

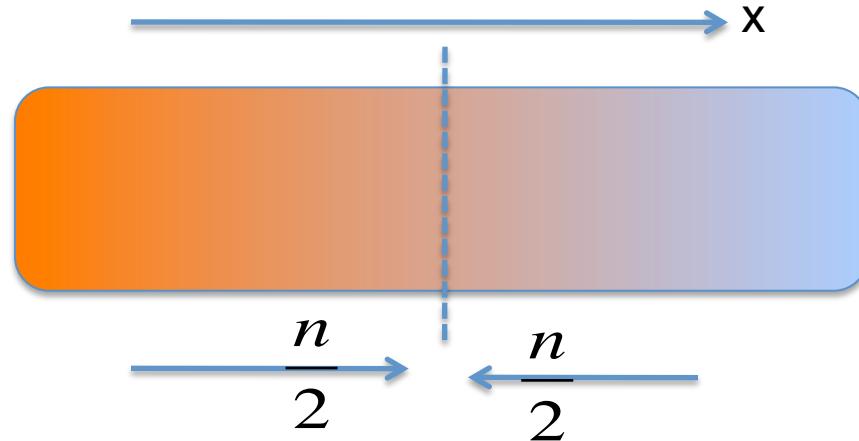
The Drude Theory of Metals

- continued



Drude's Approach in thermal conductivity κ

$$\kappa = \frac{1}{3} v^2 \tau c_v$$



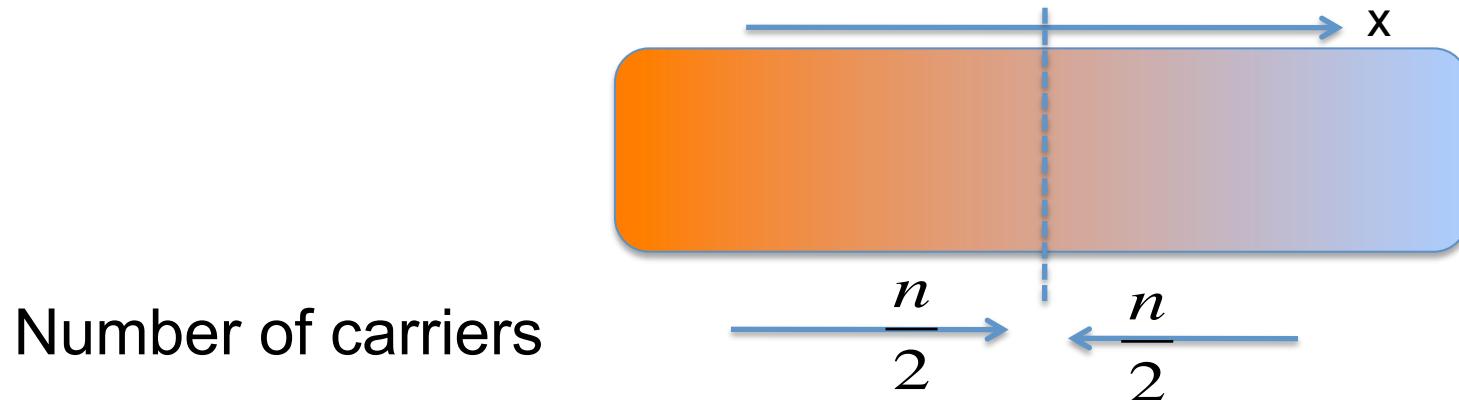
Number of carriers

$$\text{Thermal current } \frac{n}{2} v_x \epsilon [T(x - v_x \tau)] - \frac{n}{2} v_x \epsilon [T(x + v_x \tau)]$$

Assuming v is location independent

In reality, v is location dependent, i.e., $v=v(x)$

When considering $v=v(x)$



Mean electronic
velocity

$$v_Q = \frac{1}{2} [v(x - v\tau) - v(x + v\tau)] = -v\tau \frac{dv}{dx} = -\tau \frac{d}{dx} \left(\frac{v^2}{2} \right)$$

