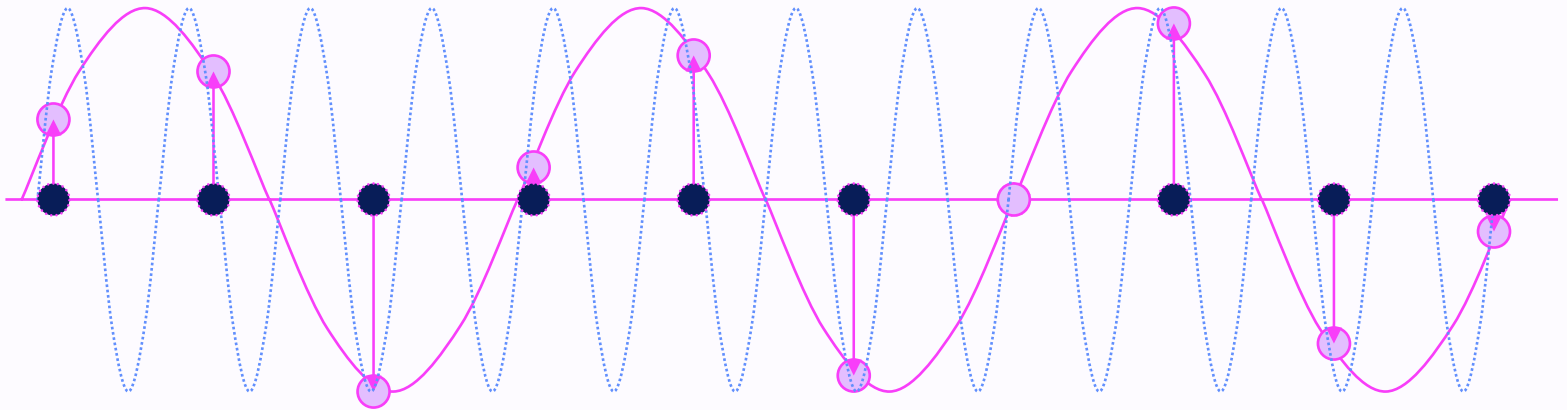# Phonons I - Crystal Vibrations
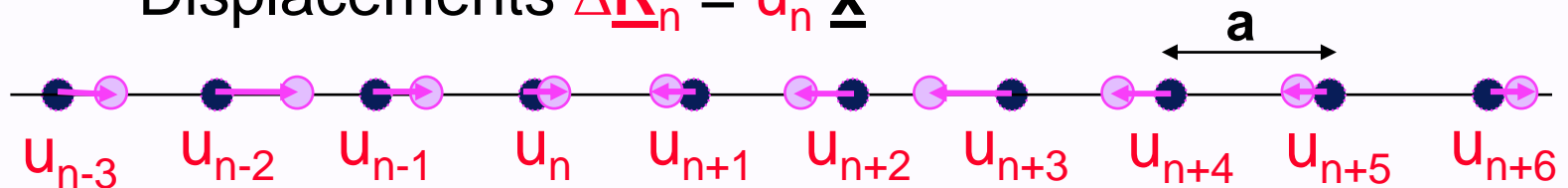# (Kittel Ch. 4)

Outline

- **Vibrations of atoms in crystals**

- **Normal modes of harmonic crystal - exact solution of the problem of an infinite number of coupled oscillators with a few lines of algebra**

- **Relation to sound waves for long wavelength**

- **Role of Brillouin Zone**
  - relation to Bragg Diffraction

- **Quantization and Phonons**

- **(Read Kittel Ch 4)**
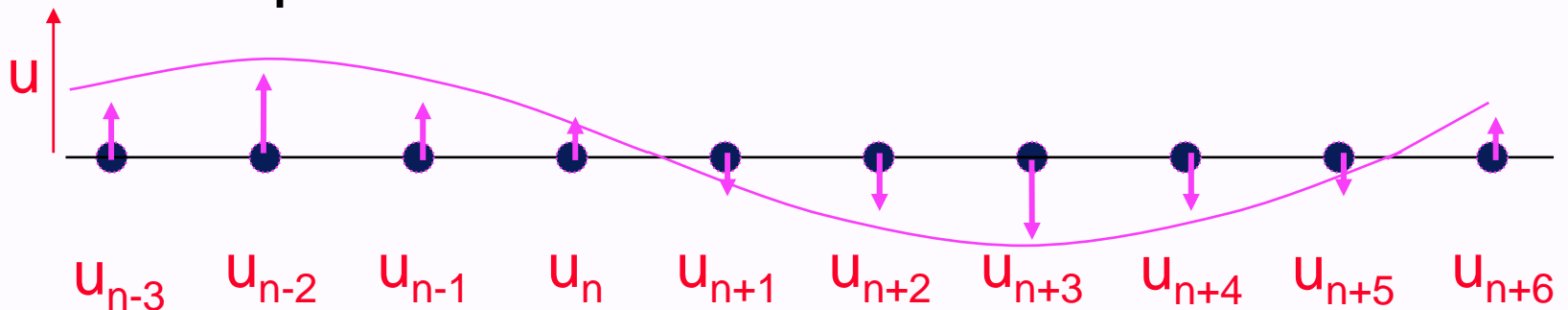
Vibration of atoms in a linear chain

Consider atoms in a line restricted to move along the line

Equilibrium positions $\underline{R}_n^0 = n\,a\,\hat{\underline{x}}$

Displacements $\Delta\underline{R}_n = u_n\,\hat{\underline{x}}$

u_{n-3} u_{n-2} u_{n-1} u_n u_{n+1} u_{n+2} u_{n+3} u_{n+4} u_{n+5} u_{n+6}

Plot of displacements u

u_{n-3} u_{n-2} u_{n-1} u_n u_{n+1} u_{n+2} u_{n+3} u_{n+4} u_{n+5} u_{n+6}
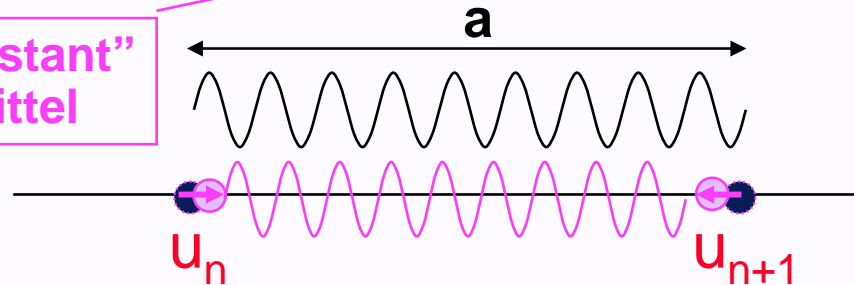
Energy due to Displacements

- The energy of the crystal changes if the atoms are displaced.

- Analogous to springs between the atoms

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

$$\Delta E = \tfrac{1}{2} C (u_{n+1} - u_n)^2$$
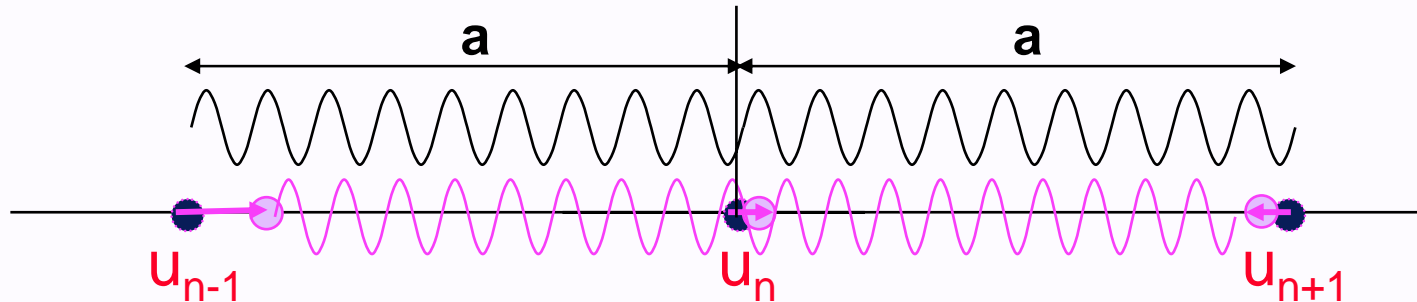
C = "spring constant"
Notation in Kittel

a

u_n u_{n+1}

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

Force due to Displacements

- The force on atom n is due to the two springs on the right and left sides of the atom

$$F_n = C \left[(u_{n+1} - u_n) - (u_n - u_{n-1}) \right]$$
$$= C \left[u_{n+1} + u_{n-1} - 2 u_n \right]$$

- The right spring is compressed more than the left one. Thus the force on atom n is to the left

- Note: For simplicity we consider only springs connecting nearest neighbors – in general there can be interactions with more distant neighbors

