

# Metallic Bonding

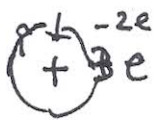
Ex: Li metal

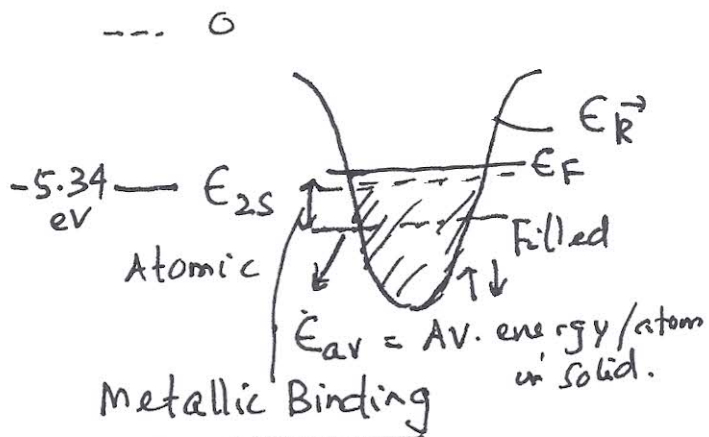
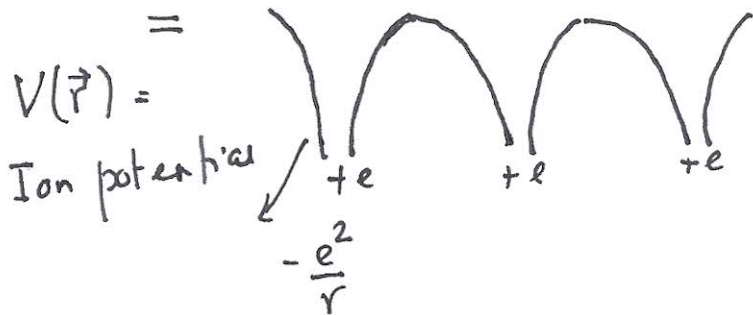
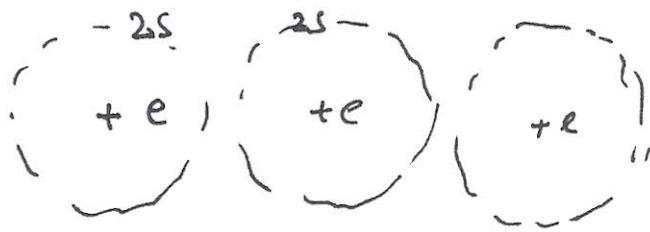
$1s^2, 2s^1$



1s electrons are tightly bound (core electrons)

2s " are loosely bound (conduction electrons)

Ion Core:   $\Rightarrow + Z_{eff}e, Z_{eff} = 1$



## Physical reasons for metallic binding

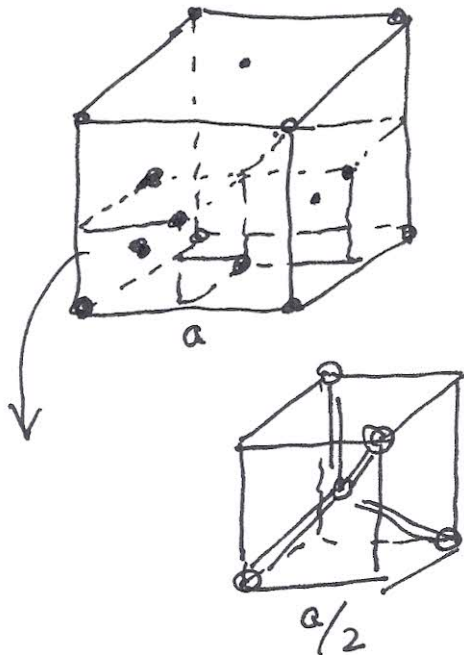
- ① Delocalization reduces Kinetic energy
- ② Exchange interaction keeps parallel spins apart  $\rightarrow$  reduces Coulomb repulsion.
- ③ Average Coulomb repulsion balanced by electron-ion attraction.
- ④ Coulomb correlation (many-body effect)

# Covalent bonding

Quite strong — comparable to ionic bonds  
 4-5 eV/atom Cohesive energy.

