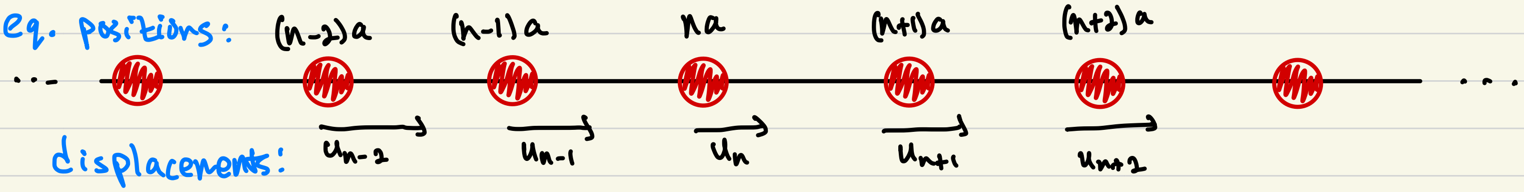
Lattice dynamics of crystals (G and P chapter IX)

- 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:

force on nuclei i

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

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

$$E_0(\{u_n\}) = E_0(0) + \frac{1}{2}\sum_{n,n'} \left.\frac{\partial^2 E_0}{\partial u_n \partial u_{n'}}\right|_0 u_n u_{n'}$$

$$+ \frac{1}{3!}\sum_{n,n',n''} \left.\frac{\partial^3 E_0}{\partial u_n \partial u_{n'} \partial u_{n''}}\right|_0 u_n u_{n'} u_{n''} + \ldots$$

- 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:

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

↑ "force constant matrix"

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

← proportionality coeff between Force and displacement

- Symmetries of D:

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

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

$\sum_{n'} D_{nn'} = 0$ (Forces vanish when all atoms are moved rigidly)

- Equation of motion for nuclei n:

← second time derivative, i.e., acceleration

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

↑ nuclear mass

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

- Anzatz for solution: $u_n(t) = A e^{i(qna - \omega t)}$

↓ periodic in space

↑ periodic in time

- Plug in to EOM:

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

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

↓ Fourier transform of $D_{nn'}$

↓ 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 chages in q of $2\pi n$, independent values of q are confined to $-\pi/a < q \le \pi/a$

- Under Born-von Karman boundary conditions, discrete q in BZ with values $m(2\pi/Na)$

* Now consider case of just nearest neighbor interactions!

$D_{nn} = 2C$, $D_{nn\pm1} = -C$, all other elements are zero

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

$$E_0^{harm} = \frac{1}{2} C \sum_n \left(2u_n^2 - u_n u_{n+1} - u_n u_{n-1}\right)$$

$$= \frac{1}{2} C \left[\sum_n u_n^2 + \sum_n u_{n+1}^2 - \sum_n u_n u_{n+1} - \sum_n u_{n+1} u_n\right]$$

$$= \frac{1}{2} C \sum_n \left(u_n - u_{n+1}\right)^2$$

- Classical EOM:

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

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

$$-M\omega^2 A e^{i(qna - \omega t)} = -AC\left[2e^{i(qna - \omega t)} - e^{i(qna + qa - \omega t)} - e^{i(qna - qa - \omega t)}\right]$$

$$\Rightarrow M\omega^2 = C\left[2 - e^{-iqa} - e^{iqa}\right] = C\left[2 - 2\cos(qa)\right] = 2C\left[1 - \cos(qa)\right]$$

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

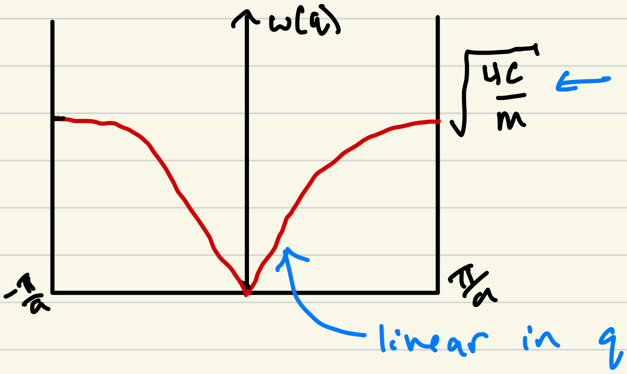
$$M\omega^2 = 4C \sin^2\left(\frac{qa}{2}\right) \Rightarrow \omega = \sqrt{\frac{4C}{M}} \left|\sin\left(\frac{1}{2}qa\right)\right|$$

