6.730 Physics for Solid State Applications

Lecture 3: Metal as a Free Electron Gas

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Generalizations from Molecules to Solids

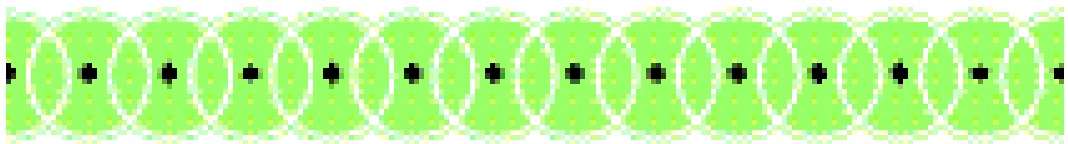
- The source of the binding energy is primarily the electrostatic potential between the nuclei and the electrons. The localization energy can also play a role (metal).

- Nuclear motions of the ions contribute a very small part to the binding energy.

- Sharing electrons between nuclei lowers the energy of the solid.

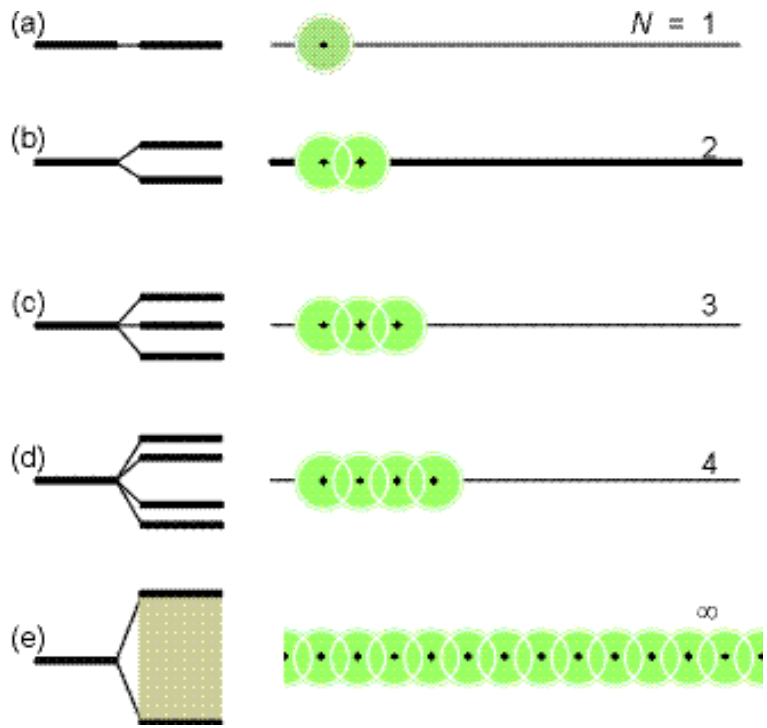
- The potential between the nuclei is of the same form as the molecule.

- Exicted states exists.



Assumptions for Electronic States

- One electron energy levels
- No spin or exchange energies
- LCAO a good approximation
- Ignore motion of the nuclei
  to first order



Overview of Electron Transport

Goal: Calculate electrical properties (eg. resistance) for solids

Approach:

- Macroscopic theory: *V, I, R* $V = IR$
- Microscopic theory: *J, E, σ* $\mathbf{J} = \sigma \mathbf{E}$ $\frac{l}{\sigma A} = R$
- Phenomenological model of transport: *n, τ, m* $\sigma = \frac{ne^2\tau}{m}$
- Relate parameters in phenomenological theory to electronic energy levels and wavefunction

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

$$\tau_k = \Sigma_{k'} \frac{2\pi}{\hbar} \left\langle \psi_{fin,k'}(\mathbf{r}) | \hat{V}_{scat} | \psi_{ini,k}(\mathbf{r}) \right\rangle \qquad \tau = \langle\langle \tau_k \rangle\rangle$$

Overview of Electron Transport

Goal: Calculate electrical properties (eg. resistance) for solids

Approach:
In the end calculating resistance boils down to calculating the electronic energy levels and wavefunctions; to knowing the *bandstructure*

You will be able to relate a bandstructure to macroscopic parameters for the solid

Why this approach ?:
This first principles approach will make assumptions and approximations explicit. The phenomenological theory fails for modern devices – the channel in the MOSFET on the Pentium chip.

