

# Chapter 4

## The Statistical Physics of non-Isolated systems: The Canonical Ensemble

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## 4 The Statistical Physics of non-Isolated systems: The Canonical Ensemble

In principle the tools of Chap. 3 suffice to tackle all problems in statistical physics. In practice the microcanonical ensemble considered there for isolated systems ( $E, V, N$  fixed) is often complicated to use since it is usually (i.e., except for ideal, non-interacting systems) very difficult to calculate all possible ways the energy can be split between all the components (atoms). However, we may also consider non-isolated systems, and in this chapter we consider systems in contact in with a heat reservoir, where temperature  $T$  is fixed rather than  $E$ . This then leads us to the **canonical ensemble**. In Chap. 3, we have introduced the canonical ensemble as many copies of a thermodynamic system, all in thermal contact with one another so energy is exchanged to keep temperature constant throughout the ensemble. In this chapter we will introduce the **Boltzmann distribution** function by focusing on one copy and considering the rest copies as a giant heat reservoir:

$$\text{Canonical Ensemble} = \text{System} + \text{Reservoir.}$$

The important point to note is that for a macroscopic system the two approaches are essentially identical. Thus, if  $T$  is held fixed the energy will statistically fluctuate, but, as we have seen, the fractional size of the fluctuations  $\propto 1/\sqrt{N}$  (we will verify this explicitly later). Thus, from a macroscopic viewpoint, the energy is constant to all intents and purposes, and it makes no real difference whether the heat reservoir is present or not, i.e., whether we use the microcanonical ensemble (with  $E, V, N$  fixed) or the canonical ensemble (with  $T, V, N$  fixed). The choice is ours to make, for convenience or ease of calculations. We will see canonical ensemble is much more convenience.

As we see below, the canonical ensemble leads to the introduction of something called **the partition function**,  $Z$ , from which all thermodynamic quantities ( $P, E, F, S, \dots$ ) can be found. At the heart of the partition function lies the Boltzmann distribution, which gives the probability that a system in contact with a heat reservoir at a given temperature will have a given energy.

## 4.1 The Boltzmann distribution

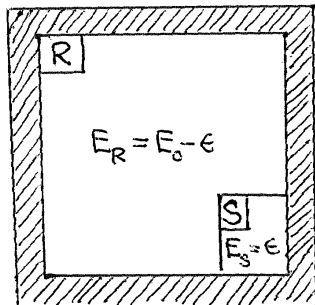


Figure 1

Consider a system  $S$  in contact with a heat reservoir  $R$  at temperature  $T$  as shown in Figure 1. The whole,  $(R + S)$ , forms an isolated system with fixed energy  $E_0$ . Heat can be exchanged between  $S$  and  $R$ , but  $R$  is so large that its temperature remains  $T$  if heat is exchanged. We now ask: What is the probability  $p_i$  that the system  $S$  is in a particular microstate with energy  $E_i$ ?

We assume that  $S$  and  $R$  are independent of each other. The total number of microstates

$$\Omega = \Omega_R \times \Omega_S.$$

Now, if we specify the microstate of  $\Omega_S$  to be the  $i$ th microstate,  $\Omega_S = 1$ , we have

$$\Omega = \Omega(E_0, E_i) = \Omega_R(E_0 - E_i) \times 1.$$

Thus, the probability  $p_i$  of  $S$  being in a state with energy  $E_i$  depends on the number of microstates of  $R$  with energy  $E_0 - E_i$ ,

$$p_i = p_i(E_i) = \frac{\Omega_R(E_0 - E_i)}{\Omega(E_0)} = \frac{\text{number of microstates of } (S + R) \text{ with } S \text{ in state } i}{\text{total number of microstates of } (S + R)}.$$

Now, use the Boltzmann relation  $S = k_B \ln \Omega$  from Eq. (1) of Chap. 3,

$$\Omega_R(E_0 - E_i) = \exp \left[ \frac{1}{k_B} S_R(E_0 - E_i) \right].$$

If  $R$  is a good reservoir it must be much bigger than  $S$ . So, let's Taylor expand around  $E_0$ :

$$S_R(E_0 - E_i) = S_R(E_0) - E_i \left[ \left( \frac{\partial S_R}{\partial E} \right)_{V,N} \right]_{E=E_0} + \frac{1}{2!} E_i^2 \left[ \left( \frac{\partial^2 S_R}{\partial E^2} \right)_{V,N} \right]_{E=E_0} + \dots$$

But, from the thermodynamic relations involving partial derivative of  $S$ ,

$$\begin{aligned}\left(\frac{\partial S_R}{\partial E}\right)_{V,N} &= \frac{1}{T}, \\ \left(\frac{\partial^2 S_R}{\partial E^2}\right)_{V,N} &= \left[\frac{\partial(1/T)}{\partial E}\right]_{V,N} = -\frac{1}{T^2} \left(\frac{\partial T}{\partial E}\right)_{V,N} = -\frac{1}{T^2 C_V}.\end{aligned}$$

Thus,

$$S_R(E_0 - E_i) = S_R(E_0) - \frac{E_i}{T} - \frac{E_i^2}{2T^2 C_V^{(R)}} + O(E_i^3).$$

If  $R$  is large enough,  $C_V^{(R)}T \gg E_i$  and only the first two terms in the expansion are nonzero,

$$p_i \propto \Omega_R(E_0 - E_i) = \exp\left[\frac{1}{k_B} S_R(E_0 - E_i)\right] = \exp\left[\frac{S_R(E_0)}{k_B} - \frac{E_i}{k_B T}\right] = \text{const.} \times e^{-E_i/k_B T}$$

since  $S_R(E_0)$  is a constant, independent of the microstate index  $i$ . Call this constant of proportionality  $1/Z$ , we have

$$p_i = \frac{1}{Z} e^{-E_i/k_B T}, \quad (1)$$

where  $Z$  is determined from normalization condition. So if we sum over all microstates

$$\sum_i p_i = 1$$

we have

$$Z = \sum_i e^{-E_i/k_B T}, \quad (2)$$

where sum on  $i$  runs over all distinct microstates.  $p_i$  of Eq. (1) is the Boltzmann distribution function and  $Z$  is called the partition function of the system  $S$ . As we will see later, partition function  $Z$  is very useful because all other thermodynamic quantities can be calculated through it.

The internal energy can be calculated by the average

$$\langle E \rangle = \sum_i E_i p_i = \frac{1}{Z} \sum_i E_i e^{-E_i/k_B T}. \quad (3)$$

We will discuss calculation of other thermodynamic quantities later. We want to emphasize also that the index  $i$  labels the microstates of  $N$ -particles and  $E_i$  is the

total energy. For example, a microstate for the case of an spin-1/2 paramagnet of  $N$  independent particles is a configuration of  $N$  spins (up or down):

$$i = (\uparrow, \uparrow, \downarrow, \dots, \downarrow).$$

For a gas of  $N$  molecules, however,  $i$  represents a set of values of positions and momenta as

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

as discussed in Chap. 3

[Ref.: (1) Mandl 2.5; (2) Bowley and Sánchez 5.1-5.2]

## 4.2 The independent-particle approximation: one-body partition function

If we ignore interactions between particles, we can represent a microstate of  $N$ -particle system by a configuration specifying each particle's occupation of the one-body states,

$$i = (k_1, k_2, \dots, k_N), \quad (4)$$

meaning particle 1 in single-particle state  $k_1$ , particle 2 in state  $k_2$ , etc., (e.g., the spin configurations for a paramagnet). The total energy in the microstate of the  $N$  particles is then simply the sum of energies of each particle,

$$E_i = \epsilon_{k_1} + \epsilon_{k_2} + \dots + \epsilon_{k_N},$$

where  $\epsilon_{k_1}$  is the energy of particle 1 in state  $k_1$  etc. The partition function of the  $N$ -particle system of Eq. (2) is then given by,

$$Z = Z_N = \sum_i e^{-E_i/k_B T} = \sum_{k_1, k_2, \dots, k_N} \exp \left[ -\frac{1}{k_B T} (\epsilon_{k_1} + \epsilon_{k_2} + \dots + \epsilon_{k_N}) \right].$$

If we further assume that  $N$  particles are **distinguishable**, summations over  $k$ 's are independent of one another and can be carried out separately as

$$\begin{aligned} Z_N &= \sum_{k_1, k_2, \dots, k_N} e^{-\epsilon_{k_1}/k_B T} e^{-\epsilon_{k_2}/k_B T} \dots e^{-\epsilon_{k_N}/k_B T} \\ &= \left( \sum_{k_1} e^{-\epsilon_{k_1}/k_B T} \right) \left( \sum_{k_2} e^{-\epsilon_{k_2}/k_B T} \right) \dots \left( \sum_{k_N} e^{-\epsilon_{k_N}/k_B T} \right). \end{aligned} \quad (5)$$

We notice that in the last equation, the summation in each factor runs over the same complete single-particle states. Therefore, they are all equal,

$$\sum_{k_1} e^{-\epsilon_{k_1}/k_B T} = \sum_{k_2} e^{-\epsilon_{k_2}/k_B T} = \dots = \sum_{k_N} e^{-\epsilon_{k_N}/k_B T}.$$

Hence, the  $N$ -particle partition function in the independent-particle approximation is,

$$Z_N = (Z_1)^N$$

where

$$Z_1 = \sum_{k_1} e^{-\epsilon_{k_1}/k_B T}$$

is the one-body partition function. We notice that the index  $k_1$  in the above equation labels **single particle state** and  $\epsilon_{k_1}$  is the corresponding energy of the single particle, contrast to the index  $i$  used earlier in Eqs. (1) and (2), where  $i$  labels the microstate of total  $N$ -particle system and  $\epsilon_i$  is the corresponding total energy of the system.

