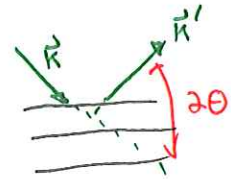
Physics 410/510 – Solid State Physics
Spring 2015
Monday, Week 4:

Review:

$$\vec{k}' - \vec{k} = \vec{G} \iff \vec{k}\cdot\left(\tfrac{1}{2}\vec{G}\right) = \left(\tfrac{1}{2}G\right)^2 \iff 2d\sin\theta = n\lambda$$

- 

- $\vec{k}$ must go from origin of reciprocal space to BZ!

$$I_{(hkl)} \propto |S_{(hkl)}|^2$$

$$S(\vec{G}) \equiv \int_{\substack{\text{unit}\\\text{cell}}} V(\vec{x})\, e^{i\vec{G}\cdot\vec{x}}\, d\vec{x}$$

$$= \sum_j f_j\, e^{i\vec{G}\cdot\vec{x}_j}$$ [Structure factor of the basis]

$f_j \rightarrow$ Atomic form factor

CsCl:

$$S_{(hkl)} = f_{Cl} + f_{Cs}(-1)^{h+k+l}$$

- <u>Cesium bcc</u>

<u>Basis</u>

$$C_s = [0,0,0]$$
$$C_s = [1/2, 1/2, 1/2]$$

$$S_{(hkl)} = f_{Cs}\, e^{i\vec{G}\cdot\vec{0}} + f_{Cs}\, e^{i\vec{G}\cdot(1/2,1/2,1/2)a}$$

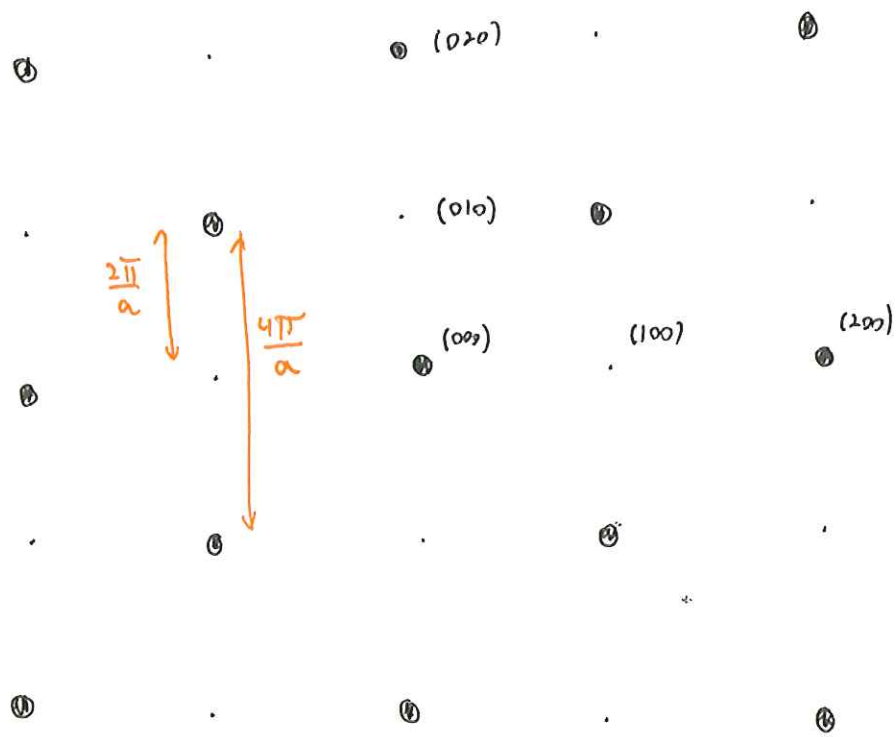
$$= f_{Cs} + f_{Cs}\, e^{i\,2\pi i\,(h,k,l)\cdot(1/2,1/2,1/2)}$$

$$= f_{Cs}\left(1 + e^{i\pi(h+k+l)}\right)$$

$$= f_{Cs}\left(1 + (-1)^{h+k+l}\right)$$

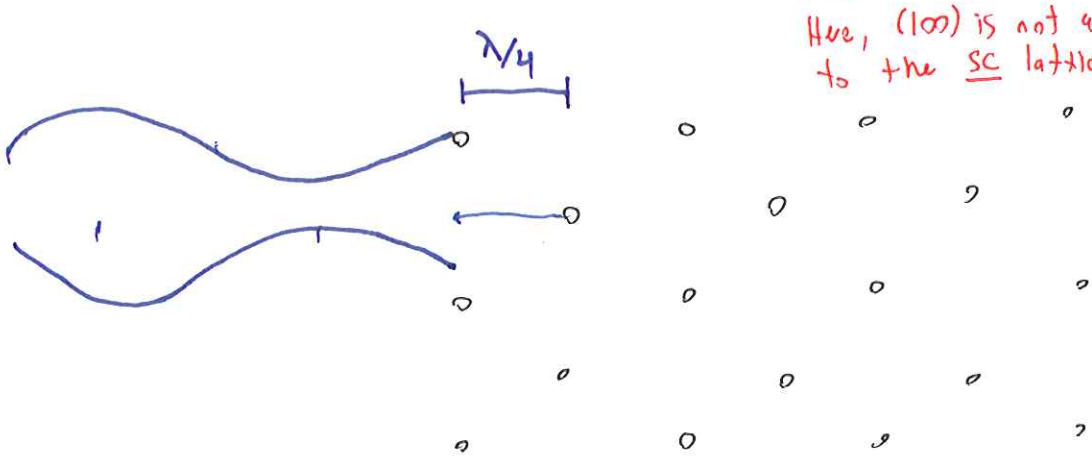
$$= \begin{cases} 2f_{Cs} & h+k+l = \text{even} \\ 0 & h+k+l = \text{odd} \end{cases} \rightarrow \text{Systematic Absences}$$

Here $l=0$,
If we look at $l=\pm1$ plane,
we get FCC!!



why? bcc is being viewed in conventional cubic unit cell, & planes of atoms sit halfway between other to cause destructive interference.

