figure 22.3 is not zero above the locked point. It is of importance that this distribution function does not depend on the initial size distribution function of grains. From this one can estimate the typical time τ of grain growth during which the grain size varies significantly due to the attachment and evaporation processes. According to formulae (22.21) we have for this time

$$\tau \sim \frac{n}{r_o D N_b \Delta c} \quad (22.22)$$

where n is the typical number of atoms per grain, Δc is the typical difference between the concentration of “free atoms” and the critical concentration for the average size of grains. This time is relatively large because, on the one hand, the diffusion coefficient D is relatively small, and, on the other, the number density of “free atoms” which are found in equilibrium with bound atoms is also relatively small.

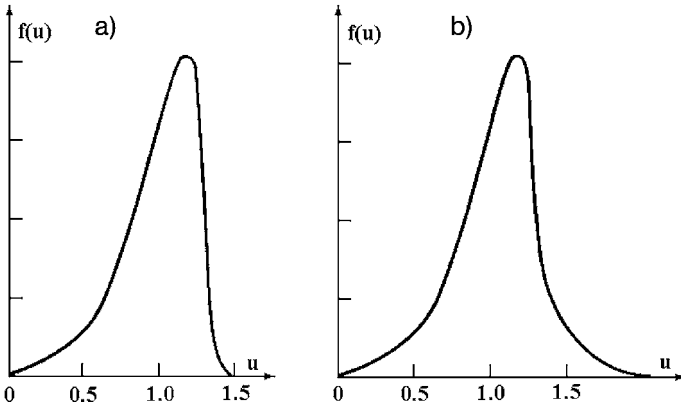


Figure 22.3. The asymptotic distribution function for grain growth in a solid solution due to Ostwald ripening in the zero-th (a) and first (b) approximation (V.V. Slezov, V.V. Sagalovich. *Sov. Phys. Usp.* 30, 62, 1987; E.M. Lifshitz, L.P. Pitaevskii. *Physical Kinetics*. Oxford, Pergamon Press, 1981).

22.5 Character of Growth of Charged Clusters in a Plasma

We now consider the growth of charged clusters in a dense buffer gas, so that the coagulation process is prohibited by the cluster charge, and the size evolution of clusters results from equilibrium with an atomic vapor. As before, the number density of free atoms N is small in comparison with the number density N_b of cluster atoms $N_b \gg N$, but because the diffusion coefficient is relatively large in this case, i.e. the parameter of formula (22.17) $\alpha \gg 1$, the diffusion of atoms in a gas is a fast process and does not influence the rate of cluster growth. The competition between attachment and evaporation processes leads to the equilibrium number density of atoms N_{cr} at which the rates of atom attachment and atom evaporation are equalized for a cluster consisting of a given number n of atoms, where $n \gg 1$. According to formula (12.45), the equilibrium number density is given by

$$N_{cr} = N_{sat}(T) \exp\left(\frac{\Delta\varepsilon}{Tn^{1/3}}\right) \quad (22.23)$$

Here T is the temperature of clusters and free atoms, $\Delta\varepsilon = 2A/3$, and A is the specific surface energy of a liquid cluster which is defined by formula (7.26).

The evolution of the size distribution function of metallic clusters with a large number n of atoms is described by the kinetic equation (12.48), which has the following form in this case

$$\frac{\partial f_n}{\partial t} = -\frac{\partial j_n}{\partial n}, \quad j_n = k_o n^{2/3} f_n \left[N - N_{sat}(T) \exp\left(\frac{\Delta\varepsilon}{Tn^{1/3}}\right) \right] \quad (22.24)$$

Thus in this regime cluster growth proceeds according to the scheme (21.1), but a small proportion of atoms are free and take part in this process.

Formula (22.24) for the collision integral shows that small clusters evaporate, large clusters grow, and the critical size n_{cr} , at which the rates of attachment and evaporation processes are

equalized, is determined by the relation

$$N = N_{\text{sat}}(T) \exp \left(\frac{\Delta \varepsilon}{T n_{\text{cr}}^{1/3}} \right) \quad (22.25)$$

It is convenient to divide clusters into two size groups whose boundary is $n = n_{\text{cr}}$. Denoting the number densities of bound atoms for clusters of the first and second groups by N_1 and N_2 respectively, we have $N_1 + N_2 = N_b \gg N$. In the course of evolution of cluster size, transitions of clusters of one group into clusters of the other group are prohibited.

We now consider the asymptotic regime of coalescence, when the size distribution function of clusters becomes asymptotic and does not vary its form in reduced variables $u = r_o/r_{\text{cr}} = (n/n_{\text{cr}})^{1/3}$. Of course, the reduced distribution function differs from that of Figure 22.3, when the diffusion of atoms to the cluster surface and back is of importance, but both functions have an analogous form, and hence we now consider both cases. The asymptotic regime is established at large cluster sizes if

$$n_{\text{cr}}^{1/3} \gg \frac{\Delta \varepsilon}{T} \quad (22.26)$$

In this case $N_b \Delta c \sim N_{\text{sat}}(T) \Delta \varepsilon / (T n_{\text{cr}}^{1/3})$ in formula (22.22), and since $r_o = r_W n^{1/3}$, where r_W is the Wigner–Seitz radius, we obtain the asymptotic character of the time dependence on the basis of formula (22.22)

$$\bar{n}(t) \sim \frac{T}{\Delta \varepsilon} D r_W N_{\text{sat}}(T) \cdot t, \quad \Delta c \sim \frac{N_{\text{sat}}(T)}{N_b} \frac{\Delta \varepsilon}{T \bar{n}^{1/3}} \sim t^{-1/3} \quad (22.27)$$

where $\bar{n}(t)$ is the average cluster size. In this case of the coalescence process for charged clusters in a dense buffer gas we have by a change in the factor $D r_o$ by $k_o n^{2/3}$

$$\bar{n}(t) \sim \left(\frac{T}{\Delta \varepsilon} k_o N_{\text{sat}}(T) \cdot t \right)^{3/2} \quad (22.28)$$

Correspondingly, the number of grains or clusters varies at large times as $\sim 1/t$ in the first case and $\sim t^{-3/2}$ in the second case.

The additional relation follows from the conservation of the number density of free and bound atoms. In particular, we have

$$\frac{dN_b}{dt} = \sum_n n \frac{\partial f_n}{\partial t} = \int_0^\infty k_o(T) n^{2/3} f_n \left[N - N_{\text{sat}}(T_{cl}) \exp \left(\frac{\Delta \varepsilon}{T_{cl} n^{1/3}} \right) \right] dn = 0 \quad (22.29)$$

As we can see, the number density of bound atoms is conserved because of the equality of rates of attachment and the evaporation process. In the same manner, we find the conservation of the number density of free atoms during typical times of this equilibrium. But these values vary over large times. We represent the balance equation for the average cluster size $\bar{n}(t)$ in the form

$$\frac{d\bar{n}}{dt} = \gamma k_o N_{\text{sat}}(T) \bar{n}^{2/3} \quad (22.30)$$

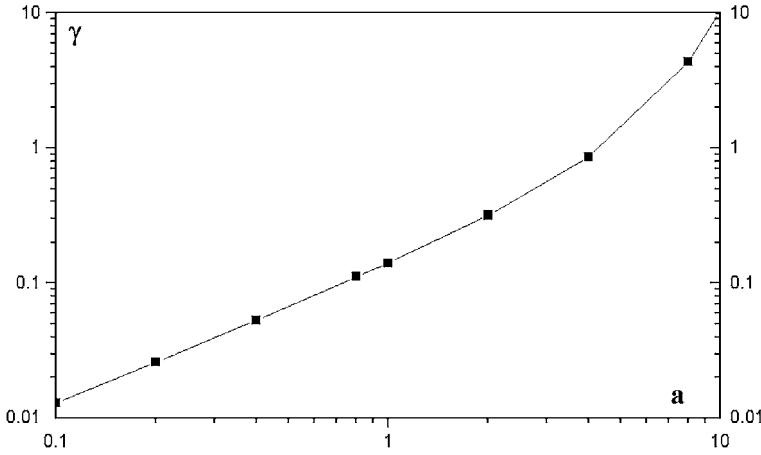


Figure 22.4. The dependence of the parameter γ in equation (21.30) on the parameter $a = \Delta\varepsilon/(T\bar{n}^{1/3})$.

where the value γ depends on the parameter $a = \Delta\varepsilon/(T\bar{n}^{1/3})$, which follows from the expression (12.48) for the collision integral. Figure 22.4 gives this dependence.

If clusters are neutral and their growth proceeds through the coagulation process (21.1), this equation according to (22.11) has the form

$$\frac{d\bar{n}}{dt} = 3.5N_b k_o \bar{n}^{1/6} \quad (22.31)$$

This formula corresponds to the growth of neutral clusters, and though it corresponds to a weak dependence of the growth rate on cluster size, in this case the rate of cluster growth is higher than for charged clusters, because this process includes all the bound atoms. Next, the rate (22.30) depends strongly on the temperature, because the proportion of free atoms drops strongly with decreasing temperature. Note that the temperature dependence of the growth rate for the coagulation process according to formula (22.31) is weak.

Let us consider as an example the case when the WF_6 molecules are inserted in a plasma with mean number density $1 \cdot 10^{16} \text{ cm}^{-3}$, where the plasma and buffer gas temperature is $T = 3700 \text{ K}$ and the average cluster size is $\bar{n} = 1000$. At this temperature $N_{\text{sat}} = 6.4 \cdot 10^{13} \text{ cm}^{-3}$, and the equilibrium number density of free atoms is $N = 1.3 \cdot 10^{14} \text{ cm}^{-3}$, so that most of the metallic atoms are found in clusters, and under these conditions $a \approx 1$. Thus, the number density of bound atoms $N_b = 1 \cdot 10^{16} \text{ cm}^{-3}$ significantly exceeds the number density of free atoms. According to formulae (22.30) and (22.31), the growth rate $d\bar{n}/dt$ is equal to $1 \cdot 10^5 \text{ s}^{-1}$ and $1.6 \cdot 10^7 \text{ s}^{-1}$ for charged and neutral clusters respectively. Thus, when clusters become charged, the coagulation process stops because of repulsion between identically charged clusters, and the growth rate for clusters in a plasma is small at low temperatures.

We have that a local equilibrium between clusters and their atomic vapor is determined by the equality of the total rate of atom attachment to clusters and the total rate of evaporation of atoms. But this system is not stable because small clusters are evaporated and large clusters

grow, i.e. the size distribution function of clusters f_n varies with time. As a result of this instability, the coalescence regime of cluster growth is realized.

22.6 Peculiarities of Nucleation on Surfaces

The growth of clusters in gases and plasmas has an analogy with nucleation processes on surfaces. In order to demonstrate this analogy, we analyze now the growth of a condensed phase from the gaseous one on a surface. If chemical processes are absent in this case, free atoms attach to the surface and propagate along it due to diffusion motion. As a result of the motion of individual atoms along the surface and their joining, *islands* are formed on the surface, and these islands are similar to growing clusters in the case of nucleation from the gaseous phase in a free space.

One can see the realization of all three mechanisms of nucleation which are given in Figure 22.1. Indeed, initially surface atoms are joined in small islands, and other surface atoms attach to these islands, which corresponds to the nucleation mechanism of Figure 21.1a. While the islands are small, they can move along the surface, so that their joining corresponds to the coagulation mechanism of nucleation (Figure 22.1b). When the islands become large, their motion along the surface as a result of diffusion stops because of the small diffusion coefficient. Then the subsequent evolution of islands proceeds through individual surface atoms which are formed by the evaporation of islands and then attach themselves to islands, so that “free” surface atoms are in equilibrium with islands through evaporation and attachment processes. As a result of these processes, small islands evaporate and large islands grow, and this is the nucleation mechanism of coalescence or Arrhenius ripening (Figure 22.1c) for the growth of islands. Thus, we have an analogy between the mechanisms of growth of clusters in a free space and the formation of islands of a new phase from the gaseous phase on a surface.

Of course, each nucleation process has specific characteristics, and chemical processes can lead to new mechanisms for the growth of a new phase on a surface. Chemical processes lead to *surface reconstruction*, and can be different. We will not consider this aspect of the nucleation problem. Another specific feature of island growth on a surface is the shape of the island, which for simplicity is assumed to be semispherical. We consider, for simplicity, the case in which rare gas atoms attach to a regular metallic surface, assuming the lattice constants of the metal surface and rare gas crystal to be identical. There are two possibilities for atom location on the metal surface at small numbers of attached atoms in comparison with that formed by a one-atom film on the metal surface. In the first case atoms cover the metallic surface in a layer that is one atom thick, so that each rare gas atom borders metallic atoms. In the second case atoms of rare gas atoms are joined in clusters – islands on the metallic surface – and these clusters occupy a small part of the metallic surface, while most of the atoms have rare gas atoms as nearest neighbors. The optimal form of atom location depends on the energetic parameters of this system. Taking D , the binding energy for two rare gas atoms, and D' , the binding energy between a metallic atom and a rare gas atom, we have the total binding energy per rare gas atom to be $6D$ in a large rare gas cluster of the face-centered cubic structure according to formula (7.28). This value is $3D + 3D'$ if rare gas atoms cover the metallic surface in the direction $\{111\}$ in a single layer (we ignore here cluster surface effects). From this it follows that the criterion of formation of cluster islands on the metallic

surface at zero temperature has the form

$$D > D' \quad (22.32)$$

If this criterion is fulfilled, the formation of large clusters of rare gas atoms on a metallic surface is profitable for a given metallic surface. In the case of the opposite criterion, rare gas atoms cover the metallic surface with a monatomic layer at zero temperature.

We now consider the structure when condensed rare gas covers the metal surface and forms at least several lattice layers. We assume the metal has the polycrystal structure. Evidently, the optimal conditions of construction of this system relate to the case in which the parameters of the metal and rare gas crystal lattices are found in correspondence. Rare gases have the face-centered cubic (fcc) lattice, so that only metals with the face-centered cubic or hexagonal lattice are suitable as a target. Table 22.1 gives values of the lattice constant a for metals of the fcc lattice structure (a is the edge length of the cell of this lattice, so that the distance between nearest neighbors equals $a/\sqrt{2}$). In this table the constants of the lattices of rare gases are given, and the distances between nearest neighbors of these lattices are represented in parentheses.

Table 22.1. Lattice constants for metals of the fcc structure of the lattice and for lattices of rare gases. Distances between nearest neighbors for rare gases are given in parentheses.

