

Free electron gas

We will build a super simplistic solids model.

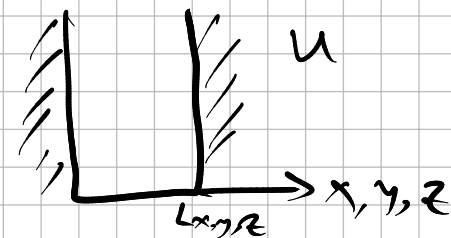
We will assume that all atoms freed their electrons and the electrons are free to move, moreover, we assume that electrons do not interact.

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}

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

to a bunch of the single particle Hamiltonians

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

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

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

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

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

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

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 \uparrow or \downarrow electrons)

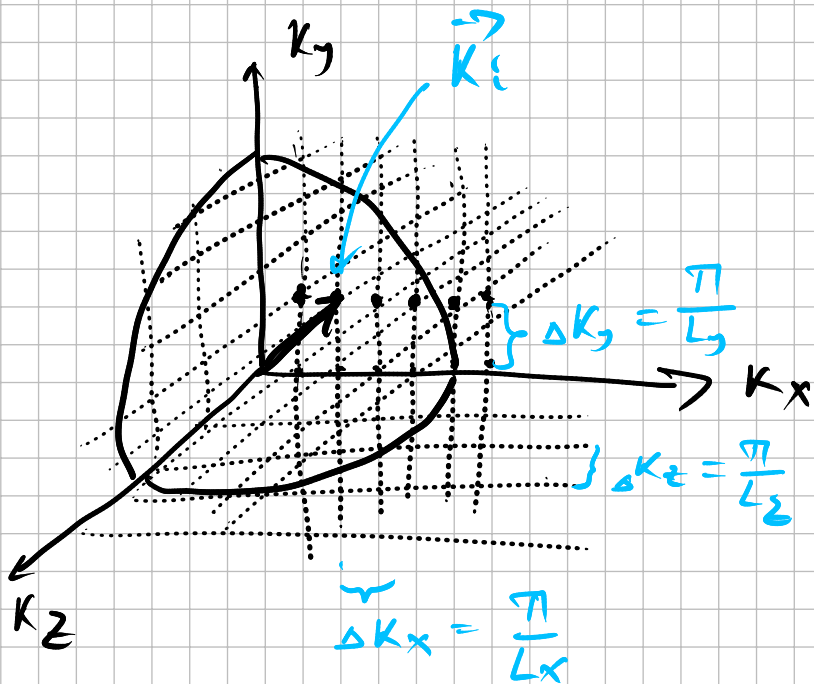
$$E_{tot} = 2 \sum_{n_x, n_y, n_z} E_{n_x, n_y, n_z} = 2 \cdot \frac{\hbar^2}{2m_f} \cdot \underbrace{\sum \left[\left(\frac{n_x}{L_x}\right)^2 + \left(\frac{n_y}{L_y}\right)^2 + \left(\frac{n_z}{L_z}\right)^2 \right]}_{N \text{ terms}}$$

$\left. \begin{array}{l} \vdots \\ \vdots \\ \vdots \\ \vdots \end{array} \right\} \text{non repeating sets}$

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

\nearrow mass of fermion

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



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

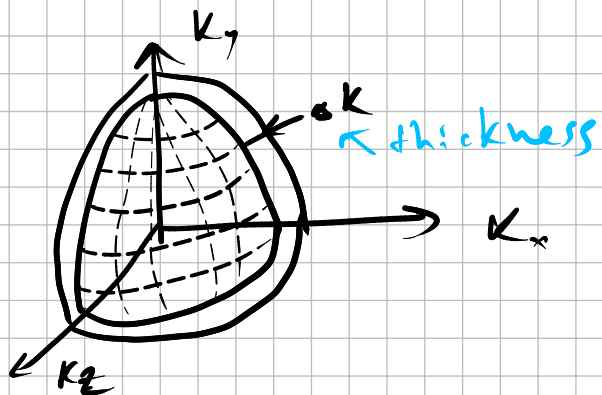
$$V_1 = \Delta k_x \cdot \Delta k_y \cdot \Delta k_z = \frac{\pi^3}{L_x L_y L_z} = \frac{\pi^3}{V}$$

unit volume in 'k' space

well volume

different units!

Now let's look at the $\sum \vec{k}_i$ in a spherical shell



$$\sum_{\text{in shell}} \vec{k}_i = N_k k^2 \approx \frac{V_k}{V_1} k^2 = \frac{4\pi k^2 \Delta k}{8} \frac{V_{\text{shell}}}{V_1} k^2$$

Number of slots in the shell

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

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

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

$k_{\max} = k_F$
 Fermi

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

How to find k_F ?

Recall the volume of octant of a sphere contained

$$\frac{N}{2} \text{ nodes} \Rightarrow \frac{N}{2} = \frac{1}{8} \frac{4\pi}{3} k_F^3 \frac{1}{V_1} \approx \frac{1}{2} \frac{\pi}{3} k_F^3 \cdot \frac{V}{\pi^3}$$

each node
occupied
twice

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

density of
particles
(fermions)

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

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 $\frac{M_{\text{nucleus}}}{M_{\text{electron}}} \rightarrow 1000 = \frac{m_{\text{proton}}}{m_e}$

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 $\frac{E_{\text{tot}}}{N} \sim E_f < \frac{3}{2} k_B T \approx k_B T$

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

$$N \sim ? \quad N_{\text{el}} = \frac{M_{\text{total}}}{M_{\text{Atom}}} \quad \begin{array}{l} \# \text{ protons} \\ \text{per atom} \\ \uparrow \\ m_A / m_{\text{proton}} \end{array} = \frac{M_{\text{total}}}{m_{\text{proton}}} \cdot \frac{1}{2}$$

#proton = #neutron

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

↑
mass density

Let's take Carbon \rightarrow diamond density
 $\rho_m = 3.5 \cdot 10^3 \frac{\text{kg}}{\text{m}^3}$

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

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

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

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

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

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

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

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

What about Pressure?

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

All this moving particles 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} :

$$\Delta E_{\text{tot}} = \frac{dE_{\text{tot}}}{dV} \cdot \Delta V = \underbrace{P(-\Delta V)}_{\substack{\text{Work done by outside} \\ \text{pressure}}} \quad \leftarrow \text{assuming constant Pressure}$$

change of internal energy Thermo 101

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

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

so called degeneracy pressure