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

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

- linear in q
- V_s is "sound velocity"

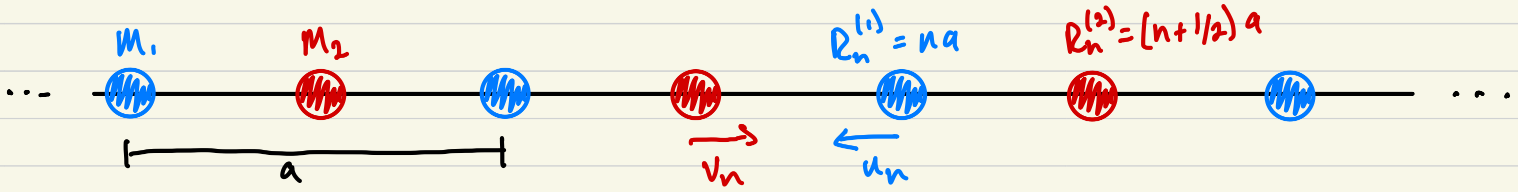
- Dispersion :



typical cutoff frequencies order 10s of meV

linear in q near q=0

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

- Plug into EOM:

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

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

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

similarly:

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

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

- 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 $q \to 0$ limit:

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

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

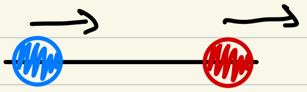
for small x, $\sqrt{A-x} = \sqrt{A} - \frac{x}{2\sqrt{A}} - \dots$

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

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

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

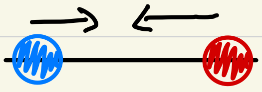
also: $\frac{A_1}{A_2} \approx \frac{2C - O(q^2)}{2C - m_1\,O(q^2)} \approx 1$ so $A_1 = A_2$ and both sublattices move together:



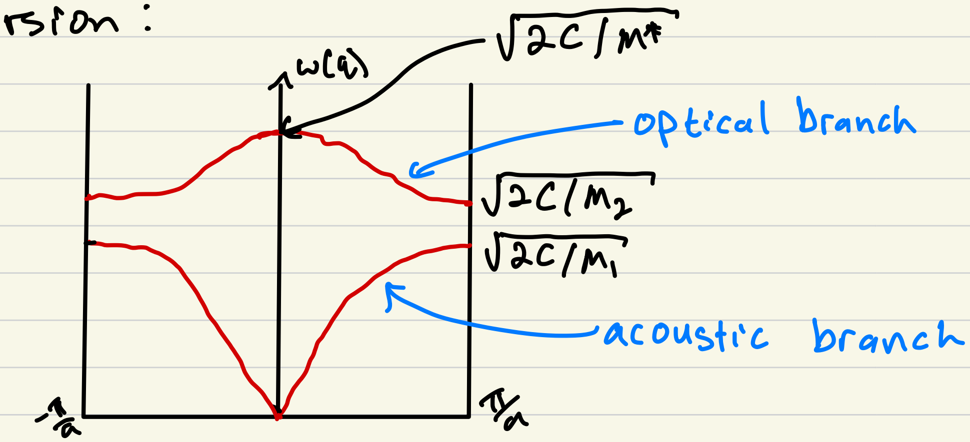
Other branch: (+) "Optical branch"

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

$\frac{A_1}{A_2} \approx \frac{2C}{2C\left(1 - \frac{m_1}{m_1} - \frac{m_1}{m_2}\right)} = -\frac{m_2}{m_1}$ so $A_1 M_1 = -A_2 M_2$ 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 $\vec{d}_\nu$

- Label atoms by $(\overset{\text{unit cell}}{n}\underset{\text{sublattice}}{\nu})$

* Expansion of E_0 up to harmonic term:

$$E_0^{harm}(\{\vec{u}_{n\nu}\}) = E_0(0) + \frac{1}{2}\sum_{n\nu\alpha,\, n'\nu'\overset{\alpha = x,y,z}{\alpha'}} D_{n\nu\alpha,n'\nu'\alpha'}\, u_{n\nu\alpha}\, u_{n'\nu'\alpha'}$$

sum runs over unit cells, sublattices, directions

- where: $D_{n\nu\alpha,n'\nu'\alpha'} = \left.\dfrac{\partial^2 E_0}{\partial u_{n\nu\alpha}\,\partial u_{n'\nu'\alpha'}}\right|_0$