Metal	a , Å	Rare gases	a , Å
Sc	4.541	Ne	4.446 (3.156)
Ni	3.524	Ar	5.311 (3.755)
Cu	3.615	Kr	5.709 (3.992)
Mo	4.16	Xe	6.202 (4.335)
Pd	3.890		
Ag	4.086		
Pt	3.923		
Au	4.079		
Pb	4.950		

From the data of Table 22.1 it follows that the lattice constants of rare gases significantly exceed those of metals of the fcc structure, and our goal is to combine these lattices and find optimal conditions for this operation. In order to create the minimum tension at the interface between the metal and rare gas lattices, it is convenient to distribute atoms as shown in Figure 22.5, when some positions on the metal surface remain free. Figure 22.5 represents the interface between metal and rare gas lattices when the lattice parameters are different but the lattices are compatible. In the case of the $\{100\}$ boundary face, the lattices are compatible if their constants differ by a factor of $\sqrt{2}$ (see Figure 22.5a). In this case the more compatible systems for Kr are Ag, Pt and Au, the lattice parameters of which differ by 2%, or Pd, where this difference is 3%, whereas for Xe it is Mo that is most compatible, where the difference between the lattice parameters is 4%. In these cases one can expect the highest reliability of experiments because of the small strains on the boundary between the metallic target and the rare gas crystal. In the case of the $\{110\}$ metal surface, atoms of a rare gas form on this

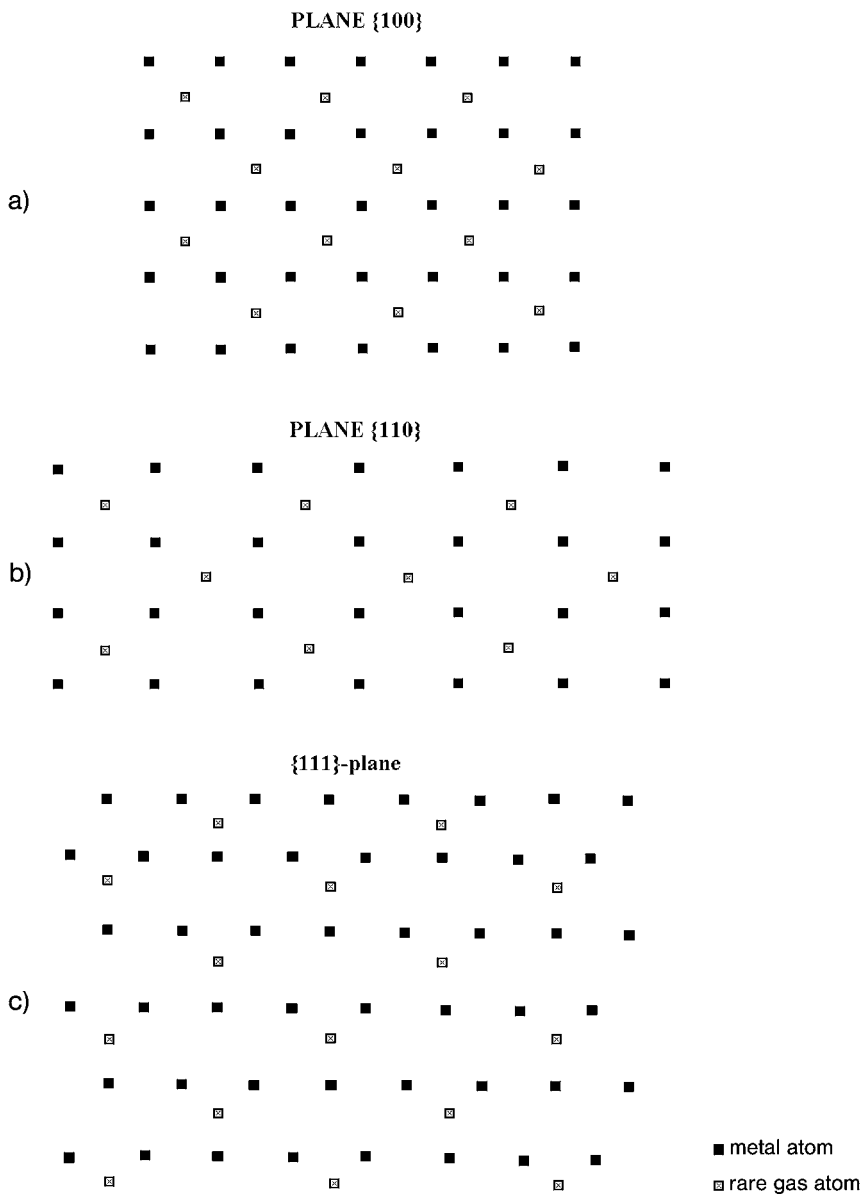


Figure 22.5. Positions of rare gas atoms on the metal surface of a solid rare gas; (a) the metal and rare gas border by the plane $\{100\}$, and the lattice constant of the rare gas lattice exceeds that of the metal in $\sqrt{2}$ times; (b) the same for the $\{110\}$ boundary plane; (c) the metal and rare gas border by the plane $\{100\}$, and the lattice constant of the rare gas lattice exceeds that of the metal in $\sqrt{3}$ times.

surface a distorted $\{111\}$ surface (see Figure 22.5b), so that the distances on this plane are $a\sqrt{3/2} = 1.22a$ and $a\sqrt{2} = 1.41a$, and the average value is $a\sqrt{2\sqrt{2/3}} = 1.28a$. In this case Mo is suitable for Ar, and Pb is suitable for Xe, but distortion at the boundaries correspond to lattice deformations of about 10%. When lattices border a $\{111\}$ plane (Figure 22.5c), their constants differ by a factor of $\sqrt{3}$. Then the Xe lattice is compatible with Ni, Cu and Pd lattices, where the distortion at the interface does not exceed 5%.

The question is which distortions do not violate the stability of the interface. According to a simple estimate, lattice distortion is not essential if the difference of the lattice constants do not exceed the amplitude of atomic vibrations. It follows from the Debye approximation for atom vibrations that the mean square displacement of a lattice atom is equal to

$$\Delta r^2 = \frac{9\hbar^2}{4m\theta_D} \quad (22.33)$$

where m is the atom mass and θ_D is the Debye temperature. In particular, using the Debye temperatures for rare gas crystals (Chapter 3), we find $\Delta r = 0.18 \text{ \AA}$ for Ar, $\Delta r = 0.14 \text{ \AA}$ for Kr and $\Delta r = 0.12 \text{ \AA}$ for Xe. Next, the surface and interface displacement are more than those inside the crystal, which follows from general grounds. From this one can conclude that distortions of several per cent in the lattice constants do not violate interface stability. Thus the general conclusion of this analysis is that the lattices of a metal substrate and rare gas layer must be identical. The greater the difference between the parameters of these lattices, the more defects are contained in the rare gas layers. The loss of uniformity of the rare gas lattice influences the quality and repeatability of structures for systems with metal surfaces covered by rare gas atoms. The above analysis shows that although the process of growth of islands on a surface is analogous to cluster growth, surface growth has additional peculiarities, even in the absence of chemical processes.

23 Cluster Growth in Expanding Gases and Plasmas

23.1 Transformation of Atomic Vapor in Clusters in an Expanding Gas

We consider the regime of cluster growth from an atomic vapor which is an admixture to an expanding buffer gas. As a result of this process, admixture atoms join in clusters. The first stage of transformation of an atomic vapor of the admixture in clusters is the *three-body process*, which proceeds according to the scheme



where M is an atom of a condensing admixture, and X is an atom of a buffer gas. Correspondingly, the number density of diatomic molecules N_2 is determined by the balance equation

$$\frac{dN_2}{dt} = K N_a N^2$$

where K is the rate constant of this three-body process, N_a is the number density of atoms of a buffer gas and N is the number density of free atoms of a nucleating vapor. We assume that, starting from diatomic molecules, the cluster growth process results from pair processes (21.1), that is, the forming diatomic molecules are the nuclei of condensation for clusters. Under the criterion

$$K N_a N \tau_{\text{ex}} \ll 1 \quad (23.2)$$

the formation of diatomic molecules does not influence the balance of admixture atoms. In this regime of nucleation we estimate the typical time of transformation of an atomic vapor into clusters. The three-body process delays the growth of clusters if

$$G = \frac{k_o}{K N_a} \gg 1 \quad (23.3)$$

i.e. the number density N_a of buffer gas atoms is restricted. We assume here that the criterion (23.3) holds true.

According to the balance equation, the number density of diatomic molecules formed through a time τ from the beginning is estimated as

$$N_2 \sim K N_a N^2 \tau$$

Then each molecule is a nucleus of condensation on which a cluster grows with a rate (11.15), so that after a time τ the typical cluster size is

$$n \sim (k_o N \tau)^3$$

The nucleation process is finished when all the atoms become bonded, that is

$$N_2 n \sim N$$

From this we find the typical nucleation time of an atomic vapor in a buffer gas τ and a typical cluster size n at this time

$$\tau \sim \frac{1}{k_o N} \cdot G^{1/4}; \quad n \sim (k_o N \tau)^3 \sim G^{3/4} \quad (23.4)$$

Because of the criterion (23.3), clusters are large during the transformation of an atomic vapor in clusters. Taking typical values of the parameters in this formula $k_o \sim 10^{-11} \text{ cm}^3/\text{s}$, $K \sim 10^{-33} \text{ cm}^6/\text{s}$ and $N_a \sim 10^{18} \text{ cm}^{-3}$, we obtain $G \sim 10^4$, $N\tau \sim 10^{12} \text{ cm}^{-3}\text{s}$ and $n \sim 10^3$. Hence large clusters are formed under such conditions.

In order to understand the nature of the nucleation process for the transformation of an atomic metallic vapor into clusters in a buffer gas, we analyze in detail the regime of cluster growth, when owing to the process (21.1) only a small part of an expanding vapor is transformed in clusters, but due to the criterion (23.3) these clusters are large. The balance equation for the number density N of free metallic atoms has the form

$$\frac{dN_b}{dt} = -\frac{dN}{dt} = \int N k_o n^{2/3} f_n dn + K N^2 N_a, \quad \frac{dN_{cl}}{dt} = K N^2 N_a \quad (23.5)$$

where N_b is the total number density of bound atoms, N_{cl} is the number density of clusters, f_n is the size distribution function of clusters that satisfies to the normalization conditions

$$N_{cl} = \int f_n dn, \quad N_b = \int n f_n dn \quad (23.6)$$

and k_n , the rate constant of atom attachment to a cluster of n atoms within the framework of the liquid drop model, is given by formulae (11.15) and (11.16), where we assume the probability of atom sticking to the cluster surface to be one

$$k_n = k_o n^{2/3}, \quad k_o = \sqrt{\frac{8T}{\pi m}} \pi r_W^2$$

where m is the atom mass and r_W is the Wigner–Seitz radius for a cluster material.

The set (23.5) of balance equations describes the character of cluster growth for conditions under consideration. One can see that the ratio of the first and second terms of the right-hand side of the first balance equation (23.5) is of the order $G n^{2/3}$, where n is a current cluster size n , and since $G \gg 1$, $n \gg 1$, one can neglect the second term in the first balance equation. In addition, we assume here that a typical cluster size n is large compared with the critical cluster size that allows us to neglect the processes of cluster evaporation in the set of balance equations (23.5). We below solve this set of balance equations where we ignore cluster evaporation processes and for simplicity we assume in these equations $N = \text{const}$, until N_b reaches the value N . Then relation

$$N_b(\tau) = N$$

gives us the time τ of the nucleation process.

For determination of the size distribution function f_n of clusters we note that a size $n(t)$ of the cluster satisfies to the equation

$$\frac{dn}{dt} = k_o n^{2/3} N$$

if a diatomic molecule, a condensation nuclei for this cluster, is formed at $t = 0$. From this it follows that the size of this cluster at time t is

$$n = \left(\frac{N k_o t}{3} \right)^3 \quad (23.7)$$

Taking into account that $f_n dn$, the number density of clusters with sizes from n to $n + dn$, is proportional to the time range dt when diatomic molecules form nuclei of condensation, i.e. $f_n dn \sim dt$, we obtain on the basis of formula (23.7) for the size distribution function of clusters

$$f_n = \frac{C}{n^{2/3}}, \quad n < n_{\max} \quad (23.8)$$

where C is the normalization constant, $n_{\max}$ is the maximum cluster size at this time, and $f_n = 0$ if $n > n_{\max}$. This formula may be obtained directly from the kinetic equation (22.24) for the distribution function f_n if we neglect evaporation processes

$$\frac{\partial f_n}{\partial t} = -\frac{\partial}{\partial n} (N k_o n^{2/3} f_n)$$

and, as we have seen, formula (23.8) is a solution of this equation.

We now determine the parameters describing the kinetics of cluster growth. On the basis of the normalization relations (23.6) we have, using the distribution function (23.8), at the end of the nucleation process

$$C = \frac{4N}{3n_{\max}^{4/3}}, \quad N_{cl} = 3Cn_{\max}^{1/3} = \frac{4N}{n_{\max}}, \quad \bar{n} = \frac{n_{\max}}{4} \quad (23.9a)$$

where $\bar{n}$ is the average cluster size, and we use the relation (23.7) for the maximum cluster size at the end of the nucleation process:

$$n_{\max}(\tau) = \left(\frac{N k_o \tau}{3} \right)^3 = \left(\frac{\zeta}{3} \right)^3$$

where $\zeta = N k_o \tau$. Next, we integrate the balance equations (19.11) over the time of nucleation, neglecting the second term on the right-hand side of the second equation. This gives

$$N_{cl} = K N^2 N_a \tau = N \frac{\zeta}{G}, \quad N_b(\tau) = \int N k_o C n_{\max} dt = \frac{1}{4} \zeta C n_{\max} = N \quad (23.9b)$$

where we use the relation (23.7). Within the framework of this model, all the free atoms become bound at the end of the nucleation process.

This simplified scheme for the nucleation of an atomic vapor allows us to express the cluster parameters at the end of the nucleation process through the parameter G according to formula (23.3). Indeed, comparing the expressions for N_{cl} from formulae (23.9a) and (23.9b), we have

$$n_{\max} = \frac{4G}{\zeta} \quad (23.10)$$

and using the expression for $n_{\max}$ in accordance with formula (23.7), we get for the reduced nucleation time

$$\zeta = 3 \left(\frac{4}{3} G \right)^{1/4} = 3.2 G^{1/4}, \quad \tau_{cl} = \frac{3.2 G^{1/4}}{k_o N} \quad (23.11a)$$

where τ_{cl} is the time of transformation of an atomic vapor in a gas of clusters for this model, and the reduced nucleation time is large because $G \gg 1$. This leads also to large cluster sizes at the end of the nucleation process

$$n_{\max} = 1.2 G^{3/4}, \quad \bar{n} = 0.31 G^{3/4}, \quad N_{cl} = 3.2 N G^{-3/4} \quad (23.11b)$$

Thus, in considering the nucleation of an atomic vapor in a dense buffer gas, we use a simple realistic scheme for this process that allows us to analyze real cases of cluster generation. Then we will connect the parameters of the nucleation process with the parameters of other processes for a certain scheme of cluster generation. Note that although we consider the formation of pure metallic clusters from their atoms, in reality the generation of some compounds of these metals is possible. For example, a small oxygen admixture can give clusters of metal oxides. We note that in this regime of nucleation, criterion (23.2) prevents the main part of an atomic vapor from formation of diatomic molecules, and criterion (22.12) provides a large size of forming clusters. These criteria can be compatible if the condition (23.3) holds true. Typical values of the rate constants are $k_o \sim 10^{-11} \text{ cm}^3/\text{s}$ and $K \sim 10^{-33} \text{ cm}^6/\text{s}$, so that the regime of nucleation considered is valid if $N_b \ll 10^{22} \text{ cm}^{-3}$.

Let us use the connection between the cluster size n at the end of the process and the time t of formation of diatomic molecules which are the nuclei of condensation for these clusters. Clusters, which result from diatomic molecules formed at moment t , have the following size:

$$n = \left(\frac{k_o N \tau_{ex}}{3} \right)^3 \exp \left(-\frac{3t}{\tau_{ex}} \right) = n_{\max} \exp \left(-\frac{3t}{\tau_{ex}} \right)$$

where N is the number density of metallic atoms at the initial time. Next, the rate of formation of nucleation centers at time t is equal to

$$\frac{dN_2}{dt} = K N_a N^2 \exp \left(-\frac{3t}{\tau_{ex}} \right)$$

Because the cluster size n is definitively connected with the time of formation of a condensation nucleus, we have from these equations for the the distribution function f_n of clusters of size n in the end of the process from the relation $f_n dn \sim dN_2$ and formula 23.7:

$$f_n = \frac{C}{n^{2/3}} \exp \left(-\frac{9n^{1/3}}{k_o N \tau_{ex}} \right) \quad (23.12)$$

where C is the normalization factor. The most of atoms remains free under the criterion

$$KN_a N \tau_{ex} (k_o N \tau_{ex})^3 \ll 1 \quad \text{or} \quad k_o N \tau_{ex} \ll G^{1/4} \quad (23.13)$$

Thus the criterion that the number density of bound atoms is small compared with that of free atoms is given by

$$\tau_{ex} \ll \frac{G^{1/4}}{k_o N} \quad (23.14)$$

all the atoms are bonded in the end, and formula 23.8 for the distribution function, as well as formulas 23.11 for cluster parameters in the end of the process hold true. In the case

$$\tau_{ex} < \tau_{cl} \quad (23.15)$$

where τ_{cl} is a typical time of cluster growth (formula 23.11a), and the most part of atoms remains free in the end of the expansion process.

We now consider another regime of cluster growth when initially metallic atoms are bonded in gaseous molecules, so that metallic atoms are formed in the course of cluster growth, and the typical time τ_{ch} of formation of free atoms as a result of the decay of molecules is large compared with an atom's lifetime with respect to its attachment to clusters. For example, this regime is realized by the formation of clusters M_n as a result of the injection of gaseous molecules MX_6 into a buffer gas, where M is a metal atom and X is a halogen atom. In the first stage of the process molecules are destroyed, and then the metallic atoms join into clusters. Of course, this takes place over some temperature range, where the $M-X$ bonds are broken and stronger bonds $M-M$ are stable. We assume that diatomic metallic molecules are formed in three-body collisions of metallic atoms and the atoms of a buffer gas, and diatomic molecules are the nuclei of condensation for cluster growth. The set of balance equations describing this regime of cluster growth has the form

$$\frac{dN}{dt} = Q - N_{cl} k_o n^{2/3} N - K N^2 N_a, \quad \frac{dN_{cl}}{dt} = K N^2 N_a, \quad \frac{dn}{dt} = k_o n^{2/3} N \quad (23.16)$$

where Q is the rate of formation of free metallic atoms as a result of the decomposition of molecules. The second equation of this relations (23.16) takes into account that diatomic molecules are nuclei of condensation and are later converted into clusters.

