LECTURE #16

FREE ELECTRON THEORY

ASSUME THAT THE ELECTRONS IN A SOLID EXPERIENCE NO FORCES EXCEPT AT THE IMPENETRABLE WALLS:

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

THE ALLOWED ENERGIES OF A PARTICLE IN A 3-D BOX ARE:

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

WHERE k IS THE MAGNITUDE OF THE WAVE VECTOR:

$$\vec{k} = (k_x, k_y, k_z)$$

$$k_{x,y,z} = \frac{\pi n_{x,y,z}}{l_{x,y,z}}, \quad n_{x,y,z} = 1, 2, \ldots$$

IMAGINE A 3-D SPACE WITH AXES k_x, k_y, k_z ("k-SPACE") WITH PLANES DRAWN IN AT $k_x = \frac{\pi}{l_x}, \frac{2\pi}{l_x}, \frac{3\pi}{l_x}, \ldots$, $k_y = \frac{\pi}{l_y}, \frac{2\pi}{l_y}, \frac{3\pi}{l_y}, \ldots$, AND $k_z = \frac{\pi}{l_z}, \frac{2\pi}{l_z}, \frac{3\pi}{l_z}, \ldots$

$\Rightarrow$ EACH INTERSECTION REPRESENTS A DISTINCT STATIONARY STATE; EACH BLOCK IN THE GRID (AND, HENCE, EACH STATE) OCCUPIES A k-SPACE VOLUME:

$$\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V} \leftarrow \text{REAL SPACE VOLUME}$$

AT $T = 0K$, BOSONS OR DISTINGUISHABLE PARTICLES WOULD SETTLE TO THE GROUND STATE ψ_{111}.

HOWEVER, ELECTRONS ARE FERMIONS THAT OBEY THE PAULI EXCLUSION PRINCIPLE. HENCE, ONLY TWO (BECAUSE OF SPIN) CAN OCCUPY EACH STATE.

$\Rightarrow$ N ELECTRONS WILL FILL UP ONE OCTANT OF A SPHERE IN K-SPACE WHOSE RADIUS K_F IS DETERMINED BY THE FACT THAT EACH PAIR OF ELECTRONS REQUIRES A VOLUME π^3/V

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

$$\therefore K_F = (3\pi^2 n)^{1/3}$$

WHERE $n = \frac{N}{V}$ = # OF ELECTRONS PER UNIT VOLUME

THE BOUNDARY BETWEEN OCCUPIED AND UNOCCUPIED STATES IN K-SPACE AT $T=0K$ IS CALLED THE FERMI SURFACE.

THE CORRESPONDING ENERGY IS THE FERMI ENERGY:

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$$

HOW MANY e^- EXIST BETWEEN K AND $K + dK$?

TWO APPROACHES:

(1) MULTIPLY THE SURFACE AREA BY dk AND DIVIDE BY THE K-SPACE VOLUME PER STATE:

$$dN = \frac{\frac{1}{8}(4\pi k^2)\,dk}{\pi^3/2V} = \frac{V}{\pi^2} k^2 dk$$

$$\therefore \quad dn = \frac{k^2}{\pi^2} dk$$

(2) DETERMINE THE TOTAL # OF STATES AS A FUNCTION OF k AND DIFFERENTIATE.

FOR EXAMPLE, FOR A SPHERICAL FERMI SURFACE, WE SHOWED THAT $k = (3\pi^2 n)^{1/3}$

$$\Downarrow$$

$$n = \frac{k^3}{3\pi^2}$$

$$\therefore \quad dn = \frac{k^2}{\pi^2} dk \qquad \text{(CONSISTENT WITH APPROACH \#1)}$$

SINCE $E = \frac{\hbar^2 k^2}{2m}$, $dE = \frac{\hbar^2 k}{m} dk$,

$$dn = \frac{1}{\pi^2} \frac{2mE}{\hbar^2} \frac{m}{\hbar^2 k} dE$$

$$= \frac{1}{\pi^2} \frac{2m^2 E}{\hbar^4} \frac{\hbar}{\sqrt{2mE}} dE = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

$$\therefore \quad \boxed{g(E) = \frac{dn}{dE} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}} \qquad \text{"DENSITY OF STATES"}$$

NOTE: $E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$

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

$$\therefore\ g(E_F) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{E_F^{3/2}}{E_F}$$

$$= \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(\frac{\hbar^2}{2m}\right)^{3/2}\frac{3\pi^2 n}{E_F} = \frac{3}{2}\frac{n}{E_F}$$

$$\therefore\ \boxed{g(E_F) = \frac{3}{2}\frac{n}{E_F}}$$

WHAT IS THE TOTAL ENERGY OF THE FREE ELECTRON GAS?

$$dn = \frac{k^2}{\pi^2}dk \Rightarrow dN = \frac{V}{\pi^2}k^2 dk$$

EACH OF THE ELECTRONS IN THE SHELL BETWEEN k AND $k+dk$ CARRIES AN ENERGY $\hbar^2 k^2/2m$.

