

# Chapter 5

## Ensembles

### 5.1 Characteristic variables

In chapter 3 we have introduced various thermodynamic functions, with differentials

$$dU = TdS - PdV + \mu dN \quad (5.1)$$

$$dH = TdS + VdP + \mu dN \quad (5.2)$$

$$dA = -SdT - PdV + \mu dN \quad (5.3)$$

$$dG = -SdT + VdP + \mu dN \quad (5.4)$$

So, for example, instead of using  $S$ ,  $V$  and  $N$  as independent variables for the energy  $U$ , we changed to  $T$ ,  $V$  and  $N$  as independent variables for the free energy  $A$ .

Each thermodynamic function is associated with a special set of variables, called its characteristic variables. These characteristic variables are exactly the terms appearing after the differentials “d” in the list above. Knowing a thermodynamic function as a function of its characteristic variables, we know everything there is to know (thermodynamically speaking) about the system.

Let us first consider the internal energy  $U$ . Suppose we are given  $U$  as a function of entropy and volume,  $U = U(S, V)$  (for brevity we ignore the dependence on  $N$ ). Then

$$U = U(S, V) \quad (5.5)$$

$$T = \left( \frac{\partial U}{\partial S} \right)_V = T(S, V) \quad (5.6)$$

$$P = - \left( \frac{\partial U}{\partial V} \right)_S = P(S, V). \quad (5.7)$$

This is all there is. All other thermodynamic quantities can now be calculated. For

example the heat capacity at constant volume:

$$T = T(S, V) \rightarrow S = S(T, V) \quad (5.8)$$

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V = C_V(T, V), \quad (5.9)$$

or, if inverting to  $S(T, V)$  is too difficult,

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V = \frac{T}{\left( \frac{\partial T}{\partial S} \right)_V} = \frac{\left( \frac{\partial U}{\partial S} \right)_V}{\left( \frac{\partial^2 U}{\partial S^2} \right)_V} = C_V(S, V). \quad (5.10)$$

On the other hand, if we are given the energy  $U$  as a function of temperature and volume,  $U = F(T, V)$ , we *cannot* know everything about the system:

$$U = F_1 \left( \left( \frac{\partial U}{\partial S} \right)_V, V \right) \rightarrow \left( \frac{\partial U}{\partial S} \right)_V = F_2(U, V) \quad (5.11)$$

$$\left( \frac{\partial S}{\partial U} \right)_V = F_3(U, V) \quad (5.12)$$

$$S(U, V) = F_4(V) + \int^U F_3(U, V) dU. \quad (5.13)$$

So we can find the energy dependence of the entropy, but not its volume dependence because we cannot derive the function  $F_4(V)$ . We are lacking information.

This example shows why  $S$  and  $V$  are called the characteristic variables of the energy  $U$ . In the same way it may be shown that the number of particles  $N$  is also a characteristic variable of the energy  $U$ . The characteristic variables of the thermodynamic functions we have encountered up to now are given by:

$$U = U(N, V, S) \quad (5.14)$$

$$H = H(N, P, S) \quad (5.15)$$

$$A = A(N, V, T) \quad (5.16)$$

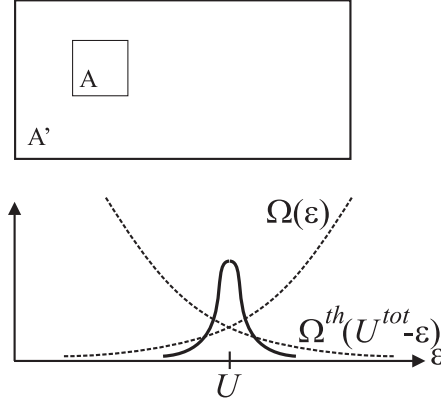
$$G = G(N, P, T). \quad (5.17)$$

## 5.2 The canonical ensemble (N, V, T)

We will now explore how we can change variables in statistical physics.

Consider a system A immersed in a very large thermal reservoir A', see Fig. 5.1 (top). The boundaries between A and A' are impenetrable to particles, but they allow for energy to be exchanged. The composite system of A+A' is adiabatically sealed from the rest of the universe and has a total energy  $U^{tot}$ . If at any time the system A is in a state characterised by an energy  $\epsilon$ , then the reservoir must have an

Figure 5.1: (top) A given system A immersed in a thermal reservoir A'. Exchange of energy (heat) is possible. (bottom) The density of states in A is a sharply increasing function of the system's energy  $\epsilon$ . The density of states in A' is a sharply decreasing function of  $U^{tot} - \epsilon$ . The integrand of Eq. (5.18) is therefore sharply peaked around some value  $\epsilon = U$ .



energy  $U^{tot} - \epsilon$ . The total number of ways to combine the density of states  $\Omega^{th}$  of the thermal reservoir with the density of states  $\Omega$  of the system is therefore

$$\Omega^{tot} = \int d\epsilon \Omega^{th}(U^{tot} - \epsilon)\Omega(\epsilon). \quad (5.18)$$

The integrand of this equation is a sharply peaked function around some value  $\epsilon = U$ , see Fig. 5.1 (bottom). We are therefore only interested in values of  $\epsilon$  close to  $\epsilon = U$ . Using the same arguments as in section 4.1 it is easy to show that the maximum occurs when

$$T = T^{th}, \quad (5.19)$$

as expected for a system in contact with a thermal reservoir. For the density of states of the thermal reservoir we now write

$$\begin{aligned} \Omega^{th}(U^{tot} - \epsilon) &= \Omega^{th}(U^{tot} - U + U - \epsilon) \\ &= \exp \left[ \frac{S^{th}(U^{tot} - U + U - \epsilon)}{k_B} \right] \\ &\approx \exp \left[ \frac{S^{th}(U^{tot} - U)}{k_B} + \frac{\partial S^{th}}{\partial U} \Big|_{U^{tot}-U} \frac{U - \epsilon}{k_B} \right] \\ &= \exp \left[ \frac{S^{th}(U^{tot} - U)}{k_B} + \beta(U - \epsilon) \right], \end{aligned} \quad (5.20)$$

where we have made a first order Taylor expansion around  $\epsilon = U$ , and defined  $\beta = 1/(k_B T)$ . The total density of states of the composite system is therefore

$$\begin{aligned} \Omega^{tot} &= \int d\epsilon \Omega^{th}(U^{tot} - \epsilon)\Omega(\epsilon) \\ &= \exp \left[ \frac{S^{th}(U^{tot} - U)}{k_B} \right] \exp(\beta U) \int d\epsilon \exp(-\beta\epsilon) \Omega(\epsilon). \end{aligned} \quad (5.21)$$

The last integral defines the *partition function*  $Q$ .<sup>1</sup> The entropy of the composite system can now be expressed as

$$\begin{aligned} S^{tot} &= k_B \ln \Omega^{tot} \\ &= S^{th}(U^{tot} - U) + \frac{U}{T} + k_B \ln Q \end{aligned} \quad (5.22)$$

$$= S^{th} + S. \quad (5.23)$$

The entropy of the system is therefore given by

$$S = \frac{U}{T} + k_B \ln Q. \quad (5.24)$$

Making use of Eq. (3.9) the free energy  $A$  of the system can now be expressed as

$$\boxed{A = U - TS = -k_B T \ln Q.} \quad (5.25)$$

Note that  $Q$  depends on the variables  $N$ ,  $V$ , and  $T$ . Of all the thermodynamic functions it is the free energy  $A$  that is directly proportional to  $\ln Q$ . This is no coincidence, since  $A$  is the thermodynamic function whose characteristic variables are also  $N$ ,  $V$ , and  $T$ . Knowing  $Q$  as a function of these variables allows us to calculate all thermodynamic properties of the system (Problem 5-1). Depending on the representation of the energy states, the partition function  $Q$  may be expressed as an integral

$$Q = \int d\epsilon \Omega(\epsilon) e^{-\beta\epsilon}, \quad (5.26)$$

as a sum over all states<sup>2</sup>

$$Q = \sum_i e^{-\beta\epsilon_i}, \quad (5.27)$$

or as a sum over energy levels

$$Q = \sum_n \Omega_n e^{-\beta E_n}, \quad (5.28)$$

where  $\Omega_n$  is the degeneracy of energy level  $n$ .

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<sup>1</sup>Do not confuse the partition function with the total amount of heat  $Q$  added to a system. It will always be clear from the context which is implied.

<sup>2</sup>This is why  $Q$  is sometimes also referred to as the *sum-of-states*

### 5.3 Canonical treatment of the ideal gas

In section 2.2.4 we have treated the ideal gas of  $N$  particles in a box of size  $V = L^3$ , the energy of which is given by

$$E_{n_1, \dots, n_{3N}} = \frac{h^2}{8mL^2} (n_1^2 + \dots + n_{3N}^2). \quad (5.29)$$

We will now try to find the free energy  $A$  of the ideal gas by first calculating its partition function. Each of the quantum numbers  $n_i$  can have a non-negative integer value, so  $Q$  is calculated as

$$Q = \frac{1}{N!} \sum_{n_1=1}^{\infty} \dots \sum_{n_{3N}=1}^{\infty} e^{-\left(\frac{\beta h^2}{8mL^2}\right)n_1^2} \times \dots \times e^{-\left(\frac{\beta h^2}{8mL^2}\right)n_{3N}^2} = \frac{q^{3N}}{N!} \quad (5.30)$$

$$\begin{aligned} q &\equiv \sum_{n=1}^{\infty} e^{-\left(\frac{\beta h^2}{8mL^2}\right)n^2} \approx \int_0^{\infty} dn e^{-\left(\frac{\beta h^2}{8mL^2}\right)n^2} \\ &= \sqrt{\frac{\pi 8mL^2}{4\beta h^2}} = L \sqrt{\frac{2\pi m k_B T}{h^2}}. \end{aligned} \quad (5.31)$$

Note that we have taken into account an additional factor  $N!$  because of quantum symmetry. The free energy is now given by

$$A = -k_B T \ln \left( \frac{q^{3N}}{N!} \right) = -N k_B T \ln \left[ \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} e \frac{V}{N} \right]. \quad (5.32)$$

All thermodynamic quantities can now be calculated. In Problem 5-2 you are asked to calculate the energy  $U$  and pressure  $P$ .

### 5.4 Canonical treatment of the harmonic crystal

In section 2.2.3 we have introduced the harmonic crystal and shown that its energy is given by

$$E_{n_1, \dots, n_{3N}} = \hbar\omega \left( n_1 + \frac{1}{2} \right) + \dots + \hbar\omega \left( n_{3N} + \frac{1}{2} \right). \quad (5.33)$$

Each of the quantum numbers  $n_i$  can have any non-negative integer value. Therefore the partition function  $Q$  is given by<sup>3</sup>

$$\begin{aligned}
 Q &= \sum_{n_1=0}^{\infty} \dots \sum_{n_{3N}=0}^{\infty} e^{-\beta\hbar\omega(n_1+\frac{1}{2})} \times \dots \times e^{-\beta\hbar\omega(n_{3N}+\frac{1}{2})} \\
 &= \exp\left(-\frac{3N}{2}\beta\hbar\omega\right) \left[ \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} \right]^{3N} \\
 &= \exp\left(-\frac{3N}{2}\beta\hbar\omega\right) \left[ \frac{1}{1 - e^{-\beta\hbar\omega}} \right]^{3N}.
 \end{aligned} \tag{5.34}$$

The free energy is then

$$A = -k_B T \ln Q = \frac{3N}{2} \hbar\omega + 3N k_B T \ln(1 - e^{-\hbar\omega/k_B T}). \tag{5.35}$$

All thermodynamic quantities can now be calculated. For example, the entropy is found from  $S = -(\partial A/\partial T)_{N,V}$  and the heat capacity from  $C_V = T(\partial S/\partial T)_{N,V} = -T(\partial^2 A/\partial T^2)_{N,V}$ , yielding the same result as Eq. (3.27) obtained through another route! (Problem 5-3.)

