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,

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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.