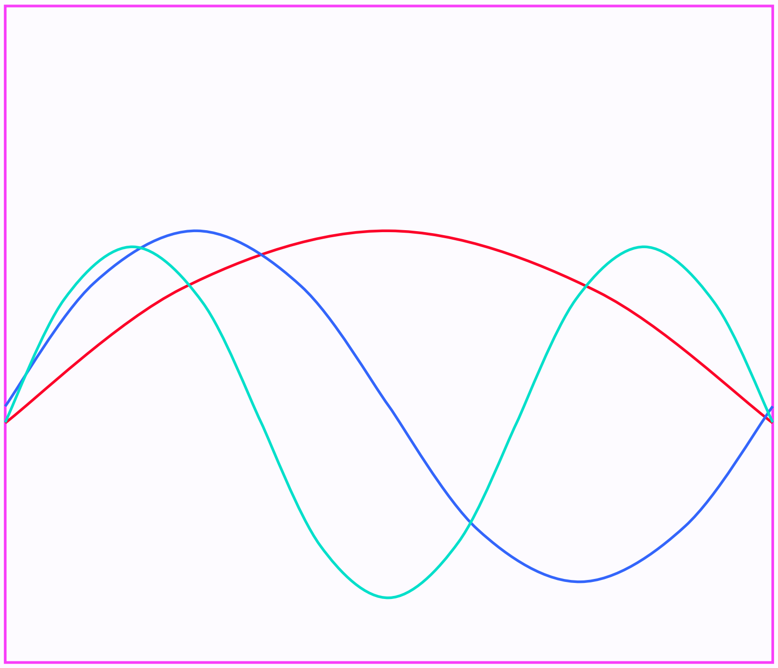
Free Electron Fermi Gas
(Kittel Ch. 6)

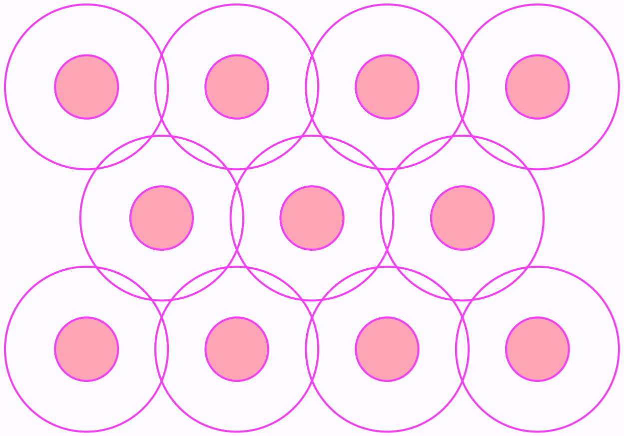


Role of Electrons in Solids

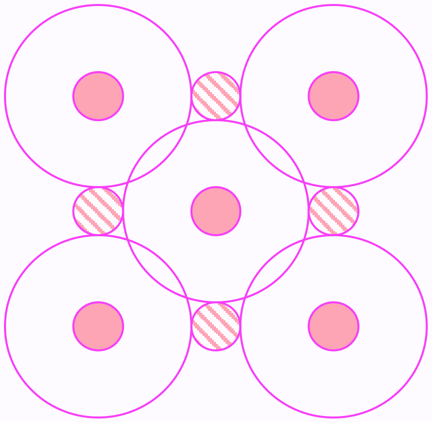
- Electrons are responsible for binding of crystals -- they are the "glue" that hold the nuclei together
  - Types of binding (see next slide)
    - Van der Waals - electronic polarizability
    - Ionic - electron transfer
    - Covalent - electron bonds

- Electrons are responsible for important properties:
  - Electrical conductivity in metals
  - (But why are some solids insulators?)
  - Magnetism
  - Optical properties
  - . . . .

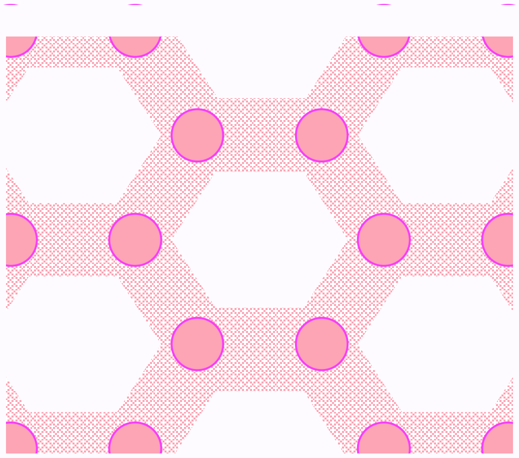
Characteristic types of binding



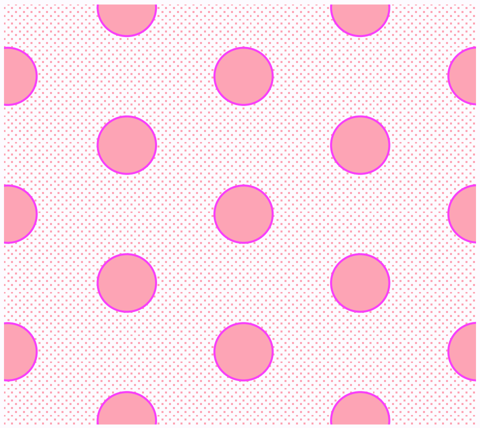
Closed-Shell Binding
Van der Waals



Ionic Binding



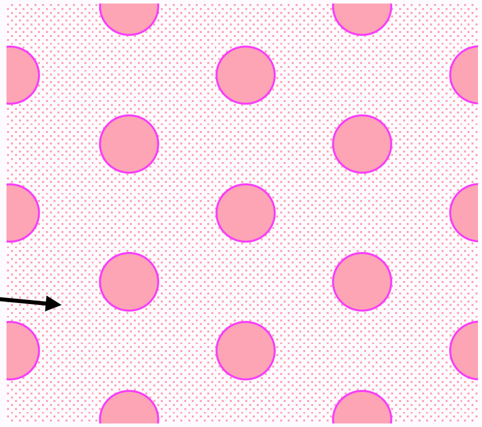
Covalent Binding



Metallic Binding

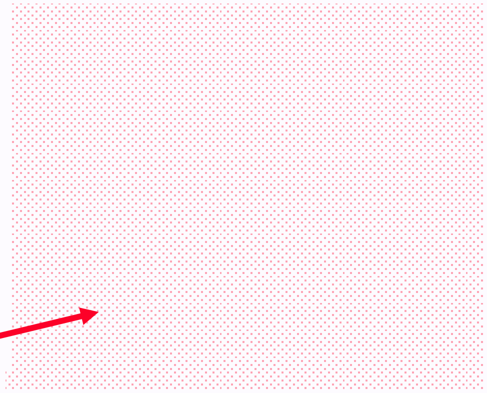
Starting Point for Understanding Electrons in Solids

- **Nature of a metal: Electrons can become "free of the nuclei" and move between nuclei since we observe electrical conductivity**



- **Electron Gas**

  Simplest possible model for a metal - electrons are completely "free of the nuclei" - nuclei are replaced by a smooth background -- "Electrons in a box"



Electron Gas - History

- **Electron Gas model predates quantum mechanics**

- **Electrons Discovered in 1897**

- **Drude-Lorentz Model (1905)- Electrons - classical particles free to move in a box**
- **Model: All electrons contribute to conductivity. Works! Still used!**

- **But same model predicted that all electrons contribute to heat capacity. Disaster. Heat capacity is MUCH less than predicted.**

Quantum Mechanics

- **1911: Bohr Model for H**
- **1923: Wave Nature of Particles Proposed**
  Prince Louis de Broglie
- **1924-26: Development of Quantum Mechanics - Schrodinger equation**
- **1924: Bose-Einstein Statistics for Identical Particles (phonons, ...)**
- **1925-26: Pauli Exclusion Principle, Fermi-Dirac Statistics (electrons, ...)**
- **1925: Spin of the Electron (spin = 1/2)**
  G. E. Uhlenbeck and S. Goudsmit

