

The background of the slide is a light gray gradient, decorated with numerous realistic water droplets of various sizes. Some droplets are in the top left corner, others are scattered along the bottom edge, and a few are on the right side. The droplets have highlights and shadows, giving them a three-dimensional appearance.

Free Electron Fermi Gas In Metals

Many solids conduct electricity.

There are **electrons** that are **not bound** to atoms but are able to move through the whole crystal.

Conducting solids fall into two main classes; metals and semiconductors.

$\rho(RT)_{metals}; 10^{-6} - 10^{-8} \Omega - m$ And increases by the addition of small amounts of impurity.

The resistivity normally decreases monotonically with decreasing temperature.

$\rho(RT)_{pure-semiconductor} \gg \rho(RT)_{metal}$ And can be reduced by the addition of small amounts of impurity.

Semiconductors tend to become insulators at low T.

Free Electron Model

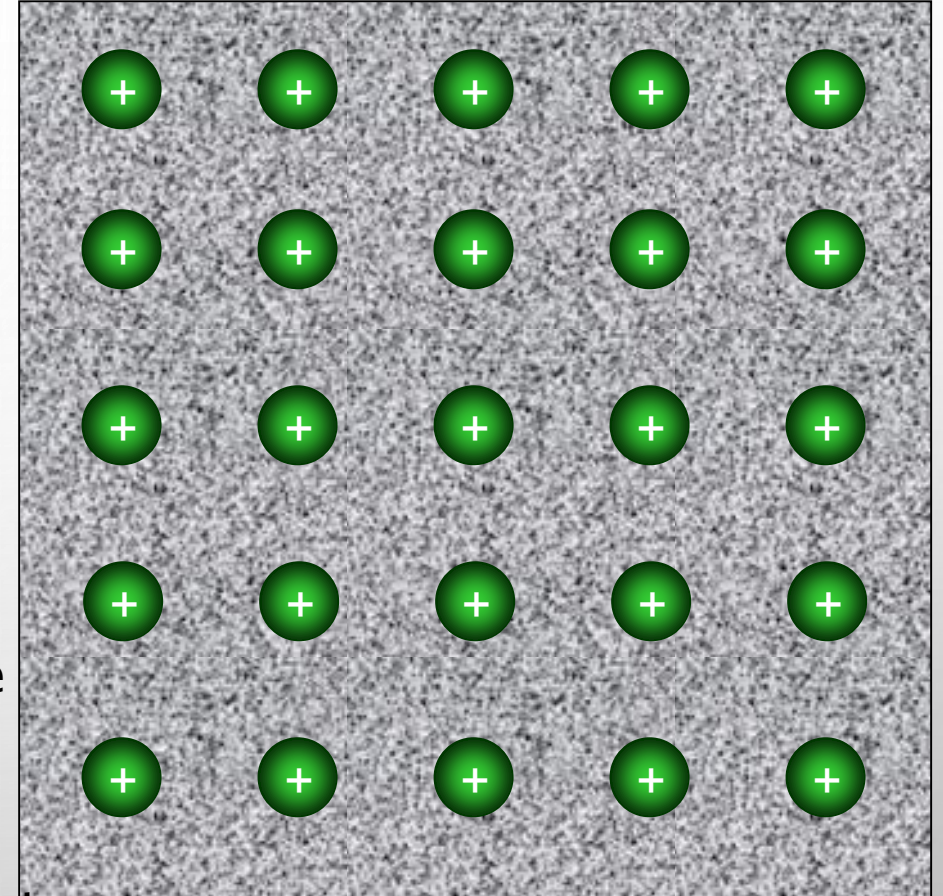
Schematic model of metallic crystal, such as Na, Li, K, etc.

The equilibrium positions of the atomic cores are positioned on the crystal lattice and surrounded by a sea of conduction electrons.

For Na, the conduction electrons are from the 3s valence electrons of the free atoms. The atomic cores contain 10 electrons in the configuration: $1s^2 2s^2 p^6$.

In this model, electrons are completely free to move about, free from collisions, except for a surface potential that keeps the electrons inside the metal.

In the alkali metals, with a bcc structure, the cores take up about 15% of the volume of the crystal, but in the noble metals (Cu, Ag, Au), with an fcc structure, the atomic cores are relatively larger and maybe close to contacting or in contact with each other.



PAUL Drude



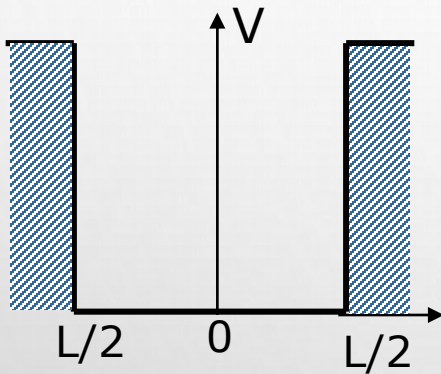
- resistivity ranges from $10^{-8} \Omega \cdot \text{m}$ (Ag) to $10^{20} \Omega \cdot \text{m}$ (polystyrene)
- Drude (circa 1900) was asking why? He was working prior to the development of quantum mechanics, so he began with a classical model:
 - positive ion cores within an electron gas that follows Maxwell-Boltzmann statistics
 - following the kinetic theory of gases- the electrons in the gas move in straight lines and make collisions only with the ion cores – no electron-electron interactions.
- He envisioned instantaneous collisions in which electrons lose any energy gained from the electric field.
- The mean free path was approximately the inter-ionic core spacing.
- Model successfully determined the form of **Ohm's law** in terms of free electrons and a **relation between electrical and thermal conduction** σ / κ , but failed to explain electron heat capacity and the magnetic susceptibility of conduction electrons, and mean free path

Fermi Gas model

- The removal of the valence electrons leaves a positively charged ion.
- The charge density associated the positive ion cores is spread uniformly throughout the metal so that the electrons move in a constant electrostatic potential. All the details of the crystal structure is lost when this assumption is made.
- According to FEM this potential is taken as zero and the repulsive force between conduction electrons are also ignored.
- Therefore, these conduction electrons can be considered as moving independently in a square well of finite depth and the edges of well corresponds to the edges of the sample.

Energy Levels In One Dimension

Consider a metal with a shape of cube with edge length of L ,
 Ψ and E can be found by solving schrödinger equation



$$H\Psi = E\Psi$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$$

Since $V = 0$

- By means of periodic boundary conditions Ψ 's are running waves.

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

Energy Levels In One Dimension

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

Orbital: solution of a 1-e Schrodinger equation

Since the $\psi_n(x)$ is a continuous function and is equal to zero beyond the length L , the boundary conditions for the wave function are

