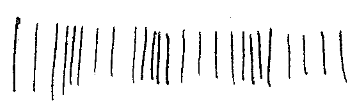
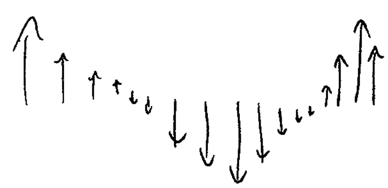
Lattice Vibrations

- So far we assumed atoms fixed in space → of course this isn't really true, so let's do better.

- Atoms vibrate about their equilibrium positions due to thermal / quantum fluctuations. eg:



compression wave



shear wave

(• Atoms also respond to external forces → elasticity)

- These phenomena are important for many reasons:

  - Vibrations can store / transmit energy, contribute to properties like heat capacity, thermal conductivity
  - Thermal expansion of solids
  - Question: Do thermal / quantum fluctuations destroy or modify Bragg peaks in a scattering experiment?

Model (very general)

potential describing interactions among atoms.

$$H = \sum_\alpha \frac{\vec{p}_\alpha}{2M_\alpha} + U(\{\vec{r}_\alpha\})$$

$\hookrightarrow$ labels atomic positions

• ~~Recall: In 1st lecture, we estimated~~

• Recall: Interaction energy between ions is much larger than kinetic energy. So we may expect deviations from equilibrium positions to be small.

$\longrightarrow$

• Expand about equilibrium positions: $\vec{r}_\alpha = \vec{r}_\alpha^{\,0} + \vec{u}_\alpha$

give minimum of U.

(μ,ν are vector indices)

$$U(\{\vec{r}_\alpha\}) = \text{Const.} + \frac{1}{2}\sum_{\alpha,\beta} u_\alpha^\mu D_{\alpha\beta}^{\mu\nu} u_\beta^\nu + \cancel{\mathcal{O}(u^3)} + \dots$$

Neglect: harmonic approximation.

Notation: Label atoms by equilibrium position $\vec{r}_\alpha^{\,0} \longrightarrow \vec{r}_\alpha$

(drop the "0")

$$U_\alpha^\mu \to U^\mu(\vec{r}_\alpha) \; ; \quad D_{\alpha\beta}^{\mu\nu} \to D^{\mu\nu}(\vec{r}_\alpha, \vec{r}_\beta)$$

$$P_\alpha^\mu \to P^\mu(\vec{r}_\alpha) \; ; \quad [U^\mu(\vec{r}_\alpha), P^\nu(\vec{r}_\beta)] = i\hbar\,\delta_{\mu\nu}\,\delta_{\alpha\beta}$$

- We will treat this problem quantum mechanically to start with, even though we will first be interested in classical limit. Reason is that we will need to make various changes of variables, and in QM the commutation relations help us keep track of effects of such changes. (Could do using Hamiltonian classical mechanics & Poisson brackets, too.) We can always take the classical limit later if we need to.

- This general form is a bit complicated ...

Work with simple case : 1d monatomic Bravais lattice.

lattice constant.

- $\vec{r}_\alpha \to R = na$; $\vec{u} \to u$; $\vec{p} \to p$; $[u_R, p_{R'}] = i\hbar\, \delta_{RR'}$.

$$H = \frac{1}{2M} \sum_R p_R^2 + \frac{1}{2} \sum_{R,R'} D(R,R')\, u_R u_{R'}$$

- Periodic b.c. : $u_0 \equiv u_{Na}$; $L = Na$

- Exploit discrete translation symmetry : $D(R,R') = D(R-R')$

- Also, must be true that H doesn't change under a uniform shift of the whole crystal, $u_R \to u_R + \delta u$

  (Can show this requires $\sum_R D(R) = 0$.)

Simplify further:

$$H = \frac{1}{2M}\sum_R P_R^2 + \frac{K}{2}\sum_R (u_R - u_{R+a})^2$$

- Goal: Find normal modes (i.e., reduce the problem to a bunch of harmonic oscillators)

- Expect normal modes are plane waves
  $\rightarrow$ Guess: $u_R = \sum_k e^{ikR} u_k$

  $\hookrightarrow k = \frac{2\pi n}{L} = \frac{2\pi n}{Na}$, as appropriate for periodic boundary conditions.