3D

$$\vec{v}_Q = -\tau \frac{d}{dT} \left(\frac{v^2}{6} \right) \nabla T$$

$E = Q \nabla T$ -- **thermoelectric field**

\rightarrow **Seebeck coefficient or thermopower**

$$\vec{v}_E = -e \vec{E} \tau / m$$

Drude's Approach in thermopower Q

$$\vec{v}_Q = -\tau \frac{d}{dT} \left(\frac{v^2}{6} \right) \nabla T$$

$$\vec{v}_E = -e \vec{E} \tau / m$$

They are in opposite direction

At the equilibrium, $\vec{v}_E = -\vec{v}_Q$



$$Q = - \left(\frac{1}{3e} \right) \frac{d}{dT} \left(\frac{mv^2}{2} \right)$$

$$= - \frac{C_v}{3ne} ?$$

No $C_v \neq \frac{3}{2} nk_B$ $\frac{1}{2} mv^2 \neq \frac{3}{2} k_B T$

Why had Drude made incorrect estimate on c_v and kinetic energy?

$$c_v \neq \frac{3}{2} nk_B \quad \frac{1}{2} mv^2 \neq \frac{3}{2} k_B T$$

Electrons cannot be treated as an ideal gas (classic)
– Maxwell-Boltzmann distribution

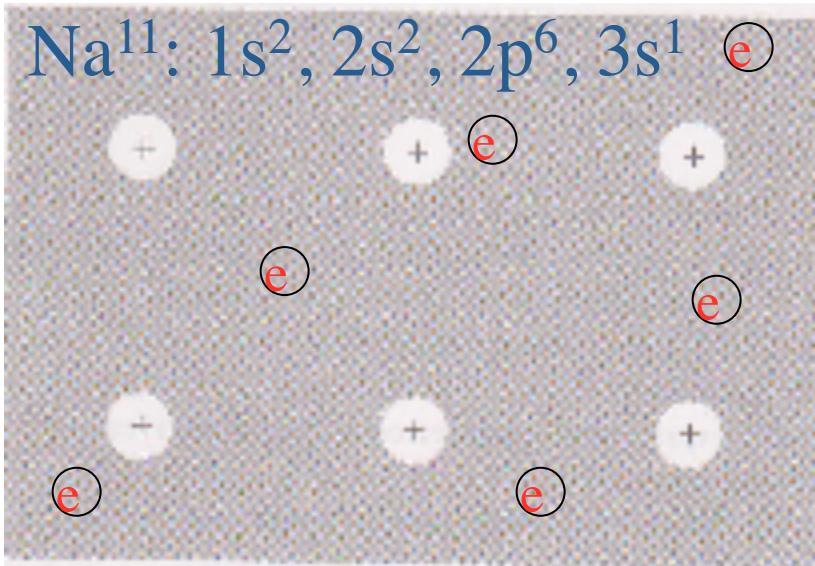
Drude did not consider Pauli exclusion principle



died in 1906



born in 1900



Electrons have to obey the
Pauli exclusion principle

-- no two electrons can have all
their quantum numbers identical

The Sommerfeld Theory of Metals

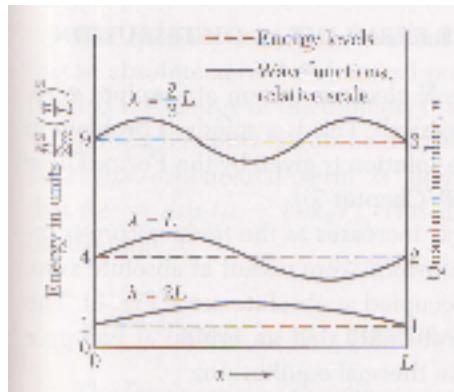


(1868 – 1951)

- Treat electrons with quantum Fermi-Dirac distribution
- 4 of his students received Nobel Prizes

Energy Levels

Considering a one-dimensional system with N electrons and length L,
the electron in the energy level ε_n has wavefunction ψ_n



$$\mathcal{H}\psi_n = \varepsilon_n \psi_n = -\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} \quad \text{For free-electron case}$$