Schrodinger

Schrodinger Equation

- Basic equation of Quantum Mechanics

$$[\ - (\hbar/2m)\ \Delta^2 + V(\underline{r})\ ]\ \Psi(\underline{r}) = E\ \Psi(\underline{r})$$

where

m = mass of particle
$V(\underline{r})$ = potential energy at point $\underline{r}$
$\Delta^2 = (d^2/dx^2 + d^2/dy^2 + d^2/dz^2)$
E = eigenvalue = energy of quantum state
$\Psi(\underline{r})$ = wavefunction
$n(\underline{r}) = |\Psi(\underline{r})|^2$ = probability density

Schrodinger Equation – 1D line

- Suppose particles can move freely on a line with position x, $0 < x < L$

- Schrodinger Eq. In 1D with $V = 0$

  $$-\left(\hbar^2/2m\right) d^2/dx^2\, \Psi(x) = E\, \Psi(x)$$

- Solution with $\Psi(x) = 0$ at $x = 0, L$ ← **Boundary Condition**

  $$\Psi(x) = 2^{1/2} L^{-1/2} \sin(kx)\,, \quad k = n\pi/L,\ n = 1,2, \ldots$$

  (Note similarity to vibration waves)

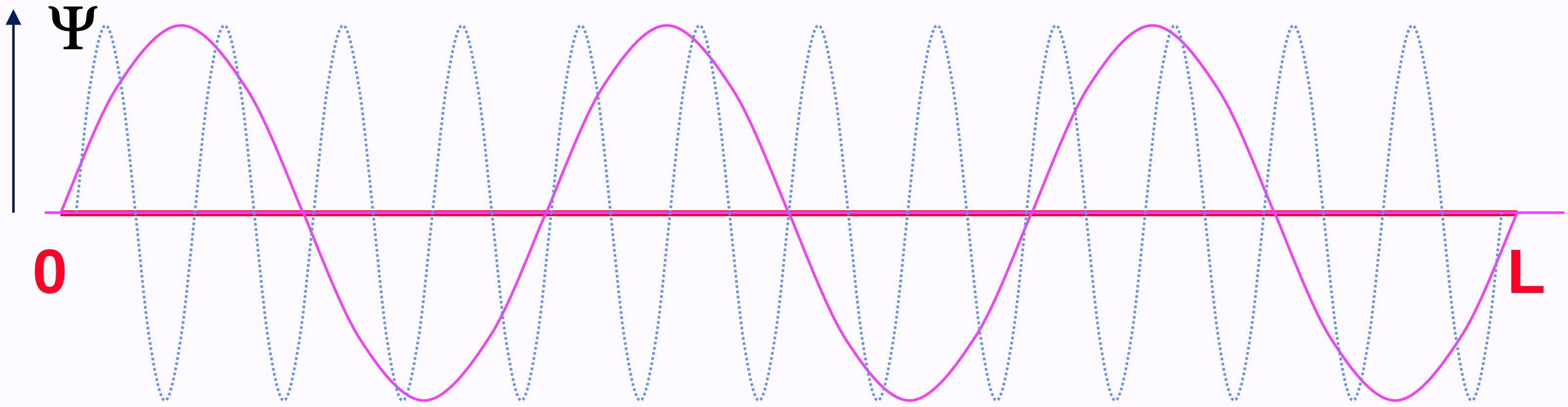
  Factor chosen so $\int_0^L dx\, |\Psi(x)|^2 = 1$

- $E(k) = \left(\hbar^2/2m\right) k^2$

Electrons on a line

- Solution with $\Psi(x) = 0$ at $x = 0,L$

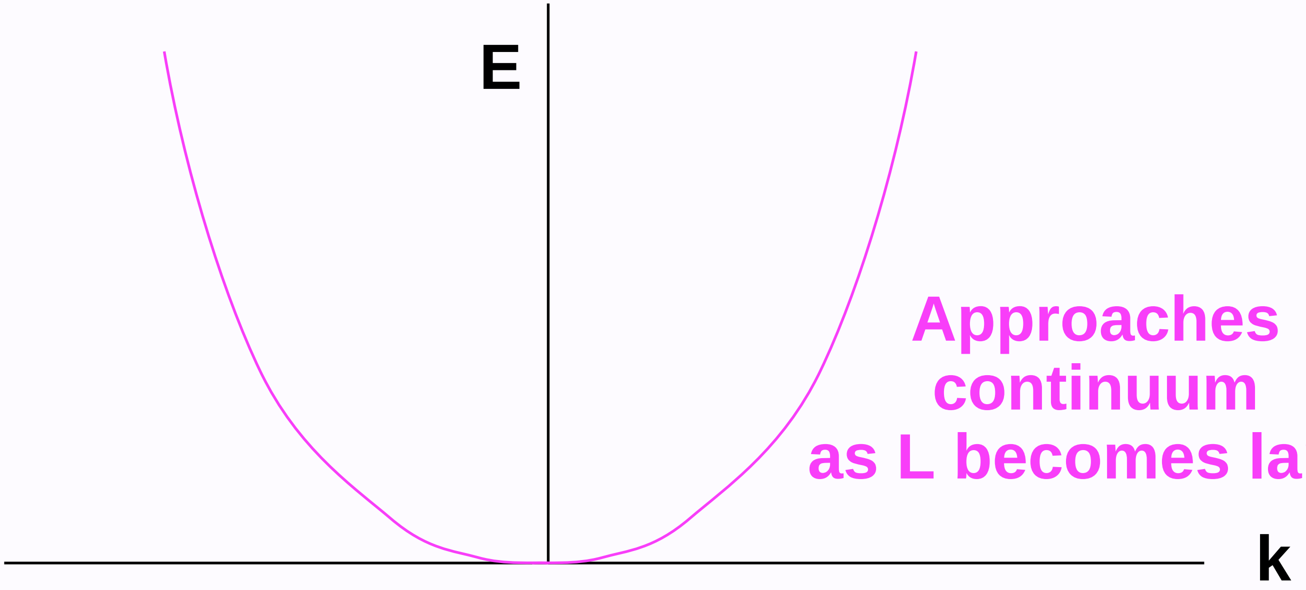
  Examples of waves - same picture as for lattice vibrations except that here $\Psi(x)$ is a continuous wave instead of representing atom displacements



Electrons on a line

- For electrons in a box, the energy is just the kinetic energy which is quantized because the waves must fit into the box

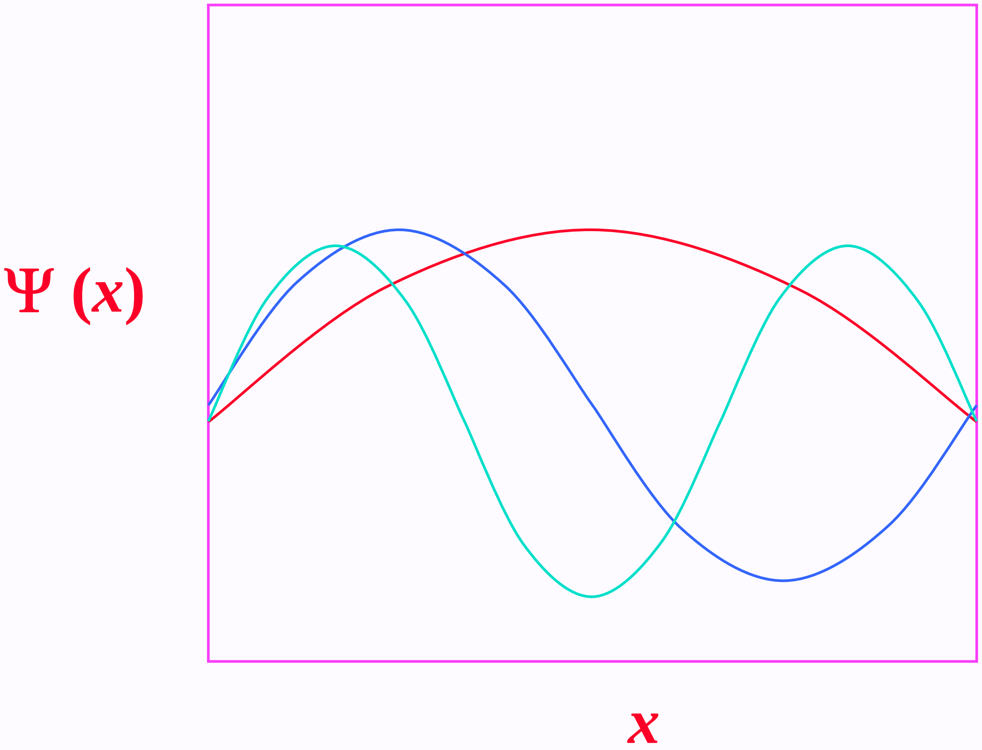
$E(k) = (\hbar^2/2m)\,k^2$, $k = n\pi/L$, $n = 1,2,\ldots$



