

## Chapter 4

# Grand canonical ensemble

In the previous chapter we described the canonical ensemble which consists of a system in equilibrium with a large heat reservoir at fixed temperature. In the grand canonical ensemble the system is in thermal contact with a reservoir at a fixed temperature which can also exchange particles with the system. The exchange of particles is controlled by the chemical potential  $\mu$  which is the energy required to add an additional particle to the system.

### 4.1 Chemical Potential

If we change the number of particles in a system by  $dN$  then there is an additional contribution to the internal energy  $\mu dN$ . Here  $\mu$  is the energy cost of adding another particle, and is called the *chemical potential*. We can use the properties of functions of state to derive expressions for the chemical potential

$$dU = TdS - pdV + \mu dN \Rightarrow \mu = \left( \frac{\partial U}{\partial N} \right)_{S,V} \quad (4.1)$$

$$dS = \frac{1}{T}(dU + pdV - \mu dN) \Rightarrow \mu = T \left( \frac{\partial S}{\partial N} \right)_{U,V} \quad (4.2)$$

Often it is useful to determine the average number of particles from the chemical potential. This can be done using a thermodynamic potentials called the grand potential, which is defined by the expression

$$\Phi = U - TS - \mu N \quad (4.3)$$

For an ideal gas, a small change in the grand potential is given by

$$d\Phi = -pdV - Nd\mu - SdT \quad (4.4)$$

Using this expression the number of particles is given by

$$N = - \left( \frac{\partial \Phi}{\partial \mu} \right)_{T,V} \quad (4.5)$$

We can also determine the entropy and the pressure from this expression

$$p = - \left( \frac{\partial \Phi}{\partial V} \right)_{T,\mu} \quad S = - \left( \frac{\partial \Phi}{\partial T} \right)_{\mu,V} \quad (4.6)$$

For a closed system partitioned into two, we can use the chemical potential to find the equilibrium of the system. If we have  $N$  particles in total,  $N_A$  in subsystem  $A$  and  $N_B$  in subsystem  $B$ , then the entropy change is given by

$$dS = -\frac{1}{T} (\mu_A dN_A + dN_B \mu_B) \quad (4.7)$$

If the total number of particles is  $N = N_A + N_B$  then

$$dS = -\frac{dN_A}{T} (\mu_A - \mu_B) \quad (4.8)$$

i.e. the system is in equilibrium when  $\mu_A = \mu_B$ . If the chemical potentials are not equal then the particles will move to the system with the lowest chemical potential so that the entropy change is positive.

### Ideal gas

Consider a single particle in a box with only translational degrees of freedom (no vibrational, rotational or other degrees of freedom). The statistical mechanics follows from the partition function. We can calculate this using the density of states in energy. For ideal particles in a box they have energy

$$E = \frac{\hbar^2 k^2}{2m}, \quad (4.9)$$

where the  $k$  is the wavevector, and  $m$  is the particle mass. If we differentiate this expression we find  $dE = \frac{\hbar^2 k}{m} dk$ , or  $dE = \hbar \sqrt{2E/m} dk$ . We calculated earlier in the course the density of states in  $k$  space as  $D(k)dk = \frac{V}{2\pi^2} k^2 dk$ . If we convert this to a density of states in energy we find

$$D(E)dE = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E} dE \quad (4.10)$$

We can use this to calculate the partition function for 1 particle in a box

$$Z_1 = \sum_k e^{-E_k/(k_B T)} \quad (4.11)$$

$$= \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty e^{-E/(k_B T)} \sqrt{E} dE \quad (4.12)$$

$$= V \left( \frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} = n_Q(T) V \quad (4.13)$$

where  $n_Q(T)$  is called the quantum concentration. To obtain the partition function for  $N$  particles one might naively multiply  $N$  of these partition functions together. This is incorrect because it assumes all the particles are indistinguishable. A crude way to correct for this is to include a factor of  $N!$  in the partition function

$$Z = \frac{Z_1^N}{N!} \quad (4.14)$$

As a result the free energy calculated from this partition function is extensive

$$F = -k_B T \ln Z = -k_B T \left( N \ln \frac{Z}{N} + N \right) = -k_B T N \left( \ln \frac{n_Q(T) V}{N} + 1 \right) \quad (4.15)$$

From this expression we can calculate the the chemical potential.

$$\mu = \frac{\partial F}{\partial N} = -k_B T \ln \frac{N}{n_Q(T) V} \quad (4.16)$$

From this expression it is clear that as we add more particles to the system the density increases, and hence so does the chemical potential. External factors also contribute to the chemical potential, for example gravitational, magnetic or electric fields would shift the chemical potential in the same way they shift the energy of an isolated particle. A gas molecule at height  $h$  in a gravitational field would have an additional term  $mgh$  added to the chemical potential.

