# PYL 102

Thursday, Sept. 19, 2024

Drude and Sommerfeld model

# Drude Model

- Positive charges immobile and 'valence' electrons get detached and wander freely in metals.
- Neglect e-e interaction.
- Neglect electron-core interaction.
- Only way electron 'sees' core is by scattering.

# Basic assumption of Drude model

1. Between collisions electrons move in straight line - effect of electron-electron interaction is ignored (reasonably valid) – effect of electron-ion in ignored (completely invalid).
2. Mean free time between collisions is $\tau$ (probability of collision per unit time is $1/\tau$; probability of having a collision in infinitesimal time interval dt is $dt/\tau$
3. Relaxation time is independent of position and velocity of electron.

4. Electrons achieve thermal equilibrium by collisions with lattice – they emerge after collision at a random direction with speed appropriate to the temperature of the region where collision happened – the hotter the region; the higher the speed of the emerging electrons.

Note: electrons (unlike gas molecules) are charged and are moving in the background of other charged entities; electron densities also large ($\sim 10^{28}/cm^3$ ); still Drude applied kinetic theory (valid for neutral dilute classical gas) to metals.

# Application of Drude model: DC Electrical Conductivity of metal

If $n$ = number of charges e per unit volume, what is the

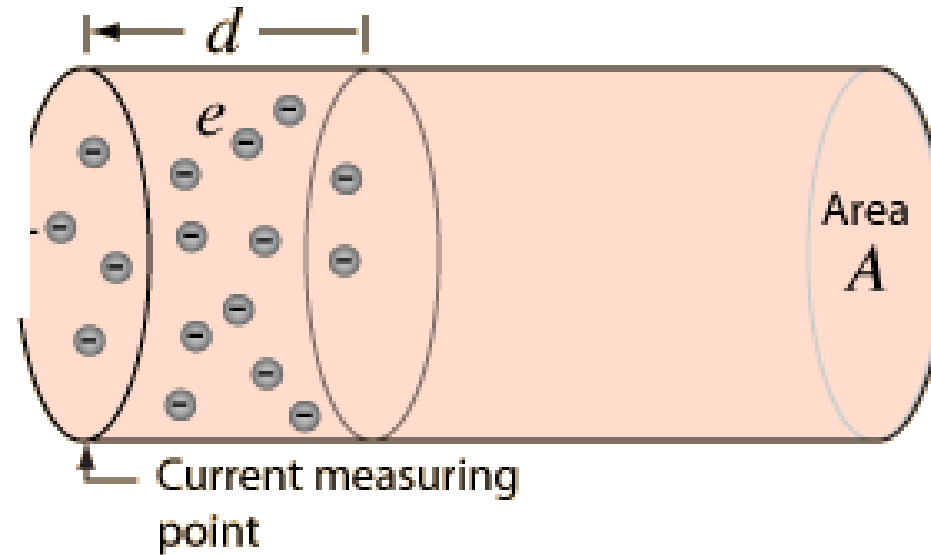total mobile charge in length d of the conductor
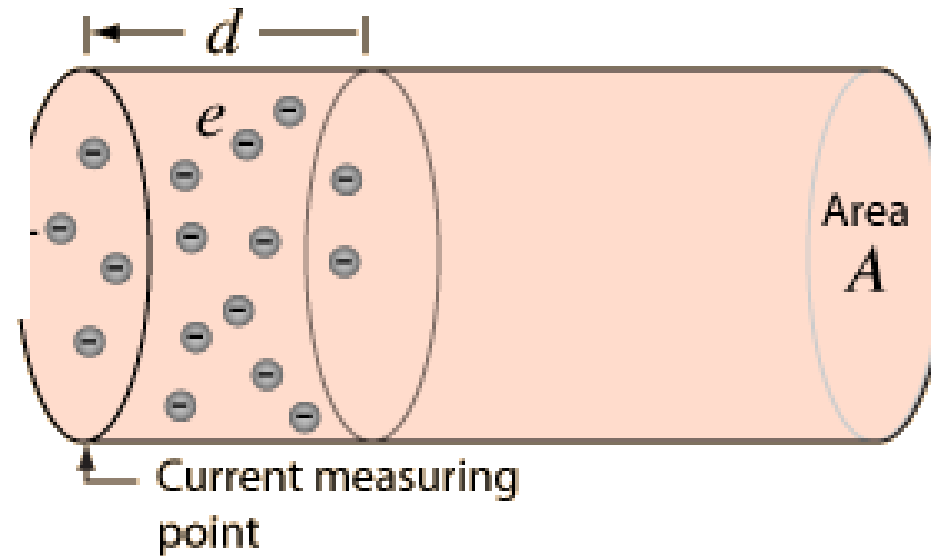
# Application of Drude model: DC Electrical Conductivity of metal