N.B. If (hkl) doesn't lead to diffraction, then this means it's not a reciprocal lattice vector. Here, (100) is not a $\vec{G}$, since we're referring the bcc to the SC lattice & it's not in 1-1 corr. w/ family of lattice planes.



(100) has $\lambda = d = \frac{2\pi}{a}$

(200) has $\lambda = \frac{2\pi}{2a} = \frac{1}{2}\left(\frac{2\pi}{a}\right)$ ✓

- Copper fcc:

Basis: [0,0,0]
[½,0,½]
[½,½,0]
[0,½,½]

$$S_{(hkl)} = f_{Cu}\left(1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)}\right)$$

Selection Rules:

SC	all h, k, l allowed
bcc	h+k+l = even
fcc	h, k, l all odd or even ; No
	(111) (222) (212) or (100)

Don't require all axes of lattice to have same length

- Diamond : fcc w/ basis

$$[0,0,0],\ [\tfrac{1}{2},\tfrac{1}{2},0],\ [\tfrac{1}{2},0,\tfrac{1}{2}],\ [0,\tfrac{1}{2},\tfrac{1}{2}]$$

$$\text{"} + \underbrace{[\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4}]}_{\vec{v}} \quad \text{"} + \vec{v} \quad \text{"} + \vec{v} \quad \text{"} + \vec{v}$$

$$S_{(hkl)} = f_c\, e^{i2\pi(h,k,l)\cdot(0,0,0)} + f_c\, e^{i2\pi(h,k,l)\cdot(\frac{1}{2},\frac{1}{2},0)}$$

$$+ \cdots + f_c\, e^{i2\pi(hkl)\cdot(000)}\, e^{i2\pi(hkl)\cdot(\frac{1}{4},\frac{1}{4},\frac{1}{4})}$$

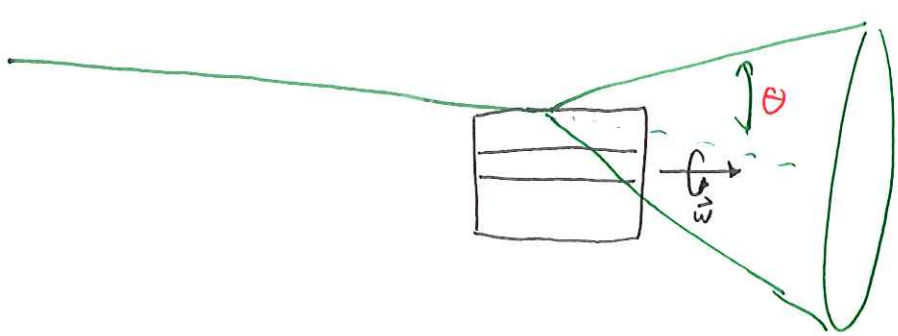
$$+ \cdots$$

$$= f_c \underbrace{\left(1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)}\right)}_{\text{fcc lattice}} \times \underbrace{\left(1 + e^{i2\pi(hkl)(\frac{1}{4}\frac{1}{4}\frac{1}{4})}\right)}_{\text{basis}}$$

This was also the case for fcc & bcc lattices viewed from sc lattice, through the $S_{(hkl)} = 1$ for an sc lattice.

Methods of Scattering Experiments:

- Laue Method : Single crystal, vary $\vec{k}$
- Rotating Crystal Method : Rotate specimen
- Powder diffraction : Debye-Scherrer Method



Example PrO_2: Pr $[0,0,0]$

O $[1/4, 1/4, 1/4]$

$[1/4, 1/4, 3/4]$

☆ PDT

The multiplicity of planes leads to:

$$I_{\{hkl\}} \propto M_{\{hkl\}} \left| S_{\{hkl\}} \right|^2$$

$$d_{(hkl)} = \frac{\lambda}{2\sin\theta} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

$$\frac{a^2}{d^2} = h^2 + k^2 + l^2 \equiv N$$

peak a

$$\frac{d_a^2}{d^2} = \frac{h^2+k^2+l^2}{h_a^2+k_a^2+l_a^2} = \frac{N}{N_a}$$

Guess N_a so other N_i's are integers.

$$\boxed{N_a = 3}$$

This gives us N_i's, which gives $\{hkl\}$, & also gives $\underline{\underline{a}}$.

What about measured intensities?

These can be explained by the scattering amplitude.

Comes from fcc lattice

$$I_{\{hkl\}} = C M_{\{hkl\}} \left| \left[b_{Pr} + b_O \left(e^{i(\frac{\pi}{2})(h+k+l)} + e^{i\frac{\pi}{2}(h+k+3l)} \right) \right] \right|^2$$

use (hkl) & across w/ measured. Can also infer b_{Pr} & b_O values (scattering lengths).

