

Chapter 6

Indistinguishable particles: quantum gases and fluids

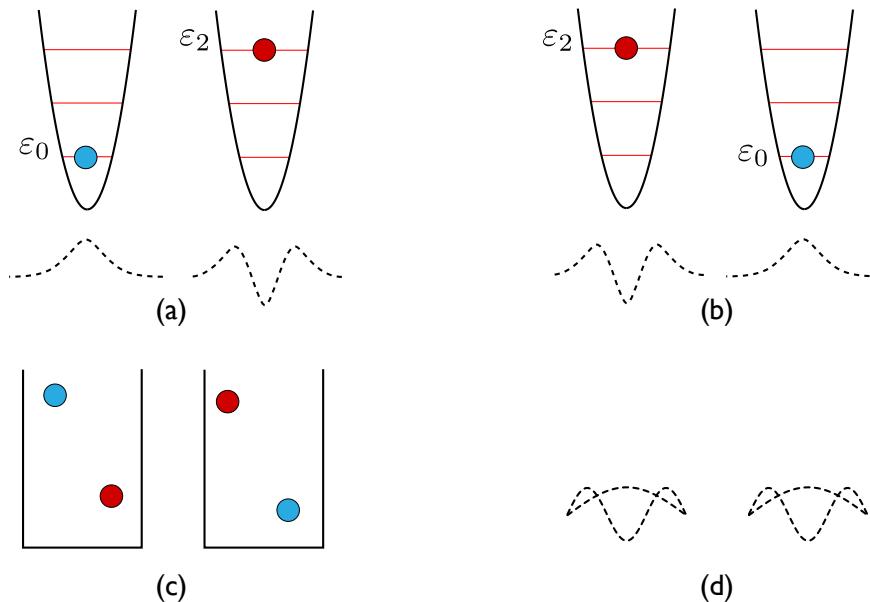
The Boltzmann statistics that we looked at in the previous section were clearly very useful, but they relied on a series of assumptions. Some were general, but some were restrictive, and we'll look to relax the restrictive ones. We'll no longer assume that the atoms are fixed in a crystal, so *they are no longer distinguishable*. We will also lose the assumption that each state has a distinct \mathcal{E} , i.e. we will allow *degeneracy*.

6.1 Distinguishability is an issue!

Indistinguishability is fundamentally a *quantum* effect. The Boltzmann statistics that we have looked at so far relied on two key concepts: we assumed that we had a set of localised, distinguishable particles, each in a well-defined 'state' labelled 'state i ' with a well-defined 'state-energy' labelled ' \mathcal{E}_i '. This has amounted to picking and choosing from the rules of quantum mechanics: there is probably not much difficulty in associating the notion of the 'state' of the atoms we discussed with an atomic eigenstate.

However, the founders of statistical physics spent most of their time thinking about *classical* gases of atoms, and had to work hard to come up with a definition of 'state'. Despite that effort, things did not work out properly and they were left with the famous 'Gibbs paradox'. The resolution of this problem required the introduction of the *full* consequences of the quantum ideas that we will proceed to look at.

Consider two adjacent atomic potentials, each containing one electron. In the first, the electron is in the state 0, and in the second, in state 2. We use the approximation of harmonic atomic potentials purely for illustration, and sketch the wavefunctions that correspond to the classical particle representation. This is shown in figure 6.1 (a). Let's now imagine swapping the particles over, so we end up with the situation shown in figure 6.1 (b). This doesn't present us with any problems.

**Figure 6.1**

Now let's try something equally innocuous: let's put the particles in a box together. If we look at figure 6.1 (c), this presents no problems for the classical particle picture, and it seems perfectly intuitive. However, if we look at figure 6.1 (d), we can see the results of swapping particles when using the quantum mechanical wavefunction picture. We have a problem here: we can't distinguish the 'before-swapping' and 'after-swapping' situation!

This difficulty is distinguishability is an *absolutely general feature of quantum mechanics*. Particles in eigenstates are *not* localised within the same potential, in this case the box. If we do not have localised particle, we do not have a mechanism for distinguishability. This example shows how we managed to both have our cake and eat it the way we set up our Boltzmann statistics: we used quantum mechanical language to set up 'states' with discrete energies, which saved us many of the problems encountered in the 19th century. However, we carefully ensured that each 'particle' was localised because we worked in a crystal lattice with pre-localised potentials.