Approaches continuum as L becomes large

Schrodinger Equation – 1D line

- $E(k) = (h^2/2m)\, k^2$, $k = n\pi/L$, $n = 1,2, \ldots$
- Lowest energy solutions with $\Psi(x) = 0$ at $x = 0, L$



Electrons in 3 dimensions

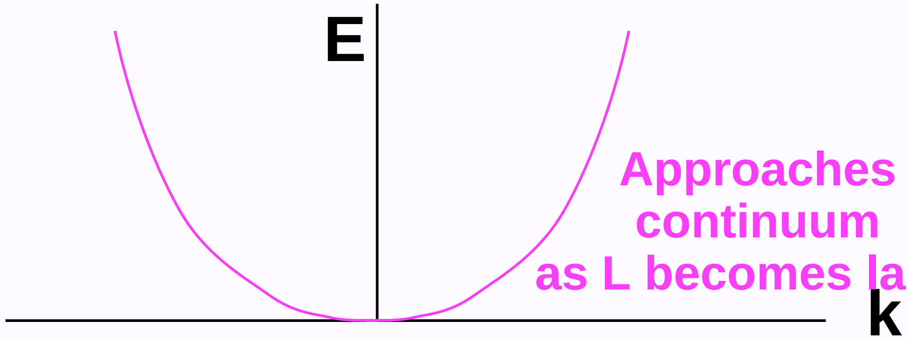
$$-(\hbar^2/2m)\,[d^2/dx^2 + d^2/dy^2 + d^2/dz^2]\,\Psi(x,y,z) = E\,\Psi(x,y,z)$$

$\Psi(x) = 0$ at $x = 0,L$; $\Psi(y) = 0$ at $y = 0,L$; $\Psi(z) = 0$ at $z = 0,L$

$$\Psi = 2^{3/2} L^{-3/2} \sin(k_x x) \sin(k_y y) \sin(k_z z) ,$$

$k_x = n\,\pi/L$, $n = 1,2, \ldots$, same for y,z

$$E(k) = (\hbar^2/2m)(k_x^2 + k_y^2 + k_z^2) = (\hbar^2/2m)\,k^2$$



Approaches continuum as L becomes large

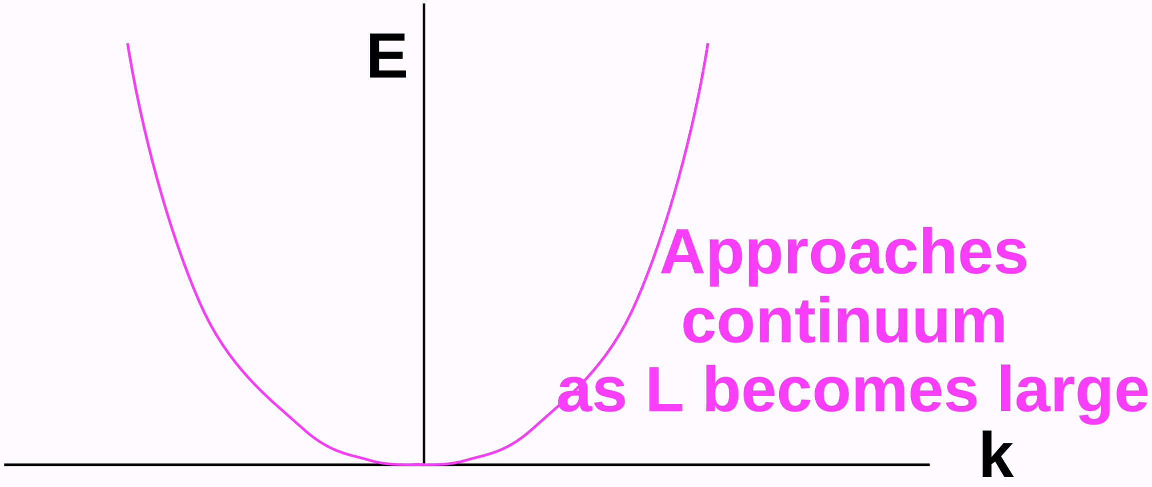
Electrons in 3 dimensions - continued

- Just as for phonons it is convenient to define Ψ with periodic boundary conditions
- Ψ is a traveling plane wave:

$$\Psi = L^{-3/2} \exp(i(k_x x + k_y y + k_z z) ,$$

$$k_x = \pm n \, (2\pi/L), \text{ etc., } n = 0,1,2,..$$

$$E\,(k) = (\, \hbar^2/2m\,)\,(k_x^2 + k_y^2 + k_z^2\,) = (\,\hbar^2/2m\,)\,k^2$$



Approaches continuum as L becomes large

Density of states

- Key point - exactly the same as for vibration waves
- We need the number of states per unit energy to find the total energy and the thermal properties of the electron gas.
- Difference: density of states is defined in terms of energy E, not angular frequency.
- D(E)dE - number of states in energy range E to E+dE
- States in interval (k, E) to (k+ Δk, E+ ΔE)

$$\Delta N = N(k)\,\Delta k = N(E)\,\Delta E$$

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

Density of States in 3D

- 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

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

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

$\Longrightarrow D(E) = (V/2\pi^2)\, k^2 / (\hbar^2/m)\, k = (V/2\pi^2)\, k / (\hbar^2/m)$

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

Kittel adds a factor of 2 for multiplicity of electrons in the same state (spin): $D(E) = (V/2\pi^2)\, E^{1/2}\, (2m / \hbar^2)^{3/2}$

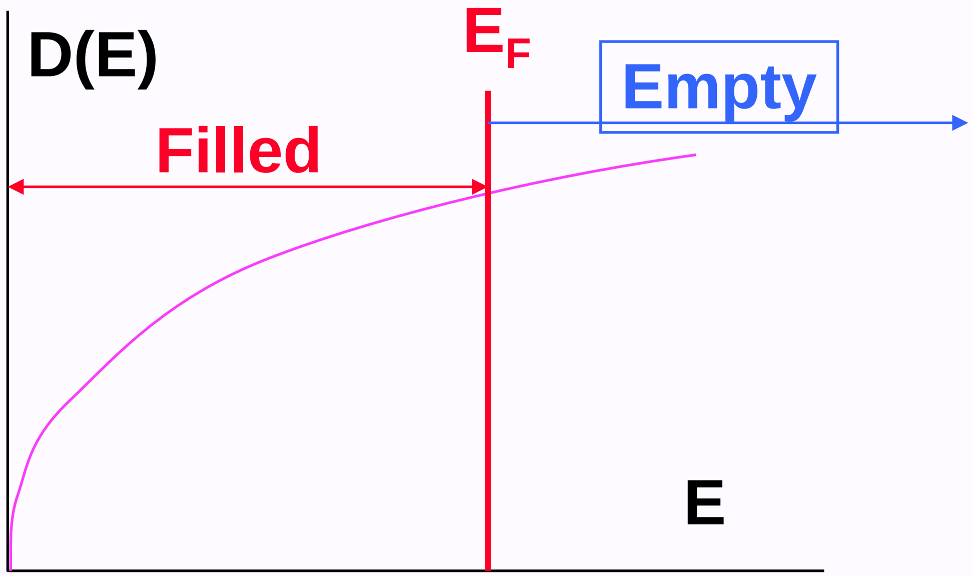
Electron orbitals

- In 1D E (k) = ($\hbar^2/2m$) k^2 , $k = n\,\pi/L$, n = 1,2, …
- In 3D E (k) = ($\hbar^2/2m$) $(k_x^2 + k_y^2 + k_z^2)$ = ($\hbar^2/2m$) k^2

