6.730 Physics for Solid State Applications

Recitation 1: Free Electron Gas and Density of States

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Quantum Free Electron Gas

Crystal as Infinite Well Potential

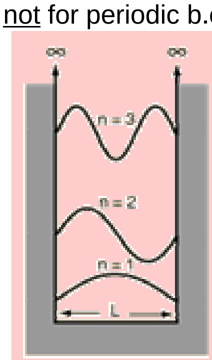
Electron confined in crystal of size *L* on a side
- no interaction with nuclei
- single particle approximation
- periodic boundary conditions

$$-\frac{\hbar^2\nabla^2}{2m}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{\mathrm{V}}}\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}$$

$$E(\mathbf{k}) = \frac{\hbar^2}{2\mathrm{m}}|\mathbf{k}|^2 = \frac{\hbar^2}{2\mathrm{m}}[\mathrm{k}_x^2 + \mathrm{k}_y^2 + \mathrm{k}_z^2]$$

<u>not</u> for periodic b.c.



(hyperphysics.phy-astr.gsu.edu)

Quantum Free Electron Gas

Periodic Boundary Conditions

$$\psi(x+L,y,z) = \psi(x,y,z)$$

$$\psi(x,y+L,z) = \psi(x,y,z)$$

$$\psi(x,y,z+L) = \psi(x,y,z)$$

$$\psi(x+L,y,z) = \frac{1}{\sqrt{V}} e^{ik_x(x+L)} e^{ik_y y} e^{ik_z z} = e^{ik_x L} \frac{1}{\sqrt{V}} e^{ik_x x} e^{ik_y y} e^{ik_z z}$$

$$= e^{ik_x L} \psi(x,y,z)$$

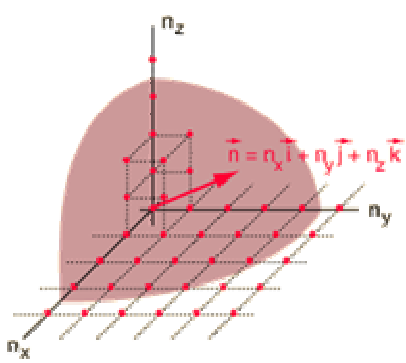
so that $k_x = \frac{2\pi}{L} n_x$, $k_y = \frac{2\pi}{L} n_y$, and $k_z = \frac{2\pi}{L} n_z$

and n_x, n_y, n_z are integers $0, \pm 1, \pm 2, \pm 3 \ldots$

$$\boxed{E(\mathrm{k}) = \mathbf{E}_{\mathbf{n_x,n_y,n_z}} = \frac{\hbar^2}{2\mathbf{m}} \left(\frac{2\pi}{\mathbf{L}}\right)^2 [\mathbf{n_x^2 + n_y^2 + n_z^2}]}$$

Limit for Large Crystals

$$E(\mathrm{k}) = \mathbf{E}_{\mathbf{n_x,n_y,n_z}} = \frac{\hbar^2}{2\mathbf{m}} \left(\frac{2\pi}{\mathbf{L}}\right)^2 [\mathbf{n_x^2 + n_y^2 + n_z^2}]$$



States fill up the lowest energies first, with two electrons (spin up and spin down) per energy level. The highest energy at zero temperature is denoted as E_{F0} and the highest k vector as k_F.

$$N = \sum_{k<k_F} 2 \qquad \text{and} \qquad E_{\text{total}} = \sum_{k<k_F} 2\frac{\hbar^2 k^2}{2m}$$

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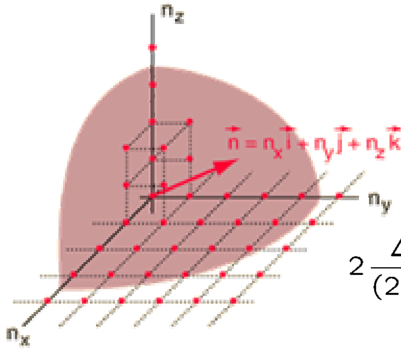


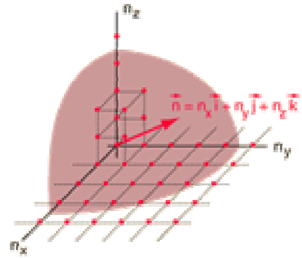
For large crystals we can use a macro-microvolume to do an integration rather than a sum.

