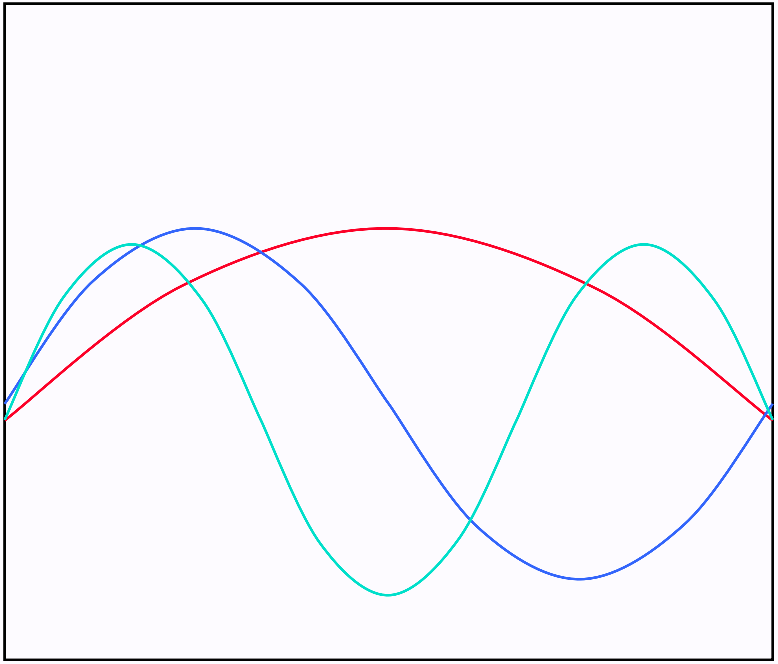
# Part II - Electronic Properties of Solids

## Lecture 12: The Electron Gas (Kittel Ch. 6)



# Outline

- Overview - role of electrons in solids

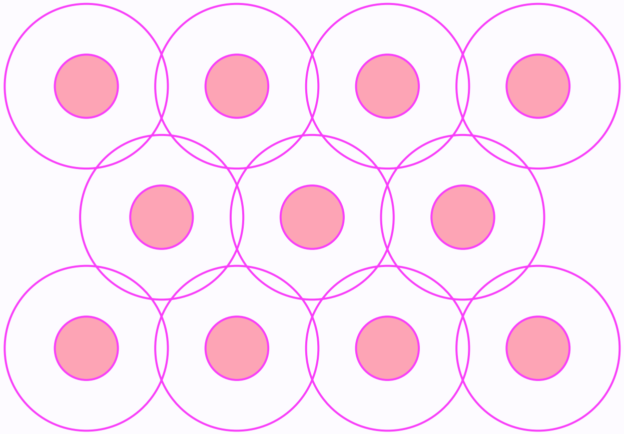
- The starting point for understanding electrons in solids is completely different from that for understanding the nuclei ( But we will be able to use many of the same concepts! )
- Simplest model - Electron Gas
  - Failure of classical mechanics
  - Success of quantum mechanics
  - Pauli Exclusion Principle, Fermi Statistics
  - Energy levels in 1 and 3 dimensions
- Similarities, differences from vibration waves
- Density of States, Heat Capacity
- (Read Kittel Ch 6)

# Role of Electrons in Solids

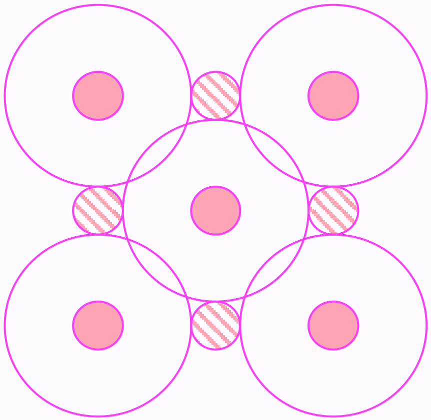
- Electrons are responsible for binding of crystals -- they are the "glue" that hold the nuclei together
  - Types of binding (see next slide)
    - Van der Waals - electronic polarizability
    - Ionic - electron transfer
    - Covalent - electron bonds
    - Metallic - more about this soon