Boundary conditions: $\psi_n(0) = 0 \quad \psi_n(L) = 0$

$$\boxed{\psi_n(x) = A \sin\left(\frac{2\pi}{\lambda_n} x\right) \quad \lambda_n = \frac{2L}{n} \quad \varepsilon_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L}\right)^2}$$

N electrons go to N different orbitals

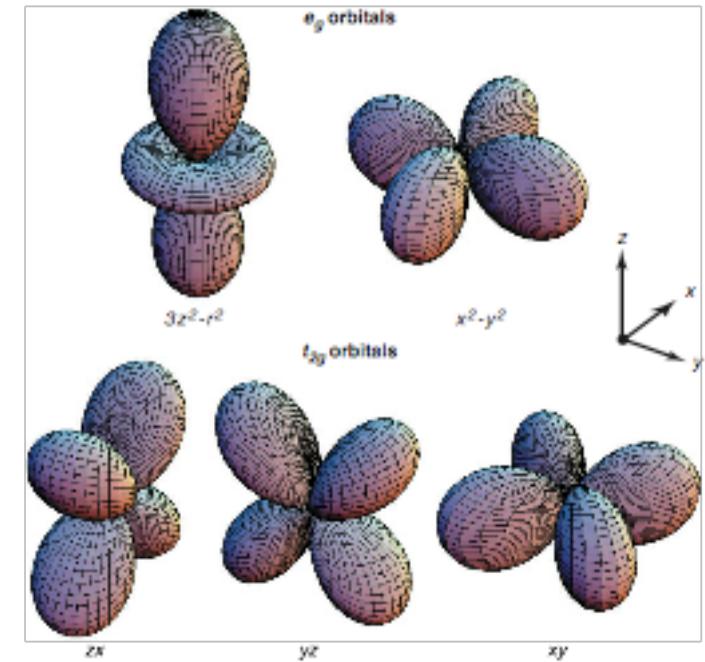
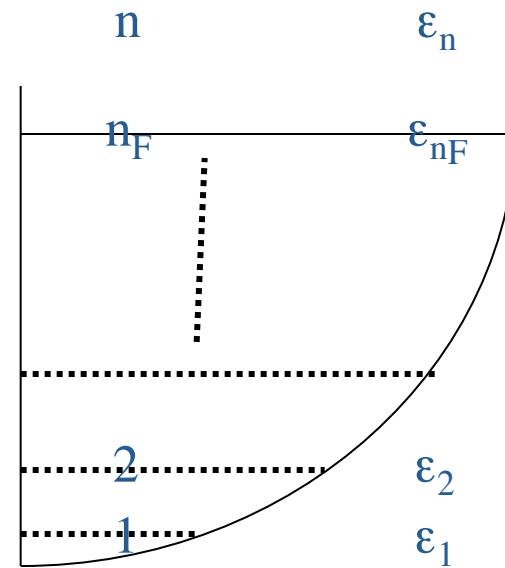
Electron orbital (n,m)

Since $m = +\frac{1}{2}$ (spin - up), $-\frac{1}{2}$ (spin - down)

Different orbitals may have the same energy.

Degeneracy: the number of orbitals with the same energy

The topmost level



Free Electron Gas In 3-Dimensions

1D

$$\mathcal{H}\psi_n = \varepsilon_n \psi_n = -\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2}$$

$$\psi_n(0) = 0 \quad \psi_n(L) = 0$$

$$\psi_n(x) = A \sin\left(\frac{n\pi}{L}x\right)$$

$$\varepsilon_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L}\right)^2$$

3D

$$\mathcal{H}\psi_n = \varepsilon_n \psi_n = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_n$$

$$\begin{aligned} \psi_n(x+L, y, z) &= \psi_n(x, y, z) \\ \psi_n(x, y+L, z) &= \psi_n(x, y, z) \\ \psi_n(x, y, z+L) &= \psi_n(x, y, z) \end{aligned}$$

$$\psi_n(r) = A \sin\left(\frac{n_x\pi}{L}x\right) \sin\left(\frac{n_y\pi}{L}y\right) \sin\left(\frac{n_z\pi}{L}z\right)$$

$$\varepsilon_n = \frac{\hbar^2}{2m} \left[\left(\frac{n_x\pi}{L}\right)^2 + \left(\frac{n_y\pi}{L}\right)^2 + \left(\frac{n_z\pi}{L}\right)^2 \right]$$

