

**METHODS
OF
STATISTICAL
PHYSICS**

by

A. I. AKHIEZER

and

S. V. PELETMINSKII

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Foreword

The present monograph by A.I. Akhiezer and S.V. Peletnitsky, dedicated to an exposition of methods of statistical mechanics, will undoubtedly occupy a special place among monographs on statistical mechanics, since it uniformly derives and studies both kinetic equations for classical and quantized systems, and equations of macroscopic physics, i.e., equations of hydrodynamics for normal and superfluid liquids and equations of macroscopic electrodynamics.

The authors have achieved uniformity in their approach to such seemingly varied problems by basing their exposition on the concept of compact description of non-equilibrium states of macroscopic systems. This compact description emerges naturally in the course of the evolution of physical systems having a large number of degrees of freedom, and therefore it is also expedient and natural to employ this description of non-equilibrium systems for deriving both kinetic equations and equations of hydrodynamics. If a system is characterized by weak particle interactions or by low particle densities, the hydrodynamic stage of the evolution is preceded by a kinetic stage, which may be studied with the aid of kinetic equations. If the particle interactions are not weak or the particle density is high, there is no kinetic stage of evolution and the hydrodynamic stage which arises immediately may be studied with the aid of the equations of hydrodynamics.

Closely adhering to this idea of a compact description, the authors construct a theory on the basis of general principles, such as the principle of the relaxation of correlations and ergodic relations, connected with the special features of the structure of Hamiltonians and with the properties of their symmetry.

The authors devote particular attention to the study of quantum systems. In addition, they preface their discussion of problems of quantum statistics with a

clear exposition of the fundamentals of quantum mechanics, including the theory of measurement.

The authors also employ the method of a compact description in their investigation of the asymptotic behaviour of such universal quantities as equilibrium two-time Green functions.

Special attention is paid to examining systems with spontaneously broken symmetry, and in particular to systems with broken gauge symmetry.

The monograph is distinguished by rigour, clarity and consistency of mathematical constructs, both as a whole and with respect to specific problems. We may note, for example, the investigation of problems related to the entropy of weakly non-ideal gases, to the quantum virial expansion in the theory of kinetic equations, and so on.

However, the reader will find here not only a presentation of the formal basis of statistical mechanics. The monograph also examines a series of concrete applications that provide good illustrations of the general theory. These include the kinetic theory of gases, the theory of Brownian motion, the theory of the slowing down of neutrons, the theory of transport phenomena in crystals, and some problems of statistical plasma theory.

The book is characterized, if one may say so, by a balance between physics and mathematics, which greatly facilitates its reading and comprehension.

This interesting and valuable book will undoubtedly benefit a wide circle of readers, including both physicists and mathematicians, who deal with problems of statistical mechanics.

Academician N.N. Bogoliubov

Preface

The properties of macroscopic bodies are to a large degree determined by their atomic-molecular structure. With the number of atoms and molecules making up macroscopic bodies being enormously large, laws arise of a special type - statistical laws which, together with the microscopic laws of the motion of atoms and molecules, determine the macroscopic properties of physical bodies.

The physical nature of the different processes occurring in macroscopic bodies can vary greatly. Thus different types of physical phenomena demand the development of different theories. However, despite the variety of theories, there is a general research method combining them all. This is the statistical mechanics method, based on the examination of macroscopic bodies defined as systems made up of an enormous number of particles. Since precise values for the coordinates and momenta of individual particles are of no relevance to macroscopic descriptions (to say nothing of the fact that in practice we do not know these values), the need arises for some sort of averaging, for which the concept of the probability of a state must be introduced.

In introducing the concept of probability we must emphasize that the use of probability is not an essential part of classical physics. We use it because it is not possible, and indeed not desirable, to follow the motion of every atom (although in principle, if the atom were subject to the laws of classical mechanics, this would be possible). In real life atoms are subject to the laws of quantum mechanics, not classical mechanics, and so the concept of probability is inherent in the nature of things. Thus the basic statistical nature of the behaviour of micro-objects does not contradict the determinism of the behaviour of macro-objects, since as we have already said, macroscopic examination assumes the averaging of the

dynamic variables of individual atoms. For a very large number of these variables the averaging that derives from the general theorems of the theory of probability leads to a very great reduction in the variations of macroscopic observations.

