

# Lecture 10 The Fermi Dirac Distribution Function and Thermal Properties of the Free Electron Model

**Kittel: Chapter 6, p136-147; Simon: Chapter 4, p27-37**

## The Fermi Function at Finite Temperatures

The overall state having the lowest total energy of a metal is the most likely for the electrons to occupy.

At zero Kelvin (when the whole system is in the ground state) this is the overall state with all energies less than  $E_F$  occupied and those above  $E_F$  empty.

Using this we can define an occupation number  $f(E)$  for each state which is the average number of electrons in each state. It can also be considered the probability of the state being occupied:

$$f(E) = \begin{cases} 1 & (0 < E \leq E_F) \\ 0 & (E > E_F) \end{cases} \quad \text{at temperature } T = 0 \text{ K.}$$

We can use this occupation number to give us the total number of electrons by combining it with the density of states function. We recall that the density of states function gives the number of available electron energy states per unit energy range.

The occupation number can also be considered as a distribution function which varies continuously as the Energy varies.

The total number of electrons is then just the integral of the density of states function.

$$N = \int_0^{E_F} n(E) dE = \int_0^{\infty} n(E) f(E) dE$$

Using  $f(E)$  allows us to change the limits of the integral making it easier to solve.

An important question to consider is: How does this distribution change as the temperature is increased? All practical systems are at finite temperatures above 0 Kelvin.

Any changes in the electron distribution will result from the finite thermal energy in the system which will excite a number of electrons out of the ground state. This is very small compared to the electron energy so any change will be a relatively small perturbation to the 0 Kelvin distribution. (Typical  $E_F$  values in metals are a few eV, compared to thermal energy 25 meV at 300 K.)

The effect of increasing temperature is to spread out the distribution of the electrons at the fermi energy  $E_F$  so the transition from  $f(E) \sim 1$  to  $f(E) \sim 0$  occurs over a region of energy.

This distribution of electrons at finite temperatures is described by the Fermi-Dirac distribution function – named after Enrico Fermi and Paul Dirac who developed it in 1927.

The Fermi-Dirac distribution is derived by requiring three constraints to be considered:

1. Conservation of energy
2. Conservation of particle number
3. Behaviour subject to the Pauli Exclusion Principle.

As electrons are quantum particles (fermions) they are indistinguishable and identical.

The derivation of the Fermi-Dirac distribution function uses these three constraints and arranges electrons in such a way as to minimise their energy (subject to the three constraints above). This is a standard problem in statistical physics.

The details of the derivation are not required for this course.

The result is important and we shall consider this further.

Fermi-Dirac Distribution Function:

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)}$$

The function is a correctly normalised statistical distribution function and therefore describes the probability of an electron occupying a state with energy  $E$ . The two parameters are  $T$  and  $E_F$ .

