Phonons I - Crystal Vibrations Continued (Kittel Ch. 4)

View of triple axis neutron scattering facility at National Research Council of Canada

http://neutron.nrc.ca/welcome.htm

Outline

- **Examples in higher dimensions**
- **How many modes are there?**
- **Quantization and Phonons**
- **Experimental observation by inelastic scattering**
- **(Read Kittel Ch 4)**

From last lecture

Energy due to Displacements

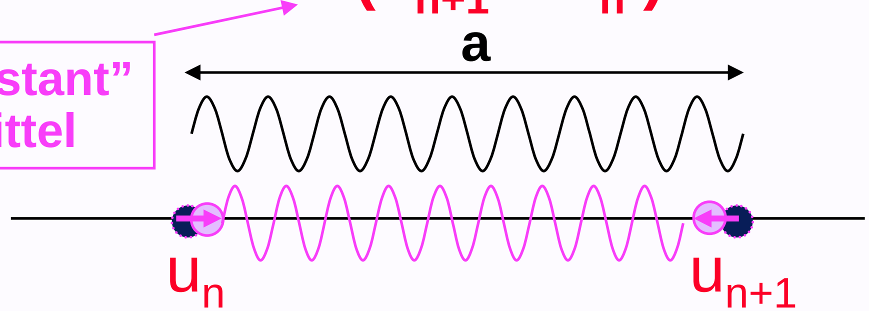
- The energy of the crystal changes if the atoms are displaced.
- Analogous to springs between the atoms

More later on this

- Suppose there is a spring between each pair of atoms in the chain. For each spring the change is energy is:

$$\Delta E = \frac{1}{2} C (u_{n+1} - u_n)^2$$

C = "spring constant"
Notation in Kittel



- Note: There are no linear terms if we consider small changes u from the equilibrium positions

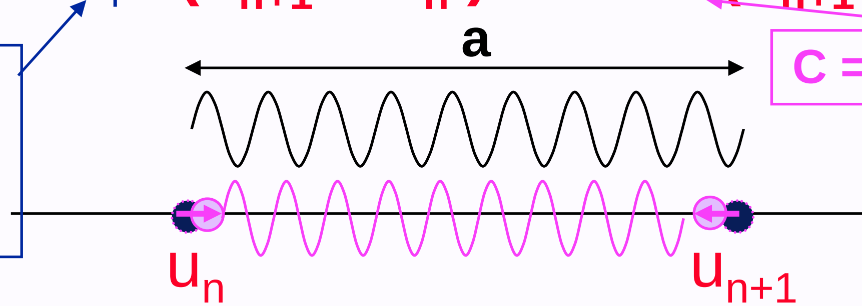
What determines the "spring constant"

- The energy of the crystal changes if the atoms are displaced – because the atoms are bound together!
- Example: Atoms in a line with binding of each pair of atoms that depends of the distance $\phi\,(|\,\underline{\mathbf{R}}_{n+1} - \underline{\mathbf{R}}_{n}\,|)$
- For each bond the change is energy is:

$$\Delta E = \tfrac{1}{2}\,\phi''\,(\mathbf{u}_{n+1} - \mathbf{u}_{n})^2 = \tfrac{1}{2}\,\mathbf{C}\,(\mathbf{u}_{n+1} - \mathbf{u}_{n})^2$$

ϕ'' = second derivative of $\phi\,(r)$

C = "spring constant"



- **Examples:** **Coulomb, Van der Waals attraction, replusive terms, etc. given before**

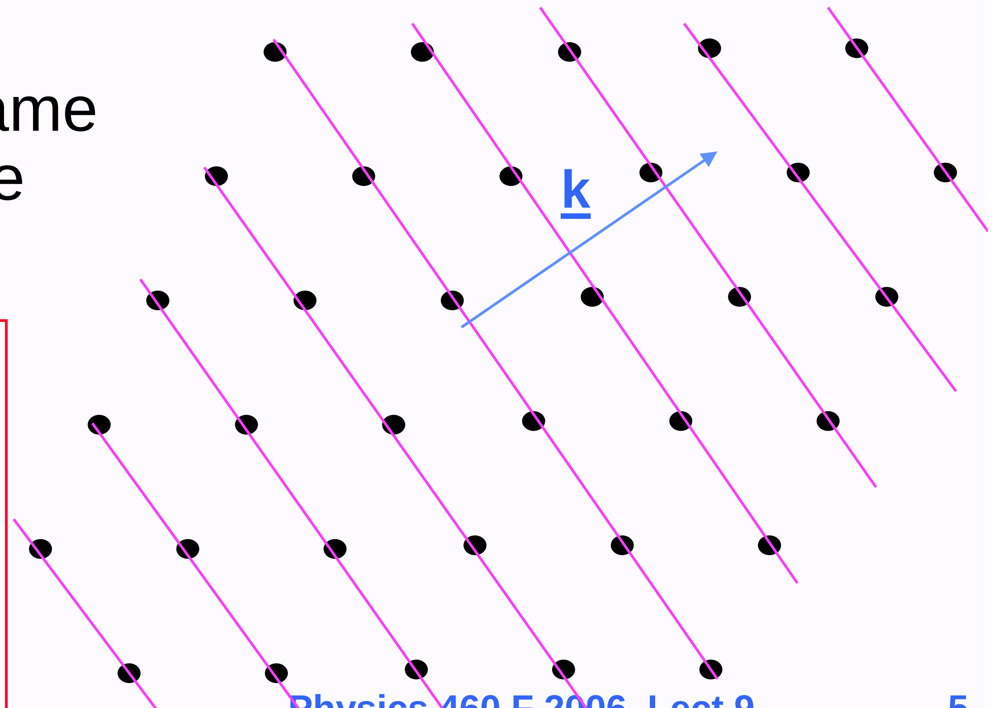
From last lecture

Vibration waves in 2 or 3 dimensions

- Newton's Law: $M\, d^2 \underline{\mathbf{u}}_n / dt^2 = \underline{\mathbf{F}}_n$
- General Solution:

$$\underline{\mathbf{u}}_n(t) = \Delta \underline{\mathbf{u}} \exp(i\underline{\mathbf{k}} \cdot \underline{\mathbf{R}}_n - i\omega t)$$