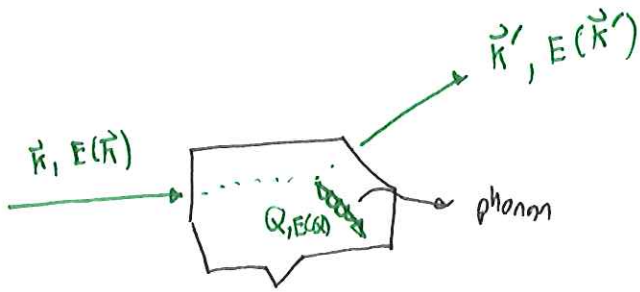
Final comments on scattering:

It's the method for determining the microscopic structure of materials:

- hemoglobin + myoglobin (N.P 1962)
- DNA (N.P 1962)
- Penicillin (1964)
- Boranes (1976)
- Photosynthetic proteins (1988)
- Ribosomes (2009)

X-rays

Inelastic Scattering:



$$\vec{Q} = \vec{k} - \vec{k}' + G \qquad \text{Momentum Conservation}$$

$$E(\vec{Q}) = E(\vec{k}) - E(\vec{k}')$$

Thus map phonon dispersion:

$$E(\vec{Q})$$

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Wednesday, Week 4:

Review:

$$S_{(hkl)} = \sum_j f_j \, e^{i 2\pi (h x_j + k y_j + l z_j)}$$

Selection Rules: Direct lattice

SC	all h,k,l allowed
bcc	$h+k+l$ = even
fcc	h,k,l = all even, all odd

Lattice + Basis:

$$S_{(hkl)} \propto S^{lattice}_{(hkl)} \times S^{basis}_{(hkl)}$$

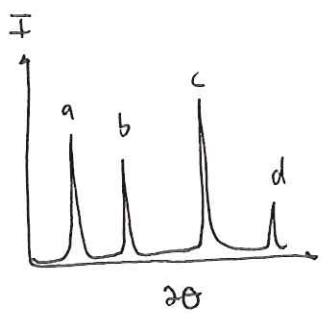
Ex Diamond

$$S_{(hkl)} = \underbrace{f_c \left(1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(h+l)} \right)}_{\text{fcc lattice}} \times \underbrace{\left(1 + e^{i 2\pi \cdot (h,k,l) \cdot (1/4, 1/4, 1/4)} \right)}_{\text{basis}}$$

Diffraction Methods:

- Debye-Scherer or Bragg Method

$$I_{\{hkl\}} \propto \underbrace{M_{\{hkl\}}}_{\text{multiplicity}} \times \left| S_{\{hkl\}} \right|^2$$

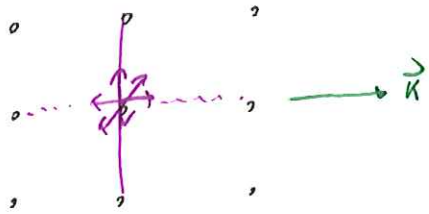


$\Rightarrow$
- Lattice
- Lattice constant
- Atomic form factors

Let's consider vibrations of crystals,

Vibrations in a 1D Monatomic Chain:

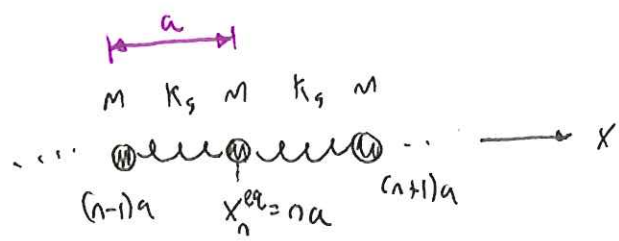
In a 3D crystal, vibrations can propagate as waves longitudinally or transversely:



1 longitudinal mode

2 transverse modes

Here, entire planes of waves move together in phase. We can learn much from the 1D version:



$\delta X_n \equiv X_n - X_n^{eq}$, then

$$M \ddot{\delta X}_n = -2K_s \delta X_n + K_s(\delta X_{n+1} + \delta X_{n-1})$$

Guess sol'n,

$$\delta X_n = A e^{-i(K X_n^{eq} - \omega t)}$$
$$= A e^{-i(K \cdot na - \omega t)}$$

N.B. X-position only defined at $X = n \cdot a$, so we will get aliasing where

$$K + G_n$$

gives same motion as K, so we can distinguish than & only K is relevant.

Then,

$$-M\omega^2 A e^{-i(K \cdot na - \omega t)} = -2K_s A e^{-i(Kna - \omega t)} + K_s\left(A e^{-i(K(n+1)a - \omega t)} + A e^{-i(K(n-1)a - \omega t)}\right)$$
$$= K_s A e^{-i(K \cdot na - \omega t)}\left[-2 + e^{-iKa} + e^{iKa}\right]$$

Cancelling common factor & using Euler's Eq.,

$$M\omega^2 = K_s\left(2 - 2\cos(ka)\right)$$

or

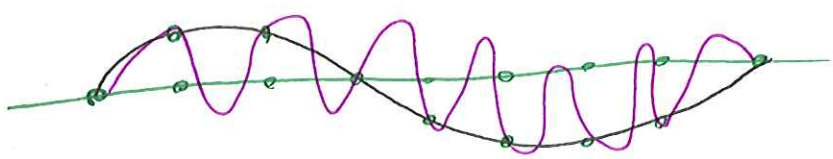
$$\boxed{\begin{aligned} \omega^2 &= \frac{2K_s}{M}\left(1-\cos(ka)\right) \\ &= \frac{4K_s}{M}\sin^2\left(\frac{ka}{2}\right) \\ \omega(k) &= 2\sqrt{\frac{K_s}{M}}\left|\sin\left(\frac{ka}{2}\right)\right| \end{aligned}}$$

From ω^2 expression, it is most clear that $\omega^2(k+g_n) = \omega^2(k)$ where $g_n = \frac{2\pi}{a}\cdot n$