$V_d$ = drift velocity or average **velocity** (not speed) of conduction electrons

If $n$ = number of charges e per unit volume,

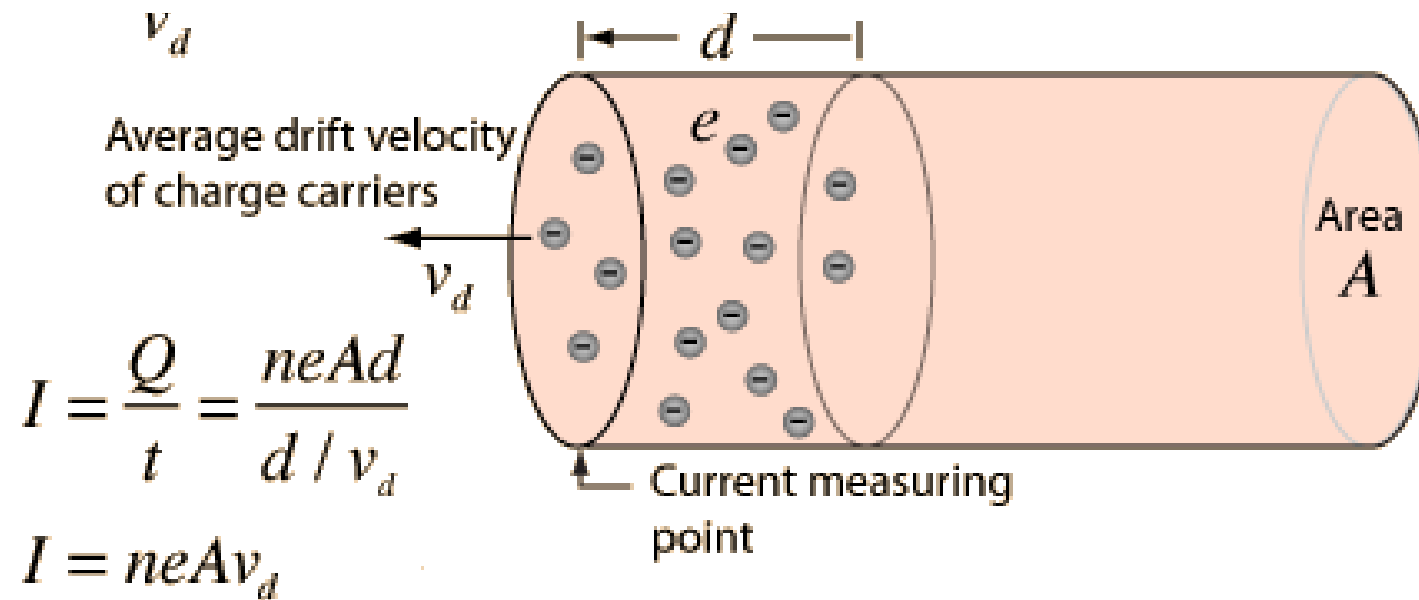$Q = neAd$ = total mobile charge in length d of the conductor

# Application of Drude model: DC Electrical Conductivity of metal

$V_d$ = drift velocity or average **velocity** (not speed) of conduction electrons

If $n$ = number of charges e per unit volume,

$Q = neAd$ = total mobile charge in length d of the conductor



$$I = \frac{Q}{t} = \frac{neAd}{d/v_d}$$

$$I = neAv_d$$

Current Density: $J = I/A$

Consider an electron, whose velocity immediately after collision (say at $t=0$) is $\vec{v}_o$. Let the electric field be $\vec{E}$. Its velocity at time $t$ would be given as

$$\vec{v}(t) = \vec{v}_o - \frac{e\vec{E}t}{m}$$

provided electron does not suffer a collision in between.

