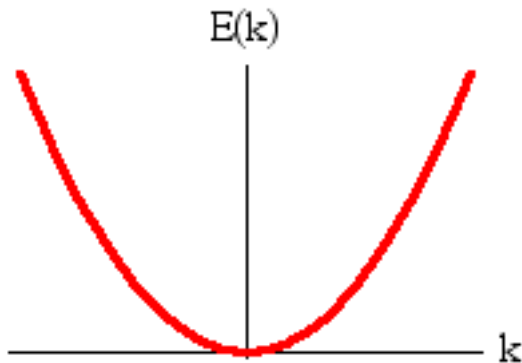


# PH575 Spring 2014

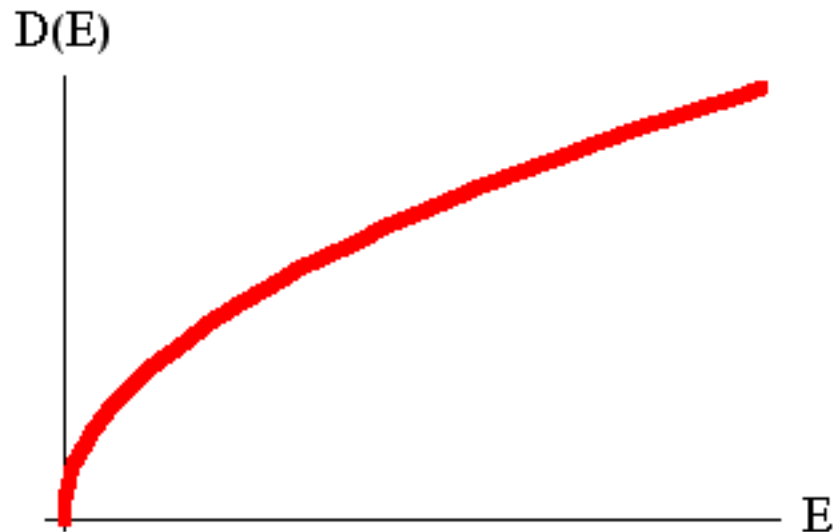
## Lecture #18

Free electron theory: Sutton Ch. 7 pp 132 -> 144;  
Kittel Ch. 6.

$$E(k) = \frac{\hbar^2 k^2}{2m}$$



$$D(E) = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$$



Assumption: electrons metal do not interact with each other, not with the potential due to the ions EXCEPT that the ion potential confines them to the region of space occupied by the material.

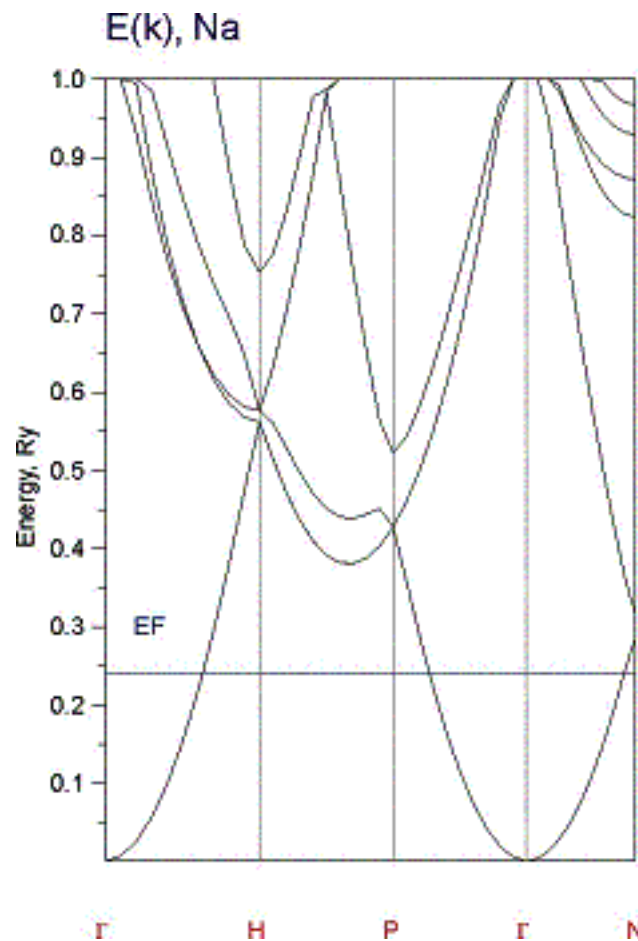
We will see that this assumption leads to a spherical Fermi surface and explains the properties of simple metals. It does not predict gaps in the band structure, but it is remarkable that the theory works as well as it does, and it improves the classical Drude model that is still used with success.



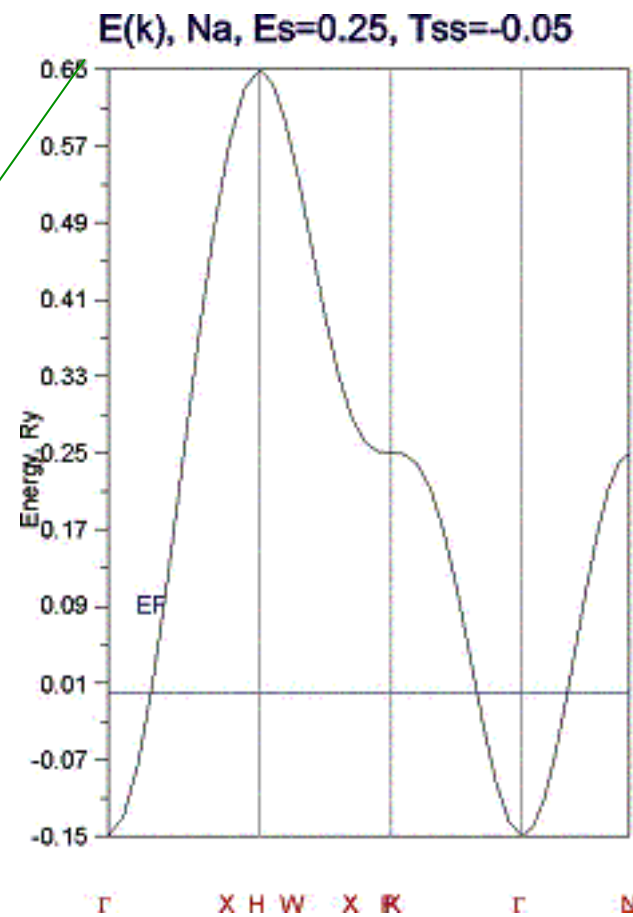
Paul Drude (1863-1906)

Free electron bands & LCAO (tight binding) bands are qualitatively similar, with important exception of gaps. (Sutton, Fig. 7.6, Ge e.g.)  
 So free electron model works well only for metals.

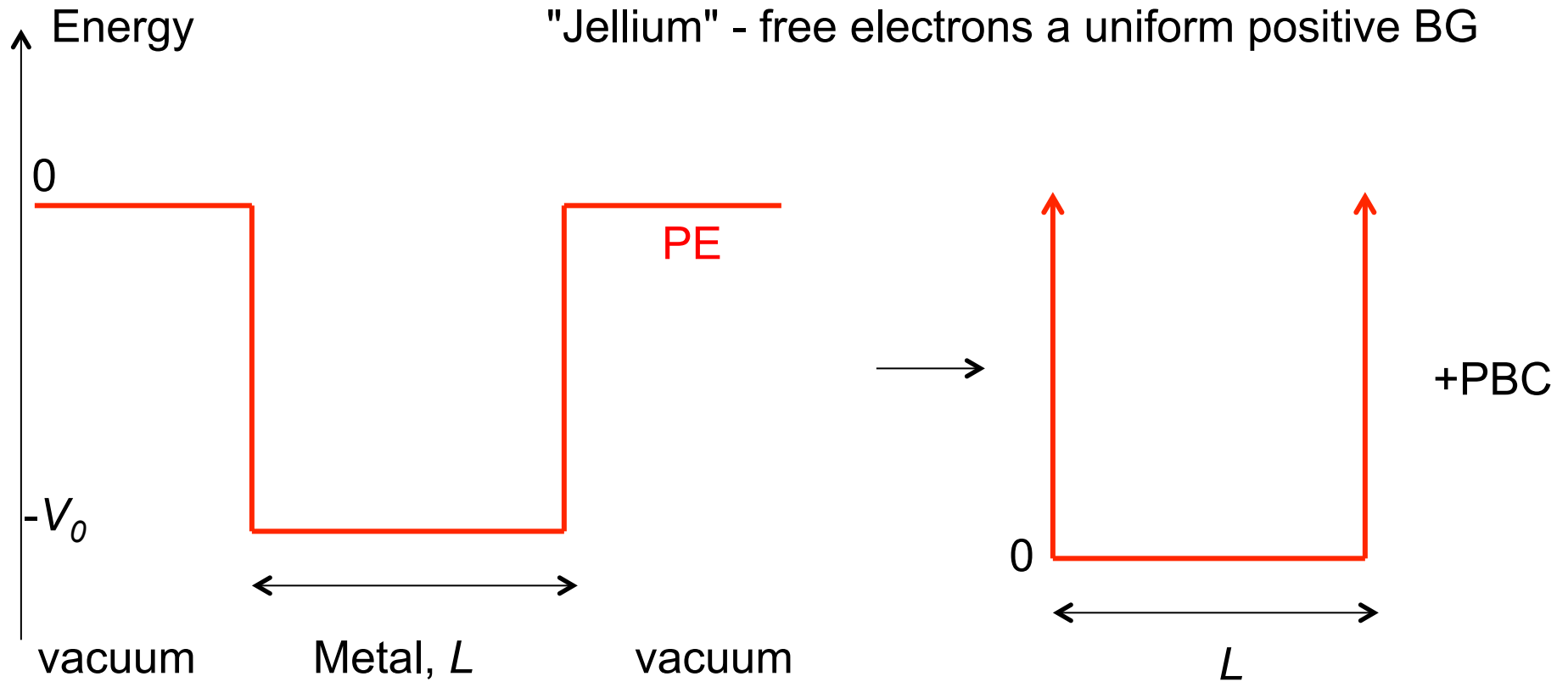
FE bands (Na)