## 5.5 The grand canonical ensemble ( $\mu$ , $V$ , $T$ )

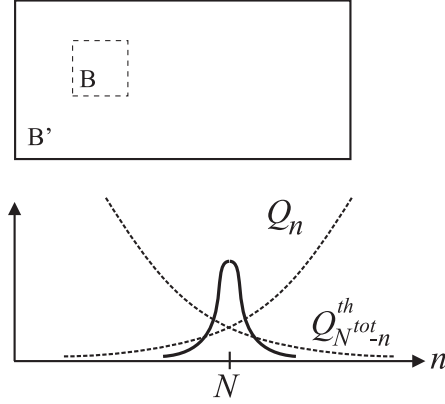
Consider a system B immersed in a very large system B', see Fig. 5.2 (top). The composite system B+B' is immersed in a thermal reservoir and enclosed by walls which allow for energy to be exchanged. The boundaries between B and B', however, are open, i.e. they allow for both particles and energy to be exchanged. B' could for instance be a certain small, but still macroscopically large, region of the composite system. If at any time the system B is in a state characterised by a number of particles  $n$ , then the reservoir B' must have  $N^{tot} - n$  particles, where  $N^{tot}$  is the total number of particles in the composite system. Because B and B' are in thermal contact, and B' is in contact with an external thermal reservoir, the temperature  $T$  is constant throughout the composite system. For each value of  $n$  we may therefore treat B and B' in the canonical ensemble, and sum over all possible values of  $n$ . The total partition function then reads

$$Q^{tot} = \sum_{n=0}^{N^{tot}} Q_{N^{tot}-n}^{th} Q_n. \tag{5.36}$$

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<sup>3</sup>Note that, because of the localisation of the particles to the lattice points, they are in principle distinguishable. In this case we therefore do not include the factor  $N!$  in the partition function.

Figure 5.2: (top) A given system B immersed in a thermal and particle reservoir B'. Exchange of both energy (heat) and particles is possible. (bottom) The partition function of B is a sharply increasing function of the system's number of particles  $n$ , while the partition function of B' is a sharply decreasing function of  $n$ . The product  $Q_{N^{tot}-n}^{th} Q_n$  is therefore sharply peaked around some value  $n = N$ .



The partition function  $Q_n$  of the system B is a sharply increasing function of  $n$ , while the partition function  $Q_{N^{tot}-n}^{th}$  of the reservoir B' is a sharply decreasing function of  $n$ . The product  $Q_{N^{tot}-n}^{th} Q_n$  consequently is a sharply peaked function around some value  $n = N$ , see Fig. 5.2 (bottom). The maximum occurs when

$$\begin{aligned} \frac{d}{dn} Q_{N^{tot}-n}^{th} Q_n &= Q_{N^{tot}-n}^{th} Q_n \frac{d}{dn} \ln \{ Q_{N^{tot}-n}^{th} Q_n \} \\ &= Q_{N^{tot}-n}^{th} Q_n \left\{ \frac{\mu^{th}}{k_B T} - \frac{\mu}{k_B T} \right\} = 0, \end{aligned} \quad (5.37)$$

where we have used that  $\mu = (\partial A / \partial n)_{V,T}$  and Eq. (5.25). The maximum is therefore determined by the condition that the chemical potential in the system B equals the chemical potential of the reservoir B',

$$\mu = \mu^{th}. \quad (5.38)$$

Making a first order Taylor expansion around  $n = N$  we find

$$\begin{aligned} Q_{N^{tot}-n}^{th} &= \exp \{ -\beta A_{N^{tot}-n}^{th} \} \\ &= \exp \left\{ -\beta \left[ A_{N^{tot}-N}^{th} + \left. \frac{\partial A_{N^{tot}-n}^{th}}{\partial n} \right|_{n=N} (n - N) \right] \right\} \\ &= \exp \{ -\beta A_{N^{tot}-N}^{th} - \beta \mu (N - n) \} \end{aligned} \quad (5.39)$$

$$Q^{tot} = \exp \{ -\beta A_{N^{tot}-N}^{th} - \beta \mu N \} \sum_{n=0}^{N^{tot}} Q_n e^{\beta \mu n}. \quad (5.40)$$

The last sum defines the *grand canonical partition function*  $\Xi$ . Since the reservoir B' is assumed to be much larger than the system B, the total number of particles  $N^{tot}$  is much larger than  $N$  and may for all practical purposes be considered infinite:

$$\Xi \equiv \sum_{n=0}^{\infty} Q_n e^{\beta \mu n}. \quad (5.41)$$

The free energy of the composite system B+B' is now expressed as

$$A^{tot} = -k_B T \ln Q^{tot} = A_{N^{tot}-N}^{th} + \mu N - k_B T \ln \Xi. \quad (5.42)$$

We therefore identify the free energy of the system B as

$$A = \mu N - k_B T \ln \Xi. \quad (5.43)$$

Since  $\mu N$  is the Gibbs free energy, see Eq. (3.80), we find the following relation

$$\boxed{PV = k_B T \ln \Xi.} \quad (5.44)$$

Of all thermodynamic functions, it is  $PV$  that is directly proportional to  $\ln \Xi$ . Again this is no coincidence:  $\Xi$  depends on the variables  $\mu$ ,  $V$ , and  $T$ , which are exactly the characteristic variables of  $PV$ , see Problem 5-4. Knowing  $\Xi$  as a function of these variables allows us to calculate all thermodynamic properties of the system (Problem 5-5).



## Problems

**5-1. Thermodynamic properties from the canonical partition function.** Suppose we know the canonical partition function  $Q(N, V, T)$ . Using thermodynamic relations, show that we can express the energy, pressure, and entropy as

$$\begin{aligned} U &= k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V, N} \\ P &= k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{T, N} \\ S &= k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_{V, N} + k_B \ln Q. \end{aligned}$$

**5-2. Energy and pressure of an ideal gas.** Starting from Eq. (5.32), calculate the energy  $U$  and pressure  $P$  of an ideal gas as a function of  $(N, V, T)$ .

**5-3. Entropy and specific heat of the harmonic crystal.** Starting from the free energy of a harmonic crystal, Eq. (5.35), calculate its entropy and specific heat at constant volume.

**5-4. Characteristic variables of  $PV$ .** Show that the thermodynamic function  $PV$  has characteristic variables  $\mu$ ,  $V$ , and  $T$ . Hint: Gibbs-Duhem.

**5-5. Thermodynamic properties from the grand canonical partition function.** Suppose we know the grand canonical partition function  $\Xi(\mu, V, T)$ . Using thermodynamic relations, prove the following relations

$$\begin{aligned} P &= k_B T \left( \frac{\partial \ln \Xi}{\partial V} \right)_{T, \mu} \\ S &= k_B T \left( \frac{\partial \ln \Xi}{\partial T} \right)_{V, \mu} + k_B \ln \Xi \\ N &= k_B T \left( \frac{\partial \ln \Xi}{\partial \mu} \right)_{V, T} \\ U &= k_B T \left[ \mu \left( \frac{\partial \ln \Xi}{\partial \mu} \right)_{V, T} + T \left( \frac{\partial \ln \Xi}{\partial T} \right)_{V, \mu} \right]. \end{aligned}$$



# Chapter 6

## Ideal gases

### 6.1 Quantum description of an ideal gas

In this chapter we are going to focus on the statistical mechanics of non-interacting systems, also referred to as ideal gases. We will start with a quantum mechanical description.

Suppose we have  $N$  identical non-interacting particles. The Hamiltonian of such a system is the sum of  $N$  independent contributions<sup>1</sup>

$$\mathcal{H}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^N h(\mathbf{r}_i). \quad (6.1)$$

To describe the state of the system we will first focus on single particle states, which are the eigenfunctions  $\psi_n(\mathbf{r})$  of  $h(\mathbf{r})$ :

$$h\psi_n = \epsilon(n)\psi_n. \quad (6.2)$$

We can construct system states by attributing a state  $\psi_n$  to each particle. One possible realisation is

$$\Psi_{n_1, \dots, n_N}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \psi_{n_1}(\mathbf{r}_1) \times \dots \times \psi_{n_N}(\mathbf{r}_N), \quad (6.3)$$

which would correspond to an energy

$$E_{n_1, \dots, n_N} = \epsilon(n_1) + \dots + \epsilon(n_N). \quad (6.4)$$

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<sup>1</sup>For simplicity, in our notation of the wave function we do not explicitly indicate the spin of the particles. This implies that each of the  $\psi_n(\mathbf{r}_i)$  is the product of an 'orbital' and a spin function.  $n$  therefore includes a spin quantum number. The (anti-) symmetry requirements of the next page actually apply to these combined 'spin-orbitals'.

So the eigenfunctions of a sum of independent Hamiltonians are products of the eigenfunctions of the individual Hamiltonians, with eigenvalues equal to the sum of the individual eigenvalues (like it was in classical mechanics).

The above wave function  $\Psi$  is however not yet correct! In an ideal gas each particle can occupy every position in the box. Consequently, it is relevant to ask about the probability of a particular configuration of particles, which differs from another one by the interchange of two particles. Obviously in the case of indistinguishable particles the probability distribution for both configurations should be the same, i.e.

$$|\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N)|^2 = |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)|^2. \quad (6.5)$$

In general condition can be met by stating

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N) = e^{i\gamma} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N),$$

where  $\gamma$  is some phase. It turns out that in nature only  $\gamma = 0$  and  $\gamma = \pi$  are encountered. Therefore:  $\Psi$  must remain the same or it must change sign upon exchange of two particles. In the first case we call the particles *bosons*, in the second case we call them *fermions*,

$$\begin{aligned} \text{bosons :} \quad & \Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N) = \Psi(\mathbf{r}_1, \dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N), \\ \text{fermions :} \quad & \Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N) = -\Psi(\mathbf{r}_1, \dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N). \end{aligned}$$

Particles with integer spin, like photons, are bosons. Particles with half-integer spin, like electrons, protons and neutrons, are fermions. Particles composed of a number of other particles can be either bosons or fermions, depending on their total spin. Hence, many nuclei are in fact bosons. For example the  $\alpha$ -particle (a  ${}^4\text{He}$  nucleus) is a boson. Let us now see how to construct a (anti-)symmetrised product of single particle states.

**Bosons.** Suppose we have just two bosons in our system. It is easy to verify that a properly symmetrised state function, which remains the same upon exchange of the two particles, is given by

$$\Psi_{n_1, n_2}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \{ \psi_{n_1}(\mathbf{r}_1) \psi_{n_2}(\mathbf{r}_2) + \psi_{n_1}(\mathbf{r}_2) \psi_{n_2}(\mathbf{r}_1) \}. \quad (6.6)$$

In the general case of  $N$  particles the symmetrised state function is

$$\Psi_{n_1, \dots, n_N} = \frac{1}{\sqrt{N!}} \sum_P \psi_{n_1}(\mathbf{r}_{P1}) \times \dots \times \psi_{n_N}(\mathbf{r}_{PN}), \quad (6.7)$$

where the sum over  $P$  denotes *all* possible permutations of the coordinates ( $N!$  in total).

Note that permutations of the quantum numbers  $n_i$  do not result in new states. We are therefore free to choose the order in which they occur in Eq. (6.7). We may for instance order them according to

$$n_i \leq n_{i+1}. \quad (6.8)$$

This will be useful when we treat quantum gases.

**Fermions.** Suppose we have just two fermions in our system. Again it is easy to verify that a properly antisymmetrised state function, which changes sign upon exchange of the two particles, is given by

$$\Psi_{n_1, n_2}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \{ \psi_{n_1}(\mathbf{r}_1) \psi_{n_2}(\mathbf{r}_2) - \psi_{n_1}(\mathbf{r}_2) \psi_{n_2}(\mathbf{r}_1) \}. \quad (6.9)$$

In the general case of  $N$  particles the antisymmetrised state function is

$$\Psi_{n_1, \dots, n_N} = \frac{1}{\sqrt{N!}} \sum_P \epsilon^P \psi_{n_1}(\mathbf{r}_{P1}) \times \dots \times \psi_{n_N}(\mathbf{r}_{PN}), \quad (6.10)$$

where again the sum over  $P$  denotes *all* possible permutations of the coordinates. The variable  $\epsilon^P$  is either +1 or -1,

$$\begin{aligned} \epsilon^P &= +1 && \text{even permutations} \\ &= -1 && \text{odd permutations.} \end{aligned}$$

where an even permutation means that an even number of pair exchanges was needed to establish that permutation, and similarly for odd permutations.

