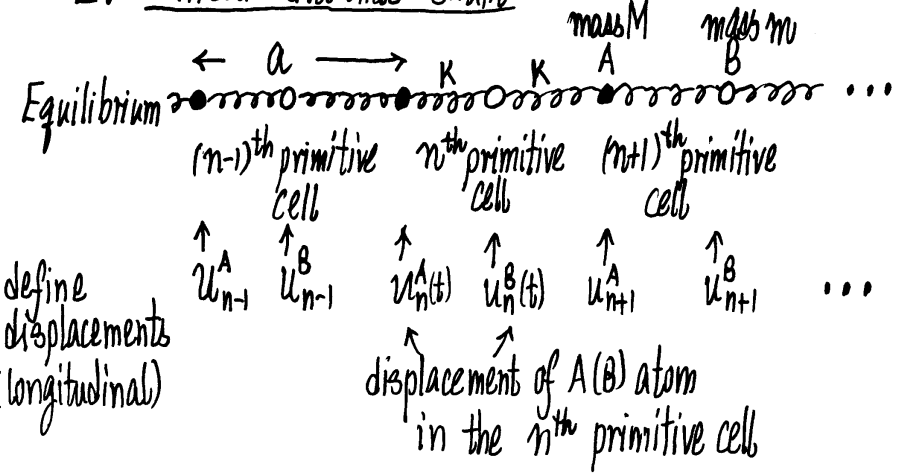
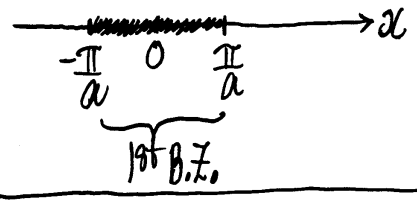
E. Linear diatomic chain



N(>>1) unit cells in crystal

Description of crystal structure:

- 1D lattice of lattice constant a + basis of 2 atoms



Equations of motion:

- for atom A in n^{th} primitive cell

$$M\ddot{u}^A_n = -K(u^A_n - u^B_{n-1}) - K(u^A_n - u^B_n)$$

- for atom B in n^{th} primitive cell

$$m\ddot{u}^B_n = -K(u^B_n - u^A_n) - K(u^B_n - u^A_{n+1})$$

Applying periodic B.C.

⇒ the two equations of motion hold for atoms in ALL primitive cells (all n)

Normal modes:

$$\begin{cases} u^A_n(t) = \underbrace{A e^{iqna}}_{\text{Bloch's theorem}} e^{-i\omega t} \\ u^B_n(t) = B e^{iqna} e^{-i\omega t} \end{cases} \leftarrow \text{same time dependence}$$

But A-atom and B-atom are different atoms, thus we need two (possibly complex) amplitudes A and B.

Substituting into eqns. of motion:

$$-\omega^2 MA = -K(2A - Be^{-iqa} - B)$$
$$-\omega^2 mB = -K(2B - A - Ae^{iqa})$$

which can be written as

$$\begin{pmatrix} \frac{2K}{M} - \omega^2 & -\frac{K}{M}(1+e^{-iqa}) \\ -\frac{K}{m}(1+e^{iqa}) & \frac{2K}{m} - \omega^2 \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = 0$$

or

$$\begin{pmatrix} \frac{2K}{M} & -\frac{K}{M}(1+e^{-iqa}) \\ -\frac{K}{m}(1+e^{iqa}) & \frac{2K}{m} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = \omega^2 \begin{pmatrix} A \\ B \end{pmatrix}$$

Thus, there will be 2 values of ω^2 for a given q.
[$q \in 1^{st}$ B.Z. is sufficient]

$$|\text{Determinant}| = 0$$

$$\Rightarrow Mm\omega^4 - 2K(M+m)\omega^2 + 2K^2(1-\cos qa) = 0$$

$$\Rightarrow \omega^2(q) = \frac{K(M+m)}{Mm} \pm K\sqrt{\left(\frac{M+m}{Mm}\right)^2 - \frac{4}{Mm}\sin^2\left(\frac{qa}{2}\right)} \quad \text{(Ex.)}$$

[phonon dispersion relation : 1D diatomic chain]

Each $q \Rightarrow$ two ω's (two branches in q-ω plot) (see figure)

What if 3 atoms in the basis?