LCAO band (Na)



"Jellium" - free electrons a uniform positive BG



$$\hat{H}|\psi_k\rangle = E_k|\psi_k\rangle$$

$$\frac{-\hbar^2}{2m} \left[ \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right] |\psi_k\rangle = E_k |\psi_k\rangle$$

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

Similar to  
Bloch form

$$\frac{-\hbar^2}{2m} \left[ \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right] \psi_k(\vec{r}) = E_k \psi_k(\vec{r})$$

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

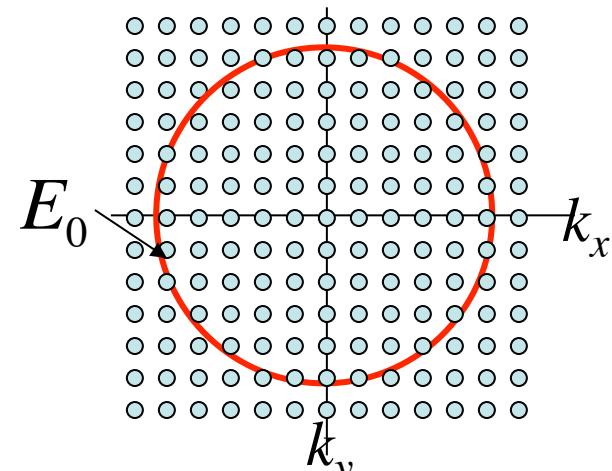
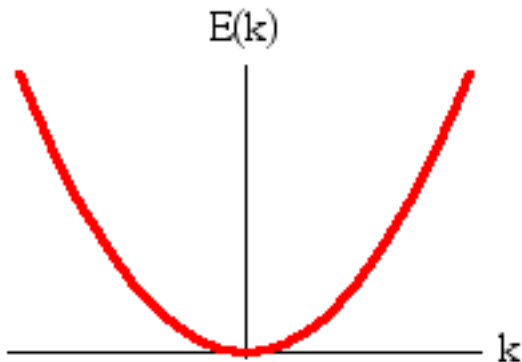
$$\vec{r} = x\hat{x} + y\hat{y} + z\hat{z}; \quad r = |\vec{r}| = \sqrt{x^2 + y^2 + z^2}$$

$$\vec{k} = k_x\hat{x} + k_y\hat{y} + k_z\hat{z}; \quad k = |\vec{k}| = \sqrt{k_x^2 + k_y^2 + k_z^2}$$

$$E(\vec{k}) = ?; \quad k_x = ? \quad k_y = ? \quad k_z = ?$$

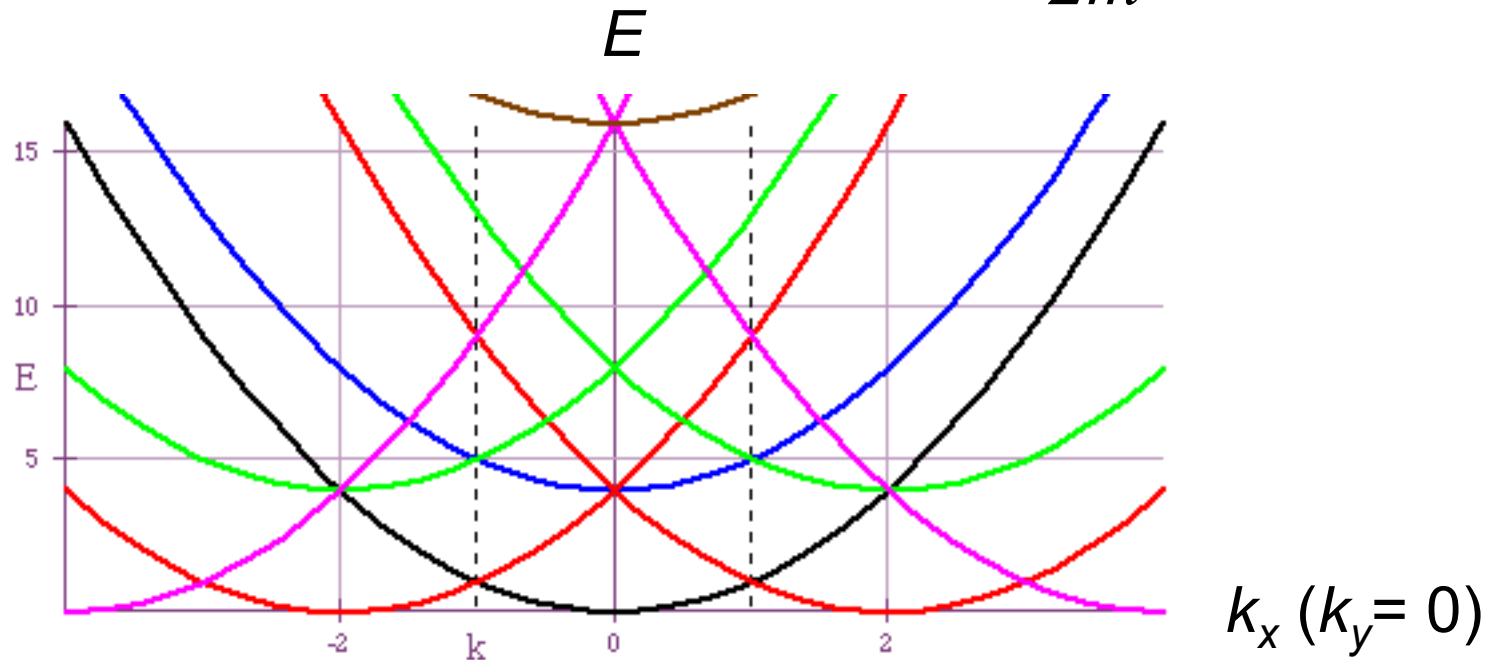
$$E(k) = \frac{\hbar^2 k^2}{2m}$$

$$k_x = n_x \frac{2\pi}{L}; \quad k_y = n_y \frac{2\pi}{L}; \quad k_z = n_z \frac{2\pi}{L}$$