What's Ex: (Purely covalent)

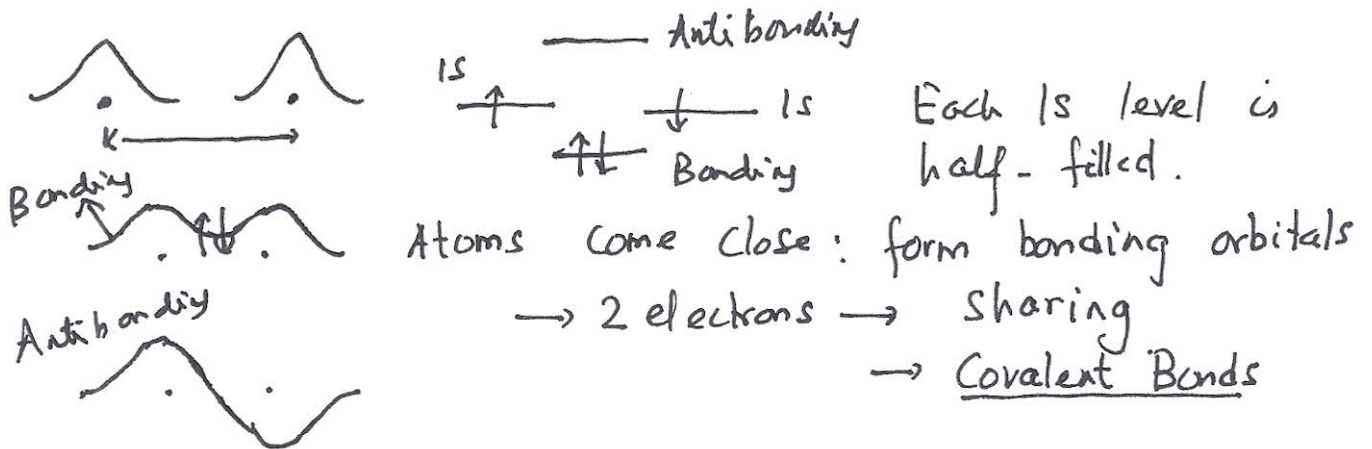
- Carbon, Si, Ge,
- Graphite, Graphene,
- Bucky balls, Nanotubes ...
- organic solids



Each C atom bonds with Every 4 other C atoms  
 C: Forms a tetrahedron.

What's the physical origin of <sup>covalent-</sup>binding?

Look at H<sub>2</sub> molecule.



Generalize this concept to C solid

Bonds Vs Bands.

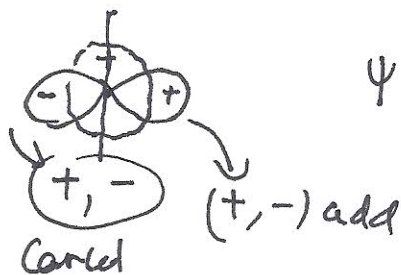
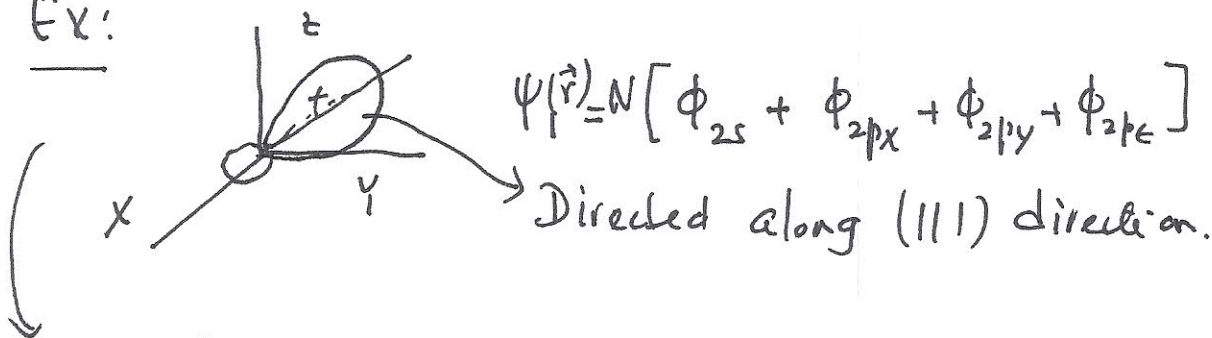
# Carbon atom

$2p^2$   $\begin{array}{|c|c|c|} \hline \uparrow & \uparrow & \\ \hline p_x & p_y & p_z \end{array}$  P-orbitals are partially filled -  
 $2s^2$   $\begin{array}{|c|} \hline \uparrow\downarrow \\ \hline s \end{array}$  can form covalent bonds, but only 3  
 In C solid we need 4 bonds for each C atom.