Oscillations of linear chain

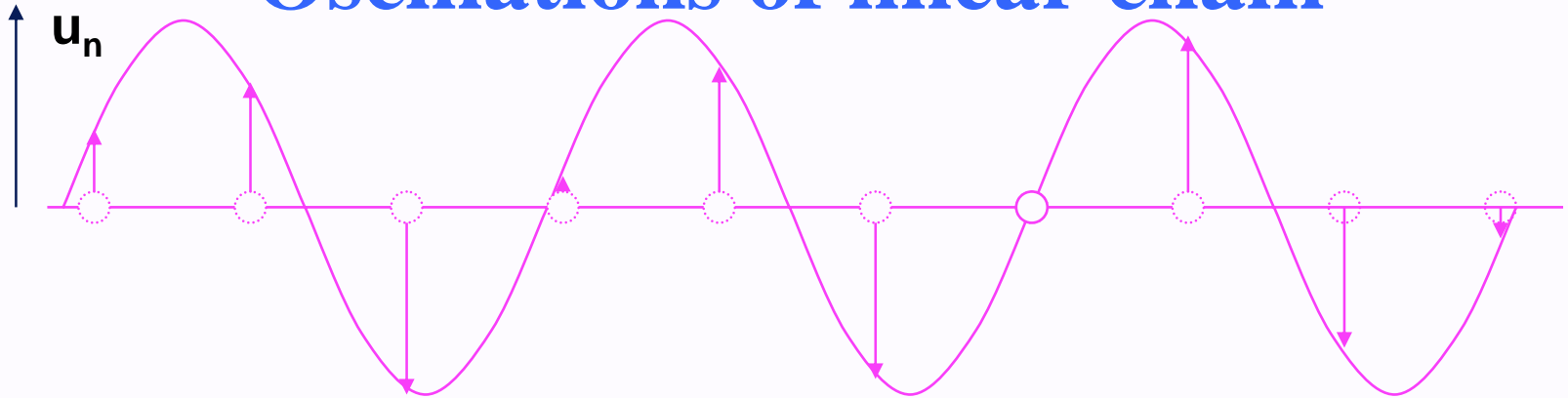$$M \, d^2 \, u_n \, / \, dt^2 = F_n = C \, [\, u_{n+1} + u_{n+1} - 2 \, u_n]$$
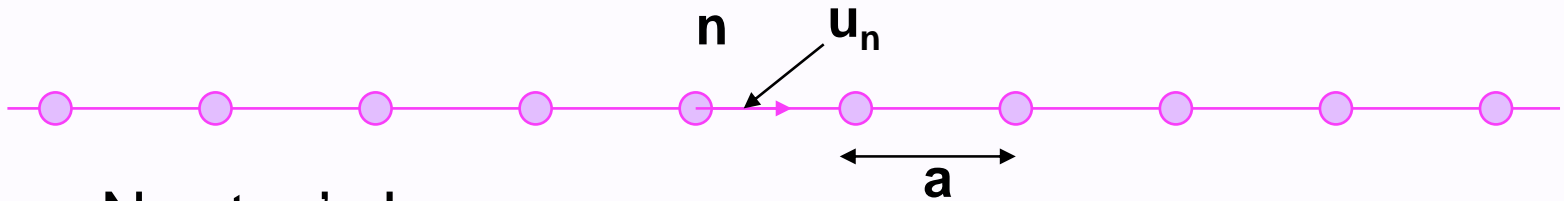
- Newton's Law:
  $$M \, d^2 \, u_n \, / \, dt^2 = F_n = C \, [\, u_{n+1} + u_{n+1} - 2 \, u_n]$$

- Time dependence: Let $u_n(t) = u_n \exp(-i\omega t)$
  ($\sin(\omega t)$ or $\cos(\omega t)$ are also correct but harder to use)
  Then
  $$M \, \omega^2 \, u_n = C \, [u_{n+1} + u_{n+1} - 2 \, u_n]$$

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

Oscillations of linear chain

u_n

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

$$u_n = u \exp(ikna) \qquad k = 2\pi/\lambda$$

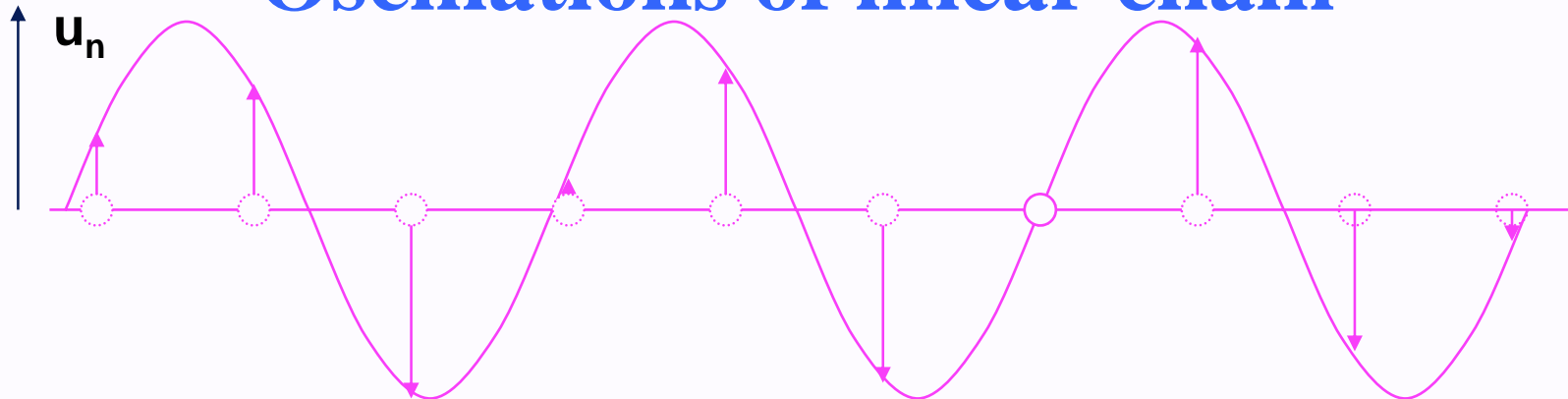**Imaginary number** **Integer n denotes the atom**

- Then

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

or

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

Oscillations of linear chain

u_n

- A more convenient form is
$$\omega^2 = (C / M) [2 \cos(ka) - 2]$$
$$= 4 (C / M) \sin^2(ka/2)$$

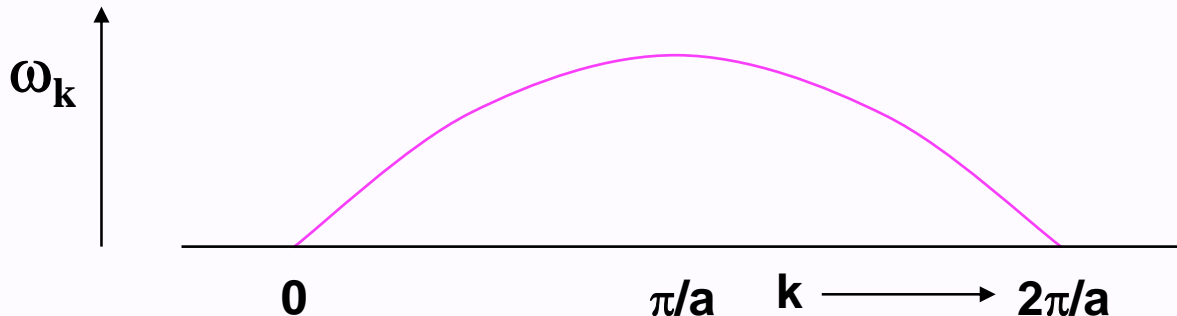(using $\cos(x) = \cos(x/2) - \sin^2(x/2) = 1 - 2 \sin^2(x/2)$)

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

Oscillations of 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

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

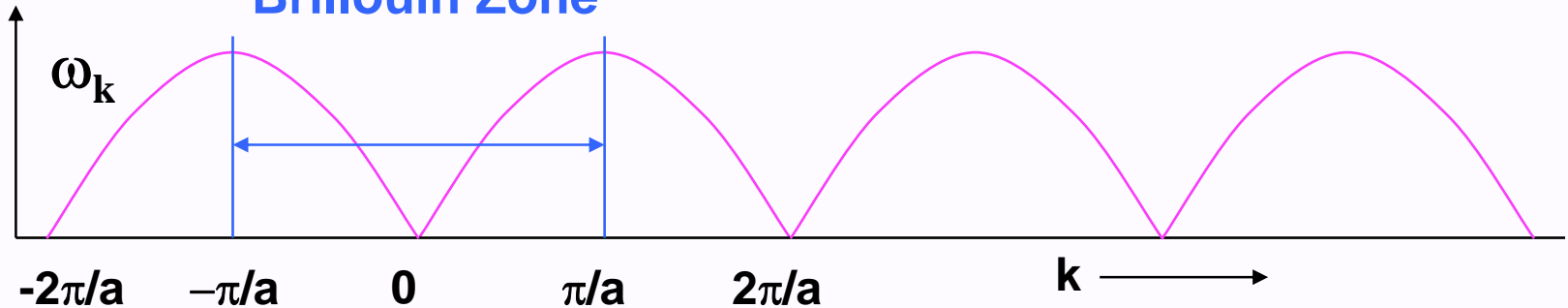- **The relation ω_k as a function of k is called a dispersion curve**

