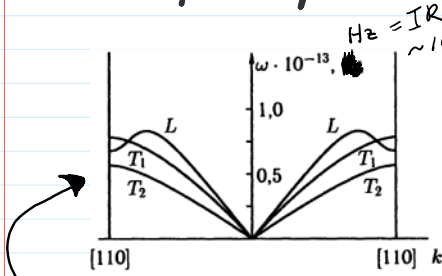


# Energetic spectrum of acoustic phonons

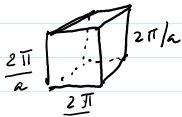


Dispersion curves of Al in [110]

As you recall there can be only 3 waves in a crystal, so for any specific direction  $\vec{k}$  there will be 3 dispersion curves ( $\omega(\vec{k})$ ) or we say 3 branches of acoustic waves. Because of the large number of possible directions, we can instead describe a crystal via the surfaces of constant frequency  $\omega = \omega_i(\vec{k})$  for each branch  $i$ .

Note,  $\omega$  dependence on  $k$  is a periodic function with the period defined by the size of **Brillouin zone** = which is an area which is symmetric wrt to  $k=0$ . For a chain of size  $a = 2\pi/a$

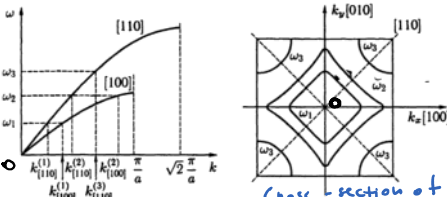
For 2D  $(k_x, k_y) = \begin{matrix} \square \\ 2\pi/a \end{matrix} \cdot 2\pi/a$ . In general the shape in 3D is defined by symmetry of a crystalline lattice.



← it contains all possible values of  $k$ . So once you have this for 1 BZ, you have it determined for the whole crystal.  $\Rightarrow \omega(\vec{k}) = \omega(\vec{k} + n\vec{g})$ , where  $\vec{g}$  is the crystal momentum.

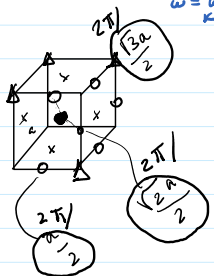
where  $n = 1, 2, 3, \dots$

3 Consider the case of a square lattice, of size  $a$



Dispersion curves for phonons in [110] and [100]

Cross section of  $\omega = \omega(\vec{k})$   $k_2 = 0$



- 1) The closest points to  $k=0$  are the points located to the center of the cube faces.  $\times$
- 2) next are the center of the edges of the cube  $\circ$
- 3) and the further ones are the corners of the cube  $\Delta$

To determine the shape of the phonon curves consider e.g. [010] for  $\omega_1$ ,  $\omega_2$  and  $\omega_3$  and  $k_2 = 0$

5 Note for small  $k$  all branches are linear in all directions. However depending on direction the distance to the BZ can be different so in the direction with closer distance dispersion changes faster than for a direction furthest to the BZ edge. This causes the distortion of the constant surface shape as shown in fig. above.

## SPECTRAL DENSITY OF PHONONS

the distortion of the constant surface shape as shown in fig. above.

### SPECTRAL DENSITY OF PHONONS

In real crystals the real spectrum is very complex, and we may need to know the exact shape of  $\omega = \omega_i(\mathbf{k}) = \text{const}$  for  $i=1,2,3$ . Those surfaces define a very important quantity  $D(\omega) = \frac{dn}{d\omega}$

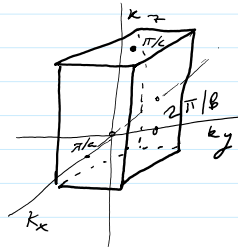
= SPECTRAL DENSITY OF PHONONS = # of phonons in the interval of freq.  $d\omega$

$$n(\omega) = n_{||} + n_{\perp 1} + n_{\perp 2} \Rightarrow D(\omega) = \sum_{i=1}^3 \frac{dn_i(\omega)}{d\omega} = \sum_{i=1}^3 D_i(\omega)$$

Clearly  $\int_0^\infty D(\omega) d\omega = \text{total number of allowed states in the BZ.}$

e.g. single atom xtal:  $k_{q_x} = \frac{2\pi q_x}{L_x}$   $q_x = \pm 1, \pm 2, \dots, \frac{L_x}{2a}$   
 $L_x, L_y, L_z$  and so on.

All allowed values of  $\mathbf{k}$  must be inside the 1st BZ with volume  $\frac{(2\pi)^3}{(abc)}$



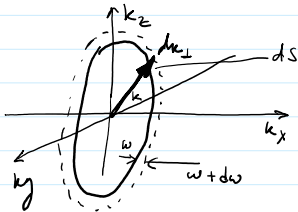
The elementary volume available for 1 state:

$$\frac{(2\pi)^3}{(L_x L_y L_z)} = \frac{(2\pi)^3}{V} : \text{the total \# of states } \frac{(2\pi)^3}{(abc)} \frac{1}{(2\pi)^3} \Rightarrow \frac{V}{(abc)} = N$$

The total number of acoustic waves =  $3N$  which is true for any single atom lattices.

2

Let's calculate  $D_i(\omega) = dn_i/d\omega$  we need to calculate the change of  $dn_i$  for  $d\omega$ . Consider 2 surfaces  $\omega_i(\mathbf{k}) = \text{const}$  and  $d\omega + \omega_i(\mathbf{k}) = \text{const}$



the volume for the arc  $ds$  is  $ds \cdot dk_{\perp}$ . The total volume between  $\omega$  and  $\omega + d\omega$

$$\Delta = \int_{S(\omega)} ds dk_{\perp} = \int_{S(\omega)} \frac{d\omega ds}{|v_g(\mathbf{k})|} = d\omega \int_{S(\omega)} \frac{ds}{|v_g(\mathbf{k})|}$$

The volume for a single state  $(2\pi)^3/V$  and hence

$$dn = \frac{\Delta}{(2\pi)^3/V} = \frac{V d\omega}{(2\pi)^3} \int_{S(\omega)} \frac{ds}{|v_g(\mathbf{k})|} \Rightarrow$$

$$D(\omega) = \frac{dn}{d\omega} = \frac{V}{(2\pi)^3} \int \frac{ds}{|v_{g_i}(\mathbf{k})|}$$

the integration is along the close surface for each branch  $i$

Because each branch has max  $\omega_i^m$  the result for 3D

$$D_i(\omega) = \begin{cases} \frac{V}{(2\pi)^3} \oint_{S(\omega_i)} \frac{ds}{|v_{g_i}|} & \text{for } \omega \leq \omega_i^m \\ 0 & \omega > \omega_i^m \end{cases}$$

