# Phonons I - Crystal Vibrations
(Kittel Ch. 4)
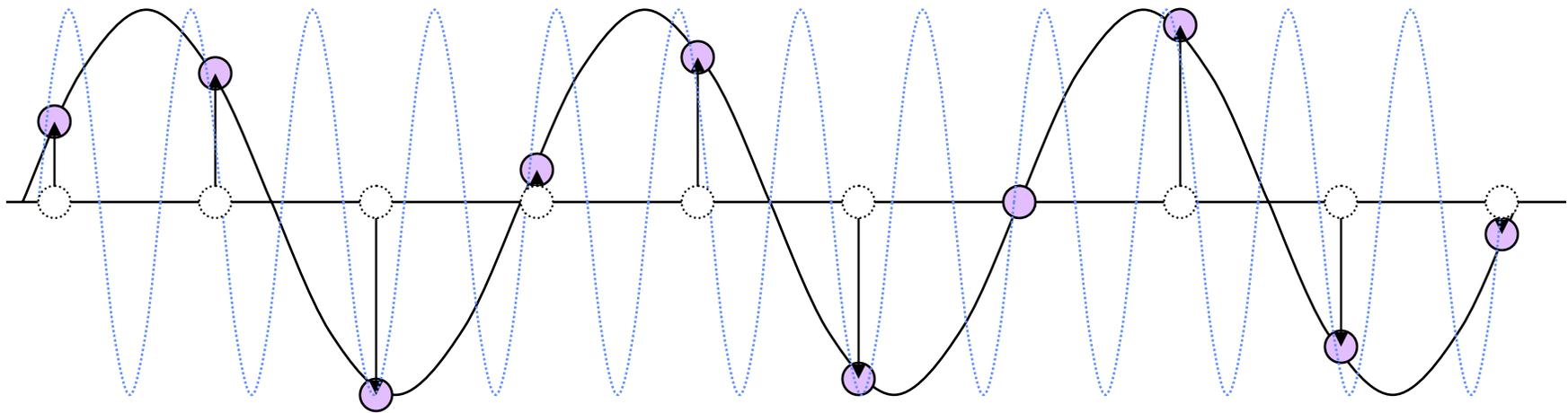
Displacements of Atoms

- Positions of atoms in their perfect lattice positions are given by:

$$\underline{R}^0(n_1, n_2, n_3) = n_1^0 \, \underline{x} + n_2^0 \, \underline{y} + n_3^0 \, \underline{z}$$

For simplicity here we consider
only one atom per cell and assume
an orthogonal coordinate system
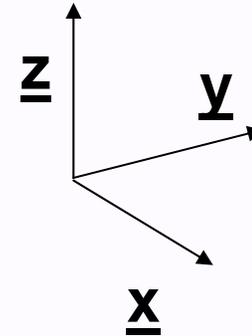
For convenience let $\underline{n}_i = (n_{i1}^0, n_{i2}^0, n_{i3}^0)$ denote atom i which has position $\underline{R}^0_i$

- The displacement of atom i can be written

$$\Delta \underline{R}_i = u_i \, \underline{x} + v_i \, \underline{y} + w_i \, \underline{z} = (n_{1i} - n_{1i}^0) \, \underline{x} + (n_{2i} - n_{2i}^0) \, \underline{y} + (n_{3i} - n_{3i}^0) \, \underline{z}$$

Energy & Force due to Displacements

- The energy of the crystal changes if the atoms are displaced.
- The change in energy can be written as a function of the positions of all the atoms:

$$E(\underline{R}_1, \underline{R}_2, \underline{R}_3, \ldots) = E(\underline{R}_1^0 + \Delta\underline{R}_1, \ \underline{R}_2^0 + \Delta\underline{R}_2, ..)$$

- There are no linear terms if we expand about the equilibrium positions – equilibrium defined by $dE/d\underline{R}$ $(R=R^0)=0$

- To lowest order in the displacements the energy is quadratic - Hooke's law - harmonic limit

$$E = E_0 + (1/2) \, \Sigma_{ij} \, \Delta\underline{R}_i \cdot D_{ij} \cdot \Delta\underline{R}_j + \ldots.$$

Energy & Force due to Displacements

- The general expression for force on atom s is
$$\underline{\mathbf{F}}_s = - dE/d\ \underline{\mathbf{R}}_s$$

- From the harmonic expression the force is given by
$$\underline{\mathbf{F}}_s = - \Sigma_j\ D_{sj} \cdot \Delta\underline{\mathbf{R}}_j$$

- The D's are called force constants - the ratio of force on atom s to displacement of atom j - the generalization of the force constant of a spring

- There are no forces at the equilibrium positions.

- The force is due to the displacement of atoms i and the lowest order terms are linear in the displacements

- Note that D_{ss} exists and its sign is negative!

- What matters is the distance between $\underline{R}_i$ and $\underline{R}_s$

Linear chain

- Consider atoms in a line restricted to move along the line

i $u_i = \Delta R_i$

a
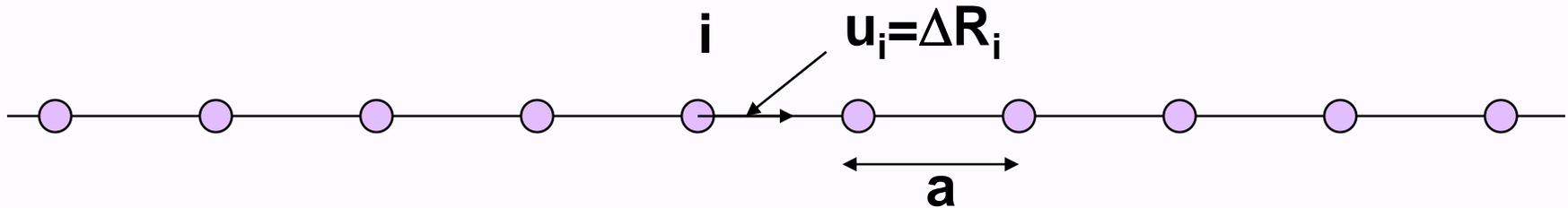
- $F_s = - \sum_j D_{sj} \cdot u_j$

- Consider the case of only nearest neighbor interactions.
- $F_s = - (D_{s\,s-1} \cdot u_{s-1} + D_{s\,s} \cdot u_s + D_{s\,s-1} \cdot u_{s-1})$

- Or, in analogy with elastic springs,
  assume that force depends on the relative displacements
- $F_s = - \sum_i C (u_s - u_{s+i})$

- $F_s = -C [(u_s - u_{s+1}) + [(u_s - u_{s-1})]$
  $= C [u_{s+1} + u_{s-1} - 2 u_s]$

Oscillations of linear chain

sa   **u$_s$**

a
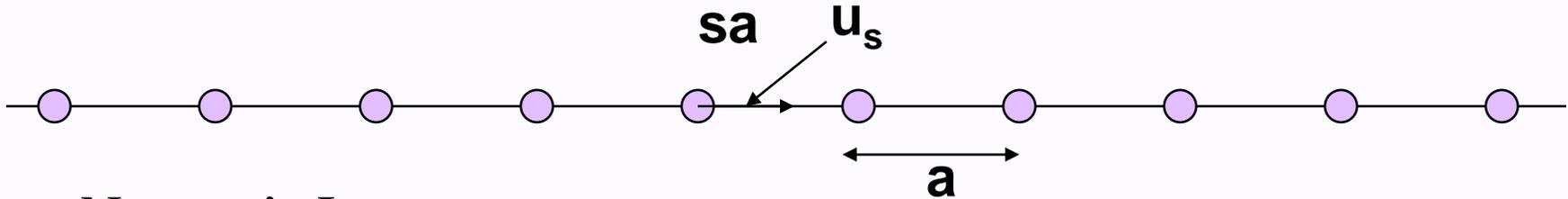
- Newton's Law:

  $M \, d^2 u_s / dt^2 = F_s = C \, [\, u_{s+1} + u_{s-1} - 2 \, u_s]$

- Time dependence: Let $u_s(t) = u_s \exp(-i\omega t)$)
  (also sin or cos is correct but not as elegant)
  Then

  $M \, \omega^2 \, u_s = C \, [\, u_{s+1} + u_{s-1} - 2 \, u_s]$

- How to solve? Looks complicated - an infinite number of coupled oscillators!

