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Statistical Physics I

Equilibrium Statistical Mechanics

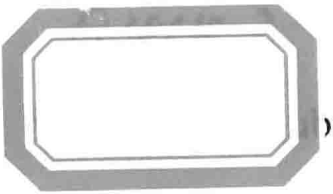
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统计物理学 第 1 卷

M. Toda R. Kubo N. Saitô

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Equilibrium Statistical Mechanics

Second Edition
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Foreword to Statistical Physics I and II

The search to discover the ultimate structure of matter, from molecules to atoms, from atoms to electrons and nuclei, to nucleons, to elementary particles, and now to quarks, has formed the mainstream of modern physics. The ultimate structure is still elusive, but the efforts of mankind from the beginning of this century to probe the fundamentals of the physical world have been extremely successful in revealing the grandeur of the order in nature. The glory of this success may even outshine another great endeavor of modern physics, which is, however, equally important. This other endeavor is directed towards the synthesis of analyzed elements into organized systems which are encountered in our more common experience. Analysis and synthesis are the two sides of the evolution of science. They are very often so interconnected that they cannot be separated in any simple way. Briefly stated, statistical physics is the methodology of synthesis. It is the subject of this text.

The construction of macroscopic systems from microscopic elements analyzed at the microscopic level is not only limited to physics. Macrosystems are synthesized from microscopic structure and dynamics in biology, the social sciences, psychology and other sciences as well. This activity of synthesizing is undoubtedly one of the most powerful tools of science. However, we may say that it is best developed in physics. This is, of course, because the objects studied in physics are simpler and more concrete than those in other sciences, and theories can be more easily tested through experiments.

The synthesis of a macroscopic system from microscopic elements is not simply a collecting of fragments. The macroscopic system is an entity characteristically different from that existing at the microscopic level. The most typical example is perhaps given by the second law of thermodynamics. Despite the reversibility of the microscopic dynamics, macroscopic phenomena are indeed irreversible, and entropy always increases.

As is well known, the law of increasing entropy is interpreted in terms of probability. In order to describe a macroscopic system consisting of an enormous number of microscopic elements, the extremely complex motion of the microscopic elements has to be projected, so to speak, onto a much smaller number of macroscopic variables. This projection is necessarily of a statistical character. In this sense, it is statistical physics that synthesizes the microscopic world to the macroscopic world. Statistical physics covers a very large area, from statistical thermodynamics (that is, the statistical mechanics which con-

structs thermodynamics) to the generalized statistical mechanics of irreversible processes and the kinetic theories which inherit the tradition of the classical kinetic theory of gases. The great breadth of these subjects makes it impossible to treat them all within this text. Fortunately, two volumes of the *Iwanami Series in Fundamental Physics* are also included in this series[1] and are devoted to the physics of condensed matter with various applications of statistical physics. Therefore the emphasis in this book will be placed upon methodological aspects rather than upon specific applications.

The year 1972, during which the first Japanese edition of this book was prepared, was the hundredth anniversary of the proposal of the Boltzmann equation. This equation determines the evolution of the velocity distribution function of molecules in a dilute gas. The stationary solution of this equation gives the Maxwell–Boltzmann distribution law on which the statistical thermodynamics of dilute gases was founded. An even more important aspect of this equation is that it provided a method for calculating the properties of dilute gases in nonequilibrium states. The Boltzmann equation was the prototype of the general kinetic method which treats the temporal evolution of the distribution functions of microscopic elements.

Although the kinetic method is very useful and powerful, generalizing it to apply to denser systems is very difficult. It can hardly be regarded as the general basis of statistical thermodynamics. Here again, Boltzmann made a great contribution and in so doing created statistical mechanics. He recognized that the assumption of equal weights of microscopic states is sufficient to build a general scheme for the statistical mechanics of equilibrium states, namely statistical thermodynamics. The inscription

$$S = k \log W$$

on Boltzmann's gravestone in the central cemetery of Vienna is the essence of this work, by means of which Max Planck summarized Boltzmann's somewhat obscure statements. Statistical mechanics was born through this simple equation. The whole structure was beautifully reconstructed by W. Gibbs some years later. Although there was a difference in viewpoints between Boltzmann and Gibbs, this is no longer so important.

The true mechanics of the microscopic world is quantum mechanics. Thus, statistical mechanics, based on classical mechanics, was doomed to show inconsistencies when applied to real physical problems. The best known case of this was the problem of blackbody radiation, which led Planck to the discovery of energy quanta. Moreover, the quantal structure of nature is reflected in the very existence of thermodynamics. For example, the Gibbs paradox for the extensivity of entropy cannot be resolved by the classical picture. If nature had a different structure, macroscopic thermodynamics would have been totally different from what we know in the physical world. The logical structure of statistical

[1] S. Nakajima, Y. Toyozawa, R. Abe: *The Physics of Elementary Excitations*. T. Matsubara (ed): *The Structure and Properties of Matter*, Springer Ser. Solid-State Sci., Vols. 12 and 28, respectively.

mechanics, particularly that constructed by Gibbs, received the new mechanics as if it had been anticipated. The logic bridging the microscopic and macroscopic worlds does not much depend upon the mechanics governing the former. Here we see the general character of the methods of statistical physics.