But wait: R is discrete, does this matter?

Suppose: $K = \frac{2\pi}{a} \cdot n$, and $k' = k + K$, then

$$e^{ik'R} = e^{ikR} e^{iKR} = e^{ikR} e^{i\frac{2\pi n}{a} \cdot an'} = e^{ikR}$$

$$\Rightarrow \boxed{k \text{ and } k+K \text{ are not distinct Fourier components}}$$

$\Rightarrow$ • Restrict $k \in [-\frac{\pi}{a}, \frac{\pi}{a})$

(i.e. $k = -\frac{\pi}{a} + \frac{2\pi n}{Na}$; $n = 0, \ldots, N-1$)

notice: N allowed k-points

• Recall, $K = \frac{2\pi n}{a}$ are RLV's

→ "k is only defined modulo a RLV"

→ k chosen to lie in a primitive cell of RL, in particular, in the 1st Brillouin Zone ("BZ")

Try again:

$$u_R = \frac{1}{\sqrt{N}} \sum_{k \in B.Z.} e^{ikR} u_k$$

$$u_k = \frac{1}{\sqrt{N}} \sum_{R} e^{-ikR} u_R$$

do same for p_R & p_k.

Note: $u_R^\dagger = u_R \Leftrightarrow u_k^\dagger = u_{-k} \Rightarrow$ u_k & u_{-k} are not independent.

(Same for p's)

Plug in:

$$H = \overset{\text{kinetic}}{H_K} + \overset{\text{potential}}{H_p}$$

$$H_K = \frac{1}{2M} \sum_R p_R^2 = \frac{1}{2MN} \sum_R \sum_{kk'} e^{ikR} e^{ik'R} p_k p_{k'}$$

$$= \frac{1}{2M} \sum_{kk'} \delta_{k,-k'} \, p_k p_{k'}$$

$$= \frac{1}{2M} \sum_k p_k^\dagger p_k$$

$$H_p = \frac{K}{2} \sum_R (u_R - u_{R+a})(u_R - u_{R+a})$$

$$= \frac{K}{2N} \sum_R \sum_{k,k'} \left[e^{ikR} u_k - e^{ikR} e^{ika} u_k \right] \left[e^{ik'R} u_{k'} - e^{ik'R} e^{ik'a} u_{k'} \right]$$

$$= \frac{K}{2N} \sum_R \sum_{k,k'} e^{iR(k+k')} (1 - e^{ika})(1 - e^{ik'a}) u_k u_{k'}$$

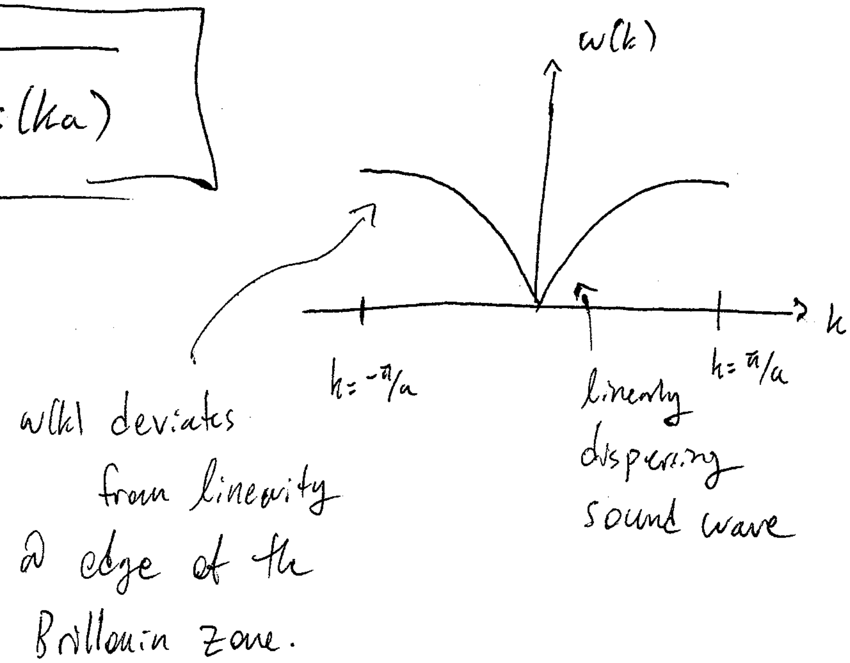
$$= \frac{K}{2M} \sum_{k,k'} \delta_{k,-k'} (1 - e^{ika})(1 - e^{+ik'a}) u_k u_{k'}$$

