Free electron gas

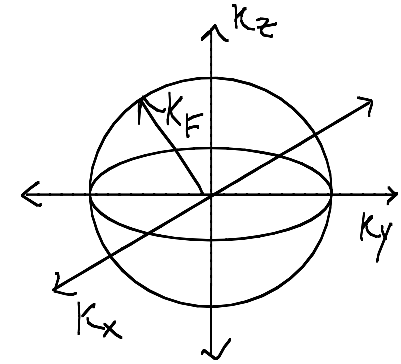
What if we have an even larger number of electrons, like in a metal or plasma? What is the ground state, consistent with the Pauli exclusion principle?

If the electrons are not confined by any potential, and we ignore electron-electron Coulomb interactions, our Hamiltonian is trivial:

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi \longrightarrow \psi \propto e^{i\vec{k}\cdot\vec{r}} \quad \left(|\vec{k}| = \frac{\sqrt{2mE}}{\hbar}\right)$$

Our states are therefore labeled by k_x, k_y, and k_z components of $\vec{k}$.

We can fill states from the lowest energy $(\vec{k}=\vec{0})$, until all electrons in the system are accounted for.



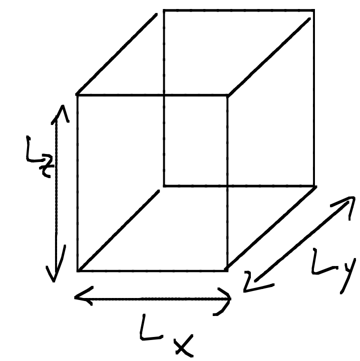
Since $E = \frac{\hbar^2}{2m}(k_x^2+k_y^2+k_z^2)$, the surface of the volume of filled states in $\vec{k}$-space is a "Fermi sphere", with volume $\Omega = \frac{4}{3}\pi k_F^3$. The radius k_F ("Fermi wavenumber") depends on the number of filled states and the volume each state excludes.

Density of States

Our free electron gas is not confined by any external potential, and so has infinite volume V and infinite total # of electrons N.

However, the electron density $n = \frac{N}{V}$ is fixed. Due to full translational symmetry, we can assert arbitrary periodicity.

For example, cut space into identical cubes: $\longrightarrow$



Now, apply periodic boundary conditions: $\Psi(\vec{r}) = \Psi(\vec{r} + L_x\hat{x}) = \Psi(\vec{r} + L_y\hat{y}) = \Psi(\vec{r} + L_z\hat{z})$

Using our planewave eigenfunctions, we have e.g. $e^{i\vec{k}\cdot\vec{r}} = e^{i\vec{k}\cdot(\vec{r}+L_x\hat{x})} = e^{i\vec{k}\cdot\vec{r}}e^{i\vec{k}\cdot L_x\hat{x}}$.

So, $\vec{k}\cdot L_x\hat{x} = k_x L_x = 2\pi \cdot$ integer, and spacing of states along k_x is $\Delta k_x = \frac{2\pi}{L_x}$.

In 3d $\vec{k}$ space, $\Delta^3 k = \frac{(2\pi)^3}{V} \leftarrow L_x L_y L_z$ per state labeled by k_x, k_y, k_z, and half as much when including spin (up/down) degeneracy.

For Fermi sphere w/ volume $\frac{4}{3}\pi k_F^3$, $N = \frac{\frac{4}{3}\pi k_F^3}{\underbrace{(2\pi)^3/2V}_{\text{spin}}} \longrightarrow n = \frac{k_F^3}{3\pi^2}$

Properties of a "typical" Fermi sphere

In a typical monovalent metal $n \sim 10^{23}\ cm^{-3}$

"Fermi wavenumber" $K_F = (3\pi^2 n)^{1/3} \sim 10^8\ cm^{-1}$

On the surface of the Fermi sphere,

"Fermi velocity" $V_F = \frac{\hbar K_F}{m} = \frac{6.6\times10^{-16}\ eV\cdot s \cdot 10^8\ cm^{-1}}{5\times10^5\ eV / 9\times10^{20}\ \frac{cm^2}{s^2}} \sim 10^8\ \frac{cm}{s}$

