STATISTICAL MECHANICS

by RYUZO ABE

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PREFACE

In the last decade, a number of new techniques, such as Feynman diagrams, the Green's function method and the linear response theory, have been developed and applied to many physical problems in statistical mechanics. This book is intended to be an introduction to such new techniques at an elementary level. In chapters 1 and 2, the basic ideas in statistical mechanics are discussed, and in chapter 3, the cumulant expansion technique is introduced as a general method. By using this technique, one of the traditional problems in statistical mechanics, i.e. the cluster expansion of an imperfect gas, is discussed. Quantum mechanics plays a major role after chapter 5 where the method of second quantization, which is followed by the perturbational treatment of problems in chapters 6 and 7, is introduced. Chapter 8 is devoted to the Green's function method, while the perturbation method used as a systematic method of calculating the Green's functions, is discussed in chapter 9. This method is then applied in chapter 10 to the electron-phonon system. Until this chapter, the concern has mainly been with systems in thermal equilibrium. The linear response theory is introduced in chapter 11, and the expression for electrical conductivity which will then be exploited to calculate the electrical resistivity due to impurities in the last chapter is derived. The arguments in this book are maintained at an elementary level, being restricted to simple mathematics such as ordinary calculus, Stirling's formula, elementary contour integrals, etc.

I have omitted some interesting subjects such as superfluidity, superconductivity, phase transitions, etc. in view of the fact that these topics are too advanced for a book at this level. I believe that the methods of tackling problems in statistical mechanics can, however, be learned through the rather limited number of topics selected for this book.

R.A.

CONTENTS

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Chapter 1

CLASSICAL STATISTICAL MECHANICS OF SYSTEMS IN THERMAL EQUILIBRIUM·

1.1 INTRODUCTION

The materials we find about us are made up of a large number of particles. For example, 1 cm³ of a gas at 0°C and standard pressure contains 2.7×10^{19} molecules. Also, approximately 10^{22} electrons are moving in 1 cm³ of a metal such as copper or aluminum. The motion of such many-body systems may be described by a mechanical equation of motion. In classical theory, if the position and momentum of a system at a specific time is known, then the motion of the system can be determined uniquely. In quantum mechanics, causality in the classical sense does not hold true, but a causal description is still possible in that the motion of the system can be described by the Schrödinger equation.

However, it is extremely difficult to calculate the mechanical motion of a many-body system. This is apparent from the problems created by 3-body systems, for example, that of the sun, earth and moon which plagued nineteenth-century physicists and mathematicians. Moreover, even if we can calculate the motion of 10^{19} particles, what good is it? We do not observe microscopic motion, but macroscopic properties such as pressure and specific heat in the case of a gas. Statistical mechanics gives us the necessary macroscopic information from a microscopic standpoint. In this chapter we shall explain the basic ideas of statistical mechanics under the condition that the systems under consideration are in thermal equilibrium. Let us first consider some examples in which the motion is classically described.

1.2 SIMPLE EXAMPLES IN CLASSICAL MECHANICS

Example 1: One-dimensional Simple Harmonic Oscillator
Consider a one-dimensional simple harmonic oscillator of mass m

and angular frequency ω. Let the coordinate and momentum be x and $p \, (=m\dot{x})$, respectively. The energy of this oscillator is a constant of motion and is given by

$$e = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2}. \tag{1.1}$$

The right-hand side of Eq. (1.1) is called the Hamiltonian $H(x, p)$ and the equation of motion can be written as

$$\dot{x} = \frac{\partial H}{\partial p}, \quad \dot{p} = -\frac{\partial H}{\partial x}. \tag{1.2}$$

It is convenient to describe the motion of the oscillator in an x–p plane which is called the phase space or μ space. From Eq. (1.1) we see that the orbit in μ space is an ellipse (Fig. 1).
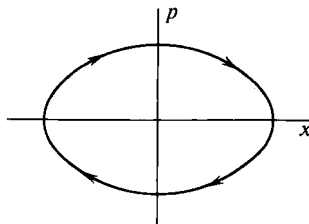
Fig. 1

Example 2: A Free Particle in a Box

Let us assume there is a particle in a cubic box of side L, with no forces acting on it. We shall further assume that collisions between the particle and walls of the box are smooth and completely elastic. That is, on collision, the normal component of the velocity changes sign only, while the tangential component remains the same. Therefore, in the plane spanned by the coordinate x and the momentum p_x, the point representing the particle performs the motion indicated in Fig. 2.