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

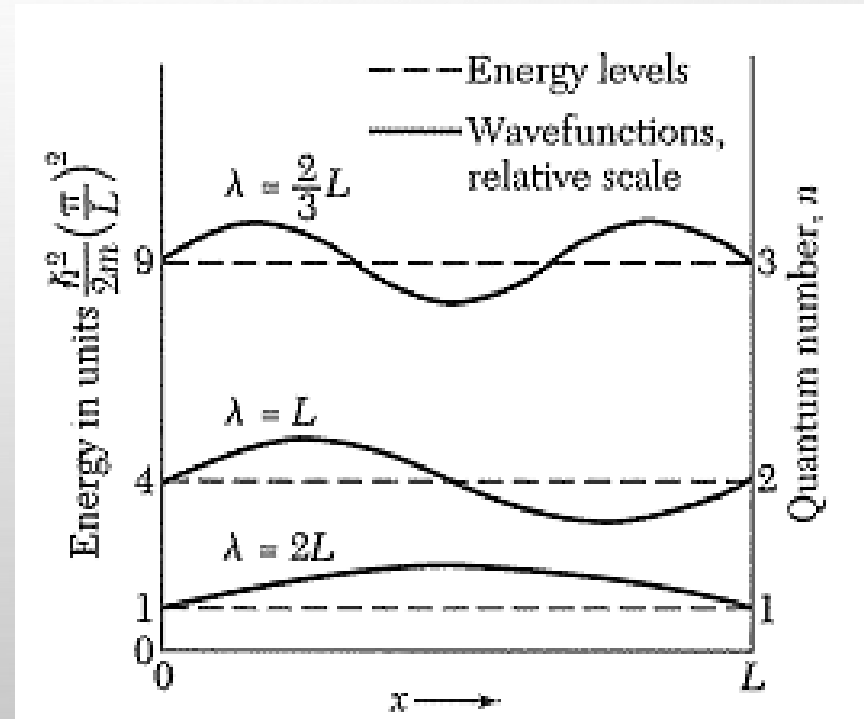
$$\psi_n = A \sin\left(\frac{n\pi}{L}x\right) = A \sin\left(\frac{2\pi}{\lambda_n}x\right)$$

$$n = 1, 2, \dots \quad \lambda_n = \frac{2}{n}L$$

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

These solutions correspond to standing waves with a different number of nodes within the potential well as is shown in Fig.

Particle in a box



Pauli-exclusion principle: No two electrons can occupy the same quantum state.

Quantum numbers for free electrons: (n, m_s) $m_s = \uparrow, \downarrow$

where n describes the orbital $\psi_n(x)$, and m_s describes the projection of the spin momentum on a quantization axis

Degeneracy: number of orbitals having the same energy.

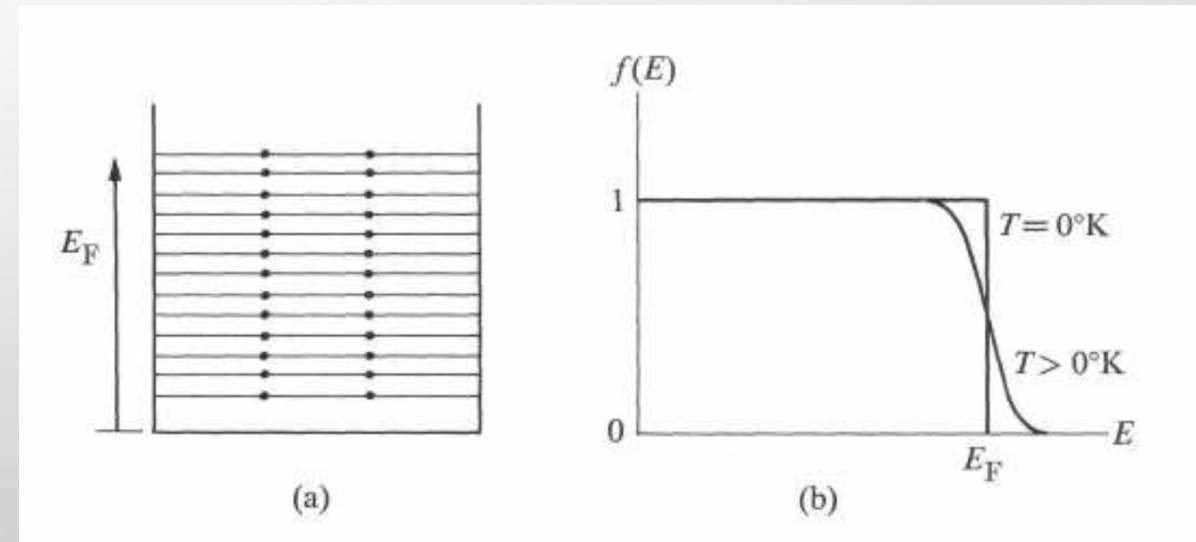
Fermi energy ε_F = energy of topmost filled orbital when system is in ground state (at $T=0\text{K}$).

For the onedimensional system of N electrons we find

$$\varepsilon_F = \frac{\hbar^2}{2m} \left(\frac{n_F \pi}{L} \right)^2 \quad n_F = \frac{N}{2} \quad \text{N number of valence electrons}$$

In metals the value of the Fermi energy is of the order of 5 eV.

(a) Occupation of energy levels according to the Pauli exclusion principle, (b) The distribution function $f(E)$, at $T = 0^\circ\text{K}$ and $T > 0^\circ\text{K}$.



Effect Of Temperature On The Fermi–Dirac Distribution

Fermi-Dirac distribution : $f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}$ $\beta = \frac{1}{k_B T}$

Fermi distribution function determines the probability of finding an electron at the energy E .

Chemical potential $\mu = \mu(T)$ is determined by $N = \int d\varepsilon g(\varepsilon) f(\varepsilon)$ $g = \text{density of states}$

At $T = 0$: $f(\varepsilon) = \begin{cases} 1 & \text{for } \varepsilon < \mu \\ 0 & \text{for } \varepsilon > \mu \end{cases}$

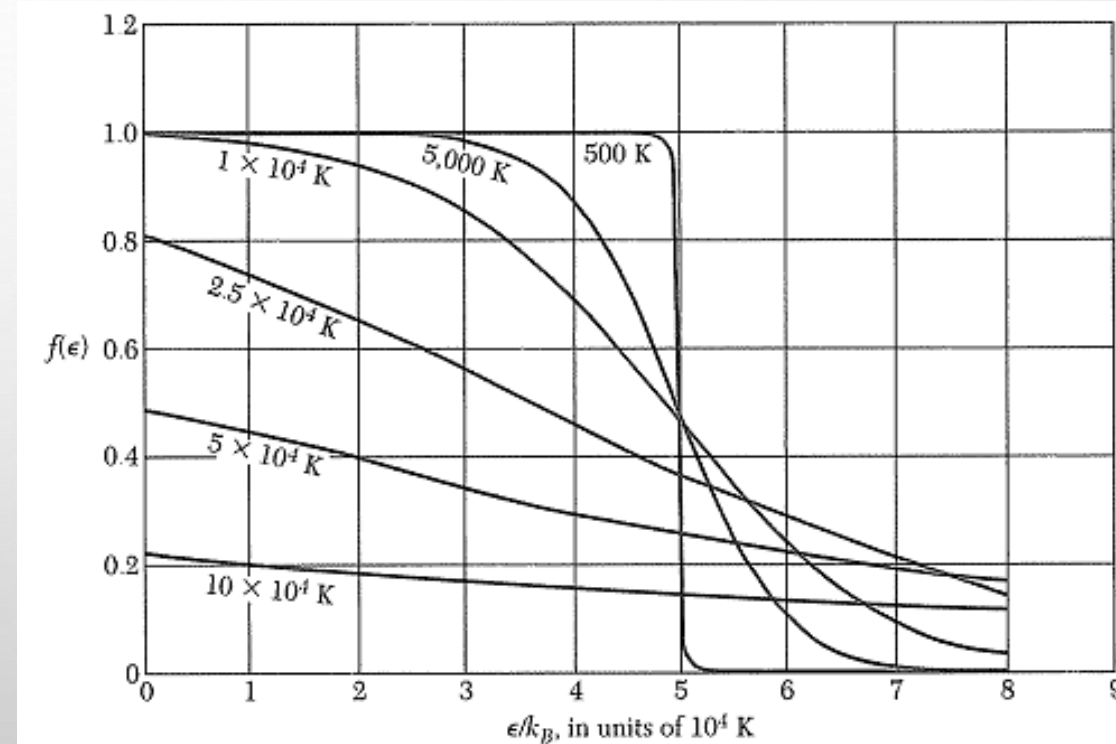
$\rightarrow \mu(0) = \varepsilon_F$

For all T : $f(\mu) = \frac{1}{2}$

At $T = 0$, Fermions occupy the lowest energy levels.
Near $T = 0$, there is little chance that thermal agitation will kick a **Fermion** to an energy greater than E_F .

