CMP
Lecture 13

School of Physics
The University of Sydney

THE UNIVERSITY OF
SYDNEY

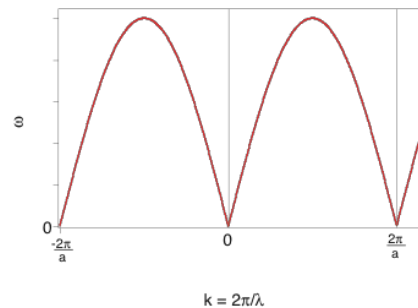## Examples of dispersion relations

1. Vibrations in a 1D chain

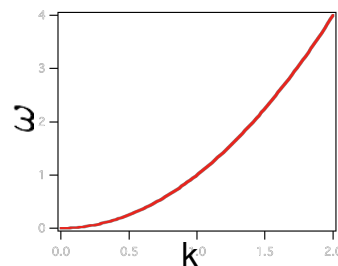$$\omega(k) = 2\sqrt{\frac{\kappa}{M}}\,|\sin\frac{ka}{2}|$$

k = 2π/λ

2. A quantum mechanical particle

$$E(k) = \hbar\omega(k) = \frac{\hbar^2 k^2}{2m}$$

$$\omega(k) = \frac{\hbar k^2}{2m}$$

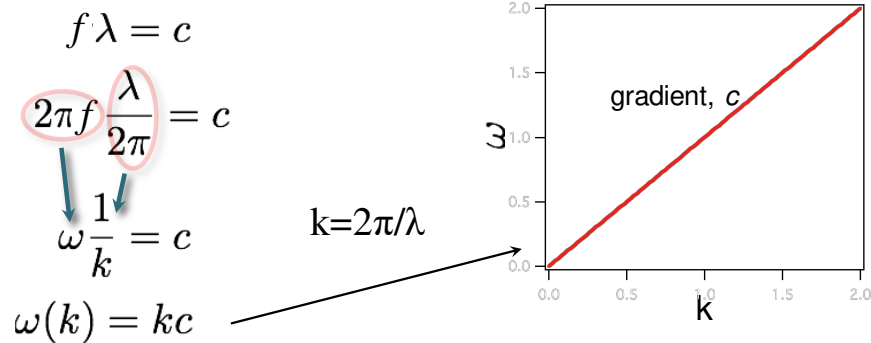$$v_g = \frac{\partial\omega(k)}{\partial k} = \frac{\hbar k}{m} = \frac{p}{m}$$

p = momentum

Examples of dispersion relations
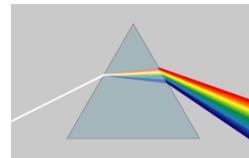
3. Light in vacuum

f is frequency, c speed of light in vacuum

$$f\lambda = c$$

$$2\pi f \frac{\lambda}{2\pi} = c$$

$$\omega \frac{1}{k} = c$$

$k = 2\pi/\lambda$

$$\omega(k) = kc$$

gradient, c

In vacuum the dispersion relation of light is *linear*.
Light travels with c independent of the frequency.

4. Light in matter – c depends on ω
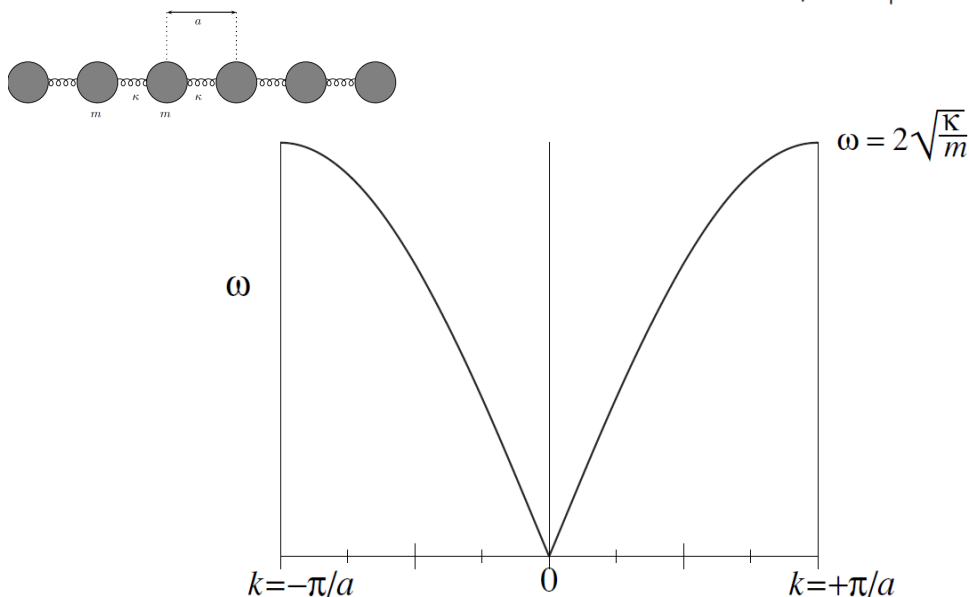
$$\omega(k) = kc(\omega)$$

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Dispersion of 1D chain

Solid State Basics, Ch. 9,10; Ashcroft & Mermin Ch. 22

Recall dispersion relation for 1D chain below:
Doesn't hold for all k – only particular k,
k is quantised.