$$2\,\frac{\Delta k_x}{(2\pi/L)}\frac{\Delta k_y}{(2\pi/L)}\frac{\Delta k_z}{(2\pi/L)} \longrightarrow 2\,V\frac{d^3\mathbf{k}}{(2\pi)^3}$$

$$N \approx \underbrace{\int\!\!\int\!\!\int}_{k<k_F} 2\,V\frac{d^3\mathbf{k}}{(2\pi)^3} \qquad E_{\text{total}} \approx \underbrace{\int\!\!\int\!\!\int}_{k<k_F} \frac{\hbar^2 k^2}{2m} 2\,V\frac{d^3\mathbf{k}}{(2\pi)^3}$$

Zero-Temperature Limit
Fermi Energy and Temperature

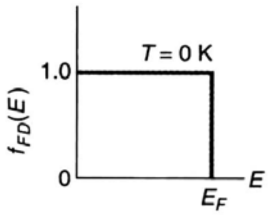
$$n = \frac{N}{V} = \frac{2}{(2\pi)^3}\frac{4\pi}{3}k_F^3$$



$$k_F = \left(3\pi^2 n\right)^{1/3} \sim 1\text{Å}^{-1} \qquad E_{Fo} = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3} \sim 4\,\text{eV}$$

$$v_F = \frac{\hbar \mathbf{k_F}}{m} \sim 10^8\text{cm/sec} \qquad T_F = \frac{E_F}{k_B} \sim 50,000\,\text{K}$$

Zero-Temperature Limit
Electronic Energy



$$E_{\text{total}} \approx \underbrace{\int\int\int}_{k<k_F} \frac{\hbar^2 k^2}{2m} 2\,V \frac{d^3\mathbf{k}}{(2\pi)^3}$$

$$\frac{E_{\text{total}}}{V} = \frac{3}{5} n E_{Fo}$$

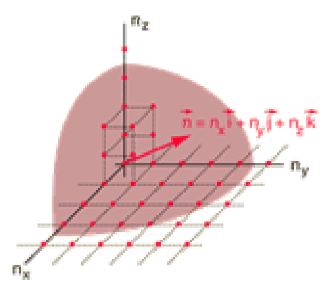
Average energy per electron:

$$\frac{E_{\text{total}}}{N} = \frac{3}{5} E_{Fo}$$

Ensemble Averages at ZeroTemperatures

Where F_k is any property of the electron

$$\frac{F_{\text{tot}}}{V} = \int_0^{E_{F0}} F_{\mathbf{k}}\; 2 \frac{d^3\mathbf{k}}{(2\pi)^3}$$



$$\frac{F_{tot}}{\text{V}} = \int_0^{E_{F0}} F(E)\, g(E)\; dE$$

where *g(E)* is number of states at E per unit volume

By comparing the above two expressions…

$$\frac{2}{(2\pi)^3} 4\pi k^2 dk = g(E) dE \quad \Longrightarrow \quad g(E) = \frac{mk}{\hbar^2 \pi^2} \qquad \text{for} \qquad E > 0$$

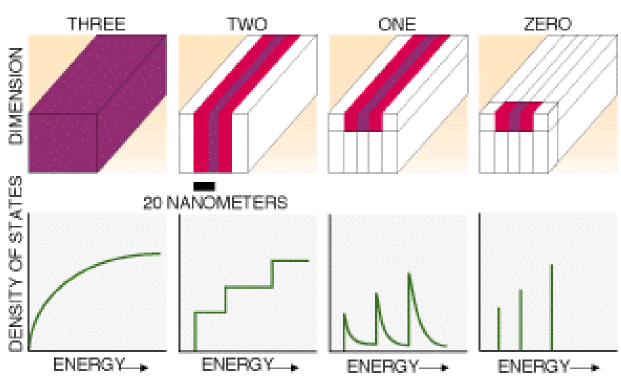
Density of States in Large 3D Solid

$$g(E) = \frac{mk}{\hbar^2\pi^2} \qquad \text{for} \qquad E > 0$$

$$E(\mathbf{k}) = \frac{\hbar^2}{2\mathrm{m}}|\mathbf{k}|^2 = \frac{\hbar^2}{2\mathrm{m}}[\mathbf{k}_x^2 + \mathbf{k}_y^2 + \mathbf{k}_z^2]$$

$$g(E) = \begin{cases} \dfrac{1}{2\pi^2}\dfrac{(2m)^{3/2}}{\hbar^2}E^{1/2} = \frac{3}{2}\frac{n}{E_{F0}}\left(\frac{E}{E_{F0}}\right)^{1/2} & E > 0 \quad \left[\dfrac{\text{states}}{\text{J-m}^3}\right] \\ 0 & E < 0 \end{cases}$$

