X. Lattice Vibrations

A. Normal modes

(oscillates along x-axis only, for simplicity)

Set up 3 equations of motion (Newton's second law)

- u_1, u_2, u_3 are displacements
- Key step : $u_i = u_{0i} e^{-i\omega t}$, $i = 1,2,3$

same ω $\underbrace{\text{(an unknown)}}_{\text{normal mode frequencies}}$

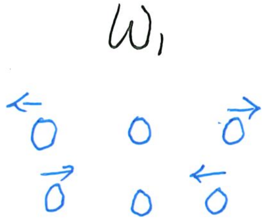
Plug in eqs. of motion ⇒ 3×3 matrix equation for u_{01}, u_{02}, u_{03} ["ω" enters through $\frac{d^2(\dots)}{dt^2}$]

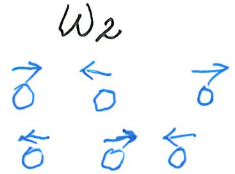
⇒ $\boxed{\text{3 normal mode frequencies}}$

why "3"? (do accounting)

ω = 0 mode

(translation mode/no relative motions)





"linear triatomic molecules"

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† This is a brief version of Balkanski and Wallis Ch.7

Key concepts

- Each normal mode involves motions of all atoms at the normal mode frequency
- Assuming Hooke's law applies, the normal modes are independent of each other

meaning: If there are only harmonic potential energy terms, the statement is correct.

When there are anharmonic terms, there are remaining coupling

SSP generalization

Anharmonic terms lead to some remaining coupling between phonons (phonon-phonon interaction)

meaning: Any oscillation $=$ Combinations (superposition) of normal modes

SSP generalization

Normal modes → $\omega(\vec{q})$

Each $\omega(\vec{q})$ is $\underbrace{\text{an oscillator}}_{\text{excitations}}$ ⇔ phonons $\left\{\begin{array}{l}\hbar\omega(\vec{q})\\ \hbar\vec{q}\end{array}\right.$

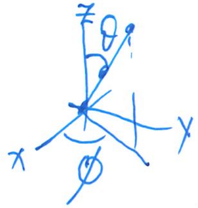
Phonons $\underbrace{\text{don't interact}}_{\text{independent of each other}}$ (harmonic terms only)

Linear Molecules in 3D

"3N-5" vibrational modes (N = # atoms) (our example: N=3)

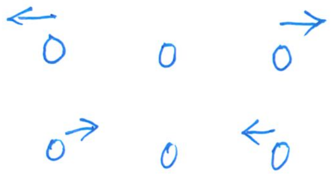
What is that "5"?

- Translational modes (in $\hat{x}$, $\hat{y}$, $\hat{z}$) ∴ three $\omega = 0$ modes (3D) [thus 3]
- Linear  its orientation (pointing to which direction) needs two angles

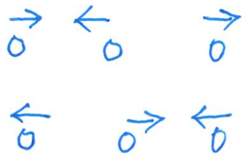


[thus 2]
(rotational modes)

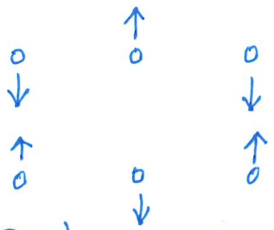
- Apart from 3 $\omega=0$ modes, there are (9-5) normal (vibrational) modes



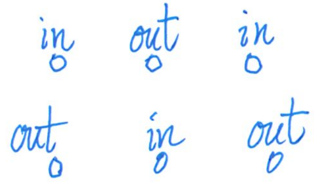
"symmetric stretching"
"longitudinal" (SSP)



"asymmetric stretching"
"longitudinal" (SSP)



Bending (up/down)
"transverse" (SSP)



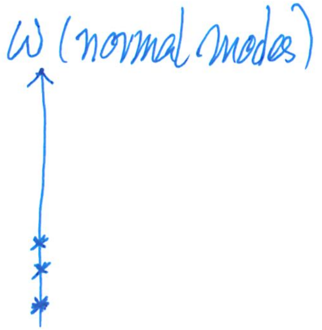
Bending (in/out of page)
"transverse" (SSP)

↖ same ω (degenerate) ↗

Summary -

springs ⇔ bonding ⇔ due to electron distribution ($|\psi|^2$) in molecule
(same idea works in solids)

- 
- must do this problem
- Along the line of atoms $\left\{\begin{array}{l}\left.\begin{array}{l}\text{asymmetric}\\ \text{symmetric}\end{array}\right\rangle \text{stretching}\\ \omega=0\end{array}\right.$



