

Heat capacity at low temperatures

The energy increase when we rise the temperature is

$$\Delta U = U(T) - U(0)$$

$$U(T) = \int_0^{\infty} dE E D(E) f(E) \quad f(E) = \frac{1}{\exp[(E-\mu)/k_B T] + 1}$$

$$U(0) = \int_0^{E_F} dE E D(E)$$

The number of available states is

$$\begin{aligned} N &= \int_0^{E_F} D(E) dE = \int_0^{\infty} D(E) f(E) dE \\ &= \left[\int_0^{E_F} dE + \int_{E_F}^{\infty} dE \right] D(E) f(E) \end{aligned}$$

Coming back to the energy:

$$\Delta U = \int_0^{\infty} dE E D(E) f(E) + N E_F - N E_F - \int_0^{E_F} dE E D(E)$$

$$N E_F = \left[\int_0^{E_F} dE + \int_{E_F}^{\infty} dE \right] E_F D(E) f(E)$$

$$= \int_0^{E_F} dE E_F D(E)$$

$$= \int_0^{E_F} dE E D(E) f(E) + \int_{E_F}^{\infty} dE E D(E) f(E) + \int_0^{E_F} dE E_F D(E)$$

$$- \left[\int_0^{E_F} dE + \int_{E_F}^{\infty} dE \right] E_F D(E) f(E) - \int_0^{E_F} dE E D(E)$$

$$\begin{aligned}
&= \int_0^{E_F} dE D(E) f(E) (E - E_F) + \int_0^{E_F} dE D(E) (E_F - E) \\
&\quad + \int_{E_F}^{\infty} dE D(E) f(E) (E - E_F) \\
&= \int_0^{E_F} dE D(E) f(E) (E - E_F) - \int_0^{E_F} dE D(E) (E - E_F) \\
&\quad + \int_{E_F}^{\infty} dE D(E) f(E) (E - E_F) \\
&= \int_0^{E_F} dE D(E) (E - E_F) (f(E) - 1) + \int_{E_F}^{\infty} dE D(E) f(E) (E - E_F) \\
&= \int_0^{E_F} dE D(E) (E_F - E) (1 - f(E)) \left. \begin{array}{l} \text{Both contributions} \\ \text{are positive!} \end{array} \right\} \\
&\quad + \int_{E_F}^{\infty} dE D(E) f(E) (E - E_F)
\end{aligned}$$

① Energy to take an e^- up to E_F from orbitals below E_F

② Energy to take an e^- from E_F to an orbital with $E > E_F$

The heat capacity is obtained

$$C_{el} = \frac{\partial \Delta U}{\partial T} \quad \text{only } f(E) \text{ depends on } T$$

$$\begin{aligned}
C_{el} = \frac{\partial \Delta U}{\partial T} &= \int_0^{E_F} dE D(E) (E_F - E) \left(-\frac{\partial f}{\partial T} \right) \\
&\quad + \int_{E_F}^{\infty} dE D(E) (E - E_F) \frac{\partial f}{\partial T}
\end{aligned}$$

$$= \int_0^{E_F} dE D(E) (E - E_F) \frac{\partial f}{\partial T} + \int_{E_F}^{\infty} dE D(E) (E - E_F) \frac{\partial f}{\partial T}$$

$$C_{el} = \int_0^{\infty} dE D(E) (E - E_F) \frac{\partial f}{\partial T}$$

when $k_B T / E_F \ll 0.01$, $\frac{\partial f}{\partial T}$ has huge positive peaks around E_F . therefore

$$\frac{\partial f}{\partial T} \approx \delta(E - E_F)$$

$$C_{el} \approx D(E_F) \int_0^{\infty} dE (E - E_F) \frac{\partial f}{\partial T}$$

$\mu \approx E_F$ at low temperatures

$$\frac{\partial f}{\partial T} = \frac{\partial}{\partial T} \frac{1}{\exp\left[\frac{E - E_F}{k_B T}\right] + 1} = \frac{E - E_F}{k_B T^2} \frac{\exp\left[\frac{E - E_F}{k_B T}\right]}{\left\{\exp\left[\frac{E - E_F}{k_B T}\right] + 1\right\}^2}$$