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

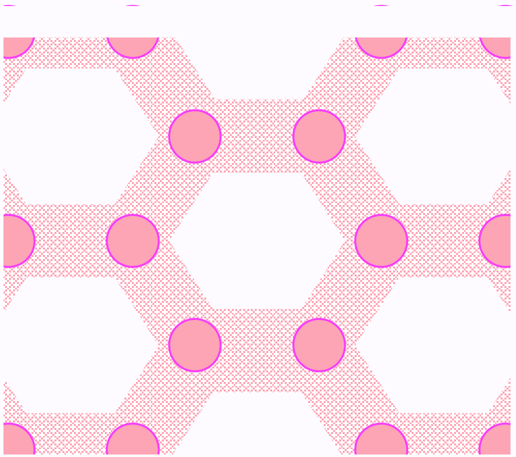
# Characteristic types of binding



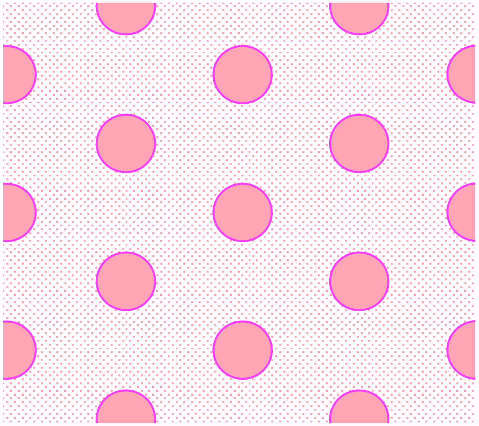
Closed-Shell Binding
Van der Waals



Ionic Binding



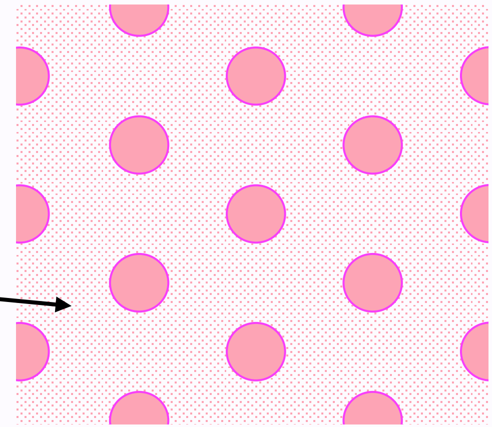
Covalent Binding



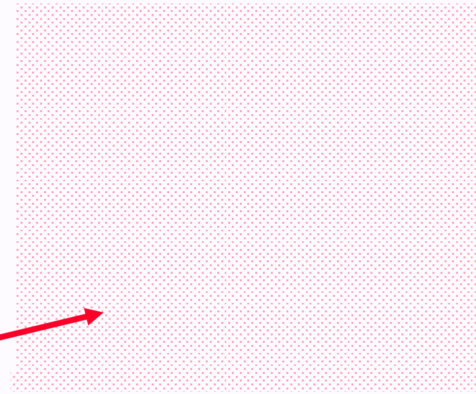
Metallic Binding

# 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**



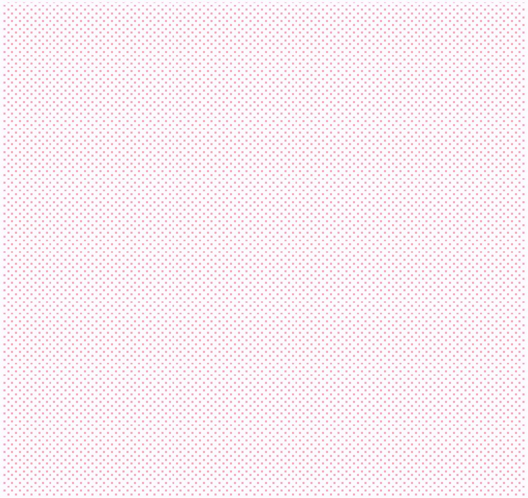
- **Electron Gas**
  **Simplest possible model for a metal - electrons are completely "free of the nuclei" - nuclei are replaced by a smooth background -- "Electrons in a box"**



# Electron Gas - History

- Electron Gas model predates quantum mechanics

- Electrons Discovered in 1897
  - J. J. Thomson



- Drude-Lorentz Model -
  Electrons - classical particles free to move in a box

# Drude-Lorentz Model (1900-1905)

- **Electrons as classical particles moving in a box**
- **Model: All electrons contribute to conductivty. Works! Still used!**
- **But same model predicted that all electrons contribute to heat capacity. Disaster. Heat capacity is MUCH less than predicted.**

**Paul Drude**

# Quantum Mechanics

- 1911: Bohr Model for H
- 1923: Wave Nature of Particles Proposed
  Prince Louie 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

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

where

m = mass of particle

$V(\underline{r})$ = potential energy at point $\underline{r}$

$\nabla^2 = (d^2/dx^2 + d^2/dy^2 + d^2/dz^2)$

E = eigenvalue = energy of quantum state

$\Psi(\underline{r})$ = wavefunction

$n(\underline{r}) = |\Psi(\underline{r})|^2$ = probability density

$\nabla$

# Schrodinger Equation - 1d line

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

0 L

- Schrodinger Eq. In 1d with V = 0

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

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

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

  (Note similarity to vibration waves)