In fact, (as will become apparent in solid state physics), even this localisation of the atomic potentials far from guarantees localisation of the electrons in the crystal, (conduction, anyone?) and we'll have some more work to do to justify the simple model that we set up in previous sections. It's not wasted, however, as the model *can* be justified as at least being approximately correct in some circumstances.

Our discussion of distinguishability illustrates another fundamental issue: it also reminds us that in a quantum system, e.g. quantum particles in a box, the quantised energy levels are those of *the whole system*, not N copies of those of each of the system's particles. From now on, we need to think 'fully quantum' about the entire system. This will require awareness of some more fundamental rules of quantum mechanics, which you already gained last semester.

If we think about our example of trying to swap two particles in a box, note that the diagram only featured the *amplitudes* of the wavefunctions when illustrating indistinguishability. If we consider the

phase of the wavefunction, then it turns out that there are two possible outcomes for the overall two-particle wave function, which either *maintains* or *reverses* its sign every time a swap between two particles is made. If the sign is maintained, the particles described by the wave function are called *bosons*, while if it is reversed, the particles are called *fermions*. It also turns out that bosons have integer spin, while fermions (for example, electrons) have half-integer spin.

The rule that will be key to us, concerns how states can be occupied. Bosons can multiply occupy a state without restriction, but fermions are subject to the *Pauli exclusion principle* which says that: “*No two identical fermions can occupy the same quantum state.*” These considerations lead to some remarkable features which we will now explore.

phase factor	particle	2-particle wave function	“rules” for particle	spin	examples
$e^{i\delta} = +1$	boson	$\psi_S(1, 2)$	multiple occupancy possible	$s = 0, 1, 2, \dots$	photons, He-4
$e^{i\delta} = -1$	fermion	$\psi_A(1, 2)$	Pauli exclusion principle	$s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$	$e^-, p, n, He-3$

Table 6.1: Differences between bosons and fermions.

6.2 Quantum counting statistics

Let’s start by considering **bosons**: for any energy level \mathcal{E}_i there could be g_i allowed states, each of which can be occupied by any number of particles. Unlike the case described by equation 5.12, these particles are indistinguishable. With a wee bit of thought, the combination counting turns out to be very simple: figure 6.2 shows a way of representing the distribution of bosons across the different states (all of the same energy) that together make up a degenerate energy level. In the example shown, the degeneracy of the energy level is 6. The ‘|’ symbol (often called a ‘pipe’ by those that use it often enough to name it!) represents a non-physical division between states for the purposes of counting them, so two adjacent pipes represents an un-occupied state. We can look at this like the ‘heads and tails’ problem: if we think of the \circ as a ‘head’ and the $|$ as a ‘tail’ then we can see that if we have n_i bosons in a level with energy \mathcal{E}_i and degeneracy g_i then we are doing the equivalent of making combinations of n_i heads and $(g_i - 1)$ tails. We only need $(g_i - 1)$ tails because we only

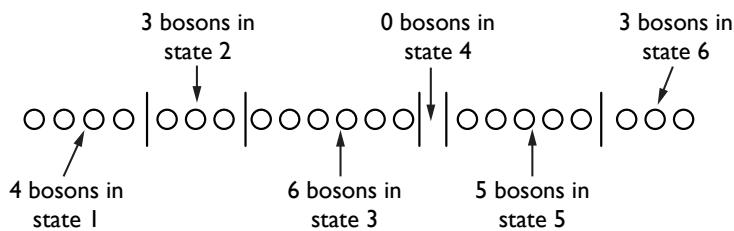


Figure 6.2: Schematic of a single energy level with degeneracy of 6 showing a possible distribution of 21 bosons among the states that make up the energy level.