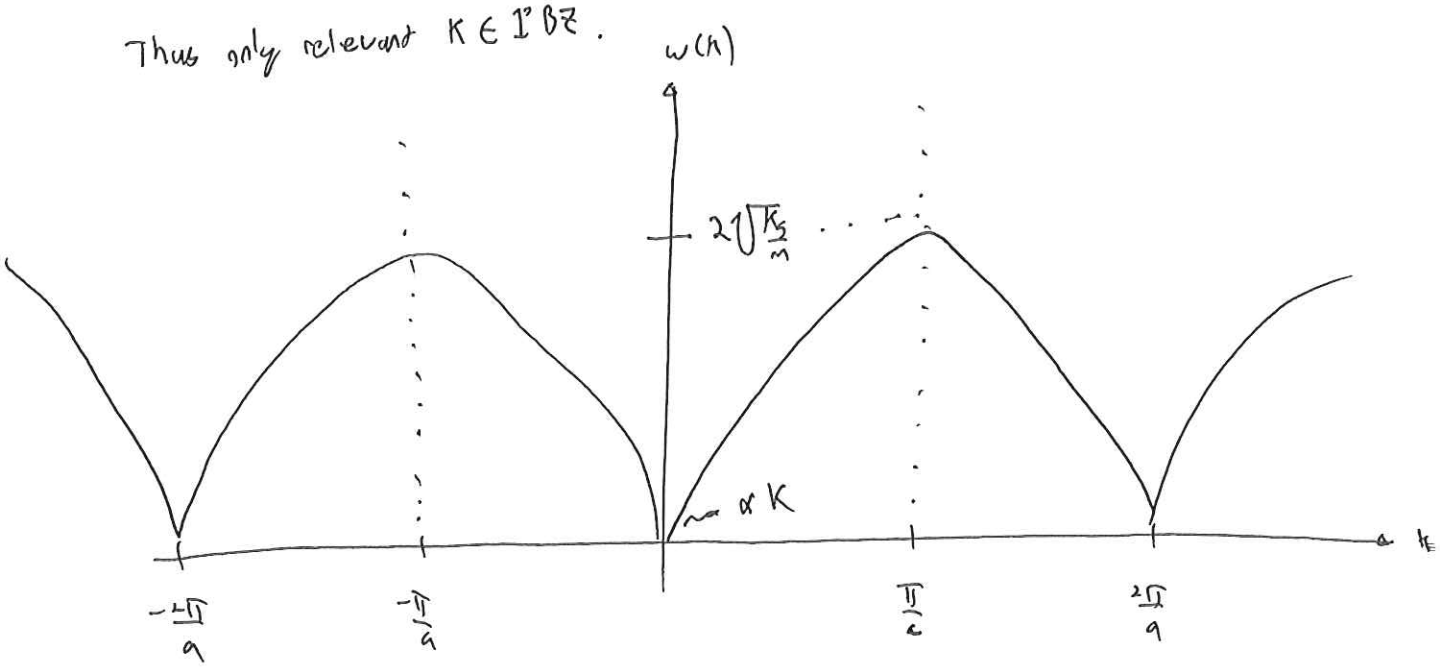
So

$$\begin{aligned} \xi X_n(k+g_n) &= A e^{-i\left((k+g_n)\cdot na - \omega(k+g_n)t\right)} \\ &= A e^{-i(k\cdot na - \omega t)} \\ &= \xi X_n(k) \end{aligned}$$

& Have differing λ, but are the same physically.



Thus only relevant $k \in 1^{\circ}$ BZ.



Remarks:

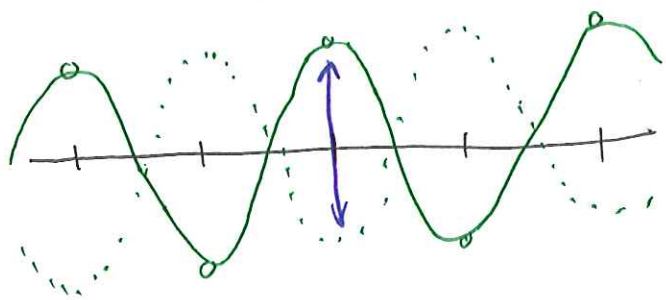
- BZ edge, $K = \pm \frac{\pi}{a}$ gives standing waves.

$$\delta x_n = A e^{-i(\pm\frac{\pi}{a}\cdot na - \omega t)}$$
$$= A e^{i\omega t} \cdot e^{\mp i\pi n}$$
$$= (-1)^n A e^{i\omega t}$$

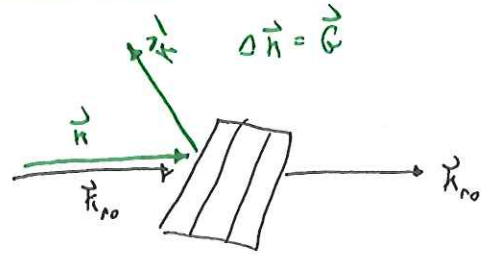
$$\Rightarrow A e^{-i(\frac{\pi}{a}\cdot na - \omega t)} + A e^{-i(-\frac{\pi}{a}\cdot na - \omega t)}$$

$\parallel$

standing waves!