Brillouin Zone

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

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

Brillouin Zone

ω_k

| -2π/a | −π/a | 0 | π/a | 2π/a | k → |

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

- 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 $k \sim 2\pi/3$

$\sin((k + 2\pi/a)\, a/2)$
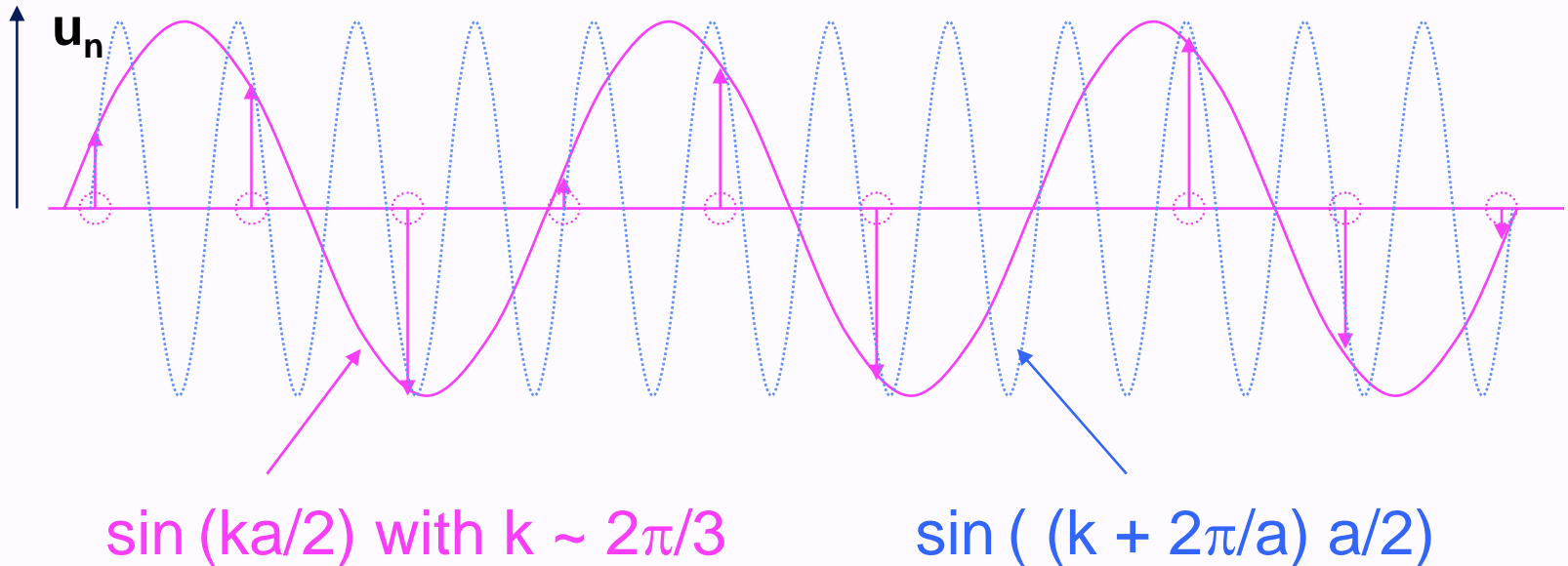
Meaning of Periodicity in Reciprocal space -- II

- This is a general result valid in all crystals in all dimensions (more later on 2 and 3 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.
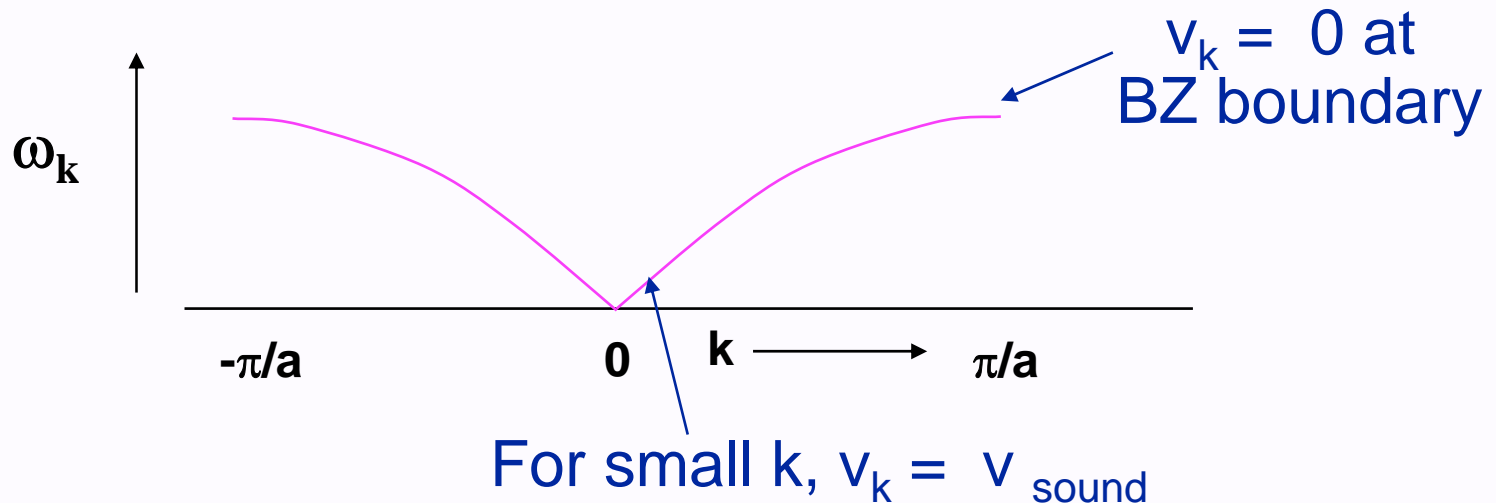
Group velocity of vibration wave

- The wave $u_n = u \exp(ik(na) - i\omega t)$ is a traveling wave
- 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

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

ω_k

$v_k = 0$ at BZ boundary

$-\pi/a$ 0 $k \longrightarrow$ π/a

For small k, $v_k = v_{sound}$

Sound Velocity

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

- Atoms act like a continuum for $ka = 2\pi a/\lambda \ll 1$

- Speed of sound: $v_k = d\,\omega_k / dk = \omega_k/k = v$ independent of k for small k

- From previous silde: $v_{sound} = a (C / M)^{1/2}$

- Homework to show the relation to elastic waves

ω_k

$-\pi/a$ 0   k $\longrightarrow$ π/a

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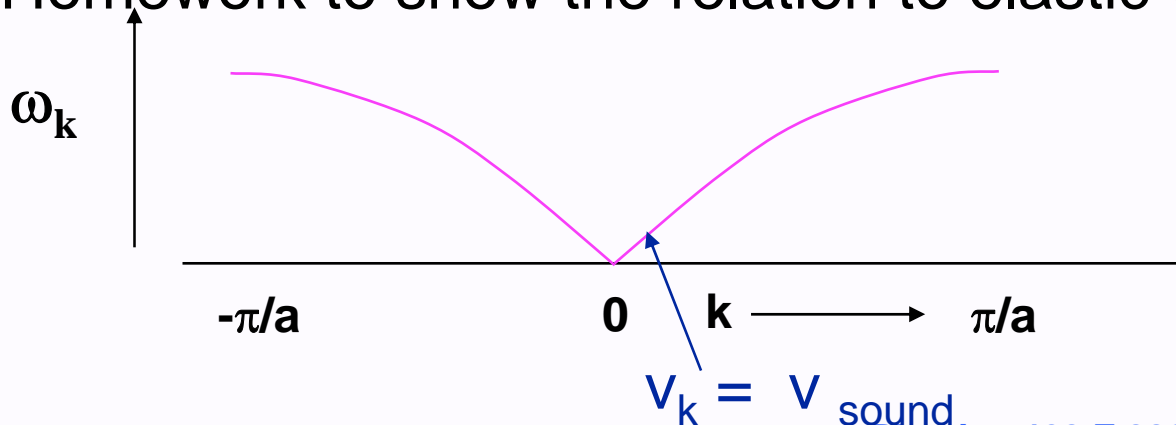
What is significance of zero Group velocity at BZ Boundary?

- 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

ω_k

$v_k = 0$ at BZ boundary

k outside BZ

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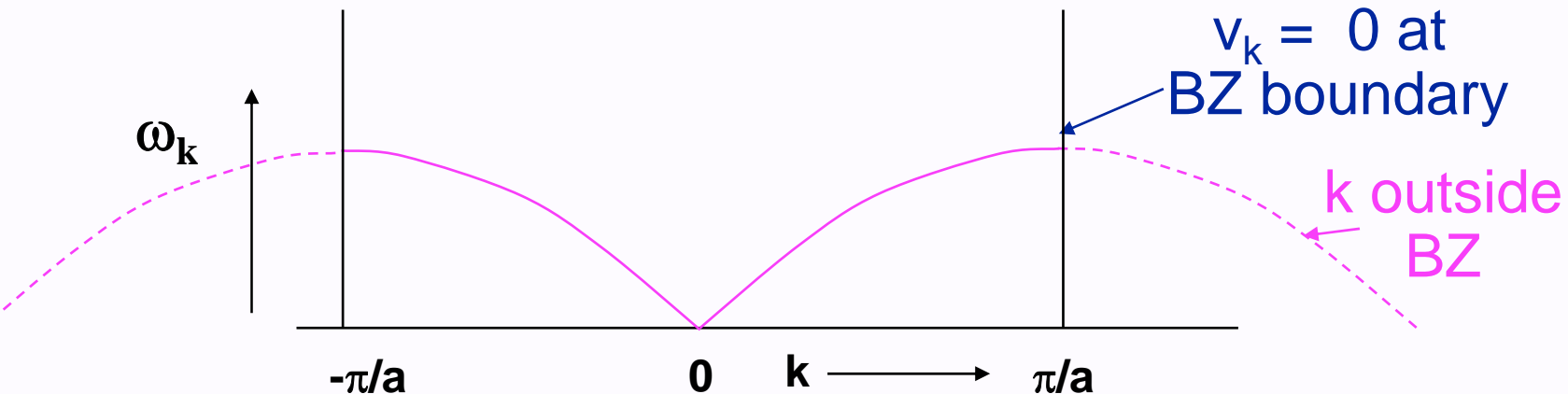
What is significance of zero Group velocity at BZ Boundary?

- Example of Bragg Diffraction!