- $\underbrace{\text{Perpendicular}}_{\text{two directions}}$ to line of atoms $\left\{\begin{array}{l}\text{bending}\\ \omega=0\end{array}\right.$
- All these ideas carry over to "phonon dispersion relations" for solids
- Harmonic approximation: Normal modes are independent of each other
- Anharmonic terms: Remaining coupling
- For solids, we don't need to care about rotational Motions

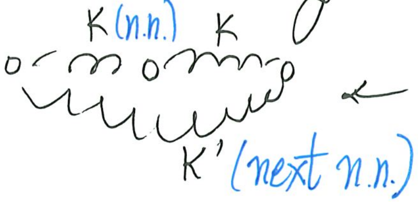
B. Monaatomic Linear Chain

equilibrium separation a

spring: due to solution of Band problem $(|\psi_0|^2)$

$$\underset{\substack{\uparrow \\ \text{"size" of 1D crystal}}}{L} = \underbrace{N_1}_{\substack{\uparrow \\ \#\text{ unit cells}}}\ \underbrace{a}_{\text{lattice constant}}$$

could have longer-range interaction



← Picture

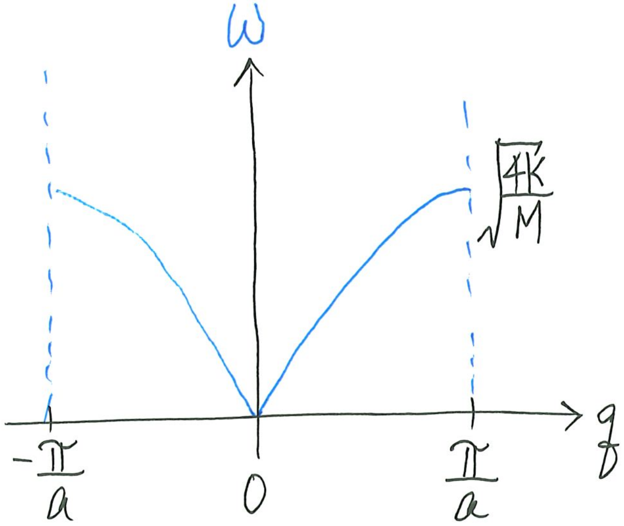
- N_1 eqs. of motion

$$\boxed{M\frac{d^2u_n}{dt^2} = K(u_{n+1} - 2u_n + u_{n-1})} \qquad (1)$$

- Periodicity ⇒ 1st B.Z. (N_1 k-values (called them q-values)) (∵ periodic B.C.)

$$\underset{\uparrow}{u_n} = A\,e^{iqx_n^0}e^{-i\omega t} \qquad (2)$$

- how the atom at unit cell "n" at x_n^0 moves
- $q \in$ 1st B.Z. [so each q-value is a separate problem]
- n.n. springs ⇒ $\omega(q) = \sqrt{\frac{4K}{M}}\left|\sin\left(\frac{qa}{2}\right)\right|$ (3) normal mode frequencies (longitudinal motions)



← N_1 allowed q-values →

- "Line" contains N_1 values of ω

∴ N_1 normal mode frequencies each labelled by q (q_x is it is in x-direction)

∴ $\boxed{\text{Exactly } N_1 \text{ normal modes in the dispersion relation } \omega(q)}$

It exhausted all possible normal modes (NO MORE!!)$^{+}$ if vibrations are restricted to along the chain.

$^{+}$ It is important conceptually. For $\hat{H}_0\psi = E\psi$ band problem, we get infinitely many bands (each $k \Rightarrow$ a $\infty \times \infty$ matrix problem $\Rightarrow$ infinite $\mathcal{E}$ for a k-value). Here, each q, Eq.(1) gives a 1×1 problem $\Rightarrow$ 1 value of ω.

Reason: All we need to solve are N_1 variables $[u_1, u_2, \cdots, u_{N_1}]$

In band problem, $\psi(\vec{r})$

$\vec{r}$ is infinitely many places in a unit cell!

