CHAPTER 4: QUANTUM STATISTICS

LECTURE 10

The material in this chapter is covered in section 9-1 of the text. After studying the chapter you will be able to:

- describe the Maxwell-Boltzmann distribution function and explain its origin;
- discuss the concept of indistinguishability and the Pauli exclusion principle; and
- describe the Bose-Einstein and Fermi-Dirac distribution functions.

One of the great successes of 19th century physics was the explication of thermodynamics in terms of the behaviour of large numbers of molecules — the subject we call kinetic theory. In this chapter we explore what new insights were brought to this subject by quantum mechanics.

The key idea is that you can get a lot of information about a thermodynamic system simply by assuming that the molecules can interchange energy, so that at thermal equilibrium the total energy of the system is distributed among all the molecules in a random way. In classical physics there is an infinitely continuous spectrum of energies that any one particle can have, so it is difficult to do any counting of possibilities. So we imagine that the allowable energies are actually very finely spaced discrete states. Each one of these we call a microstate. And, in order that we can truly talk about the particles’ distributions’ being random we will take as a basic principle that all microstates occur with the same probability.

4.1 The classical thermodynamic distribution function

As an introductory example, consider a system consisting of only six particles, which can only take energy values $E$, $2E$, $3E$, … . Let the total energy of the system be some small integral multiple of $E$. We choose $8E$. Now write down every single configuration that the system can be in, that is, enumerate all the microstates. The complete tabulation is shown in figure 4.1.

![Figure 4.1: Different configurations of the 6 particle system (SMM, Fig 9.1)](image)

It is straightforward, though time-consuming, to calculate the total number of microstates represented by the 20 different configurations. These are already shown in figure 4.1. And by
adding all those numbers together, you get the total number of microstates that the 6-particle system can have if its total energy is 8\(E\). This number is \(\text{1287}\). Hence, if each of these is equally likely to occur, we can say that:

\[
\text{Probability of occurrence of any single microstate} = \frac{1}{1287} \quad (4.1)
\]

You already know how many particles there are, so (in principle) you know the density of this system. You know the total energy (8\(E\)), therefore you know the average energy per particle (1.333 \(E\)), which is related to its temperature. For further thermodynamic understanding you need to work out the average distribution of energy among all the particles—on average, how many of them have 8 units of energy? how many have 7 units? and so on to how many have no energy? Having made the assumption that all microstates are equally probable enables us to do this calculation easily. It is merely a matter of counting.

Let us ask, for example, how many particles in the box on average have, say, 4 units of energy? In the configuration (2,1) there are 2 particles, and only 2, with energy 4\(E\). There are 15 different microstates in this configuration, each which has a probability of (1/1287). So if this were the only configuration that produced particles with 4\(E\), you could say that there were 15 chances in 1287 that the number of particles with 4\(E\) is 2; and there are 1272 chances in 1287 that the number of particles with 4\(E\) is zero. So the average number of particles with 4\(E\) is 2 \times (15/1287) or 0.02331.

But we know that this configuration is not the only way to get at least one particle with 4\(E\). The configurations (2,4), (2,5), (3,1) or (3,2) also have at least one particle on the 4\(E\) rung. So when we calculate the average number of particles with 4\(E\) we must take account of all of these. The final calculation looks like this:

\[
\text{Average no. with } 4E = 2 \times \frac{15}{1287} + 1 \times \frac{120}{1287} + 1 \times \frac{60}{1287} + 1 \times \frac{180}{1287} + 1 \times \frac{30}{1287} = 0.3258 \quad (4.2)
\]

It is similarly not difficult to find the average number with 0\(E\), 1\(E\), 2\(E\) ... 8\(E\).

Since there are 6 particles in the box we can convert these figures into a measure of the probability that any particular particle has 0\(E\), 1\(E\), 2\(E\) ... 8\(E\), by dividing these numbers by 6. The final results are given in this table and plotted as a function of energy.