Compare to classical velocity @ RT: $K_BT \sim \frac{1}{2}mv^2 \rightarrow v \sim \sqrt{\frac{2K_BT}{m}} = c\sqrt{\frac{1/40\ eV}{5\times10^5 eV}} \sim 10^{-4}c \cong 10^6\frac{cm}{s}$

"Fermi energy" $E_F = \frac{\hbar^2 K_F^2}{2m} = \frac{(6.6\times10^{-16} eVs)^2 (10^8 cm^{-1})^2}{2\ 5\times10^5\ eV/c^2} \sim 1-10\ eV$

"Fermi Temperature" $T_F = E_F/K_B = \frac{10\ eV}{1\ eV/ 40/300K} \sim 10^5 K \rightarrow$ properties of ground state ($T=0$) are a very good approximation to RT ($T=300K$) behavior!

Total energy

Sum over energy contributions from every electron in Fermi sphere

$$E = 2 \sum_{|\vec{k}|<k_F} \frac{\hbar^2 k^2}{2m}$$

Spin degeneracy

Since $\Delta^3 k = \frac{(2\pi)^3}{V}$, $E = \frac{2 \cdot V}{(2\pi)^3} \sum_{|\vec{k}|<k_F} \frac{\hbar^2 k^2}{2m} \Delta^3 k \longrightarrow \frac{2V}{(2\pi)^3} \int_{\substack{\text{Fermi}\\ \text{sphere}}} \frac{\hbar^2 k^2}{2m} d^3k$

Energy is a function only of $|\vec{k}|$, so we have spherical symmetry:

$d^3k \to 4\pi k^2 dk$, so $E = \frac{2V}{(2\pi)^3} \int_0^{k_F} \frac{\hbar^2 k^2}{2m} 4\pi k^2 dk = \frac{V\hbar^2}{2\pi^2 m} \frac{k^5}{5} \Big|_0^{k_F} = \frac{\hbar^2 k_F^5}{10\pi^2 m} V.$

Then, Energy density $u = \frac{E}{V} = \frac{\hbar^2 k_F^5}{10\pi^2 m}$, and average energy per electron

$$\frac{u}{n} = \frac{\frac{\hbar^2 k_F^5}{10\pi^2 m}}{k_F^3/3\pi^2} = \frac{3}{10} \frac{\hbar^2 k_F^2}{m} = \frac{3}{5} E_F$$

Fermi Pressure

$$P = -\left.\frac{\partial E}{\partial V}\right|_N = -\frac{\partial}{\partial V}\left[\tfrac{3}{5}E_F N\right]\Big|_N = -\frac{3}{5}N\frac{\partial}{\partial V}\left[\frac{\hbar^2}{2m}\left(3\pi^2\frac{N}{V}\right)^{2/3}\right]\Big|_N$$

$$= -\frac{3}{5}N\frac{\hbar^2}{2m}\frac{\left(3\pi^2\frac{N}{V}\right)^{2/3}}{V}\left(-\tfrac{2}{3}\right) = \tfrac{2}{5}E_F n$$

Assuming $n \sim 10^{23}\,\text{cm}^{-3}$, $E_F \sim 10\,\text{eV}$, Then we have $P \sim 10^{24}\,\text{eV}/\text{cm}^3$. Convert to more useful units:

$$10^{24}\,\text{eV}/\text{cm}^3 \cdot \frac{1.6\times10^{-19}\,\text{J}}{\text{eV}}\;\frac{10^6\,\text{cm}^3}{\text{m}^3} \simeq 10^{11}\,\frac{\text{N}}{\text{m}^2} \sim 10^6\,\text{atm}. \quad \text{Huge!}$$

What are the physical consequences of such a large degeneracy pressure?

$$\text{"compressivity"} = -\frac{dV}{\frac{dp}{V}} \longrightarrow \text{"bulk modulus"}\quad B = \frac{1}{\text{compressivity}} = -V\frac{dp}{dV}$$

Since $P \propto V^{-5/3}$, $B = -V\left(-\frac{5}{3}\frac{P}{V}\right) = \tfrac{5}{3}P \sim \frac{2}{3}E_F n \sim 10^6\,\text{atm}.$

This confirms the empirically negligible compressibility of metals.