Week 3: Free Electron Model of a metal

- Box ($V = L_x\, L_y\, L_z$) containing N electrons.

  $\hat{H} = -\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2})$, states $\Phi(x, y, z) = Ae^{ik_x x}\, e^{ik_y y}\, e^{ik_z z} = Ae^{i\mathbf{k}\cdot\mathbf{r}}$.

- Periodic boundary conditions (PBCs): $\Phi(x, y, z) = \Phi(x + L_x, y, z)$ etc.

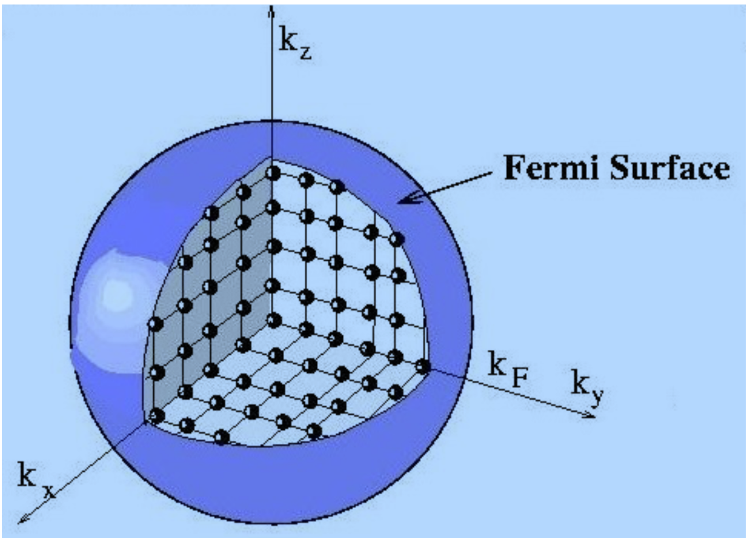
  Let right-going wave out of box at one face and at same time enter at opposite face. PBCs suited for 'large' systems where the properties far from boundaries are wanted. (Video games use them $\cdots$).

- PBCs give $e^{ik_x L_x} = 1 = e^{ik_y L_y} = e^{ik_z L_z}$ and $\mathbf{k} = 2\pi(\frac{n_x}{L_x}, \frac{n_y}{L_y}, \frac{n_z}{L_z})$ with n_x, n_y and n_z integers. In $\mathbf{k}$-space, states picked out on a regular mesh of points, with volume elements $\frac{2\pi}{L_x} \cdot \frac{2\pi}{L_y} \cdot \frac{2\pi}{L_z} = \frac{(2\pi)^3}{V}$.

- For system of N electrons in the box, each state can be occupied by 2 electrons (2 spin values, $\uparrow$ and $\downarrow$).

The Fermi Energy, E_F, and Fermi Surface

- Fill up the states with the N electrons. In *reciprocal* wavevector **k**-space, fill a sphere up to a radius k_F, the Fermi wave number. The surface of the sphere defines the Fermi surface for the model of a metal.



- $N = 2(\frac{4\pi k_F^3}{3})/(\frac{(2\pi)^3}{V}) = \frac{Vk_F^3}{3\pi^2}$.

  2 for spin $\times$ volume of sphere in k-space /volume per state.

- So the Fermi wave number $k_F = (3\pi^2\rho)^{\frac{1}{3}}$ where $\rho = \frac{N}{V}$, the electron density and the magnitude of the Fermi velocity $v_F = \frac{\hbar k_F}{m}$.

- The Fermi energy $E_F = \frac{\hbar^2}{2m}k_F^2 = \frac{\hbar^2}{2m}(3\pi^2\rho)^{\frac{2}{3}}$ also in terms of the electron density and $N = \frac{V}{3\pi^2}(\frac{2mE_F}{\hbar^2})^{\frac{3}{2}}$.

- For Li and Al, with ρ of 4.7 10^{28} and 18.1 10^{28} valence electrons per m^3 respectively, the Fermi energies are estimated to be 4.74 eV and 11.7 eV.