## 4.2 The Grand partition function

### Gibbs distribution

In the grand canonical ensemble the system is in equilibrium with a reservoir of fixed temperature and chemical potential. Suppose that the combined system has total energy  $U$  and total number of particles  $N$ . The probability that the system occupies a particular state is proportional to the number of available states in the reservoir. Hence the probability that the system has energy  $E_i$ , and number of particles  $N_i$  is given by

$$p(E_i, N_i) \propto W_{\text{res}}(U - E_i, N - N_i) \quad (4.17)$$

$$\propto \exp \left( \ln W_{\text{res}}(U, N) - E_i \frac{\partial \ln W_{\text{res}}(U, N)}{\partial U} - N_i \frac{\partial \ln W_{\text{res}}(U, N)}{\partial N} + \dots \right) \quad (4.18)$$

$$\Rightarrow p(E_i, N_i) \propto e^{-\beta(E_i - \mu N_i)} \quad (4.19)$$

where we have used the results that  $\frac{\mu}{T} = \frac{\partial S}{\partial N}$  and  $\frac{1}{T} = \frac{\partial S}{\partial U}$ , and abbreviated  $\beta = \frac{1}{k_B T}$ . This is called the *Gibbs factor*. To construct a normalised distribution we must divide this Gibbs factor by the *Grand partition function*

$$\Xi = \sum_i e^{-(E_i - \mu N_i)/(k_B T)} \quad (4.20)$$

where the sum is over all states. The Gibbs distribution is then

$$p(E_i, N_i) = \frac{e^{-\beta(E_i - \mu N_i)}}{\Xi} \quad (4.21)$$

### Grand Potential relation to the grand partition function

If we substitute the Gibbs potential into the expression for the Gibbs entropy then we obtain a connection between the thermodynamic grand potential  $\Phi$  and the Grand partition function.

$$S = -k_B \sum_i p_i \ln p_i \quad (4.22)$$

$$= -k_B \sum_i p_i (-\beta(E_i - \mu N_i) - \ln \Xi) \quad (4.23)$$

$$\Rightarrow TS = \underbrace{\sum_i p_i E_i}_{\langle E \rangle} - \mu \underbrace{\sum_i p_i N_i}_{\langle N \rangle} + k_B T \ln \Xi \quad (4.24)$$

$$\Rightarrow \Phi = \langle E \rangle - TS - \mu \langle N \rangle = -k_B T \ln \Xi \quad (4.25)$$

This equation provides an important link between thermodynamics and statistical physics.

## 4.3 Identical particles

In classical physics if we have identical particles then there are some repercussions in how we count the number of particles – we must account for the fact that we cannot tell the difference between them. Quantum mechanically identical particles have an additional complication.

For identical fermions (particles with half integer spin) the wavefunction must be antisymmetric under particle exchange (i.e. change sign when we exchange two particles), and so the probability two particles being in the same place is zero. This is the Pauli exclusion principle – two fermions cannot occupy the same quantum state.

For identical bosons the wavefunction must be symmetric under particle exchange (i.e. no sign change when we exchange two particles). This gives an enhanced probability of two bosons occupying the same state.

We can use this knowledge to calculate the statistical mechanics of non-interacting fermions and bosons.

### Fermi-Dirac distribution

Let us consider the grand partition function for a particular state corresponding to a wavefunction  $\psi_k$  (labelled by its wavevector  $k$ ). For fermions we can have  $n_k = 0, 1$  corresponding to an empty or filled state. The grand partition function is thus

$$\Xi = \sum_k e^{-(E_k - \mu N_k)/(k_B T)} = \underbrace{1}_{n_k=0} + \underbrace{e^{-\beta(E_k - \mu)}}_{n_k=1} \quad (4.26)$$

The average number of particles in this state is given by

$$\langle n_k \rangle = \frac{e^{-\beta(E_k - \mu)}}{1 + e^{-\beta(E_k - \mu)}} = \frac{1}{e^{\beta(E_k - \mu)} + 1} \quad (4.27)$$

This is called the Fermi-Dirac distribution.

### Bose-Einstein distribution

For bosons we can have any number of particles in the state, so all values of  $n_k$  are permitted. The grand partition function is thus

$$\Xi = \sum_k e^{-(E_k - \mu N_k)/(k_B T)} = \sum_k \left( e^{-\beta(E_k - \mu)} \right)^{n_k} \quad (4.28)$$

$$= \frac{1}{1 - e^{-\beta(E_k - \mu)}} \quad (4.29)$$

The grand potential  $\Phi$  can be calculated for this particular energy level.

$$\Phi_k = -k_B T \ln \Xi = k_B T \ln \left( 1 - e^{-\beta(E_k - \mu)} \right) \quad (4.30)$$

We can calculate the average number of particles in the energy level  $E_k$  by using the grand potential.

$$\langle n_k \rangle = -\frac{\partial \Phi}{\partial \mu} = \frac{1}{e^{\beta(E_k - \mu)} - 1} \quad (4.31)$$

Note that  $\langle n_k \rangle \rightarrow \infty$  as  $\mu \rightarrow E_k$  since the denominator vanishes. This is called the Bose-Einstein distribution.