- Any wave (vibrations or other waves) is diffracted if k is on a BZ boundary – Recall from the description of Bragg Diffraction – Kittel, Ch. 2, Lecture 3, 5
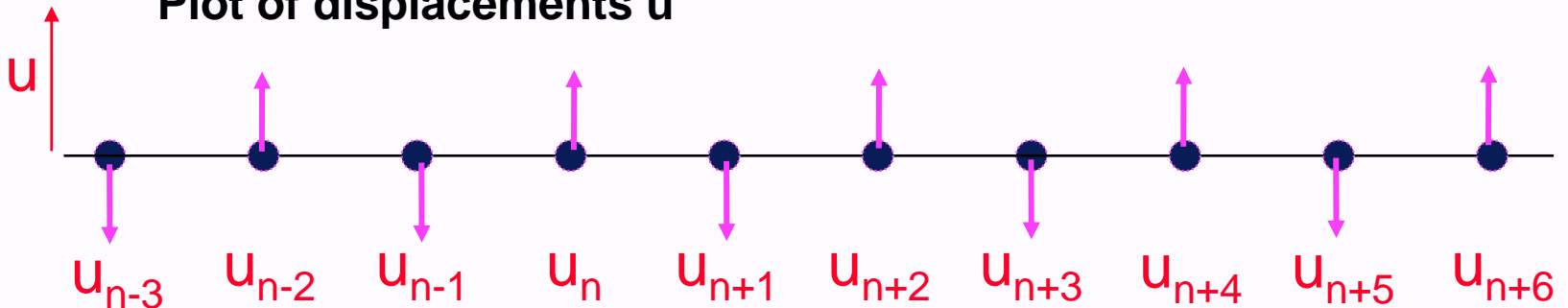
- Leads to standing wave with group velocity = 0

$v_k = 0$ at BZ boundary

ω_k

$-\pi/a$ 0   k $\longrightarrow$ π/a
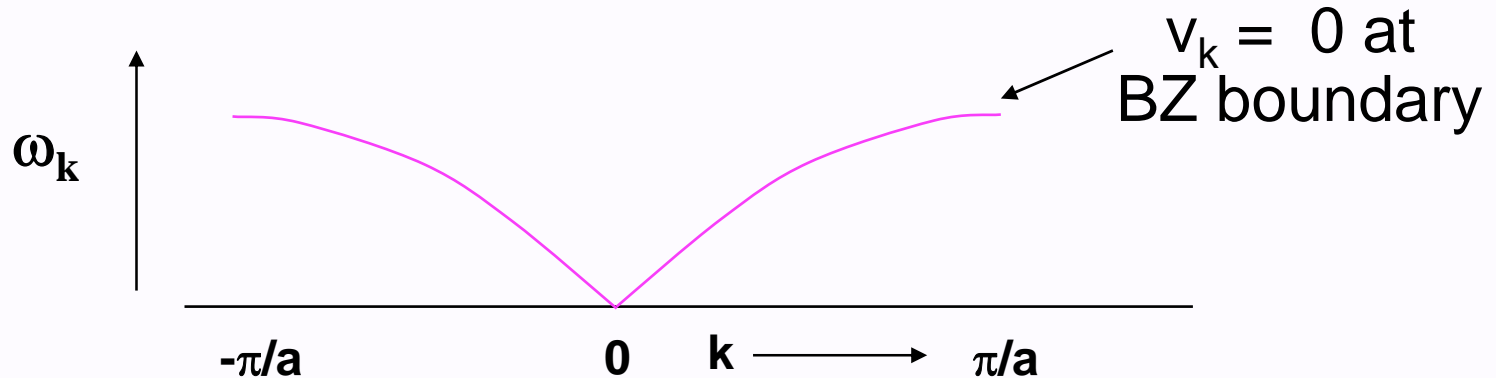
Vibration at the BZ Boundary

At the boundary of the Brillouin Zone in one dimension
k = π/a

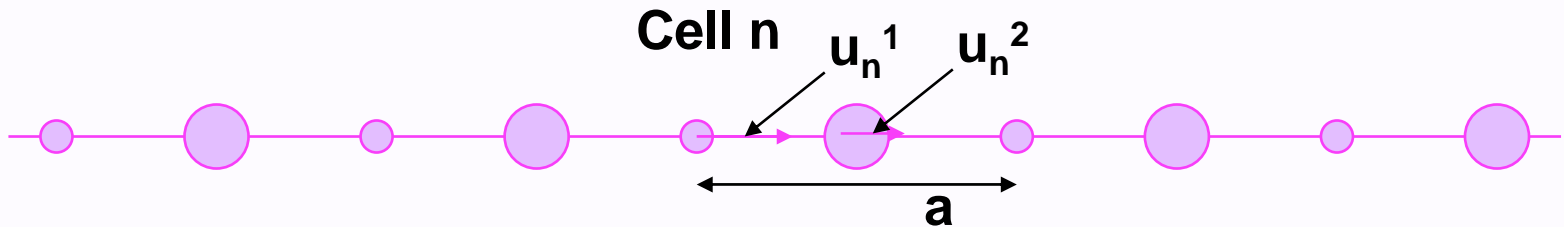The displacement is $u_n = u \exp(ikna) = u \exp(in\pi)$
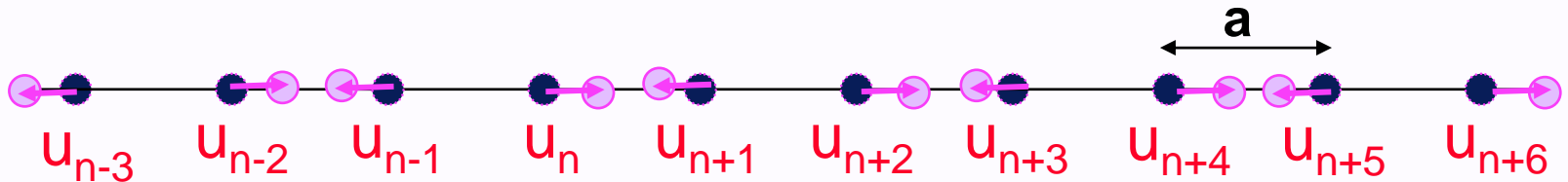
Plot of displacements u

The vibration at the BZ boundary is a standing wave!

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

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

$$F_n^1 = K [u_{n-1}^2 + u_n^2 - 2 u_n^1] = M_1 d^2 u_n^1 / dt^2$$

and

$$F_n^2 = K [u_{n+1}^1 + u_n^1 - 2 u_n^2] = M_2 d^2 u_n^2 / dt^2$$

Note subscripts - Each atom has one neighbor in the same cell and one neighbor in the next cell, left or right

Oscillations with two atoms per cell

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

$$u_n^1 = u^1 \exp(ik\,(n\,a) - i\omega t\,)$$
$$u_n^2 = u^2 \exp(ik\,(n\,a) - i\omega t\,)$$

- Inserting in Newton's equations gives the coupled equations

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

and

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

- Or

$$[2\,K - M_1\,\omega^2\,]\,u^1 - K\,(\exp(-ik\,a) + 1)\,u^2 = 0$$

and

$$[2\,K - M_2\,\omega^2\,]\,u^2 - K\,(\exp(\,ik\,a) + 1)\,u^1 = 0$$

Oscillations with two atoms per cell

- From the previous slide

$$2K - M_1 \omega^2 u^1 - K(\exp(-ik\,a) + 1)\, u^2 = 0$$

and

$$2K - M_2 \omega^2 u^2 - K(\exp(ik\,a) + 1)\, u^1 = 0$$
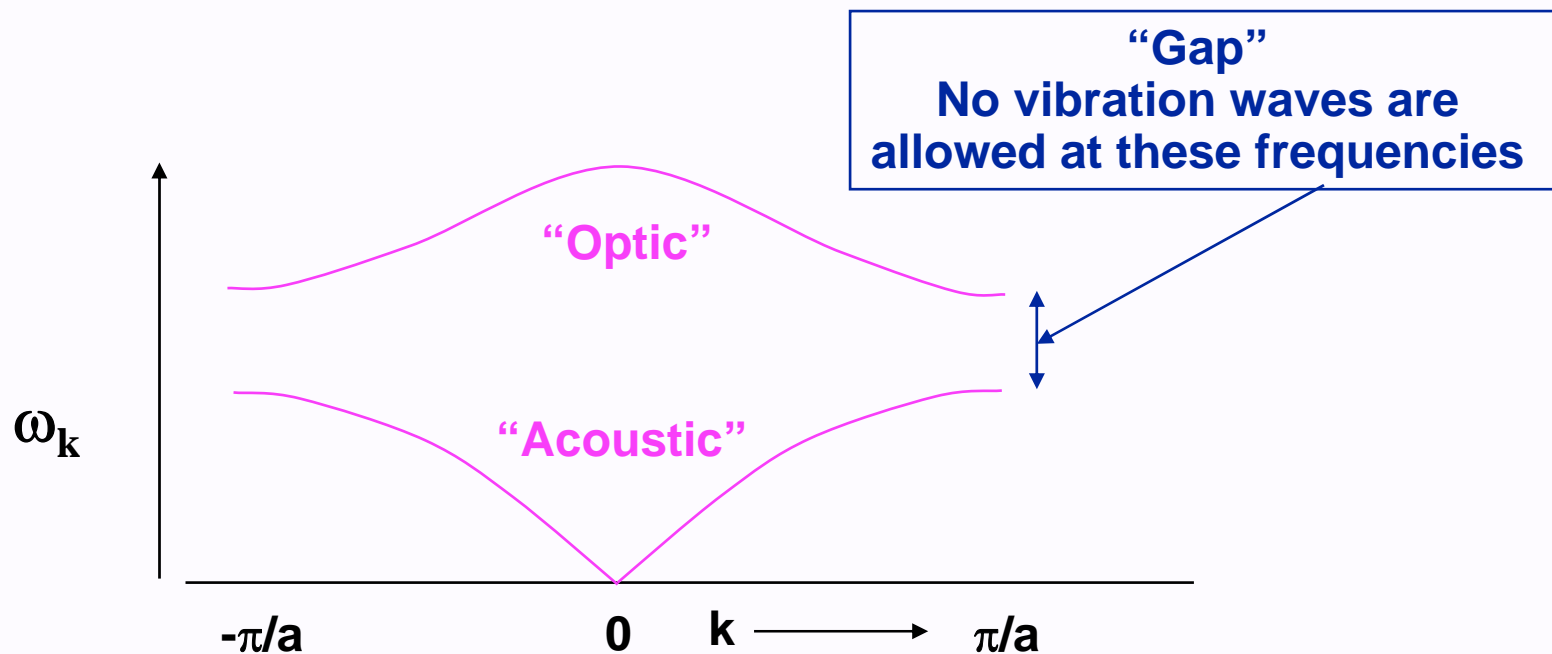
These two equations can be written in matrix form:

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

- The solution is that the determinant must vanish:

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

Oscillations with two atoms per cell

- There are two solutions for each wave vector k

"Gap"
No vibration waves are
allowed at these frequencies

"Optic"

"Acoustic"

ω_k

$-\pi/a$ 0   k $\longrightarrow$ π/a

Oscillations with two atoms per cell

- Limits:

- $k \sim 0$

  Acoustic - Total Mass

  Optic - Reduced Mass
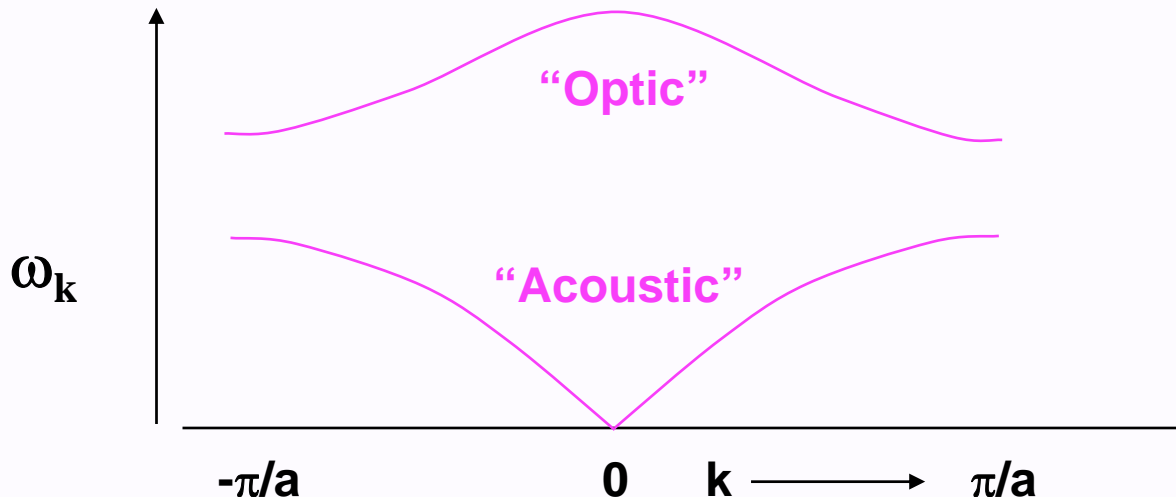
  Acoustic: $\omega^2 = (1/2) (K / (M_1 + M_2)) k^2 a^2$
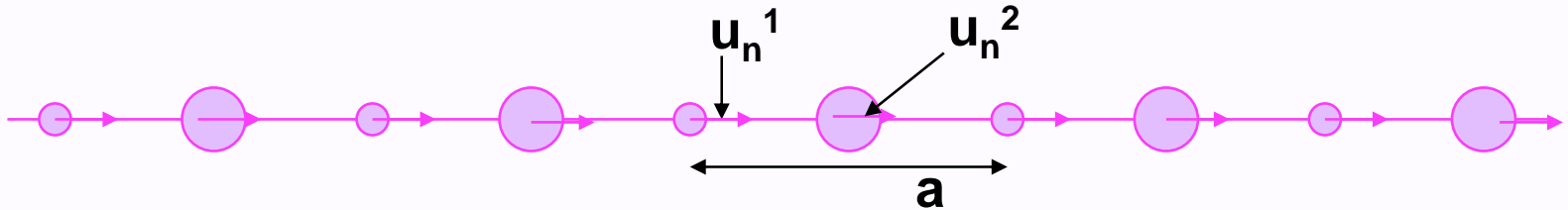 Optic: $\omega^2 = 2 K [(1 / M_1) + (1/M_2)] = 2 K / \mu$

- $k = \pi/a$
  Acoustic: $\omega^2 = 2 K / M_{large}$ Optic: $\omega^2 = 2 K / M_{smaLL}$

"Optic"
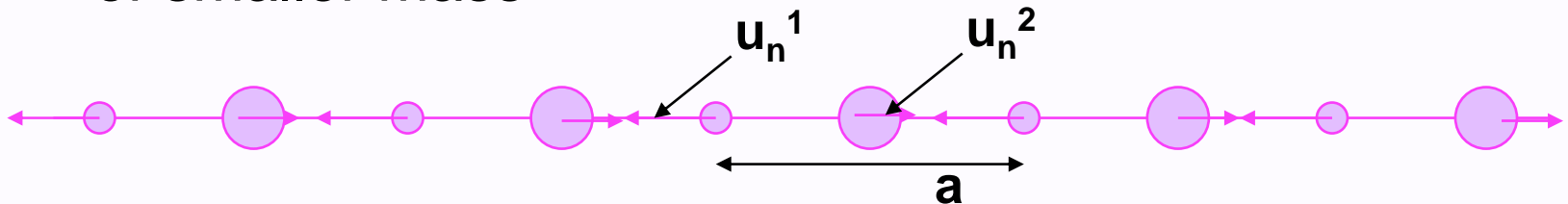
"Acoustic"

ω_k

$-\pi/a$ 0 $k \longrightarrow$ π/a

Modes for k near 0

- Acoustic at k near 0 - motion of cell as a whole

$$u_n^1 \qquad u_n^2$$

$$a$$

- Optic at k = 0 - opposed motion - larger displacement of smaller mass
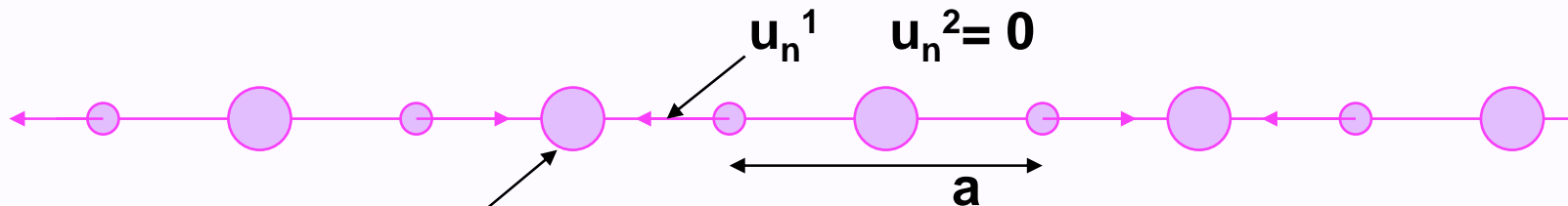
$$u_n^1 \qquad u_n^2$$

$$a$$

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 atoms moving

- Acoustic at k = π/a - motion of larger mass

$$u_n^1 = 0 \qquad u_n^2$$
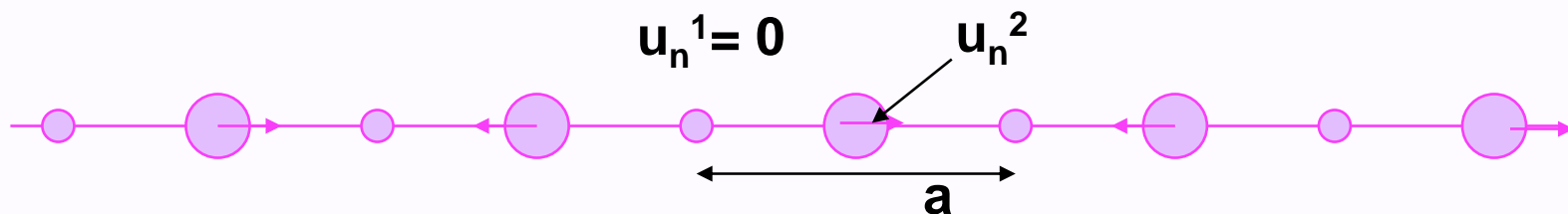
- Optic at k = π/a - motion of smaller mass

