

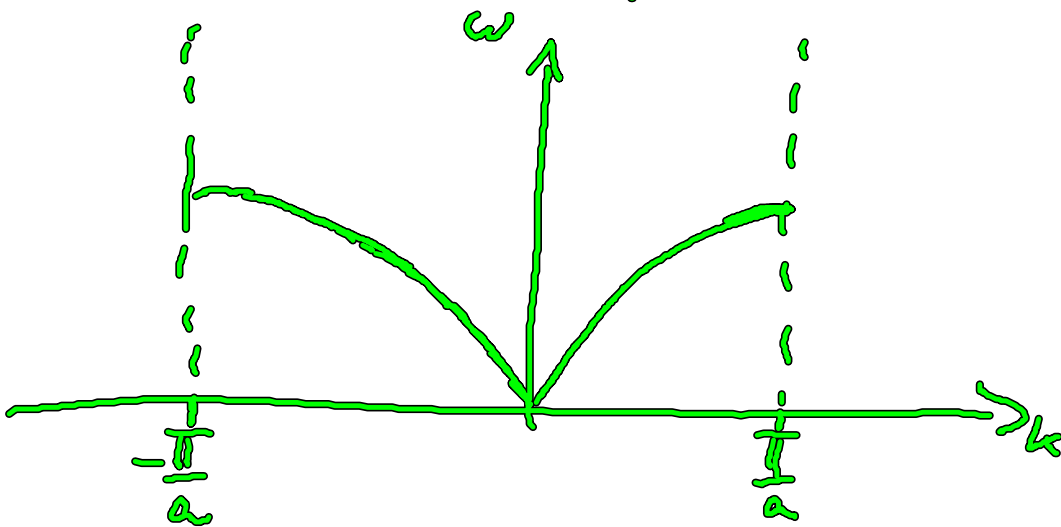
General case:

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

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...  $\rightarrow$  linear chain (lat)

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



$$k \rightarrow 0 : \omega \rightarrow \underbrace{a \cdot \sqrt{\frac{F}{M}}}_{\text{"group velocity"}} \cdot k$$

$$S_n = \frac{1}{\sqrt{M}} c \cdot e^{i(kan - \underbrace{\omega t}_{\uparrow})}$$

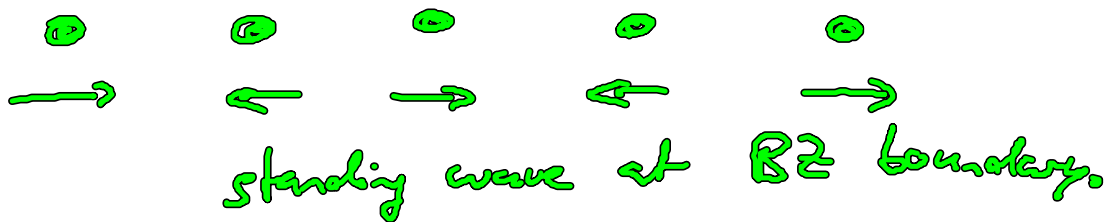
• traveling wave  $\rightarrow$  sound wave!

"acoustic branch"

