

# **Chapter 3**

## **The Statistical Theory of Thermodynamics**

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### 3 Statistical theory of thermodynamics

In this chapter, we will focus on two topics: (a) foundation of statistical mechanics and (b) application to isolated systems.

So far, we have only calculated the entropy changes but never the absolute value. The classical theory of thermodynamics leaves important questions unanswered, e.g.,

- What really is entropy?
- Why does entropy increase?
- Can we deduce equation of state of real thermodynamic systems from first principles?

The statistical theory addresses these. In particular, we all say that entropy is a measure of disorder but how do we measure disorder? In addressing this question, we need to know the state of each particle's motion in the system, i.e., microstates of a thermodynamic system. Hence we may say

$$\text{Entropy} \rightarrow \text{Disorder} \rightarrow \text{Microstates}$$

and we will provide a precise relation between these. We will be able to answer why always  $\Delta S \geq 0$  in a probabilistical way, namely, the opposite direction of the changes are very unlikely.

#### 3.1 Macrostate and Microstate

As discussed in Chapter 1, a **macrostate** of a thermodynamic system is described by a few thermodynamic variables, such as  $P, V, T$  and  $E, S$  etc. for a gas system. These quantities are the measure of collective behaviors of atoms in the gas.

A **microstate**, however, specifies the system with the physical quantities of the constituent particles. For a single particle, we cannot speak of  $P, V$ , and  $T$ . But we can specify its physical state of motion. In **classical mechanics**, the state of a single particle is specified by its position and momentum at a moment,  $(\mathbf{r}; \mathbf{p})$ . For  $N$  particles in a box, a microstate is specified by a set of values of their positions and momenta

$$(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N) .$$

Since each of these vectors has three components, the whole lot represents a  $6N$ -dimensional space. This is the **phase space** of the  $N$ -particle system.

In **quantum mechanics**, we use wavefunctions to describe the physical motion of a single particle and these wavefunctions are usually specified by a set of **quantum**

**numbers.** For example, a state of an electron in hydrogen atom is specified by a set of quantum numbers  $(n, l, m, \sigma)$ , where  $n$  is the principle number,  $l$  the angular momentum number,  $m$  the  $z$ -component number of angular momentum, and finally  $\sigma = \pm 1/2$  is its spin quantum number. Notice that quantum states are discrete [i.e., the parameters  $(n, l, m, \sigma)$  are discrete numbers], contrast to the classical states, where the state parameters  $(\mathbf{r}; \mathbf{p})$  are continuous variables. For a quantum particle moving in a box, its state is a plane-wave specified by three **discrete** components of momenta  $\mathbf{p} = (p_x, p_y, p_z)$  together with its spin  $\sigma$ . We will discuss this in details later. For a system of  $N$  quantum particles in a box, the collection of all quantum numbers

$$(\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N; \sigma_1, \sigma_2, \dots, \sigma_N)$$

are in general used to specify the microstates of the  $N$ -particle system in the so-called independent particle approximation (ignoring the interactions between particles). Later, we will consider a system of  $N$  localized spins in a solid, for which a microstate is specified by a given spin configuration  $(\sigma_1, \sigma_2, \dots, \sigma_N)$ . We notice immediately that the possible numbers of microstates are huge numbers when  $N$  is large.

**A Simple Example of microstates:** Suppose we have a  $6 \times 6$  checkerboard. Each square of the board represents a localised spin-1/2 particle with two possible spin orientations, one spin-up marked by  $X$  and the other spin-down marked by  $O$ . A particular configuration of this up and down spins corresponds a microstate. Many different patterns are possible, such as those shown below.