One matter of great relevance is the fact that in the process of the evolution which every physical system undergoes with time the character of the probabilistic description changes; or to put it more precisely, at each stage of the evolution of a physical system the form of the probability of a state has a different structure, the structure becoming simplified with time. This indicates that the probability for the state of a system over a long period of time is defined in practice by a limited number of functions, i.e. the probability is a functional of those functions which can be used for the macroscopic description of physical systems. These functions satisfy particular equations - at different stages of the evolution of a physical system, the kinetic equations for the particle distribution function, the equations of hydrodynamics and other transport equations.

This book describes the general methods of statistical mechanics, based on the idea of a contracted description of systems with a large number of degrees of freedom. A range of applications of these methods is also described.

We begin with a study of kinetic equations in classical systems (Chapter One). We introduce many-particle distribution functions, which at the kinetic stage of the evolution are functionals of the single-particle distribution function. For these functionals we construct a chain of coupled integral equations equivalent to the chain of integral equations of Bogolyubov, Born, Green, Kirkwood and Yvon and the 'boundary condition' of Bogolyubov, which is in turn connected with the principle of the weakening of correlations in macroscopic systems. In this chapter we also set out the theory of transport phenomena based on Boltzmann's kinetic equation and derive the Fokker-Planck equation for slow processes. These are applied to an examination of the theory of Brownian motion and the slowing-down theory of neutrons. Chapter One also contains an examination of the basic questions of the statistical mechanics of charged particles. The chapter concludes with a consideration of aspects of the reversibility of mechanical motion and the irreversibility of macroscopic processes.

In Chapter Two we set out the basic principles of the statistical mechanics of quantum systems. Here, along with the general principles of quantum mechanics, ergodic relations of macroscopic quantum systems and the principle of the weakening of correlations are examined. Chapter Three is devoted to the theory of equilibrium states of quantum systems. Questions of the thermodynamic perturbation theory and the quantum virial expansion are examined. Using the quasi-average method we

develop a theory of the superfluidity of boson and fermion gases.

Chapter Four is devoted to methods of investigating non-equilibrium states of quantum systems. The reaction of a system to external disturbances is introduced, the properties of Green functions are investigated, and a general theory of relaxation processes based on the concept of a contracted description of macroscopic systems is developed. We examine in detail the low-frequency asymptotics of Green functions.

In Chapter Five we examine kinetic equations for quantum systems. We derive kinetic equations for cases of weak interaction and of low density. We study the question of the entropy of a weakly non-ideal non-equilibrium quantum gas. We derive kinetic equations for particles in a variable external field and establish the link between these equations and the low-frequency asymptotics of Green functions for both normal and degenerate systems. We also obtain kinetic equations for particles and radiation interacting with a medium. We apply these to such matters as zero-sound theory and the theory of the thermal conductivity of dielectrics.

In Chapter Six we examine the hydrodynamic stage of the evolution and derive equations for the hydrodynamics of both normal and superfluid liquids. In this chapter we obtain equations for macroscopic electrodynamics and establish the properties of electrodynamic Green functions.

As we have already indicated, our approach is based on the idea of a contracted description of systems with a large number of particles. Therefore we have not considered matters lying outside this area. For example, the theory of equations for the diagonal elements of a statistical operator, developed by Prigogine and Van Hove, is not examined. We have not covered the diagram technique, since its basic results can be obtained by the contracted description method. In this regard our bibliography cannot be considered exhaustive, and we beg in advance the pardon of those authors whose work on the methods of statistical physics has not found expression in our bibliography.

We wish to express our gratitude to V.P. Prikhodko, A.I. Sokolovsky and V.K. Fedyanin for their valuable comments and assistance in the preparation of the manuscript for publication.

A.I. Akhiezer

S.V. Peletminsky

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CHAPTER 1

Kinetic Equations for Classical Systems

1.1. MANY-PARTICLE DISTRIBUTION FUNCTIONS

1.1.1. Boltzmann's Kinetic Equation

In contrast to statistical thermodynamics, which is concerned with the study of equilibrium states of macroscopic systems consisting of a large number of particles, physical kinetics is concerned with the study of the various physical processes taking place in such systems.

Upon the passage of a sufficient amount of time (called the relaxation time), every macroscopic system, if left to itself, undergoes a transition into a state of statistical equilibrium. For this reason, physical kinetics must take statistical thermodynamics into account as a limiting case. However, from general considerations it is clear that the ultimate equilibrium state must be described much more simply than those processes as a result of which this state is achieved. And in fact, all thermodynamic properties of any macroscopic body can be studied with the aid of the universal *Gibbs ensemble* [42]

$$w(x_1, \dots, x_N) = \exp\{\beta(F - H(x_1, \dots, x_N))\}, \quad (1.1.1)$$

which links the equilibrium probability density $w(x_1, \dots, x_N)$ that separate particles of a system have given coordinates and momenta $x_i = (\vec{x}_i, \vec{p}_i)$, with the Hamiltonian of the system $H(x_1, \dots, x_N)$ and with such macroscopic quantities as temperature $T = \beta^{-1}$ and free energy F .