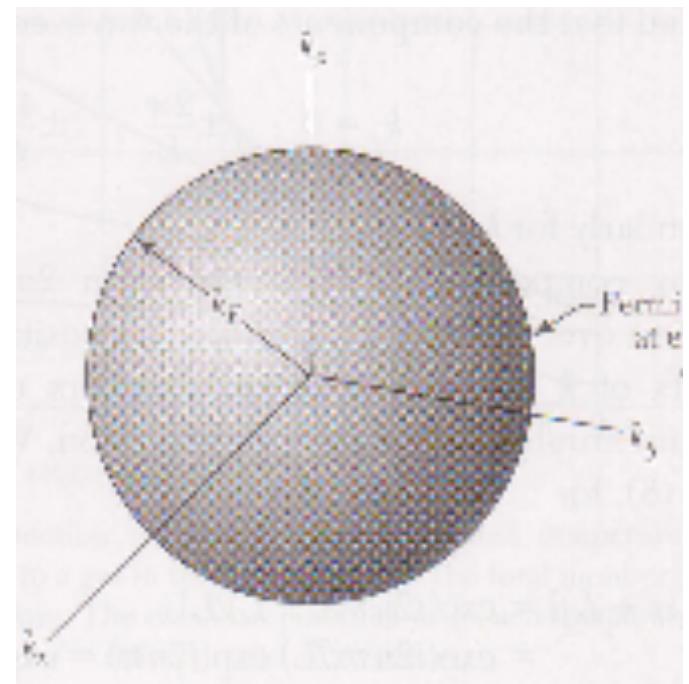
3D System in k-Space

$$\mathcal{H}\psi_k = \varepsilon_k \psi_k = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_k$$

↓

$$\psi_k(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})$$

$$\varepsilon_k = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m} [k_x^2 + k_y^2 + k_z^2]$$