$$u_n^1 \qquad u_n^2 = 0$$
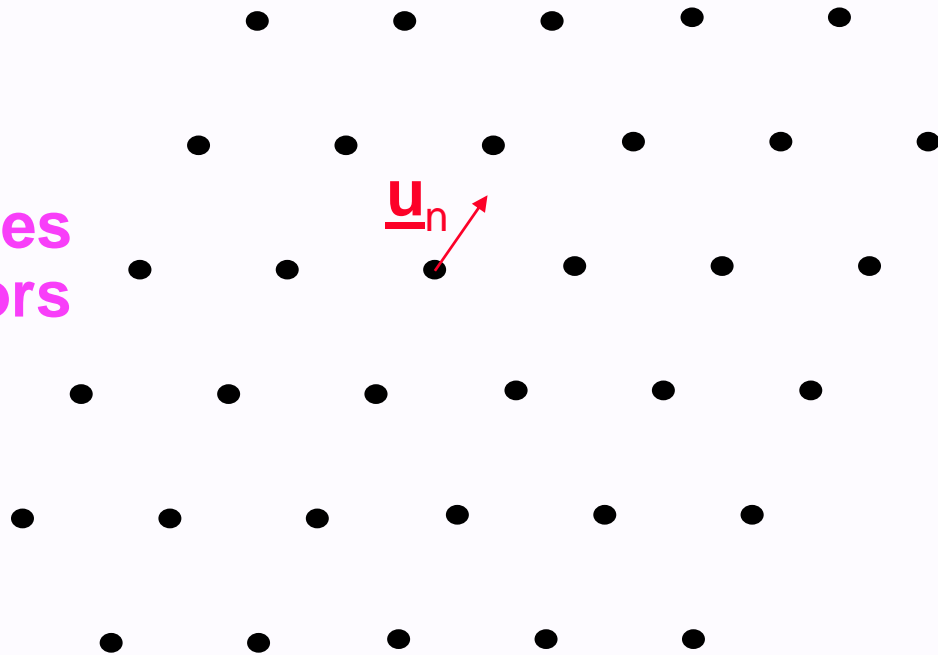
Atom 2 does not move because there are no forces on it!

Vibration waves in 2 or 3 dimensions

- The position $\underline{R}_n{}^0$ and displacement $\underline{u}_n$ are vectors
  $$\underline{R}_n = \underline{R}_n{}^0 + \underline{u}_n$$

- The force on an atom is a vector $\underline{F}_n$ that depends upon the displacements of all the neighbors

Looks complicated

Each atom exerts forces on each of its neighbors

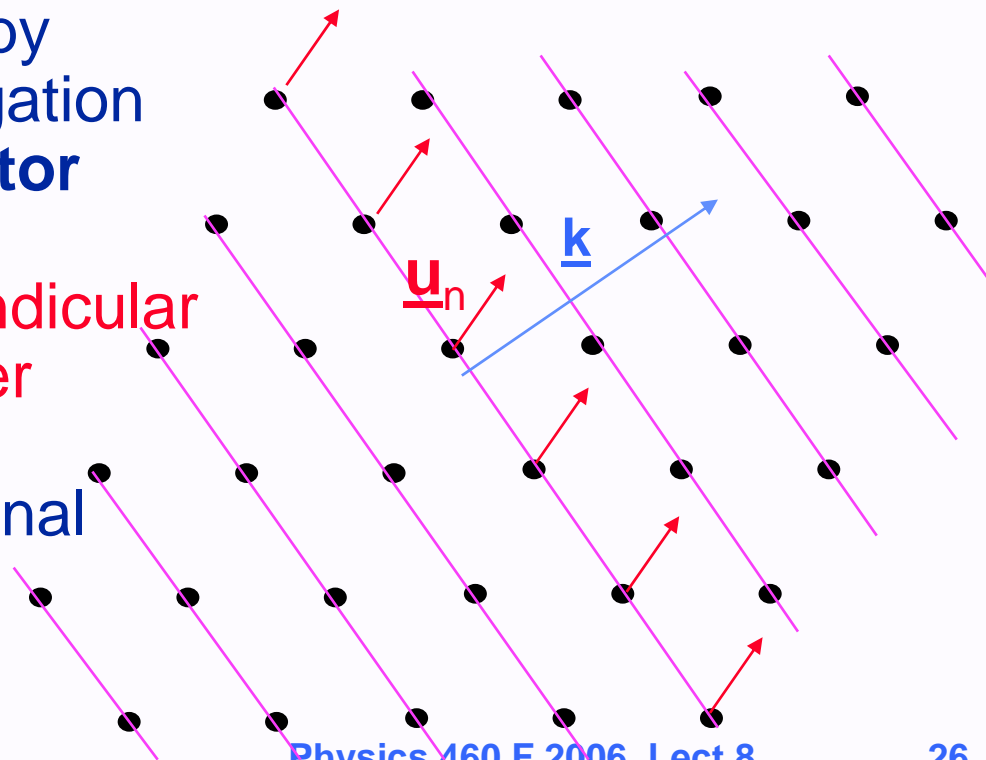**How do we deal with this?**

$\underline{u}_n$

Vibration waves in 2 or 3 dimensions

- We can understand vibrations waves in 2 and 3 dimensional crystals using the same ideas as for vibrations of atoms in a line

A wave is defined by the direction of propagation of the wave – **k-vector**

Planes of atoms perpendicular to **k** move together

Like a one-dimensional problem!

$\underline{u}_n$

$\underline{k}$

Vibration waves in 2 or 3 dimensions

- Every atom in a plane has the same displacement $\underline{u}_n$ and the same force $\underline{F}_n$ on it

- Thus it is sufficient to solve equations for one atom in each plane – all the other atoms obey the same equations
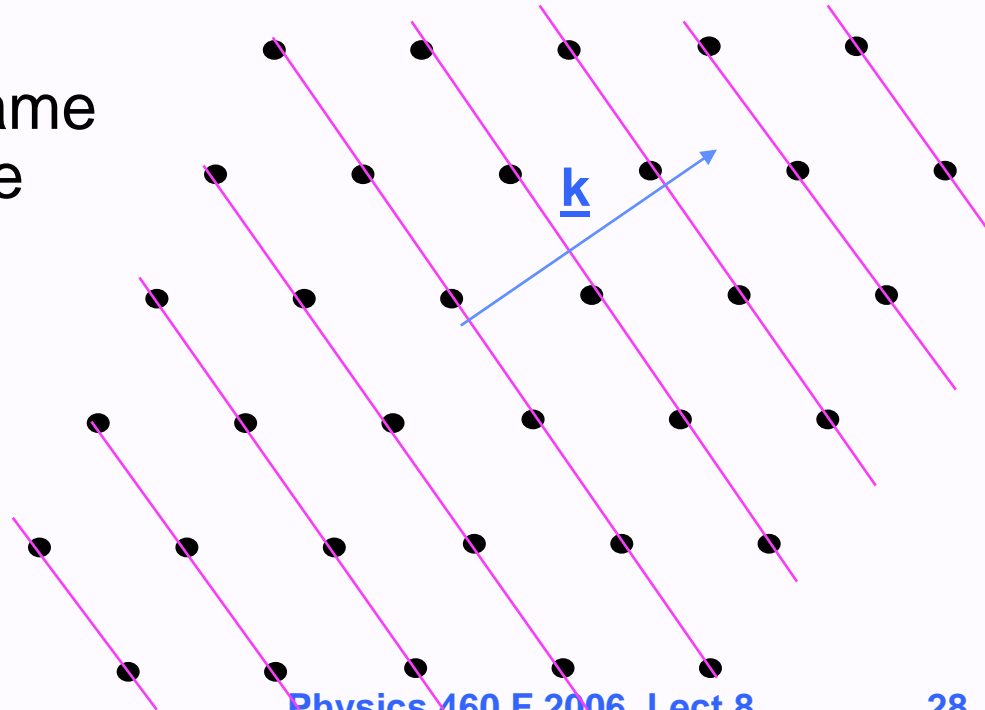
$\underline{k}$
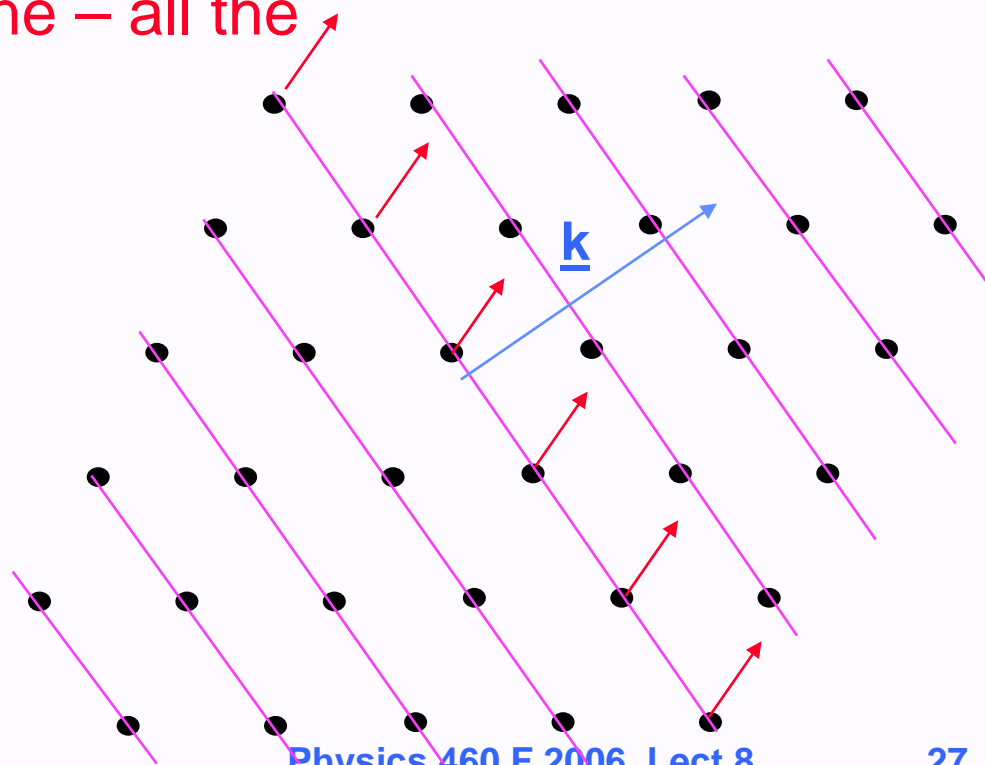
Vibration waves in 2 or 3 dimensions

- 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 **k**

k

Vibration waves in 2 or 3 dimensions

- Normal modes of vibrations in any crystal can be described as waves in which planes move rigidly (Note that there are different sets of planes for different directions of the k vector!)