Vector dot product - same for all atoms in plane perpendicular to $\underline{\mathbf{k}}$



Consider the motion to be vibrations of planes of atoms

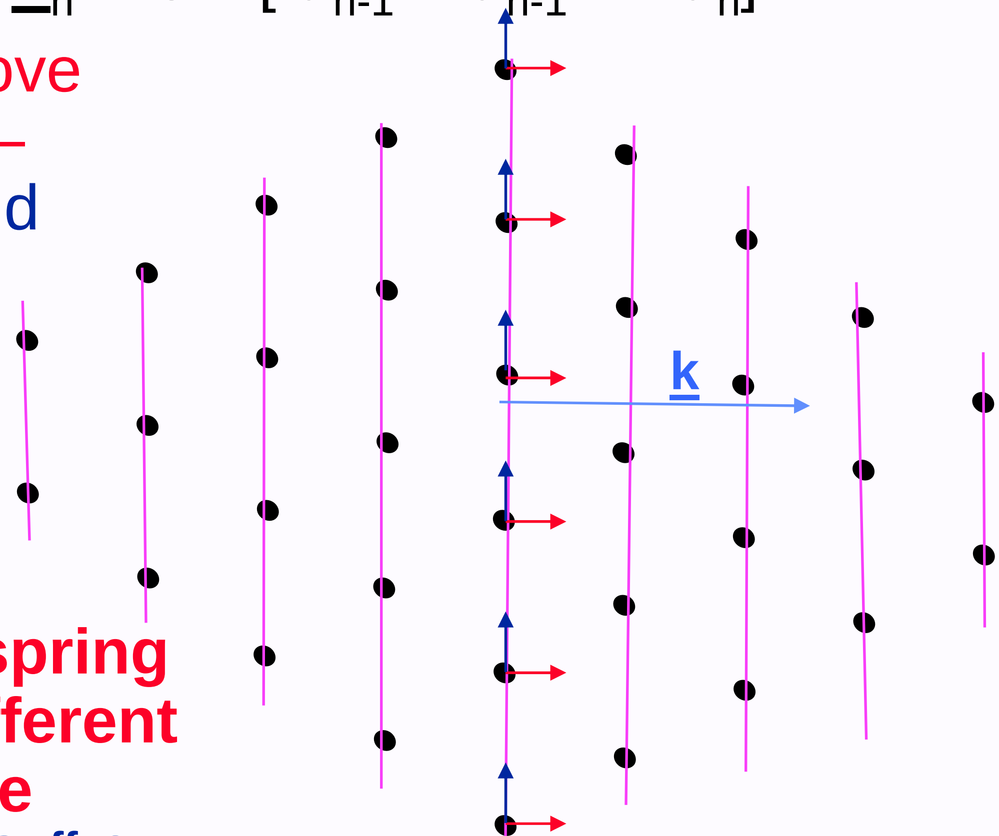
Like a chain in one dimension!

Vibration waves in 2 or 3 dimensions

- Easier to see with planes vertical and k vector horizontal
- Then Newton's equations become

$$M\, d^2 \underline{\mathbf{u}}_n / dt^2 = \underline{\mathbf{F}}_n = C^{eff} [\, \mathbf{u}_{n-1} + \mathbf{u}_{n-1} - 2\, \mathbf{u}_n]$$

- Each plane can move in three directions – one longitudinal and two transverse



Like one dimension!

But the effective spring constant C^{eff} is different for each mode

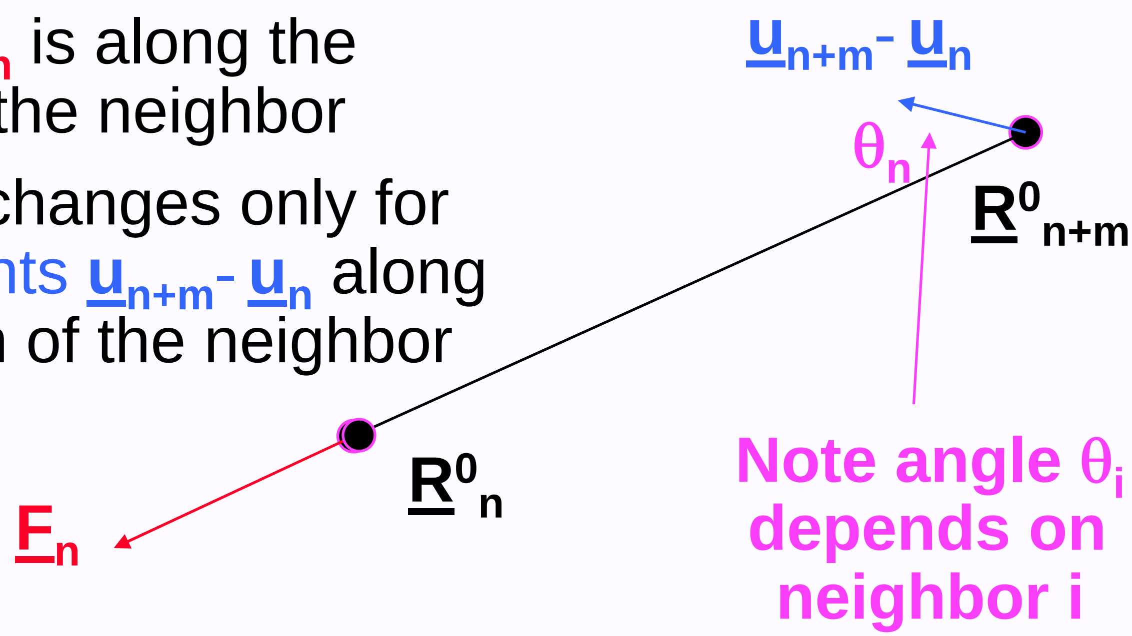
How do we find C^{eff} ?