$q \to 0$ modes:
$$\omega(q) \approx \sqrt{\frac{4K}{m}} \cdot \frac{qa}{2} = \sqrt{\frac{K}{m}}\, a \cdot q$$
$$= \sqrt{\frac{Ka}{\frac{m}{a}}} \cdot q \qquad (4)$$

speed of sound

i.e. $\boxed{\omega = v_s \cdot q}$

linear

long wavelength limit

Force required to increase separation from a to r $= K(r-a)$

$$\text{Force} = \text{elastic modulus} \times \text{Strain}$$
$$= C \cdot \frac{(r-a)}{a}$$

(q→0, long $\underbrace{\text{wavelength}}_{\gg a}$ motions ⇒ continuum description is Valid)

$\therefore \quad Ka = C$ (elastic modulus)

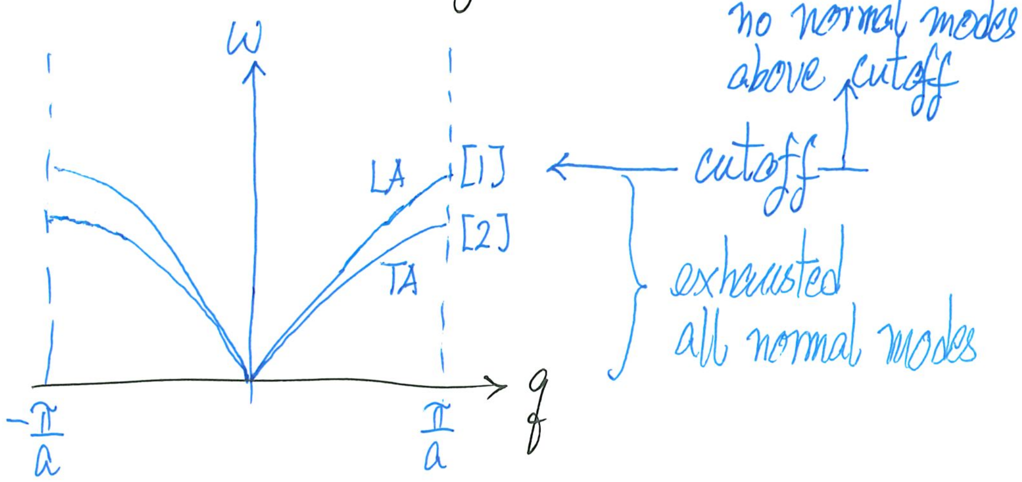
$\frac{m}{a} = \frac{\text{mass}}{\text{length}}$ (mass per unit length of a continuous chain)

$$\omega(q) = \sqrt{\frac{C}{\rho}} \cdot q = v_s \cdot q$$

as expected for a continuous chain (sound mode)

[This "branch" of $\omega(q)$ is called "Longitudinal Acoustic" branch (LA)]

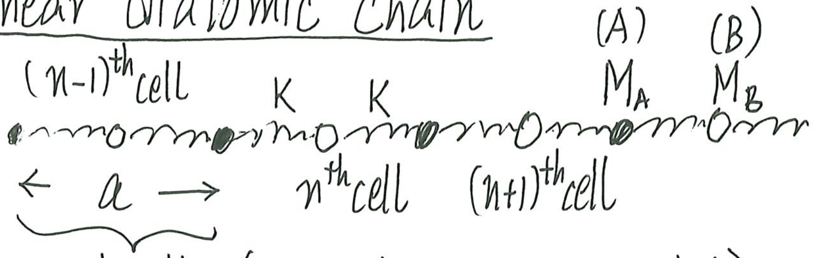
If we allow vibrations perpendicular to chain (though strictly speaking it is not a strictly 1D problem), we would have two degenerate "transverse acoustic" branches.



$$\text{There are } \underbrace{\text{3N normal modes}}_{\text{3 branches}}$$

[Each branch, N q-values in 1st B.Z.]

C. Linear diatomic chain



unit cell (N unit cells in crystal)

[relevant to Semiconductors (2 basis atoms)]

Accounting:

- 2N atoms
- Say, allow motions along chain

$$\Downarrow$$

expect 2N normal modes

For atom A in n^{th} cell

$$M_A \ddot{u}_n^A = -K(u_n^A - u_{n-1}^B) - K(u_n^A - u_n^B)$$

For atom B in n^{th} cell

$$M_B \ddot{u}_n^B = -K(u_n^B - u_n^A) - K(u_n^B - u_{n+1}^A)$$

(5) (Newton's law)

For normal modes:

$$u_n^A(t) = A\, e^{iqna} e^{-i\omega t}$$

$$u_n^B(t) = B\, e^{iqna} e^{-i\omega t}$$

(A and B are different because of two different atoms)

Eqs. of motion give
$$\begin{cases} -\omega^2 M_A A = -K(2A - Be^{iqa} - B) \\ -\omega^2 M_B B = -K(2B - A - Ae^{iqa}) \end{cases}$$