<table>
<thead>
<tr>
<th>(p(E))</th>
<th>Probability of finding a particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>0(E)</td>
<td>0.385</td>
</tr>
<tr>
<td>1(E)</td>
<td>0.256</td>
</tr>
<tr>
<td>2(E)</td>
<td>0.167</td>
</tr>
<tr>
<td>3(E)</td>
<td>0.0978</td>
</tr>
<tr>
<td>4(E)</td>
<td>0.0543</td>
</tr>
<tr>
<td>5(E)</td>
<td>0.0272</td>
</tr>
<tr>
<td>6(E)</td>
<td>0.0117</td>
</tr>
<tr>
<td>7(E)</td>
<td>0.00388</td>
</tr>
<tr>
<td>8(E)</td>
<td>0.000777</td>
</tr>
</tbody>
</table>

Figure 4.2: Distribution function for 6 particles sharing 8 units of energy (SMM, Fig 9.2)

What you see is that the probability decreases rapidly with energy (it is approximately an exponential decrease). That tells us it is much more likely to find the energy distributed among many particles of the system than concentrated in a few particles.

We did that calculation for only a small number of particles. Had we been able to do a similar thing for a very large number, like Avogadro’s number, then we would have found a result which was qualitatively similar, which can be stated like this:
For a system with a fixed numbers of particles \(N\), and with fixed total energy \(E_{\text{tot}}\), then the probability of finding a particle with one of its allowable energies \(E_i\) is denoted by the symbol \(f\), given by

\[
f = Ae^{-\beta E_i}
\]  

(4.3)

The two constants \(A\) and \(\beta\) are related to the quantities \(N\) and \(E_{\text{tot}}\). You can make a rough estimate of \(\beta\) by observation of Figure 4.4. At the average value of the energy \((1.33E)\) the probability has fallen to about half its maximum value. That means:

\[
e^{-\beta E} \sim 0.5 \quad \text{or} \quad \beta \sim \frac{0.7}{E}
\]  

(4.4)

You know enough thermodynamics already to know that the average value of a collection of particles is essentially a measure of its temperature. Indeed in every system you have met, the average energy is of the order of \(k_B T\), where \(k_B\) is known as Boltzmann’s constant. A careful study of this thermodynamical relationship will show that the form of Equation 4.3 which is valid for all (classical) systems is

\[
f_{\text{MB}} = Ae^{-E_i/k_B T}
\]  

(4.5)

This is known as the Maxwell-Boltzmann distribution function.

There is a further complication to take into account. It often happens that the molecules have other forms of energy, and there can be many different states with a single energy. The energy states are said to be degenerate. When you perform calculations which involve counting energy states, we must take into account possible degeneracies. If the number of states with the same energy \(E_i\) is \(g_i\), then the number of particles, \(n_i\), with energy \(E_i\) is given by:

\[
n_i = g_i f_{\text{MB}} = g_i Ae^{-E_i/k_B T}
\]  

(4.6)

When the number of particles gets very large, and the energies involved are substantial, it is too difficult ever to calculate \(g_i\) for each and every single particle state. Instead we try to estimate \(g\) as a function of \(E\), and write the number of single particle states with energy between \(E\) and \(E + \Delta E\) as \(g(E)\Delta E\). Then the number of particles with energies between \(E\) and \(E + \Delta E\) is given by:

\[
n(E) \Delta E = g(E)Ae^{-E_i/k_B T} \Delta E
\]  

(4.7)

The quantity \(g(E)\) is called the density of states.

### 4.2 The statistics of quantum particles

Let us revisit the simple counting exercise, and ask where was the critical point at which we assumed something about the nature of the particles we were dealing with. It was at the point where we were talking about energy configurations (or microstates) and said that there were a number of ways of achieving any configuration because there were many different particles that could have a particular amount of energy.

Now the logic in that statement is that, if particle A is in a certain energy state, and particle B is in a state with the same energy; then it is equally possible to imagine that particle B is in the first energy state, and particle A is in the other state with the same energy—and these two are equally probable and must both be counted when doing statistics. But in the limit where atoms have just wave properties and no particle properties, that doesn’t make sense. Two atoms with the same energy means one wave of twice the amplitude in the matter field. In what sense is it sensible to say that such a wave must be counted twice?

In the usual formulation of quantum mechanics it is believed that all electrons (or protons or neutrons etc.) are absolutely identical with one another. There is no way, even in principle, that you could tell two of them apart (unless of course they were a long way apart to start with). An absolutely critical property, which must be taken into account in any statistical argument is this fundamental indistinguishability.
Look again at the table of possible configurations in Figure 4.1. In the pure wave way of looking at things, each of these is a single microstate. The total number of these microstates is 20 (much less that it was before). Hence when we calculated, for example, the average number of particles with 4E, the result is now:

\[
\text{Average no. with } 4E = 2 \times \frac{1}{20} + 1 \times \frac{1}{20} + 1 \times \frac{1}{20} + 1 \times \frac{1}{20} + 1 \times \frac{1}{20} = 0.30 \quad (4.8)
\]

Again, since there are 6 particles in the box we can convert these figures into a measure of the probability that any particular particle has 0E, 1E, 2E ... 8E, by dividing these numbers by 6. The new results show a new distribution which tends to have more particles at the lowest energy levels than the previous curve. At higher energies the two curves come together, and decrease in probability with increasing energy.