$$H_P = \frac{K}{2} \sum_k \left| 1 - e^{ika} \right|^2 u_k^\dagger u_k$$

$$= \frac{K}{2} \sum_k \left[2(1-\cos(ka)) \right] u_k^\dagger u_k$$

$$\Rightarrow \boxed{H = \frac{1}{2M} \sum_k p_k^\dagger p_k + \frac{1}{2} \sum_k (M\omega^2(k))\, u_k^\dagger u_k},$$

$$\boxed{\omega(k) = \sqrt{\frac{2K}{M}} \sqrt{1-\cos(ka)}}$$



- Almost looks like bunch of decoupled oscillators (normal modes),

but:
- u_k, p_k aren't Hermitian
- commutation relations?
- u_k, u_{-k} not independent

Can show: $[u_k, p_{k'}] = i\hbar\, \delta_{k,-k'}$

$$\Rightarrow \quad [u_k, p_{k'}^\dagger] = i\hbar\, \delta_{kk'}$$

Want Hermitian operators $\rightarrow$ take real, imaginary parts.

$$u_k = \frac{u_k^R + i u_k^I}{\sqrt{2}} \qquad p_k = \frac{p_k^R + i p_k^I}{\sqrt{2}}$$

$$\Rightarrow \left\{ \begin{aligned} [u^R_k, p^R_{k'}] &= i\hbar\, \delta_{kk'} \\ [u^I_k, p^I_{k'}] &= i\hbar\, \delta_{kk'} \\ [u^R_k, p^I_{k'}] &= 0 \\ [u^I_k, p^R_{k'}] &= 0 \end{aligned} \right.$$

Now we have Hermitian operators with canonical commutation relations ✓

- Next, $u_k^\dagger = u_{-k} \Rightarrow \begin{cases} u_k^R = u_{-k}^R \\ u_k^I = -u_{-k}^I \end{cases}$

- Can fix lack of independence by summing only over $k \geq 0$.

write: $\sum_k{}' \equiv \sum_{k \geq 0}$

$$\Rightarrow \quad H = \frac{1}{4M} \sum_k \left[(p_k^R)^2 + (p_k^I)^2 \right] + \frac{1}{4} \sum_k \left[M(\omega(k))^2 \right] \left[(u_k^R)^2 + (u_k^I)^2 \right]$$

$$= \frac{1}{2M} \sum_k{}' \left[(p_k^R)^2 + (p_k^I)^2 \right] + \frac{1}{2} \sum_k{}' \left[M\omega^2(k) \right] \left[(u_k^R)^2 + (u_k^I)^2 \right]$$

- So we indeed have N normal modes, labeled by k, with frequency $\omega(k)$.

- Because $\omega(k) = \omega(-k)$ (inversion symmetry), we could have just naively concluded this from Hamilton in terms of u_k & $u_k^\dagger$, would have been correct!

Physical meaning of u^R's u^I's:

~~Suppose at time t=0 $u_k^{R/I} = 0$, except~~

Suppose $u_k^R = A\cos(\omega_k t + \phi)$; all others zero.

$$\Rightarrow \quad u_R(t) \propto \cos(kR)\cos(\omega_k t + \phi) \rightarrow \text{standing wave}$$

~~Other~~

$u_k^R(t) = A\cos(\omega_k t)$; $u_k^I(t) = A\sin(\omega_k t)$

On the other hand: $u_k(t) = A\, e^{i\omega_k t}$; others zero

$$\Rightarrow \quad u_R(t) \propto \cos(kR + \omega_k t) \rightarrow \text{traveling wave}$$

Significance of k? $\longrightarrow$ Return to more general case...

