STATISTICAL MECHANICS

AN ADVANCED COURSE WITH PROBLEMS AND SOLUTIONS

RYOGO KUBO

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RYOGO KUBO
University of Tokyo

in cooperation with

HIROSHI ICHIMURA
Tokyo Institute of Technology

TSUNEMARU USUI
Kyoto University

NATSUKI HASHIZUME
Ochanomizu University

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PREFACE TO ENGLISH EDITION

The original text of this volume is part of the book "Problems and Solutions in Thermodynamics and Statistical Mechanics", itself one of the "University Series" published by the Shokabo Publishing Company. At the request of the present publisher, the English edition is being published in two volumes, one on thermodynamics and the other on statistical mechanics. Considering the more urgent interest of university students in statistical mechanics, this volume has been translated and published first. The volume on thermodynamics is expected to be published within a year.

The translation was made from the Japanese text by the original authors, together with a few collaborators. As the editor of the original Japanese edition and of the English edition, I wish to express my deep appreciation to Drs. Masaji Kubo, Toshihiko Tsuneto and Satoru Miyake who did the translation work with the authors, and particularly to Professor Donald C. Worth of International Christian University, Tokyo, who kindly took the trouble of helping us with linguistic difficulties. The authors are also indebted to Miss N. Tokuda for the preparation of the manuscript.

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PREFACE TO JAPANESE EDITION

Thermodynamics and statistical mechanics are indispensable tools in studying the physics of the properties of matter. Statistical mechanics, together with quantum mechanics, provides a foundation for modern physics which aims at the thorough understanding of physical phenomena from the microscopic viewpoint of atomic physics. Fundamental knowledge and training in statistical mechanics are therefore of vital importance not only for students studying the physical properties of matter but also for those who study nuclear physics or even astrophysics. Outside the realm of physics, its importance is rapidly penetrating into chemistry, biology and into those vast areas of technology which owe their growth to the advances in modern physics.

Thermodynamics belongs completely to classical physics and is sometimes regarded as unimportant by students of physics who are over-occupied in learning modern physics. Even for students in chemistry, the present is different from the time some decades ago when physical chemistry was almost nothing but chemical thermodynamics. However, it must be stressed here that the usefulness and unique significance of thermodynamics as a fundamental science remain as basic today as they were in the latter half of the last century. Thermodynamics teaches us the value of a phenomenological approach. It avoids explicit use of physical images or models such as atoms and molecules. Instead it deals with relations between somewhat abstract quantities such as energy, entropy, free energy and so forth. Admittedly it does not give intuitive pictures as atomic theories do, which is one of the reasons why students find it difficult to gain sufficient understanding and familiarity to use thermodynamics in real problems. But the simplicity of the logic of thermodynamics sometimes makes us see more clearly into the nature of the basic physics of a given problem from very general principles. This is the great advantage of a phenomenological approach.

Obviously, however, it is impossible to explore more deeply the underlying atomic processes in a given physical phenomenon if we confine our attention to thermodynamics. Such progress is made possible only by quantum mechanics and statistical mechanics. Statistical mechanics provides us with a means to link the physical laws of the microscopic world to those of the macroscopic world. Without close cooperation with statistical mechanics, quantum mechanics itself would not be able to represent the physics of the real world. In this sense, statistical mechanics is indispensable as one of the keystones of modern physics.

Like any other science, statistical mechanics cannot be mastered easily just by learning its principles once. One has to think by oneself a great deal before one grasps the way in which to use the statistical approach in one's thinking, and to apply statistical mechanics to real physical problems. In statistical mechanics and in thermodynamics, there are certain aspects which are quite different from other fields of physics. We often meet students who find difficulty in mastering thermodynamics or statistical mechanics, lacking confidence in applying it to real problems, although they know the principles. Such difficulties are due to insufficient and inadequate training.

The purpose of the present book is to provide a guide for students studying and acquiring facility in thermodynamics and statistical mechanics. Thus it contains fundamental topics, examples and a fairly large number of problems with complete solutions. The fundamental topics are rather condensed, but still they cover all of the points which are basic. This book is meant to be readable without reference to other textbooks. By reading through these topics only, one would be able to obtain fundamental knowledge of thermodynamics and statistical mechanics. The examples are partly to supplement the fundamental topics, but they are primarily meant to show the reader how the principles are applied to physical problems.