For $\varepsilon \gg \mu$: $f(\varepsilon) \approx e^{-\beta(\varepsilon-\mu)}$

(Boltzmann distribution)



Free Electron Gas In Three Dimensions

$$H\psi(\mathbf{r}) = -\frac{\hbar^2}{2m} \left(\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} \right) = \varepsilon \psi(\mathbf{r})$$

If the electrons are confined to a cube of edge L , the solution is the standing wave

Particle in a box (fixed) boundary conditions:

$$\psi_n(0, y, z) = \psi_n(L, y, z) = \psi_n(x, 0, z) = \psi_n(x, L, z) = \psi_n(x, y, 0) = \psi_n(x, y, L) = 0$$

$$\rightarrow \psi_n = A \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right) \quad n_i = 1, 2, \dots \quad \text{Standing waves}$$

Periodic boundary conditions: our wavefunction is periodic in x , y , and z directions with period L ,

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

$$\rightarrow \psi_k = A e^{i\mathbf{k} \cdot \mathbf{r}} \quad k_i = \frac{2n_i \pi}{L} \quad n_i = 0, \pm 1, \pm 2, \dots \quad \text{Traveling waves}$$

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m}$$

$$E_k = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2).$$

$$\mathbf{p} \psi_{\mathbf{k}} = \frac{\hbar}{i} \nabla \psi_{\mathbf{k}} = \hbar \mathbf{k} \psi_{\mathbf{k}}$$

$$\mathbf{p} = \hbar \mathbf{k} \quad \mathbf{v} = \frac{\hbar \mathbf{k}}{m}$$

In the ground state a system of N electrons occupies states with lowest possible energies. Therefore all the occupied states lie inside the sphere of radius k_F

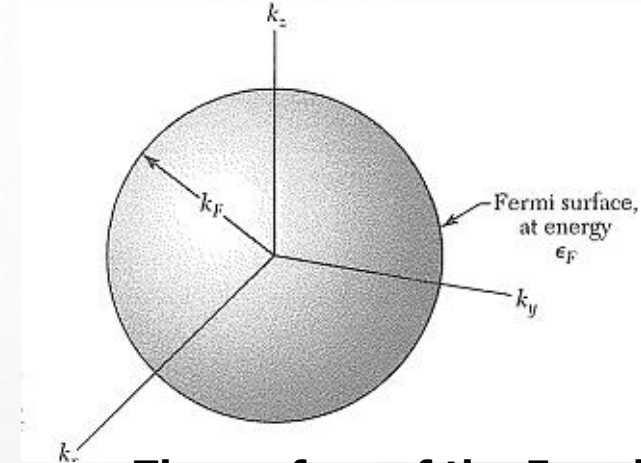
- The Fermi energy and the Fermi wavevector (momentum) are determined by the number of valence electrons in the system.
- In order to find the relationship between N and k_F , we need to count the total number of orbitals in a sphere of radius k_F which should be equal to N . There are two available spin states for a given set of k_x , k_y , and k_z .
- The volume in the \mathbf{k} space which is occupied by this state is equal to $(2\pi / L)^3$. Thus in the sphere of $(4 / 3) \pi k_F^3$ the total number of states is

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

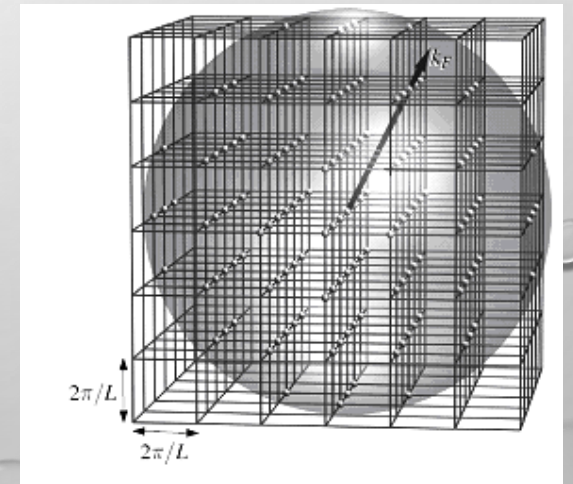
which depends only of the electron concentration

$$\text{Fermi velocity } v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m} \left(\frac{3\pi^2 N}{V} \right)^{1/3}$$

→ $\psi_{\mathbf{k}}$ is a momentum eigenstate with eigenvalue $\hbar \mathbf{k}$.



The surface of the Fermi sphere represent the boundary between occupied and unoccupied \mathbf{k} states at absolute zero for the free electron gas.



Only at temperatures above T_F will the free electron gas behave like a classical gas.

Fermi (degeneracy) Temperature T_F by

$$E_F = k_B T_F$$

A few estimates for Na: Na has bcc structure with cubic lattice parameter $a=4.2\text{\AA}$ and one valence electron per atom. Since there are 2 atoms in a unit cell, the electron concentration is $N/V = 2/(4.2\text{\AA}^3) = 3 \cdot 10^{22} \text{cm}^{-3}$. Then, the Fermi momentum is $k_F \approx (3 \cdot 10 \cdot 3 \cdot 10^{22} \text{cm}^{-3})^{1/3} \approx 10^8 \text{cm}^{-1} = 1\text{\AA}^{-1}$.

The Fermi energy is given by $E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2ma_0^2} k_F^2 a_0^2 \approx 13.6 \text{eV} \cdot 0.25 \approx 3.5 \text{eV}$. The Fermi temperature is defined $T_F = E_F / k_B \approx 40000 \text{K}$ (1eV corresponds to $1.16 \cdot 10^4 \text{K}$). The Fermi velocity

can be found from $\frac{v_F}{c} = \frac{\hbar}{mca_0} k_F a_0 = \frac{\hbar}{mc} \frac{me^2}{\hbar^2} k_F a_0 = \frac{e^2}{\hbar c} k_F a_0 \approx \frac{1}{137} 0.5 \approx 4 \cdot 10^{-3}$, which results in

$v_F \approx 10^8 \frac{\text{cm}}{\text{s}}$. We see that the velocity of electrons is relatively large.

Density of states:

- The Density of States $D(E)$ specifies how many states exist at a given energy E .

- The Fermi Function $f(E)$ specifies how many of the existing states at energy E will be filled with electrons.

