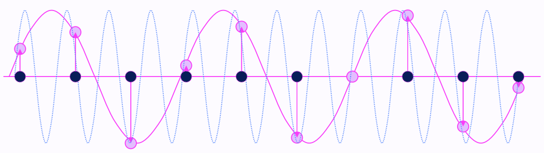
Lecture 8 - Crystal Vibrations

Phonons I - Crystal Vibrations (Kittel Ch. 4)



Outline

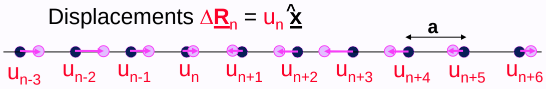
- Vibrations of atoms in crystals
- Normal modes of harmonic crystal - exact solution of the problem of an infinite number of coupled oscillators with a few lines of algebra
- Relation to sound waves for long wavelength
- Role of Brillouin Zone
  - relation to Bragg Diffraction
- Quantization and Phonons
- (Read Kittel Ch 4)

Vibration of atoms in a linear chain

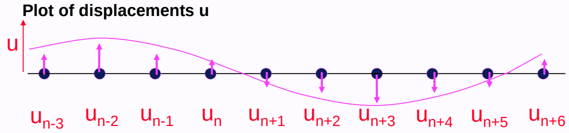
Consider atoms in a line restricted to move along the line

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

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



Plot of displacements u

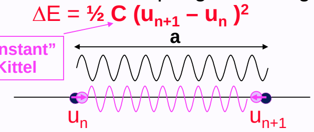


Energy due to Displacements

- 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:

$$\Delta E = ½\, C\, (u_{n+1} - u_n)^2$$

C = "spring constant" Notation in Kittel

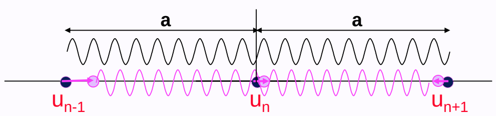


- Note: There are no linear terms if we consider small changes u from the equilibrium positions

Force due to Displacements

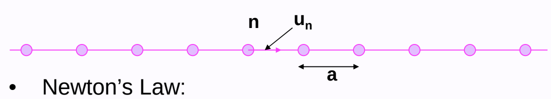
- The force on atom n is due to the two springs on the right and left sides of the atom

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



- 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

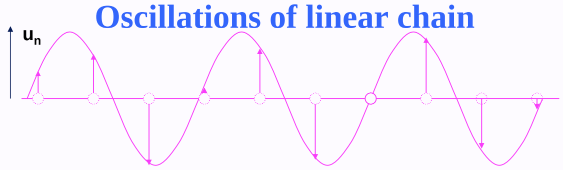
Oscillations of linear chain



- 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(ωt) or cos(ωt) 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!

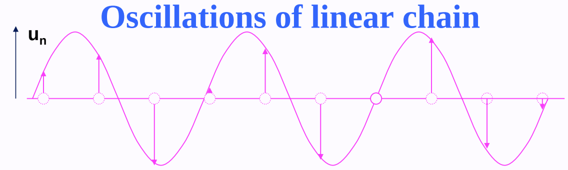
Lecture 8 - Crystal Vibrations

Oscillations of linear chain



- 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) **k=2π/λ**
  Imaginary number Integer n denotes the atom
- Then
  M ω^2 u = C [exp(ika) + exp(-ika) - 2] u
  or
  ω^2 = (C / M) [2 cos(ka) - 2]

Oscillations of linear chain

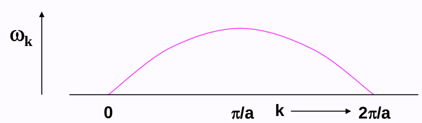


- A more convenient form is
  ω^2 = (**C** / M) [2 cos(ka) - 2]
  = 4 (**C** / M) $\sin^2(ka/2)$

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

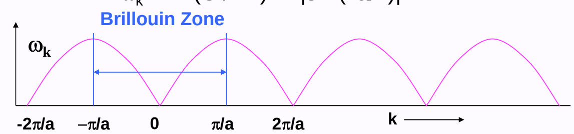
Oscillations of linear chain

- **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

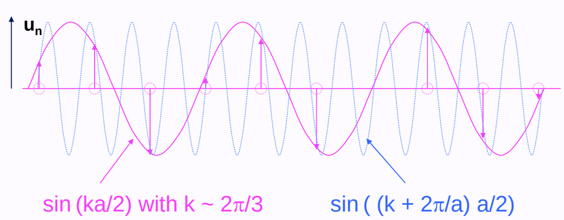
- Consider k ranging over all reciprocal space. The expression for ω_k is periodic
  $\omega_k = 2 (C / M)^{1/2} |\sin(ka/2)|$



- 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



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.