Again permutations of the quantum numbers do not result in new states. What distinguishes fermions from bosons is that states with two or more quantum numbers equal don't exist! (Explain why?) We can therefore order the quantum numbers according to

$$n_i < n_{i+1}. \quad (6.11)$$

## 6.2 Ideal gas partition function: Maxwell-Boltzmann statistics

The partition function of a system of bosons or fermions is given by, respectively,

$$Q^B = \sum_{n_1, \dots, n_N}^B \exp \{ -\beta \epsilon(n_1) - \dots - \beta \epsilon(n_N) \} \quad (6.12)$$

$$Q^F = \sum_{n_1, \dots, n_N}^F \exp \{ -\beta \epsilon(n_1) - \dots - \beta \epsilon(n_N) \}, \quad (6.13)$$

where the superscripts  $B$  and  $F$  indicate a sum restricted to the boson and fermion symmetry requirements, respectively. Before solving these partition functions exactly, let us first consider what happens if we can neglect the symmetry restrictions:

$$\sum_{n_1, \dots, n_N} \exp \{-\beta\epsilon(n_1) - \dots - \beta\epsilon(n_N)\} = \left[ \sum_n \exp \{-\beta\epsilon(n)\} \right]^N = q^N, \quad (6.14)$$

where we have defined the single particle partition function  $q$ . In this sum every state with no two quantum numbers equal to each other is counted  $N!$  times. In  $q^N/N!$  these are counted like they should be counted both for bosons and for fermions.

At high temperatures, the number of states contributing to  $Q$  is extremely high (Problem 6-1); the great majority of them has all quantum numbers different; therefore

$$Q^B = \frac{q^N}{N!} (1 - C^B) \quad C^B \ll 1 \quad (6.15)$$

$$Q^F = \frac{q^N}{N!} (1 - C^F) \quad C^F \ll 1, \quad (6.16)$$

where  $C^B$  and  $C^F$  are some very small numbers. The free energy is therefore given by

$$\begin{aligned} A^B &= -k_B T \ln Q^B \\ &= -k_B T \ln \frac{q^N}{N!} - k_B T \ln (1 - C^B) \approx -k_B T \ln \frac{q^N}{N!} \end{aligned} \quad (6.17)$$

$$\begin{aligned} A^F &= -k_B T \ln Q^F \\ &= -k_B T \ln \frac{q^N}{N!} - k_B T \ln (1 - C^F) \approx -k_B T \ln \frac{q^N}{N!}. \end{aligned} \quad (6.18)$$

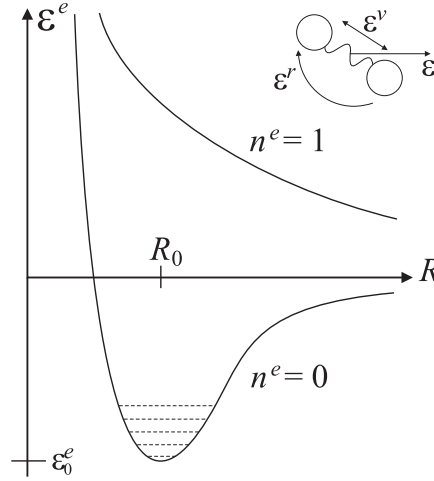
So at high temperatures the distinction between bosons and fermions becomes irrelevant. In this regime the particles are said to obey Maxwell-Boltzmann statistics:

$$\boxed{Q = \frac{q^N}{N!}} \quad (6.19)$$

### 6.3 The two-atomic molecular ideal gas

Up to this point we have assumed that the ideal gas particles have *no internal structure*. If the particles do have internal structure, the total energy should also include energy terms representing changes in the internal structure. As an example we will treat now an ideal gas of two-atomic molecules. The two atoms may be the

Figure 6.1: Sketch of the effective (electronically averaged) potential energy of a two-atomic molecule as a function of the distance between the nuclei. For each electronic state  $n^e$  there is a different curve; only the first two are depicted here. The ground state energy has a minimum  $\epsilon_0^e$  at a distance  $R_0$ . Vibrations around this minimum are approximated by a (quantum mechanical) harmonic oscillator, with energy levels indicated by the dashed lines.



same, in which case we speak of homonuclear molecules ( $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ , etc). If the two atoms are different, we speak of heteronuclear molecules ( $\text{CO}$ ,  $\text{NO}$ , etc).

As we have seen in section 1.3.6 the energy of a two-atomic molecule consists of several parts: The electronic, vibrational, rotational, and translational energy. A sketch is given in Fig. 6.1. The total energy and single particle (or molecular) partition function may therefore be written as:

$$\epsilon(n) = \epsilon(n^e, n^v, n^r, n^t) = \epsilon^e(n^e) + \epsilon^v(n^v) + \epsilon^r(n^r) + \epsilon^t(n^t) \quad (6.20)$$

$$q = q^e q^v q^r q^t. \quad (6.21)$$

We will now treat each contribution in more detail.

For the electrical contribution we have

$$q^e = \omega_0^e \exp \{-\beta \epsilon_0^e\}, \quad (6.22)$$

where  $\omega_0^e$  is the degeneracy of the ground state. Usually there is just one ground state,  $\omega_0^e = 1$ . Notable exceptions are  $\text{O}_2$ , for which  $\omega_0^e = 3$ , and  $\text{NO}$ , for which  $\omega_0^e = 2$ .

The vibrations of the two nuclei are approximately harmonic, so summing over all possible quantum numbers gives (see Problem 6-2)

$$\epsilon^v(n^v) = \left( n^v + \frac{1}{2} \right) \hbar \omega \quad (6.23)$$

$$q^v = \frac{\exp \left\{ -\frac{1}{2} \beta \hbar \omega \right\}}{1 - \exp \left\{ -\beta \hbar \omega \right\}} = \frac{\exp \left\{ -\frac{1}{2} \Theta^v / T \right\}}{1 - \exp \left\{ -\Theta^v / T \right\}}, \quad (6.24)$$

where we have defined the vibrational temperature  $\Theta^v \equiv \hbar \omega / k_B$ . Typical  $\Theta^v$  range from 300 K (for  $\text{H}_2$ ) to 6000 K.

The vibrations are usually much faster than the rotations. To a good approximation, the molecule therefore rotates as a rigid body, with the nuclei fixed at the equilibrium distance  $R_0$ . The moment of inertia for rotations around an axis through the centre of the molecule, perpendicular to the axis connecting the two nuclei, is therefore

$$I = \frac{m_1 m_2}{m_1 + m_2} R_0^2 = \mu R_0^2, \quad (6.25)$$

where  $\mu$  is the reduced mass of the molecule. According to quantum mechanics the possible energies of a rigid rotator, and the degeneracy, are given by

$$\epsilon_J^r = \frac{\hbar^2}{2I} J(J+1) \quad (6.26)$$

$$\omega_J = 2J + 1, \quad (6.27)$$

where  $J = 0, 1, 2, \dots$ . Calculating the rotational partition function  $q^r$  we now replace the sum by an integral:

$$\begin{aligned} q^r &= \sum_J (2J+1) e^{-\beta \frac{\hbar^2}{2I} J(J+1)} \\ &\approx \int_0^\infty dJ (2J+1) e^{-\beta \frac{\hbar^2}{2I} J(J+1)} \\ &= \frac{2I}{\beta \hbar^2} = \frac{T}{\Theta^r}, \end{aligned} \quad (6.28)$$

where  $\Theta^r \equiv \hbar^2/(2Ik_B)$  is the rotational temperature. Typical  $\Theta^r$  range from 0.05 K (for  $\text{H}_2$ ) to 80 K (for  $\text{I}_2$ ). Replacing the sum by an integral is only justified if the distance between consecutive energy levels is much smaller than  $k_B T$ , that is if

$$\frac{\beta \hbar^2}{2I} (J+1)(J+2) - \frac{\beta \hbar^2}{2I} J(J+1) = \frac{\beta \hbar^2}{I} (J+1) \ll 1. \quad (6.29)$$

When applying Eq. (6.28) we have to convince ourselves that the temperature is high enough to obey Eq. (6.29).

Finally, for the translational partition function we again consider the energy of a particle in a box of size  $V = L^3$ . Similarly to Eq. (5.31) (but now  $q^t$  stands for three dimensions instead of one) we find

$$q^t = V \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2}, \quad (6.30)$$

where now  $m = m_1 + m_2$  is the total mass of the molecule.

There is one subtlety related to the nuclear spin. This is where we find that homonuclear molecules behave differently from heteronuclear molecules. According



to quantum mechanics, for homonuclear molecules the nuclei must be indistinguishable. Specifically, the nuclear spin function either changes sign under exchange of the two nuclei, or it doesn't change at all. Even though the nuclear spins do not take part in the thermal fluctuations, there is a way in which they influence the partition function: a rotation of  $180^\circ$  around an axis through the centre of the molecule, perpendicular to the axis connecting the two nuclei, is the same as exchanging the two nuclei. Therefore, the nuclear spin functions and rotational functions are coupled. Analysis shows that if the nuclear spin is integer only even  $J$  values are allowed, and if the nuclear spin is half-integer only odd  $J$  values are allowed. Therefore, for homonuclear molecules, Eq. (6.28) should be replaced with

$$q^r = \sum_{J=\text{even}} (2J+1)e^{-\beta\frac{h^2}{2I}J(J+1)} \approx \frac{T}{2\Theta^r} \quad (6.31)$$

$$q^r = \sum_{J=\text{odd}} (2J+1)e^{-\beta\frac{h^2}{2I}J(J+1)} \approx \frac{T}{2\Theta^r}. \quad (6.32)$$

Note that both even and odd nuclear spin yield the same answer. In general, the rotational partition function is denoted as  $T/(\sigma\Theta^r)$ , with  $\sigma = 1$  for heteronuclear and  $\sigma = 2$  for homonuclear two-atomic molecules.

In summary, for an ideal gas of two-atomic molecules, the free energy is given by  $A = -k_B T \ln Q$ , with  $Q = q^N/N!$  and

$$q = \omega_0^e \exp\{-\beta\epsilon_0^e\} \frac{\exp\{-\frac{1}{2}\Theta^v/T\}}{1 - \exp\{-\Theta^v/T\}} \left(\frac{T}{\sigma\Theta^r}\right) V \left(\frac{2\pi mk_B T}{h^2}\right)^{3/2}. \quad (6.33)$$

In Problem 6-3 you are asked to calculate the entropy and specific heat of an ideal gas of two-atomic molecules.

## 6.4 Boson gas

We have seen in section 6.2 that at high temperatures the distinction between bosons and fermions becomes irrelevant. In that regime the particles obey Maxwell-Boltzmann statistics. In this and the next section we will analyse the more general case, also applicable to low temperatures. As it turns out, it is quite difficult to treat the statistics of bosons or fermions in the canonical ensemble, but much easier in the grand canonical ensemble. We will show why.