The average (drift) velocity of all the electrons would be given by.

$$\vec{v}_D = \langle \vec{v} \rangle = -\frac{e\vec{E}\tau}{m}$$

If $n$ is the total number of electrons per unit volume, then current density is given as follows.

$$\vec{J} = -ne\vec{v}_D = \frac{ne^2\tau}{m}\vec{E}$$

# Ohm's Law

$$\vec{J} = \sigma \vec{E}$$

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

$$\rho = \frac{1}{\sigma}$$

$v = \lambda/\tau$

$\lambda$ - mean free path (path travelled before collision)

$\sigma$ is called conductivity, while $\rho$ is called resistivity of the metals.
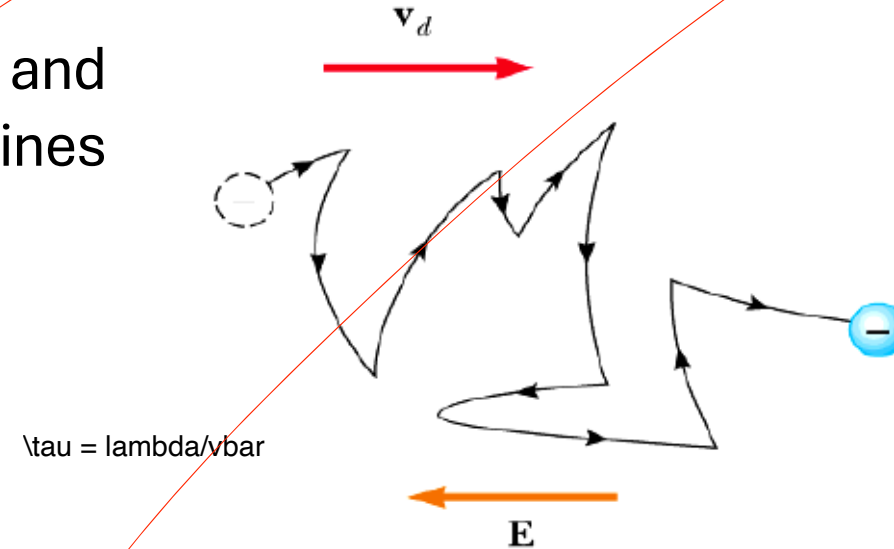
# Microscopic Description of Ohm's Law

Collisions between electrons and atoms in a conductor determines the conductivity
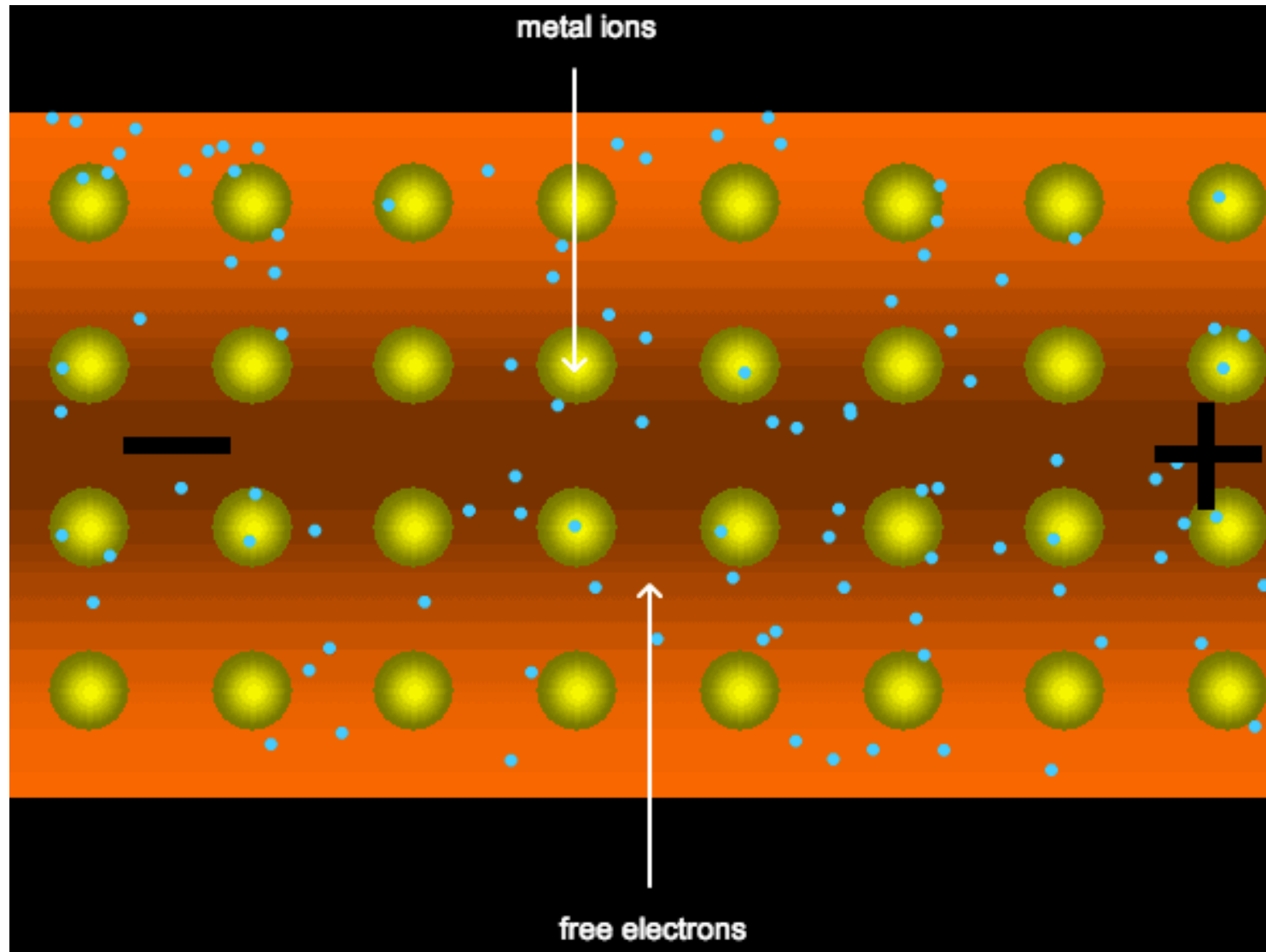
$$\sigma = \frac{n\lambda e^2}{m_e \bar{v}}$$