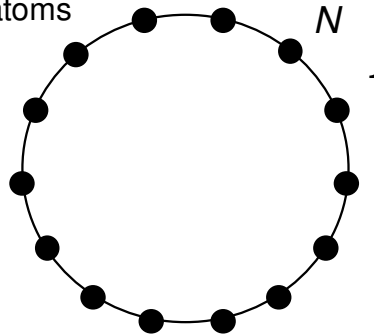$$\omega = 2\sqrt{\frac{\kappa}{m}}\left|\sin\left(\frac{ka}{2}\right)\right|$$

$\omega = 2\sqrt{\frac{\kappa}{m}}$

ω

$k=-\pi/a$ 0 $k=+\pi/a$

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Periodic boundary conditions
Max Born and Theodore von Karman (1912)

Chain with *N* atoms:

$$u_{N+n}(t) = u_n(t)$$

How many discrete *k* values depends on how many atoms *N* there are in the chain

Called *Born von Karman boundary conditions* – or periodic boundary conditions

A finite chain with no end! can describe travelling waves

Counting normal modes
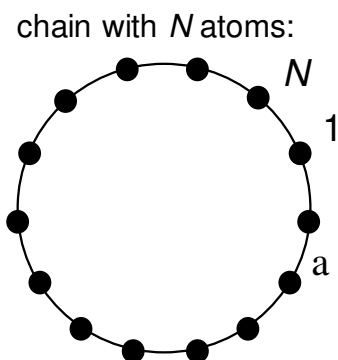## Periodic boundary conditions

$$x_{n+N} = x_n$$

chain with *N* atoms:

Must have wave ansatz satisfied
Recall: $\delta x_n = A e^{i\omega t - ikna}$

$$e^{i\omega t - ikna} = e^{i\omega t - ik(N+n)a}$$

$$= e^{i\omega t - ikna} e^{ikNa}$$

must have $e^{ikNa} = 1$ to hold true

must then have $k = \dfrac{2\pi p}{Na} = \dfrac{2\pi p}{L}$ $(since\ e^{ikNa} = e^{i2\pi pNa/Na} = e^{i2\pi p} = 1)$
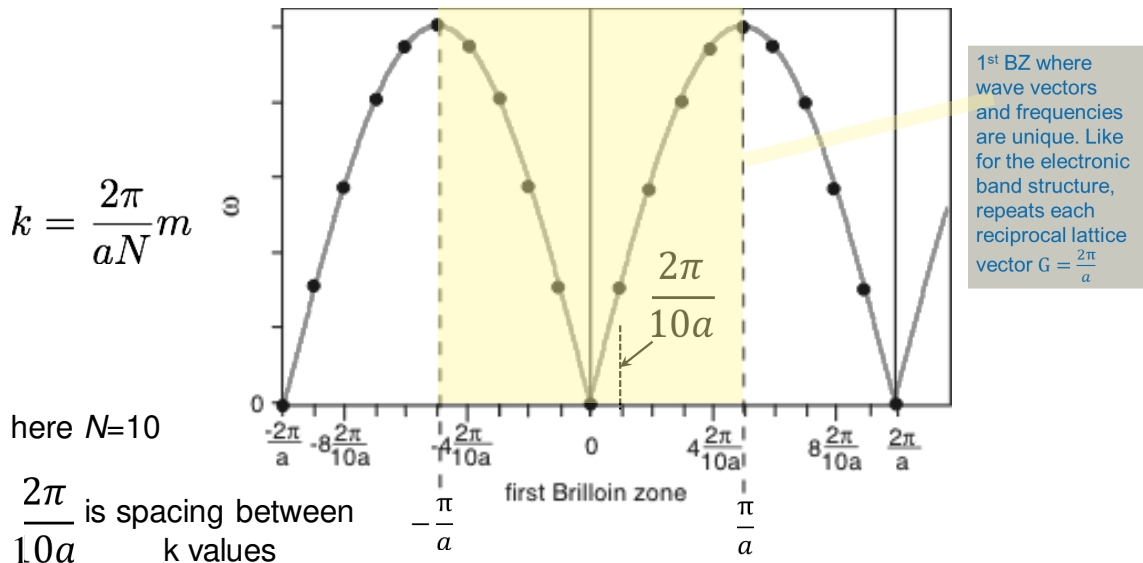
L =Na, is the length around the circle

Length of first Brillouin zone

$$\text{Total Number of Modes} = \frac{\text{Range of } k}{\text{Spacing between neigboring } k} = \frac{2\pi/a}{2\pi/(Na)} = N$$

Example: finite chain with 10 unit cells and one atom per unit cell

$$k = \frac{2\pi}{aN}m$$

1st BZ where wave vectors and frequencies are unique. Like for the electronic band structure, repeats each reciprocal lattice vector $G = \frac{2\pi}{a}$

$$\frac{2\pi}{10a}$$

here $N=10$

$\frac{2\pi}{10a}$ is spacing between k values

- N atoms give N so-called normal modes of vibration.
- For long but finite chains, the points are very dense.
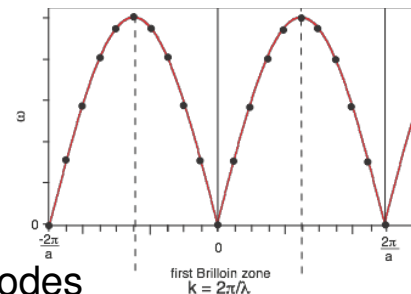
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Counting normal modes...

From boundary conditions $\qquad k = \frac{2\pi}{aN}m$

k-points

Chain with 1 atom / unit cell and N unit cells
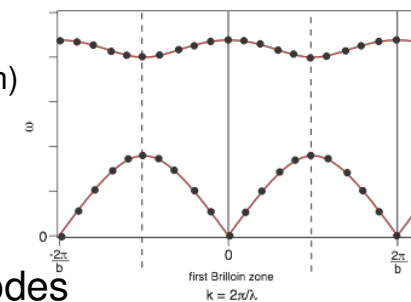
N x 1 modes

eigenvalues per k-point

(since we have N degrees of freedom i.e. each atom can move left or right (x-direction) in 1D chain)