The above analysis are valid for models of solids and paramagnets where particles are localized hence distinguishable. However, particles of a gas are identical and are moving around the whole volume; they are indistinguishable. The case of  $N$  **indistinguishable** particles is more complicated. The fact that permutation of any two particles in a configuration  $(k_1, k_2, \dots, k_N)$  of Eq. (3) does not produce a new microstate imposes restrictions on the sum  $\sum_i = \sum_{k_1, k_2, \dots, k_N}$ ; the number of microstates is hence much reduced and sums over  $k$ 's are not longer independent of each other. The simple separation method of Eq. (5) is invalid. For a classical ideal gas, if we assume the  $N$  particles are in different single-particle states (imagine  $N$  molecules in  $N$  *different* cubicles of size  $h^3$  in the phase-space  $(\mathbf{r}, \mathbf{p})$ ), the overcounting factor is clearly  $N!$  as there are  $N!$  permutations for the same microstate  $(k_1, k_2, \dots, k_N)$ . We hence approximate the partition function of  $N$  classical particles as,

$$Z_N \approx \frac{1}{N!} (Z_1)^N.$$

Summary of the partition function in the independent-particle approximation

- $N$  distinguishable particles (models of solids and paramagnets):

$$Z_N = (Z_1)^N; \tag{6}$$

- $N$  indistinguishable classical particles (classical ideal gas):

$$Z_N \approx \frac{1}{N!} (Z_1)^N; \tag{7}$$

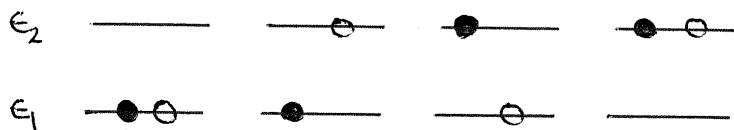
- In both Eqs. (6) and (7),

$$Z_1 = \sum_{k_1} e^{-\epsilon_{k_1}/k_B T} \tag{8}$$

is the one-body partition function, with  $\epsilon_{k_1}$  the single-particle energy.

**Example.** Consider a system of two free (independent) particles. Assuming that there are only two single-particle energy levels  $\epsilon_1, \epsilon_2$ , by enumerating all possible two-body microstates, determine the partition functions  $Z_2$  if these two particles are (a) distinguishable and (b) indistinguishable.

**Solution:** (a) We list all four possible microstates of two distinguishable particles in the following **occupation diagram**:



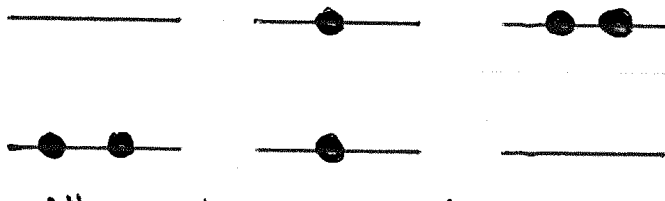
Notice that the 2nd and 3rd states are different states as two particles are distinguishable. By definition, the partition function of the two-particle system is given by

$$Z_2 = \sum_i e^{-E_i/k_B T} = e^{-2\epsilon_1/k_B T} + 2e^{-(\epsilon_1+\epsilon_2)/k_B T} + e^{-2\epsilon_2/k_B T} = (e^{-\epsilon_1/k_B T} + e^{-\epsilon_2/k_B T})^2 = Z_1^2,$$

agreed with the general formula  $Z_N = (Z_1)^N$  of Eq. (6). The average energy of the two-particle system is given by, according to Eq. (3)

$$\langle E \rangle = \frac{1}{Z} \sum_i E_i e^{-E_i/k_B T} = \frac{1}{Z_2} \left[ (2\epsilon_1) e^{-2\epsilon_1/k_B T} + 2(\epsilon_1 + \epsilon_2) e^{-(\epsilon_1+\epsilon_2)/k_B T} + (2\epsilon_2) e^{-2\epsilon_2/k_B T} \right].$$

(b) For two identical particles, there are only three microstates as shown in the following occupation-number diagram.



The corresponding partition function is then given by

$$Z_2 = \sum_i e^{-E_i/k_B T} = e^{-2\epsilon_1/k_B T} + e^{-(\epsilon_1+\epsilon_2)/k_B T} + e^{-2\epsilon_2/k_B T}.$$

Notice that this partition function of two identical particles  $Z_2 \neq \frac{1}{2!} Z_1^2$  as given by Eq. (7). Only the middle term has same weight as given by  $\frac{1}{2!} Z_1^2$ . The average energy of the two-particle system is

$$\langle E \rangle = \frac{1}{Z} \sum_i E_i e^{-E_i/k_B T} = \frac{1}{Z_2} \left[ (2\epsilon_1) e^{-2\epsilon_1/k_B T} + (\epsilon_1 + \epsilon_2) e^{-(\epsilon_1+\epsilon_2)/k_B T} + (2\epsilon_2) e^{-2\epsilon_2/k_B T} \right].$$

For the case of a two-particle system with three states, see Q1 of Example Sheet 9.

Note:

- (a) It is important to note that the sum in Eq. (8) runs over all single-particle states  $k_1$ , and not over all different energies. A given energy eigenvalue  $\epsilon_{k_1}$  may be degenerate, i.e., belong to more than one (different) state. We can also express Eq. (8) alternatively as a sum over distinct energy levels, as

$$Z_1 = \sum_{k_1} e^{-\epsilon_{k_1}/k_B T} = \sum_{\epsilon_{k_1}} g(\epsilon_{k_1}) e^{-\epsilon_{k_1}/k_B T}, \quad (9)$$

where  $g(\epsilon_{k_1})$  is the degeneracy factor at energy level  $\epsilon_{k_1}$ .

- (b) One-body partition function  $Z_1$  is a useful quantity for determining  $N$ -particle partition function in the independent-particle approximation.  $Z_1$  itself has no physical meaning as temperature is undefined for a single particle system.
- (c) Even if we ignore interaction completely (i.e., in the independent-particle approximation) and restrict to classical mechanics, many-body effects still appear for  $N$  identical particles as demonstrated by the  $1/N!$  factor.
- (d) Equation (6) is invalid in the low temperature limit where quantum effects dominate (e.g., a significant portion of particles of a quantum gas are in the zero-momentum state: the Bose-Einstein condensation). A proper way to tackle the problems of identical particles is to introduce occupation-number configurations and to employ **grandcanonical ensemble**. A third-year course (*Fermions and Bosons*) will discuss this subject in details.

[Ref.: (1) Mandl 7.1]

### 4.3 Examples of partition function calculations

We will see later all thermodynamic quantities ( $E, S, F, P$  etc.) can be determined via the partition function  $Z$ . So it is important to learn how to calculate the partition function. In general, calculation of partition function of a thermodynamic system is complicated due to the interactions between particles. In this section, we show a few examples in the independent-particle approximation in which interactions are ignored, using Eqs. (6)-(8) of the last section.

**Example 1.** The ideal spin-1/2 paramagnet. Only 2 energy states for each spin,  $k_1 = \uparrow, \downarrow$ , with energies

$$\epsilon_{\uparrow} = -\mu B, \quad \epsilon_{\downarrow} = +\mu B,$$



where  $\mu$  is the magnetic moment of one spin particle and  $B$  is the magnetic field. The one-body partition function is therefore

$$Z_1 = \sum_{k_1} e^{-\epsilon_{k_1}/k_B T} = e^{\mu B/k_B T} + e^{-\mu B/k_B T} = 2 \cosh(\mu B/k_B T).$$

The partition function for the  $N$  spins (distinguishable particles) is

$$Z_N = [2 \cosh(\mu B/k_B T)]^N. \quad (10)$$

**Example 2.** A simple model for a one-dimensional solid consists of  $M$  independent oscillators, each with energy

$$\epsilon(x, p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2,$$

where  $\omega$  is the angular frequency. The state of a classical particle is specified by  $k = (x, p)$  and the sum becomes integral

$$\sum_k = \frac{1}{h} \int dx dp,$$

as discussed in Chap. 3.5. The one-body partition function is therefore given by

$$\begin{aligned} Z_1 &= \sum_k e^{-\epsilon_k/k_B T} = \frac{1}{h} \int dx dp e^{-\epsilon(x,p)/k_B T} \\ &= \frac{1}{h} \int_{-\infty}^{\infty} dp e^{-p^2/2mk_B T} \int_{-\infty}^{\infty} dx e^{-m\omega^2 x^2/2k_B T} \\ &= \frac{1}{h} \sqrt{2\pi mk_B T} \sqrt{\frac{2\pi k_B T}{m\omega^2}} = \frac{2\pi k_B T}{h\omega}, \end{aligned}$$

where we have used the Gaussian integral

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}, \quad a > 0.$$

The partition function of  $M$  oscillators (distinguishable) is

$$Z_M = (Z_1)^M = \left( \frac{2\pi k_B T}{h\omega} \right)^M. \quad (11)$$

**Example 3.** The classical ideal gas of  $N$  particles in a volume  $V$ . In this case, the single particle energy is

$$\epsilon(\mathbf{r}, \mathbf{p}) = \epsilon(p) = \frac{p^2}{2m} = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2).$$

The one-body partition function is

$$Z_1 = \frac{1}{h^3} \int d^3r d^3p e^{-\epsilon(p)/k_B T}.$$

As the energy  $\epsilon(p)$  is  $r$  independent, the integral over real space produces a factor of volume  $V$  and the integral over momentum is,

$$\begin{aligned} \int d^3p e^{-p^2/2mk_B T} &= \left( \int_{-\infty}^{\infty} dp_x e^{-p_x^2/2mk_B T} \right) \left( \int_{-\infty}^{\infty} dp_y e^{-p_y^2/2mk_B T} \right) \left( \int_{-\infty}^{\infty} dp_z e^{-p_z^2/2mk_B T} \right) \\ &= \sqrt{2\pi mk_B T} \cdot \sqrt{2\pi mk_B T} \cdot \sqrt{2\pi mk_B T} = (2\pi mk_B T)^{3/2}, \end{aligned}$$

where we have again used the Gaussian integral formula given above. The one-body partition function is

$$Z_1 = V \left( \frac{2\pi mk_B T}{h^2} \right)^{3/2} \quad (12)$$

and the partition function for a classical ideal gas of  $N$  identical molecules in a volume  $V$  is

$$Z_N = \frac{1}{N!} Z_1^N = \frac{V^N}{N!} \left( \frac{2\pi mk_B T}{h^2} \right)^{3N/2}. \quad (13)$$

Later, we will see the importance of the factor  $1/N!$  when we calculated thermodynamic quantities such as energy, entropy, etc.

