

## Introduction

This particular result is known as the Fermi-Dirac distribution function and is used particularly in the theory of metals to describe the electron gas at low temperature and high concentration (Chapter 7).

The classical distribution function used in the derivation of the ideal gas law is just the limit of (10) when the occupancy  $P(1, \epsilon)$  is much less than 1:

$$P(1, \epsilon) \approx \exp[(\mu - \epsilon)/\tau]. \quad (11)$$

The properties of the ideal gas are developed from this result in Chapter 6.

The Helmholtz free energy  $F \equiv U - \tau\sigma$  appears as an important computational function, because the relation  $(\partial F/\partial \tau)_{N, V} = -\sigma$  offers the easiest method for finding the entropy, once we have found out how to calculate  $F$  from the energy eigenvalues (Chapter 3). Other powerful tools for the calculation of thermodynamic functions are developed in the text. Most of the remainder of the text concerns applications that are useful in their own right and that illuminate the meaning and utility of the principal thermodynamic functions.

Thermal physics connects the world of everyday objects, of astronomical objects, and of chemical and biological processes with the world of molecular, atomic, and electronic systems. It unites the two parts of our world, the microscopic and the macroscopic.

## Chapter 1

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### States of a Model System

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*But although, as a matter of history, statistical mechanics owes its origin to investigations in thermodynamics, it seems eminently worthy of an independent development, both on account of the elegance and simplicity of its principles, and because it yields new results and places old truths in a new light in departments quite outside of thermodynamics.*

J. W. Gibbs

*A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts.*

A. Einstein

Thermal physics is the fruit of the union of statistical and mechanical principles. Mechanics tells us the meaning of work; thermal physics tells us the meaning of heat. There are three new quantities in thermal physics that do not appear in ordinary mechanics: entropy, temperature, and free energy. We shall motivate their definitions in the first three chapters and deduce their consequences thereafter.

Our point of departure for the development of thermal physics is the concept of the stationary quantum states of a system of particles. When we can count the quantum states accessible to a system, we know the entropy of the system, for the entropy is defined as the logarithm of the number of states (Chapter 2). The dependence of the entropy on the energy of the system defines the temperature. From the entropy, the temperature, and the free energy we find the pressure, the chemical potential, and all other thermodynamic properties of the system.

For a system in a stationary quantum state, all observable physical properties such as the energy and the number of particles are independent of the time. For brevity we usually omit the word stationary; the quantum states that we treat are stationary except when we discuss transport processes in Chapters 14–15. The systems we discuss may be composed of a single particle or, more often, of many particles. The theory is developed to handle general systems of interacting particles, but powerful simplifications can be made in special problems for which the interactions may be neglected.

Each quantum state has a definite energy. States with identical energies are said to belong to the same energy level. The multiplicity or degeneracy of an energy level is the number of quantum states with very nearly the same energy. It is the number of quantum states that is important in thermal physics, not the number of energy levels. We shall frequently deal with sums over all quantum states. Two states at the same energy must always be counted as two states, not as one level.

Let us look at the quantum states and energy levels of several atomic systems. The simplest is hydrogen, with one electron and one proton. The low-lying energy levels of hydrogen are shown in Figure 1.1. The zero of energy in the figure is taken at the state of lowest energy. The number of quantum states belonging to the same energy level is in parentheses. In the figure we overlook that the proton has a spin of  $\frac{1}{2}\hbar$  and has two independent orientations, parallel

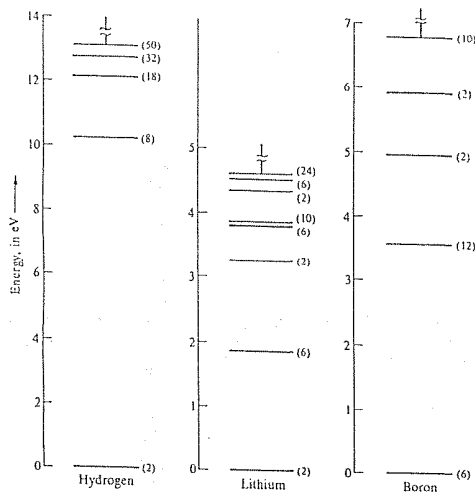


Figure 1.1 Low-lying energy levels of atomic hydrogen, lithium, and boron. The energies are given in electron volts, with  $1 \text{ eV} = 1.602 \times 10^{-12} \text{ erg}$ . The numbers in parentheses give the number of quantum states having the same energy, with no account taken of the spin of the nucleus. The zero of energy in the figure is taken for convenience at the lowest energy state of each atom.

or antiparallel to the direction of an arbitrary external axis, such as the direction of a magnetic field. To take account of the two orientations we should double the values of the multiplicities shown for atomic hydrogen.

An atom of lithium has three electrons which move about the nucleus. Each electron interacts with the nucleus, and each electron also interacts with all the

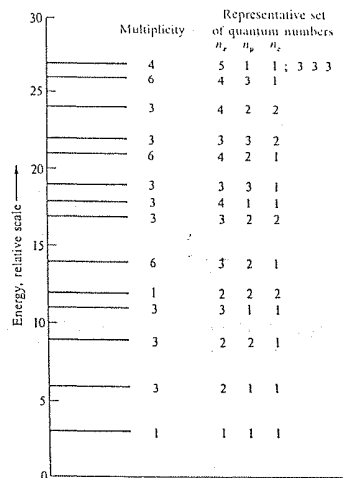


Figure 1.2 Energy levels, multiplicities, and quantum numbers  $n_x, n_y, n_z$  of a particle confined to a cube.

other electrons. The energies of the levels of lithium shown in the figure are the collective energies of the entire system. The energy levels shown for boron, which has five electrons, are also the energies of the entire system.

The energy of a system is the total energy of all particles, kinetic plus potential, with account taken of interactions between particles. A quantum state of the system is a state of all particles. Quantum states of a one-particle system are called orbitals. The low-lying energy levels of a single particle of mass  $M$  confined to a cube of side  $L$  are shown in Figure 1.2. We shall find in Chapter 3

that an orbital of a free particle can be characterized by three positive integral quantum numbers  $n_x, n_y, n_z$ . The energy is

$$\epsilon = \frac{h^2}{2M} \left( \frac{\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2). \quad (1)$$

The multiplicities of the levels are indicated in the figure. The three orbitals with  $(n_x, n_y, n_z)$  equal to  $(4, 1, 1)$ ,  $(1, 4, 1)$ , and  $(1, 1, 4)$  all have  $n_x^2 + n_y^2 + n_z^2 = 18$ ; the corresponding energy level has the multiplicity 3.

To describe the statistical properties of a system of  $N$  particles, it is essential to know the set of values of the energy  $\epsilon_s(N)$ , where  $\epsilon$  is the energy of the quantum state  $s$  of the  $N$  particle system. Indices such as  $s$  may be assigned to the quantum states in any convenient arbitrary way, but two different states should not be assigned the same index.

It is a good idea to start our program by studying the properties of simple model systems for which the energies  $\epsilon_s(N)$  can be calculated exactly. We choose as a model a simple binary system because the general statistical properties found for the model system are believed to apply equally well to any realistic physical system. This assumption leads to predictions that always agree with experiment. What general statistical properties are of concern will become clear as we go along.

## BINARY MODEL SYSTEMS

The binary model system is illustrated in Figure 1.3. We assume there are  $N$  separate and distinct sites fixed in space, shown for convenience on a line. Attached to each site is an elementary magnet that can point only up or down, corresponding to magnetic moments  $\pm m$ . To understand the system means to count the states. This requires no knowledge of magnetism: an element of the system can be any site capable of two states, labeled as yes or no, red or blue, occupied or unoccupied, zero or one, plus one or minus one. The sites are numbered, and sites with different numbers are supposed not to overlap in physical space. You might even think of the sites as numbered parking spaces in a car parking lot, as in Figure 1.4. Each parking space has two states, vacant or occupied by one car.

Whatever the nature of our objects, we may designate the two states by arrows that can only point straight up or straight down. If the magnet points up, we say that the magnetic moment is  $+m$ . If the magnet points down, the magnetic moment is  $-m$ .

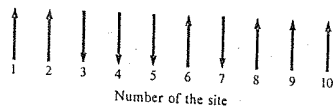


Figure 1.3 Model system composed of 10 elementary magnets at fixed sites on a line, each having magnetic moment  $\pm m$ . The numbers shown are attached to the sites; each site has its own magnet. We assume there are no interactions among the magnets and there is no external magnetic field. Each magnetic moment may be oriented in two ways, up or down, so that there are  $2^{10}$  distinct arrangements of the 10 magnetic moments shown in the figure. If the arrangements are selected in a random process, the probability of finding the particular arrangement shown is  $1/2^{10}$ .

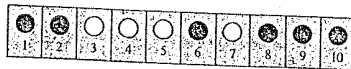
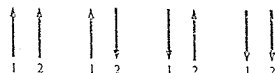


Figure 1.4 State of a parking lot with 10 numbered parking spaces. The  $\odot$ 's denote spaces occupied by a car; the  $\circ$ 's denote vacant spaces. This particular state is equivalent to that shown in Figure 1.3.

Now consider  $N$  different sites, each of which bears a moment that may assume the values  $\pm m$ . Each moment may be oriented in two ways with a probability independent of the orientation of all other moments. The total number of arrangements of the  $N$  moments is  $2 \times 2 \times 2 \times \dots \times 2 = 2^N$ . A state of the system is specified by giving the orientation of the moment on each site; there are  $2^N$  states. We may use the following simple notation for a single state of the system of  $N$  sites:

↑↑↑↑↑↑↑↑↑↑

Figure 1.5 The four different states of a system of two elements numbered 1 and 2, where each element can have two conditions. The element is a magnet which can be in condition ↑ or condition ↓.



The sites themselves are assumed to be arranged in a definite order. We may number them in sequence from left to right, as we did in Figure 1.3. According to this convention the state (2) also can be written as

$$\uparrow_1 \downarrow_2 \downarrow_3 \downarrow_4 \downarrow_5 \downarrow_6 \downarrow_7 \downarrow_8 \downarrow_9 \downarrow_{10} \cdots \quad (3)$$

Both sets of symbols (2) and (3) denote the same state of the system, the state in which the magnetic moment on site 1 is  $+m$ ; on site 2, the moment is  $+m$ ; on site 3, the moment is  $-m$ ; and so forth.

It is not hard to convince yourself that every distinct state of the system is contained in a symbolic product of  $N$  factors:

$$(f_1 + \downarrow_1)(f_2 + \downarrow_2)(f_3 + \downarrow_3) \cdots (f_N + \downarrow_N). \quad (4)$$

The multiplication rule is defined by

$$(f_1 + \downarrow_1)(f_2 + \downarrow_2) = f_1 f_2 + f_1 \downarrow_2 + \downarrow_1 f_2 + \downarrow_1 \downarrow_2. \quad (5)$$

The function (4) on multiplication generates a sum of  $2^N$  terms, one for each of the  $2^N$  possible states. Each term is a product of  $N$  individual magnetic moment symbols, with one symbol for each elementary magnet on the line. Each term denotes an independent state of the system and is a simple product of the form  $f_1 f_2 f_3 \cdots f_N$ , for example.