Central Forces

- For Central Forces the depends only on the distance between the atoms
- The energy per atom is

$$E = (1/2(1/N) \Sigma_{nm} \phi_{nm} (| \underline{\mathbf{R}}_n - \underline{\mathbf{R}}_{n+m} |)$$
$$= E_0 + (1/4N) \Sigma_{nm} \phi_{nm}'' (\Delta| \underline{\mathbf{R}}_n - \underline{\mathbf{R}}_{n+m} |)^2 + \ldots.$$

- The force $\underline{\mathbf{F}}_n$ is along the direction of the neighbor
- The length changes only for displacements $\underline{\mathbf{u}}_{n+m} - \underline{\mathbf{u}}_n$ along the direction of the neighbor

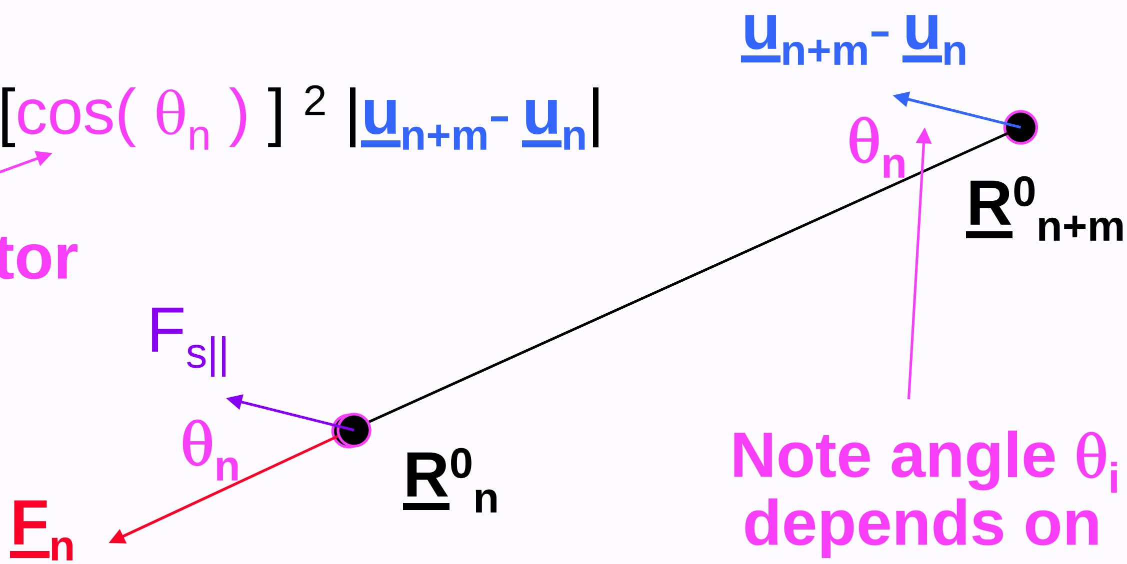


Geometric factors for Central Forces

- We will consider waves with each atom displaced in the same direction – for simplicity – then we always need the force in the direction of the motion $F_{n||}$

- $F_{s||} = - \Sigma_i \, \phi_i'' \, [\cos(\theta_n)]^2 \, |\underline{u}_{n+m} - \underline{u}_n|$