$\tau$ = lambda/vbar

$\mathbf{v}_d$

$\mathbf{E}$

$\lambda$: mean free path of an electron in the conductor, i.e., the average traveling distance of an electron that will not collide with an atom or other electron.

$n$: bulk electron density in a conductor

$\bar{v}$: average speed of an electron

# Microscopic Description of Ohm's Law

# Example:

$$\tau = m / (\rho n e^2) \qquad v_d = \Delta x / \tau$$

Calculate the average time between collisions $\tau$ for electrons in copper at 273 K.

| | Valence | $\sigma$ $(10^7\,\Omega^{-1}\,m^{-1})$ | $\rho$ $(10^{-8}\,\Omega\,m)$ | $n$ $(10^{28}\,m^{-3})$ |
|---|---|---|---|---|
| Sodium | 1 | 2.38 | 4.20 | 2.65 |
| Copper | 1 | 6.45 | 1.55 | 8.50 |
| Silver | 1 | 6.80 | 1.47 | 5.86 |
| Gold | 1 | 4.88 | 2.05 | 5.90 |
| Magnesium | 2 | 2.54 | 3.94 | 8.60 |
| Zinc | 2 | 1.82 | 5.50 | 13.2 |
| Aluminium | 3 | 4.00 | 2.50 | 18.1 |
| Tin | 4 | 0.87 | 11.5 | 14.5 |
| Lead | 4 | 0.52 | 19.2 | 13.2 |

Assuming that the average speed for free electrons in copper is 1.6 x $10^6$ m/s calculate their <u>mean free path</u>.

How reasonable is the formula $\sigma = \dfrac{ne^2\tau}{m}$

Estimate mean free path in equilibrium: $l = v_d \times \tau$

$$\frac{1}{2}mv^2 = \frac{3}{2}kT$$

Relaxation time ~ $10^{-14}$ s and v ~ $10^5$ m/s makes mean free path ~ Angstroms (lattice constant)

The mean free path gives an expected number.

# Problems with Drude model

- Conductivity depends on temperature, purity, crystalline quality.

- Much larger mean free paths have been observed experimentally (~ cm at low temperature).

- Observed small contribution to specific heat.

# Electronic heat capacity

The Drude model predicts the electronic heat capacity to be the classical "equipartition of energy" $C_{el} = 3/2\ nk_B$ This is independent of temperature.

Experimentally, the low-temperature heat capacity of metals follows the relationship $C_V = \gamma T + AT^3$ . The second term is obviously the phonon (Debye) component, leading us to suspect that $C_{el} = \gamma T$. Even at room temperature, the electronic component of the heat capacity of metals is much smaller than the Drude prediction. This is a severe failing of the model.