<table>
<thead>
<tr>
<th>Energy</th>
<th>Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>0E</td>
<td>0.408</td>
</tr>
<tr>
<td>1E</td>
<td>0.258</td>
</tr>
<tr>
<td>2E</td>
<td>0.150</td>
</tr>
<tr>
<td>3E</td>
<td>0.0750</td>
</tr>
<tr>
<td>4E</td>
<td>0.0500</td>
</tr>
<tr>
<td>5E</td>
<td>0.0250</td>
</tr>
<tr>
<td>6E</td>
<td>0.0167</td>
</tr>
<tr>
<td>7E</td>
<td>0.00833</td>
</tr>
<tr>
<td>8E</td>
<td>0.000833</td>
</tr>
</tbody>
</table>

Figure 4.3: Distribution for 6 indistinguishable particles sharing 8 energy units (SMM, Fig 9.6)

### 4.3 The Bose-Einstein distribution

Again, when we consider systems with large numbers of particles (like Avogadro’s number), a continuous distribution can be rigorously derived (although we certainly won’t bother doing it). By maximizing the number of ways of distributing the indistinguishable quantum particles among the allowed energy states, again subject to the constraints of a fixed number of particles (\(N\)) and fixed total energy (\(E_{\text{tot}}\)), we find this distribution function:

\[
f_{BE} = \frac{1}{B e^{E/k_B T} - 1} \quad (4.9)
\]

where \(B\) is a slowly increasing function of energy, different from the quantity \(A\) in Equation 4.5. This formula is known as the **Bose-Einstein distribution function**.

We should say immediately that not all quantum particles obey this distribution law. There are two distinct classes of quantum particles. One class, called **fermions**, are governed by an extra physical law, called the **Pauli principle**, which we will discuss in next lecture. The rest of them do not have this extra constraint, and their behaviour in large numbers are therefore described by the analysis we just went through. This class of quantum particles are called **bosons**.

It should be clear that, at high energies the term \((-1)\) in the denominator of Equation 4.9 is much smaller than the exponential term, and can be safely ignored. Under those conditions the Bose-Einstein distribution function has the same form as the Maxwell-Boltzmann distribution. So the thermodynamic behaviour of the two must be very similar. However at low energies and low temperatures that \((-1)\) could, in principle, lead to a singularity. So we would expect that it is only at very low temperatures that quantum behaviour will become noticeable.
4.4 The Pauli exclusion principle and electron spin

In the early 1920s two proposals were put forward, to help understanding of a number of puzzling observations. Firstly Wolfgang Pauli put forward the following rule, which he argued had to be obeyed in any quantum system:

*No two electrons in a multielectron atom can be in the same quantum state.*

He could give no justification for this other than it seemed to be necessary. It was only later that it came to be seen as a fundamental property of all quantum particles, and was associated with other mathematical constraints.

The second came from an observation made by Otto Stern and Walter Gerlach that all electrons behaved in a sense like little bar magnets which could only point along and opposite to some applied magnetic field. It is usually said that electrons are spinning, and

*Any electron has a spin which can take one of two eigenvalues, \( \pm \frac{1}{2} \hbar \).*

The key idea coming out of this is that two electrons, oppositely aligned so that they cancel out any magnetic effect, can now inhabit what we have thought of till now as a single energy state. But no more than two—with two electrons the energy state is filled.

You can read up elsewhere about how these two propositions explain to an astonishing degree the periodic table (see for example Section 8.6 of the textbook). For us here, they will clearly have a dramatic impact when we come to count states as we do when we study quantum statistics.

4.5 The Fermi-Dirac distribution

Let us return to the simplified system we discussed in Section 4.1 and discard any configurations that involved there being more than two particles in any energy level. This in fact leaves only three microstates, configurations (2,4), (2,7) and (3,1). The total number of these microstates is now only 3 so the probability of each is 1/3, and the number of particles is still 6. So the average number of particles with any energy is particularly easy to calculate.