Microscopic Variables for Electrical Transport

Drude Theory

Balance equation for forces on electrons:

$$m\frac{d\mathbf{v}(r,t)}{dt} = -\underbrace{m\frac{\mathbf{v}(r,t)}{\tau}}_{\text{DRAG FORCE}} \underbrace{-e\left[\mathbf{E}(\mathbf{r},\mathbf{t}) + \mathbf{v}(\mathbf{r},\mathbf{t}) \times \mathbf{B}(\mathbf{r},\mathbf{t})\right]}_{\text{LORENTZ FORCE}}$$

In steady-state when $\mathbf{B}$=0:

$$\mathbf{v} = -\frac{e\tau}{m}\mathbf{E}_{\mathrm{DC}}$$

$$\mathbf{J} = -ne\mathbf{v} = \frac{ne^2\tau}{m}\mathbf{E}_{\mathrm{DC}}$$

$$\boxed{\mathbf{J} = \sigma\mathbf{E}_{\mathrm{DC}} \quad \text{and} \quad \sigma = \frac{\mathbf{ne^2\tau}}{\mathbf{m}}}$$

Microscopic Variables for Electrical Transport

$$\mathbf{J} = \sigma \mathbf{E}_{\mathsf{DC}} \quad \text{and} \quad \sigma = \frac{\mathbf{n e^2 \tau}}{\mathbf{m}}$$

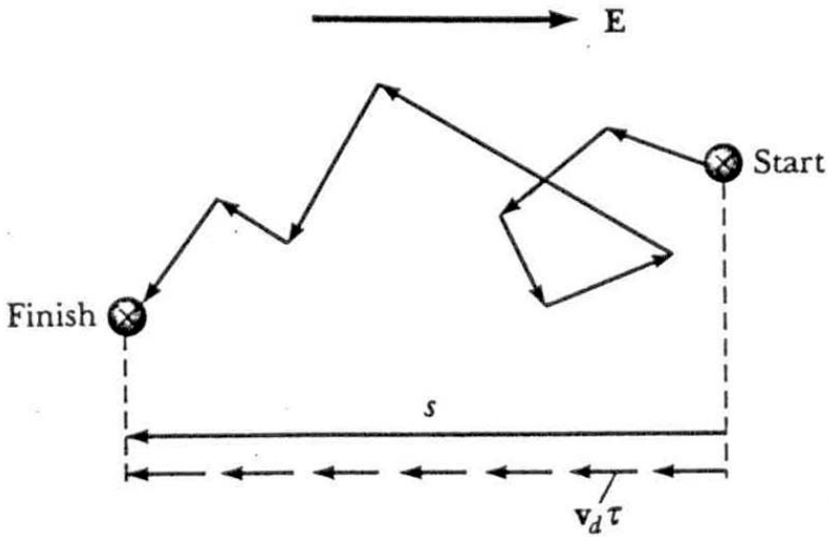
Recovering macroscopic variables:

$$I = \int \mathbf{J} \cdot d\mathbf{a} = \sigma \int \mathbf{E} \cdot \mathbf{da} = \sigma \frac{\mathbf{V}}{\mathbf{l}} \mathbf{A}$$

$$V = I \left(\frac{l}{\sigma A} \right) = IR$$

Microscopic Variables for Electrical Transport

$$\mathbf{J} = \sigma \mathbf{E}_{DC} \quad \text{and} \quad \sigma = \frac{\mathbf{n e^2 \tau}}{\mathbf{m}}$$



