Lattice Dynamics and Phonons

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Crystal Dynamics

- In previous chapters we have assumed that the atoms were at rest at their equilibrium position. this can not be entirely correct (against to the hup); atoms vibrate about their equilibrium position at absolute zero.
- The energy they possess as a result of zero point motion is known as zero point energy.
- The amplitude of the motion increases as the atoms gain more thermal energy at higher temperatures.
- In this chapter we discuss the nature of atomic motions, sometimes referred to as lattice vibrations.
- In crystal dynamics we will use the harmonic approximation , amplitude of the lattice vibration is small. at higher amplitude some unharmonic effects occur.

From the theory viewpoint,
a solid is a system with a
VERY LARGE
number of coupled atoms.

The form of the coupling between the atoms depends on the type of bonding that holds the solid together.

- **Thermal lattice vibrations are responsible for:**

⟶ Thermal conductivity of insulators is due to dispersive lattice vibrations (e.g., thermal conductivity of diamond is 6 times larger than that of metallic copper).

→ They reduce intensities of diffraction spots and allow for inellastic scattering where the energy of the scatter (e.g., neutron) changes due to absorption or creation of a phonon in the target.

→ Electron-phonon interactions renormalize the properties of electrons (**electrons become heavier**).

→ Superconductivity (conventional BCS) arises from multiple electron-phonon scattering between time-reversed electrons.

Lattice Dynamics

lattice dynamics (LD) extends the concept of crystal lattice to an array of atoms with finite masses that are capable of motion. This motion is not random but a coherent superposition of vibrations of atoms around their equilibrium sites due to the interaction with neighbor atoms. A collective vibration of atoms in the crystal forms a wave with given **wavelength** and **amplitude**

The problem of lattice dynamics is to find the normal modes of vibration of a crystal and to calculate their energies (**or frequencies, ω)** as a function of their **wavevector k** . The relationship ω(k) is called **phonon dispersion** .

LD offers two different ways of finding the dispersion relation:
Quantum-mechanical approach
Semiclassical treatment of lattice vibrations

Semiclassical treatment of lattice vibrations

This is a ***Classical Treatment!*** , this treatment makes no direct reference to ***PHONONS***. This is because

Phonons are Quantum Mechanical Quasiparticles.

Here, first we'll outline the method to find the **classical** normal modes. Once those are found, then we can quantize & start talking about Phonons

- Crystal lattices at zero temperature posses long range order – translational symmetry (e.g., generates sharp diffraction pattern)
- At $T>0$ ions vibrate with an amplitude that depends on temperature – because of lattice symmetries, thermal vibrations can be analyzed in terms of collective motion of ions which can be populated and excited just like electrons – unlike electrons, **phonons are bosons** (**no Pauli principle, phonon number is not conserved**).

Sound Waves

- mechanical waves are waves which propagate through a material medium (solid, liquid, or gas) at a wave speed which depends on the elastic and inertial properties of that medium. there are two basic types of wave motion for mechanical waves: **longitudinal** waves and **transverse** waves.

- Sound waves propagate through solids. this tells us that wavelike lattice vibrations of wavelength long compared to the interatomic spacing are possible. the detailed atomic structure is unimportant for these waves and their propagation is governed by the macroscopic elastic properties of the crystal.

- We discuss sound waves since they must correspond to the low frequency, long wavelength limit of the more general lattice vibrations considered later in this chapter.

- At a given frequency and in a given direction in a crystal it is possible to transmit three sound waves, differing in their direction of polarization and in general also in their velocity.

Types of polarization

- There are two possible polarizations for the vibrations of atoms in a crystal: **longitudinal and transverse**

In case of **longitudinal** modes the displacement of the atoms from their equilibrium position coincides with the propagation direction of the wave, whereas for **transverse** modes, atoms move perpendicular to the propagation of the wave.

For **one atom** per unit cell the phonon dispersion curves are represented only by **acoustical** branches. However, if we have **more than one atom** in the unit cell **optical** branches will appear additionally.

The difference between acoustical and optical branches arises because of the options for the vibration of the atoms in the unit cell. For example, atoms A and B of diatomic cell can move together **in phase** (acoustical branch) or **out of phase** (optical branch).

Elastic Waves

A solid is composed of discrete atoms, however when the wavelength is very long, one may disregard the atomic nature and treat the solid as a continous medium. Such vibrations are referred to as elastic waves.

$$\rho \frac{\partial^2 u}{\partial t^2} = C \frac{\partial^2 u}{\partial x^2}$$

Which is the wave eqn. with an offered sol'n and velocity of sound waves ;

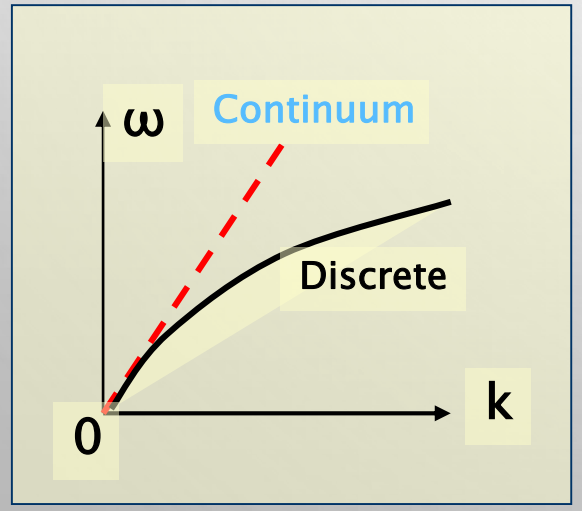
$$u = Ae^{i(kx-\omega t)}$$

- **k = wave number (2π/λ)**
- **ω = frequency of the wave**
- **A = wave amplitude**

$$\omega = v_s k$$

$$v_s = \sqrt{C/\rho}$$

- the relation connecting the frequency and wave number is known as the dispersion relation.



- At small λ $k \rightarrow \infty$ (scattering occurs)
- At long λ $k \rightarrow 0$ (no scattering)

- When k increases velocity decreases. As k increases further, the scattering becomes greater since the strength of scattering increases as the wavelength decreases, and the velocity decreases even further.

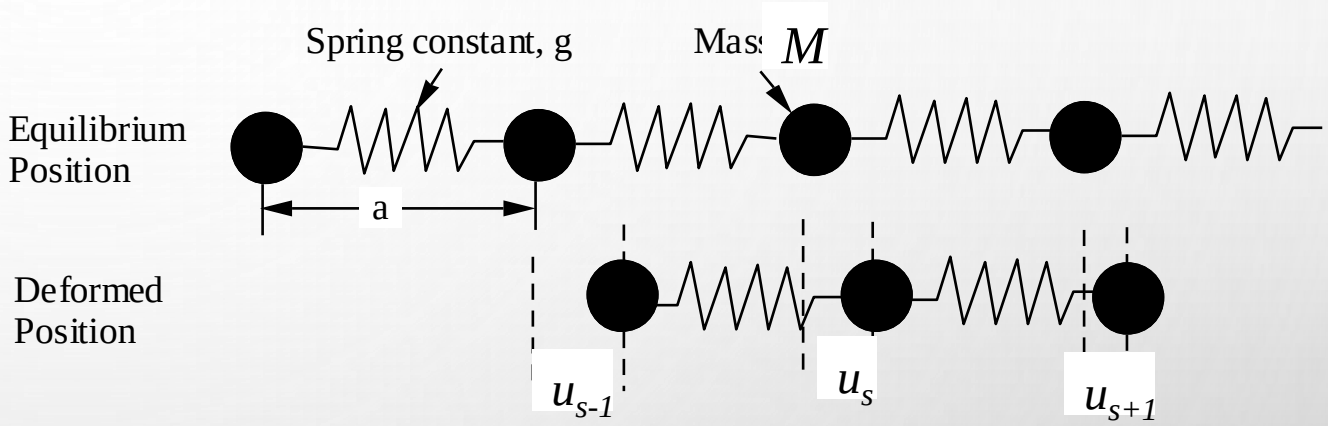
* Slope of the curve gives the velocity of the wave.