OR
$$\begin{pmatrix} \frac{2K}{M_A} - \omega^2 & -\frac{K}{M_A}(1+e^{iqa}) \\ -\frac{K}{M_B}(1+e^{iqa}) & \frac{2K}{M_B} - \omega^2 \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = 0 \qquad (6)$$

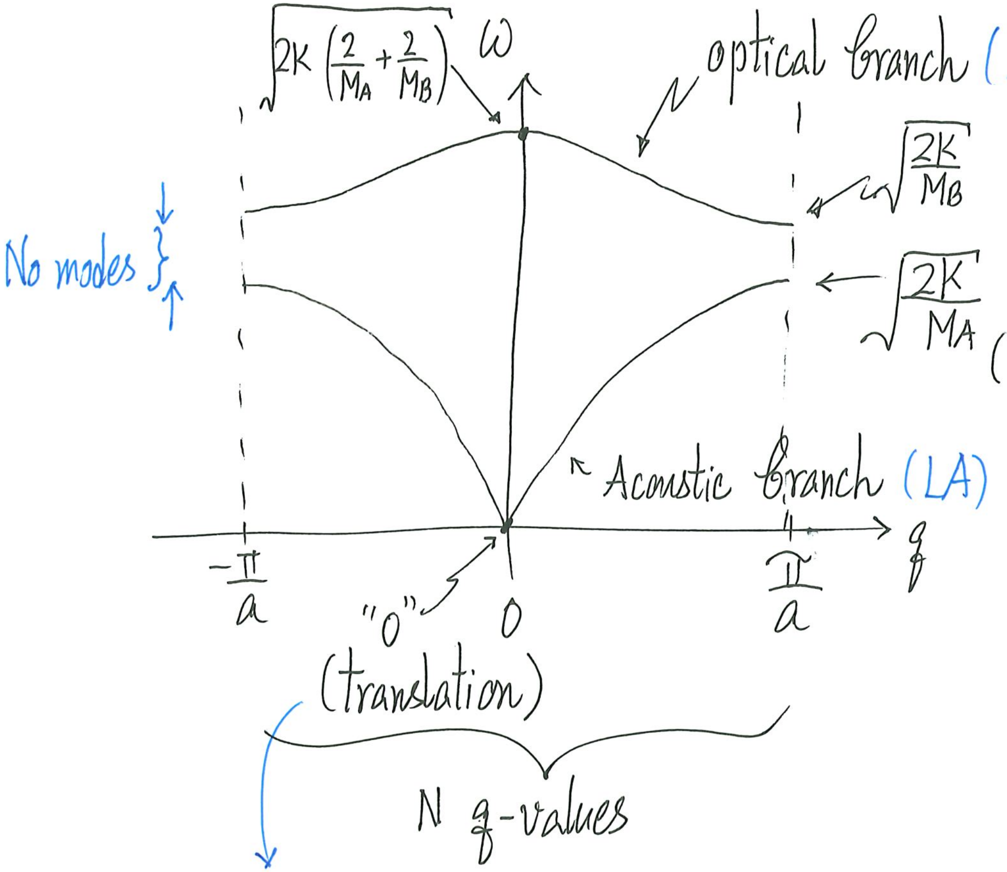
|Determinant| = 0 ⇒ quadratic eq. in ω^2

$$\Rightarrow \boxed{\omega^2(q) = \frac{K(M_A+M_B)}{M_A M_B} \pm \sqrt{K\left(\frac{M_A+M_B}{M_A M_B}\right)^2 - \frac{4}{M_A M_B}\sin^2\left(\frac{qa}{2}\right)}} \qquad (7)$$

- Each q, 2 values of ω
- N q-values in 1st B.Z. ⇒ $2N$ values of ω's

Accounting

- Each q gives 2x2 problem
- N q-values in 1st B.Z.
- $2N$ ω's (OK)



(assumed $M_B < M_A$) (only lighter atoms oscillate and heavier atoms at rest)

(only heavier atoms oscillate and lighter atoms at rest)

Total 2N modes

$A = B$ ($q = 0$ mode)

Acoustic Branch

As $q \to 0$, $\omega \cong \underbrace{a\sqrt{\frac{K}{M_A+M_B}}}_{v_s} \cdot q$