This distribution, established by Gibbs in 1901, is true for any macroscopic system; of the microscopic quantities pertaining to the system, it contains only the Hamiltonian of the system, and of the macroscopic quantities it includes parameters which characterize the equilibrium state, i.e. the temperature, volume and number

of particles (the free energy is a function of temperature T , volume V and number of particles N).

The universality of the Gibbs ensemble, which in principle encompasses all statistical thermodynamics, is related to the fact that it describes equilibrium states. In the transition from equilibrium states to non-equilibrium states this universality is lost, and for the time dependence of various processes at various stages of the system's evolution, physical kinetics obtains various relationships which cannot be united in a single universal formula of the Gibbs type, which includes only temperature and volume.

Statistical thermodynamics and physical kinetics are based on the kinetic theory of gases developed by Maxwell and Boltzmann in the second half of the 19th century. And it is precisely on the basis of a gas, which is the simplest physical system, that the relationship between statistical thermodynamics and physical kinetics - the two component parts of statistical physics - can be most easily understood.

If in the first approximation the interaction between gas particles is not taken into account, its Hamiltonian will have the form

$$H(x_1, \dots, x_N) = \sum_{1 \leq \ell \leq N} \left(\frac{\vec{p}_\ell^2}{2m} + U(\vec{x}_\ell) \right),$$

where \vec{p}_ℓ and \vec{x}_ℓ are the momentum and radius-vector of the ℓ -th particle, $U(\vec{x}_\ell)$ is its potential energy in a given external field, m is the particle mass and N is the number of particles (the particles are assumed to be identical). This form of the Hamiltonian leads to a decomposition of probability $w(x_1, \dots, x_N)$ into a product of single-particle distribution functions $f_0(\vec{x}_\ell, \vec{p}_\ell)$

$$w(x_1, \dots, x_N) \propto \prod_{1 \leq \ell \leq N} f_0(\vec{x}_\ell, \vec{p}_\ell),$$

$$f_0(\vec{x}, \vec{p}) = C \exp \left\{ -\beta \frac{\vec{p}^2}{2m} - \beta U(\vec{x}) \right\}, \quad (1.1.2)$$

where C is a normalization constant.

The function $f_0(\vec{x}, \vec{p})$ is called the *Maxwell-Boltzmann distribution*. It determines (after multiplication by $d^3\vec{x} d^3\vec{p}$) the number of particles whose coordinates and momenta lie within the ranges $d^3\vec{x}$ and $d^3\vec{p}$ close to the given values of \vec{x} and \vec{p} after the passage of a long (compared to the relaxation time τ_r) time, after which the gas has acquired a state of statistical equilibrium.

But the question may arise, how does a single-particle distribution function behave at times t that are shorter than the relaxation time τ_r , and how does the

ultimate transition to the Maxwell-Boltzmann distribution occur? This question is one of the simplest, and at the same time one of the most fundamental questions of physical kinetics. It was solved by Boltzmann, who established an equation which is satisfied by the non-equilibrium single-particle distribution function $f(\vec{x}, \vec{p}, t)$ in the case of a gas with a low density [33]. This equation, called the Boltzmann kinetic equation, has the following form:

$$\frac{\partial f}{\partial t} + (\vec{v} \cdot \frac{\partial f}{\partial \vec{x}}) + (\vec{F} \cdot \frac{\partial f}{\partial \vec{p}}) = (\frac{\partial f}{\partial t})_c, \quad (1.1.3)$$

where $\vec{v} = \vec{p}/m$ is particle velocity, $\vec{F} = -dU/d\vec{x}$ is the external force acting on the particle, and $(df/dt)_c$ is the so-called collision integral. The distribution function determines (after multiplying by $d^3\vec{x} d^3\vec{p}$) the number of particles whose coordinates and momenta lie at time t within the volume element $d^3\vec{x} d^3\vec{p}$, and satisfies the normalization condition

$$\int d^3\vec{x} d^3\vec{p} f(\vec{x}, \vec{p}, t) = N.$$

The terms $(\vec{v} \cdot df/d\vec{x})$ and $(\vec{F} \cdot df/d\vec{p})$ in the kinetic equation define the change in the distribution function caused by the arrival and departure of particle in the element $d^3\vec{x} d^3\vec{p}$ of the coordinate and momentum space as a result of the motion of particles under the action of an external force; the quantity $(df/dt)_c$ defines the change in the distribution function caused by the interaction of gas particles with each other.