<table>
<thead>
<tr>
<th>Energy</th>
<th>Probability of finding a particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>0E</td>
<td>0.333</td>
</tr>
<tr>
<td>1E</td>
<td>0.278</td>
</tr>
<tr>
<td>2E</td>
<td>0.167</td>
</tr>
<tr>
<td>3E</td>
<td>0.167</td>
</tr>
<tr>
<td>4E</td>
<td>0.167</td>
</tr>
<tr>
<td>5E</td>
<td>0.056</td>
</tr>
<tr>
<td>6E</td>
<td>0.000</td>
</tr>
<tr>
<td>7E</td>
<td>0.000</td>
</tr>
<tr>
<td>8E</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

Figure 4.4: Distribution function for 6 indistinguishable particles obeying the exclusion principle sharing 8 units of energy (SMM, Fig 9.7)

We now see a distinctly different distribution from the Maxwell-Boltzmann or Bose-Einstein curves. Although it is not entirely clear that the results plotted actually do lie on the smooth curve, consideration of systems with more than 6 particles shows this to be the case. For very large numbers of particles, the corresponding continuous distribution function is:

\[
f_{FD} = \frac{1}{He^{E/kBT} + 1}
\]

where \( H \) is another slowly increasing function of energy, different from the quantities \( A \) in Equation 4.5 or \( B \) in Equation 4.9. This formula is known as the **Fermi-Dirac distribution function**.
LECTURE 11

The material in this chapter is covered in the text sections: 9-2, 9–3

After studying the chapter you will be able to:

• discuss quantitatively condition for using quantum vs classical statistics;
• describe the differences between fermions and bosons;
• describe quantitatively the meaning of the Fermi energy;
• discuss applications of BE statistics, including superfluidity; and.
• discuss applications of FD statistics, including electrons in a metal.

4.5.1 Classical vs quantum distributions

Before we examine the quantum distributions in detail let us ask under what conditions is it necessary to use the quantum distributions, and when are classical statistics accurate enough. Remember the decisive question is whether the atoms are behaving like particles or like waves. If they behave purely like waves, then their thermodynamic behaviour must show quantum effects. But if they behave like little billiard balls, then their thermodynamic behaviour must be classical. The in-between case is when they are behaving like wave packets. Then the deciding feature is: how spread out are the packets? After all if two particles are behaving like two very narrow packets far apart from one another, even though they are indistinguishable in principle, you can in practice tell them apart by where they are at any time. So the mathematical model you use to describe their behaviour can legitimately follow the Maxwell-Boltzmann line of reasoning.

We can quantify this by saying that the Maxwell-Boltzmann distribution is valid when the average distance between particles, $d$, is large compared with the quantum uncertainty in the positions of the particles, $\Delta x$, or

$$d >> \Delta x. \quad (4.11)$$

This statement is equivalent to saying that you can use the classical distribution function provided the temperature is well above a certain value, which depends on the number of particles per unit volume. This is true when:

$$\frac{\sqrt{2mk_B T}}{\hbar} >> \left(\frac{N}{V}\right)^{1/3}. \quad (4.12)$$

If you want to see where this comes from, then here is the mathematical argument which is in four steps:

• Uncertainty in position is related to uncertainty in momentum, $\Delta x > h/\Delta p$,
• uncertainty in momentum is related to average kinetic energy, $\Delta p = \sqrt{p^2} = \sqrt{2mKE}$,
• and average kinetic energy is related to temperature, $KE \sim k_BT$.
• On the other side, average separation is related to number density, $d \sim (V/N)^{1/3}$.

Combine these four expressions and you get Equation 4.12.

Example 1  Hydrogen gas at standard temperature and pressure

• At temperature 300 K, $k_BT = 1.38 \times 10^{-23}$ J K$^{-1}$, $300 K = 4.14 \times 10^{-21}$ J
• $m_H = 3.34 \times 10^{-27}$ kg, $\hbar = 1.05 \times 10^{-34}$ Js, therefore left hand side = $5.01 \times 10^{10}$ m$^{-1}$.
• 1 mole of hydrogen gas has $6.02 \times 10^{23}$ molecules and it occupies a volume of $2.24 \times 10^{-4}$ m$^3$
• Therefore right hand side = $3.00 \times 10^8$ m$^{-1}$. 