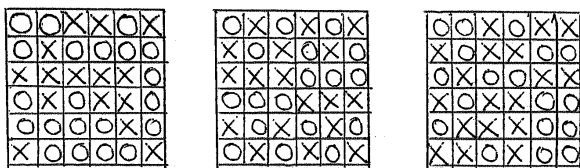


Figure 1

Later we will make an assumption that every configuration is equally likely, i.e., each one has the same probability  $1/\Omega$ , with  $\Omega = 2^{36} \approx 6.9 \times 10^{10}$  (assumption of equal a priori probabilities). Define a macrostate here to be simply specified by the number,  $n_\uparrow$ , of  $X$ 's (and hence  $(N - n_\uparrow)$  of  $O$ 's, here with  $N = 36$ ). For example, if the macrostate is "13 up spins" the following are a few of the allowed microstates:

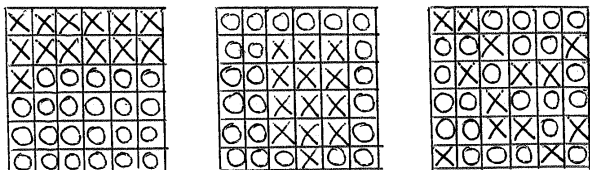


Figure 2

How many possible such microstates are there? This is just the common combinatorial

problem of splitting a group of  $N$  identical objects into two smaller groups  $n_{\uparrow}$  and  $(N - n_{\uparrow})$  without caring about the ordering in each group. The number of ways is

$$\frac{N!}{n_{\uparrow}!(N - n_{\uparrow})!}.$$

(Think first of  $N$  different (distinguishable) spins on  $N$  squares,  $N!$  ways. But if  $n_{\uparrow}$  of them are identical, there are  $n_{\uparrow}!$  ways of arranging the up spins among themselves without changing the pattern; similarly  $(N - n_{\uparrow})!$  ways of arranging the down spins). Here  $N = 36$  and  $n_{\uparrow} = 13$ , so the total is  $2.31 \times 10^9$ . Similarly for  $n_{\uparrow} = 15$  there are only  $5.57 \times 10^9$  ways, whereas for  $n_{\uparrow} = 18$  there are  $9.08 \times 10^9$  ways (this is the maximum for this case).

Note: the numbers  $N!/ [n!(N - n)!]$  are called the binomial coefficients, and are often written as either

$$C_N^n \quad \text{or} \quad \binom{N}{n},$$

from binomial expansion

$$(a + b)^N = \sum_{n=0}^N C_N^n a^{N-n} b^n.$$

See Q3 of Example Sheet 7 for more examples of microstates of various systems.

### 3.2 Basic statistical hypotheses

As discussed earlier, classical thermodynamics describes macroscopic systems (i.e., ones which contain very large numbers of atoms) in terms of a few thermodynamic variables  $P, V, T, E$  etc. But we know such systems are really made of atoms, and a microscopic description would be in terms of the underlining states of all of the atoms. Hence we need a bridge between the microstate and macrostate description. This bridge is provided by **statistical mechanics**.

As the atoms interact the microstates change very rapidly (maybe  $10^{35}$  times/second). We can in principle take two approaches in averaging:

- (a) Time-average. Suppose  $X$  is some observed macroscopic quantity (i.e., a state variable) e.g., internal energy  $E$ , we could take a time average over some (long) time  $\tau$ :

$$X_{\text{observable}} = \frac{1}{\tau} \int_{t_0}^{t_0+\tau} X(t) dt$$

and, at equilibrium (independent of  $\tau$ )

$$\langle X \rangle \equiv X_{\text{observable}} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_{t_0}^{t_0+\tau} X(t) dt.$$

But, this notion of time-average is impossible to compute in practice even though it's what we actually measure in an experiment.

- (b) Average by distribution (ensemble). It's clear that many different microstates all correspond to the same macrostate (see the earlier example of 36 spins). Suppose we take a movie film of the progression in time of the system. Eventually we expect to see all possible microstate configurations consistent with given macrostate (described, e.g., by  $E, V, N$ ). Suppose the value of the variable  $X$  in microstate  $i$  is  $X_i$ , and let the probability that the  $i$ th microstate appears in the movie of the system be  $p_i$ . Then, we can average over microstates to get the observed value  $\langle X \rangle$  in the macrostate

$$\langle X \rangle = \sum_i p_i X_i.$$

This idea of taking an **ensemble average** (see below) is clearly much easier in practice than the much more complicated time-averaging, provided we know the probabilities  $p_i$ .

