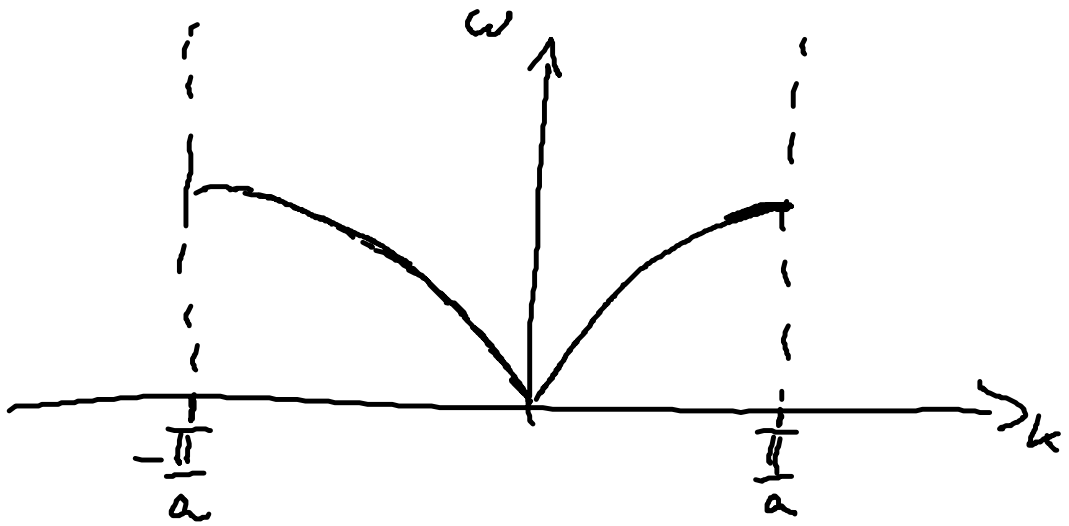
General case:

$$\omega^2 c_{\alpha,\mu} = \sum_{\beta\nu} D^{\beta\nu}_{\alpha\mu}(\underline{k})\, c_{\beta\nu}$$

... → linear chain (1at)

$$\omega(k) = 2\sqrt{\frac{f}{M}}\left|\sin\left(\frac{ka}{2}\right)\right|$$



$k \to 0$: $\omega \to a \cdot \sqrt{\frac{f}{M}} \cdot k$

"group velocity"

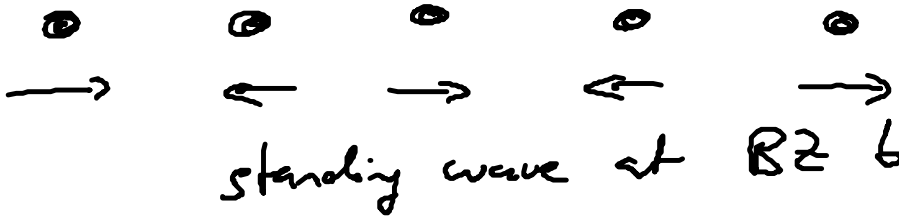
$$S_n = \frac{1}{\sqrt{M}}\, c \cdot e^{i(kan - v_g t)}$$

• traveling wave ⟶ sound wave!

"acoustic branch"