The value of  $\omega_{max}$  is determined from:  $\int_0^{\omega_{max}} D_i(\omega) d\omega = \int_0^{\omega_{max}} D_i(\omega) d\omega = N$

$$D_i^{2D}(\omega) = \int_{\Sigma} \frac{d\ell^s}{(2\pi)^2}$$

The value of  $\omega_{max}$  is determined from:  $\int_0^{\omega_{max}} D_i(\omega) d\omega = \int_0^{\omega_{max}} D_j(\omega) d\omega = N$

$$D_i^{2D}(\omega) = \left\{ \left( \frac{L}{2\pi} \right)^2 \oint \frac{d\ell^s}{\ell(\omega_i) |v_{g_i}(\omega)|} \right\} \text{ and } D_i^{1D}(\omega) = \left\{ \frac{L}{2\pi} \frac{1}{v_g} \right\}$$

element of line of constant  $\omega$  for  $i$ -th branch of spectrum

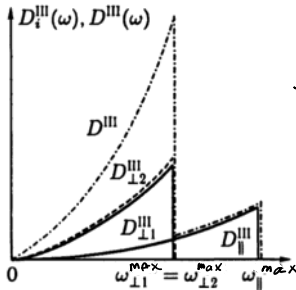
3 In general, it's very hard to calculate  $D(\omega)$  so we need to refer to some simple model. The simplest model was introduced by Debye for isotropic xtal, with isotropic BZ.

$v_{\perp 1} = v_{\perp 2}$  and  $v_{\parallel}$  independent of  $k$   
 In this model we have  $\omega_{\parallel} = v_{\parallel} |k|$   $v_{\perp} = v_{\perp} |k|$

The surface of const freq. are spheres:  $\uparrow$  double degenerate  
 of radius  $k_{\parallel} = \frac{\omega_{\parallel}}{v_{\parallel}}$ ,  $k_{\perp} = \frac{\omega_{\perp}}{v_{\perp}} \Rightarrow |v_g| = \text{const} \Rightarrow$

$$D_i^{3D}(\omega) = \int_0^{\omega} \left( \frac{V}{(2\pi)^3} \right) \cdot \frac{1}{|v_g|} \oint ds = \frac{V}{(2\pi)^3} \frac{4\pi \omega^2}{|v_g|^3} = \frac{V \omega^2}{2\pi^2 |v_g|^3}$$

$\left( 4\pi k_i^2 = 4\pi \left( \frac{\omega}{v_{\parallel, \perp}} \right)^2 \right)$



Spectral distribution of  $D_{\parallel}$  and  $D_{\perp 1}$  and  $D_{\perp 2}$

The total  $D(\omega) = \sum_{2 \times 1, \parallel} D_i(\omega)$ ; The  $\omega^{max}$  is determined by

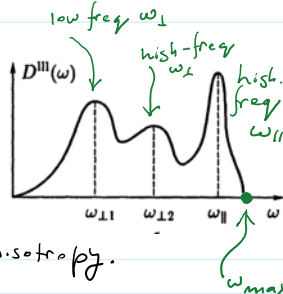
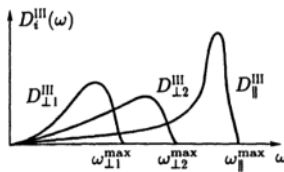
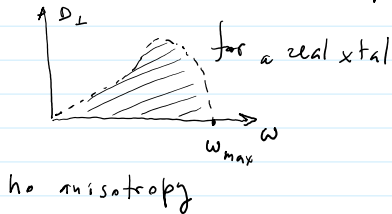
from  $\int_0^{\omega_i^{max}} D_i(\omega) d\omega = N$  or  $\frac{V (\omega_i^{max})^3}{6\pi^2 |v_g|^3} = N$

or  $\omega_i^{max} = |v_g| \left( \frac{6\pi^2 N}{V} \right)^{1/3}$   
 $\omega_{\parallel}^{max} > \omega_{\perp 1} = \omega_{\perp 2}$   
 $\uparrow$   $n = \text{density of phonon modes}$

Derive  $\omega_i^{max}$  for the 2D and 1D cases.

Note: Debye model is the only model with an analytical result.

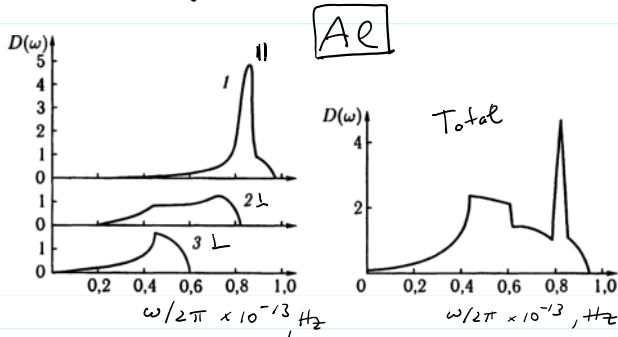
Some complications: 1) no single  $k^{max}$  since it's not a sphere but BZ which is often has complex topology as the result  $\omega(\omega)$  will stop at the zone boundary.



And here is the real calculation for Al based on DFT.

$D(\omega) \uparrow$   $\parallel$  Al

calculation for AE based on DFT.



## VAN Hove Singularities

if you compare the Debye model and DFT you notice that we have a very similar behaviour. But in DFT we see many sharp features. Why?

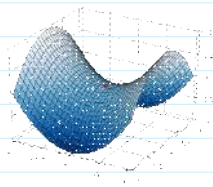
The reason for kind of behavior is that we have those "spikes" when we reach the frequencies corresponding to  $\omega$  in the BZ with some critical points, meaning that at those points

$$v_g = \nabla_{\mathbf{k}} \omega(\mathbf{k}) = 0 \Rightarrow D_i(\omega) = \frac{V}{(2\pi)^3} \oint \frac{dS}{|v_g(\mathbf{k})|} \rightarrow \infty$$

There are four kinds of critical points in the BZ:

2 points - MIN and MAX

2 points - saddle



singularities in DOS ( $D_i(\omega)$ ) corresponding to those points are called

the VAN HOVE SINGULARITIES.