Free electron bands: square lattice

$$E = \frac{\hbar^2 |\vec{k} + \vec{G}|^2}{2m}$$



Real space

$$\vec{a}_1 = a(1,0)$$

$$\vec{a}_2 = a(0,1)$$

Reciprocal

$$\vec{g}_1 = \frac{2\pi}{a}(0,1)$$

$$\vec{g}_2 = \frac{2\pi}{a}(1,0)$$

$$\vec{G} = \frac{2\pi}{a}(0,0)$$

$$\vec{G} = \frac{2\pi}{a}(\pm 1,0)$$

$$\vec{G} = \frac{2\pi}{a}(0,1)$$

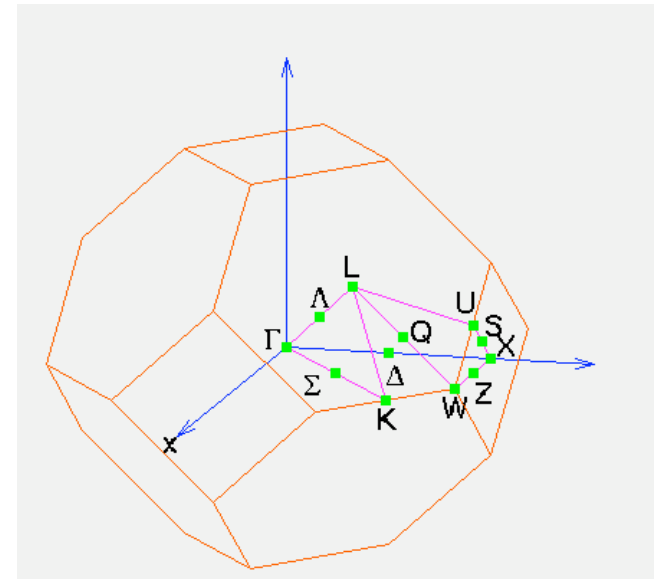
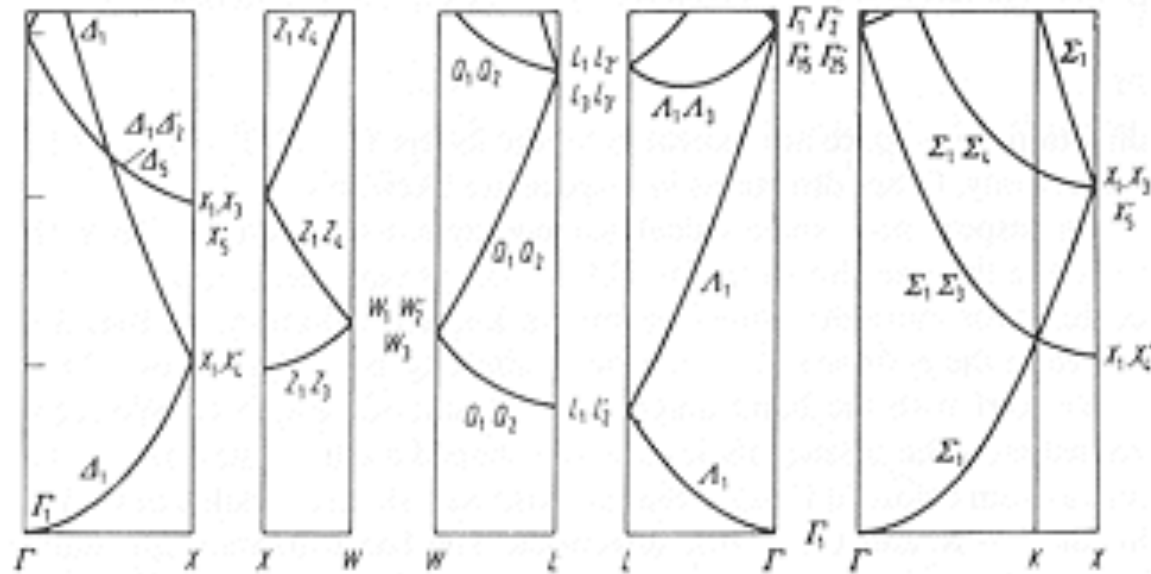
$$\vec{G} = \frac{2\pi}{a}(\pm 1,\pm 1)$$

$$\vec{G} = \frac{2\pi}{a}(0,2)$$

$$\vec{G} = \frac{2\pi}{a}(\pm 2,0)$$

# Free electron bands: fcc lattice

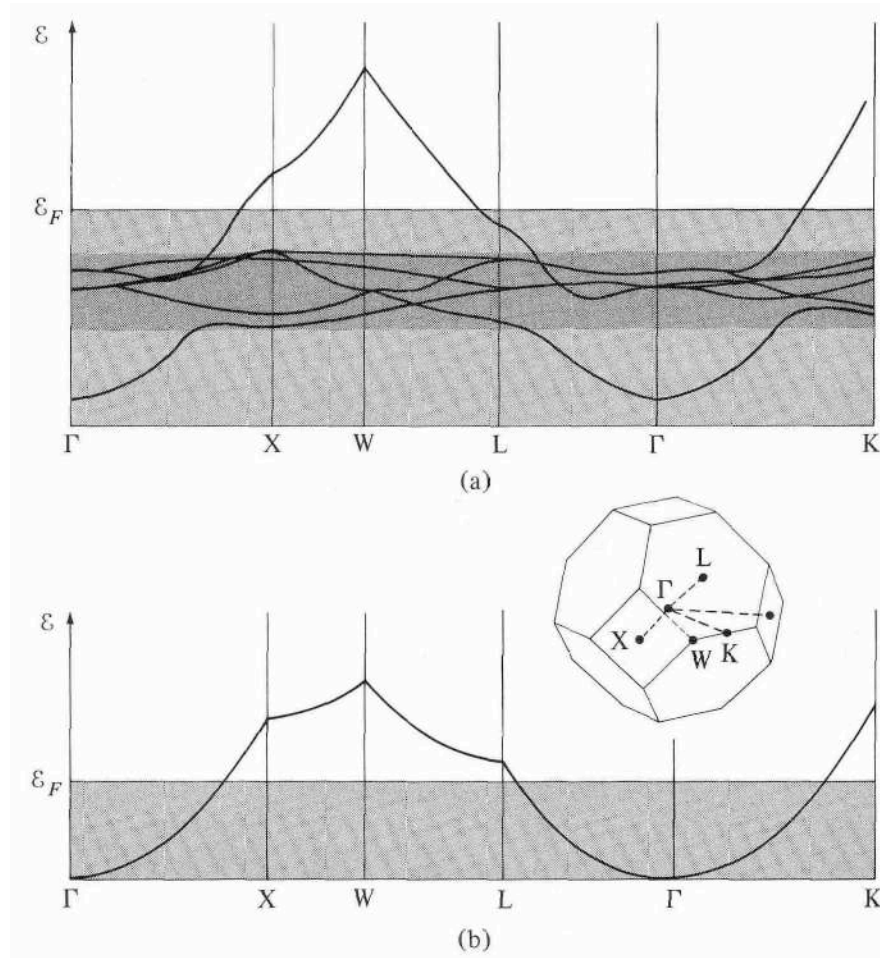
$$E = \frac{\hbar^2 |\vec{k} + \vec{G}|^2}{2m}$$



# Free electron bands: fcc lattice Example Copper

$$E = \frac{\hbar^2 |\vec{k} + \vec{G}|^2}{2m}$$

<- Calculated with  
pseudopotential methods.  
Note d-bands!