$sp^3$  bonds:  $\psi_i = C_{is} \phi_{2s} + C_{i\mu} \phi_{2p_\mu}$   $\mu = x, y, z$   
 $i = 1, 2, 3, 4$

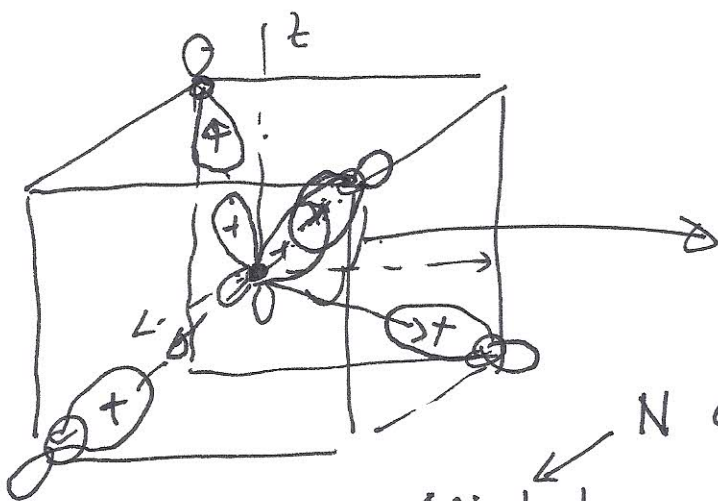
oriented orbitals  $\rightarrow$  ideal to form bonds.

Ex:



$\psi = \phi_{2s} + \phi_{2p_x} \Rightarrow$

oriented towards +x dir



— Anti bonding

$\uparrow\downarrow$  Bonding

$N$  atoms  $\rightarrow 4N$   $sp^3$  orbitals

$4N$  electrons

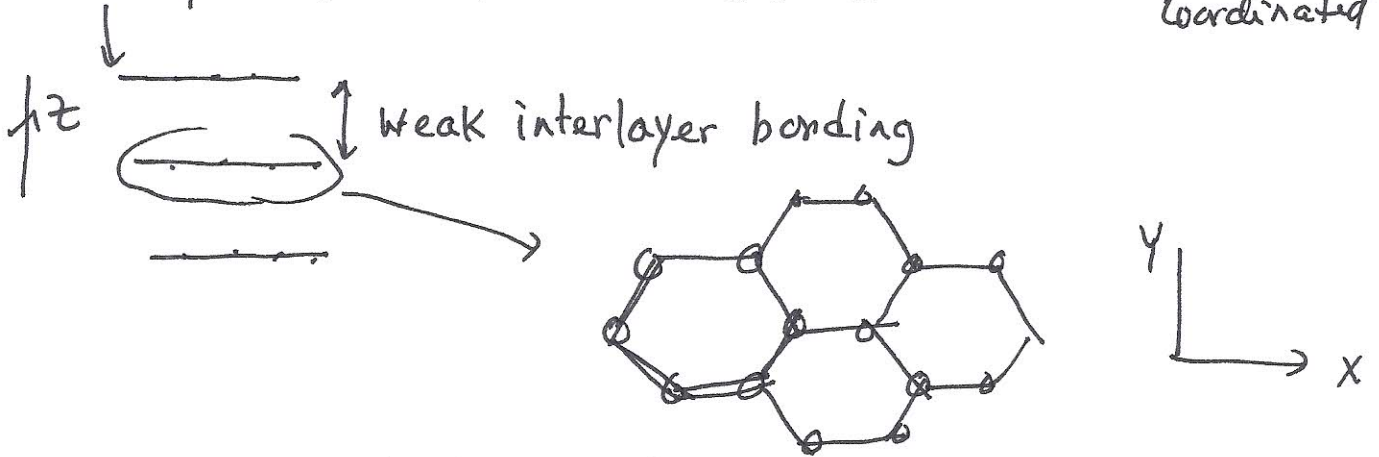
$2N$  Bonding

$2N$  Anti - "