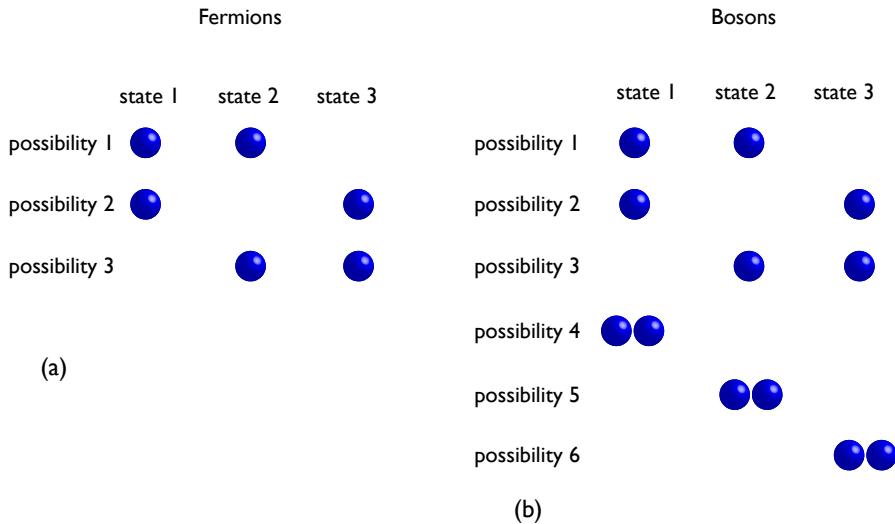


Figure 6.3: The ways of distributing $n_i = 2$ indistinguishable particles among 3 states of energy E_i , if the particles are (a) fermions and (b) bosons.

require $(g_i - 1)$ of | symbols to define the ways of arranging particles between g_i states. Hence the number of ways of arranging the n_i bosons is

$$\frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \quad (6.1)$$

When we take into account the full set of available energy levels, then the total Ω is

$$\Omega_b = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \quad (6.2)$$

where the ‘b’ subscripts denotes the fact that we are talking about bosons.

The case is simpler for **fermions**: for any energy level E_i there could be g_i allowed states, but each of these can only be occupied by a maximum of one particle. Each of the n_i occupied states is like a ‘head’ in our coin model and each empty state is like a ‘tail’. This means that

$$\Omega_f = \prod_i \frac{g_i!}{n_i! (g_i - n_i)!} \quad (6.3)$$

where the subscript ‘f’ denotes that we are talking about fermions. (Note that what we have just done to get the term inside the product, is to work out Ω for a two state system as described by equation 3.5, where the two states are ‘occupied’ (n_i) and ‘unoccupied’ ($g_i - n_i$). Obviously, if there are g_i states and n_i are occupied, then $g_i - n_i$ must be unoccupied.)

Let’s illustrate the difference between equations 5.12, 6.2 and 6.3 with an example: consider a quantised energy E_i shared by three quantum states (so $g_i = 3$). In **Boltzmann statistics** (to which we apply eq. 5.12), E_i and g_i define 3 quantum states of a *single, distinguishable* atom (which is part of a larger assembly of atoms). They refer only to *this* atom, so only it can occupy them, and so there are 3 ways of doing this. ($n_i = 1$, so $g_i^{n_i}/n_i! = 3^1/1 = 3$.) In **quantum statistics**, however, E_i and g_i define 3 quantum states of a *whole assembly*. Figure 6.3 shows how we could distribute (say) $n_i = 2$ particles among those states.

6.3 Quantum distribution functions

Let's begin with **bosons**:

$$\Omega_b = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \quad (6.2)$$

When we discussed the counting for bosons, we took care to explain the role of the '-1' in the bracketed terms. It may seem a shame, then, that the first thing we do is neglect it: in a real assembly, the degeneracies and particle numbers will be so large in comparison that we can ignore it:

$$\Omega_b \approx \prod_i \frac{(n_i + g_i)!}{n_i! g_i!} \quad (6.4)$$

We'll take the same approach to maximising Ω_b as we have to maximising Ω previously: we seek to maximise $\ln \Omega_b$, which we approximate using Stirling's formula (3.4):

$$\ln \Omega_b \approx \sum_i [(n_i + g_i) \ln(n_i + g_i) - n_i \ln n_i - g_i \ln g_i] \quad (6.5)$$

(There are no sums over n_i and g_i in the above expression as the numerator gives a term $-(n_i + g_i)$, whilst the denominator gives a term $n_i + g_i$, and these obviously cancel. Try it and convince yourself.) We take the differential and set to zero as before. (Note: g_i are fixed for all i , so $dg_i = 0$):

$$\begin{aligned} d(\ln \Omega_b) &= \sum_i (\ln(n_i + g_i)) dn_i - \ln n_i dn_i \\ &= \sum_i \ln \left(\frac{n_i + g_i}{n_i} \right) dn_i = 0 \end{aligned} \quad (6.6)$$

