FREE ELECTRON MODEL

Lecture 15

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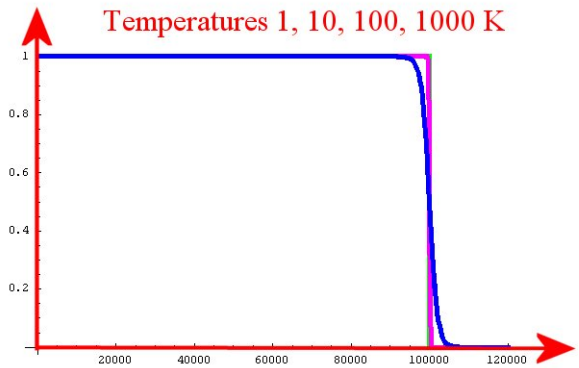
6.3 Thermal Behaviour of free electron gas

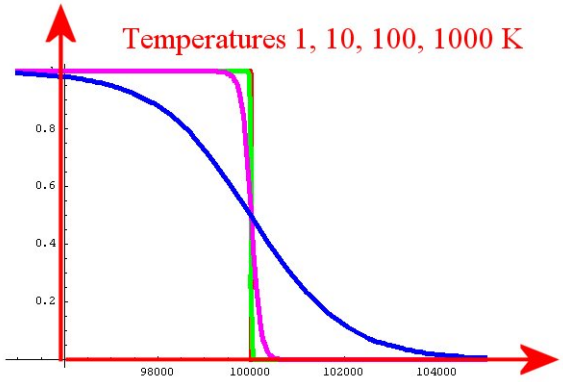
6.3.1 Review of Fermi function

The key point about electrons in a metal is that the Fermi temperature T_F is *high* – about 10^5 K.

$$f_{FD} = \frac{1}{\exp((e-\mu)/k_B T)+1}$$



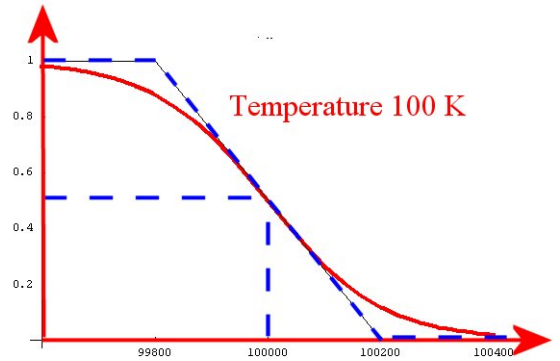
Even if we zoom in, we can only just see the change from the step function at normal temperatures.



This means that temperature has very little effect on the energy distribution of the electrons.

6.3.2 Electronic specific heat

To a good approximation, we can approximate the effect of temperature by drawing a straight line passing through $f_{FD}(E_F) = \frac{1}{2}$, falling from $f_{FD}(E_F - 2k_B T) = 1$ to $f_{FD}(E_F + 2k_B T) = 0$.



Thus the effect of increasing temperature changes the energy of the number of electrons in a triangular region of height $g(E_\mathrm{F})/2$ and width $2k_\mathrm{B}T$, that is, $\frac{1}{2}g(E_\mathrm{F})k_\mathrm{B}T$. These have their energy increased by about $k_\mathrm{B}T$ ($\frac{4}{3}k_\mathrm{B}T$ if we keep to the triangular model), so that

$$E_\mathrm{total} \approx E_0 + \frac{1}{2}g(E_\mathrm{F})k_\mathrm{B}T \times k_\mathrm{B}T,$$

so that the electronic specific heat is

$$C_v = \frac{\mathrm{d}E}{\mathrm{d}T} \approx g(E_\mathrm{F}){k_\mathrm{B}}^2 T.$$

Note that

$$\begin{aligned}
g(E_\mathrm{F}) &= \frac{Vm}{\pi^2\hbar^3}\ \sqrt{2mE_\mathrm{F}} \\
&= V\,\frac{\sqrt{2m^3}}{\pi^2\hbar^3}\ \sqrt{E_\mathrm{F}} \\
E_\mathrm{F} &= \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N_e}{V}\right)^{2/3} \\
&= \frac{1}{2m}\left(\frac{3\pi^2\hbar^3 N_e}{V}\right)^{2/3} \\
\pi^2\hbar^3 &= \frac{V}{3N_e}\left(2mE_\mathrm{F}\right)^{3/2} \\
g(E_\mathrm{F}) &= V\ \frac{3N_e}{V}\left(\frac{1}{2mE_\mathrm{F}}\right)^{3/2}\sqrt{2m^3}\sqrt{E_\mathrm{F}} \\
&= \frac{3N_e}{2E_\mathrm{F}}.
\end{aligned}$$

so

$$C_v = \frac{3N_e{k_\mathrm{B}}^2 T}{2E_\mathrm{F}}.$$

A more accurate evaluation gives

$$C_v = \frac{\pi^2}{3}g(E_\mathrm{F}){k_\mathrm{B}}^2 T,$$

or

$$C_v = \frac{\pi^2 N_e{k_\mathrm{B}}^2 T}{2E_\mathrm{F}}.$$

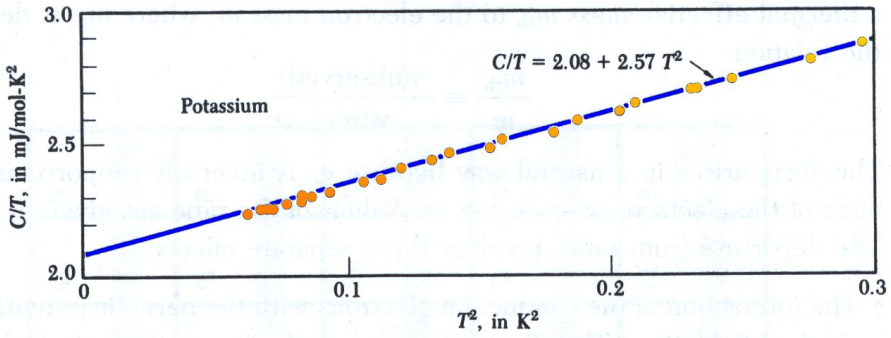
If we take a typical $E_\mathrm{F} \approx 5$ eV then at 300 K $C_v \approx 0.2$ J K^{-1}mol^{-1} This is less than one percent of the specific heat from vibrations ($\approx$ 25 J K^{-1}mol^{-1}.