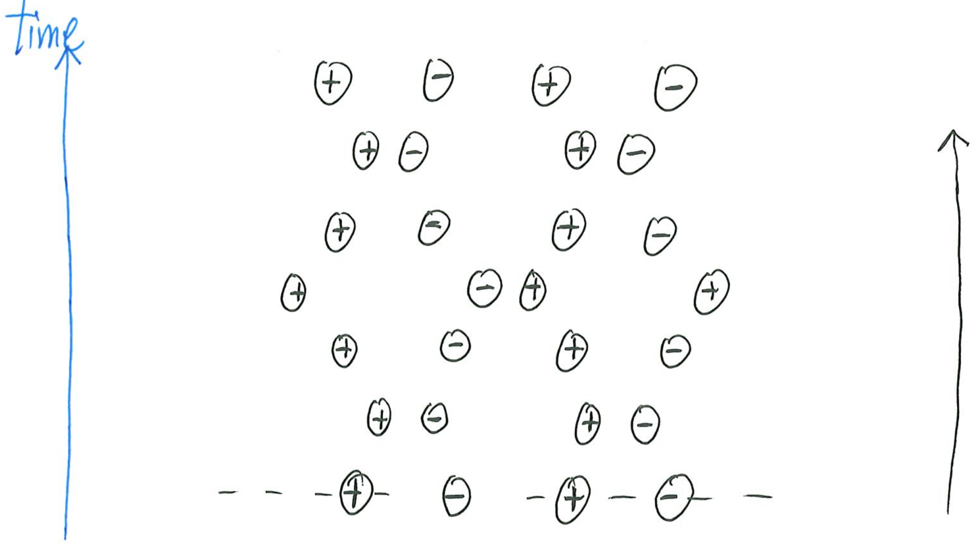
Optical Branch ($q = 0$)

- $\omega \neq 0$ $\left(\omega = \sqrt{2K\left(\frac{2}{M_A}+\frac{2}{M_B}\right)}\right)$
- $B = -\frac{M_A}{M_B} A$

oscillating in antiphase (center of mass at rest)

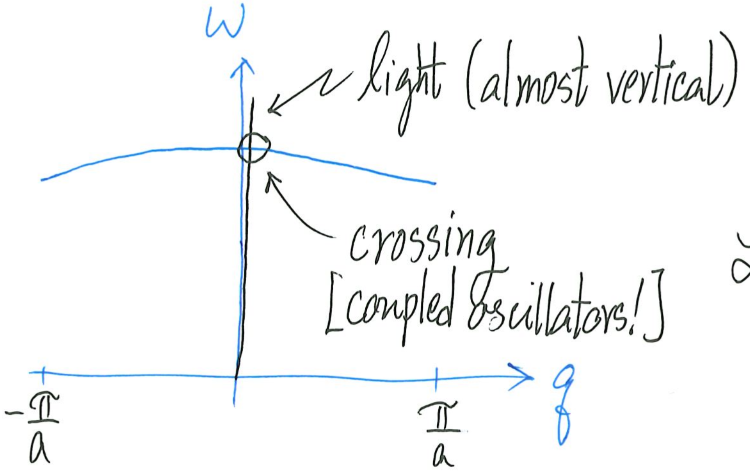
$q = 0$ mode of Optical branch

- If M_A and M_B are cation/anion (GaAs)



oscillating electric dipoles possible to couple with EM waves at frequency $\omega \sim \sqrt{\frac{2K}{\mu}}$

$$\frac{1}{\mu} = \frac{1}{M_A} + \frac{1}{M_B}$$



Light: $ck = \omega$
↑
slope of ω vs k very big!

D. What are the Springs and Spring Constants

- 3D + 1 atom per unit cell (each atom is labelled by $\vec{R}$)

$\vec{u}(\vec{R})$ = displacement of atom whose equilibrium position is at $\vec{R}$

$= \left(u_x(\vec{R}),\ u_y(\vec{R}),\ u_z(\vec{R})\right)$

Generally, potential energy V of the system is a function of positions of all N atoms

$$V = V(\vec{\mathcal{R}}_1, \vec{\mathcal{R}}_2, \cdots, \vec{\mathcal{R}}_N) = V(\{\vec{\mathcal{R}}_i\})$$

$$= V(\{\underset{\substack{\uparrow\\ \text{equilibrium}}}{\vec{R}_i} + \underset{\substack{\nwarrow\\ \text{displacement (from equilibrium)}}}{u(\vec{R}_i)}\})$$

$$= \underbrace{V(\{\vec{R}_i\})}_{\substack{\text{minimum}\\ \text{(all atoms at}\\ \text{preferred separations)}}} + \underset{\swarrow\ 0}{1^{st}\text{ order}} + \frac{1}{2}\sum_{\underset{\uparrow\,x,y,z}{\alpha},\,\underset{\uparrow\,x,y,z}{\beta}}\ \sum_{\vec{R}_i,\vec{R}_j} \underbrace{\frac{\partial^2 V}{\partial u_\alpha(\vec{R}_i)\,\partial u_\beta(\vec{R}_j)}}_{\Phi_{\alpha\beta}(\vec{R}_i|\vec{R}_j)} \cdot \overbrace{u_\alpha(\vec{R}_i)\,u_\beta(\vec{R}_j)}^{\text{harmonic terms}} + \underbrace{\text{Higher order term}}_{\text{anharmonic terms}}$$