We have the same constraints on particle number and energy as we had in section 4.1:

$$\sum_i dn_i = 0 \quad \text{and} \quad \sum_i \mathcal{E}_i dn_i = 0 \quad (4.5, 4.6)$$

so we use Lagrange multipliers to state

$$\ln \left(\frac{n_i + g_i}{n_i} \right) + \alpha - \beta \mathcal{E}_i = 0 \quad (6.7)$$

which leads us to

$$\frac{n_i + g_i}{n_i} = e^{(-\alpha + \beta \mathcal{E}_i)} \quad (6.8)$$

so

$$\frac{n_i}{g_i} = \frac{1}{e^{(-\alpha + \beta \mathcal{E}_i)} - 1} \quad (6.9)$$

Now consider **fermions**: begin with

$$\Omega_f = \prod_i \frac{g_i!}{n_i! (g_i - n_i)!} \quad (6.3)$$

then use Stirling's approximation to get

$$\ln \Omega_f \approx \sum_i [(n_i - g_i) \ln(g_i - n_i) - n_i \ln n_i + g_i \ln g_i] \quad (6.10)$$

so

$$d(\ln \Omega_f) = \sum_i \ln \left(\frac{g_i - n_i}{n_i} \right) dn_i \quad (6.11)$$

then by setting $d(\ln \Omega) = 0$ and doing the whole Lagrange multiplier method again, you should be able to arrive at

$$\frac{n_i}{g_i} = \frac{1}{e^{(-\alpha + \beta \mathcal{E}_i)} + 1} \quad (6.12)$$

The expressions for bosons and fermions are similar to look at, but the different signs of the '1' in the denominator have profound consequences.

Since the distinction between fermions and bosons is purely quantum mechanical, one would expect that there would be a limit in which it doesn't matter whether we are dealing with fermions or bosons, as we know that in general there is a classical limit in which we don't need to worry about quantum effects. If we look at equations 6.11 and 6.12, then we can see that when $g_i \gg n_i$, then the exponential term on the bottom of each expression must be $\gg 1$, so the ± 1 can be neglected in both expressions and then either can be expressed as

$$\frac{n_i}{g_i} = e^{\alpha - \beta \mathcal{E}_i} \quad (6.13)$$

This is just the same as equation 5.11 that we arrived at when accounting for degeneracy when setting up Boltzmann statistics. On reflection, this shouldn't be terribly surprising, as it tells us that the quantum effects are only felt when the quantum rules for bosons and fermions matter, which is when there is competition for the available quantum states. If $g_i \gg n_i$, then the degeneracy is so large that there is very little probability of the system trying to put two particles into the *same* state, so the fact that the system is composed of fermions or bosons doesn't matter. This is a quick first look at the idea of the '*classical limit*', which we will return to later.

We now need to consider whether it's appropriate to continue to work with discrete energies etc. in large statistical systems in which the potential is shared by all the particles. The energy levels involved are, of course, still discrete (this is definitely a quantum system) but they are incredibly closely spaced. This can be demonstrated by looking at elementary quantum mechanics, and the *particle-in-a-box* problem. We solve Schrödinger's equation for a particle in a box of width L and obtain the usual set of sinusoidal eigenstates, which are clearly eigenstates of the energy operator. However, they *clearly can't also be eigenstates of momentum* as the particle is restricted in x (it's in a well, after all!) and the uncertainty principle tell us that the particle cannot therefore have a definite momentum. The relationship $E = p^2/2m$ *still holds*, however, and there is *no inconsistency*: this expression can only tell us the *magnitude* of p , and not its direction.

So, what does the above brief discussion have to do with what we have been talking about? If we consider the *reverse* of the argument given in the above paragraph, then we can see that the energy eigenvalues (and hence their spacing) are controlled by the uncertainty principle. If we have a large box, then \mathcal{E}_i and $\Delta\mathcal{E}_i$ will be *tiny* (think about what making L really large does when calculating the energy spacings in the square well case). Because \mathcal{E}_i and $\Delta\mathcal{E}_i$ are so small, we can write expressions for the number of quantum particles that have energy in the range $\mathcal{E} \rightarrow \mathcal{E} + d\mathcal{E}$.