## 4.4 Ideal quantum gases

We have seen the factor of the quantum density  $n_Q$  in the expression for the partition function of an ideal gas. The importance of this density, and the cross over to quantum mechanical behaviour

can be demonstrated by calculating the thermal de Broglie wavelength. For a particle with thermal energy  $E = k_B T$ , its momentum is  $p = mv = \sqrt{2k_B T m}$ . The de Broglie wavelength of this particle is

$$\lambda \sim \frac{h}{p} = \sqrt{\frac{h^2}{2mk_B T}}. \quad (4.32)$$

Hence when the density of the particles approaches  $\frac{1}{\lambda^3} = \left(\frac{2mk_B T}{h^2}\right)^{3/2} \sim n_Q(T)$  the wavefunctions start to overlap in real space, and quantum effects become important. Depending on the type of particles (fermions or bosons) we will get different behaviour of the gas. To illustrate the difference between these two cases we will calculate the average number of particles occupying the energy states.

### Bose-Einstein Condensation

For a Bose gas the number of atoms is given by

$$N = \int n(E) D(E) dE = \frac{V}{4\pi^2} \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\infty \frac{\sqrt{E}}{e^{(E-\mu)/(k_B T)} - 1} dE. \quad (4.33)$$

Note that  $\mu < 0$  otherwise we'll have a divergence in  $n(E)$  for some energy  $E = \mu$ . The largest value of  $N$  is when  $\mu = 0$ , but for  $T \rightarrow 0$  the integral goes to zero. What has happened to all the particles in this case? The problem comes in converting the sum over all energy states to an integral. As  $T \rightarrow 0$  all the particles occupy the lowest energy states  $E = 0$ , i.e.

$$n(E) = \begin{cases} N & E = 0 \\ 0 & E > 0 \end{cases} \quad (4.34)$$

For a very small temperature suppose there are  $N_{\text{ex}}$  excited particles, and  $N - N_{\text{ex}}$  particles in the ground states. We can calculate  $N_{\text{ex}}$  as before, but with  $\mu = 0$

$$N_{\text{ex}} = \frac{V}{4\pi^2} \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\infty \frac{\sqrt{E}}{e^{E/(k_B T)} - 1} dE = N \left(\frac{T}{T_0}\right)^{3/2}. \quad (4.35)$$

where  $T_0 = \frac{2\pi\hbar^2}{mk_B} \left(\frac{N}{2.612V}\right)^{2/3}$  is the Bose-Einstein condensation temperature. For example in helium-4 it is approximately 3K. There is a characteristic signature in the heat capacity below  $T_0$ . By integrating the energy of the remaining particles it can be shown that the specific heat  $C_V \propto T^{3/2}$ .

### Fermi Gas

The Fermi-Dirac distribution at low temperature just becomes a step function, i.e.

$$n(E) = \begin{cases} 0 & E < \mu \\ 1 & E > \mu \end{cases} \quad (4.36)$$

If we have  $N$  particles in the system then it is useful to define the Fermi-wavevector  $k_F$ . This is the maximum value of  $k$  that is filled at  $T = 0$

$$N = \frac{1}{8} \underbrace{\left(\frac{4}{3}\pi k_F^3\right)}_{\text{volume of sphere}} / \underbrace{(\pi^3/V)}_{\text{volume per point in k-space}} \quad (4.37)$$

From this the Fermi-energy and Fermi-temperature can be defined:

$$E_F = \frac{\hbar^2 k_F^2}{2m} \quad ; \quad T_F = \frac{E_F}{k_B} \quad (4.38)$$

At a finite temperature the chemical potential for a fixed number of particles is defined by

$$N = \int n(E)D(E)dE = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{\sqrt{E}}{e^{(E-\mu)/(k_B T)} + 1} dE. \quad (4.39)$$

The heat capacity of this system can be calculated (approximately) by a simple argument. At high temperature only those particles close to the Fermi-level can be excited (as they need empty states to occupy). Each of these particles has thermal energy  $\sim k_B T$ . Hence the average energy is

$$\langle E \rangle \sim (k_B T)^2 D(E_F) \quad (4.40)$$

So the heat capacity is

$$C_V \sim 2k_B^2 T D(E_F) \quad (4.41)$$