Making connections: Born-Oppenheimer Approximation

In the electronic band problem, we assumed the ions/nuclei (the "atoms" in the present discussion) to sit in a periodic array labelled by $\{\vec{R}\}$.

We can imagine that even for a Bravais lattice, one can try the band calculations for many different lattice constants (e.g. $a = 1.3\,\text{Å}$, then $a = 1.4\,\text{Å}$, $1.5\,\text{Å}$, etc.) At the end, there is a preferred value of a that the electronic energy is lowest. This is the particular periodic structure the solid takes on, and then the atoms sit at $\{\vec{R}\}$. These positions $\{\vec{R}\}$ provide the potential energy (periodic) function

$$\underset{\substack{\uparrow \\ \text{electron's coordinates}}}{U(\vec{r})} = \sum_{\vec{R}_i} U_{\text{atomic}}(\vec{r} - \vec{R}_i)$$ in the band problem.

After solving the band problem, the electrons (forming bonds) provide the springs connecting the atoms. Here

$V(\{\vec{R}_i\})$ is the total potential energy when all atoms at sitting at $\{\vec{R}_i\}$.

When atoms deviate from their equilibrium positions, $V(\{\vec{R}_i\})$ is higher than $V(\{\vec{R}_i\})$.

This is the spirit of the Born-Oppenheimer approximation

- Let atoms be fixed for electronic part of problem
- Electrons create potential energy profile for atoms' vibrations

$$V \cong V(\{\vec{R}_i\}) + \frac{1}{2}\sum_{\alpha,\beta}\sum_{\vec{R}_i,\vec{R}_j} \Phi_{\alpha\beta}(\vec{R}_i|\vec{R}_j)\, u_\alpha(\vec{R}_i)\, u_\beta(\vec{R}_j) \qquad (8)$$

(this is the harmonic approximation)

Physical Meaning

$$-\sum_{\beta=x,y,z} \underbrace{\Phi_{\alpha\beta}(\vec{R}_i|\vec{R}_j)}_{\text{like spring constants}}\, u_\beta(\vec{R}_j) =$$

α^{th} component of force on atom at $\vec{R}_i$ due to displacement $\vec{u}(\vec{R}_j)$ $(u_x(\vec{R}_j), u_y(\vec{R}_j), u_z(\vec{R}_j))$ of atom at $\vec{R}_j$ (9)

($\vec{R}_i$ and $\vec{R}_j$ can be apart, not restricted to nearest neighbors)

(2^{nd} derivatives of $V(\{\vec{a}_i\})$ about minimum)

General Equation of motion:

$$m\frac{d^2 u_\alpha(\vec{R}'')}{dt^2} = -\underbrace{\sum_{\vec{R}'}}\sum_{\beta=x,y,z} \Phi_{\alpha\beta}(\vec{R}''|\vec{R}')\, u_\beta(\vec{R}') \qquad (10)$$

due to α^{th} component of forces from all $\vec{R}'$ (in general)

Normal mode analysis: $\vec{u}(\vec{R}'') = \vec{A}\, e^{i\vec{q}\cdot\vec{R}''} e^{-i\omega t}$ (11) ($q \in 1^{st}$ B.Z.)

amplitude [one atom only in each cell]

all atoms (same ω)

Equation of motion gives: $-m\omega^2 A_\alpha e^{i\vec{q}\cdot\vec{R}''} = -\sum_{\vec{R}'}\sum_{\beta} \Phi_{\alpha\beta}(\vec{R}''|\vec{R}')\, A_\beta\, e^{i\vec{q}\cdot\vec{R}'}$

$$\Rightarrow \sum_{\beta} \underbrace{\left[\frac{1}{m}\sum_{\vec{R}'} \Phi_{\alpha\beta}(\vec{R}''|\vec{R}')\, e^{-i\vec{q}\cdot(\vec{R}''-\vec{R}')}\right]}_{\equiv D_{\alpha\beta}(\vec{q})} A_\beta = \omega^2 A_\alpha$$

$$\Rightarrow \sum_{\beta} D_{\alpha\beta}(\vec{q}) A_\beta = \omega^2 A_\alpha \quad \text{OR} \quad \begin{pmatrix} D_{xx}(\vec{q}) & D_{xy}(\vec{q}) & D_{xz}(\vec{q}) \\ D_{yx}(\vec{q}) & D_{yy}(\vec{q}) & D_{yz}(\vec{q}) \\ D_{zx}(\vec{q}) & D_{zy}(\vec{q}) & D_{zz}(\vec{q}) \end{pmatrix} \begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix} = \omega^2 \begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix} \quad (12)$$