k-points

Chain with 2 atom / unit cell and N unit cells

N x 2 modes

eigenvalues per k-point

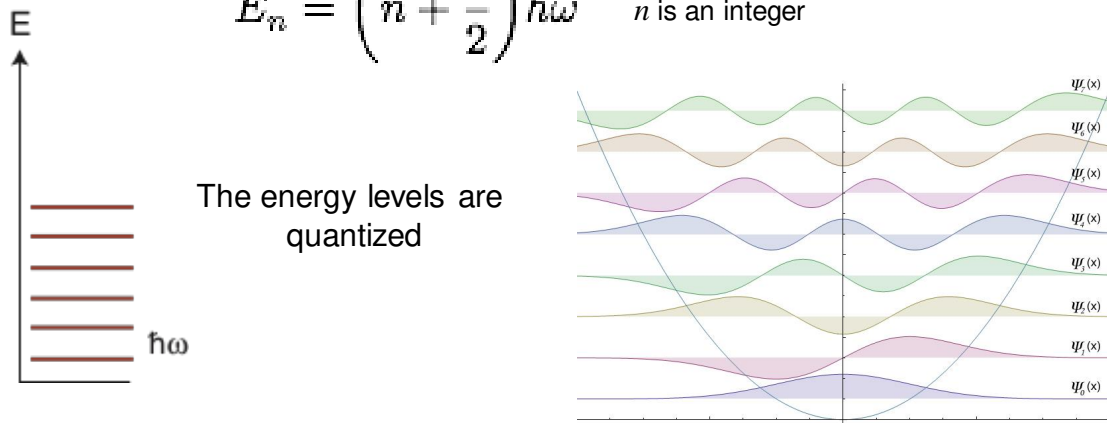(since we have 2xN degrees of freedom)

Will look at 2 atom chain later

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Quantum modes: phonons

Single harmonic oscillator: quantum model

Correspondence: for classical harmonic system with normal oscillation mode at frequency ω, corresponding quantum system will have eigenstates with energy:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad n \text{ is an integer}$$

E

The energy levels are quantized

$\hbar\omega$

$\Psi_7(x)$
$\Psi_6(x)$
$\Psi_5(x)$
$\Psi_4(x)$
$\Psi_3(x)$
$\Psi_2(x)$
$\Psi_1(x)$
$\Psi_0(x)$

In our chain, harmonic oscillator can be a collective normal mode, not just motion of a single particle.

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Quantum modes: phonons

The ground state being $n=0$ eigenstate, and has zero-point energy $\hbar\omega(k)/2$

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$
if n=1, corresponds to one phonon
if n=2, corresponds to two phonons

The lowest energy excitation is of energy $\hbar\omega(k)$ greater than the ground state, corresponding to $n=1$ eigenstate.
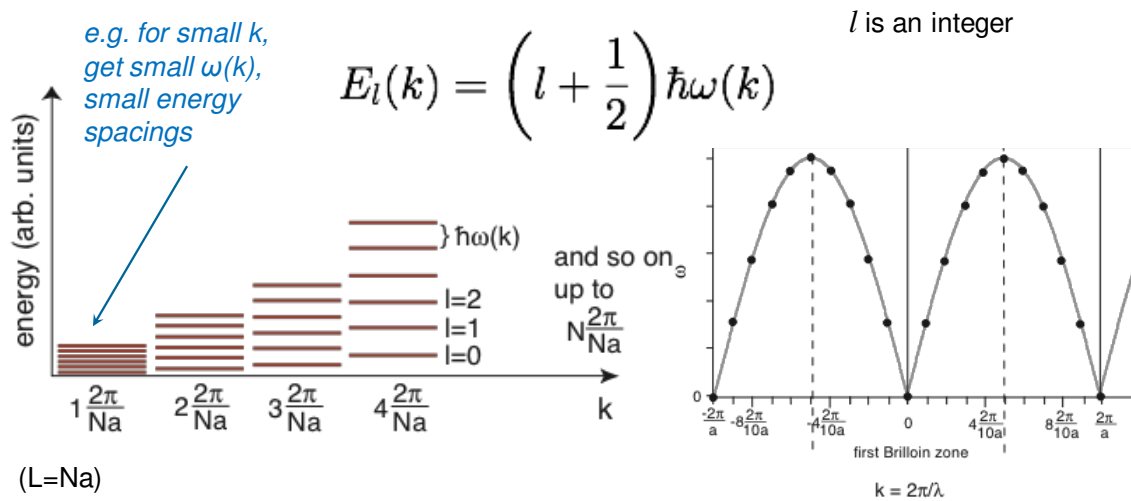
Each excitation of this normal mode by a step up (increasing quantum number n) is known as a phonon.

A phonon is a discrete quantum of vibration

Analogous to quantum of light

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Long chain: quantum model

l is an integer

$$E_l(k) = \left(l + \frac{1}{2}\right)\hbar\omega(k)$$

energy (arb. units)

} $\hbar\omega(k)$

and so on
up to
$N\frac{2\pi}{Na}$

l=2
l=1
l=0

$1\frac{2\pi}{Na}$ $2\frac{2\pi}{Na}$ $3\frac{2\pi}{Na}$ $4\frac{2\pi}{Na}$ k

ω

$\frac{-2\pi}{a}$ $-8\frac{2\pi}{10a}$ $-4\frac{2\pi}{10a}$ 0 $4\frac{2\pi}{10a}$ $8\frac{2\pi}{10a}$ $\frac{2\pi}{a}$
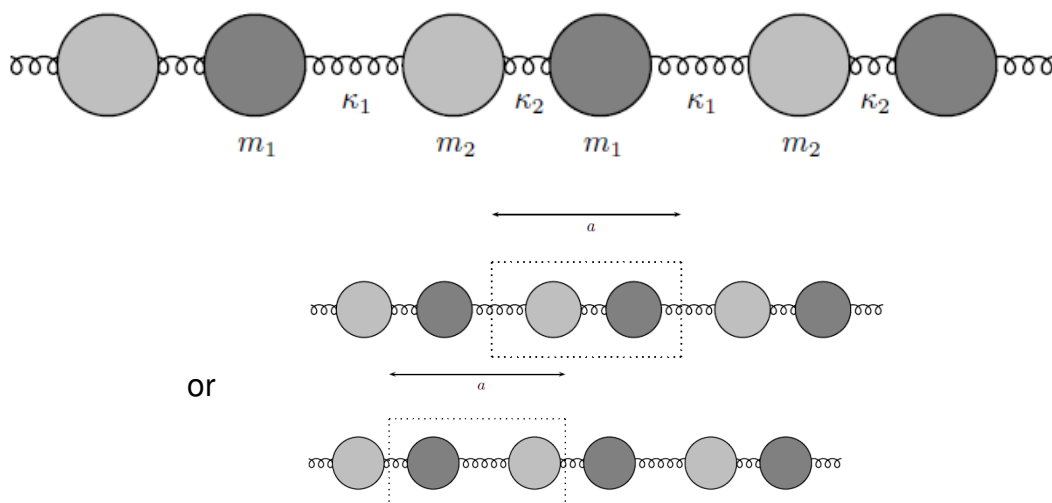
first Brilloin zone