For a system of two elementary magnets, we multiply  $(f_1 + \downarrow_1)$  by  $(f_2 + \downarrow_2)$  to obtain the four possible states of Figure 1.5:

$$(f_1 + \downarrow_1)(f_2 + \downarrow_2) = f_1 f_2 + f_1 \downarrow_2 + \downarrow_1 f_2 + \downarrow_1 \downarrow_2. \quad (6)$$

The sum is not a state but is a way of listing the four possible states of the system. The product on the left-hand side of the equation is called a generating function; it generates the states of the system.

The generating function for the states of a system of three magnets is

$$(f_1 + \downarrow_1)(f_2 + \downarrow_2)(f_3 + \downarrow_3).$$

This expression on multiplication generates  $2^3 = 8$  different states:

Three magnets up:	$\uparrow_1 \uparrow_2 \uparrow_3$	
Two magnets up:	$\uparrow_1 \uparrow_2 \downarrow_3$	$\uparrow_1 \downarrow_2 \uparrow_3$
One magnet up:	$\uparrow_1 \downarrow_2 \downarrow_3$	$\downarrow_1 \uparrow_2 \uparrow_3$
None up:	$\downarrow_1 \downarrow_2 \downarrow_3$	

The total magnetic moment of our model system of  $N$  magnets each of magnetic moment  $m$  will be denoted by  $M$ , which we will relate to the energy in a magnetic field. The value of  $M$  varies from  $Nm$  to  $-Nm$ . The set of possible values is given by

$$M = Nm, (N-2)m, (N-4)m, (N-6)m, \cdots, -Nm. \quad (7)$$

The set of possible values of  $M$  is obtained if we start with the state for which all magnets are up ( $M = Nm$ ) and reverse one at a time. We may reverse  $N$  magnets to obtain the ultimate state for which all magnets are down ( $M = -Nm$ ).

There are  $N+1$  possible values of the total moment, whereas there are  $2^N$  states. When  $N \gg 1$ , we have  $2^N \gg N+1$ . There are many more states than values of the total moment. If  $N = 10$ , there are  $2^{10} = 1024$  states distributed among 11 different values of the total magnetic moment. For large  $N$  many different states of the system may have the same value of the total moment  $M$ . We will calculate in the next section how many states have a given value of  $M$ .

Only one state of a system has the moment  $M = Nm$ ; that state is

$$\uparrow \uparrow \uparrow \cdots \uparrow \uparrow \uparrow. \quad (8)$$

There are  $N$  ways to form a state with one magnet down:

$$\downarrow \uparrow \uparrow \cdots \uparrow \uparrow \uparrow \quad (9)$$

is one such state; another is

$$\uparrow \downarrow \uparrow \cdots \uparrow \uparrow \uparrow. \quad (10)$$

and the other states with one magnet down are formed from (8) by reversing any single magnet. The states (9) and (10) have total moment  $M = Nm - 2m$ .

### Enumeration of States and the Multiplicity Function

We use the word spin as a shorthand for elementary magnet. It is convenient to assume that  $N$  is an even number. We need a mathematical expression for the number of states with  $N_1 = \frac{1}{2}N + s$  magnets up and  $N_2 = \frac{1}{2}N - s$  magnets down, where  $s$  is an integer. When we turn one magnet from the up to the down orientation,  $\frac{1}{2}N + s$  goes to  $\frac{1}{2}N + s - 1$  and  $\frac{1}{2}N - s$  goes to  $\frac{1}{2}N - s + 1$ . The difference (number up - number down) changes from  $2s$  to  $2s - 2$ . The difference

$$N_1 - N_2 = 2s \quad (11)$$

is called the spin excess. The spin excess of the 4 states in Figure 1.5 is 2, 0, 0, -2, from left to right. The factor of 2 in (11) appears to be a nuisance at this stage, but it will prove to be convenient.

The product in (4) may be written symbolically as

$$(\uparrow + \downarrow)^N.$$

We may drop the site labels (the subscripts) from (4) when we are interested only in how many of the magnets in a state are up or down, and not in which particular sites have magnets up or down. If we drop the labels and neglect the order in which the arrows appear in a given product, then (5) becomes

$$(\uparrow + \downarrow)^2 = \uparrow\uparrow + 2\uparrow\downarrow + \downarrow\downarrow;$$

further,

$$(\uparrow + \downarrow)^3 = \uparrow\uparrow\uparrow + 3\uparrow\uparrow\downarrow + 3\uparrow\downarrow\downarrow + \downarrow\downarrow\downarrow.$$

We find  $(\uparrow + \downarrow)^N$  for arbitrary  $N$  by the binomial expansion

$$(x + y)^N = x^N + Nx^{N-1}y + \frac{1}{2}N(N-1)x^{N-2}y^2 + \dots + y^N \\ = \sum_{i=0}^N \frac{N!}{(N-i)!i!} x^{N-i}y^i. \quad (12)$$

We may write the exponents of  $x$  and  $y$  in a slightly different, but equivalent, form by replacing  $i$  with  $\frac{1}{2}N - s$ :

$$(x + y)^N = \sum_{s=-\frac{1}{2}N}^{\frac{1}{2}N} \frac{N!}{(\frac{1}{2}N + s)! (\frac{1}{2}N - s)!} x^{N+s} y^{N-s}. \quad (13)$$

With this result the symbolic expression  $(\uparrow + \downarrow)^N$  becomes

$$(\uparrow + \downarrow)^N = \sum_s \frac{N!}{(\frac{1}{2}N + s)! (\frac{1}{2}N - s)!} \uparrow^{N+s} \downarrow^{N-s}. \quad (14)$$

The coefficient of the term in  $\uparrow^{N+s} \downarrow^{N-s}$  is the number of states having  $N_1 = \frac{1}{2}N + s$  magnets up and  $N_2 = \frac{1}{2}N - s$  magnets down. This class of states has spin excess  $N_1 - N_2 = 2s$  and net magnetic moment  $2sm$ . Let us denote the number of states in this class by  $g(N, s)$ , for a system of  $N$  magnets:

$$g(N, s) = \frac{N!}{(\frac{1}{2}N + s)! (\frac{1}{2}N - s)!} = \frac{N!}{N_1! N_2!} \quad (15)$$

Thus (14) is written as

$$(\uparrow + \downarrow)^N = \sum_{s=-\frac{1}{2}N}^{\frac{1}{2}N} g(N, s) \uparrow^{N+s} \downarrow^{N-s}. \quad (16)$$

We shall call  $g(N, s)$  the multiplicity function; it is the number of states having the same value of  $s$ . The reason for our definition emerges when a magnetic field is applied to the spin system: in a magnetic field, states of different values of  $s$  have different values of the energy, so that our  $g$  is equal to the multiplicity of an energy level in a magnetic field. Until we introduce a magnetic field, all states of the model system have the same energy, which may be taken as zero. Note from (16) that the total number of states is given by

$$\sum_{s=-\frac{1}{2}N}^{\frac{1}{2}N} g(N, s) = (1 + 1)^N = 2^N. \quad (17)$$

Examples related to  $g(N, s)$  for  $N = 10$  are given in Figures 1.6 and 1.7. For a coin, "heads" could stand for "magnet up" and "tails" could stand for "magnet down."

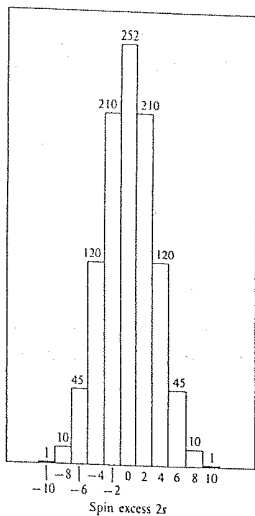


Figure 1.6 Number of distinct arrangements of  $5 + s$  spins up and  $5 - s$  spins down. Values of  $g(N, s)$  are for  $N = 10$ , where  $2s$  is the spin excess  $N \uparrow - N \downarrow$ . The total number of states is

$$2^{10} = \sum_{s=-5}^5 g(10, s)$$

The values of the  $g$ 's are taken from a table of the binomial coefficients.

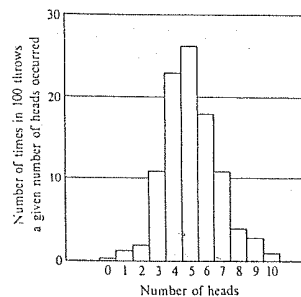


Figure 1.7 An experiment was done in which 10 pennies were thrown 100 times. The number of heads in each throw was recorded.

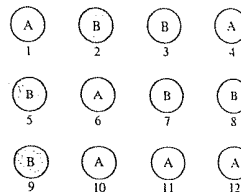


Figure 1.8 A binary alloy system of two chemical components A and B, whose atoms occupy distinct numbered sites.

### Binary Alloy System

To illustrate that the exact nature of the two states on each site is irrelevant to the result, we consider an alternate system—an alloy crystal with  $N$  distinct sites, numbered from 1 through 12 in Figure 1.8. Each site is occupied by either an atom of chemical species A or an atom of chemical species B, with no provision for vacant sites. In brass, A could be copper and B zinc. In analogy to (3), a single state of the alloy system can be written as

$$A_1 B_2 B_3 A_4 B_5 A_6 B_7 B_8 B_9 A_{10} A_{11} A_{12} \dots \quad (18)$$

Every distinct state of a binary alloy system on  $N$  sites is contained in the symbolic product of  $N$  factors:

$$(A_1 + B_1)(A_2 + B_2)(A_3 + B_3) \cdots (A_N + B_N), \quad (19)$$

in analogy to (4). The average composition of a binary alloy is specified conventionally by the chemical formula  $A_{1-x}B_x$ , which means that out of a total of  $N$  atoms, the number of A atoms is  $N_A = (1-x)N$  and the number of B atoms is  $N_B = xN$ . Here  $x$  lies between 0 and 1.

The symbolic expression

$$(A + B)^N = \sum_{r=0}^N \frac{N!}{(N-r)!r!} A^{N-r} B^r \quad (20)$$

is analogous to the result (12). The coefficient of the term in  $A^{N-r} B^r$  gives the number  $g(N,r)$  of possible arrangements or states of  $N-r$  atoms A and  $r$  atoms B on  $N$  sites:

$$g(N,r) = \frac{N!}{(N-r)!r!} = \frac{N!}{N_A! N_B!}, \quad (21)$$

which is identical to the result (15) for the spin model system, except for notation.

### Sharpness of the Multiplicity Function

We know from common experience that systems held at constant temperature usually have well-defined properties; this stability of physical properties is a major prediction of thermal physics. The stability follows as a consequence of the exceedingly sharp peak in the multiplicity function and of the steep variation of that function away from the peak. We can show explicitly that for a very large system, the function  $g(N,s)$  defined by (15) is peaked very sharply about the value  $s = 0$ . We look for an approximation that allows us to examine the form of  $g(N,s)$  versus  $s$  when  $N \gg 1$  and  $|s| \ll N$ . We cannot look up these values in tables: common tables of factorials do not go above  $N = 100$ , and we may be interested in  $N \approx 10^{20}$ , of the order of the number of atoms in a solid specimen big enough to be seen and felt. An approximation is clearly needed, and a good one is available.