Each $q \Rightarrow$ three ω's (three branches in q-ω plot)

1 longitudinal acoustic branch ($q \to 0$, $\omega \to 0$)

2 longitudinal optical branches

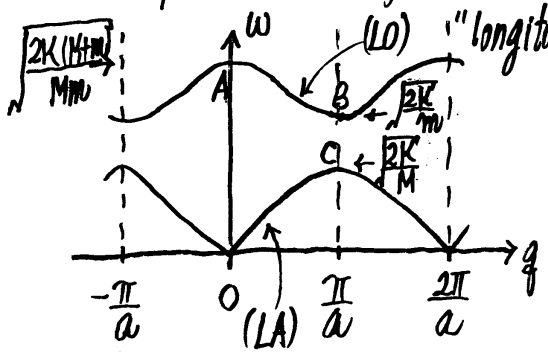
[consider longitudinal motions only]

N allowed q-values in 1^{st} B.Z.

$\Rightarrow$ 3N modes = # degrees of freedom

= 3N (basis atoms) × 1 (primitive cell) ← consider longitudinal motion only

Dispersion relation of a diatomic chain



- at A: M and m oscillate in antiphase
- at B: light mass m is oscillating and M is at rest
- at C: heavy mass M is oscillating and m is at rest

Features:

- Periodic in q with period of $\frac{2\pi}{a}$
- In addition to acoustic branch ($\omega \sim q$ as $q \to 0$), we have one optical branch ($\omega \to$ finite as $q \to 0$).

  [Q: What if we have a basis of 3 atoms?]
- There is a gap between the 2 branches, i.e., no propagating modes (with real q) for

$$\sqrt{\frac{2K}{M}} < \omega < \sqrt{\frac{2K}{m}}$$

Remark: In recent years, a new research area on "phononic crystals" emerges. A simple 1D phononic crystal is

↑ ↑ different sound velocities (moduli)

- The upper cutoff of the optical branch is at $\omega_{cutoff} = \sqrt{\frac{2K}{\mu}}$ where $\frac{1}{\mu} = \frac{1}{M} + \frac{1}{m}$ ← reduced mass

- Acoustic branch: as $q \to 0$, $\omega \sim q$

As $q \to 0$, $\omega \simeq a\sqrt{\frac{K}{2(M+m)}}\, q = v_s q$ (continuum limit)

where v_s = sound velocity $= a\sqrt{\frac{K}{2(M+m)}}$

Periodic B.C. (Mode Counting)

- N unit cells in the system
- Periodic B.C. $\Rightarrow$ q can be chosen to be within 1st B.Z.

$-\frac{\pi}{a} < q \leq \frac{\pi}{a}$ (there are N allowed values of q)

$q = \frac{2\pi}{Na} \cdot p$ ← integer

Number of modes:

N unit cells, 2 atoms per unit cell, longitudinal motions

$\Rightarrow$ 2N degrees of freedom

Now, N q-values in 1st B.Z.

Each q $\to$ 2 ω's (2 branches)

$\Rightarrow$ 2N normal mode frequencies.

Motions of the $q \to 0$ modes

From eqn. of motion: $\frac{B}{A} = \frac{2K - \omega^2 M}{K(1 + e^{-iqa})}$

$\frac{B}{A}$ ← ratio of amplitudes

- For $qa \ll 1$ (i.e. $\approx$ B.Z. center), $\sin\frac{qa}{2} \approx \frac{qa}{2}$,

$$\omega^2 \approx \frac{K(M+m)}{Mm}\left[1 \pm \sqrt{1 - \frac{mM}{(M+m)^2} q^2a^2}\right]$$

$$\approx \frac{K(M+m)}{Mm}\left[1 \pm \left(1 - \frac{mM}{2(m+M)^2} q^2a^2\right)\right]$$

$$\approx \underbrace{\frac{K q^2 a^2}{2(M+m)}} \quad \text{or} \quad \underbrace{\frac{2K(M+m)}{Mm}} = \frac{2K}{\mu}$$

LA branch as $q \to 0$ (pt. 0): $\omega = \left(\sqrt{\frac{K}{2(M+m)}}\, a\right) \cdot q$ ← sound mode

LO branch as $q \to 0$ (pt. A)

$\frac{B}{A} = \frac{2K - \frac{K q^2 a^2}{2(M+m)} M}{K(1+1)}$

≈ 1 $(q \to 0)$ (pt. 0)