(L=Na)

$k = 2\pi/\lambda$

- The excitations of these oscillators (normal modes) are called phonons.

- The dispersion is often called a phonon dispersion curve.

Vibrations of a 1D diatomic chain

Oxford Basics, Ch.10

κ_1 κ_2 κ_1 κ_2

m_1 m_2 m_1 m_2

a

or

a

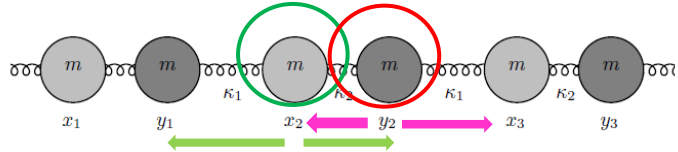Consider same masses
different spring constants

$$m_1 = m_2 = m$$

κ_1 , κ_2

Vibrations of a 1D diatomic chain

As for the 1D chain with one mass write down Newton's equations of motion for deviation of the equilibrium position

$$m\,\ddot{\delta x_n} = \kappa_2(\delta y_n - \delta x_n) + \kappa_1(\delta y_{n-1} - \delta x_n) \qquad (1)$$

$$m\,\ddot{\delta y_n} = \kappa_1(\delta x_{n+1} - \delta y_n) + \kappa_2(\delta x_n - \delta y_n) \qquad (2)$$

Similarly to before, Ansatz (mathematical guess):

$$\delta x_n = A_x e^{i\omega t - ikna}$$
$$\delta y_n = A_y e^{i\omega t - ikna}$$

Values of k that differ by $\dfrac{2\pi}{a}$ are equivalent so focus on first Brillouin zone

$$-\pi/a \leqslant k < \pi/a$$

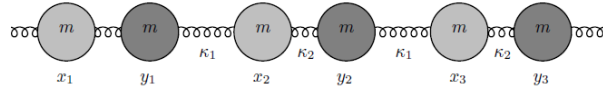If system has N unit cells, $L=Na$, and using boundary conditions as before:

$$k \text{ is quantised in units of } 2\pi/(Na) = 2\pi/L$$

As before, dividing range of k by spacing between k's, we get N different values of k; one k per unit cell

Vibrations of a 1D diatomic chain

Substitute Ansatz into the equations of motion (1) and (2):

$$-\omega^2 m A_x e^{i\omega t - ikna} = \kappa_2 A_y e^{i\omega t - ikna} + \kappa_1 A_y e^{i\omega t - ik(n-1)a} - (\kappa_1 + \kappa_2) A_x e^{i\omega t - ikna}$$
$$-\omega^2 m A_y e^{i\omega t - ikna} = \kappa_1 A_x e^{i\omega t - ik(n+1)a} + \kappa_2 A_x e^{i\omega t - ikna} - (\kappa_1 + \kappa_2) A_y e^{i\omega t - ikna}$$

gives:

$$-\omega^2 m A_x = \kappa_2 A_y + \kappa_1 A_y e^{ika} - (\kappa_1 + \kappa_2) A_x$$
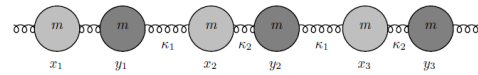$$-\omega^2 m A_y = \kappa_1 A_x e^{-ika} + \kappa_2 A_x - (\kappa_1 + \kappa_2) A_y$$

or as an eigenvalue equation:

$$m\omega^2 \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} (\kappa_1 + \kappa_2) & -\kappa_2 - \kappa_1 e^{ika} \\ -\kappa_2 - \kappa_1 e^{-ika} & (\kappa_1 + \kappa_2) \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix}$$

Vibrations of a 1D diatomic chain

Find solutions by finding zero's of the secular determinant

$$0 = \begin{vmatrix} (\kappa_1 + \kappa_2) - m\omega^2 & -\kappa_2 - \kappa_1 e^{ika} \\ -\kappa_2 - \kappa_1 e^{-ika} & (\kappa_1 + \kappa_2) - m\omega^2 \end{vmatrix}$$

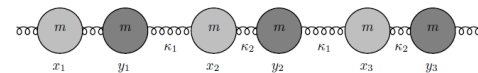$$= \left| (\kappa_1 + \kappa_2) - m\omega^2 \right|^2 - \left| \kappa_2 + \kappa_1 e^{ika} \right|^2$$

so

$$m\omega^2 = (\kappa_1 + \kappa_2) \pm \left| \kappa_1 + \kappa_2 e^{ika} \right|$$

and the second term becomes:

$$\left| \kappa_1 + \kappa_2 e^{ika} \right| =$$

$$\sqrt{(\kappa_1 + \kappa_2 e^{ika})(\kappa_1 + \kappa_2 e^{-ika})} = \sqrt{\kappa_1^2 + \kappa_2^2 + 2\kappa_1\kappa_2 \cos(ka)}$$
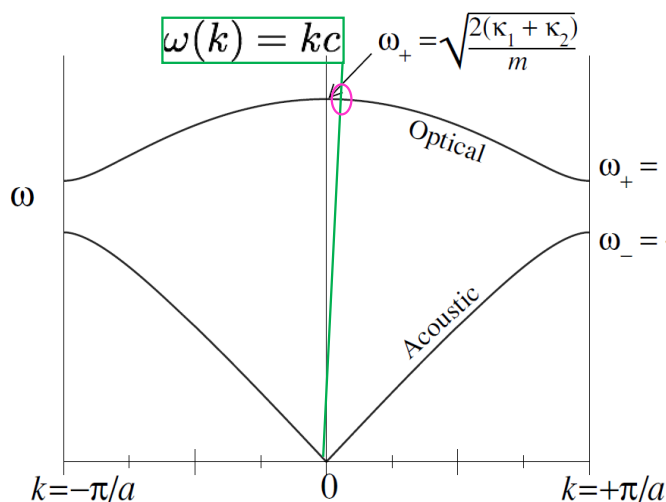
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Vibrations of a 1D diatomic chain