Also recall that $K = \pm \frac{\pi}{a}$ satisfy Bragg / Laue diffraction conditions, so this gives us another view of diffraction: $\vec{K}$ that diffract don't propagate or waves through crystals



- In long wavelength limit;

$$\lambda \propto \frac{1}{K} \gg 1 \quad \text{or} \quad K \ll 1$$

$$\omega(K) = 2\sqrt{\frac{K_s}{M}}\left|\sin\left(\frac{Ka}{2}\right)\right|$$
$$\approx a\sqrt{\frac{K_s}{M}} \cdot K$$
$$= V_{sound} \cdot K$$

where the group (speed of wave packets) & phase (speed of individual min or max) velocities are equal:

$$V_g \equiv \frac{d\omega}{dk} = V_{sound}$$

$$V_p \equiv \frac{\omega}{k} = V_{sound}$$

- $V_g\left(\pm \frac{\pi}{a}\right) = 0$

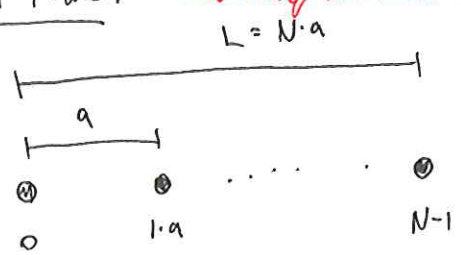
<u>Counting Normal Modes:</u> How many modes are there in our system?

<u>N atoms</u>

$\parallel$

N degree of freedom for 1D system

3N if atoms have 3 DOF each.



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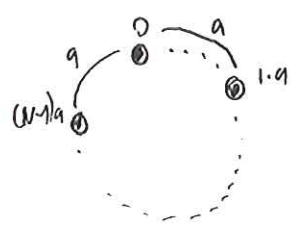


So $$e^{-i(k\cdot na - \omega t)} = e^{-i(k(n+N)a - \omega t)}$$

$$= \underbrace{e^{-ik\cdot Na}}_{1} e^{-i(k\cdot na - \omega t)}$$

[Born-Von Karman]

$$k\cdot Na = 2\pi\cdot n$$

so

$$\boxed{k_n = \frac{2\pi}{Na}\cdot n = \frac{2\pi}{L}\cdot n}$$

So each mode occupies

$$\delta k = \frac{2\pi}{N\cdot a} = \left(\frac{N\cdot a}{2\pi}\right)^{-1} \quad \text{of } k\text{-space}$$

& the density of states is thus:

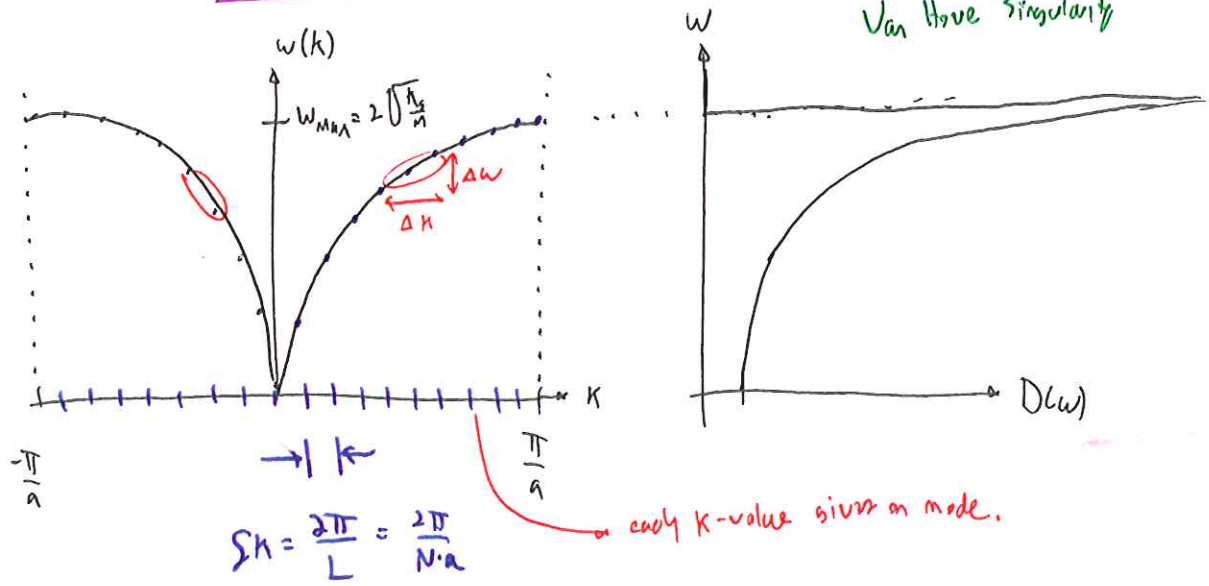
$$\boxed{DOS_k = \left(\frac{N\cdot a}{2\pi}\right)} = \frac{L}{2\pi}$$

$$\left[\begin{matrix}\text{Density of States}\\ \text{in } k\text{-space}\end{matrix}\right] = \left[\frac{\#\text{ states}}{\text{length in } k\text{-space}}\right]$$

In the 1° BZ, which has width $\frac{2\pi}{a}$, there are

$$\underbrace{\left(\frac{N\cdot a}{2\pi}\right)}\cdot\frac{2\pi}{a} = \underline{N \text{ modes}} \quad \checkmark \quad \underline{= \sum_k} = \frac{Na}{2\pi}\int_{-\pi/a}^{\pi/a} dk$$

Can Have Singularity



$$\delta k = \frac{2\pi}{L} = \frac{2\pi}{N\cdot a}$$

each k-value gives one mode.

$$D(\omega) \equiv \frac{\#\text{ states}}{\Delta\omega \rightarrow \text{interval in freq. space}}$$

$$= \frac{DOS_k\cdot\Delta k}{\Delta\omega}$$

$$\boxed{D(\omega) = 2\times\left(\frac{L}{2\pi}\right)\frac{1}{|d\omega/dk|}}$$

[Density of States in frequency]

