5.3 Solids

In solid state, a few of the loosely bound e^-s (<u>valence e^-'s</u>) are free to roam around.

We will look at <u>Sommerfeld's</u> <u>approach</u> to electron gas theory:

1.) Ignore all forces (except the confining boundaries)

2.) Treat the wandering electrons as "free" particle in a box
3-dim analog to an infinitely deep square well

Pauli Exclusion Principle accounts for the "solidity" of objects

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Free Electron Gas:

1.) Assume a rectangular solid with dimensions l_x, l_y, l_z

2.) Assume $V_{ee} \cong 0$ and the only force the electrons experience are the impenetrable walls

$$V(x,y,z) = \begin{cases} 0 & \text{for } 0 < x < l_x \quad 0 < y < l_y \quad 0 < z < l_z \\ \infty & \text{otherwise} \end{cases}$$

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

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} = E_x X \qquad -\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} = E_y Y \qquad -\frac{\hbar^2}{2m}\frac{d^2Z}{dz^2} = E_z Z$$

where $E = E_x + E_y + E_z$ $\quad k_x = \frac{\sqrt{2mE_x}}{\hbar} \quad k_y = \frac{\sqrt{2mE_y}}{\hbar} \quad k_z = \frac{\sqrt{2mE_z}}{\hbar}$

<u>Boundary</u> <u>Conditions:</u> $X(x) = A_x \sin k_x x \qquad Y(y) = A_y \sin k_y y \qquad Z(z) = A_z \sin k_z z$

and $k_x l_x = n_x\pi \qquad k_y l_y = n_y \pi \qquad k_z l_z = n_z \pi \qquad n = \text{pos. integer}$

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In general $\psi(x,y,z) = \sqrt{\dfrac{8}{l_x l_y l_z}} \sin\left(\dfrac{n_x \pi}{l_x} x\right) \sin\left(\dfrac{n_y \pi}{l_y} y\right) \sin\left(\dfrac{n_z \pi}{l_z} z\right)$

And the allowed energies are:

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right) = \frac{\hbar^2 k^2}{2m}$$

where k = magnitude of the wave vector $\vec{k} = k_x \hat{i} + k_y \hat{j} + k_z \hat{k}$

Each cell in k-space has nodes (or intersection points) every

$$\frac{\pi}{l_x}, \frac{2\pi}{l_x}, \frac{3\pi}{l_x} \dots \quad \frac{\pi}{l_y}, \frac{2\pi}{l_y}, \frac{3\pi}{l_y} \dots \quad \frac{\pi}{l_z}, \frac{2\pi}{l_z}, \frac{3\pi}{l_z}$$

where each node represents a distinct (one particle) stationary state. Or there is one state for every "block" bounded by the intersection points.

The volume of a block in k-space $= \dfrac{\pi^3}{l_x l_y l_z} = \dfrac{\pi^3}{V}$

For example, let's say we have <u>N atoms</u> ~ Avagadro's number and q electrons for each atom ~ 1-2

If electrons were distinguishable particles or bosons $\longrightarrow \psi_{111}$ (g.s.)

But electrons are <u>fermions</u> subject to the Pauli exclusion principle.

So, only 2 electrons can occupy a state in k space.

As more electron occupy the allowed quantum states in k-space, they fill on octant of a sphere whose radius is k_F, the Fermi radius.

Each pair of electrons $(\uparrow\downarrow)$ requires a volume of $\frac{\pi^3}{V}$ in k-space.

N_A $\quad$ 1-2 e^-s

So, the volume of k-space (one octant) occupied by Nq electrons is:

size of a single cell in k-space

$$\frac{1}{8}\left(\frac{4}{3}\pi k_F^3\right) = \frac{Nq}{2}\left(\frac{\pi^3}{V}\right)$$

$2e^-$ in a state

Define $\rho \equiv \frac{Nq}{V}$ = free electron density = $\frac{\text{\# of free electrons}}{\text{unit volume}}$

Then: $\frac{1}{6}\pi k_F^3 = \frac{1}{2}\rho\pi^3$ $\quad$ or $\quad$ $\boxed{k_F = \left(3\rho\pi^2\right)^{1/3}}$

The boundary separating occupied and unoccupied state in k-space is called the <u>Fermi surface</u>. The corresponding energy for states at the surface is:

$$E_F = \frac{\hbar^2}{2m}\left(3\rho\pi^2\right)^{2/3}$$

What is the total energy of the electron gas?

A shell of thickness dk contains a volume in k-space $= \frac{1}{8}\left(4\pi k^2\right) dk$

# of electrons in the shell $\rightarrow 2 \dfrac{V(\text{k-space})}{V(\text{cell})} = \dfrac{2\left(\frac{1}{2}\pi k^2 dk\right)}{(\pi^3/V)}$

# of electrons in the shell $\rightarrow \dfrac{V k^2 dk}{\pi^2}$

Energy in the shell of thickness dk is: $dE = \left(\dfrac{\hbar^2 k^2}{2m}\right)\left(\dfrac{V k^2}{\pi^2} dk\right)$

$$E_{TOT} = \int_0^{k_F} dE = \frac{\hbar^2 V}{2\pi^2 m} \int_0^{k_F} k^4 \, dk = \frac{\hbar^2 V}{10\pi^2 m} k_F^5$$

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

$$E_{TOT} \xleftrightarrow{\text{analogous}} U \text{ (internal energy in thermodynamics)}$$

The "change in energy" if the box expands by an amount dV, the total energy decreases by:

$$dE_{TOT} = -\frac{2}{3} \frac{\hbar^2}{10\pi^2 m} (3\pi^2 N_q)^{5/3} V^{-5/3} dV$$

$$\boxed{dE_{TOT} = -\frac{2}{3} E_{TOT} \frac{dV}{V}}$$

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Recall from thermodynamics that $đQ = dU + đW$

In our case: $đQ = 0$ So, $\underset{\text{our } dE_{TOT}}{dU} = -đW = -\underset{\text{pressure}}{p}\, dV$

So, $-\frac{2}{3} E_{TOT} \frac{dV}{V} = -p\, dV$

So, $\boxed{p = \frac{2}{3} \frac{E_{TOT}}{V}} = \frac{2}{3}\left(\frac{\hbar^2 V k_F^5}{10\pi^2 m}\right)\frac{1}{V}$

$$p = \frac{2}{3}\left(\frac{\hbar^2}{10\pi^2 m}\right)\left(3\pi^2 \rho\right)^{5/3} = \frac{(3\pi^2)^{2/3}\hbar^2}{5m}\rho^{5/3}$$

$\boxed{p = \frac{(3\pi^2)^{2/3}}{5m}\hbar^2 \rho^{5/3}}$ is the degeneracy pressure.