### 6.4.1 Bose-Einstein statistics

First we consider an ideal gas of  $N$  identical bosons. We can select the quantum numbers such that

$$n_i \leq n_{i+1} \quad i = 1, \dots, N \quad (6.34)$$

There is an alternative way to label the state of the system, namely by means of *occupation numbers*  $m_n$ , such that

$$\sum_{n=0}^{\infty} m_n = N. \quad (6.35)$$

The occupation number  $m_n$  is, in a way, equal to the *number* of particles in state  $n$ . We need to keep in the back of our minds that these  $m_n$  particles are, of course, not a distinct set of particles; quantum mechanics requires that all (identical) particles are indistinguishable. All particles therefore play an identical role. But often it is useful to think of the occupation number in this way. For example:

$$\begin{aligned} n &= 0, 1, 2, 3, 4, 5, 6, \dots \\ m_n &= 2, 0, 0, 0, 1, 1, 0, \dots \end{aligned}$$

means that 2 particles are in state  $n = 0$ , 1 particle in state  $n = 4$ , and 1 particle in state  $n = 5$ , i.e.

$$n_1 = 0, n_2 = 0, n_3 = 4, n_4 = 5.$$

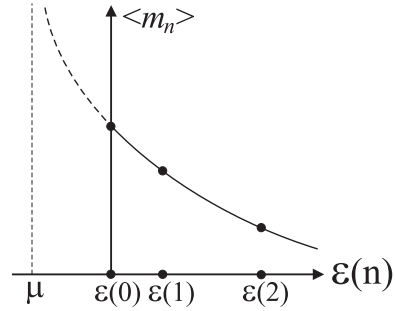
In terms of occupation numbers, the (canonical) partition function reads

$$Q_N = \underbrace{\sum_{m_0=0}^{\infty} \sum_{m_1=0}^{\infty} \dots \sum_{m_{\infty}=0}^{\infty}}_{\sum_n m_n = N} e^{-\beta \sum_n m_n \epsilon(n)}, \quad (6.36)$$

where we have labeled  $Q$  with a subscript  $N$  to make explicit its dependence on the number of particles  $N$ . The condition Eq. (6.35) makes this sum a restricted sum, which is very hard to evaluate. If we imagine the Bose gas to be coupled to an external reservoir of identical bose particles at chemical potential  $\mu$ , the grand canonical partition function reads

$$\begin{aligned} \Xi &= \sum_{N=0}^{\infty} \underbrace{\sum_{m_0=0}^{\infty} \sum_{m_1=0}^{\infty} \dots \sum_{m_{\infty}=0}^{\infty}}_{\sum_n m_n = N} e^{-\beta \sum_n m_n \epsilon(n)} e^{\beta \mu \sum_n m_n} \\ &= \sum_{m_0=0}^{\infty} \sum_{m_1=0}^{\infty} \dots \sum_{m_{\infty}=0}^{\infty} e^{-\beta \sum_n m_n (\epsilon(n) - \mu)} \\ &= \prod_{n=0}^{\infty} \left\{ \sum_{m_n=0}^{\infty} e^{-\beta m_n (\epsilon(n) - \mu)} \right\} \\ &= \prod_{n=0}^{\infty} \frac{1}{1 - e^{-\beta (\epsilon(n) - \mu)}}. \end{aligned} \quad (6.37)$$

Figure 6.2: Average occupation number of a Bose gas as a function of the energy  $\epsilon(n)$  of state  $n$ . The energy of the lowest energy state is  $\epsilon(0)$ . The chemical potential  $\mu$  must be lower than this.



In going from the first to the second line we have used the fact that a restricted sum, when summed over all possible values for the restriction ( $N$ ), is the same as an unrestricted sum (see Appendix A for a simple case). This is why this problem is much simpler to solve in the grand canonical ensemble than in the canonical ensemble.

Now the thermodynamic potential associated with the grand canonical ensemble is the function  $PV(\mu, V, T)$ . It is equal to

$$\begin{aligned} PV &= k_B T \ln \Xi \\ &= -k_B T \sum_{n=0}^{\infty} \ln (1 - e^{-\beta(\epsilon(n)-\mu)}). \end{aligned} \quad (6.38)$$

We are now ready to do thermodynamics. For example, because the differential of  $PV$  is

$$d(PV) = SdT + PdV + Nd\mu, \quad (6.39)$$

the (average) number of particles, at given chemical potential  $\mu$ , volume  $V$ , and temperature  $T$ , is given by

$$\begin{aligned} N &= \left( \frac{\partial PV}{\partial \mu} \right)_{T,V} \\ &= \sum_{n=0}^{\infty} \frac{e^{-\beta(\epsilon(n)-\mu)}}{1 - e^{-\beta(\epsilon(n)-\mu)}} = \sum_{n=0}^{\infty} \frac{1}{e^{\beta(\epsilon(n)-\mu)} - 1} = \sum_{n=0}^{\infty} \langle m_n \rangle. \end{aligned} \quad (6.40)$$

In the last line  $\langle m_n \rangle$  is the average occupation number of state  $n$  (a proof will be given in chapter 7). The average occupation number is plotted as a function of  $\epsilon(n)$  in Fig. 6.2. Notice the singularity when  $\mu = \epsilon(n)$ . We want our mathematics to be correct, and extract from this physical results. In order for the derivation of

Eq. (6.37) to be valid we need

$$\sum_{m_n=0}^{\infty} e^{-\beta m_n(\epsilon(n)-\mu)} < \infty \quad \Leftrightarrow \quad \mu < \epsilon(n) \quad (\forall n) \quad (6.41)$$

$$\frac{1}{\Xi} = \prod_{n=0}^{\infty} (1 - e^{-\beta(\epsilon(n)-\mu)}) < \infty \quad \Leftrightarrow \quad \sum_n e^{-\beta(\epsilon(n)-\mu)} < \infty. \quad (6.42)$$

So we see that the chemical potential  $\mu$  in an ideal Bose gas is necessarily lower than the lowest energy state  $\epsilon_0$ , and that there are certain requirements on the speed with which  $\exp(-\beta(\epsilon(n) - \mu))$  tends to zero as  $n$  increases.

### 6.4.2 Bose-Einstein condensation

An ideal Bose gas has the peculiar property that at a low but *finite* temperature all particles tend to pile into the single-particle state of lowest energy. Let us see why this happens.

Suppose we have a fixed amount of  $N$  Bose particles at temperature  $T$  in a volume  $V$ . Using the results derived above, we can express  $N$  in terms of the chemical potential  $\mu$  (as well as  $V$  and  $T$ ). If the spacing between consecutive energy levels is small compared to  $k_B T$ , we can replace the sum Eq. (6.40) with an integral over the single-particle density of states  $\rho(\epsilon)$ :

$$N = \sum_{n=0}^{\infty} \langle m_n \rangle \approx \int_0^{\infty} d\epsilon \rho(\epsilon) \frac{1}{e^{\beta(\epsilon-\mu)} - 1}. \quad (6.43)$$

Here we have shifted the energy states such that the single particle state of lowest energy corresponds to  $\epsilon = 0$ . For an ideal particle of spin  $s$  (be it a Bose or Fermi particle), contained in a box of volume  $V = L^3$ , the single-particle density of states is given by (see Problem 6-4)

$$\rho(\epsilon) = (2s + 1) \left( \frac{2m}{\hbar^2} \right)^{3/2} \frac{V}{4\pi^2} \sqrt{\epsilon}, \quad (6.44)$$

leading to (Problem 6-5)

$$N = \frac{2s + 1}{4\pi^2} \left( \frac{2m}{\beta\hbar^2} \right)^{3/2} V \int_0^{\infty} dx \frac{\sqrt{x}}{e^{-\beta\mu} e^x - 1}. \quad (6.45)$$

This can in principle be inverted to

$$\mu = \mu(N, V, T). \quad (6.46)$$

We see that  $\mu < 0$  because otherwise the integrand is singular. Notice that the integral in Eq. (6.45) becomes *larger* when  $-\beta\mu$  (a positive quantity) becomes *smaller*. Notice also that the factor in front of the integral becomes smaller when  $\beta$  becomes larger. Therefore, if at constant  $N$  and  $V$  we increase  $\beta$  (i.e. we decrease  $T$ ), the first factor goes down, so the second factor must go up. Therefore  $-\beta\mu$  must go down. We have done this difficult exercise to prove that  $\mu$  approaches 0 faster than  $\beta^{-1}$ .

We now find the interesting result that, as we lower the temperature of a Bose gas, at a certain critical temperature  $T_c$  we encounter a situation where  $\beta\mu = 0$ . Below this temperature most of the available particles will start to go into the lowest accessible quantum state ( $n = 0$ ). This collapse of Bose particles into a single quantum state is called *Bose-Einstein condensation*. It was predicted by Albert Einstein, by generalising Satyendra Nath Bose's work on massless photons to massive atoms.

We can find the critical temperature by first using  $\beta\mu = 0$  and  $\beta = \beta_c = 1/(k_B T_c)$  in Eq. (6.45):

$$N = \frac{2s+1}{4\pi^2} \left( \frac{2m}{\beta_c \hbar^2} \right)^{3/2} V \int_0^\infty dx \frac{\sqrt{x}}{e^x - 1} \quad (T = T_c) \quad (6.47)$$

The last integral equals  $\zeta(\frac{3}{2})\frac{1}{2}\sqrt{\pi}$ , where  $\zeta$  is the Riemann zeta function which at  $3/2$  is approximately 2.6124. Inverting yields

$$T_c = \frac{1}{k_B} \frac{2\pi\hbar^2}{m} \left[ \frac{N}{V} \frac{1}{2s+1} \frac{1}{\zeta(\frac{3}{2})} \right]^{2/3}. \quad (6.48)$$

This is a good estimate for  $T_c$ .

Below  $T_c$  the sum over states can no longer be replaced by an integral. The largest error comes from the fact that more and more particles go into the lowest quantum state  $n = 0$ , whereas according to Eq. (6.44) the single particle density of states  $\rho(\epsilon)$  equals zero at  $\epsilon = 0$ . It turns out that the integral approach can still be used, provided that the number of particles in the ground state is added separately. Let us call the number of particles in the ground state  $N_0$ . We can then approximate the number of particles for  $T < T_c$  as

$$N = N_0 + \frac{2s+1}{4\pi^2} \left( \frac{2m}{\beta\hbar^2} \right)^{3/2} V \int_0^\infty dx \frac{\sqrt{x}}{e^x - 1} \quad (T < T_c) \quad (6.49)$$

Here we have used that for  $T < T_c$  the chemical potential is essentially zero. For  $T = T_c$  the number of particles in the lowest quantum state is still very small, which is why we were allowed to use Eq. (6.47) to estimate  $T_c$ . Again using Eq. (6.47), we

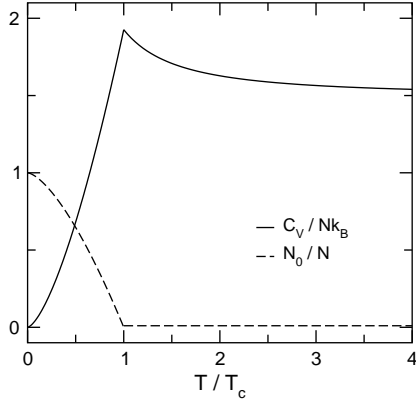


Figure 6.3: The fraction  $N_0/N$  of particles in the lowest quantum state (dashed line) and the specific heat  $C_V/(Nk_B)$  (solid line) of a Bose gas as a function of temperature. Note the discontinuity in the derivative of  $C_V$  at the critical temperature  $T_c$ .

can express the fraction  $N_0/N$  of particles condensed in the lowest quantum state (see dashed line in Fig. 6.3) as

$$\frac{N_0}{N} \approx 1 - \left(\frac{T}{T_c}\right)^{3/2}. \quad (6.50)$$

The dependence of the specific heat of a Bose gas on temperature is also quite peculiar. Knowing the occupation number and the density of states, we can find the total energy of the system:

$$U(\mu, V, T) = \sum_{n=0}^{\infty} \langle m_n \rangle \epsilon(n) \approx \int_0^{\infty} d\epsilon \epsilon \rho(\epsilon) \frac{1}{e^{\beta(\epsilon-\mu)} - 1}. \quad (6.51)$$

Note that the lowest quantum state need not be included because its energy is set to zero by definition. The specific heat is the derivative of  $U$  to  $T$  at constant  $(N, V)$ , whereas we have available  $U$  as a function of  $(\mu, V, T)$ . The chemical potential  $\mu$  needs to be determined at each temperature  $T$  such that the total number of particles equals  $N$ . In general it is therefore a difficult exercise to calculate the specific heat from this equation. However, we can easily calculate  $C_V$  for  $T < T_c$ . In that case  $\mu = 0$  and there is no temperature dependence of  $\mu$ . Using  $x = \beta\epsilon$ , the energy for  $T < T_c$  can be expressed as

$$U = \frac{2s+1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} V \beta^{-5/2} \int_0^{\infty} dx \frac{x^{3/2}}{e^x - 1} \quad (T < T_c) \quad (6.52)$$

Differentiating with respect to  $T$  gives

$$C_V = \frac{5}{2} k_B \frac{2s+1}{4\pi^2} \left(\frac{2m}{\beta\hbar^2}\right)^{3/2} V \int_0^{\infty} dx \frac{x^{3/2}}{e^x - 1} \quad (T < T_c) \quad (6.53)$$

The last integral equals  $\zeta(\frac{5}{2}) \frac{3}{4} \sqrt{\pi}$ , where the Riemann zeta function at  $5/2$  is approximately 1.3415. With the use of Eq. (6.47) this may be expressed as

$$C_V = \frac{15}{4} N k_B \left(\frac{T}{T_c}\right)^{3/2} \frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})} \approx 1.926 N k_B \left(\frac{T}{T_c}\right)^{3/2} \quad (T < T_c) \quad (6.54)$$

More elaborate calculations are needed for  $T > T_c$ . The result, to very good approximation, is:<sup>2</sup>

$$C_V \approx 1.496Nk_B + 0.341Nk_B \left(\frac{T_c}{T}\right)^{3/2} + 0.089Nk_B \left(\frac{T_c}{T}\right)^3 \quad (T > T_c) \quad (6.55)$$

Figure 6.3 (solid line) shows the very peculiar shape of  $C_V(T)$ . Note that the derivative  $dC_V/dT$  is discontinuous at  $T = T_c$ .