- The values of k_x k_y k_z are equally spaced: $\Delta k_x = 2\pi/L$,

Thus the volume in k space per state is $(2\pi/L)^3$

and the number of states N with $|k| < k_0$ is

$$N = (4\pi/3) k_0^3 / (2\pi/L)^3 = V/6\pi^2 k_0^3 \quad L^3=V$$

- The density of states per unit energy is

$$D(E) = dN/dE = (dN/dk) (dk/dE)$$

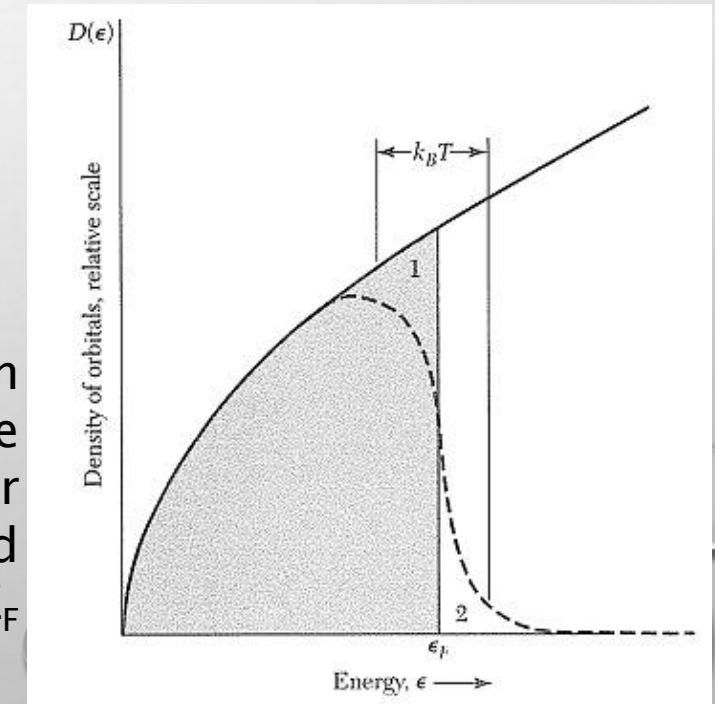
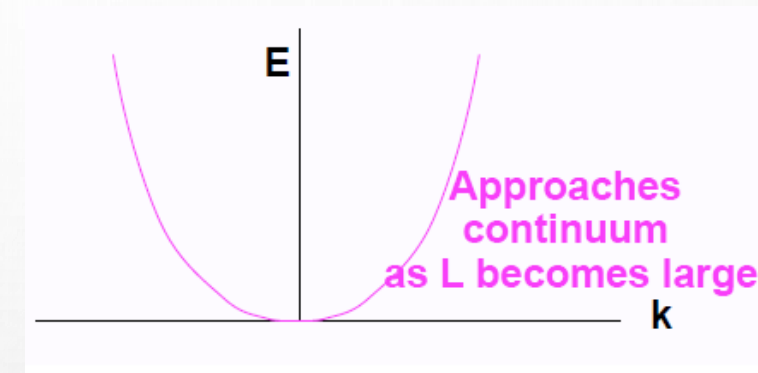
$$E = (\hbar^2/2m) k^2, \quad dE/dk = (\hbar^2/m) k$$

$$\Rightarrow D(E) = (V/2\pi^2) k^2 / (\hbar^2/m) k = (V/2\pi^2) k / (\hbar^2/m) \\ = (V/4\pi^2) E^{1/2} (2m / \hbar^2)^{3/2}$$

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

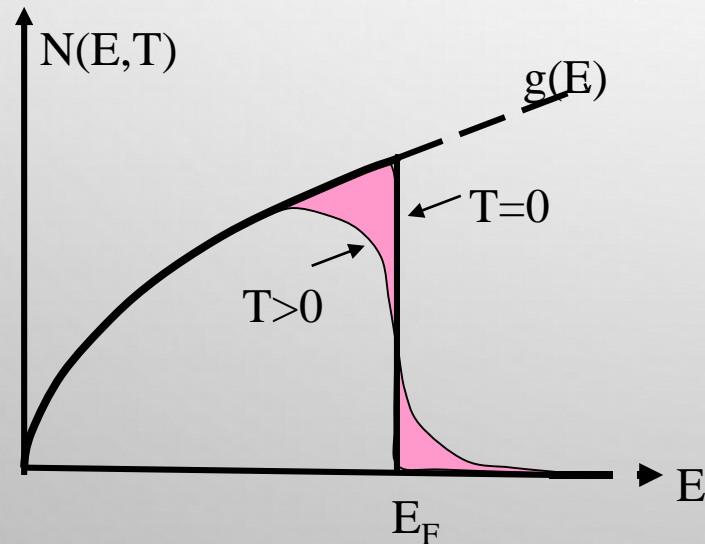
$$D(\epsilon) = \frac{3}{2} \frac{N}{\epsilon_F} \sqrt{\frac{\epsilon}{\epsilon_F}} \quad D(\epsilon_F) = \frac{3}{2} \frac{N}{\epsilon_F}$$

Fermi-Dirac distribution function is a symmetric function; at finite temperatures, the same number of levels below E_F is emptied and same number of levels above E_F are filled by electrons.



Heat Capacity Of The Free Electron Gas

- From the diagram of $N(E,T)$ the change in the distribution of electrons can be resembled into triangles of height $(\frac{1}{2})g(E_F)$ and a base of $2k_B T$ so $(\frac{1}{2})g(E_F)k_B T$ electrons increased their energy by $k_B T$.
- The electron energy levels are mostly filled up to the Fermi energy.
- So, only a small fraction of electrons, approximately T/T_F , can be excited to higher levels – because there is only about $k_B T$ of thermal energy available.
- $N(E,T) \rightarrow$ number of free electrons per unit energy range is just the area under $N(E,T)$ graph.



$$N(E,T) = g(E) f(E,T)$$

- The difference in thermal energy from the value at $T=0^\circ\text{K}$

$$E(T) - E(0) \approx \frac{1}{2} g(E_F) (k_B T)^2$$

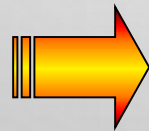
- Differentiating With Respect To **T** Gives The Heat Capacity At Constant Volume,