$\overleftrightarrow{D} \equiv$ Dynamical Matrix

Problem is to find eigenvalues $\omega^2(\vec{q})$ and eigenvectors of $\overleftrightarrow{D}$

Note that $$D_{\alpha\beta}(\vec{q}) = \frac{1}{m}\sum_{\vec{R}'}\Phi_{\alpha\beta}(\vec{R}''|\vec{R}')\,e^{i\vec{q}\cdot(\vec{R}'-\vec{R}'')}$$
$$= \frac{1}{m}\sum_{\vec{R}}\Phi_{\alpha\beta}(\vec{R}''|\vec{R}''+\vec{R})\,e^{i\vec{q}\cdot\vec{R}}$$
$$= \frac{1}{m}\sum_{\vec{R}}\Phi_{\alpha\beta}(\vec{0}|\vec{R})\,e^{i\vec{q}\cdot\vec{R}}$$

as interaction should depend only on separation between atoms (not exactly where the two atoms are) due to periodicity

$\overleftrightarrow{D}$ is 3×3 (for each $\vec{q} \in 1^{st}$ B.Z)

$\Rightarrow$ 3N eigenvalues $\Rightarrow$ 3 acoustic branches

Fitting experimental data with calculations (which require $\Phi_{\alpha\beta}$ and thus V) is a way to extract information about Φ and V (e.g. needs interaction beyond n.n.) and thus the interatomic forces.

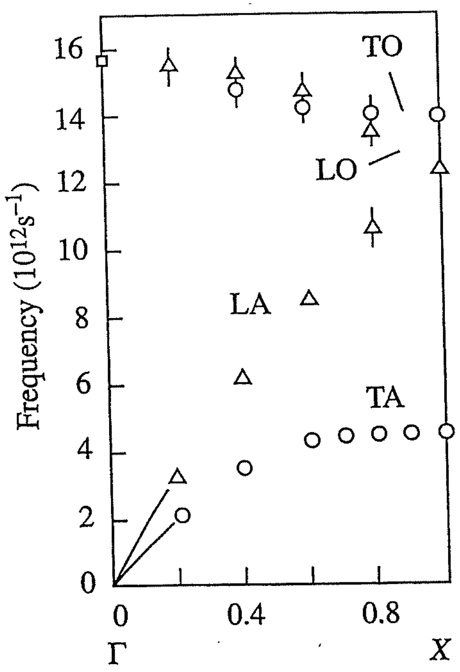
E. Higher Dimensions

- 3D + 1 atom per unit cell ⇒ $\underbrace{3N \text{ modes}}_{3 \text{ acoustic branches}}$ [N unit cells]

- 3D + 2 atoms per unit cell ⇒ $\underbrace{6N \text{ modes}}_{3 \text{ acoustic branches} + 3 \text{ optical branches}}$

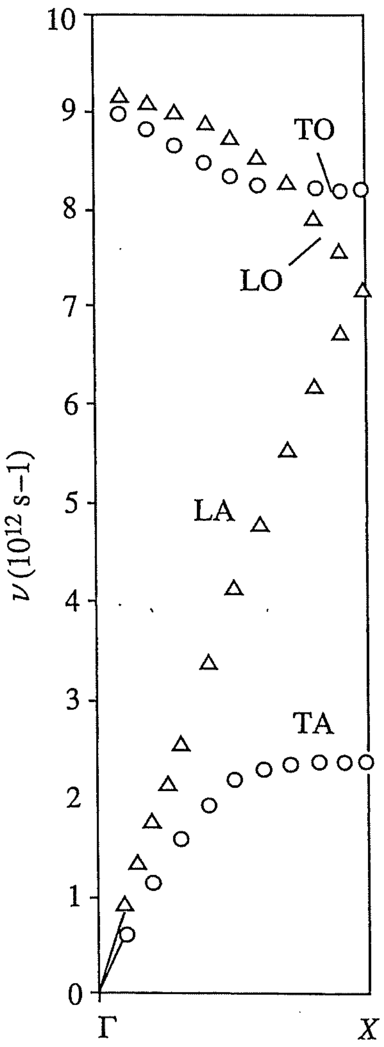
- 3D + 3 atoms per unit cell ⇒ $\underbrace{9N \text{ modes}}_{\underbrace{3 \text{ acoustic branches}}_{\text{at most 3 acoustic branches (at most 3 translation modes)}} + 6 \text{ optical branches}}$

etc.



