

Lecture 7

Continue calculating the ~~the~~ specific heat of the Fermi sea.

Internal electronic energy per volume:

$$u = 2 \int \frac{d\vec{k}}{(2\pi)^3} \epsilon_k n_F(\epsilon_k)$$

Since the integrand only depends on \vec{k} through the energy $\epsilon_k = \frac{\hbar^2 k^2}{2m}$, it is convenient to transform the 3D integral over \vec{k} into a 1D integral over energy.

$$d\vec{k} = k^2 dk \sin\theta d\theta d\phi \quad - \text{in spherical coordinates.}$$

Since ϵ_k doesn't ~~depend~~ depend on the direction of \vec{k} , we can integrate over θ and ϕ . The integral gives 4π .

$$\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi = 4\pi$$

$$d\vec{k} = 4\pi k^2 dk$$

Express this in terms of ϵ_k :

$$\epsilon_k = \frac{\hbar^2 k^2}{2m} \Rightarrow k = \sqrt{\frac{2m\epsilon_k}{\hbar^2}}$$

$$dk = \sqrt{\frac{m}{2\hbar^2}} \frac{d\varepsilon}{\sqrt{\varepsilon}} \quad - I \text{ will drop the subscript } k \text{ henceforth.}$$

$$4\pi k^2 dk = 4\pi \frac{2m\varepsilon}{\hbar^2} \sqrt{\frac{m}{2\hbar^2}} \frac{d\varepsilon}{\sqrt{\varepsilon}} =$$

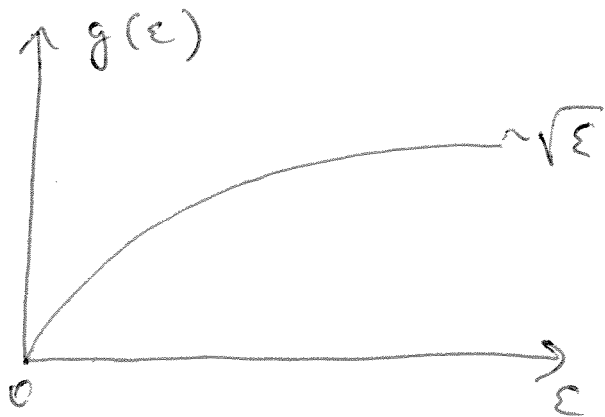
$$= \frac{4\pi m}{\hbar^2} \sqrt{\frac{2m\varepsilon}{\hbar^2}} d\varepsilon$$

Then \mathcal{U} can be written as:

$$\mathcal{U} = \int_0^\infty d\varepsilon \frac{m}{\hbar^2 \hbar^2} \sqrt{\frac{2m\varepsilon}{\hbar^2}} \varepsilon n_F(\varepsilon)$$

$$g(\varepsilon) = \frac{m}{\hbar^2 \hbar^2} \sqrt{\frac{2m\varepsilon}{\hbar^2}} \quad - \text{density of states.}$$

Physical meaning: $g(\varepsilon)d\varepsilon =$ number of states in the energy interval $(\varepsilon, \varepsilon+d\varepsilon)$ per unit volume.



free electron density of states

$$\mathcal{U} = \int_0^\infty d\varepsilon g(\varepsilon) \varepsilon n_F(\varepsilon)$$

$$C_v = \frac{\partial U}{\partial T} = \int_0^\infty d\varepsilon g(\varepsilon) \varepsilon \frac{\partial n_F(\varepsilon)}{\partial T}$$

Electron density:

$$\cancel{U} U = \int_0^\infty d\varepsilon g(\varepsilon) n_F(\varepsilon)$$

$$\frac{\partial U}{\partial T} = 0 = \int_0^\infty d\varepsilon g(\varepsilon) \frac{\partial n_F(\varepsilon)}{\partial T}$$

Multiply this by ε_F and subtract from the expression for C_v :

$$C_v = \int_0^\infty d\varepsilon g(\varepsilon) (\varepsilon - \varepsilon_F) \frac{\partial n_F(\varepsilon)}{\partial T}$$

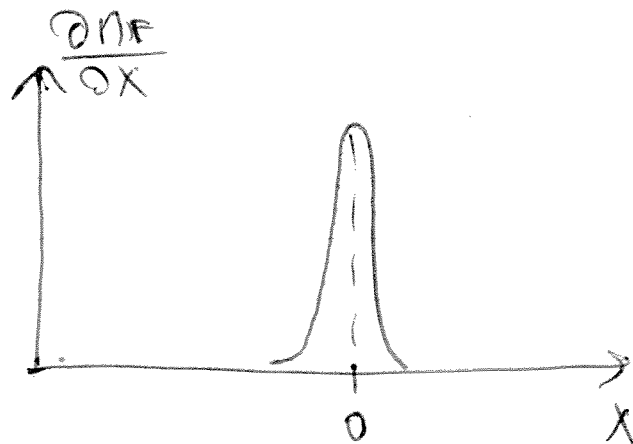
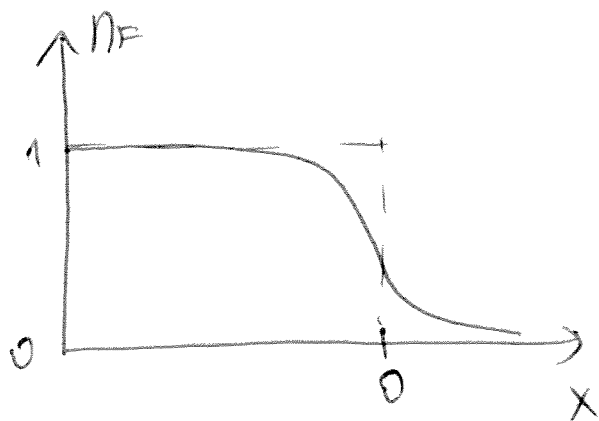
$$n_F(\varepsilon) = \frac{1}{e^{\frac{\varepsilon - \mu}{k_B T}} + 1} \approx \frac{1}{e^{\frac{\varepsilon - \varepsilon_F}{k_B T}} + 1}$$

