

MIT OpenCourseWare
<http://ocw.mit.edu>

5.62 Physical Chemistry II
Spring 2008

For information about citing these materials or our Terms of Use, visit: <http://ocw.mit.edu/terms>.

Phonons: 1-D Linear Chain of Atoms

An atomic description of the vibrations of a solid. This will be a more realistic description than Einstein's or Debye's, which are continuum models. Debye's model works well at low T (T^3 law) and high T, but not so well at intermediate T.

Linear chain in 1D of atoms connected by harmonic springs of force constant k ; atoms are labeled as $(n-2), (n-1), n, (n+1), (n+2), \dots$

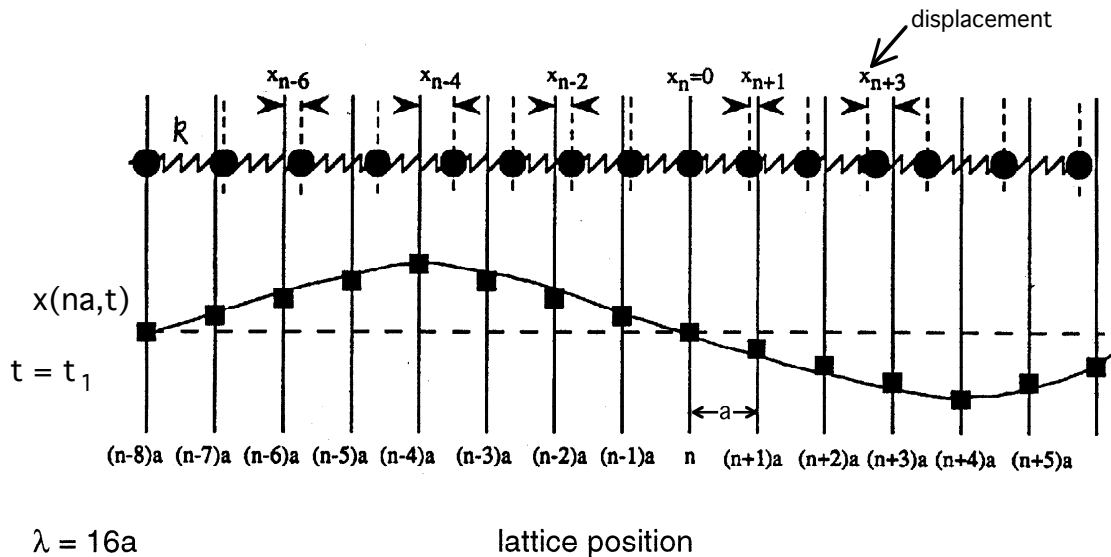
Lattice positions or equilibrium positions of atoms along the chain are labeled as

$$(n-1)a, na, (n+1)a, \dots \text{ where } a \text{ is the lattice spacing}$$

N ... total number of atoms in chain

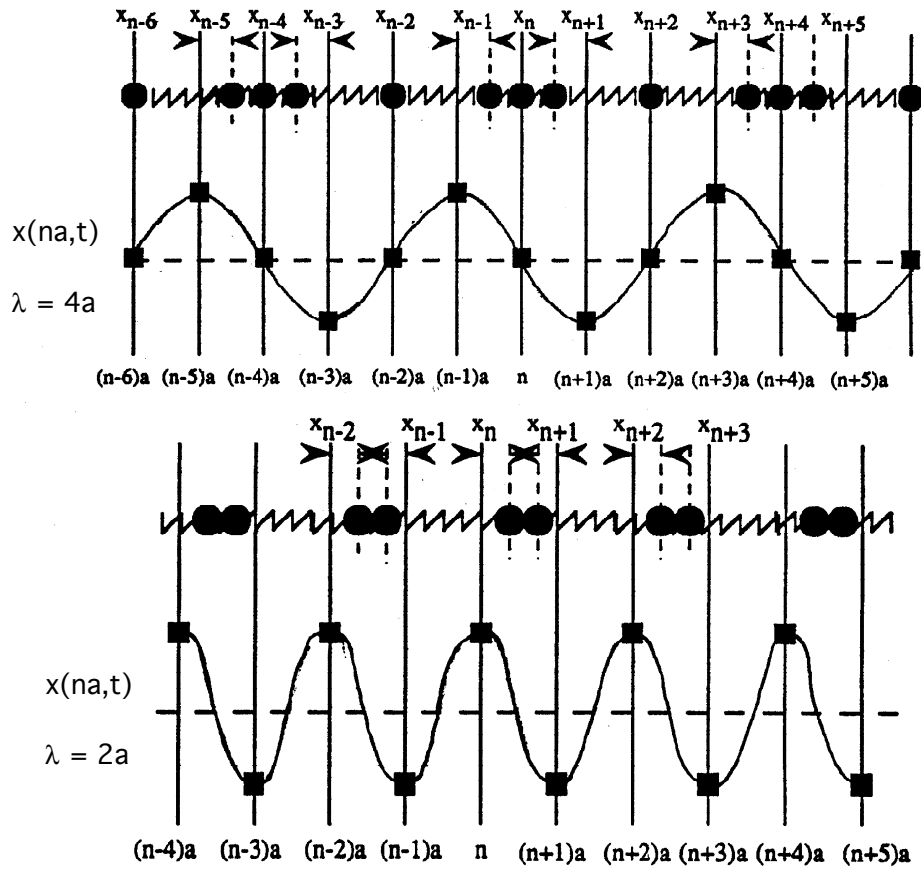
x_n ... instantaneous displacement of n^{th} atom from equilibrium position