The problems are classified into three groups, A, B and C, in order of increasing difficulty. If a reader has enough time he may go through all problems in each chapter. But, if not, it is recommended that he studies first the problems in group A throughout the whole book and then later comes back to try B and C. By just finishing group A problems, he will find himself to have obtained a much better understanding of physics. The number of group A problems is fairly large, so that he may even select about half of these and come back later to the other half. The subjects in the fundamental topics and examples which are marked by $^+$ are not needed in solving problems in group A.

In this book†, thermodynamics and statistical mechanical problems are mostly limited to those of equilibrium states. It might be desirable to include kinetic methods and extensions of thermodynamics and statistical mechanics

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† The reader is reminded that this text is a translation of the Preface to the original Japanese edition, in which thermodynamics and statistical mechanics are contained in one volume.

which apply to non-equilibrium problems. We had, however, to content ourselves in treating such topics in a limited way only in the last chapter (Chapter 6 of the present English edition). This is because the whole volume had become much larger than the original plan and also because such non-equilibrium problems are certainly somewhat advanced.

As mentioned previously in this preface, quantum mechanics is the fundamental dynamics of the microscopic world. In this sense, statistical mechanics ought to be essentially quantum-statistics. However, since the present book devotes itself to clear understanding of the nature of statistical considerations, only an elementary knowledge of quantum mechanics is required in studying problems in groups A and B. Therefore, even those students who are not specializing in physics but have only an elementary background in quantum mechanics will not find any serious difficulty in starting to study this book.

What is most important in studying a physical problem is to grasp it as a problem in *physics*. Mathematical manipulations may sometimes be tedious and sometimes may require specialized techniques. Training in mathematical methods should not be ignored, but it would be a serious mistake if one was to be dazzled by the mathematics and to forget the physics. Teachers often meet students' papers in which the student seems to be in no doubt about the numerical answers although they are in error by two or three orders of magnitudes or are dimensionally incorrect. Professor H. Nagaoka (a pioneer physicist in Japan) was carrying out calculations on a blackboard in his class. He changed the sign of his answer saying "It is plus rather than minus. Isn't it?" Mathematical calculations may very often be in error. A physical mind is very important, for this can give you the right sign even when your calculation betrays you. An answer obtained by calculation is in many cases easily understood, at least qualitatively. It may not be guessed before making calculations, but one should not forget to think it over again in order to see if one can see some physical meaning contained in it. Such remarks are not given in each solution of the problems, so that we should like to emphasize here the importance of such reasoning.

Here and there between the pages some comments † are inserted under the title "Divertissement". While giving seminars to students we sometimes take a rest to drink a cup of tea and chat. We hope that the reader will spare a few minutes at these spots to listen to a chat from the authors, drinking tea or coffee or just smoking.

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† These are revised in this English edition.

The fundamental topics were mostly written by R. K. Examples and problems were selected after repeated discussion by all the authors. The final check of the solutions was made by R. K. and the whole design of the book was made by N. H. The authors would appreciate it if readers would kindly point out any mistakes which may have escaped our notice.

Five years have passed since this book was originally planned, and two years since we started actually to write it. The undertaking proved to be much more difficult than we anticipated. The authors are particularly grateful to Mr. K. Endo, editor of Shokabo Publishing Company, for his continual encouragement and help.

January, 1961 RYOGO KUBO

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Fundamental Topics

CHAPTER 1

PRINCIPLES OF STATISTICAL MECHANICS

Thermodynamics is a phenomenological theory based upon a few fundamental laws derived from empirical facts. In contrast to this, statistical mechanics aims to provide a deductive method which leads us from the microscopic physical world to the macroscopic world starting from the atomic or molecular structure of matter and the fundamental dynamical principles of the atomic world and combining with these the logic of probability theory. It answers the questions what are the physical laws of the microscopic world behind the thermodynamic laws, how the thermodynamics can be "explained" from such laws and why a specific physical system exhibits such thermodynamic characteristics. The fundamental principles of statistical mechanics involve, in fact, very profound and difficult questions if one meditates upon them, but it would not be very wise for the beginners to be too much concerned with such questions. The most important thing is to learn how one thinks in statistical mechanics and how one applies statistical considerations to physical problems.