An **ensemble** is a collection of a large number of copies of the system, each in one of the allowed microstates. Let  $\Omega$  be the number of microstates consistent with a given macrostate, and let  $\nu$  be the number of copies of the system in the ensemble. Clearly, if  $\nu \gg \Omega$ , the number of copies of the  $i$ th microstates is simply  $\nu_i = p_i \nu$ . Then if we use  $\lambda = 1, 2, \dots, \nu$  to label the copies and  $i = 1, 2, \dots, \Omega$  to label the microstates

$$\langle X \rangle = \frac{1}{\nu} \sum_{\lambda=1}^{\nu} X_{\lambda} = \frac{1}{\nu} \sum_{i=1}^{\Omega} \nu_i X_i = \sum_{i=1}^{\Omega} p_i X_i.$$

We shall meet 3 kinds of ensembles which are used a lot in statistical mechanics, viz.,

- (a) **the microcanonical ensemble** pertains to isolated systems (i.e., at fixed  $E, V, N$ ); the copies in the ensemble are also isolated from each other (i.e., a single isolated system). The key state function is entropy  $S(E, V, N)$ .
- (b) **the canonical ensemble** pertains to systems in contact with a heat bath (i.e., at fixed  $T, V, N$ ); the copies in this ensemble are assumed to be in thermal contact, so that they may exchange energy with each other. Thus, all the copies act as a heat bath for any individual copy. The key state function in this approach is Helmholtz free energy  $F(T, V, N)$ .
- (c) **the grand canonical ensemble** pertains to systems in contact with a reservoir with which they can exchange both heat and particles (i.e., at fixed  $T, V, \mu$ ). The copies are assumed to be in both thermal and diffusive contact, so that they may exchange both heat and particles with each other.

Let us start by considering an **isolated system**, i.e., microcanonical ensemble. The big question now is how to weight the various microstates, i.e., how to find  $p_i$ . Really, we should have to solve the equations of motion for the whole macroscopic system ( $\approx 10^{23}$  atoms or so!), an impossible task. Instead we make:

**Assumption 1 (The Postulate of equal a priori probabilities):**  
**All microstates consistent with a given macrostate of an isolated system (i.e., given  $E, V, N$ ) are equally probable.**

i.e.,

$$p_i = \frac{1}{\Omega},$$

where  $\Omega = \Omega(E, V, N)$  is the total number of microstates, or **statistical weight**, or the volume of region of motion. Note that we have normalization

$$\sum_{i=1}^{\Omega} p_i = \Omega \cdot \frac{1}{\Omega} = 1.$$

This postulate is otherwise known as the ergodic hypothesis. In principle it should be provable (or disprovable) from classical or quantum mechanics. Birkhoff spent most of his life trying to prove it with no general success.

[Refs.: (1) Mandl 2.1-2.2; (2) Bowley and Sánchez 4.1]

### 3.3 Boltzmann's assumption of entropy

To make the connection of the statistical approach with thermodynamics we proceed through the entropy,  $S$

(i)  $S$  as a measure of randomness: We know spontaneous changes in systems out of equilibrium lead to an increase in  $S$ ; we also know that as  $S$  increases so does the 'randomness' or 'degrees of disorder'. We have already introduced  $\Omega = \Omega(E, V, N)$  as the statistical weight of a given macrostate = the number of distinguishably different microstates that correspond to it. System tend to evolve, if out of equilibrium, to maximize  $\Omega$ . Clearly  $\Omega$  and  $S$  seem to be related. But how?

(ii) Counting arguments: Consider 2 isolated systems,

- total entropy  $S = S_1 + S_2$
- total number of microstates  $\Omega = \Omega_1 \Omega_2$

The above arguments strongly suggest for the entropy of a thermodynamic system at equilibrium:

**Assumption 2** (Boltzmann 1844-1906)

$$S = k \ln \Omega, \quad \Omega = \Omega(E, V, N), \quad S = S(E, V, N).$$

We will see later that the constant  $k = k_B = R/N_A$ , the Boltzmann constant.