Oscillations of linear chain

u_s

New
representation
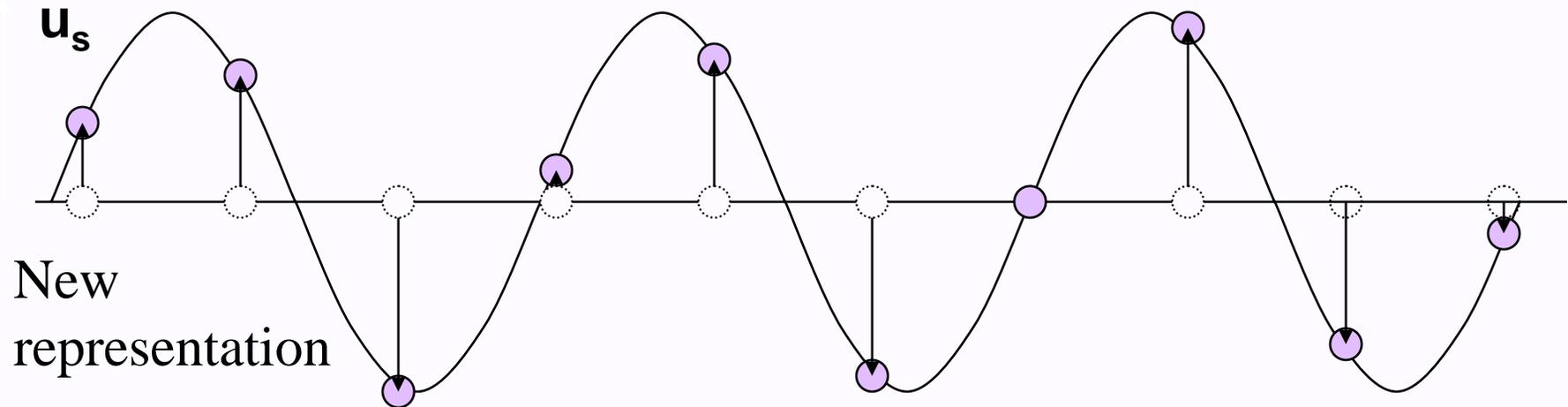
- Since the equation is the same at each s, the solution must have the same form at each s differing only by a phase factor. This is most easily written

$$u_s = u \exp(ik (s a))$$

- Then

$$M \omega^2 u = C [\exp(ik a) + \exp(- ik a) - 2] u$$

or

$$\omega^2 = (C/ M) [2 \cos(ka) - 2]$$

Oscillations of linear chain
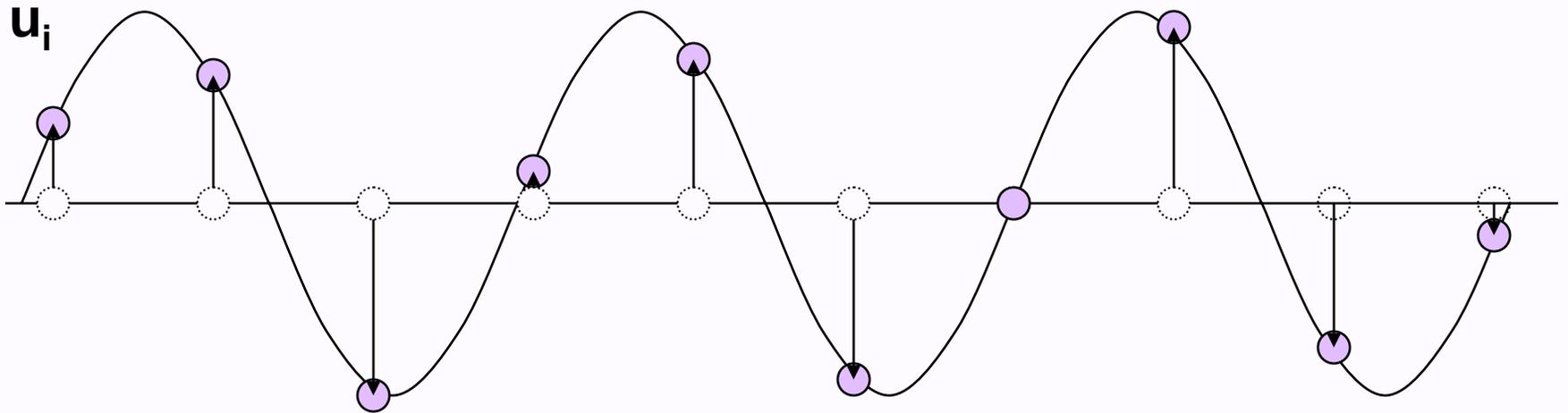
- A more convenient form is

$$\omega^2 = (C/M)[2\cos(ka) - 2]$$
$$= 4(C/M)\sin^2(ka/2)$$

(using $\cos(x) = \cos^2(x/2) - \sin^2(x/2) = 1 - 2\sin^2(x/2)$)

- Finally: $\omega = 2(C/M)^{1/2} |\sin(ka/2)|$

Oscillations of a linear chain

- We have solved the infinite set of coupled oscillators!

- The solution is an infinite set of independent oscillators, each labeled by k (wavevector) and having a frequency
$$\omega_k = 2 \, (\, C \, / \, M \,)^{1/2} \, | \sin (ka/2) \, |$$

- The relation ω_k as a function of k is called the dispersion curve
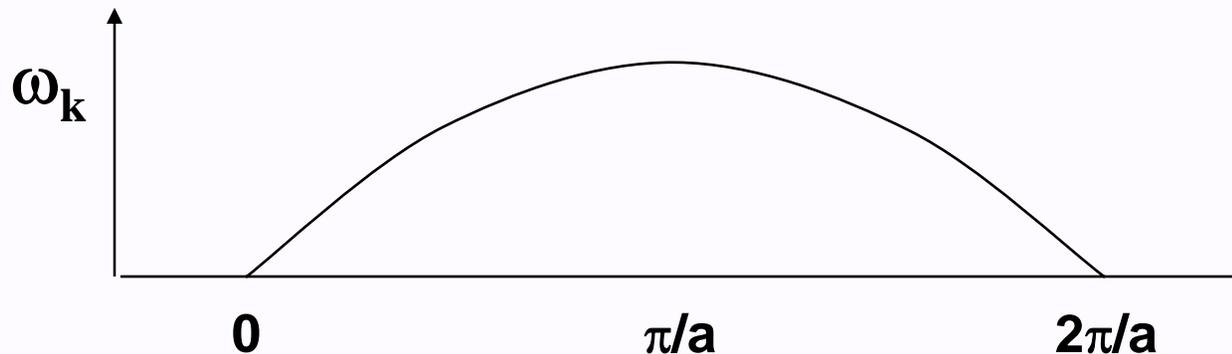
Brillouin Zone

- Consider k ranging over all reciprocal space.
  The expression for ω_k is periodic

$$\omega_k = 2 (C/M)^{½} |\sin(ka/2)|$$

Brillouin Zone

-2π/a   −π/a   0   π/a   2π/a
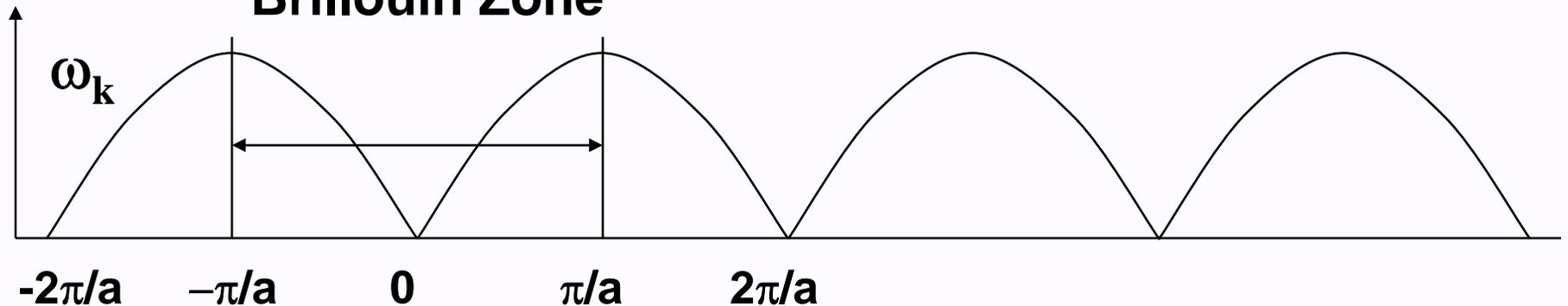
- All the information is in the first Brillouin Zone - the rest is repeated with periodicity 2π/a - that is, the frequencies are the same for ω_k and ω_{k+G} where G is any reciprocal lattice vector G = integer times 2π/a

- What does this mean?

Meaning of periodicity in reciprocal space

- In fact the motion of atoms with wavevector k is identical to the motion with wavevector k + G

- All independent vibrations are described by k inside BZ

$\sin (ka/2)$ with $k \sim 2\pi/3$ $\sin ((k + 2\pi/a) \, a/2)$
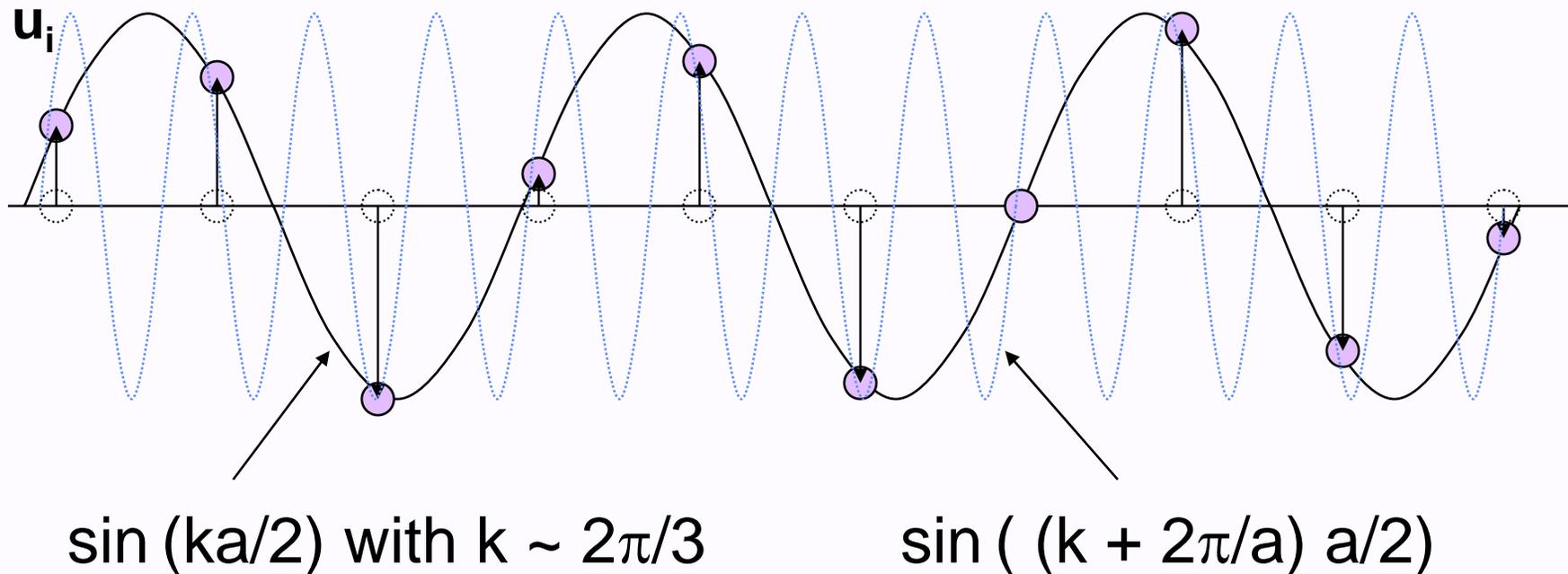
Group velocity of vibration wave