It is convenient to work with  $\log g$ . Except where otherwise specified, all logarithms are understood to be log base  $e$ , written here as log. The international standard usage is ln for log base  $e$ , but it is clearer to write log when there is no ambiguity whatever. When you confront a very, very large number such as

$2^N$ , where  $N = 10^{20}$ , it is a simplification to look at the logarithm of the number. We take the logarithm of both sides of (15) to obtain

$$\log g(N,s) = \log N! - \log\left(\frac{1}{2}N + s\right)! - \log\left(\frac{1}{2}N - s\right)!, \quad (22)$$

by virtue of the characteristic property of the logarithm of a product:

$$\log xy = \log x + \log y; \quad \log(x/y) = \log x - \log y. \quad (23)$$

With the notation

$$N_1 = \frac{1}{2}N + s; \quad N_2 = \frac{1}{2}N - s \quad (24)$$

for the number of magnets up and down, (22) appears as

$$\log g(N,s) = \log N! - \log N_1! - \log N_2!. \quad (25)$$

We evaluate the logarithm of  $N!$  in (25) by use of the Stirling approximation, according to which

$$N! \approx (2\pi N)^{1/2} N^N \exp[-N + 1/(12N) + \cdots], \quad (26)$$

for  $N \gg 1$ . This result is derived in Appendix A. For sufficiently large  $N$ , the terms  $1/(12N) + \cdots$  in the argument may be neglected in comparison with  $N$ . We take the logarithm of both sides of (26) to obtain

$$\log N! \approx \frac{1}{2} \log 2\pi + (N + \frac{1}{2}) \log N - N. \quad (27)$$

Similarly

$$\log N_1! \approx \frac{1}{2} \log 2\pi + (N_1 + \frac{1}{2}) \log N_1 - N_1; \quad (28)$$

$$\log N_2! \approx \frac{1}{2} \log 2\pi + (N_2 + \frac{1}{2}) \log N_2 - N_2. \quad (29)$$

After rearrangement of (27),

$$\log N! \approx \frac{1}{2} \log(2\pi/N) + (N_1 + \frac{1}{2} + N_2 + \frac{1}{2}) \log N - (N_1 + N_2), \quad (30)$$

where we have used  $N = N_1 + N_2$ . We subtract (28) and (29) from (30) to obtain for (25):

$$\log g \approx \frac{1}{2} \log(1/2\pi N) - (N_1 + \frac{1}{2}) \log(N_1/N) - (N_2 + \frac{1}{2}) \log(N_2/N). \quad (31)$$



This may be simplified because

$$\begin{aligned} \log(N_1/N) &= \log \frac{1}{2}(1 + 2s/N) = -\log 2 + \log(1 + 2s/N) \\ &\cong -\log 2 + (2s/N) - (2s^2/N^2) \end{aligned} \quad (32)$$

by virtue of the expansion  $\log(1+x) = x - \frac{1}{2}x^2 + \dots$ , valid for  $x \ll 1$ . Similarly,

$$\log(N_2/N) = \log \frac{1}{2}(1 - 2s/N) \cong -\log 2 - (2s/N) - (2s^2/N^2). \quad (33)$$

On substitution in (31) we obtain

$$\log g \cong \frac{1}{2} \log(2/\pi N) + N \log 2 - 2s^2/N. \quad (34)$$

We write this result as

$$g(N,s) \cong g(N,0) \exp(-2s^2/N), \quad (35)$$

where

$$g(N,0) \cong (2/\pi N)^{1/2} 2^N. \quad (36)$$

Such a distribution of values of  $s$  is called a Gaussian distribution. The integral\* of (35) over the range  $-\infty$  to  $+\infty$  for  $s$  gives the correct value  $2^N$  for the total number of states. Several useful integrals are treated in Appendix A.

The exact value of  $g(N,0)$  is given by (15) with  $s = 0$ :

$$g(N,0) = \frac{N!}{(\frac{1}{2}N)! (\frac{1}{2}N)!}. \quad (37)$$

\* The replacement of a sum by an integral, such as  $\sum_i f(i)$  by  $\int f(x) dx$ , usually does not introduce significant errors. For example, the ratio of

$$\sum_{s=0}^N s = \frac{1}{2}(N^2 + N) \quad \text{to} \quad \int_0^N s ds = \frac{1}{2}N^2$$

is equal to  $1 + (1/N)$ , which approaches 1 as  $N$  approaches  $\infty$ .

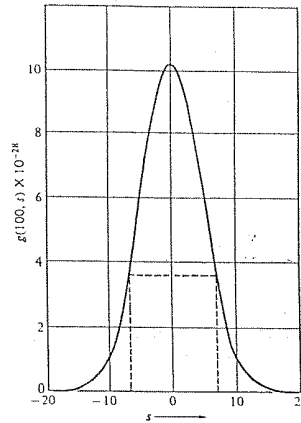


Figure 1.9 The Gaussian approximation to the binomial coefficients  $g(100,s)$  plotted on a linear scale. On this scale it is not possible to distinguish on the drawing the approximation from the exact values over the range of  $s$  plotted. The entire range of  $s$  is from  $-50$  to  $+50$ . The dashed lines are drawn from the points at  $1/e$  of the maximum value of  $g$ .

For  $N = 50$ , the value of  $g(50,0)$  is  $1.264 \times 10^{14}$ , from (37). The approximate value from (36) is  $1.270 \times 10^{14}$ . The distribution plotted in Figure 1.9 is centered in a maximum at  $s = 0$ . When  $s^2 = \frac{1}{2}N$ , the value of  $g$  is reduced to  $e^{-1}$  of the maximum value. That is, when

$$s/N = (1/2N)^{1/2}, \quad (38)$$

the value of  $g$  is  $e^{-1}$  of  $g(N,0)$ . The quantity  $(1/2N)^{1/2}$  is thus a reasonable measure of the fractional width of the distribution. For  $N \approx 10^{22}$ , the fractional width is of the order of  $10^{-11}$ . When  $N$  is very large, the distribution is exceedingly sharply defined, in a relative sense. It is this sharp peak and the continued sharp variation of the multiplicity function far from the peak that will lead to a prediction that the physical properties of systems in thermal equilibrium are well defined. We now consider one such property, the mean value of  $s^2$ .

## AVERAGE VALUES

The average value, or mean value, of a function  $f(s)$  taken over a probability distribution function  $P(s)$  is defined as

$$\langle f \rangle = \sum_s f(s) P(s), \quad (39)$$

provided that the distribution function is normalized to unity:

$$\sum_s P(s) = 1. \quad (40)$$

The binomial distribution (15) has the property (17) that

$$\sum_s g(N,s) = 2^N, \quad (41)$$

and is not normalized to unity. If all states are equally probable, then  $P(s) = g(N,s)/2^N$ , and we have  $\sum P(s) = 1$ . The average of  $f(s)$  over this distribution will be

$$\langle f \rangle = \sum_s f(s) P(N,s). \quad (42)$$

Consider the function  $f(s) = s^2$ . In the approximation that led to (35) and (36), we replace in (42) the sum  $\sum$  over  $s$  by an integral  $\int \dots ds$  between  $-\infty$  and  $+\infty$ . Then

$$\begin{aligned} \langle s^2 \rangle &= \frac{(2/\pi N)^{1/2} 2^N \int ds s^2 \exp(-2s^2/N)}{2^N}, \\ &= (2/\pi N)^{1/2} (N/2)^{3/2} \int_{-\infty}^{\infty} dx x^2 e^{-x^2} \\ &= (2/\pi N)^{1/2} (N/2)^{3/2} (\pi/4)^{1/2}, \end{aligned}$$

whence

$$\langle s^2 \rangle = \frac{1}{2} N; \quad \langle (2s)^2 \rangle = N. \quad (43)$$

The quantity  $\langle (2s)^2 \rangle$  is the mean square spin excess. The root mean square spin excess is

$$\langle (2s)^2 \rangle^{1/2} = \sqrt{N}, \quad (44)$$

and the fractional fluctuation in  $2s$  is defined as

$$\mathcal{F} \equiv \frac{\langle (2s)^2 \rangle^{1/2}}{N} = \frac{1}{\sqrt{N}}. \quad (45)$$

The larger  $N$  is, the smaller is the fractional fluctuation. This means that the central peak of the distribution function becomes relatively more sharply defined as the size of the system increases, the size being measured by the number of sites  $N$ . For  $10^{20}$  particles,  $\mathcal{F} = 10^{-10}$ , which is very small.

## Energy of the Binary Magnetic System

The thermal properties of the model system become physically relevant when the elementary magnets are placed in a magnetic field, for then the energies of the different states are no longer all equal. If the energy of the system is specified, then only the states having this energy may occur. The energy of interaction of a single magnetic moment  $m$  with a fixed external magnetic field  $B$  is

$$U = -m \cdot B. \quad (46)$$

This is the potential energy of the magnet  $m$  in the field  $B$ .

For the model system of  $N$  elementary magnets, each with two allowed orientations in a uniform magnetic field  $B$ , the total potential energy  $U$  is

$$U = \sum_{i=1}^N U_i = -B \cdot \sum_{i=1}^N m_i = -2smB, \quad (47)$$

using the expression  $M$  for the total magnetic moment  $2sm$ . In this example the spectrum of values of the energy  $U$  is discrete. We shall see later that a continuous or quasi-continuous spectrum will create no difficulty. Furthermore, the spacing between adjacent energy levels of this model is constant, as in Figure 1.10. Constant spacing is a special feature of the particular model, but this feature will not restrict the generality of the argument that is developed in the following sections.

The value of the energy for moments that interact only with the external magnetic field is completely determined by the value of  $s$ . This functional dependence is indicated by writing  $U(s)$ . Reversing a single moment lowers  $2s$  by  $-2$ , lowers the total magnetic moment by  $-2m$ , and raises the energy by  $2mB$ . The energy difference between adjacent levels is denoted by  $\Delta\epsilon$ , where

$$\Delta\epsilon = U(s) - U(s \pm 1) = 2mB. \quad (48)$$

$s$	$U(s)/mB$	$g(s)$	$\log g(s)$
-5	+10	1	0
-4	+8	10	2.30
-3	+6	45	3.81
-2	+4	120	4.79
-1	+2	210	5.35
0	0	252	5.53
+1	-2	210	5.35
+2	-4	120	4.79
+3	-6	45	3.81
+4	-8	10	2.30
+5	-10	1	0

Figure 1.10 Energy levels of the model system of 10 magnetic moments  $m$  in a magnetic field  $B$ . The levels are labeled by their  $s$  values, where  $2s$  is the spin excess and  $\frac{1}{2}N + s = 5 + s$  is the number of up spins. The energies  $U(s)$  and multiplicities  $g(s)$  are shown. For this problem the energy levels are spaced equally, with separation  $\Delta\epsilon = 2mB$  between adjacent levels.