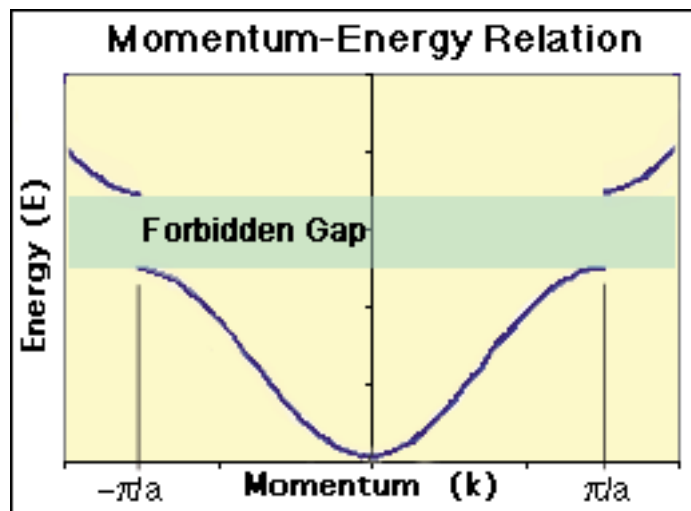


<- Free electron bands



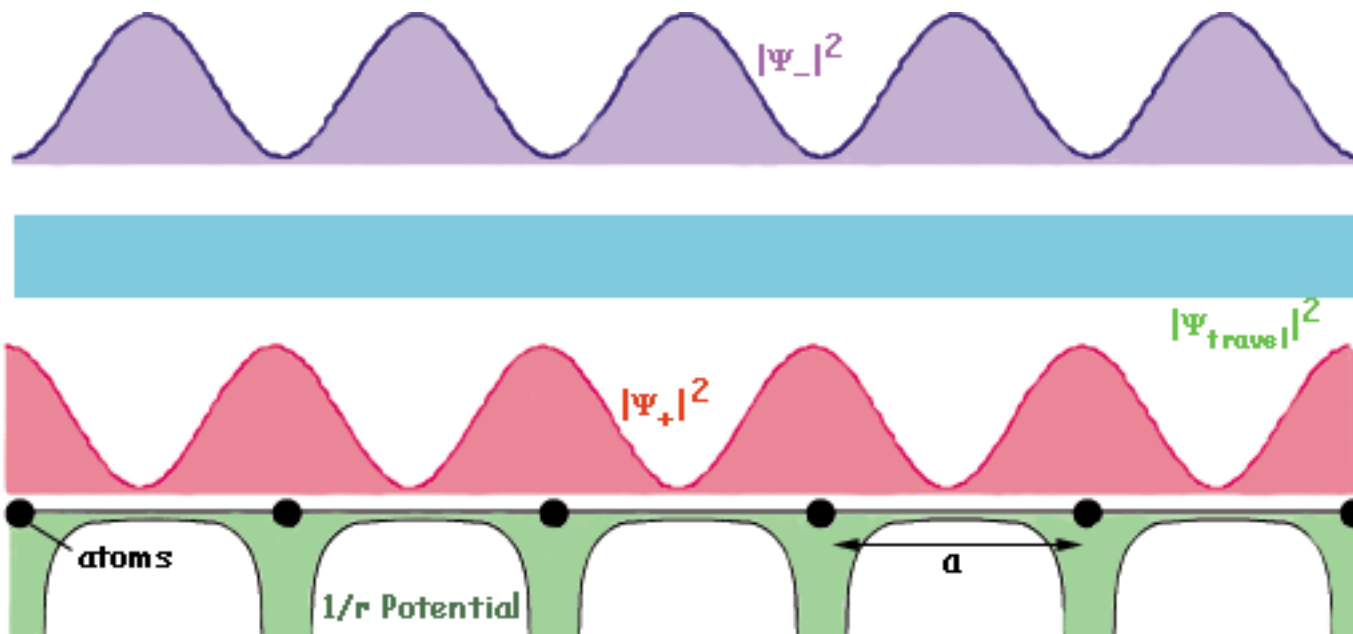
There is a gap in the energy spectrum!

This same result can be obtained by treating the periodic ion potential as a perturbation of the smooth potential (we won't do this, but it's discussed in Kittel, for example)



Free electrons (plane waves) don't interact with the lattice much until the wave vector becomes comparable with  $1/a$ , then they are Bragg reflected and there is interference between oppositely directed plane waves (*standing waves*).

Lower energy state piles up electron density on the atoms (stronger Coulomb attraction to cores), while the higher energy state piles up electron density between the atoms. Thus there is a gap in the energy spectrum!



$$e^{ikx} - e^{-ikx} \\ \sim \sin(kx)$$

$$e^{ikx} + e^{-ikx} \\ \sim \cos(kx)$$

Constant energy surfaces are spheres in  $k$  space

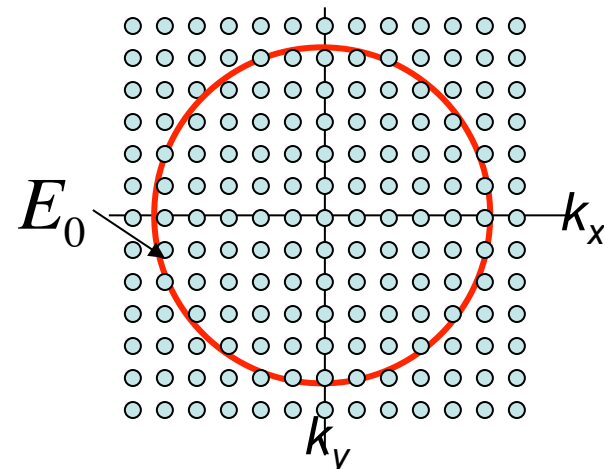
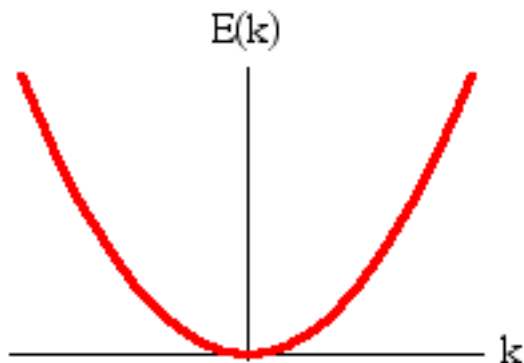
Each state occupies  $8\pi^3/L^3$  in  $k$ -space

When all  $N$  valence electrons have filled up  $k$ -states, reach the **Fermi Energy**  $E_F$  and the sphere has radius **Fermi wave vector**  $k_F$

$$N \frac{8\pi^3}{V} \frac{1}{2} \equiv \frac{4\pi k_F^3}{3} \quad E_F = \frac{\hbar^2 k_F^2}{2m}$$

Factor of 2 is from spin (2 electrons/state)

$$E(k) = \frac{\hbar^2 k^2}{2m} \quad k_x = n_x \frac{2\pi}{L}; \quad k_y = n_y \frac{2\pi}{L}; \quad k_z = n_z \frac{2\pi}{L}$$



Fermi parameters (see Kittel Ch.6, Table I):

$$k_F = \left( 3\pi^2 \frac{n}{\# e/vol} \right)^{1/3} \quad k_F = 0.92 \times 10^8 \text{ cm}^{-1}:$$

$$E_F = \frac{\hbar^2 k_F^2}{2m} \quad E_F = 3.2 \text{ eV: kinetic energy of Fermi level } e$$

$$T_F = \frac{E_F}{k_B} \quad T_F = 37,500 \text{ K: temp. above which } e \text{ obey classical statistics (can ignore quantum effects)}$$

$$v_F = \frac{\hbar k_F}{m} \quad v_F = 1.1 \times 10^8 \text{ cm s}^{-1} : 1\% c$$

Sodium:  $n = 2.65 \times 10^{22} \text{ e-/cm}^3$

Reminder: 3-D Density of states for free electron:

S counts the states.

$$D(E) = \frac{dS}{dE} \Rightarrow dS = D(E)dE$$

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

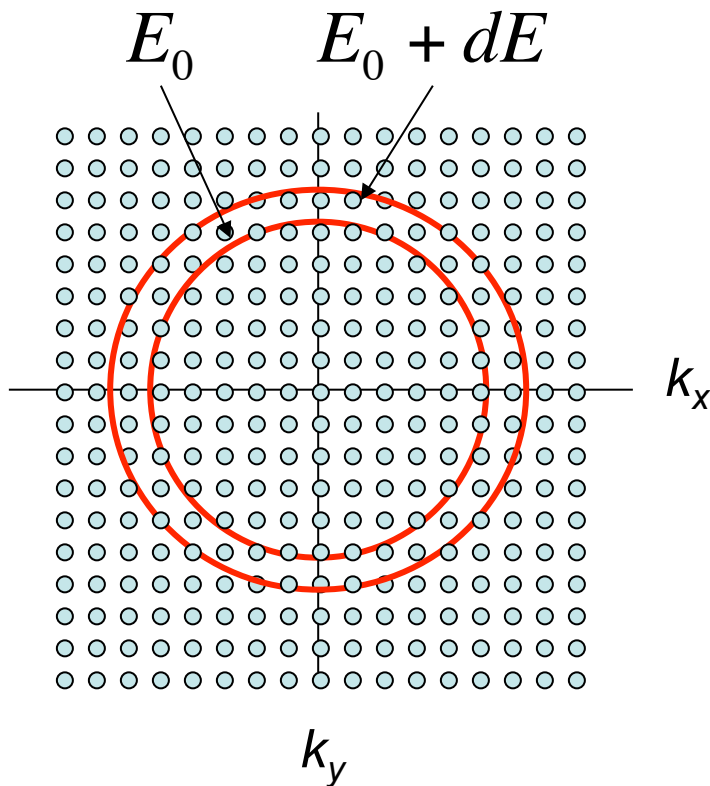
$$dS_{\uparrow\downarrow} = D_{\uparrow\downarrow}(k) \times \text{annular vol of k-space}$$