The ratio of the second and third terms of the right-hand side of the first equation is of the order of the current cluster size n , and since $n \gg 1$ one can neglect the third term. In this regime of cluster growth, the values N and N_{cl} grow during the first stage of the process. During the second stage the number density of clusters does not vary, while that of free atoms falls. Denoting by $t_{\max}$ the time when the number density of free atoms reaches a maximum, we have for the parameters of this process

$$\begin{aligned} t_{\max} &\sim \frac{G^{1/8}}{\sqrt{Q k_o}}, \quad N(t_{\max}) \sim Q t_{\max} \sim G^{1/8} \sqrt{\frac{Q}{k_o}}, \\ N_{cl} &\sim G^{-5/8} \sqrt{\frac{Q}{k_o}}, \quad n(t_{\max}) \sim G^{3/4} \end{aligned} \quad (23.17)$$

We have the following estimate for the rate of decay of molecules $Q \sim N_b/\tau_{ch}$, where N_b is the total number density of bound atoms in clusters when the nucleation process finishes, and τ_{ch} is the typical time of decay of molecules containing metallic atoms. At the end of the nucleation process we have for the typical cluster size

$$n \sim \frac{N_b}{N_{cl}} \sim G^{5/8} \sqrt{Q k_o} \tau_{ch} \quad (23.18)$$

Thus, according to this analysis, the two limiting regimes of nucleation of an atomic metallic vapor in a buffer gas proceed to different stages of nucleation. When criterion (23.3) holds true, the clusters are mostly large, but metallic atoms may be free or bound. Cluster growth proceeds due to processes (21.1) for free metallic atoms and according to the scheme (22.1) when these atoms are bound in clusters. In the regime in which cluster growth is determined by the attachment of free atoms to nuclei of condensation, and a pair process of cluster growth starts from diatomic molecules, the average cluster size is estimated on the basis of formulae (23.4) or (23.11b) when all the atomic vapor is converted into clusters. After this the cluster growth is determined by cluster coagulation (22.1), and the average cluster size is given by formula (22.11). Under the condition $N \gg N_b$, cluster growth is determined by the processes (21.1), and in the other regime, when the opposite criterion $N \ll N_b$ holds true, the cluster growth proceeds according to the process (22.1). The character of cluster growth does not depend on the charge of the clusters in the first case, whereas for clusters of identical charge sign the coagulation process stops.

The above analysis allows us to extract the following stages of transformation of an atomic vapor located in a buffer gas into a gas of clusters. In the first stage of nucleation, when atoms are mostly free, the process of formation of clusters is delayed due to the three-body formation of diatomic molecules. The diatomic molecules that form become the nuclei of condensation, and the subsequent growth of clusters from them proceeds quickly. Therefore, when all the atomic vapor is transformed into clusters, the clusters formed are large at the end, even if most of the atoms are free. The second stage of the nucleation process, the coagulation process (22.1), proceeds if the clusters are neutral. For charged clusters their charge prevents contact between clusters. Then cluster growth proceeds via an atomic vapor which is found in equilibrium with the clusters. The interaction between an atomic vapor and clusters leads to the evaporation of small clusters and the growth of large clusters (*coalescence* or *Ostwald ripening*). As a result, clusters grow and their number decreases. In this case the rate of cluster growth is lower than for the coagulation process, and the temperature dependence of this rate is sharp.

23.2 Heat Regime of Cluster Growth in Expanding Gas

In the case of joining of two clusters, the binding energy of atoms in a forming cluster exceeds the total binding energy of atoms in clusters at the beginning. Hence, a heat release results from the process (22.1). The energy excess of this process can be consumed on release of atoms, i.e. the coagulation process is accompanied by the formation of free atoms. In addition, this heat release can influence the heat regime of the cluster growth process. In particular, let us consider from this standpoint a method of generation of cluster beams by free

jet expansion of a pure atomic vapor. As a result of vapor expansion, the gaseous temperature decreases and the vapor becomes supersaturated. Then the vapor is converted into clusters, i.e. an atomic beam is converted into a cluster beam. In this process the energy of gas compression is used for cooling in the course of expansion. But the energy of gas compression per atom usually does not exceed the thermal atom energy, while the binding energy of cluster atoms per atom significantly exceeds the typical thermal energy of an atom. Hence the process of formation and growth of clusters as a result of vapor expansion influences the heat regime of the expansion process. In particular, the total transformation of atoms of an expanding vapor into clusters is practically impossible without a buffer gas that removes the excess energy.

Let us determine the number of released atoms resulted from the joining of two large clusters according to the scheme (22.1) if the released energy is consumed on liberation of atoms. An excited cluster resulting from the joining of two clusters can subsequently emit several atoms, and we have a more complicated process compared with (22.1) which proceeds according to the scheme:



Note that an excited cluster with a pair interaction of atoms emits only isolated atoms, because the evaporation of molecules and fragments is characterized by a small probability. Taking the binding energy of atoms of a large cluster consisting of n atoms in the form (formulas (7.24), (12.43))

$$E = \varepsilon_o n - An^{2/3}$$

we find the energy release as a result of the process (23.15)

$$\Delta E = A \left[m^{2/3} + (n - m)^{2/3} - n^{2/3} \right]$$

In particular, for $l = n/2$, when this function of l at a given n has a maximum, we get

$$\Delta E_{\max} = 0.25An^{2/3}$$

As we can see, this released energy is created by the surface cluster energy. Assuming the temperature of colliding and forming clusters to be identical, we find the maximum number of released atoms

$$p_{\max} = \frac{\Delta E_{\max}}{\varepsilon_o} = 0.25 \frac{An^{2/3}}{\varepsilon_o}$$

Since $A \sim \varepsilon_o$ and $n \gg 1$, the number of released atoms is relatively small: $p_{\max} \ll n$. Therefore, below we neglect this effect.

Now we analyze the heat character of expansion of a nucleating vapor which is located in a buffer gas. This is an *adiabatic process* which is accompanied by energy exchange between different degrees of freedom of an expanding gas. For the analysis of this process, let us take a gas volume V in which n_b atoms of a buffer gas and n_v atoms of a vapor are located, with these atoms being free at the beginning. The variation of the total energy of this volume is equal to

$$dE = dQ + p dV$$

where Q is the thermal energy of clusters in this volume and p is the gaseous pressure. Assuming the concentration of vapor atoms in a buffer gas to be small, we neglect the thermal energy of vapor atoms. Then the variation of the thermal energy is equal to

$$dQ = \frac{3}{2}n_a dT - \sum_k E_k dn_k$$

where dT is the temperature variation, n_k is the number of clusters consisting of k atoms and located in a given volume, and E_k is the total binding energy of atoms in a cluster containing k atoms. Introducing the number density of a buffer gas N_a and using its definition $N_a = n_a/V$, we obtain $p dV = -n_a T dn_a/N_a$, where we use the equation of the gas state $p = N_a T$. From the adiabatic character of the expansion process $dE = 0$, we obtain, accounting for the above relations:

$$dE = dQ + p dV = \frac{3}{2}n_a dT - n_a T \frac{dN_a}{N_a} - \sum_k E_k dn_k = 0 \quad (23.20)$$

If we neglect the nucleation process, equation (23.20) gives the adiabatic law (6.11) of expansion of a monatomic gas, that is $N_a \sim T^{3/2}$. Below we assume that the flow of a buffer gas maintains cylindrical symmetry during free jet expansion. Denote the beam radius by R and take into account that the atom flux $J = \pi R^2 N_a u$ is conserved during expansion, where the drift velocity of atoms u is assumed to be independent of the temperature. Then we have $N_a/N_o = R_o^2/R^2$, where N_o and R_o are the initial values of the beam parameters. Substituting this in equation (23.16), we get

$$\frac{3}{2}n_a dT - 2n_a T dR/R - \sum_k E_k dn_k = 0$$

Now let us assume that at the beginning all the vapor atoms are free, and condensation takes place in a narrow temperature range near T_* . The solution of this equation under these conditions has the form

$$T = T_o \left(\frac{R_o}{R} \right)^{4/3} \exp \left(\frac{2\varepsilon c}{3T_*} \right) \quad (23.21)$$

where $c = n_v/n_a$ is the concentration of vapor atoms and ε is the cluster binding energy per atom. From this it follows that the nucleation process does not influence the character of gas expansion if the criterion

$$c \ll T_*/\varepsilon$$

holds true. In the opposite case, the thermal effect of the nucleation process stops this process, so that only some of the free atoms can form clusters. For this reason a buffer gas is required for the total nucleation of an expanding vapor in order to remove the excess energy.

Now let us determine the maximum concentration of atoms in forming clusters as a result of the free expansion of a pure vapor. We assume that the formation of clusters proceeds in a narrow range of temperatures near T_* and use equation (23.16) in the form

$$\frac{3}{2}n dT - nT \frac{dN}{N} - \sum_k E_k dn_k = 0$$

where n is the total number of atoms in the expanding volume being considered, and N and T are the number density of atoms and the temperature. We take the initial values of these parameters to be N_o and T_o , and suppose at the beginning of nucleation these values to be N_* and T_* . During the first stage of expansion, when nucleation is absent, the vapor state is governed by the equation

$$\frac{3}{2} dT - T \frac{dN}{N} = 0$$

so that $N \sim T^{3/2}$ in accordance with formula (6.11), and we have before nucleation

$$N_* = N_o \left(\frac{T_*}{T_o} \right)^{3/2}$$

At the next stage of the process $dT = 0$, and we obtain

$$\frac{dN}{N} + \sum_k E_k \frac{dn_k}{n} = 0$$

The nucleation process starts at a temperature T_* when the formation of diatomic molecules as nuclei of condensation is possible. Hence this temperature can be estimated from the relation $N_2(T_*) \sim N$, where $N_2(T_*)$ is the number density of molecules under thermodynamic equilibrium. Let us assume that the forming clusters are large, so that the binding energy per atom is close to that of the bulk, which we denote by ε_o . Then the above equation of the heat balance takes the form

$$\frac{3}{2} n dT - nT \frac{dN}{N} - \varepsilon_o n dc = 0$$

where c is the concentration of bound atoms, i.e. it is the ratio of the number of bound atoms to the total number of atoms in a given volume. This regime of nucleation without a buffer gas corresponds to the criterion

$$KN^2\tau_{\text{ex}} \ll 1$$

where K is the rate constant of the three-body process $3A \rightarrow A_2 + A$, and τ_{ex} is the expansion time. If the nucleation process is limited by heat release, it proceeds at a constant temperature and leads to the maximum concentration of bound atoms at the end of the process, which according to the solution of this equation is equal to

$$c_{\text{max}} = \frac{T_*}{\varepsilon_o} \ln \frac{N_*}{N_f} \quad (23.22)$$

where N_f is the final number density of free atoms when the nucleation process finishes. According to equation (23.7), the end of the cluster growth $\Delta n \sim 1$ corresponds to the condition

$$k_o N_f \tau_{\text{ex}} n_{\text{max}}^{2/3} \sim 1$$

where $n_{\max}$ is the typical number of cluster atoms at the end of the process, which according to formula (22.10) is equal to

$$n_{\max} \sim (k_o N_* \tau_{\text{ex}})^3$$

Thus the maximum concentration of bound atoms at the end of the expansion process with accuracy up to numerical values under the logarithm is equal to

$$c_{\max} = \frac{T_*}{\varepsilon_o} \ln n_{\max} \quad (23.23)$$

Note that $n_{\max}$ is the cluster size due to the attachment process only. In reality, $T_*/\varepsilon_o \sim 0.1$, so that the real maximum degree of nucleation in a pure vapor is several tens per cent.

23.3 Mechanisms of Nucleation in Free Jet Expansion

We now ascertain the sequence of nucleation mechanisms in free jet expansion. As a result of free jet expansion, the temperature drops sharply, so that the gas or vapor pressure increases and exceeds the saturated vapor pressure, starting from some temperature. Moreover, we assume the supersaturation degree [formula (12.42)] of a vapor to be large, so that one can ignore evaporation processes in the process of cluster growth. We consider below the role of attachment and coagulation processes in free jet expansion of a buffer gas with a nucleating vapor.

In the first stage of nucleation cluster growth results, involving free atoms and including processes (21.1) and (23.1). At the next stage, the coagulation process (22.1) determines cluster growth. It follows from equation (23.2) that the number density of clusters is estimated as

$$N_2 \sim K N_a N^2 t \sim \frac{N}{G} n^{1/3}$$

where $n \sim (N k_o t)^3$ is a typical cluster size at time t . The number density of bound atoms at that time is given by

$$N_b \sim \frac{N}{G} n^{4/3}$$

From this it follows that when all the atoms become bonded, $N_b \sim N$, the typical cluster size is

$$n \sim G^{3/4}$$

Let us determine the contribution of the coagulation process to a cluster size. According to formula (22.11) we have for a cluster size due to the coagulation process

$$n_{\text{coag}} \sim (N_b k_o t)^{1.2} \sim \left(\frac{n^{5/3}}{G} \right)^{1/2} \sim G^{1/8}$$

where we assume that cluster growth results from the attachment of free atoms to clusters. One can see that the contribution of the coagulation process is small compared to the mechanism of atom attachment.

Thus the expansion of a buffer gas with an admixture of a vapor is accompanied by a nucleation process resulting from the formation of clusters and attachment of atoms to clusters. Coagulation makes a small contribution to cluster growth at this stage of the process. When all the atoms become bonded, the coagulation mechanism determines cluster growth. But the attachment and coagulation mechanisms of nucleation in free jet expansion are separate and act on different stages of the nucleation process.

We now demonstrate this in an example: a buffer gas containing a concentration $c = 1\%$ of nucleating metallic atoms is expanded through a nozzle, and after expansion its number density is $N_a \sim 10^{18} \text{ cm}^{-3}$, and at the final temperature $T \sim 1000 \text{ K}$ an admixture metallic vapor becomes supersaturated and is transformed into clusters. Then taking typical values for the parameters of the nucleation process $k_o \sim 10^{-11} \text{ cm}^3/\text{s}$ and $K \sim 10^{-33} \text{ cm}^6/\text{s}$, we obtain $G \sim 10^4$, and the average cluster size according to formula (23.6) is $n \approx 10^3$ at the end of the nucleation processes (21.1) and (23.1). Under these conditions, formula (23.6) gives for the typical time of transformation of metallic atoms in clusters as a result of attachment processes involving free metallic atoms $\tau \sim 2 \cdot 10^{-4} \text{ s}$. It follows from formula (22.31) that the coagulation process leads to subsequent cluster growth during a typical time $\tau_{coag} \sim 10^{-3} \text{ s}$. Hence the processes of cluster growth due to the attachment of free atoms to clusters and the coagulation of clusters are separated in time under these conditions.

23.4 Nucleation in Free Jet Expansion in Pure Gas

We now consider the peculiarities of cluster growth during *free jet expansion* of a pure gas when the nucleation process proceeds according to the scheme



This scheme assumes a strong supersaturation of the gas, so that inverse processes of cluster evaporation are negligible. We analyze this regime from the standpoint of the above results.

We use formulae (11.15) and (11.39) for the rate constants of the pair and three-body collisions and clusters with a pair interaction of atoms for which according to Table 7.3 we have $r_W = 0.64R_e$. Then the parameter G , which is given by formula (23.4) and characterizes the cluster growth process, is equal to

$$G = \frac{k_o}{KN} = \frac{0.34}{R_e^3 N} \gg 1 \quad (23.25)$$

This parameter is assumed to be large. Then the formation of diatomic molecules requires a long time in comparison with the subsequent growth of a cluster. The diatomic molecules are the nuclei of condensation, and the average cluster size is large even during the initial stage of the cluster growth process. As a matter of fact, this corresponds to the case of zero temperature, when the critical cluster size is zero also. In this case the Zeldovich formula (21.22) is not valid because the equilibrium distribution function of clusters diverges at high cluster sizes n . For this reason the nucleation process is not stationary in this case.

Hence, within the framework of the above nucleation theory, we neglect the evaporation process taking $B_n = 0$, which gives for the flux of attaching atoms

$$j_n = A_n f_n = N k_n f_n = N k_o n^{2/3} f_n$$

and the kinetic equation for the cluster growth has the form

$$\frac{\partial f_n}{\partial n} = -\frac{\partial j_n}{\partial n}$$

The distribution function f_n is zero at large n , and the boundary cluster size $n_{\max}$, above which the distribution function is zero, increases with time. This value can be found from the balance equation

$$\frac{dn}{dt} = k_o n^{2/3} N$$

and from this equation we have for the maximum cluster size

$$n_{\max} = \left(\frac{N k_o t}{3} \right)^3$$

We assume here that at time t atoms are mostly free, so that the number density of free atoms N is almost independent of time.