↑ two types of atom oscillate with same amplitude and phase

$\frac{B}{A} = \frac{2K - \frac{2K(M+m)}{Mm} M}{2K}$

$= -\underbrace{\frac{M}{m}}$ (pt. A)

oscillating in antiphase and center of mass at rest

Motion of the $q \to \pm \frac{\pi}{a}$ modes

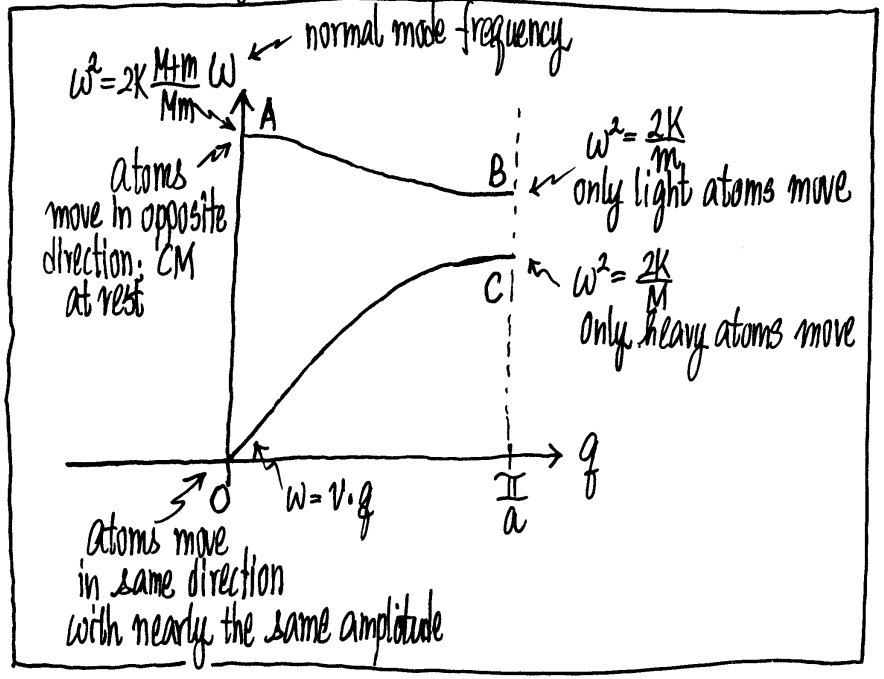
- $q \to \pm \frac{\pi}{a}$ ("B.Z. edge") (short wavelength)
- $\omega^2 = \frac{2K}{m}$ or $\frac{2K}{M}$ (pt. B / pt. C)

$$\frac{B}{A} = \frac{2K - \frac{2K}{m}\cdot M}{K(1 + e^{-iga})}, \quad e^{-iga} \to -1, \quad = \infty$$

→ lighter mass m oscillates and larger mass M at rest

$$\frac{B}{A} = \frac{2K - 2K}{K(1 + e^{-iga})} = 0$$

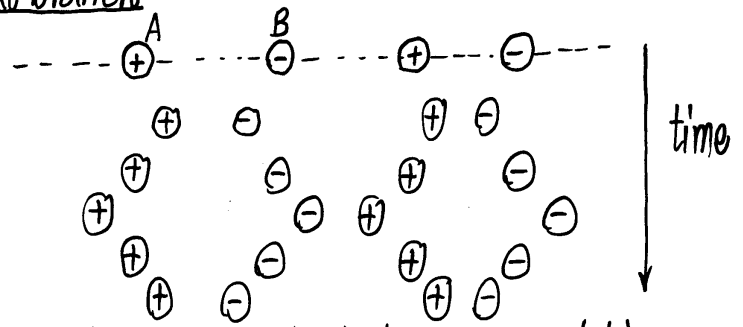
→ larger mass M oscillates and lighter mass m at rest



Acoustic branch

- characterized by $\omega \sim v \cdot q$, so that $q \to 0$, $\omega \to 0$.
- $q \to 0 \Rightarrow$ long wavelength limit (continuum limit)
- Very long wavelength, $A \approx B$ and $e^{iqna} \sim 1$
  - $\Rightarrow$ ALL atoms move together
  - $\Rightarrow$ the whole crystal moves ($\omega = 0$ mode)
- Since the crystal can move (at most in real world) in three directions (longitudinal + 2 transverse directions), we have <u>at most three acoustic branches</u> (1LA + 2TA)

Optical branch



oscillating electric dipoles! (ionic crystals)

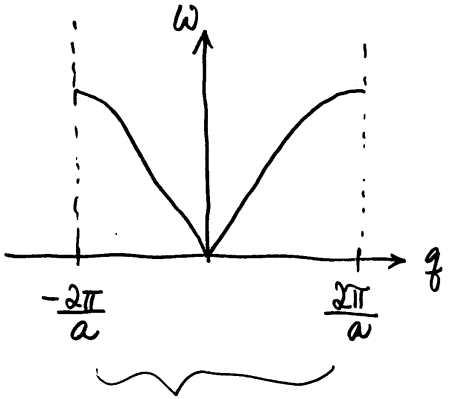
Thus, this mode will couple strongly to EM waves at the frequency $\omega \sim \sqrt{\frac{2K}{\mu}}$ $\Rightarrow$ affects optical properties of solid

thus "optical branch"

Remarks:

(a) What if $m = M$?