In this way the second law of thermodynamics has become a statistical statement, viz., systems evolve toward equilibrium because equilibrium is the *most likely* state consistent with the constraints. In principle, if the increase in entropy is just a probabilistic result, hence it is possible that it might also spontaneously decrease through a statistical fluctuations. But, we will see later this is overwhelmingly unlikely for a macroscopic system.

Note:  $k_B$  has dimension of entropy.  $k_B = R/N_A \approx 1.381 \times 10^{-23} \text{ J K}^{-1} \approx 8.617 \times 10^{-5} \text{ eV K}^{-1}$ .  $k_B T \approx \frac{1}{40} \text{ eV}$  for  $T = 300 \text{ K}$ , room temperature.)

Together with those thermodynamics relations involving entropy  $S = S(E, V, N)$  discussed earlier, we have the basic formulas for **statistical mechanics of isolated systems**:

$$S = k_B \ln \Omega \tag{1}$$

where

$$\Omega = \Omega(E, V, N)$$

is the total number of microstates of the system consistent with a given macrostate  $(E, V, N)$ ; other thermodynamic quantities are calculated by the relations derived from the fundamental thermodynamic relations as

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{V, N} \tag{2}$$

$$\frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{E, N}. \tag{3}$$

Eq. (2) is the energy equation  $E = E(T, V)$  and Eq. (3) gives equation of state.

Therefore, the key to the microcanonical ensemble approach, i.e., isolated systems, is to find the statistical weight  $\Omega(E, V, N)$ . All other physical properties are obtained by the above Eqs. (1-3). We will apply this approach to paramagnet of spin-1/2 system in the following, where it is relative easy to count the statistical weight  $\Omega(E, V, N)$ . Furthermore, Eq. (2) gives a precise definition of temperature for an isolated system, from microscopic point of view, namely, if we can find the statistical weight  $\Omega(E, V, N)$  of the system as a function of its energy, we can find its temperature.

[Refs.: (1) Mandl 2.3; (2) Bowley and Sánchez 4.1, 4.5.]

### 3.4 Independent localized spin systems: the ideal spin-half paramagnet

We now try to evaluate  $\Omega$  for some simple systems, hence physics becomes a counting problem. Consider: (i) localized systems of fixed sites (e.g., crystalline solids); (ii) the particles are assumed to be independent (i.e., not to interact with each other, not to feel each other's present): ideal systems; (iii) each particles has a set of energy levels  $\epsilon_0, \epsilon_1, \epsilon_2, \dots$ .

A very simple example is a system in which each particle has just 2 energy levels, e.g., **the ideal spin-1/2 paramagnet**. At each of  $N$  sites we have an atom with spin  $S = 1/2$ . By quantum mechanics, the  $z$ -component has only 2 values:  $S_z = -1/2$  for down-state ( $\downarrow$ ) and  $S_z = 1/2$  for up-state ( $\uparrow$ ). If we apply a magnetic field  $\mathbf{B}$  in the  $z$ -direction, each spin has a magnetic moment  $-\mu_0$  ( $\downarrow$ ) or  $\mu_0$  ( $\uparrow$ ). The total magnetic moment will be

$$m = n_{\uparrow}\mu_0 + n_{\downarrow}(-\mu_0) = (n_{\uparrow} - n_{\downarrow})\mu_0 = (2n_{\uparrow} - N)\mu_0$$

where  $n_{\uparrow}$  = number of spin-up atoms and  $n_{\downarrow}$  = number of spin-down atoms. Obviously,  $n_{\uparrow} + n_{\downarrow} = N$ . In an external magnetic field  $\mathbf{B}$  the energy of a magnetic dipole  $\mu$  is  $-\mu \cdot \mathbf{B}$ . Hence, in our case the total energy is

$$E = n_{\uparrow}(-\mu_0 B) + n_{\downarrow}(\mu_0 B) = -(2n_{\uparrow} - N)\mu_0 B = -mB. \quad (4)$$