To illustrate a point, we will not assume translation symmetry for the moment.

$$H = \frac{1}{2M}\sum_R P_R^2 + \frac{1}{2}\sum_{R,R'} D(R,R')\, u_R u_{R'}$$

$$H_p = \frac{1}{2N} \sum_{R,R'} \sum_{k,k'} e^{ikR} e^{ik'R'} D(R,R') u_k u_{k'}$$

$$= \frac{1}{2\cancel{N}} \sum_{k,k'} \left\{ u_k u_{k'} \left[\frac{1}{N} \sum_{R,R'} e^{ikR} e^{ik'R'} D(R,R') \right] \right\}$$

$$\equiv \frac{1}{2} \sum_{k,k'} \tilde{D}(k,k') u_k u_{k'}$$

- In general, $\tilde{D}(k,k') \neq 0$ for $k \neq k'$ $\rightarrow$ does <u>not</u> diagonalize H_p into decoupled oscillators.

- But, suppose $D(R,R') = D(R-R')$, then

$$\tilde{D}(k,k') = \frac{1}{N} \sum_{R,R'} e^{ikR} e^{ik'R'} D(R-R')$$

shift $R \rightarrow R+R'$

$$= \cancel{N} \left[\frac{1}{N} \sum_{R} e^{ikR} D(R) \right] \left[\sum_{R'} e^{iR'(k'+k)} \right]$$

$$= \delta_{k,-k'} \tilde{D}(k) \quad \longrightarrow \quad \text{Does diagonalize } H_p.$$

$\Rightarrow$

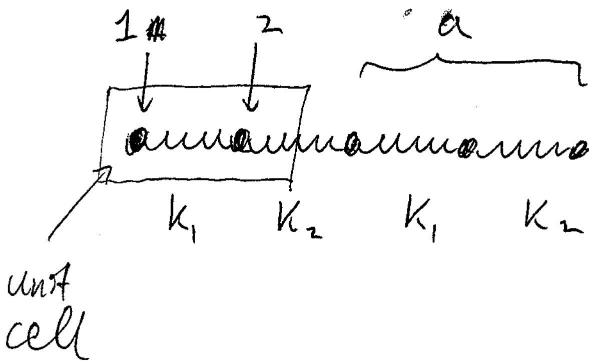
- k labels normal modes in the presence of discrete translation symmetry.

- More generally (will study this later), k is a conserved quantity analogous to the usual momentum.
  - Recall that momentum conservation follows from continuous translation invariance.
  - k-conservation follows from discrete translation invariance.

$\rightarrow$ $\boxed{k \text{ is called "crystal momentum"}}$

- Now we want to start building up to the more realistic 3d case. Turns out to be useful to first consider 1d lattice but with a basis ...

1d Harmonic Chain with 2-site basis



- $R = na$ are Bravais lattice vectors
- a is spacing between unit cells, not between atoms.

$$u_R \to u_{Ri} \;; \quad p_R \to p_{Ri}$$

$i = 1, 2$ is basis index, atoms #1 and #2 as shown.

$$H = \underbrace{\frac{1}{2M}\sum_R \sum_{i=1}^{2} p_{Ri}^2}_{H_K} + \underbrace{\frac{K_1}{2}\sum_R (u_{R1} - u_{R2})^2}_{H_{p1}} + \underbrace{\frac{K_2}{2}\sum_R (u_{R2} - u_{R+a,1})^2}_{H_{p2}}$$

To decompose into normal modes, let's try:

$$u_{Ri} = \frac{1}{\sqrt{N_c}} \sum_{k \in B.Z.} e^{ikR} u_{ki}$$

$$u_{ki} = \frac{1}{\sqrt{N_c}} \sum_R e^{-ikR} u_{Ri}$$

- Still have $k \in [-\frac{\pi}{a}, \frac{\pi}{a})$ (Because a is size of unit cell.)
- Now, N_c = # unit cells in crystal and $\frac{1}{\sqrt{N_c}}$ is used for normalization.
- Note also $L = N_c a$.