- then monatomic chain with period $\frac{a}{2}$ and $2N$ unit cells,
- so we know the answer should be



Q: Why "$\frac{2\pi}{a}$" but not $\frac{\pi}{a}$?

$2N$ allowed q values between $-\frac{2\pi}{a}$ and $\frac{2\pi}{a}$ $\Rightarrow$ $2N$ modes

(2N unit cells)(1 atom/cell)

(b) So we can understand the diatomic chain result in the following way:

(a) When $m \neq M$ (but the mass difference is so small that it is negligible)†, we only need to consider the effect of the change in the lattice.

† In electronic band theory, this is analogous to the "empty lattice" model.

Change from:

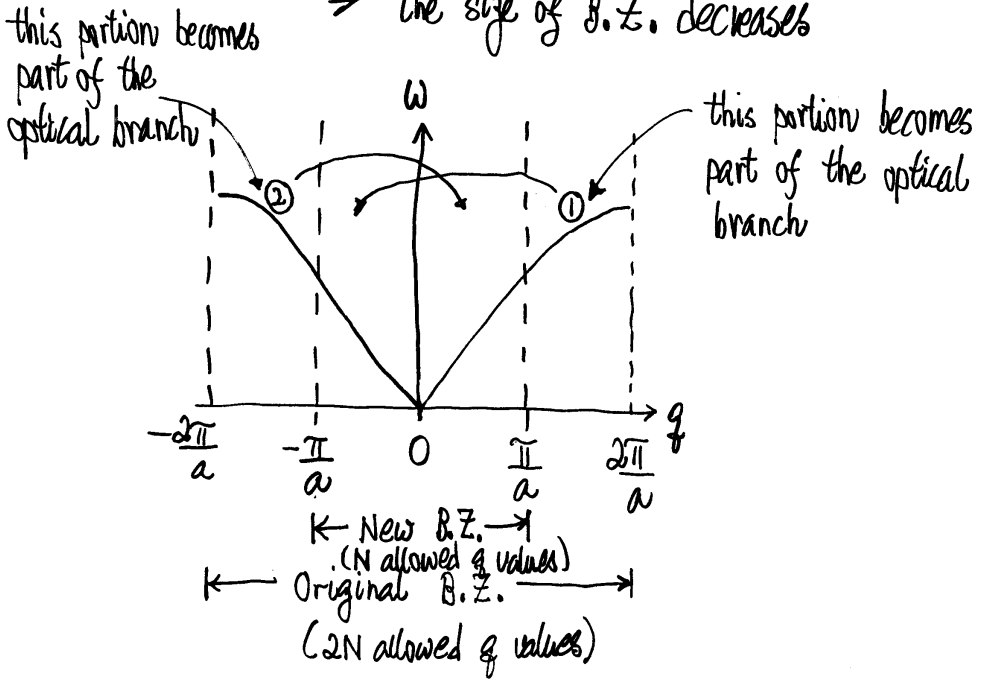
2N unit cells + Basis of 1 atom, lattice constant $= \frac{a}{2}$

→ TO →

N unit cells + Basis of 2 atoms, lattice constant $= a$

i.e. lattice constant increased in direct lattice

$\Rightarrow$ the size of B.Z. decreases

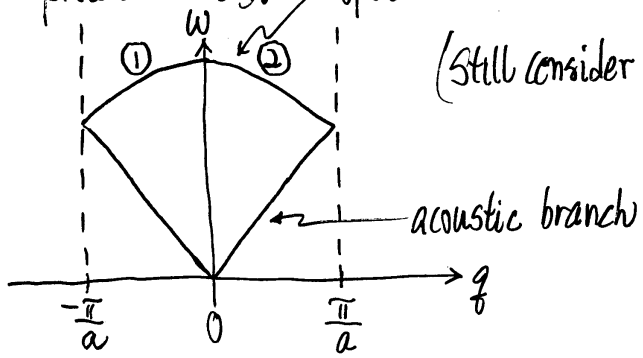


But we know that it is sufficient to include q only in the 1st B.Z. in order to include all the normal modes since waves of shorter wavelengths describe displacements corresponding to that of longer wavelengths within the 1st B.Z.

q' outside B.Z. is equivalent to the motions described by q inside B.Z., and q' and q are related by $\boxed{q' = q + \text{reciprocal lattice vector}}$