Let me illustrate this phenomenon in a 3D system:

We use a Taylor expansion in the vicinity of a singularity  $\mathbf{k}_0$

$$\omega(\mathbf{k}) = \omega_0 + a_x (\mathbf{k}_x - \mathbf{k}_{0x})^2 + a_y (\mathbf{k}_y - \mathbf{k}_{0y})^2 + a_z (\mathbf{k}_z - \mathbf{k}_{0z})^2$$

We do not have any linear terms since at  $\mathbf{k} = \mathbf{k}_0$   $\nabla_{\mathbf{k}} \omega(\mathbf{k}) = 0$

$a_{x,y,z} > 0$  for local min,  $< 0$  for local max

As you noticed  $\omega(\mathbf{k}) = \text{const} \Rightarrow$  an ellipsoid in the BZ with axis  $a, b, c$

$$a = \sqrt{\frac{\omega - \omega_0}{a_x}} \dots \dots \dots \quad \left| \text{for min} \right.$$

$$a = \sqrt{\frac{\omega - \omega_0}{-a_x}} \dots \dots \dots \quad \left| \text{for max} \right.$$

The volume  $\Omega_{\omega}$  in the BZ limited by this surface at the vicinity of min and max

$$\Omega_{\omega} = \frac{4}{3} \pi abc = \frac{4}{3} \pi \frac{|\omega - \omega_0|^{3/2}}{\sqrt{|a_x| |a_y| |a_z|}}$$

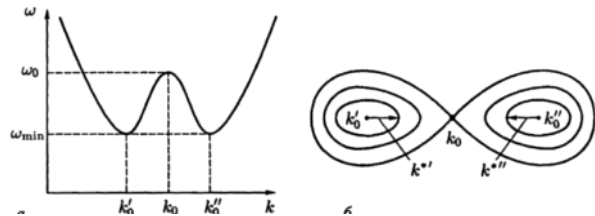
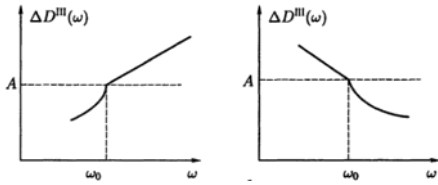
$$\Omega_{\omega} = \frac{4}{3} \pi abc = \frac{4}{3} \pi \frac{|\omega - \omega_0|^{1/2}}{\sqrt{|\alpha_x| |\alpha_y| |\alpha_z|}}$$

The number of phonon states  $N$  inside of this ellipsoid

$$N = \frac{V \Omega_{\omega}}{(2\pi)^3} \Rightarrow \Delta D^{3D} = \frac{dN}{d\omega} = \frac{V}{(2\pi)^2} \frac{|\omega - \omega_0|^{1/2}}{\sqrt{|\alpha_x| |\alpha_y| |\alpha_z|}}$$

As you see  $\Delta D^{3D}$  around singularity is still analytical. But

$\frac{d \Delta D^{3D}}{d\omega} \rightarrow \infty$ . For example, the presence of a saddle point in the phonon spectrum means that in the BZ there are 2 local minimum at  $k'_0$  and  $k''_0$ .



Repeat this calculation  
For 2D and 1D

### STATISTICS OF ACOUSTIC PHONONS (MAYBE OPTIONAL)

In our lattice we can excite an unlimited number of phonons simultaneously, i.e. in a quantum state  $\omega$  we can have unlimited number of phonons (b/c. they are bosons!).  
So the total number of phonons is really defined by the thermal equilibrium condition:

$$\left( \frac{\partial F}{\partial N} \right)_{P,T} = 0 \quad \text{but} \quad \frac{\partial F}{\partial N} = \mu \equiv \text{chem. potential} \Rightarrow$$

chem. potential of phonons is ZERO.

Now consider any branch of the phonon spectrum, the corresponding mode of oscillation is treated as an oscillator:

$$E_{n_g}^{\uparrow} = \hbar \omega_g \left( n_g + \frac{1}{2} \right) \quad n_g = 0, 1, 2, \dots$$

From Gibbs distribution: the probability that oscillator with  $\omega_g$  is in the state  $n_g$  has energy  $E_{n_g}$ :

$$W_{n_g} = A_g e^{-E_{n_g}/k_B T} \Rightarrow A_g \text{ is from } \sum_{n_g=0}^{\infty} W_{n_g} = 1$$

$$A_g = \frac{1}{\sum_{n_g=0}^{\infty} e^{-(E_{n_g}^{\uparrow}/k_B T)}} = \left[ 1 - e^{-\hbar \omega_g / k_B T} \right] e^{\hbar \omega_g / 2 k_B T} \Rightarrow$$

↑  
geometric series

$$W_{n_q} = \left[ 1 - e^{-\hbar\omega_q/k_B T} \right] e^{-n_q \hbar\omega_q/k_B T}$$

↑  
geometric series

Now lets calculate the average number of phonons:

$$n_q^{av} = \sum_{n_q=0}^{\infty} n_q W_{n_q} ; \text{ lets call } \hbar\omega_q/k_B T = x$$

$$\sum_{n_q=0}^{\infty} n_q e^{-\frac{n_q \hbar\omega_q}{k_B T}} = \sum_{n_q=0}^{\infty} n_q e^{-n_q x} = -\frac{d}{dx} \left( \sum_{n_q=0}^{\infty} e^{-n_q x} \right) = -\frac{d}{dx} \left( \frac{1}{1 - \exp(-x)} \right)$$

thus we end up:

$$n_q^{av} = \frac{[1 - e^{-x}] e^{-x}}{(1 - e^{-x})^2} = \frac{1}{e^{\hbar\omega_q/k_B T} - 1}$$

$$n_q^{av} = \frac{1}{e^{-\hbar\omega_q/k_B T} - 1}$$

Next we can calculate the average energy of the excited oscillator with freq.  $\omega_q$  at given  $T$ , i.e. the energy of the  $\omega_q$  phonon mode.

$$E_q^{av} = \sum_{n_q=0}^{\infty} E_{n_q} W_{n_q} = \frac{\hbar\omega}{2} + \hbar\omega_q \sum_{n_q=0}^{\infty} n_q W_{n_q}$$

inserting  $W_{n_q}$  from above we get:

$$E_q^{av} = \frac{\hbar\omega_q}{2} + n_q^{av} \hbar\omega_q = \frac{\hbar\omega_q}{2} + \frac{\hbar\omega_q}{e^{-\hbar\omega_q/k_B T} - 1}$$

$$= \frac{\hbar\omega_q}{2} + U_q^{av}$$

↑  
"0" oscillations

↑  
the average thermal energy due to phonons.