$$= \frac{2V}{(2\pi)^3} \times 4\pi k^2 dk$$

$$D_{\uparrow\downarrow}(E)dE = \frac{2V}{(2\pi)^3} 4\pi k^2 dk$$

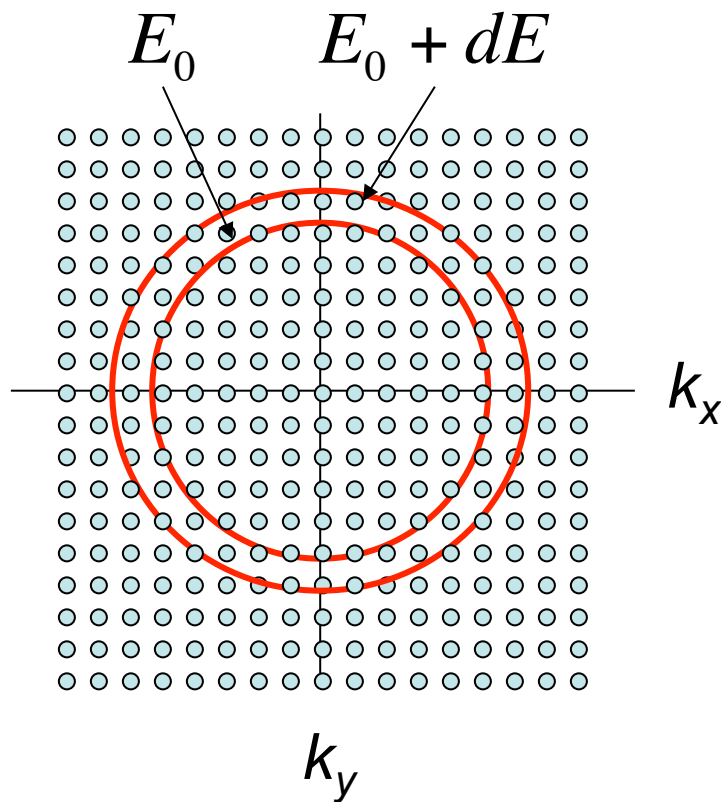
$$D_{\uparrow\downarrow}(E) = \frac{8\pi k^2 V}{(2\pi)^3} \frac{dk}{dE}$$

$$D_{\uparrow\downarrow}(E) = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$$



Example: Find total energy at  $T = 0$  (homework)  
 Will use this later for electronic specific heat.

$$E_{Tot} = \int_0^{E_F} E D(E) dE$$



Total energy at  $T \neq 0$

$$\begin{aligned} E_{Tot} &= \int_0^{\infty} E f(E) D(E) dE \\ &= \int_0^{\infty} E \frac{1}{e^{(E-E_F)/k_B T} + 1} D(E) dE \end{aligned}$$

# Fermi Function

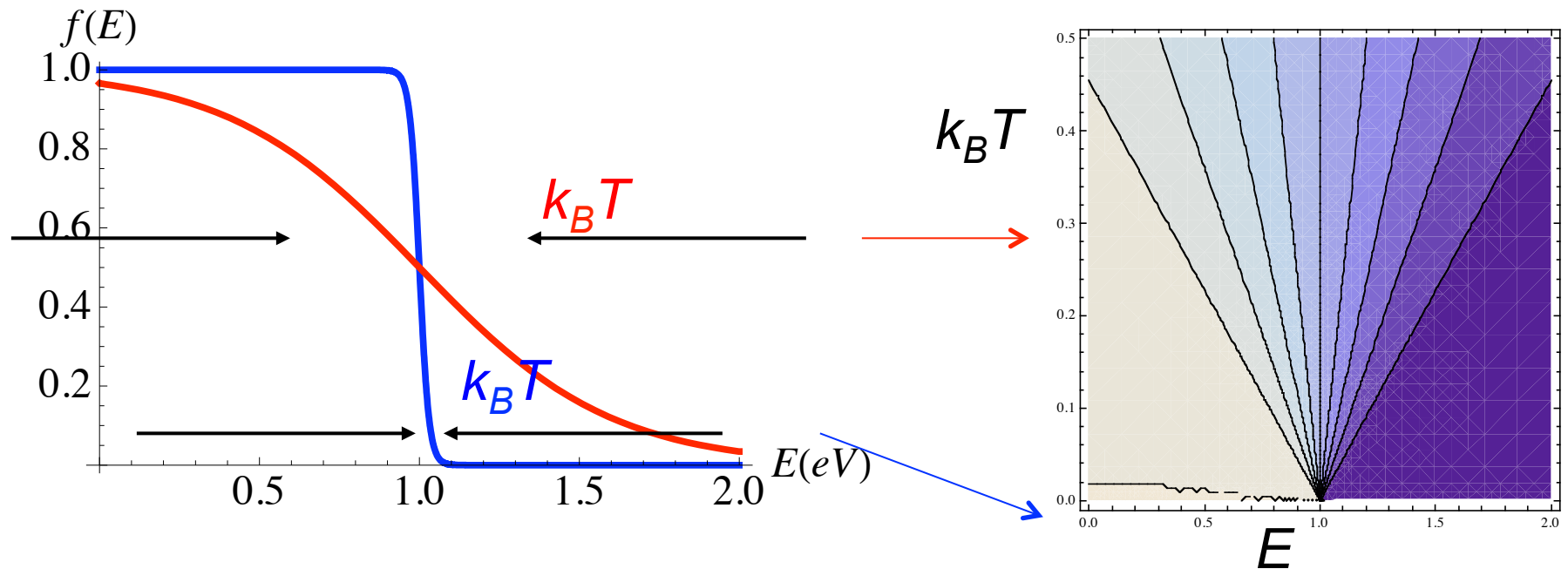
- Probability that a state of energy  $E$  is occupied at temperature  $T$ .
- $f(\mu) = 0.5$
- Varies sharply over width of  $\approx k_B T$  about  $E_F$ . Step function  $T = 0$ .