$$C_v = \frac{\partial E}{\partial T} = g(E_F) k_B^2 T$$

$$N = \frac{2}{3} E_F g(E_F)$$

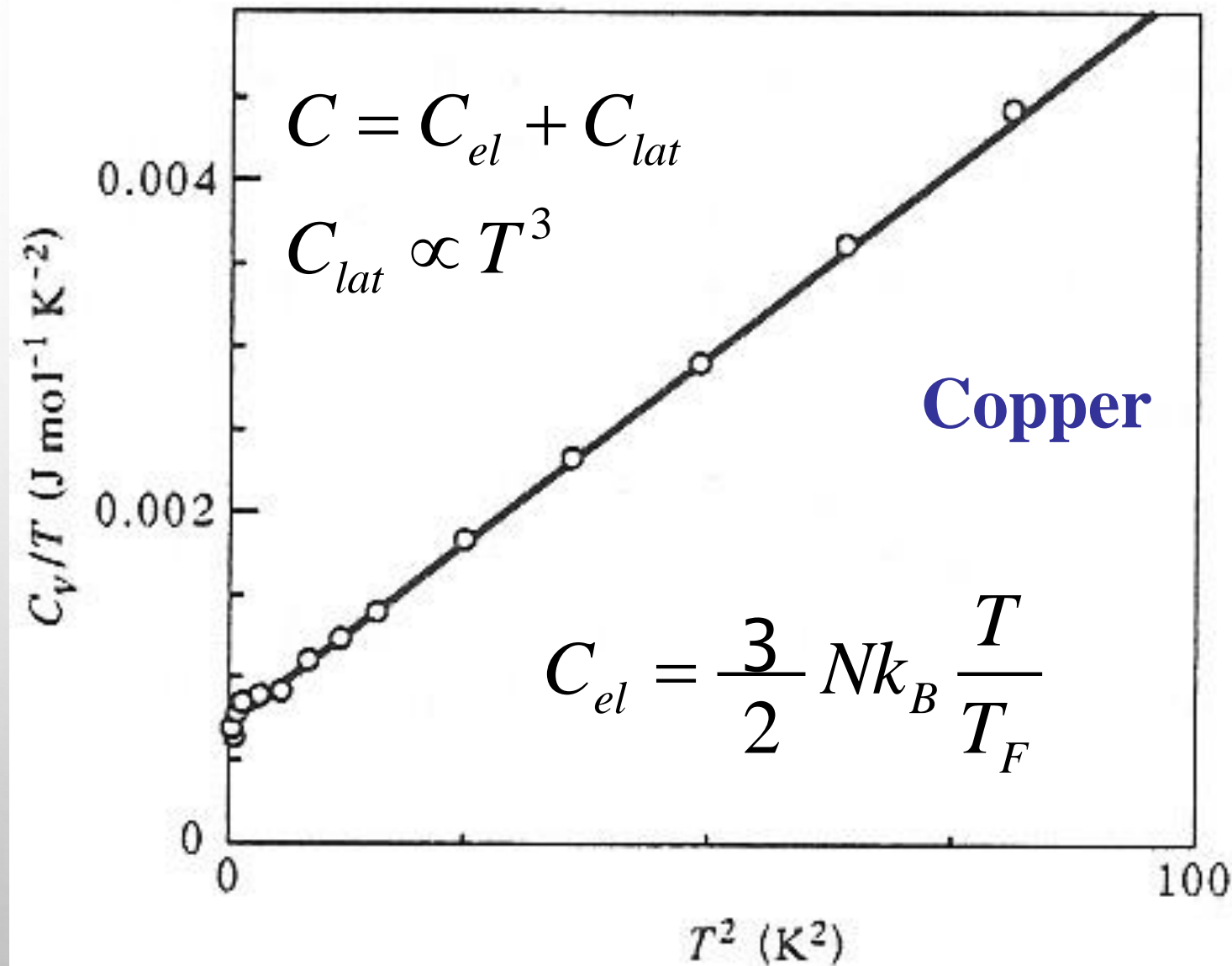
**Heat Capacity of
Free Electron Gas**

$$g(E_F) = \frac{3}{2} \frac{N}{E_F} = \frac{3N}{2k_B T_F} \quad C_v = g(E_F) k_B^2 T = \frac{3N}{2k_B T_F} k_B^2 T$$



$$C_v = \frac{3}{2} N k_B \left(\frac{T}{T_F} \right)$$

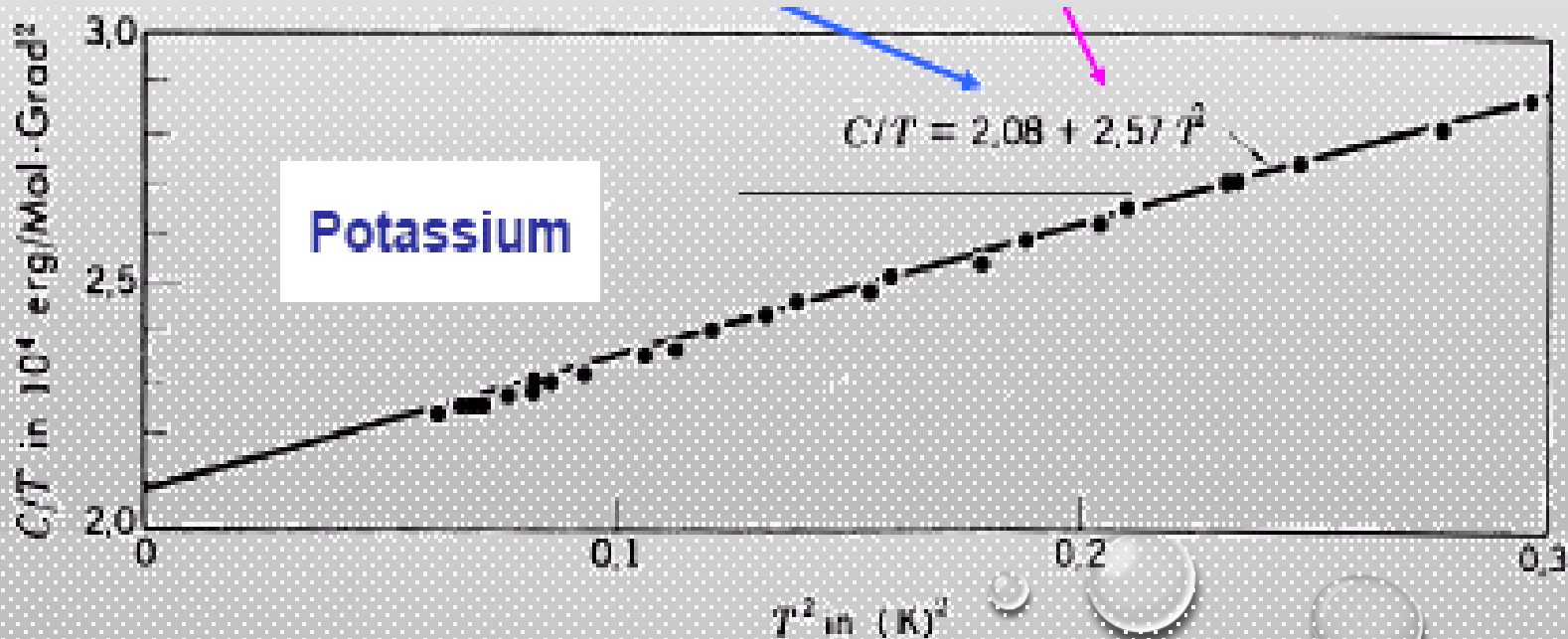
Low-Temperature Heat Capacity

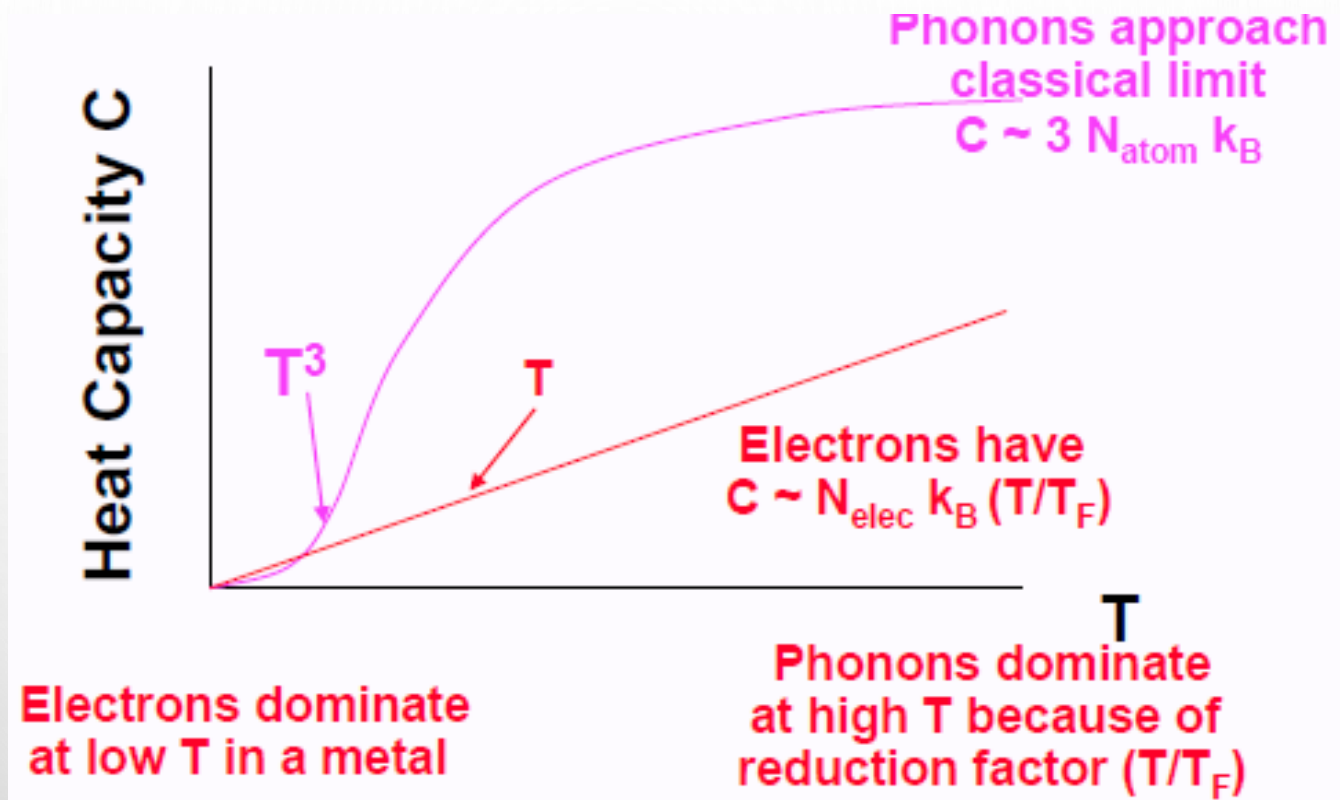


- Total metallic heat capacity at low temperatures

$$C = \underbrace{\gamma T}_{\text{Electronic Heat capacity}} + \underbrace{\beta T^3}_{\text{Lattice Heat Capacity}}$$