For fermions, we have the **Fermi-Dirac distribution**:

$$n(\mathcal{E}) d\mathcal{E} = \frac{g(\mathcal{E}) d\mathcal{E}}{e^{-\alpha + \mathcal{E}/k_B T} + 1} \quad (6.14)$$

and for bosons we have the **Bose-Einstein distribution**:

$$n(\mathcal{E}) d\mathcal{E} = \frac{g(\mathcal{E}) d\mathcal{E}}{e^{-\alpha + \mathcal{E}/k_B T} - 1} \quad (6.15)$$

expressions which rank alongside the partition function in terms of importance. If you understand their origins and consequences, then you'll have mastered one of the most important parts of statistical mechanics.

6.4 Calculation of the density of states $g(\mathcal{E}) d\mathcal{E}$

We start with the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = \mathcal{E} \psi \quad (6.16)$$

Let's impose the boundary conditions for a hard-walled cubic box, of side L : $\psi = 0$ at $x, y, z = 0$ and L . The solutions to the Schrödinger equation are standing waves

$$\psi = \left(\frac{2}{L}\right)^{3/2} \sin k_x x \sin k_y y \sin k_z z \quad (6.17)$$

where

$$k_x = \frac{n_x \pi}{L} \quad k_y = \frac{n_y \pi}{L} \quad k_z = \frac{n_z \pi}{L} \quad n_x, n_y, n_z = 1, 2, 3 \dots \quad (6.18)$$

These allowed values of k form a cubic array of closely-spaced points in the first octant (eighth-sphere) of a standard coordinate system. $k = (k_x^2 + k_y^2 + k_z^2)^{1/2}$ gives the magnitude of the vector from the origin of k -space to the location of a state defined by k_x , k_y and k_z .

Each state is separated along each of the k axes by (π/L) and occupies a volume in k -space of $(\pi/L)^3$, as shown in figure 6.4.

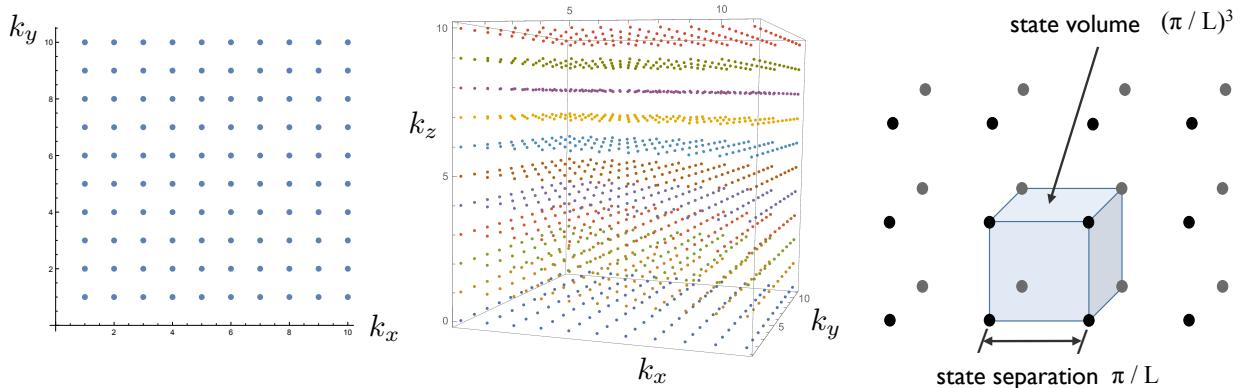


Figure 6.4: Points in k -space, state separation, state volume.