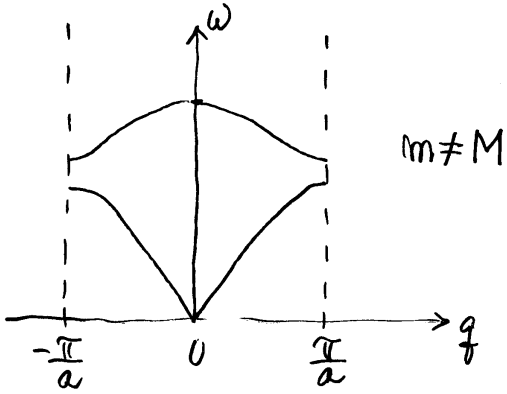
Hence, we translate portion ①, which is outside B.Z., by $-\frac{2\pi}{a}\hat{x}$ (a reciprocal lattice vector of the new reciprocal lattice); and translate portion ② by $+\frac{2\pi}{a}\hat{x}$ (also a reciprocal lattice).

2N modes



(Still consider $m \equiv M$)

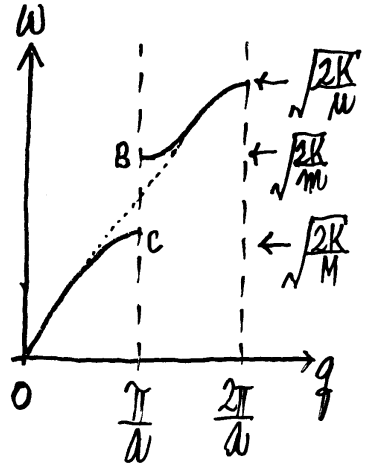
When $m \neq M$, a gap opens up at the B.Z. edge:



$m \neq M$ gap opens up.

- So, the $q \to 0$ mode of the optical branch originally comes from the mode at the B.Z. edge of the original lattice.

Summary:



$\frac{1}{\mu} = \frac{1}{M} + \frac{1}{m}$

In the limit $m \to M$, pts. B and C come together.

(c) An appreciation of periodicity

- Important to appreciate the simplicity that periodicity brings in.

e.g. Monatomic 1D chain (N unit cells + Basis of 1 atom)

Without periodicity	With periodicity
⇓	Periodicity → • can use q to label modes†
A big N-atom molecule	• N allowed q values in 1st B.Z.
⇓	Plus one equation for each q (1×1 eigenvalue problem, N times)
N × N eigenvalue problem	$\frac{2KA}{M}(\cos qa - 1)A = -\omega^2 A$
$(N \sim 10^6)$	$\Rightarrow \omega = \sqrt{\frac{4K}{M}}\left\lvert \sin\frac{qa}{2} \right\rvert$ ← {dispersion relation

† Technically, we say "q" becomes a good label (quantum number) of the normal modes.

e.g. diatomic chain

N unit cells + Basis of 2 atoms

Without periodicity ⇒ a $2N \times 2N$ eigenvalue problem

With periodicity → $q \in$ 1st B.Z. and N allowed q-values in 1st B.Z.

↳ plus a 2×2 eigenvalue problem for each q

(a total of N eigenvalue problems, each dealing with a 2×2 matrix)

i.e. periodicity highly simplifies calculations of phonon dispersion relation.

(d) How about...

more than nearest-neighbor interactions?

as long as interactions are harmonic ⇒ solvable

or can find normal mode frequencies

allow transverse motions?

higher dimensions?

(e) Key point: normal modes ⇒ independent oscillators

Thus, $$H = \sum_{\substack{\text{normal}\\ \text{modes } i}} \frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 x_i^2$$

i labels normal modes

⇒ solvable!

F. Allowing for transverse motions

- Longitudinal: displacements of atom $\parallel \vec{q}$
- Transverse: displacements of atom $\perp \vec{q}$

e.g. 1D monatomic chain

Equilibrium ... • ← a → • • ... → $\hat{x}$

Consider displacements in $\hat{y}$-direction (or $\hat{z}$-direction) only

... • u_{n-1} u_n u_{n+1} u_{n+2} ... ↑ $\hat{y}$ (or $\hat{z}$)

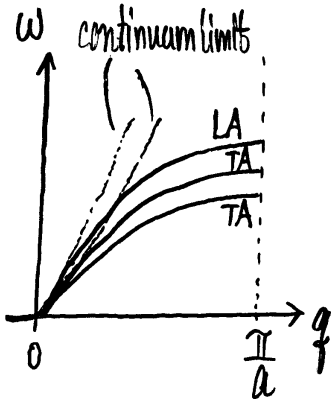
- Set up equations of motion and look for normal modes, we will get $\omega(q)$
- acoustic branch – since $q \to 0$ mode must be $\omega \to 0$ as there must be a mode for the whole system to move in $\hat{y}$-direction (or $\hat{z}$-direction)
- two transverse branches: $\hat{y}$ or $\hat{z}$ (generally, 2 directions $\perp \vec{q}$)

∴ Given a $\vec{q}$, there are

1 longitudinal and 2 transverse branches

If 1 atom/primitive cell, these are <u>acoustic branches</u>.