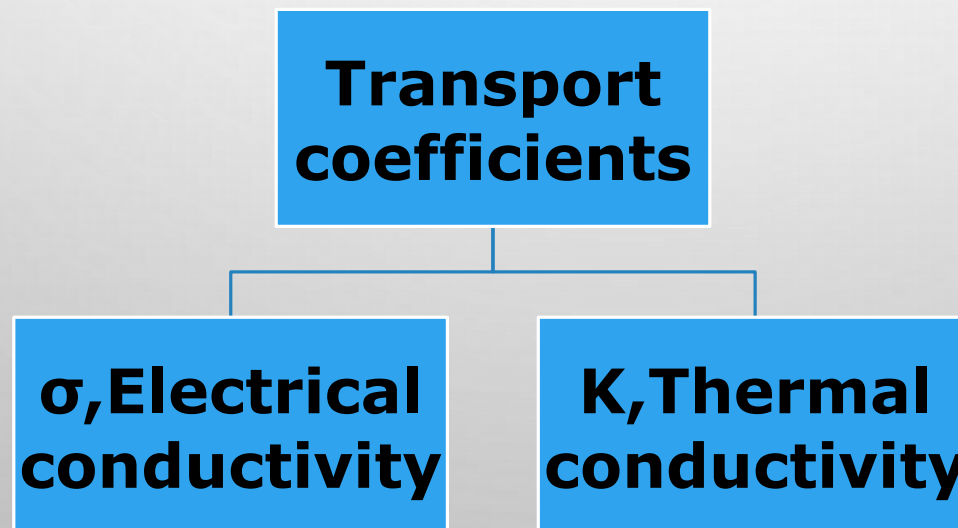
Where γ & β are constants found plotting c_v/T as a function of T^2





Transport Properties Of Conduction Electrons

- Fermi–Dirac distribution function describes the behaviour of electrons only at equilibrium.
- If there is an applied field (E or B) or a temperature gradient the transport coefficient of thermal and electrical conductivities must be considered.



- Equation of motion of an electron with an applied electric and magnetic field.

$$m_e \frac{d\vec{v}}{dt} = -e\vec{E} - e\vec{v} \times \vec{B}$$

- This is just newton's law for particles of mass m_e and charge $(-e)$.
- The use of the classical equation of motion of a particle to describe the behaviour of electrons in plane wave states, which extend throughout the crystal. A particle-like entity can be obtained by superposing the plane wave states to form a wavepacket.

- The velocity of the wavepacket is the group velocity of the waves. Thus

$$\vec{v} = \frac{d\omega}{d\vec{k}} = \frac{1}{\hbar} \frac{dE}{d\vec{k}} = \frac{\hbar \vec{k}}{m_e} = \frac{\vec{p}}{m_e}$$

$$E = \hbar\omega = \frac{\hbar^2 k^2}{2m_e}$$
$$p = \hbar k$$

- So one can use equation of $m d\vec{v}/dt$

$$m_e \left(\frac{d\vec{v}}{dt} + \frac{\vec{v}}{\tau} \right) = -e\vec{E} - e\vec{v} \times \vec{B} \quad (*)$$

τ = mean free time between collisions. An electron loses all its energy in time τ

- In the absence of a magnetic field, the applied E results a constant acceleration but this will not cause a continuous increase in current. Since electrons suffer collisions with
 - Phonons
 - Electrons
- The additional term $m_e \left(\frac{\vec{v}}{\tau} \right)$ cause the velocity v to decay exponentially with a time constant τ when the applied E is removed.

The Electrical Conductivity

- In The Presence Of DC Field Only, Eq.(*) Has The Steady State Solution

$$\vec{v} = - \underbrace{\frac{e\tau}{m_e}} \vec{E}$$

a constant of
proportionality
(mobility)

$$\mu_e = \frac{e\tau}{m_e} \quad \text{Mobility for electron}$$

- Mobility Determines How Fast The Charge Carriers Move With An E.

- Electrical Current Density, J

$$J = n(-e)v \quad \vec{v} = -\frac{e\tau}{m_e} \vec{E} \quad n = \frac{N}{V}$$

- Where n Is The Electron Density And v Is Drift Velocity. Hence

$$\vec{J} = \frac{ne^2\tau}{m_e} \vec{E}$$

Ohm's law

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

$$\sigma = \frac{ne^2\tau}{m_e}$$

Electrical conductivity

Electrical Resistivity and Resistance

$$\rho = \frac{1}{\sigma} \quad R = \frac{\rho L}{A}$$

Collisions

- In a perfect crystal; the collisions of electrons are with thermally excited lattice vibrations (scattering of an electron by a phonon).
- This electron-phonon scattering gives a temperature dependent collision time $\tau_{ph}(T)$ which tends to infinity as $T \rightarrow 0$.
- In real metal, the electrons also collide with impurity atoms, vacancies and other imperfections, this result in a finite scattering time τ_0 even at $T=0$.

- The total scattering rate for a slightly imperfect crystal at finite temperature;

$$\frac{1}{\tau} = \frac{1}{\underbrace{\tau_{ph}(T)}} + \frac{1}{\underbrace{\tau_0}}$$

Due to phonon

Due to imperfections

- So the total resistivity ρ ,

$$\rho = \frac{m_e}{ne^2\tau} = \frac{m_e}{ne^2\tau_{ph}(T)} + \frac{m_e}{ne^2\tau_0} = \rho_I(T) + \rho_0$$

Ideal resistivity

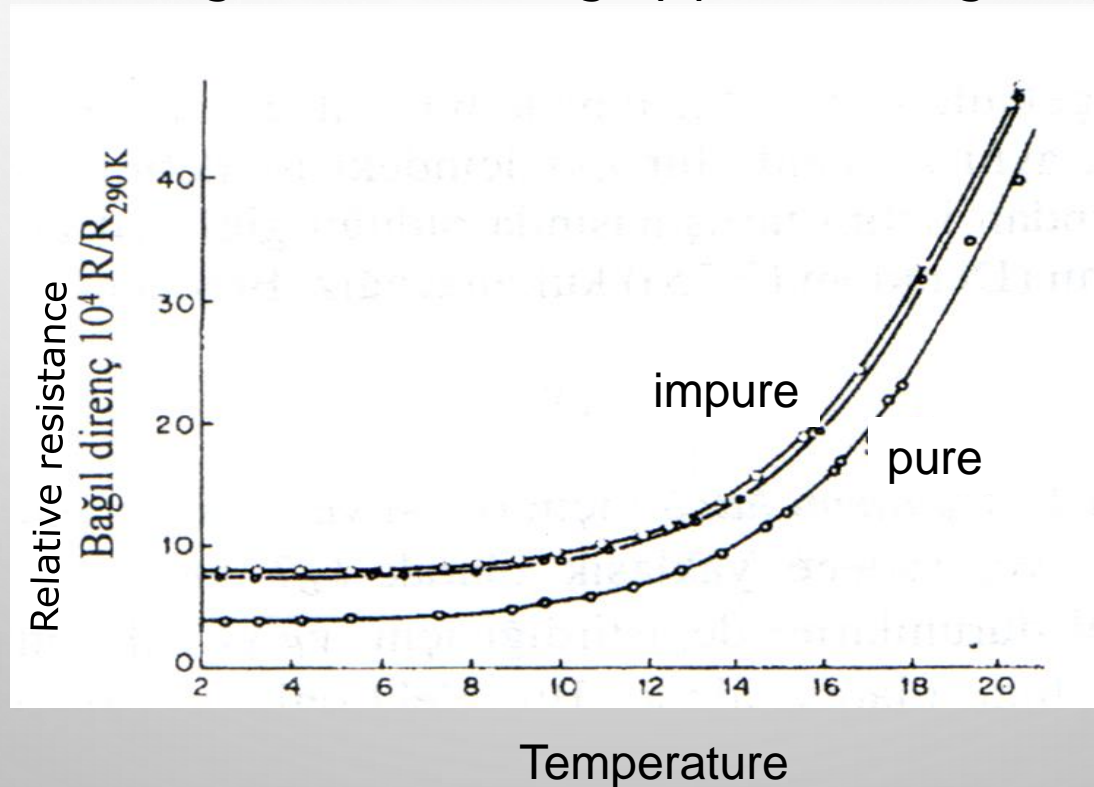
Residual resistivity

This is known as **mattheisen's rule** and illustrated in following figure for sodium specimen of different purity.