Note: $[u_{ki}, p^\dagger_{k'j}] = i\hbar\,\delta_{kk'}\delta_{ij}$

Plug this in:

~~Hp~~

$$H_K = \frac{1}{2M}\sum_{k\in BZ}\sum_{i=1}^{2} p^\dagger_{ki}p_{ki}$$

$$H_{p1} = \frac{K_1}{2N}\sum_R\sum_{k,k'} e^{ikR}e^{ik'R}(u_{k1}-u_{k2})(u_{k'1}-u_{k'2})$$

$$= \frac{K_1}{2}\sum_k (u_{k1}-u_{k2})^\dagger(u_{k1}-u_{k2})$$

$$H_{p2} = \frac{K_2}{2N}\sum_R\sum_{k,k'} e^{ikR}e^{ik'R}(u_{k2}-e^{ika}u_{k1})(u_{k'2}-e^{ik'a}u_{k'1})$$

$$= \frac{K_2}{2}\sum_k (u_{k2}-e^{ika}u_{k1})(u_{-k2}-e^{-ika}u_{-k1})$$

$$= \frac{K_2}{2}\sum_k (u_{k2}-e^{ika}u_{k1})^\dagger(u_{k2}-e^{ika}u_{k1})$$

Combine into this form:

$$H = \frac{1}{2M} \sum_{k,i} p^\dagger_{ki} p_{ki} + \frac{1}{2} \sum_{\vec{k}} u^\dagger_{ki} \underbrace{D_{ij}(k)}_{2\times 2 \text{ matrix}} u_{kj}$$

$$D_{ij}(k) = \begin{pmatrix} K_1+K_2 & -K_1-K_2 e^{-ika} \\ -K_1-K_2 e^{ika} & K_1+K_2 \end{pmatrix}$$

- We didn't quite succeed in diagonalizing H_p. But, all we need to do is just diagonalize the 2×2 Hermitian matrix $D(k)$.
- Let $S(k)$ be the unitary matrix that diagonalizes $D(k)$,

so $S^\dagger(k) D(k) S(k) = \begin{pmatrix} \lambda_1(k) & 0 \\ 0 & \lambda_2(k) \end{pmatrix}$

- Then if $u_{ki} = S_{ij}(k) u'_{kj}$ (and same for p_{ki}), we have:

$$H = \frac{1}{2M} \sum_{k,i} (p'_{ki})^\dagger p'_{ki} + \frac{1}{2} \sum_{k} (u'_{ki})^\dagger \begin{pmatrix} \lambda_1(k) & 0 \\ 0 & \lambda_2(k) \end{pmatrix}_{ij} u'_{kj}$$

• Also note, we still have

$$[u'_{ki}, (p')^\dagger_{kj}] = S_{im}(k) S^*_{jn}(k') [u_{km}, p^\dagger_{k'n}]$$
$$= S_{im}(k) S^*_{jn}(k') (i\hbar \delta_{mn} \delta_{kk'})$$
$$= i\hbar (S(k) S^\dagger(k))_{ij} \delta_{kk'} = i\hbar \delta_{ij} \delta_{kk'}$$

⇒ We've succeeded in finding the normal modes ... just need to know $\lambda_{1,2}(k)$, and the frequencies are:

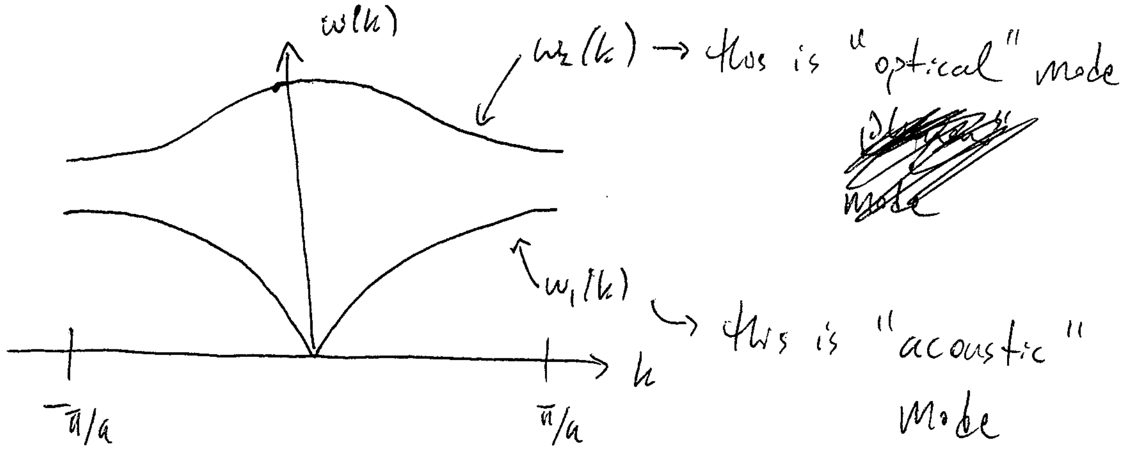
$$\omega_1(k) = \sqrt{\frac{\lambda_1(k)}{M}} \; ; \quad \omega_2(k) = \sqrt{\frac{\lambda_2(k)}{M}}$$