One can solve the kinetic equation taking $j_n = \text{const}$ at $n < n_{\max}$ and a sharp boundary of the distribution function. This gives

$$f_n = \frac{C}{n^{2/3}}$$

Next, the total number density of clusters N_{cl} is equal to the number density of nuclei of condensation $\int K N^3 dt$, which gives $C = N/G$ or

$$f_n = \frac{N}{G n^{2/3}} \quad (23.26)$$

This allows us to find the maximum cluster size at the end of the attachment process because the total number density of bound atoms $\int f_n n dn$ is less than the initial number density N_o of free atoms. This gives

$$n_{\max} < \left(\frac{3}{4} G \right)^{3/4} \gg 1 \quad (23.27)$$

Using this in formula (23.19), we have for the maximum concentration of bound atoms at the end of the process

$$c_{\max} = \frac{3T_*}{4\varepsilon_o} \ln G \quad (23.28)$$

We here neglect factors of the order of one under the logarithm. Evidently, the typical time of the attachment process

$$t_{\text{at}} \sim \frac{G^{1/4}}{N_o k_o}$$

is comparable in this case with the time of expansion τ_{ex} . This condition $t_{\text{at}} \sim \tau_{\text{ex}}$ chooses a temperature T_* at which the nucleation process proceeds.

Note that this regime of nucleation when cluster growth results only from the attachment of free atoms to clusters takes place at low number densities of free atoms, when one can ignore the coagulation process. Comparing formula (23.28) with that for the nucleation process (21.1) when the maximum concentration of bound atoms follows from formula (23.11b), we have the criterion for this regime of nucleation

$$G \gg (N_o k_o \tau_{\text{ex}})^{1.6} \quad (23.29)$$

In practice, this is fulfilled at pressures below 1 atm.

23.5 Hagedorn Approximation for Nucleation Rate

According to the above analysis, the rate of cluster growth for the coagulation regime of nucleation can be expressed through the parameter

$$x = N_o k_o \tau_{\text{ex}} \quad (23.30)$$

where N_o is the initial number density of condensing atoms, k_o is given by formula (11.16), and τ_{ex} is the typical time of expansion which is connected with the nozzle diameter. Hagedorn introduced an empirical parameter Γ which is similar to this parameter and which we will call the *Hagedorn parameter*:

$$\Gamma = N_o d^q T_o^{0.25-1.5} \quad (23.31)$$

where N_o and T_o are the initial number density and temperature of an atom beam, d is the nozzle diameter, and the parameter q lies in the range 0.5–1.0 and is chosen from experimental data; its optimal value is 0.85. It is convenient to use the reduced Hagedorn parameter Γ^* according to the formula

$$\Gamma^* = \frac{\Gamma}{\Gamma_{ch}}, \quad \Gamma_{ch} = r_{ch}^{3-q} T_{ch}^{0.25q-1.5}, \quad r_{ch} = \left(\frac{m}{\rho} \right)^{1/3} \quad (23.32)$$

Here m is the atom mass, ρ is the bulk density, T_{ch} is the sublimation energy per atom for bulk expressed in kelvins, and the value r_{ch} is proportional to the Wigner–Seitz radius r_W , which is given by formulae (7.25) and (11.13b) ($r_{ch} = 0.62r_W$). Table 23.1 gives the values of the reduced Hagedorn parameters for some vapors and gases.

Various parameters of a cluster beam can be expressed through the reduced Hagedorn parameter, and Figure 23.1 is a demonstration of this for the average cluster size $\bar{n}$ after the nozzle. The threshold character of this dependence is because the three-body process at the first stage of nucleation delays cluster growth. In spite of the fact that the Hagedorn formula is rough, it is based on experimental data and allows one to estimate the parameters of the clusters resulting from free jet expansion.

Table 23.1. The reduced Hagena parameter for some gases and vapors*.

Gas, vapor	$\Gamma_{ch}, m^{-2.15} K^{-1.29}$	Gas, vapor	$\Gamma_{ch}, m^{-2.15} K^{-1.29}$
Ar	350	Ga	5.8
Kr	210	In	5.6
Na	12	Ge	3.4
K	9.1	Rb	6.4
Cs	7.8	Fe	5.0
Cu	6.3	Ni	6.6
Ag	6.0	Zn	18
Au	4.3	Cd	17
Al	5.5	Hg	32

*Hagena, O. F. (1987) *Z. Phys.* 4D, 291.

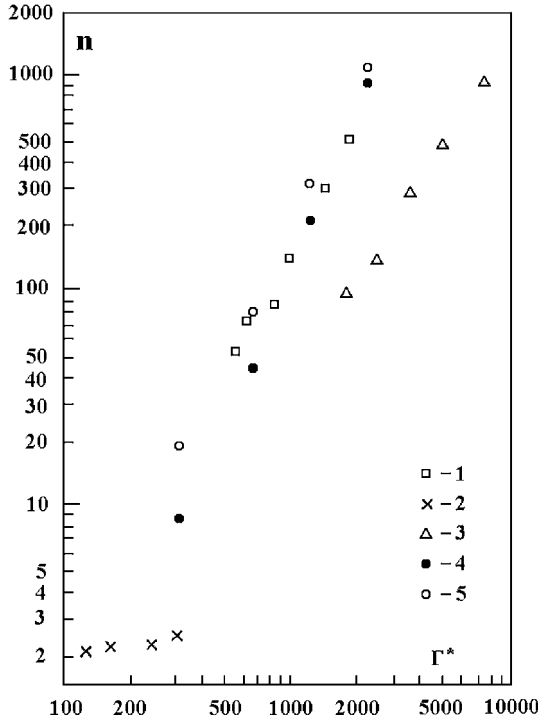


Figure 23.1. The dependence of the average cluster size on the reduced Hagena parameter. 1,2,3 – experimental results for rare gases, 4,5 – formula (23.11b) with the three-body rate constants $K = 1 \cdot 10^{-32} \text{ cm}^6/\text{s}$ and $K = 2 \cdot 10^{-32} \text{ cm}^6/\text{s}$ correspondingly.

23.6 Character of Nucleation in Pure Gas

We considered above the different mechanisms of cluster growth which are given in Figure 22.1, and below we sum up the character of nucleation for the simplest system, as a pure gas. This is given in Figure 23.2, where the role of different mechanisms of nucleation is

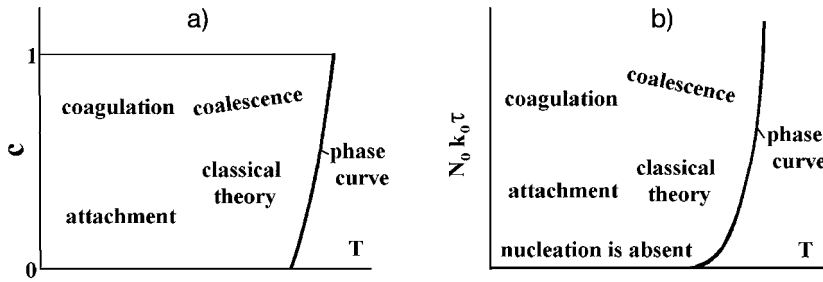


Figure 23.2. The mechanisms of cluster growth depending on parameters of a pure nucleating gas or vapor, where the absciss axis is the gas temperature and the ordinate axis is the concentration of bound atoms (a) and the reduced parameter of the number density of atoms (b) (N_o is the total number density of free and bound atoms, k_o is the rate constant (11.16) of atom collisions, τ is a time of growth or expansion).

given depending on the gas temperature, and also on the concentration of bound atoms c or on the reduced density or time parameter $N_o k_o \tau$. Briefly, all the nucleation processes proceed if the gas density exceeds that at the saturated vapor pressure, i.e. it is possible to the left of the phase curve where the gas pressure is equal to the saturated vapor pressure. The coagulation and coalescence mechanisms are realized if the concentration of bound atoms is remarkable and the coalescence mechanism takes place at high temperatures. If the atoms are mostly free, one can extract two limiting cases. In the case of the classical theory of nucleation, the size distribution of liquid clusters corresponds to thermodynamic equilibrium. Then the rates of atom attachment to clusters are almost equal to the rate of atom evaporation from the cluster surfaces, and their difference, which determines the rate of the nucleation process, is relatively small. In the other limiting case, when the degree of gas supersaturation is high enough, one can neglect the evaporation process. Then the size distribution function of clusters does not correspond to thermodynamic equilibrium and is determined by the kinetics of the atom attachment process. Correspondingly, the nucleation process becomes non-stationary in this case.

23.7 Instability of Clusters in a Nonhomogeneous Vapor

A uniform buffer gas with an admixture of a nucleating vapor is unstable with respect to the formation of clusters, and the processes of cluster growth and cluster evaporation lead to transformations of clusters into an atomic vapor or a condensed bulk system depending on the temperature. One may expect this instability to disappear in a nonhomogeneous plasma with a temperature gradient. Above (see Section 17.10) we considered cluster instability when, due to a temperature gradient in the buffer gas, metallic atoms of a metallic admixture drift from a hot region to a cold one where they attach to clusters. As a result, all the metallic atoms are bonded in a cold region in the form of clusters. One can expect clusters to drift to a hot region and evaporate there, and this establishes an equilibrium of the metallic component in a

nonuniform buffer gas, so that the flux of metallic atoms to a cold region of a discharge plasma is equal to the flux of clusters to a hot region.

But this scheme is not realized for a dense buffer gas with a metallic admixture due to cluster instability (see Section 17.10), which follows from the size dependencies of the rate of cluster growth and the cluster diffusion coefficient in a buffer gas. In order to analyze this phenomenon, we now study the evolution of an individual cluster located in a cold region. In this region the evaporation process is not significant, so that the evolution of the cluster size n (the number of cluster atoms) is governed by the process of atom attachment, the rate of which is given by formula (11.15) (we take the probability of an atom sticking to the cluster surface on contact to be $\xi = 1$). Hence the balance equation is given by (23.7)

$$\frac{dn}{dt} = k_o n^{2/3} N$$

where N is the number density of free metallic atoms. The cluster distance z from an initial point in the temperature gradient direction is determined by the diffusion motion of a test cluster and is given by the equation

$$\frac{d\bar{z}^2}{dt} = 2D_n \quad (23.33)$$

where an average is taken over the possible positions of the cluster, and D_n is the diffusion coefficient in a buffer gas for a cluster consisting of n atoms. We use the size dependence for the cluster diffusion coefficient according to formula (17.32a) $D_n = D_o/n^{2/3}$, and we obtain the equation for cluster growth in a cold plasma region with removal of this cluster from an initial point

$$\frac{d\bar{z}^2}{dn} = \frac{2D_o}{k_o n^{4/3} N} \quad (23.34)$$

It follows from this equation that the removal of clusters becomes slower with increasing size. For a large cluster, the average value of the distance squared $\bar{z}^2(t)$ is, at the end of the process,

$$\bar{z}^2(\infty) = \frac{\Delta^2}{n^{1/3}}, \quad \Delta^2 = \frac{6D_o}{k_o N} \quad (23.35)$$

and a large cluster remains in the cluster region. Because $D_o \sim 1/N_o$, we have $\Delta \sim 1/\sqrt{N_o N}$, i.e. the value $\Delta\sqrt{N_o N}$ does not depend on the density of the buffer gas. Table 23.2 contains the reduced values of D_o and Δ at $T = 1000$ K for metallic clusters in argon as a buffer gas. One can see a weak dependence of the diffusion coefficient on the cluster material, and an average of the data of Table 23.2 gives for the average reduced diffusion coefficient of metallic clusters in argon $D_o = 1.0 \pm 0.1$ cm²/s. From the data of Table 23.2 for typical values $N_o \sim 10^{19}$ cm⁻³ and $N \sim 10^{13}$ – 10^{15} cm⁻³ we have $\Delta \sim 0.01$ – 0.1 cm. This implies the existence of cluster instability under real conditions when a metallic admixture is located in a buffer gas.

Table 23.2. The reduced diffusion coefficient D_o for large clusters in argon at the normal number density $N_o = 2.69 \cdot 10^{19} \text{ cm}^{-3}$ [formula (17.32)], and the reduced shift Δ [formula (23.35)] for large clusters in argon at temperature $T = 1000 \text{ K}$.

Element	$D_o, \text{cm}^2/\text{s}$	$\Delta\sqrt{N_o N}, 10^{15} \text{ cm}^{-2}$	Element	$D_o, \text{cm}^2/\text{s}$	$\Delta\sqrt{N_o N}, 10^{15} \text{ cm}^{-2}$
Ti	0.91	1.59	Pd	1.01	2.16
V	1.05	3.51	Ta	0.90	2.19
Fe	1.17	2.13	W	0.98	2.42
Co	1.20	2.22	Re	1.01	2.49
Ni	1.22	2.31	Os	1.05	2.60
Zr	0.74	1.52	Ir	1.01	2.51
Nb	0.90	1.85	Pt	0.98	2.45
Mo	0.98	2.05	Au	0.93	2.32
Rh	1.05	2.23	U	0.81	2.11

24 Conclusions

Statistical physics and physical kinetics have existed since the 19th century, starting with the Maxwell distribution and the Boltzmann kinetic equation. Having grown from thermodynamics, which deals with the average values of parameters for particles of a system of many particles, statistical physics uses the same concepts and parameters, such as temperature and entropy, as thermodynamics. But the language of statistical physics for the description of ensembles of interacting particles is based on the probabilities of an individual particle of the ensemble and on the distribution functions for its particles. If thermodynamics studies the equilibrium states of the particle ensembles, within the framework of statistical physics this equilibrium can be violated both between some parts of the ensemble – subsystems of particles – and between the degrees of freedom for this ensemble. Usually statistical physics operates with stationary systems, whereas the evolution of non-equilibrium systems is analyzed within the framework of physical kinetics, and the corresponding mathematical apparatus is based on the kinetic equation for particles.

Thus the foundations of statistical physics and physical kinetics and their basic concepts were formulated in the 19th century. Their subsequent development has resulted from the expansion of a number of objects and phenomena, as well as their features, to which these concepts may be applied. As may be seen from the contents of this book, these problems relate to various pure physical objects, such as solids, liquids, gases, plasmas and clusters which include atoms or molecules of the same chemical elements, and to aggregate states of various compounds which form mixtures, solutions, alloys and more complex compounds which can form polymers, gels and other structures, including fractal ones. Various aspects of the properties of these objects are the subject of study for statistical physics. Transitions between aggregate states of these objects are accompanied by specific phenomena, such as the phase and glassy transitions and nucleation phenomena. On the one hand, the general methods and concepts of statistical physics can be applied to the study of new problems for these objects and phenomena, allowing one to understand their nature from a common standpoint. On the other hand, the study of these objects and their new features provides new content for statistical physics and enriches it. Some aspects of this mutual influence of contemporary statistical physics and the problems of physical objects and phenomena are reflected in this book.