- The forces between planes can be described by an effective spring constant C^{eff} – we will discuss how to determine the effective constant next time

- Then Newton's equations become

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

- Note: n denotes a plane of atoms, n+1 and n-1 denote the neighboring planes

- $\underline{u}_n$ is an atom in plane n; $\underline{u}_{n+1}$ an atom in plane n+1, etc.

- The same as a one-dimensional problem!

Vibration waves in 2 or 3 dimensions

- Thus all normal modes of vibrations in any crystal can be described in the same way as a one dimensional chain – but be careful to interpret the results properly!

  - There are different sets of planes for different directions of the k vector

  - The effective spring constant C^{eff} must be determined – it is different for different directions of k and for different types of motion

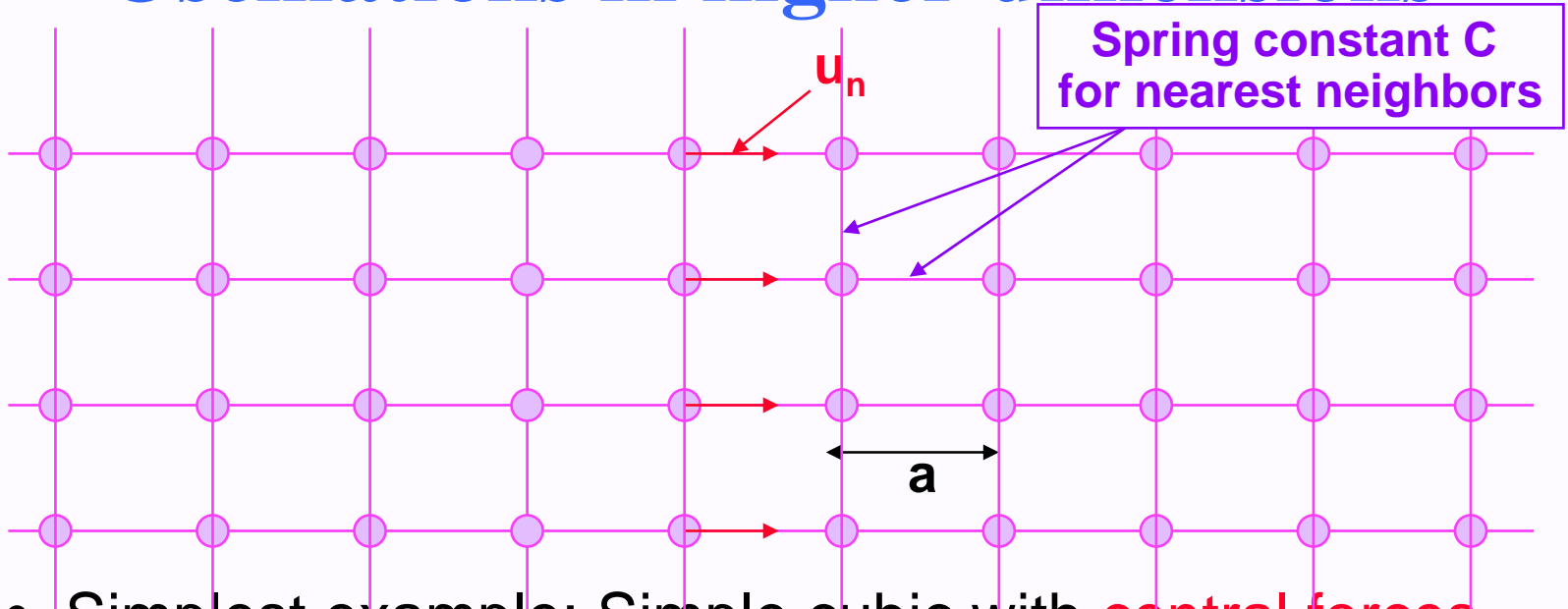 - In 2 and 3 dimensions there can be longitudinal and transverse motions

k
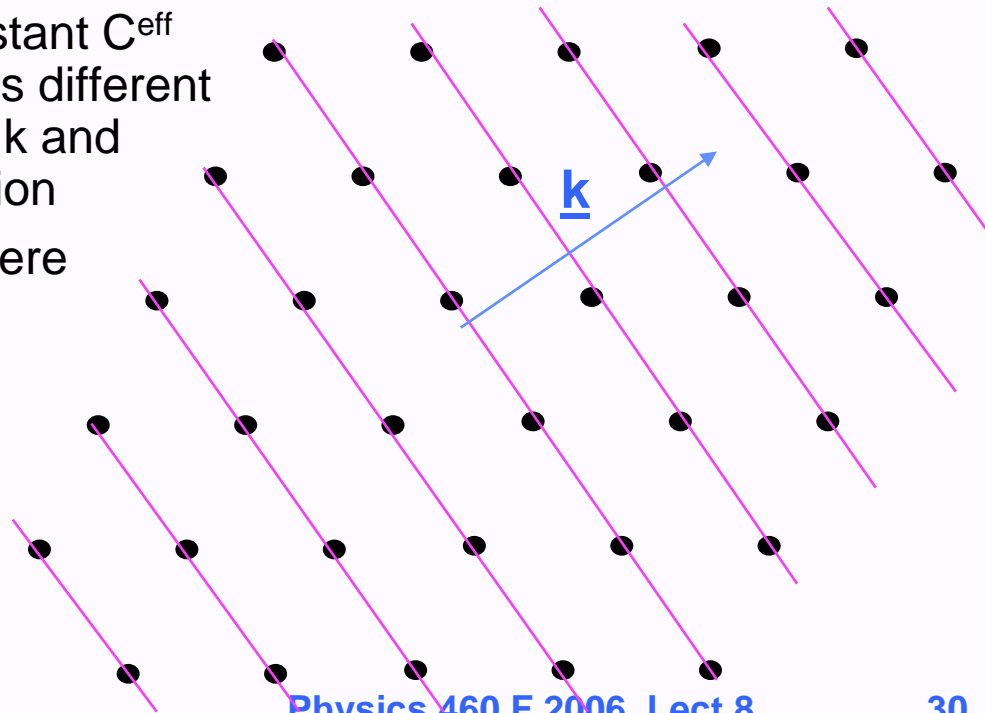
Vibration waves in 2 or 3 dimensions

- It is easier to visualize if we turn the crystal to orient the planes vertical and the k vector horizontal

- Longitudinal motion
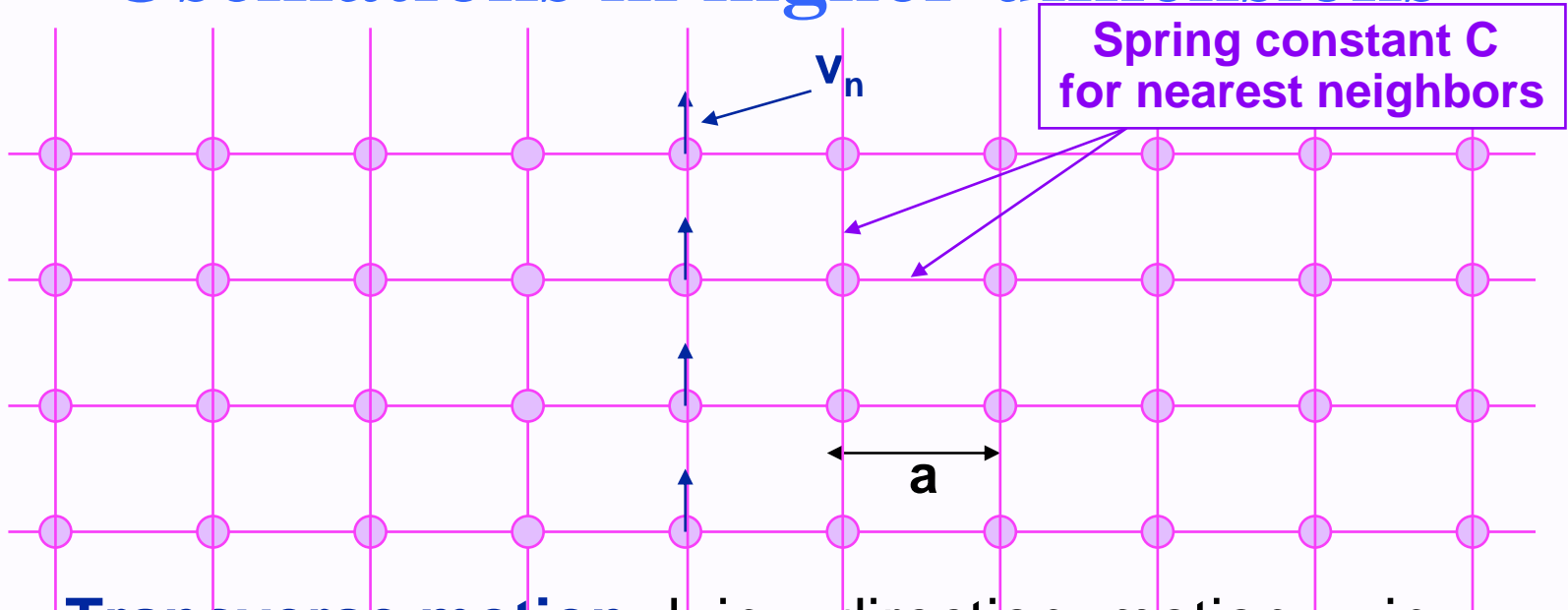
- Transverse motion