# Sommerfeld Model

1. Treats electrons using Fermi Dirac statistics.

2. Recognizes that their energies are discrete – treats them like a particle in a box of constant energy.

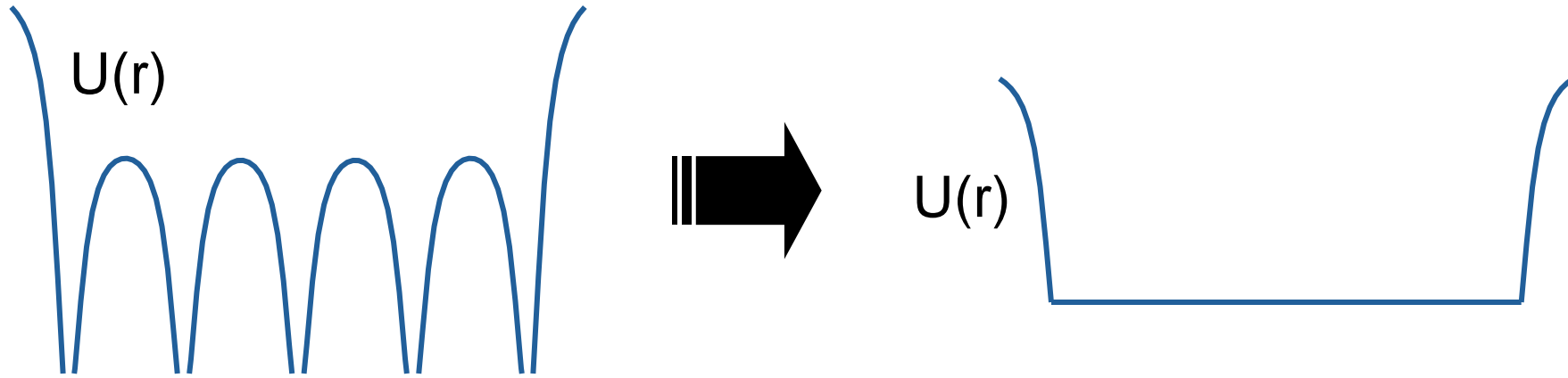3. Uses Pauli principle to distribute them in the available energy states.

# Improvement to the Drude Model

- Sommerfeld recognized we needed to utilize Pauli's exclusion principle Electrons cannot all be in the lowest energy state, since this would violate the Pauli Principle.
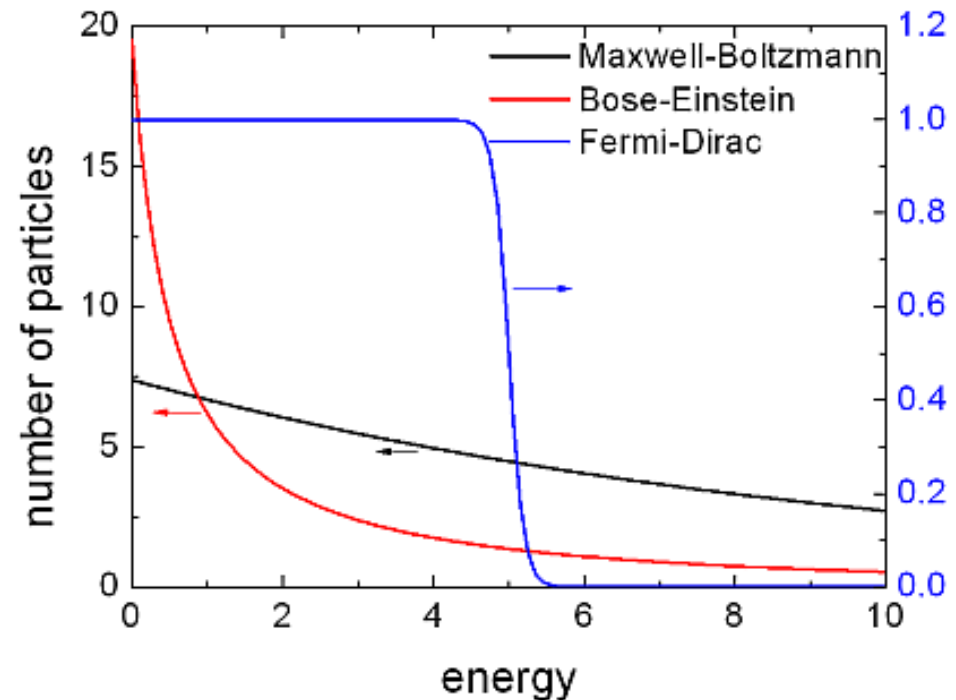
# Sommerfeld still assumes the free electron approximation



Neglect periodic potential & scattering

Reasonable for "simple metals" (Alkali Li,Na,K,Cs,Rb)

# Ground state of ideal electron gas

- These conduction electrons can be considered as moving independently in a square well and the edges of well corresponds to the edges of the sample. (ignores periodic potential from atoms)