Crystal Vibration of a Monoatomic Linear Chain

Longitudinal wave of a 1-D Array of Spring Mass System

Lets consider a linear chain of identical atoms of mass M spaced at a distance a, the lattice constant, connected by Hook's law springs.

- Atoms are separated by a distance of "a".
- Atoms move only in a direction parallel to the chain.
- Only nearest neighbours interact (short-range forces).

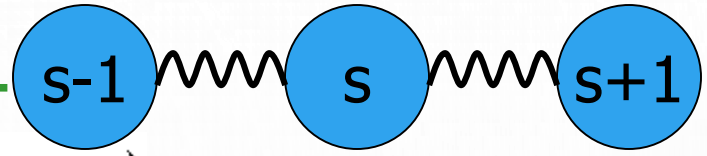


u_s: displacement of the s^{th} atom from its equilibrium position

Us−1=displacement of atom s−1 from its equilibrium position

Us+1=displacement of atom s+1 from its equilibrium position

Solution of Lattice Dynamics `1



Hawk's law

$F_s = C\Delta u$

F=ma

The force on atom s will be given by its displacement and the displacement of its nearest neighbors

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

Same M

$$M\frac{d^2u_s}{dt^2} = C(u_{s+1} + u_{s-1} - 2u_s)$$

Wave solution:

$u(x,t) \sim u\exp(-i\omega t + iKx)$

Travelling wave

where C is a spring constant

Time dep.: $\exp(-i\omega t)$ $\quad d^2u_s/dt^2 = -\omega^2 u_s$

ω: frequency

K: wavelength

$$-M\omega^2 u_s = C(u_{s+1} + u_{s-1} - 2u_s)$$

$$u_{s\pm1} = u\exp(isKa)\exp(\pm iKa) = u\exp(-i\omega t)exp(isKa)\exp(\pm iKa)$$

$$-\omega^2 Mu\exp(isKa) = Cu\{\exp[i(s+1)Ka] + \exp[i(s-1)Ka] - 2\exp(isKa)\}$$

cancel

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

Identity: $2\cos Ka = \exp(iKa) + \exp(-iKa)$

$$\omega^2 = (2C/M)(1 - \cos Ka)$$

Trig: $\omega^2 = (4C/M)\sin^2 \tfrac{1}{2}Ka$; $\quad \omega = (4C/M)^{1/2}|\sin \tfrac{1}{2}Ka|$

This dispersion relation have a number of important properties

(i) Reducing to the first Brillouin zone. The frequency and the displacement of the atoms do not change when we change k by k+2π/a. This means that these solutions are physically identical. This allows us to set the range of independent values of k within the first Brillouin zone $-\pi/a<K<\pi/a$

$$k_s = k + \frac{2\pi s}{a}$$

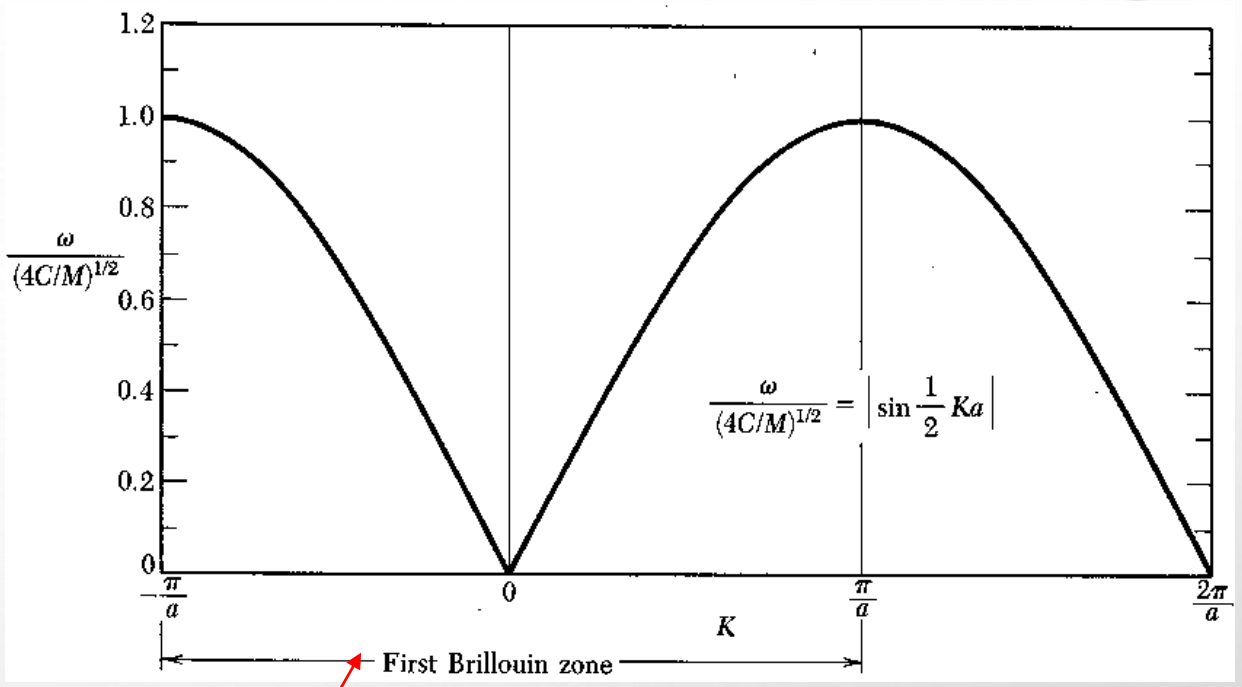
(ii)The maximum frequency is $\sqrt{\frac{4C}{m}}$.

The frequency is symmetric with respect to the sign change in k, i.e. ω(k)= ω(−k). This is not surprising because a mode with positive k corresponds to the wave traveling in the lattice from the left to the right and a mode with a negative k corresponds to the wave traveling from the right tot the left. Since these two directions are equivalent in the lattice the frequency does not change with the sign change in k.