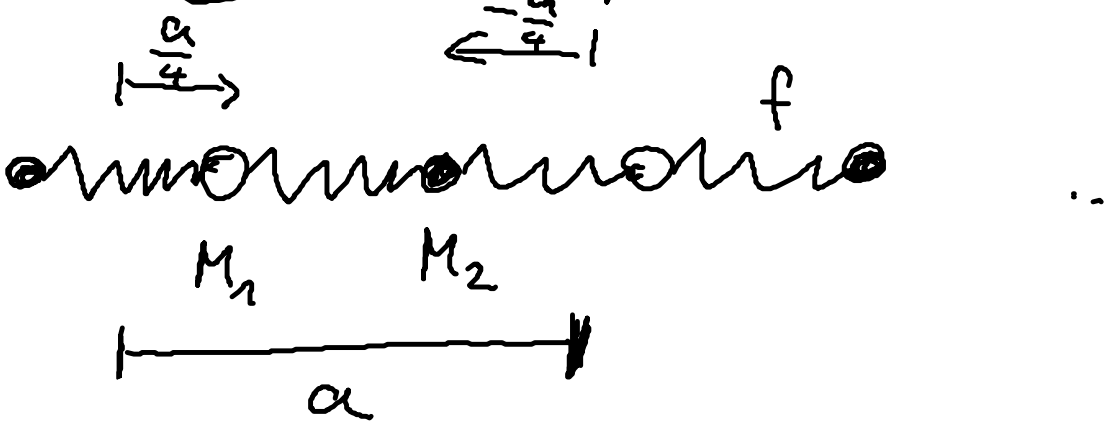
Real crystal: every crystal should have 3 acoustic branches!

$$k \to \frac{\pi}{a}: \quad s_n = \frac{1}{\sqrt{M}}\, c\, \underbrace{e^{i\pi n}}_{\pm 1 \text{ for } n \text{ even, odd}}\, e^{-i\omega t}$$



standing wave at BZ boundary.

What about: Two atomic species



$$M_1 \ddot{s}_n^{(1)} = -f\left(2s_n^{(1)} - s_n^{(2)} - s_{n-1}^{(2)}\right)$$

$$M_2 \ddot{s}_n^{(2)} = -f\left(2s_n^{(2)} - s_{n+1}^{(1)} - s_n^{(1)}\right)$$

Wave ansatz: $s_n^{(1)} = \frac{1}{\sqrt{M_1}} c_1 e^{i\left(k\left(n-\frac{1}{4}\right)a - \omega t\right)}$

$s_n^{(2)} = \frac{1}{\sqrt{M_2}} c_2 e^{i\left(k\left(n+\frac{1}{4}\right)a - \omega t\right)}$

$$\Rightarrow \quad -\omega^2 c_1 = -\frac{2f}{M_1} c_1 + \frac{2f}{\sqrt{M_1 M_2}} c_2 \cos\frac{ka}{2}$$

$$-\omega^2 c_2 = +\frac{2f}{\sqrt{M_1 M_2}} \cos\frac{ka}{2} - \frac{2f}{M_2} c_2$$

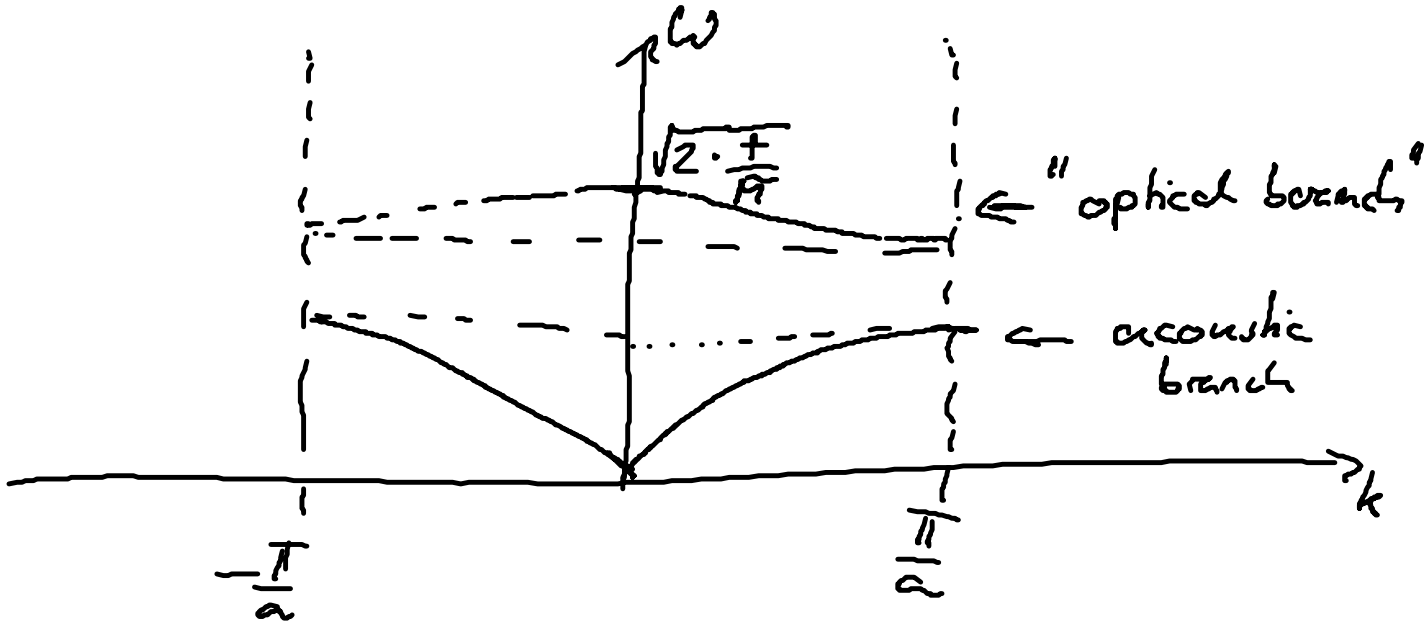
or:

$$\begin{vmatrix} \frac{2f}{M_1} - \omega^2 & \frac{2f}{\sqrt{M_1 M_2}} \cos\frac{ka}{2} \\ \frac{2f}{\sqrt{M_1 M_2}} \cos\frac{ka}{2} & \frac{2f}{M_2} - \omega^2 \end{vmatrix} = 0$$

quadratic equation $\Rightarrow$ two solutions

$$\Rightarrow \quad \omega_{\pm}^2 = f \cdot \left(\frac{1}{M_1} + \frac{1}{M_2}\right) \pm f \sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^2 - \frac{4}{M_1 M_2} \sin^2\frac{ka}{2}}$$

$$\frac{1}{M_1} + \frac{1}{M_2} =: \frac{1}{\tilde{M}} \quad \text{"reduced mass"}$$



BZ boundary: $M_1 < M_2$

$$\omega_- = \sqrt{\frac{2f}{M_2}}$$

$$\omega_+ = \sqrt{\frac{2f}{M_1}}$$

} gap between both branches

if $M_1 = M_2$ → gap closes

monatomic chain would be recovered but BZ then $\frac{2\pi}{a}$ –

acoustic branch:

→ atoms in unit cell vibrate in phase

optical branch:

M_1, M_2 vibrate against each other

Phonon band structure in 3D

Still $\det \left| \hat{D}(\underline{k}) - \omega^2 \underline{\underline{1}} \right| = 0$

$\hat{D}(\underline{k})$ ↑ dynamical matrix

In practice: Dynamical matrix from Hessian of $V^{BO}(\{\underline{R}_I\})$:

$$\underline{\underline{\Phi}}^{\beta\nu}_{\alpha\mu}(n - n')$$

need Hessian:

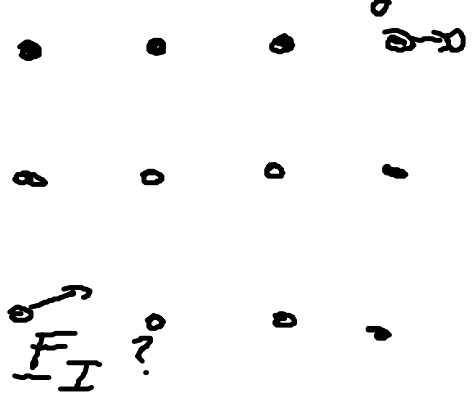
- between all atoms α, β in unit cell
- for sufficiently large $n - n'$ ≡ unit cell distance