- D is Force constant matrix in 3D
- D is real and symmetric
- $D_{n\nu\alpha,n'\nu'\alpha'} = D_{m\nu\alpha,m'\nu'\alpha'}$ if $\vec{t}_n - \vec{t}_{n'} = \vec{t}_m - \vec{t}_{m'}$
- "Acoustic sum rule": $\sum_{n'\nu'} D_{n\nu\alpha,n'\nu'\alpha'} = 0$

* Equations of motion:

$$M_\nu\, \ddot{u}_{n\nu\alpha} = -\sum_{n'\nu'\alpha'} D_{n\nu\alpha,n'\nu'\alpha'}\, u_{n'\nu'\alpha'}$$

- Look for solutions of the form:

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

↳ "polarization vectors"

- Plug in to equations of motion:

$$-M_{\nu}\,\omega^2 A_{\nu\alpha} = -\sum_{n'\nu'\alpha'} D_{n\nu\alpha,n'\nu'\alpha'}\, e^{-i\vec{q}\cdot(\vec{t}_n-\vec{t}_{n'})} A_{\nu'\alpha}$$

- Dynamical matrix: $D_{\nu\alpha,\nu'\alpha}(\vec{q}) = \sum_{n'} D_{n\nu\alpha,n'\nu'\alpha'}\, e^{-i\vec{q}\cdot(\vec{t}_n-\vec{t}_{n'})}$

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

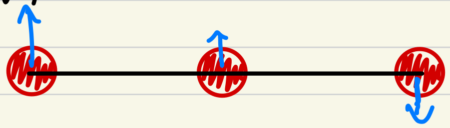
$$\det\left| D_{\nu\alpha,\nu'\alpha}(\vec{q}) - M_{\nu}\,\omega^2 \delta_{\alpha\alpha'}\delta_{\nu\nu'} \right| = 0$$

* Some comments about vibrational modes in 3D crystals:

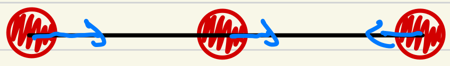
- $D(\vec{q})$ is $3n_\nu \times 3n_\nu$ matrix, so there are $3n_\nu$ modes at each $\vec{q}$
  ↑ number of atoms in unit cell

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

- Consider a polarization vector $\vec{A}_\nu(\vec{q},n)$
  - → Mode is transverse if $\vec{A} \perp \vec{q}$

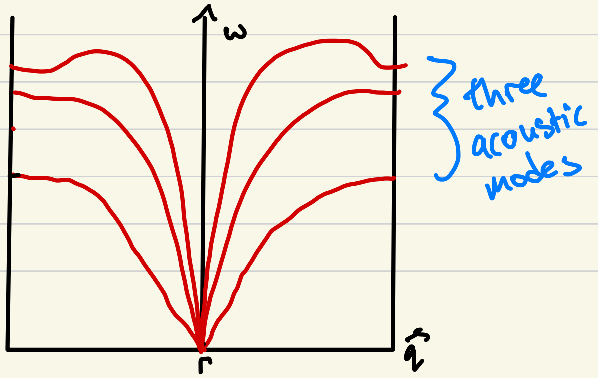


  - → mode is longitudinal if $\vec{A} \parallel \vec{q}$

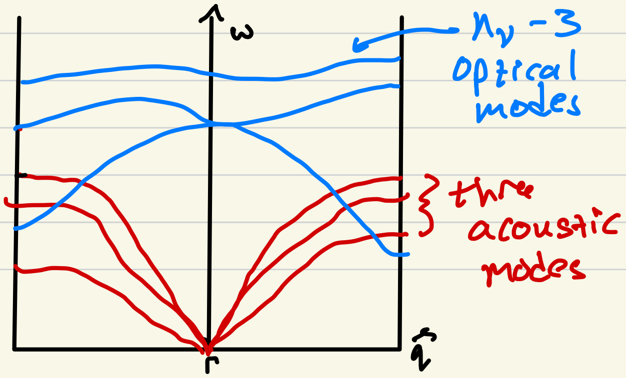


- Dispersions have optical modes if they have a basis. Always have 3 acoustic modes in 3D.

Simple lattice



lattice with basis:



Nuclear dynamics: What have we learned?

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

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

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

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