  $k_{x,}\ k_y\ k_z = \pm n\ (2\pi/L)$, etc., n = 0,1,2,..
- Thus $E_{1D}\ (k) = n^2\ (\hbar^2/2m)\ (\pi/L)^2$
- $E_{3D}\ (k) = (n_x+n_y+n_z)^2\ (\hbar^2/2m)\ (2\pi/L)^2$
- To describe a system of N_{elec} electrons, we assign the electrons to orbitals of increasing energy, until all orbitals are filled.
- Order of filling: n=1, 2, .. n_F
- n_F - topmost filled energy level (Fermi level)

Electron orbitals

- $D(E) = (V/2\pi^2)\, E^{1/2}\, (2m / h^2)^{3/2}$



- Now we need to figure out how many electrons are on a given orbital (electron occupancy)

What is special about electrons?

- Fermions - obey exclusion principle
- Fermions have spin s = 1/2 - two electrons (spin up and spin down) can occupy each state
- Kinetic energy = ($p^2/2m$) = ($\hbar^2/2m$) k^2
- Thus if we know the number of electrons per unit volume N_{elec}/V,

  the lowest energy allowed state is for the lowest $N_{elec}/2$ states to be filled with 2 electrons each,

  and all the (infinite) number of other states to be empty.
- The number of states with $|k| < k_0$ is $N = (V/6\pi^2)\, k_0^3$ (from before)

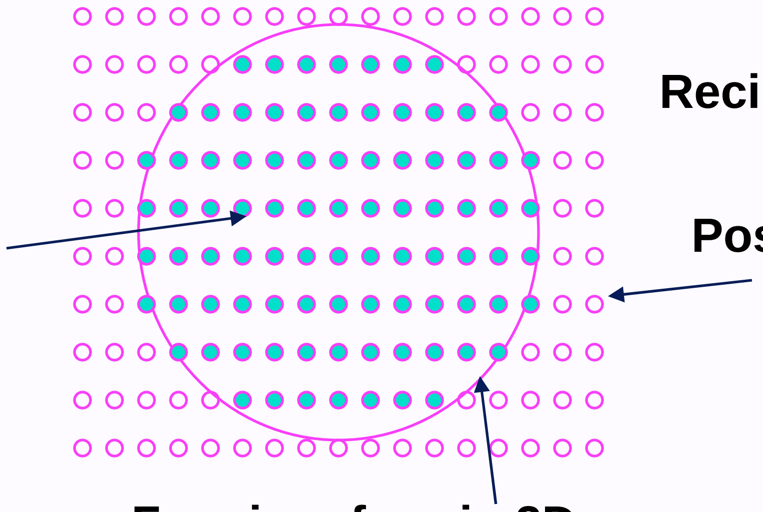
Fermi momentum and energy

Thus all states are filled up to the Fermi momentum k_F and Fermi energy $E_F = (\hbar^2/2m)\, k_F^2$, given by

$N_{elec}/2 = (V/6\pi^2)\, k_F^3$

$\Rightarrow$

$k_F = (3\pi^2 N_{elec}/V)^{1/3}$ and $E_F = (\hbar^2/2m)\,(3\pi^2 N_{elec}/V)^{2/3}$



Reciprocal space

Filled states

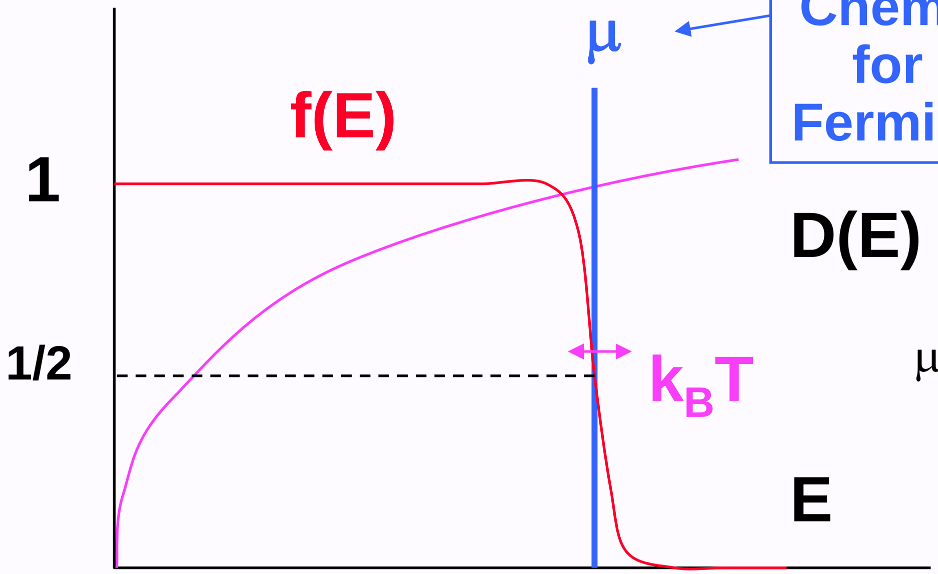
Possible k values

Fermi surface in 2D

Fermi Distribution

- At finite temperature, electrons are not all in the lowest energy states
- Applying the fundamental law of statistics to this case (occupation of any state and spin only can be 0 or 1) leads to the Fermi Distribution giving the probability that an orbital of energy E is occupied (Kittel appendix)

$$f(E) = 1/[\exp((E-\mu)/k_BT) + 1]$$



Chemical potential for electrons = Fermi energy at T=0

μ is temperature dependent

Ex. How does the Fermi distribution

$$f(E) = 1/[\exp((E-\mu)/k_BT) + 1]$$

compare with the Planck distribution for phonons?

$$n(E) = 1 / [\exp (E / k_B T) - 1]$$

Sketch them as a function of energy for different temperatures.

Typical values for electrons?

- Here we count only valence electrons (see Kittel table)

Element	N_{elec}/atom	E_F	$T_F = E_F/k_B$
Li	1	4.7 eV	5.5×10^4 K
Na	1	3.23eV	3.75×10^4 K
Al	3	11.6 eV	13.5×10^4 K

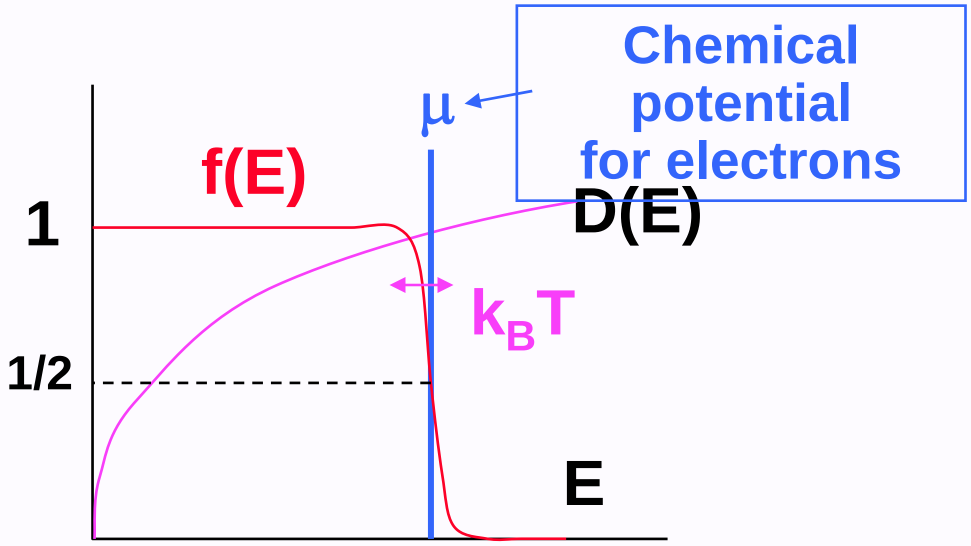
- For typical metals the Fermi energy temperature is much greater than ordinary temperatures – transition from f(E)=1 to f(E)=0 is sharp at room temperature