The left hand side is two orders of magnitude bigger than the right hand side, so Maxwell-Boltzmann statistics can be used with impunity.

Example 2  Liquid helium at its boiling point

- At temperature 4.2 K, \( k_B T = 5.8 \times 10^{-23} \text{ J} \)
- \( m_{He} = 6.68 \times 10^{-27} \text{ kg} \), so left hand side of Equation 4.12 = \( 8.4 \times 10^{+9} \text{ m}^{-1} \).
- density of helium at 4 K = 145 kg m\(^{-3}\), therefore \( N/V = 2.18 \times 10^{28} \text{ atoms per m}^{-3} \)
- Therefore the right hand side = \( 2.78 \times 10^{9} \text{ m}^{-1} \)

The left and right hand sides are very much the same order of magnitude, so the thermodynamics of liquid helium cannot be described classically, but could be expected to show very clear quantum effects.

4.6 Bosons or fermions?

The next question is: which particles are supposed to obey Bose-Einstein statistics, and which Fermi-Dirac? For reasons which are not well understood, the deciding feature lies with the spin of the particle. It is found that any particle which has the same kind of magnetic moment as an electron, that is which can point in two different directions only (or if you like, which has a spin of \( \pm \frac{1}{2} \hbar \)) is a fermion. On the other hand, a particle which has no magnetic moment, or consists of matched pairs of particles with magnetic moments which are arranged contrary to one another and cancel out, is a boson.

We should mention here that it is possible for particles with magnetic moments to combine inside other particles so that the magnitude of their total spins are greater than \( \frac{1}{2} \hbar \). We don’t want to go into the question of how to calculate the spin of collections of particles here: that is another area of quantum mechanics altogether. It is enough to state as a general rule that any particle with the magnitude of its total spin \( 0, 1\hbar, 2\hbar, \ldots \) etc is a fermion. It is observed that the three “fundamental” matter particles—electrons, protons and neutrons—all have spin \( \frac{1}{2} \hbar \), and are all fermions.

Just what the connection is between magnetic moment, or spin, and whether or not more than one particles can be in one energy level (or two counting spin states) is one of those mysteries of quantum mechanics—and there are many such mysteries in quantum mechanics. It can be traced to a mathematical property of the wave function which describes a pair of particles—whether the wave function is symmetric or antisymmetric as regards the coordinates of the two particles. It doesn’t really help much. It just pushes back the question to: what is the connection between that property and the particles’ spin? So we won’t pursue that here.

It is known that photons obeyed Bose-Einstein statistics. We have no way of knowing what the spin of a photon is at this point. Certainly it doesn’t have any magnetic moment, but then it doesn’t carry a charge either. But in Section 4.7 we saw that Helium atoms are bosons too. That is consistent with what we have been saying. A Helium nucleus consists of two protons with cancelling spins; and two neutrons whose spins also cancel. And it has two electrons in its lowest electronic shell also with cancelling spins. Hence we shouldn’t be surprised to find that Helium (gas or liquid) obeys Bose-Einstein statistics. And we shall see in the next section, that it exhibits the phenomenon of superfluidity. Equally noteworthy, however, is the fact that there is an isotope of helium, \(^3\text{He}\), and it is found that when \(^3\text{He}\) gas condenses to a liquid, it does not become superfluid!

4.7 Application of Bose-Einstein statistics: superfluidity

A simple theory of the liquid state is not yet completely available. On a naive level we believe that a liquid consists of a collection of particles almost as dense as a solid, but with enough random motion for the particles to resist forming rigid structures. One of their most important properties
is **viscosity**—stickiness or wetness. When objects move through liquids, or liquids move through pipes they lose energy, mainly by setting individual particles in random motion. In quantum terms energy is taken up by the molecules, causing transitions to higher kinetic energy states. The role of heat is to distribute molecules among levels. If there are any purely quantum effects, they are hidden among thermal fluctuations.

However when scientists started achieving really low temperatures, strange effects were noticed. Landmarks in this story are: the liquefaction of helium in 1908 by Heike Kammerlingh-Onnes; the discovery in 1937 by Peter Kapitza of superfluidity; and the first theoretical understanding by Lev Landau in 1941.

What Kapitza discovered was that liquid helium had some very strange properties.