Geometric factor depends on neighbor i



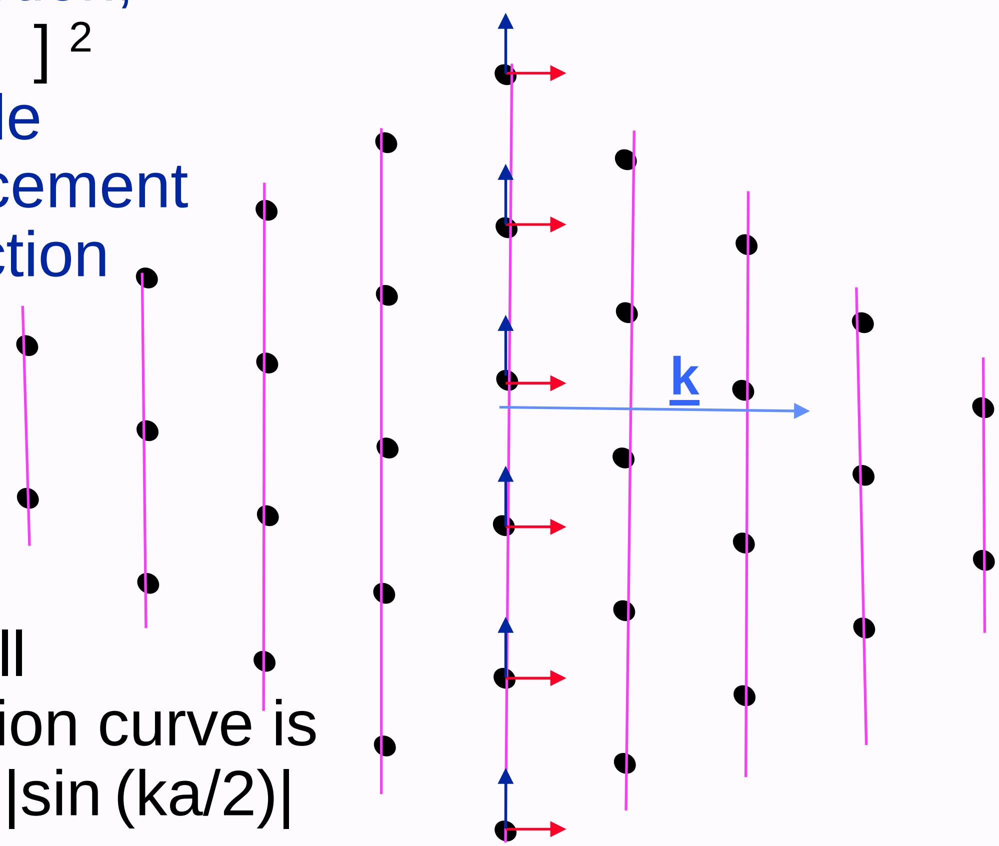
Note angle θ_i depends on neighbor i

Vibration waves in 2 or 3 dimensions

- Newton's equations

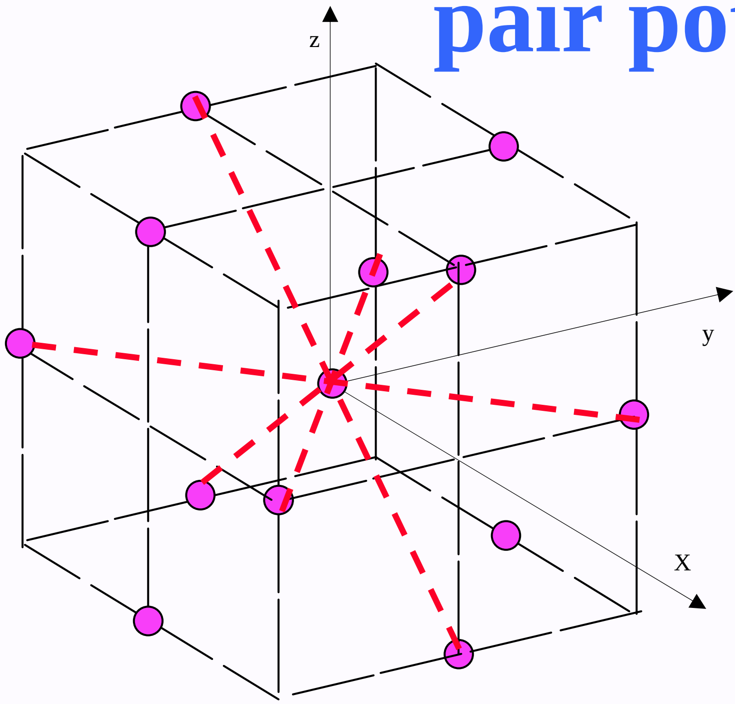
$$M\, d^2 \underline{\mathbf{u}}_n / dt^2 = \underline{\mathbf{F}}_n = C^{eff} [\, \mathbf{u}_{n+1} + \mathbf{u}_{n-1} - 2\, \mathbf{u}_n]$$

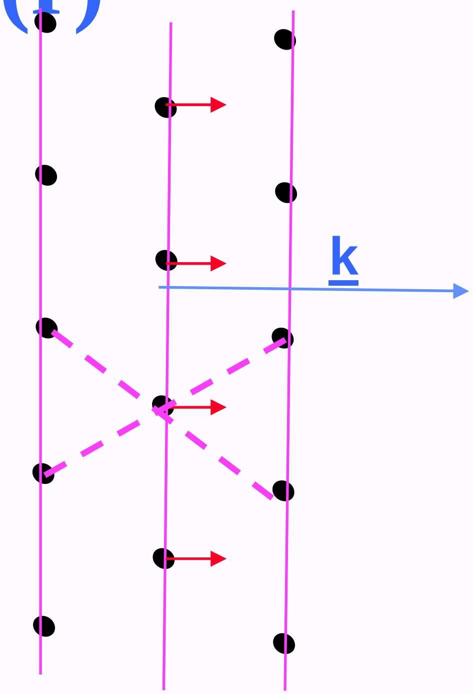
For each type of motion,
$C^{eff} = \Sigma_i\, \phi_i'' \, [\cos(\theta_i)\ ]^2$
where θ_i is the angle between the displacement vector and the direction to neighbor i



For one atom per cell
the resulting dispersion curve is
$\omega_k = 2\, (C^{eff} / M)^{1/2}\, |\sin(ka/2)|$