Plot of $x(na, t)$ vs. position along lattice at some $t = t_1$ represents a collective vibrational mode, a *phonon*, of the solid



longitudinal phonon — displacements parallel to direction of motion (top)
 transverse phonon — displacements perpendicular to direction of motion.

Phonons of many λ 's can be supported



$l = 2a$ is the shortest physically sensible wavelength; in the continuum model, there is no limit to the shortness of l .

$$\text{wavevector magnitude } k = \frac{2\pi}{\lambda} = q$$

[Reserve k for force constant and for wavevector of photons, *but not phonons*.]

GOAL: want to determine allowed values of λ or q but phonons are unlike photons, for which

$$v = \frac{c}{\lambda} \quad 2\pi v = \omega = cq \quad (\text{photons})$$

PROBLEM: for phonons, in general

$$\omega \neq cq$$

especially at large q (short wavelength), ω does not vary linearly with q .

DISPERSION RELATION

GOAL: for phonons, find allowed values of q and find the relationship between ω and q .

Phonon described by

$$x(na, t) = A \cos\left(\frac{2\pi}{\lambda} \overset{\substack{\text{integer : site \#} \\ \downarrow}}{na} - \omega t\right) = A \cos(qna - \omega t)$$

↑
lattice spacing

The constant phase point moves according to

$$n(t)a = \frac{\omega t}{q}$$

so the *phase velocity* is ω/q .

Equation of motion for n -th atom in lattice is

$$f = ma = m \frac{d^2 x(na, t)}{dt^2} \quad m = \text{mass of atom}$$

Force between atoms for harmonic potential

$$f = -k\Delta x \quad \text{Hooke's law force} \quad [\text{NOTE: This } k \text{ is force constant, not wave vector}]$$

Force on n^{th} atom including only nearest neighbor interactions.

$$\begin{aligned} f &= -k(x_n - x_{n+1}) + -k(x_n - x_{n-1}) \\ &= kx_{n+1} + kx_{n-1} - 2kx_n \end{aligned}$$

So

$$\begin{aligned} m \frac{d^2 x(na, t)}{dt^2} &= kx_{n+1} + kx_{n-1} - 2kx_n \\ m \frac{d^2 \cos(qna - \omega t)}{dt^2} &= k \cos(qna + qa - \omega t) + k \cos(qna - qa - \omega t) \\ &\quad - 2k \cos(qna - \omega t) \\ \cos \alpha + \cos \beta &= 2 \cos\left(\frac{\alpha + \beta}{2}\right) \cos\left(\frac{\alpha - \beta}{2}\right) \\ -m\omega^2 \cos(qna - \omega t) &= 2k \cos(qna - \omega t) \cos(qa) - 2k \cos(qna - \omega t) \\ &= 2k \cos(qna - \omega t) [\cos(qa) - 1] \end{aligned}$$

$$-m\omega^2 = 2k \cos(qa) - 2k$$

$$\omega^2 = \frac{2k}{m} [1 - \cos(qa)]$$

$$\omega = \left[\frac{2k}{m} (1 - \cos qa) \right]^{1/2}$$

DISPERSION RELATION (ω vs. q)

