Free electron gas

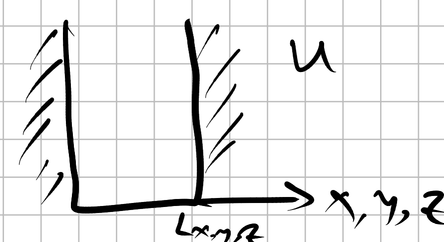
We will build a <u>super</u> <u>simplistic</u> solids model.

We will assume that all atoms freed their electrons and the electrons are free to move, moreover, we assume that electrons <u>do not interact</u>. But there are bounds which they cannot escape.

This is **Sommerfeld model.**

On a first glance it looks like the ideal gas model, but there is a QM twist: it is more like a particle in 3D square well, except there are many.

$$U(x,y,z) = \begin{cases} 0, & 0 < x,y,z < L \\ \infty, & \text{otherwise} \end{cases}$$



Since particles do not interact, we do separation of variables and split $\hat{H}$ to a bunch of the single particle Hamiltonians

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi \quad , \quad \psi(x,y,z) = X(x)Y(y)Z(z)$$

$$X(x) = \sqrt{\frac{2}{L_x}} \sin\left(\frac{\pi}{L_x} x\right)$$

$$Y(y) = \sqrt{\frac{2}{L_y}} \sin\left(\frac{\pi}{L_y} y\right)$$

$$Z(z) = \sqrt{\frac{2}{L_z}} \sin\left(\frac{\pi}{L_z} z\right)$$

$$\Rightarrow E_{n_x n_y n_z} = E_x + E_y + E_z = $$

$$= \frac{\hbar^2 \pi^2}{2m_f}\left[\left(\frac{n_x}{L_x}\right)^2 + \left(\frac{n_y}{L_y}\right)^2 + \left(\frac{n_z}{L_z}\right)^2\right]$$

$$n_x, n_y, n_z = 1, 2, 3 \ldots \infty$$

Suppose we have N particles.

If they were bosons they all would sit on the ground level and the total energy would be $E_{tot} = N \cdot E_{111}$

But we have electrons which are fermions so each energy level can be occupied only 2 times (with spin ↑ or ↓ electrons)

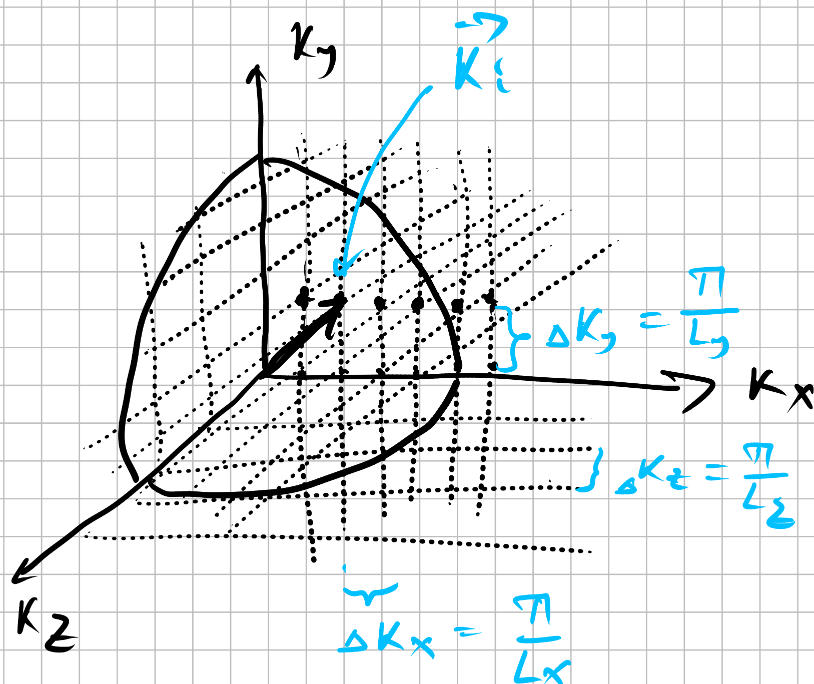
$$E_{tot} = 2 \sum_{\substack{n_x, n_y, n_z \\ 1\ \ 1\ \ 1 \\ 2\ \ 2\ \ 2 \\ 3\ \ 3\ \ 3 \\ \vdots\ \ \vdots\ \ \vdots}} E_{n_x n_y n_z} = 2 \cdot \frac{\hbar^2}{2 m_f} \cdot \underbrace{\sum \left[\underbrace{\left(\pi \frac{n_x}{L_x}\right)^2}_{=k_x^2} + \underbrace{\left(\pi \frac{n_y}{L_y}\right)^2}_{=k_y^2} + \underbrace{\left(\pi \frac{n_z}{L_z}\right)^2}_{=k_z^2}\right]}_{N \text{ terms}}$$