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

$$\mu = 1 \text{ eV}$$

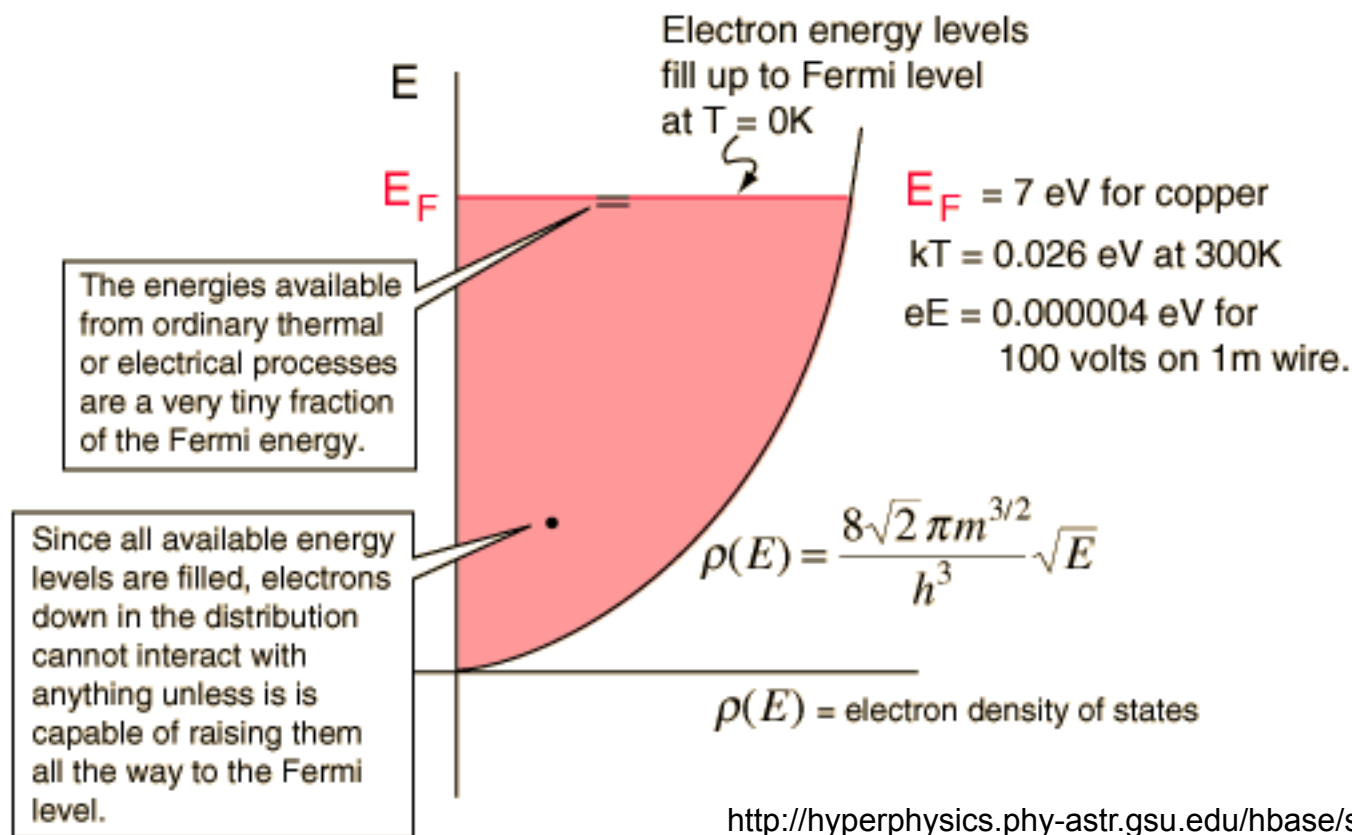
$$T = 0.015 \text{ eV} = ?\text{K}$$

$$T = 0.3 \text{ eV} = ?\text{K}$$



## Electronic specific heat

- Electrons are a repository of energy in metals and contribute to the specific heat. Dominant contribution at low T where phonons are frozen out.
- If electrons are a "classical gas" (no QM), equipartition theorem => electronic energy is  $E_{elec} = (3/2)k_B T$ .  
Electronic specific heat is  $C_{elec} = dE_{elec}/dT = (3/2)k_B$
- Actual values in metals at low temperatures are less than 1% of this, and are NOT temperature independent.





## Electronic specific heat

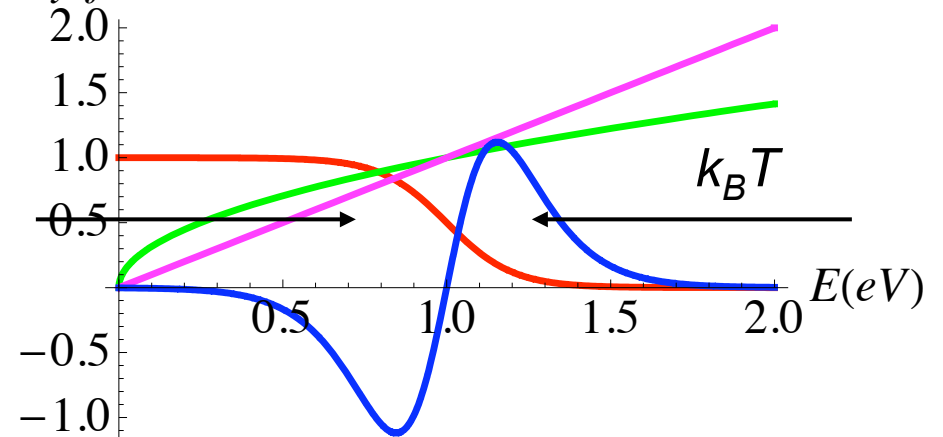
Nearly free electrons are a repository of energy in metals and contribute to the specific heat. At low temperatures, when phonons (lattice vibrations) are frozen out, this contribution dominates.

$$E_{Tot} = \int_0^{\infty} E f(E) D(E) dE$$
$$= \int_0^{\infty} E \frac{1}{e^{(E-\mu)/k_B T} + 1} D(E) dE$$

$$\frac{df(E, T)}{dT}$$

$$D(E) = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$$

many functions



$$C_v = \frac{dE_{Tot}}{dT} = \int_0^{\infty} E \frac{df(E, T)}{dT} D(E) dE$$

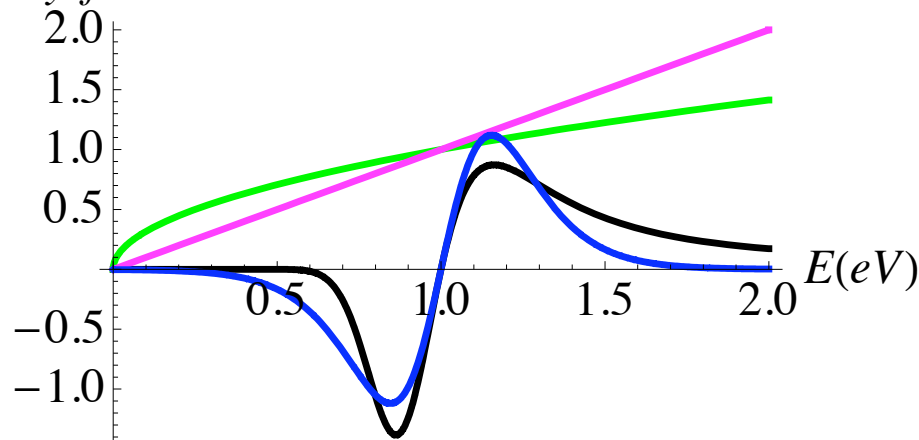
Area under black curve is electronic specific heat.

Very slight asymmetry is crucial!

Easy enough to calculate numerically, but let's look for analytical insight.

What is dominant contribution? Weakest?

*many functions*



$$E_F = 1 \text{ eV}$$

$$k_B T = 0.1 \text{ eV}$$

$$C_v = \frac{dE_{Tot}}{dT} = \int_0^{\infty} E \frac{df(E, T)}{dT} D(E) dE$$

$D(E)$  varies slowly - remove from integral (but what value?

Why can lower limit of integration be extended to  $-\infty$ ?

$$\frac{df(E, T)}{dT} = ?$$

Change variables:  $x = \frac{E - \mu}{2k_B T}$

Helpful:  $\int_{-\infty}^{\infty} \frac{x^2}{\cosh^2 x} dx = \frac{\pi^2}{6}$

$$C_v = \frac{dE_{Tot}}{dT} = \int_0^{\infty} E \frac{df(E, T)}{dT} D(E) dE$$

$$C_v = \frac{\pi^2}{2} D(E_F) k_B^2 T$$

Interpretation:

Depends linearly on temperature - NOT independent

Size depends only on density of states at Fermi surface -  
small for semimetals; large for so-called “heavy fermions”

Also interpreted as each electron near Fermi surface  
contributing roughly  $k_B$  to heat capacity:

$$C_v = D(E_F) k_B T \times k_B$$

$$C_v = \frac{dE_{Tot}}{dT} = \int_0^{\infty} E \frac{df(E, T)}{dT} D(E) dE$$

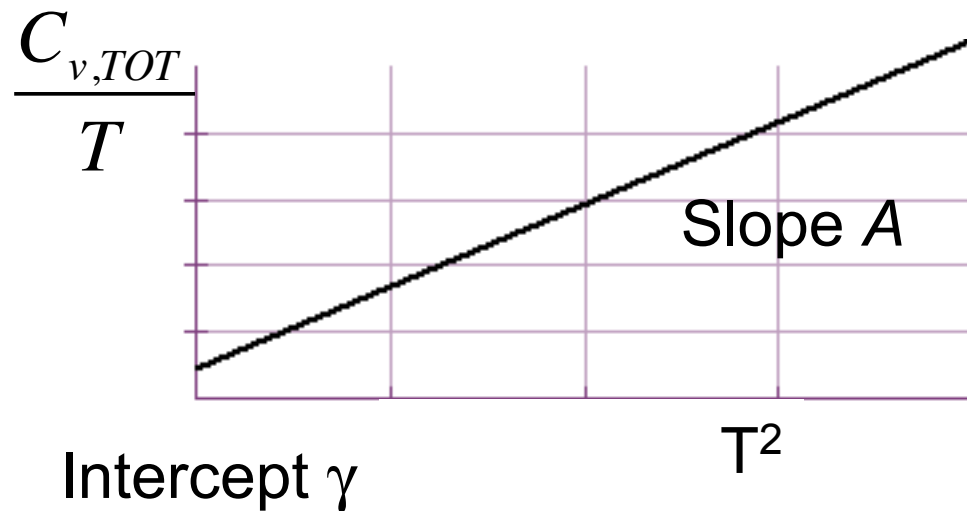
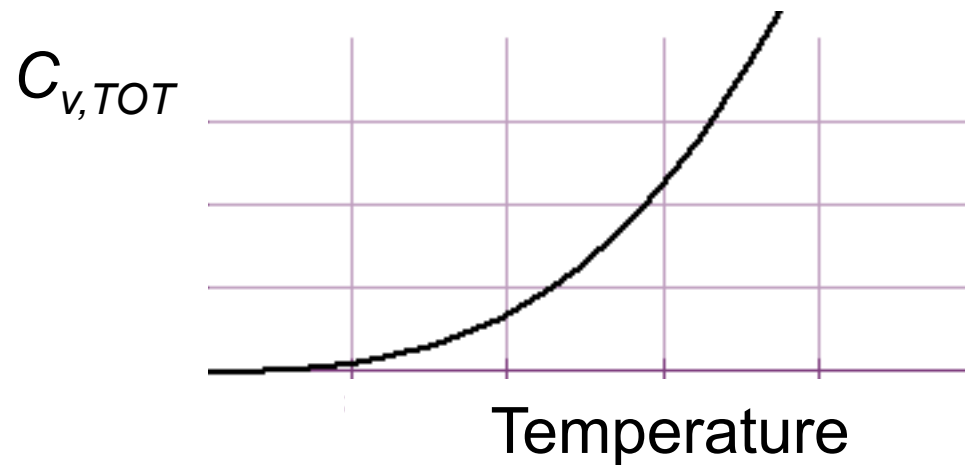
$$C_v = \frac{\pi^2}{2} D(E_F) k_B^2 T$$