Heat Capacity for Electrons

Just as for phonons the definition of heat capacity is $C = dU/dT$ where U = total internal energy

- When heated from $T=0$ only electrons within an energy range k_BT of the Fermi energy can be excited thermally
- For $T << T_F = E_F / k_B$ roughly $U \sim U_0 + N_{elec} (T/ T_F)\, k_B\, T$ so that

$$C = dU/dT \sim N_{elec}\, k_B\, (T/ T_F)$$



Chemical potential for electrons

Heat Capacity for Electrons

- More precisely, the change in energy when heated from 0 to T is

$$\Delta U = \int_0^{\infty} dE\ E\ D(E)\ f(E) - \int_0^{E_F} dE\ E\ D(E)$$

- Using the fact that $T << T_F$:

$$C = dU/dT = \int_0^{\infty} dE\ (E - E_F)\ D(E)\ (df(E)/dT)$$
$$\approx D(E_F) \int_0^{\infty} dE\ (E - E_F)\ (df(E)/dT)$$

- The integral can be done almost exactly (exact in the low T limit) to give

$C = (\pi^2/3)\ D(E_F)\ k_B^2\ T$ (valid for any metal)

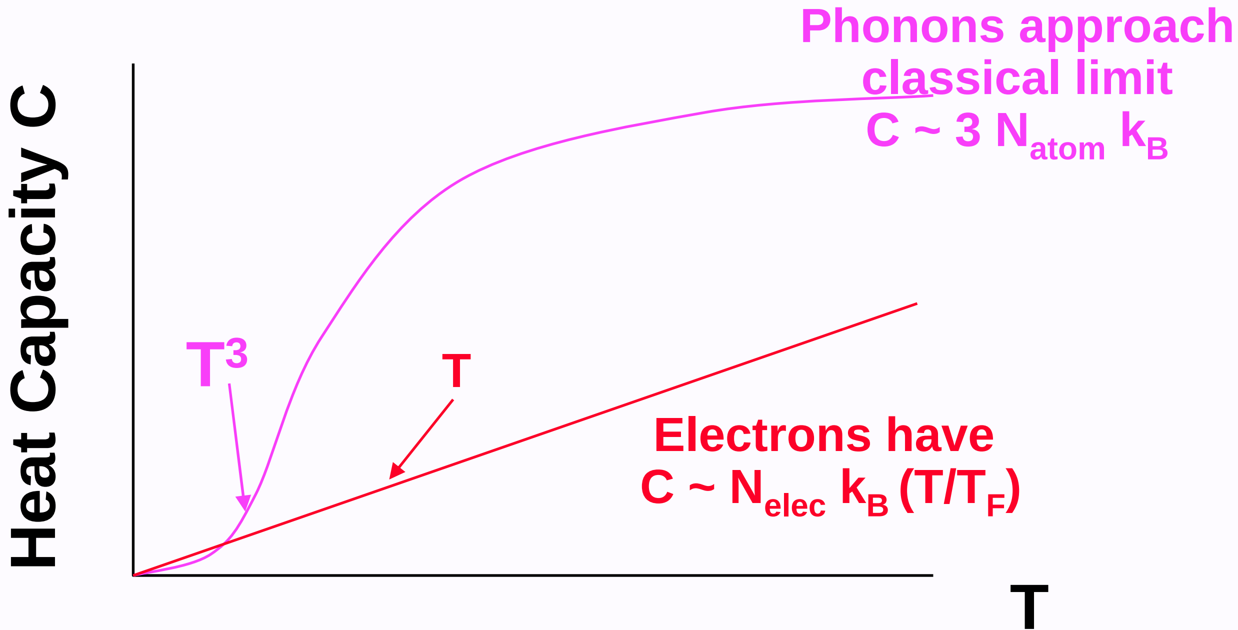
$\rightarrow (\pi^2/2)\ (N_{elec}/E_F)\ k_B^2\ T$ (for the electron gas)

(using $D(E_F) = 3\ N_{elec}/2E_F$)

- Key result: $C \sim T$ - agrees with experiment!

Heat capacity

- Comparison of electrons in a metal with phonons



Phonons approach classical limit $C \sim 3\, N_{atom}\, k_B$

Electrons have $C \sim N_{elec}\, k_B\, (T/T_F)$

Electrons dominate at low T in a metal

Phonons dominate at high T because of reduction factor (T/T_F)

Heat capacity

- Experimental results for metals

$$C/T = \gamma + A\,T^2 + \ldots.$$

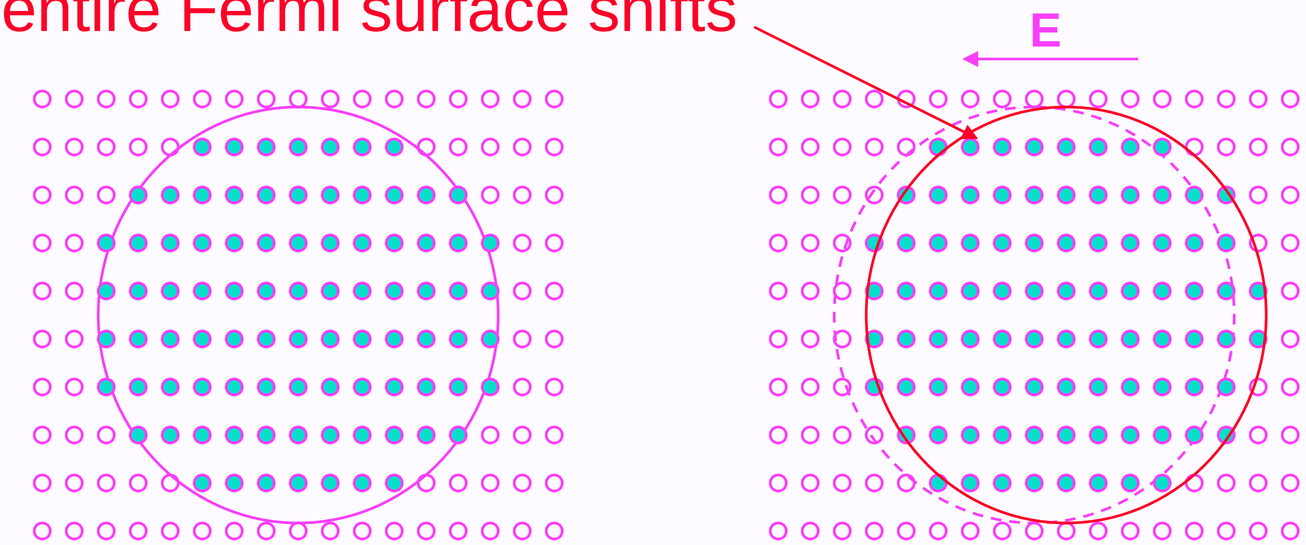
- Find the ratio γ / γ_{free}, $\gamma_{free} = (\pi^2/2)\,(N_{elec}/E_F)\,k_B^2$ is the free electron gas result. Equivalently since $E_F \propto 1/m$, we can consider the ratio $\gamma / \gamma_{free} = m_{free}/m_{th}^*$, where m_{th}^* is an thermal effective mass for electrons in the metal

Metal	m_{th}^*/ m_{free}
Li	2.18
Na	1.26
K	1.25
Al	1.48
Cu	1.38

- m_{th}^* close to m(free) is the “good”, “simple metals” !