Residual Resistance Ratio

Residual resistance ratio = room temp. Resistivity/ residual resistivity

And it can be as high as 10^6 for highly purified single crystals.



Collision Time

$$\sigma(RT)_{sodium} = 2.0 \times 10^7 (\Omega - m)^{-1}$$

$$\sigma_{residual_{pureNa}} = 5.3 \times 10^{10} (\Omega - m)^{-1}$$

τ can be found by taking

$$m_e = m$$

$$n = 2.7 \times 10^{28} m^{-3}$$



$$\tau = \frac{m\sigma}{ne^2} \square 2.6 \times 10^{-14} s \quad \text{at RT}$$

$$\square 7.0 \times 10^{-11} s \quad \text{at T=0}$$

Taking $v_F = 1.1 \times 10^6 m/s$; and $l = v_F \tau$

$$l(RT) = 29 nm$$

$$l(T = 0) = 77 \mu m$$

These mean free paths are much longer than the interatomic distances, confirming that the free electrons do not collide with the atoms themselves.

Thermal Conductivity, K

Due to the heat transport by the conduction electrons

$$K_{\text{metals}} \gg K_{\text{non-metals}}$$

Electrons coming from a hotter region of the metal carry more thermal energy than those from a cooler region, resulting in a net flow of heat. The thermal conductivity

$$K = \frac{1}{3} C_V v_F l \quad \text{where } C_V \text{ is the specific heat per unit volume}$$

v_F is the mean speed of electrons responsible for thermal conductivity since only electron states within about $k_B T$ of ε_F change their occupation as the temperature varies.

l is the mean free path; $l = v_F \tau$ and Fermi energy $\varepsilon_F = \frac{1}{2} m_e v_F^2$

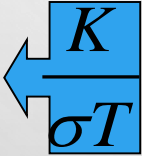
$$K = \frac{1}{3} C_V v_F^2 \tau = \frac{1}{3} \frac{\pi^2}{2} \frac{N}{V} k_B \left(\frac{T}{T_F} \right) \frac{2}{m_e} \varepsilon_F \tau = \frac{\pi^2 n k_B^2 T \tau}{3 m_e} \quad \text{where } C_V = \frac{\pi^2}{2} N k_B \left(\frac{T}{T_F} \right)$$

Wiedemann–Franz Law

$$\sigma = \frac{ne^2\tau}{m_e}$$

$$K = \frac{\pi^2 nk_B^2 T \tau}{3m_e}$$

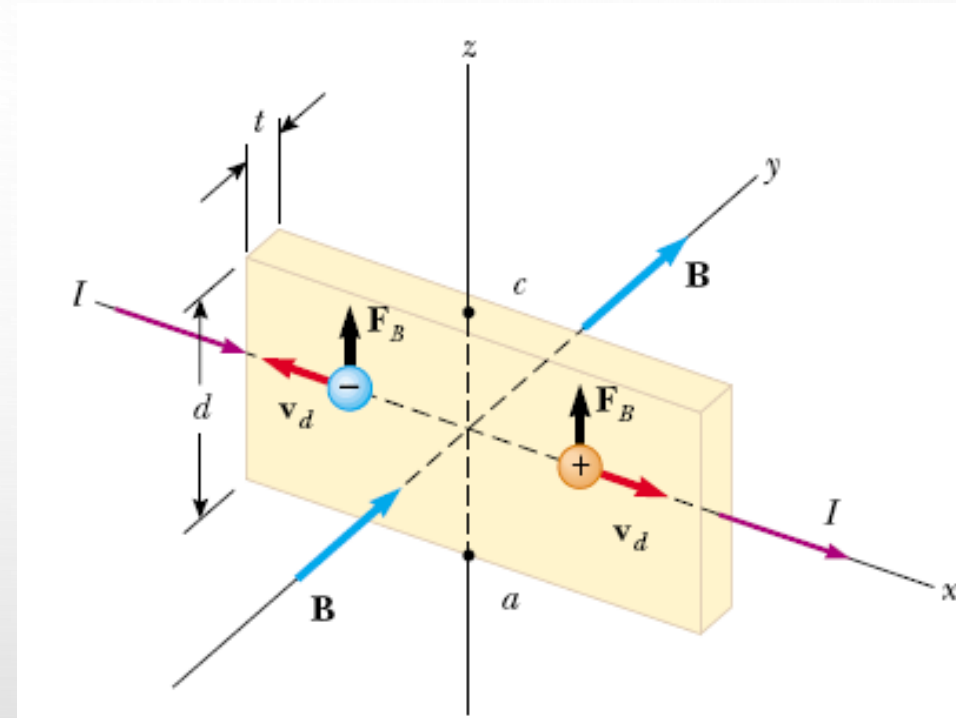
The ratio of the electrical and thermal conductivities is independent of the electron gas parameters;

Lorentz number  $= \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 = 2.45 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$

$$L = \frac{K}{\sigma T} = 2.23 \times 10^{-8} \text{ W}\Omega\text{K}^{-2} \quad \text{For copper at 0 C}$$

Hall Effect

- A uniform magnetic field B is applied in the y -direction.
- If the charge carriers are electrons moving in the negative x -direction with a velocity v_d , they will experience an upward magnetic force f_b .
- The electrons will be deflected upward, making the upper edge negatively charged and the lower edge positively charged.



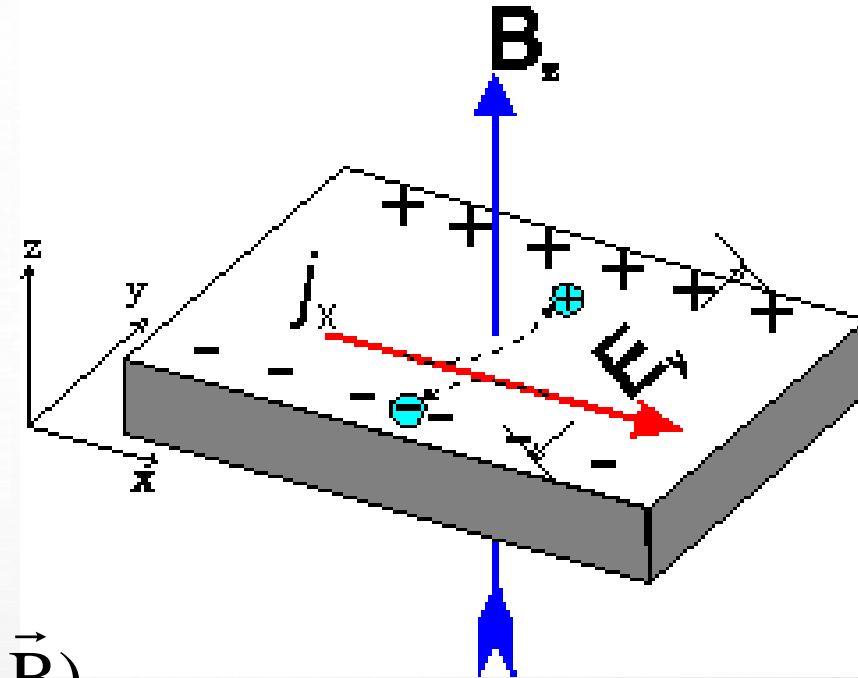
Hall Effect

Initially, $\vec{v} = v_x \hat{x} + v_y \hat{y} + v_z \hat{z}$

$$\vec{E} = E_x \hat{x}$$

$$\vec{B} = B_z \hat{z}$$

$$\vec{F} = m \left(\frac{d}{dt} + \frac{1}{\tau} \right) \vec{v} = -e(\vec{E} + \vec{v} \times \vec{B})$$