**Example 4.** The Einstein model of a one-dimensional solid. Revisit Example 2 above but now consider the oscillators are quantum mechanical. A single quantum oscillator has energies

$$\epsilon_n = \hbar\omega \left( n + \frac{1}{2} \right), \quad n = 0, 1, 2, 3, \dots$$

The one-particle partition function is

$$\begin{aligned} Z_1 &= \sum_{n=0,1,2,\dots} e^{-\epsilon_n/k_B T} = e^{-\hbar\omega/2k_B T} \sum_{n=0,1,2,\dots} e^{-\hbar\omega n/k_B T} \\ &= e^{-\hbar\omega/2k_B T} \frac{1}{1 - e^{-\hbar\omega/k_B T}} = \frac{1}{2 \sinh(\hbar\omega/2k_B T)}, \end{aligned}$$

where in the third equation, we have used the formula

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}.$$

The partition function of  $M$  quantum oscillators is

$$Z_M = (Z_1)^M = \frac{1}{[2 \sinh(\hbar\omega/2k_B T)]^M}.$$

We will see later the thermodynamics of quantum oscillators reduces to the classical one in the high temperature limit but is completely different in the low temperature limit.

In the next sections, we will discuss how to calculate energy, entropy and other thermodynamic quantities from partition functions.

[Ref.: (1) Mandl 2.5; (2) Bowley and Sánchez 5.1-5.2]

#### 4.4 The partition function and other state functions

Although the partition function,  $Z = \sum_i e^{-E_i/k_B T}$ , has appeared just as a normalization constant, its usefulness is much deeper than that. Loosely, whereas for an isolated system (at fixed  $E, N, V$ ) all the thermodynamic properties  $S, T, P, \dots$  could be derived from  $\Omega(E, N, V)$ , as for a system in thermal equilibrium at temperature  $T$  the same role is played by  $Z = Z(T, N, V)$  for a hydrostatic system (or  $Z = Z(T, N, B)$  for a magnetic system, etc.). In the last section we have calculated  $Z$  of several systems in the independent-particle approximation. Here we discuss in general how to calculate other properties from  $Z$ .

First, we consider the energy  $E$ . The average energy  $\langle E \rangle$  is calculated for the canonical ensemble (with  $\nu$  copies of the system and  $\nu_i$  of these copies in the  $i$ -microstate, recall Chap. 3.2) as

$$\langle E \rangle = \frac{1}{\nu} \sum_{\lambda=1}^{\nu} E_{\lambda} = \frac{1}{\nu} \sum_i \nu_i E_i = \sum_i p_i E_i,$$

or

$$\langle E \rangle = \frac{1}{Z} \sum_i E_i e^{-E_i/k_B T} = \frac{\sum_i E_i e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}},$$

As given by Eq. (3) in Sec. 4.1. Now, in this expression, the numerator can be obtained from the denominator by differentiating the denominator with respect to  $(-1/k_B T)$ . That is a bit awkward, so let's define

$$\beta \equiv \frac{1}{k_B T}. \tag{14}$$

Hence

$$\langle E \rangle = \frac{\sum_i E_i e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}} = -\frac{1}{Z} \left( \frac{\partial Z}{\partial \beta} \right)_{N, V},$$

or, more formally

$$\langle E \rangle = - \left( \frac{\partial \ln Z}{\partial \beta} \right)_{N,V} = k_B T^2 \left( \frac{\partial \ln Z}{\partial T} \right)_{N,V}. \quad (15)$$

Next, we consider entropy. Clearly, if the system is in a given (fixed) microstate it has no entropy. Instead, we talk now about the entropy of the ensemble since the many copies can be in many different microstates. So, let the ensemble have  $\nu$  copies of the system and the ensemble entropy,  $S_\nu = \nu \langle S \rangle$ , where  $\langle S \rangle$  is the average system entropy. Let the ensemble have  $\nu_i$  copies in the  $i$ th microstate, so the total number of ways of arranging this is

$$\Omega_\nu = \frac{\nu!}{\nu_1! \nu_2! \nu_3! \cdots}.$$

Use Stirling formula, we have

$$\ln \Omega_\nu = \nu \ln \nu - \nu - \sum_i (\nu_i \ln \nu_i - \nu_i) = \sum_i \nu_i (\ln \nu - \ln \nu_i) = - \sum_i \nu_i \ln \frac{\nu_i}{\nu},$$

but  $p_i = \nu_i/\nu$ ,

$$\ln \Omega_\nu = -\nu \sum_i p_i \ln p_i.$$

So, from Boltzmann's formula:  $S_\nu = k_B \ln \Omega_\nu$  and  $\langle S \rangle = S_\nu/\nu$ , we have system entropy

$$\langle S \rangle = -k_B \sum_i p_i \ln p_i. \quad (16)$$

Let us now apply the general Eq. (16) to the case of a system in thermal equilibrium at a temperature  $T$ , where  $p_i$  is given by the Boltzmann distribution of Eq. (1),

$$\begin{aligned} \langle S \rangle &= -k_B \sum_i p_i \ln \frac{e^{-\beta E_i}}{Z} = -k_B \sum_i p_i (-\beta E_i - \ln Z) \\ &= k_B \beta \sum_i p_i E_i + k_B Z \sum_i p_i = k_B \beta \langle E \rangle + k_B \ln Z \end{aligned}$$

where we have used the definition  $\langle E \rangle = \sum_i p_i E_i$  and normalization condition  $\sum_i p_i = 1$ . Rearrange the above equation

$$k_B T \ln Z = -(\langle E \rangle - T \langle S \rangle) = -\langle F \rangle$$

where  $F \equiv E - TS$  is the Helmholtz free energy. Hence we write

$$\langle F \rangle = -k_B T \ln Z. \quad (17)$$

The other thermodynamic quantities can then be calculated by partial derivatives of  $F$  as given in Chap. 2.

Summary of basic formulas for canonical ensemble

- First calculate partition function

$$Z_N = \sum_i e^{-E_i/k_B T}. \quad (18)$$

- Then the Helmholtz free energy

$$F = -k_B T \ln Z_N. \quad (19)$$

- The entropy and equation of state are obtained by

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V,N}; \quad P = - \left( \frac{\partial F}{\partial V} \right)_{T,N}. \quad (20)$$

- The internal energy can be calculated using

$$E = - \left( \frac{\partial \ln Z_N}{\partial \beta} \right)_{N,V} = k_B T^2 \left( \frac{\partial \ln Z}{\partial T} \right)_{N,V}, \quad (21)$$

or simply from

$$E = F + TS. \quad (22)$$

In the above formulas, we have dropped the average notation  $\langle \rangle$  for  $F$ ,  $E$  and  $S$ . This is because in the large  $N$  limit, the fluctuations around the average value very small, typically proportional to  $1/\sqrt{N}$ . In the next section we will discuss these fluctuations for the energy  $\langle E \rangle$ .

Note:

- For magnetic systems the term  $-PdV$  is replaced by  $-m dB$ ; and hence we have  $m = -(\partial F/\partial B)_{T,N}$  instead.]
- Equations (19)-(20) are very reminiscent of those we met in the case of an isolated system in Chap. 3 (Eqs. (1)-(3)). Whereas the entropy  $S$  played a central role for isolated systems, that role is now played by  $F$  for system in contact with a heat bath. It is no real surprise that  $F$  is now the key state function for system at fixed  $T$ , since that is just how it was introduced in thermodynamics.
- In the independent-particle approximation discussed in Sec. 4.2, the partition function can be written as

$$Z_N \begin{cases} = (Z_1)^N, & \text{distinguishable particles;} \\ \approx \frac{1}{N!} (Z_1)^N, & \text{indistinguishable particles,} \end{cases}$$

where  $Z_1$  is the one-body partition function. After taking log, we have

$$\ln Z_N \begin{cases} = N \ln Z_1, & \text{distinguishable particles;} \\ \approx N \ln Z_1 - \ln N!, & \text{indistinguishable particles,} \end{cases}$$

we have, for both the distinguishable and indistinguishable particles,

$$E = E_N = - \left( \frac{\partial \ln Z_N}{\partial \beta} \right)_{N,V} = -N \left( \frac{\partial \ln Z_1}{\partial \beta} \right)_{N,V} = N E_1,$$

where  $E_1 = -\partial \ln Z_1 / \partial \beta$  is the average energy of a single particle. Namely, in the independent-particle approximation, the total internal energy of  $N$  particles (distinguishable or indistinguishable) is equal to  $N$  times the average energy of a single particle.

We have calculated the partition functions  $Z_N$  for a number of systems in Section 4.3. Using Eqs. (19)-(21), it is straightforward to calculate other thermodynamic quantities. In the rest of the chapter we will do just that and also discuss the physical implications of our results.

[Refs.: (1) Mandl 2.5; (2) Bowley and Sánchez 5.3-5.6.]