1LA + 2TA



Schematic phonon dispersion relation

1D monatomic chain allowing for <u>longitudinal and transverse motions</u>

- N primitive cells + 1 atom/cell + 3 directions
  ⇒ 3N degrees of motion
- N allowed q-values in 1st B.Z. (periodic B.C.)
  + 3 branches (3 ω's for each q)
  ⇒ 3N normal modes

e.g. <u>1D diatomic chain</u>

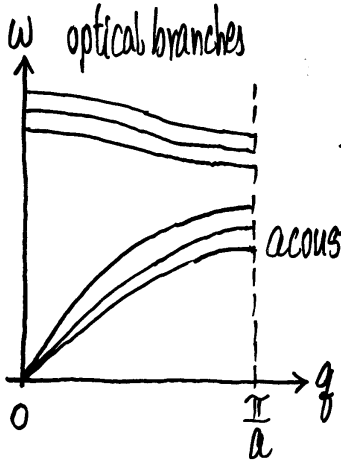
- Expect to have
  - acoustic and optical branches
  - at most 3 acoustic branches, since the whole system can move in 3 directions.

N primitive cells + 2 atoms/cell + 3 directions
⇒ 6N degrees of freedom

3 acoustic branches (1LA + 2TA) ⇒ 3N modes

∴ 3N modes should be optical branches

⇒ 3 optical branches (1LO + 2TO)



Schematic
1D diatomic chain

<u>Remark</u>:

- Some branches may overlap due to symmetry reasons (degenerate)

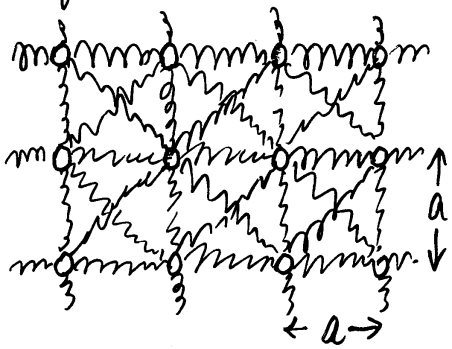
How about s atoms in basis? 3 acoustic branches (3N modes)
(3s-3) optical branches ((3s-3)N modes)
Total = 3sN modes

G. Lattice Vibrations in Higher Spatial Dimensions

Basically, all results can be carried over to 2D and 3D.

- Bloch's theorem ✓ (rely on periodicity)
- $q \to \vec{q}$ (lives in reciprocal space)
- $\vec{q} \in 1^{st}$ B.Z. ✓ (rely on $e^{i\vec{G}\cdot\vec{R}} = 1$)
- finite crystal with N primitive cells
  $\Rightarrow$ N allowed $\vec{q}$ in 1^{st} B.Z. ✓ (periodic B.C.)
- At most 3 acoustic branches ✓ (∵ can translate the solid in 3 directions), others are optical branches ✓ (rely on mode counting)
- Normal modes are independent of each other ✓
  (rely on only harmonic terms in potential energy)
- Using normal modes, each $\omega(\vec{q})$ characterizes an oscillator
  $\Rightarrow$ $3Ns$ independent harmonic oscillators ✓
  (s atoms/basis) (rely on harmonic approximation)

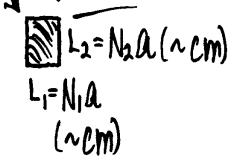
e.g. 2D crystal



Square lattice
1 atom in basis

$\vec{a}_1 = a\hat{x}$
$\vec{a}_2 = a\hat{y}$

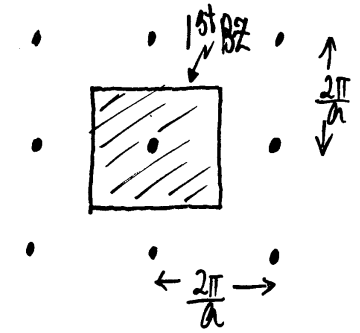
sample / zoom in



Size of sample: $\begin{cases} N_1 \text{ cells in } \vec{a}_1 \text{ direction} \\ N_2 \text{ cells in } \vec{a}_2 \text{ direction} \end{cases}$

$\therefore N = \#$ primitive cells in sample $= N_1 \cdot N_2$

Reciprocal lattice: $\vec{b}_1 = \frac{2\pi}{a}\hat{x}$, $\vec{b}_2 = \frac{2\pi}{a}\hat{y}$



Reciprocal lattice

Periodicity $\Rightarrow$ $\vec{q}$ can be chosen to be in 1^{st} B.Z.