Lecture 8 - Crystal Vibrations

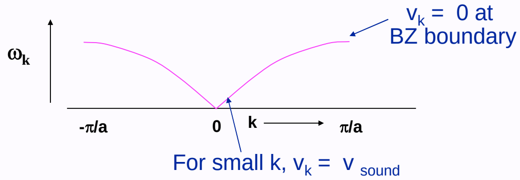
Group velocity of vibration wave

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

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

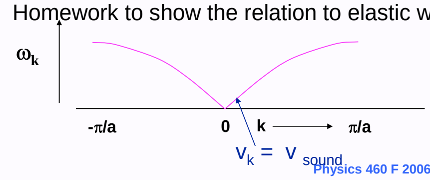
so

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



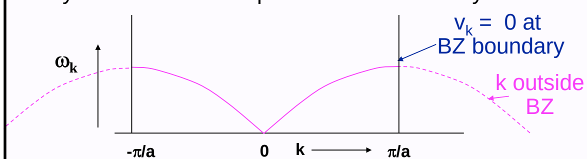
Sound Velocity

- 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 $ka = 2\pi a/\lambda << 1$
- 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



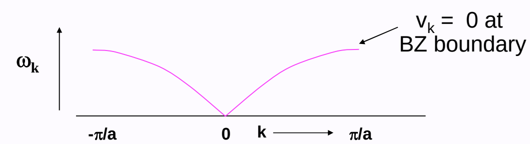
What is significance of zero Group velocity at BZ Boundary?

- 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



What is significance of zero Group velocity at BZ Boundary?

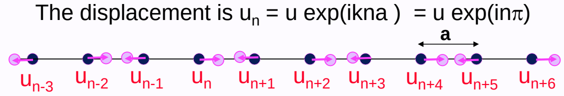
- Example of Bragg Diffraction!
- Any wave (vibrations or other waves) is diffracted if k is on a BZ boundary – Recall from the description of Bragg Diffraction – Kittel, Ch. 2, Lecture 3, 5
- Leads to standing wave with group velocity = 0



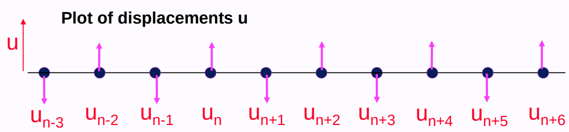
Vibration at the BZ Boundary

At the boundary of the Brillouin Zone in one dimension
$k = \pi/a$

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



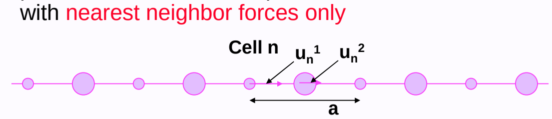
Plot of displacements u



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

Lecture 8 - Crystal Vibrations

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

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

and

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

- Or

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

and

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

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:

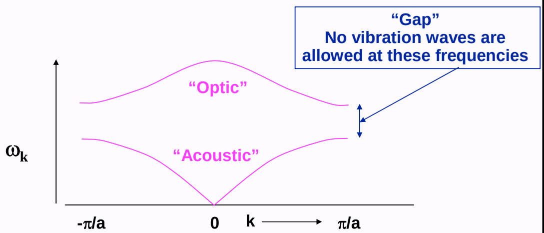
$$\begin{bmatrix} 2K - M_1 \omega^2 & -K(\exp(-ik a) + 1) \\ -K(\exp(ik a) + 1) & 2K - M_2 \omega^2 \end{bmatrix} \begin{bmatrix} u^1 \\ u^2 \end{bmatrix} = 0$$