$$\tau = \frac{m}{ne^2\rho}$$

$$\tau = \frac{9.1 \times 10^{-31}\text{kg}}{(10^{28}\text{m}^{-3})(1.6 \times 10^{-19}\text{C})^2(1 \times 10^{-4}\Omega\text{-m})}$$

$$= 3.6 \times 10^{-13}\text{s} = 360\,\text{fs}$$

Microscopic Variables for Electrical Transport

Balance equation for energy of electrons:

$$\frac{dE}{dt} = -\frac{\Delta E}{\tau} + IV$$

In steady-state:

$$\Delta E = \tau IV$$

In the continuum models, we assume that electron scattering is sufficiently fast that all the energy pumped into the electrons is randomized; all additional energy heats the electrons

How do we relate ΔE and T ?

Equipartition Theorem

Balance equation for energy of electrons:

The theorem of equipartition of energy states that molecules in thermal equilibrium have the same average energy associated with each independent degree of freedom of their motion

$$< u >_{\text{thermal}} = \frac{3}{2} k_B T \qquad \text{Equi-partition theorem}$$

$$\frac{E_{\text{total}}}{V} = \frac{N}{V} u = \frac{3}{2} n k_B T$$

So in this simple theory, ΔE and T are proportional to each other…

Specific Heat and Heat Capacity

Again assume that the heat and change in internal energy are the same:

$$c_V = \left(\frac{dQ}{dT}\right)_V = \left(\frac{dE_{\text{total}}}{dT}\right)_V \qquad \text{(heat capacity)}$$

Take constant volume since this ensures
none of the extra energy is going into *work*
(think ideal gas)

$$C_V = \frac{1}{V}\frac{d}{dT}\left(\frac{3}{2}Nk_BT\right) = \frac{3}{2}nk_B \qquad \text{(specific heat)}$$

$$C_v = 2 \times 10^6 \frac{\text{erg}}{\text{cm}^3\text{-K}} = 11 \frac{\text{Joule}}{\text{mole-K}}$$

Specific heat is independent of temperature…Law of Dulong and Petit

Specific Heat Measurements

(hyperphysics.phy-astr.gsu.edu)

Specific heat is independent of temperature…NOT TRUE !

To get this correct we will need to (a) quantize electron energy levels, (b) introduce discreteness of lattice and (c) the heat capacity of lattice

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

not for periodic b.c.

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

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

$$E(\mathbf{k}) = \frac{\hbar^2}{2m}|\mathbf{k}|^2 = \frac{\hbar^2}{2m}[k_x^2 + k_y^2 + k_z^2]$$

(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 $0, \pm1, \pm2, \pm3 \ldots$

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

Estimating Electron Number

$$E(\mathbf{k}) = \frac{\hbar^2}{2m}|\mathbf{k}|^2 = \frac{\hbar^2}{2m}[k_x^2 + k_y^2 + k_z^2]$$

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

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

Total number of electrons:

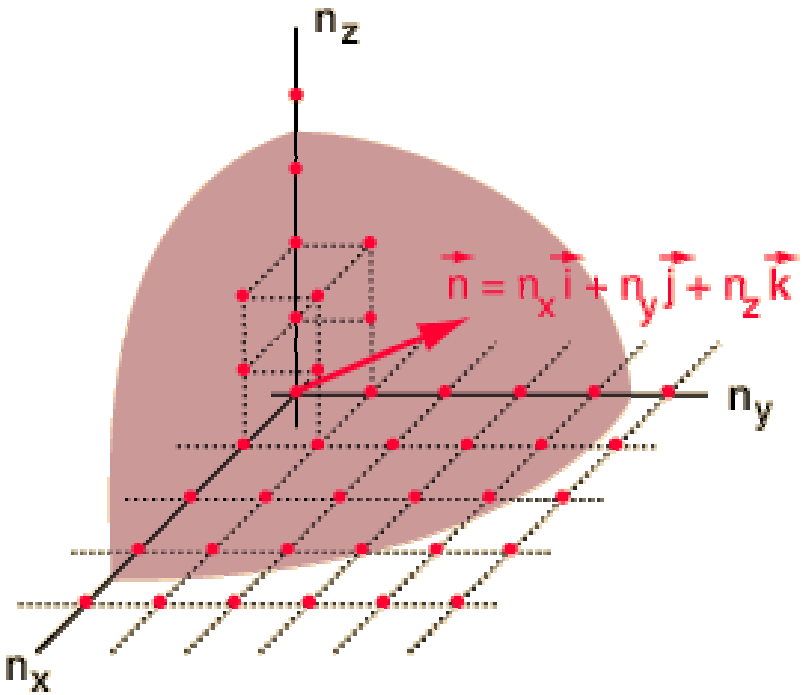
$$N = \sum_{l=0}^{\infty} \frac{1}{1 + e^{(E_l-\mu)/k_B T}}$$

