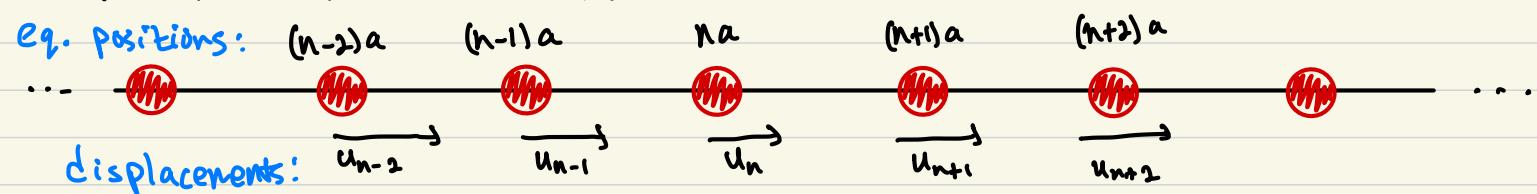


Lattice dynamics of crystals (G and P chapter 1x)

- Previously, we have been focused on the electronic system, taking the nuclei as fixed
- But the nuclei are always dynamic, even at 0 K due to zero-point motion
- To understand the implications of these dynamics we need to understand small vibrations of nuclei, which follow the normal modes of the crystal
- We begin with the simplest case: Dynamics of a 1D monatomic chain:



* N atoms of mass M , u_n is longitudinal displacement of n^{th} atom from equilibrium position $t_n = na$

* Ground-state energy with fixed (possibly displaced) nuclei positions $R_n = na + u_n$ is $E_0(\{R_n\})$

- Under the adiabatic approximation (i.e., Born-Oppenheimer approx), $E_0(\{u_n\})$ is given by solving the electron-nuclear system at fixed nuclear configuration

* Assume also that forces on nuclei just depend on u_n :

$$F_i = - \frac{\partial E_0(\{u_n\})}{\partial u_i}$$

↓ force on nuclei i

* To treat small u_n , we expand E_0 around equilibrium ($u_n=0$):

$$\begin{aligned} E_0(\{u_n\}) &= E_0(0) + \frac{1}{2} \sum_{n,n'} \left. \frac{\partial^2 E_0}{\partial u_n \partial u_{n'}} \right|_0 u_n u_{n'} \\ &\quad + \frac{1}{3!} \sum_{n,n',n''} \left. \frac{\partial^3 E_0}{\partial u_n \partial u_{n'} \partial u_{n''}} \right|_0 u_n u_{n'} u_{n''} + \dots \end{aligned}$$

- No linear term since $\frac{\partial E_0}{\partial u_n} \Big|_0 = 0$ which is the definition of equilibrium

- We make the "harmonic approximation," truncate at second order derivative:

$$E_0^{\text{harm}}(\{u_n\}) = E_0(0) + \frac{1}{2} \sum_{nn'} D_{nn'} u_n u_{n'}, \quad D_{nn'} = \frac{\partial^2 E_0}{\partial u_n \partial u_{n'}} \Big|_0$$

↑ "force constant matrix"

proportionality coeff between force and displacement

- $F_n = -\frac{\partial E_0^{\text{harm}}}{\partial u_n} = -\sum_{n'} D_{nn'} u_{n'}$

- Symmetries of D :

$$D_{nn'} = D_{n'n} \quad (\text{from partial derivative})$$

$$D_{nn'} = D_{mm'} \quad \text{if} \quad t_n - t_{n'} = t_m - t_{m'} \quad (\text{translational symmetry})$$

$$\sum_n D_{nn'} = 0 \quad (\text{Forces vanish when all atoms are moved rigidly})$$

- Equation of motion for nuclei n :

$$M \ddot{u}_n = -\sum_{n'} D_{nn'} u_{n'}$$

↑ second time derivative, i.e., acceleration

nuclear mass

- We would like to solve the set of N coupled differential equations for $u_n(t)$.