**Example: Multiplicity function for harmonic oscillators.** The problem of the binary model system is the simplest problem for which an exact solution for the multiplicity function is known. Another exactly solvable problem is the harmonic oscillator, for which the solution was originally given by Max Planck. The original derivation is often felt to be not entirely simple. The beginning student need not worry about this derivation. The modern way to do the problem is given in Chapter 4 and is simple.

The quantum states of a harmonic oscillator have the energy eigenvalues

$$\epsilon_s = s\hbar\omega, \quad (49)$$

where the quantum number  $s$  is a positive integer or zero, and  $\omega$  is the angular frequency of the oscillator. The number of states is infinite, and the multiplicity of each is one. Now consider a system of  $N$  such oscillators, all of the same frequency. We want to find the number of ways in which a given total excitation energy

$$\epsilon = \sum_{i=1}^N s_i \hbar\omega = n\hbar\omega \quad (50)$$

can be distributed among the oscillators. That is, we want the multiplicity function  $g(N, n)$  for the  $N$  oscillators. The oscillator multiplicity function is not the same as the spin multiplicity function found earlier.

We begin the analysis by going back to the multiplicity function for a single oscillator, for which  $g(1, n) = 1$  for all values of the quantum number  $s$ , here identical to  $n$ . To solve the problem of (53) below, we need a function to represent or generate the series

$$\sum_{n=0}^{\infty} g(1, n)t^n = \sum_{n=0}^{\infty} t^n. \quad (51)$$

All  $\sum$  run from 0 to  $\infty$ . Here  $t$  is just a temporary tool that will help us find the result (53), but  $t$  does not appear in the final result. The answer is

$$\frac{1}{1-t} = \sum_{n=0}^{\infty} t^n, \quad (52)$$

provided we assume  $|t| < 1$ . For the problem of  $N$  oscillators, the generating function is

$$\left(\frac{1}{1-t}\right)^N = \left(\sum_{s=0}^{\infty} t^s\right)^N = \sum_{n=0}^{\infty} g(N, n)t^n, \quad (53)$$

because the number of ways a term  $t^n$  can appear in the  $N$ -fold product is precisely the number of ordered ways in which the integer  $n$  can be formed as the sum of  $N$  non-negative integers.

We observe that

$$\begin{aligned} g(N, n) &= \lim_{t \rightarrow 0} \frac{1}{n!} \left(\frac{d}{dt}\right)^n \sum_{s=0}^{\infty} g(N, s)t^s \\ &= \lim_{t \rightarrow 0} \frac{1}{n!} \left(\frac{d}{dt}\right)^n (1-t)^{-N} \\ &= \frac{1}{n!} N(N+1)(N+2) \cdots (N+n-1). \end{aligned} \quad (54)$$

Thus for the system of oscillators,

$$g(N, n) = \frac{(N+n-1)!}{n!(N-1)!}. \quad (55)$$

This result will be needed in solving a problem in the next chapter.

## SUMMARY

1. The multiplicity function for a system of  $N$  magnets with spin excess  $2s = N_1 - N_2$  is

$$g(N, s) = \frac{N!}{(\frac{1}{2}N + s)! (\frac{1}{2}N - s)!} = \frac{N!}{N_1! N_2!}$$

In the limit  $s/N \ll 1$ , with  $N \gg 1$ , we have the Gaussian approximation

$$g(N, s) \approx (2/\pi N)^{1/2} 2^N \exp(-2s^2/N).$$

2. If all states of the model spin system are equally likely, the average value of  $s^2$  is

$$\langle s^2 \rangle = \int_{-\infty}^{\infty} ds s^2 g(N, s) / \int_{-\infty}^{\infty} ds g(N, s) = \frac{1}{2} N,$$

in the Gaussian approximation.

3. The fractional fluctuation of  $s^2$  is defined as  $\langle s^2 \rangle^{1/2}/N$  and is equal to  $1/2N^{1/2}$ .
4. The energy of the model spin system in a state of spin excess  $2s$  is

$$U(s) = -2smB,$$

where  $m$  is the magnetic moment of one spin and  $B$  is the magnetic field.

## Chapter 2

## Entropy and Temperature

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Note on problems: The method of this chapter can be used to solve some problems, as illustrated by Problems 1, 2, and 3. Because much simpler methods are developed in Chapter 7 and later, we do not emphasize problem solving at this stage.

*One should not imagine that two gases in a 0.1 liter container, initially unmixed, will mix, then again after a few days separate, then mix again, and so forth. On the contrary, one finds . . . that not until a time enormously long compared to  $10^{100}$  years will there be any noticeable unmixing of the gases. One may recognize that this is practically equivalent to never. . . .*

*L. Boltzmann*

*If we wish to find in rational mechanics an a priori foundation for the principles of thermodynamics, we must seek mechanical definitions of temperature and entropy.*

*J. W. Gibbs*

*The general connection between energy and temperature may only be established by probability considerations. [Two systems] are in statistical equilibrium when a transfer of energy does not increase the probability.*

*M. Planck*

We start this chapter with a definition of probability that enables us to define the average value of a physical property of a system. We then consider systems in thermal equilibrium, the definition of entropy, and the definition of temperature. The second law of thermodynamics will appear as the law of increase of entropy. This chapter is perhaps the most abstract in the book. The chapters that follow will apply the concepts to physical problems.

## FUNDAMENTAL ASSUMPTION

The fundamental assumption of thermal physics is that a closed system is equally likely to be in any of the quantum states accessible to it. All accessible quantum states are assumed to be equally probable—there is no reason to prefer some accessible states over other accessible states.

A closed system will have constant energy, a constant number of particles, constant volume, and constant values of all external parameters that may influence the system, including gravitational, electric, and magnetic fields.

A quantum state is accessible if its properties are compatible with the physical specification of the system: the energy of the state must be in the range within which the energy of the system is specified, and the number of particles must be in the range within which the number of particles is specified. With large systems we can never know either of these exactly, but it will suffice to have  $\delta U/U \ll 1$  and  $\delta N/N \ll 1$ .

Unusual properties of a system may sometimes make it impossible for certain states to be accessible during the time the system is under observation. For example, the states of the crystalline form of  $\text{SiO}_2$  are inaccessible at low temperatures in any observation that starts with the glassy or amorphous form: fused silica will not convert to quartz in our lifetime in a low-temperature experiment. You will recognize many exclusions of this type by common sense. We treat all quantum states as accessible unless they are excluded by the specification of the system (Figure 2.1) and the time scale of the measurement process. States that are not accessible are said to have zero probability.

Of course, it is possible to specify the configuration of a closed system to a point that its statistical properties as such are of no interest. If we specify that the

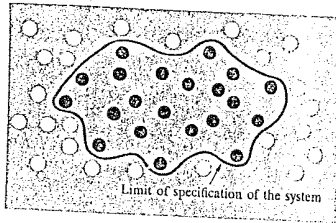


Figure 2.1 A purely symbolic diagram: each solid spot represents an accessible quantum state of a closed system. The fundamental assumption of statistical physics is that a closed system is equally likely to be in any of the quantum states accessible to it. The empty circles represent some of the states that are not accessible because their properties do not satisfy the specification of the system.

system is exactly in a stationary quantum state  $s$ , no statistical aspect is left in the problem.

## PROBABILITY

Suppose we have a closed system that we know is equally likely to be in any of the  $g$  accessible quantum states. Let  $s$  be a general state label (and not one-half the spin excess). The probability  $P(s)$  of finding the system in this state is

$$P(s) = 1/g \quad (1)$$

if the state  $s$  is accessible and  $P(s) = 0$  otherwise, consistent with the fundamental assumption. We shall be concerned later with systems that are not closed, for which the energy  $U$  and particle number  $N$  may vary. For these systems  $P(s)$  will not be a constant as in (1), but will have a functional dependence on  $U$  and on  $N$ .

The sum  $\sum_s P(s)$  of the probability over all states is always equal to unity, because the total probability that the system is in some state is unity:

$$\sum_s P(s) = 1. \quad (2)$$

The probabilities defined by (1) lead to the definition of the average value of any physical property. Suppose that the physical property  $X$  has the value  $X(s)$  when the system is in the state  $s$ . Here  $X$  might denote magnetic moment, energy, square of the energy, charge density near a point  $r$ , or any property that can be observed when the system is in a quantum state. Then the average of the observations of the quantity  $X$  taken over a system described by the probabilities  $P(s)$  is

$$\langle X \rangle = \sum_s X(s)P(s). \quad (3)$$

This equation defines the average value of  $X$ . Here  $P(s)$  is the probability that the system is in the state  $s$ . The angular brackets  $\langle \dots \rangle$  are used to denote average value.

For a closed system, the average value of  $X$  is

$$\langle X \rangle = \sum_s X(s)(1/g), \quad (4)$$

because now all  $g$  accessible states are equally likely, with  $P(s) = 1/g$ . The average in (4) is an elementary example of what may be called an ensemble average: we imagine  $g$  similar systems, one in each accessible quantum state. Such a group of systems constructed alike is called an ensemble of systems. The average of any property over the group is called the ensemble average of that property.

An ensemble of systems is composed of many systems, all constructed alike. Each system in the ensemble is a replica of the actual system in one of the quantum states accessible to the system. If there are  $g$  accessible states, then there will be  $g$  systems in the ensemble, one system for each state. Each system in the ensemble is equivalent for all practical purposes to the actual system. Each system satisfies all external requirements placed on the original system and in this sense is "just as good" as the actual system. Every quantum state

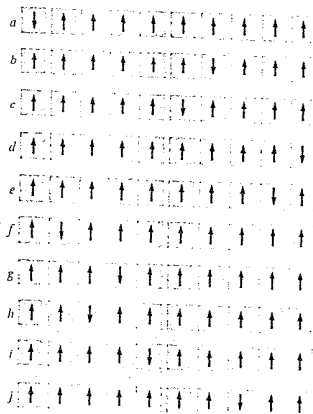


Figure 2.2 This ensemble *a* through *j* represents a system of 10 spins with energy  $-8mb$  and spin excess  $2s = 8$ . The multiplicity  $g(N, s)$  is  $g(10, 4) = 10$ , so that the representative ensemble must contain 10 systems. The order in which the various systems in the ensemble are listed has no significance.

accessible to the actual system is represented in the ensemble by one system in a stationary quantum state, as in Figure 2.2. We assume that the ensemble represents the real system—this is implied in the fundamental assumption.

**Example: Construction of an ensemble.** We construct in Figure 2.3 an ensemble to represent a closed system of five spins, each system with spin excess  $2s = 1$ . The energy of each in a magnetic field is  $-mb$ . (Do not confuse the use of  $s$  in spin excess with our frequent use of  $s$  as a state index or label.) Each system represents one of the multiples of

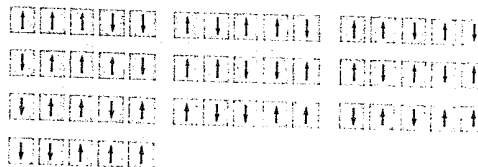


Figure 2.3 The ensemble represents a system with  $N = 5$  spins and spin excess  $2s = 1$ .