## 4.5 The energy fluctuations

In this section we will focus on the energy fluctuations and show it is small in the large  $N$  limit. From  $\langle E \rangle$  we can calculate heat capacity

$$\langle C_V \rangle = \left( \frac{\partial \langle E \rangle}{\partial T} \right)_{N,V} = k_B \beta^2 \left( \frac{\partial^2 \ln Z}{\partial \beta^2} \right)_{N,V}. \quad (23)$$

$\langle E \rangle$  in canonical ensemble is only known as an *average*. It will also statistically fluctuate. We can also examine the *fluctuations*, and see how big they are. We define

$$(\Delta E)^2 \equiv \langle E^2 \rangle - \langle E \rangle^2.$$

Clearly

$$\langle E^2 \rangle = \frac{\sum_i E_i^2 e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = \frac{1}{Z} \left( \frac{\partial^2 Z}{\partial \beta^2} \right)_{N,V}.$$

Hence, (all derivatives in the followings are at constant  $N, V$ )

$$\begin{aligned} (\Delta E)^2 &= \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left( -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 = \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) = \left( \frac{\partial^2 \ln Z}{\partial \beta^2} \right)_{N,V} \\ &= - \left( \frac{\partial \langle E \rangle}{\partial \beta} \right)_{N,V} = - \left( \frac{\partial \langle E \rangle}{\partial T} \right)_{N,V} \frac{dT}{d\beta} = k_B T^2 \langle C_V \rangle. \end{aligned}$$

or

$$(\Delta E)^2 = \left( \frac{\partial^2 \ln Z}{\partial \beta^2} \right)_{N,V} = k_B T^2 C_V. \quad (24)$$

Note: For a normal macroscopic system  $\langle E \rangle \propto Nk_B T$ , and  $C_V \propto Nk_B$ , hence

$$\frac{\Delta E}{\langle E \rangle} \propto \frac{\sqrt{N} k_B T}{N k_B T} = \frac{1}{\sqrt{N}}.$$

So, if  $N \approx 10^{24}$ ,  $\Delta E / \langle E \rangle \approx 10^{-12}$ , an unobservable tiny number! So, for most normal macroscopic systems the fluctuations are totally negligible and we can forget the notation  $\langle \rangle$ , and write  $\langle E \rangle \rightarrow E$ ,  $\langle C_V \rangle \rightarrow C_V$ , etc., and there is no real difference between an isolated system of fixed energy  $E$  and one in contact with a heat bath at the same temperature  $T = (\partial E / \partial S)_{N,V}$ .

[Note: A notable exception occurs near critical points, where the distinction between 2 phases disappears. Near critical points  $\langle C_V \rangle$  can be very large and the fluctuations may not be negligible. This can sometimes be observed as "critical opalescence" where the meniscus between the liquid and gas phases disappears, and the mixture becomes milky-looking and opaque as it scatters light.]

[Ref.: (1) Mandl 2.5]

## 4.6 Example: The ideal spin-1/2 paramagnet

Now we revisit the problem of the ideal spin-1/2 paramagnet at fixed temperature. We consider  $N$  spins in a magnetic field  $B$ . Each spin has only two states, either up with energy ( $\epsilon_\uparrow = -\mu B$ ) or down with energy ( $\epsilon_\downarrow = +\mu B$ ).

From Sec. 4.3, the partition function of the paramagnet is calculated as

$$Z_N = (Z_1)^N = [2 \cosh(\beta \mu B)]^N, \quad \ln Z_N = N \ln (2 \cosh(\beta \mu B)),$$

where  $\beta = 1/k_B T$ . We can now calculate the total average energy easily using Eq. (21)

$$E = -\frac{\partial \ln Z_N}{\partial \beta} = -\frac{N}{\cosh(\beta \mu B)} \cdot \sinh(\beta \mu B) \cdot (\mu B),$$

hence

$$E = -N \mu B \tanh \frac{\mu B}{k_B T}. \quad (25)$$

The heat capacity at constant magnetic field is calculated as

$$C_B = \left( \frac{\partial E}{\partial T} \right)_B = -N \mu B \operatorname{sech}^2 \frac{\mu B}{k_B T} \cdot \left( -\frac{\mu B}{k_B T^2} \right) = N \frac{\mu^2 B^2}{k_B T^2} \operatorname{sech}^2 \frac{\mu B}{k_B T}, \quad (26)$$

where we have used  $\frac{d}{dx} \tanh x = \text{sech}^2 x$ , and  $\text{sech} x \equiv 1/\cosh x$ .

We can plot  $E$  and  $C_B$  as function of  $T$  using the fact that, as  $x \rightarrow 0$ ,  $\sinh x \rightarrow x$  and  $\cosh x \rightarrow 1$ ; and as  $x \rightarrow \infty$ ,  $\sinh x \rightarrow e^x/2$  and  $\cosh x \rightarrow e^x/2$ . Hence, from Eq. (25)

$$E \rightarrow -N\mu B, \quad T \rightarrow 0$$

just as expected, since all spins will be in lowering energy spin-up state. On the other hand,  $\tanh x \rightarrow x$  as  $x \rightarrow 0$ , hence

$$E \rightarrow -\frac{N\mu^2 B^2}{k_B T}, \quad T \rightarrow \infty$$

again, as expected since as  $T \rightarrow \infty$ , the number of up spins and down spins become nearly equal and their energies cancel each other out. These behaviors are shown in Figure 2.

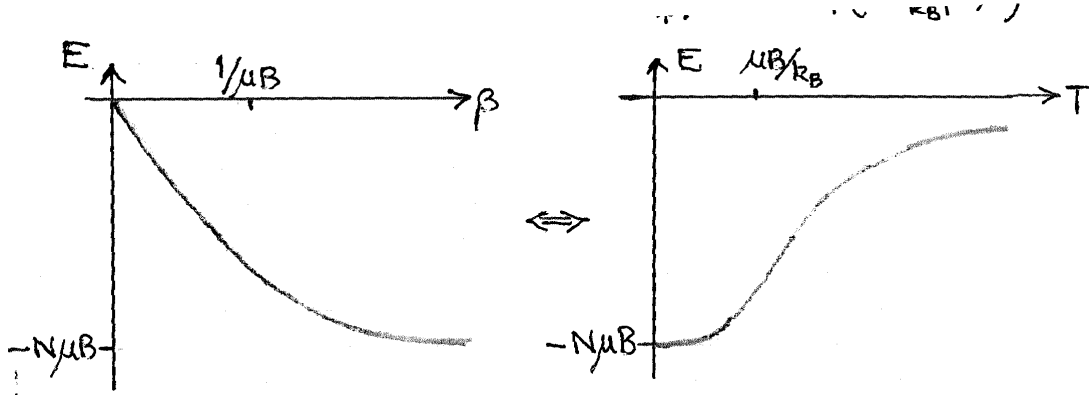


Figure 2

We can similarly plot  $C_B$ . From Eq. (26), in the limit  $T \rightarrow 0$  ( $\beta \rightarrow \infty$ ),

$$C_B \rightarrow N k_B (\mu B \beta)^2 4 e^{-2\mu B \beta} = N k_B \left( \frac{2\mu B}{k_B} \right)^2 \frac{1}{T^2} e^{-2\mu B/k_B T}$$

or, using the fact that exponential  $\rightarrow 0$  faster than  $1/T^2 \rightarrow \infty$ ,

$$C_B \rightarrow 0, \quad T \rightarrow 0.$$

This behavior, which is quite general, is also easy to understand. Thus, at low  $T$ , thermal fluctuations that flip a spin are rare  $\rightarrow$  very difficult for the system to absorb heat. Quantization of energy levels  $\rightarrow$  there is always a minimum excitation energy for any system, and hence, if  $T$  is low enough, the system can't absorb heat.



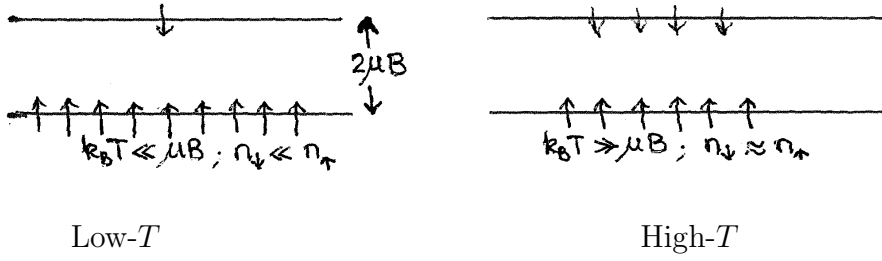


Figure 3

At the opposite limit,

$$C_B \rightarrow \frac{N\mu^2 B^2}{k_B} \frac{1}{T^2}, \quad T \rightarrow \infty.$$

The high  $T$  behavior arises because  $n_\downarrow$  is always smaller than  $n_\uparrow$ . As  $T \rightarrow \infty$ ,  $n_\downarrow$  approaches  $n_\uparrow$  and raising  $T$  even higher makes no difference, i.e., the system has no further capacity to absorb heat. However, this behavior is not universal, since most systems have an infinite number of energy levels of higher and higher energies. Hence in general there is no max. energy and the heat capacity won't fall to zero in the high- $T$  limit. In our case, it is pictorially shown in Figure 3. We sketch the behaviors of  $C_B$  as a function of  $T$  in Figure 4.