ALLOWED VALUES OF q

long chain — N very large — ends of chain destroy collective modes — don't care about ends — join them (periodic boundary condition) because math is convenient

$$x(na, t) = x(na + Na, t)$$

allowed values of q will come from this boundary condition

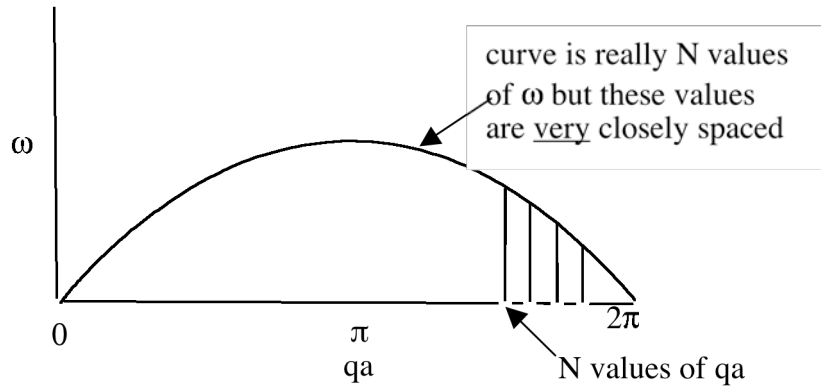
$$\cos(qna - \omega t) = \cos(qna - \omega t + qNa)$$

This will be true for one cycle or for an integer number of cycles later — 1 cycle = 2π so

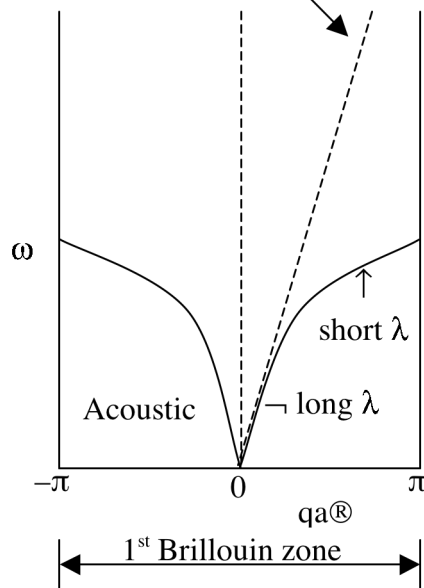
$$qNa = p2\pi \quad \text{where } p = 1, 2, \dots, N$$

$$qa = p \frac{2\pi}{N}$$

allowed values of qa run from ~ 0 to 2π
nearly continuously because N is so large



DISPERSION CURVE usually plotted from $qa = -\pi$ to $+\pi$
 $\omega = (k/m)^{1/2} qa$



Limit of w when $qa \rightarrow 0$ (very long l)

$$\omega = \left[\frac{2k}{m} (1 - \cos qa) \right]^{1/2}$$

$$\cos qa \cong 1 - \frac{1}{2} (qa)^2 + \dots \quad \text{when } qa \rightarrow 0$$

$$\omega \cong \left(\frac{k}{m} \right)^{1/2} |qa| \quad \text{linear in } qa \text{ at small } |q|.$$

At small (q) we have *acoustic waves*: where ω is linear in q , ω/q is the speed of sound.

Similar to a light wave, where $\omega/q = c$. All ω 's have the same velocity. A disturbance composed of a range of ω 's moves through the lattice without spreading.

At short λ ($qa \Rightarrow \pi$), the wavelength becomes comparable to the lattice spacing, and the linear variation of ω with q breaks down. We call this *dispersion* because a disturbance composed of a range of ω 's spreads as it propagates in the lattice.