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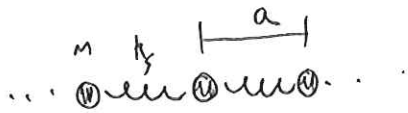
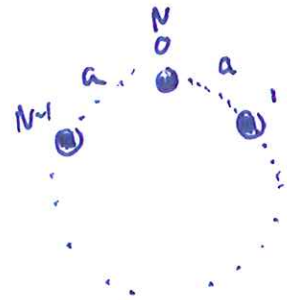
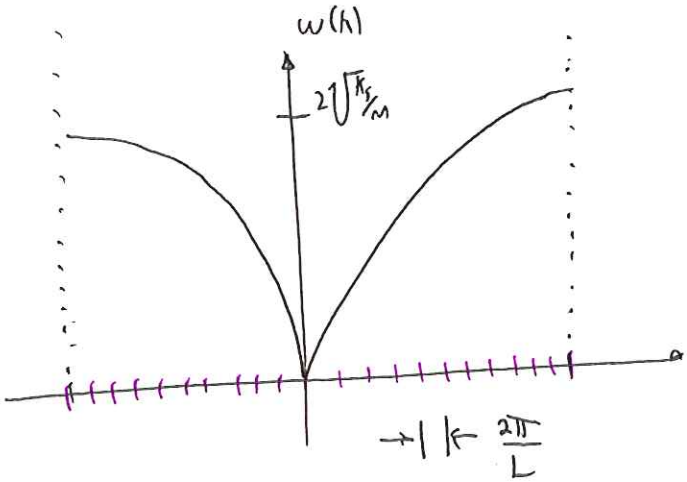




$$\omega(k) = 2\sqrt{\frac{k_s}{m}}\left|\sin\left(\frac{ka}{2}\right)\right|$$



$$\Sigma x_n = Ae^{-i(k(n+N)a-\omega t)}$$
$$= Ae^{-i(kna-\omega t)}$$

$$\Rightarrow \quad kNa = 2\pi \cdot n$$

$$\boxed{k_n = \frac{2\pi}{Na}\cdot n = \frac{2\pi}{L}\cdot n}$$

$$\boxed{\begin{aligned} DOS_k &= \frac{Na}{2\pi} = \frac{L}{2\pi} \\ D(\omega) &= 2\left(\frac{L}{2\pi}\right)\frac{1}{|d\omega/dk|} \end{aligned}}$$

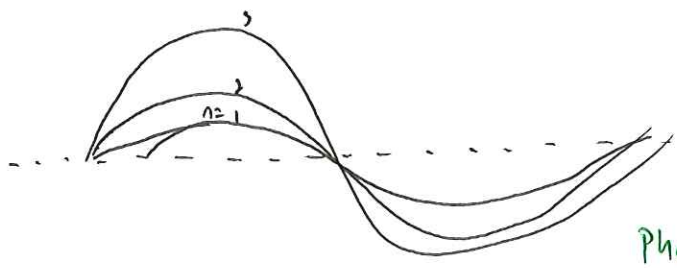
Density of States

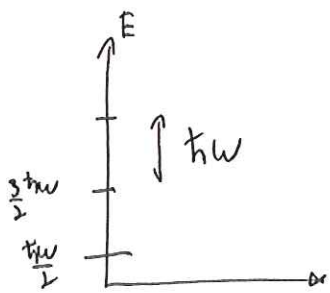
Quantum Modes: Phonons

- Quantum correspondence: A classical quadratic Hamiltonian mode w/ frequency ω has energy eigenstates:

$$E_n = \hbar\omega(n + 1/2) \qquad n \in \mathbb{Z}^+$$

Higher $n \Rightarrow$ larger amplitude





Phonons:

Each excitation by a step up the harmonic oscillator ladder is a "phonon."

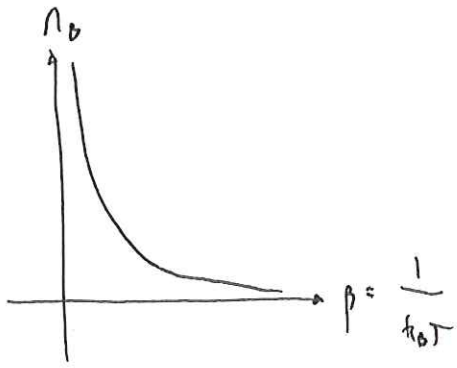
A phonon is a discrete quantum of vibration.

Like photons, phonons are bosons so the occupation # of a mode of freq. $\omega(k)$ is

$$n_B(\beta \cdot \hbar\omega) = \frac{1}{e^{\beta\hbar\omega} - 1} \qquad \beta \equiv \frac{1}{k_B T}$$

[Bose Occupation factor]

so



Then the energy of a mode is:

$$E_k = \hbar\omega(k)\left(n_B(\beta\hbar\omega(k)) + \tfrac{1}{2}\right)$$

& the total energy

$$U_{total} = \sum_k \hbar\omega(k)\left(n_B(\beta\hbar\omega(k)) + \tfrac{1}{2}\right)$$

$$= \frac{Na}{2\pi}\int_{-\pi/a}^{\pi/a} \hbar\omega(k)\left(n_B(\omega(k)) + \tfrac{1}{2}\right) dk$$

$$= \int \frac{Na}{2\pi}\frac{d\omega}{dk}(\ldots)\, dk$$

$$= \int_0^{\omega_{max}} D(\omega)\cdot\hbar\omega\left(n_B(\beta\hbar\omega) + \tfrac{1}{2}\right) d\omega$$