- The wave $u_s = u \exp(ik (s a) - i\omega t)$ is a traveling wave
- Phase velocity $v_\phi = \omega / k$
- Group velocity $v_k = d \omega_k / dk$ = slope of ω_k vs k

$$\omega_k = 2 (C / M)^{1/2} \sin (ka/2)$$

so

$$v_k = a (C / M)^{1/2} \cos (ka/2)$$

$v_k = 0$ at BZ boundary

ω_k

$-\pi/a$ 0 π/a

$v_k = V_{sound}$
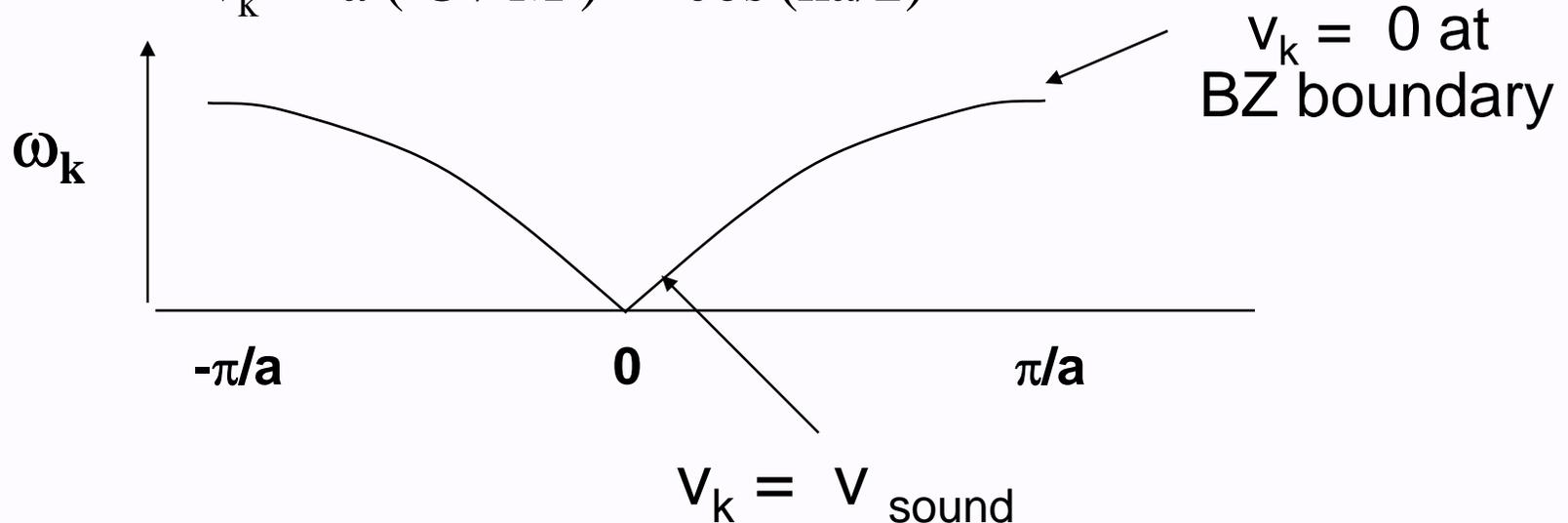
What is significance of zero Group velocity at BZ Boundary?

- Fundamentally different from elastic wave in a continuum
- Since ω_k is periodic in k it **must** have $v_k = d\,\omega_k\,/\,dk\ = 0$ somewhere!
- Occurs at BZ boundary because ω_k **must** be symmetric about the points on the boundary

$v_k = 0$ at BZ boundary

ω_k

$-\pi/a$ 0 π/a
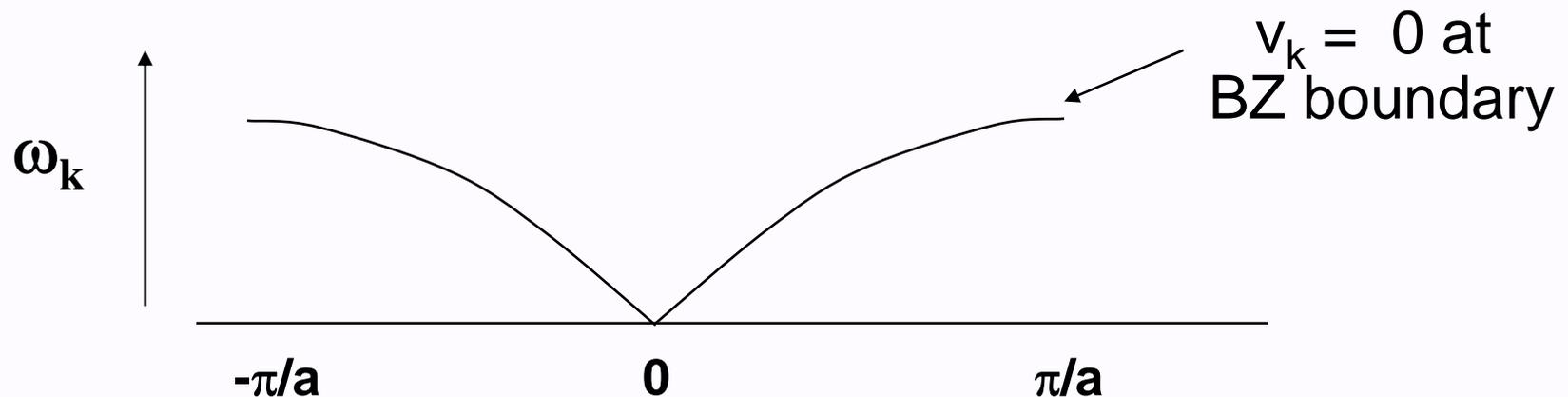
What is significance of zero group velocity at BZ Boundary?

- Example of Bragg Diffraction!

- Any wave (vibrations or other waves) is diffracted if k is on a BZ boundary

- $u_s = u \exp(ik (s a)) = u \exp(\pm is\pi) = u(-1)^s$

- Leads to standing wave with group velocity = 0
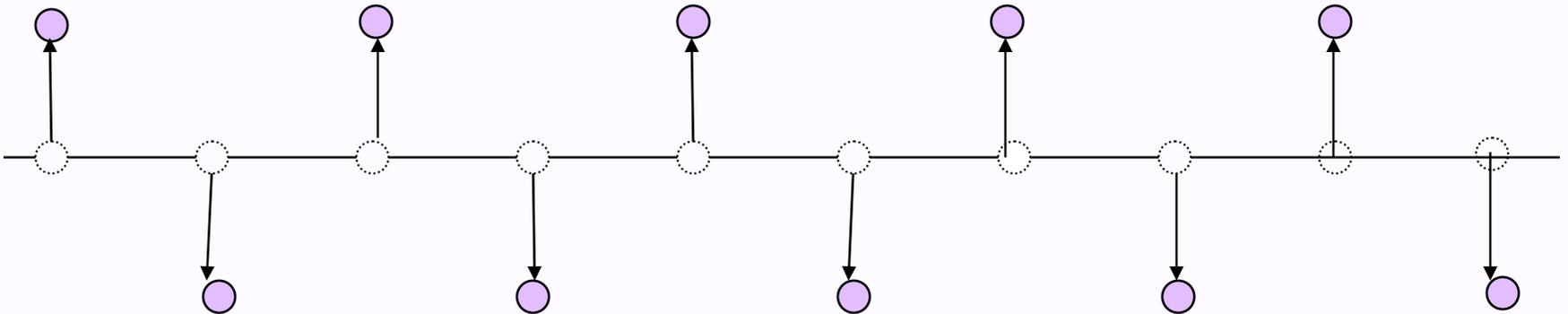
Meaning of periodicity in reciprocal space -- II

- This is a general result valid in all crystals in all dimensions
- The vibrations are an example of excitations. The atoms are not in their lowest energy positions but are vibrating.
- The excitations are labeled by a wavevector k and are periodic functions of k in reciprocal space.
- All the excitations are counted if one considers only k inside the Brillouin zone (BZ). The excitations for k outside the BZ are identical to those inside and are not independent excitations.