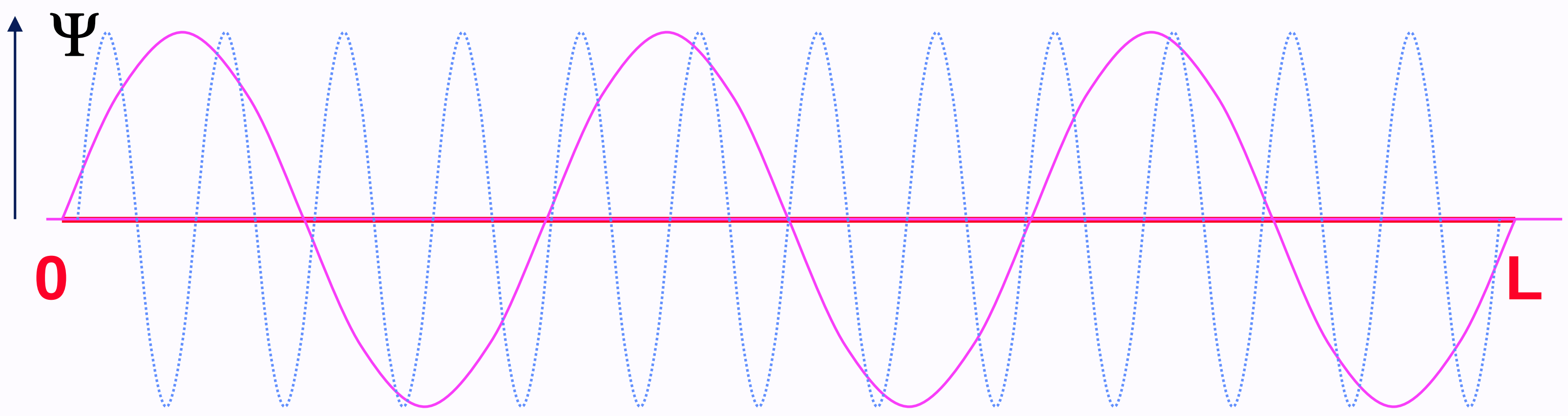
  Factor chosen so $\int_0^L dx \, | \Psi(x) |^2 = 1$

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

# Electrons on a line

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

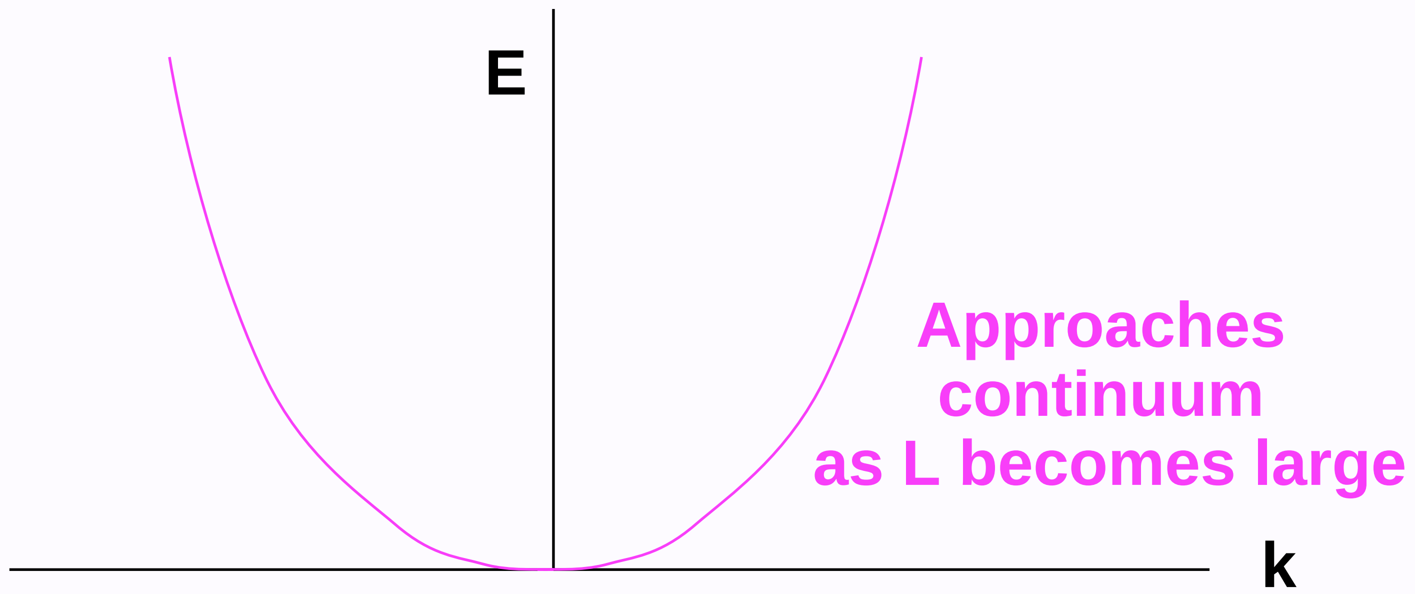
  Examples of waves - same picture as for lattice vibrations except that here $\Psi(x)$ is a continuous wave instead of representing atom displacements