- 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



Oscillations with two atoms per cell

- Limits:

Acoustic - Total Mass   Optic - Reduced Mass

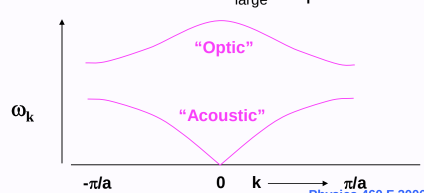
- $k \sim 0$

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

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

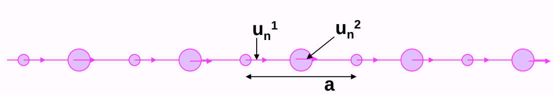
- $k = \pi/a$

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

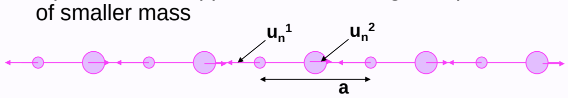


Modes for k near 0

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

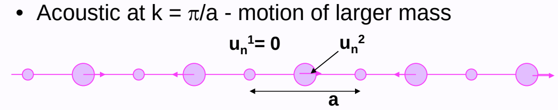


- Optic at k = 0 - opposed motion - larger displacement of smaller mass

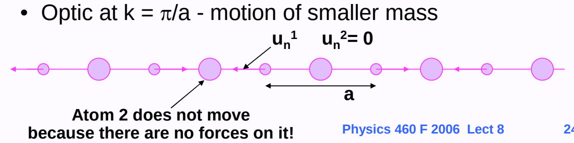


Modes for k at BZ boundary

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



- Optic at $k = \pi/a$ - motion of smaller mass



Lecture 8 - Crystal Vibrations

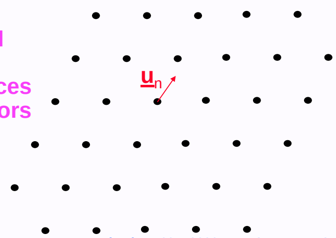
Vibration waves in 2 or 3 dimensions

- The position $\underline{\mathbf{R}}_n^0$ and displacement $\underline{\mathbf{u}}_n$ are vectors
  $\underline{\mathbf{R}}_n = \underline{\mathbf{R}}_n^0 + \underline{\mathbf{u}}_n$
- The force on an atom is a vector $\underline{\mathbf{F}}_n$ 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?



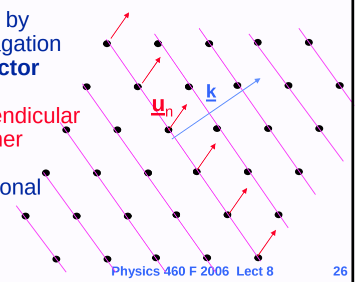
Vibration waves in 2 or 3 dimensions

- 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**

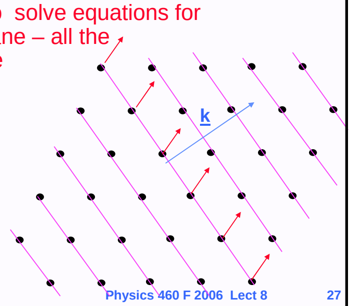
Planes of atoms perpendicular to **k** move together

Like a one-dimensional problem!



Vibration waves in 2 or 3 dimensions

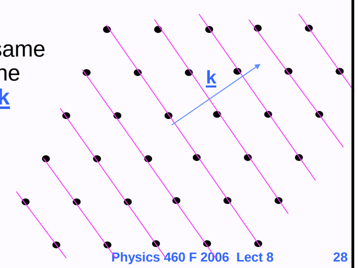
- Every atom in a plane has the same displacement $\underline{\mathbf{u}}_n$ and the same force $\underline{\mathbf{F}}_n$ on it
- Thus it is sufficient to solve equations for one atom in each plane – all the other atoms obey the same equations