Then

$$C_{el} = D(E_F) \int_0^{\infty} dE \frac{(E - E_F)^2 \exp\left[\frac{E - E_F}{k_B T}\right]}{k_B T^2 \left\{\exp\left[\frac{E - E_F}{k_B T}\right] + 1\right\}^2}$$

Change the variable $x = \frac{E - E_F}{k_B T}$

$$dx = \frac{1}{k_B T} dE \Rightarrow dE = k_B T dx$$

$$\frac{(E - E_F)^2}{k_B T^2} = x^2 k_B$$

$$C_{el} = D(E_F) k_B^2 T \int_{-\frac{E_F}{k_B T}}^{\infty} \frac{x^2 e^x}{(e^x + 1)^2} dx$$

As we are interested in the low T regime

$E_F/k_B T \gg 1$ and we can approximate the lower limit by $-\infty$

$$C_{el} = D(E_F) k_B^2 T \int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x + 1)^2} dx$$
$$= D(E_F) k_B^2 T \frac{\pi^2}{3}$$

From previous lecture: $D(E_F) = \frac{3N}{2E_F} = \frac{3N}{2k_B T_F}$

$$C_{el} = \frac{3N}{2k_B T_F} k_B^2 T \frac{\pi^2}{3}$$

$$C_{el} = \frac{\pi^2}{2} N k_B \left(\frac{T}{T_F} \right)$$

Experimental heat capacity of metals

At T below Debye's Θ and Fermi's T_F , the heat capacity of a metal may be written as

$$C = \gamma T + \beta T^3$$

where γ, β are constants characteristics of the material.

The observed values of γ and β are of the order of magnitude that are expected, but often they do not agree closely with the values calculated for free electrons.

It is common to express this discrepancy as a thermal effective mass

$$m_{th} = \frac{\delta(\text{obs})}{\delta(\text{pred})} m$$

These discrepancies come from three aspects

- e^- interact with the periodic potential of the crystal
- e^- interact with phonons
- e^- interact with each other

Electric conductivity

The momentum of an electron is related to its wavevector:

$$\vec{p} = \hbar \vec{k} = m \vec{v}$$

In an electric field \vec{E} and magnetic field \vec{B} , the force on the electron is given by Lorentz force

$$\vec{F} = -e(\vec{E} + \vec{v} \times \vec{B})$$

$$\vec{F} = m \vec{a} = \frac{d\vec{p}}{dt} = \hbar \frac{d\vec{k}}{dt} = m \frac{d\vec{v}}{dt}$$

In the absence of \vec{B} -field

$$\vec{F} = -e\vec{E} = \hbar \frac{d\vec{k}}{dt} \Rightarrow \vec{k}(t) - \vec{k}(0) = -\frac{e\vec{E}}{\hbar} t$$

If the \vec{E} -field is applied at $t=0$ to an e^- gas that fills the Fermi sphere centered at the origin of \vec{k} -space, then after time t it will

be centered at $\delta\vec{k} = -\frac{e\vec{E}}{\hbar}t$

The whole sphere is displaced because every e^- is displaced by the same $\delta\vec{k}$

Because of collisions of e^- with impurities, lattice imperfections and phonons, the displaced sphere reaches a steady state.

If the mean time between collision is τ (τ is also called the collision time), then the displacement is maintained at

$$\vec{k}_0 = -\frac{e\vec{E}\tau}{\hbar}$$

The drift velocity $\vec{v}_0 = \frac{\hbar\vec{k}_0}{m} = -\frac{e\vec{E}\tau}{m}$

If we are in a constant \vec{E} -field, and we have n electrons of charge $q = -e$ per unit volume the density of the current

$$\vec{J} = nq\vec{v}_0 = \frac{ne^2\tau}{m}\vec{E}$$

$$\boxed{\vec{J} = \frac{ne^2\tau}{m}\vec{E}} \quad \text{Ohm's law}$$

We can define $\sigma = \frac{ne^2\tau}{m}$: conductivity

$$\vec{J} = \sigma\vec{E}$$

We can also define $\rho = \frac{1}{\sigma} = \frac{m}{ne^2\tau}$: resistivity

Conductivity

- ⊕ we expect the charge transported is proportional to the density of charge n_e .
- ⊗ the factor e/m enters here because the acceleration in an \vec{E} -field is proportional to e and inverse prop. to m .
- ⊗ the longer τ , the more the charge can move