ω-*K* Relation: Dispersion Relation

(iii) One important feature of the dispersion curve is the periodicity of the function. For unit cell length **a** , the repeat period is equal to the unit cell length in the reciprocal lattice. Therefore the useful information is contained in the waves with wave vectors lying between the limits

$-\pi/a < K < \pi/a$



$$k_{max} = \frac{\pi}{a} \qquad \lambda_{min} = \frac{2\pi}{k_{max}} = 2a$$

$$\omega_{max} = 2\sqrt{\frac{C}{m}}$$

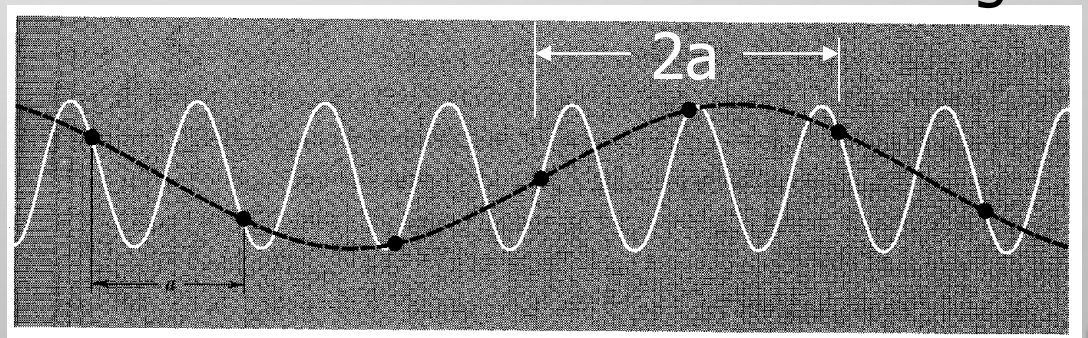
$K = 2\pi/\lambda$

$\lambda_{min} = 2a$

$K_{max} = \pi/a$

$-\pi/a < K < \pi/a$

λ: wavelength



Lattice is Low-pass filter

The physical distinction between the two velocities is that v_p is the velocity of the propagation of the plane wave, whereas the v_g is the velocity of the propagation of the wave packet. The latter is the velocity for the propagation of energy in the medium

Phase velocity

$$V_p = \frac{\omega}{k}$$

$$V_p = \frac{2\sqrt{\frac{C}{M}}\left|sin\frac{ka}{2}\right|}{k} \qquad \times \div \frac{a}{2}$$

$$V_p = \frac{\sqrt{\frac{Ca^2}{M}}\left|sin\frac{ka}{2}\right|}{\frac{ka}{2}}$$

❖ At the Brillion zone boundary $k = \pm\frac{\pi}{a}$

$$V_p = \frac{2a}{\pi}\sqrt{\frac{C}{M}}$$

Group velocity

$$V_g = \frac{d\omega}{dK}$$

$$V_g = \sqrt{\frac{Ca^2}{M}}\left|cos\frac{ka}{2}\right|$$

❖ At the Brillion zone boundary $k = \pm\frac{\pi}{a}$

$$V_g = 0$$

The wave is standing wave

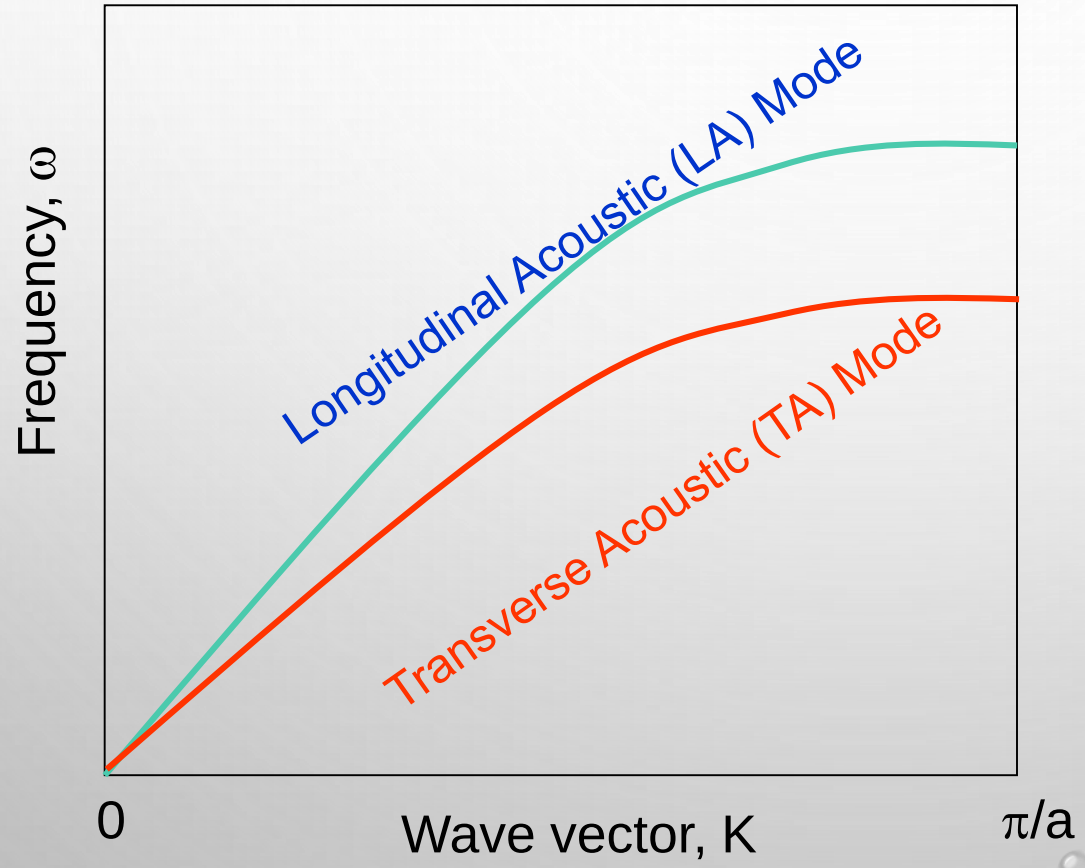
$$u_s = Ae^{iska}e^{-i\omega t} = Ae^{\pm is\pi}e^{-i\omega t}$$

$$= A(-1)^s e^{-i\omega t}$$

Polarization and Velocity

$$\omega^2 M = C\left[2 - \exp(-iKa) - \exp(iKa)\right] = 2C(1 - \cos Ka)$$

$$\omega = \sqrt{\frac{2C}{M}}(1 - \cos Ka)^{1/2}$$



Group Velocity:

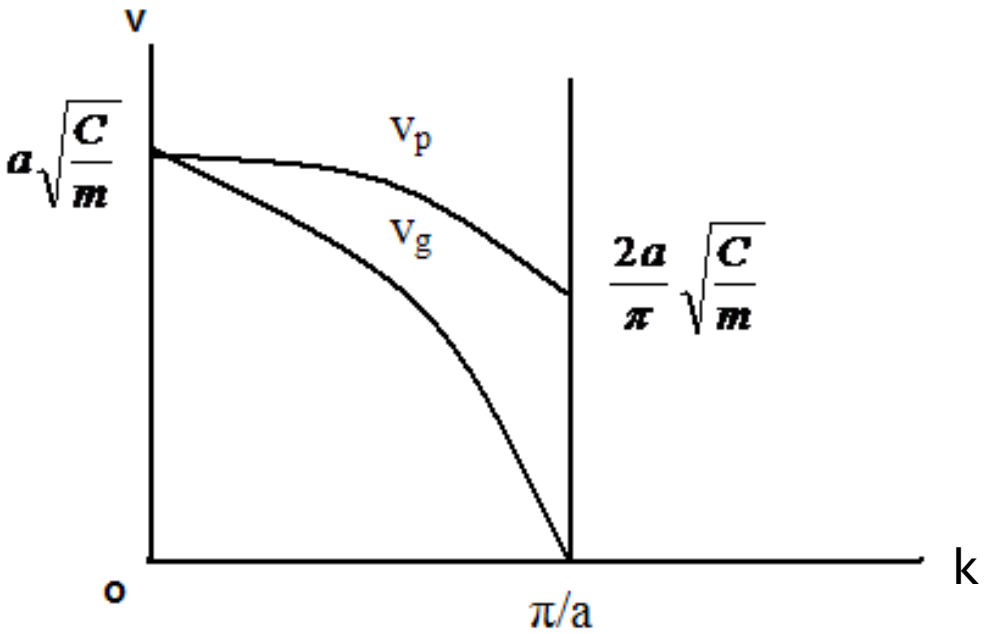
$$v_g = \frac{d\omega}{dK}$$

For small K

$$v_g = v_s = \lim_{K \to 0} \frac{d\omega}{dK}$$

Speed of Sound

$$= a\sqrt{\frac{C}{M}}$$



Relations between phase and group velocity and wave-vector

Long wavelength Limit

When the wavelength is very long

$ka \ll 1$, or $\lambda \gg a$

We expand $\sin\frac{ka}{2} = \frac{ka}{2} - \frac{(ka)^3}{3!} + \frac{(ka)^5}{5!} - \cdots\cdots \approx \frac{ka}{2}$

$$\omega = 2\sqrt{\frac{C}{M}}sin\frac{ka}{2} \approx 2\sqrt{\frac{C}{M}}\frac{ka}{2} = \sqrt{\frac{Ca^2}{M}}\mathrm{k}$$

We see that the frequency of vibration is proportional to the wavevector. This is equivalent to the statement that velocity is independent of frequency.

In this case

$$V_p = \sqrt{\frac{C}{M}}a$$

This is the velocity of sound for the one dimensional lattice which is consistent with the expression for elastic waves.

Chain Of Two Types Of Atom

- This is the simplest possible model of an ionic crystal.
- Since a is the repeat distance, the nearest neighbors separations is a/2

- Two different types of atoms of masses M1 and M2 are connected by identical springs of spring constant f;
- We will consider only the first neighbour interaction although it is a poor approximation in ionic crystals because there is a long range interaction between the ions.
- The model is complicated due to the presence of two different types of atoms which move in opposite directions.

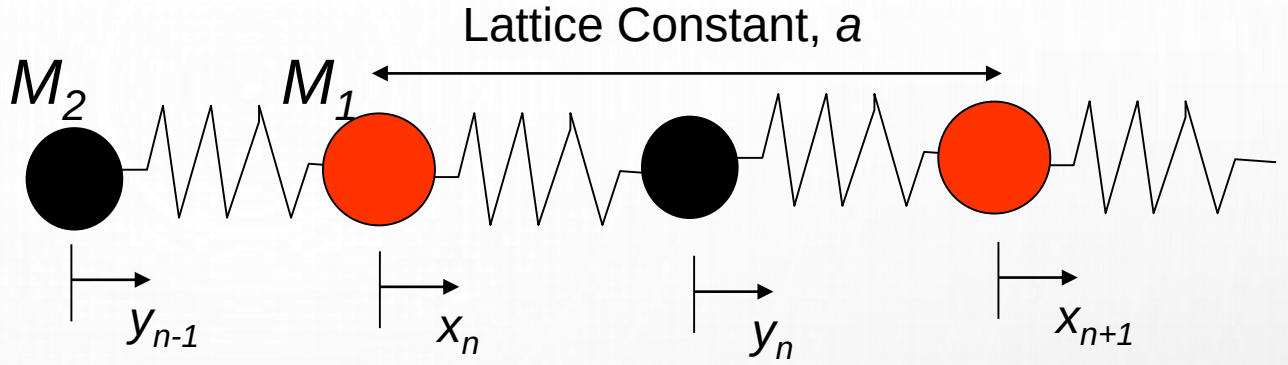
our aim is to obtain ω-k relation for diatomic lattice

Two equations of motion must be written;

One for mass M1, and
One for mass M2.

Two Atoms Per Unit Cell

Consider a lattice with two kinds of atoms – that is a lattice with a basis of two atoms in the primitive cell. Now we have to write two solutions for the displacement corresponding to the two masses M1 and M2. The equations of motion are:



$$M_1 \frac{d^2 x_n}{dt^2} = f\left(y_n + y_{n-1} - 2x_n\right)$$

f: spring constant

$$M_2 \frac{d^2 y_n}{dt^2} = f\left(x_{n+1} + x_n - 2y_n\right)$$

Solution:

$$\omega^2 = f\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \pm f\left[\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^2 - \frac{4}{M_1 M_2}\sin^2\frac{Ka}{2}\right]^{1/2}$$

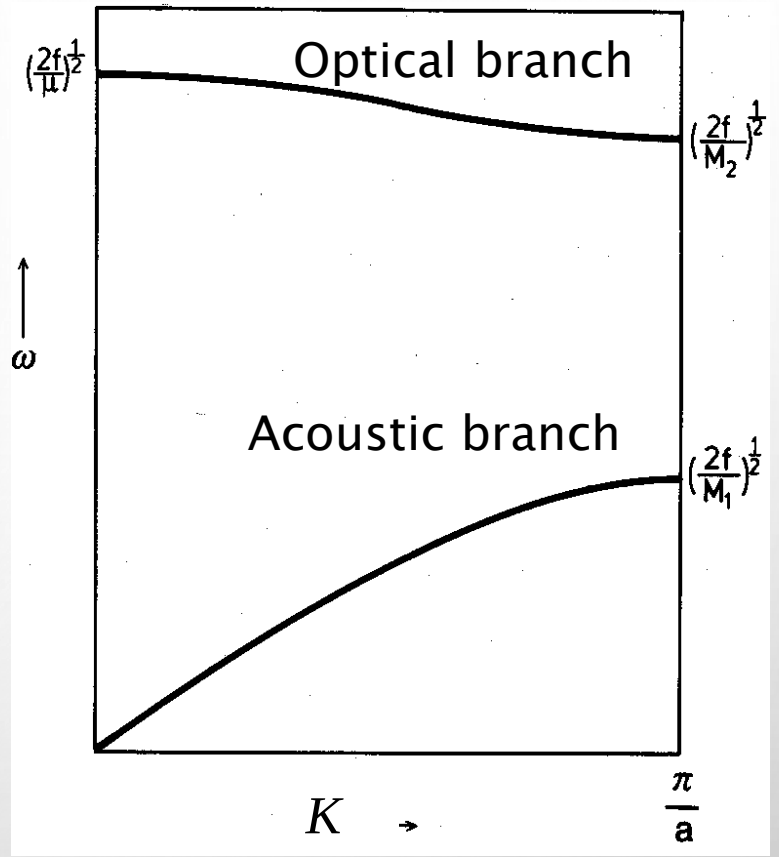
Depending on sign in this formula there are two different solutions corresponding to two different dispersion curve