• Note that the counting of normal modes works as expected: $2N_c = N$ normal modes.

• λ's are roots of: $(K_1 + K_2 - \lambda)^2 - |K_1 + K_2 e^{ika}|^2 = 0$

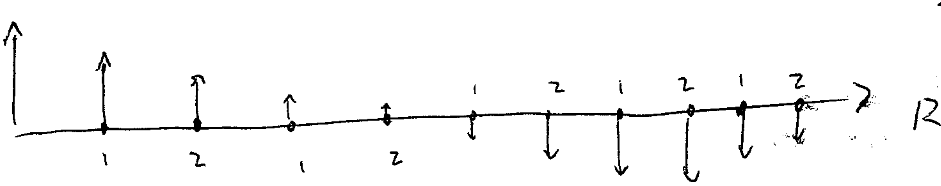
$$\Rightarrow \lambda_1 = K_1 + K_2 - \sqrt{K_1^2 + K_2^2 + 2K_1K_2\cos(ka)}$$
$$\lambda_2 = K_1 + K_2 + \sqrt{K_1^2 + K_2^2 + 2K_1K_2\cos(ka)}$$

Typical values of K_1, K_2:



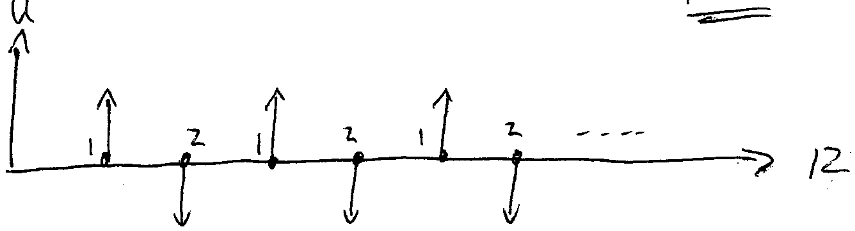
- Near $k=0$, acoustic mode is just a usual compression wave ...

Acoustic



- Optical mode looks different ...

Optical



→ Sharp variations within unit cell.

Acoustic vs. Optical Modes

- For a 1d crystal like this, if there are k atoms in the unit cell, there will <u>always</u> be 1 acoustic mode (i.e. has $\omega(k=0)=0$) and $(k-1)$ optical modes ($\omega(k) \neq 0$ for all k)

  Why?

- In such a case we have displacements u_{Ri} ($i=1,\dots,k$).

— Energy can't change under uniform shift $u_{Ri} \to u_{Ri} + \delta u$

— Instead, consider a shift $u_{Ri} \to u_{Ri} + \delta u \cdot \cos(kR)$

(Instead of R, I could put the actual position of each atom, but it won't affect the conclusion.)

— By continuity, $\delta E(k) \to 0$ as $k \to 0$.

— Strongly suggests there should be a mode with vanishingly small potential energy cost and hence $\omega(k) \to 0$ as $k \to 0$.

— But this argument only gives one mode that behaves this way, so <u>generically</u> expect just one acoustic mode.

- Actually, if other ~~phonons~~ modes had $\omega(k) \to 0$, this would signal an instability of the crystal structure, leading e.g. to a spontaneous distortion. After the distortion, we'd be back again to just one acoustic mode.

Three dimensional case (monatomic Bravais lattice, for simplicity)