A Physical Constants and Units

A.1 Some Physical Constants

Velocity of light	$c = 2.99792 \times 10^{10}$ cm/s
Planck constant	$h = 6.62619 \times 10^{-27}$ erg· s
	$\hbar = 1.05459 \times 10^{-27}$ erg · s
Electron charge	$e = 4.8032 \times 10^{-10}$ CGSE
	$e^2 = 2.3071 \times 10^{-19}$ erg · cm
Electron mass	$m_e = 9.1095 \times 10^{-28}$ g
Proton mass	$m_p = 1.6726 \times 10^{-24}$ g
Atomic unit of mass	1.6605×10^{-24} g
Avogadro number	6.0221×10^{23} mol ⁻¹
Stefan–Boltzmann constant	$\sigma = 5.669 \times 10^{-12}$ W/(cm ² K ⁴)

A.2 Conversion Factors for Energy Units

	erg	eV	cal/mol	cm ⁻¹	K
erg	1	6.242×10^{11}	1.4395×10^{16}	5.0346×10^{15}	7.243×10^{15}
eV	1.602×10^{-12}	1	2.306×10^4	8.0660×10^3	1.1605×10^4
cal/mol	6.947×10^{-17}	4.3359×10^{-5}	1	0.34973	0.50319
cm ⁻¹	1.986×10^{-16}	1.2398×10^{-4}	2.8592	1	1.4386
K	1.3806×10^{-16}	8.671×10^{-5}	1.9873	0.69509	1

1 J = 10⁷ erg

A.3 Numerical Coefficients in Some Relationships of Physics

Relationship	Formula	Factor C	Units used
$v = \sqrt{2\varepsilon/m}$, v : velocity, ε : energy, m : mass	$v = C\sqrt{\varepsilon/m}$	5.931×10^7 cm/s 1.389×10^6 cm/s 5.506×10^5 cm/s 1.289×10^4 cm/s	ε in eV, m in emu* ε in eV, m in amu* ε in K, m in emu* ε in K, m in amu*
$\omega = \varepsilon/\hbar$ ε : photon energy, ω : frequency	$\omega = C\varepsilon$	1.520×10^{15} s ⁻¹	ε in eV
$\omega = 2\pi c/\lambda$ λ : wavelength	$\omega = C/\lambda$	1.885×10^{11} s ⁻¹	λ in cm
$\omega_p = \sqrt{4\pi N_e e^2/m_e}$ ω_p : plasma frequency	$\omega_p = C\sqrt{N_e}$	5.642×10^4 s ⁻¹	N_e in cm ⁻³
$r_D = \sqrt{T/(8\pi N_e e^2)}$ r_D : Debye–Hückel radius	$r_D = \sqrt{T/N_e}$	525.6 cm 4.879 cm	N_e in cm ⁻³ , T in eV N_e in cm ⁻³ , T in K
$\omega_H = eH/(mc)$ ω_H : Larmor frequency, H: magnetic field	$\omega_H = CH/m$	1.759×10^6 s ⁻¹ 9649 s ⁻¹	H in Gs, m in emu*) H in Gs, m in amu*)
$r_H = v/\omega_H$ r_H : electron Larmor radius	$r_H = C\sqrt{\varepsilon m}/H$	3.372 cm	ε in eV, H in Gs
$N = p/T$ p : pressure, N : number density	$N = Cp/T$	7.340×10^{21} cm ⁻³ 9.658×10^{18} cm ⁻³	p in atm, T in K p in Torr, T in K
$D = 3\sqrt{2\pi T/\mu}/(16N\sigma)$ D : diffusion coefficient	$D = C\sqrt{T/\mu}/(N\sigma)$	4.278×10^{19} cm ² /s	T in K, μ in amu*) N in cm ⁻³ , σ in Å ²
μ : reduced mass σ : mean cross section		1.595 cm ² /s	the same T , μ , σ , $N = 2.689 \times 10^{19}$ cm ⁻³
$x = eE/(TN\sigma)$	$x = CE/(TN\sigma)$	1.160×10^{20}	E in V/cm, T in K, σ in Å ² , N in cm ⁻³
Factor of Saha formula $f = [mT/(2\pi\hbar^2)^{3/2}]$	$f = CT^{3/2}$	7.635×10^{19} cm ⁻³ 3.018×10^{21} cm ⁻³ 1.879×10^{20} cm ⁻³	T in 10 ³ K, m in emu T in eV, m in emu T in K, m in amu

*emu – electron mass unit ($m_e = 9.108 \times 10^{-28}$ g), amu – atomic mass unit ($m_a = 1.6605 \times 10^{-24}$ g).

B Physical Parameters in the Form of the Periodical Table of Elements

B.1 Mobilities of Atomic Ions in Parent Gases

n	Shell of valence electrons					
	ns		ns ²		np ⁶	
1	1.008	12 8.4	11 7.6	4.003		
	¹ H	0.31	0.28	² He		
	Hydrogen	0.58	0.52	Helium		
2	6.491	1.1 0.74	9.012	1.8 1.3	4.0 2.8	20.179
	³ Li	0.027	⁴ Be	0.047	0.10	¹⁰ Ne
	Lithium	0.051	Berillium	0.091	0.19	Neon
3	22.990	0.92 0.63	24.305	0.80 0.56	1.6 1.1	39.948
	¹¹ Na	0.024	¹² Mg	0.021	0.041	¹⁸ Ar
	Sodium	0.044	Magnesium	0.038	0.077	Argon
4	39.098	0.29 0.20	40.08	0.44 0.31		
	¹⁹ K	0.0074	²⁰ Ca	0.011		
	Potassium	0.014	Calcium	0.021		
4	0.49 0.33	63.546	0.58 0.42	65.38	0.86 0.60	83.80
	0.013	²⁹ Cu	0.015	³⁰ Zn	0.022	³⁶ Kr
	0.023	Copper	0.029	Zinc	0.042	Krypton
5	85.468	0.18 0.12	87.62	0.27 0.18		
	³⁷ Rb	0.0045	³⁸ Sr	0.0071		
	Rubidium	0.0082	Strontium	0.013		
5	0.35 0.24	107.87	0.41 0.28	112.41	0.52 0.36	131.29
	0.0090	⁴⁷ Ag	0.011	⁴⁸ Cd	0.013	⁵⁴ Xe
	0.016	Silver	0.020	Cadmium	0.025	Xenon
6	132.90	0.12 0.084	137.33	0.17 0.12		
	⁵⁵ Cs	0.0032	⁵⁶ Ba	0.0045		
	Cesium	0.0058	Barium	0.0083		
6	0.31 0.21	196.97	0.36 0.25	200.59	0.31 0.23	[222]
	0.0079	⁷⁹ Au	0.0094	⁸⁰ Hg	0.0080	⁸⁶ Rn
	0.015	Gold	0.017	Mercury	0.016	Radon

Mobility of atomic ions in a parent atomic gas in cm²/V·s at temperatures of 300K (left) and 800K

Atomic weight — 137.33
 Symbol — Ba
 Atomic number — 56
 Element — Barium

0.17 0.12
 0.0045
 0.0083

Diffusion coefficient of atomic ions in a parent atomic gas in cm²/s at temperatures of 300K (up) and 800K (down).

B.2 Ionization Potentials for Atoms and Their Ions

Group Period	I	II			
1	1.008 $1s$ 1 H $2s_{1/2}$ 13.598 Hydrogen	24.588 $1s^2$ 4.003 54.418 $1s_0$ 2 He Helium	III	IV	V
2	6.491 $2s$ 5.392 11 Li $2s_{1/2}$ 75.64 122.4 Lithium	9.012 $2s^2$ 9.323 4 Be $1s_0$ 18.211 153.9 Beryllium 217.7	8.298 $2p$ 10.81 25.155 $2p_{1/2}$ 5 B 37.931 259.38 Boron	11.260 $2p^2$ 12.011 24.384 $3p_0$ 6 C 47.89 64.49 Carbon	14.534 $2p^3$ 14.007 29.602 $4s_{3/2}$ 7 N 47.45 77.47 Nitrogen
3	22.990 $3s$ 5.139 11 Na $2s_{1/2}$ 47.287 71.620 Sodium 98.92	24.305 $3s^2$ 7.646 12 Mg $1s_0$ 15.035 80.144 Magnesium 109.27	5.986 $3p$ 26.982 18.829 $2p_{1/2}$ 13 Al 28.448 119.99 Aluminium	8.152 $3p^2$ 28.086 16.346 $3p_0$ 14 Si 33.493 45.142 Silicon	10.437 $3p^3$ 30.974 19.770 $4s_{3/2}$ 15 P 30.203 51.444 Phosphorus
4	39.098 $4s$ 4.341 19 K $2s_{1/2}$ 31.63 45.81 Potassium 60.91	40.08 $4s^2$ 6.113 20 Ca $1s_0$ 11.872 50.913 Calcium 67.3	44.956 $3d4s^2$ 6.562 21 Sc $2d_{3/2}$ 12.800 21 Scandium 73.49	47.88 $3d^24s^2$ 6.82 22 Ti $3f_2$ 13.58 27.49 Titanium 43.27	50.942 $3d^34s^2$ 6.74 23 V $4f_{3/2}$ 14.66 29.31 Vanadium 46.71
	7.726 $3d^{10}4s$ 63.546 20.293 $2s_{1/2}$ 29 Cu 36.84 57.4 Copper	9.394 $4s^2$ 65.38 17.964 $1s_0$ 30 Zn 39.72 59.57 Zinc	5.999 $4p$ 69.72 20.51 $2p_{1/2}$ 31 Ga 30.7 64.2 Gallium	7.900 $4p^2$ 72.59 15.935 $3p_0$ 32 Ge 34.2 45.7 Germanium	9.789 $4p^3$ 74.922 18.59 $4s_{3/2}$ 33 As 28.4 50.1 Arsenic
5	85.468 $5s$ 4.177 37 Rb $2s_{1/2}$ 27.290 39.2 Rubidium 52.6	87.62 $5s^2$ 5.694 38 Sr $1s_0$ 11.030 42.88 Strontium 56.28	88.906 $4d5s^2$ 6.217 39 Y $2d_{3/2}$ 12.24 20.525 Yttrium 60.61	91.22 $4d^25s^2$ 6.837 40 Zr $3f_2$ 13.13 23.1 Zirconium 34.419	92.906 $4d^45s$ 6.88 41 Nb $6d_{1/2}$ 14.32 25.0 Niobium 37.7
	7.576 $4d^{10}5s$ 107.87 21.49 $2s_{1/2}$ 47 Ag 34.8 Silver	8.994 $5s^2$ 112.41 16.908 $1s_0$ 48 Cd 37.47 Cadmium	5.786 $5p$ 114.82 18.87 $2p_{1/2}$ 49 In 28.0 57.0 Indium	7.344 $5p^2$ 118.69 14.632 $3p_0$ 50 Sn 30.50 40.74 Tin	8.609 $5p^3$ 121.75 16.53 $4s_{3/2}$ 51 Sb 25.32 44.16 Antimony
6	132.90 $6s$ 3.894 55 Cs $2s_{1/2}$ 23.15 33.4 Cesium 46	137.33 $6s^2$ 5.212 56 Ba $1s_0$ 10.004 35.8 Barium 47	138.90 $5d6s^2$ 5.577 57 La $2d_{3/2}$ 11.1 19.18 Lanthanum 49.9	178.49 $5d^26s^2$ 6.8 72 Hf $3f_2$ 14.9 23.3 Hafnium 33.4	180.95 $5d^36s^2$ 7.89 73 Ta $4f_{3/2}$ Tantalum
	9.226 $5d^{10}6s$ 196.97 20.5 $2s_{1/2}$ 79 Au 34 43 Gold	10.438 $5d^{10}6s^2$ 200.59 18.76 $1s_0$ 80 Hg 34.2 46 Mercury	6.108 $6p$ 204.38 20.43 $2p_{1/2}$ 81 Tl 29.85 Thallium	7.417 $6p^2$ 207.2 15.033 $3p_0$ 82 Pb 31.94 42.33 Lead	7.286 $6p^3$ 208.98 16.7 $4s_{3/2}$ 83 Bi 25.56 45.3 Bismuth
7	$[223]$ $7s$ 4.0 87 Fr $2s_{1/2}$ Francium	226.02 $7s^2$ 5.278 88 Ra $1s_0$ 10.15 Radium	227.03 $6d7s^2$ 5.2 11.75 89 Ac $2d_{3/2}$ 20 Actinium		

Actinides

$6d^27s^2$ 6.1 232.04 $3f_2$ 11.9 90 Th $3f_2$ 18.3 Thorium 28.7	$5f^26d7s^2$ 6.0 231.04 $4k_{11/2}$ 91 Pa $4k_{11/2}$ Protactinium	$5f^36d7s^2$ 6.194 238.03 11.9 92 U $5l_6$ 20 37 Uranium	$5f^46d7s^2$ 6.266 237.05 93 Np $6l_{11/2}$ Neptunium	$5f^67s^2$ 6.06 $[244]$ 94 Pu $7f_0$ Plutonium	$5f^77s^2$ 6.0 $[243]$ 95 Am $8s_{7/2}$ Americium

			Shell of valence electrons Atomic weight Symbol Atomic number 95.94 42 Mo Molybdenum 4d⁵5s 7S₃ 16.16 27.2 46.4 Element Electron term Ionization potentials of the atom and first three ions	
VI	VII	VIII		
13.618 2p ⁴ 15.999 35.118 3p ₂ ² 8 54.936 77.414 Oxygen	17.423 2p ⁵ 18.998 34.971 2p _{3/2} ² 9 62.71 87.14 Fluorine	21.565 2p ⁶ 20.179 40.963 1s ₀ ¹⁰ 10 63.46 97.12 Neon		
10.360 3p ⁴ 32.06 23.338 3p ₂ ² 16 34.83 47.305 Sulfur	12.968 3p ⁵ 35.453 23.814 2p _{3/2} ² 17 39.61 53.47 Chlorine	15.760 2p ⁶ 39.948 27.630 1s ₀ ¹⁸ 18 40.911 59.81 Argon		
51.996 3d ⁵ 4s 6.766 24Cr 7S ₃ 16.50 Chromium 31.0 49.2	54.938 3d ⁵ 4s ² 7.434 25Mn 6S ₂ 15.640 Manganese 33.67 51.2	55.847 3d ⁶ 4s ² 7.902 26Fe 5D ₄ 16.188 Iron 30.65 54.8	58.933 3d ⁷ 4s ² 7.86 27Co 4F _{9/2} 17.084 Cobalt 33.5 51.3	58.69 3d ⁸ 4s ² 7.637 28Ni 3F ₄ 18.169 Nickel 35.3 54.9
9.752 4p ⁴ 78.96 21.16 3p ₂ ² 34 30.82 42.95 Selenium	11.814 4p ⁵ 79.904 21.81 2p _{3/2} ² 35 35.90 47.3 Bromine	14.000 4p ⁶ 83.80 24.360 1s ₀ ³⁶ 36 36.95 52.5 Krypton		
95.94 4d ⁵ 5s 7.099 42Mo 7S ₃ 16.16 Molybdenum 27.2 46.4	[98] 4d ⁵ 5s ² 7.28 43Tc 6S ₂ 15.26 Technetium 29.5	101.07 4d ⁷ 5s 7.366 44Ru 5F ₅ 16.76 Ruthenium 28.5	102.91 4d ⁸ 5s 7.46 45Rh 4F _{9/2} 18.08 Rhodium 31.1	106.42 4d ¹⁰ 8.336 46Pd 1S ₀ 19.43 Palladium 32.9
9.010 5p ⁴ 127.60 18.6 3p ₂ ² 52 27.96 37.42 Tellurium	10.451 5p ⁵ 126.90 19.131 2p _{3/2} ² 53 33.0 Iodine	12.130 5p ⁶ 131.29 20.98 1s ₀ ⁵⁴ 54 31.0 45 Xenon		
183.85 5d ⁴ 6s ² 7.98 74W 5D ₀ Tungsten	186.21 5d ⁵ 6s ² 7.88 75Re 6S ₂ Rhenium	190.2 5d ⁶ 6s ² 8.73 76Os 5D ₄ Osmium	192.22 5d ⁷ 6s ² 9.05 77Ir 4F _{9/2} Iridium	195.08 5d ⁹ 6s 8.96 78Pt 3D ₃ 18.56 Platinum
8.417 6p ⁴ [209] 3p ₂ ² 84 Polonium	9.0 6p ⁵ [210] 2p _{3/2} ² 85 Astatine	10.75 6p ⁶ [222] 1s ₀ ⁸⁶ 86 Radon		

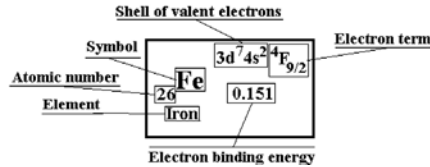
Lanthanides

4f ⁵ d ⁶ s ² 5.539 140.12 10.8 58Ce ¹ G ⁴ 20.20 Cerium 39.76	4f ³ 6s ² 5.47 140.91 10.6 59Pr ⁴ 9/2 21.62 Praseodymium 38.98	4f ⁴ 6s ² 5.525 144.24 10.7 60Nd ⁵ I ⁴ 22.1 Neodymium 40.4	4f ⁵ 6s ² 5.58 [145] 10.9 61Pm ⁶ H ⁵ 22.3 Promethium 41.0	4f ⁶ 6s ² 5.644 150.36 11.1 62Sm ⁷ F ⁰ 23.4 Samarium 41.4	151.96 4f ⁷ 6s ² 5.670 63Eu ⁸ S ^{7/2} 24.9 Europium 42.7	4f ⁷ 5d ⁶ s ² 6.150 157.25 12.1 64Gd ⁹ D ² 20.6 Gadolinium 44.0
4f ⁹ 6s ² 5.864 158.92 11.5 65Tb ⁶ H ^{15/2} 21.9 Terbium 39.4	4f ¹⁰ 6s ² 5.939 162.50 11.7 66Dy ⁵ I ⁸ 22.8 Dysprosium 41.4	4f ¹¹ 6s ² 6.022 164.93 11.8 67Ho ⁵ I ^{15/2} 22.8 Holmium 42.5	4f ¹² 6s ² 6.108 167.26 11.9 68Er ³ H ⁶ 22.7 Erbium 42.7	4f ¹³ 6s ² 6.184 168.93 12.1 69Tm ² F ^{7/2} 23.7 Thulium 42.7	4f ¹⁴ 6s ² 6.254 173.04 12.18 70Yb ¹ S ⁰ 25.05 Ytterbium 43.6	4f ¹⁴ 5d ⁶ s ² 5.426 174.97 13.9 71Lu ² D ^{3/2} 20.96 Lutetium 45.25