Fundamental Topics

§ 1.1. MICROSCOPIC STATES

Microscopic and macroscopic states: A physical system which one observes usually consists of a great number of atoms or molecules and so has an enormously large number of degrees of dynamical freedom. But in the usual case, only a few physical quantities, say the temperature, the pressure and the density, are measured, by means of which the "state" of the system is specified. A state defined in this crude manner is called a *macroscopic state* (example: a thermodynamic state). On the other hand, from a dynamical point of view, each state of a system can be defined, at least in principle, as precisely as possible by specifying all of the dynamical variables of the system. Such a state is called a *microscopic state.*

Classical statistical mechanics and quantum statistical mechanics: The statistical mechanics based on classical mechanics is called *classical statistical mechanics* and that based on quantum mechanics is called *quantum statistical mechanics.* Since rigorous mechanics in the atomic world is quantum mechanics, rigorous statistical mechanics must be quantum statistical mechanics and so classical statistical mechanics may be said to be useful only as a certain approximation to quantum statistical mechanics. But the classical theory has even today a great value from theoretical and educational points of view because it makes us understand more clearly the basic ways of thinking in statistical mechanics.

Classical phase space: Let $(q_1, q_2, \ldots q_f)$ be the generalized coordinates of a system with f degrees of freedom and $(p_1, p_2, \ldots p_f)$ their conjugate momenta. A microscopic state of the system is defined by specifying the values of $(q_1, q_2, \ldots q_f, p_1, p_2, \ldots p_f)$. The $2f$-dimensional space constructed from these $2f$ variables as the coordinates is the *phase space* of the system. Each point in the phase space (phase point) corresponds to a microscopic state. Therefore the microscopic states in classical statistical mechanics make a continuous set of points in phase space.

If the Hamiltonian of the system is denoted by $\mathscr{H}(q, p)$, the motion of the system is determined by the canonical equation of motion

$$\dot{p}_j = -\frac{\partial \mathscr{H}}{\partial q_j}, \qquad \dot{q}_j = \frac{\partial \mathscr{H}}{\partial p_j}, \qquad (j = 1,2 \ldots, f). \tag{1.1}$$

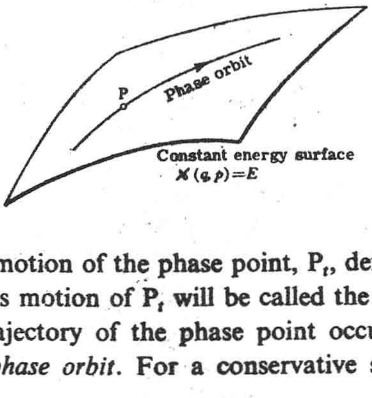

Fig. 1.1.

This determines the motion of the phase point, P_t, defining the state of the system at time t. This motion of P_t will be called the *natural motion* in the phase space. The trajectory of the phase point occurring during natural motion is called a *phase orbit*. For a conservative system, the energy is constant, i.e.

$$\mathscr{H}(q, p) = E. \tag{1.2}$$

Therefore the phase orbit must lie on a surface of constant energy (ergodic surface).

Quantum states: According to quantum mechanics, p and q cannot be specified simultaneously (the uncertainty principle of Heisenberg), so that classical phase space loses its rigorous meaning. In quantum statistical mechanics, a microscopic state is a state defined in a quantum mechanical sense. In particular, a stationary dynamical state of a system must be one of the quantum states determined by the equation

$$\mathscr{H}\varphi_l = E_l\varphi_l \qquad (l = 1, 2, \ldots). \tag{1.3}$$

Here $\mathscr{H}$ is the Hamiltonian of the system, E_l the energy of the quantum state l and φ_l is the wave function representing the quantum state l.

The set of microscopic states in quantum statistical mechanics is thus a discrete denumerable set of quantum states denoted by the quantum number l. (In statistical mechanics, one usually considers a system confined in a limited space, so that the quantum number l is usually discrete. A system with infinite extension is considered as the limit of one of finite extension.)

§ 1.2. STATISTICAL TREATMENT

Whenever a system is kept in equilibrium and remains constant according to macroscopic observations, it never stays constant from the microscopic point of view, and so one can never say precisely in which microscopic state the system is found. One can only define the probability for the set of all possible microscopic states of the system.