Electrical Conductivity & Ohm's Law

- Consider electrons in an external field E. They experience a force $F = -eE$
- Now $F = dp/dt = \hbar\, dk/dt$, since $p = \hbar k$
- Thus in the presence of an electric field all the electrons accelerate and the k points shift, i.e., the entire Fermi surface shifts

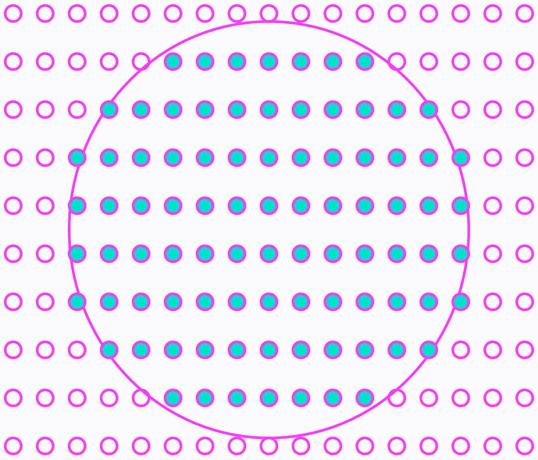


Equilibrium - no field

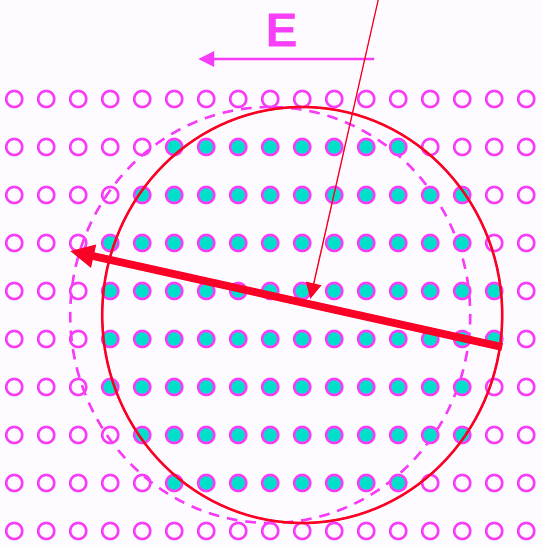
With applied field

Electrical Conductivity & Ohm’s Law

- What limits the acceleration of the electrons?
- Scattering increases as the electrons deviate more from equilibrium
- After field is applied a new equilibrium results as a balance of acceleration by field and scattering



Equilibrium - no field



With applied field

Electrical Conductivity and Resistivity

- The conductivity σ is defined by $j = \sigma E$,
  where j = current density
- How to find σ?
- From before $F = dp/dt = m\, dv/dt = \hbar\, dk/dt$
- Equilibrium is established when the rate that k increases due to E equals the rate of decrease due to scattering, then $dk/dt = 0$
- If we define a scattering time τ and scattering rate $1/\tau$
  $$\hbar\,(dk/dt + k/\tau) = F = q E \quad (q = \text{charge})$$
- Now $j = n q v$ (where n = density) so that
  $$j = n q (\hbar k/m) = (n q^2/m)\, \tau E$$
  $$\Rightarrow \boxed{\sigma = (n q^2/m)\, \tau}$$
- Resistance: $\rho = 1/\sigma \propto m/(n q^2 \tau)$

Note: sign of charge does not matter

Scattering mechanisms

- Impurities - wrong atoms, missing atoms, extra atoms, ….

  Proportional to concentration

- Lattice vibrations - atoms out of their ideal places

  Proportional to mean square displacement

- (Really these conclusions depend upon ideas from the next section that there is no scattering in a perfect crystal.)

Electrical Resistivity

- Resistivity ρ is due to scattering: Scattering rate inversely proportional to scattering time τ

$$\rho \propto \text{scattering rate} \propto 1/\tau$$

- Matthiesson's rule - scattering rates add

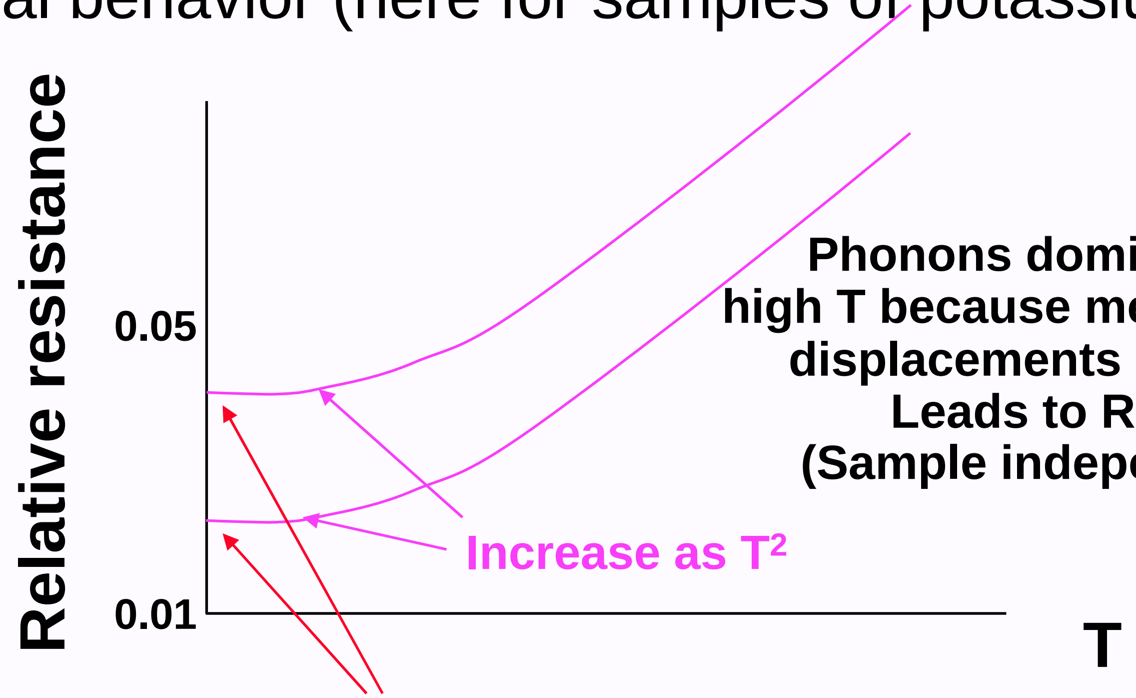
$$\rho = \rho_{\text{vibration}} + \rho_{\text{impurity}} \propto 1/\tau_{\text{vibration}} + 1/\tau_{\text{impurity}}$$

Temperature dependent
$\propto \langle u^2 \rangle$

Temperature independent
- sample dependent

Electrical Resistivity

- Consider relative resistance R(T)/R(T=300K)
- Typical behavior (here for samples of potassium)



Increase as T^2

Phonons dominate at high T because mean square displacements $\langle u^2 \rangle \propto T$

Leads to $R \propto T$

(Sample independent)

Inpurity scattering dominates at low T in a metal

(Sample dependent)