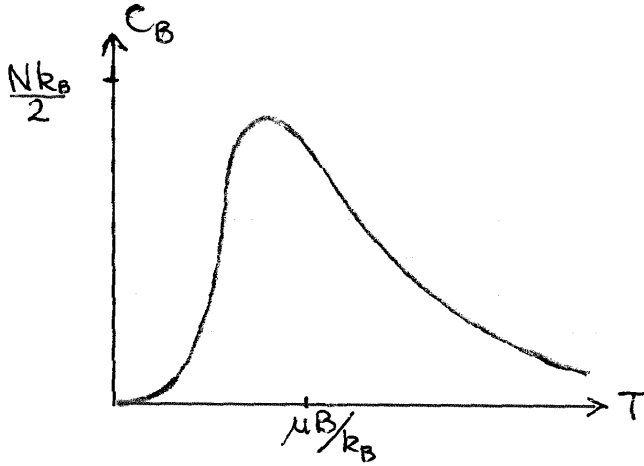


Figure 4

The Helmholtz free energy is calculated as, using Eq. (19)

$$F = -k_B T \ln Z_N = -Nk_B T \ln \left( 2 \cosh \frac{\mu B}{k_B T} \right).$$

The entropy and magnetization are calculated by Eqs. (20)

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

Hence, for the entropy

$$S = Nk_B \{ \ln[2 \cosh(\beta\mu B)] - \beta\mu B \tanh(\beta\mu B) \}. \quad (27)$$

Consider the limits:

(i)  $T \rightarrow 0$  (or  $\beta \rightarrow \infty$ )

$$S \rightarrow Nk_B \{ \ln[2 \times \frac{1}{2} e^{\beta\mu B}] - \beta\mu B \cdot 1 \} \rightarrow 0, \quad T \rightarrow 0$$

which is as expected, since as  $T \rightarrow 0$  all spins are up, i.e. no disorder!

(ii)  $T \rightarrow \infty$  (or  $\beta \rightarrow 0$ )

$$S \rightarrow Nk_B \{ \ln 2 - (\beta\mu B)^2 \} \rightarrow Nk_B \ln 2$$

again, as expected, since as  $T \rightarrow \infty$ , the spins are equally likely to be up or down, entropy per spin is  $k_B \ln 2$  as we have seen in Chap. 3.

The net magnetic moment is given by,

$$m = - \left( \frac{\partial F}{\partial B} \right)_{T,N} = N\mu \tanh(\beta\mu B) = -\frac{E}{B}$$

as expected, since  $E = -mB$  is the equation of state for the ideal paramagnet. The limits:

(i)  $T \rightarrow 0$  (or  $\beta \rightarrow \infty$ )

$$m \rightarrow N\mu$$

for all spins are up; and

(ii)  $T \rightarrow \infty$  (or  $\beta \rightarrow 0$ )

$$\begin{aligned} m &\rightarrow \frac{N\mu^2 B}{k_B T}, \quad \text{Curies's law} \\ &\rightarrow 0 \end{aligned}$$

again, as expected, since nearly equal number of up and down spins.

We plot  $S$  and  $m$  versus  $T$  for several different external fields as shown in Figure 5.

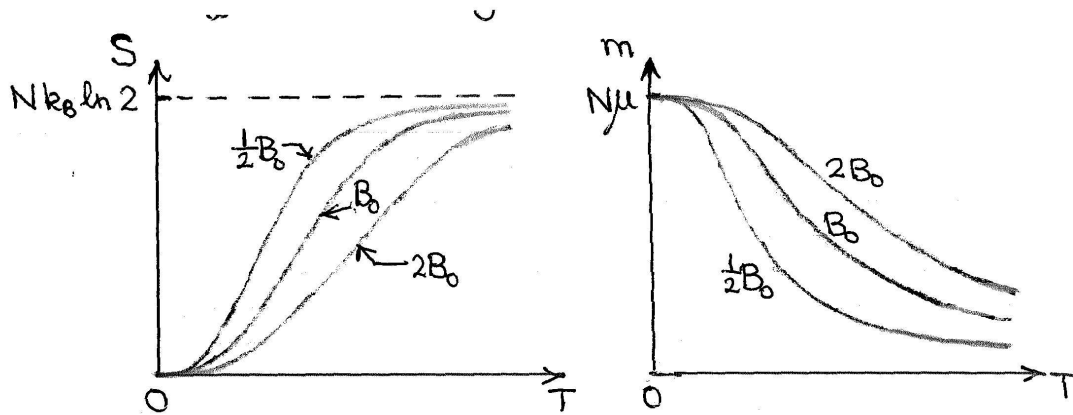


Figure 5

Note: As we have seen above, the entropy  $S \rightarrow 0$  as  $T \rightarrow 0$  as all spins align. This is generally true, namely, a system has no disorder in the limit of  $T \rightarrow 0$ . This is **the third law of thermodynamics**:

**The entropy of any system  $S \rightarrow 0$  as  $T \rightarrow 0$ .**

In the next section, we discuss a way to reach low temperature limit using paramagnets.

[Refs.: (1) Mandl 3; (2) Bowley and Sánchez 5.7.]

#### 4.7 Adiabatic demagnetization and the third law of thermodynamics

By magnetizing and demagnetizing a paramagnet sample, while controlling the heat flow, we can lower its temperature. Thus, referring to the above  $S$  vs.  $T$  curves for the ideal paramagnet:

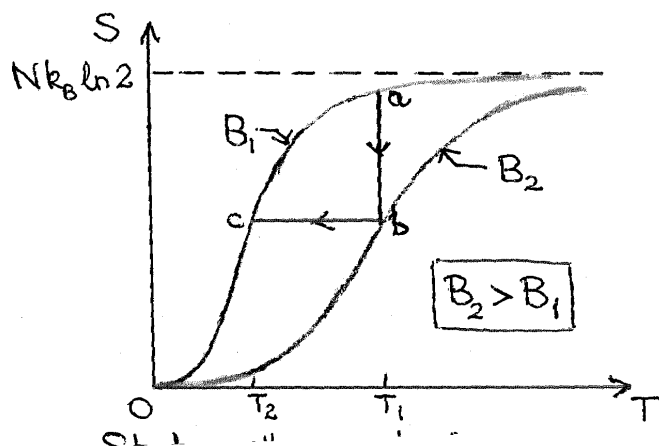
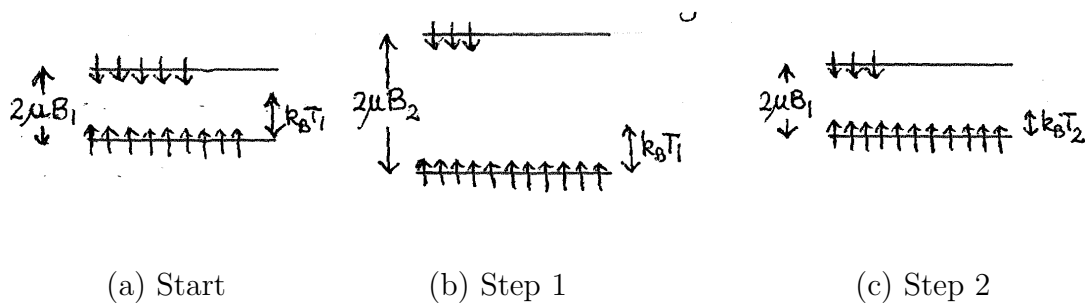


Figure 6

Start with sample in magnetic field  $B_1$  at an (already fairly low) temperature  $T_1$ .

- Step 1: **isothermal magnetization**: increase the field from  $B_1 \rightarrow B_2$  at constant  $T$  (i.e., in contact with heat bath). Entropy  $S$  hence decreases as spins align in stronger field (i.e., more ordered).
- Step 2: **adiabatic demagnetization**: now isolate the system and demagnetize (i.e., reduce  $B$  from  $B_2 \rightarrow B_1$ ).  $\Delta Q = 0$ , and if the process is quasistatic and reversible,  $\Delta S = 0$ . From the plot we see  $T$  reduces  $T_1 \rightarrow T_2$ ; or from Eq. (15)  $S$  is a function of  $B/T$  only, hence for constant  $S$  and  $B$  reduces,  $T$  must reduce by a same factor.

The figures below show what happens to the spins:



In the step 1, we increase the level spacing but keep  $T$  constant; population of upper level falls. In step 2 we reduce the level spacing again, but as the process is now adiabatic (spins isolated) there is no change in level occupations, the temperature is lowered.

This is actually a practical way to reach quite low temperatures, to small fractions of 1 K. If we start with a large sample we could repeat the process with a small sub-sample, with rest acting as a heat bath. However at each repeat of Steps 1 and 2 we would reduce the temperature by less and less, as the curves come together as  $T \rightarrow 0$ . **Thus it is impossible to reach  $T \rightarrow 0$  in a finite number of steps in this way.** This is just one example of **the third law of thermodynamics**: namely, either

- absolute zero is unattainable (in a finite number of steps) or, more precisely,
- The entropy of any aspect of any system,  $S \rightarrow 0$  as  $T \rightarrow 0$ .

Note: The (b) statement implies that the ground state is non-degenerate so that all particles fall into the same state as  $T \rightarrow 0$ .

[Ref.: (1) Mandl 5.6.]

Thus, we can colloquially state:

The laws of thermodynamics

1. You can't win, you can only break even at best
2. You can only break even at  $T = 0$
3. You can't attain  $T = 0$

Even more snappily, and slightly more cryptically:

The laws of thermodynamics (as played in Monte Carlo)

1. You can't win!
2. You can't even break even!
3. You can't leave the game!

## 4.8 Example: The classical ideal gas

Now it is time to revisit the ideal gas we discussed often in thermodynamics. We hinted before that it would be a challenge problem using microcanonical ensemble approach. We will show that this is not the case using canonical ensemble approach.

We have calculated the partition function of classical ideal gas of  $N$  identical molecules at fixed temperature  $T$  in a volume  $V$  as, Eq. (12)-(13),

$$Z_N = \frac{1}{N!} Z_1^N = \frac{V^N}{N!} \left( \frac{2\pi m k_B T}{h^2} \right)^{3N/2},$$

hence, using Stirling approximation,  $N! \approx (N/e)^N$ ,

$$\ln Z_N = N \ln \left[ e \frac{V}{N} \left( \frac{2\pi m k_B T}{h^2} \right)^{3N/2} \right] \quad (28)$$

Now we follow the standard calculations of canonical ensemble to obtain other thermodynamic quantities. The Helmholtz free energy is obtained from Eq. (19)

$$F = -k_B T \ln Z_N = -k_B T N \left[ \frac{3}{2} \ln \left( \frac{2\pi m k_B T}{h^2} \right) + \ln \frac{V}{N} + 1 \right]. \quad (29)$$

Note: If we did not include the  $1/N!$  factor in  $Z_N$ , the second term in Eq. (29) would be  $\ln V$  instead of the intensive quantity  $\ln(V/N)$ , and  $F$  would not be extensive as required.