Let us first consider  $B = 0$  (zero external magnetic field). In this case all microstates have the same energy and are equally likely. This is just like our checkerboard example in Sec. 3.1. Thus, macrostates can be characterized by their magnetic moment  $m$  (or, equivalently, magnetization  $M = m/V$ ; and microstates by the list of spins at each site. e.g. for  $N = 3$  we have 4 macrostates and  $2^3 = 8$  microstates.

$$\begin{array}{ll} m &= 3\mu_0 & \uparrow\uparrow\uparrow \\ m &= \mu_0 & \uparrow\uparrow\downarrow, \uparrow\downarrow\uparrow, \downarrow\uparrow\uparrow \\ m &= -\mu_0 & \uparrow\downarrow\downarrow, \downarrow\uparrow\downarrow, \downarrow\downarrow\uparrow \\ m &= -3\mu_0 & \downarrow\downarrow\downarrow \end{array}$$

Next, we consider number of microstates under an applied magnetic field. Since the simple linear relation between  $E$  and  $n_{\uparrow}$  from Eq. (4), a given energy  $E$  implies a given number of up spins  $n_{\uparrow}$ . Therefore, the statistical weight is the number of microstates for a given  $n_{\uparrow}$ , i.e.,  $\Omega = \Omega(N, n_{\uparrow})$ .

Q: How many microstates for a given macrostate  $(N, n_{\uparrow})$ ?

A: Choose first particle in  $N$  ways, second in  $(N - 1)$  ways, third in  $(N - 2)$  ways, etc.



So there are  $N!$  ways of ordering the particles. But the microstates do not distinguish the orderings of particles in the same spin state

$$\Omega(N, n_{\uparrow}) = \frac{N!}{n_{\uparrow}!(N - n_{\uparrow})!} \quad (5)$$

as number of microstates of given  $n_{\uparrow}$ . If we sum over all  $n_{\uparrow}$  we get

$$\sum_{n_{\uparrow}=0}^N \Omega(N, n_{\uparrow}) = \sum_{n_{\uparrow}}^N \frac{N!}{n_{\uparrow}!(N - n_{\uparrow})!} = 2^N = \Omega(N) \quad (6)$$

namely, the total number of microstates. The proof is easy if we write

$$(1+x)^N = 1 + Nx + \frac{N(N-1)}{2!}x^2 + \frac{N(N-1)(N-2)}{3!}x^3 + \dots + x^N = \sum_{n=0}^N \frac{N!}{n!(N-n)!}x^n$$

and putting  $x = 1$ .

Let's plot  $\Omega(N, n)$  normalized to 1 at the peak, as a function of  $n/N$  for different values of  $N$  (and see Ex. Sheet 8).

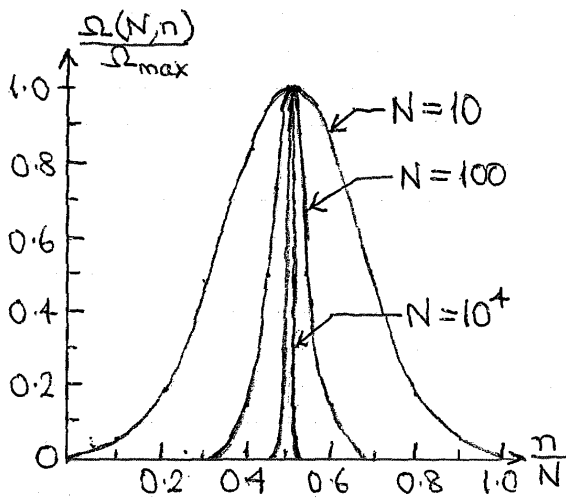


Figure 3

As  $N$  increases the function  $\Omega(N, n)$  is more and more sharply peaked around its maximum at  $n = N/2$  and it's more and more likely that when  $B = 0$  there will be equal numbers  $n_{\uparrow} = n_{\downarrow}$  of up and down spin, giving zero magnetization. In the limit  $N \gg 1$  the curve is very well approximated by a Gaussian

$$\Omega(N, n) \approx \sqrt{\frac{2}{\pi N}} 2^N \exp \left[ -\frac{(n - N/2)^2}{N/2} \right], \quad N \rightarrow \infty. \quad (7)$$