Interpretation of Ohm's law
Electrons act like a gas

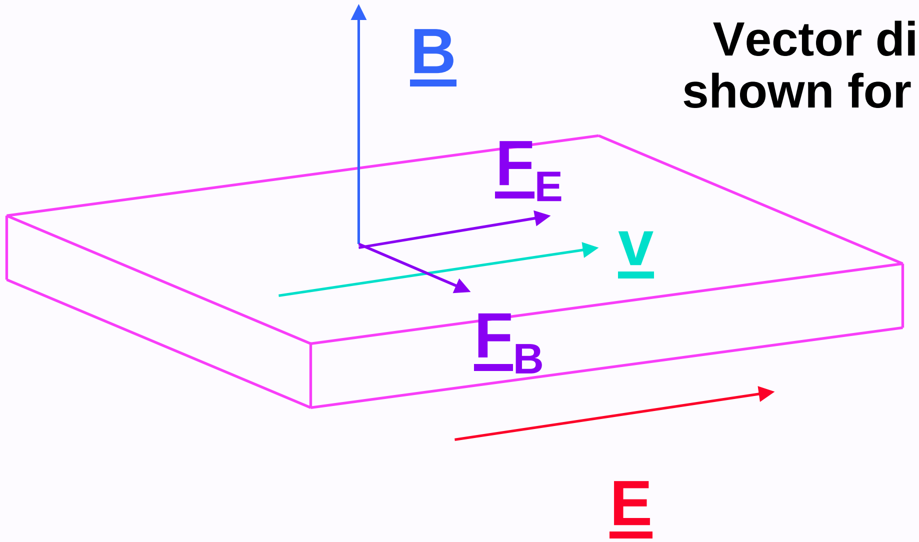
- A electron is a particle - like a molecule.
- Electrons come to equilibrium by scattering like molecules (electron scattering is due to defects, phonons, and electron-electron scattering).
- Electrical conductivity occurs because the electrons are charged, and it shows the electrons move and equilibrate
- What is different from usual molecules?
  Electrons obey the exclusion principle. This limits the allowed scattering which means that electrons act like a weakly interacting gas.

Hall Effect I

- Electrons moving in an electric and a perpendicular magnetic field
- Now we must carefully specify the vector force

$$\underline{F} = q(\,\underline{E} + (1/c)\,\underline{v} \times \underline{B}\,) \quad \text{(note: } c \rightarrow 1 \text{ for SI units)}$$

(q = -e for electrons)

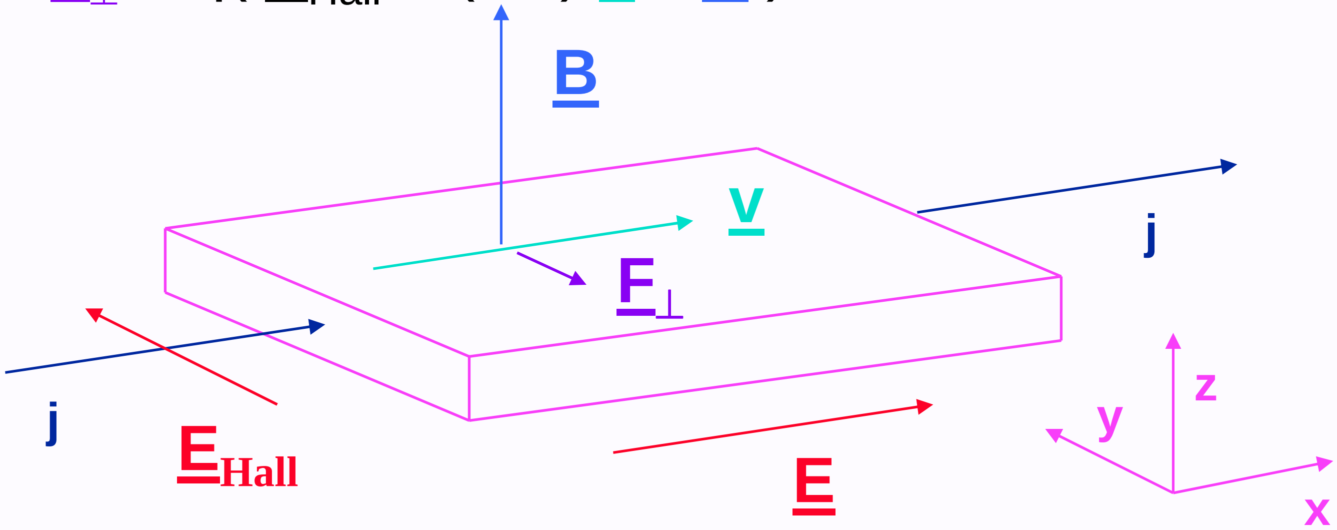


Vector directions shown for positive q

Hall Effect II

- Relevant situation: current $j = \sigma E = nqv$ flowing along a long sample due to the field $\underline{\mathbf{E}}$
- But NO current flowing in the perpendicular direction
- This means there must be a Hall field $\underline{\mathbf{E}}_{\mathrm{Hall}}$ in the perpendicular direction so the net force $\underline{\mathbf{F}}_{\perp} = 0$

$$\underline{\mathbf{F}}_{\perp} = q(\underline{\mathbf{E}}_{\mathrm{Hall}} + (1/c)\, \underline{\mathbf{v}} \times \underline{\mathbf{B}}) = 0$$



Hall Effect III

- Since

$$\underline{\mathbf{F}}_\perp = q(\,\underline{\mathbf{E}}_{\mathrm{Hall}} + (1/c)\,\underline{\mathbf{v}} \times \underline{\mathbf{B}}\,) = 0 \quad \text{and } v = j/nq$$

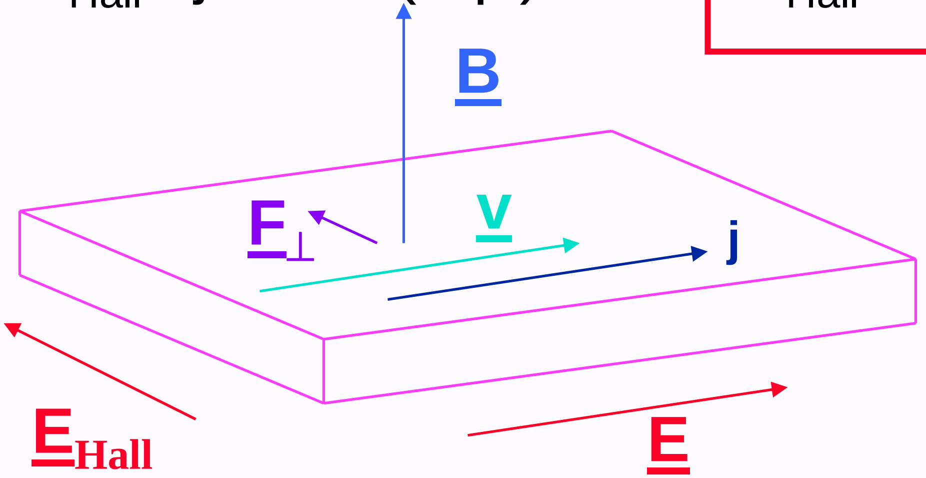
then defining $v = (\underline{\mathbf{v}})_x$, $E_{\mathrm{Hall}} = (\underline{\mathbf{E}}_{\mathrm{Hall}})_y$, $B = (\underline{\mathbf{B}})_z$,

$$E_{\mathrm{Hall}} = -\,(1/c)\,(j/nq)\,(-\,B)$$

Sign from cross product

and the Hall coefficient is

$$R_{\mathrm{Hall}} = E_{\mathrm{Hall}} / j\,B = 1/(nqc) \quad \text{or} \quad \boxed{R_{\mathrm{Hall}} = 1/(nq) \text{ in SI}}$$