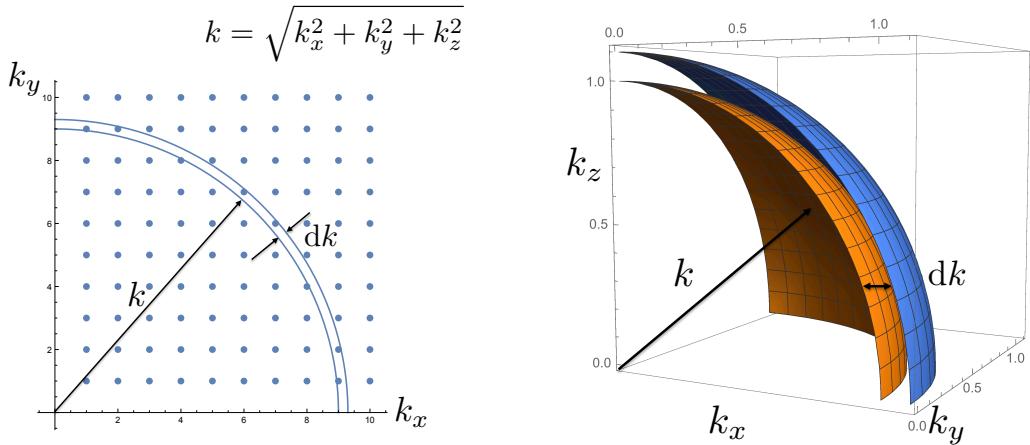


Figure 6.5: Number of states in the interval $k \rightarrow k + dk$ (i.e. in a slice of thickness dk at k).

Now we want to count the number of states in the interval $k \rightarrow k + dk$ (see figure 6.5):

$$g(k) dk = \frac{\text{vol. of shell at } k}{\text{vol. per } k} = \frac{1}{8} 4\pi k^2 \left(\frac{L}{\pi}\right)^3 dk = \frac{V}{2\pi^2} k^2 dk \quad (6.19)$$

There is always a function relating \mathcal{E} to k , and as long as this is used in the conversion from k to \mathcal{E} , then

$$g(\mathcal{E}) d\mathcal{E} = g(k) dk \quad (6.20)$$

For massive particles with mass m , we relate \mathcal{E} to k with

$$\mathcal{E} = \frac{\hbar^2 k^2}{2m} \quad (6.21)$$

and hence

$$dk = \frac{m}{\hbar^2 k} d\mathcal{E} \quad \text{and} \quad k = \left(\frac{2m\mathcal{E}}{\hbar^2}\right)^{1/2} \quad (6.22)$$

and equation 6.19 becomes

$$\begin{aligned} g(\mathcal{E}) d\mathcal{E} &= \frac{1}{8} 4\pi \frac{2m\mathcal{E}}{\hbar^2} \frac{L^3}{\pi^3} \frac{m}{\hbar^2} \left(\frac{\hbar^2}{2m\mathcal{E}}\right)^{1/2} d\mathcal{E} \cdot G \\ &= V \frac{m^{3/2}}{\sqrt{2}\pi^2\hbar^3} \mathcal{E}^{1/2} d\mathcal{E} \cdot G \end{aligned} \quad (6.23)$$

The exact form of equation 6.23 depends on the dimensions of our box (three is appropriate for this course, but two or even one dimensions can be realised for electrons in semiconductor devices) and the appropriate $\mathcal{E} - k$ relationship.

The spin factor G is introduced to $g(\mathcal{E}) d\mathcal{E}$ to account for the G sets of states we get from each possible spin direction. For e.g. electrons with spin $s = 1/2$ we get $G = 2$, corresponding to spin up or down.

Chapter 7

The Fermi-Dirac distribution in more detail

The Fermi-Dirac distribution is

$$n(\mathcal{E}) d\mathcal{E} = \frac{g(\mathcal{E}) d\mathcal{E}}{e^{-\alpha + \mathcal{E}/k_B T} + 1} \quad (6.14)$$

We will choose to write $\alpha = \mu/k_B T$, which is more conventional. μ is a quantity (with units of energy) known as the **chemical potential**. We'll talk more about what physical significance μ has later.

Now that we have introduced μ , we can rewrite equation 6.14 in the more conventional form:

$$n(\mathcal{E}) d\mathcal{E} = \frac{g(\mathcal{E}) d\mathcal{E}}{e^{(\mathcal{E}-\mu)/k_B T} + 1} \quad (7.1)$$