Example – fcc with nearest-neighbor pair potential $\phi(r)$





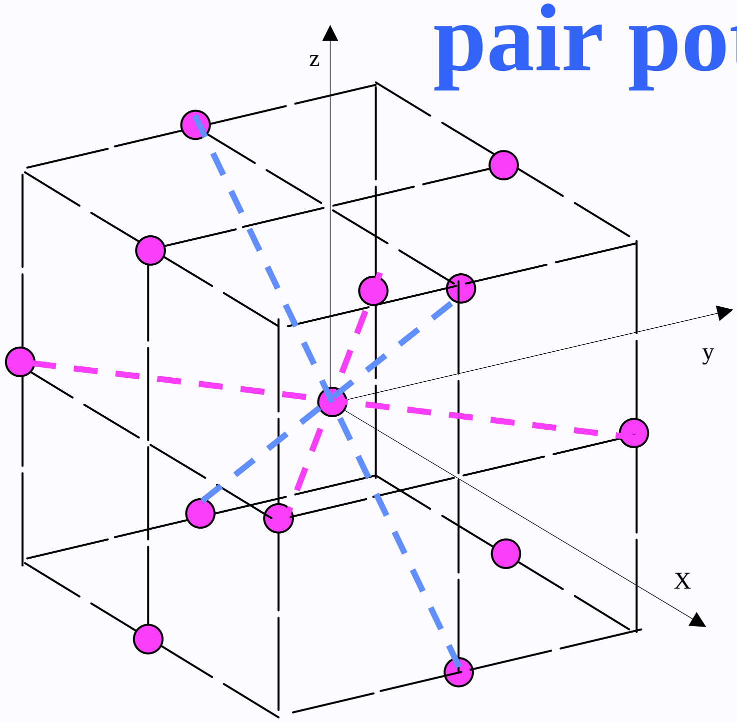
Consider waves with k in x direction

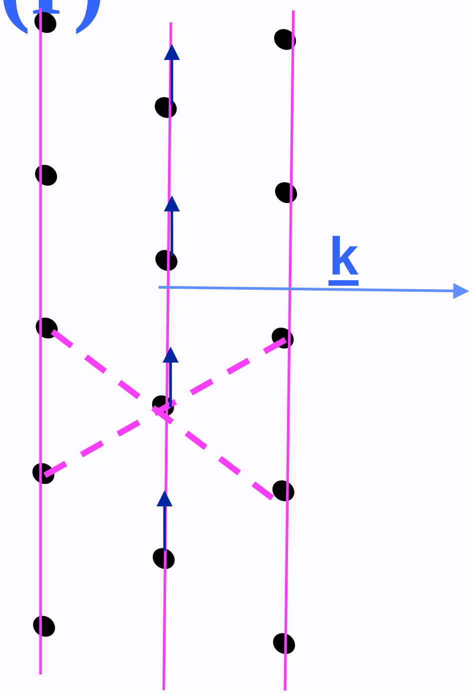
Longitudinal motion in x direction

Each atom has 4 neighbors in each of the two neighboring planes with $\cos(\theta)^2 = ½$

$C^{eff} = 4\,\phi_i''/2 \qquad \omega_k = 2^{3/2}\,(\phi_i''/M\,)^{1/2}\,|\sin\,(ka/2)|$

Example – fcc with nearest-neighbor pair potential $\phi(r)$





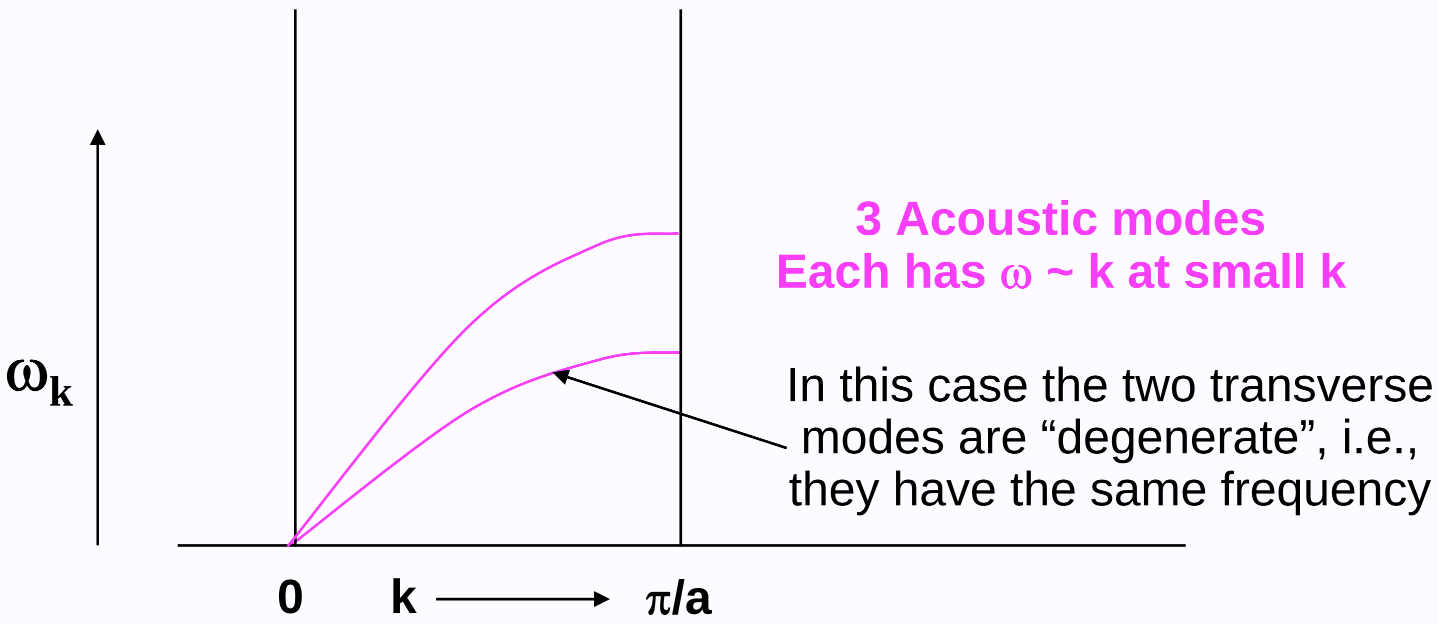
Consider waves with k in x direction

Transverse motion in y direction

Each atom has 2 neighbors in each of the two neighboring planes with $\cos(\theta)^2 = ½$ and 2 neighbors with $\cos(\theta) = 0$