The same is true for the y and z directions, hence, μ space is 6-dimensional.

In future we use vector notation for the sake of convenience and set

$$\boldsymbol{x} = (x, y, z), \quad \boldsymbol{p} = (p_x, p_y, p_z).$$

The volume element in μ space is denoted by

$$d\boldsymbol{x}d\boldsymbol{p} = dxdydzdp_xdp_ydp_z. \tag{1.3}$$
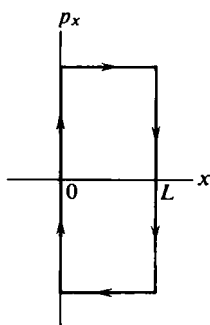
Fig. 2

1.3 ENSEMBLE OF ALMOST INDEPENDENT PARTICLES

Consider N simple harmonic oscillators, as described in the preceding section, and assume that the oscillators are not all independent but can transfer energy through very weak interactions. These interactions are assumed to be so weak that the total energy may be written as the sum of the individual energies

$$E = e^{(1)} + e^{(2)} + \cdots + e^{(N)}, \tag{1.4}$$

where $e^{(i)}$ is the energy of the i-th oscillator.

Now consider a phase space spanned by $x^{(1)}, x^{(2)}, \cdots, x^{(N)}, p^{(1)}, p^{(2)}, \cdots, p^{(N)}$. A point in this space defines a state of all the oscillators. We shall call this phase space of the entire system Γ space.

A point in Γ space moves with time along an orbit obeying the rule of mechanics. If all of the oscillators are independent, then each oscillator moves along the ellipse in Fig. 1 with a constant energy in each μ space. If interactions are present, however small, the quantity e is no longer a constant but is a function of time, and the orbit in μ space deviates from an ellipse (Fig. 3).
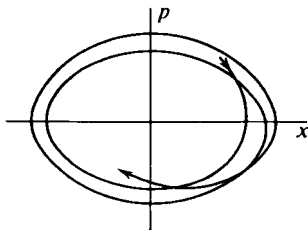
Fig. 3

Let us now put N points representing all of the oscillators in one μ space and let the number of points in an infinitesimal volume $dxdp$ at a certain time be n. The quantity n/N is considered to be the probability of occurrence of a state in which one oscillator is in the volume $dxdp$. Our task is to determine this probability.

We have used simple harmonic oscillators in the above example, but the situation is the same for a system of free particles. In example 2 of the preceding section, Γ space is $6N$-dimensional consisting of $x^{(i)}$ and $p^{(i)}$, where $i = 1, 2, \cdots, N$ and N is the total number of particles. Our problem is to find the probability of the occurrence of that state in which one particle is in an infinitesimal volume $dxdp$ in μ space. Again, we assume that there are no interactions among the particles other than collisions.

Ergodic Hypothesis

In the previous models, the ensemble of simple harmonic oscillators and the ensemble of free particles, we assumed that the total energy E was given. However, a system is usually exchanging energy with its surroundings, and therefore it would be appropriate to assume that the energy of the system lies within a small region about E. Hence we will assume that the energy of the system is between E and $E + \Delta E$. Therefore the representative point in Γ space undergoes motion in the region

$$E \leqq H(q_1, q_2, \cdots, q_f, p_1, p_2, \cdots, p_f) \leqq E + \Delta E,$$

where f is the degree of freedom, $q_1, q_2, \cdots, q_f, p_1, p_2, \cdots, p_f$ are the generalized coordinates and momenta, and H is the Hamiltonian.

We assume that the motion of the point in Γ space covers the above region uniformly. More precisely, *the probability that the representative point is found in a specified volume is independent of the position of that volume*. This is a very fundamental assumption in statistical mechanics and is called the ergodic hypothesis.

There are many mathematical problems involved in the ergodic hypothesis, but we will not go into these in detail. This hypothesis is true not only for the almost independent particles mentioned above, but also for the total Γ space for a general system in which particles are interacting with each other.