# Electrons on a line

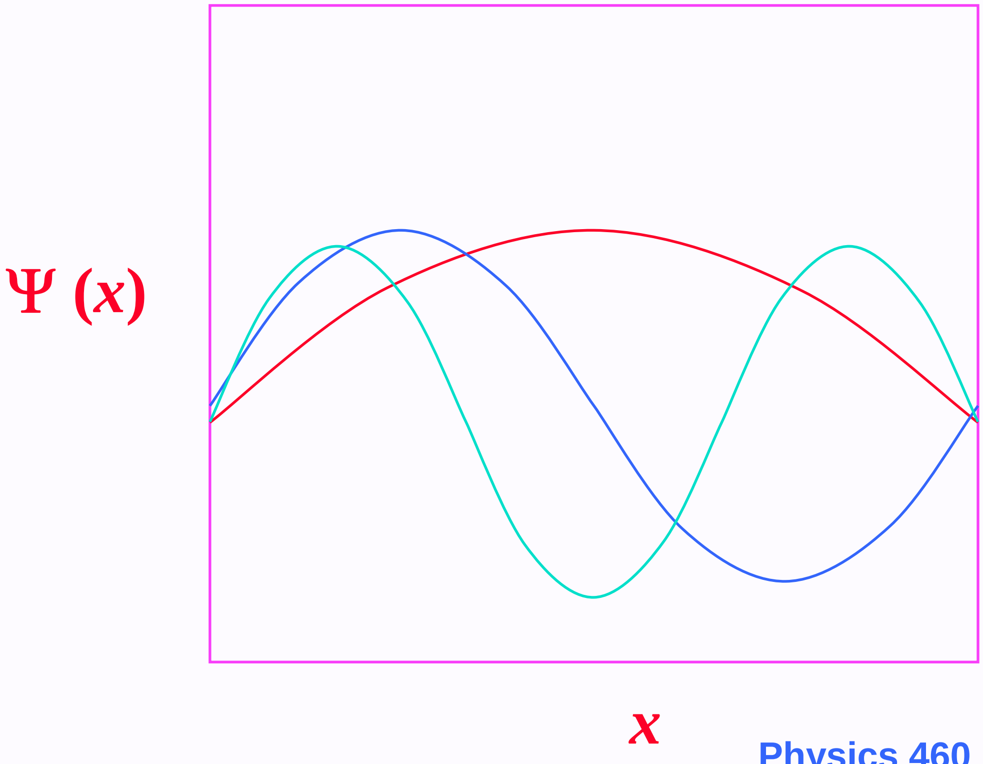
- For electrons in a box, the energy is just the kinetic energy which is quantized because the waves must fit into the box