B.3 Electron Binding Energies in Negative Ions of Atoms

Group Period	I				
1	$1s^2\ 1S_0$ 1H 0.75420 Hydrogen	II	III	IV	V
2	$2s^2\ 1S_0$ 3Li 0.6180 Lithium	$2p^2\ 2P_{1/2}$ 4Be absent Beryllium	$2p^2\ 3P_0$ 0.27972 5B Boron	$4s_{3/2}\ 1.2621\ 2p^3$ 6C $2D_{3/2}\ 0.033$ Carbon	$2p^4\ 3P_0$ absent 7N Nitrogen
3	$3s^2\ 1S_0$ 11Na 0.54793 Sodium	$3p^2\ 2P_{1/2}$ 12Mg absent Magnesium	$3p^2$ $3P_0\ 0.4328\ 13\text{Al}$ $1D_2\ 0.11$ Aluminium	$4s_{3/2}\ 1.385\ 3p^3$ $2D_{3/2}\ 0.5272\ 14\text{Si}$ $2D_{5/2}\ 0.5255\ 15\text{P}$ $2P_{1/2}\ 0.029$ Silicon	$3p^4\ 3P_0$ 0.7465 15P Phosphorus
4	$4s^2\ 1S_0$ 19K 0.5015 Potassium	$4p^2\ 2P_{1/2}$ 20Ca 0.0245 Calcium	$3d4s^2 4p$ 21Sc $3F_2\ 0.19$ $3D_1\ 0.04$ Scandium	$3d^3 4s^2 4F_{3/2}$ 22Ti 0.08 Titanium	$4d^4 4s^2 5D_0$ 23V 0.52 Vanadium
	$3d^{10} 4s^2 1S_0$ 1.235 29Cu Copper	$4p^2\ 2P_{1/2}$ absent 30Zn Zinc	$4p^2\ 3P_0$ 0.43 31Ga Gallium	$4s_{3/2}\ 1.2327\ 4p^3$ $2D_{3/2}\ 0.4014\ 32\text{Ge}$ $2D_{5/2}\ 0.3773$ Germanium	$4p^4\ 3P_0$ 0.81 33As Arsenic
5	$5s^2\ 1S_0$ 37Rb 0.48592 Rubidium	$5p^2\ 2P_{1/2}$ 38Sr 0.048 Strontium	$4d5s^2 5p$ 39Y $3F_2\ 0.31$ $3D_1\ 0.16$ Yttrium	$4d^3 5s^2 4F_{3/2}$ 40Zr 0.43 Zirconium	$5d^4 5s^2 5D_0$ 41Nb 0.89 Niobium
	$4d^{10} 5s^2 1S_0$ 1.302 47Ag Silver	$5p^2\ 2P_{1/2}$ absent 48Cd Cadmium	$5p^2\ 3P_0$ 0.40 49In Indium	$4s_{3/2}\ 1.1121\ 5p^3$ $2D_{3/2}\ 0.3976\ 50\text{Sn}$ $2D_{5/2}\ 0.3046$ Tin	$5p^4$ $3P_2\ 1.047\ 51\text{Sb}$ $3P_1\ 0.714\ 52\text{Te}$ $3P_0\ 0.700\ 53\text{I}$ $1D_2\ 0.131$ Antimony
6	$6s^2\ 1S_0$ 55Cs 0.47163 Cesium	$6p^2\ 2P_{1/2}$ 56Ba 0.15 Barium	$5d^2 6s^2 3F_2$ 57La 0.5 Lanthanum	$5d^3 6s^2 4F_{3/2}$ 58Hf absent Hafnium	$5d^4 6s^2 5D_0$ 73Ta 0.32 Tantalum
	$5d^{10} 6s^2 1S_0$ 2.30863 79Au Gold	$6p^2\ 2P_{1/2}$ absent 80Hg Mercury	$6p^2\ 3P_0$ 0.4 81Tl Thallium	$6p^3\ 4S_{3/2}$ 0.364 82Pb Lead	$6p^4\ 3P_0$ 0.95 83Bi Bismuth
7	$7s^2\ 1S_0$ 87Fr 0.46 Francium				

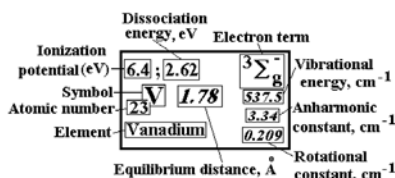
		VIII			
		$2s^2 2s_{1/2}$ ^2He absent Helium			
VI	VII				
$2p^5 2p_{3/2}$ 1.4611103 ^8O Oxygen	$2p^6 1s_0$ 3.401190 ^9F Fluorine	$2p^6 3s^2 2s_{1/2}$ absent ^{10}Ne Neon			
$3p^5 2p_{3/2}$ 2.077104 ^{16}S Sulfur	$3p^6 1s_0$ 3.61269 ^{17}Cl Chlorine	$3p^6 4s^2 2s_{1/2}$ absent ^{18}Ar Argon			
$3d^5 4s^2 6s_{5/2}$ ^{24}Cr Chromium 0.66	$3d^6 4s^2 5d_4$ ^{25}Mn Manganese absent	$3d^7 4s^2 4f_{9/2}$ ^{26}Fe Iron 0.151	$3d^8 4s^2 3f_4$ ^{27}Co Cobalt 0.662	$3d^9 4s^2 2d_{5/2}$ ^{28}Ni Nickel 1.16	
$4p^5 2p_{3/2}$ 2.02067 ^{34}Se Selenium	$4p^6 1s_0$ 3.363590 ^{37}Br Bromine	$4p^6 5s^2 2s_{1/2}$ absent ^{36}Kr Krypton			
$4d^5 5s^2 6s_{5/2}$ ^{42}Mo Molybdenum 0.748	$4d^6 5s^2 5d_4$ ^{43}Tc Technetium 0.6	$4d^7 5s^2 4f_{9/2}$ ^{44}Ru Ruthenium 1.0	$4d^8 5s^2 3f_4$ ^{45}Rh Rhodium 1.137	$4d^9 5s^2 2d_{5/2}$ ^{46}Pd Palladium 0.562	
$5p^5 2p_{3/2}$ 1.9708 ^{52}Te Tellurium	$5p^6 1s_0$ 3.05904 ^{53}I Iodine	$5p^6 6s^2 2s_{1/2}$ absent ^{54}Xe Xenon			
$5d^5 6s^2 6s_{5/2}$ ^{74}W Tungsten 0.815	$5d^6 6s^2 5d_4$ ^{75}Re Rhenium 0.2	$5d^7 6s^2 4f_{9/2}$ ^{76}Os Osmium 1.1	$5d^8 6s^2 3f_4$ ^{77}Ir Iridium 1.5638	$5d^9 6s^2 2d_{5/2}$ ^{78}Pt Platinum 2.128	
$6p^5 2p_{3/2}$ 1.9 ^{84}Po Polonium	$6p^6 1s_0$ 2.8 ^{85}At Astatine	$6p^6 7s^2 2s_{1/2}$ absent ^{86}Rn Radon			



B.4 Parameters of Diatomic Molecules

Group Period	I	II			
1	15.43; 4.478 $1\Sigma_g^+$ $1H$ 0.741 4401 Hydrogen 121.3 60.85	$1\Sigma_g^+$ 22.22; 0.001 2.97 $2He$ Helium 0.96	III	IV	V
2	5.145; 1.05 $1\Sigma_g^+$ $3Li$ 2.67 351.4 Lithium 2.59 0.672	7.45; 0.098 $1\Sigma_g^+$ $4Be$ 2.45 275.3 Beryllium 12.5 0.615	$1\Sigma_g^+$ 8.8; 2.8 1059 1.60 $5B$ Boron 15.66 1.216	$1\Sigma_g^+$ 12.15; 5.36 1855 1.24 $6C$ Carbon 13.27 1.899	$1\Sigma_g^+$ 15.581; 9.579 2359 1.098 $7N$ Nitrogen 14.95 1.998
3	4.90; 0.731 $1\Sigma_g^+$ $11Na$ 3.08 51.08 Sodium 0.725 0.155	6.7; 0.053 $1\Sigma_g^+$ $12Mg$ 3.89 51.08 Magnesium 1.62 0.093	$3\Pi_u$ 4.84; 0.46 284.2 2.47 $13Al$ Aluminium 2.02 0.205	$3\Sigma_g^-$ 7.4; 3.24 510.9 2.24 $14Si$ Silicon 2.02 0.239	$1\Sigma_g^+$ 10.56 780.3 1.89 $15P$ Phosphorus 2.83 0.304
4	4.064; 0.551 $1\Sigma_g^+$ $19K$ 3.92 92.09 Potassium 0.233 0.165	5.2; 0.13 $1\Sigma_g^+$ $20Ca$ 4.28 64.9 Calcium 1.09 0.047	1.69 $5\Sigma_u^-$ $21Sc$ 2.21 238.9 Scandium 0.93 0.153	6.2; 1.4 $3\Delta_g$ $22Ti$ 1.94 407.9 Titanium 1.08 0.187	6.4; 2.62 $3\Sigma_g^-$ $23V$ 1.78 537.5 Vanadium 3.34 0.209
	$1\Sigma_g^+$ 7.89; 1.99 2.21 $29Cu$ Copper 0.60 0.022	$1\Sigma_g^+$ 9.0; 0.034 25.7 4.8 $30Zn$ Zinc 0.60 0.022	$3\Pi_u$ 6.5; 1.18 158 2.76 $31Ga$ Gallium 1.0 0.063	$3\Sigma_g^-$ 7.2; 2.5 259 2.44 $32Ge$ Germanium 0.8 0.078	$1\Sigma_g^+$? 12.0; 3.96 429.6 2.103 $33As$ Arsenic 1.12 0.102
5	3.45; 0.495 $1\Sigma_g^+$ $37Rb$ 4.17 266.4 Rubidium 1.03 0.109	4.74; 0.13 $1\Sigma_g^+$ $38Sr$ 4.45 39.6 Strontium 0.45 0.019	1.6 $1\Sigma_g^+$ $39Y$ 2.8 206.5 Yttrium 0.043	1.5 $1\Sigma_g^+$ $40Zr$ 2.3 373 Zirconium 0.070	6.37; 5.48 $3\Sigma_g^-$ $41Nb$ 2.1 424.9 Niobium 0.94 0.084
	$1\Sigma_g^+$ 7.66; 1.65 135.8 2.53 $47Ag$ Silver 0.50 0.049	$1\Sigma_g^+$ 0.013 22.5 5.1 $48Cd$ Cadmium 0.4 0.011	$3\Pi_u$ 0.83 111 3.14 $49In$ Indium 0.8 0.030	$3\Sigma_g^-$ 7.32; 2.0 186.2 2.75 $50Sn$ Tin 0.261 0.038	$1\Sigma_g^+$ 8.8; 3.09 269.9 2.34 $51Sb$ Antimony 0.58 0.050
6	3.64; 0.452 $1\Sigma_g^+$ $55Cs$ 4.65 42.02 Cesium 0.082 0.013	$1\Sigma_g^+$ $56Ba$ 4.6 34.1 Barium 0.16 0.009	$57La$ Lanthanum	$58Hf$ Hafnium	$73Ta$ Tantalum
	$1\Sigma_g^+$ 9.2; 2.31 190.9 2.47 $79Au$ Gold 0.42 0.028	$0\Sigma_g^+$ 9.4; 0.055 18.5 3.65 $80Hg$ Mercury 0.27 0.013	$3\Sigma_g^-$ 6.3; 0.001 80 3.0 $81Tl$ Thallium 0.5 0.018	$3\Sigma_g^-$ 6.4; 0.83 110.2 2.93 $82Pb$ Lead 0.327 0.019	$1\Sigma_g^+$ 7.4; 2.08 173.1 2.66 $83Bi$ Bismuth 0.376 0.023

VI	VII	VIII
$3\Sigma_g^-$ 12.071 ; 5.12 1580 1.207 $8O$ 11.98 Oxygen 1.445	$1\Sigma_g^+$ 15.686 ; 1.66 916.6 1.41 $9F$ 11.24 Fluorine 0.89	$1\Sigma_g^+$ 20.4 ; 0.037 31.3 3.09 $10Ne$ 6.48 Neon 0.175
$3\Sigma_g^-$ 9.4 ; 4.37 725.6 1.89 $16S$ 2.28 Sulfur 0.295	$1\Sigma_g^+$ 11.50 ; 2.576 559.7 1.99 $17Cl$ 2.68 Chlorine 0.244	$1\Sigma_g^+$ 14.54 ; 0.012 30.68 3.76 $18Ar$ 2.42 Argon 0.060
6.8 ; 1.66 $1\Sigma_g^+$ $24Cr$ 1.68 470 14.1 Chromium 0.23	6.5 ; 0.79 $1\Sigma_g^+$ $25Mn$ 2.52 68.1 1.05 Manganese 0.097	6.3 ; 0.9 $1\Sigma_g^+$ $26Fe$ 2.02 412.0 1.4 Iron 0.148
$3\Sigma_g^-$ 8.88 ; 2.9 385.3 2.16 $34Se$ 0.963 Selenium 0.89	$1\Sigma_g^+$ 10.52 ; 2.05 325 2.28 $37Br$ 1.08 Bromine 0.082	$1\Sigma_g^+$ 12.97 ; 0.017 24.1 4.01 $36Kr$ 1.34 Krypton 0.025
6.2 ; 4.1 $1\Sigma_g^+$ $42Mo$ 2.2 477 1.51 Molybdenum 0.072	$43Tc$ Technetium	$44Ru$ Ruthenium
$3\Sigma_g^-$ 8.29 ; 2.7 249.1 2.56 $52Te$ 0.537 Tellurium 0.040	$1\Sigma_g^+$ 9.3 ; 1.542 214.5 2.67 $53I$ 0.615 Iodine 0.037	$1\Sigma_g^+$ 11.13 ; 0.024 21.12 4.36 $54Xe$ 0.65 Xenon 0.0135
6.9 $74W$ 336.8 1.0 Tungsten $-$	$75Re$ Rhenium	$76Os$ Osmium
$84Po$ Polonium	$85At$ Astatine	$86Rn$ Radon



B.5 Parameters of Positively Charged Diatomic Molecules

Group Period	I	II			
1	15.43; 2.65 $2\Sigma_g^+$ $1H$ 1.06 2323 Hydrogen 67.5 35.3 30.21	$2\Sigma_g^+$ 22.22; 2.47 $2He$ 1.08 1698.5 Helium 7.21	III	IV	V
2	5.145; 1.28 $1\Sigma_g^+$ $3Li$ 3.12 263.1 Lithium 1.61 0.49	7.45; 1.9 $2\Sigma_g^+$ $4Be$ 502 4.2 Beryllium 0.752 0.181	$2\Sigma_g^+$ 8.8; 1.9 $5B$ 4.15 357 Boron 12.1 1.41	$4\Sigma_g^-$ 12.15; 5.3 $6C$ 1351 1.41 Carbon 12.1 1.41	$2\Sigma_g^+$ 15.581; 8.713 $7N$ 2207 1.12 16.2 Nitrogen 1.932
3	4.90; 0.98 $2\Sigma_g^+$ $11Na$ 3.54 120.8 Sodium 0.46 0.113	6.7; 1.3 $2\Sigma_g^+$ $12Mg$ 502 4.2 Magnesium 0.752 0.181	$2\Sigma_g^+$ 4.84; 1.4 $13Al$ 178 2.0 Aluminium 0.122	$2\Pi_u$ 7.4; 3.24 $14Si$ 528 2.19 Silicon 0.25	$2\Pi_u$ 10.56; 5.0 $15P$ 672 2.74 Phosphorus 0.276
4	4.064; 0.81 $2\Sigma_g^+$ $19K$ 4.6 73.4 Potassium 0.2 0.042	5.2; 1.04 $2\Sigma_g^+$ $20Ca$ 3.7 119 Calcium 0.053	$2\Sigma_g^+$ 6.5; 1.27 $21Sc$ 108 3.24 Scandium 0.046	6.0; 2.44 $22Ti$ 1351 1.41 Titanium 12.1 1.41	6.36; 3.14 $23V$ 430 1.9 Vanadium 0.125
5	3.45; 0.75 $2\Sigma_g^+$ $37Rb$ 4.8 44.5 Rubidium 0.017	4.74; 1.1 $2\Sigma_g^+$ $38Sr$ 3.9 86 Strontium 0.54 0.025	$2\Sigma_g^+$ 9.0; 0.42 $39Y$ 108 3.24 Yttrium 0.046	$4\Sigma_g^-$ 7.2; 2.91 $40Zr$ 256 2.32 Zirconium 0.036	$2\Sigma_g^+$ 9.64; 4.11 $41Nb$ 430 1.9 Niobium 0.125
6	3.76; 0.61 $2\Sigma_g^+$ $55Cs$ 4.44 32.4 Cesium 0.051 0.013	$2\Sigma_g^+$ 9.4; 0.96 $56Ba$ 2.8 91.6 Barium 0.301 0.021	$2\Sigma_g^+$ 9.4; 0.96 $57La$ 2.8 91.6 Lanthanum 0.301 0.021	7.38; 1.96 $49In$ 50 Indium 50	8.7; 3.2 $51Sb$ 51 Antimony 51
	$2\Sigma_g^+$ 9.2; $79Au$ 143.4 Gold 0.18	$2\Sigma_g^+$ 9.4; 0.96 $80Hg$ 143.4 Mercury 0.18	$2\Sigma_g^+$ 9.4; 0.96 $81Tl$ 143.4 Thallium 0.18	6.1; 1.7 $82Pb$ 143.4 Lead 0.18	$2\Pi_g$ 7.4; 1.89 $83Bi$ 143.4 Bismuth 0.18