At $qa = \pi$,

$$\frac{2\pi}{\lambda}a = \pi \quad \text{so } \lambda = 2a \text{—smallest physically realistic wavelength}$$

$$\omega = \left[\frac{2k}{m}(1 - \cos qa) \right]^{1/2} = 2 \left(\frac{k}{m} \right)^{1/2} \quad (qa = \pi, \cos \pi = -1)$$

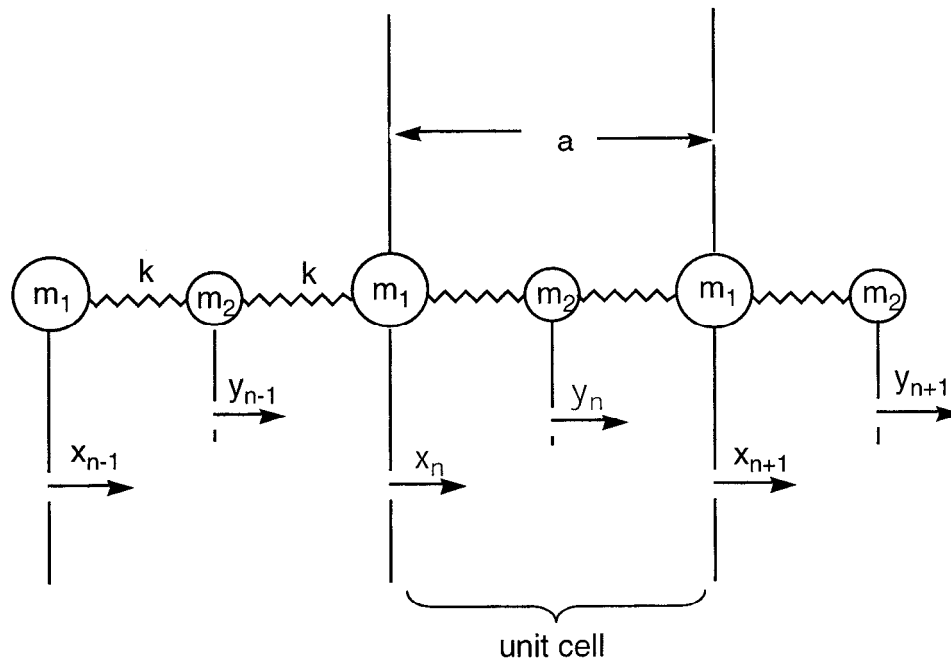
$c = \omega(q)/q$ is not independent of q .

COMPARISON TO DEBYE MODEL

In the Debye model, $\omega \propto \lambda^{-1}$. Debye model gave excellent results at low T ($C_v \propto T^3$). At low T , only low- ω phonons are excited. It is in the low frequency range where $\omega \propto q$, according to the dispersion curve, so the goodness of the Debye model is expected. At higher T , the Debye model is not so good because the dispersion curve has the form $\omega \neq \text{constant} * q$.

1D DIATOMIC MOLECULE CHAIN

The presence of two different atoms in the chain leads to *optical phonons* in addition to *acoustic phonons*. Consider a 1D chain consisting of alternating atoms of mass m_1 and m_2 interacting harmonically with force constant k



$x_n \equiv$ displacement of n^{th} m_1 atom

$y_n \equiv$ displacement of n^{th} m_2 atom

GOAL: find dispersion relation for a diatomic molecule chain

Force on n^{th} m_1 atom

$$f = -k(x_n - y_n) + -k(x_n - y_{n-1}) = ky_n + ky_{n-1} - 2kx_n$$

Equation of motion

$$m_1 \frac{d^2 x_n}{dt^2} = k(y_n + y_{n-1} - 2x_n)$$

For n^{th} m_2 atom

$$f = -k(y_n - x_{n+1}) + -k(y_n - x_n) = kx_{n+1} + kx_n - 2ky_n$$

$$m_2 \frac{d^2 y_n}{dt^2} = k(x_{n+1} + x_n - 2y_n)$$

Now, consider the following proposal for $x_n(t)$ and $y_n(t)$:

$$x_n = A e^{i(qna - \omega t)} \quad y_n = B e^{i(qna - \omega t)}$$

This is a specific linear combination of cos and sin that is easier to use than cos.