If we divide through by $g(\mathcal{E}) d\mathcal{E}$ we define the *state occupation function*:

$$f(\mathcal{E}) = \frac{1}{e^{(\mathcal{E}-\mu)/k_B T} + 1} \quad (7.2)$$

What does this function look like, and what does it signify? Let's first consider the case at $T = 0$ (or if you are pedantic enough to care about the real-life chances of actually getting there, infinitesimally close to zero...), as shown in figure 7.1. $f(\mathcal{E})$ looks 'badly behaved': for any potential $\mathcal{E} < \mu$, the exponential has a massive negative argument, and so $f = 1$. As soon as $\mathcal{E} > \mu$, the exponential has a huge positive argument and diverges, so $f = 0$. So, at $T = 0$, $f(\mathcal{E})$ looks like a step function. What this signifies is, that on average, every available quantum state in the system contains one particle until a certain energy, μ , at which all the particles are allocated to their state and there are no more to fill the higher energy states. A quantum gas at low temperatures is often referred to as 'degenerate' (meaning that all states filled, independent of degeneracy). At zero temperature, μ is equal to the *Fermi energy*, which is the energy of the highest-energy occupied state at zero temperature (hence the \mathcal{E}_F indicated on the energy axis of figure 7.1).

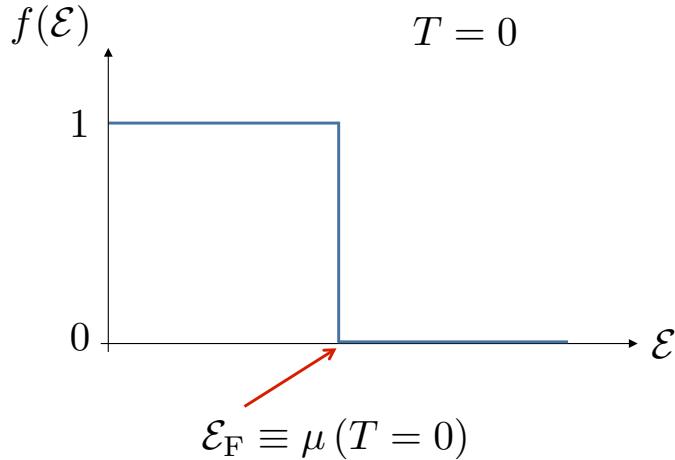


Figure 7.1: The state occupation function $f(\mathcal{E})$ for fermions at zero temperature.

At the Fermi energy, the allowed states in a Fermi gas at zero temperature suddenly change from being completely filled to being completely empty. It can be shown that \mathcal{E}_F for a 3D system is given by

$$\mathcal{E}_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} \quad (7.3)$$

where N/V is the number of fermions per unit volume. This has a very definite physical meaning: if you try to put fermions into the same potential well at $T = 0$, the application of the Pauli exclusion principle means that even when you have done your very best to minimise the internal energy, the fermions will range in energy from zero to a maximum value of \mathcal{E}_F .

7.1 The meaning of the Fermi temperature

If the Fermi energy is known, we can define a temperature

$$T_F = \frac{\mathcal{E}_F}{k_B} \quad (7.4)$$

This is not a real temperature, but it has a real meaning. Recall from earlier courses the classical notion of *equipartition of energy*, namely that for a classical particle

$$\frac{1}{2}mv^2 \propto k_B T \quad (7.5)$$

The meaning of T_F is therefore the *fictional* temperature that one would have to heat a gas of classical particles up to in order for them to have the same kinetic energy as the most energetic particles sitting in the quantum gas at $T = 0$!

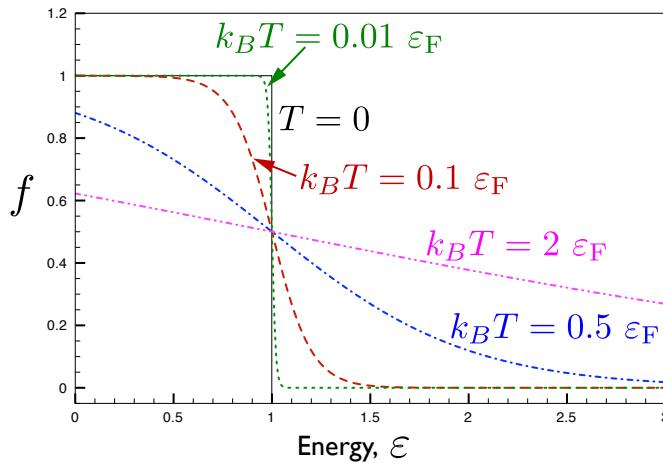


Figure 7.2: Plots of the state occupation function $f(\mathcal{E})$ for $\mathcal{E}_F = 1$ for a range of temperatures, assuming a temperature independent $\mu = 1$.