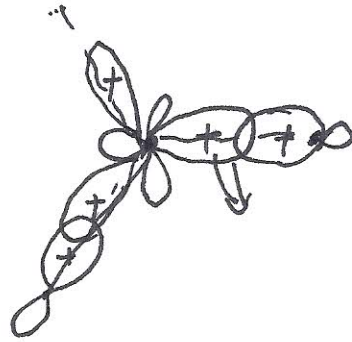


# Graphite / Graphene

C: atoms are 3-fold coordinated

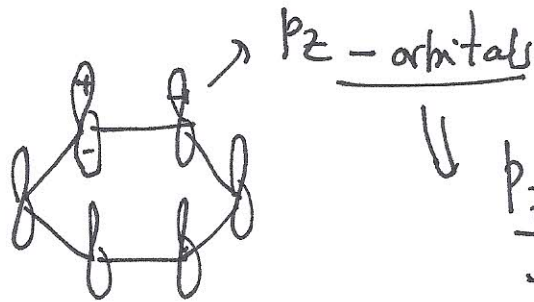


$s, p_x, p_y$  or  $sp^2$  bonding.



—  $3 \frac{N}{2}$  antibonding  
 —  $3 \frac{N}{2}$  bonding  
~~6N~~ electrons  
 (3N)

But there are 4N electrons.



↓ p\_z-bonds.



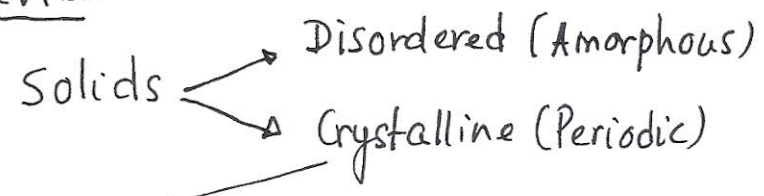
Graphite is metallic

Graphene is another story

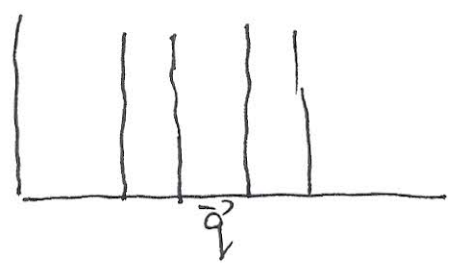
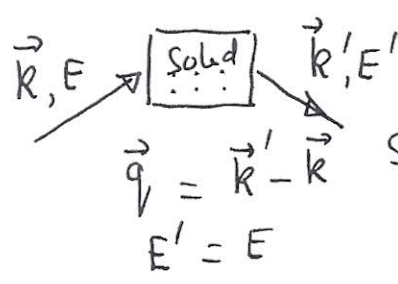
# Lattice Vibrations, Normal Modes, Phonons etc.

Ch. 4,5

## Quick Review



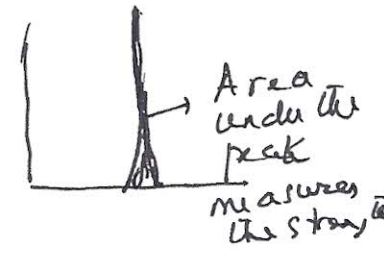
Structure: Diffraction (X-ray, Electron, Neutron...)  
Elastic scattering



Bragg peaks

$\vec{q} = \vec{G}$   
Reciprocal lattice vectors.

In reality: Experimental Resolution  $\Delta\vec{q}$

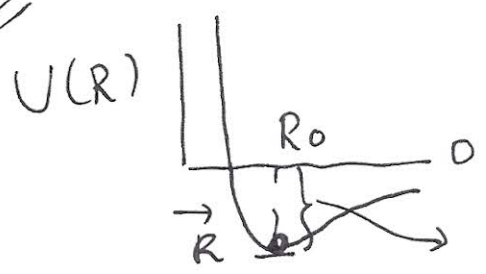


## Physics of Binding (Cohesion)

$E = E_{\text{kin (atoms)}} + E_{\text{rest}}$

$E_{\text{rest}} = E_{\text{Nuc-Nuc}} + E_{\text{el}} \Rightarrow U(R)$

Assume  $\epsilon = 0$



- $E_{\text{coh.}}$
- Metallic
  - Ionic
  - Covalent
  - Van der Waal

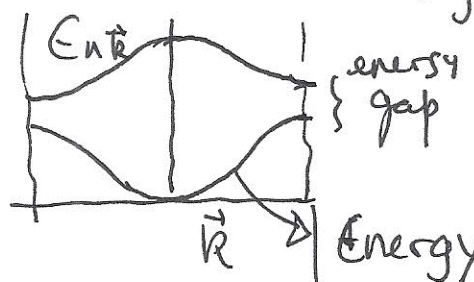
# Electronic Structure (static periodic lattice)

Periodic potential  $V(\vec{r}) = V(\vec{r} + \vec{R})$   
 $\vec{R}$  direct lattice vector

$E_{n\vec{k}}$  : Energy states that electrons can occupy.