Finally, the dispersion relation is:

$$\omega_\pm = \sqrt{\frac{\kappa_1 + \kappa_2}{m} \pm \frac{1}{m}\sqrt{\kappa_1^2 + \kappa_2^2 + 2\kappa_1\kappa_2 \cos(ka)}}$$

$$\boxed{w(k) = kc}$$

$$\omega_+ = \sqrt{\frac{2(\kappa_1 + \kappa_2)}{m}}$$

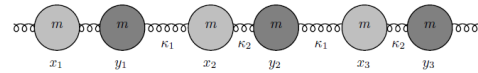*When phonons interact with light (photons) it is with the upper "optical" branch, hence name*

Optical

$$\omega_+ = \sqrt{\frac{2\kappa_2}{m}}$$

Group velocity $d\omega/dk$ goes to zero at zone boundary and for optical modes at $k=0$

$$\omega_- = \sqrt{\frac{2\kappa_1}{m}}$$

ω

Acoustic

plotted for:

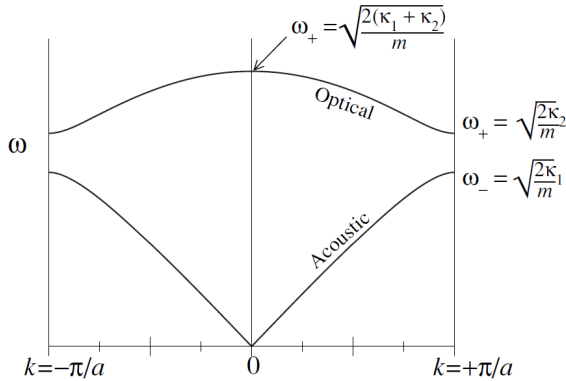$$\kappa_2 = 1.4\kappa_1$$

$k=-\pi/a$ 0 $k=+\pi/a$

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Vibrations of a 1D diatomic chain

Finally, the dispersion relation is:

$$\omega_\pm = \sqrt{\frac{\kappa_1 + \kappa_2}{m} \pm \frac{1}{m}\sqrt{\kappa_1^2 + \kappa_2^2 + 2\kappa_1\kappa_2 \cos(ka)}}$$

$$\omega_+ = \sqrt{\frac{2(\kappa_1 + \kappa_2)}{m}}$$

Optical

$$\omega_+ = \sqrt{\frac{2\kappa_2}{m}}$$

$$\omega_- = \sqrt{\frac{2\kappa_1}{m}}$$

Acoustic

ω

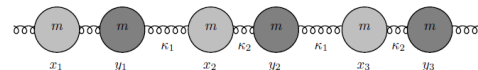$k=-\pi/a$ 0 $k=+\pi/a$

Look at acoustic branch for $k=0$:
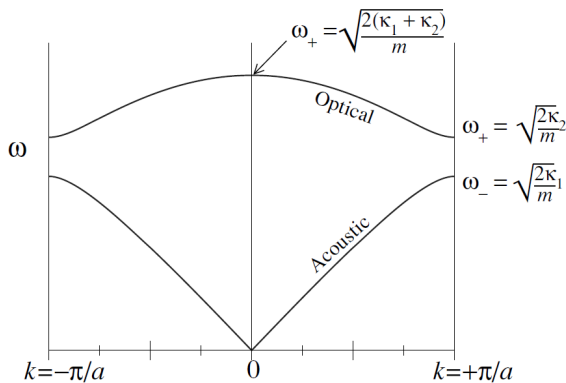
Look at acoustic branch for $k=\pi/a$:

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Vibrations of a 1D diatomic chain

Finally, the dispersion relation is:

$$\omega_\pm = \sqrt{\frac{\kappa_1 + \kappa_2}{m} \pm \frac{1}{m}\sqrt{\kappa_1^2 + \kappa_2^2 + 2\kappa_1\kappa_2 \cos(ka)}}$$
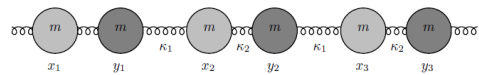
$$\omega_+ = \sqrt{\frac{2(\kappa_1 + \kappa_2)}{m}}$$

Optical

$$\omega_+ = \sqrt{\frac{2\kappa_2}{m}}$$

$$\omega_- = \sqrt{\frac{2\kappa_1}{m}}$$

Acoustic

ω

$k=-\pi/a$ 0 $k=+\pi/a$

Look at optical mode for $k=0$:

Look at optical mode for $k=\pi/a$:

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Vibrations of a 1D diatomic chain

Expanding for small k, can show we recover expression for sound waves:

$$\omega_\pm = \sqrt{\frac{\kappa_1 + \kappa_2}{m} \pm \frac{1}{m}\sqrt{\kappa_1^2 + \kappa_2^2 + 2\kappa_1\kappa_2\cos(ka)}}$$

$$v_{sound} = \frac{d\omega_-}{dk} = \sqrt{\frac{a^2\kappa_1\kappa_2}{2m(\kappa_1+\kappa_2)}}$$

Using the small angle approximation $\cos(ka) = (1-1/2(ka)^2)$

Could have derived this sound velocity – recall, we had earlier:

$$v = \sqrt{\frac{B}{\rho}} = \sqrt{\frac{1}{\rho\beta}} \qquad v = \sqrt{\frac{\kappa a^2}{m}}$$

(bulk modulus $B = 1/\beta$ inverse of compressibility $\beta = \frac{1}{\kappa a}$)

Effective spring constant:

$$\tilde{\kappa} = (\kappa_1\kappa_2)/(\kappa_1+\kappa_2)$$

Density of chain $\rho = 2m/a$

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Vibrations of a 1D diatomic chain

But what do the atomic motions look like?