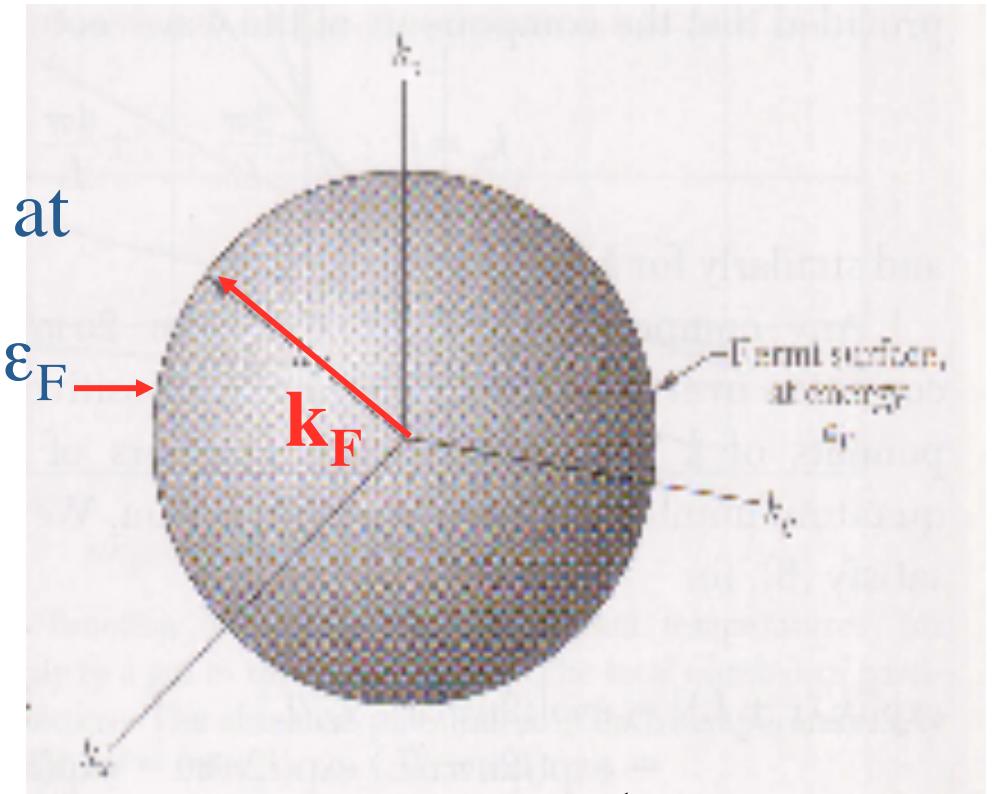
Fermi Surface

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

Fermi surface at

Fermi energy ϵ_F

At T = 0 K, all electrons
(N) reside within the sphere



$$N = 2 \frac{4\pi k_F^3 / 3}{(2\pi/L)^3}$$

Total volume

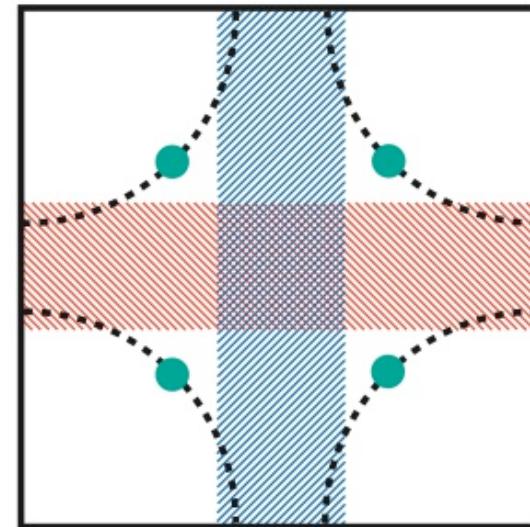
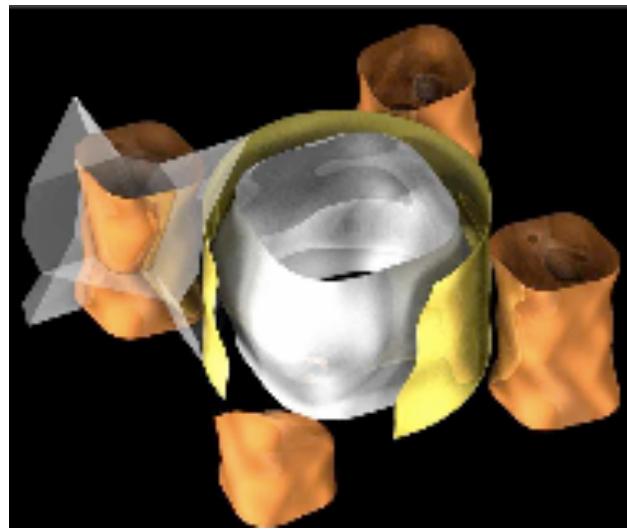
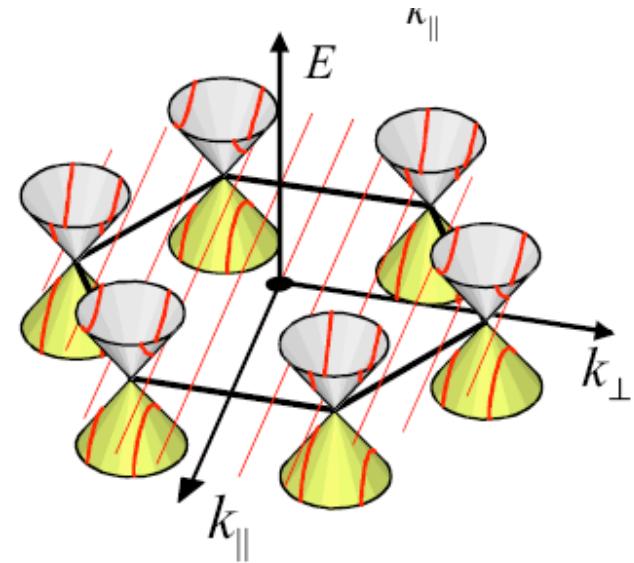
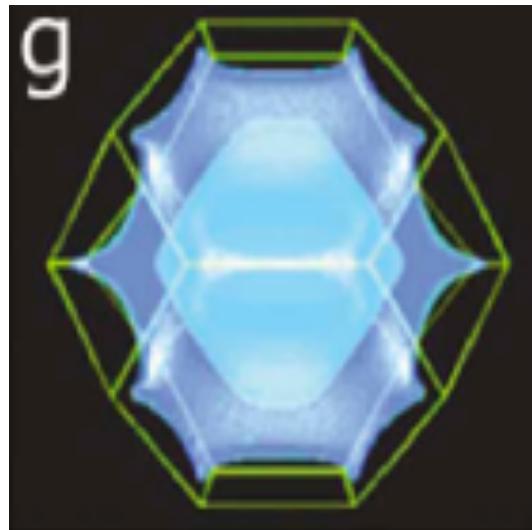
Volume/allowed K