## 6.5 Fermi gas

### 6.5.1 Fermi-Dirac statistics

We now consider an ideal gas of  $N$  identical fermions. We can select quantum numbers such that

$$n_i < n_{i+1}. \quad (6.56)$$

The treatment is similar to the treatment of the Bose gas. We will again turn to a description in terms of occupation numbers  $m_n$ . Since for fermions states with two or more quantum numbers equal do not exist, the occupation number of a state is either 0 or 1. The (canonical) partition function is therefore given by

$$Q_N = \underbrace{\sum_{m_0=0}^1 \sum_{m_1=0}^1 \dots \sum_{m_\infty=0}^1}_{\sum_n m_n = N} e^{-\beta \sum_n m_n \epsilon(n)}, \quad (6.57)$$

and the grand canonical partition function by

$$\begin{aligned} \Xi &= \sum_{N=0}^{\infty} Q_N e^{\beta \mu N} \\ &= \sum_{m_0=0}^1 \dots \sum_{m_\infty=0}^1 e^{-\beta \sum_n (\epsilon(n) - \mu) m_n} \\ &= \prod_{n=0}^{\infty} (1 + e^{-\beta(\epsilon(n) - \mu)}), \end{aligned} \quad (6.58)$$

<sup>2</sup>Note that this is an approximation, but the accuracy is at least 0.3% over the full range of temperatures. For example the high temperature limit should be  $C_V = 3/2Nk_B$ , whereas the approximation yields a prefactor 1.496.

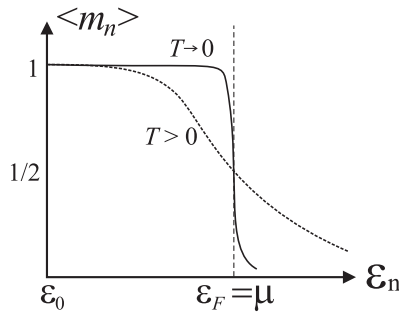


Figure 6.4: Average occupation number of a Fermi gas as a function of the energy  $\epsilon_n = \epsilon(n)$  of state  $n$ . At very low temperatures  $T \rightarrow 0$ , all lower states are occupied by one particle. The energy of the highest occupied state at  $T = 0$  is called the Fermi energy  $\epsilon_F$ .

where again we have used the fact that a restricted sum, when summed over all possible restriction, is an unrestricted sum. The thermodynamic function  $PV$  is now equal to

$$PV = k_B T \sum_{n=0}^{\infty} \ln(1 + e^{-\beta(\epsilon(n) - \mu)}). \quad (6.59)$$

The number of particles, at given chemical potential  $\mu$ , volume  $V$ , and temperature  $T$ , is given by

$$N = \left( \frac{\partial PV}{\partial \mu} \right)_{T,V} = \sum_{n=0}^{\infty} \frac{1}{e^{\beta(\epsilon(n) - \mu)} + 1} = \sum_{n=0}^{\infty} \langle m_n \rangle. \quad (6.60)$$

The average occupation number  $\langle m_n \rangle$  is plotted as a function of  $\epsilon(n)$  in Fig. 6.4. Notice that as  $T \rightarrow 0$ , all lower level states become occupied by exactly one particle. Remember that this is the maximum occupation number allowed for fermions. The energy of the highest occupied state at  $T = 0$  is also called the Fermi energy  $\epsilon_F$ . It is equal to the chemical potential  $\mu$  at  $T = 0$  (can you explain why?).

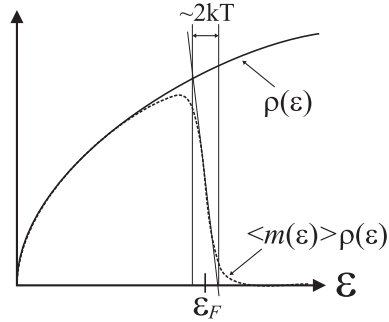
### 6.5.2 Specific heat of free electrons in a metal

Consider a block of metal. In metals, the highest energy electrons are not “bound” to any specific nucleus. Rather, they move almost freely in the entire volume  $V$  of the metal, which is why they are called free electrons. We may now ask what is the contribution of these  $N$  free electrons to the specific heat of the metal? In fact, this is an age old problem, which could not be solved prior to the development of quantum mechanics. Classically, one would expect  $C_V \approx \frac{3}{2} N k_B$ , at least at high enough temperature. Experiments on metals, however, show that  $C_V$  is proportional to  $N k_B T$ , i.e. linear in the temperature  $T$ .

To show why, consider the free electrons to form an ideal Fermi gas, contained in the volume  $V$  of the block of metal. The single-particle density of states, according



Figure 6.5: Density of states  $\rho(\epsilon)$  and average occupation number times density of states  $\rho(\epsilon) \langle m(\epsilon) \rangle$  of a Fermi gas. The integral over the latter gives the number of particles  $N$ . The width of the transition zone between the two vertical lines is approximately  $2k_B T$ .



to Eq. (6.44), is given by (remember that the spin of an electron is  $\frac{1}{2}$ ):

$$\rho(\epsilon) = \left( \frac{2m}{\hbar^2} \right)^{3/2} \frac{V}{2\pi^2} \sqrt{\epsilon}. \quad (6.61)$$

The number of free electrons is related to the Fermi energy  $\epsilon_F$  by

$$N = \int_0^\infty d\epsilon \rho(\epsilon) \frac{1}{e^{\beta(\epsilon-\mu)} + 1}, \quad (6.62)$$

where we have put the lowest energy  $\epsilon_0$  of the free electrons equal to zero. A plot of the integrand, i.e. the number of particles between energy  $\epsilon$  and  $\epsilon + d\epsilon$ , is given in Fig. 6.5. The argument is now as follows. The electrons can only gain energy if they move into a free state in their energetic neighbourhood. Only a few of the electrons can do this, namely the ones with an energy near  $\mu$ . The width of the transition zone (between the vertical lines in Fig. 6.5) is of order  $2k_B T$ , whereas for a typical metal  $\epsilon_F/k_B \approx 10^5$  K. Therefore  $\mu \approx \epsilon_F$  also at room temperature. Because the specific heat is proportional to the number of electrons which can move into a free state, we predict that  $C_V$  will be linear in  $T$ .

Now a more precise calculation. The integral in Eq. (6.62) is particularly easy at  $T = 0$  K, because all states up to  $\epsilon_F$  are occupied by one particle, whereas all higher energy states are unoccupied:

$$N = \int_0^{\epsilon_F} d\epsilon \left( \frac{2m}{\hbar^2} \right)^{3/2} \frac{V}{2\pi^2} \sqrt{\epsilon} = \frac{V}{3\pi^2} \left( \frac{2m\epsilon_F}{\hbar^2} \right)^{3/2}. \quad (6.63)$$

Now suppose we heat the metal from 0 K to a temperature  $T$ , assuming the volume and number of free electrons remain constant. We may then write the increase in energy of the free electrons, and the number of free electrons as

$$U(T) = \int_0^\infty d\epsilon \epsilon \rho(\epsilon) \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \quad (6.64)$$

$$\epsilon_F N = \epsilon_F \int_0^\infty d\epsilon \rho(\epsilon) \frac{1}{e^{\beta(\epsilon-\mu)} + 1}. \quad (6.65)$$

Differentiating Eqs. (6.64) and (6.65) with respect to  $T$  yields

$$C_V = \int_0^\infty d\epsilon \epsilon \rho(\epsilon) \frac{\partial}{\partial T} \left( \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \right) \quad (6.66)$$

$$0 = \int_0^\infty d\epsilon \epsilon_F \rho(\epsilon) \frac{\partial}{\partial T} \left( \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \right). \quad (6.67)$$

Subtracting Eq. (6.67) from Eq. (6.66) we find for the specific heat

$$C_V = \int_0^\infty d\epsilon (\epsilon - \epsilon_F) \rho(\epsilon) \frac{\partial}{\partial T} \left( \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \right). \quad (6.68)$$

As we have seen, the  $\partial/\partial T(\ )$  term is only significant in a small region around  $\epsilon = \epsilon_F$ . We may therefore approximate  $\rho(\epsilon) \approx \rho(\epsilon_F)$  in this integral. Furthermore, the chemical potential  $\mu$  changes only very slowly with temperature  $T$  and is approximately  $\epsilon_F$  throughout the entire solid state range of a metal. We therefore write

$$\begin{aligned} C_V &\approx \rho(\epsilon_F) \int_0^\infty d\epsilon (\epsilon - \epsilon_F) \frac{\frac{\epsilon - \epsilon_F}{k_B T^2} e^{\beta(\epsilon - \epsilon_F)}}{[e^{\beta(\epsilon - \epsilon_F)} + 1]^2} \\ &\approx k_B^2 T \rho(\epsilon_F) \int_{-\infty}^\infty dx \frac{x^2 e^x}{(e^x + 1)^2} \\ &= k_B^2 T \rho(\epsilon_F) \frac{\pi^2}{3}. \end{aligned} \quad (6.69)$$

In the second line we have used that  $\epsilon_F \gg k_B T$ . Note that in this last derivation we have made no assumptions about the precise form of  $\rho(\epsilon)$ . We do know the precise form, namely Eq. (6.61), which may be expressed as

$$\rho(\epsilon) = \rho(\epsilon_F) \left( \frac{\epsilon}{\epsilon_F} \right)^{1/2}, \quad (6.70)$$

allowing us to write (again assuming  $\epsilon_F \gg k_B T$ )

$$N \approx \int_0^{\epsilon_F} \rho(\epsilon) d\epsilon = \frac{2}{3} \rho(\epsilon_F) \epsilon_F. \quad (6.71)$$

Our final result for the (electronic) specific heat of a metal is therefore

$$C_V = \frac{\pi^2}{2} N k_B \left( \frac{T}{T_F} \right), \quad (6.72)$$

where  $T_F = \epsilon_F/k_B$  is the Fermi temperature. That this result is linear in the temperature is entirely due to quantum effects.

## 6.6 The classical limit: Maxwell-Boltzmann revisited

Let us now show how Maxwell-Boltzmann statistics arise for a Bose gas at high temperatures. We have argued that, at constant  $N$  and  $V$ ,  $-\beta\mu$  increases as the temperature increases (and  $\mu < \epsilon(n)$  for all  $n$ ). Therefore at high enough temperature we have  $\exp\{\beta(\epsilon(n) - \mu)\} \gg 1$ . In that case

$$\begin{aligned} PV &= -k_B T \sum_n \ln(1 - e^{-\beta(\epsilon(n) - \mu)}) \\ &\approx k_B T \sum_n e^{-\beta(\epsilon(n) - \mu)} \end{aligned} \quad (6.73)$$

$$= k_B T e^{\beta\mu} q. \quad (6.74)$$

The chemical potential can be related to the number of particles by writing

$$N = \left( \frac{\partial PV}{\partial \mu} \right)_{T,V} = e^{\beta\mu} q \quad (6.75)$$

$$\mu = -k_B T \ln \left( \frac{q}{N} \right). \quad (6.76)$$

Note that the above implies  $PV = Nk_B T$ . We can now express the free energy as

$$\begin{aligned} A &= G - PV = N\mu - PV \\ &= -Nk_B T \ln \left( \frac{q}{N} \right) - Nk_B T = -Nk_B T \ln \left( \frac{qe}{N} \right) \\ &= -k_B T \ln \left( \frac{q^N}{N!} \right). \end{aligned} \quad (6.77)$$

This is in exact agreement with Maxwell-Boltzmann statistics Eq. (6.19).