For low  $T$ :  $T \ll \hbar\omega_q/k_B$

$$n_q^{av} \text{ and } U_q^{av} \text{ are very small} \Rightarrow n_q^{av} = e^{-\hbar\omega_q/k_B T}$$

$$U_q^{av} \approx \hbar\omega_q e^{-\hbar\omega_q/k_B T}$$

In high  $T > \hbar\omega_q/k_B$  both grow as  $T \Rightarrow$

$$n_q^{av} \sim k_B T$$

$$g = \frac{1}{\hbar \omega_g}$$

Recall the number of modes, or waves with freq.  $\omega_g$  in each branch of acoustic phonons =  $N$  atoms in lattice. And the total number =  $3N$

$$U_g^{av} \approx k_B T$$

But the number of phonons in each mode with freq.  $\omega_g$  is unlimited and is determined only by  $T$ .

Also remember for each mode we have MAX freq.:

$\omega_{\perp, \parallel}^{max}$  so we end up with some characteristic  $T^*$ :  
 $\frac{\hbar \omega^{max}}{k_B}$ , meaning the probability of excitation

of one phonon with max  $\omega_{max} = 0.272$   
 two = 0.086  
 three = 0.232

\* But at  $T > T^*$  we excite ALL modes from  $\omega^{min}$  to  $\omega^{max}$  in the give phonon branch. Further increasing  $T$  only increase the number of phonons in each mode.

### DEBYE TEMPERATURE $\Theta_D$ or $T_D$

$T_D$  is the temperute when energy of thermal oscillations of lattice  $\approx E_{avg}^{av}$  of high frequency phonon modes

It enters all interesting thermodynamic parameters!

Only for 1D chain:  $T_D = \frac{\hbar \omega^{max} = \omega^D}{k_B} = \Theta_D / k_B$  so in this case the  $\omega^{MAX} = \omega^D$ .

In real 3D crystals we have 3 different branches

so we need to think of  $\Theta_{D\parallel}, \Theta_{D\perp 1}, \Theta_{D\perp 2}$  so we have to average over those frequencies.

Debye suggested to approximate it by

$$D_i(\omega) = \frac{V \omega^2}{2\pi v_{a,i}^3} \quad \text{for } \omega < \omega_i^{max}$$

and assume that  $v_{a,i} = \text{const}$ , for each branch  
 For even simple cubic lattice we have a complication  
 since  $v_{||,a}$  and  $v_{\perp,a}$  depend on  $\vec{k}$ . That is we  
 the notion of an average speed of sound is very  
 uncertain.

For small  $k$ ,  $v(k)$  is linear and we can approximate it  
 $|K_i(\omega)|^2 = k_x^2 + k_y^2 + k_z^2$  and  $v_{i,a} = \frac{\omega}{k_i(\omega)}$

and since  $v_{i,a} = \text{const}$

$$\bar{\omega}_i^{\text{max}} = v_{i,a} \left( \frac{6\pi^2 N}{V} \right)^{1/3}$$

and from  $\bar{\theta}_D = \hbar \bar{\omega}_i^{\text{max}}$  etc we can  
 calculate  $\bar{\theta}_D$ .

Also Debye approximated  $D(\omega)$  by the parabolic dependence

$$D_i^{3D}(\omega) = \left\{ \frac{V \omega^2}{2\pi^2 v_a^3} \right.$$

so we can find  $\bar{\omega}^{\text{max}}$  from

$$\int_0^{\bar{\omega}^{\text{max}}} D(\omega) d\omega = 3N \quad \text{where } D(\omega) = \sum_{i=1}^3 D_i(\omega) =$$

$$= \frac{V \omega^2}{2\pi^2} \left( \frac{1}{v_{a,||}^3} + \frac{1}{v_{a,\perp 1}^3} + \frac{1}{v_{a,\perp 2}^3} \right) \Rightarrow \bar{\omega} = \bar{v}_a \left( \frac{6\pi^2 N}{V} \right)^{1/3}$$

where  $\frac{3}{\bar{v}_a^3}$  →

and thus  $\bar{\theta}_D = \hbar \bar{\omega}^{\text{max}}$

To summarize, the physical meaning of  $\theta_D$  is

to characterize the energy state of a crystal

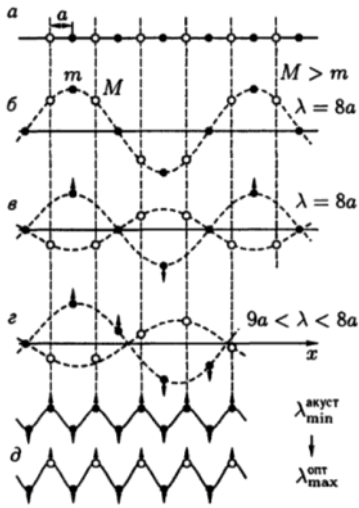
by separating the temperature scale into 2 regions:

1)  $k_B T \ll \bar{\theta}_D$  we get only long wavelength  
 excitations with  $\hbar \omega \ll \bar{\theta}_D$

2)  $k_B T \gg \bar{\theta}_D$  we have all possible excitations  
 including those with  $\hbar \omega \sim \bar{\theta}_D$  & no more modes.



THE END OF PHONONS THEM!



If your crystal has

- i) atoms of a different kind
- ii) more than one atom per unit cell

there will be another kind of excitations called - OPTICAL PHONONS (OP)

The key distinction for OPs is the fact that near neighbours oscillate OUT OF PHASE.

Those modes are excited by light that's why OPs.

Thus for any given  $k_y = 2\pi/\lambda_y$  we have 2 waves for the same  $k_y$  - acoustic and optical.

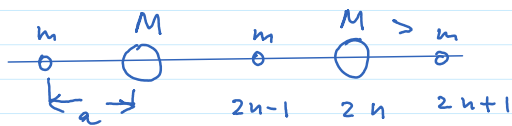
Note: since nn are out of phase the frequency for OPs is close to the  $\omega_{acoustic}^{max}$  and is almost independent of  $k$ .

So in general we have 6 branches:

$$\omega_{||}^a, \omega_{\perp,1}^a, \omega_{\perp,2}^a \text{ and } \omega_{1,2,3}^o$$

DISPERSION OF OPs.