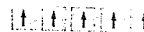


Figure 2.4 With  $N = 5$  and  $2s = 5$ , a single system may represent the ensemble. This is not a typical situation.

quantum states at this energy. The number of such states is given by the multiplicity function (1.15):

$$g(5, 1) = \frac{5!}{3!2!} = 10.$$

The 10 systems shown in Figure 2.3 make up the ensemble.

If the energy in the magnetic field were such that  $2s = 5$ , then a single system comprises the ensemble, as in Figure 2.4. In zero magnetic field, all energies of all  $2^5 = 2^5 = 32$  states are equal, and the new ensemble must represent 32 systems, of which 1 system has  $2s = 5$ ; 5 systems have  $2s = 3$ ; 10 systems have  $2s = 1$ ; 5 systems have  $2s = -3$ ; and 1 system has  $2s = -5$ .

### Most Probable Configuration

Let two systems  $\mathcal{S}_1$  and  $\mathcal{S}_2$  be brought into contact so that energy can be transferred freely from one to the other. This is called thermal contact (Figure 2.5). The two systems in contact form a larger closed system  $\mathcal{S} = \mathcal{S}_1 + \mathcal{S}_2$  with constant energy  $U = U_1 + U_2$ . What determines whether there will be a net flow of energy from one system to another? The answer leads to the concept of temperature. The direction of energy flow is not simply a matter of whether the energy of one system is greater than the energy of the other, because the

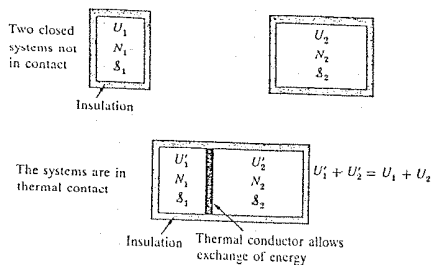


Figure 2.5 Establishment of thermal contact between two systems  $\mathcal{S}_1$  and  $\mathcal{S}_2$ .

systems can be different in size and constitution. A constant total energy can be shared in many ways between two systems.

The most probable division of the total energy is that for which the combined system has the maximum number of accessible states. We shall enumerate the accessible states of two model systems and then study what characterizes the systems when in thermal contact. We first solve in detail the problem of thermal contact between two spin systems, 1 and 2, in a magnetic field which is introduced in order to define the energy. The numbers of spins  $N_1, N_2$  may be different, and the values of the spin excess  $2s_1, 2s_2$  may be different for the two systems. All spins have magnetic moment  $m$ . The actual exchange of energy might take place via some weak (residual) coupling between the spins near the interface between the two systems. We assume that the quantum states of the total system  $\mathcal{S}$  can be represented accurately by a combination of any state of  $\mathcal{S}_1$  with any state of  $\mathcal{S}_2$ . We keep  $N_1, N_2$  constant, but the values of the spin excess are allowed to change. The spin excess of a state of the combined system will be denoted by  $2s$ , where  $s = s_1 + s_2$ . The energy of the combined system is directly proportional to the total spin excess:

$$U(s) = U_1(s_1) + U_2(s_2) = -2mB(s_1 + s_2) = -2mBs. \quad (5)$$

The total number of particles is  $N = N_1 + N_2$ .

We assume that the energy splittings between adjacent energy levels are equal to  $2mB$  in both systems, so that the magnetic energy given up by system 1 when one spin is reversed can be taken up by the reversal of one spin of system 2 in the opposite sense. Any large physical system will have enough diverse modes of energy storage so that energy exchange with another system is always possible. The value of  $s = s_1 + s_2$  is constant because the total energy is constant, but when the two systems are brought into thermal contact a redistribution is permitted in the separate values of  $s_1, s_2$  and thus in the energies  $U_1, U_2$ .

The multiplicity function  $g(N, s)$  of the combined system  $\mathcal{S}$  is related to the product of the multiplicity functions of the individual systems  $\mathcal{S}_1$  and  $\mathcal{S}_2$  by the relation:

$$g(N, s) = \sum_{s_1} g_1(N_1, s_1) g_2(N_2, s - s_1), \quad (6)$$

where the multiplicity functions  $g_1, g_2$  are given by expressions of the form of (1.15). The range of  $s_1$  in the summation is from  $-\frac{1}{2}N_1$  to  $\frac{1}{2}N_1$ , if  $N_1 < N_2$ . To see how (6) comes about, consider first that configuration of the combined system for which the first system has spin excess  $2s_1$  and the second system has spin excess  $2s_2$ . A configuration is defined as the set of all states with specified values of  $s_1$  and  $s_2$ . The first system has  $g_1(N_1, s_1)$  accessible states, each of which may occur together with any of the  $g_2(N_2, s_2)$  accessible states of the second system. The total number of states in one configuration of the combined system is given by the product  $g_1(N_1, s_1)g_2(N_2, s_2)$  of the multiplicity functions of  $\mathcal{S}_1$  and  $\mathcal{S}_2$ . Because  $s_2 = s - s_1$ , the product of the  $g$ 's may be written as

$$g_1(N_1, s_1)g_2(N_2, s - s_1). \quad (7)$$

This product forms one term of the sum (6).

Different configurations of the combined system are characterized by different values of  $s_1$ . We sum over all possible values of  $s_1$  to obtain the total number of states of all the configurations with fixed  $s$  or fixed energy. We thus obtain (6), where  $g(N, s)$  is the number of accessible states of the combined system. In the sum we hold  $s, N_1,$  and  $N_2$  constant, as part of the specification of thermal contact.

The result (6) is a sum of products of the form (7). Such a product will be a maximum for some value of  $s_1$ , say  $\bar{s}_1$ , to be read as " $s_1$  hat" or " $s_1$  caret". The configuration for which  $g_1 g_2$  is a maximum is called the most probable configuration; the number of states in it is

$$g_1(N_1, \bar{s}_1)g_2(N_2, s - \bar{s}_1). \quad (8)$$

$$= k + S = (L \cdot f)^{\infty}$$

$$k = k_{\text{Boltz}} \quad L = 10^{\text{C}}$$



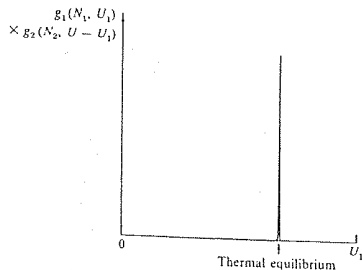


Figure 2.6 Schematic representation of the dependence of the configuration multiplicity on the division of the total energy between two systems,  $S_1$  and  $S_2$ .

If the systems are large, the maximum with respect to changes in  $s_1$  will be extremely sharp, as in Figure 2.6. A relatively small number of configurations will dominate the statistical properties of the combined system. The most probable configuration alone will describe many of these properties.

Such a sharp maximum is a property of every realistic type of large system for which exact solutions are available; we postulate that it is a general property of all large systems. From the sharpness property it follows that fluctuations about the most probable configuration are small, in a sense that we will define.

The important result follows that the values of the average physical properties of a large system in thermal contact with another large system are accurately described by the properties of the most probable configuration, the configuration for which the number of accessible states is a maximum. Such average values (used in either of these two senses) are called thermal equilibrium values.

Because of the sharp maximum, we may replace the average of a physical quantity over all accessible configurations (6) by an average over only the most probable configuration (8). In the example below we estimate the error involved in such a replacement and find the error to be negligible.

**Example: Two spin systems in thermal contact.** We investigate for the model spin system the sharpness of the product (7) near the maximum (8) as follows. We form the product of the multiplicity functions for  $g_1(N_1, s_1)$  and  $g_2(N_2, s_2)$ , both of the form of (1.35):

$$g_1(N_1, s_1)g_2(N_2, s_2) = g_1(0)g_2(0) \exp\left(-\frac{2s_1^2}{N_1} - \frac{2s_2^2}{N_2}\right), \quad (9)$$

where  $g_1(0)$  denotes  $g_1(N_1, 0)$  and  $g_2(0)$  denotes  $g_2(N_2, 0)$ . We replace  $s_2$  by  $s - s_1$ :

$$g_1(N_1, s_1)g_2(N_2, s - s_1) = g_1(0)g_2(0) \exp\left(-\frac{2s_1^2}{N_1} - \frac{2(s - s_1)^2}{N_2}\right). \quad (10)$$

This product\* gives the number of states accessible to the combined system when the spin excess of the combined system is  $2s$ , and the spin excess of the first system is  $2s_1$ .

We find the maximum value of (10) as a function of  $s_1$ , when the total spin excess  $2s$  is held constant; that is, when the energy of the combined systems is constant. It is convenient to use the property that the maximum of  $\log y(x)$  occurs at the same value of  $x$  as the maximum of  $y(x)$ . The calculation can be done either way. From (10),

$$\log g_1(N_1, s_1)g_2(N_2, s - s_1) = \log g_1(0)g_2(0) - \frac{2s_1^2}{N_1} - \frac{2(s - s_1)^2}{N_2}. \quad (11)$$

This quantity is an extremum when the first derivative with respect to  $s_1$  is zero. An extremum may be a maximum, a minimum, or a point of inflection. The extremum is a maximum if the second derivative of the function is negative, so that the curve bends downward.

At the extremum the first derivative is

$$\frac{\partial}{\partial s_1} \{\log g_1(N_1, s_1)g_2(N_2, s - s_1)\} = -\frac{4s_1}{N_1} + \frac{4(s - s_1)}{N_2} = 0, \quad (12)$$

where  $N_1$ ,  $N_2$ , and  $s$  are held constant as  $s_1$  is varied. The second derivative  $\partial^2/\partial s_1^2$  of Equation (11) is

$$-4\left(\frac{1}{N_1} + \frac{1}{N_2}\right)$$

\* The product function of two Gaussian functions is always a Gaussian.

and is negative, so that the extremum is a maximum. Thus the most probable configuration of the combined system is that for which (12) is satisfied:

$$\frac{s_1}{N_1} = \frac{s - s_1}{N_2} = \frac{s_2}{N_2}. \quad (13)$$

The two systems are in equilibrium with respect to interchange of energy when the fractional spin excess of system 1 is equal to the fractional spin excess of system 2.