← Very flat

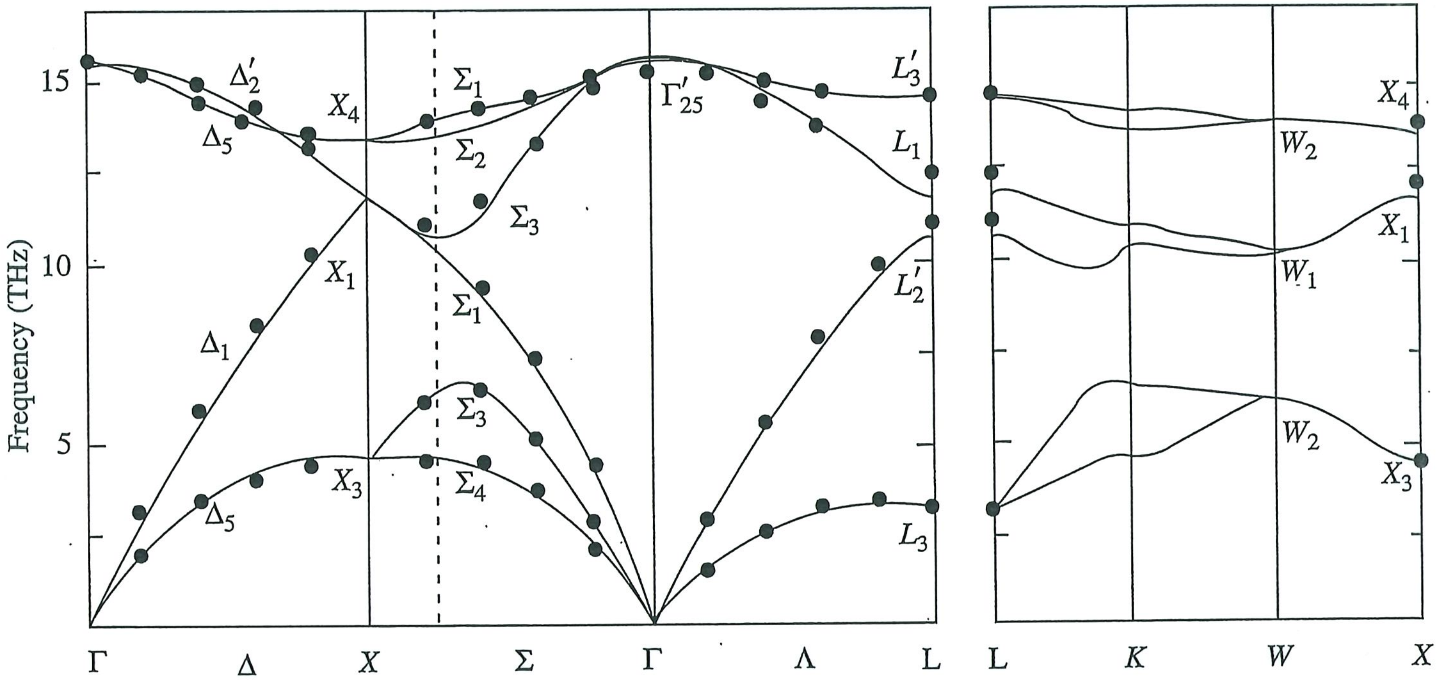
Phonon spectrum for Si in the [100] direction



← Very flat (degenerate)

Phonon spectrum for Ge in the [100] direction

Note $\omega \sim 10^{13}\ s^{-1}$ range (IR range)



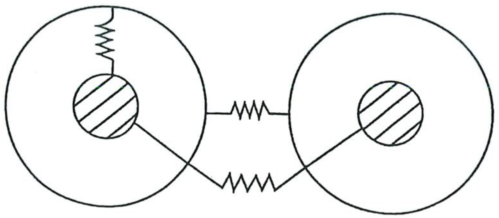
3 optical branches

3 acoustic branches

Silicon • exp'tal data lines: theory

flat acoustic branches needs more complicated model

needs interactions (springs) beyond n.n.'s



Schematic representation of shell model interactions.