Diffraction and the Brillouin Zone

- Brillouin Zone formed by
  perpendicular bisectors
  of G vectors

- Special Role of Brillouin Zone

  (Wigner-Seitz cell of recip. lat.)

  as opposed to any other primitive cell

- No diffraction for any k
   inside the first Brillouin Zone

- Now we see that there are no independent excitations
 outside of the first Brilluin Zone
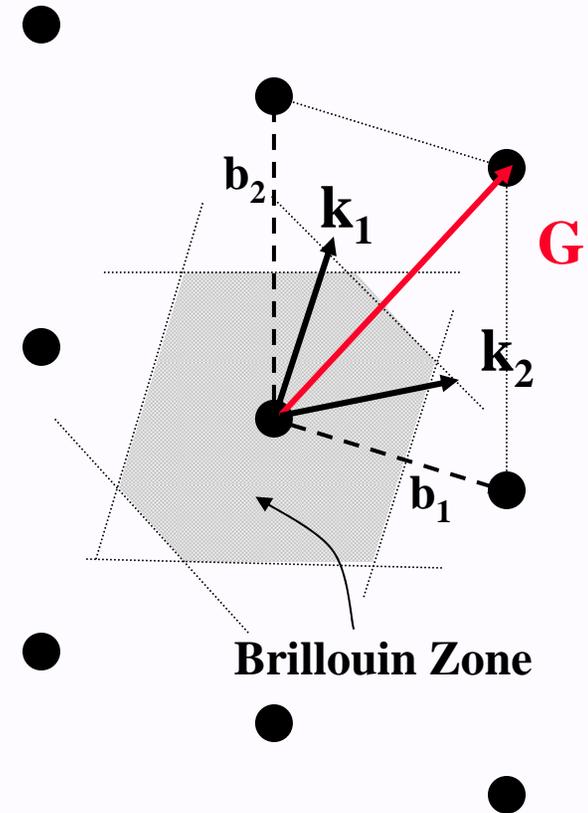
Sound Velocity

- In the long wavelength (small k) limit the atomic vibration wave $u_s = u \exp(ik(s\,a) - i\omega t)$ is an elastic wave

- Atoms act like a continuum for $ka \ll 1$

- $$\omega_k = (C/M)^{1/2} ka$$

- Sound velocity

$$v_{sound} = a(C/M)^{1/2}$$

ω_k

$-\pi/a$ 0 π/a

$V_k = V_{sound}$
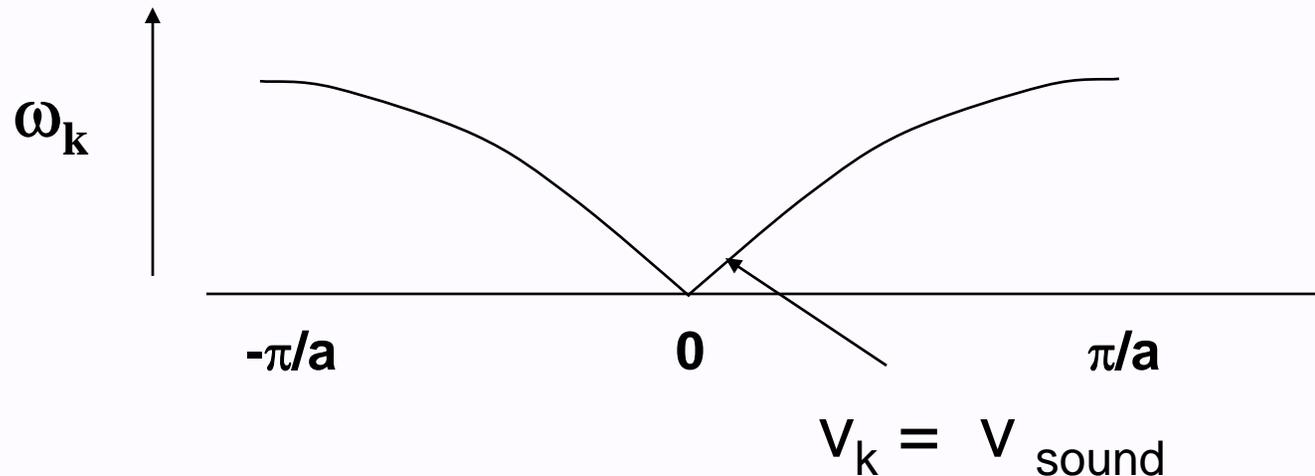
Normal modes of a finite set of oscillators

- N independent oscillators, each labeled by k (wavevector) and having a frequency

$$\omega_k = 2 (C / M)^{1/2} | \sin (ka/2) |$$

- Leading to a wave $u_s = u \cos (ksa - \omega t)$
- If end atoms are fixed at $u_s = 0$, possible wavelenghts
  $\Rightarrow$ k=πn/(N-1)a, N values <=π/a
- If periodic boundary conditions $u_{N+s} = u_s$

  $\Rightarrow$ k=+-2πn/Na, N values<= π/a

These discrete choices for waves are called the normal modes of
crystal excitations.

The normal modes serve as a basis for describing arbitrarily
 complex excitations.

Oscillations in higher dimensions
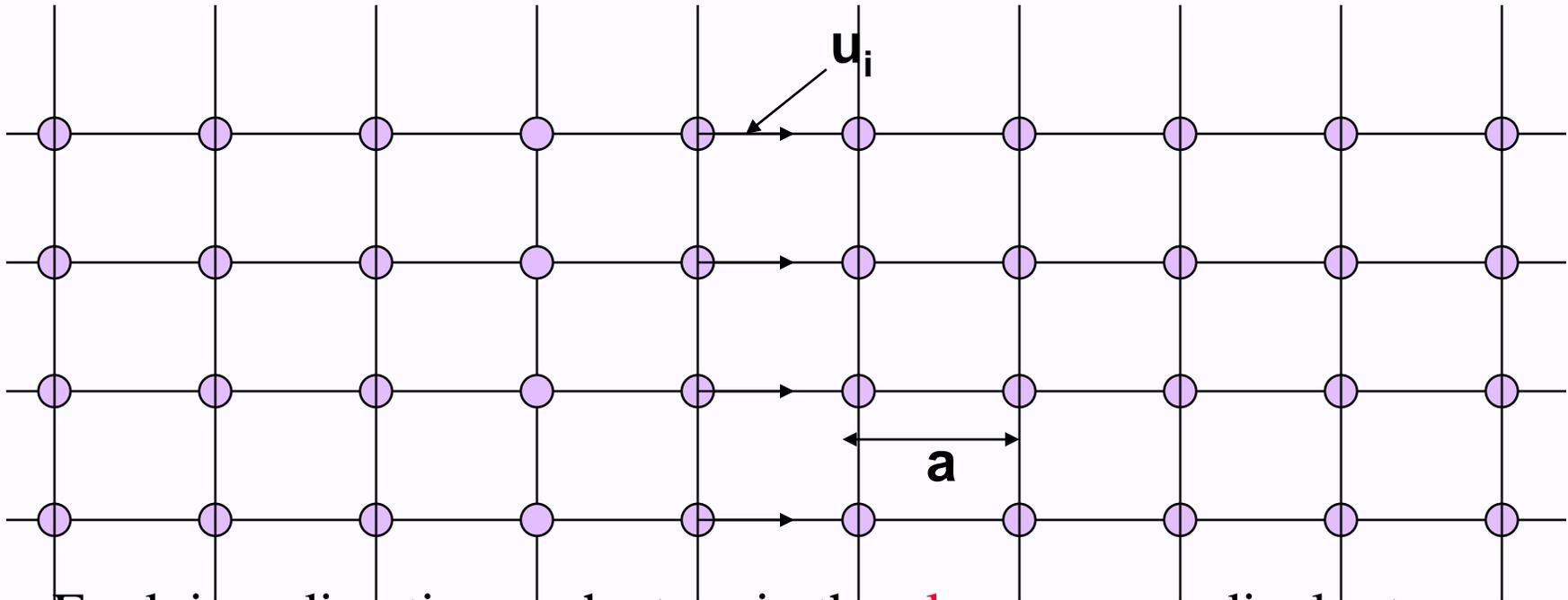
- For k in x direction each atom in the planes perpendicular to x moves the same:

$$u_s = u \exp(ik (s a) - i\omega t)$$

- For motion in x direction, same as linear chain

$$\omega = 2 (C / M)^{1/2} | \sin (ka/2) |$$

- longitudinal wave

Oscillations in higher dimensions
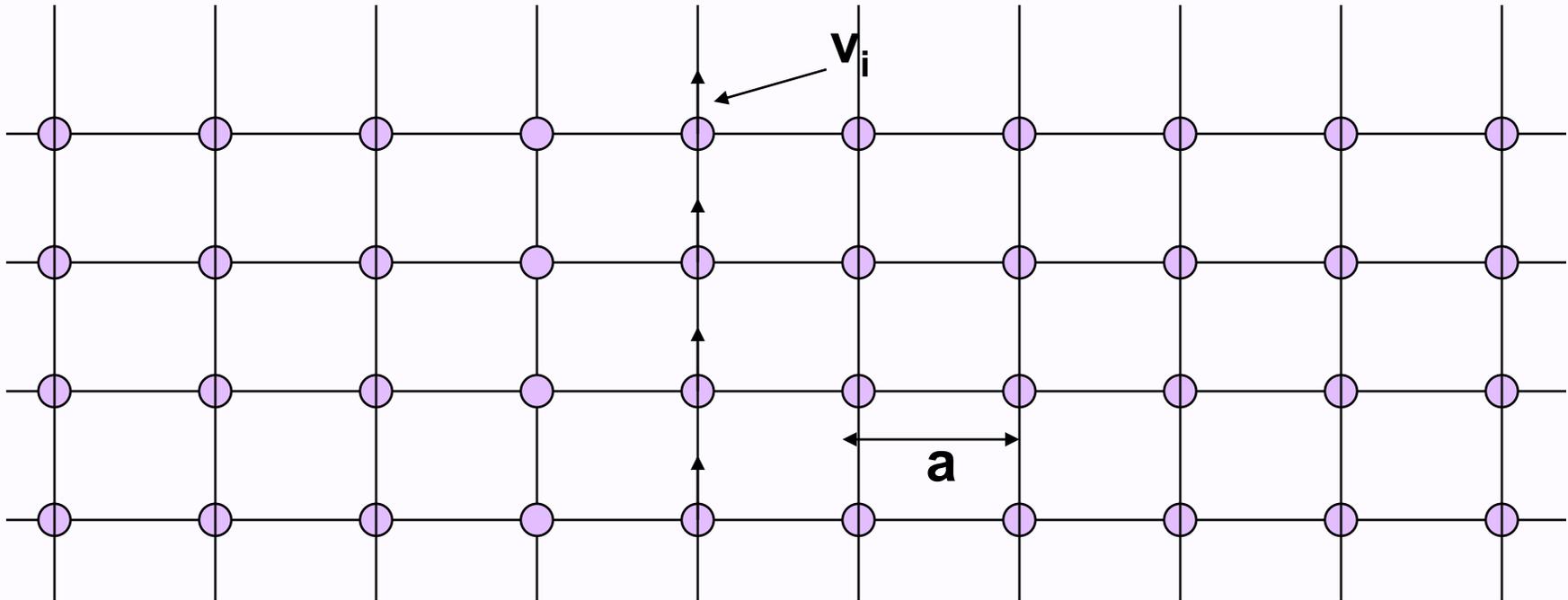
- Transverse motion: k in x direction; motion v_s in y direction

  $$v_s = v \exp(ik (s\, a) - i\omega t)$$

- Central forces give no restoring force! Unstable!

- Need other forces - non-central or second neighbor

Oscillations in higher dimensions
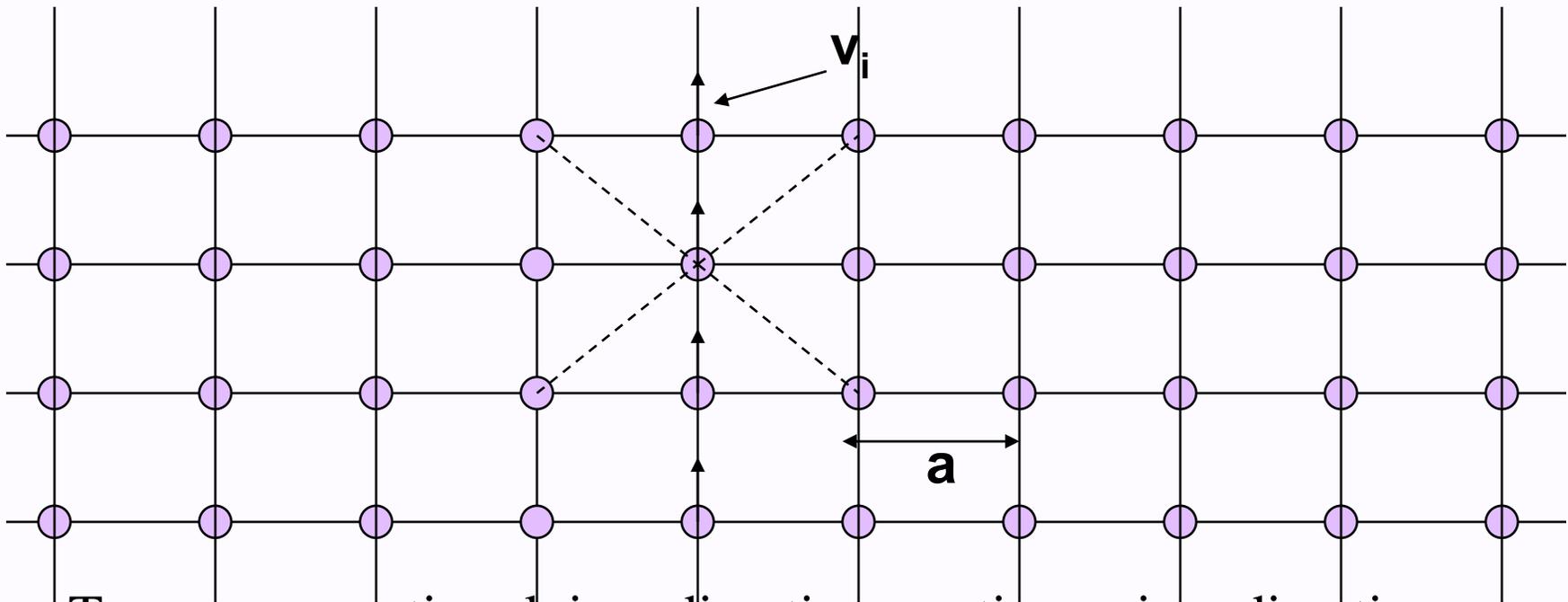
- Transverse motion: k in x direction; motion v_s in y direction

$$v_s = v \exp(ik (s a) - i\omega t)$$

- Second neighbor forces

$$\omega^2 = (1/2)(C / M) [4 \cos(ka) - 4]$$

4 neighbors

Geometric factor = $\cos^2(p/4)$

- The end result is the same!

Two atoms per cell - Linear chain

- To illustrate the effect of having two different atoms per cell, consider the simplest case atoms in a line with nearest neighbor forces only

Cell s u_s^1 u_s^2

a
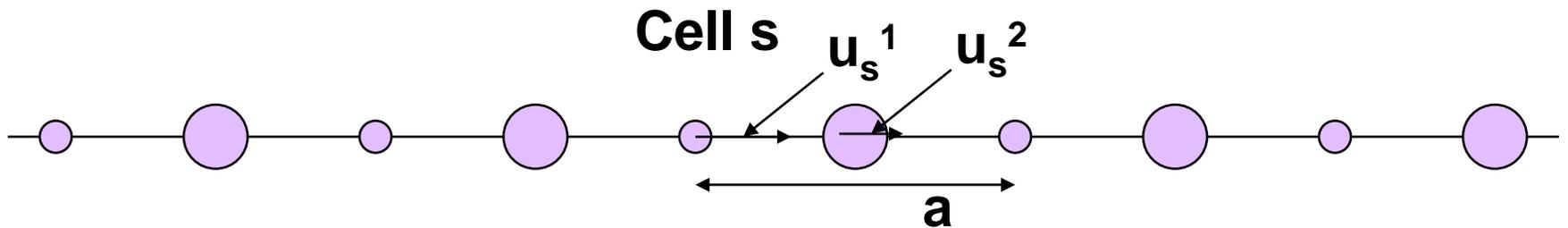
- Now we must calculate force and acceleration of each of the atoms in the cell

$$F_s^1 = C \left[u_{s-1}^2 + u_s^2 - 2 u_s^1 \right] = M_1 \, d^2 u_s^1 / dt^2$$

and

$$F_s^2 = C \left[u_{s+1}^1 + u_s^1 - 2 u_s^2 \right] = M_2 \, d^2 u_s^2 / dt^2$$

Note subscripts

Oscillations with two atoms per cell

- Since the equation is the same for each cell s, the solution must have the same form at each s differing only by a phase factor. This is most easily written

$$u_s{}^1 = u^1 \exp(ik\,(s\,a) - i\omega\,t\,)$$
$$u_s{}^2 = u^2 \exp(ik\,(s\,a) - i\omega\,t\,)$$

- Inserting in Newton's equations gives the coupled equations

$$-M_1\,\omega^2\,u^1 = C[(\exp(-ik\,a) + 1)\,u^2 - 2\,u^1]$$

and

$$-M_2\,\omega^2\,u^2 = C\,[(\exp(\,ik\,a) + 1)\,u^1 - 2\,u^2]$$

$$\begin{vmatrix} 2\,C - M_1\,\omega^2 & -\,C(\exp(-ik\,a) + 1) \\ -\,C(\exp(\,ik\,a) + 1) & 2\,C - M_2\,\omega^2 \end{vmatrix} = 0$$

Oscillations with two atoms per cell

$$\begin{vmatrix} 2C - M_1 \omega^2 & -C(\exp(-ik\,a) + 1) \\ -C(\exp(ik\,a) + 1) & 2C - M_2 \omega^2 \end{vmatrix} = 0$$

- Exercise: Find the simplest form of the equation connecting ω and k
- Use $\cos(x) = \cos^2(x/2) - \sin^2(x/2) = 1 - 2\sin^2(x/2))$

- How many dispersion relations (branches) does this correspond to?