The entropy is calculated as, according to Eq. (20),

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V,N} = k_B N \left( \frac{3}{2} \ln \frac{2\pi m k_B T}{h^2} + \ln \frac{V}{N} + \frac{5}{2} \right), \quad (30)$$

which can be compared with Q2(a) of Example Sheet 5

$$S = k_B N \left( \frac{3}{2} \ln \frac{T}{T_0} + \ln \frac{V}{V_0} \right) + \text{const.}$$

Eq. (30) is referred as Sackur-Tetrode equation. It gives **absolute** value of the entropy of a gas at a given temperature  $T$ . (See Q2 of Example Sheet 11 for more details). Apart from the factor  $m$  of atomic mass, it is the same for every substance. At high enough temperature and low enough densities **all** substances behave as ideal gases, and so the Sackur-Tetrode formula can be checked experimentally. Good agreement is found.

The equation of state is obtained by Eq. (20) for pressure,

$$P = - \left( \frac{\partial F}{\partial V} \right)_{T,N} = k_B T N \cdot \frac{1}{V}$$

or, the familiar formula

$$PV = Nk_B T. \tag{31}$$

The internal energy of an ideal gas can be calculated by partial derivative of Eq. (21), or simply from  $F = E - TS$  of Eq. (22)

$$E = F + TS = \frac{3}{2} k_B N T, \tag{32}$$

which is independent of volume  $V$  as expected. The heat capacity at constant volume is

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = \frac{3}{2} k_B N.$$

Note: The entropy  $S$  of Eq. (30) has wrong low- $T$  behavior as  $S \rightarrow -\infty$  in the limit  $T \rightarrow 0$ , in conflict with the 3rd law which states  $S \rightarrow 0$  in the limit  $T \rightarrow 0$ . Two reasons for the problem:

- (a) We have ignored interactions between particles when calculating partition function  $Z_N$ ; these interactions are responsible for the particles condensing into liquids or forming solids at low temperature.
- (b) We have also ignored quantum effects (significant at low temperature) when we considered the properties of indistinguishable particles by assuming particles are in different single-particle state (hence the over-counting factor is simple  $N!$ ). The quantum effect of many particles in the zero-momentum state is responsible for the Bose-Einstein condensation.

Inclusion either of the above two effects will result correct low temperature behavior for the entropy. More detailed discussion for validity of the classical  $Z_N$  above is given by Mandl 7.3.

## 4.9 Vibrational and rotational energy of diatomic molecules

In the last section we consider the classical ideal gas of  $N$  particles. If these particles are diatomic molecules, in addition to the translational motion for the center-of-mass of a molecule, there are also vibrational and rotational motions. We consider

these three motions are independent of one another, hence write the partition function of  $N$  diatomic molecules as

$$Z_N = \frac{1}{N!} (Z_1)^N, \quad Z_1 = Z_1^t Z_1^v Z_1^r \quad (33)$$

where  $Z_1^t$  is the one-body partition function of translational motion, given by Eq. (12),  $Z_1^v$  is that of vibrational motion, and  $Z_1^r$  is that of rotational motion. Here we consider  $Z_1^r$  and  $Z_1^v$  by quantum treatment.

**Vibrational energy contribution.** The energy levels of a quantum simple harmonic oscillator of angular frequency  $\omega$  are

$$\epsilon_n = \left( n + \frac{1}{2} \right) \hbar\omega, \quad n = 0, 1, 2, \dots$$

Hence, the one-body partition function is the same as calculated by Eq. (14) as

$$Z_1 = \sum_{n=0}^{\infty} e^{-(n+1/2)\hbar\omega\beta} = \frac{1}{2 \sinh(\hbar\omega\beta/2)}.$$

Hence, the vibrational energy per molecule at temperature  $T$  is

$$\frac{E^v}{N} = - \left( \frac{\partial \ln Z_1}{\partial \beta} \right) = \frac{1}{2 \sinh(\hbar\omega\beta/2)} \cdot 2 \cosh(\hbar\omega\beta/2) \cdot (\hbar\omega/2)$$

or

$$\frac{E^v}{N} = \frac{1}{2} \hbar\omega \coth(\hbar\omega\beta/2). \quad (34)$$

The two temperature limits:

(i)  $T \rightarrow 0$  ( $\beta \rightarrow \infty$ ),  $\coth(\hbar\omega\beta/2) \rightarrow 1$

$$\frac{E^v}{N} \rightarrow \frac{1}{2} \hbar\omega,$$

just the zero-point energy;

(ii)  $T \rightarrow \infty$  ( $\beta \rightarrow 0$ ),  $\coth(\hbar\omega\beta/2) \rightarrow \frac{2}{\hbar\omega\beta}$ ,

$$\frac{E^v}{N} \rightarrow \frac{1}{\beta} = k_B T.$$



Note: For most diatomic molecules, the high- $T$  limit is reached for  $T \geq 1000$  K.

**Rotational energy contribution.** In classical mechanics the energy of a rigid rotor with moment of inertia  $I$ , rotating with angular velocity  $\omega$  (or angular momentum  $L = I\omega$ ) is  $\epsilon = I\omega^2/2 = L^2/2I$ . In quantum mechanics, the angular momentum is quantized as

$$L^2 \rightarrow l(l+1)\hbar^2, \quad l = 0, 1, 2, \dots$$

and hence the energy levels are

$$\epsilon_l = \frac{l(l+1)\hbar^2}{2I}, \quad l = 0, 1, 2, \dots$$

Also, for each eigenvalue  $l$  we have  $g(\epsilon_l) = (2l+1)$  degenerate magnetic sublevels, specified by quantum number  $m_l = -l, -l+1, \dots, l-1, l$ , all with same energy  $\epsilon_l$ . Hence the one-body partition function is

$$Z_1^r = \sum_{l=0}^{\infty} (2l+1) e^{-l(l+1)\hbar^2\beta/2I}. \quad (35)$$

For general  $\beta$ , we can not specify the above  $Z_1$  further. However, we can look at the low- and high- $T$  limits as follows:

- (a)  $T \rightarrow 0$  ( $\beta \rightarrow \infty$ ), for a good approximation, keeping only the first two terms,

$$Z_1 \rightarrow 1 + 3e^{-\hbar^2\beta/2I}$$

and the rotational energy per molecule is

$$\frac{E^r}{N} \rightarrow 0.$$

- (b)  $T \rightarrow \infty$  ( $\beta \rightarrow 0$ ). In this limit ( $k_B T \gg \hbar^2/2I$ ) there are many thermally accessible energy levels, and the discrete series can be well approximated by a continuum, i.e.,

$$Z_1^r \rightarrow \int_0^{\infty} dl (2l+1) e^{-l(l+1)\hbar^2\beta/2I}$$

and luckily this integral can be exactly evaluated by making the substitution  $x = l(l+1)$  and  $dx = (2l+1)dl$ . And we obtain

$$Z_1^r \rightarrow \frac{2I}{\hbar^2\beta} = \frac{2Ik_B T}{\hbar^2}. \quad (36)$$

and the rotational energy per molecule, using  $\frac{E^r}{N} = -\frac{\partial}{\partial\beta} \ln Z_1^r$

$$\frac{E^r}{N} \rightarrow \frac{1}{\beta} = k_B T, \quad T \rightarrow \infty. \quad (37)$$

For details, see Example Sheet 10. Note: For typical diatomic molecules,  $\hbar^2/2I \approx 10^{-3}$  eV, and so the high- $T$  limit is reached well below room temperature.

**Translational energy contribution.** From Eq. (32) of Sec. 4.8, we have the translational energy per molecule as

$$\frac{E^t}{N} = \frac{3}{2} k_B T. \quad (38)$$

We obtained this result using classical mechanics approach. In the next section we obtain the same result using quantum treatment.

We will see later in Sec. 4.11 that it is no accident that there is a simple relation between energies per molecule in the high- $T$  limit for these three motions. They are examples of the more general equipartition theorem.

[Refs.: (1) Bowley and Sánchez 5.11, 5.12.]

## 4.10 Translational energy of molecules: Quantum treatment

We have calculated the one-body partition function and the energy for the translation motion of  $N$  particles, using classical mechanics approach. Here we repeat the calculation using quantum mechanics. We will see that  $Z_1$  is the same as classical result.