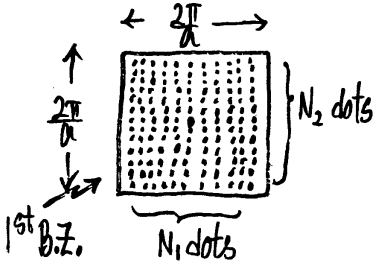
- Applying Periodic B.C. $\Rightarrow$ densely packed discrete allowed $\vec{q}$ in 1st B.Z.

$$q_x = \frac{2\pi}{N_1 a} p_x \quad , \quad p_x = \text{integers}$$

$$q_y = \frac{2\pi}{N_2 a} p_y \quad , \quad p_y = \text{integers}$$

$\therefore$ $\vec{q} = (q_x, q_y)$ (2D) a vector in reciprocal space

$\therefore$ There are $N_1 \cdot N_2 = N$ allowed $\vec{q}$'s in 1st B.Z.



Each dot represents a $\vec{q}$ (from (0,0) to the dot)

1 atom in basis

For each $\vec{q}$, 3 normal mode frequencies

1 LA + 2 TA

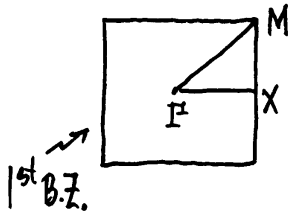
All $\vec{q}$'s in 1st B.Z.

$\Rightarrow$ 3N modes $\Rightarrow$ 3 branches (1 LA + 2 TA)

$N_1, N_2 \gg 1 \Rightarrow$ allowed $\vec{q}$'s are densely packed

To express $\omega(\vec{q})$, we need a 3D plot.

OR show $\omega(\vec{q})$ along some special directions in 1st B.Z.



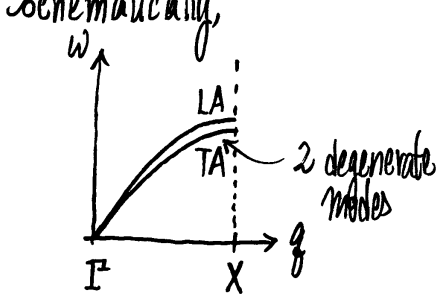
Γ- point : $\vec{q} = (0,0)$ "zone center"

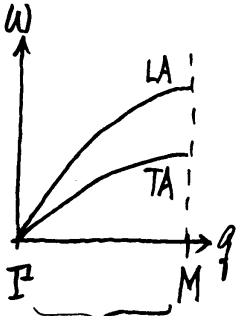
X- point : $\vec{q} = (\frac{\pi}{a}, 0)$ or equivalent

M- point : $\vec{q} = (\frac{\pi}{a}, \frac{\pi}{a})$ or equivalent

Typically, plot ω vs q for $\vec{q}$'s along $\Gamma \to X$, $\Gamma \to M$, $X \to M$, etc.

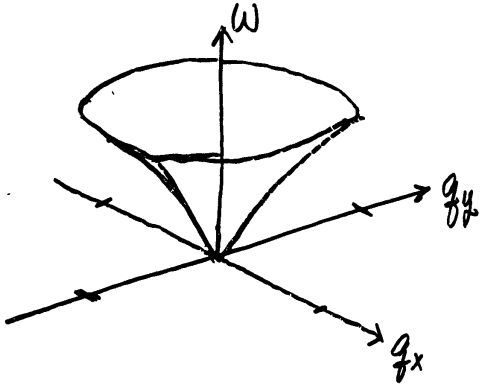
schematically,





longer than $\Gamma \to X$

Showing $\omega(\vec{q})$ or $\omega(q_x, q_y)$ in 3D plot, one branch will look like:



$\Gamma \to X$, $\Gamma \to M$, $X \to M$, etc

$\Rightarrow$ different cuts

But can't do this in 3D systems!