Hall Effect IV

- Finally, define the Hall resistance as

$$\rho_{Hall} = R_{Hall}\, B = E_{Hall} / j$$

Each of these quantities can be measured directly

which has the same units as ordinary resistivity

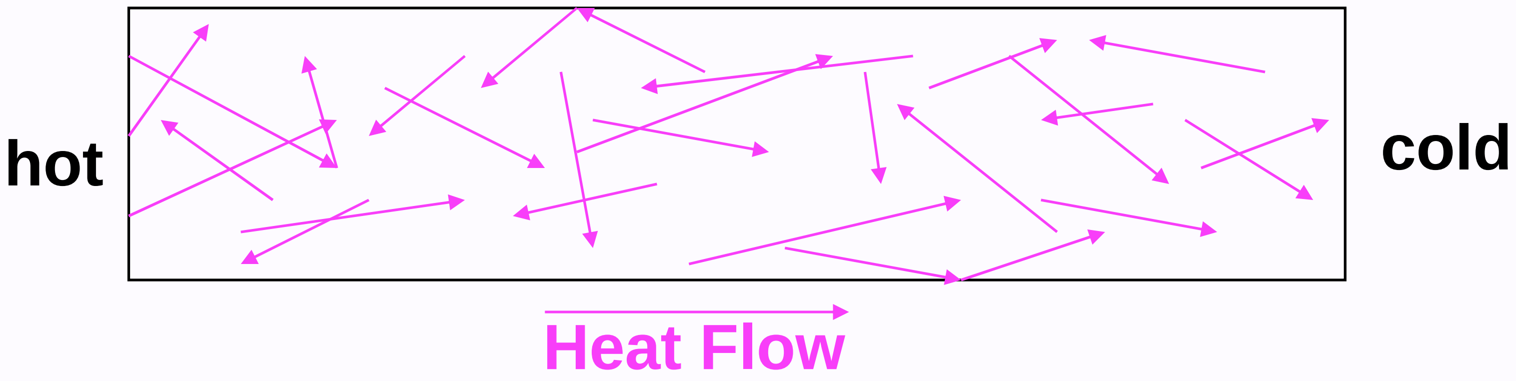
- $R_{Hall} = E_{Hall} / j\, B = 1/(nq)$
- Note: R_{Hall} determines sign of charge q

Since magnitude of charge is known R_{Hall} also determines density n

- The sign of charge in several metals (Mg, Al) is positive

Electrons act like gas - heat transport

- A electron is a particle that carries energy - just like a molecule.
- Electrical conductivity shows the electrons move, scatter, and equilibrate
- What is different from usual molecules? Electrons obey the exclusion principle. This limits scattering and helps them act like weakly interacting gas.



Heat Transport due to Electrons

- Definition (just as for phonons):
  $j_{thermal}$ = heat flow (energy per unit area per unit time)
  $= - K\, dT/dx$
- If an electron moves from a region with local temperature T to one with local temperature T - ΔT, it supplies excess energy c ΔT, where c = heat capacity per electron. (Note ΔT can be positive or negative).
- On average :
  $\Delta T = (dT/dx)\, v_x\, \tau$, where τ = mean time between collisions
- Then $j_{thermal} = -\underbrace{\underset{\text{Density}}{n}\ v_x}_{\text{Flux}}\, c\, v_x\, \tau\, dT/dx = -n\ c\, v_x^2\, \tau\, dT/dx$

Electron Heat Transport - continued

- Just as for phonons:
  Averaging over directions gives $(v_x^2)_{\text{average}} = (1/3) v^2$
  and
  $$j = - (1/3)\, n\, c\, v^2\, \tau\, dT/dx$$

- Finally we can define the mean free path $L = v \tau$
  and $C = nc$ = total heat capacity,
  Then
  $$j = - (1/3)\, C\, v\, L\, dT/dx$$
  and
  $K = (1/3)\, C\, v\, L = (1/3)\, C\, v^2\, \tau$ = thermal conductivity

  (just like an ordinary gas!)

Electron Heat Transport - continued

- What is the appropriate v?
- The velocity at the Fermi surface = v_F
- What is the appropriate τ ?
- Same as for conductivity (almost).

- Results using our previous expressions for C:

$$K = (\pi^2/3)\ (n/m)\ \tau\ k_B^2\ T$$

- Relation of K and σ -- From our expressions:

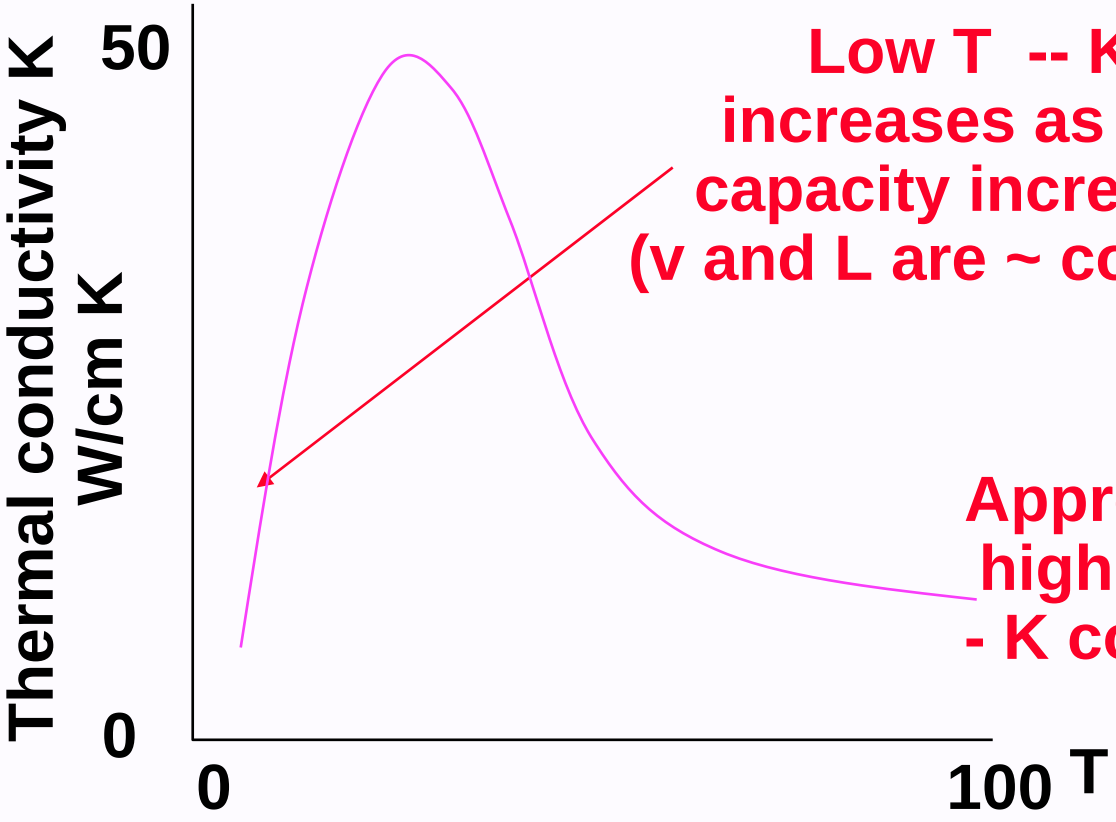
$$K / \sigma = (\pi^2/3)\ (k_B/e)^2\ T$$

- This justifies the Weidemann-Franz Law that

$$K / \sigma \propto T$$

Electron Heat Transport - continued

- K ∝ σ T
- Recall σ → constant as T → 0, σ → 1/T as T → large



Low T -- K increases as heat capacity increases (v and L are ~ constant)

Approaches high T limit - K constant

Electron Heat Transport - continued

- Comparison to Phonons

  Electrons dominate in good metal crystals

  Comparable in poor metals like alloys

  Phonons dominate in non-metals

Summary

- **Electrical Conductivity - Ohm's Law**

  $\sigma = (n\, q^2/m)\, \tau \qquad \rho = 1/\sigma$

- **Hall Effect**

  $\rho_{Hall} = R_{Hall}\, B = E_{Hall} / j$

  and ρ_{Hall} determine n and the charge of the carriers

- **Thermal Conductivity**

  $K = (\pi^2/3)\ (n/m)\, \tau\, k_B^2\, T$

  Weideman :

  $K / \sigma = (\pi^2/3)\, (k_B/e)^2\, T$

- **Metallic Binding**

  Kinetic repulsion

  Coulomb attraction to nuclei

  (not included in gas model - must be added)