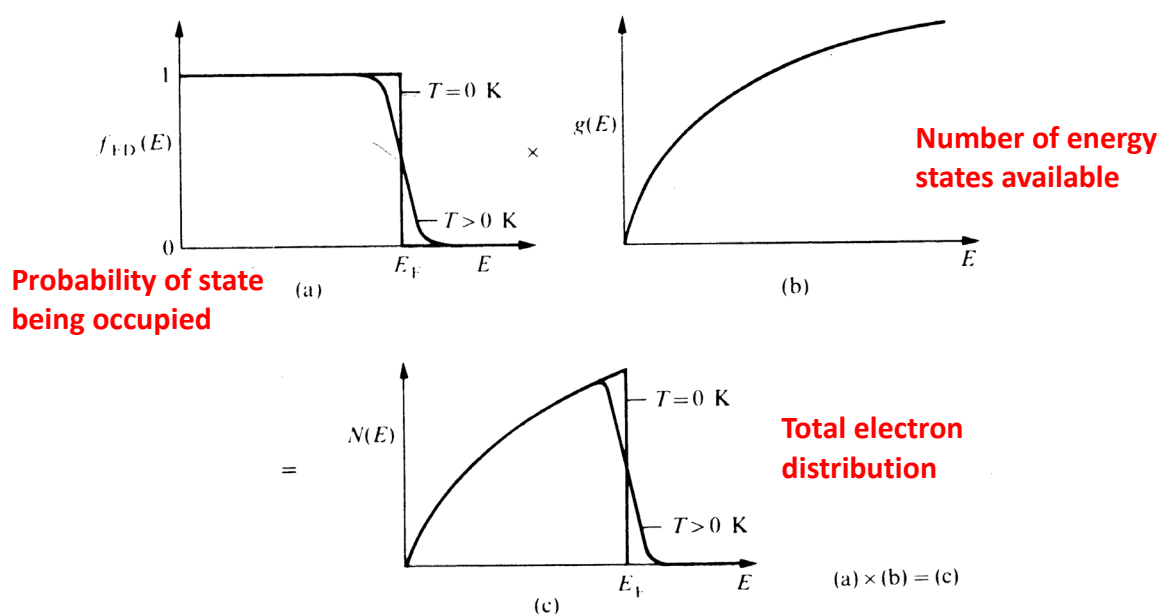


FIG. 7.3. The calculation of the density of occupied electron states  $N(E)$ . (a) The Fermi-Dirac function; (b) the density of states; (c)  $N(E) = g(E) \cdot f_{FD}(E)$ . The shaded regions of Fig. 7.2 correspond to (c).

## Behaviour of Fermi Dirac Distribution

We now consider the behaviour of electrons as described by the Fermi-Dirac distribution function in different regimes.

At low temperatures when  $k_B T \ll E_F$

a. When  $E < E_F$

If  $k_B T$  is small then  $(E - E_F) / k_B T$  is large and negative so the exp is very small and  $f(E) \sim 1$ .

b. When  $E > E_F$

In this case  $(E - E_F) / k_B T$  is large and positive so the exp is very large and  $f(E) \sim 0$ .

This becomes the zero temperature form of  $f(E)$  as  $T \rightarrow 0$ . The Fermi energy is set at a value which accommodates all the electrons in the system.

c. When  $E \sim E_F$

The transition between  $f(E) = 1$  and  $f(E) = 0$  occurs over a narrow energy interval whose width is approximately  $k_B T$  either side of the fermi energy.

In metals at room temperature we always have  $k_B T \ll E_F$ . This is a consequence of the high concentration of electrons in metals.

For low densities of electrons (for example in semiconductors and insulators)  $f(E) \ll 1$ .

This gives:

$$f(E) \approx \exp\left(-\frac{E - E_F}{k_B T}\right) \approx \exp\left(\frac{-E}{k_B T}\right)$$

where we neglect  $E_F$  which is very small. This is the result of classical physics – the Maxwell Boltzmann distribution. In other words low electron density systems (such as semiconductors and insulators) can be modelled using a classical distribution function.

A very small or low fermi-energy means the electron density  $n$  is very low. In this case it behaves more as a classical system where the interaction between electrons has little impact.

The figure below shows the impact of temperature on the Fermi-Dirac distribution and the impact on the free electron energy distribution. Electrons occupy the shaded region.

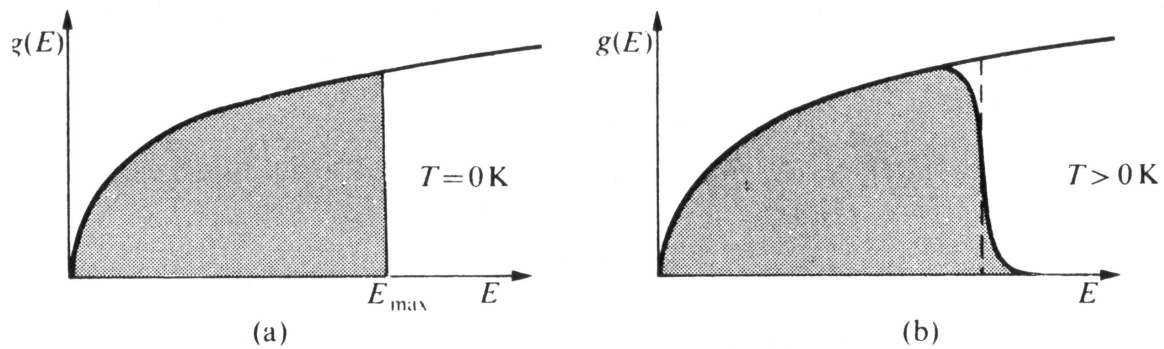


FIG. 7.2. The density of states  $g(E)$  as a function of energy for the free-electron model. (a) At 0 K all states are occupied up to  $E_{\text{max}}$ . (b) At higher temperatures the occupation of states in the region of  $E_{\text{max}}$  is smeared out.