Acoustic and Optical Branches

$$\omega^2 = f\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm f\left[\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4}{M_1 M_2}\sin^2\frac{Ka}{2}\right]^{1/2}$$

μ is the effective mass

$$1/\mu = 1/M_1 + 1/M_2$$



Dispersion curve of a diatomic linear chain with a mass ratio $M_1/M_2 = 5$. With increasing mass ratio, the optical branch becomes progressively flatter

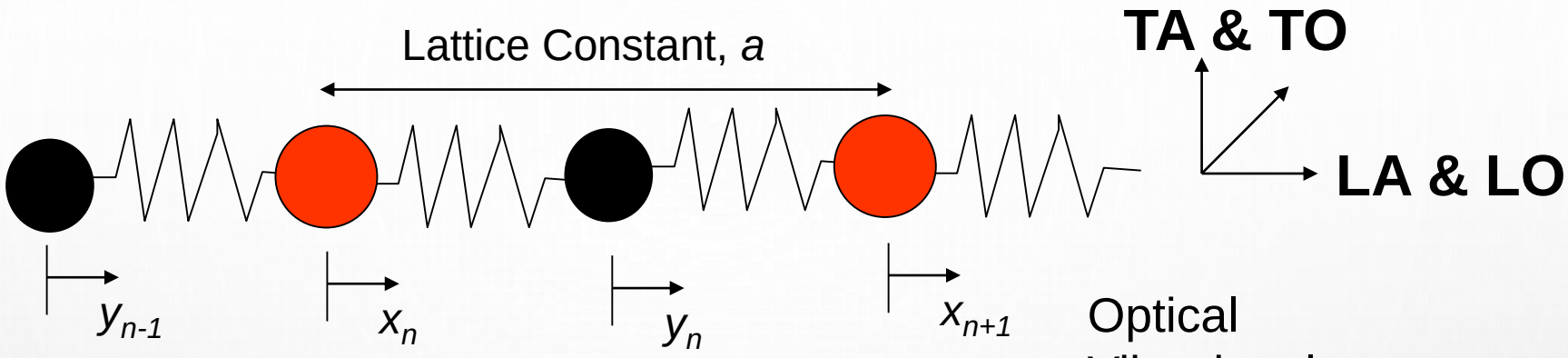
The lower curve is called the acoustic branch, while the upper curve is called the optical branch. The acoustic branch begins at k=0 and ω=0. Then with increasing k the frequency increases in a linear fashion. This is why this branch is called acoustic: it corresponds to elastic waves or sound. Eventually this curve saturates at the edge of the Brillouin zone. On the other hand, the optical branch has a nonzero frequency at zero k

$$\omega_0 = \sqrt{2f\left(\frac{1}{M_1}+\frac{1}{M_2}\right)} = \sqrt{\frac{2f}{\mu}}$$

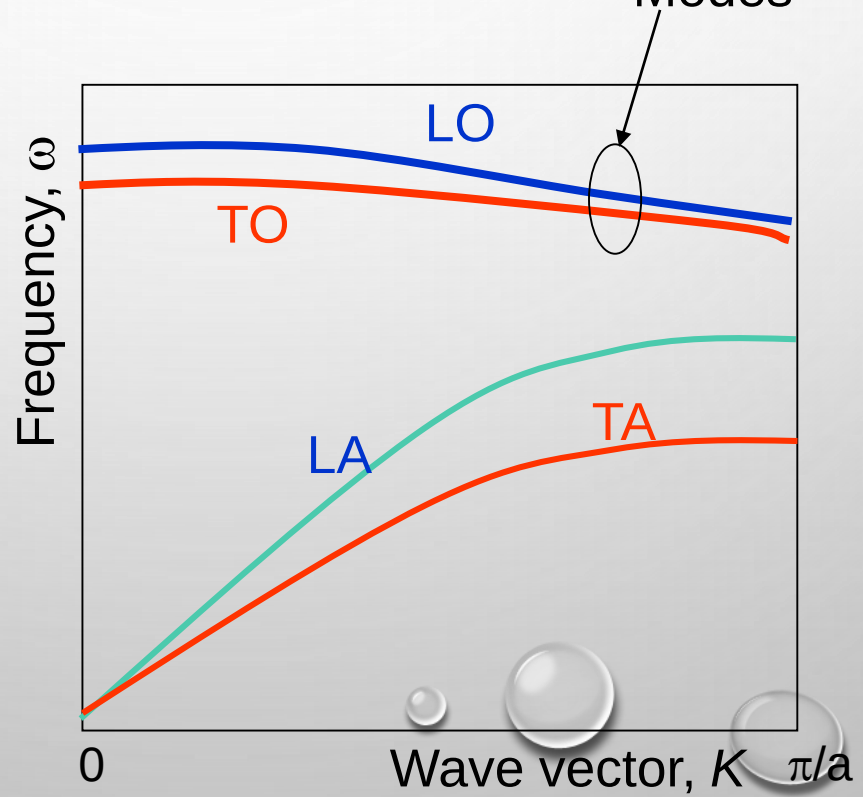
What is the group velocity of the optical branch?

What if $M_1 = M_2$?

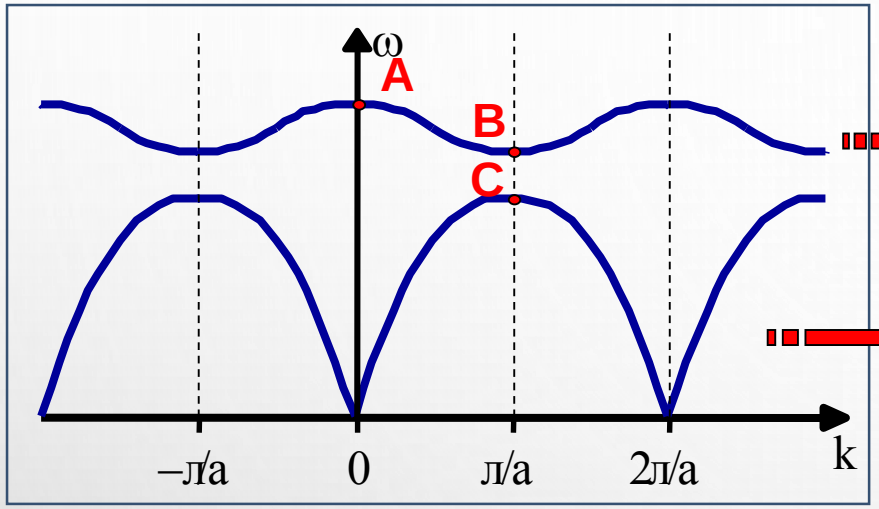
Polarization



Total 6 polarizations



- ω versus k relation for diatomic chain;



Optical Branch

Upper branch is due to the +ve sign of the root.