Distribution of Maximum Probabilities

Now, returning to simple harmonic oscillators, we divide μ space for one simple harmonic oscillator into small equal sections of size a. Regarding the magnitude of a; classically it is arbitrary, but in quantum

mechanical analysis it is appropriate to choose a equal to h, Planck's constant, in the light of the uncertainty relation $\Delta x \cdot \Delta p \geq h$. However, since the final result is independent of the magnitude of a, we shall merely assume it to be reasonably small. Now, we divide μ space into numbered boxes of size a. Let the energy of each box be e_1, e_2, e_3, $\cdots$. We do the same for N oscillators, and therefore the volume of the boxes in Γ space corresponding to this division is obviously a^N. According to the ergodic hypothesis, in the part of Γ space between E and $E + \Delta E$, the probability that the representative point is found in any one of the boxes is equal. Now assume, that among N oscillators, n_1 oscillators are in the first box, n_2 in the second and n_i in the i-th box. The number of such distributions, according to permutation theory, is

$$P = \frac{N!}{n_1! \, n_2! \cdots n_i! \cdots},\tag{1.5}$$

and the volume in Γ space corresponding to it is Pa^N. That is, the probability of a given distribution $n_1, n_2, \cdots, n_i, \cdots$ occurring is proportional to P.

We assume that P attains its maximum value at thermal equilibrium, i.e., the most probable P is realized at thermal equilibrium. Let us now determine n_i's so that P is maximized. First take the natural logarithm of P:

$$\ln P = \ln N! - \sum_i \ln n_i!.\tag{1.6}$$

According to Stirling's formula, we know that for a large positive integer M

$$\ln M! \approx M(\ln M - 1)\tag{1.7}$$

and therefore, we have

$$\ln P = N(\ln N - 1) - \sum n_i(\ln n_i - 1)$$
$$= N \ln N - \sum n_i \ln n_i.$$

To maximize P, we set

$$\delta \ln P = - \sum(\ln n_i + 1)\delta n_i = 0.\tag{1.8}$$

However, the δn_i's are not all independent, but are subject to the constraints:

$$\sum n_i = N \qquad \therefore \sum \delta n_i = 0\tag{1.9}$$

and

$$\sum e_i n_i = E \qquad \therefore \sum e_i \delta n_i = 0. \tag{1.10}$$

It is convenient to use the Lagrange multiplier method to solve such a problem. The operation $-(1.8)+(1.9)\times\alpha+(1.10)\times\beta$ yields

$$\sum (\ln n_i + \alpha + \beta e_i) \, \delta n_i = 0. \tag{1.11}$$

In Eq. (1.11), we may treat the δn_i's as if they are independent, and therefore we obtain

$$\ln n_i + \alpha + \beta e_i = 0,$$

$$\therefore \quad n_i = \frac{N}{f} e^{-\beta e_i}. \tag{1.12}$$

The quantities β and f can be determined using Eqs. (1.9) and (1.10), namely

$$f = \sum e^{-\beta e_i} \tag{1.13}$$

and

$$E = \frac{N}{f} \sum e_i \, e^{-\beta e_i}. \tag{1.14}$$

The Physical Meaning of β and f

To determine the physical meaning of β, we shall consider 2 ensembles, A and B, consisting of different types of oscillators, and assume that these 2 systems can exchange energy freely. The number of oscillators in A is N_A and there are N_B oscillators in B. Let the number of oscillators in A of energies e_1, e_2, $\cdots$ be n_1, n_2, $\cdots$, and those in B of energies e_1', e_2', $\cdots$ be n_1', n_2', $\cdots$. The number of such distributions is

$$P = \frac{N_A!}{n_1! \, n_2! \cdots} \frac{N_B!}{n_1'! \, n_2'! \cdots}, \tag{1.15}$$

which is to be maximized under the following conditions:

$$\sum n_i = N_A,$$

$$\sum n_i' = N_B,$$

$$\sum e_i n_i + \sum e_j' n_j' = E.$$

As before, we obtain

$$\sum (\ln n_i + \alpha + \beta e_i) \delta n_i + \sum (\ln n_j' + \alpha' + \beta e_j') \delta n_j' = 0.$$

Hence

$$n_i = \frac{N_A}{f_A} e^{-\beta e_i}, \quad n_j' = \frac{N_B}{f_B} e^{-\beta e_j'}. \tag{1.16}$$

From these equations we see that the constant β is common to both systems when they can exchange energy. According to thermodynamics, the temperatures of two systems are equal if they exchange energy and are in thermal equilibrium. Therefore the quantity β corresponds to temperature in thermodynamics.