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



# Schrodinger Equation - 1d line

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



# Electrons in 3 dimensions

- Schrodinger Eq. In 3d with V = 0

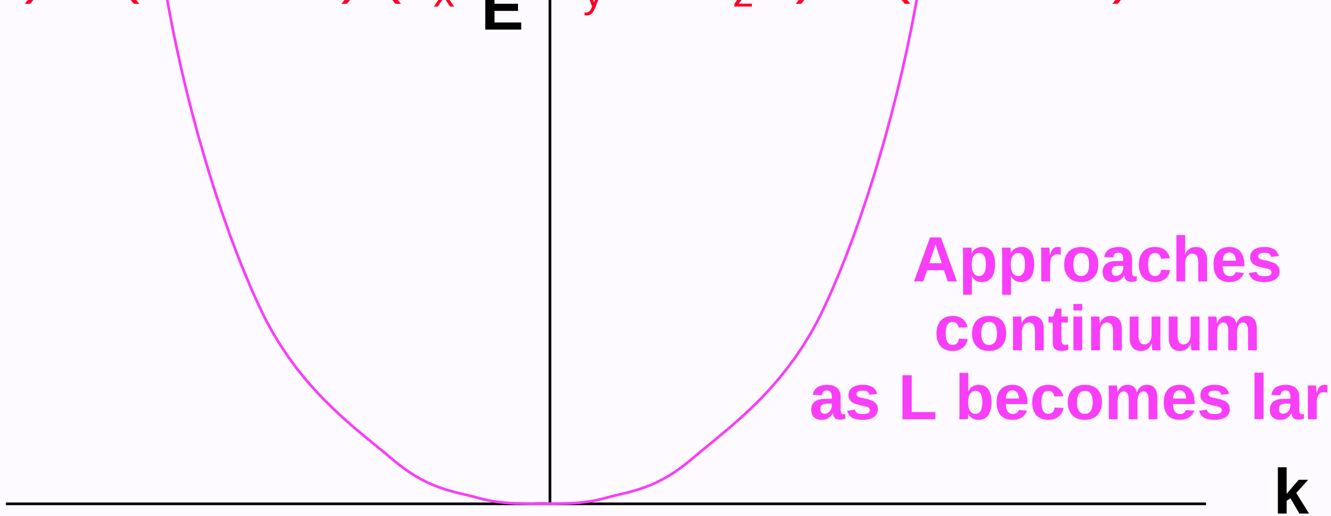
  $-(\hbar^2/2m)\,[d^2/dx^2 + d^2/dy^2 + d^2/dz^2]\,\Psi(x,y,z) = E\,\Psi(x,y,z)$

- Solution

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

  $k_x = m\,\pi/L$, m = 1,2, …, same for y,z

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



# Electrons in 3 dimensions

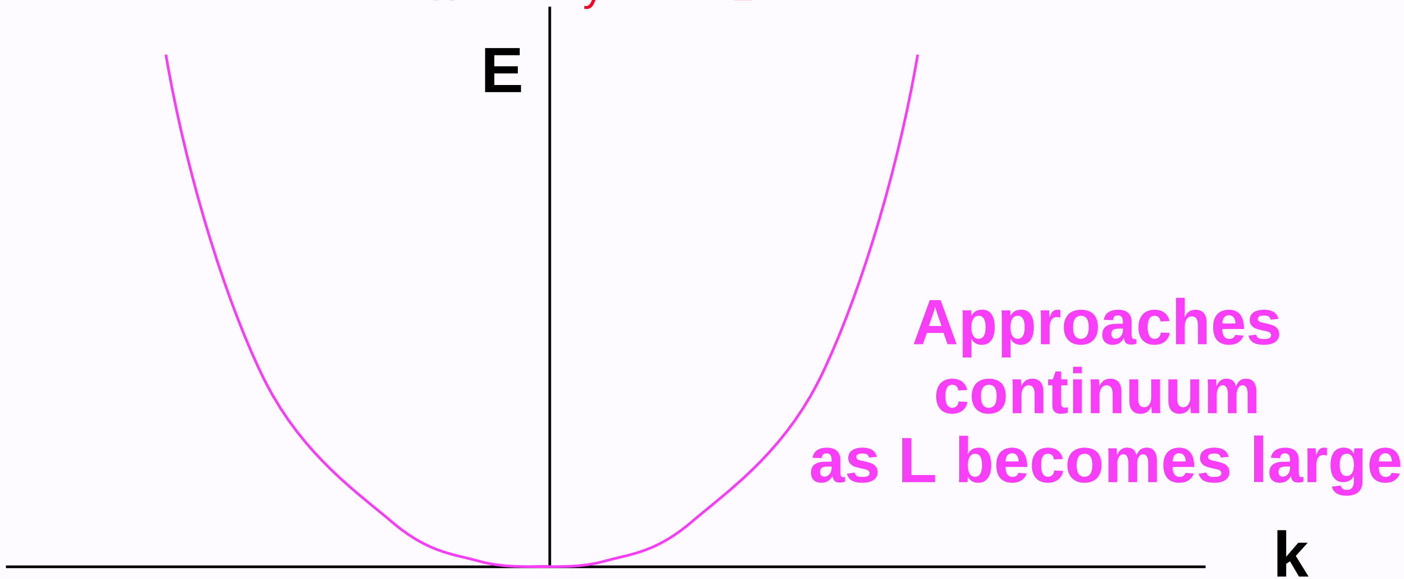
- Just as for phonons it is convenient to define $\Psi$ with periodic boundary conditions

- $\Psi$ is a traveling plane wave:

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

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

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



# Density of States 3 dimensions

- Key point - exactly the same as for vibration waves - the values of $k_x$ $k_y$ $k_z$ are equally spaced - $\Delta k_x = 2\pi/L$ , etc.
- Thus the volume in k space per state is $(2\pi/L)^3$ and the number of states N per unit volume $V = L^3$, with $|k| < k_0$ is

  $$N = (4\pi/3)\, k_0^3 / (2\pi/L)^3 \;\Rightarrow\; N/V = (1/6\pi^2)\, k_0^3$$

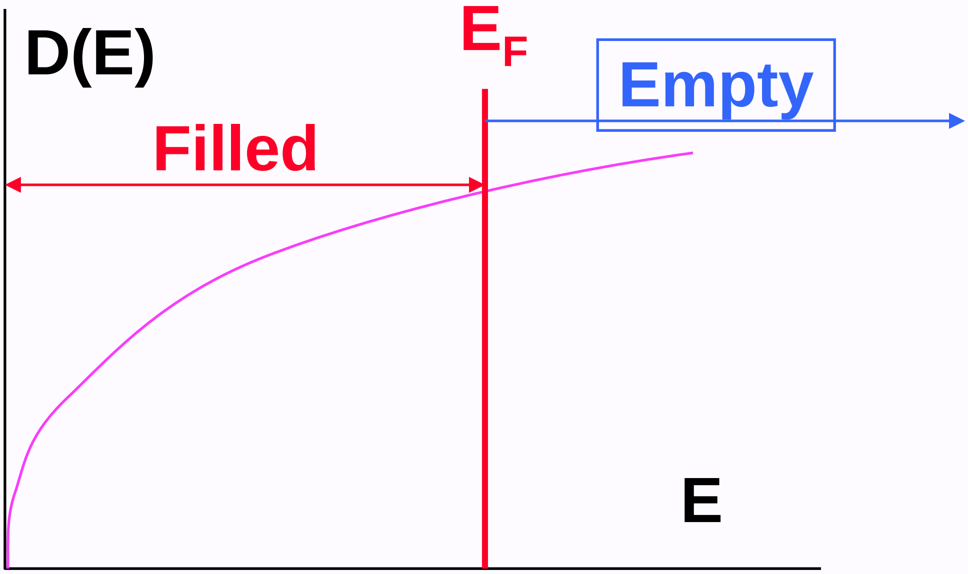
- $\Rightarrow$ density of states per unit energy per unit volume is $D(E) = d(N/V)/dE = (d(N/V)/dk)\,(dk/dE)$
  Using $E = (\hbar^2/2m)\, k^2$ , $dE/dk = (\hbar^2/m)\, k$

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

- (NOTE - Kittel gives formulas that already contain a factor of 2 for spin)