Nearly free electron approx } "Energy gaps"  
 Tight binding approx } "Bands"

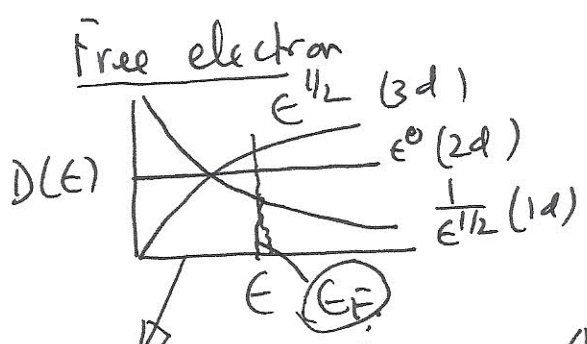
1<sup>st</sup> Brillouin zone



Energy dispersion  
 Brillouin Zone boundary.

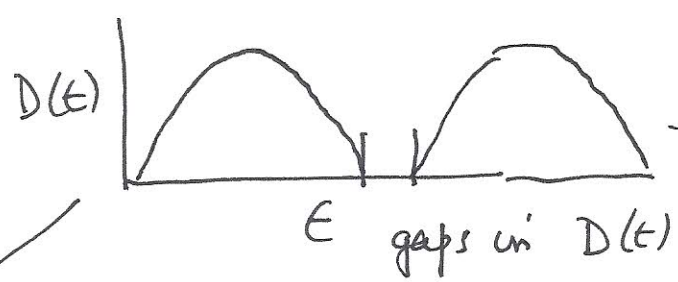
## Density of States

D(E)



Always a metal  
 (Why?)

## Band electrons (3d)



Position of  $E_F$  depends on  $N_{el}$  = Number of electrons.

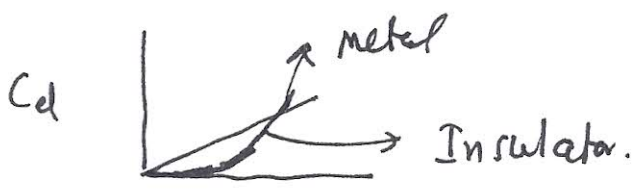
- ① Metal:  $E_F$  lies in the band
- ② Insulator or Semiconductor  $E_F$  lies in the band gap

How do we differentiate between a metal and insulator.

### Heat capacity

Metals:  $C_{el} \sim \gamma T$   $T \ll T_F$

Insulators:  $C_{el} \sim e^{-\Delta/k_B T}$   $k_B T \ll E_g$



Now we want to see what happens when atoms are allowed to move:  $E_{kin, atom} \neq 0$

As long as  $E_{kin, atom}$  not too large:

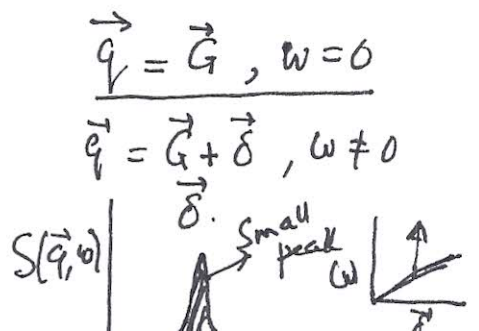
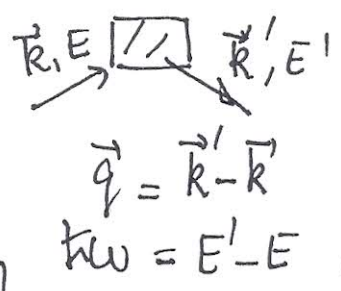
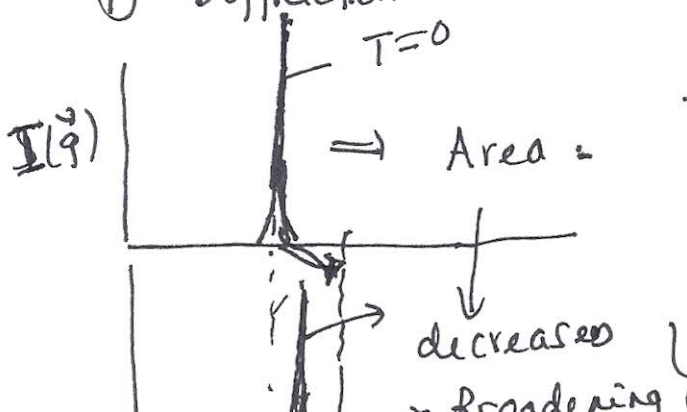
→ Vibration of atoms about their static eq.