Consider a single free particle (acted on by no forces, potential  $V = 0$ ), contained in a box of lengths  $L_x, L_y, L_z$  with sides parallel, respectively to the  $x, y, z$  axes. Its wavefunction  $\psi = \psi(x, y, z)$  satisfies the free Schrödinger equation inside the box

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(x, y, z) = E \psi(x, y, z).$$

We assume the box is impenetrable so that  $\psi$  vanishes everywhere on the boundaries of the box and outside it. The Schrödinger equation with this boundary condition is easily seen to be satisfied by the solution

$$\psi(x, y, z) = \begin{cases} A \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right), & \text{inside box;} \\ 0, & \text{outside box,} \end{cases}$$

where  $n_x, n_y, n_z = 1, 2, \dots$  and  $A$  is a normalization constant. The corresponding energy eigenvalues are  $E = \epsilon_{n_x, n_y, n_z}$

$$\epsilon_{n_x, n_y, n_z} = \left[ \left( \frac{n_x \pi}{L_x} \right)^2 + \left( \frac{n_y \pi}{L_y} \right)^2 + \left( \frac{n_z \pi}{L_z} \right)^2 \right] \frac{\hbar^2}{2m} \equiv \frac{\hbar^2 k^2}{2m},$$

where  $k^2 = k_x^2 + k_y^2 + k_z^2$  and  $k_x = n_x \pi / L_x$ ,  $k_y = n_y \pi / L_y$  and  $k_z = n_z \pi / L_z$ . Hence, the one-particle partition function for this free translational motion is

$$Z_1^t = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-\beta \epsilon_{n_x, n_y, n_z}}.$$

This sum can be further evaluated only in the limit  $k_B T \gg \hbar^2 \pi^2 / 2mL^2$ , the energy level spacing. Even for  $L = 1$  cm,  $m = m_H$  (hydrogen mass),  $\hbar^2 \pi^2 / 2mL^2 \approx 2 \times 10^{-18}$  eV, a truly tiny energy, and for all attainable temperature the condition  $k_B T \gg \hbar^2 \pi^2 / 2mL^2$  always satisfies. Thus, for all macroscopic boxes and even at the lowest temperature ever reached, we can replace the sums by integrals. Putting  $n_x = k_x L_x / \pi$ , etc., we replace

$$\sum_{n_x=1}^{\infty} \dots \rightarrow \int_0^{\infty} \frac{L_x}{\pi} dk_x \dots,$$

etc. We rewrite  $Z_1$  as

$$Z_1^t = \frac{L_x}{\pi} \frac{L_y}{\pi} \frac{L_z}{\pi} \int_0^{\infty} dk_x \int_0^{\infty} dk_y \int_0^{\infty} dk_z e^{-\beta \epsilon(k)} = \frac{V}{8\pi^3} \int d^3 k e^{-\beta \epsilon(k)},$$

where  $V = L_x L_y L_z$  and  $\epsilon(k) \equiv \hbar^2 k^2 / 2m$ . Rewrite the above equation as

$$Z_1^t = \frac{V}{(2\pi)^3} \int d^3 k e^{-\beta \epsilon(k)}, \quad \epsilon(k) \equiv \frac{\hbar^2 k^2}{2m}. \quad (39)$$

Furthermore, in spherical coordinates  $d^3 k = k^2 dk \sin \theta d\theta d\phi$ , we rewrite Eq. (21), after integration of the angles to yield  $4\pi$ ,

$$Z_1^t = \int_0^{\infty} dk D(k) e^{-\beta \epsilon(k)}, \quad D(k) = \frac{V k^2}{2\pi^2}, \quad (40)$$

where  $D(k)$  is usually referred to as **density of states** in  $k$ -space, i.e.,  $D(k)dk$  is the number of states within the spherical shell from  $k \rightarrow k + dk$ .

Finally, we can insert  $\epsilon(k) = \hbar^2 k^2 / 2m$  and evaluate the integral of Eq. (40). Substitute  $k = \sqrt{2m/\beta \hbar^2} x$ ,

$$Z_1^t = \frac{V}{2\pi^2} \left( \frac{2m}{\beta \hbar^2} \right)^{3/2} \int_0^{\infty} dx x^2 e^{-x^2} = V \left( \frac{m}{2\pi \beta \hbar^2} \right)^{3/2}, \quad (41)$$

where we have used Gaussian integral

$$\int_0^\infty x^2 e^{-x^2} dx = \frac{\sqrt{\pi}}{4}.$$

From  $Z_1^t$  we can calculate the average energy per molecule

$$\frac{E^t}{N} = -\frac{\partial \ln Z_1^t}{\partial \beta} = \frac{3}{2} \frac{1}{\beta} = \frac{3}{2} k_B T,$$

same as Eq. (32) by classical approach. This is not surprising as we have taken the continuous limit (converting the summations into integrals). The discrete nature of the energy levels will show up only at temperature  $T < \hbar^2/(k_B m V^{2/3}) \approx 10^{-14}$  K.

Note: (a) In Eq. (40),  $D(k)$  acts for the continuum  $k$ -variable like the degeneracy factor  $g(\epsilon_k)$  in the discrete  $\epsilon_k$ -variable in the discrete sum for  $Z_1$  of Eq. (9). (b) We want to emphasize that although quantum mechanical  $Z_1$  obtained here is the same as classical result shown earlier, the formula for the total partition function

$$Z_N = \frac{1}{N!} Z_1^N$$

is the classical approximation. Namely we have ignored the quantum effects of many-body systems.

[Refs.: (1) Mandl 7.1-7.3.; (2) Bowley and Sánchez 5.9,7.2.]

## 4.11 The equipartition theorem

The last three results (for vibrational, rotational and translational motion) provide examples of the **equipartition theorem**: for each degree of freedom of a system with an energy which is quadratic in either the coordinate or the momentum, the average energy is  $k_B T/2$  and its contribution to the heat capacity is  $k_B/2$ , at high enough temperatures. Here are the examples we have discussed earlier:

- vibrations:

$$E_{\text{vib}} = \frac{1}{2} m \dot{x}^2 + \frac{1}{2} k x^2$$

2 quadratic d.o.f.  $\rightarrow E \rightarrow k_B T$  as  $T \rightarrow \infty$ .

- rotations: 2 perpendicular axes about which it can rotate,

$$E_{\text{rot}} = \frac{1}{2} I_1 \dot{\theta}_1^2 + \frac{1}{2} I_2 \dot{\theta}_2^2$$

2 quadratic d.o.f., hence  $E \rightarrow k_B T$  as  $T \rightarrow \infty$ ;

- translations:

$$E_{\text{tr}} = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$$

3 quadratic d.o.f., hence  $E \rightarrow 3k_B T/2$  as  $T \rightarrow \infty$ .

The equipartition theorem is a classical theorem. From our present statistical mechanics treatment we see it breaks down when the separation between energy levels is small compared with  $k_B T$ . If this happens the heat capacity of this d.o.f. will be reduced, dropping to zero at low temperatures. The corresponding d.o.f. is then said to be frozen out; e.g., this is typically the situation for the vibrational degrees of freedom at room temperature. More specifically, equipartition holds

- for vibrations, when  $T \gg \hbar\omega/k_B \approx 10^3$  K;
- for rotations, when  $T \gg \hbar^2/Ik_B \approx 10 - 100$  K;
- for translations, when  $T \gg \hbar^2/(mV^{2/3}k_B) \approx 10^{-14}$  K.

Thus, at room temperature, only the rotational and translational degrees of freedom can be treated classically, giving  $C_V = 3R/2$  for monatomic gases and  $C_V = 5R/2$  for diatomic gases, for the molar heat capacity. The following diagram is an example for a diatomic gas (e.g.,  $\text{H}_2$ ).

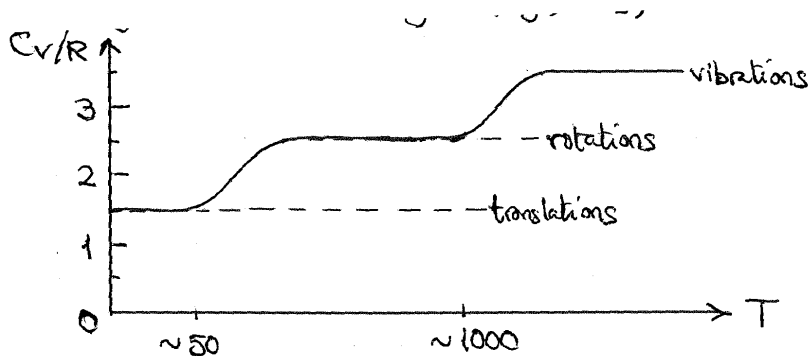


Figure 8

We can predict the heat capacities of other substances using equipartition, simply by counting the quadratic degrees of freedom. An example is a solid, for which we expect the molar heat capacity to be  $3R$  since each atom is free to vibrate in 3 directions. This is the **Dulong-Petit law**, which works well for many solids at room temperature

Note: Equipartition only holds for quadratic degrees of freedom. An example is for an ultra-relativistic gas, for which  $\epsilon = cp = c\hbar k$ , is linear (instead of quadratic).

Two important points:

- (a)  $T \rightarrow 0$ , quantum effects dominate. In fact, for all quantum systems including quantum gases,  $C_V \rightarrow 0$  as  $T \rightarrow 0$ , consistent with the 3rd law of thermodynamics.
- (b) We only discussed energy per molecule and specific heat here using the equipartition theorem and avoided discussing other properties such as entropy or equation of state which require the full  $N$ -body partition function  $Z_N$  (and the property of identical particles matter).

[Refs.: (1) Mandl 7.9; (2) Bowley and Sánchez 5.14.]

## 4.12 The Maxwell-Boltzmann velocity distribution

In this section we derive the Maxwell-Boltzmann velocity distribution for an ideal classical gas you have learned in your year one module.

Consider a gas of  $N$  molecules in a volume  $V$ , in thermal equilibrium at a temperature  $T$ . From Boltzmann distribution function, the probability of an average molecule in the state  $(\mathbf{r}, \mathbf{p})$  is

$$p(\mathbf{r}, \mathbf{p}) = \frac{1}{Z_1} e^{-\epsilon(\mathbf{r}, \mathbf{p})/k_B T}$$

where  $\epsilon(\mathbf{r}, \mathbf{p})$  is the energy of the a single molecule at state  $(\mathbf{r}, \mathbf{p})$ . The average number of molecules at state  $(\mathbf{r}, \mathbf{p})$  inside the volume  $d^3r d^3p/h^3$  is then given by

$$Np(\mathbf{r}, \mathbf{p}) \frac{d^3r d^3p}{h^3}$$

The Maxwell-Boltzmann velocity distribution function  $f(v)$  is obtained by setting translational energy  $\epsilon(\mathbf{r}, \mathbf{p}) = p^2/2m$  with  $p = mv$ , and integrating over spatial  $d^r$  and solid angle  $\sin \theta d\theta d\phi$  of the momentum as

$$f(v)dv = \frac{Nm^3}{Z_1 h^3} \int d^3r \int \sin \theta d\theta d\phi e^{-mv^2/2k_B T} v^2 dv = \frac{Nm^3 V}{Z_1 h^3} e^{-mv^2/2k_B T} v^2 dv,$$

hence

$$f(v) = \frac{Nm^3 V}{Z_1 h^3} v^2 e^{-mv^2/2k_B T}.$$

Using the result

$$Z_1 = V \left( \frac{mk_B T}{2\pi \hbar^2} \right)^{3/2},$$

we have

$$f(v) = N \sqrt{\frac{2}{\pi}} \left( \frac{m}{k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}. \quad (42)$$

Notice the normalization

$$\int_0^\infty f(v) dv = N.$$

We can also define distribution function for an average particle as  $P(v) = f(v)/N$  and the normalization equation is

$$\int_0^\infty P(v) dv = 1.$$

This is the well-known Maxwell-Boltzmann velocity distribution. We plot distribution  $P(v)$  of Eq. (42) in Figure 9.