Later we'll see Debye & Einstein models for U_{total} differ in what the dispersion relation is:

$\omega(k) = v_{sound}\, k$ (Debye)

$\omega(k) = \omega_0$ (Einstein)

Where we also note,

$$\sum_k = \int_{-\pi/a}^{\pi/a}\left(\frac{Na}{2\pi}\right) dk$$

$$= \int D(\omega)\, d\omega$$

<u>Crystal Momentum (Phonon Momentum):</u>

The momentum of a photon is $\hbar\vec{k}$, so it is tempting to write the phonon momentum as

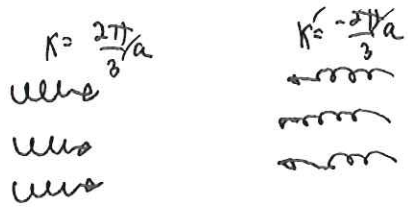
$$\hbar\vec{k}$$

But the phonon mode is the same physically for $\vec{k} + \vec{G}$, so $\hbar\vec{k}$ is ambiguous. In a crystal, the quantity $\hbar\vec{k}$ is known as the crystal momentum & it is conserved modulo $\vec{G}$:

$$\hbar\vec{k}' = \hbar\vec{k} + \hbar\vec{G} \quad \text{for some } \vec{G}$$

However energy is conserved.

Ex

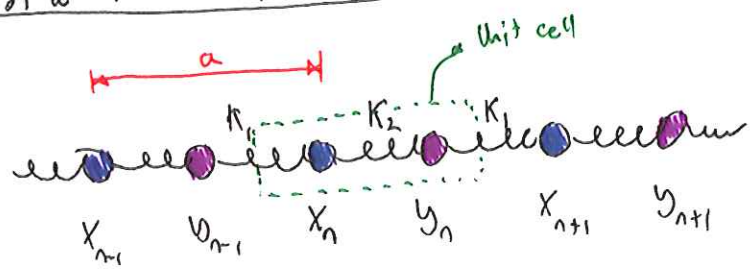


$$\sum k = 2\pi/a \qquad \Rightarrow \qquad \sum k = \sum k' + 2 \times \frac{2\pi}{a} \qquad \square$$
$$\sum k' = -2\pi/a$$

However, energy will always be conserved:

$$\hbar\omega(\vec{k}) = \hbar\omega(-\vec{k})$$

Vibrations of a 1D Diatomic chain:



Assume masses are equal:

$$m\,\delta\ddot{x}_n = -(k_1+k_2)\,\delta x_n + k_1\,\delta y_{n-1} + k_2\,\delta y_n$$
$$m\,\delta\ddot{y}_n = -(k_1+k_2)\,\delta y_n + k_1\,\delta x_{n+1} + k_2\,\delta x_n$$

Now δx_n, δy_n may have different amplitudes:

$$\delta x_n = A_x e^{-i(kna-\omega t)}$$

$$\delta y_n = A_y e^{-i(kna-\omega t)}$$

$$-m\omega^2 A_x e^{-i(kna-\omega t)} = -(k_1+k_2)A_x e^{-i(kna-\omega t)} + k_1 A_y e^{-i(kna-\omega t)} e^{ika} + k_2 A_y e^{-i(kna-\omega t)}$$

$$-m\omega^2 A_y e^{-i(kna-\omega t)} = -(k_1+k_2)A_y e^{-i(kna-\omega t)} + k_1 A_x e^{-i(kna-\omega t)} e^{-ika} + k_2 A_x e^{-i(kna-\omega t)}$$

Cancelling common factors, we have,

$$-m\omega^2 A_x = -(k_1+k_2)A_x + k_1 A_y e^{ika} + k_2 A_y$$
$$-m\omega^2 A_y = -(k_1+k_2)A_y + k_1 A_x e^{-ika} + k_2 A_x$$

or in matrix form,

$$m\omega^2 \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} k_1+k_2 & -k_1 e^{ika} - k_2 \\ -k_1 e^{-ika} - k_2 & k_1+k_2 \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix}$$

A solution is found by the det $=0$:

$$\begin{vmatrix} (k_1+k_2)-m\omega^2 & -k_2-k_1 e^{ika} \\ -k_2-k_1 e^{-ika} & (k_1+k_2)-m\omega^2 \end{vmatrix} = (k_1+k_2-m\omega^2)^2 - |k_2+k_1 e^{ika}|^2 = 0$$

or

$$m\omega^2 = (k_1+k_2) \pm \underbrace{|k_1 + k_2 e^{ika}|}$$

$$\sqrt{(k_1+k_2 e^{ika})(k_1+k_2 e^{-ika})} = \sqrt{k_1^2+k_2^2+k_1k_2(e^{ika}+e^{-ika})}$$
$$= \sqrt{k_1^2+k_2^2+2k_1k_2\cos(ka)}$$

$$\Rightarrow \boxed{\omega_\pm = \left(\frac{k_1+k_2}{m} \pm \frac{1}{m}\sqrt{k_1^2+k_2^2+2k_1k_2\cos(ka)}\right)^{1/2}}$$