A similar argument holds for the case of a Fermi gas at high temperatures, with the same outcome.

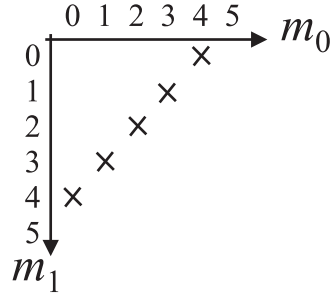


Figure 6.6: Example of a summation over occupation numbers  $m_0$  and  $m_1$  with the constraint that the total number of particles  $N = 4$ . When a final summation over  $N$  is made, each combination of  $m_0$  and  $m_1$  is encountered exactly once.

## Appendix

In this appendix we will show for a simple case why the summation over  $N$  in Eq. (6.37) effectively removes the restriction that  $\sum_n m_n$  must be equal to  $N$ .

Suppose we have just two states,  $n = 0$  and  $n = 1$ , and a total of  $N = 4$  particles. When performing the sums over the occupation numbers for  $m_0$  and  $m_1$ , we will have as an added constraint that  $\sum_n m_n = N$ , i.e.  $m_0 + m_1 = 4$ . The occupation numbers can then be chosen according to the crosses in figure 6.6. Now if we perform a sum over the total number of particles  $N$ , other diagonal rows of crosses will be added until we have encountered each combination of  $m_0$  and  $m_1$  exactly once. The same argument applies to a larger number of states.

## Problems

**6-1. The classical limit.** Calculate  $n_x$ ,  $n_y$ ,  $n_z$ , for the case  $n_x = n_y = n_z$  for a hydrogen atom in a box of  $1 \text{ cm}^3$  if the particle has an energy of  $U = \frac{3}{2}k_B T$  and  $T = 300 \text{ K}$ . What significant fact does this calculation illustrate?

**6-2. Vibrational molecular partition function.** Give a proof of Eq. (6.24).

**6-3. Entropy and specific heat of an ideal gas of two-atomic molecules.** Prove that the entropy and specific heat of an ideal gas of two-atomic molecules are given by

$$\begin{aligned} \frac{S}{Nk_B} &= \ln \left[ \left( \frac{2\pi mk_B T}{h^2} \right)^{3/2} e^{5/2} \frac{V}{N} \right] + \ln \left( \frac{T}{\sigma \Theta^r} e \right) \\ &\quad + \frac{\Theta^v/T}{e^{\Theta^v/T} - 1} - \ln(1 - e^{-\Theta^v/T}) + \ln \omega_0^e \\ \frac{C_V}{Nk_B} &= \frac{5}{2} + \left( \frac{\Theta^v}{T} \right)^2 \frac{e^{\Theta^v/T}}{(e^{\Theta^v/T} - 1)^2}. \end{aligned}$$

**6-4. Single-particle density of states.** Consider a quantum particle of spin  $s$  in a box of volume  $V = L^3$ . Prove that the single-particle density of states at energy  $\epsilon$  is given by Eq. (6.44). (Hint: what is the number of realisations for  $s_z$  for a particle of spin  $s$ ? Use the result of Problem 1-9 for the energy of the particle.)

**6-5. Number of particles in a Bose gas at chemical potential  $\mu$ .** Prove Eq. (6.45) from Eqs. (6.43) and (6.44).

**6-6. Molecular adsorption on a surface.** Consider a gas in contact with a solid surface. The molecules of the gas can adsorb on  $M$  specific sites on the surface. All these sites are identical and we assume, for simplicity, that these sites do not interact with each other. Each site can accommodate at most two molecules from the gas; each site has an energy that we take as zero when the site is empty,  $\epsilon_1$  if the site is singly occupied, and  $\epsilon_2$  if it is doubly occupied. If we consider the surface as our system, the total energy of the system is

$$E = \sum_{i=1}^M \epsilon(n_i),$$

where  $n_i$  is the number of adsorbed molecules at site  $i$ , and  $\epsilon(0) = 0$ ,  $\epsilon(1) = \epsilon_1$ , and  $\epsilon(2) = \epsilon_2$ . The total number of adsorbed molecules can be expressed as

$$N = \sum_{i=1}^M n_i.$$

We assume the surface is in equilibrium with the gas, which has a temperature  $T$  and chemical potential  $\mu$ .

Show that the average number of molecules adsorbed per site is given by

$$\frac{\langle N \rangle}{M} = \frac{e^{-\beta(\epsilon_1 - \mu)} + 2e^{-\beta(\epsilon_2 - 2\mu)}}{1 + e^{-\beta(\epsilon_1 - \mu)} + e^{-\beta(\epsilon_2 - 2\mu)}},$$

and that the average energy per site is given by

$$\frac{\langle E \rangle}{M} = \frac{\epsilon_1 e^{-\beta(\epsilon_1 - \mu)} + \epsilon_2 e^{-\beta(\epsilon_2 - 2\mu)}}{1 + e^{-\beta(\epsilon_1 - \mu)} + e^{-\beta(\epsilon_2 - 2\mu)}}.$$

(Hint: Show that the grand canonical partition function can be written as  $\Xi = z^M$ , with  $z = 1 + \exp\{-\beta(\epsilon_1 - \mu)\} + \exp\{-\beta(\epsilon_2 - 2\mu)\}$ . Then use the results of Problem 5-5.)

**6-7. An ideal gas of atoms.** In this exercise we will consider an ideal gas of real *atoms*. Besides the translational energy associated with point particles, atoms also have an electronic contribution to the single particle energy. Since these two types of energy contributions are independent, the single particle partition function of an ideal gas of atoms factorizes into two parts:

$$q = q^e q^t$$

where  $q^t$  is the translational partition function of a particle in a box, and  $q^e$  is given by

$$q^e = \sum_{n^e} \omega^e(n^e) \exp \{-\beta \epsilon^e(n^e)\}$$

Here  $\omega^e(n^e)$  is the degeneracy of the  $n^e$ 'th electronic energy level. For hydrogen  $\omega^e(0) = 2$ , for carbon  $\omega^e(0) = 9$ , and for oxygen  $\omega^e(0) = 5$ ,  $\omega^e(1) = 3$  and  $\omega^e(2) = 1$ . We are allowed to set the ground state energy of all atoms to zero:  $\epsilon^e(0) \equiv 0$ . The other energy levels may then be measured experimentally by analysing the adsorption spectra of the atoms: photons (light) are adsorbed by the atoms at frequencies  $\nu$ , the energies  $h\nu$  of which correspond to the distance between the different electronic energy levels. As it turns out, for most atoms even the first level is much higher than the ground state, giving no contribution to the electronic partition function. Notable exceptions are atomic oxygen and fluor. Oxygen has a first excitation at  $158.5 \text{ cm}^{-1}$  and a second at  $226.5 \text{ cm}^{-1}$ . The next is at  $15867.6 \text{ cm}^{-1}$ . Using  $1 \text{ cm}^{-1} = 1.986 \times 10^{-23} \text{ J}$ , we see that the last excitation gives a contribution only when  $T \approx 15000 \text{ K}$ .

Calculate the atomic entropy (per mole) of carbon atoms and that of oxygen atoms at standard temperature ( $T^0 = 298.15 \text{ K}$ ) and standard pressure ( $P^0 = 1.048 \times 10^5 \text{ Pa}$ ). (You may use that the molar entropy of atomic hydrogen equals  $114.71 \text{ J/mol/K}$ .) Experimentally:  $S(\text{C}) = 158.10 \text{ J/mol/K}$  and  $S(\text{O}) = 161.06 \text{ J/mol/K}$ .

**6-8. Chemical potential in an ideal gas mixture.** Suppose we make an ideal gas mixture of  $N_A$  molecules A and  $N_B$  molecules B. Because the mixture is ideal, the molecules do not interact, and the canonical partition function may be written as

$$Q = \frac{q_A^{N_A} q_B^{N_B}}{N_A! N_B!}$$

a Show that the total free energy  $A$  is given by

$$A = -N_A k_B T \ln \left( \frac{q_A^e}{N_A} \right) - N_B k_B T \ln \left( \frac{q_B^e}{N_B} \right)$$

Since we have not specified the exact nature of the molecules A and B, we do not know much about the partition function. However, we do know that the translations of the molecules lead to the appearance of the volume  $V$  in the single particle partition function. We denote the remaining part of the single particle partition function by  $q'$ . Specifically, for molecule A:

$$q_A = \frac{q_A}{V} V \equiv q'_A(T) V$$

Note that  $q'_A(T)$  only depends on the temperature, *not* on the volume of the system.

- b Show that the chemical potential of A, defined as  $\mu_A = \left( \frac{\partial A}{\partial N_A} \right)_{N_B, V, T}$ , may be written as

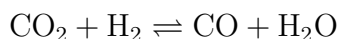
$$\mu_A(P, T) = \mu_A^*(T) + k_B T \ln(P x_A)$$

where  $x_A = N_A/(N_A + N_B)$  is the fraction of A molecules,  $P = (N_A + N_B) k_B T / V$  the pressure, and  $\mu_A^*(T)$  a function that only depends on temperature.

Note the  $\mu_A^*(T)$  depends on our choice for the unit of pressure. In the literature it is common practice to express everything in molar quantities and the pressure  $P$  in units of atmosphere, so that  $\mu_A^*(T)$  is the chemical potential per mole at temperature  $T$  and standard pressure  $P^0$ :

$$\mu_A(P, T) = \mu_A^*(T) + RT \ln((P/P^0)x_A).$$

**6-9. Chemical equilibrium.** We consider the following chemical reaction:



at a temperature of  $T = 2000$  K and reference temperature  $P = P^0 = 1$  atm. Under these conditions the reaction takes place entirely in the gas phase, which we may assume to be an ideal gas mixture.

Denoting the chemical potentials of the components in the mixture by  $\mu_i$  (see end of previous exercise), thermodynamic equilibrium is reached when

$$\sum_i \mu_i \nu_i = 0$$

where  $\nu_i$  are the stoichiometric coefficients of the reaction (i.e. +1 for CO and H<sub>2</sub>O, and -1 for CO<sub>2</sub> and H<sub>2</sub>).

## 6. IDEAL GASES

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- a Show that the above condition implies that  $K_p$ , defined as  $K_p = \prod_i (Px_i)^{\nu_i}$ , can be expressed as

$$K_p = \exp\left(-\frac{\Delta\mu_r^*(T)}{RT}\right)$$

where  $x_i = N_i/N$  is the mole fraction of component  $i$  and  $\Delta\mu_r^*(T) = \sum_i \mu_i^*(T)\nu_i$  is the change in chemical potential (per mole) of the reaction at temperature  $T$  and standard pressure  $P^0$ . Note that for this particular reaction the pressure dependence of  $K_p$  falls out:

$$K_p = \frac{(Px_{CO})(Px_{H_2O})}{(Px_{CO_2})(Px_{H_2})} = \frac{x_{CO}x_{H_2O}}{x_{CO_2}x_{H_2}}$$

- b Calculate  $\Delta\mu_r^*(2000\text{K})$  of the reaction using the table given below. Hint: consider Eq. (3.89).

species	$h^0$ kJ/mol	$s^0$ J/mol/K	$c_p$ J/mol/K
CO	-110.53	197.54	29.14
H <sub>2</sub> O	-241.82	188.72	33.60
CO <sub>2</sub>	-393.52	213.69	37.05
H <sub>2</sub>	0	130.57	29.16

- c Suppose we start with 1 mole of CO<sub>2</sub> and 1 mole of H<sub>2</sub> at  $T = 2000$  K and standard pressure. Our reaction will take place. How many moles of CO<sub>2</sub>, H<sub>2</sub>, CO, and H<sub>2</sub>O are there in equilibrium? Hint: suppose  $\alpha$  mole of CO<sub>2</sub> have reacted, how many moles of the other components are there?