7.2 More about the chemical potential μ

To get equation 6.14 into the form 7.1, we re-wrote the Lagrange multiplier α as $\mu/k_B T$, but didn't discuss any possible temperature dependence of μ itself. A simple argument does in fact show that it *must* be temperature dependent.

For the total number of particles in our system we can write

$$N = \int_0^\infty n(\mathcal{E}) d\mathcal{E} = \int_0^\infty g(\mathcal{E}) f(\mathcal{E}) d\mathcal{E} = \int_0^\infty \frac{g(\mathcal{E}) d\mathcal{E}}{e^{(\mathcal{E}-\mu)/k_B T} + 1} \quad (7.6)$$

Let us assume that the density of states $g(\mathcal{E})$ is not temperature dependent. If we look at figure 7.2 which shows plots of $f(\mathcal{E})$ at various temperatures assuming a constant μ , we'll see that their integral is clearly NOT constant. However, N has to be constant (we are not making or destroying any particles, after all) so the only fix that we have for this is a temperature-dependent μ , namely one that must decrease from \mathcal{E}_F as T increases.

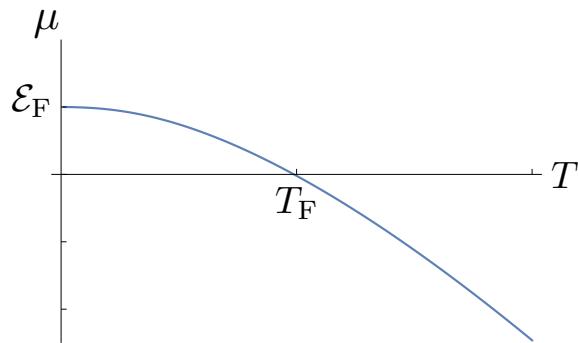


Figure 7.3 The temperature dependence of the chemical potential for fermions.

As can be inferred from figure 7.3 the temperature dependence of μ is very small if $k_B T \ll \mathcal{E}_F$. At these low temperatures μ is given approximately by

$$\mu(T) \approx \mathcal{E}_F \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right] \quad \text{for } T \ll T_F \quad (7.7)$$

At high temperatures, the chemical potential becomes negative. (Per definition $\mu(T=0) \equiv \mathcal{E}_F$.)

μ does in fact have a definite physical meaning in terms of the number or flow of particles. To look at this, we are going to briefly depart from our assumption that every system that we talk about contains a fixed number of particles, i.e a fixed quantity of matter, and imagine considering a system in which this is *not* fixed. (This is of great importance when considering chemical reactions, or the consequences of changes in phase, or even something conceptually simpler, such as a container of gas with a hole in it.) We'll confine ourselves to having just one type of particle in our system.

The central equation of thermodynamics is

$$dU = TdS - PdV \quad (7.8)$$

which applies to a system in which the quantity of matter is fixed. If we allow the quantity of matter to change, then we need to modify equation 7.8, to account for a change in U due to the energy associated with the particles that are being added (or taken from) the system.

This results in an additional term to account for the change in particle number, and if the number of particles, N , changes by dN , then equation 7.8 is modified to become

$$dU = TdS - PdV + \mu dN \quad (7.9)$$

The chemical potential μ is defined as the increase in the internal energy for each particle that we add under conditions of constant entropy and constant volume, i.e.

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} \quad (7.10)$$

One simple way to see the consistency of this with the behaviour of the Fermi-Dirac function is to consider what happens if we add a single fermion to a Fermi gas at zero temperature (and thus at zero entropy by the third law of thermodynamics) and fixed volume. If N/V is large enough, then we can neglect any change in the Fermi energy due to adding one more particle. At zero temperature, all the states are filled up to \mathcal{E}_F , so the added particle will have energy \mathcal{E}_F . The extra internal energy the system has is thus $dU = \mathcal{E}_F$ and as $dN = 1$, this is consistent with equations 7.9, 7.10 and the statement that $\mu = \mathcal{E}_F$ when $T = 0$.

If two systems free to transfer particles are put in contact, there will be a net flow of particles between them unless their chemical potentials are equal.