Let's evaluate $\omega_\pm$ @ $k=0$ & $k=\frac{\pm\pi}{a}$

$$\omega_\pm(0) = \left(\frac{k_1+k_2}{m} \pm \frac{1}{m}\sqrt{(k_1+k_2)^2}\right)^{1/2} =$$

$$= \left(\frac{k_1+k_2}{m} \pm \frac{k_1+k_2}{m}\right)^{1/2}$$

$$= \boxed{\begin{cases} 0 & - \\ \sqrt{\frac{2(k_1+k_2)}{m}} & + \end{cases}}$$

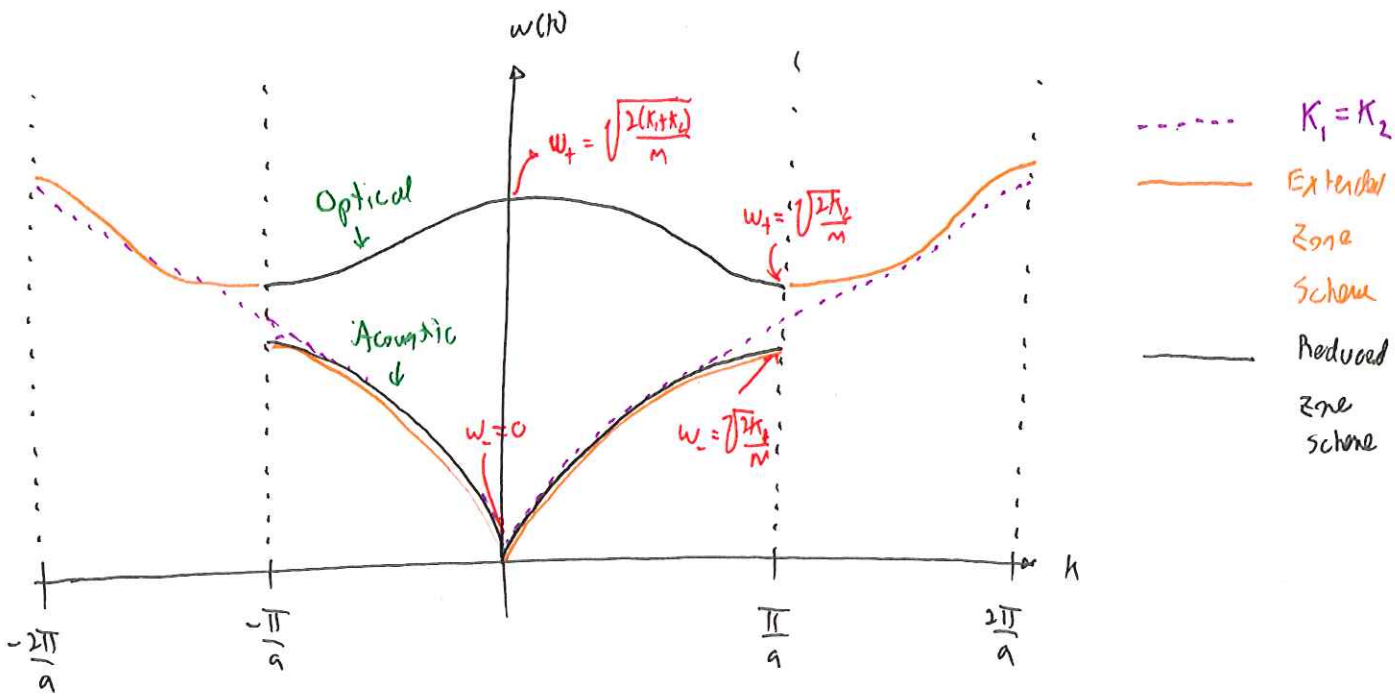
$$\omega_\pm\left(\frac{\pm\pi}{a}\right) = \left(\frac{K_1+K_2}{m} \pm \frac{K_2-K_1}{m}\right)^{1/2}$$

$\downarrow$

1st BZ

$$= \boxed{\begin{cases} \sqrt{\frac{2K_1}{m}} & - \\ \sqrt{\frac{2K_2}{m}} & + \end{cases}}$$

Assume $K_2 > K_1$



Remarks:

- For the 2-atom basis, there are 2 unique values of $\omega(\vec{k})$ per $\vec{K}$. These are called dispersion branches.

  - In general, the number of dispersion branches will equal the number of DOF of the unit cell, but there will only be one acoustic branch per DOF of an atom (up to 3), & the rest will be optical branches:

    # of Acoustic Branches = 3 — In 3D with

    # of optical modes = $3(n-1)$ — n basis atoms

- Allowed K-vectors still determined by Born-von Karman & Lattice: $K_n = \frac{2\pi}{Na}\cdot n = \frac{2\pi}{L}\cdot n$

- The optical branch has a finite ω @ $K \to 0$, $\lambda \to \infty$. It's name arises because

$$\omega_{photon} = c \cdot K$$

$$\omega_{phonon} = \begin{cases} \omega_0 & \text{optical} \\ v_{sound} K & \text{acoustic} \end{cases} \quad K \to 0$$

Since $cK \gg v_{sound} K$ for all K, we cannot get conservation of energy by coupling to the acoustic mode,

For the optical mode, we can find some K such that,

$$\boxed{c \cdot K \approx \omega_0}$$

So photons will interact with optical phonons.

- Viewing $\omega(K)$ in the extended zone scheme (or by going up the ω_- first, then the optical branch from $\pm \pi/a$) we see that the Bragg condition is met for vibrational waves at the edges of the 1° & 2° BZ!

Here $\frac{d\omega}{dK} = 0$

So no waves can propagate.

- There is a $\Delta\omega$ gap at $K = \pm \pi/a$:

$$\Delta\omega = \sqrt{\frac{2K_2}{m}} - \sqrt{\frac{2K_1}{m}}$$

& as $K_1 \to K_2$ $\Delta\omega = 0$

but we get a monatomic basis with $a_{lattice} = \frac{a}{2}$ so $K = \pm \frac{2\pi}{a}$ is 1° BZ,