Plugging trial forms of x_n and y_n into equations of motion

$$\begin{aligned} k(1 + e^{-iqa})B + (\omega^2 m_1 - 2k)A &= 0 \\ k(1 + e^{iqa})A + (\omega^2 m_2 - 2k)B &= 0 \end{aligned}$$

Non-trivial solution exists only if determinant of the coefficients of A and B = 0

$$\omega^2 = k \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \pm k \left[\frac{1}{m_1^2} + \frac{1}{m_2^2} + \frac{2}{m_1 m_2} \cos qa \right]^{1/2}$$

– solutions ACOUSTIC PHONONS

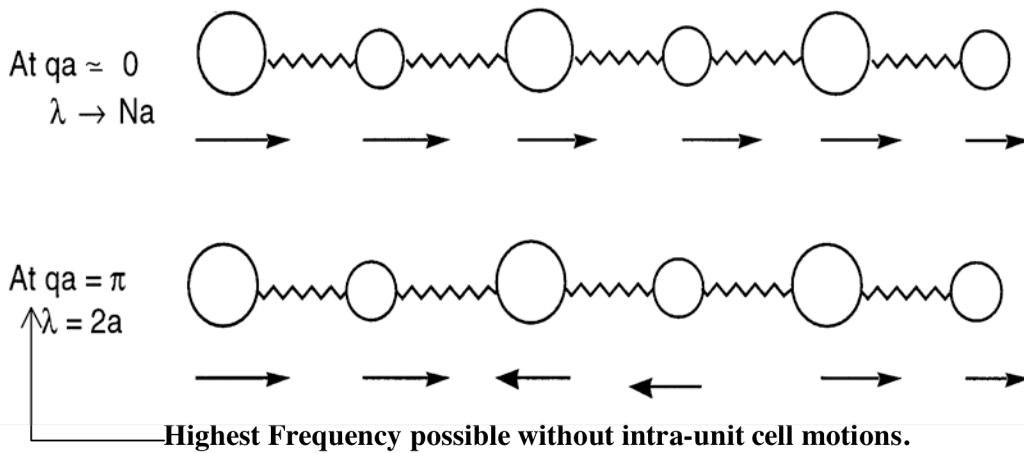
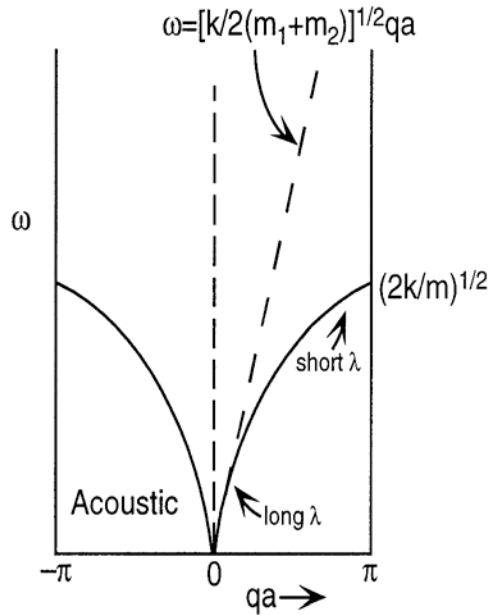
+ solutions OPTICAL PHONONS

Allowed values of qa run from $-\pi$ to π (or ~ 0 to 2π)

ACOUSTIC MODES - DIATOMIC CHAIN (– solution)