# Density of States 3 dimensions

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



# 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.
- 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

$$N_{elec}/2V = (1/6\pi^2)\, k_F^3 \text{ or } N_{elec}/V = (1/3\pi^2)\, k_F^3$$

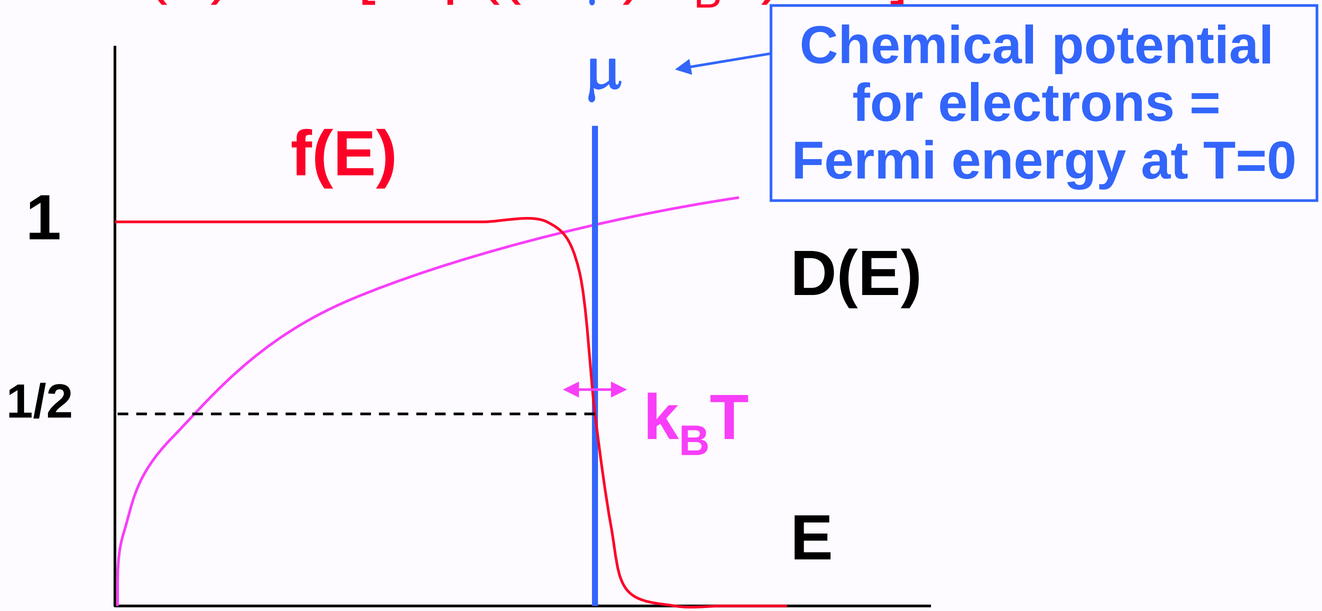
$\Rightarrow$

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

# Fermi Distribution

- At finite temperature, electrons are not all in the lowest energy states
- Applying the fundamental law of statistics to this case (occcupation of any state and spin only can be 0 or 1) leads to the Fermi Distribution (Kittel appendix)

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



# Typical values for electrons?

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

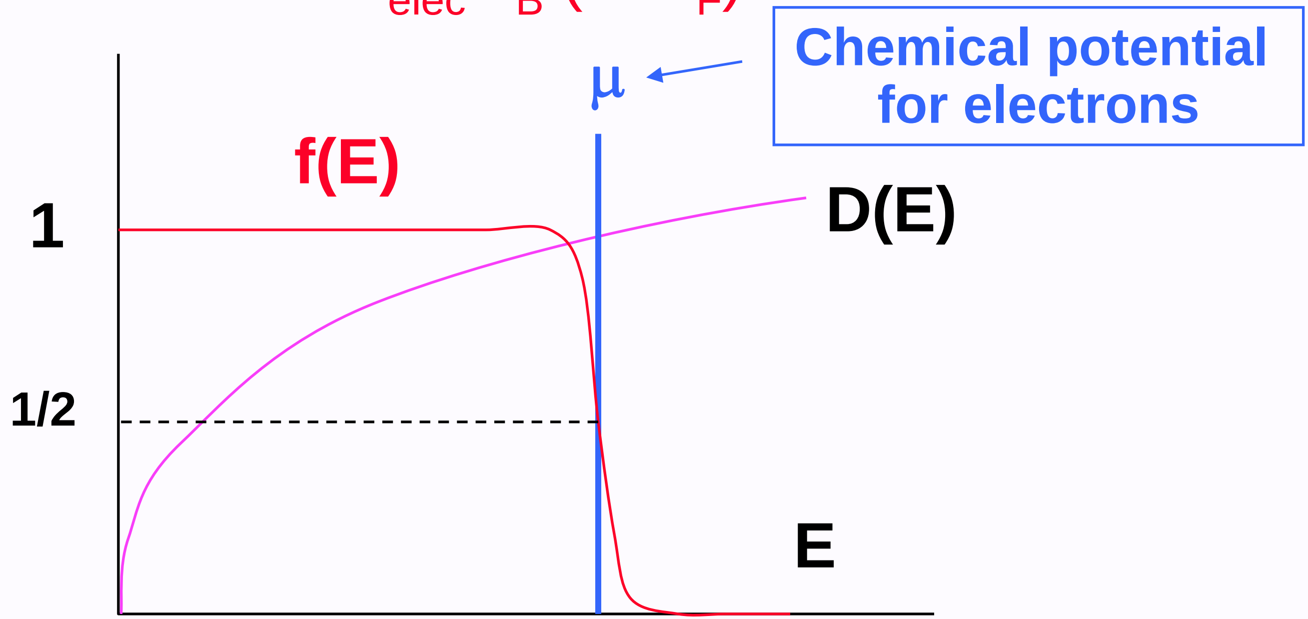
| Element | $N_{elec}$/atom | $E_F$ | $T_F = E_F/k_B$ |
|---|---|---|---|
| Li | 1 | 4.7 eV | 5.5 x$10^4$ K |
| Na | 1 | 3.23eV | 3.75 x$10^4$ K |
| Al | 3 | 11.6 eV | 13.5 x$10^4$ K |

- Conclusion: For typical metals the Fermi energy (or the Fermi temperature) is much greater than ordinary temperatures

# Heat Capacity for Electrons

- Just as for phonons the definition of heat capacity is $C = dU/dT$ where U = total internal energy
- For $T << T_F = E_F / k_B$ it is easy to see that roughly $U \sim U_0 + N_{elec} (T/ T_F) k_B T$ so that

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



# Heat Capacity for Electrons

- Quantitative evaluation:
  $U = \int_0^{\infty} dE\, E\, D(E)\, f(E) - \int_0^{E_F} dE\, E\, D(E)$