- It flows through very narrow tubes—its viscosity is less than $1/10\text{,}000$ of hydrogen gas!
- If it is placed in an open container it will rise up the sides and flow over the top.
- If a light is shone into a beaker of superfluid and there is an exit at the top the fluid will form a fountain and shoot out of the top exit.
- If the fluid’s container is rotated from stationary, the fluid inside does not move. The viscosity of the liquid is zero. Any part of the liquid or its container can be moving at any speed without affecting any of the surrounding fluid.
- It has very high thermal conductivity, over 200 times faster than purest copper.
- It exhibits an extremely rapid change in specific heat at a temperature of $2.18$ K. This temperature has been named the **lambda point**, because of the shape of the graph of specific heat capacity against temperature.

![Figure 4.5: The variation of specific heat of liquid Helium near the lambda point](image)

This figure gives the clue to what is happening. Clearly there is a change of phase occurring (think of how the specific heat of water varies as it goes from ice to water to ice or form water to steam, when latent heat has to be put in). Above the lambda point, helium behaves like an ordinary liquid. This phase is called He I. Below this temperature, a new phase starts to appear, called He II, which because of its strange properties is called a **superfluid** or a **quantum liquid**.

Because these atoms obey Bose-Einstein statistics there is a tendency for all the atoms to fall into the ground state (remember the singularity that seemed to be possible in Equation 4.9). Once they’re in it, the thermal energy of surrounding atoms is not enough to push them into the next excited state. We can think of the superfluid as being in a single quantum state made up of a very large number of atoms. These atoms behave in a cooperative way, giving the fluid its unusual properties. This kind of phase change is called **Bose-Einstein condensation**.

There are many other applications of Bose-Einstein statistics, most importantly the theory of **blackbody radiation** and the theory of quantized lattice waves, or **phonons**. The general area
of Bose-Einstein condensates is an active field of research these days. Make sure you read about these in the textbook — MMS, pp.356–61, 376–7.

4.8 The Fermi Energy

If you compare the formulas for the three statistical distribution functions, Maxwell-Boltzmann (4.5), Bose-Einstein (4.9) and Fermi-Dirac (4.10), you will see that an important difference between the three functions is in the energy dependence of the “constants” $A$, $B$ and $H$. For both MB and BE statistics these quantities vary only slowly with energy, but for FD, $H$ is strongly dependent on $T$, and the dependence is usually approximately exponential, so $H$ is written as $e^{-E_F/kT}$ and so the usual way of writing the Fermi-Dirac distribution function is:

$$f_{FD} = \frac{1}{e^{(E-E_F)/kT} + 1} \quad (4.13)$$

The quantity $E_F$ is known as the **Fermi energy**. It is sometimes useful to calculate the speed of an electron whose kinetic energy is equal to this value. This is known as the **Fermi speed**.

$$v_F = \sqrt{2E_F/m_e} \quad (4.14)$$

Consider the properties of the Fermi-Dirac distribution. For values of $E > E_F$, when $T$ is small the exponential factor becomes large and $f_{FD}$ goes to zero just like $f_{MB}$ and $f_{BE}$. However when $E < E_F$ the story is very different. The term $(E - E_F)$ is negative and the exponential term goes to zero for small $T$. Therefore $f_{FD} \approx 1$. The occupation probability is therefore only one per quantum state, just as required by the Pauli Principle. Even at very low temperatures, fermions do not “condense” into the lowest energy level.

Don’t forget incidentally, that there is a degeneracy factor $g = 2$ because of the two possible spin eigenvalues ($\pm \frac{\hbar}{2}$) which has to be taken into account. So in reality the occupation probability is two per energy level.

A plot of the Fermi-Dirac distribution with fixed Fermi energy at different temperatures looks like this:

![Fermi-Dirac distribution with fixed Fermi energy at different temperatures](image)

**Figure 4.6:** The Fermi-Dirac distribution function with $E_F = 10,000 \text{ K}$ for three different temperatures. (Compare with SMM Fig 9.12)

At $T = 0$, all the energy levels up to $E_F$ are occupied ($f_{FD} = 1$), and all the energy levels above $E_F$ are empty. As $T$ increases, some levels above $E_F$ are partially occupied ($f_{FD} > 0$), while some levels below $E_F$ are partially empty ($f_{FD} < 1$). The higher the temperature, the more “spread out” the distribution becomes.