(c.f. standard Gaussian  $\propto \exp[-(x - \bar{x})^2/2\sigma^2]$  with  $\bar{n} = N/2$  and  $\sigma = \sqrt{N}/2$  and  $\sigma/\bar{n} = 1/\sqrt{N}$ , namely, fractional size of fluctuations is proportional to  $1/\sqrt{N}$ . For example, for a macroscopic sample with  $N = 10^{24}$ ,  $\sigma/\bar{n} = 10^{-12}$ , and even a 1000 fluctuation would need an accuracy measurement of better than one part in  $10^{10}$ , since  $1000/\bar{n} = 10^{-10}$ .)

So we see that for macroscopic systems, the macroscopic (thermodynamic) properties are extremely sharply defined, and statistical fluctuations are imperceptible. Thus, the milk in my coffee will 'never' spontaneously separate. It is just too unlikely.

The largest value of  $\Omega(N, n)$ , namely  $\Omega_{\max}$ , clearly occurs when  $n = N/2$ . In order to work with  $\Omega$ , it is useful to use **Stirling's approximation**

$$n! \approx \sqrt{2\pi n} n^n e^{-n}, \quad n \gg 1 \quad (8)$$

which is better known in its logarithmic form

$$\ln n! \approx n \ln n - n + O(\ln n), \quad (9)$$

known as Stirling's formula. We find

$$\ln \Omega_{\max} = \ln \Omega(N, N/2) = \ln \left[ \frac{N!}{[(N/2)!]^2} \right] \approx N \ln N - N - 2 \left[ \frac{N}{2} \ln \frac{N}{2} - \frac{N}{2} \right] = N \ln 2$$

and hence,  $S = Nk_B \ln 2$  or,  $S = k_B \ln \Omega_{\max}$ . i.e., in the sum for  $S = \ln \Omega(N) = \ln \sum_{n=0}^{\infty} \Omega(N, n)$ , we can replace the sum by the its largest term. At first sight this seems strange, but it is a simple consequence of  $N$  being large and logarithms be present. Thus, clearly

$$\Omega(N, N/2) < \Omega(N) < N \cdot \Omega(N, N/2)$$

Since all terms are positive, we can take logs

$$\ln \Omega(N, N/2) < \ln \Omega(N) < \ln \Omega(N, N/2) + \ln N$$

But  $\ln N \ll \ln \Omega(N, N/2) \approx N \ln 2$  and  $N \gg \ln N$ , hence

$$\ln \Omega(N) = \ln \Omega(N, N/2)$$

It is quite common in statistical mechanics to find such examples where sums can, to a very good approximation, be replaced by their largest term - it is always a consequence (as here) of the very sharply peaked nature of the function in the sum. Next, we discuss the thermodynamics of spin paramagnet using the statistical mechanics formulas discussed earlier.

**Example:** The thermodynamics of the isolated ideal spin-1/2 paramagnet in an external magnetic field. The key question is to determine the internal energy and magnetization as a function of temperature.

In this case the work term  $dW = -PdV$  is replaced by  $dW = -mdB$ . The fundamental thermodynamic relation is

$$dE = TdS - mdB$$

or

$$dS = \frac{1}{T}dE + \frac{m}{T}dB.$$

Hence, we have  $S = S(E, B, N)$  with

$$\left(\frac{\partial S}{\partial E}\right)_{B,N} = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial B}\right)_{E,N} = \frac{m}{T}. \quad (10)$$