## The Free Electron Heat Capacity

The electronic heat capacity of a crystal determined by using the free electron quantum model will be smaller than in the classical model. This is because only a small number of electrons with energies near the fermi energy  $E_F$  are able to absorb any energy when the temperature is increased. If an electron is not able to move from an occupied to an empty state it cannot absorb any energy and the overall electron distribution does not change.

This restriction (originating from the Pauli Exclusion Principle) is not present in the classical model.

When an electron absorbs energy (thermal, EM radiation etc.) it will be promoted to a higher energy state. If there is not a vacant energy state for the electron to move to then the energy cannot be absorbed by the electron.

Example of free electron model: Simple calculation for heat capacity of **electrons**

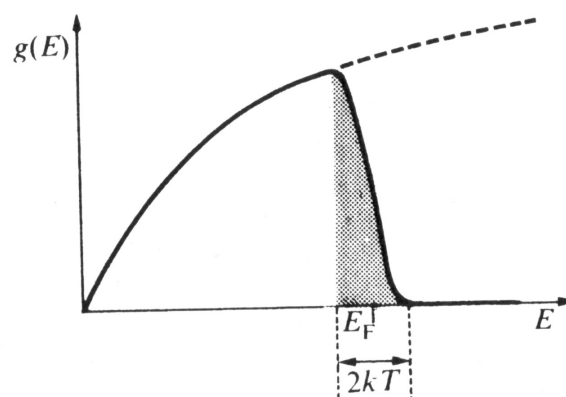


FIG. 7.4. Calculation of the electronic specific heat. Only electrons with energies in the neighbourhood of  $E_F$  can change their state as the temperature is raised, and so the electronic specific heat is small.

This begins by assuming that the number of electrons with energies close to  $E_F$  that are excited to energies above  $E_F$  is approximately  $n(E_F)k_B T$  where  $n(E_F)$  is the density of states per unit energy range evaluated at the fermi energy  $E_F$ . The extra energy received by the electron is  $k_B T$ . It is *assumed* that  $T$  represents the change in temperature  $\Delta T$  when starting from a 0 K distribution.

The increase in the internal energy of the system can be obtained from the Density of States function at the fermi energy.

If  $n(E_F)$  is the Density of states at the fermi energy then the number of electrons involved in a thermal excitation process is  $n(E_F)k_B T$  and the increase in the internal energy of the system is then obtained from the number of electrons involved  $\times$  the change in thermal energy of each electron  $k_B T$

$$U(T) - U(0) = n(E_F) (k_B T)^2$$

where  $n(E_F)$  is the density of states at the fermi energy

The heat capacity is then:

$$c_V = \frac{dU}{dT} \approx 2 n(E_F) k_B^2 T$$

This also assumes that  $n(E_F)$  is constant over the range  $\Delta T$  which is an approximation. We need to determine the value of the Density of States Function evaluated at the Fermi energy  $n(E_F)$ . We can write the total number of electrons as a function of the Density of States function. This enables us to evaluate the Density of States function at the Fermi Energy as a function of other known parameters:

$$N = n(E_F) E_F V \Rightarrow n(E_F) = \frac{N}{E_F V}$$

From lecture 9 we recall that:

$$n = \frac{(E_F 2m_e)^{\frac{3}{2}}}{3\pi^2 \hbar^3}$$

finally we get:

$$n(E_F) = \frac{3}{2} \frac{N}{E_F V}$$

The specific heat per electron is then:

$$c_V \approx \frac{3}{2} k_B \left( \frac{2k_B T}{E_F} \right)$$

The specific heat is thus reducing from the classical value by a factor of  $2k_B T / E_F$ . This is the **electronic specific heat**. There is another contribution to the specific heat which involves phonons (as explored in Lecture 7). Typically the phonon contribution is smaller than the electronic contribution to the specific heat.