Acoustical Branch

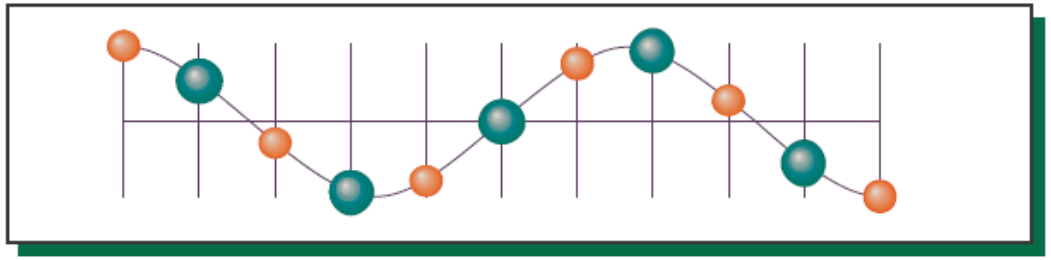
Lower branch is due to the -ve sign of the root.

- **Normal mode frequencies of a chain of two types of atoms.**

At A, the two atoms are oscillating in antiphase with their center of mass at rest;
at B, the lighter mass M2 is oscillating and M1 is at rest;
at C, M1 is oscillating and M2 is at rest.

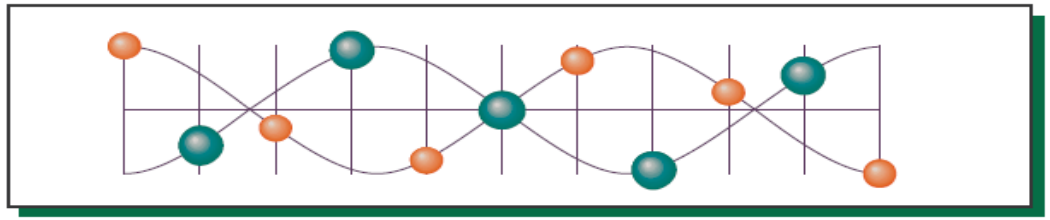
Acoustic modes

Neighbouring atoms in phase

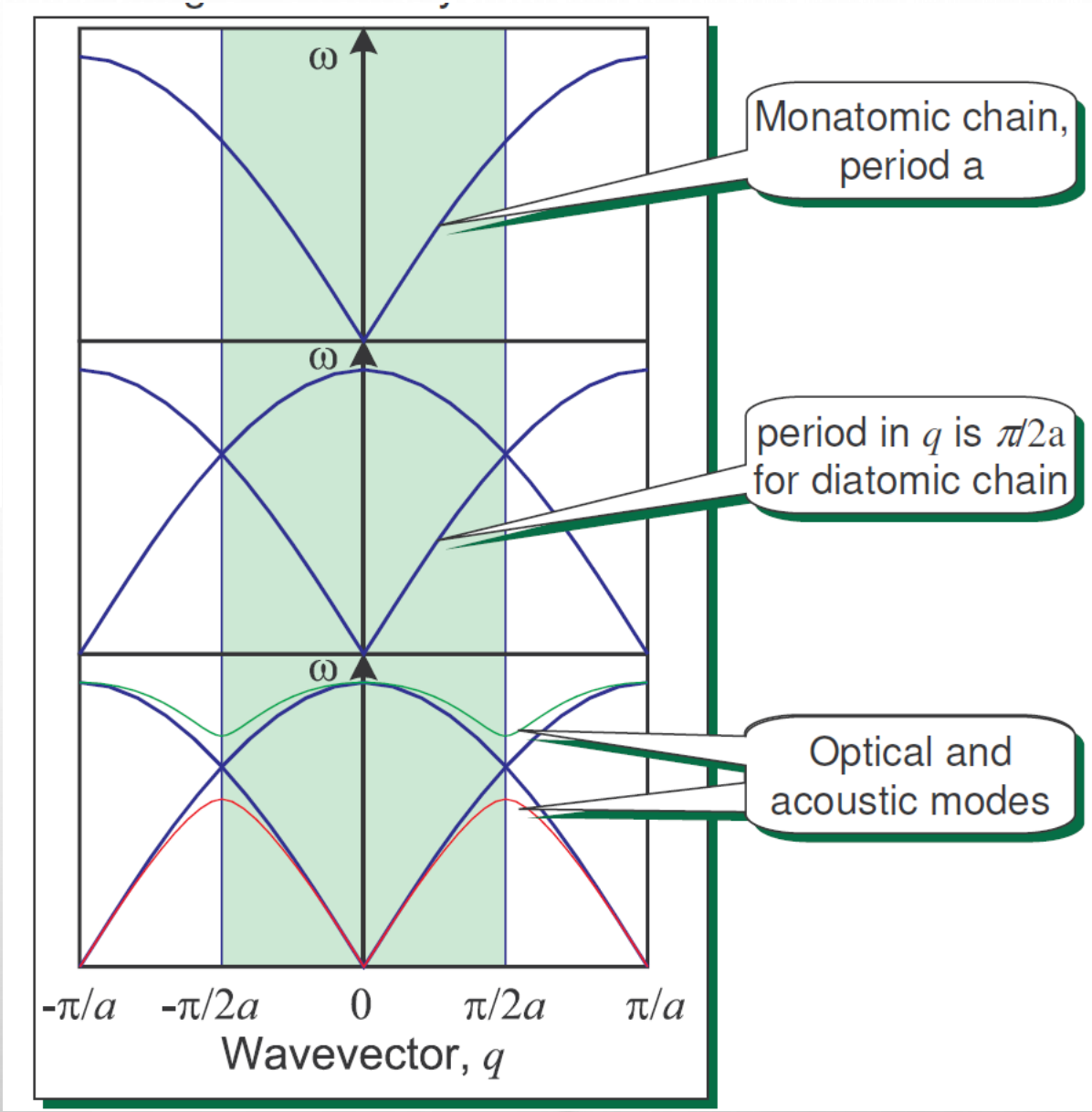


Optical modes:

Neighbouring atoms out of phase



The modes of the diatomic chain can be seen to arise from those of a monatomic chain.



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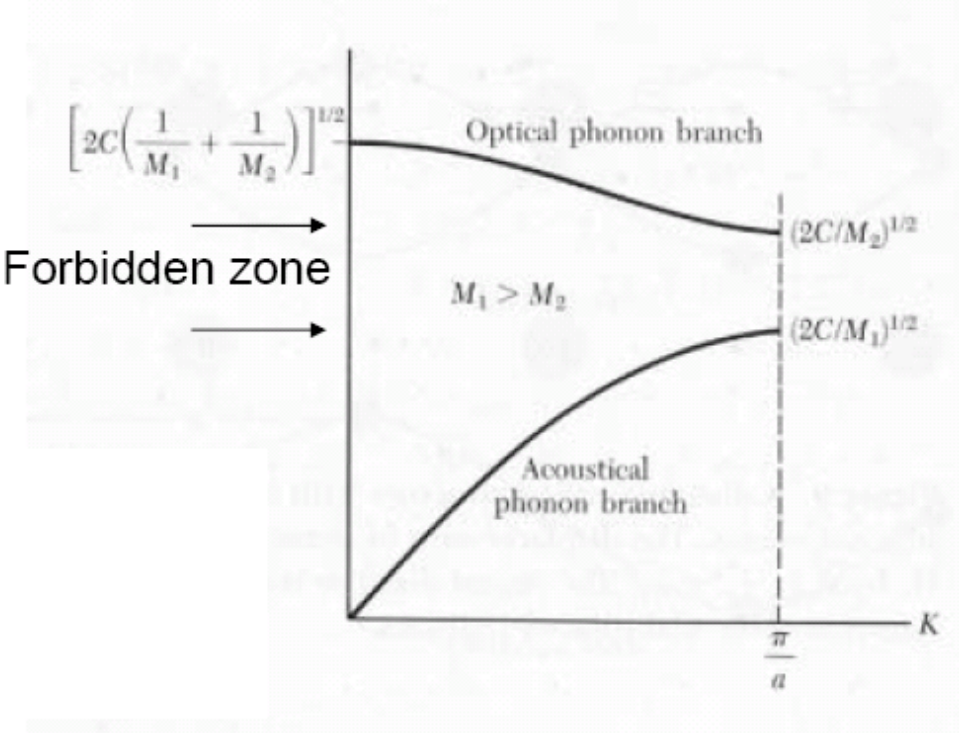
Forbidden frequencies