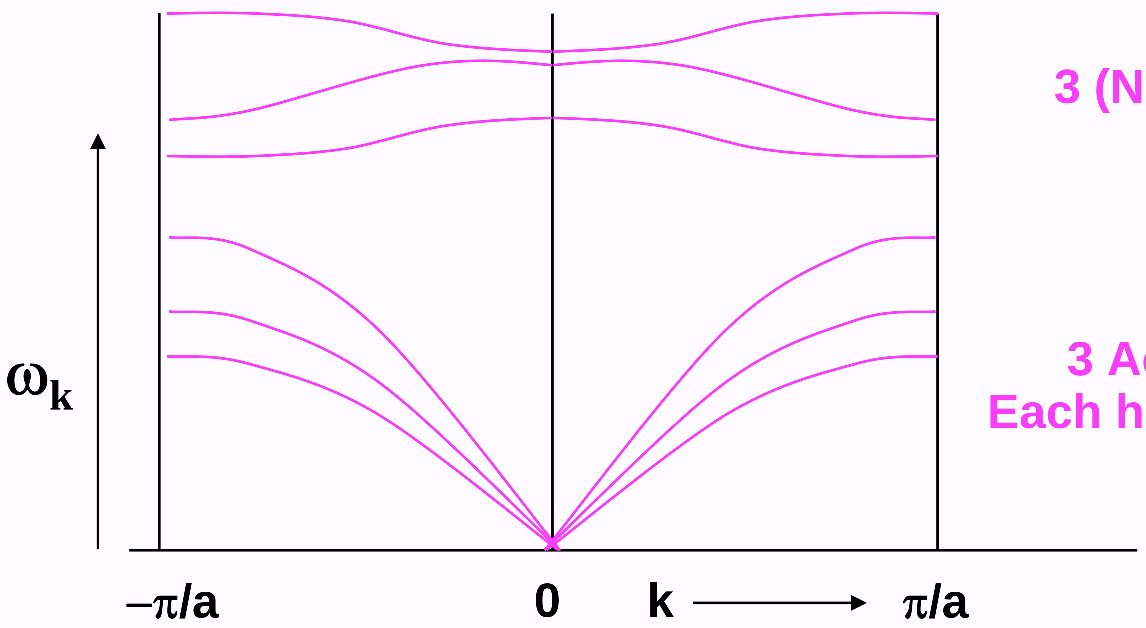
$C^{eff} = 2\,\phi_i''/2$ $\quad\quad \omega_k = 2\,(\phi_i''/M)^{1/2}\,|\sin(ka/2)|$

Waves traveling in x direction in fcc crystal with one atom per cell



In the case of nearest neighbor forces, the longitudinal ω_k is higher than the transverse ω_k by the factor $2^{1/2}$

Oscillations in general 3 dimensional crystal with N atoms per cell



3 (N -1) Optic Modes

3 Acoustic modes
Each has $\omega \sim k$ at small k

Quantization of Vibration waves

- **Max Planck - The beginning of quantum mechanics in 1901**
- **There were observations and experimental facts that showed there were serious issues that classical mechanics failed to explain**
- **One was radiation – the laws of classical mechanics predicted that light radiated from hot bodies would be more intense for higher frequency (blue and ultraviolet) – totally wrong!**

- **Planck proposed that light was emitted in "quanta" – units with energy E = h $\nu = \hbar\omega$**
- **Planck's constant h --- "h bar" = $\hbar$ = h/2π**

- **The birth of quantum mechanics**
- **Applies to all waves!**

Quantization of Vibration waves

- Each independent harmonic oscillator has quantized energies:

$$e_n = (n + 1/2)\, h\nu = (n + 1/2)\hbar\omega$$

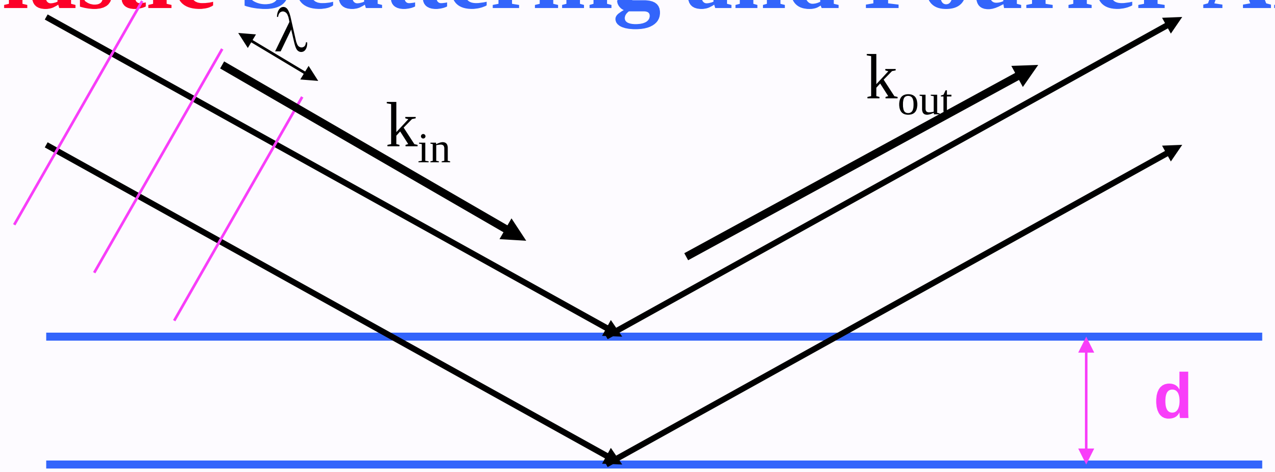
- We can use this here because we have shown that vibrations in a crystal are independent waves, each labeled by **k** (and index for the type of mode - 3N indices in a 3 dimen. crystal with N atoms per cell)