Oscillations with two atoms per cell

- **Solution**

"Optic"

"Gap" frequencies at which no vibrations can occur

"Acoustic"

ω_k

0   π/a $2\pi/a$
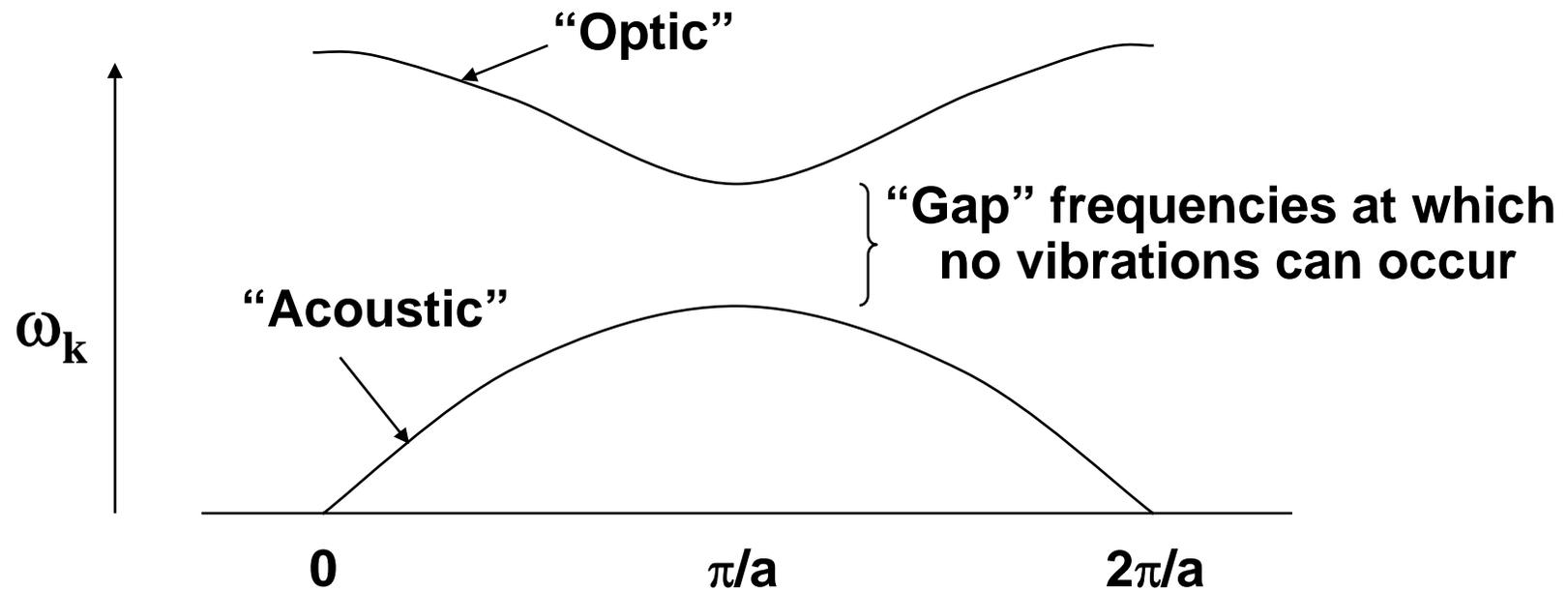
Oscillations with two atoms per cell

- Limits:
- $k \sim 0$

Acoustic - Total Mass

Optic - Reduced Mass

Acoustic: $\omega^2 = (1/2) (C/ (M_1 + M_2)) k^2 a^2$

Optic: $\omega^2 = 2 C[(1 / M_1) + (1/M_2)] = 2 C/\mu$

- $k = \pi/a$

Acoustic: $\omega^2 = 2 C/ M_{large}$ Optic: $\omega^2 = 2 C/ M_{small}$

"Optic"

"Acoustic"

ω_k

}"Gap" frequencies at which no vibrations can occur

0   π/a 2π/a
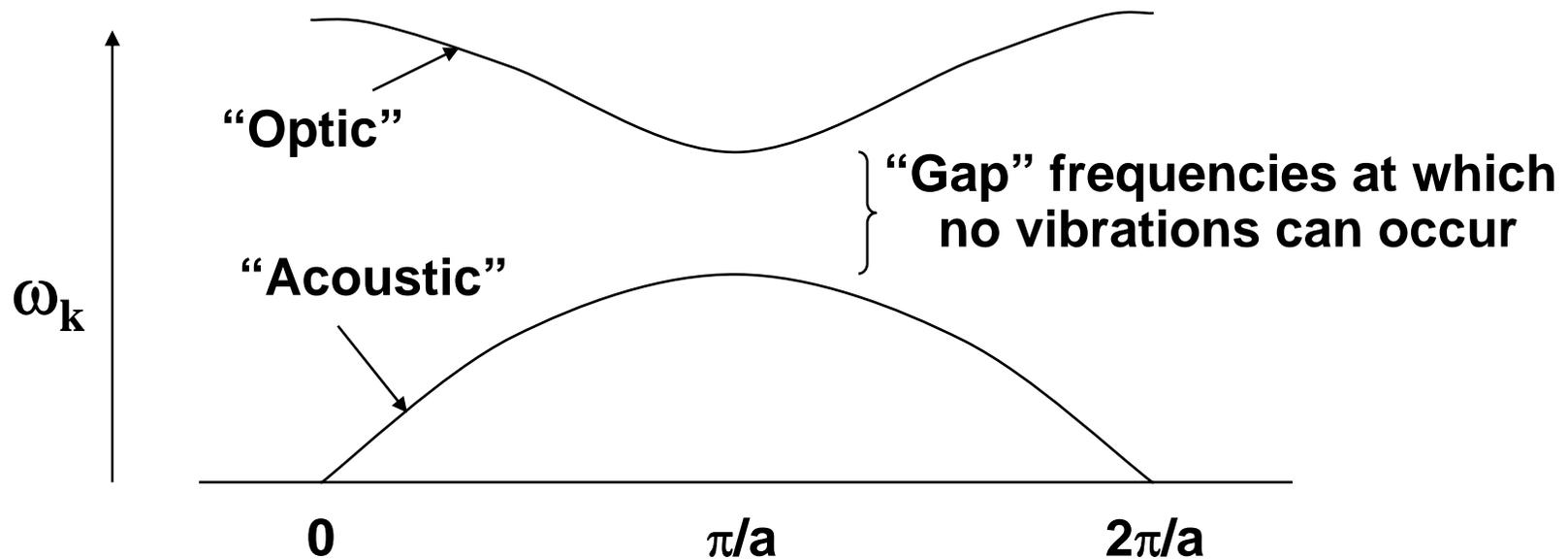
Modes for k near 0

- **Acoustic at k near 0 - motion of cell as a whole**
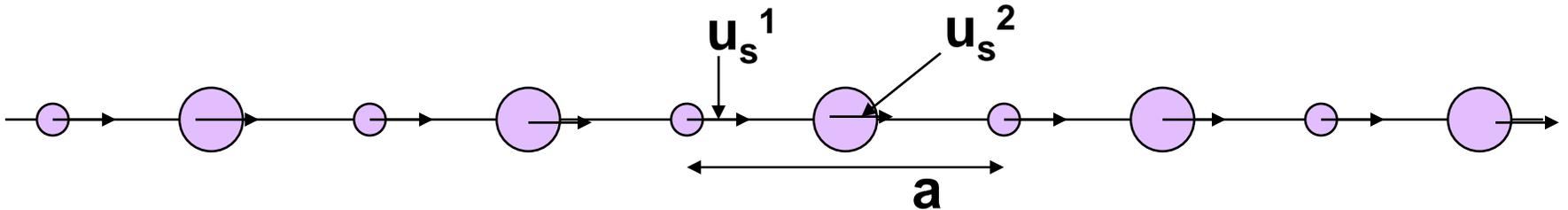
- **Optic at k = 0 - opposed motion - larger displacement of smaller mass**
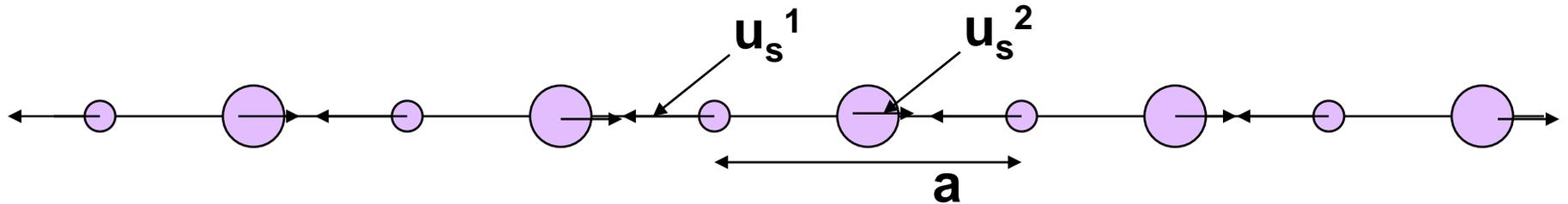
Modes for k at BZ boundary