$$N = 2 \sum_{k=-\infty}^{\infty} \frac{1}{1 + e^{(E_k-\mu)/k_B T}}$$

spin

Limit for Large Crystals

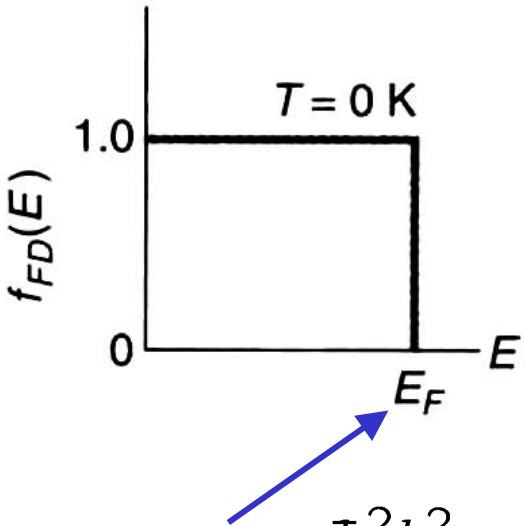
$$2\,\frac{\Delta k_x}{(2\pi/L)}\,\frac{\Delta k_y}{(2\pi/L)}\,\frac{\Delta k_z}{(2\pi/L)} \longrightarrow 2\,V\frac{d^3\mathbf{k}}{(2\pi)^3}$$

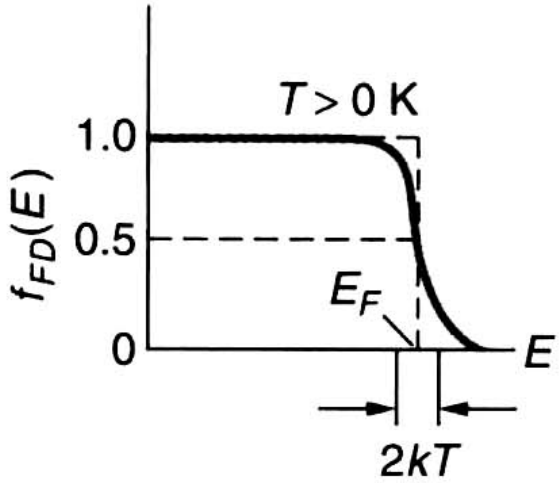


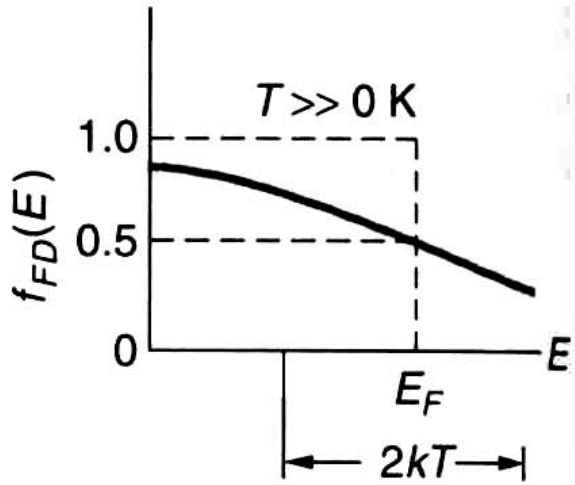
$$n = \frac{N}{V} = \int_{-\infty}^{\infty} \frac{1}{1 + e^{(E_{\mathbf{k}} - \mu)/k_B T}}\, 2\frac{d^3\mathbf{k}}{(2\pi)^3}$$