At least as far as thermodynamic properties are concerned, quantum-statistical mechanics is the most general scheme for elucidating the properties of a macroscopic system on the basis of its microscopic structure. Developments since 1930 in the modern physics of condensed matter have been theoretically supported by quantum mechanics and quantum-statistical mechanics. Some of the basic problems will be treated in this book, but most of the physical problems had to be left to the two volumes of this series mentioned previously. It should be kept in mind that there is no distinct boundary between statistical physics and condensed matter physics. Indeed, progress in the former was made through efforts in the latter. Theoretical methods were developed in the treatment of real physical problems. It is only in the last decades that statistical physics has grown into quantum-statistical physics, which includes some general aspects of nonequilibrium theories. In these years this progress was truly remarkable and was made hand in hand with developments in solid-state physics and related fields.

This text includes such recent developments in the fundamentals of statistical physics. It is not possible to cover the entirety of these subjects in these few pages. Our intention is to make this an elementary introduction to the subjects on the one hand, and to indicate to the reader the directions of future developments on the other.

The treatment is divided into two volumes. *Statistical Physics I*[2] is on equilibrium theories and *Statistical Physics II*[3] is on nonequilibrium theories. The first three chapters of Volume I form an introduction to statistical thermodynamics, specifically to the statistical mechanics of equilibrium states. The reader is expected to be acquainted only with elementary mechanics, such as the Hamiltonian equation of motion in classical mechanics and the concepts of quantum states in quantum mechanics.

Chapter 1(I) discusses some elements of mechanics and treats some simple problems which use only the concept of the average. These do not depend upon the precise meaning of the average and are therefore very illuminating. Chapter 2(I) reviews the skeleton structure of statistical mechanics. As mentioned earlier, statistical mechanics is based on a probabilistic assumption for microscopic states, namely the principle of equal weight. The logical problem of justifying this principle is discussed later in Chap. 5(I). Here the principle is accepted as a postulate, and we will see how the whole structure of statistical

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[2] M. Toda, R. Kubo, N. Saitô: *Statistical Physics I*, Equilibrium Statistical Mechanics, Springer Ser. Solid-State Sci., Vol. 30 (henceforth denoted by I).

[3] R. Kubo, M. Toda, N. Hashitsume: *Statistical Physics II*, Nonequilibrium Statistical Mechanics, Springer Ser. Solid-State Sci., Vol. 31 (henceforth denoted by II).

thermodynamics is constructed on this basis. This is a standpoint commonly taken in textbooks, so that the construction in this chapter is not much different from that in other books. A beginner should study this chapter carefully.

Chapter 3(I) is devoted to a few applications. Their number is limited for reasons of space. These problems are basic and will be a good preparation for further study.

Chapter 4(I) treats the problem of phase change within the limitations of statistical thermodynamics. The dynamic aspects are not treated and remain as future problems. Even within this limitation, the problem is the most difficult and fascinating one in statistical physics. The first successful theory of the so-called "order–disorder" problem was the Weiss theory of ferromagnets, from which followed a number of approximate theories. Except for one- and two-dimensional models, no rigorous theory of phase transition exists. Rigorous treatments are discussed in this chapter for examples of lattice gases and low-dimensional Ising models. Approximations for three dimensions are discussed. Recently, more examples of rigorous solutions have been found and their intrinsic relations elucidated. These solutions are highly mathematical and are not treated here. While our treatment is also somewhat mathematical, a beginner need not read this through in detail. The problem of singularities associated with a second-order phase transition has been a central topic of statistical mechanics in recent years and is related to many important aspects of statistical physics. This is briefly touched upon along with the problem of critical indices. The reader is referred to other textbooks on the scaling and renormalization group theories.

Chapter 5(I) is devoted to a fundamental consideration of the mechanical basis of statistical mechanics, namely ergodic problems. We have limited ourselves primarily to classical ergodic problems based on classical mechanics. Quantum-mechanical ergodic theories are only briefly sketched. It is questionable whether classical ergodic theories can really be meaningful as a foundation of statistical mechanics; nevertheless, such theories have their own significance as a branch of physics and have made remarkable progress in recent years. Still, it is indeed a great pity for those engaged in research work in statistical physics that basic principles such as that of equal weight lack rigorous proof. The hope that someone among the readers may someday accomplish this ambitious task is one reason why this chapter was incorporated.