To look at this situation more closely, let us return to Eqs. (1.13) and (1.14) for a single system and examine how $\ln f$ varies from β to $\beta + d\beta$:

$$d(\ln f) = - \frac{\sum e_i e^{-\beta e_i}}{\sum e^{-\beta e_i}} d\beta = - \frac{E}{N} d\beta. \tag{1.17}$$

Now compare this equation with an equation in thermodynamics of the same form. Let the Helmholtz free energy and the absolute temperature be F and T, respectively. Then we have for constant volume V,

$$d\left(\frac{F}{T}\right) = - E \frac{dT}{T^2}. \tag{1.18}$$

Equations (1.17) and (1.18) imply that $\beta \propto 1/T$. Hence, we set

$$\beta = 1/k_B T \tag{1.19}$$

where k_B is the Boltzmann constant, the value of which will be determined later. We also know that the Helmholtz free energy is given by

$$F = - N k_B T \ln f. \tag{1.20}$$

By substituting Eq. (1.19) into Eq. (1.12), we obtain

$$n_i = \frac{N}{f} e^{-e_i/k_B T} \tag{1.21}$$

This is the Maxwell-Boltzmann distribution law.

So far, we have considered only simple harmonic oscillators, but this distribution law, Eq. (1.21), holds true in general for any system consisting of almost free particles.

Application to an Ideal Gas

Let us apply the above distribution law to an ideal gas. Suppose there are N identical molecules in a volume V, with no forces acting between them. We assume that internal motions such as rotation and vibration can be neglected. Therefore, the μ space to be considered is 6-dimensional, (x, y, z, p_x, p_y, p_z). The kinetic energy of a single molecule is

$$e = \frac{(p_x^2 + p_y^2 + p_z^2)}{2m}.$$

From Eq. (1.21), the average number of molecules in a volume a in μ space is

$$n = \frac{N}{f}\exp\left(-\frac{p_x^2 + p_y^2 + p_z^2}{2mk_BT}\right). \tag{1.22}$$

From Eq. (1.13), we have

$$f = \frac{1}{a}\int \cdots \int \exp\left(-\frac{p_x^2 + p_y^2 + p_z^2}{2mk_BT}\right)dx\,dy\,dz\,dp_x\,dp_y\,dp_z$$

$$= \frac{V(2\pi mk_BT)^{3/2}}{a}, \tag{1.23}$$

where we have used the reaction

$$\int_{-\infty}^{\infty} e^{-\alpha x^2}\,dx = \left(\frac{\pi}{\alpha}\right)^{1/2} \qquad (\alpha > 0). \tag{1.24}$$

Hence, the Helmholtz free energy is given by

$$F = -Nk_B\,T\ln\left[\frac{V}{a}(2\pi mk_BT)^{3/2}\right]. \tag{1.25}$$

The pressure p is given by the thermodynamic relation

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_BT}{V}. \tag{1.26}$$

This is the equation of state for an ideal gas, and if we take N as N_0, Avogadro's number, we obtain $pV = N_0 k_B T$. Comparing this equation with the thermodynamic relation $pV = RT$, we conclude that

$$k_B = \frac{R}{N_0} = 1.380 \times 10^{-16} \quad \text{erg/deg}. \tag{1.27}$$

1.4   CANONICAL ENSEMBLE

We assumed in the preceding section that the interaction between particles is very weak and that the total energy is the sum of the energies of the individual particles. This assumption is true for the kinetic energy but fails for the potential energy. We now discuss a general method which is applicable to such a system. The system considered in the preceding section is, of course, included as a special case.

Consider a system consisting of many particles (e.g., a gas in a box,