$$C_{v,FE} = \frac{\pi^2}{2} N k_B \frac{T}{T_F}$$

*Much* smaller than expected from classical theory:

$$C_{v,class} = \frac{3}{2} N k_B$$

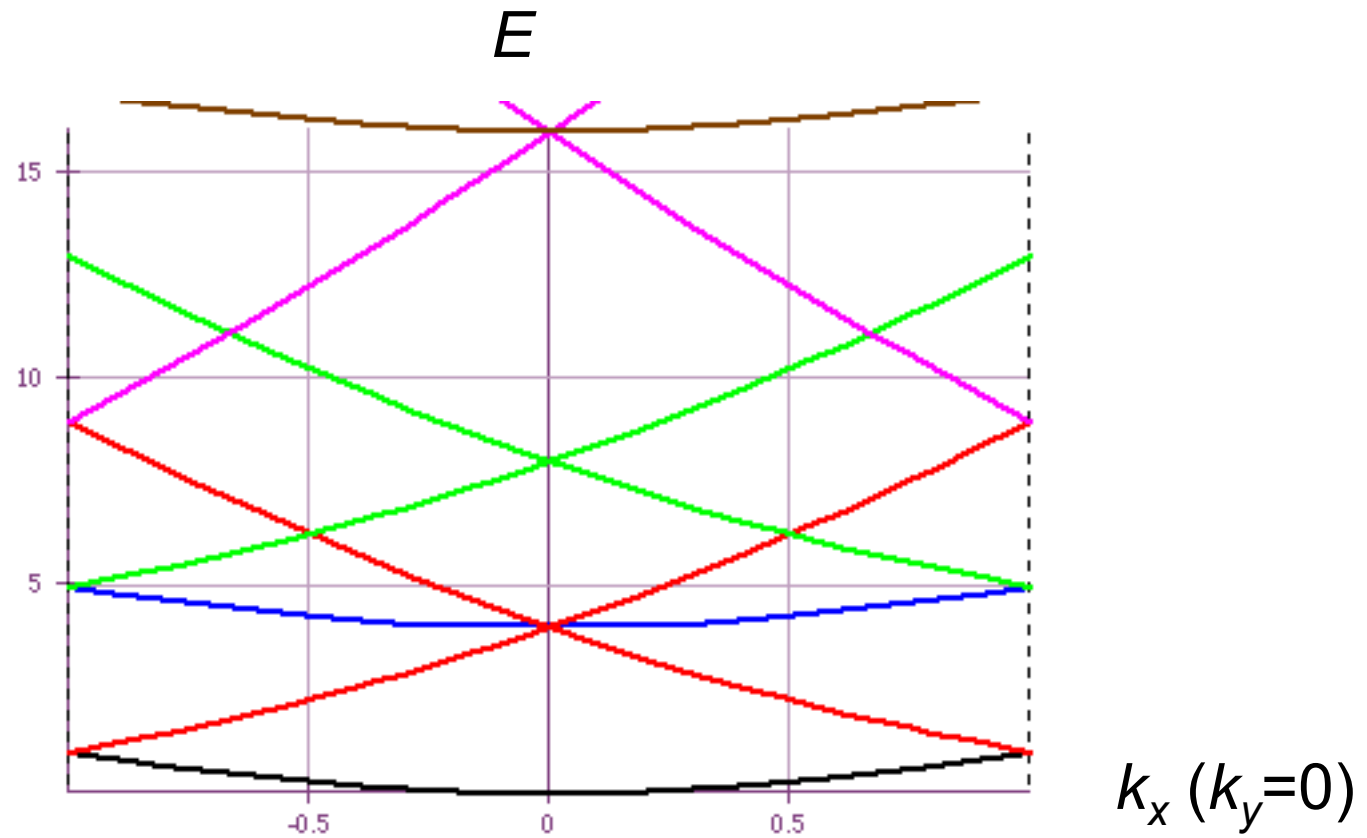
$$C_{v,TOT} = \overbrace{\gamma T}^{\text{electronic}} + \overbrace{AT^3}^{\text{phonon}}$$



	$\gamma_{\text{expt}}$ (mJ/mol/K <sup>2</sup> )	$\gamma_{\text{fe}}$ (mJ/mol/K <sup>2</sup> )
Na	1.38	1.09
K	2.08	1.67
Cu	0.70	0.51
Zn	0.64	0.75
Ag	0.65	0.65