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 $\underline{\mathbf{k}}$

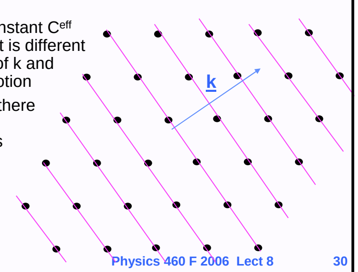


Vibration waves in 2 or 3 dimensions

- 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
  $M\, d^2 \underline{\mathbf{u}}_n / dt^2 = \underline{\mathbf{F}}_n = C^{eff} [\, \mathbf{u}_{n-1}^2 + \mathbf{u}_n^2 - 2\, \mathbf{u}_n^1]$
- Note: n denotes a plane of atoms, n+1 and n-1 denote the neighboring planes
- $\underline{\mathbf{u}}_n$ is an atom in plane n; $\underline{\mathbf{u}}_{n+1}$ an atom in plane n+1, etc.
- The same as a one-dimensional problem!

Vibration waves in 2 or 3 dimensions

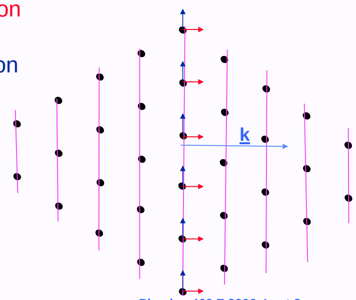
- Thus all normal modes of vibrations in any crystal can be described in the same way as a one dimensional chain – but be careful to interpret the results properly!
  - There are different sets of planes for different directions of the k vector
  - The effective spring constant C^{eff} must be determined – 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



Lecture 8 - Crystal Vibrations

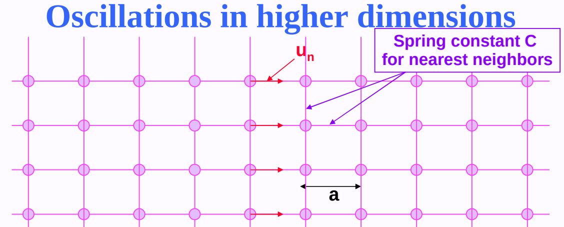
Vibration waves in 2 or 3 dimensions

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



Physics 460 F 2006 Lect 8 31

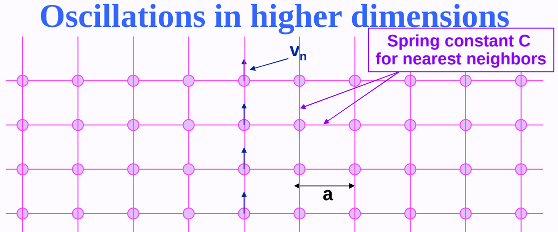
Oscillations in higher dimensions



- Simplest example: Simple cubic with central forces
- For k in x direction each atom in the vertical planes moves the same: $\mathbf{u}_n = \mathbf{u}_n = \mathbf{u} \exp(ik\,(n\,a) - i\omega\,t)$
- **Longitudinal motion:** for u_n in x direction: the problem is exactly the same as a linear chain
  $\omega = 2\,(C_L^{eff} / M)^{1/2}\,|\sin(ka/2)|$ where $C_L^{eff} = C$

Physics 460 F 2006 Lect 8 32

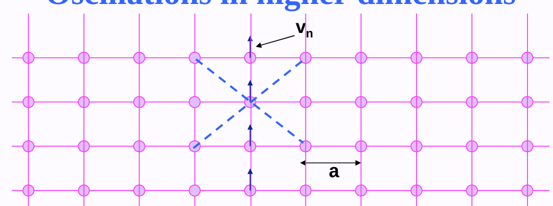
Oscillations in higher dimensions



- **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

Physics 460 F 2006 Lect 8 33

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

Physics 460 F 2006 Lect 8 34

Meaning of Periodicity in Reciprocal space -- Again

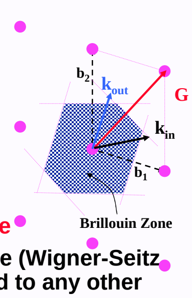
- The same logic that we used for one dimension applies to 2 and 3 dimensions
- The vibrations are an example of excitations. The atoms are not in their lowest energy positions but are vibrating.
- The excitations are labeled by a wavevector k and are periodic functions of k in reciprocal space.
- All 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**

Physics 460 F 2006 Lect 8 35

From Lecture 5

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**

Physics 460 F 2006 Lect 8 36

Lecture 8 - Crystal Vibrations

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)**