

Boris M. Smirnov

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Distributions, Structures, Phenomena,
Kinetics of Atomic Systems



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Boris M. Smirnov

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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

$$z = \sum_{k=1}^n z_k \tag{2.1}$$

Introduce the *characteristic functions*:

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

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

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

This gives:

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

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).