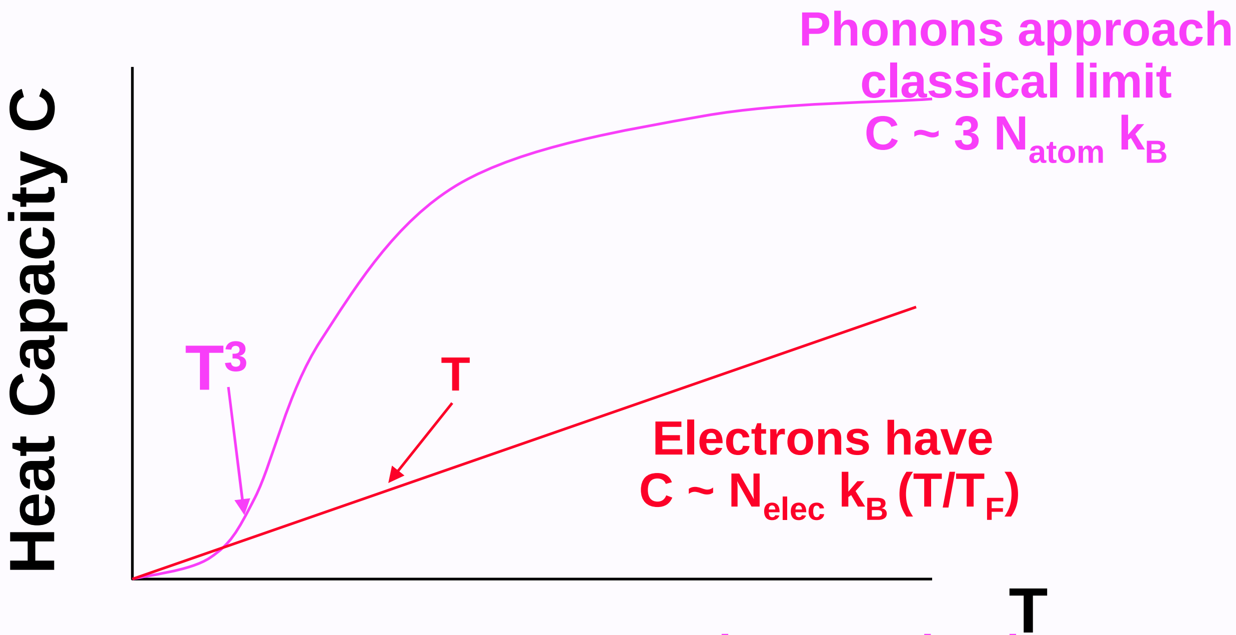
- Using the fact that $T << T_F$:
  $C = dU/dT = \int_0^{\infty} dE\, (E - E_F)\, D(E)\, (df(E)/dT)$
  $\approx D(E_F) \int_0^{\infty} dE\, (E - E_F)\, (df(E)/dT)$

- Finally, using transformations discussed in Kittel, the integral can be done almost exactly for $T << T_F$
  $\rightarrow C = (\pi^2/3)\, D(E_F)\, k_B^2\, T$ (valid for any metal)
  $\rightarrow (\pi^2/2)\, (N_{elec}/E_F)\, k_B^2\, T$ (for the electron gas)
  $D(E_F) = 3\, N_{elec}/2E_F$ for gas

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

# Heat capacity

- Comparison of electrons in a metal with phonons




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

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

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

| Metal | $m_{th}^*/ m(\text{free})$ |
|---|---|
| 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” !

# Outline

- Overview - role of electrons in solids
  - Determine binding of the solid
  - "Electronic" properties (conductivity, … )
- The starting point for understanding electrons in solids is completely different from that for understanding the nuclei ( But we will be able to use many of the same concepts! )
- Simplest model - Electron Gas
  - Failure of classical mechanics
  - Success of quantum mechanics
  - Pauli Exclusion Principle, Fermi Statistics
  - Energy levels in 1 and 3 dimensions
- Similarities, differences from vibration waves
- Density of States, Heat Capacity
- (Read Kittel Ch 6)

# Next time

- **Continue free electron gas (Fermi gas)**
- **Electrical Conductivity**
- **Hall Effect**
- **Thermal Conductivity**
- **(Read Kittel Ch 6)**
- **Remember: EXAM Wednesday, October 11**

# Comments on Exam

- **Wed. October 11**

- **Closed Book**
  **You will be given constants, etc.**

- **Three types of problems:**

- **Short answer questions**
- **Order of Magnitudes**
- **Essay questions**
- **Quantitative problems – not difficult**