"Modern" theory: DFT – LDA
– GGA

a) "linear response"
calculating the Hessian directly by derivative of $E_{DFT}[n]$

b) Finite differences
(frozen phonons)

calculate numerically
Force on atom I
if we displace atom J



$$\Phi_{IJ} = \frac{F_I(s_J)}{s_J}$$

restores discrete k points

$$n - n' = 1, 2, 3, \ldots$$
$$\frac{\Pi}{2a} \quad \frac{\Pi}{3a} \quad \frac{\Pi}{4a} \quad \ldots$$

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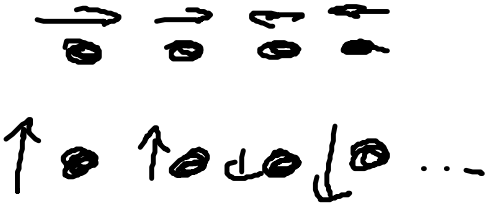
examples: 3D, monatomic

- 3 acoustic branches
  - 1 "longitudinal"
  - 2 "transversal"



- at BZ boundary, derivatives are 0.

3D, diatomic case

- 3 acoustic branches
- $3r - 3 = 3$ optical branches ($r = 2$)
- $M_1 = M_2$ (Si)
  → optical, acoustic branches overlap
- $M_1 \neq M_2$ (Sb: Al large ratio)
  ⇒ clearly separated branches

Energy scales: $\omega \sim \frac{1}{\sqrt{M}}$

Rh: 30 meV $\sim kT$

lighter elements $\sim$ 80, 100 meV?

but always $\sim kT$ at RT

Quantum theory of the harmonic crystal

Atoms & electrons: quantum mech particles

but so far: classical theory for $\omega(\underline{k})$

ok ??

all we need for $\omega(k)$ is to diagonalize Hamiltonian given by $V^{BO}(\{R_I\})$

ok as long as BO approx holds

But qm becomes important as soon as individual excitations or their statistics.

Finding a good quantum description:

Consider 1D harmonic oscillator (no periodicity!)

$$H_{1D} = T + V = \frac{p^2}{2m} + \frac{m\omega^2}{2} q^2$$

$$f = m\omega^2$$

QM: $\quad p = -i\hbar \frac{\partial}{\partial q}$

$$[p, q] = i\hbar$$

Define:

"lowering operator": $\quad a = \sqrt{\frac{m\omega}{2\hbar}}\, q + i \sqrt{\frac{1}{2\hbar m\omega}}\, p$

"raising operator": $a^+ =$ – " – – i · – " –

(ladder operators)

can show $[a, a^+] = 1$

$$H_{1D} = \hbar\omega \left(a^+ a + \frac{1}{2} \right)$$

(proof: just insert and calculate)

H_{1D} has eigenstates

$|0\rangle, |1\rangle, |2\rangle$

with eigenvalues: $E_n = \langle n | H_{1D} | n \rangle$

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

"n vibrations" excited

zero point energy

Could prove this only using ladder operators

→ QM textbooks (Cohen-Tannoudji)

$$a^+ |n\rangle = (n+1)^{1/2} |n+1\rangle$$

$$a |n\rangle = n^{1/2} |n-1\rangle$$

$$a |0\rangle = 0$$

a^+ "creation" operator

a "annihilation" operator

3D harmonic oscillator:

(monatomic for simplicity)

$$H = \sum_{I=1}^{M} \frac{P_I^2}{2M_I} + \underbrace{V^{BO}\left(\{\underline{R}_I^0\}\right)}_{\text{constant}} + \frac{1}{2} \sum_{I,J}^{M,M} \sum_{\mu,\nu}^{3,3} s_{I\mu}\, \bar{\Phi}_{\mu\nu}(\underline{R}_I \underline{R}_J)\, s_{J\nu}$$

transform to diagonal form:

(eigenmodes $s_I(\underline{k})$)

$$H_{vib} = \underbrace{\sum_{i=1}^{3}}_{\text{monatomic}} \sum_{\underline{k}} \frac{P_{(i)}^2(\underline{k})}{2M} + \frac{1}{2} \sum_{i=1}^{3} \sum_{\underline{k}} \omega(\underline{k}) \left| s^{(i)}(\underline{k}) \right|^2$$