We prove that nearly all the accessible states of the combined systems satisfy or very nearly satisfy (13). If  $\bar{s}_1$  and  $\bar{s}_2$  denote the values of  $s_1$  and  $s_2$  at the maximum, then (13) is written as

$$\frac{\bar{s}_1}{N_1} = \frac{\bar{s}_2}{N_2} = \frac{s}{N}. \quad (14)$$

To find the number of states in the most probable configuration, we insert (14) in (9) to obtain

$$(g_1 g_2)_{\max} \equiv g_1(\bar{s}_1) g_2(s - \bar{s}_1) = g_1(0) g_2(0) \exp(-2s^2/N). \quad (15)$$

To investigate the sharpness of the maximum of  $g_1 g_2$  at a given value of  $s$ , introduce  $\delta$  such that

$$s_1 = \bar{s}_1 + \delta; \quad s_2 = \bar{s}_2 - \delta. \quad (16)$$

Here  $\delta$  measures the deviation of  $s_1, s_2$  from their values  $\bar{s}_1, \bar{s}_2$  at the maximum of  $g_1 g_2$ . Square  $s_1, s_2$  to form

$$s_1^2 = \bar{s}_1^2 + 2\bar{s}_1\delta + \delta^2; \quad s_2^2 = \bar{s}_2^2 - 2\bar{s}_2\delta + \delta^2,$$

which we substitute in (9) and (15) to obtain the number of states

$$g_1(N_1, s_1) g_2(N_2, s_2) = (g_1 g_2)_{\max} \exp\left(-\frac{4\bar{s}_1\delta}{N_1} - \frac{2\delta^2}{N_1} + \frac{4\bar{s}_2\delta}{N_2} - \frac{2\delta^2}{N_2}\right).$$

We know from (14) that  $\bar{s}_1/N_1 = \bar{s}_2/N_2$ , so that the number of states in a configuration of deviation  $\delta$  from equilibrium is

$$g_1(N_1, \bar{s}_1 + \delta) g_2(N_2, \bar{s}_2 - \delta) = (g_1 g_2)_{\max} \exp\left(-\frac{2\delta^2}{N_1} - \frac{2\delta^2}{N_2}\right). \quad (17)$$

As a numerical example in which the fractional deviation from equilibrium is very small, let  $N_1 = N_2 = 10^{22}$  and  $\delta = 10^{12}$ ; that is,  $\delta/N_1 = 10^{-10}$ . Then  $2\delta^2/N_1 = 200$ , and the

product  $g_1 g_2$  is reduced to  $e^{-400} \approx 10^{-174}$  of its maximum value. This is an extremely large reduction, so that  $g_1 g_2$  is truly a very sharply peaked function of  $s_1$ . The probability that the fractional deviation will be  $10^{-10}$  or larger is found by integrating (17) from  $\delta = 10^{12}$  out to a value of the order of  $s$  or of  $N$ , thereby including the area under the wings of the probability distribution. This is the subject of Problem 6. An upper limit to the integrated probability is given by  $N \times 10^{-174} = 10^{-152}$ , still very small. When two systems are in thermal contact, the values of  $s_1, s_2$  that occur most often will be very close to the values of  $\bar{s}_1, \bar{s}_2$  for which the product  $g_1 g_2$  is a maximum. It is extremely rare to find systems with values of  $s_1, s_2$  perceptibly different from  $\bar{s}_1, \bar{s}_2$ .

What does it mean to say that the probability of finding the system with a fractional deviation larger than  $\delta/N_1 = 10^{-10}$  is only  $10^{-152}$  of the probability of finding the system in equilibrium? We mean that the system will never be found with a deviation as much as 1 part in  $10^{10}$ , small as this deviation seems. We would have to sample  $10^{152}$  similar systems to have a reasonable chance of success in such an experiment. If we sample one system every  $10^{-12}$  s, which is pretty fast work, we would have to sample for  $10^{140}$  s. The age of the universe is only  $10^{18}$  s. Therefore we say with great surety that the deviation described will never be observed. The estimate is rough, but the message is correct. The quotation from Boltzmann given at the beginning of this chapter is relevant here.

We may expect to observe substantial fractional deviations only in the properties of a small system in thermal contact with a large system or reservoir. The energy of a small system, say a system of 10 spins, in thermal contact with a large reservoir may undergo fluctuations that are large in a fractional sense, as have been observed in experiments on the Brownian motion of small particles in suspension in liquids. The average energy of a small system in contact with a large system can always be determined accurately by observations at one time on a large number of identical small systems or by observations on one small system over a long period of time.

## THERMAL EQUILIBRIUM

The result for the number of accessible states of two model spin systems in thermal contact may be generalized to any two systems in thermal contact, with constant total energy  $U = U_1 + U_2$ . By direct extension of the earlier argument, the multiplicity  $g(N, U)$  of the combined system is:

$$g(N, U) = \sum_{U_1} g_1(N_1, U_1) g_2(N_2, U - U_1), \quad (18)$$

summed over all values of  $U_1 \leq U$ . Here  $g_1(N_1, U_1)$  is the number of accessible states of system 1 at energy  $U_1$ . A configuration of the combined system is specified by the value of  $U_1$ , together with the constants  $U, N_1, N_2$ . The number of accessible states in a configuration is the product  $g_1(N_1, U_1) g_2(N_2, U - U_1)$ . The sum over all configurations gives  $g(N, U)$ .

The largest term in the sum in (18) governs the properties of the total system in thermal equilibrium. For an extremum it is necessary that the differential\* of  $g(N, U)$  be zero for an infinitesimal exchange of energy:

$$dg = \left( \frac{\partial g_1}{\partial U_1} \right)_{N_1} g_2 dU_1 + g_1 \left( \frac{\partial g_2}{\partial U_2} \right)_{N_2} dU_2 = 0; \quad dU_1 + dU_2 = 0. \quad (19)$$

We divide by  $g_1 g_2$  and use the result  $dU_2 = -dU_1$  to obtain the thermal equilibrium condition:

$$\frac{1}{g_1} \left( \frac{\partial g_1}{\partial U_1} \right)_{N_1} = \frac{1}{g_2} \left( \frac{\partial g_2}{\partial U_2} \right)_{N_2}, \quad (20a)$$

which we may write as

$$\left( \frac{\partial \log g_1}{\partial U_1} \right)_{N_1} = \left( \frac{\partial \log g_2}{\partial U_2} \right)_{N_2}. \quad (20b)$$

We define the quantity  $\sigma$ , called the entropy, by

$$\sigma(N, U) \equiv \log g(N, U). \quad (21)$$

where  $\sigma$  is the Greek letter sigma. We now write (20) in the final form

$$\left( \frac{\partial \sigma_1}{\partial U_1} \right)_{N_1} = \left( \frac{\partial \sigma_2}{\partial U_2} \right)_{N_2}. \quad (22)$$

\* The notation

$$\left( \frac{\partial g_1}{\partial U_1} \right)_{N_1}$$

means that  $N_1$  is held constant in the differentiation of  $g_1(N_1, U_1)$  with respect to  $U_1$ . That is, the partial derivative with respect to  $U_1$  is defined as

$$\left( \frac{\partial g_1}{\partial U_1} \right)_{N_1} = \lim_{\Delta U_1 \rightarrow 0} \frac{g_1(N_1, U_1 + \Delta U_1) - g_1(N_1, U_1)}{\Delta U_1}.$$

For example, if  $g(x, y) = 3x^2y$ , then  $(\partial g/\partial x)_y = 6xy$  and  $(\partial g/\partial y)_x = 3x^2$ .

This is the condition for thermal equilibrium for two systems in thermal contact. Here  $N_1$  and  $N_2$  may symbolize not only the numbers of particles, but all constraints on the systems.

## TEMPERATURE

The last equality (22) leads us immediately to the concept of temperature. We know the everyday rule: in thermal equilibrium the temperatures of the two systems are equal:

$$T_1 = T_2. \quad (23)$$

This rule must be equivalent to (22), so that  $T$  must be a function of  $(\partial \sigma / \partial U)_N$ . If  $T$  denotes the absolute temperature in kelvin, this function is simply the inverse relationship

$$\frac{1}{T} = k_B \left( \frac{\partial \sigma}{\partial U} \right)_N. \quad (24)$$

The proportionality constant  $k_B$  is a universal constant called the Boltzmann constant. As determined experimentally,

$$\begin{aligned} k_B &= 1.381 \times 10^{-23} \text{ joules/kelvin} \\ &= 1.381 \times 10^{-16} \text{ ergs/kelvin.} \end{aligned} \quad (25)$$

We defer the discussion to Appendix B because we prefer to use a more natural temperature scale: we define the fundamental temperature  $\tau$  by

$$\frac{1}{\tau} = \left( \frac{\partial \sigma}{\partial U} \right)_N. \quad (26)$$

This temperature differs from the Kelvin temperature by the scale factor,  $k_B$ :

$$\tau = k_B T. \quad (27)$$

Because  $\sigma$  is a pure number, the fundamental temperature  $\tau$  has the dimensions of energy. We can use as a temperature scale the energy scale, in whatever unit

may be employed for the latter—joule or erg. This procedure is much simpler than the introduction of the Kelvin scale in which the unit of temperature is arbitrarily selected so that the triple point of water is exactly 273.16 K. The triple point of water is the unique temperature at which water, ice, and water vapor coexist.

Historically, the conventional scale dates from an age in which it was possible to build accurate thermometers even though the relation of temperature to quantum states was as yet not understood. Even at present, it is still possible to measure temperatures with thermometers calibrated in kelvin to a higher precision than the accuracy with which the conversion factor  $k_B$  itself is known—about 32 parts per million. Questions of practical thermometry are discussed in Appendix B.

*Comment.* In (26) we defined the reciprocal of  $\tau$  as the partial derivative  $(\partial\sigma/\partial U)_N$ . It is permissible to take the reciprocal of both sides to write

$$\tau = (\partial U/\partial\sigma)_N. \quad (28)$$

The two expressions (26) and (28) have a slightly different meaning. In (26), the entropy  $\sigma$  was given as a function of the independent variables  $U$  and  $N$  as  $\sigma = \sigma(U, N)$ . Hence  $\tau$  determined from (26) has the same independent variables,  $\tau = \tau(U, N)$ . In (28), however, differentiation of  $U$  with respect to  $\sigma$  with  $N$  constant implies  $U = U(\sigma, N)$ , so that  $\tau = \tau(\sigma, N)$ . The definition of temperature is the same in both cases, but it is expressed as a function of different independent variables. The question “What are the independent variables?” arises frequently in thermal physics because in some experiments we control some variables, and in other experiments we control other variables.

## ENTROPY

The quantity  $\sigma \equiv \log g$  was introduced in (21) as the entropy of the system: the entropy is defined as the logarithm of the number of states accessible to the system. As defined, the entropy is a pure number. In classical thermodynamics the entropy  $S$  is defined by

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_N. \quad (29)$$

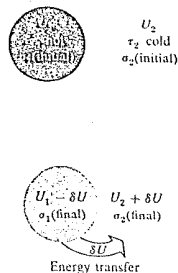


Figure 2.7 If the temperature  $\tau_1$  is higher than  $\tau_2$ , the transfer of a positive amount of energy  $\delta U$  from system 1 to system 2 will increase the total entropy  $\sigma_1 + \sigma_2$  of the combined systems over the initial value  $\sigma_1(\text{initial}) + \sigma_2(\text{initial})$ . In other words, the final system will be in a more probable condition if energy flows from the warmer body to the cooler body when thermal contact is established. This is an example of the law of increasing entropy.

$$\sigma_1(\text{final}) + \sigma_2(\text{final}) > \sigma_1(\text{initial}) + \sigma_2(\text{initial})$$

As a consequence of (24), we see that  $S$  and  $\sigma$  are connected by a scale factor:

$$S = k_B \sigma. \quad (30)$$

We will call  $S$  the conventional entropy.