Consider 1D chain with N atoms of two types, M and m.



equation of motion is given by

$$\begin{cases} M \frac{\partial^2 \xi_{2n}}{\partial t^2} = \beta_1 (\xi_{2n+1} + \xi_{2n-1} - 2\xi_{2n}) \\ m \frac{\partial^2 \xi_{2n+1}}{\partial t^2} = \beta_1 (\xi_{2n+2} + \xi_{2n} - 2\xi_{2n+1}) \end{cases}$$

we search for a solution in the form:

$$\begin{cases} \xi_{2n} = \mu e^{i(\omega t + 2nka)} \\ \xi_{2n+1} = \eta e^{i(\omega t + (2n+1)ka)} \end{cases} \Rightarrow$$

$$\begin{cases} -M \mu \omega^2 = \beta_1 \eta [e^{ika} + e^{-ika}] - 2\beta_1 \mu \\ \dots \dots \dots \beta_1 \mu [e^{ika} - e^{-ika}] - 2\beta_1 \eta \end{cases} \Rightarrow$$

$$\begin{cases} -M\mu\omega^2 = \beta_1\eta [e^{ika} + e^{-ika}] - 2\beta_1\mu \\ -m\eta\omega^2 = \beta_1\mu [e^{ika} + e^{-ika}] - 2\beta_1\eta \end{cases} \Rightarrow$$

$$\begin{vmatrix} (2\beta_1 - \omega^2 M) & (-2\beta_1 \cos ka) \\ (-2\beta_1 \cos ka) & (2\beta_1 - \omega^2 m) \end{vmatrix} = 0 \Rightarrow$$

$$\omega_{\pm}^2 = \beta_1 \left( \frac{1}{m} + \frac{1}{M} \right) \pm \beta_1 \sqrt{\left( \frac{1}{m} + \frac{1}{M} \right)^2 - \frac{4\sin^2 ka}{mM}}$$

Notice  $\omega^2$  is independent of  $\eta$ .

Consider  $\omega_+$ ,  $\omega_-$  for  $ka \ll 1$

$$\omega_+ \sim \sqrt{2\beta_1 \left( \frac{1}{m} + \frac{1}{M} \right)} \quad \omega_- \sim \left( \frac{2\beta_1}{M+m} \right)^{1/2} ka$$

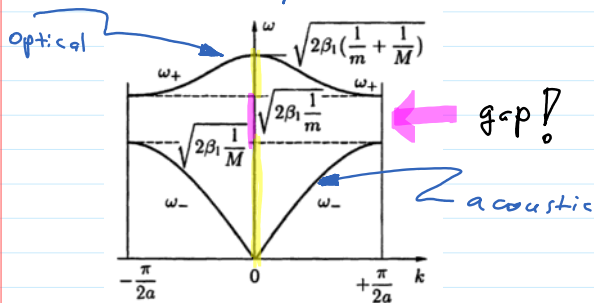
First consider  $\omega_-(ka)$  we have  $v_a'' = \frac{\partial \omega_-}{\partial k} = a \sqrt{\frac{2\beta_1}{M+m}}$

But we also have another branch:  $\omega_+(ka)$ , to understand its phys. meaning let's take the ratio:

$$\frac{M}{\eta} \text{ (just plug } \omega_+ \text{ or } \omega_- \text{ in } \dots)$$

$\frac{M}{\eta} = -\frac{M}{m}$  which is  $M\mu + m\eta = 0$  which means the amplitude of the center of gravity motion = 0 (for  $ka \ll 1$ ) i.e. the atoms move in antiphase.

Let's plot those 2 branches



e.g. for  $k=0$

$$\omega_+^{\max} = \sqrt{2\beta_1 \left( \frac{1}{m} + \frac{1}{M} \right)}$$

and  $\frac{\partial \omega_+}{\partial k} = 0$  at  $k=0$

$$k \rightarrow \pm \frac{\pi}{2a} \quad \omega_+^{\min} = \sqrt{\frac{2\beta_1}{m}}$$

and for  $k = \frac{\pi}{2a}$   $\frac{\partial \omega_+}{\partial k} = 0$

The spectrum of allowed oscillations is confined into:

$$0 < \omega < \sqrt{\frac{2\beta_1}{m}} \text{ - acoustic}$$

and also we have a GAP!

$$\sqrt{\frac{2\beta_1}{m}} < \omega < \sqrt{2\beta_1 \left( \frac{1}{m} + \frac{1}{M} \right)} \text{ - optical}$$

Note, for  $M \gg m$  the spectrum of optical phonons is very narrow.

$$\omega_+^{\max} = \sqrt{2\beta_1 \left( \frac{1}{m} + \frac{1}{M} \right)} \approx \left( 1 + \frac{m}{2M} \right) \sqrt{2\beta_1 \frac{1}{m}} \approx \sqrt{\frac{2\beta_1}{m}}$$

$$\omega_{+}^{\max} = \sqrt{2\beta_1 \left(\frac{1}{m} + \frac{1}{M}\right)} \approx \left(1 + \frac{m}{2M}\right) \sqrt{2\beta_1 \frac{1}{M}} \sim \sqrt{\frac{2\beta_1}{M}}$$

★ for a 2 atom chain the dispersion is limited to  $|k| < \pm \frac{\pi}{2a}$  NOT  $\pm \frac{\pi}{a}$ !

The allowed wave numbers can be found from

$$\xi_{2n} = \xi_{2n+N} \quad \text{or} \quad \xi_{2n+1} = \xi_{2n+1+N} \quad (\text{periodic boundary cond})$$

$$k_g = 2\pi \frac{g}{Na} = 2\pi \frac{a}{L}, \quad g = \pm 1, \pm 2, \dots, \pm \frac{N}{4}$$

for each  $k_g$  we have  $\lambda_g = \frac{2\pi}{k_g}$   $4a < \lambda_g < L$

The number of modes for each branch is defined by the number of discrete values of  $k_g$  between  $-\frac{\pi}{2a}$  to  $+\frac{\pi}{2a}$

$$\left(\frac{\pi}{a}\right) / \left(\frac{2\pi}{L}\right) = \frac{L}{2a} = N/2 \quad (N/2 \text{ for optical and } N/2 \text{ for acoustic})$$

The discrete spectrum of  $\omega_g$  is defined by the set of  $k_g$  from  $\pm \frac{\pi}{2a}$  which is the BZ for the di-atomic chain.

For acoustic and optical branches for each  $\omega_g$  there are 2 waves with  $k_g$  and  $-k_g$  and symmetric around  $k=0$

Problem: What happens with  $\omega(k)$  vs  $k$  when  $m=M$ ? do we have a gap?