- Electron confined in a cube of sides L, potential inside the cube is constant (take it to be zero) – potential at boundaries. Assume non-interacting electrons $\Psi(r_{1,}r_{2,...}r_N) = \Psi(r_1)\Psi(r_2)\ldots\ldots\Psi(r_N)$
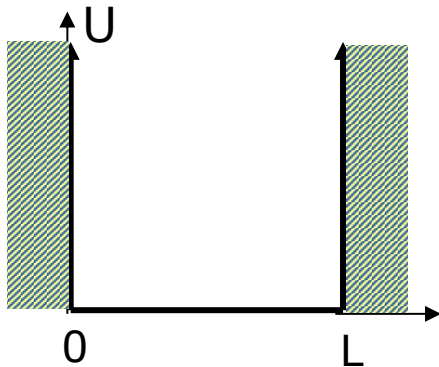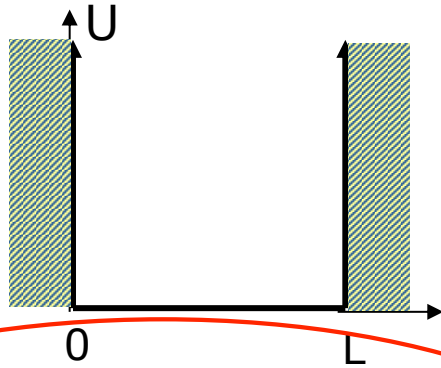
$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)\right]\psi = \varepsilon\psi$$

$\varepsilon$ is the total energy of the system. The square of the wave function ($\psi\,\psi^*$) is equal to the probability of finding the particle at a particular region of space.

U

0            L

Cube V=L$^3$

Electrons in crystals are moving through atomic potentials. Sommerfield/Drude models ignore those; use flat average.

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

U

0    L

Eigenstates $\psi(\vec{r}) = \frac{1}{\sqrt{V}}e^{i\vec{k}\bullet\vec{r}}$

with eigenvalues $\varepsilon = \frac{\hbar^2 k^2}{2m}$

Dispersion relation for e's

Possible Boundary conditions
1. Ψ(0)=0 and Ψ(L)=0
2. Ψ(x,y,z)= Ψ(x+L,y,z)

where $k = \frac{n\pi}{L}$ in 3D:

$$k_x = \frac{n_x\pi}{L}, k_y = \frac{n_y\pi}{L}, k_z = \frac{n_z\pi}{L}$$

Where $n_x$, $n_y$ and $n_z$ are integers

$$e^{i\vec{k}_x L} = 1 = e^{i\vec{k}_y L} = e^{i\vec{k}_z L}$$

For large N the filled states form a sphere in k-space – its radius is $k_F$ (this is called the Fermi wave-vector) and volume $\frac{4}{3}\pi k_F^3$. This is the Fermi sphere. At T = 0

$$N = 2 \times \frac{4}{3}\pi k_F^3 \times \frac{1}{\left(\frac{2\pi}{L}\right)^3}$$

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

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

Total energy of the electronic system is

$$E = 2 \times \sum_{k<k_F}\frac{\hbar^2 k^2}{2m}$$

For large N; the values of k are arbitrarily close to each other – can treat as continuum:

$$E = 2\frac{V}{8\pi^3}\int\frac{\hbar^2 k^2 dk}{2m} = \frac{1}{10}\frac{\hbar^2 k_F^5}{\pi^2 m}$$

Average energy per particle is

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

In contrast to a classical gas, the degenerate quantum mechanical electron gas has appreciable ground-state energy.
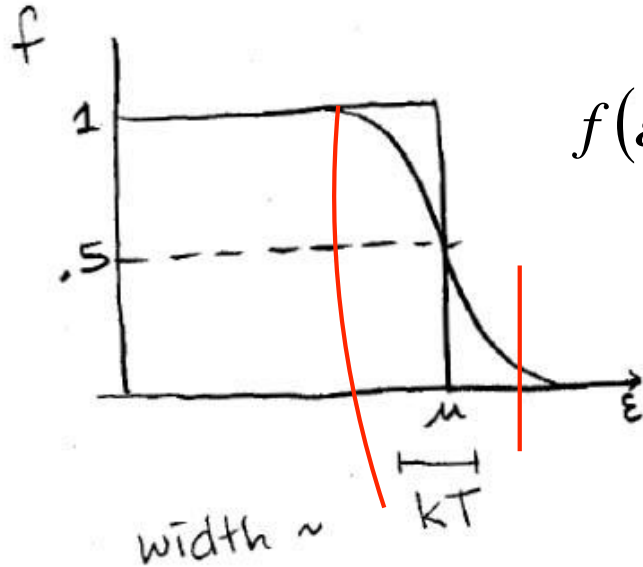
# Fermi Energy for Sodium

Density=0.971 g/cc

Atomic Weight=22.99

$$\frac{N}{V} = \frac{6.02 \times 10^{23} \times 0.971}{22.99} \times 10^{6}$$

$$= 2.543 \times 10^{28}$$

Substituting we get

$E_F$=3.16 eV

# Fermi-Dirac Distribution Function



$$f(\varepsilon, T) = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1}$$

Becomes a step function at T= 0.
Low E:  f ~ 1.
High E:  f ~ 0.