The more states that are accessible, the greater the entropy. In the definition of  $\sigma(N, U)$  we have indicated a functional dependence of the entropy on the number of particles in the system and on the energy of the system. The entropy may depend on additional independent variables: the entropy of a gas (Chapter 3) depends on the volume.

In the early history of thermal physics the physical significance of the entropy was not known. Thus the author of the article on thermodynamics in the *Encyclopaedia Britannica*, 11th ed. (1905), wrote: “The utility of the conception of entropy . . . is limited by the fact that it does not correspond directly to any directly measurable physical property, but is merely a mathematical function of the definition of absolute temperature.” We now know what absolute physical property the entropy measures. An example of the comparison of the experimental determination and theoretical calculation of the entropy is discussed in Chapter 6.

Consider the total entropy change  $\Delta\sigma$  when we remove a positive amount of energy  $\Delta U$  from 1 and add the same amount of energy to 2, as in Figure 2.7.

The total entropy change is

$$\Delta\sigma = \left(\frac{\partial\sigma_1}{\partial U_1}\right)_{N_1}(-\Delta U) + \left(\frac{\partial\sigma_2}{\partial U_2}\right)_{N_2}(\Delta U) = \left(-\frac{1}{\tau_1} + \frac{1}{\tau_2}\right)\Delta U. \quad (31)$$

When  $\tau_1 > \tau_2$  the quantity in parentheses on the right-hand side is positive, so that the total change of entropy is positive when the direction of energy flow is from the system with the higher temperature to the system with the lower temperature.

**Example: Entropy increase on heat flow.** This example makes use of the reader's previous familiarity with heat and specific heat.

(a) Let a 10-g specimen of copper at a temperature of 350 K be placed in thermal contact with an identical specimen at a temperature of 290 K. Let us find the quantity of energy transferred when the two specimens are placed in contact and come to equilibrium at the final temperature  $T_f$ . The specific heat of metallic copper over the temperature range 15°C to 100°C is approximately  $0.389 \text{ J g}^{-1} \text{ K}^{-1}$ , according to a standard handbook.

The energy increase of the second specimen is equal to the energy loss of the first; thus the energy increase of the second specimen is, in joules,

$$\Delta U = (3.89 \text{ J K}^{-1})(T_f - 290 \text{ K}) = (3.89 \text{ J K}^{-1})(350 \text{ K} - T_f),$$

where the temperatures are in kelvin. The final temperature after contact is

$$T_f = \frac{1}{2}(350 + 290) \text{ K} = 320 \text{ K}.$$

Thus

$$\Delta U_1 = (3.89 \text{ J K}^{-1})(-30 \text{ K}) = -11.7 \text{ J},$$

and

$$\Delta U_2 = -\Delta U_1 = 11.7 \text{ J}.$$

(b) What is the change of entropy of the two specimens when a transfer of 0.1 J has taken place, almost immediately after initial contact? Notice that this transfer is a small fraction of the final energy transfer as calculated above. Because the energy transfer considered is small, we may suppose the specimens are approximately at their initial temperatures of 350 and 290 K. The entropy of the first body is decreased by

$$\Delta S_1 = \frac{-0.1 \text{ J}}{350 \text{ K}} = -2.86 \times 10^{-4} \text{ J K}^{-1}.$$

The entropy of the second body is increased by

$$\Delta S_2 = \frac{0.1 \text{ J}}{290 \text{ K}} = 3.45 \times 10^{-4} \text{ J K}^{-1}.$$

The total entropy increases by

$$\Delta S_1 + \Delta S_2 = (-2.86 + 3.45) \times 10^{-4} \text{ J K}^{-1} = 0.59 \times 10^{-4} \text{ J K}^{-1}.$$

In fundamental units the increase of entropy is

$$\Delta\sigma = \frac{0.59 \times 10^{-4}}{k_B} = \frac{0.59 \times 10^{-4} \text{ J K}^{-1}}{1.38 \times 10^{-23} \text{ J K}^{-1}} = 0.43 \times 10^{19}, \quad (32)$$

where  $k_B$  is the Boltzmann constant. This result means that the number of accessible states of the two systems increases by the factor  $\exp(\Delta\sigma) = \exp(0.43 \times 10^{19})$ .

### Law of Increase of Entropy

We can show that the total entropy always increases when two systems are brought into thermal contact. We have just demonstrated this in a special case. If the total energy  $U = U_1 + U_2$  is constant, the total multiplicity after the systems are in thermal contact is

$$g(U) = \sum_{U_1} g_1(U_1)g_2(U - U_1), \quad (33)$$

by (18). This expression contains the term  $g_1(U_{10})g_2(U - U_{10})$  for the initial multiplicity before contact and many other terms besides. Here  $U_{10}$  is the initial energy of system 1 and  $U - U_{10}$  is the initial energy of system 2. Because all terms in (33) are positive numbers, the multiplicity is always increased by establishment of thermal contact between two systems. This is a proof of the law of increase of entropy for a well-defined operation.

The significant effect of contact, the effect that stands out even after taking the logarithm of the multiplicity, is not just that the number of terms in the summation is large, but that the largest single term in the summation may be very, very much larger than the initial multiplicity. That is,

$$(g_1 g_2)_{\max} \equiv g_1(U_1)g_2(U - U_1) \quad (34)$$

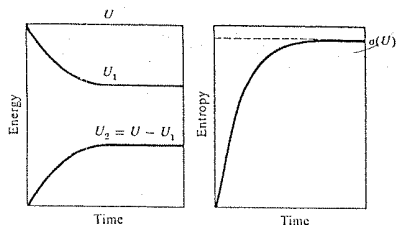


Figure 2.8 A system with two parts, 1 and 2, is prepared at zero time with  $U_2 = 0$  and  $U_1 = U$ . Exchange of energy takes place between two parts and presently the system will be found in or close to the most probable configuration. The entropy increases as the system attains configurations of increasing multiplicity or probability. The entropy eventually reaches the entropy  $g(U)$  of the most probable configuration.

may be very, very much larger than the initial term

$$g_1(U_{10})g_2(U - U_{10}). \quad (35)$$

Here  $\bar{U}_1$  denotes the value of  $U_1$  for which the product  $g_1g_2$  is a maximum. The essential effect is that the systems after contact evolve from their initial configurations to their final configurations. The fundamental assumption implies that evolution in this operation will always take place, with all accessible final states equally probable.

The statement

$$\sigma_{\text{final}} \approx \log(g_1g_2)_{\text{max}} \geq \sigma_{\text{initial}} = \log(g_1g_2)_0 \quad (36)$$

is a statement of the law of increase of entropy: the entropy of a closed system tends to remain constant or to increase when a constraint internal to the system is removed. The operation of establishing thermal contact is equivalent to the removal of the constraint that  $U_1$ ,  $U_2$  each be constant; after contact only  $U_1 + U_2$  need be constant.

The evolution of the combined system towards the final thermal equilibrium configuration takes a certain time. If we separate the two systems before they

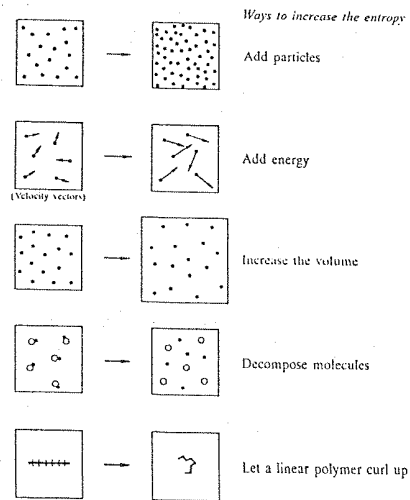


Figure 2.9 Operations that tend to increase the entropy of a system.

reach this configuration, we will obtain an intermediate configuration with intermediate energies and an intermediate entropy. It is therefore meaningful to view the entropy as a function of the time that has elapsed since removal of the constraint, called the time of evolution in Figure 2.8.

Processes that tend to increase the entropy of a system are shown in Figure 2.9; the arguments in support of each process will be developed in the chapters that follow.

For a large system\* (in thermal contact with another large system) there will never occur spontaneously significant differences between the actual value of the entropy and the value of the entropy of the most probable configuration of the system. We showed this for the model spin system in the argument following (17); we used "never" in the sense of not once in the entire age of the universe,  $10^{18}$  s. We can only find a significant difference between the actual entropy and the entropy of the most probable configuration of the macroscopic system very shortly after we have changed the nature of the contact between two systems, which implies that we had prepared the system initially in some special way. Special preparation could consist of lining up all the spins in one system parallel to one another or collecting all the molecules in the air of the room into the system formed by a small volume in one corner of the room. Such extreme situations never arise naturally in systems left undisturbed, but arise from artificial operations performed on the system.

Consider the gas in a room: the gas in one half of the room might be prepared initially with a low value of the average energy per molecule, while the gas in the other half of the room might be prepared initially with a higher value of the average energy per molecule. If the gas in the two halves is now allowed to interact by removal of a partition, the gas molecules will come very quickly<sup>†</sup> to a most probable configuration in which the molecules in both halves of the room have the same average energy. Nothing else will ever be observed to happen. We will never observe the system to leave the most probable configuration and reappear later in the initial specially prepared configuration. This is true even though the equations of motion of physics are reversible in time and do not distinguish past and future.

## LAWS OF THERMODYNAMICS

When thermodynamics is studied as a nonstatistical subject, four postulates are introduced. These postulates are called the laws of thermodynamics. In essence, these laws are contained within our statistical formulation of thermal physics, but it is useful to exhibit them as separate statements.

**Zeroth law.** If two systems are in thermal equilibrium with a third system, they must be in thermal equilibrium with each other. This law is a consequence

\* A large or macroscopic system may be taken to be one with more than  $10^{19}$  or  $10^{23}$  atoms.

† The calculation of the time required for the process is largely a problem in hydrodynamics.

of the condition (20b) for equilibrium in thermal contact:

$$\left(\frac{\partial \log g_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \log g_2}{\partial U_2}\right)_{N_2}; \quad \left(\frac{\partial \log g_2}{\partial U_2}\right)_{N_2} = \left(\frac{\partial \log g_3}{\partial U_3}\right)_{N_3}.$$

In other words,  $\tau_1 = \tau_2$  and  $\tau_2 = \tau_3$  imply  $\tau_1 = \tau_3$ .

**First law.** Heat is a form of energy. This law is no more than a statement of the principle of conservation of energy. Chapter 8 discusses what form of energy heat is.

**Second law.** There are many equivalent statements of the second law. We shall use the statistical statement, which we have called the law of increase of entropy, applicable when a constraint internal to a closed system is removed. The commonly used statement of the law of increase of entropy is: "If a closed system is in a configuration that is not the equilibrium configuration, the most probable consequence will be that the entropy of the system will increase monotonically in successive instants of time." This is a looser statement than the one we gave with Eq. (36) above.