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

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

The existence of a Fermi surface is a direct consequence of the Pauli exclusion Principle, which allows a maximum of one electron per quantum state.

Fermi Surface



Fermi velocity

-- electron velocity at the Fermi surface

Fermi momentum $p_F = mv_F = \hbar k_F$

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

Note $v_F \propto \frac{1}{m}$

Energy Density of Electrons

$$\frac{E}{V} \equiv \frac{1}{4\pi^3} \int_{k \leq k_F} d^3k \frac{\hbar^2 k^2}{2m} = \frac{1}{4\pi^3} \int_{k \leq k_F} (4\pi k^2) dk \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 k_F^5}{10m\pi^2}$$

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

$$\frac{N}{V} = \frac{k_F^3}{3\pi^2}$$



$$\frac{E}{N} = \frac{3}{5} \left(\frac{\hbar^2 k_F^2}{2m} \right) = \frac{3}{5} \epsilon_F$$

Fermi Temperature

Definition: $\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} = k_B T_F$

$$T_F = \frac{\varepsilon_F}{k_B} = \frac{\hbar^2 k_F^2}{2mk_B}$$



$$\frac{E}{N} = \frac{3}{5} \varepsilon_F = \frac{3}{5} k_B T_F$$

Recall Drude gives:

$$\frac{E}{N} = \frac{3}{2} k_B T$$

**FERMI ENERGIES, FERMI TEMPERATURES, FERMI WAVE VECTORS, AND
FERMI VELOCITIES FOR REPRESENTATIVE METALS^a**

ELEMENT	r_s/a_0	\mathcal{E}_F	T_F	k_F	v_F
Li	3.25	4.74 eV	5.51×10^4 K	1.12×10^8 cm $^{-1}$	1.29×10^8 cm/sec
Na	3.93	3.24	3.77	0.92	1.07
K	4.86	2.12	2.46	0.75	0.86
Rb	5.20	1.85	2.15	0.70	0.81
Cs	5.62	1.59	1.84	0.65	0.75
Cu	2.67	7.00	8.16	1.36	1.57
Ag	3.02	5.49	6.38	1.20	1.39
Au	3.01	5.53	6.42	1.21	1.40
Be	1.87	14.3	16.6	1.94	2.25
Mg	2.66	7.08	8.23	1.36	1.58
Ca	3.27	4.69	5.44	1.11	1.28
Sr	3.57	3.93	4.57	1.02	1.18
Ba	3.71	3.64	4.23	0.98	1.13
Nb	3.07	5.32	6.18	1.18	1.37
Fe	2.12	11.1	13.0	1.71	1.98
Mn	2.14	10.9	12.7	1.70	1.96
Zn	2.30	9.47	11.0	1.58	1.83
Cd	2.59	7.47	8.68	1.40	1.62
Hg	2.65	7.13	8.29	1.37	1.58
Al	2.07	11.7	13.6	1.75	2.03
Ga	2.19	10.4	12.1	1.66	1.92
In	2.41	8.63	10.0	1.51	1.74
Tl	2.48	8.15	9.46	1.46	1.69
Sn	2.22	10.2	11.8	1.64	1.90
Pb	2.30	9.47	11.0	1.58	1.83
Bi	2.25	9.90	11.5	1.61	1.87
Sb	2.14	10.9	12.7	1.70	1.96