	Dissociation energy, eV	Electron term
Diatom ionization potential (eV)	4.90; 0.98	$2\Sigma_g^+$
Symbol	Na	3.54
Atomic number	11	120.8
Element	Sodium	0.46
		0.113
	Equilibrium distance, Å	Rotational constant, cm ⁻¹

VI	VII	VIII		
$^3\Sigma_g^-$ 12.071 ; 6.66 ^{1905} 1.12 ^8O 16.3 1.689 Oxygen	$^2\Pi_g$ 15.47 ; 3.34 ^{1073} 1.32 ^9F 9.13 1.015 Fluorine	$^2\Sigma_g^+$ 20.4 ; 1.2 ^{586} 1.75 ^{10}Ne 5.4 0.544 Neon		
$^2\Pi_u$ 9.4 ; 5.4 ^{806} 1.82 ^{16}S 3.33 0.318 Sulfur	$^2\Pi_g$ 11.50 ; 3.95 $^{645.6}$ 1.88 ^{17}Cl 3.02 0.265 Chlorine	$^2\Sigma_g^+$ 14.54 ; 1.23 $^{308.9}$ 2.43 ^{18}Ar 1.66 0.143 Argon		
6.8 ; 1.8 ^{24}Cr Chromium	6.47 ; 1.3 ^{25}Mn Manganese	6.3 ; 2.7 ^{26}Fe Iron	6.0 ; 2.75 ^{27}Co Cobalt	7.43 ; 2.35 ^{28}Ni Nickel
$^2\Pi_u$ 8.88 ; 4.4 ^{450} 2.07 ^{34}Se --- 0.10 Selenium	$^2\Pi_g$ 10.52 ; 2.96 ^{376} 2.3 ^{37}Br 1.13 0.088 Bromine	$^2\Sigma_g^+$ 12.97 ; 1.15 ^{178} 2.8 ^{36}Kr 0.82 0.051 Krypton		
6.2 ; 5.0 ^{42}Mo Molybdenum	^{43}Tc Technetium	^{44}Ru Ruthenium	^{45}Rh Rhodium	7.7 ^{46}Pd Palladium
8.2 ; 3.5 ^{52}Te Tellurium	$^2\Pi_g$ 9.3 ; 1.92 ^{243} 2.58 ^{53}I --- 0.040 Iodine	$^2\Sigma_g^+$ 11.13 ; 1.1 ^{123} 3.25 ^{54}Xe 0.63 0.026 Xenon		
^{74}W Tungsten	^{75}Re Rhenium	^{76}Os Osmium	^{77}Ir Iridium	8.7 ; 3.26 ^{78}Pt Platinum
^{84}Po Polonium	^{85}At Astatine	$^1\Sigma_g^+$ ^{86}Rn Radon		

B.6 Parameters of Negatively Charged Diatomic Molecules

Group Period	I	II	III	IV
2	0.7 ; 0.88 $2\Sigma_u^+$ ${}^3\text{Li}$ 2.8 233.1 Lithium 1.92 0.516	0.4 ; 2.8 $2\Sigma_g^+$ ${}^4\text{Be}$ 2.3 620 Beryllium ---	1.7 ; 4.2 $2\Sigma_g^+$ ${}^5\text{B}$ 1781 Boron 11.7 1.746	3.27 ; 8.5 $2\Sigma_g^+$ ${}^6\text{C}$ 1.27 Carbon
3	0.43 ; 0.44 $2\Sigma_u^+$ ${}^{11}\text{Na}$ Sodium	${}^{12}\text{Mg}$ Magnesium	${}^4\Sigma_g^-$ 1.1 ; 2.4 ${}^{33}\text{Al}$ 2.65 335 Aluminium 0.178	2.19 ; 3.3 $2\Sigma_g^+$ ${}^{14}\text{Si}$ Silicon
4	0.49 ; $2\Sigma_u^+$ ${}^{19}\text{K}$ Potassium	${}^{20}\text{Ca}$ Calcium	${}^{21}\text{Sc}$ Scandium	${}^{22}\text{Ti}$ Titanium
	$2\Sigma_u^+$ 0.84 ; 1.57 ${}^{196}\text{Cu}$ 2.34 29 Copper 0.7 0.097	${}^{30}\text{Zn}$ Zinc	${}^4\Sigma_g^-$ 6.5 ; 1.18 ${}^{158}\text{Ga}$ 2.76 31 Gallium 1.0 0.063	${}^{32}\text{Ge}$ Germanium
5	0.5 ; 0.5 $2\Sigma_u^+$ ${}^{37}\text{Rb}$ 4.8 28.3 Rubidium --- 0.017	${}^{38}\text{Sr}$ Strontium	${}^{39}\text{Y}$ Yttrium	${}^{40}\text{Zr}$ Zirconium
	$2\Sigma_u^+$ 1.03 ; 1.37 ${}^{145}\text{Ag}$ 2.6 47 Silver 0.9 0.046	${}^{48}\text{Cd}$ Cadmium	${}^{49}\text{In}$ Indium	${}^{50}\text{Sn}$ Tin
6	0.47 ; 0.45 $2\Sigma_u^+$ ${}^{55}\text{Cs}$ 4.8 28.4 Cesium 0.042 0.011	${}^{56}\text{Ba}$ Barium	${}^{57}\text{La}$ Lanthanum	${}^{58}\text{Hf}$ Hafnium
	$2\Sigma_u^+$ 1.94 ; 1.9 ${}^{79}\text{Au}$ Gold	3.65 ${}^{80}\text{Hg}$ Mercury	${}^{81}\text{Tl}$ Thallium	$2\Pi_g$ 1.66 ; 1.37 ${}^{129}\text{Pb}$ 2.81 82 Lead 0.2 0.021

B.7 Cross Sections of Resonant Charge Exchange

Group Period	I	II			
1	1.008 $1s^2 S_{1/2}$ 1 H 1.000 6.12 Hydrogen 2.00 4.82 3.65	$1s^2 1S_0$ 4.003 2 He 1.344 2.87 Helium 2.1	III	IV	V
2	6.491 $2s^2 S_{1/2}$ 3 Li 0.630 26 Lithium 0.82 22 18	9.012 $2s^2 1S_0$ 4 Be 0.828 13 Beryllium 1.6 10 8.3	$2p^2 P_{1/2}$ 10.81 14 0.781 5 B 12 0.88 Boron 9.0	$2p^2 3P_0$ 12.011 9.9 0.910 6 C 8.2 1.3 Carbon 6.6	$2p^3 4S_{3/2}$ 14.007 7.7 1.034 7 N 6.4 1.5 Nitrogen 5.2
3	22.990 $3s^2 S_{1/2}$ 11 Na 0.615 31 Sodium 0.74 26 21	24.305 $3s^2 1S_0$ 12 Mg 0.750 18 Magnesium 1.3 15 12	$3p^2 P_{1/2}$ 26.982 21 0.663 13 Al 19 0.61 Aluminium 17	$3p^2 3P_0$ 28.086 17 0.774 14 Si 14 1.1 Silicon 12	$3p^3 4S_{3/2}$ 30.974 14 0.878 15 P 12 1.6 Phosphorus 10
4	39.098 $4s^2 S_{1/2}$ 19 K 0.565 40 Potassium 0.52 34 28	40.08 $4s^2 1S_0$ 20 Ca 0.670 25 Calcium 0.95 21 17	44.956 $3d4s^2 2D_{3/2}$ 21 0.693 24 Sc 1.1 20 Scandium 16	47.88 $3d^2 4s^2 3F_2$ 22 Ti 0.708 22 Titanium 1.2 19 15	50.942 $3d^3 4s^2 4F_{3/2}$ 23 V 0.704 23 Vanadium 1.2 19 16
	$3d^{10} 4s^2 S_{1/2}$ 63.546 19 0.754 29 Cu 16 1.3 Copper 13	$4s^2 1S_0$ 65.38 15 0.831 30 Zn 12 1.7 Zinc 10	$4p^2 P_{1/2}$ 69.72 26 0.664 31 Ga 22 0.60 Gallium 18	$4p^2 3P_0$ 72.59 20 0.762 32 Ge 17 1.3 Germanium 14	$4p^3 4S_{3/2}$ 74.922 15 0.850 33 As 13 1.6 Arsenic 11
5	85.468 $5s^2 S_{1/2}$ 37 Rb 0.554 45 Rubidium 0.48 38 32	87.62 $5s^2 1S_0$ 38 Sr 0.647 29 Strontium 0.86 25 20	88.906 $4d5s^2 2D_{3/2}$ 39 Y 0.682 21 Yttrium 1.0 18	91.22 $4d^2 5s^2 3F_2$ 40 Zr 0.709 23 Zirconium 1.2 20 16	92.906 $4d^4 5s^2 6D_{1/2}$ 41 Nb 0.711 23 Niobium 1.2 19 16
	$4d^{10} 5s^2 S_{1/2}$ 107.87 20 0.746 47 Ag 17 1.2 Silver 14	$5s^2 1S_0$ 112.41 16 0.813 48 Cd 14 1.6 Cadmium 11	$5p^2 P_{1/2}$ 114.82 28 0.652 49 In 24 0.58 Indium 20	$5p^2 3P_0$ 118.69 22 0.735 50 Sn 19 1.0 Tin 15	$5p^3 4S_{3/2}$ 121.75 20 0.797 51 Sb 17 1.7 Antimony 14
6	132.90 $6s^2 S_{1/2}$ 55 Cs 0.535 51 Cesium 0.41 44 36	137.33 $6s^2 1S_0$ 56 Ba 0.619 35 Barium 0.78 30 25	138.90 $5d6s^2 2D_{3/2}$ 57 La 0.640 32 Lanthanum 0.90 27 23	178.49 $5d^2 6s^2 3F_2$ 72 Hf 0.740 22 Hafnium 1.3 18 15	180.95 $5d^3 6s^2 4F_{3/2}$ 73 Ta 0.762 20 Tantalum 1.4 17 14
	$5d^{10} 6s^2 S_{1/2}$ 196.97 16 0.823 79 Au 14 1.6 Gold 11	$5d^{10} 6s^2 1S_0$ 200.59 14 0.876 80 Hg 12 1.9 Mercury 10	$6p^2 P_{1/2}$ 204.38 26 0.670 81 Tl 22 0.55 Thallium 18	$6p^2 3P_0$ 207.2 22 0.738 82 Pb 19 1.1 Lead 16	$6p^3 4S_{3/2}$ 208.98 26 0.732 83 Bi 22 1.4 Bismuth 19
7	$[223]$ $7s^2 S_{1/2}$ 87 Fr 0.542 53 Franchium 0.49 45 38	226.02 $7s^2 1S_0$ 88 Ra 0.623 35 Radium 0.78 30 25	227.03 $6d7s^2 2D_{3/2}$ 89 Ac 0.636 33 Actinium 0.70 28 24		

Actinides

$6d^2 7s^2 3F_2$ 232.04 0.675 28 90 Th 0.94 24 Thorium 20	$5f^2 6d 7s^2 4K_{11/2}$ 231.04 0.647 30 91 Pa 0.70 25 Protactinium 21	$5f^3 6d 7s^2 5L_6$ 238.03 0.670 28 92 U 0.89 24 Uranium 20	$5f^4 6d 7s^2 6L_{11/2}$ 237.05 0.580 46 93 Np 0.70 39 Neptunium 33	$5f^6 7s^2 7F_0$ $[244]$ 0.612 38 94 Pu 0.73 32 Plutonium 27	$5f^7 7s^2 8S_{7/2}$ $[243]$ 0.569 72 95 Am 0.70 49 Americium 36

VI	VII	VIII			
$2p^4\ ^3P_2$ 8.3 1.000 6.9 1.3 5.6 8O Oxygen	$2p^5\ ^2P_{3/2}$ 5.7 1.132 4.7 1.132 3.7 1.6 9F Fluorine	$2p^6\ ^1S_0$ 4.1 1.259 3.2 1.8 2.6 10Ne Neon	Shell of valence electrons Electron term Atomic weight Symbol Atomic number Element 137.33 56 Ba Barium $6s^2\ ^1S_0$ 0.619 35 30 25 Cross section of resonant charge exchange (in 10^{-15} cm^2 at 0.1, 1, 10 eV in the laboratory frame) Asymptotic parameters		
$3p^4\ ^3P_2$ 13 0.873 10 1.1 8.6 16S Sulfur	$3p^5\ ^2P_{3/2}$ 9.6 0.976 8.0 0.976 6.6 1.8 17Cl Chlorine	$2p^6\ ^1S_0$ 7.0 1.076 5.8 2.0 4.7 2.0 18Ar Argon	$5s^4\ ^3P_2$ 51.996 24Cr Chromium	$3d^5\ 4s^2\ ^7S_3$ 33 0.705 19 1.1 16 25Mn Manganese	$3d^5\ 4s^2\ ^6S_{5/2}$ 54.938 20 0.739 17 1.3 14 26Fe Iron
$4p^4\ ^3P_2$ 16 0.847 14 1.5 12 34Se Selenium	$4p^5\ ^2P_{3/2}$ 12 0.932 10 0.932 8.2 1.8 35Br Bromine	$4p^6\ ^1S_0$ 9.0 1.014 7.5 2.1 6.2 36Kr Krypton	$5s^8\ ^3P_2$ 58.933 27Co Cobalt	$3d^7\ 4s^2\ ^4F_{9/2}$ 19 0.760 16 1.4 13 28Ni Nickel	$3d^8\ 4s^2\ ^3F_4$ 58.69 20 0.749 17 1.4 14 29Cu Copper
$5p^4\ ^3P_2$ 18 0.814 16 1.6 13 52Te Tellurium	$5p^5\ ^2P_{3/2}$ 14 0.876 12 0.876 10 1.9 53I Iodine	$5p^6\ ^1S_0$ 12 0.944 10 2.2 8.6 54Xe Xenon	$4d^8\ 5s^2\ ^4F_{9/2}$ 102.91 45Rh Rhodium	$4d^{10}\ ^1S_0$ 106.42 46Pd Palladium	$4d^{10}\ ^1S_0$ 106.42 46Pd Palladium
$5d^4\ 6s^2\ ^5D_0$ 183.85 74W Tungsten	$5d^5\ 6s^2\ ^6S_{5/2}$ 186.21 75Re Rhenium	$5d^6\ 6s^2\ ^5D_4$ 190.2 76Os Osmium	$5d^7\ 6s^2\ ^4F_{9/2}$ 192.22 77Ir Iridium	$5d^9\ 6s^3\ ^3D_3$ 195.08 78Pt Platinum	$5d^9\ 6s^3\ ^3D_3$ 195.08 78Pt Platinum
$6p^4\ ^3P_2$ 17 0.788 15 1.5 12 84Po Polonium	$6p^5\ ^2P_{3/2}$ 18 0.813 15 0.813 13 1.9 85At Astatine	$6p^6\ ^1S_0$ 15 0.889 13 2.3 11 86Rn Radon			