$$\text{At } qa = 0 \quad \omega = 0$$

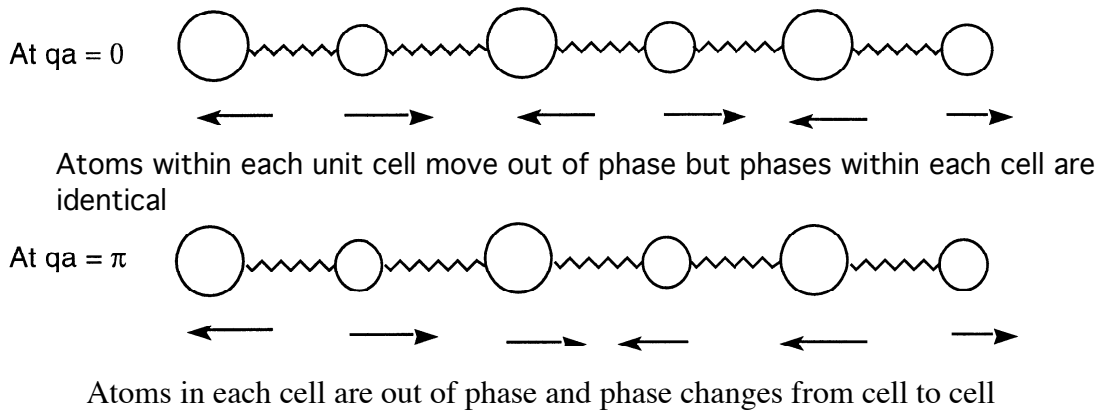
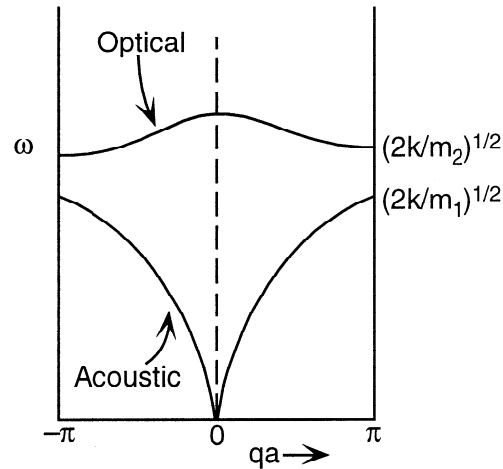
$$\text{At } qa = \pi \quad \omega = \left(\frac{2k}{m_1} \right)^{1/2} \quad (m_1 > m_2)$$



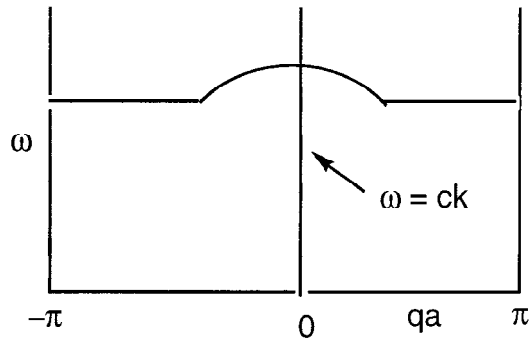
In acoustic modes, both atoms in each unit cell move in phase. At $qa = \pi$, both atoms move in phase but phase changes from one unit cell to the next unit cell.

OPTICAL MODES — DIATOMIC CHAIN (+ solution)

$$\begin{aligned} \text{At } qa = 0 \quad \omega &= \left[2k \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \right]^{1/2} \\ \text{At } qa = \pi \quad \omega &= \left(\frac{2k}{m_2} \right)^{1/2} \quad (m_1 > m_2) \end{aligned}$$



Optical phonons — the out of phase motion of 2 different atoms in a unit cell sets up a dynamical oscillating dipole moment which can couple to an external oscillating electric field — the optical vibrations are IR active. They absorb at the frequency where the dispersion curve for light [$v = ck/2\pi$] crosses the optical dispersion curve. At this special point the light frequency and the vibrational frequency match, and also the light wavelength and the vibrational wavelength match! So when IR light enters the crystal and excites the vibration, the vibration moves through the crystal along with the light, at the speed of the IR light! But thermally excited optical phonons at other wavelengths, that don't match the light dispersion curve, don't move through the crystal.



Since $c = 3 \times 10^{10}$ cm/s for photons and $c \cong 3 \times 10^5$ cm/s for phonons, the photon dispersion curve intersects the phonon curve at $qa \cong 0$

Reststrahlen Absorption

CsI	63 cm^{-1}	GaAs	263 cm^{-1}
KBr	114 cm^{-1}	LiH	588 cm^{-1}
NaCl	164 cm^{-1}	SiC	800 cm^{-1}

These are the absorption frequencies calculated for the + solution at $qa \approx 0$.

3D SOLID LATTICES

1 atom/unit cell — 3 branches of acoustic modes — 1 longitudinal and 2 transverse where displacement is perpendicular to direction of wave. All crystals have 3 acoustic branches.

2 atoms/unit cell — 3 acoustic modes and 3 optical modes where 1 is longitudinal and 2 are transverse.

Each phonon branch has N allowed wavevectors.

$3N$ total acoustic phonon modes, $3N$ total optical phonon modes.

If n atoms per unit cell, then $(3n - 3)$ optical phonon branches.

$3n$ total degrees of freedom, 3 of which are the acoustic phonons.