FREE — ELECTRON GAS

Arnold Sommerfeld worked out a simplified model for metals: neglect all interactions among electrons and nuclei, and imagine the metal as a quantum well full of wandering electrons, subject exclusively to Pauli's exclusion principle. Stimulated by the discussion about the ground state of atoms, obtained following Hund's rules, we ask ourselves: what is the ground state of a system composed by a large number of electrons, such as in a metal or plasma, that is consistent with Pauli's exclusion principle?

If we ignore all interactions, the wavefunction of an electron state is:

$$\psi \propto e^{i\vec{k}\cdot\vec{x}}$$: Schroedinger's equation is in fact trivial: $-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$

$$|\vec{k}| = \sqrt{2mE}/\hbar$$ (free particle!)

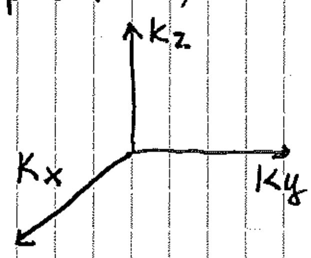
Our states are therefore labelled by k_x, k_y, k_z, the components of $\vec{k}$.
Let us imagine our free electrons are confined in a volume of dimension L_x, L_y, L_z. Boundary conditions force a constraint on $\vec{k}$:

$$k_x = \frac{\pi}{L_x} n_x \qquad k_y = \frac{\pi}{L_y} n_y \qquad k_z = \frac{\pi}{L_z} n_z$$

The energy of a state identified by $\vec{k}$ can be written:

$$E_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) = \frac{\hbar^2 k^2}{2m}$$

Let us move to a 3-d $\vec{k}$ space, i.e., let us picture three axes with k_x, k_y and k_z coordinates:



In this space, each point with coordinates $\left(\frac{n_x \pi}{L_x}, \frac{n_y \pi}{L_y}, \frac{n_z \pi}{L_z}\right)$ represent a distinct state. How far are distinct states? Multiples of π/L_x along the K_x axis, multiple of π/L_y along the K_y axis, multiples of π/L_z along the K_z axis.

In other words, each state occupies a volume $\pi^3/(L_x \cdot L_y \cdot L_z) = \frac{\pi^3}{V}$ in $\vec{K}$ space. When I include spin, I notice that each π^3/V volume can contain 2 states (one with spin up, one with spin down), so the volume occupied by an electron state is: $\pi^3/2V$, where V is the volume in 3-d $\vec{r}$ space occupied by my gas of free electrons.

Suppose I have n electrons in my system. They will occupy the states with lowest $\vec{K}$, one electron per state, and fill up an octant of radius K_F such that:

$$\frac{1}{8}\left(\frac{4}{3}\pi K_F^3\right) = n \cdot \frac{\pi^3}{2V}$$

- $\frac{1}{8}$: $K_x, K_y, K_z > 0$: states fill one octant of the sphere
- $\frac{4}{3}\pi K_F^3$: spherical volume in K-space occupied by electron states
- n: number of electrons
- $\frac{\pi^3}{2V}$ → volume in K-space occupied by an electron state (it scales with $1/V$, V = actual volume of metal in 3d space

$$K_F = \underline{\text{Fermi wavenumber}} = (3\rho\pi^2)^{1/3}$$

where $\rho = n/V$ = density of free electrons in metal model

$$E_F = \frac{\hbar^2 K_F^2}{2m} = \frac{\hbar^2}{2m}(3\rho\pi^2)^{2/3} \quad \underline{\text{Fermi energy}}$$

The Fermi surface is the boundary between occupied and unoccupied states. In the $\vec{K}$ space, it is the sphere with radius K_F.

Some typical values: $\rho \sim 10^{23}\ cm^{-3}$

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

v_F = Fermi velocity = $\frac{\hbar K_F}{m} \sim \frac{6.6\cdot 10^{-16}\ eV\cdot s\cdot 10^8\ cm^{-1}}{0.5\cdot 10^6 eV/(3\cdot 10^{10} cm/s)^2} \sim 10^8$ cm/s

compare to classical velocity at 300K:

$$\frac{1}{2} m v^2 \sim K_B\cdot T \Rightarrow v \sim \sqrt{\frac{2K_BT}{m}} \sim c\cdot\left(\frac{0.025\,eV}{0.5\cdot 10^6 eV}\right)^{1/2} \sim 10^{-4} c \sim 10^6\ cm/s$$

E_F = Fermi energy = $\frac{\hbar^2 K_F^2}{2m} \sim \frac{(6.6\cdot 10^{-16} eVs)^2\cdot 10^{16}\ cm^{-2}}{2\cdot 0.5\cdot 10^6 eV/(3\cdot 10^{10} cm/s)^2} \sim 1\text{-}10\,eV$

T_F = Fermi temperature = $\frac{E_F}{K_B} \sim \frac{10\,eV}{1/40\,eV/300K} \sim 10^5\ K$ ← very hot! In practice, properties of ground state ($T\sim 0$) are very good approximation of room-temperature behavior ($T\sim 300K$)

How do I find the total energy of a free electron gas?

Each electron in Fermi sphere contributes to energy:

$$E_{TOTAL} = 2 \sum_{electrons} \frac{\hbar^2 K^2}{2m} =$$

(2 ↖ spin degeneracy)

$$= 2\cdot\frac{V}{\pi^3}\sum \frac{\hbar^2 K^2}{2m}\Delta^3 K \longrightarrow \frac{2V}{\pi^3}\int_{\text{octant of radius } K_F} \frac{\hbar^2 K^2}{2m} d^3\vec{K} = \frac{V\hbar^2}{\pi^3 m}\int_0^{\pi/2} d\phi \int_0^1 d\cos\theta \int_0^{K_F} K^4 dK$$

$$E_{TOTAL} = \frac{\hbar^2 V K_F^5}{10\pi^2 m} = \frac{\hbar^2 (3\pi n)^{5/3}}{10\pi^2 m} V^{-2/3}$$

[$K_F \propto \rho^{1/3} = (n/V)^{1/3}$ density of free electrons]