$\omega(q_x, q_y, q_z)$

3D crystals

- $\vec{q}$ lives in 3D reciprocal space
- $\vec{q} = (q_x, q_y, q_z)$ in 1st B.Z.
- N primitive cells in sample

  $\Rightarrow$ N allowed values of $\vec{q}$ in 1st B.Z.
- 3 acoustic branches, the rest are optical branches

  $\therefore$ s atoms/basis

  $\begin{cases} \text{3 acoustic branches (1LA + 2TA)} \\ \text{3(s-1) optical branches ((s-1)LO + 2(s-1)TO)} \end{cases}$

  $\therefore$ 3sN normal modes

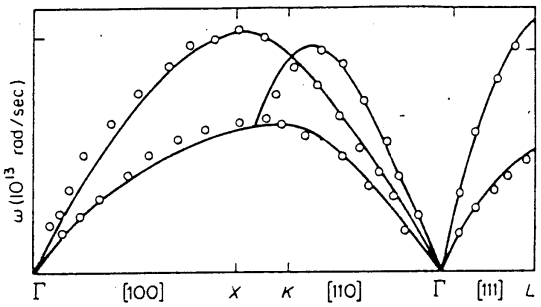
To show $\omega(\vec{q})$ or $\omega(q_x, q_y, q_z)$ [which needs a 4D plot], we usually display $\omega(\vec{q})$ along some lines in 1st B.Z.

e.g. Aluminum

Direct lattice: fcc lattice (monatomic, basis of 1 atom)

Note: ω typically goes $\sim 10^{13} s^{-1}$ (IR range)

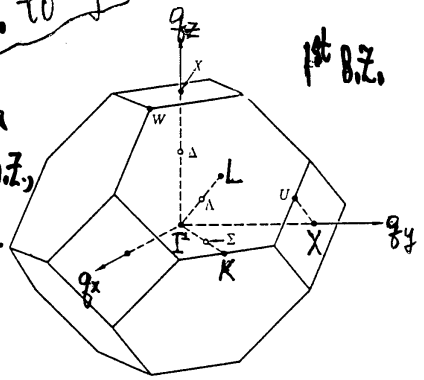
Aluminum
- direct: fcc
- reciprocal: bcc



Calculated (continuous curve) and measured (circles) phonon spectrum of aluminum.

1st B.Z. to fcc (also Wigner-Seitz cell of bcc)

Every $\vec{q}$ in 1st B.Z., 3 values of ω.



(a)

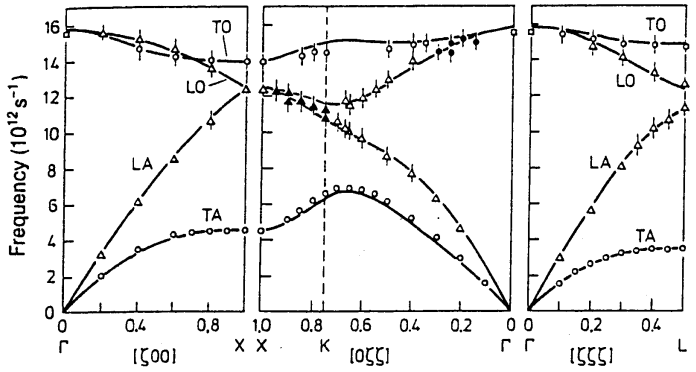
Standard labels of the symmetry points and axes of the Brillouin zones of the fcc lattices. The zone centers are Γ. In (a) the boundary point at $(2\pi/a)(100)$ is X; the boundary point at $(2\pi/a)(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ is L; the line Δ runs between Γ and X.

Remark: This is an important 1st B.Z. since most semiconductors are fcc in direct lattice.

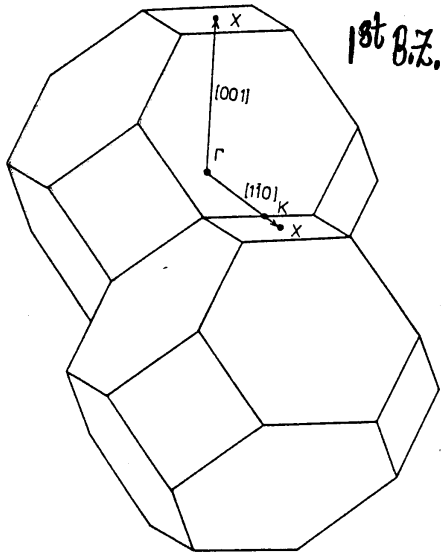
Note: In the plot, the x-axis is labeled [100] when we plot $\vec{q}$ along $\Gamma \to X$, this is because $\Gamma \to X$ is along the $\vec{G} = 1\vec{b}_1 + 0\cdot\vec{b}_2 + 0\cdot\vec{b}_3$ in reciprocal lattice and hence is perpendicular to [100] planes in direct lattice.

e.g. Silicon

Si (diamond structure) fcc + basis of 2 atoms



- Dispersion relation can be experimentally probed by inelastic scattering of neutrons.



1st B.Z.

Before neutron scattering is used, the consequences of $\omega(\vec{q})$ were tested by averaged contributions only, e.g. in T-dependence of heat capacity.