- Since the energy of an oscillator is 1/2 kinetic and 1/2 potential, the mean square displacement is given by $(1/2)\, M\, \omega^2\, u^2 = (1/2)\,(n + 1/2)\, \hbar\omega$
where M and u are appropriate to the particular mode (e.g. total mass for acoustic modes, reduced mass for optic modes , ….)

Quantization of Vibration waves

- Quanta are called phonons
- Each phonon carries energy $\hbar\omega$
- For each independent oscillator (i.e., for each independent wave in a crystal), there can be any integer number of phonons
- These can be viewed as particles
- They can be detected experimentally as creation or destruction of quantized particles
- Later we will see they can transport energy just like a gas of ordinary particles (like molecules in a gas).

Inelastic Scattering and Fourier Analysis



- The in and out waves have the form:

  exp(i $\underline{k}_{in}$· r - i ω_{in}t) and exp(i $\underline{\mathbf{k}}_{out}$· r - i ω_{out}t)

- For elastic scattering we found that diffraction occurs only for $\underline{\mathbf{k}}_{in}$ - $\underline{\mathbf{k}}_{out}$ = $\underline{\mathbf{G}}$
- For inelastic scattering the lattice planes are vibrating and the phonon supplies wavevector $\underline{\mathbf{k}}_{phonon}$ and frequency ω_{phonon}

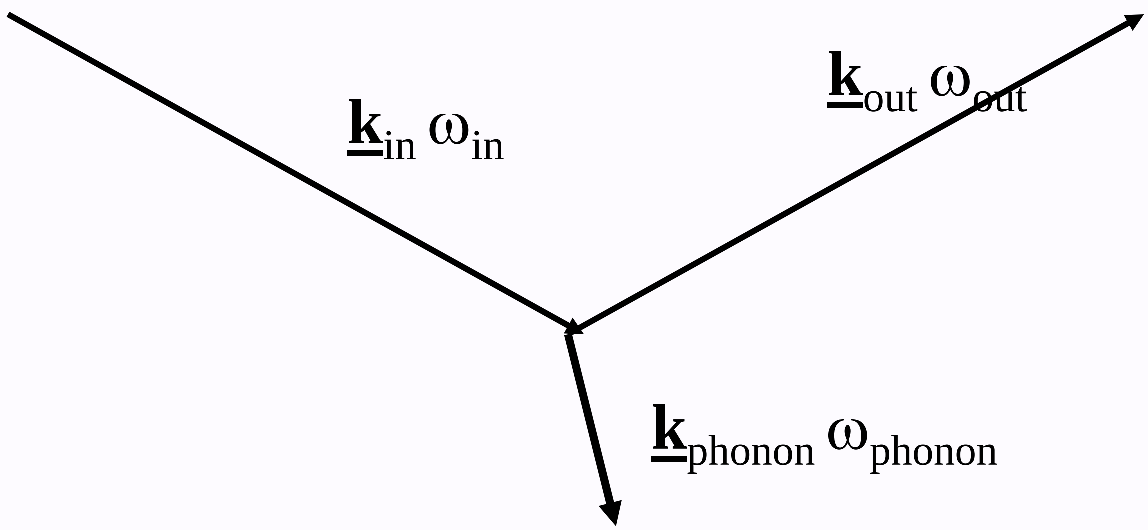
Inelastic Scattering and Fourier Analysis

- Result:
- Inelastic diffraction occurs for

$$\underline{\mathbf{k}}_{in} - \underline{\mathbf{k}}_{out} = \underline{\mathbf{G}} \pm \underline{\mathbf{k}}_{phonon}$$

$$\omega_{in} - \omega_{out} = \pm\, \omega_{phonon} \text{ or } \boxed{E_n - E_{out} = \pm\, \hbar\omega_{phonon}}$$