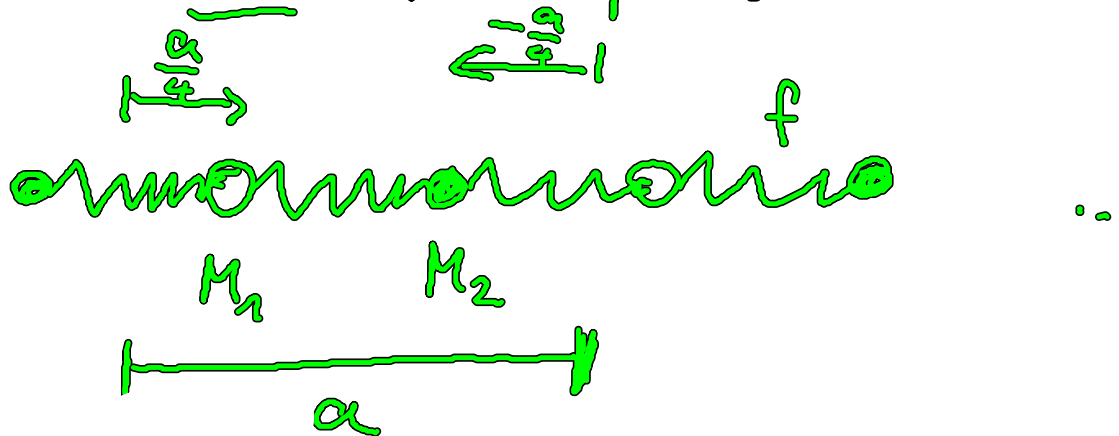
Real crystal: every crystal should have 3 acoustic branches!

$$k \rightarrow \frac{\pi}{a} : s_n = \frac{1}{\sqrt{M}} c \underbrace{e^{i\pi n}}_{\pm 1} e^{-iat}$$

for n even, odd



What about: Two atomic species



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

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

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

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

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

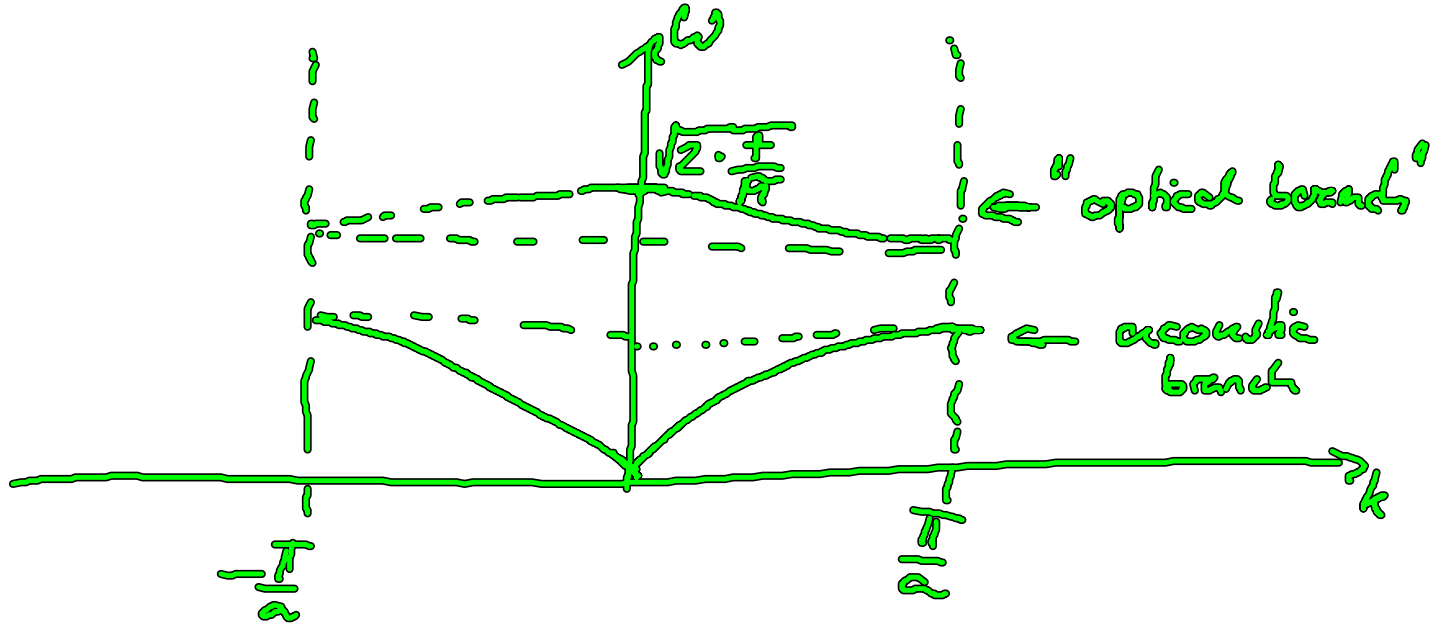
$$-\omega^2 c_2 = +\frac{2f}{\sqrt{M_1 M_2}} c_1 \cos \frac{ka}{2} - \frac{2f}{M_2} c_2$$