Zero-Temperature Limit

$$\mu(T) \approx \mu(0) = E_{Fo} = \mu_o$$







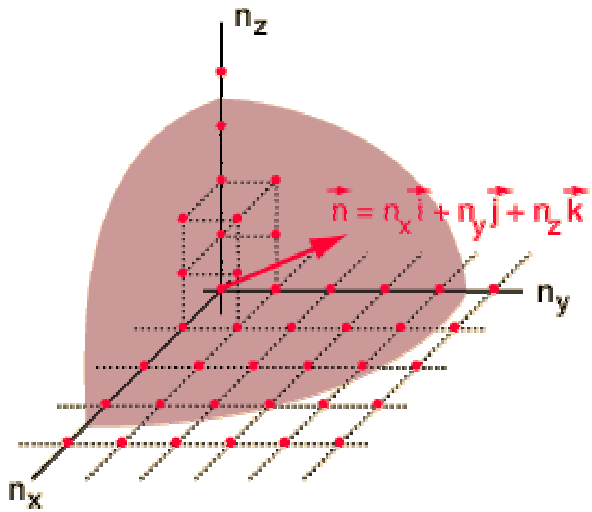
$$E_F = \frac{\hbar^2 k_F^2}{2m}$$

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

$$N \approx \underbrace{\int\int\int}_{k<k_F} 2\, V \frac{d^3\mathbf{k}}{(2\pi)^3}$$

Zero-Temperature Limit
Fermi Energy and Temperature

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



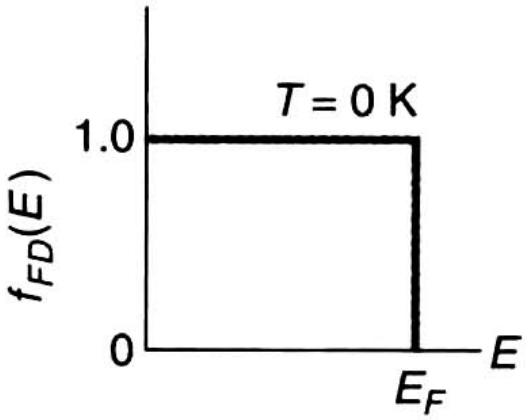
$$k_f = \left(3\pi^2 n\right)^{1/3} \sim 1\text{Å}^{-1}$$