$\mu$ = chemical potential gives the probability of occupation of a state of energy E

$\mu(T=0)=\varepsilon_F$ Fermi energy

$$f(\varepsilon = \mu) = \frac{1}{1 + 1}$$   Right at the Fermi level:  f = 1/2.

Turning to the finite T figure, *f* only varies significantly within $k_B$T of μ. This has two implications.

1. As kBT≪EF, this implies that μ ≈ EF.

2. Only electrons with energies within kBT of μ, i.e. EF, will be able to contribute to thermal processes, transport etc.. Electrons further below μ will be unable to acquire sufficient thermal energy to be excited into empty states; states more than ~ kBT above μ will be empty

# DOS for 3-D crystal

The periodicity in atomic arrangement in a crystal give rise to a corresponding periodicity in the internal electric potential due to ion cores. Incorporating this periodic potential into the Schrödinger equation results in the allowed plane wave functions that are modulated by the lattice periodicity.

$$\Psi(r) = u_k(r)e^{ikr}$$

Where $u_k(r)$ has the property $u_k(r) = u_k(r+T)$, where T is lattice translations vector. Let us consider one dimensional case, with periodic boundary condition.

$$\Psi(x) = \Psi(x+L)$$

$$e^{ikx} = e^{ik(x+L)} \Rightarrow 1 = e^{ikL}$$

$$\Rightarrow k = \frac{2\pi n}{L} ; \Delta k = \frac{2\pi}{L}$$

Difference between consecutive k values is fixed.

For a 3D crystal, k space volume occupied by each wave vector state will be $8\pi^3/L^3$.

Now we will find out number of allowed states between sphere of radius k and k+dk

$$g(k)_{3D}\, dk = 2 \times \frac{4\pi k^2\, dk L^3}{8\pi^3} = \frac{k^2\, dk L^3}{\pi^2}$$

2 is introduced for spin up and spin down conditions for a given k value.

$$k = \sqrt{\frac{2mE}{\hbar^2}} \Rightarrow dk = \left(\frac{2mE}{\hbar^2}\right)^{-1/2} \frac{m}{\hbar^2}\, dE$$

$$N(E)_{3D}\, dE = \frac{2mE}{\pi^2\hbar^2}\left(\frac{2mE}{\hbar^2}\right)^{-1/2} \frac{m}{\hbar^2}\, dE = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}\, dE$$

<u>The electronic density of states at E ≈ EF</u> As only the electrons within ~ kBT of EF are able to take part in thermal processes, only the density of electron states at the Fermi energy, g(EF), will be particularly important in many calculations.
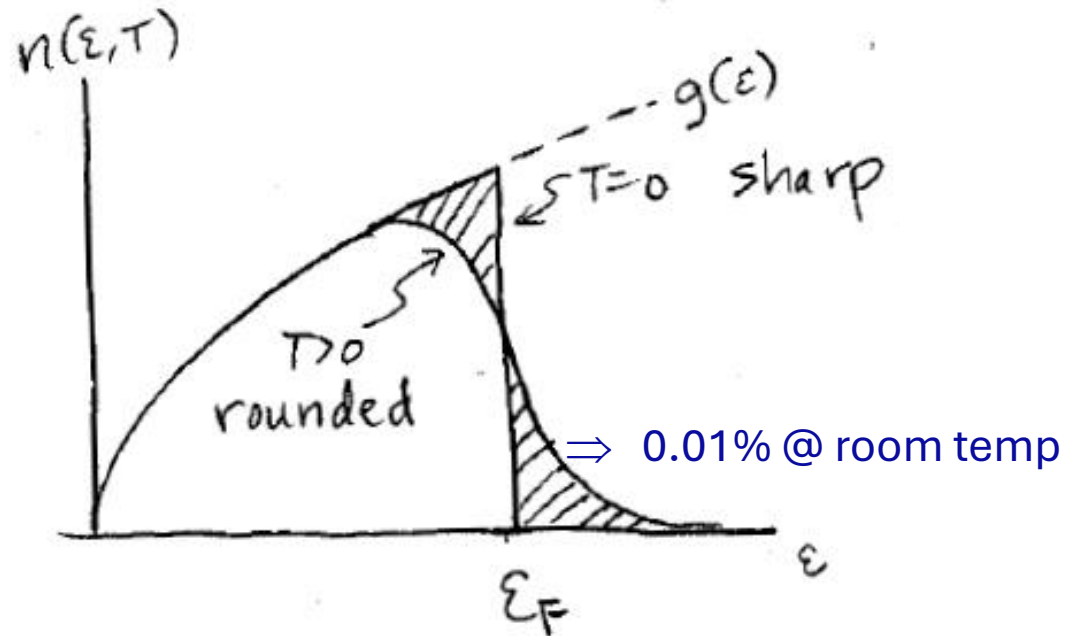In the free-electron approximation, the Fermi energy is given by $\quad E_F = \dfrac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3}$