net force in
-x direction

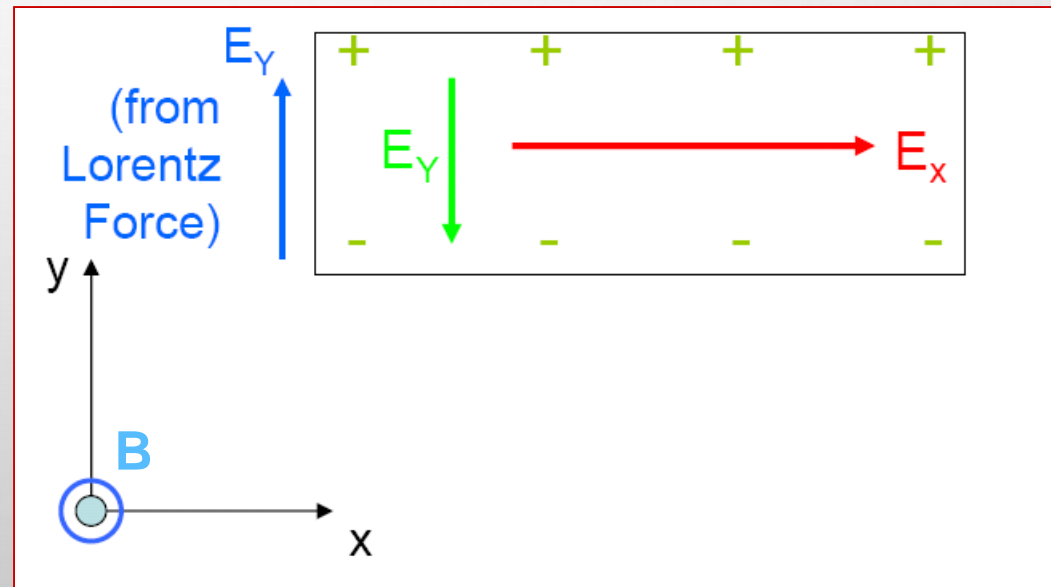
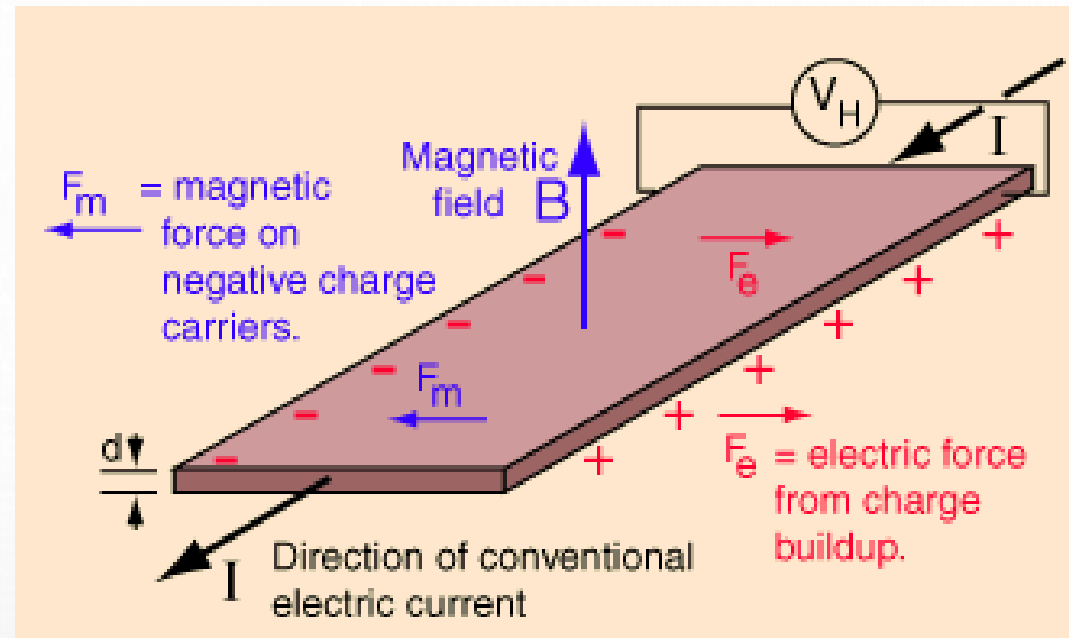
$$F_x = m \left(\frac{d}{dt} + \frac{1}{\tau} \right) v_x = -e(E_x + v_y B)$$

net force in
-y direction

$$F_y = m \left(\frac{d}{dt} + \frac{1}{\tau} \right) v_y = e(v_x B)$$

Hall Effect

As a result, electrons move in the $-y$ direction and an electric field component appears in the y direction, E_y . This will continue until the Lorentz force is equal and opposite to the electric force due to the buildup of electrons – that is, a steady condition arises.



Hall Effect

Steady State
Condition

$$\frac{mv_x}{\tau} = -e(E_x + v_y B)$$

$$\frac{mv_y}{\tau} = -e(E_y + v_x B)$$

Let

$$\omega_C = \frac{eB}{m}$$



$$\begin{aligned} v_x &= -\frac{e\tau E_x}{m} - \omega_C v_y \tau \\ v_y &= -\frac{e\tau E_y}{m} + \omega_C v_x \tau \end{aligned}$$

Hall Effect

$$v_y = -\frac{e\tau E_y}{m} + \omega_C v_x \tau = 0$$
$$\Rightarrow E_y = m \frac{\omega_C v_x}{e}$$

$$v_x = -\frac{e\tau}{m} E_x$$
$$\Rightarrow E_x = -m \frac{v_x}{e\tau}$$

$$E_y = -\omega_C \tau E_x = -\frac{eB\tau}{m} E_x$$

Hall Effect

The sign and magnitude of R_H gives the sign of the charge carriers and their density. In most metals, the charge carriers are electrons and the charge density determined from the Hall effect measurements agrees with calculated values for metals which release a single valence electron and charge density is approximately equal to the number of valence electrons per unit volume.

The Hall coefficient is defined as:

$$R_H = \frac{E_y}{j_x B} = - \frac{\frac{eB\tau}{m} E_x}{\frac{ne^2\tau}{m} E_x B} = - \frac{1}{ne}$$

For copper:

$$n = 8.47 \times 10^{28} \text{ electrons/m}^3.$$

Conduction
Electron
Density

Failure of Fermi gas model

- The Hall Effect experiment suggests that a carrier can have a positive charge.
- These carriers are “holes” in the electron sea - the absence of an electron acts as a net positive charge. These were first explained by Heisenberg.
- We can't explain why this would happen with our free electron theory.

Some successes:

1. electrical conductivity
2. heat capacity
3. thermal conductivity

Some failures:

1. physical differences between conductors, insulators, semiconductors, semi-metals
2. positive Hall coefficients – positive charge carriers ??