  For a neutron star with mass density of 7.0 10^{17} kg-m^{-3} find its $E_F \cdots$

- $$
\begin{aligned}
E_F &= \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \\
&\approx \frac{(1.05\times10^{-34})^2}{2\times1.67\times10^{-27}}\left(30\times\frac{7.0\times10^{17}}{1.67\times10^{-27}}\right)^{2/3} \\
&\approx 1.8\times10^{-11}\text{J}\approx 110\ \text{MeV}
\end{aligned}
$$

The Density of States $n(E)$ and calculating properties.

- Below E_F, $E < E_F$, $N(E)$ of the N electrons fill up the states, i.e. $N(E) = \frac{V}{3\pi^2}(\frac{2mE}{\hbar^2})^{\frac{3}{2}}$.

- So between two close energies $E + \Delta E$ and E, can count the number of states and find how closely packed the states are. The limit of $\frac{(N(E+\Delta E)-N(E))}{\Delta E}$ for vanishing small ΔE (large system and continuum of states) gives the density of states $n(E)$.

  (*Note - in Thermal Physics $g(E)$ is used to define it*).

- $n(E) = \frac{V}{2\pi^2}(\frac{2m}{\hbar^2})^{\frac{3}{2}}\, E^{\frac{1}{2}}$.

- Use it to calculate stuff, e.g. the total energy of the N electron system.

  $E_{tot} = 2\sum_{n=1}^{\frac{N}{2}} E_n = \int_0^{E_F} E\, n(E) dE.$

  This leads to $E_{tot} = \frac{3}{5}N\, E_F = \frac{3}{5}N\frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{\frac{2}{3}}$. The average energy per electron is $E_{tot}/N = \frac{3}{5}E_F$

- Find expressions for the pressure $P = -\frac{\partial E_{tot}}{\partial V}$ and bulk modulus $B = -V\frac{\partial P}{\partial V}\cdots$.

- N is fixed so get $P = \frac{2}{5} N \frac{\hbar^2}{2m} \left(3\pi^2 N\right)^{\frac{2}{3}} V^{-\frac{5}{3}} = \frac{2NE_F}{5V}$ and then $B = \frac{2NE_F}{3V}$

Temperature effects and magnetic fields

- At $T \neq 0$K, involve the Fermi-Dirac distribution (see Thermal Physics). $N = \int_0^\infty f(E,\mu,T)\, n(E) dE$ where μ is the chemical potential ($= E_F$ at $T = 0$K).

- The total energy $E_{tot}(T) = \int_0^\infty f(E,\mu,T)\, E\, n(E) dE$ and $(E_{tot}(T) - E_{tot}(0)) \propto T^2$ so that the specific heat $C_v = \frac{dE_{tot}}{dT} \propto T$, a signature property of a metal.

- In a magnetic field, $-B\hat{\mu}_s$ is added to Hamiltonian. $E_\uparrow = \frac{\hbar^2 k^2}{2m} + \mu_B B$, $E_\downarrow = \frac{\hbar^2 k^2}{2m} - \mu_B B$. Induced magnetisation $M = \mu_B (N_\downarrow - N_\uparrow) \approx \mu_B^2 n(E_F)\, B$ so that susceptibility $\frac{dM}{dB} = \mu_B^2 n(E_F)$.

Probability Current Density in QM

- Conservation: $\boldsymbol{\nabla} \cdot \mathbf{j} = -\frac{\partial \rho}{\partial t}$. Analogy with fluid flow, **j** is a probability current density (NB vector quantity). (In 1-D, $\frac{\partial j}{\partial x} = -\frac{\partial \rho}{\partial t}$).

- Using $\rho = \psi^\star(x,y,z,t)\, \psi(x,y,z,t)$ and the Schrodinger equation, can find an expression for $\frac{\partial \rho}{\partial t} = \psi^* \frac{\partial \psi}{\partial t} + \frac{\partial \psi^*}{\partial t} \psi$ which can be cast into a form $-\boldsymbol{\nabla} \cdot \boldsymbol{j}$ so that the corresponding current density can be identified. It turns out to be $\boldsymbol{j} = \frac{\hbar}{2im} \left(\psi^* \boldsymbol{\nabla} \psi - \psi \boldsymbol{\nabla} \psi^*\right)$. For $\psi = Ae^{i(\mathbf{k}\cdot\mathbf{r} - Et/\hbar)}$, $\boldsymbol{j} = \frac{\hbar\, \mathbf{k}}{m} A^* A$, i.e. velocity times density.