Consider acoustic and optical phonon as $k \to 0$, we had:

$$m\omega^2 \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} (\kappa_1+\kappa_2) & -\kappa_2 - \kappa_1 e^{ika} \\ -\kappa_2 - \kappa_1 e^{-ika} & (\kappa_1+\kappa_2) \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix}$$

which becomes, $\omega^2 \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \frac{\kappa_1+\kappa_2}{m} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} A_x \\ A_u \end{pmatrix}$

Acoustic mode, which has $\omega = 0$ is solved by, $\begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$

Says the two atoms move together for the acoustic mode in the long wavelength limit
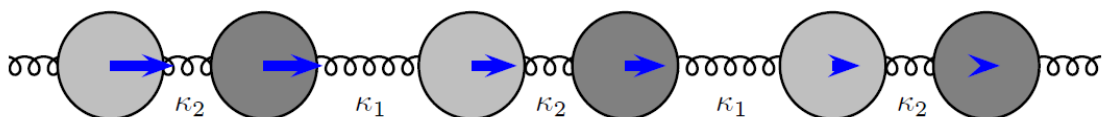
Start in phase near zone centre, and become more and more out of phase

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Vibrations of a 1D diatomic chain
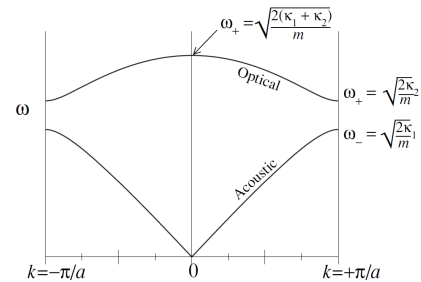
As $k \to 0$, we had

$$\omega^2 \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \frac{\kappa_1 + \kappa_2}{m} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix}$$
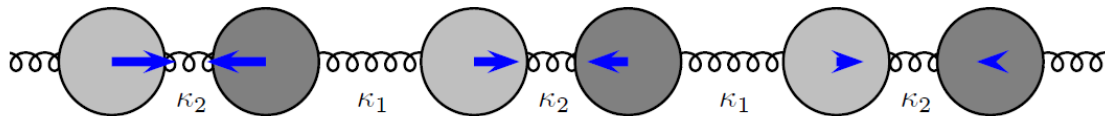
The optical mode at $k = 0$ has frequency:

$$\omega^2 = \frac{2(\kappa_1 + \kappa_2)}{m}$$

Sub in for ω^2 and can find eigenvector

$$\begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

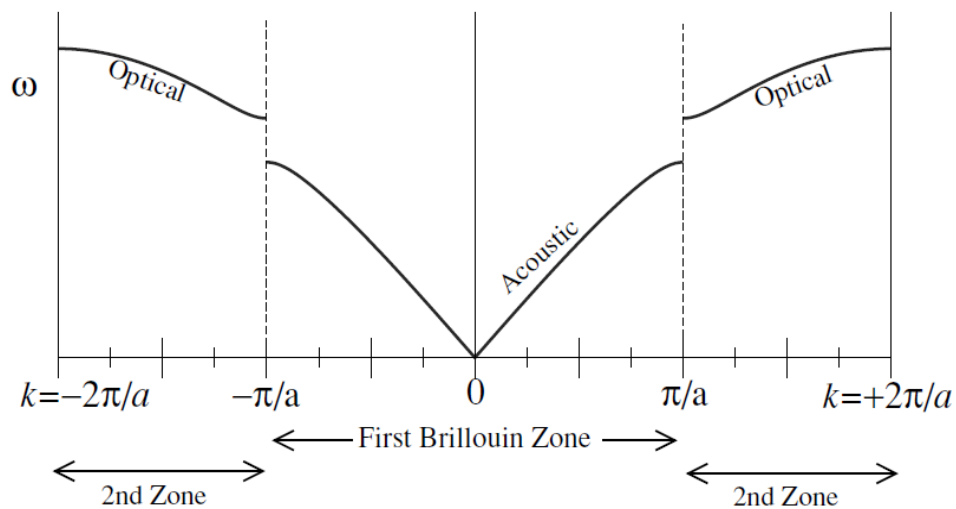*(can sub in for $A_{x,y}$ and show it's true)*

Tells the two atoms move in opposite directions

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Vibrations of a 1D diatomic chain

As for electronic states,
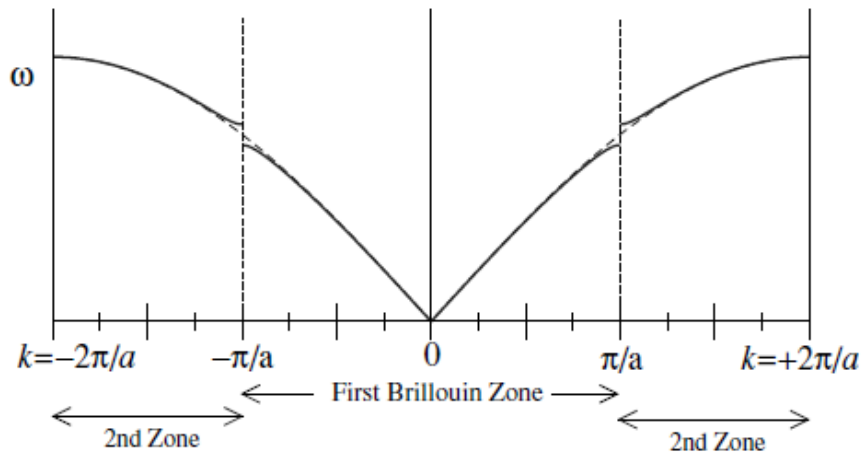can unfold into the "extended zone scheme"
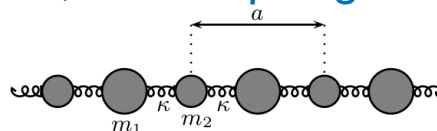

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Vibrations of a 1D diatomic chain

Full curve κ_1 κ_2 very similar; dashed curve identical.