↑ periodic in space

$$\text{Ansatz for solution: } u_n(t) = A e^{i(q_n a - \omega t)}$$

↑ periodic in time

- Plug in to EOM:

$$-M \omega^2 A e^{i(q_n a - \omega t)} = -\sum_{n'} D_{nn'} A e^{i(q_{n'} a - \omega t)}$$

Fourier transform of $D_{nn'}$

$$M \omega^2 = \sum_{n'} D_{nn'} \bar{e}^{i q (n a - n' a)} = D(q)$$

Note, does not depend on specific value of n because of translational symmetry

- Equation $M\omega^2(q) = D(q)$ gives dispersion relation for frequencies ω
- As with electron wavevector, since u_n is not affected by charges in q of $2\pi/a$, independent values of q are confined to $-\pi/a \leq q \leq \pi/a$
- Under Born-Von Karman boundary conditions, discrete q in BZ with values $m(2\pi/Na)$

* Now consider case of just nearest neighbor interactions:

$$D_{nn} = 2C, \quad D_{n\pm 1} = -C, \quad \text{all other elements are zero}$$

- Take $E_0(0) = 0$, then:

$$\begin{aligned} E_0^{\text{harm}} &= \frac{1}{2} C \sum_n (2u_n^2 - u_n u_{n+1} - u_n u_{n-1}) \\ &= \frac{1}{2} C \left[\sum_n u_n^2 + \sum_n u_{n+1}^2 - \sum_n u_n u_{n+1} - \sum_n u_{n+1} u_n \right] \\ &= \frac{1}{2} C \sum_n (u_n - u_{n+1})^2 \end{aligned}$$

- Classical EOM:

$$m \ddot{u}_n = -C(2u_n - u_{n+1} - u_{n-1})$$

look for solutions of the form $A e^{i(qna - \omega t)}$:

$$\begin{aligned} -M\omega^2 A e^{i(qna - \omega t)} &= -AC \left[2e^{i(qna - \omega t)} - e^{i(qna + qa - \omega t)} - e^{i(qna - qa - \omega t)} \right] \\ \Rightarrow M\omega^2 &= C \left[2 - e^{-iqa} - e^{iqa} \right] = C \left[2 - 2 \cos(qa) \right] = 2C \left[1 - \cos(qa) \right] \end{aligned}$$

use half-angle formula: $2 \sin^2(\frac{x}{2}) = 1 - \cos(x)$

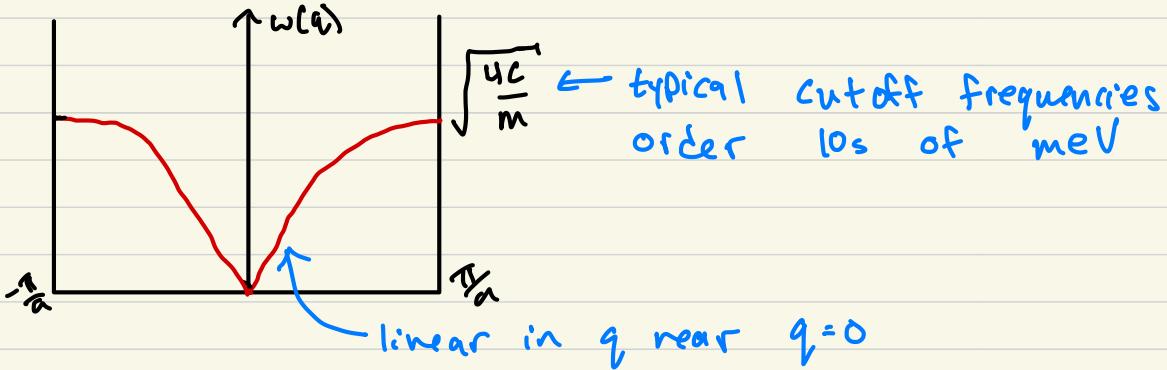
$$M\omega^2 = 4C \sin^2\left(\frac{qa}{2}\right) \Rightarrow \omega = \sqrt{\frac{4C}{m}} |\sin(\frac{1}{2}qa)|$$

Take "long-wavelength limit": $q \rightarrow 0$

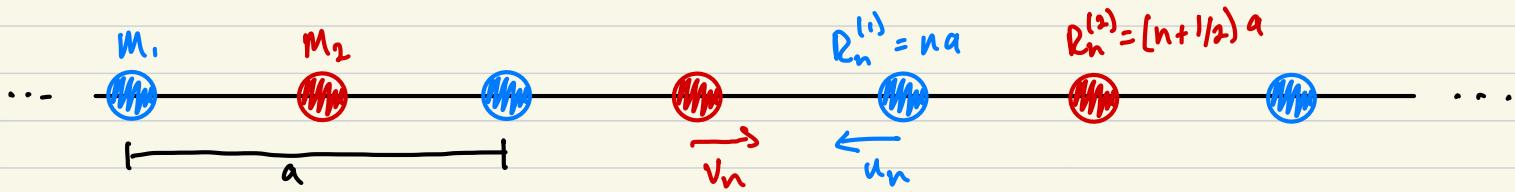
$$\omega \approx \sqrt{\frac{4C}{m}} \frac{1}{2} qa = \sqrt{\frac{C}{m}} a q \equiv v_s q$$