k

Oscillations in higher dimensions

u_n

a
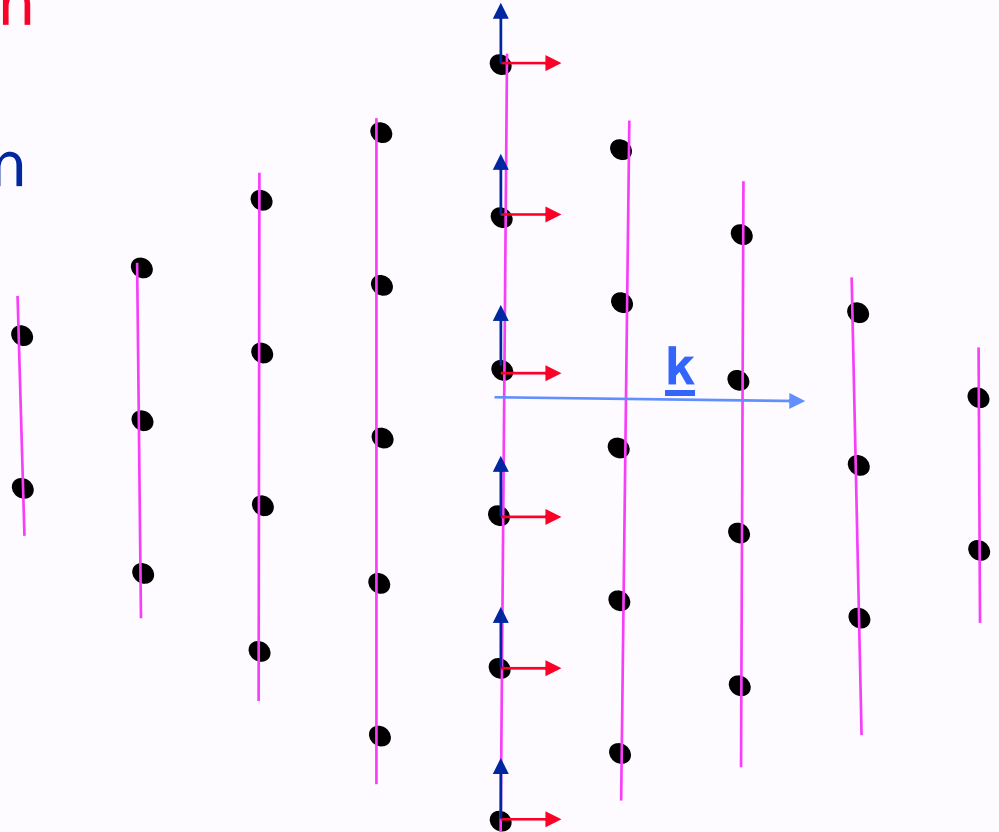
- Simplest example: Simple cubic with central forces

- For k in x direction each atom in the vertical planes moves the same: $u_n = u_n = u \exp(ik (n a) - i\omega t)$

- **Longitudinal motion:** for u_n in x direction: the problem is exactly the same as a linear chain

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

Oscillations in higher dimensions
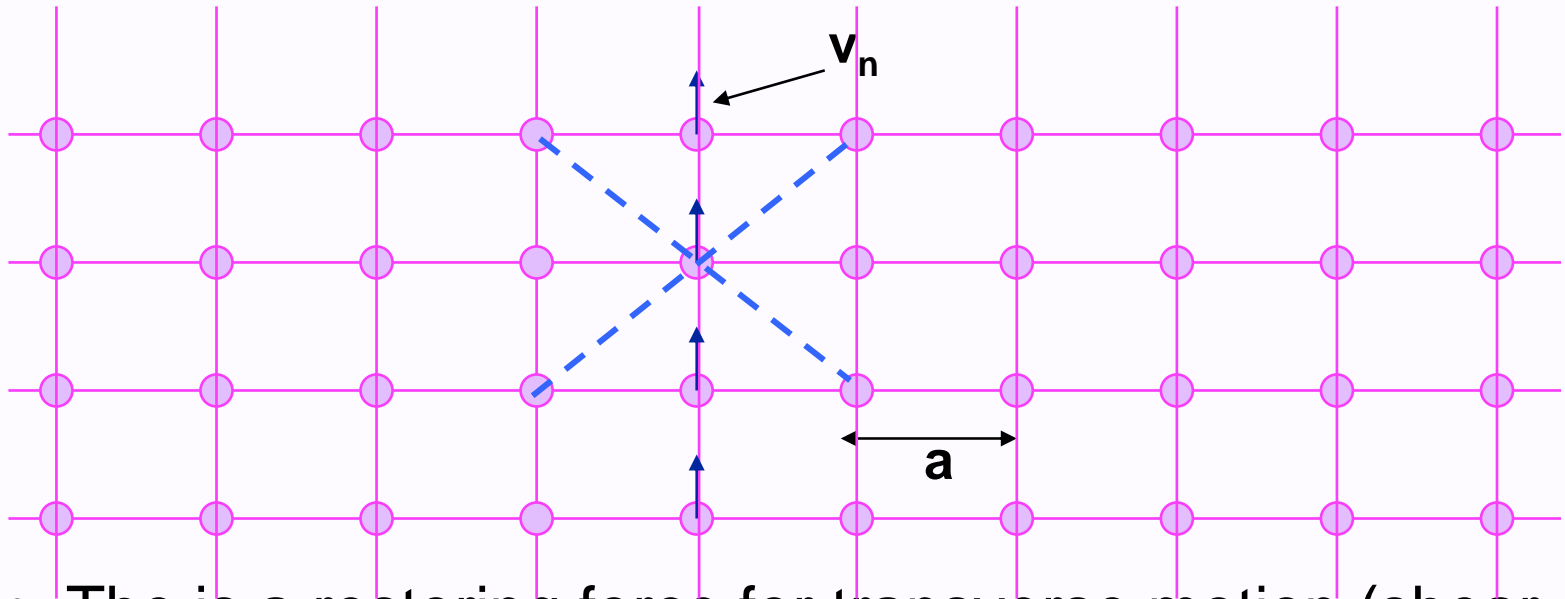
Spring constant C for nearest neighbors

- **Transverse motion:** k in x direction; motion v_n in y direction

$$v_n = v_n = v \exp(ik (n a) - i\omega t)$$

- Central forces give no restoring force! Unstable!

- Need other forces - non-central or second neighbor

Oscillations in higher dimensions

- The is a restoring force for transverse motion (shear motion) if there are **second neighbor forces**

$$\omega^2 = (1/2)(C_2 / M) [4 \cos(ka) - 4]$$
$$= 2 (C_2 / M)^{1/2} | \sin (ka/2) |$$

4 neighbors

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

Second neighbor

Meaning of Periodicity in Reciprocal space -- Again

- The same logic that we used for one dimension applies to 2 and 3 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.

- **This is a general result valid in all crystals in all dimensions**

Diffraction and the Brillouin Zone

- **Brillouin Zone formed by perpendicular bisectors of G vectors**

- **Consequence: No diffraction for any k inside the first Brillouin Zone**

- **Special Role of Brillouin Zone (Wigner-Seitz cell of recip. lat.) as opposed to any other primitive cell**

- **Important later in course -- Here we have example for vibrations -- later for electrons**

b_2

k_{out}

G

k_{in}

b_1

Brillouin Zone
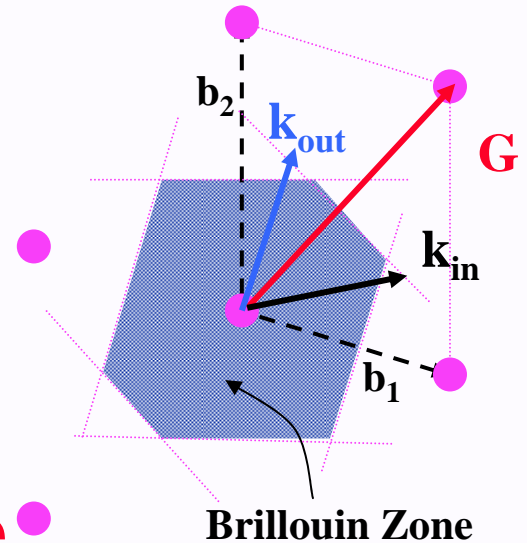
Summary

- Normal modes of vibrations in a crystal with harmonic forces :
  - Independent oscillators are labeled by wavevector **k** and have frequency ω_k
  - The relation ω_k as a function of k is called a dispersion curve
  - ω_k periodic as a function of **k** in reciprocal space
  - All independent oscillations are described by wavevectors **k** inside the Brillouin Zone
  - For more than one atom per cell there are acoustic and optic modes of vibration
- Sound waves are long wavelength (small **k**) acoustic modes
- Group velocity of the waves vanish at BZ boundary Bragg scattering!
- **Linear chain, planes in crystals – more next time**

Next time

- **Why do vibrations in crystals act like atoms connected by springs?**

- **How do we determine the effective spring constant from the forces that bind the atoms together?**

- **Quantization and Phonons**

- **Is phonon "momentum" real?**

- **Experimental Measurements**

- **(Read Kittel Ch 4)**