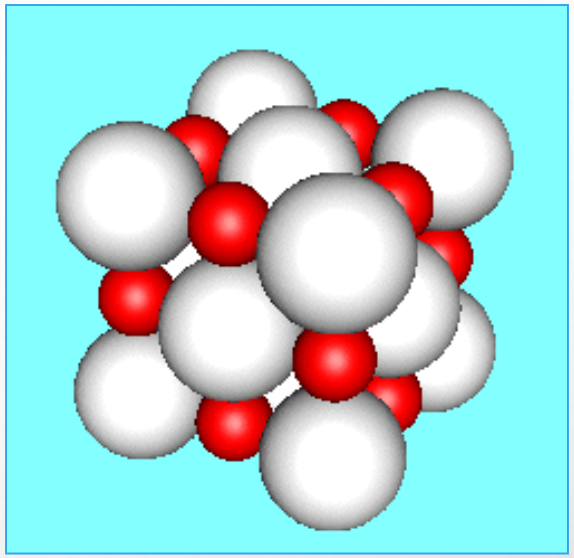
- Note that for polyatomic lattices ($M_1 \neq M_2$), there is a gap for certain frequencies at the zone boundary (K = +/- π/a)
- This is a characteristic feature for elastic waves.
- If you look for solutions for ω in this region, you will find complex solutions of K (which means that the wave is damped out and it cannot exist in the lattice)



Three Dimensions

For each mode in a given propagation direction,
the dispersion relation yields acoustic and optical branches:

- Acoustic
  - Longitudinal (LA)
  - Transverse (TA)
- Optical
  - Longitudinal (LO)
  - Transverse (TO)



NaCl – two atoms per primitive cell

6 branches:

1 LA

1 LO

2 TA

2 TO

Generally, for N atoms per unit cell there will be 3N branches, 3 acoustical branches (1 longitudinal and 2 transverse) and 3N-3 optical branches (N-1 longitudinal and 2N-2 transverse)

Summary

Acoustic modes:

correspond to sound-waves in the long wavelength limit. Hence the name.

$\omega \rightarrow 0$ as $k \rightarrow 0$

Optical modes:

- In the long-wavelength limit, optical modes interact strongly with electromagnetic radiation in polar crystals. Hence the name.
- Strong optical absorption is observed (Photons annihilated, phonons created).

$\omega \rightarrow$ finite value as $k \rightarrow 0$

- Optical modes arise from folding back the dispersion curve as the lattice periodicity is doubled (halved in k-space).

Zone boundary:

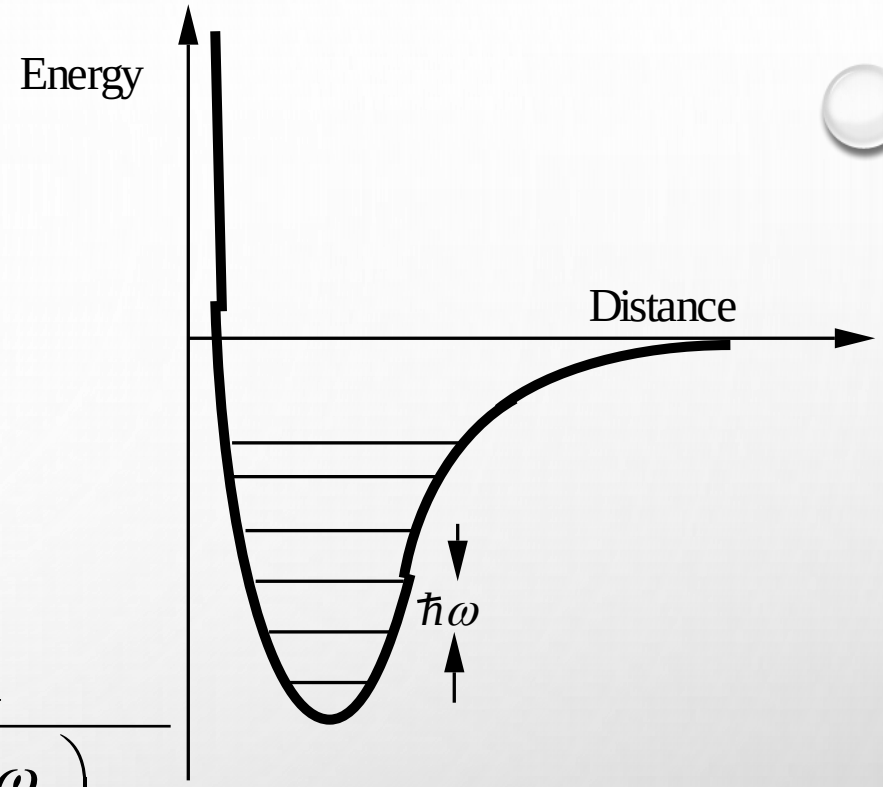
- All modes are standing waves at the zone boundary, $\partial\omega/\partial k = 0$: a necessary consequence of the lattice periodicity.
- In a diatomic chain, the frequency-gap between the acoustic and optical branches depends on the mass difference. In the limit of identical masses the gap tends to zero.

Phonon

- The linear atom chain can only have *N* discrete *K* → ω is also discrete

- The energy of a lattice vibration mode at frequency ω was found to be

$$u = \left(n + \frac{1}{2}\right)\hbar\omega$$



- where $\hbar\omega$ can be thought as the energy of a particle called *phonon*, as an analogue to *photon*

- *n* can be thought as the total number of phonons with a frequency ω, and follows the Bose-Einstein statistics:

$$\langle n \rangle = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

Equilibrium distribution

- It is quantized, in the form of phonons, similar to the quantization of light, as both are derived from a discrete harmonic oscillator model.
- Elastic waves in crystals are made up of phonons.
- Thermal vibrations are thermally excited phonons.