- Normal modes, Diff. type of modes,
- Dispersion of modes  $\omega_{\vec{k}j}$  (Similar to  $E_n(\vec{k})$ )
- Density of States
- Phonons
- Thermal properties

⇒ How do atomic vibrations show up in experiment?

① Diffraction

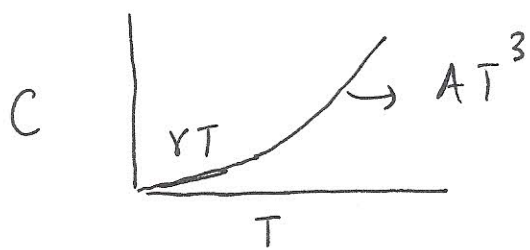
② Inelastic scattering





# Thermal properties

Heat Capacity: Metals:  $C = C_{el} + C_{latt}$   
 $= \gamma T + \underbrace{AT^3}_{\omega} + \dots$



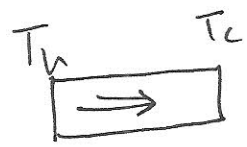
At very low T,  $C_{el}$  dominates (Why).  
 low density of states associated with lattice vib. modes.

## Insulators

$$C = B e^{-\Delta/k_B T} + AT^3$$

At low T,  $C_{latt}$  dominates (Why)  
 electronic excitations are suppressed due to energy gap.

## Thermal Conductivity $K$



$$K = K_{el} + K_{latt}$$

$J_{heat} \propto \nabla T$  Metals:  $K_{el} \approx K_{latt}$   
 $= -K \nabla T$  Insulators:  $K_{latt}$  dominates.

Electrons interact with "phonons" ~~the~~ vibrating lattice.

# Some basic things about lattice vibrations



Solid: N atoms : Bead/spring model

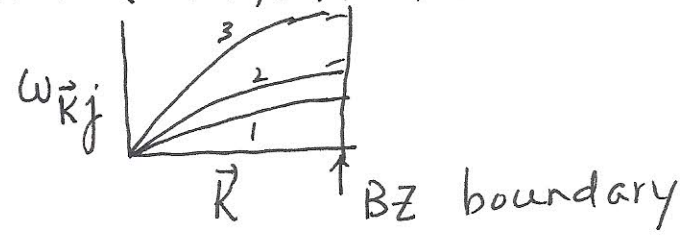
Each atom: moves in 3d (unless there are constraints)

3N degrees of freedom  
= 3N normal modes

Bravais Lattice

Normal mode frequencies  $\omega_{\vec{k}j}$   
 $\vec{k} \in 1^{st}$  Brillouin zone (N allowed  $\vec{k}$  values)  
~~for~~  $j=1,2,3$

If  $\vec{k}$  is along symmetry directions  
Cubic:  $(1,0,0), (0,1,0), (0,0,1)$  or  $(1,1,0)$  - -

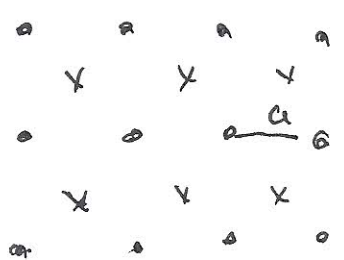


Longitudinal, Transverse



For general  $\vec{k}$  : L & T get mixed up.

Bravais Lattice with Basis



N Bravais Lattice sites

$Nr = \#$  of atoms  $r = \#$  of atoms/BL point  
 $r=2$

3Nr modes

For a given  $\vec{k}$  : there are 3r modes. (More next time)