Density of States in Different Solids



(Scientific American)

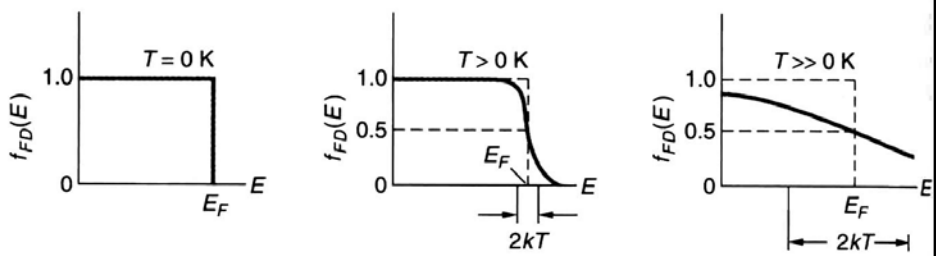
So at zero temperature

$$n = \int_0^{E_{F0}} g(E)\, dE \qquad \text{and} \qquad \frac{E}{V} = \int_0^{E_{F0}} E\, g(E)\, dE$$

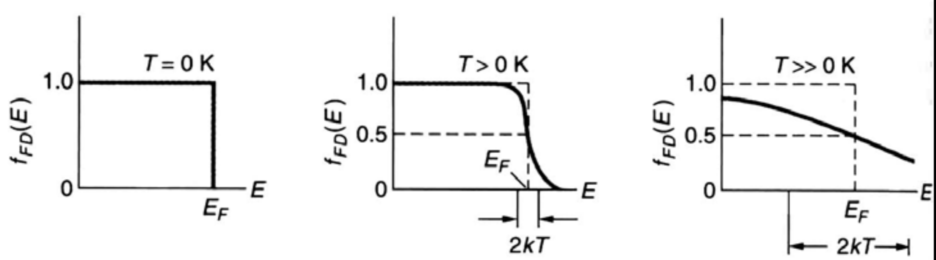
Finite Temperature Limit

Probability of a particular energy level being occupied by an electron:

$$f(E-\mu) = \frac{1}{1+e^{(E-\mu)/k_BT}}$$



Finite Temperatures



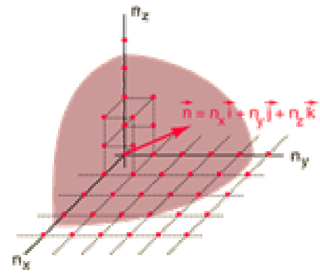
$$n = \frac{N}{V} = \int_{-\infty}^{\infty} \frac{1}{1+e^{(E_{\mathbf{k}}-\mu)/k_BT}} \, 2\frac{d^3\mathbf{k}}{(2\pi)^3}$$

$$\frac{E_{\text{total}}}{V} = \int_{-\infty}^{\infty} E_{\mathbf{k}} \frac{1}{1+e^{(E_{\mathbf{k}}-\mu)/k_BT}} \, 2\frac{d^3\mathbf{k}}{(2\pi)^3}$$

Ensemble Averages at Finite Temperatures

Where F_k is any property of the electron

$$\frac{F_{\text{tot}}}{V} = \int_{-\infty}^{\infty} F_{\mathbf{k}} \frac{1}{1+e^{(E_{\mathbf{k}}-\mu)/k_B T}} 2\frac{d^3\mathbf{k}}{(2\pi)^3}$$



$$\frac{F_{tot}}{V} = \int_{-\infty}^{\infty} F(E)g(E)\frac{1}{1+e^{(E-\mu)/k_B T}}dE$$

where $g(E)$ is number of states at E per unit volume.
It is the same as at zero temperature.

By comparing the above two expressions…

$$\frac{2}{(2\pi)^3}4\pi k^2 dk = g(E)dE \Longrightarrow g(E) = \frac{mk}{\hbar^2\pi^2} \quad \text{for} \quad E > 0$$