- **Each type of atom moves in opposite directions in adjacent cells**
- **Leads to two modes, each with only one type of atom moving**
- **Acoustic at k = π/a - motion of larger mass**

$$u_s^1 = 0 \qquad u_s^2$$

$$a$$
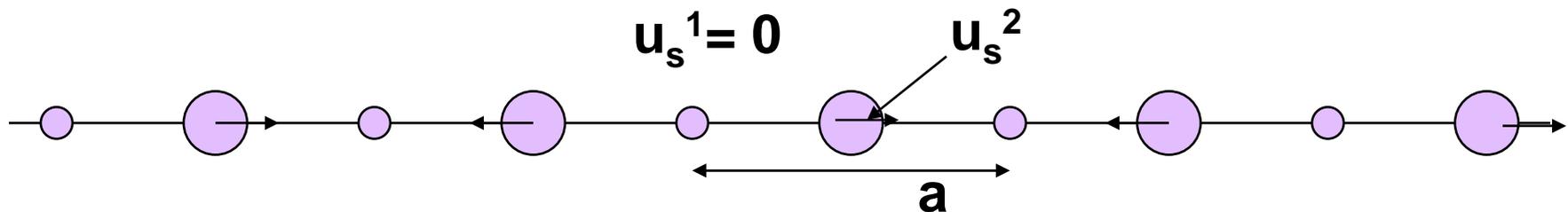
- **Optic at k = π/a - motion of smaller mass**

$$u_s^1 \qquad u_s^2 = 0$$

$$a$$
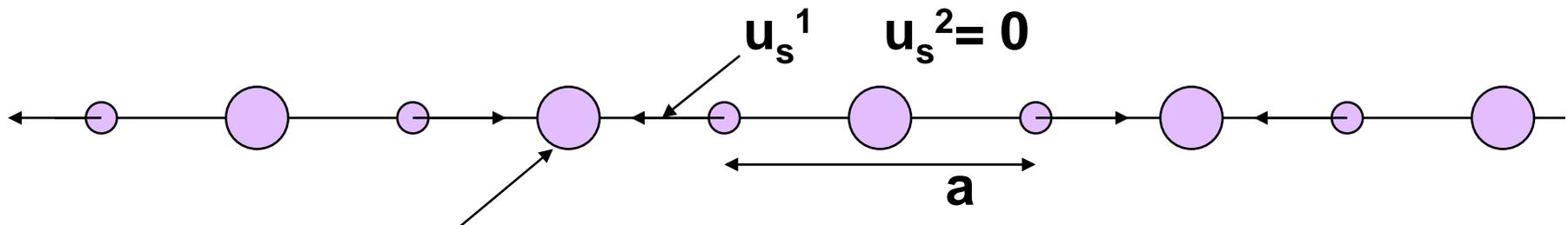
**Atom 2 does not move
because there are no forces on it!**

Oscillations in 3 dimension with N atoms per cell

- **Result**

3 (N -1) Optic Modes

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

ω_k

0   π/a $2\pi/a$
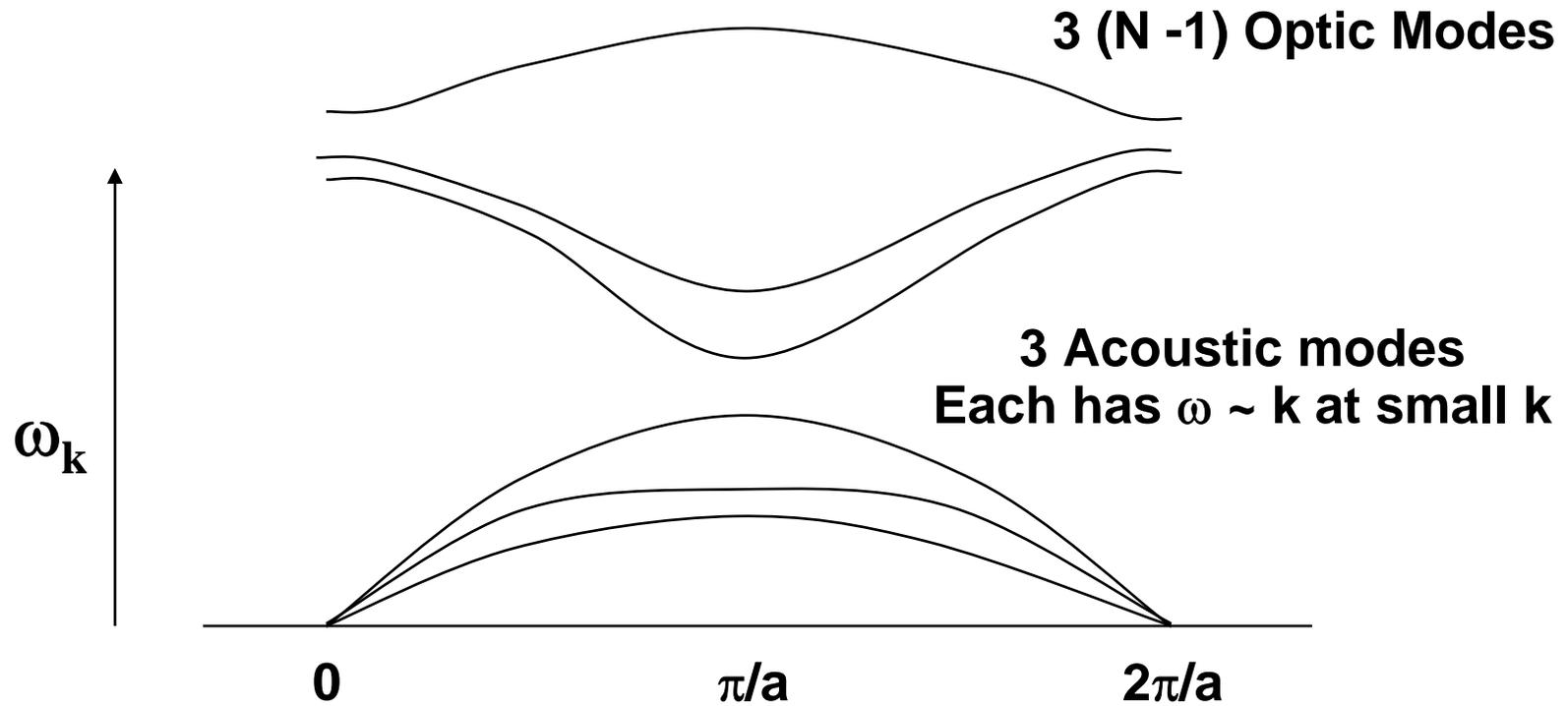
Quantization of Vibration waves

- 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
  $$(1/2) \, M \, \omega^2 \, u^2 = (1/2) \, (n + 1/2) \, h\omega$$
  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
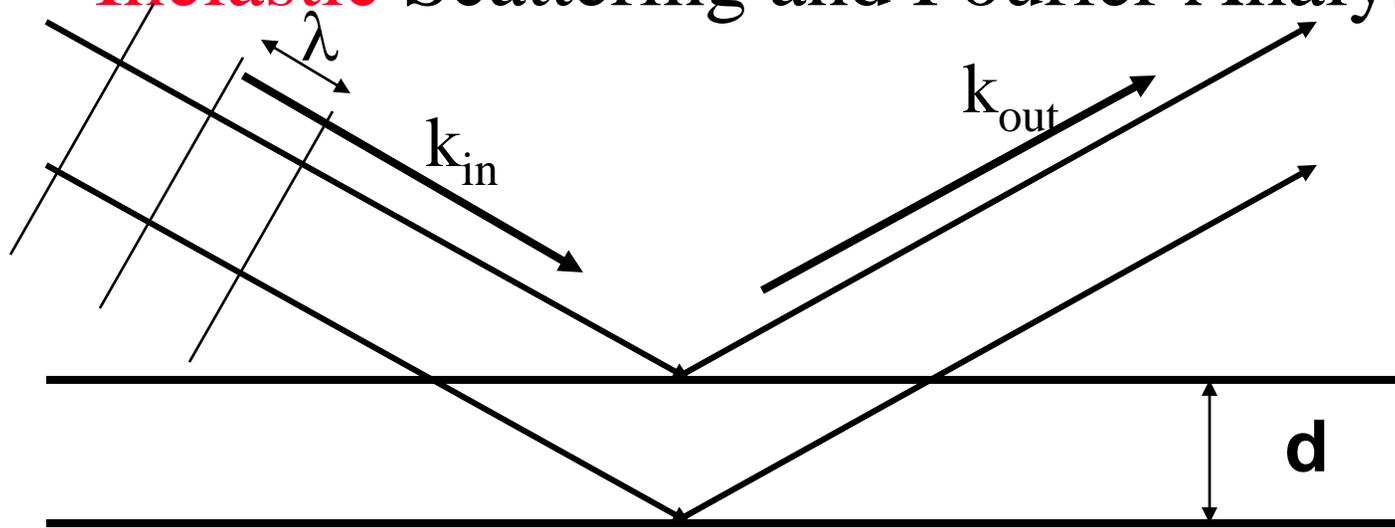
- The in and out waves have the form:
  $\exp(i\,\underline{k}_{in} \cdot r - i\,\omega_{in}t)$ and $\exp(i\,\underline{k}_{out} \cdot r - i\,\omega_{out}t)$
- For elastic scattering we found that diffraction occurs only for $\underline{k}_{in} - \underline{k}_{out} = \underline{G}$
- For inelastic scattering the lattice planes are vibrating and the phonon supplies wavevector $\underline{k}_{phonon}$ and frequency ω_{phonon}

Inelastic Scattering and Fourier Analysis

- Result:

- Inelastic diffraction occurs for

Quantum Mechanics

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

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

$\underline{k}_{in} \, \omega_{in}$

$\underline{k}_{out} \, \omega_{out}$

$\underline{k}_{phonon} \, \omega_{phonon}$
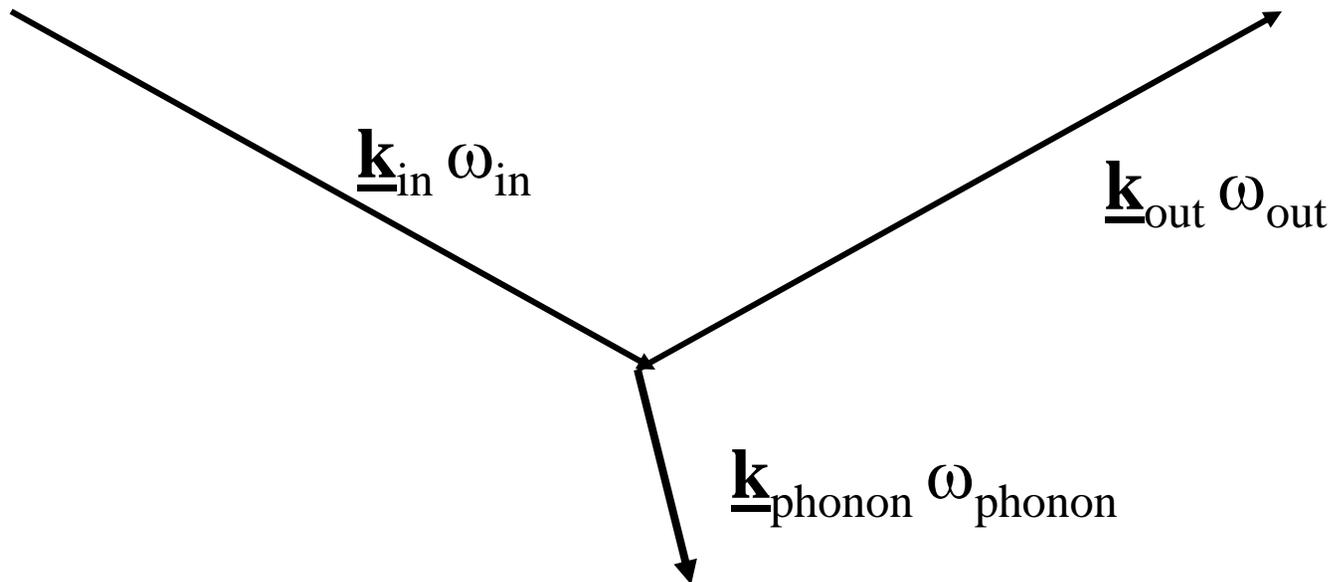
Experimental Measurements of Dispersion Curves

- 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
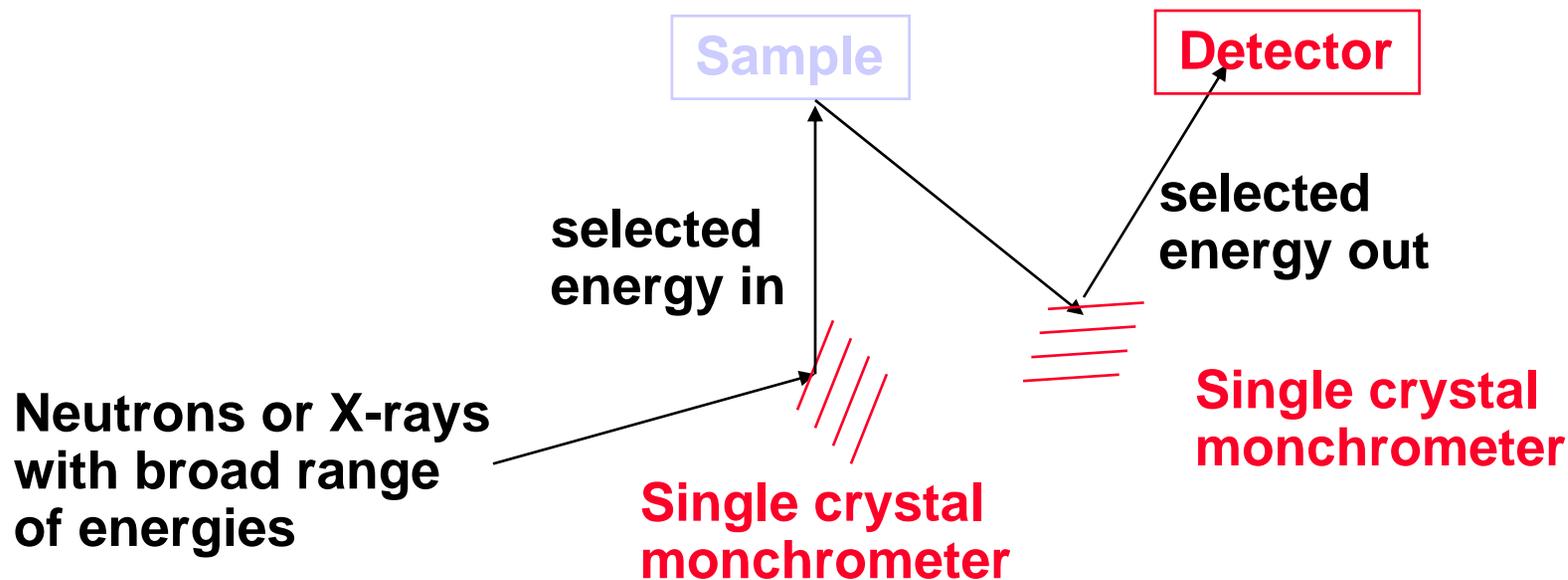
Experimental Measurements of Dispersion Curves

- **Alternate approach for Neutrons**
  Use neutrons from a sudden burst, e.g., at the new "spallation" source being built at Oak Ridge

- **Measure in and out energies by "time of flight"**

Sample

Mechanical chopper selects velocity, i.e., energy in

Timing at detector selects energy out

Detector

Burst of neutrons at measured time (broad range of energies)
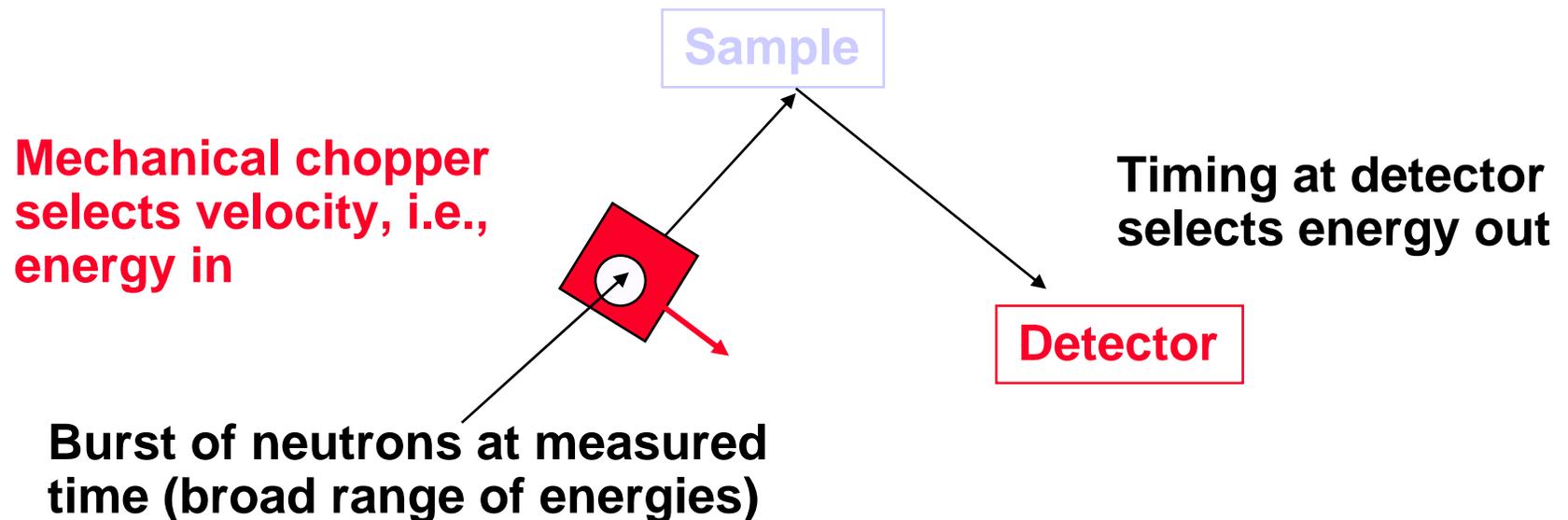
More on Phonons as Particles

- Quanta are called phonons, each with energy $\hbar\omega$

- $\underline{k}$ can be interpreted as "momentum"

- What does this mean?
  NOT really momentum - a phonon does not change the total momentum of the crystal
  But $\underline{k}$ is "conserved" almost like real momentum - when a phonon is scattered it transfers "$\underline{\mathbf{k}}$" plus any reciprocal lattice vector, i.e.,
  $$\Sigma\, \underline{\mathbf{k}}_{\mathbf{b}\text{efore}} = \Sigma\, \underline{\mathbf{k}}_{\text{after}} + \underline{\mathbf{G}}$$

- Example : scattering of particles
  $$\underline{\mathbf{k}}_{\underline{i}n} = \mathbf{k}_{out} + \underline{\mathbf{G}} \pm \underline{\mathbf{k}}_{phonon}$$
  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 <u>G</u> vector

- Measured directly by inelastic diffraction - difference in in
  and out energies is the quantized phonon energy

- Neutrons, X-rays, …..