This also shows that the electronic specific heat is proportional to  $T$ .

A more accurate calculation is followed in Kittel page 141-144 which gives a more accurate result by differentiating the Fermi function. We have assumed that the Density of State function is constant over the energy range  $2k_B T$  which is an approximation. Kittel does the full derivation (not required for this course).

The result of this calculation is that the heat capacity *per electron*:

$$C_{el} = \frac{1}{3} \pi^2 k_B^2 \frac{T}{E_F}$$

This is generally written as  $\gamma T$  where  $\gamma = \frac{\pi^2}{3} \frac{k_B^2}{E_F}$

Note this differs from our simpler approximation in the example above by a factor of  $\frac{\pi^2}{3}$ . **Error corrected to 3<sup>2</sup> - 24 April 2018**

Plot shows experimental data compared with our example above.

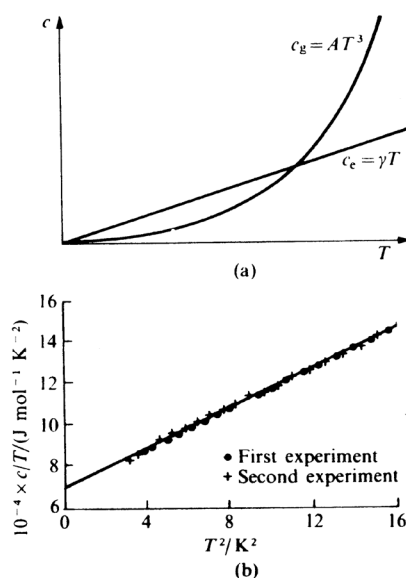


FIG. 7.5. The specific heat of metals at low temperatures. (a) In the helium region the electronic contribution  $c_e$  can dominate that of the lattice,  $c_g$ . (b) A plot of  $c/T$  against  $T^2$  for copper, showing the very good linear relationship which is obtained (C. A. Bailey (1959), D. Phil. Thesis, Oxford University).

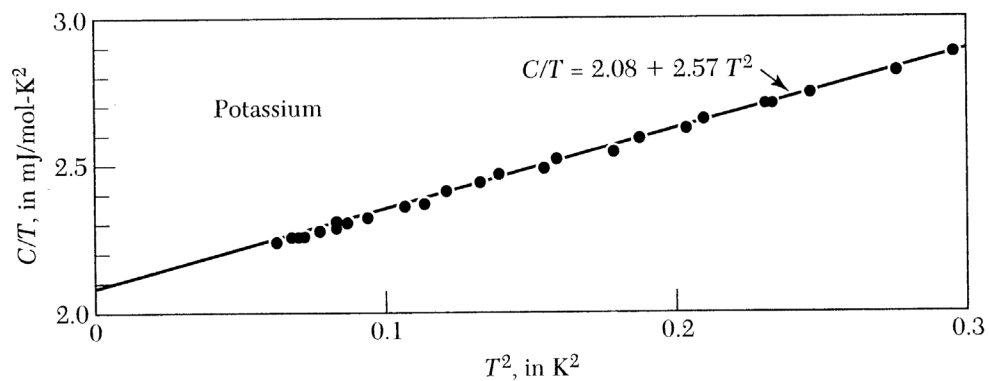
To fully understand this plot we must consider the contribution of both phonons and electrons to the specific heat.

The Debye law predicts the contribution of phonons to be  $\propto T^3$  (see earlier lecture).

The contribution of electrons is predicted above to be  $\propto T$

It is normal to plot this in the form of  $c/T$  versus  $T^2$  giving a straight line.

Data for Copper and potassium shown which agree with these predictions.



**Figure 9** Experimental heat capacity values for potassium, plotted as  $C/T$  versus  $T^2$ . (After W. H. Lien and N. E. Phillips.)

This data confirms the validity of the free electron model at describing the experimentally observed heat capacity of electrons in metals.