Fundamental assumption for observed values of physical quantities: Suppose a physical quantity A is observed for the system under consideration. A is a dynamical quantity from the microscopic point of view and is a function of microscopic states. The microscopic value of A is represented by $A(q, p) = A(\mathrm{P})$ in classical mechanics (P is a phase point) and by the expectation value†

$$A_l = \int \varphi_l^* A \varphi_l \, \mathrm{d}\tau \equiv \langle l | A | l \rangle \tag{1.4}$$

in the quantum state l in quantum mechanics. The observed value A_{obs} in the macroscopic sense must be a certain average of microscopic A: i.e.

$$A_{\text{obs}} = \bar{A}. \tag{1.5}$$

Realization probability of a microscopic state: Let $\mathfrak{M}$ be the set of all possible microscopic states which can be realized by the system under a certain macroscopic condition. $\mathfrak{M}$ is classically a certain subspace of the phase space and quantum-mechanically it is a set of quantum states of the system. The probability that these microscopic states are realized is defined as the

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† The integration in the following expression is carried out over the variables which are used to represent the wave function, say $q_1, q_2, \ldots q_f$. Here $\mathrm{d}\tau$ is a volume element of the space of these variables. Note that a quantum state corresponds to a phase orbit in classical mechanics and so A_l corresponds to the average taken over such an orbit.

probability that one of the microscopic states in the volume element $\Delta\Gamma$ of phase space is realized:

$$Pr(\Delta\Gamma) = \int_{\Delta\Gamma} f(\mathrm{P})\,\mathrm{d}\Gamma, \qquad (\Delta\Gamma \in \mathfrak{M}) \tag{1.6a}$$ †

or the probability that the quantum state l is realized:

$$Pr(l) = f(l), \qquad (l \in \mathfrak{M}) \tag{1.6b}$$

that is, by giving the probability density $f(\mathrm{P}) = f(q, p)$ or the probability $f(l)$. $f(\mathrm{P})$ and $f(l)$ are sometimes called simply the distribution functions.†† When the distribution functions are given, the average value (1.5) is explicitly written as

$$A_{\text{obs}} = \bar{A} = \int_{\mathfrak{M}} A(\mathrm{P}) f(\mathrm{P})\,\mathrm{d}\Gamma, \tag{1.7a}$$

$$\bar{A} = \sum_{\mathfrak{M}} A_l f(l). \tag{1.7b}$$

Statistical ensembles: In order to make the probabilistic idea as clear as possible, let us consider an hypothetical ensemble consisting of a great number of systems each of which has the same structure as the system under observations, and assume that the probability that a system arbitrarily chosen from this ensemble is found to be in a particular microscopic state is given by (1.6a) or (1.6b). For this hypothetical ensemble, (1.5) may be written as

$$A_{\text{obs}} = \text{ensemble average of } A \equiv \bar{A}\,. \tag{1.8}$$

A statistical ensemble is defined by the distribution function which characterizes it. The most fundamental ensemble is the micro-canonical ensemble to be discussed later, but many other ensembles can be considered corresponding to various physical conditions (see (1.12) and (1.13)).

Ideal gas – Γ space and μ-space: So far the whole system in question is considered as the object of statistical treatment. This is the general standpoint of statistical mechanics established, in particular, by Gibbs. If the system under consideration is an ideal gas or a nearly ideal gas, it is possible to take each molecule as a statistical unit and regard the gas as a real ensemble

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† A volume element of phase space is denoted by $\mathrm{d}\Gamma$: $\mathrm{d}\Gamma = \mathrm{d}q_1\,\mathrm{d}q_2 \ldots \mathrm{d}q_f\,\mathrm{d}p_1\,\mathrm{d}p_2 \ldots \mathrm{d}p_f$.

†† In mathematical probability theory, a distribution function is usually defined by

$$\int_{-\infty}^{x} f(x)\,\mathrm{d}x = F(x)$$

in the one-dimensional case, for example. The term "distribution function" in statistical mechanics is usually used in a loose way.

consisting of such units. This point of view was taken in the kinetic theory of gases which became the prototype of statistical mechanics. From this standpoint, the important thing is, in classical statistical mechanics, the distribution function of the position $\boldsymbol{x}$ and the momentum $\boldsymbol{p}$ of a molecule, i.e., the probability that a molecule chosen from the ensemble of gas molecules is found to have the coordinate and momentum values between $\boldsymbol{x}$ and $\boldsymbol{x} + \mathrm{d}\boldsymbol{x}$, $\boldsymbol{p}$ and $\boldsymbol{p} + \mathrm{d}\boldsymbol{p}$ is equal to

$$f(\boldsymbol{x}, \boldsymbol{p})\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{p}\,. \tag{1.9}$$

Most of the properties of dilute gases can be derived from a knowledge of this distribution function. This is a distribution in a six-dimensional space, which is often called the *μ-space*. The phase space of the N molecules of the gas is called the *Γ space*.