EXTRA SLIDES ABOUT FREE ELECTRON BANDS

# Free electron bands: square lattice, reduced zone scheme

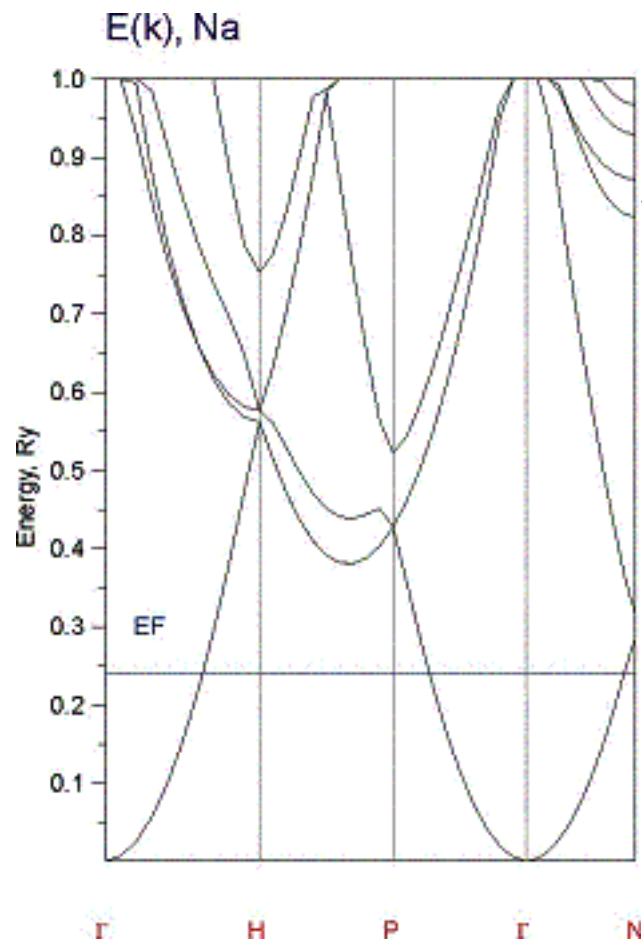


$$E = \frac{\hbar^2 |\vec{k} + \vec{G}|^2}{2m}$$

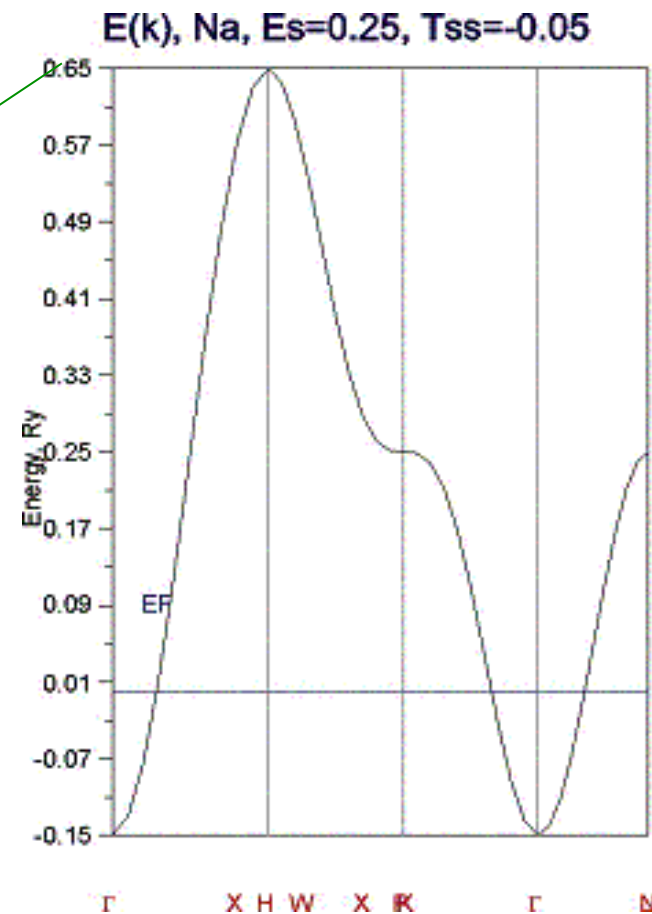


Free electron bands & LCAO (tight binding) bands are qualitatively similar, with important exception of gaps. (Sutton, Fig. 7.6, Ge e.g.)  
 So free electron model works well only for metals.

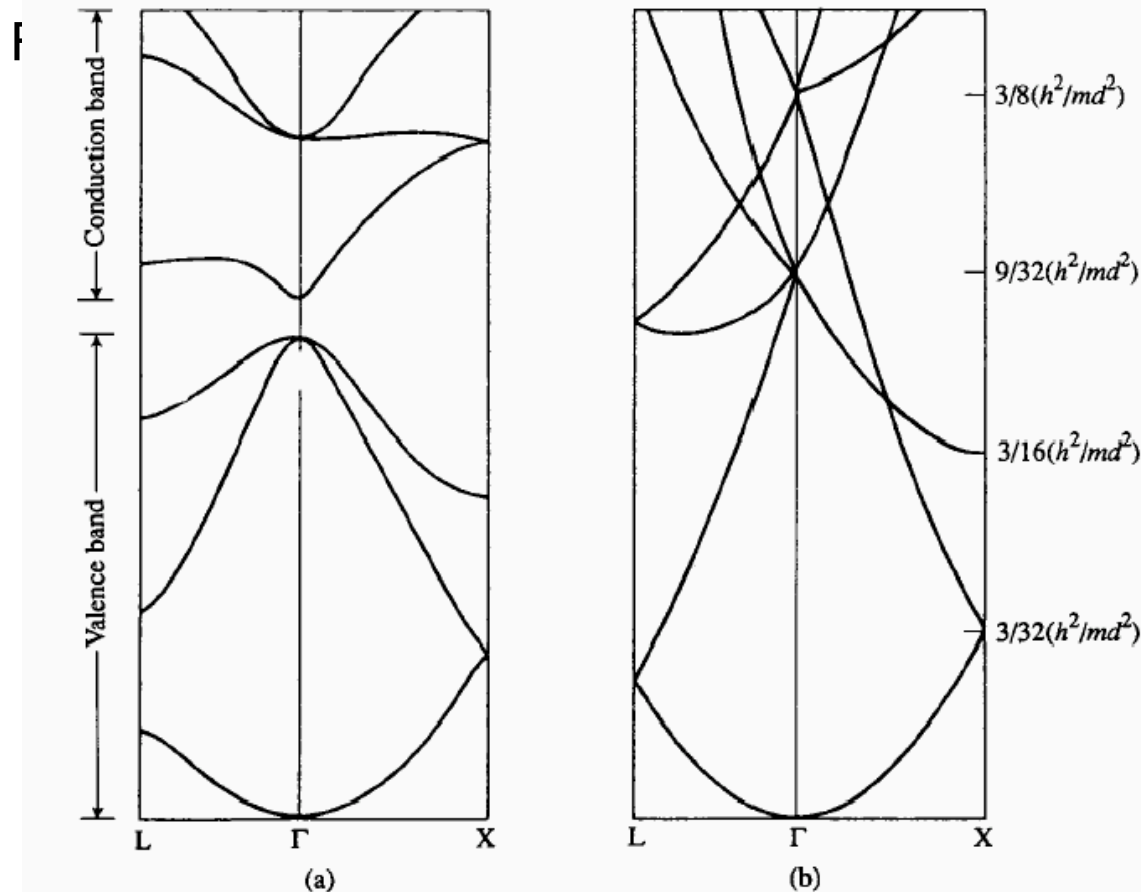
FE bands (Na - bcc)



LCAO band (Na)



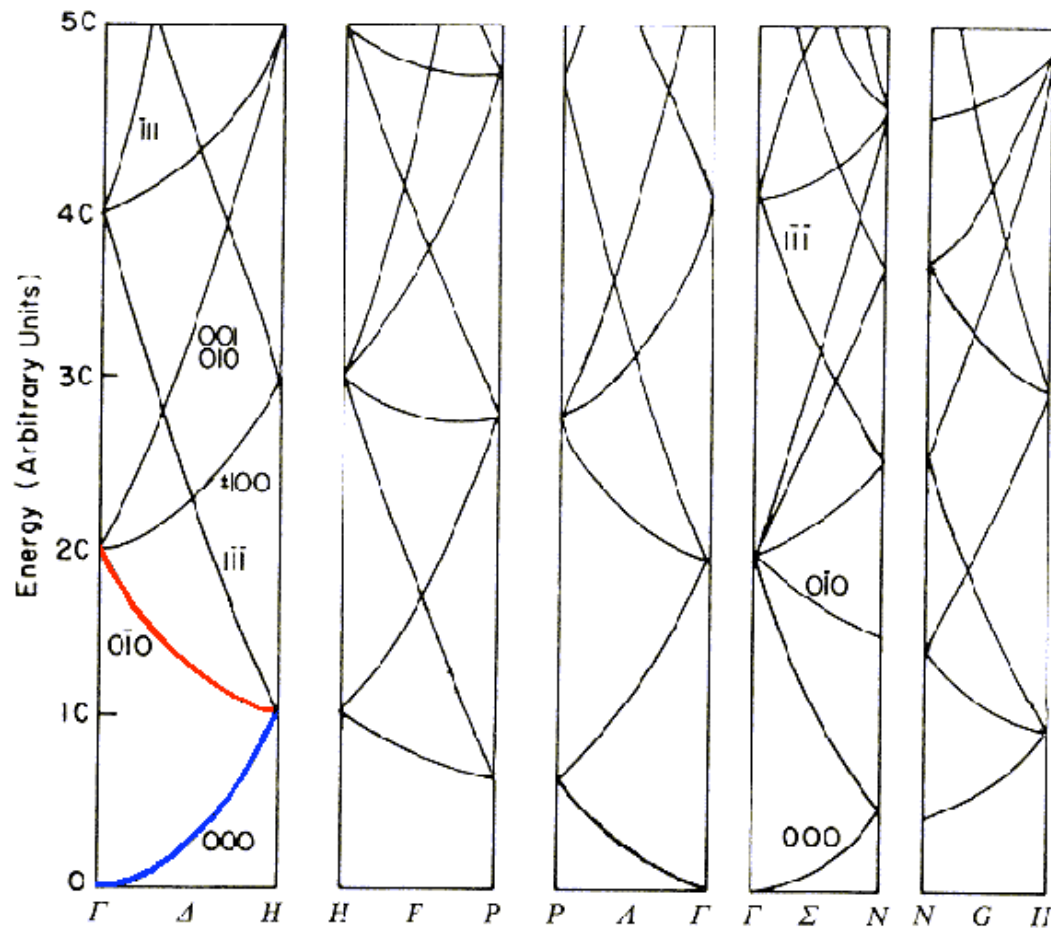
Free electron bands & LCAO (tight binding) bands are qualitatively similar, with important exception of gaps. (Sutton, Fig. 7.6, Ge e.g.)  
 So free electron model works well only for metals.



**Fig. 7.6** Comparison between the LCAO bands for Ge, computed with an  $sp^3$  basis, and the free electron bands. From Harrison (1980).

# Free electron bands: bcc lattice

$$E = \frac{\hbar^2 |\vec{k} + \vec{G}|^2}{2m}$$



[http://www.tf.uni-kiel.de/matwis/amat/semi\\_en/kap\\_2/illustr/band\\_bcc\\_free.gif](http://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_2/illustr/band_bcc_free.gif)