Can show that as $\kappa_2 \rightarrow \kappa_1$ the two atoms in cell become identical and dispersion becomes that of monoatomic dispersion (with lattice constant redefined to be a/2, giving twice as large BZ).

Vibrations of a 1D diatomic chain – different masses, same spring constant

Let x_n be the position of the nth particle of mass m_1 and y_n be the position of the nth particle of mass m_2. We assume they are connected by the same spring constant κ.

We write the equations of motion for the deviations from these equilibrium positions δx_n and δy_n.

different m

same κ

$$m_1\ddot{\delta x}_n = -\kappa(\delta x_n - \delta y_{n-1}) - \kappa(\delta x_n - \delta y_n)$$
$$m_2\ddot{\delta y}_n = -\kappa(\delta y_n - \delta x_n) - \kappa(\delta y_n - \delta x_{n+1})$$

Writing the Ansatz:

$$\delta x_n = A_x e^{ikan - i\omega t}$$
$$\delta y_n = A_y e^{ikan - i\omega t}$$

Vibrations of a 1D diatomic chain

We obtain the equations:

$$-m_1\omega^2 A_x e^{ikna} = -2\kappa A_x e^{ikna} + \kappa A_y(e^{ikna} + e^{ik(n-1)a})$$
$$-m_2\omega^2 A_y e^{ikna} = -2\kappa A_y e^{ikna} + \kappa A_x(e^{ikna} + e^{ik(n+1)a})$$

or

$$\omega^2 A_x = 2(\kappa/m_1)A_x - (\kappa/m_1)(1 + e^{-ika})A_y$$
$$\omega^2 A_y = 2(\kappa/m_2)A_y - (\kappa/m_2)(1 + e^{ika})A_x$$

which is an eigenvalue problem for ω^2. Thus we need to find the roots of the determinant

$$\begin{vmatrix} 2(\kappa/m_1) - \omega^2 & -(\kappa/m_1)(1 + e^{-ika}) \\ -(\kappa/m_2)(1 + e^{ika}) & 2(\kappa/m_2) - \omega^2 \end{vmatrix}$$

Vibrations of a 1D diatomic chain

This gives the equation:

$$0 = \omega^4 - \omega^2\left(2\kappa(1/m_1 + 1/m_2)\right) + \frac{\kappa^2}{m_1 m_2}\left(4 - (1 + e^{ika})(1 + e^{-ika})\right)$$
$$0 = \omega^4 - \omega^2\left(\frac{2(m_1 + m_2)\kappa}{m_1 m_2}\right) + \frac{\kappa^2}{m_1 m_2}(2 - 2\cos(ka))$$

with the solution (skipping a few steps):

$$\omega^2 = \frac{\kappa}{m_1 m_2}\left(m_1 + m_2 \pm \sqrt{m_1^2 + m_2^2 + 2m_1 m_2 \cos(ka)}\right)$$
$$= \frac{\kappa}{m_1 m_2}\left(m_1 + m_2 \pm \sqrt{(m_1 + m_2)^2 - 4m_1 m_2 \sin^2(ka/2)}\right)$$

At $k = 0$, $\cos(ka) = 1$, the acoustic mode has zero energy, whereas the optical mode has energy

$$\omega = \sqrt{\frac{2\kappa(m_1 + m_2)}{m_1 m_2}}$$

At the zone boundary $\cos(ka) = -1$, so the two modes have energy

$$\omega = \sqrt{\frac{2\kappa m_1}{m_1 m_2}} \quad \text{and} \quad \sqrt{\frac{2\kappa m_2}{m_1 m_2}}$$

the greater of which is the optical mode, the lesser being the acoustic mode.

Visualization

In the case of long wavelength (small k) in acoustic branch of the dispersion curve, the atoms move synchronously and deviation of every atom is about the same.

In the optical branch, the atoms move in antiphase.

For the shortest waves (large k, at zone boundary) in acoustic branch the lighter atoms are still and heavier atoms oscillate;
in the optical branch the situation is inverse.

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Vibrations / phonons
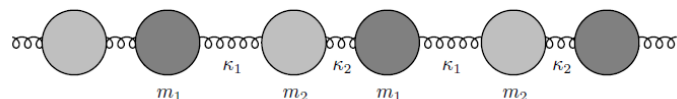
For 1-D chain atoms only move in line, one degree of freedom

Had one mass per cell, one mode per distinct value of k (acoustic, go to zero at $k = 0$)
For two masses per cell, two modes per distinct value of k (acoustic, optical)
For M atoms per cell, get M modes per distinct value of k – one will be acoustic, others optical.