6.3.3 Experimental results

At low temperatures, though, the vibrational contribution falls off as T^3, so the vibrational and electronic parts become comparable. Conventionally write

$$C_v = \gamma T + AT^3$$

at low T, and so a plot of C_v/T against T^2 should give a straight line.



Experimental heat capacity values for potassium, plotted as C/T versus T^2.

***Key point*: treating the electrons as quantum mechanical particles has shown their specific heat is reduced by a factor of about $k_{\mathrm{B}}T/E_{\mathrm{F}}$ from the classical result.**

6.4 Electrical Conductivity

6.4.1 Classical treatment

A particle acted on by a force $\mathcal{F}$ experiences a change in momentum

$$\mathcal{F} = \frac{\mathrm{d}\mathbf{p}}{\mathrm{d}t},$$

and for a classical particle

$$\mathcal{F} = m\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t}.$$

We know that the electrons in a metal have speeds ranging up to $\approx 10^6\ \mathrm{m\,s^{-1}}$, in random directions, so that there is no nett movement of electrons in a particular direction. We assume that the force adds a general tendency for the electrons to move in the direction of the force. We call the associated velocity a *drift velocity*, $\mathrm{v_d}$, and write

$$\mathcal{F} = m\frac{\mathrm{d}\mathbf{v}_{\mathrm{d}}}{\mathrm{d}t}.$$

The electrons will move freely through a perfect crystal – but the perfection is disturbed by

- **defects**
  - **– impurities (not different isotopes – these affect phonons as they have different masses but not electrons as they are electrically identical)**
  - **– dislocations**
  - **– grain boundaries**
- **phonons, locally altering the atomic spacings**
- **in addition, there may be electron-electron interactions**

6.4.2 Relaxation time

Introduce a *scattering time* or *relaxation time* τ:

- **the probability of an electron's being scattered in the time interval $\mathrm{d}t$ is $\mathrm{d}t/\tau$**
- **at each scattering event the velocity is randomised – the drift velocity is reset to zero**
- **so the rate at which v_{d} returns to zero is**

$$\left(\frac{\mathrm{d}v_{\mathrm{d}}}{\mathrm{d}t}\right)_{\mathrm{scatter}} = -\frac{v_{\mathrm{d}}}{\tau}$$

- **we may have different scattering times τ for different types of scattering – the different processes are assumed to be independent (*Matthiessen's rule*)**
- **we can also introduce a *mean free path* Λ: but note that the electrons have the Fermi velocity v_{F} as well as the drift velocity v_{d}, and $v_{\mathrm{d}} << v_{\mathrm{F}}$, so the distance travelled in the time τ is**

$$\Lambda = \tau v_{\mathrm{F}}.$$

So the evolution of $v_{\rm d}$ with time is

$$m\left[\frac{{\rm d}\mathbf{v}_{\rm d}}{{\rm d}t}+\frac{\mathbf{v}_{\rm d}}{\tau}\right]=\mathcal{F}.$$

There are two important cases:

- ***Steady state*: the time derivative is zero, so**

$$m\frac{\mathbf{v}_{\rm d}}{\tau}=\mathcal{F},$$
$$\mathbf{v}_{\rm d}=\frac{\mathcal{F}\tau}{m}.$$

- ***Zero force*: then**

$$\frac{{\rm d}\mathbf{v}_{\rm d}}{{\rm d}t}+\frac{\mathbf{v}_{\rm d}}{\tau}=0,$$
$$\mathbf{v}_{\rm d}(t)=\mathbf{v}_{\rm d}(0)e^{-t/\tau},$$

showing a *relaxation* of the drift velocity back to zero with a time constant τ.

6.4.3 Electrical conductivity

If the force arises from an electric field $\mathcal{E}$ then

$$\mathcal{F}=-e\mathcal{E}$$

(note that e is the *magnitude* of the charge on the electron – hence the minus sign).
So the steady-state drift velocity is

$$v_{\rm d}=-\frac{e\mathcal{E}\tau}{m},$$

which is often expressed in terms of a *mobility* μ,

$$\begin{aligned}\mu &\equiv \text{drift speed in unit field}\\ &=\frac{|\mathbf{v}_{\rm d}|}{|\mathcal{E}|}\\ &=\frac{e\tau}{m}.\end{aligned}$$

Now the electrical current density J is

$$\begin{aligned}\mathbf{J} &= (\text{electron charge})\times(\text{number of electrons/volume})\times(\text{drift velocity})\\ &=-e\frac{N_e}{V}\mathbf{v}_{\rm d}\\ &=\frac{N_e e^2\tau}{Vm}\mathcal{E}\\ &=\frac{N_e}{V}e\mu\mathcal{E}.\end{aligned}$$

This gives us *Ohm's law*, current proportional to field. If we write $n=N_e/V$, we have

$$\begin{aligned}\mathbf{J} &= \sigma\mathcal{E}\\ \sigma &= \frac{ne^2\tau}{m}\\ &= ne\mu.\end{aligned}$$

The quantity $\mu=e\tau/m$, which is the magnitude of the drift velocity acquired in unit field, is called the *mobility* of the electron.