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

$$v_F = \frac{\hbar \mathbf{k_F}}{m} \sim 10^8 \text{cm/sec}$$

$$T_F = \frac{E_F}{k_B} \sim 50,000\,\text{K}$$

Zero-Temperature Limit
Electronic Energy



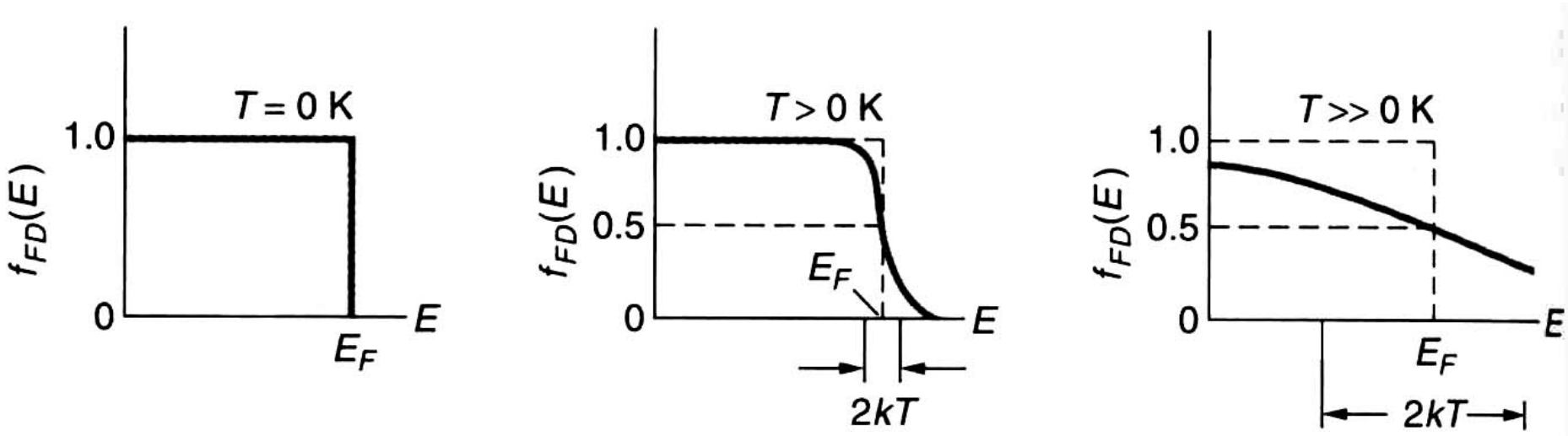
$$E_{\text{total}} \approx \underbrace{\int\int\int}_{k<k_F} \frac{\hbar^2 k^2}{2m} 2\,V \frac{d^3\mathbf{k}}{(2\pi)^3}$$

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

Average energy per electron:

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

Finite Temperatures



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

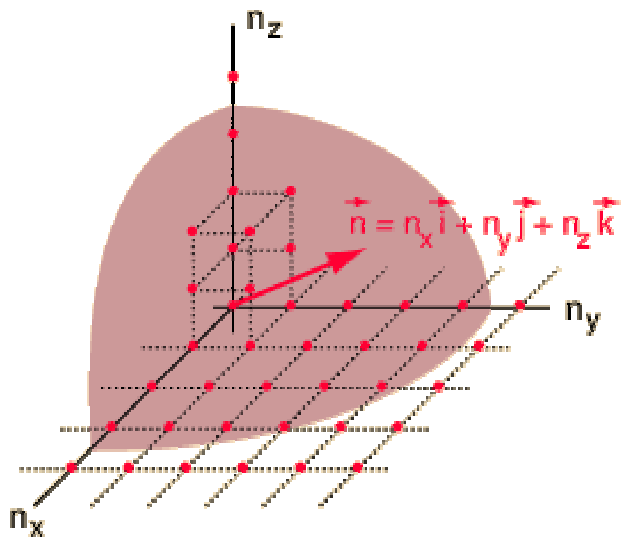
$$\frac{E_{\text{total}}}{V} = \int_{-\infty}^{\infty} E_{bfk} \frac{1}{1 + e^{(E_{\mathbf{k}} - \mu)/k_B T}} 2 \frac{d^3\mathbf{k}}{(2\pi)^3}$$

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

By comparing the above two expressions…

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

Density of States in Large 3D Solid

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

$$E(\mathbf{k}) = \frac{\hbar^2}{2\mathbf{m}}|\mathbf{k}|^2 = \frac{\hbar^2}{2\mathbf{m}}[\mathbf{k_x^2} + \mathbf{k_y^2} + \mathbf{k_z^2}]$$

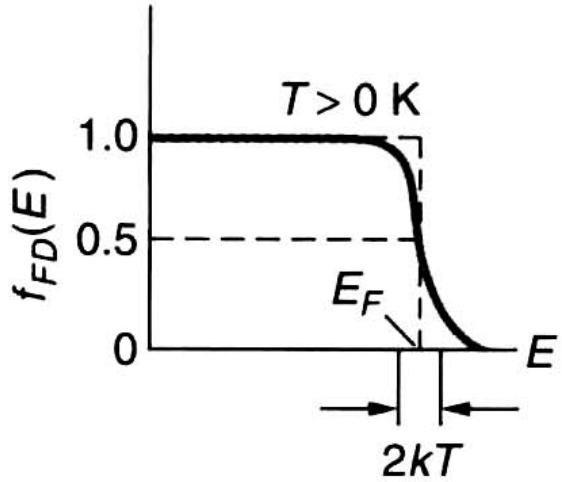
$$g(E) = \begin{cases} \dfrac{1}{2\pi^2}\dfrac{(2m)^{3/2}}{\hbar^2}E^{1/2} = \frac{3}{2}\frac{n}{E_{F0}}\left(\frac{E}{E_{F0}}\right)^{1/2} & E > 0 \quad \left[\dfrac{\text{states}}{\text{J-m}^3}\right] \\ 0 & E < 0 \end{cases}$$