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

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

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



BZ boundary:  $M_1 < M_2$

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

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

} gap between both branches

if  $M_1 = M_2 \rightarrow$  gap closes

monatomic chain

would be recovered

but BZ then  $\frac{2\pi}{a}$  -

acoustic branch:

$\rightarrow$  atoms in unit cell vibrate in phase

optical branch:

$M_1, M_2$  vibrate against each other



## Phonon band structure in 3D

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

↑  
dynamical  
matrix

In practice : Dynamical matrix

from Hessian of  $V^{\text{Bo}}(\{\underline{R}_I\}) :$

$$\Phi_{\alpha\mu}^{\beta\nu} (n-n')$$

need Hessian :

- between all atoms  $\alpha, \beta$  in unit cell
- for sufficiently large  $n - n'$   
≡ unit cell distance

"Modern" theory : DFT-LDA  
- GGA

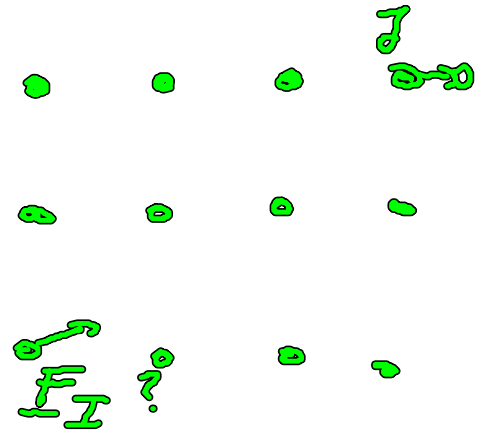
a) "linear response"  
 calculating the Hessian directly by derivatives  
 of  $E_{TOT} [u]$

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

$$h - h' = 1, 2, 3, \dots$$

$$\frac{\pi}{2a}, \frac{\pi}{3a}, \frac{\pi}{4a}, \dots$$

examples: 3D, monatomic

- 3 acoustic branches

- 1 "longitudinal"



- 2 "transverse"



- 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  $\sim kT$

light 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  $\omega(k)$

ok ??  
∴

all we need for  $\omega(\underline{k})$  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!)

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

$$f = m\omega^2$$

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

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

Define:

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



"raising operator":  $a^\dagger = -\frac{1}{i} \frac{d}{dx} - x$   
(ladder operators)

can show  $[a, a^\dagger] = 1$

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

(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)

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

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

$$a |0\rangle = 0$$

$a^\dagger$  "creation" operator

$\alpha$  "annihilation" operator

3D harmonic oscillator:

(monatomic for simplicity)

$$H = \sum_{I=1}^3 \frac{P_I^2}{2M_I} + \underbrace{V^{BO}(\{\underline{R}_I\})}_{\text{constant}} + \frac{1}{2} \sum_{I,J} \sum_{\mu,\nu} \overset{3,3}{\underline{h}_{IJ}} \xi_{I\mu} \overline{\Phi_{J\nu}}(\underline{R}_I, \underline{R}_J) \xi_{J\nu}$$

transform to diagonal form:  
(eigenmodes  $\xi_I(\underline{k})$ )

$$H_{\text{vib}} = \underbrace{\sum_{i=1}^3}_{\text{monatomic}} \sum_{\underline{k}} \frac{P_{i1}^2(\underline{k})}{2M} + \frac{1}{2} \sum_{i=1}^3 \sum_{\underline{k}} \omega(\underline{k}) |s^{(i)}(\underline{k})|^2$$