Fermi-Dirac Distribution

-- probability in finding an electron in the i^{th} level with energy of ε_i

$$f_i(\varepsilon_i) = \frac{1}{\exp\left(\frac{\varepsilon_i - \mu}{k_B T}\right) + 1}$$

-- chemical potential: $\mu = F_{N+1} - F_N$

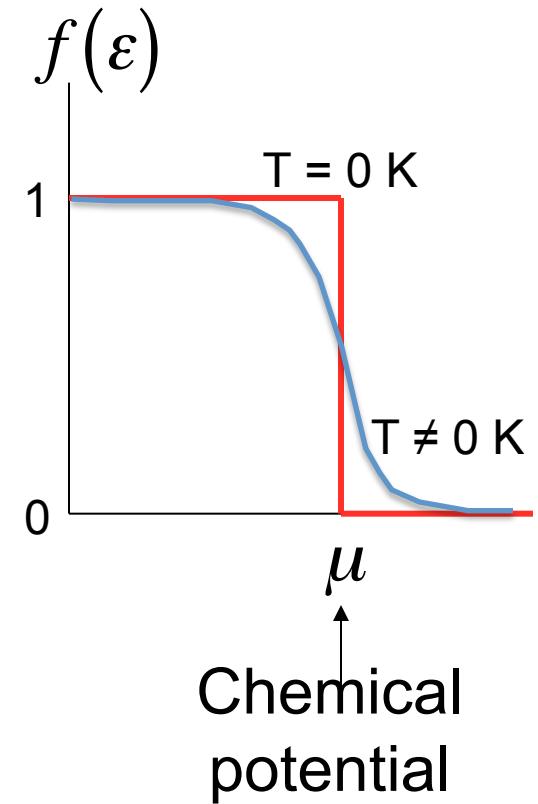
$$N = \sum_i f_i(\varepsilon_i) = \sum_i \frac{1}{\exp\left(\frac{\varepsilon_i - \mu}{k_B T}\right) + 1}$$

Electron Distribution

$$f(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{k_B T}\right) + 1}$$

$T = 0 \text{ K}$: all electrons stay
in the ground state

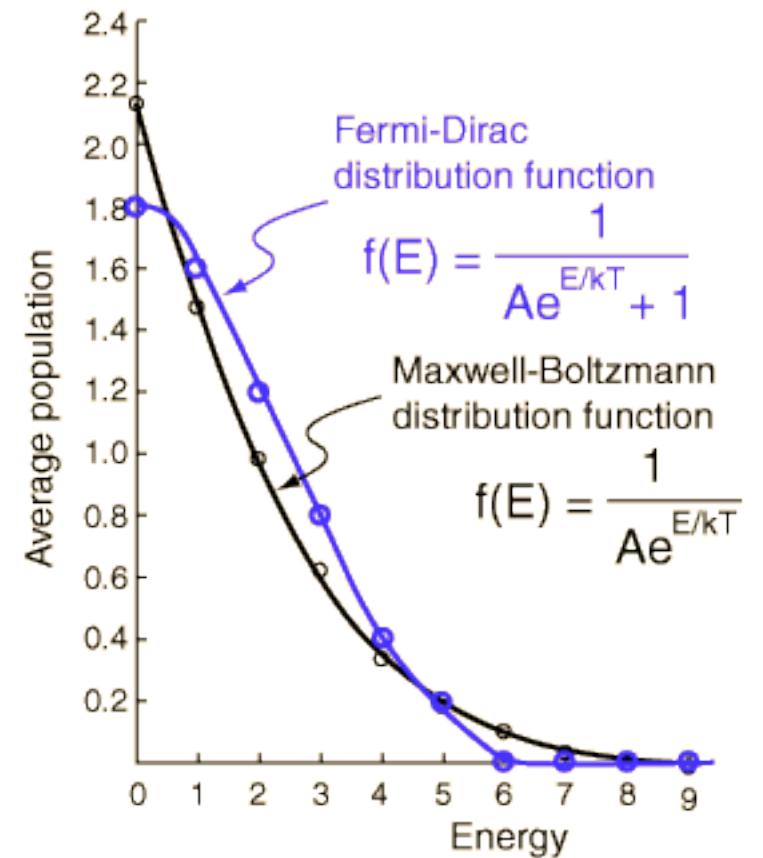
$T \neq 0 \text{ K}$: excitations due to
thermal energy