For 3-D solid atoms have three degrees of freedom

Three different acoustic modes at each k at long wavelength – one "longitudinal acoustic" (amplitude in direction of propagation) and two "transverse acoustic" (amplitude perpendicular to direction of propagation).
For M atoms per cell, $3(M\text{-}1)$ optical modes, always 3 acoustic modes – $3M$ degrees of freedom per cell.
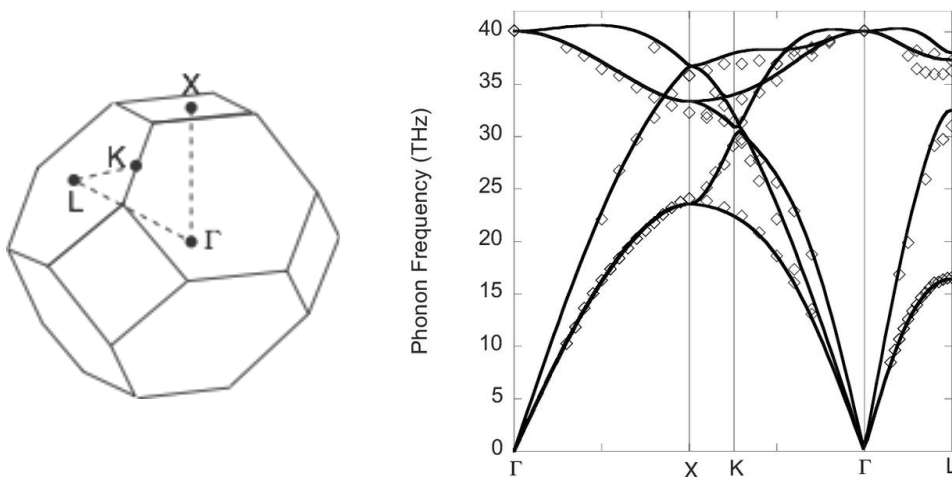
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Phonons in 3D crystals: Aluminium
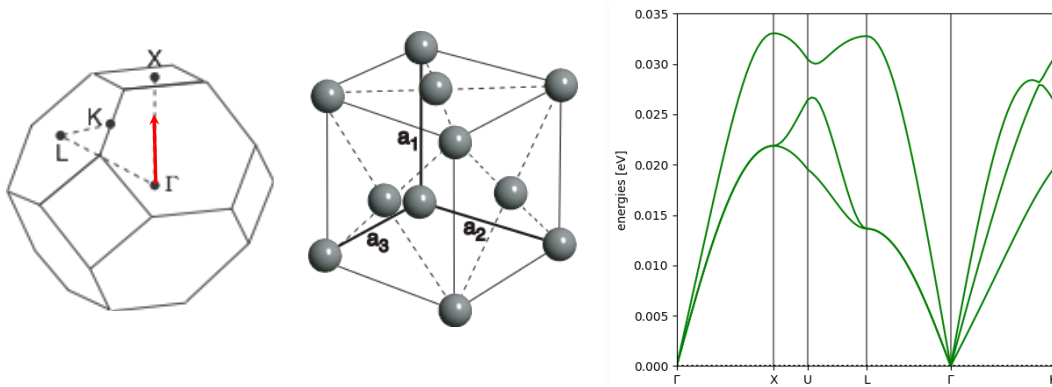
No. optical modes = 3(M-1) = 0

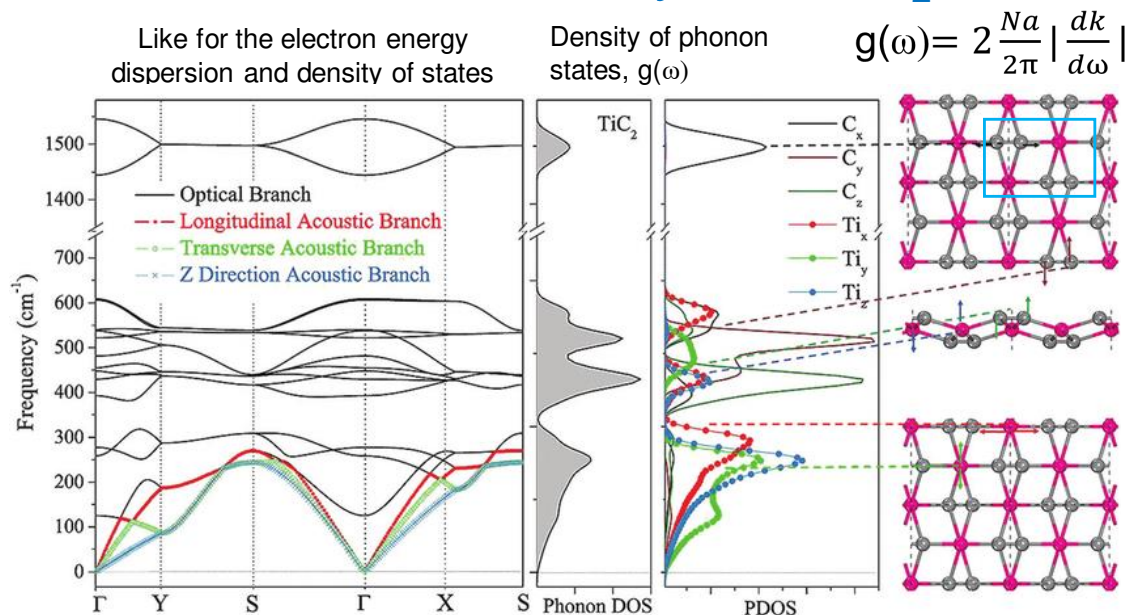One atom per cell, just 3 acoustic modes

Phonons in 3D crystals: diamond

- We see acoustic and optical phonons. 3 branches/bands for every atom per unit cell. Here two atoms, six branches three ac, three opt (3(M-1) = 3(2-1)=3).
- Important to identify Bravais lattice and basis if we want to make predictions as to vibrational properties.

Phonons in 3D crystals: TiC_2

Like for the electron energy dispersion and density of states

Density of phonon states, $g(\omega)$

$$g(\omega) = 2\frac{Na}{2\pi}\left|\frac{dk}{d\omega}\right|$$

Phonon dispersion and phonon density of states of TiC_2 as determined by DFT calculations.

6 atoms per unit cell – no. optical = 3 (6-1) = 15 opt., 3 acoustic

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Phonon dispersion curves for some structures:

http://henriquemiranda.github.io/phononwebsite/phonon.html?yaml=http://henriquemiranda.github.io/phononwebsite/tests/phonopy/band.yaml

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End