If the density of the gas is low, only binary collisions are significant, and the collision integral has the form

$$(\frac{\partial f}{\partial t})_c = \int d^3p_1 \int d\Omega |\vec{v} - \vec{v}_1| \sigma(\theta, \vec{v} - \vec{v}_1) (f'f'_1 - ff_1). \quad (1.1.4)$$

Here \vec{p} and \vec{p}_1 are the momenta of any two particles prior to the collision, \vec{p}' and \vec{p}'_1 are the momenta of these particles after the collision, linked to \vec{p} and \vec{p}_1 by the laws of conservation of momentum and energy; $d\sigma = \sigma(\theta, \vec{v} - \vec{v}_1) d\Omega$ is the differential cross-section of scattering in solid angle $d\Omega$ (θ is the angle between the vectors, $\vec{p}_1 - \vec{p}$ and $\vec{p}'_1 - \vec{p}'$) and $f = f(\vec{x}, \vec{p}, t)$, $f_1 = f(\vec{x}, \vec{p}_1, t)$, $f' = f(\vec{x}, \vec{p}', t)$, etc. The values of the momenta of the particles after the collision are clearly unambiguously defined by the quantities \vec{p} , \vec{p}_1 , θ .

We see that the collision integral includes the scattering cross-section, i.e., a quantity having a probabilistic character. This type of quantity does not occur in any dynamic equations of mechanics. Thus it may be said that the formulation

of a kinetic equation necessitates introducing a concept which is essentially new in mechanics - the concept of probability. On the other hand, the irreversibility of kinetic processes also has a probabilistic character. Therefore it is natural that kinetic equations are that mathematical apparatus which makes possible the study of irreversible processes in a gas and to determine the kinetic coefficients of a gas, i.e., the coefficients of thermal conductivity, viscosity and diffusion.

The irreversibility of kinetic processes corresponds to the increase in the system's entropy, and the kinetic equation makes it possible to prove the law of entropy increase of a gas (the *Boltzmann H-theorem*). The entropy density of the gas $s(\vec{x}, t)$ is here determined, according to Boltzmann, combinatorially:

$$s(\vec{x}, t) = - \int d^3\vec{p} f(\vec{x}, \vec{p}, t) \ln f(\vec{x}, \vec{p}, t). \quad (1.1.5)$$

From this definition and from the kinetic equation (1.1.3) it follows that

$$\begin{aligned} \frac{\partial s}{\partial t} + \operatorname{div} \vec{s} &= \\ &= - \frac{1}{4} \int d^3\vec{p}_1 \int d^3\vec{p} \int d\Omega |\vec{v} - \vec{v}_1| \sigma(\theta, \vec{v} - \vec{v}_1) (f'f'_1 - ff_1) \ln \frac{ff_1}{f'f'_1}, \\ \vec{s}(\vec{x}, t) &= - \int d^3\vec{p} \vec{v} f(\vec{x}, \vec{p}, t) \ln f(\vec{x}, \vec{p}, t), \end{aligned}$$

from which $(\partial/\partial t) \int d^3\vec{x} s(\vec{x}, t) \geq 0$. The equality sign corresponds to the state of statistic equilibrium, when the distribution function is determined by formula (1.1.2).

Since a kinetic equation contains only the first time derivative of the distribution function, the Cauchy problem may be posed for it, i.e., the problem of finding the particle distribution function $f(\vec{x}, \vec{p}, t)$ at $t \neq 0$ for a given initial distribution $f(\vec{x}, \vec{p}, 0)$. This problem has a single solution [62] but due to the specific structure of the collision integral, the function $f(\vec{x}, \vec{p}, t)$ will be positive only at $t > 0$, i.e., at subsequent moments of time in relation to the initial moment. With respect to moments of time preceding the initial moment, for them the solution of the kinetic equation may not be positive. Therefore, the solution of the kinetic equation for $t < 0$ does, generally speaking, not have a physical meaning. Thus, in the Boltzmann kinetic equation both directions of time are not equivalent. This circumstance accords with the fact that the kinetic equation is suitable for describing irreversible processes.

The method which was used by Boltzmann himself when deriving the kinetic equation had in some sense a semi-intuitive character; specifically, in the derivation it was taken for granted that a state a gas can always be described with the aid of only a single-particle distribution function, i.e., it was silently assumed that the effects related to particle correlations are always negligibly small. It is