Fermi-Dirac vs. Maxwell-Boltzmann Distribution (Drude used)

$$f_{M-B}(\varepsilon) = \exp\left(\frac{\mu - \varepsilon}{K_B T}\right)$$

$$f_{F-D}(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{K_B T}\right) + 1}$$



Electron Density of States $g(\varepsilon)$

-- the number of orbitals per unit energy range

$$g(\varepsilon) \equiv \frac{dN}{d\varepsilon} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon}$$

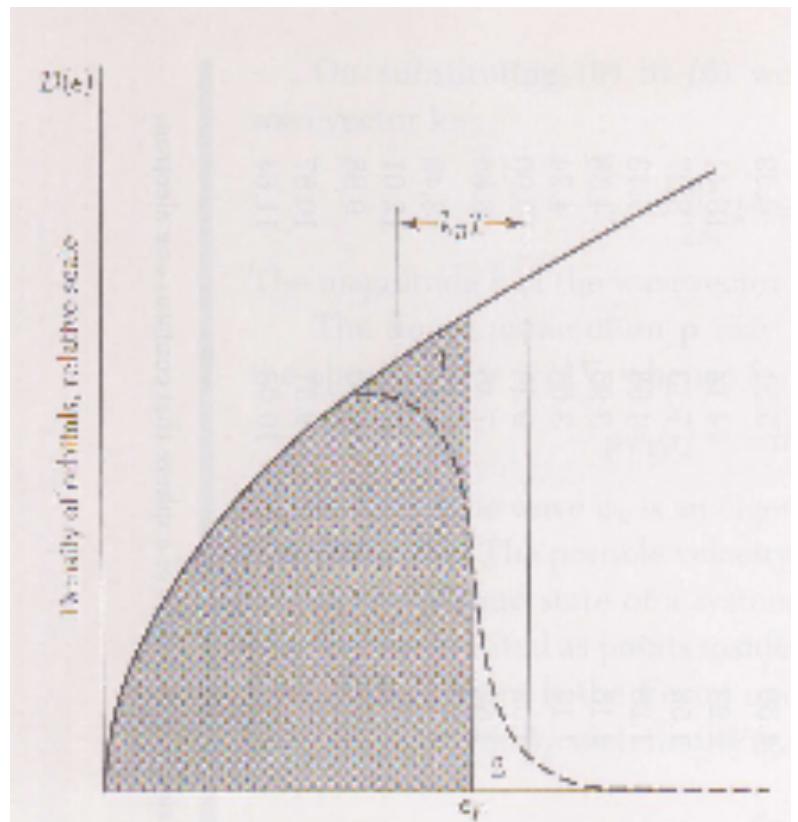
using $N = \frac{V}{3\pi^2} \left(\frac{2m\varepsilon}{\hbar^2} \right)^{3/2}$

$g(\varepsilon)$ versus ε

$$g(\varepsilon) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon} \quad \varepsilon \leq \varepsilon_F$$

$$= 0 \quad \varepsilon > \varepsilon_F$$

$$g(\varepsilon_F) = \frac{mk_F}{\hbar^2\pi^2} = \frac{3}{2} \frac{n}{\varepsilon_F}$$



Homework today (due on Sept. 16, 2010)

1. Problem 1a in page 53 (Ashcroft/Mermin)
2. Show that the kinetic energy of a three-dimensional gas of N free electrons at 0K is

$$U_0 = \frac{3}{5} N \varepsilon_F$$