$\therefore$ THE ENERGY OF EACH SHELL IS: $dE = \frac{\hbar^2 k^2}{2m}\frac{V}{\pi^2}k^2 dk$

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

$$= \frac{\hbar^2 (3\pi^2 N)^{5/3}}{10\pi^2 m} V^{-2/3}$$

THIS QUANTUM MECHANICAL ENERGY IS ANALOGOUS TO THE INTERNAL KINETIC ENERGY OF A GAS. IN PARTICULAR, IT EXERTS A PRESSURE ON THE WALLS, FOR IF THE SOLID EXPANDS BY AN AMOUNT dV, THE TOTAL ENERGY DECREASES:

$$dE_{TOTAL} = -\frac{2}{3}\frac{\hbar^2(3\pi^2 N)^{5/3}}{10\pi^2 m} V^{-5/3}\, dV = -\frac{2}{3} E_{TOTAL}\frac{dV}{V}$$

WHICH MANIFESTS ITSELF AS WORK DONE ON THE OUTSIDE ($dW = PdV$) BY THE QUANTUM PRESSURE:

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

THIS PRESSURE PARTIALLY EXPLAINS WHY A COLD SOLID OBJECT DOESN'T SIMPLY COLLAPSE. THERE IS A STABILIZING INTERNAL PRESSURE THAT HAS NOTHING TO DO WITH $e^- - e^-$ REPULSION, NUCLEAR REPULSION, OR THERMAL MOTION BUT IS STRICTLY QUANTUM MECHANICAL RESULTING FROM THE PAULI EXCLUSION PRINCIPLE FOR FERMIONS!
(a.k.a., DEGENERACY PRESSURE OR EXCLUSION PRESSURE)

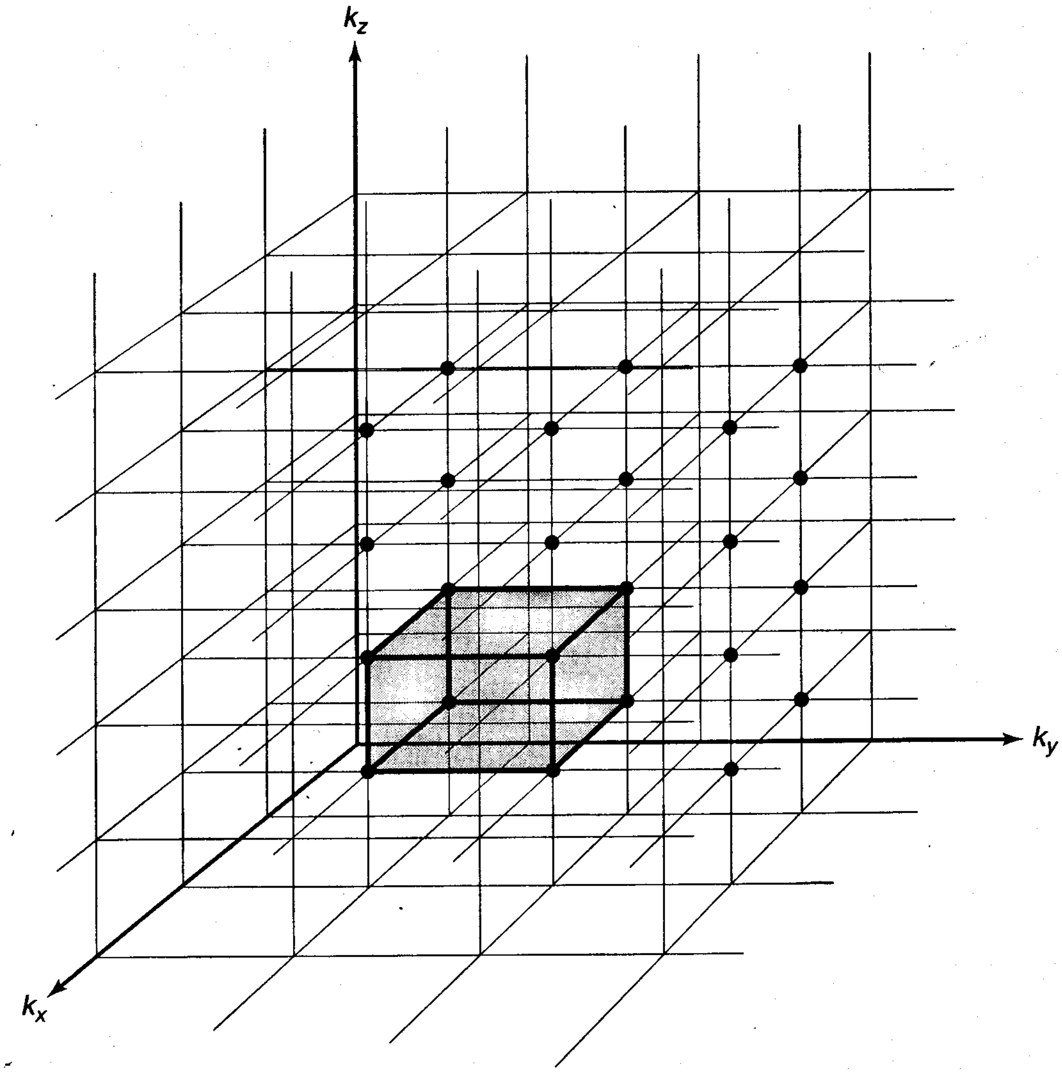

Figure 5.3: Free electron gas. Each intersection on the grid represents an allowed energy. Shading indicates one block; there is one state for every block.