- linear in q
- v_s is "sound velocity"

- Dispersion:



- Now consider diatomic 1D lattice:



- * Still consider just nearest neighbor interactions, "spring" const C

- EOMs:

$$M_1 \ddot{u}_n = -C(2u_n - v_{n-1} - v_n)$$

$$M_2 \ddot{v}_n = -C(2v_n - u_n - u_{n+1})$$

- Ansatz: $u_n(t) = A_1 e^{i(qna - \omega t)}$, $v_n(t) = A_2 e^{i(qna + q\alpha/2 - \omega t)}$

- Plug into EOM:

$$-M_1 \omega^2 A_1 = -C[2A_1 - A_2 e^{i(-qa + q\alpha/2)} - A_2 e^{i(q\alpha/2)}]$$

$$-M_1 \omega^2 A_1 = -C[2A_1 - A_2(e^{-iqa/2} + e^{iqa/2})]$$

$$(M_1 \omega^2 - 2C) A_1 = -2CA_2 \cos(q\alpha/2)$$

similarly:

$$-M_2 \omega^2 A_2 = -C[2A_2 - A_1(e^{-iqa/2} + e^{iqa/2})]$$

$$(M_2 \omega^2 - 2C) A_2 = -2CA_1 \cos(q\alpha/2)$$

- After some algebra (see G and P Sec. IX.2) :

$$\omega^2 = C \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \pm C \sqrt{\left(\frac{1}{m_1} + \frac{1}{m_2} \right)^2 - \frac{4 \sin^2(qa/2)}{m_1 m_2}}$$

↑ two branches!

and: $\frac{A_1}{A_2} = \frac{2C \cos(qa/2)}{2C - m_1 \omega^2}$

- Let's look at $q \rightarrow 0$ limit:

$$\omega^2 \approx C \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \pm C \sqrt{\left(\frac{1}{m_1} + \frac{1}{m_2} \right)^2 - \frac{q^2 a^2}{m_1 m_2}}$$

$$\approx C \frac{m_1 + m_2}{m_1 m_2} \pm C \sqrt{\left(\frac{m_1 + m_2}{m_1 m_2} \right)^2 - \frac{q^2 a^2}{m_1 m_2}}$$

for small x , $\sqrt{A-x} = \sqrt{A} - \frac{x}{2\sqrt{A}} - \dots$

$$\approx C \frac{m_1 + m_2}{m_1 m_2} \pm C \left[\frac{m_1 + m_2}{m_1 m_2} - \frac{q^2 a^2}{2 m_1 m_2} \frac{m_1 m_2}{m_1 + m_2} \right]$$

So one branch is: (-) "Acoustic branch"

$$\omega^2 = \frac{C q^2 a^2}{2(m_1 + m_2)} + O(q^4) \text{ so } \omega \text{ is linear in } q \text{ like before}$$

also: $\frac{A_1}{A_2} \approx \frac{2C - O(q^2)}{2C - m_1 O(q^2)} \approx 1 \text{ so } A_1 = A_2 \text{ and}$

both sublattices move together :



Other branch: (+) "Optical branch"