Lanthanides

$4f^1\ 5d^2\ ^1G_4$ 140.12 58Ce Cerium	$4f^3\ 5d^2\ ^4I_{9/2}$ 140.91 59Pr Praseodymium	$4f^4\ 5d^2\ ^5I_4$ 144.24 60Nd Neodymium	$4f^5\ 5d^2\ ^6H_{5/2}$ 145.91 61Pm Promethium	$4f^6\ 5d^2\ ^7F_0$ 150.36 62Sm Samarium	$4f^7\ 5d^2\ ^8S_{7/2}$ 151.96 63Eu Europium	$4f^7\ 5d\ 6s^2\ ^9D_2$ 157.25 64Gd Gadolinium
$4f^9\ 6s^2\ ^1H_{5/2}$ 158.92 65Tb Terbium	$4f^{10}\ 6s^2\ ^1S_0$ 162.50 66Dy Dysprosium	$4f^{11}\ 6s^2\ ^5I_{15/2}$ 164.93 67Ho Holmium	$4f^{12}\ 6s^2\ ^3H_6$ 167.26 68Er Erbium	$4f^{13}\ 6s^2\ ^2F_{7/2}$ 168.93 69Tm Thulium	$4f^{14}\ 6s^2\ ^1S_0$ 173.04 70Yb Ytterbium	$4f^{14}\ 5d\ 6s^2\ ^2D_{3/2}$ 174.97 71Lu Lutetium

B.8 Parameters of Evaporation for Metallic Liquid Clusters

Group Period	I	II	III	IV	V
2	454; 1615 ³ Li Lithium 1.61 0.99 1.3	1560; 2744 ⁴ Be Beryllium 3.12 1.4 23			
3	371; 1156 ¹¹ Na Sodium 1.08 0.73 0.63	923; 1363 ¹² Mg Magnesium 1.44 1.4 1.1	3,09 933; 2730 2,0 11 ¹³ Al Aluminium		
4	336; 1032 ¹⁹ K Potassium 0.91 0.62 0.37	1115; 1757 ²⁰ Ca Calcium 1.67 1.4 0.72	1814; 3103 ²¹ Sc Scandium 3.57 8	1941; 3560 ²² Ti Titanium 4.89 3.2 300	2183; 3680 ²³ V Vanadium 5.1 3.7 150
	3,40 1358; 2835 2,2 15 ²⁹ Cu Copper	1,22 693; 1180 1,5 1,6 ³⁰ Zn Zinc	2,76 303; 2680 1,5 2,0 ³¹ Ga Gallium		
5	312; 961 ³⁷ Rb Rubidium 0.82 0.54 0.28	1050; 1655 ³⁸ Sr Strontium 1.5 1.3 0.32	1795; 3618 ³⁹ Y Yttrium 4.0 4	2128; 4650 ⁴⁰ Zr Zirconium 6.12 3.8 52	2750; 5100 ⁴¹ Nb Niobium 7.35 4.5 360
	2,87 1235; 2435 2,0 15 ⁴⁷ Ag Silver	1,06 594; 1040 1,4 1,4 ⁴⁸ Cd Cadmium	2,38 430; 2353 1,5 0,17 ⁴⁹ In Indium	3,10 505; 2875 1,6 0,24 ⁵⁰ Sn Tin	1,5 904; 1860 1,04 0,03 ⁵¹ Sb Antimon
6	301; 944 ⁵⁵ Cs Cesium 0.78 0.51 0.24	1000; 1913 ⁵⁶ Ba Barium 1.71 1.4 0.17	1191; 3737 ⁵⁷ La Lanthanum 4.34 8	2510; 4876 ⁵⁸ Hf Hafnium 5.95 14	3290; 5731 ⁷³ Ta Tantalum 8.1 4.7 250
	3,65 1337; 3129 2,5 12 ⁷⁹ Au Gold	0,62 334; 630 1,23 7,7 ⁸⁰ Hg Mercury	1,78 577; 1746 1,3 2,0 ⁸¹ Tl Thallium	1,95 600; 2022 1,4 1,0 ⁸² Pb Lead	1,92 544; 1837 1,2 50 ⁸³ Bi Bismuth
7	300; 900 ⁸⁷ Fr Francium 0.7 0.1	970; 1800 ⁸⁸ Ra Radium 1.4 0.1	1320; 3470 ⁸⁹ Ac Actinium 4.1 9		

VI	VII	VIII	Melting and boiling points, K Symbol Atomic number Element ϵ_0, eV A, eV p_0, 10^{-5} atm	
2180; 2944 24Cr Chromium	1519; 2334 25Mn Manganese	1812; 3023 26Fe Iron	2750; 5017 27Co Cobalt	1728; 3100 28Ni Nickel
2886; 4912 42Mo Molybdenum	2430; 4538 43Tc Technetium	2607; 4423 44Ru Ruthenium	3237; 3968 45Rh Rhodium	1828; 3236 46Pd Palladium
3695; 5830 74W Tungsten	3459; 5880 75Re Rhenium	3100; 5300 76Os Osmium	2819; 4700 77Ir Iridium	2041; 4098 78Pt Platinum
1.2 84Po Polonium				

Actinides

2023; 5061 90Th Thorium	1845 91Pa Protactinium	1408; 4404 92U Uranium	917; 93Np Neptunium	913; 3500 94Pu Plutonium	1450; 2600 95Am Americium

B.9 Parameters of Metals at Room Temperatures

Period \ Group	I			II			III			IV			V		
2	52	2.38	0.534	97	3.92	1.85									
	³ Li	9.7		⁴ Be	25										
	Lithium	0.85		Berillium	2.0										
3	120	2.35	0.97	120	3.64	1.74	2.70	4.25	170						
	¹¹ Na	19		¹² Mg	21		34		¹³ Al						
	Sodium	1.4		Magnesium	1.6		2.4		Aluminium						
4	100	2.22	0.89	180	2.80	1.54	9	3.3	2.99	17	3.92	4.51	21	4.12	6.0
	¹⁹ K	12		²⁰ Ca	27		²¹ Sc	1.6		²² Ti	2.1		²³ V	4.6	
	Potassium	1.0		Calcium	2.0		Scandium	0.16		Titanium	0.22		Vanadium	0.31	
	8.96	4.40	240	7.14	4.24	72	5.91	3.96	27						
	⁵⁴ Cu			¹⁵ Zn			5.2		³¹ Ga						
	4.0		Copper	1.2		Zinc	0.41		Gallium						
5	170	2.35	1.53	50	2.64		9	3.3	4.47	20	3.9	6.52	36	4.0	8.57
	³⁷ Rb	7.0		³⁸ Sr	6.9		³⁹ Y	1.5		⁴⁰ Zr	2.1		⁴¹ Nb	7.2	
	Rubidium	0.58		Strontium	0.35		Yttrium	0.17		Zirconium	0.23		Niobium	0.54	
	10.5	4.3	280	8.69	4.1	280	7.31	3.8	63	7.26	4.38	47	6.68	4.08	140
	⁵⁷ Ag			¹⁷ Cd			¹¹ In			^{8.2} Sn			²³ Sb		
	4.3		Silver	0.97		Cadmium	0.82		Indium	0.67		⁵⁰ Tin	0.24		Antimony
6	41	1.81	1.93	120	2.49	3.62	10	3.3	6.15	15		13.3	35	4.12	16.4
	⁵⁵ Cs	4.4		⁵⁶ Ba	3.3		⁵⁷ La	1.5		⁵⁸ Hf	2.7		⁷³ Ta	6.9	
	Cesium	0.36		Barium	0.18		Lanthanum	0.13		Hafnium	0.23		Tantalum	0.58	
	19.3	4.30	200	13.5	4.52	5	11.8	3.7	29	11.3	4.0	26	9.79	4.4	5
	⁴⁰ Au			^{0.94} Hg			^{5.0} Tl			^{4.4} Pb			^{0.78} Bi		
	3.2		Gold	0.083		Mercury	0.46		Thallium	0.35		⁸² Lead	0.079		Bismuth

VI	VII	VIII			
			Ratio of the mean free path to the Wigner-Seitz radius Work function for polycrystal state, eV Density, g/cm³ Conductivity, 10¹⁶ s⁻¹ Thermal conductivity, $\frac{\text{W}}{\text{cm K}}$ Symbol Atomic number Element 82 4.54 19.3 74 W 17 Tungsten 1.7		
44 24 Cr Chromium 4.58 7.15 7.0 0.94	3 25 Mn Manganese 3.83 7.3 0.6 0.078	22 26 Fe Iron 4.31 7.87 9.4 0.80	60 27 Co Cobalt 4.41 8.86 14 1.0	60 28 Ni Nickel 4.50 8.90 14 0.91	
82 42 Mo Molybdenum 4.3 10.2 17 1.4	28 43 Tc Technetium 11 6 0.51	56 44 Ru Ruthenium 4.6 12.1 12 1.2	97 45 Rh Rhodium 12.4 20 1.5	40 46 Pd Palladium 4.8 12.0 8.5 0.72	
82 74 W Tungsten 4.54 19.3 17 1.7	20 75 Re Rhenium 5.0 20.8 4.3 0.48	44 76 Os Osmium 4.7 22.6 9.5 0.88	79 77 Ir Iridium 4.7 22.5 17 1.5	40 78 Pt Platinum 5.32 21.5 8.5 0.72	
9.20 2 0.2 13 84 Po Polonium					

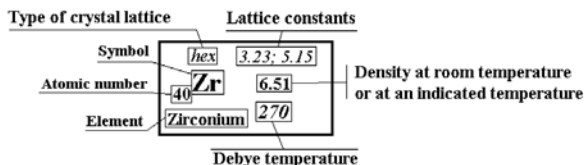
B.10 Parameters of Crystal Structures of Elements at Low Temperatures

Source: Kittel, C. *Thermal Physics*. New York, Wiley, 1970.

Group Period	I	II	III	IV	V
1	<i>hex</i> 3.76; 6.10 ¹ H 0.076 (11K) Hydrogen				
2	<i>bcc</i> 3.51 ³ Li 0.534 Lithium 370	<i>hex</i> 2.28; 3.58 ⁴ Be 1.85 Beryllium 1200	8.74; 5.07 <i>tetr</i> 2.94 ⁵ B 1250 Boron	3.57 <i>diam</i> 3.51 ⁶ C 2000 Carbon	5.64 <i>cub</i> 1.026 (23K) ⁷ N Nitrogen
3	<i>bcc</i> 4.29 ¹¹ Na 0.971 Sodium 150	<i>hex</i> 3.21; 5.21 ¹² Mg 1.74 Magnesium 360	4.05 <i>fcc</i> 2.70 ¹³ Al 410 Aluminium	5.43 <i>diam</i> 2.33 ¹⁴ Si 640 Silicon	18.5 <i>cub</i> 1.82 ¹⁵ P Phosphorus
4	<i>bcc</i> 5.04 ¹⁹ K 0.862 Potassium 100	<i>fcc</i> 5.58 ²⁰ Ca 1.55 Calcium 230	<i>hex</i> 3.31; 5.27 ²¹ Sc 2.99 Scandium 360	<i>hex</i> 2.95; 4.69 ²² Ti 4.54 Titanium 350	<i>bcc</i> 3.04 ²³ V 6.11 Vanadium 320
	3.62 <i>fcc</i> 8.96 ²⁹ Cu 330 Copper	2.66 <i>hex</i> 7.13 ³⁰ Zn 280 Zinc	4.52; 7.66; 4.52; <i>orth</i> 5.91 ³¹ Ga 280 Gallium	5.66 <i>diam</i> 5.32 ³² Ge 370 Germanium	3.76; 10.55 <i>rhdr</i> 5.78 ³³ As 280 Arsenic
5	<i>bcc</i> 5.71 ³⁷ Rb 1.53 Rubidium 56	<i>fcc</i> 6.08 ³⁸ Sr 2.54 Strontium 150	<i>hex</i> 3.62; 5.72 ³⁹ Y 4.47 Yttrium 280	<i>hex</i> 3.23; 5.15 ⁴⁰ Zr 6.51 Zirconium 280	<i>bcc</i> 3.30 ⁴¹ Nb 8.57 Niobium 250
	4.09 <i>fcc</i> 10.5 ⁴⁷ Ag 220 Silver	2.98; 5.62 <i>hex</i> 8.65 ⁴⁸ Cd 160 Cadmium	3.25; 4.95 <i>tetr</i> 7.31 ⁴⁹ In 120 Indium	6.49 <i>diam</i> 5.75 ⁵⁰ Sn 230 Tin	4.31; 11.27 <i>rhdr</i> 6.69 ⁵¹ Sb 210 Antimony
6	<i>bcc</i> 6.09 ⁵⁵ Cs 1.87 Cesium 40	<i>bcc</i> 5.02 ⁵⁶ Ba 3.59 Barium 110	<i>hex</i> 3.77; 12.17 ⁵⁷ La 6.15 Lanthanum 140	<i>hex</i> 3.20; 5.06 ⁵⁸ Hf 13.3 Hafnium 250	<i>bcc</i> 3.31 ⁷³ Ta 16.6 Tantalum 240
	4.08 <i>fcc</i> 19.3 ⁷⁹ Au 170 Gold	3.46; 6.66 <i>rhdr</i> 13.6 ⁸⁰ Hg 90 Mercury	3.45; 5.52 <i>hex</i> 11.8 ⁸¹ Tl 90 Thallium	4.95 <i>fcc</i> 11.4 ⁸² Pb 100 Lead	4.55; 11.85 <i>rhdr</i> 9.75 ⁸³ Bi 120 Bismuth

Types of crystal lattice

fcc - face-centered cubic
bcc - body-centered cubic
hex - hexagonal
tetr - tetragonal
diam - diamond
rhdm - rhombohedral
orth - orthorhombic (rhombic)
rhdr - rhombohedral
cub - cubic



		VIII			
		3.47; 5.54 <i>hex</i> 2He ⁴ Helium			
VI	VII				
5.40; 3.43; 5.09 <i>rhomb</i> 2.00 (54K) 8O Oxygen	<i>rhomb</i> 9F Fluorine	4.46 <i>fcc</i> 1.44 (24K) 10Ne 75 Neon			
10.5; 12.9; 24.5 <i>orth</i> 2.07 16S Sulfur	8.56; 6.12; 2.03 <i>tetr</i> 2.03 17Cl Chlorine	5.31 <i>fcc</i> 1.66 (40K) 18Ar 92 Argon			
<i>bcc</i> 2.88 24Cr 7.19 Chromium 540	<i>bcc</i> 8.91 25Mn 7.44 Manganese 400	<i>bcc</i> 2.87 26Fe 7.87 Iron 440	<i>fcc</i> 3.54 27Co 8.90 Cobalt 420	<i>fcc</i> 3.59 28Ni 8.90 Nickel 410	
4.37; 4.95 <i>hex</i> 4.79 34Se 90 Selenium	6.68; 8.74; 4.49; <i>orth</i> 4.05 (123K) 37Br Bromine	5.65 <i>fcc</i> 2.82 (116K) 36Kr 72 Krypton			
<i>bcc</i> 3.15 42Mo 10.2 Molybdenum 410	<i>hex</i> 2.74; 4.40 43Tc 11.5 Technetium	<i>hex</i> 2.71; 4.28 44Ru 12.4 Ruthenium 600	<i>fcc</i> 3.80 45Rh 18.4 Rhodium 480	<i>fcc</i> 3.89 46Pd 12.0 Palladium 270	
4.46; 5.93 <i>hex</i> 6.24 52Te 150 Tellurium	7.27; 9.80; 4.79; <i>orth</i> 4.93 53I Iodine	6.13 <i>fcc</i> 3.54 (161K) 54Xe 64 Xenon			
<i>bcc</i> 3.16 74W 19.3 Tungsten 360	<i>hex</i> 2.76; 4.46 75Re 21.0 Rhenium 430	<i>hex</i> 2.73; 4.32 76Os 22.6 Osmium 500	<i>fcc</i> 3.84 77Ir 22.6 Iridium 420	<i>fcc</i> 3.92 78Pt 21.45 Platinum 230	
3.34 <i>cub</i> 9.32 84Po Polonium	<i>At</i> 85 Astatine	6.6 <i>fcc</i> 86 Radon			

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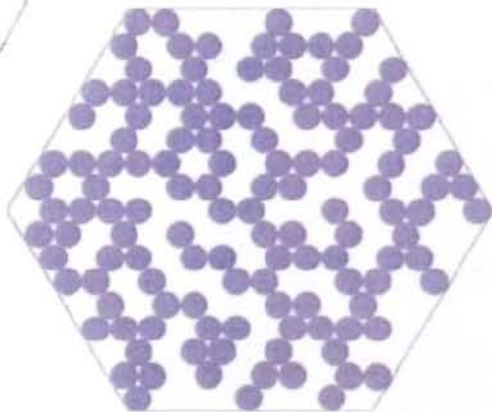
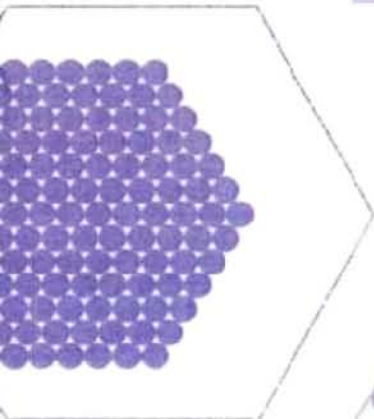
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