A Physical meaning of the gap.

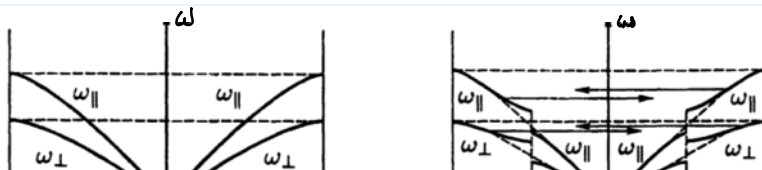
For  $m \rightarrow M$  the waves will experience Bragg reflection at  $k = \pm \pi/a$  and  $\partial\omega/\partial k = 0$ .

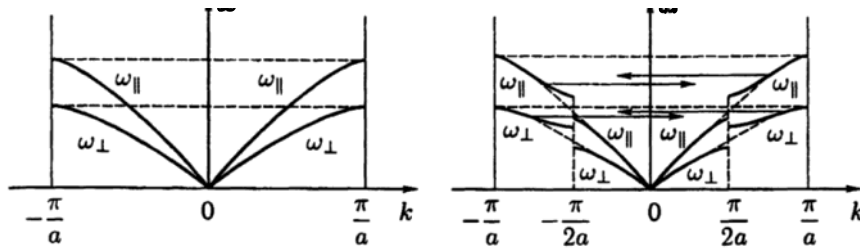
Now gradually increase the mass of even atoms  $m \neq M$  the period also changes from  $a$  to  $2a$ .

And the scattering occurs for  $k = \pm \frac{\pi}{2a}$ . Imagine  $m \approx M$  then for  $k \neq \pm \pi/2a$   $\omega(k)$  should stay unchanged and

for  $k = \pm \frac{\pi}{2a}$   $\frac{\partial\omega}{\partial k} = 0$  and to cross the lines of  $\pm \pi/2a$

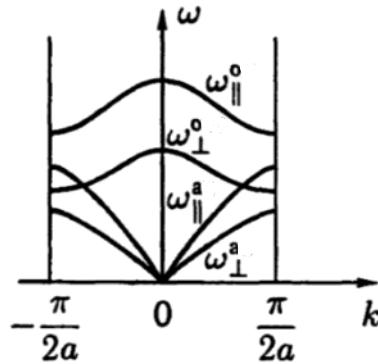
$\omega(k)$  splits into 2 branches separated by the gap.





1D chain: what happens when we double the period of the chain

In general, we can plot the complete dispersion for 3D and 2 atoms



Some comments about 3D:

- 1) for  $\omega_{\perp}$  in general there are very different branches
- 2) b/c of the anisotropy of a crystal there are no strict  $\omega_{\perp}^o$  and  $\omega_{\parallel}^o$  except when polarization of light is along high symmetry axes of the crystal.

- 3) For different directions of  $\vec{k}$  in the BZ there are different sets of  $\omega_{\perp}^o(k)$ ,  $\omega_{\parallel}^o(k)$ ,  $\omega_{\perp,1,2}^o(k)$

It's hard to plot the <sup>iso</sup> energetic surfaces of optical phonons b/c there are no linear  $\omega(k)$  part of the spectrum for OPs. for small  $k$ s.

### STATISTICS OF OPs.

OPs are bosons. But they are special since their minimal energy  $\sim$  max energy of acoustic phonons.  $\sim kT_D = \Theta_D$   
 Below  $T_D$  the number of OPs gets very small.

The total number of phonon modes in all 3 branches =  $3N/2$   
 (in each branch the # of modes =  $N/2$ )

The same is for acoustic phonons.

So the total number of modes:  $3N/2 + 3N/2 = 3N$

Again, the total number of OPs is UNLIMITED WITHIN each modes

Example: The probability of excitation of 1 phonon in each mode for  $T \sim T_0 \approx 100\%$ . It means at this  $T$  we excite  $\sim 3N/2$  OPs, on average 1 OP for each mode of oscillation; for a given  $\omega_q$ .

For  $T \sim T_0/2$  the # of OPs  $\sim 10\%$

$\sim T_0/3 \quad \sim 5\%$

$T_0/50 \quad \sim 10^{-2} N$

i.e. We say OPs rapidly freeze out with  $T$  below  $T_0$ .

### SPECTRAL DENSITY OF OPs

OPs are spread over a narrow freq. range  $> \omega_a^{\max}$

For OPs  $\frac{\partial \omega}{\partial k}$  is small and typically if  $|k| \rightarrow 0 \quad |k| \rightarrow k^{\max}$

That's why  $D_i^0(\omega)$  has narrow peaks.

It's hard to tell what's  $D_i^0(\omega)$  for a real material (DFT?)

but let's assume for  $k=0 \quad \omega = \omega_{\max}$  and also let's assume

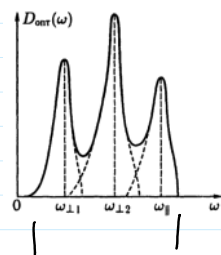
the isoenergy surface is a sphere around  $k=0$  with  $V = 4\pi k^3/3$ , for small  $k$ , long  $\lambda \quad v_g = \partial \omega / \partial k \sim 0$

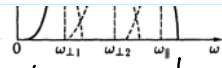
so we can assume that  $(\omega_{\max} - \omega) = \alpha k^2$

then the volume limited by  $\omega = \text{const} \sim 4\pi (\omega_{\max} - \omega)^{3/2} / 3\alpha^{3/2}$

if we divide it by  $(2\pi)^3/V$  and differentiate by  $\omega$

$$\text{we get } D_i^0(\omega)_{k \rightarrow 0} = \frac{V \sqrt{\omega_{\max} - \omega}}{16\pi^2 \alpha^{3/2}}$$





very narrow  
compared to  
acoustic phonons.