non repeating sets

mass of fermion

$$= 2 \frac{\hbar^2}{2 m_f} \sum_{i=1}^{N} \vec{k}_i^{\,2}$$

The hard part is to calculate $\sum_{i=1}^{N} \vec{K}_i^2$



$\vec{K}$ vector point to a node in the grid

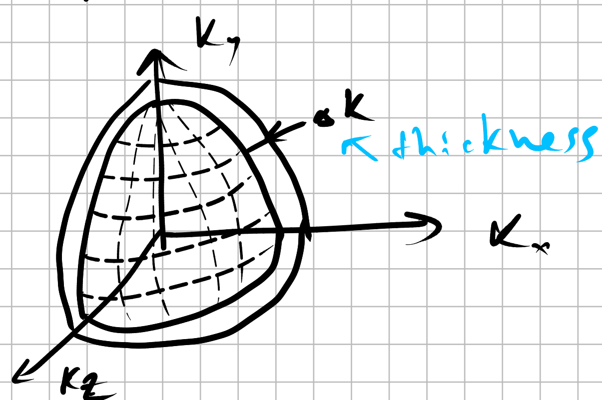
$$V_1 = \Delta K_x \cdot \Delta K_y \cdot \Delta K_z = \frac{\pi^3}{L_x L_y L_z} = \frac{\pi^3}{V}$$

unit volume in 'K' space

well volume

different units!

Now let's look at the $\sum \vec{K}_j$ in a sperical shell



shell volume

$$\sum_{\text{in shell}} \vec{K}_j = N_K K^2 \approx \frac{V_K}{V_1} K^2 = \frac{4\pi K^2 \Delta K}{8 \; V_1} K^2$$

Number of slots in the shell

all K are the same

N is huge $\Longrightarrow$ $V_1 << V_{shell}$, so we do not need to worry about edge effects

$$\Rightarrow \sum_{\text{in shell}} \vec{k}^2 = \frac{4\pi k^4}{8\, V_1}\Delta k = \frac{4\pi}{8\pi^3} V \cdot k^4 \Delta k \approx \frac{V}{2\pi^2} k^4\, dk$$

$$\Rightarrow \sum_{i=1}^{N} \vec{k}_i^{\,2} = \sum_{\#\text{shells}} \frac{V}{2\pi^2} k^4 \Delta k \approx \frac{V}{2\pi^2}\int_0^{k_{max}} k^4\, dk = \underbrace{\frac{V}{2\pi^2}\frac{k_{max}^5}{5}}$$

$$\boxed{k_{max} = k_F}$$

Fermi

$$\text{So} \quad E_{tot} = \frac{\hbar^2}{m_f}\sum_{i=1}^{N} k_i^2 = \frac{\hbar^2}{m_f}\frac{V}{2\pi^2}\frac{k_F^5}{5}$$

How to find k_F ?

Recall the volume of octant of a sphere contained $\frac{N}{2}$ nodes $\Rightarrow$ $\frac{N}{2} = \frac{1}{8}\frac{4\pi}{3}k_F^3 \frac{1}{V_1} = \frac{1}{2}\frac{\pi}{3}k_F^3 \cdot \frac{V}{\pi^3}$

each node occupied twice

$$\boxed{k_F^3 = 3\pi^2 \frac{N}{V} = 3\pi^2 \rho_f}$$

density of particles (fermions)

$$\Rightarrow \frac{\hbar^2}{2m_f}k_F^2 = \boxed{E_F = \frac{\hbar^2}{2m_f}(3\pi^2\rho_f)^{2/3}}$$

Fermi energy, or maximum energy of one particle

What about nucleus of atoms which gave up electrons? They could be fermions too..