Nonequilibrium processes for which temporal evolution is to be considered explicitly are regarded as stochastic processes. This view is discussed in Chaps. 1 and 2(II). The theory of stochastic processes is an important field of mathematics. We emphasize its physical aspects and introduce the reader to the subject using Brownian motion as an example. Brownian motion is not merely random motion of a very fine particle; in general it is random motion of a physical quantity to be observed in a macrosystem. Such random motion is idealized to ideal Brownian motion in the same way that real gases are idealized to ideal gases in statistical thermodynamics. In this sense, the subject matter of Chap. 1(II) is basic to the whole framework of statistical physics. In particular,

the fluctuation–dissipation theorem is the heart of the theory that provides a stepping-stone to the treatments in Chaps. 3–5(II).

To reach the macroscopic level of observation starting from the very fundamental microscopic level, we have to climb up successive levels of coarse graining. In going up each level of this staircase, a certain amount of information gets lost and a corresponding uncertainty is added to the probabilistic description. This is precisely the fundamental theme of statistical physics. However, it is difficult to formulate the program of coarse graining in a general way. Therefore, in Chap. 2(II) we treat a few relatively simple examples to show how this program is carried out, and finally we discuss the derivation of the master equation. Boltzmann's equation is somewhat removed from the main theme of this chapter, but we have included some basic matter on this subject. The Boltzmann equation is also important from a historical point of view, as well as from a conceptual and practical one. Difficult problems still remain in its derivation and generalization, but these are not touched upon here.

Chapters 3–5(II) review the developments in nonequilibrium statistical mechanics which have occurred in the past few decades. Chapter 3(II) is an introduction to these problems from their phenomenological side. It treats relaxation processes from nonequilibrium to equilibrium states and the response of a system near equilibrium to a weak external disturbance. These are linear irreversible processes belonging to a category of physics easily accessible as an extension of the well-founded statistical mechanics of equilibrium states. Theoretical methods for deriving from microscopic physics the relaxation and response functions for such linear processes are discussed in the linear response theory in Chap. 4(II).

Chapter 5(II) treats new developmens in quantum-statistical mechanics on the basis of Chap. 4(II). These developments are applications of the Green's functions and their perturbative calculations. These are among the most remarkable developments of recent years. The Green's function method can join the kinetic approach and equilibrium-statistical mechanics, though to a somewhat limited extent. The formalism takes advantage of the fact that microdynamics is quantum mechanics. The content of this chapter is rather condensed. For further study of the subject the reader is referred to a few well-known textbooks.

The number of pages far exceeded the total originally planned. In spite of this, there are many things which the authors regretfully omitted. We hope that the reader will feel inspired enough to go on and study the subjects at more advanced levels.

R. Kubo and *M. Toda*

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Preface to the Second Edition

In this, the second edition of *Statistical Physics*, much new material has been introduced while the general plan and arrangement of the volume remain unchanged.

The subject itself has progressed considerably in recent years, especially in relation to the theory of phase changes and various aspects of the ergodic problems. In order to include recent developments of the theory of phase changes, more than half of Chap. 4 has been rewritten. It is hoped that the inclusion of additional material will elucidate the current point of view and the new methods employed in this fascinating branch of statistical physics. Chapter 5, which is devoted to the ergodic problems, has been fully revised to present contemporary knowledge of the ergodic behavior of mechanical systems, which has been actively investigated in the last few years by means of mathematical analysis, supported by numerical computation.

The authors have also taken advantage of the opportunity to correct typographical errors, and to revise some figures.

On behalf of the authors I thank the staff of Springer-Verlag for valuable assistance during the preparation of this edition.

Tokyo,
May 1991

Morikazu Toda

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1. General Preliminaries

In this chapter, we introduce the subjects to be treated in terms of statistical mechanics. The principles of statistical mechanics, the topics of Chap. 2, are well established for the equilibrium state, while the kinetic theory of gases was developed to interpret the thermal properties of matter in the bulk. Though we will not be involved in kinetic theory in this chapter, we will clarify some important relations which can be derived by the use of averages with respect to configuration and motion of molecules.

1.1 Overview

1.1.1 Subjects of Statistical Mechanics

The macroscopic states of matter are determined by the properties and motion of the microscopic constituents such as molecules, atoms, electrons, and atomic nuclei, and the detailed behavior of electromagnetic fields. The motion of these constituents obey laws of mechanics including electromagnetic theory. However, since the number of the constituents, or the degrees of freedom, is extremely large, the laws of mechanics are not directly reflected in the properties of matter in bulk. Statistical mechanics forms bridges between microscopic and macroscopic worlds.

In the later half of the nineteenth century, there came thermodynamics which systematized general phenomenological laws of heat. Though thermodynamics may exclude considerations of the microscopic structure of matter, the results of thermodynamics can be transferred to statistical mechanics since the subjects to be discussed in both theories overlap in general. The term "statistical thermodynamics" is sometimes used to emphasize this relationship [1.1–12].

Since the number of constituents is extremely large, it is impossible to obtain a complete mechanical description of physical systems though they are microscopically subject to mechanical laws. As far as classical mechanics is concerned, it is impossible to solve the equations of motion exactly because we have as many equations as the number of constituents. Even if we could solve them, we would have to give the initial conditions concerning velocities and positions of all the constituents; but it is practically impossible to determine these initial

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