Now, if the system is isolated,  $E$  is fixed, and hence, since  $E = (N - 2n_{\uparrow})\mu B$  from Eq. (4),  $n_{\uparrow}$  is fixed. We have,  $\Omega = \Omega(n_{\uparrow}, B, N)$ ,

$$S = k_B \ln \Omega(n_{\uparrow}, B, N) = k_B \ln \left[ \frac{N!}{n_{\uparrow}!(N - n_{\uparrow})!} \right] \quad (11)$$

with

$$n_{\uparrow} = \frac{1}{2} \left( N - \frac{E}{\mu B} \right). \quad (12)$$

We use Stirling's formula again for  $\ln N!$ ,  $\ln n!$ ,  $\ln(N - n)!$ , hence

$$S = k_B \{ N \ln N - N - (n_{\uparrow} \ln n_{\uparrow} - n_{\uparrow}) - [(N - n_{\uparrow}) \ln(N - n_{\uparrow}) - (N - n_{\uparrow})] \}$$

or

$$S = k_B [N \ln N - n_{\uparrow} \ln n_{\uparrow} - (N - n_{\uparrow}) \ln(N - n_{\uparrow})]. \quad (13)$$

(a) From 1st equation of Eqs. (10),

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{B,N} = \left(\frac{\partial S}{\partial n_{\uparrow}}\right)_N \left(\frac{\partial n_{\uparrow}}{\partial E}\right)_{B,N}$$

or

$$\frac{1}{T} = k_B [-\ln n_{\uparrow} - 1 + \ln(N - n_{\uparrow}) + 1] \left( -\frac{1}{2\mu B} \right)$$

or

$$\frac{1}{T} = \frac{k_B}{2\mu B} \ln \frac{n_{\uparrow}}{n_{\downarrow}} \quad (14)$$

where  $n_{\downarrow} = N - n_{\uparrow}$ . Note: (1)  $T > 0$  since  $n_{\uparrow} > n_{\downarrow}$  (always more spins aligned along  $B$  than against it); (2)  $T = \infty$  for  $n_{\uparrow} = n_{\downarrow}$ ; (3)  $T = 0$  for  $n_{\downarrow} = 0$ . We can solve for  $n_{\uparrow}$  from Eq. (14) and then use Eq. (12) to find the energy  $E$  as a function of temperature. For details, see Q2 of Example Sheet 8.

(b) From 2nd equation of Eqs. (10),

$$\frac{m}{T} = \left( \frac{\partial S}{\partial B} \right)_{E,N} = \left( \frac{\partial S}{\partial n_{\uparrow}} \right)_N \left( \frac{\partial n_{\uparrow}}{\partial B} \right)_{E,N}$$

hence

$$\frac{m}{T} = k_B [-\ln n_{\uparrow} + \ln(N - n_{\uparrow})] \left( \frac{E}{2\mu B^2} \right)$$

or

$$\frac{m}{T} = -\frac{k_B E}{2\mu B^2} \ln \frac{n_{\uparrow}}{n_{\downarrow}}. \quad (15)$$

Combing Eqs. (14) and (15),

$$m = -\frac{k_b E}{2\mu B^2} \cdot 2\mu B k_B = -\frac{E}{B}, \quad \text{or } E = -mB,$$

as required.

### 3.5 Correspondence between classical and quantum mechanical statistical weight

As discussed in Sec. 3.1, a microstate for a quantum system is specified by a set of discrete quantum numbers. Therefore, in principle, there is no ambiguity in counting the total number of the microstates  $\Omega$  in QM. In a classical system, the same can not be said as a microstate is specified by the continuous variables  $\mathbf{r}_i, \mathbf{p}_i$ ,  $i = 1, 2, \dots, N$ . In the followings, we discuss the correspondence between counting the classical microstates and the quantum mechanical microstates by considering the case of an ideal gas.