g(E$_F$) ≡ dn/dE$_F$          ln(E$_F$) = 2/3 ln(n) + constant

g(E$_F$) = 3/2 (n/E$_F$)

# Density of Occupied States



Hand-drawn figure showing occupied density of states $n(\varepsilon, T)$ vs $\varepsilon$. The dashed curve is labeled $g(\varepsilon)$. A sharp step at $T=0$ ("T=0 sharp") and a rounded curve for $T>0$ ("T>0 rounded") are shown, with the Fermi energy $\varepsilon_F$ marked on the horizontal axis. Two shaded areas near $\varepsilon_F$ are indicated.

$\Rightarrow$ 0.01% @ room temp

n is conserved

Shaded areas are equal

# Electronic Heat Capacity

$n(\varepsilon, T)$

$g(\varepsilon)$

$\varepsilon_F$  $\varepsilon$  $T > 0$
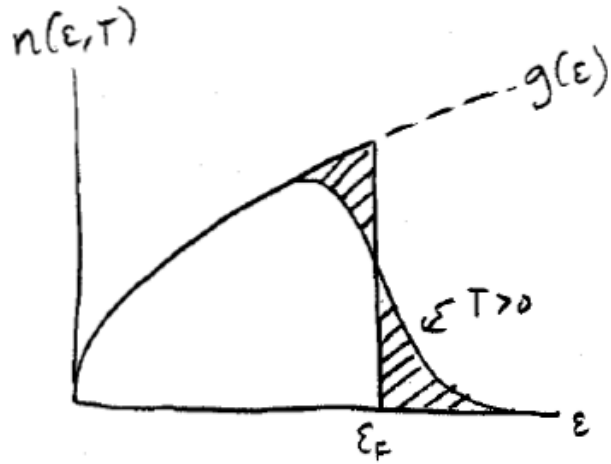
Width of shaded region ~ kT

Room temp T ~ 300K, $T_F$ ~ $10^4$ K

→ Small width

→ Few electrons thermally excited

How many electrons are excited thermally?

Shaded area ≈ triangle.  Area = (base)(height)/2

Number of excited electrons: ≈ $(g(\varepsilon_F)/2)(kT)/2 ≈ g(\varepsilon_F)(kT)/4$

Excitation energy ≈ kT (thermal)

Total thermal energy in electrons U(T):   $U(T) \, \alpha \, (kT)^2$

Why ??

## Electronic heat capacity   $C_{el} = \dfrac{dU}{dT}$

DOS $\quad g(E) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{\frac{1}{2}}$

At $T=0$

$$U(0) = \int^{E_F} E\, g(E)\, dE = \int_0^{E_F} E^{3/2} \left(\frac{1}{2\pi^2}\right) \left(\frac{2m}{\hbar^2}\right)^{3/2} dE$$

$\Rightarrow \boxed{U(0) = \frac{E^{5/2}}{5\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2}}$

At finite temp. $e's$ are excited into higher levels.

$$U(T) = \int_0^\infty E\, g(E)\, f_D(E,T)\, dE = \left(\frac{1}{2\pi^2}\right) \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{E^{3/2}}{e^{(E-\mu)/kT}+1}\, dE$$

$$U(T) = U(0) + \frac{n\pi^2 k^2 T^2}{4E_F} \quad (\text{for } \mu \simeq E_F >> kT)$$

$$C_{el} = \frac{dU(T)}{dT}$$

$$\boxed{C_{el} = \frac{1}{2} nk \left(\frac{kT}{E_F}\right)}$$

1. $C_{el}$ is proportional to T, as are experimental data
2. $C_{el}$ is a factor $\sim kT/E_F$ smaller than the classical (Drude) value, as are experimental data.