# Chapter 7

## Probabilities and fluctuations

In this chapter we will study probabilities associated with each type of ensemble. We will encounter the principle of equal *a priori* probabilities, the ergodic hypothesis, and study fluctuations of the thermodynamic variables in each of the ensembles.

### 7.1 Probabilities

#### 7.1.1 Microcanonical (N,V,U)

Suppose we have an isolated system, containing  $N$  particles in a constant volume  $V$ . Because the system is isolated, its energy  $U$  is in principle a conserved property. We have discussed in section 2.2 that perfect isolation is never possible, and small perturbations cause the system to continuously jump between any of the  $\Omega$  different states of the same energy. A measurement of a quantity  $F$  will therefore be given by some average over the expectation values of all possible states. We postulate that this average must be performed with an equal probability for each possible state. In other words, the probability to encounter the system in state  $n$  is<sup>1</sup>

$$P_n = \begin{cases} \frac{1}{\Omega} & \text{if } E_n = U, \\ 0 & \text{if } E_n \neq U. \end{cases} \quad (7.1)$$

A measurement of a quantity  $F$  then yields<sup>2</sup>

$$\langle F \rangle = \sum_n P_n F_n, \quad (7.2)$$

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<sup>1</sup>Do not confuse the notation of  $P_n$  for probability with  $P$  for pressure.

<sup>2</sup>Note that the notation  $\langle \dots \rangle$  for the *ensemble* average is similar to that of the quantum mechanical expectation value  $\langle \dots \rangle$  of an observable. Technically we should write

$$\langle\langle F \rangle\rangle = \sum_n P_n \langle F_n \rangle,$$

where  $F_n$  is the expectation value of property  $F$  in state  $n$ . The average in Eq. (7.2) is called the microcanonical average, to distinguish it from the canonical average which we will encounter in the next subsection. Eq. (7.1) is the fundamental postulate of statistical thermodynamics. It is referred to as the *principle of equal a priori probabilities*. “*A priori*” means that the principle refers to the most elementary property of the system, its quantum mechanical state, about which one cannot justify any other statement than that all outcomes are equally probable. For all kinds of derived properties it is of course no longer true that each outcome is equally probable. An analogy is this: if we shake a box containing 1000 balls, and blindly take one ball, the probability to take a certain ball is  $1/1000$ , and this probability is equal for each ball. Now suppose  $3/4$  of the balls are red and  $1/4$  are white. The colour of the ball we take can be either red or white. The probability to take a red ball is however not  $1/2$ , but  $3/4$ .

Only in an idealised case can the energy be kept exactly constant, in practice this is impossible. We therefore assume that the energy fluctuates between  $U$  and  $U + dU$ . If we say the system is thermodynamically isolated, we mean in practice that  $dU$  is very small relative to  $U$ , e.g.  $dU = 10^{-10}U$ . For a system containing  $10^{20}$  particles this would mean  $dU = 10^{10}(U/N)$ , in other words: no matter how small the fluctuation at the macroscopic scale, it will still be many orders of magnitude larger than the energy per particle. Quantum mechanically there are many states between  $U$  and  $U + dU$ . In the language of section 2.2, the density of states  $\Omega(U)$  is very large. Small perturbations therefore cause the system to jump between different states for which  $U \leq E_n < U + dU$ . The principle of equal a priori probabilities is also applied in this case, leading to

$$P_n = \begin{cases} \frac{1}{\Omega(U)dU} & U \leq E_n < U + dU, \\ 0 & \text{otherwise.} \end{cases} \quad (7.3)$$

In the above we have assumed an idealized experiment, in which an average is taken over all possible states corresponding to the macroscopic thermodynamic parameters. In other words, we have performed an *ensemble average*. In a real experiment a property  $F$  is measured by averaging of a certain amount of *time*  $T$ ,

$$\bar{F} = \frac{1}{T} \int_0^T dt F(t). \quad (7.4)$$

Since a finite amount of time is spent in each state, and the number of states between  $U$  and  $U + dU$  is so great, one may wonder whether this time average is equal to the ensemble average Eq. (7.2). Indeed, even though many different states are sampled

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where  $\langle F_n \rangle$  is the quantum mechanical expectation value of  $F$  in state  $n$ . However, this would make all our notations needlessly complicated. We stick to the notation of Eq. (7.2), assuming the reader understands from the context which average is meant.

during a typical experimental time, the actual number of states visited is still much less than the number of states between  $U$  and  $U + dU$ . Despite this we *assume* that to a good approximation

$$\boxed{\bar{F} = \langle F \rangle}. \quad (7.5)$$

This is referred to as the *ergodicity hypothesis*. We can think of the analogy of red and white balls above. If we have a huge box containing, say,  $10^{20}$  balls, we only need to take  $10^4$  balls to determine the fraction of red balls with an accuracy of 1%. If the distribution is not random, but for instance red balls are preferably surrounded by other red balls, we may need to take more balls, but never it is necessary to take all balls out of the box. Similarly a time average yields a good approximation of the ensemble average, and vice versa.

### 7.1.2 Canonical (N,V,T)

Now consider a system immersed in a thermostat at temperature  $T$ . The system and thermostat combined are enclosed by adiabatic walls. The energy  $E_n$  of the system is determined by a quantum number  $n$ , the energy  $E_m^{th}$  of the thermostat is determined by a quantum number  $m$ . The total energy of the combined system is then

$$E_{n,m}^{tot} = E_n + E_m^{th} = U^{tot}. \quad (7.6)$$

The total number of states of the combined system at total energy  $U$  is equal to the total number of states in the thermostat, summed over all commensurate states of the system:

$$\Omega^{tot}(U^{tot}) = \sum_n \Omega^{th}(U^{tot} - E_n). \quad (7.7)$$

The probability to encounter the system in state  $n$  is therefore

$$P_n = \frac{\Omega^{th}(U^{tot} - E_n)}{\Omega^{tot}(U^{tot})}. \quad (7.8)$$

As we have seen before  $\Omega^{th}$  has the general form

$$\Omega^{th}(U^{tot}) = C^{th}(N^{th}, V^{th}) (U^{tot})^{\alpha N^{th}}, \quad (7.9)$$

where  $\alpha$  is a constant of order one. We now rewrite

$$\begin{aligned}
\Omega^{th}(U^{tot} - E_n) &= C^{th}(N^{th}, V^{th}) \times (U^{tot} - E_n)^{\alpha N^{th}} \\
&= C^{th}(N^{th}, V^{th}) \times (U^{tot})^{\alpha N^{th}} \times \left(1 - \frac{E_n}{U^{tot}}\right)^{\alpha N^{th}} \\
&= \Omega^{th}(U^{tot}) \times \left(1 - \frac{\alpha N^{th}}{U^{tot}} \frac{E_n}{\alpha N^{th}}\right)^{\alpha N^{th}} \\
&\approx \Omega^{th}(U^{tot}) \times \left(1 - \beta \frac{E_n}{\alpha N^{th}}\right)^{\alpha N^{th}} \\
&= \Omega^{th}(U^{tot}) \times \exp\{-\beta E_n\}.
\end{aligned} \tag{7.10}$$

We can therefore write the probability to encounter the system in state  $n$  as

$$\boxed{P_n = \frac{1}{Q} \exp\{-\beta E_n\},} \tag{7.11}$$

where

$$\boxed{Q = \sum_n \exp\{-\beta E_n\}.} \tag{7.12}$$

The factor  $\exp\{-\beta E_n\}$  occurs very often in calculations in the canonical ensemble and is called the Boltzmann factor.

The average of any quantity  $F$  in this ensemble is again

$$\langle F \rangle = \sum_n P_n F_n, \tag{7.13}$$

where  $F_n$  is the value of property  $F$  in state  $n$ . For example the average energy of the system is

$$\begin{aligned}
\langle E \rangle &= \sum_n P_n E_n \\
&= \frac{1}{Q} \sum_n E_n e^{-\beta E_n} = -\frac{\partial}{\partial \beta} \ln Q \\
&= -\frac{dT}{d\beta} \frac{\partial \ln Q}{\partial T} = k_B T^2 \frac{\partial \ln Q}{\partial T}.
\end{aligned} \tag{7.14}$$

We may ask if this is the same as the (classical) thermodynamic energy  $U$ . The

answer is yes, as the following consistency check shows:

$$\begin{aligned}
 U &= A + TS = A - T \left( \frac{\partial A}{\partial T} \right)_{N,V} \\
 &= -k_B T \ln Q + T \frac{\partial}{\partial T} k_B T \ln Q \\
 &= k_B T^2 \frac{\partial \ln Q}{\partial T}.
 \end{aligned} \tag{7.15}$$

So indeed the average value of the energy in the canonical ensemble equals the thermodynamic energy,  $\langle E \rangle = U$ .

### 7.1.3 Grand canonical ( $\mu$ , $V$ , $T$ )

Now consider an open system in contact with a particle reservoir at chemical potential  $\mu$ . The combined system contains  $N^{tot}$  particles and is thermostatted from the outside. We can therefore treat the combined system in the canonical ensemble. The probability to encounter the system in state  $n$  and containing  $N$  particles is

$$P_{N,n} = \frac{e^{-\beta E_{N,n}} Q_{N^{tot}-N}^{th}}{\sum_N Q_N Q_{N^{tot}-N}^{th}}. \tag{7.16}$$

This probability is maximal for  $N \approx \langle N \rangle$  and quickly becomes much smaller for values of  $N$  away from  $\langle N \rangle$ . We therefore make a Taylor expansion around  $N = \langle N \rangle$ :

$$\begin{aligned}
 Q_{N^{tot}-N}^{th} &= \exp \{ -\beta A^{th}(N^{tot} - N) \} \\
 &\approx \exp \left\{ -\beta \left[ A^{th}(N^{tot} - \langle N \rangle) + \left. \frac{\partial A^{th}(N^{tot} - N)}{\partial N} \right|_{\langle N \rangle} (N - \langle N \rangle) \right] \right\} \\
 &= \exp \{ -\beta [A^{th}(N^{tot} - \langle N \rangle) - \mu(N - \langle N \rangle)] \},
 \end{aligned} \tag{7.17}$$

where  $\mu^{th} = \mu$  as before. We can now write the probability to encounter the system with  $N$  particles and in state  $n$  as

$$\boxed{P_{N,n} = \frac{1}{\Xi} e^{-\beta E_{N,n} + \beta \mu N}}, \tag{7.18}$$

where

$$\boxed{\Xi = \sum_N Q_N e^{\beta \mu N}}. \tag{7.19}$$

Averages are expressed as sums over  $P_{N,n}$  times the quantity of interest. For example, the average number of particles and average energy are given by

$$\langle N \rangle = \sum_{N,n} P_{N,n} N = \frac{1}{\Xi} \sum_N N Q_N e^{\beta \mu N} \quad (7.20)$$

$$= k_B T \frac{\partial \ln \Xi}{\partial \mu} \quad (7.21)$$

$$\langle E \rangle = \sum_{N,n} P_{N,n} E_{N,n} = -\frac{\partial \ln \Xi}{\partial \beta} + \mu \langle N \rangle. \quad (7.22)$$

Again we can make a consistency check to see if this equals the thermodynamic energy  $U$ : The differential of the characteristic thermodynamic function  $PV$  associated with  $\Xi(\mu, V, T)$  is

$$d(PV) = SdT + PdV + \langle N \rangle d\mu. \quad (7.23)$$

Therefore

$$\langle N \rangle = \frac{\partial PV}{\partial \mu} = k_B T \frac{\partial \ln \Xi}{\partial \mu} \quad (7.24)$$

$$\begin{aligned} U &= G + TS - PV \\ &= \langle N \rangle \mu + T \frac{\partial PV}{\partial T} - PV \\ &= \langle N \rangle \mu + T \frac{\partial k_B T \ln \Xi}{\partial T} - k_B T \ln \Xi \end{aligned} \quad (7.25)$$

$$= \langle N \rangle \mu + k_B T^2 \frac{\partial \ln \Xi}{\partial T}. \quad (7.26)$$

## 7.2 Average occupation numbers

In section 6.4 we introduced the concept of occupation number  $m_n$  to count the number of particles in an ideal gas that reside in a certain state  $n$ .