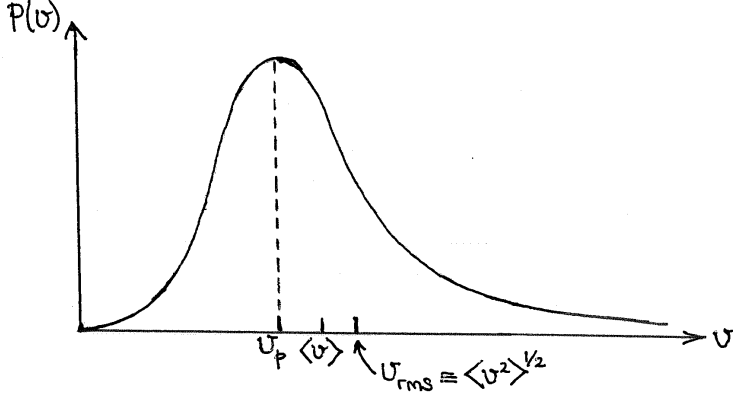


Figure 9

A few physical quantities are calculated as follows.

- most probable speed: let  $v_p$  be the point of maximum  $P(v)$ , i.e.,  $dP/dv = 0$

$$\frac{d}{dv} (v^2 e^{-mv^2/2k_B T}) = 0 \quad \rightarrow \quad (2v - v^2 m v \beta) = 0$$

we have

$$v_p = \sqrt{\frac{2k_B T}{m}} \approx 1.41 \sqrt{\frac{k_B T}{m}}. \quad (43)$$

- mean speed:

$$\begin{aligned} \langle v \rangle &= \int_0^\infty v \cdot P(v) dv = \sqrt{\frac{2}{\pi}} \left( \frac{m}{k_B T} \right)^{3/2} \int_0^\infty v^3 e^{-mv^2/2k_B T} dv \\ &= \sqrt{\frac{8k_B T}{m}} \approx 1.60 \sqrt{\frac{k_B T}{m}}. \end{aligned} \quad (44)$$

- rms speed:

$$\begin{aligned}\langle v^2 \rangle &\equiv v_{\text{rms}}^2 = \int_0^\infty v^2 \cdot P(v) dv = \sqrt{\frac{2}{\pi}} \left( \frac{m}{k_B T} \right)^{3/2} \int_0^\infty v^4 e^{-mv^2/2k_B T} dv \\ &= 3 \frac{k_B T}{m},\end{aligned}$$

or

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}} \approx 1.73 \sqrt{\frac{k_B T}{m}}. \quad (45)$$

These three speeds are marked in Figure 9.

From Eq. (45) we have

$$E_1 = \frac{1}{2} \langle mv^2 \rangle = \frac{1}{2} m v_{\text{rms}}^2 = \frac{m}{2} \cdot \frac{3k_B T}{m} = \frac{3}{2} k_B T,$$

consistent with equipartition theorem. Note also that  $\hbar$  has disappeared from the Maxwell-Boltzmann distribution of Eq. (42), which is why it can be also found from classical kinetic theory, as was done originally by Maxwell.

Note: In the above integrals, we have used the following general Gaussian integral

$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}.$$

[Refs.: (1) Mandl 7.7; (2) Bowley and Sánchez 7.4.]

### 4.13 What is next?

So far, we have completely ignored interactions between constituent particles in all of our examples, from the ideal spin-1/2 paramagnets to the classical ideal gases. How do we go from here and what is next in the physics of statistical mechanics? Clearly, investigation of the effects due to, for example, interactions between molecules of a gas is the next main task. In fact, the most interesting physics emerges from such interactions, examples are phase transitions from gases to liquids or solids as temperature is lower, and even to superfluids or superconductors at extremely low temperatures where quantum physics dominates.

Another major neglect is the quantum effects of many particles (bosons) occupying the same single-particle state (particularly the zero-momentum state) when we discussed the independent-particle approximation for identical particles. Such effects are important in the low temperature limit and inclusion of such quantum effects will result in the Bose-Einstein condensation. These effects are much easier to handle and they are covered in a thir-year course, *Bosons and Fermions*.



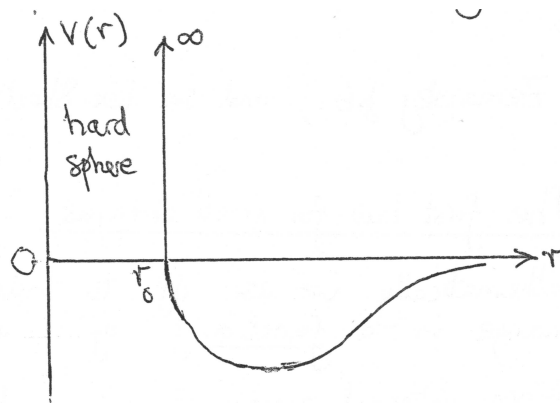
The difficult problem is the inclusion of interactions between particles. Amazingly, we have most of the fundamental formulas needed for all such further investigation, although some special techniques will be required. Let's do a little demonstration to complete our *Thermal and Statistical Physics*.

We consider a gas of  $N$  identical, classical molecules. These molecules interact with one another, and the interaction is described by a pair-wise interaction potential,  $V(r)$ , where  $r$  is the separation between the interacting pair. We draw a typical  $V(r)$  in Fig. 10. Qualitatively, we see the interaction potential consists of a hard-core (molecules repel each others strongly when they are very close) and an attractive tail which is responsible for condensation into liquids and formation of solids at low temperature.

In Chap. 1.3, we have qualitatively discussed the effects due to this interaction to the equation of state, the so-called van der Waals equation,

$$\left(P + \frac{\alpha N^2}{V^2}\right)(V - N\beta) = Nk_B T,$$

where  $\alpha$  and  $\beta$  are coefficients depending on the interaction potential. This empirical equation of van der Waals in fact provides a good description of a dense gas (recall that an ideal gas corresponds to dilute gas where interactions can be ignored) and it also predicts a phase transition from gas to liquid phase.



**Fig. 10** A schematic diagram for the interaction potential between two molecules.

One of the tasks in statistical mechanics is to derive this van der Waals equation from, say, canonical ensemble approach. In canonical-ensemble approach, as discussed

earlier, we first need to calculate the partition function of  $N$  molecules

$$Z_N = \sum_i e^{-\epsilon_i/k_B T},$$

where, as we mention before, summation over microstate index  $i$  for  $N$  classical molecules corresponds to the integral in  $6N$ -dimensional phase-space

$$\sum_i = \frac{1}{N!} \frac{1}{h^{3N}} \int d^3 r_1 d^3 p_1 \int d^3 r_2 d^3 p_2 \cdots \int d^3 r_N d^3 p_N,$$

with the factor  $1/N!$  due to the property of identical particles. The energy  $\epsilon_i$  is then the classical Hamiltonian (total energy) of interacting  $N$  molecules

$$\begin{aligned} H &= H(\mathbf{r}_1, \mathbf{r}_2, \dots; \mathbf{p}_1, \mathbf{p}_2, \dots) = K + U; \\ K &= \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \cdots + \frac{p_N^2}{2m} = \sum_{k=1}^N \frac{p_k^2}{2m}, \\ U &= V(|\mathbf{r}_1 - \mathbf{r}_2|) + V(|\mathbf{r}_1 - \mathbf{r}_3|) + \cdots = \sum_{k < l} V(|\mathbf{r}_1 - \mathbf{r}_k|) \end{aligned}$$

where  $K$  is the total kinetic energy,  $U$  the total potential energy. Hence, the partition function of the gas is written as

$$Z_N = \frac{1}{N!} \frac{1}{h^{3N}} \int d^3 r_1 d^3 p_1 \int d^3 r_2 d^3 p_2 \cdots \int d^3 r_N d^3 p_N e^{-(K+U)/k_B T}.$$

We notice, contrast to the case of an ideal gas, the above multi-dimensional integral is NOT **separable**, due the coupling terms in the potential  $U$  between molecular coordinates  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ . (The kinetic energy term  $K$  is still separable, hence the integrals over momenta  $\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N$  are still separable. Can you prove this?). Special techniques have been developed to evaluate this multi-dimensional integral. One of such techniques is the so-called cluster-expansion for the factor  $e^{-U/k_B T}$ . Corrections to the ideal gas equation of state can then be evaluated. We will stop here. For those who are interested, a good but very advanced reference book (postgraduate text book) is by K. Huang, *Statistical Mechanics*.

## **Acknowledgment**

The main parts of these lecture notes (including figures, diagrams, and example sheets) have been passed down to me from Prof. R.F. Bishop and to him from Dr. J.A. McGovern. If these materials have been useful to you, credits should go to these earlier lecturers. I have made some significant changes, including re-organizing the materials. If you find typos, mistakes, or Chinglish, they are likely mine.

## **Lecture Cancellation**

Lecture on Thursday, 2:00 pm, 01 May 2008 is canceled. Please study the last section Sec. 4.10 (available on line). Last lecture on Thursday, 08 May will focus on revision.