Density of States in Different Solids

$$n = \int_{-\infty}^{\infty} g(E) f(E-\mu) dE = \int_{-\infty}^{\infty} g(E) \frac{1}{1 + e^{(E-\mu)/k_B T}} dE$$

Low Temperature Specific Heat of the Free Electron Gas

Sommerfeld Approximation



$$\frac{\Delta E}{V} \approx \underbrace{[g(E_{Fo})k_BT]}_{\text{excited states}} \qquad \underbrace{k_BT}_{\text{increase in energy}}$$

$$C_V = \frac{\partial(\Delta E/\mathrm{V})}{\partial T} \approx 2g(E_{F0})k_B^2T$$

$$C_V \approx \left(\frac{3}{2}nk_B\right)\left(\frac{2k_BT}{E_{F0}}\right) \approx \left(\frac{3}{2}nk_B\right)(100-5000)$$

Specific Heat Measurements

(hyperphysics.phy-astr.gsu.edu)

To get this correct we will need to (a) quantize electron energy levels, (b) introduce discreteness of lattice and (c) the heat capacity of lattice

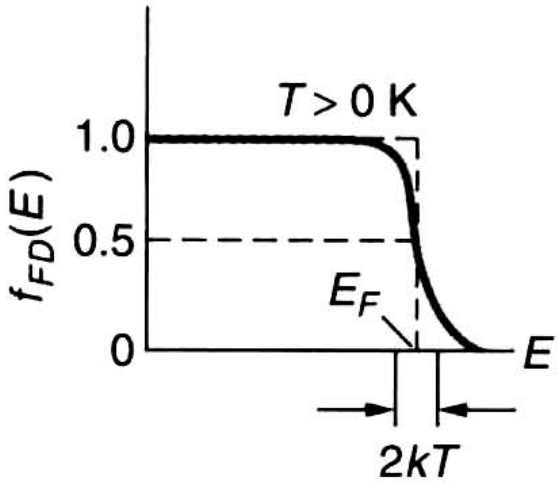
Conductivity of the Free Electron Gas

Sommerfeld Approximation

$$\mathbf{v_d} = (-e\tau/m)\mathbf{E}_{DC}$$

$$\mathbf{v} = \mathbf{v_F} - \frac{e\tau}{m}\mathbf{E}_{DC}$$

$$E = \frac{1}{2}mv^2 \approx \frac{1}{2}mv_F^2 + e\tau\mathbf{v}\cdot\mathbf{E}_{DC}$$



$$\Delta E = e\tau v_F|\mathbf{E}_{DC}|$$

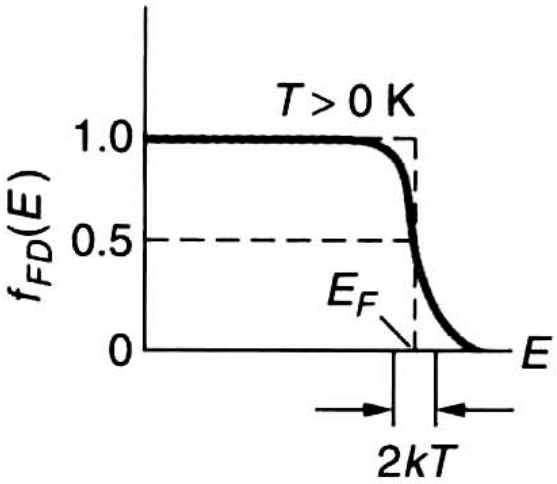
$$J = -e(\delta n)v_F$$

$$\delta n \approx g(E_F)\Delta E$$

Only electrons near E_F contribute to current !