**Example: Classical ideal gas.** From Q2 of Example Sheet 5, we calculated the entropy change of an ideal gas as:

$$S - S_0 = k_B N \ln \frac{V}{V_0} + C_V \ln \frac{T}{T_0}.$$

Now we try to relate this thermodynamic result to the Boltzmann's entropy formula of Eq. (1). For an ideal gas, setting  $C_V = 3k_B N/2$  and  $E = C_V T = 3k_B N T/2$ , we

write

$$\begin{aligned} S - S_0 &= k_B N \left[ \ln \frac{V/N}{V_0/N} + \ln \left( \frac{E/N}{E_0/N} \right)^{3/2} \right] \\ &= k_B N \ln \left[ \frac{V}{N} \left( \frac{E}{N} \right)^{3/2} \right] - k_B N \ln \left[ \frac{V_0}{N} \left( \frac{E_0}{N} \right)^{3/2} \right]. \end{aligned}$$

As first term depends only on state  $(E, V)$  and the second term on state  $(E_0, V_0)$ , we can write, in general, up to an undetermined constant  $a$ ,

$$S = k_B N \ln \left[ \left( \frac{V}{N} \right) \left( \frac{E}{N} \right)^{3/2} \right] + k_B N \ln a^{3/2} = k_B N \ln \left[ a^{3/2} \left( \frac{V}{N} \right) \left( \frac{E}{N} \right)^{3/2} \right], \quad (16)$$

where  $a$  is independent of  $(E, V, N)$ . We can consider that  $E/N$  is the average energy of each molecule and  $V/N$  is the average volume occupied by each molecule (both are therefore intensive while  $S$  is extensive). How do we relate this equation to the Boltzmann's law of Eq. (1) and how do we determine the constant  $a$ ? Clearly, if we let

$$\frac{(\Delta p)^2}{2m} = \frac{E}{N}, \quad (\Delta x)^3 = \frac{V}{N}$$

then, roughly speaking,  $\Delta p$  is the magnitude of the change of momentum of the molecules and  $\Delta x$  is that of the change of position. Now we can write the entropy as

$$S = k_B \ln \left( \frac{\Delta x \Delta p}{w} \right)^{3N} = k_B \ln \Omega,$$

with constant  $w = \sqrt{2m/a}$  and

$$\Omega = \left( \frac{\Delta x \Delta p}{w} \right)^{3N}.$$

Namely, the statistical weight  $\Omega$  for  $N$  classical particles is given by the total volume in the phase space in the unit of  $w$  (here the name of **the volume of region of motion** seems appropriate). As  $\Omega$  is dimensionless, the choice of minimum value,

$$w = h = 6.626 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1},$$

the Planck constant, gives the **unique correspondence** between classical and quantum mechanical calculation of the total number of the microstates  $\Omega$ .

We hence write the correspondence formula for a single particle,

$$\Omega_1 = \int d\Omega_1 = \frac{1}{h^3} \int d^3 r d^3 p, \quad (17)$$

where

$$\begin{aligned} d^3p &= dp_x dp_y dp_z, \quad -\infty < p_x, p_y, p_z < \infty \\ &= p^2 \sin \theta dp d\theta d\phi, \quad 0 \leq p < \infty, 0 \leq \theta < \pi, 0 \leq \phi < 2\pi . \end{aligned}$$

Extending to the  $N$ -particle gas, we need to introduce multi-particle integrals, the property of identical particles (i.e., permuting between any pair of molecules does not produce a new microstate), and the total energy-conservation condition for the isolated system, namely

$$\Omega(E, V, N) = \frac{1}{N! h^{3N}} \int_V d^3r_1 d^3r_2 \cdots d^3r_N \int d^3p_1 d^3p_2 \cdots d^3p_N \delta(H - E) \quad (18)$$

where the integrals over real space  $\int_V$  ensures particles moving inside the volume  $V$ , and  $\delta$  function  $\delta(H - E)$  with Hamiltonian  $H = H(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N; \mathbf{p}_1, \mathbf{p}_2, \cdots, \mathbf{p}_N)$  ensures energy conserving at value of  $E$ . This multi-dimensional integral of Eq. (18) is highly nontrivial and we will not discuss it further in this course. We will instead discuss the case of classical gases in the next chapter using a canonical ensemble, where Helmholtz free energy  $F$ , instead of entropy  $S$ , is the relevant thermodynamic potential, and where the corresponding integrals will become much more straightforward. Did we say  $F$  is more convenient while  $S$  is more original?

[Refs.: (1) Mandl 2.4; (2) Bowley and Sánchez 2.9.]