Phonon Momentum

$$\vec{p} = \hbar\vec{q}$$

Earlier, we saw that the elastic scattering of x-rays from the lattice is governed by the rule:

$$\vec{k}' = \vec{k} + \vec{G}$$

If the photon scattering is inelastic, with a creation of a phonon of wavevector q, then

$$\vec{k}' + \vec{q} = \vec{k} + \vec{G}$$

If the photon is absorbed, then

$$\vec{k}' = \vec{k} + \vec{G} + \vec{q}$$

Wave-vector selection-rule

Inelastic scattering

a phonon with a wavevector q will interact with particles, like neutrons, photons, electrons, as if it had a momentum (the crystal momentum)

$$\vec{p} = \hbar\vec{q}$$

- Be careful! Phonons do not carry momentum like photons do. They can interact with particles as if they have a momentum. For example, a neutron can hit a crystal and start a wave by transferring momentum to the lattice.
- However, this momentum is transferred to the lattice as a whole. The atoms themselves are not being translated permanently from their equilibrium positions.
- The only exception occurs when q = 0, where the whole lattice translates. This, of course, does carry momentum.

Measuring Phonons

Experiments: *1. Neutron scattering*

Neutrons excite lattice vibrations: measure ΔE and $\Delta \boldsymbol{k}$ of neutrons (transfer to crystal)

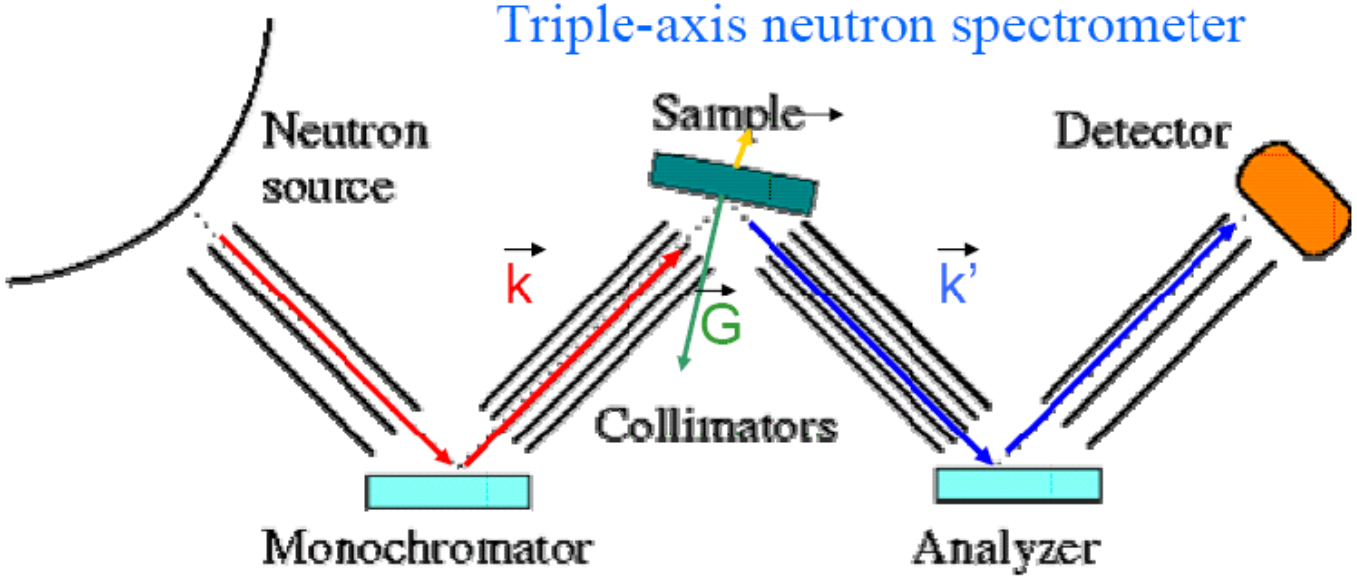
$$\vec{k}' \pm \vec{q} = \vec{k} + \vec{G}$$

- $\vec{k}'$: scattered neutron
- $\vec{q}$: phonon wavevector (+ for phonon created, – for phonon absorbed)
- $\vec{k}$: incident neutron
- $\vec{G}$: reciprocal lattice vector

Measuring Phonons

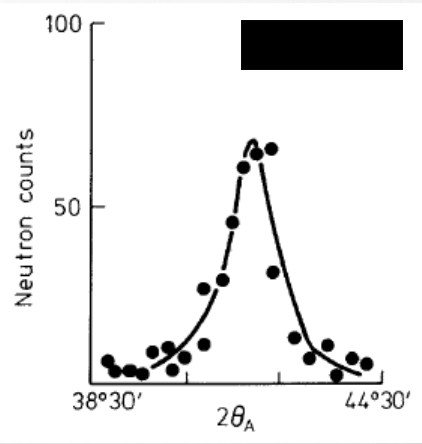
Inelastic neutron scattering

Triple-axis neutron spectrometer



Defines incoming wavelength

Defines outgoing wavelength, which may be different if the neutron lost a bit of energy to make a phonon



Measuring Phonons

Inelastic neutron scattering

- Using the conservation of energy, we can define the energy of the phonon created by:

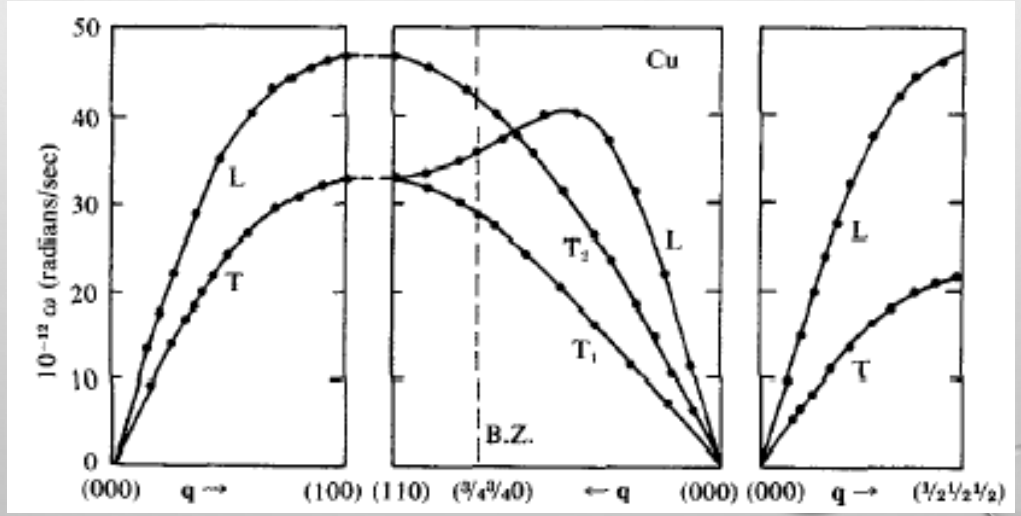
$$\frac{\hbar^2 k^2}{2M_n} = \frac{\hbar^2 k'^2}{2M_n} \pm \hbar\omega$$

Mass of neutron

Phonon energy (sign changes if phonon is created or destroyed)

Incoming neutron energy

Scattered neutron energy



Measuring Phonons

Other Techniques

- Inelastic X-ray Spectroscopy
- Raman Spectroscopy (IR, near IR, and visible light)
- Microwave Ultrasonics