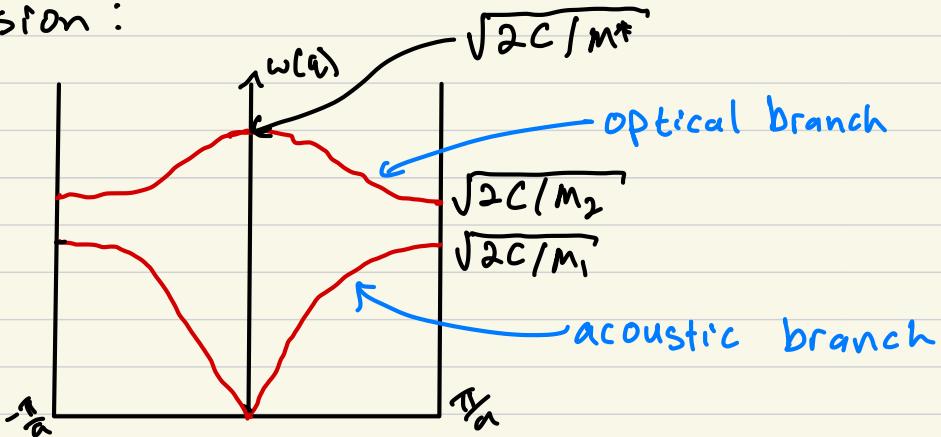
$$\omega^2 = \frac{2C}{m^*} + O(q^2), \frac{1}{m^*} = \frac{1}{m_1} + \frac{1}{m_2} \text{ so } \omega \text{ is constant at small } q$$

$$\frac{A_1}{A_2} \approx \frac{2C}{2C \left(1 - \frac{m_1}{m_1} - \frac{m_1}{m_2} \right)} = -\frac{m_2}{m_1} \text{ so } A_1 M_1 = -A_2 M_2 \text{ and}$$

Sublattices move in opposite directions



- Dispersion:



- Now we will generalize to 3D crystals

* Atomic positions described by translation vector \vec{t}_n and basis vectors \vec{c}_v

- Label atoms by $(n v)$
unit cell
sublattice

* Expansion of E_0 up to harmonic term:

$$E_0^{\text{harmon}}(\{\vec{u}_{nva}\}) = E_0(0) + \frac{1}{2} \sum_{nva, n'v'd'} D_{nva, n'v'd'} u_{nva} u_{n'v'd'} \quad \begin{matrix} \text{d} = x, y, z \\ \text{sum runs over unit cells, sublattices, directions} \end{matrix}$$

- Where: $D_{nva, n'v'd'} = \left. \frac{\partial^2 E_0}{\partial u_{nva} \partial u_{n'v'd'}} \right|_0$

- D is force constant matrix in 3D

- D is real and symmetric

- $D_{nva, n'v'd'} = D_{mva, m'v'd'} \quad \text{if} \quad \vec{t}_n - \vec{t}_{n'} = \vec{t}_m - \vec{t}_{m'}$

- "Acoustic sum rule": $\sum_{n'v'd'} D_{nva, n'v'd'} u_{n'v'd'} = 0$

* Equations of motion:

$$m_v \ddot{u}_{nva} = - \sum_{n'v'd'} D_{nva, n'v'd'} u_{n'v'd'}$$

- Look for solutions of the form:

$$\vec{u}_{n\nu}(t) = \vec{A}_\nu(\vec{q}, \omega) e^{i(\vec{q} \cdot \vec{r}_n - \omega t)}$$

↳ "polarization vectors"

- Plug in to equations of motion:

$$-M_\nu \omega^2 A_{\nu a} = - \sum_{n'n'a'} D_{n\nu a, n'n'a'} e^{-i\vec{q} \cdot (\vec{r}_n - \vec{r}_{n'})} A_{n'n'a'}$$

- Dynamical matrix: $D_{\nu a, \nu' a'}(\vec{q}) = \sum_n D_{n\nu a, n'n'a'} e^{-i\vec{q} \cdot (\vec{r}_n - \vec{r}_{n'})}$

- Solve secular equations to get \vec{A} and ω :

$$\det |D_{\nu a, \nu' a'}(\vec{q}) - M_\nu \omega^2 \delta_{aa'} \delta_{\nu \nu'}| = 0$$

* Some comments about vibrational modes in 3D crystals:

- $D(\vec{q})$ is $3N_\nu \times 3N_\nu$ matrix, so there are $3N_\nu$ modes at each \vec{q} number of atoms in unit cell

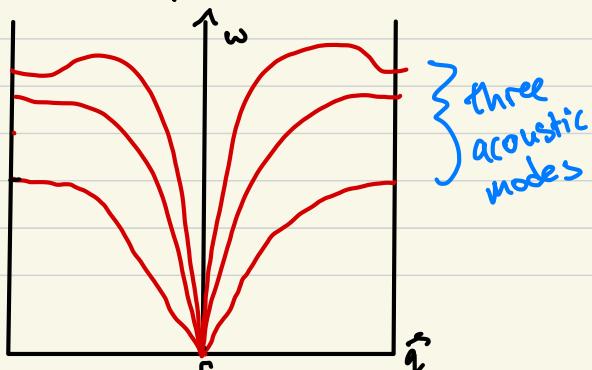
- Since there are N (number of unit cells in crystal) \vec{q} points, there are $N N$ normal modes