We would now like to know how many particles, *on average*, are in this state  $n$ . In other words, we would like to calculate the average occupation number  $\langle m_n \rangle$ . It is obvious that in an ideal gas  $\langle m_n \rangle / N$  is the probability to find a certain particle in state  $n$ . If we treat that particle as our system, and the other particles as the thermostat, we then suspect that

$$\frac{\langle m_n \rangle}{N} = \frac{1}{q} \exp \{ -\beta \epsilon(n) \}, \quad (7.27)$$

where  $q = \sum_n \exp \{ -\beta \epsilon(n) \}$ . That this is indeed the case can be shown as follows.

We first assume the particles are distinguishable. The occupation number then may be written as

$$m_n = \delta_{n_1,n} + \delta_{n_2,n} + \dots + \delta_{n_N,n} = \sum_{i=1}^N \delta_{n_i,n}. \quad (7.28)$$

Here  $\delta_{n,m}$  is the Kronecker delta, which equals 1 if  $n = m$  and 0 otherwise. In Eq. (7.28) we check each particle for  $n_i = n$ , and increase  $m_n$  by one if this is the case. The average of  $m_n$  then is

$$\begin{aligned} \langle m_n \rangle &= \sum_{n_1=0}^{\infty} \dots \sum_{n_N=0}^{\infty} m_n P_{n_1, \dots, n_N} \\ &= \frac{1}{Q} \sum_{n_1=0}^{\infty} \dots \sum_{n_N=0}^{\infty} \sum_{i=1}^N \delta_{n_i,n} \exp \{ -\beta\epsilon(n_1) - \dots - \beta\epsilon(n_N) \} \\ &= N \frac{1}{Q} \sum_{n_1=0}^{\infty} \dots \sum_{n_N=0}^{\infty} \delta_{n_1,n} \exp \{ -\beta\epsilon(n_1) - \dots - \beta\epsilon(n_N) \} \\ &= N \frac{1}{q^N} \sum_{n_1=0}^{\infty} \delta_{n_1,n} \exp \{ -\beta\epsilon(n_1) \} q^{N-1} \\ &= N \frac{1}{q} \exp \{ -\beta\epsilon(n) \}. \end{aligned} \quad (7.29)$$

So we see that Eq. (7.27) is true for distinguishable particles. If the temperature is high enough, the same result applies to indistinguishable particles. You are asked to prove this in Problem 7-1.

At low temperatures quantum mechanical effects become more important and Eq. (7.27) is no longer valid. In Problem 7-2 you are asked to calculate the average occupation number  $\langle m_j \rangle$  of a state  $j$  in a Bose gas and a Fermi gas along a different route, namely in the grand canonical ensemble:

$$\langle m_j \rangle = \frac{1}{e^{\beta(\epsilon(j)-\mu)} \mp 1}, \quad (7.30)$$

where the minus sign applies to a Bose gas and the plus sign to a Fermi gas. We have already used this result in section 6.4.

It is important to realise that the above results are not restricted to the case of an ideal gas of structureless particles. More generally, the same arguments apply if the Hamiltonian of a system consists of several independent parts. Treating the system quantum mechanically, this means that the wave function can be written as a product (or rather a sum of products) of partial wave functions and the total energy as a sum of partial energies, each associated with their own quantum numbers  $n_i$ .

The average occupation number of a certain quantum state  $n$ , then again is given by Eq. (7.27).

For example, in an ideal gas of two-atomic molecules the electronic, vibrational, rotational, and translational contributions to the energy are to a good approximation decoupled, see Eq. (6.20). The probability to find a certain molecule in a vibrational state  $n^v$  [see Eqs. (6.23) and (6.24)] is therefore

$$\frac{\langle m_{n^v} \rangle}{N} = \frac{1}{q^v} \exp \{ -\beta \epsilon^v(n^v) \}. \quad (7.31)$$

### 7.3 Fluctuations

Until now we have only studied averages. But in the canonical ensemble the energy  $E$  fluctuates, and in the grand canonical ensemble both  $E$  and  $N$  fluctuate. This can only be useful if the fluctuations are small. We will now show that, quite generally, the magnitude of the fluctuations *relative* to the average scale as  $1/\sqrt{N}$ . So indeed the fluctuations become arbitrarily small as the system size becomes macroscopically large.

In the canonical ensemble  $(N, V, T)$  are the fixed variables. The energy  $E$ , however, can fluctuate. The density of states  $\Omega$  is a strongly growing function with energy, and the probability to encounter a state of a certain energy decreases exponentially with energy like  $\exp(-\beta E)$ . Combined, we can define the probability  $P(E)dE$  to encounter the system's energy in the interval  $[E, E + dE]$ . According to Eqs. (7.11) and (7.12) the energy distribution  $P(E)$  is given by

$$P(E) = \frac{\Omega(E) \exp(-\beta E)}{Q} \quad (7.32)$$

$$Q = \int dE \Omega(E) \exp(-\beta E). \quad (7.33)$$

$P(E)$  is sharply peaked around some average  $\langle E \rangle$  with a standard deviation  $\sigma_E$ , see Fig. 7.1. The latter is defined as

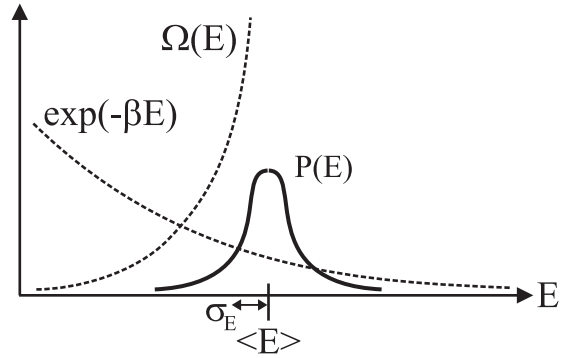
$$\sigma_E = \sqrt{\langle (E - \langle E \rangle)^2 \rangle}. \quad (7.34)$$

A little manipulation yields

$$\begin{aligned} \sigma_E^2 &= \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 - 2 \langle E \rangle E + \langle E \rangle^2 \rangle \\ &= \langle E^2 \rangle - \langle E \rangle^2. \end{aligned} \quad (7.35)$$



Figure 7.1: The density of states  $\Omega$  is a strongly growing function with energy. In the canonical ensemble, the probability to encounter a state of a certain energy decreases exponentially with energy like  $\exp(-\beta E)$ . Combined, the probability  $P(E)$  to encounter a certain energy is sharply peaked around some average  $\langle E \rangle$  with a standard deviation  $\sigma_E$ .



We can work out the average of  $E$  and  $E^2$  as follows:

$$\langle E \rangle = \frac{1}{Q} \sum_n E_n e^{-\beta E_n} = -\frac{\partial \ln Q}{\partial \beta}, \quad (7.36)$$

$$\langle E^2 \rangle = \frac{1}{Q} \sum_n E_n^2 e^{-\beta E_n}, \quad (7.37)$$

$$\begin{aligned} \frac{\partial^2 \ln Q}{\partial \beta^2} &= -\frac{\partial}{\partial \beta} \frac{1}{Q} \sum_n E_n e^{-\beta E_n} \\ &= -\frac{1}{Q^2} \left( \sum_n E_n e^{-\beta E_n} \right)^2 + \frac{1}{Q} \sum_n E_n^2 e^{-\beta E_n} \\ &= \langle E^2 \rangle - \langle E \rangle^2. \end{aligned} \quad (7.38)$$

The magnitude of the energy fluctuations is therefore related to the specific heat of the system:

$$\sigma_E^2 = \frac{\partial^2 \ln Q}{\partial \beta^2} = -\frac{\partial U}{\partial \beta} = k_B T^2 \frac{\partial U}{\partial T} = k_B T^2 C_V. \quad (7.39)$$

We can now make some estimates for the fluctuations. Usually, the energy of a system may be approximated as  $U \approx \alpha k_B T N$ , with  $\alpha$  some constant of order one. Hence  $C_V \approx \alpha k_B N$ . The *relative* magnitude of the energy fluctuations is therefore

$$\frac{\sigma_E}{U} \approx \frac{\sqrt{\alpha N}}{\alpha N} = \frac{1}{\sqrt{\alpha N}}. \quad (7.40)$$

So, even though the absolute magnitude of the fluctuations goes up with  $\sqrt{N}$ , because the average increases with  $N$  the relative magnitude goes down with  $1/\sqrt{N}$ .

In Problem 7-3 you are asked to show that the fluctuations in the number of particles in a grand canonical system grow as  $\sqrt{N}$ . So also the relative fluctuations in particle number scale as  $1/\sqrt{N}$ . In Problem 7-4 you will use the grand canonical ensemble to show that the distribution of particle numbers in an ideal gas is given by the so-called Poisson distribution.

## Problems

**7-1. Average occupation number for indistinguishable particles.** Show that Eq. (7.27) is also valid for indistinguishable particles at high temperature. (Hint: Follow the argument of Eq. (7.29). Use the fact that we may treat the particles as distinguishable, and divide by  $N!$  to correct for the indistinguishability of all states with no two quantum numbers equal. All other states can be neglected at high temperatures, see section 6.2.)

**7-2. Occupation numbers of a Bose and Fermi gas.** Show that for given chemical potential  $\mu$ , volume  $V$ , and temperature  $T$ , the average occupation number of state  $j$  in a Bose or Fermi gas is given by

$$\langle m_j \rangle^{B/F} = \frac{1}{e^{\beta(\epsilon(j)-\mu)} \mp 1},$$

where the minus sign applies to a Bose gas and the plus sign to a Fermi gas. (Hint: Write  $\langle m_j \rangle$  as a partial derivative of  $\ln \Xi$ , where  $\Xi$  is the grand-canonical partition function.)

**7-3. Particle number fluctuations in the grand canonical ensemble.**

(a) Show that in the grand canonical ensemble the particle number fluctuations, defined as  $\sigma_N = \sqrt{\langle N^2 \rangle - \langle N \rangle^2}$  may also be expressed as

$$\sigma_N^2 = k_B T \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{V,T}.$$

(b) Show that

$$\sigma_N^2 = \frac{N k_B T}{v} \kappa_T,$$

where  $v = V/N$  and  $\kappa_T$  is the isothermal compressibility defined as

$$\kappa_T \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T,N} = -\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T.$$

(Hint: Use the fact that  $V$  may be written as a function of  $N$ ,  $\mu$ , and  $T$ . Then derive

$$\left( \frac{\partial N}{\partial \mu} \right)_{T,V} = - \left( \frac{\partial N}{\partial V} \right)_{\mu,T} \left( \frac{\partial \mu}{\partial V} \right)_{N,T}^{-1} = -\frac{N}{v} \left( \frac{\partial \mu}{\partial v} \right)_{N,T}^{-1}.$$

Rewrite  $(\partial\mu/\partial v)$ , using the Gibbs-Duhem relation in the form  $d\mu = -sdT + vdP$ , where  $s = S/N$ .)

(c) Show that for an ideal gas

$$\frac{\sigma_N}{N} = \frac{1}{\sqrt{N}}.$$

**7-4. The Poisson distribution.** Suppose we have an ideal gas of  $N^{tot}$  particles in a volume  $V^{tot}$ . We now focus on a small subvolume  $V$ , where  $V \ll V^{tot}$ , and count the number of particles for different placements of this subvolume. On average we would expect to count  $\langle N \rangle = N^{tot}V/V^{tot}$  particles. Show that the probability to find  $N$  particles is given by the Poisson distribution

$$\text{Prob}(N) = \langle N \rangle^N \frac{e^{-\langle N \rangle}}{N!}.$$

(Hint: Use the grand canonical ensemble and Eq. (6.75), realising that the thermodynamic  $N$  is now  $\langle N \rangle$ , i.e.  $\langle N \rangle = e^{\beta\mu}q$ .)

**7-5. Unifying expression for the entropy.** In general, in any ensemble, the entropy is given by

$$S = -k_B \sum_n P_n \ln P_n,$$

where  $P_n$  is the probability to encounter the system in state  $n$  in that ensemble. Show that this expression is indeed correct for the microcanonical and canonical ensembles.