The traditional thermodynamic statement is the Kelvin-Planck formulation of second law of thermodynamics: "It is impossible for any cyclic process to occur whose sole effect is the extraction of heat from a reservoir and the performance of an equivalent amount of work." An engine that violates the second law by extracting the energy of one heat reservoir is said to be performing perpetual motion of the second kind. We will see in Chapter 8 that the Kelvin-Planck formulation is a consequence of the statistical statement.

**Third law.** The entropy of a system approaches a constant value as the temperature approaches zero. The earliest statement of this law, due to Nernst, is that at the absolute zero the entropy difference disappears between all those configurations of a system which are in internal thermal equilibrium. The third law follows from the statistical definition of the entropy, provided that the ground state of the system has a well-defined multiplicity. If the ground state multiplicity is  $g(0)$ , the corresponding entropy is  $\sigma(0) = \log g(0)$  as  $\tau \rightarrow 0$ . From a quantum point of view, the law does not appear to say much that is not implicit in the definition of entropy, provided, however, that the system is in its lowest set of quantum states at absolute zero. Except for glasses, there would not be any objection to affirming that  $g(0)$  is a small number and  $\sigma(0)$  is essentially zero. Glasses have a frozen-in disorder, and for them  $\sigma(0)$  can be substantial, of the order of the number of atoms  $N$ . What the third law tells us in real life is that curves of many reasonable physical quantities plotted against  $\tau$  must come in flat as  $\tau$  approaches 0.

## Entropy as a Logarithm

Several useful properties follow from the definition of the entropy as the logarithm of the number of accessible states, instead of as the number of accessible states itself. First, the entropy of two independent systems is the sum of the separate entropies.

Second, the entropy is entirely insensitive—for all practical purposes—to the precision  $\delta U$  with which the energy of a closed system is defined. We have never meant to imply that the system energy is known exactly, a circumstance that for a discrete spectrum of energy eigenvalues would make the number of accessible states depend erratically on the energy. We have simply not paid much attention to the precision, whether it be determined by the uncertainty principle  $\delta U \delta(\text{time}) \sim h$ , or determined otherwise. Define  $\Phi(U)$  as the number of accessible states per unit energy range;  $\Phi(U)$  can be a suitable smoothed average centered at  $U$ . Then  $g(U) = \Phi(U)\delta U$  is the number of accessible states in the range  $\delta U$  at  $U$ . The entropy is

$$\sigma(U) = \log \Phi(U)\delta U = \log \Phi(U) + \log \delta U. \quad (37)$$

Typically, as for the system of  $N$  spins, the total number of states will be of the order of  $2^N$ . If the total energy is of the order of  $N$  times some average one-particle energy  $\Delta$ , then  $\Phi(U) \sim 2^N/N\Delta$ . Thus

$$\sigma(U) = N \log 2 - \log N\Delta + \log \delta U. \quad (38)$$

Let  $N = 10^{20}$ ;  $\Delta = 10^{-14}$  erg; and  $\delta U = 10^{-1}$  erg.

$$\sigma(U) = 0.69 \times 10^{20} - 13.82 - 2.3. \quad (39)$$

We see from this example that the value of the entropy is dominated overwhelmingly by the value of  $N$ ; the precision  $\delta U$  is without perceptible effect on the result. In the problem of  $N$  free particles in a box, the number of states is proportional to something like  $U^N \delta U$ , whence  $\sigma \sim N \log U + \log \delta U$ . Again the term in  $N$  is dominant, a conclusion independent of even the system of units used for the energy.

*Example: Perpetual motion of the second kind.* Early in our study of physics we came to understand the impossibility of a perpetual motion machine, a machine that will give forth more energy than it absorbs.

Equally impossible is a perpetual motion machine of the second kind, as it is called, in which heat is extracted from part of the environment and delivered to another part of the environment, the difference in temperature thus established being used to power a heat engine that delivers mechanical work available for any purpose at no cost to us. In brief, we cannot propel a ship by cooling the surrounding ocean to extract the energy necessary to propel the ship. The spontaneous transfer of energy from the low temperature ocean to a higher temperature boiler on the ship would decrease the total entropy of the combined systems and would thus be in violation of the law of increase of entropy.

## SUMMARY

1. The fundamental assumption is that a closed system is equally likely to be in any of the quantum states accessible to it.
2. If  $P(s)$  is the probability that a system is in the state  $s$ , the average value of a quantity  $X$  is

$$\langle X \rangle = \sum_s X(s)P(s).$$

3. An ensemble of systems is composed of very many systems, all constructed alike.
4. The number of accessible states of the combined systems 1 and 2 is

$$g(s) = \sum_i g_1(s_1)g_2(s - s_1),$$

where  $s_1 + s_2 = s$ .

5. The entropy  $\sigma(N, U) \equiv \log g(N, U)$ . The relation  $S = k_B \sigma$  connects the conventional entropy  $S$  with the fundamental entropy  $\sigma$ .
6. The fundamental temperature  $\tau$  is defined by

$$1/\tau \equiv (\partial \sigma / \partial U)_{N, V}.$$

The relation  $\tau = k_B T$  connects the fundamental temperature and the conventional temperature.

7. The law of increase of entropy states that the entropy of a closed system tends to remain constant or to increase when a constraint internal to the system is removed.

*Handwritten note:*  
 $P(s) = \frac{1}{g(s)}$   
 $\sigma = \log g(s)$



8. The thermal equilibrium values of the physical properties of a system are defined as averages over all states accessible when the system is in contact with a large system or reservoir. If the first system also is large, the thermal equilibrium properties are given accurately by consideration of the states in the most probable configuration alone.

### PROBLEMS

1. *Entropy and temperature.* Suppose  $g(U) = CU^{3N/2}$ , where  $C$  is a constant and  $N$  is the number of particles. (a) Show that  $U = \frac{3}{2}N\tau$ . (b) Show that  $(\partial^2 \sigma/\partial U^2)_N$  is negative. This form of  $g(U)$  actually applies to an ideal gas.

2. *Paramagnetism.* Find the equilibrium value at temperature  $\tau$  of the fractional magnetization

$$M/Nm = 2\langle s \rangle/N$$

of the system of  $N$  spins each of magnetic moment  $m$  in a magnetic field  $B$ . The spin excess is  $2s$ . Take the entropy as the logarithm of the multiplicity  $g(N, s)$  as given in (1.35):

$$\sigma(s) \approx \log g(N, 0) - 2s^2/N, \quad (40)$$

for  $|s| \ll N$ . *Hint:* Show that in this approximation

$$\sigma(U) = \sigma_0 - U^2/2m^2B^2N, \quad (41)$$

with  $\sigma_0 = \log g(N, 0)$ . Further, show that  $1/\tau = -U/m^2B^2N$ , where  $U$  denotes  $\langle U \rangle$ , the thermal average energy.

3. *Quantum harmonic oscillator.* (a) Find the entropy of a set of  $N$  oscillators of frequency  $\omega$  as a function of the total quantum number  $n$ . Use the multiplicity function (1.55) and make the Stirling approximation  $\log N! \approx N \log N - N$ . Replace  $N - 1$  by  $N$ . (b) Let  $U$  denote the total energy  $n\hbar\omega$  of the oscillators. Express the entropy as  $\sigma(U, N)$ . Show that the total energy at temperature  $\tau$  is

$$U = \frac{N\hbar\omega}{\exp(\hbar\omega/\tau) - 1}. \quad (42)$$

This is the Planck result; it is derived again in Chapter 4 by a powerful method that does not require us to find the multiplicity function.

4. *The meaning of "never."* It has been said\* that "six monkeys, set to strum unintelligently on typewriters for millions of years, would be bound in time to write all the books in the British Museum." This statement is nonsense, for it gives a misleading conclusion about very, very large numbers. Could all the monkeys in the world have typed out a single specified book in the age of the universe?†

Suppose that  $10^{10}$  monkeys have been seated at typewriters throughout the age of the universe,  $10^{18}$  s. This number of monkeys is about three times greater than the present human population\* of the earth. We suppose that a monkey can hit 10 typewriter keys per second. A typewriter may have 44 keys; we accept lowercase letters in place of capital letters. Assuming that Shakespeare's *Hamlet* has  $10^5$  characters, will the monkeys hit upon *Hamlet*?

(a) Show that the probability that any given sequence of  $10^5$  characters typed at random will come out in the correct sequence (the sequence of *Hamlet*) is of the order of

$$(1/44)^{100000} = 10^{-164345}$$

where we have used  $\log_{10} 44 = 1.64345$ .

(b) Show that the probability that a *monkey-Hamlet* will be typed in the age of the universe is approximately  $10^{-164316}$ . The probability of *Hamlet* is therefore zero in any operational sense of an event, so that the original statement at the beginning of this problem is nonsense: one book, much less a library, will never occur in the total literary production of the monkeys.

5. *Additivity of entropy for two spin systems.* Given two systems of  $N_1 \approx N_2 = 10^{22}$  spins with multiplicity functions  $g_1(N_1, s_1)$  and  $g_2(N_2, s - s_1)$ , the product  $g_1 g_2$  as a function of  $s_1$  is relatively sharply peaked at  $s_1 = \bar{s}_1$ . For  $s_1 = \bar{s}_1 + 10^{12}$ , the product  $g_1 g_2$  is reduced by  $10^{-174}$  from its peak value. Use the Gaussian approximation to the multiplicity function; the form (17) may be useful.

(a) Compute  $g_1 g_2 / (g_1 g_2)_{\max}$  for  $s_1 = \bar{s}_1 + 10^{12}$  and  $s = 0$ .

(b) For  $s = 10^{10}$ , by what factor must you multiply  $(g_1 g_2)_{\max}$  to make it equal to  $\sum_{s_1} g_1(N_1, s_1) g_2(N_2, s - s_1)$ ; give the factor to the nearest order of magnitude.

\* J. Jeans, *Mysterious universe*, Cambridge University Press, 1930, p. 4. The statement is attributed to Huxley.

† For a related mathematico-literary study, see "The Library of Babel," by the fascinating Argentine writer Jorge Luis Borges, in *Ficciones*, Grove Press, Evergreen paperback, 1962, pp. 79–88.

‡ For every person now alive, some thirty persons have once lived. This figure is quoted by A. C. Clarke in 2001. We are grateful to the Population Reference Bureau and to Dr. Roger Revelle for explanations of the evidence. The cumulative number of man-seconds is  $2 \times 10^{10}$ , if we take the average lifetime as  $2 \times 10^8$  s and the number of lives as  $1 \times 10^{11}$ . The cumulative number of man-seconds is much less than the number of monkey-seconds ( $10^{18}$ ) taken in the problem.

(c) How large is the fractional error in the entropy when you ignore this factor?

6. *Integrated deviation.* For the example that gave the result (17), calculate approximately the probability that the fractional deviation from equilibrium  $\delta/N_1$  is  $10^{-10}$  or larger. Take  $N_1 = N_2 = 10^{23}$ . You will find it convenient to use an asymptotic expansion for the complementary error function. When  $x \gg 1$ ,

$$2x \exp(x^2) \int_x^\infty \exp(-t^2) dt \approx 1 + \text{small terms.}$$

## Chapter 3

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