- Consider a polarization vector $\vec{A}_\nu(\vec{q}, n)$

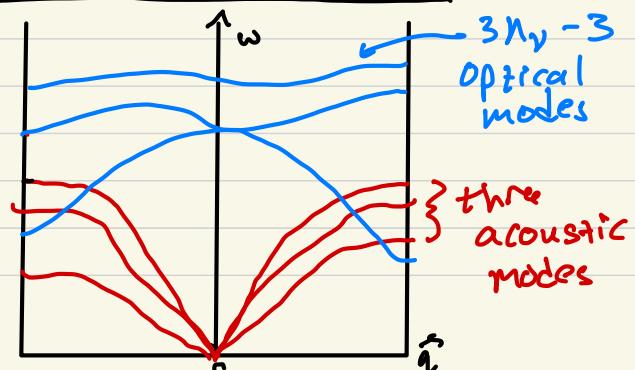
→ Mode is transverse if $\vec{A} \perp \vec{q}$

→ mode is longitudinal if $\vec{A} \parallel \vec{q}$

- Dispersions have optical modes if they have a basis. Always have 3 acoustic modes in 3D.
- Simple lattice



lattice with basis:



- What are the physical implications of vibrational modes?

* In the homework, you show that the quantum theory gives quantized vibrational modes called phonons

$$H = \sum_q k \omega(q) \left[a_q^\dagger a_q + \frac{1}{2} \right]$$

- Phonons are vibrational "quasiparticles" with quantized energy $\hbar\omega(q)$
 - These particles act as bosons
 - Average vibrational energy in a crystal

$$U_{\text{vib}}(T) = \sum_{\vec{q}, \vec{p}} \left[\frac{\hbar \omega(\vec{q}, \vec{p})}{\exp[\hbar \omega(\vec{q}, \vec{p})/k_B T] - 1} + \frac{1}{2} \hbar \omega(\vec{q}, \vec{p}) \right]$$

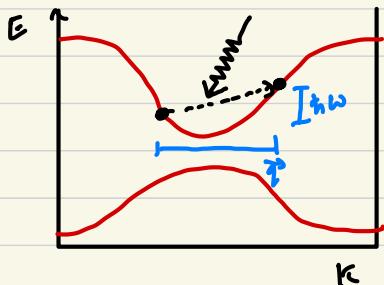
\vec{q} 's in first BZ
 branches of phonon dispersion
 Base-Einstein occupations
 "zero point" vibrations

- Note: chemical potential is zero since phonons can be created with zero energy!
 - Recall that lattice heat capacity at constant volume;

$$C_v^{\text{vib}}(T) = \frac{\partial U_{\text{vib}}}{\partial T} = \frac{\partial}{\partial T} \sum_{\vec{q}, p} \frac{k_B \omega(\vec{q}, p)}{\exp[k_B \omega(\vec{q}, p)/k_B T] - 1}$$

* Phonon scattering:

- Phonons can scatter electrons to different states:



- Allows for energy exchange between lattice and electrons

Nuclear dynamics: What have we learned?

- Under the adiabatic Born-Oppenheimer approximation: electronic energies at fixed nuclear configuration make potential energy surface for nuclei

$$* \text{Classical: } M \ddot{R}_I = \frac{\partial E_{\text{elect}}(\vec{R})}{\partial R_I}$$

$$* \text{Quantum: } \left[-\frac{\hbar^2}{2m} + E_{\text{elect}}(\vec{R}) \right] \chi(R) = \omega \chi(R)$$

- Lattice dynamics: Normal vibrational modes of crystal described by phonon band structure
 - Vibrational frequencies as a function of wavevector \vec{q}
 - D acoustic modes ($D = \# \text{ dimensions}$), linear in \vec{q} for small \vec{q} and short-ranged force constants
 - $N_{\text{atom}} - D$ ($N_{\text{atom}} = \# \text{ atoms in unit cell}$) optical modes, finite ω at $\vec{q} = 0$