Create or destroy quanta of vibrational energy

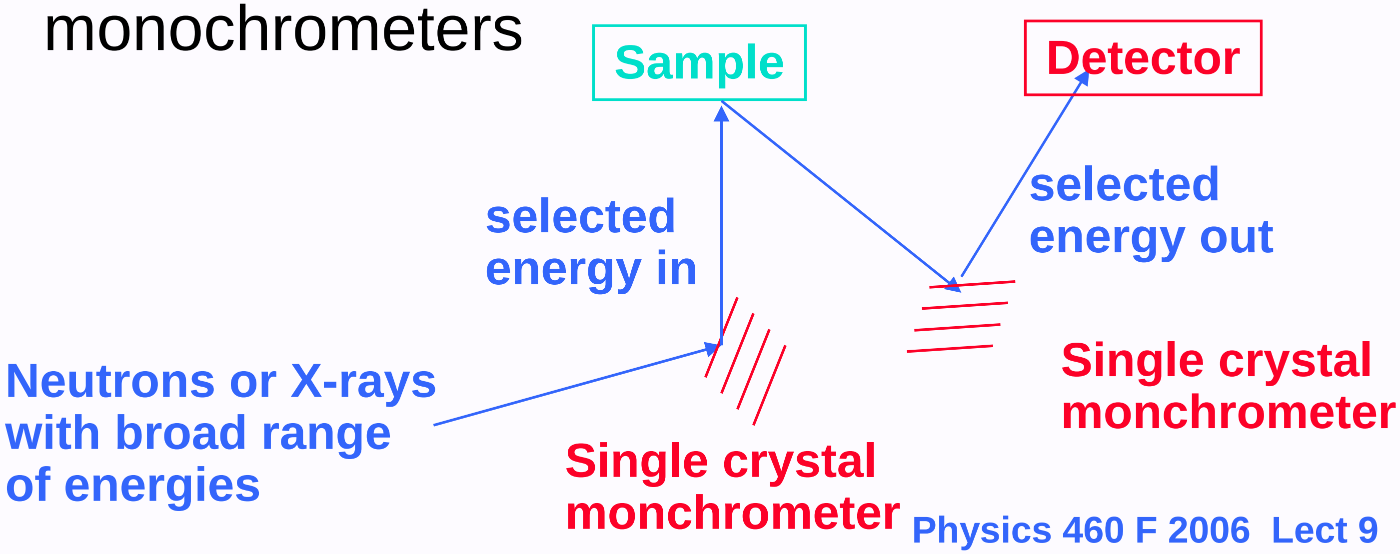


Experimental Measurements of Dispersion Curves

- Dispersion curves ω as a function of k are measured by inelastic diffraction
- If the atoms are vibrating then diffraction can occur with energy loss or gain by scattering particle
- In principle, can use any particle - neutrons from a reactor, X-rays from a synchrotron, He atoms which scatter from surfaces, …...

Experimental Measurements of Dispersion Curves

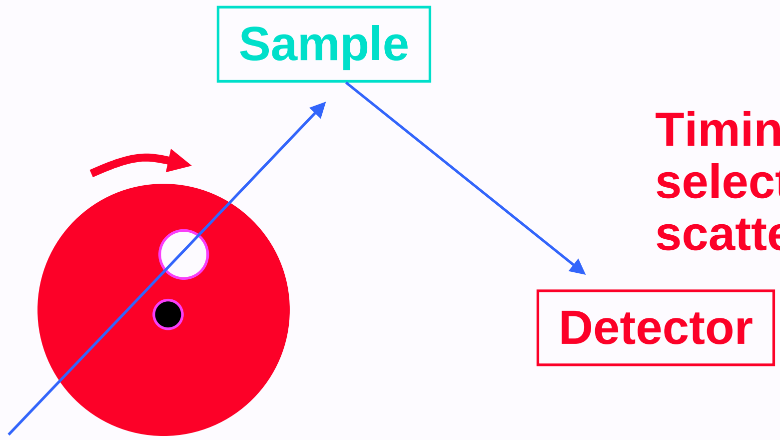
- Neutrons are most useful for vibrations
  For λ ~ atomic size, energies ~ vibration energies
  BUT requires very large crystals (weak scattering)
- X-ray - only recently has it been possible to have enough resolution (meV resolution with KeV X-rays!)
- “Triple Axis” - rotation of sample and two monochrometers



Experimental Measurements of Dispersion Curves

- Alternate approach for Neutrons
  Use neutrons from a sudden burst, e.g., at the new "spallation" source at Oak Ridge
  (Largest science project in the US this century!)
- Measure in and out energies by "time of flight"

Mechanical chopper selects velocity, i.e., energy of neutrons



Timing at detector selects energy of scattered neutrons

Burst of neutrons at measured time (broad range of energies)

More on Phonons as Particles

- Quanta are called phonons, each with energy $\hbar\omega$
- $\underline{\mathbf{k}}$ can be interpreted as "momentum"
- What does this mean?
  NOT really momentum - a phonon does not change the total momentum of the crystal
  But $\underline{\mathbf{k}}$ is "conserved" almost like real momentum - when a phonon is scattered it transfers "$\underline{\mathbf{k}}$" plus any reciprocal lattice vector, i.e.,
  $$\sum \underline{\mathbf{k}}_{\mathbf{before}} = \sum \underline{\mathbf{k}}_{\mathbf{after}} + \underline{\mathbf{G}}$$
- Example : scattering of particles
  $$\underline{\mathbf{k}}_{\mathrm{in}} = \mathbf{k}_{\mathrm{out}} + \underline{\mathbf{G}} \pm \underline{\mathbf{k}}_{\mathrm{phonon}}$$
  where + means a phonon is created, - means a phonon is destroyed

Summary

- Normal modes of harmonic crystal
  Independent oscillators labeled by wavevector k and having frequency ω_k
- The relation ω_k as a function of k is called a dispersion curve - 3N curves for N atoms/cell in 3 dimensions
- Quantized energies (n + 1/2) h ω_k
- Can be viewed as particles that can be created or destroyed - each carries energy and "momentum"
- "Momentum" conserved modulo any **G** vector
- Measured directly by inelastic diffraction - difference in in and out energies is the quantized phonon energy
- Neutrons, X-rays, …..

Next time

- Phonon Heat Capacity
- One of the early mysteries solved by quantum mechanics - obey Bose-Einstein Statistics
- Density of states of phonons
- Debye and Einstein Models
- (Read Kittel Ch 5)