From Equation 4.13 you can see that when $E = E_F$, the value of $f_{FD}$ is $\frac{1}{2}$, regardless of temperature. Thus an alternative definition of $E_F$ is:

*The Fermi energy is the energy at which the occupation probability is exactly one half.*

The Fermi energy varies only slightly with temperature for most materials, and we can usually regard it as a constant. We will see later that for electrons in a metal, $E_F$ depends on the electron density of the material, which doesn’t change much with temperature. However, for some materials, notable semiconductors, the density of *conduction* electrons can change significantly with temperature and therefore in these materials $E_F$ is temperature dependent.
4.9 Application of Fermi-Dirac statistics: Electrons in a metal

An excellent example where Fermi-Dirac statistics apply is to the conduction electrons in a metal. Since the outer electrons are weakly bound to individual atoms, we can treat the outer conduction electrons as a gas of fermions trapped within a cavity formed by the metallic surface. The first thing we must do is to count how many energy levels there are available to these electrons.

We can think of electrons as a system of matter waves whose wave functions vanish at the boundaries of the metal. Since these waves exist in three dimensions, there are many different arrangements of these waves which have any particular energy (especially at large energies). The result we want to use is:

The number of electron states, per unit volume, with energies between \( E \) and \( E + \Delta E \) is

\[
g(E) \Delta E = \frac{8 \sqrt{2} \pi m_e^{3/2}}{\hbar^3} \frac{E^{1/2} \Delta E}{e^{(E-E_F)/k_B T} + 1} \tag{4.15}\]

I’m not going to prove this result. It is purely geometric and you can follow it if you want in the textbook, SMM pp.362-363.

You can combine this result with Equation 4.13 to generate an expression for the number of electrons (per unit volume) with energies between \( E \) and \( E + \Delta E \),

\[
n(E) \Delta E = \frac{8 \sqrt{2} \pi m_e^{3/2}}{\hbar^3} \frac{E^{1/2} \Delta E}{e^{(E-E_F)/k_B T} + 1} \tag{4.16}\]

Although this expression looks a bit messy, it simplifies a lot at \( T = 0 \), and one simple calculation you can do is to integrate it over the energy range \((0-E_F)\) and get a relationship between the total number of electrons per unit volume and the Fermi energy at \( T = 0 \):

\[
\frac{N}{V} = \frac{8 \sqrt{2} \pi m_e^{3/2}}{\hbar^3} \int_0^{E_F} E^{1/2} \, dE = \frac{16 \sqrt{2} \pi m_e^{3/2}}{3 \hbar^3} E_F^{3/2} \tag{4.17}\]

As an example of what this means let us consider copper, say, and work out its Fermi energy.

<table>
<thead>
<tr>
<th>Density of copper, ( \rho )</th>
<th>( 8.960 \times 10^3 ) kg.m(^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass of copper, ( M_{mole} )</td>
<td>( 63.5 \times 10^{-3} ) kg/mole</td>
</tr>
<tr>
<td>Number density of copper, ( n )</td>
<td>( N_A \rho / M_{mole} )</td>
</tr>
<tr>
<td></td>
<td>( = 8.49 \times 10^{28} ) atoms.m(^{-3} )</td>
</tr>
<tr>
<td>Zero point Fermi Energy, ( E_F(0) )</td>
<td>( (\hbar^2/2m_e)(3n/8\pi)^{2/3} )</td>
</tr>
<tr>
<td></td>
<td>( = 1.08 \times 10^{-18} \text{ J} = 6.76 \text{ eV} )</td>
</tr>
<tr>
<td>Zero point Fermi Speed, ( v_F )</td>
<td>( (2E_F/m_e)^{1/2} )</td>
</tr>
<tr>
<td></td>
<td>( = 1.54 \times 10^6 \text{ m.s}^{-1} )</td>
</tr>
</tbody>
</table>

This particular application of Fermi-Dirac statistics is carefully covered in the textbook because it forms the basis of later chapters dealing with electrical conductivity. There are other examples which you will come across in outside reading. One interesting one is in the structure of white dwarf and neutron stars.
INTERLUDE 3

LECTURE 12

In this lecture period, it is intended to discuss extension material which can shed a different perspective on the content of chapter 4.

For the Advanced class:

Other applications of both the Bose-Einstein and Fermi-Dirac distributions will be discussed, including . After studying this lecture material students will be able to:

- discuss applications of BE statistics, including black-body radiation, and
- discuss applications of FD statistics, including white dwarf stars.

For the Normal class:

Problems and examples from the textbook will be worked.
Extra material covered in Interlude 3.