## PHONON CONTRIBUTION TO THERMODYNAMICS OBSERVABLES

Thermal energy  $U^{3D}$  at given  $T$  is  $\sum$  of  $\bar{E}_q = \frac{\hbar\omega_q}{2} + \bar{U}_q$

$$+ \bar{U}_q = \frac{\hbar\omega_q}{2} + \frac{\hbar\omega_q}{e^{\hbar\omega_q/k_B T} - 1}$$

with  $\bar{U}_q$  (per mode) =  $\frac{1}{e^{\hbar\omega_q/k_B T} - 1}$

The number of phonon modes in  $d\omega = D(\omega)d\omega$

$$U^{3D} = \int_0^\infty \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} D(\omega) d\omega$$

$D(\omega)$  is not generally known analytically so we will try to approximate it by some simple dependence, e.g. Debye like

Physics: for  $T \ll T_D$  we have  $\sqrt{\hbar\omega}$  optical phonons, and some long  $\lambda$  acoustic phonons. We can think that

the volume limited by the surface of const  $\omega$  ( $\omega_q = \omega, q$ )

$$\sim |q|^3. \text{ Also, for small } q_s \quad \omega_q \sim |q| \leq k_B T / \hbar$$

and hence  $\omega_q \sim T^3$

In short, if the density of wavevector states inside BZ is constant

hence the number of # of excited modes at  $T \sim T^3$

The average energy of each mode  $q$  with  $\hbar\omega_q < \frac{k_B T}{\hbar} \sim k_B T$

Then  $U^{3D} \sim (k_B T) \cdot T^3 \sim T^4$

Now, for  $T > T_D$  # of acoustic phonons is independent of  $T$  and  $= 3N$  in the BZ. The energy of each changes  $\sim T$ . Therefore  $U_{\text{acoustic}}^{3D} \sim 3N k_B T$

But we need to take into account OPs, which contribution growth exponentially with  $T \gg$  above  $T_D$ .

### Debye THEORY

$$\text{For } D_i(\omega) = \frac{V \omega^2}{2\pi^2 v_a^3} \Rightarrow \bar{U}_D^{3D} = \frac{\hbar V}{2\pi^2 v_a^3} \int_0^{\omega_{max}} \frac{\omega^3 d\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} =$$

$$= \frac{3V k_B T^4}{2\pi^2 \hbar^3 v_a^3} \int_0^{x_m} \frac{x^3 dx}{e^x - 1} \quad x_m = \frac{\hbar \omega_m}{k_B T}$$

Let us introduce  $T_D = \theta_D / k_B = \hbar \omega_m / k_B$ , and recall  $\omega_m = v_a \left( \frac{6\pi^2 N}{V} \right)^{1/3}$

$$\bar{U}_D^{3D} = 9 k_B N \left( \frac{T}{T_D} \right)^3 T \int_0^{T_D/T} \frac{x^3 dx}{e^x - 1} \quad \text{for } T \ll T_D \quad T/T_D \rightarrow \infty$$

$$\int_0^{\infty} \frac{x^3 dx}{e^x - 1} = 6 \zeta(4) = \pi^4/15 \quad \text{so for } T \ll T_D$$

Riemann zeta function

$$\boxed{\bar{U}_D^{3D} = 3\pi^4 \frac{k_B N T^4}{5 T_D^3}} \quad T \ll T_D$$

Now we can calculate many things; e.g. heat capacity

$$C_D^{3D} = \frac{\partial \bar{U}^{3D}}{\partial T} = \frac{12\pi^4 k_B N}{5} \left( \frac{T}{T_D} \right)^3 = \boxed{234 k_B N \left( \frac{T}{T_D} \right)^3}$$

it works very well for many solids if  $T < 0.1 T_D$

For high  $T > T_D$   $x < 1$  everywhere  $e^x \sim 1 + x + \dots$

and thus  $\bar{U}_D^{3D} = 3 k_B N T$

$$\boxed{C_D^{3D} = \frac{\partial U}{\partial T} = 3 k_B N} \quad T > T_D$$

in general

$$\boxed{C_D^{3D}(T) = \frac{\partial \bar{U}_D^{3D}}{\partial T} = 9 k_B T N \left( \frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{x^3 dx}{e^x - 1}}$$

Works very well for many metals from e.g. Al to Cu



up to their melting points.

Calculate heat capacity of 2D materials within the Debye model.

## THERMAL CONDUCTIVITY

Gradient of  $T$ ,  $\nabla T$  creates heat flow  $\vec{h} \sim \nabla T$

In isotropic solid  $\vec{h} = -\chi \nabla T$

↑ thermal conductivity

Note; heat can be carried by both electrons and phonons. Here we consider only SPINLESS dielectrics, where heat is due to phonons only.

In general, one can write down Boltzmann equation for an ideal gas of quasiparticles with relaxation time

Then  $\chi = \frac{1}{3} C \bar{v} \ell$ ,  $\ell = \bar{v} \tau$ ,  $\tau$  - relaxation time

We want apply it to our gas of phonons, where  $\bar{v}$  - is the average group velocity  $\omega/k = v_a$

$$\chi_{ph} = \frac{1}{3} C_{ph} \bar{v}_a \ell_{ph} = \frac{1}{3} C_{ph} \bar{v}_a^2 \tau_{ph}$$

Now we need to think of scattering of phonons;  $\tau_{i,ph}$

where  $\frac{1}{\tau_{i,ph}}$  is the freq. of phonon scattering, and

$\nu = \sum_i \nu_{i,ph}$  for several scattering mechanisms.

Thermal Resistance

 $\Rightarrow \omega_{ph} = \frac{1}{\chi_{ph}} = \frac{3}{C_{ph} \bar{v}_a^2 \tau_{ph}} = \frac{3 \nu_{ph}}{C_{ph} \bar{v}_a^2}$

$$\nu_{ph} = \nu_{p-p} + \nu_{p-defect} + \nu_{p-surface \text{ or grain boundary}}$$

### A. NORMAL SCATTERING PROCESSES (N-process)

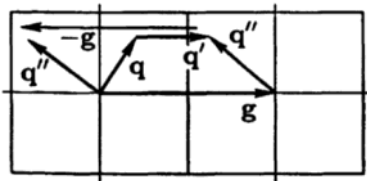
Remember heat flow is a directional motion of phonons then scattering means ph-ph interaction when the phonon after the collision gets out of the stream.

Meaning, large changes in  $\vec{k}$ . For small angle scattering there is no relaxation.

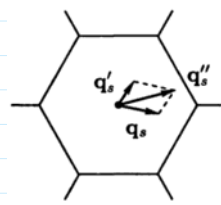
Since thermal energy is in the direction of  $\bar{v}_a$

N-pr. give no scattering.