$$\mu \approx \varepsilon_F$$

$$\text{let } x = \frac{\varepsilon - \varepsilon_F}{k_B T}$$

$$\frac{\partial n_F}{\partial T} = \frac{\partial n_F}{\partial x} \frac{\partial x}{\partial T} = - \frac{\partial n_F}{\partial x} \frac{\varepsilon - \varepsilon_F}{k_B T^2}$$

Plot $n_F(x)$ and $\frac{\partial n_F}{\partial x}$:



$\frac{\partial n_F}{\partial x}$ is very sharply peaked near $x=0$. ~~at~~
~~the origin~~

Then we can replace $g(\epsilon)$ in the expression for C_v by $g(\epsilon_F)$ ($x=0$ corresponds to $\epsilon = \epsilon_F$).

Then we obtain:

$$C_v = \int_{-\frac{\epsilon_F}{k_B T}}^{\infty} dx \, g(\epsilon_F) \cdot k_B T \cdot x \cdot k_B T \frac{x}{T} \left(-\frac{\partial n_F}{\partial x} \right) \approx \\ \approx g(\epsilon_F) k_B^2 T \int_{-\infty}^{\infty} dx \, x^2 \left(-\frac{\partial n_F}{\partial x} \right)$$

$$\frac{\partial n_F}{\partial x} = \frac{d}{dx} \frac{1}{e^x + 1} = - \frac{e^x}{(e^x + 1)^2}$$

$$C_v = g(\epsilon_F) k_B^2 T \int_{-\infty}^{\infty} dx \, x^2 \frac{e^x}{(e^x + 1)^2}$$

$\frac{\pi^2}{3}$

$$C_V = \frac{\pi^2}{3} g(E_F) k_B^2 T$$

$$g(E_F) = \frac{m}{\pi^2 \hbar^2} \sqrt{\frac{2mE_F}{\hbar^2}} = \frac{m k_F}{\pi^2 \hbar^2} = \frac{m k_F E_F}{\pi^2 \hbar^2 E_F}$$

$$k_F E_F = \frac{\hbar^2}{2m} k_F^3 = \frac{\hbar^2}{2m} 3\pi^2 n$$

$$g(E_F) = \frac{m}{\pi^2 \hbar^2 E_F} \cdot \frac{\hbar^2}{2m} \cdot 3\pi^2 n = \frac{3n}{2E_F}$$

$$C_V = \frac{\pi^2}{3} \cdot \frac{3n}{2E_F} k_B^2 T = \frac{\pi^2}{2} k_B n \frac{k_B T}{E_F}$$

$C_V \sim T$ agrees with experiment.

$$\gamma = \frac{\pi^2}{3} g(E_F) k_B^2$$

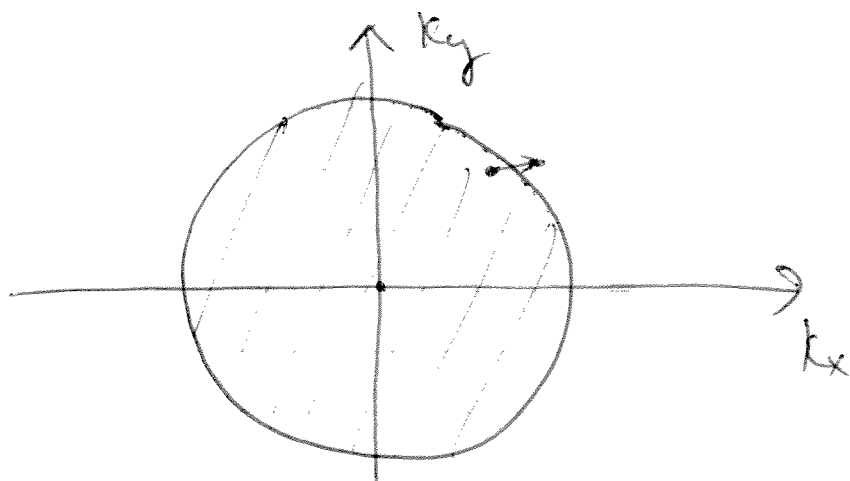
The value of γ agrees reasonably well for alkali metals (Li, Na) and for noble metals (Cu, Ag, Au)

But disagrees quite strongly (order of magnitude)

for metals like Fe, Mn, Bi, Sb.

Main problem of the free electron model: if we take this as a model of electrons in any solid, all solids will come out to be metals, which is definitely not true.

This model predicts that the ground state is the Fermi sea:



This is ~~classical~~ a model because electrons from inside the Fermi sea can always be excited to states outside \Rightarrow solid will absorb the energy of electromagnetic field of any frequency.

To do better we need to explicitly consider motion of electrons in the periodic crystal potential.

If we think about the motion of electrons in such potential classically, then it seems that ~~electrons~~ the periodic potential should severely restrict the motion of electrons: from this point of view the existence of metals with high conductivity is puzzling. All these problems are resolved by quantum mechanics.