Yes, But their mass $\frac{M_{nucleus}}{M_{electron}} > 1000 = \frac{m_{proton}}{m_e}$

so energy and pressure of them factor of 1000 smaller too

So far we neglected "classical" pressure of moving particles. When we can do so?

Energy per particle $\frac{E_{tot}}{N} \sim E_f < \frac{3}{2} k_B T \simeq k_B T$

$$E_1 = \frac{E_{tot}}{N} = \frac{\hbar^2}{m_f} \frac{V}{\pi^2} \frac{1}{10} \left(3\pi^2 \frac{N}{V}\right)^{5/3} \frac{1}{N} = \frac{\hbar^2}{\pi^2 10} \frac{(3\pi^2)^{5/3}}{m_f} \cdot \left(\frac{N}{V}\right)^{2/3}$$

$$N - ? \quad N_{el} = \frac{M_{total}}{m_{Atom}} \underbrace{\#\text{protons per atom}}_{m_A/m_{proton}} = \frac{M_{total}}{m_{proton}} \cdot \frac{1}{2}$$

#proton $\simeq$ #neutron

$$\frac{N}{V} = \frac{M_{total}}{V} \frac{1}{2} \frac{1}{m_{proton}} = \rho_m \cdot \frac{1}{2\, m_{proton}}$$

mass density

Let's take Carbon $\longrightarrow$ diamond density

$$\rho_m = 3.5 \cdot 10^3 \frac{kg}{m^3}$$

$$m_{proton} = 1.6 \cdot 10^{-27}\, kg \quad , \quad \hbar = 1.05 \cdot 10^{-34}\, J \cdot s$$

$$m_f = m_{electron} = 9 \cdot 10^{-31}\, kg$$

$$E_1 = \frac{\hbar^2 \, (3\pi^2)^{5/3}}{10 \cdot \pi^2} \cdot \frac{1}{m_f} \cdot \left(\frac{1}{2} \rho_m \frac{1}{m_{proton}} \right)^{2/3}$$

$$= 3.165 \cdot 10^{-68} \; \frac{1}{m_f} \left(\frac{1}{2} \rho_m \frac{1}{m_{proton}} \right)^{2/3}$$

$$= 3.165 \cdot 10^{-68} \cdot 1.8 \cdot 10^{50} = 3.7 \cdot 10^{-18}\, J$$

$$E_1 = k_B \cdot T_f \implies T_f = \frac{E_1}{k_B} = \frac{3.7 \cdot 10^{-18}}{1.38 \cdot 10^{-23}} =$$

$$\boxed{T_f = 2.7 \cdot 10^5\ K}$$

So in a typical solid classical contribution is negligible at Earth conditions

What about Pressure ?

$$\boxed{E_{tot} = \frac{\hbar^2}{m_f}\frac{V}{2\pi^2}\frac{1}{5}\left(3\pi^2\frac{N}{V}\right)^{5/3} = \frac{\hbar^2}{m_f}\frac{1}{10}\frac{1}{\pi^2}(3\pi^2 N)^{5/3}\cdot V^{-2/3}}$$

All this moving particle exert pressure on the sides of the well. How to find it?

Suppose we change volume by a tiny ΔV, it will change the E_{tot}:

$$\underbrace{\Delta E_{tot}}_{\text{change of internal energy}} = \frac{dE_{tot}}{dV}\cdot\Delta V = \underbrace{P(-\Delta V)}_{\text{Work done by outside pressure}}$$

assuming constant Pressure

Thermo 101

$$P_f = -\frac{dE}{dV} = +\frac{2}{3}\frac{\hbar^2(3\pi^2 N)^{5/3}}{10\pi^2 m_f}V^{-5/3}$$

$$\boxed{P_f = \frac{2}{3}\frac{E_{tot}}{V}}$$

So called degeneracy pressure