Maxwell distribution: In a thermal equilibrium state at high temperatures, the distribution function f for a dilute gas is given by

$$f(\boldsymbol{p}) = \frac{1}{(2\pi mkT)^{\frac{3}{2}}} \exp\left\{ -\frac{1}{2mkT}(p_x^2 + p_y^2 + p_z^2) \right\} \tag{1.10}$$

where T is the absolute temperature, m the mass of a molecule, and k the Boltzmann constant. This Maxwell distribution can be derived by various methods. The most general derivation will be described later § 1.15, eq. (1.100).

§ 1.3. THE PRINCIPLE OF EQUAL WEIGHT AND THE MICROCANONICAL ENSEMBLE

When a system consisting of a great number of particles (more generally a system having a great number of degrees of freedom) is isolated for a long time from its environment, it will finally reach a thermal equilibrium state. In this case, the energy of the system is constant, so that it is presumed to be fixed at the value E with a certain allowance δE. This is the prescribed macroscopic condition. The set $\mathfrak{M}(E, \delta E)$ of the microscopic states to be considered under such conditions † is

classically: the shell-like subspace of the phase space between the two constant-energy surfaces for $\mathscr{H} = E$ and $\mathscr{H} = E + \delta E$;

and quantum-mechanically: the set of quantum states having the energy eigenvalues in the interval $E < E_l < E + \delta E$.

The principle of equal weight: In a thermal equilibrium state of an isolated

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† Under certain circumstances, other constants of motion such as the total linear momentum or the total angular momentum may be prescribed. In such a case, $\mathfrak{M}$ is further restricted.

system, each of the microscopic states belonging to the set $\mathfrak{M}(E, \delta E)$ is realized with equal probability, namely:

(classically)

$$f(\mathrm{P}) = \text{constant} = \left[\int_{E<\mathscr{H}<E+\delta E} \mathrm{d}\Gamma \right]^{-1}, \qquad \mathrm{P} \in \mathfrak{M}(E, \delta E) \tag{1.11a}$$

(quantum-mechanically)

$$f(l) = \text{constant} = \left[\sum_{E<E_l<E+\delta E} 1 \right]^{-1}, \qquad l \in \mathfrak{M}(E, \delta E). \tag{1.11b}$$

The microcanonical ensemble: A statistical ensemble defined by the principle of equal weight, or more precisely by the probability distribution given by (1.11a) or (1.11b), is called a microcanonical ensemble, and the distribution is called a *microcanonical distribution.* A microcanonical ensemble thus represents an isolated system which has reached thermal equilibrium.

Classical limit ($\delta E \to 0$): Using classical considerations, one may go to the limit $\delta E \to 0$ and take the set $\sigma(E)$ on the surface of constant energy E instead of $\mathfrak{M}(E, \delta E)$. Then one has, instead of (1.6a) and (1.11a)

$$Pr(\Delta\sigma) = \int_{\Delta\sigma} f(\mathrm{P})\, \mathrm{d}\sigma, \qquad \mathrm{P} \in \sigma(E) \tag{1.12a}$$

or,

$$f(P)\, \mathrm{d}\sigma = \frac{\mathrm{d}\sigma}{|\operatorname{grad} \mathscr{H}|} \Bigg/ \int_{\mathscr{H}=E} \frac{\mathrm{d}\sigma}{|\operatorname{grad} \mathscr{H}|}, \tag{1.12b}$$

where $\mathrm{d}\sigma$ is a surface element on the constant energy surface, and

$$|\operatorname{grad} \mathscr{H}| = \left[\sum_j \left\{ \left(\frac{\partial \mathscr{H}}{\partial p_j} \right)^2 + \left(\frac{\partial \mathscr{H}}{\partial q_j} \right)^2 \right\} \right]^{\frac{1}{2}}.$$

Equation (1.7a) becomes

$$\bar{A} = \int_{\mathscr{H}=E} \frac{A(q, p)\, \mathrm{d}\sigma}{|\operatorname{grad} \mathscr{H}|} \Bigg/ \int_{\mathscr{H}=E} \frac{\mathrm{d}\sigma}{|\operatorname{grad} \mathscr{H}|}. \tag{1.13}$$

Ergodic theorem: In classical mechanics, the dynamical states of an isolated system are represented by the motion of a phase point in phase space and so a dynamical quantity A is represented by a time-dependent quantity $A_t = A(\mathrm{P}_t)$ which changes in time according to the motion of the phase point. An observed value A_{obs} of A is therefore to be considered as a time average of A_t. Since A_{obs} remains constant for the thermal equilibrium state of the system, it may be an average over a sufficiently long period of time. In this way,