Conductivity of the Free Electron Gas

Sommerfeld Approximation



$$\Delta E = e\tau v_F |\mathbf{E}_{\mathrm{DC}}|$$

$$J = -e(\delta n)v_F$$

$$\delta n \approx g(E_F)\Delta E$$

$$J = e^2 \tau v_F^2 g(E_F)|\mathbf{E}_{\mathrm{DC}}|$$

$$\sigma = e^2 v_F^2 \tau g(E_F)$$

$$\sigma \approx \frac{ne^2\tau}{m}$$

Sommerfeld recovers the phenomenological results !

Sommerfeld Expansion

$$f(E-\mu) = \lim_{T\to 0} \frac{1}{1+e^{(E-\mu)/k_B T}} = 1-u(E-\mu)$$

$$f'(E-\mu) = -\delta(E-E_{Fo})$$

$$\int_{-\infty}^{\infty} f(E-\mu)H(E)dE = \int_{-\infty}^{\mu} H(E)dE + \frac{\pi^2}{6}(k_B T)^2 H'(\mu) + O\left(\frac{k_B T}{E_{F0}}\right)^4$$

$$\int_{-\infty}^{\mu} H(E)dE = \int_{-\infty}^{E_{F0}} H(E)dE + (\mu - E_{F0})H(E_{F0}) + O\left(\frac{k_B T}{E_{F0}}\right)^4$$

Sommerfeld Expansion for Electron Density

$$n = \int_0^{E_{F0}} g(E)dE + \underbrace{\left[(\mu - E_{F0})g(E_{F0}) + \frac{\pi^2}{6}(k_B T)^2 g'(E_{F0})\right]}_{0}$$

$$\mu = E_{F0}\left\{1 - \frac{\pi^2}{6}\left(\frac{(k_B T)^2}{E_{F0}}\right)\frac{g'(E_{F0})}{g(E_{F0})}\right\}$$

$$\mu = E_{F0}\left\{1 - \frac{1}{3}\left(\frac{\pi k_B T}{2E_{F0}}\right)^2\right\}$$

Sommerfeld Expansion for Electron Energy

$$\frac{E}{V} = \int_{-\infty}^{\infty} E g(E) f(E-\mu) dE$$

$$= \int_0^{E_{F0}} E g(E) dE + E_{F0} \underbrace{\left[(\mu - E_{F0}) g(E_{F0}) + \frac{\pi^2}{6} (k_B T)^2 g'(E_{F0}) \right]}_{0}$$

$$+ \frac{\pi^2}{6} (k_B T)^2 g(E_{F0}) + O(T^4)$$

$$\frac{E}{V} = \int_0^{E_{F0}} E g(E) dE + \frac{\pi^2}{6} (k_B T)^2 g(E_{F0})$$

$$= \frac{3}{5} E_F n + \frac{\pi^2}{6} (k_B T)^2 g(E_{F0})$$

$$\boxed{C_V = \left. \frac{\partial ((E/V))}{\partial T} \right|_{V,N} = \frac{\pi^2}{3} k_B^2 T g(E_{F0}) = \gamma T}$$

Density of States is the Central Character in this Story

Goal: Calculate electrical properties (eg. resistance) for solids

Approach:
In the end calculating resistance boils down to calculating the electronic energy levels and wavefunctions; to knowing the *bandstructure*

You will be able to relate a bandstructure to macroscopic parameters for the solid

$$\sigma = e^2 v_F^2 \tau g(E_F)$$

$$C_V = \left.\frac{\partial((E/V))}{\partial T}\right|_{V,N} = \frac{\pi^2}{3} k_B^2 T g(E_{F0}) = \gamma T$$