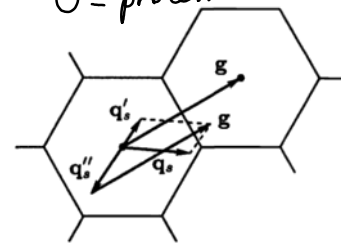
Next, thermal resistance  $W$  is determined by the so-called U-process  $q_s + q_s' = q_s'' + g$



N-process



U-process



For N process  $q + q_s' = q_s''$

$$\omega_s = v_a q_s \quad \omega_s' = v_a q_s' \quad \omega_s'' = v_a q_s''$$

The energy carried by phonons

$$\hbar \omega_s v_a + \hbar \omega_s' v_a = \hbar v_a^2 (q_s + q_s')$$

and after the interaction:  $\hbar v_a^2 q_s'' = \hbar v_a^2 (q_s + q_s')$

In N-process  $\bar{q}_s + \bar{q}_s' - \bar{q}_s'' = 0 \Rightarrow$  no energy dissipation in the N-process is possible.

The thermal resistance in ph-ph mechanism of conductivity is defined only by the so-called U-processes (Umklapp-german)

During the U-process  $q_s + q_s' = q_s'' + g$  crystal momentum

as seen  $q_s + q_s' - q_s'' \neq 0!$

and it means that each U-scattering act results in the energy dissipation.

In short for  $\nu_{p-p}$  we need only consider the U-process.

At high  $T$   $\nu_{p-p}^U \sim T$  and hence  $W_{ph} \sim T$

Once the temperature drops below  $T_D$  probability of U-scattering goes down as for low  $T$  only long wavelength phonons <sup>can</sup> participate.

And the number of highly excited phonons with  $q \sim q_D$  drops exponentially, and below  $T < T_D$   $\nu_{p-p}^U$  sharply

decreases. This can only be seen experimentally for dielectrics as for metals we have a sharp rise of electron-phonon scattering.

### PHONON SCATTERING OF DEFECTS

Since point like defects means  $\approx$  size of a (lattice const)

at  $T = T_D$   $\lambda_{ph} \approx 2a$ , and the energy  $k_B T \sim \frac{\hbar v_a}{\lambda_{ph}}$   
and for low  $T \sim$  several hundreds of a.

Long  $\lambda$  (short  $k$ ) makes scattering very inefficient.

so we ignore this process.

### PHONON SCATTERING OF INTERFACE / SURFACE

With decreasing  $T$ ,  $v$  goes down and  $\lambda_{ph}$  goes up and can reach the size of a thin film or a crystal grain. This kind of scattering may become dominant.

The type of scattering depends on the interface roughness and  $\lambda_{ph}$ . Let's consider a very simple model of diffuse scattering. In this case

$$\nu_{ph-s} = \frac{1}{\tau} = v \quad \text{and almost const with } T. \\ \text{for } \ell_{ph} > d$$

and very small if  $\ell_{ph} \ll d$

For high  $T$  we can ignore  $\nu_{ph-defect}$  and  $\nu_{ph-surface}$  interface

Since  $c(T) = \text{const}(T)$  and  $\nu_{ph-ph} \sim T$

we conclude for  $T \geq T_D$

$$W_{ph} \sim \frac{1}{v_a^2} \sim T \quad \text{and thus } \lambda_p \sim \frac{1}{T}$$

When  $T$  goes down  $\nu_{ph-ph}$  for U-processes

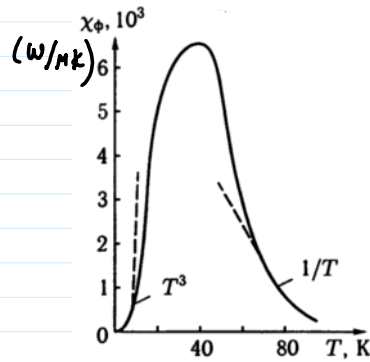
$$\nu_{ph-ph}^U \sim T^{\frac{1}{2}} e^{-\alpha T_D/T} \quad \text{where } 1 < \frac{1}{2} < 3 \\ \text{(no proof)} \\ \text{here}$$

and by ignoring  $\nu_{ph-defect}$  and  $\nu_{ph-interface}$

and  $C_{\text{electra}} = C(T)$  we get

$$W_{\text{ph}} \sim \frac{1}{C(T) v_a^2} T^3 e^{-\omega T_0/T} \quad 1 < \xi < 3$$

For  $T \ll T_D$ ,  $C \sim T^3$  and  $\nu_{\text{ph-ph}}$  goes rapidly down and only  $\nu_{\text{ph-interface}}$  can contribute.



$\chi_{\text{ph}}$  for  $\text{Al}_2\text{O}_3$  (sapphire)

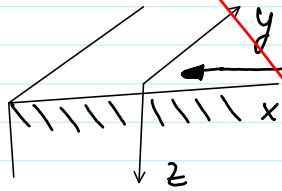
### SURFACE PHONONS

{ Possibly the story of SC in FeSe monolayer }

Surface phonon (SPs) are special acoustic waves.  
 SPs can be of 2 kinds:

- i) vertical polarization  $\perp$  to the surface/interface  
 (Rayleigh waves)  
 Rws
- ii) horizontally polarized along the surface

Rws are the only kind which can propagate on the surface



$$\frac{\partial^2 \xi}{\partial t^2} - v^2 \Delta \xi^2 = 0 \quad \xi_{\parallel} \text{ on the surface } \sigma_{\parallel}$$

$$\xi_{\perp} \perp \text{ to the surface } \sigma_{\perp}$$

no  $\xi$  inside, i.e. along  $z$ .

Let's look for a solution  $\xi = A e^{i(\omega t - kx) - \alpha z} \Rightarrow \alpha = \sqrt{k^2 - \omega^2/v^2}$

since  $z < 0$  we picked  $\oplus$  sign for  $\alpha$ .

The true  $\xi = \xi_{\parallel} + \xi_{\perp}$  with  $\sigma_{\parallel}$  and  $\sigma_{\perp}$ .

Note, for waves inside 3D crystal we would have 3 solutions, one longitudinal and 2 transverse waves.

For SPs  $\xi$  is limited by the surface. The boundary

condition for  $z=0$

$$\frac{\partial \xi_x}{\partial z} + \frac{\partial \xi_z}{\partial x} = 0$$

$$\frac{\partial \xi_z}{\partial z} + \frac{\partial \xi_z}{\partial z} = 0$$

volume expansion  $\lambda \Delta + 2\mu \frac{\partial \xi_z}{\partial z} = 0$   
 shear modulus  
 compression modulus

# 3d Bravais lattices

Read chapter: Simons book

Tuesday, October 2, 2018 5:54 PM

\* A Bravais lattice is the infinite system of geometrical points which is created via translation of a single point like this:

$$\vec{r} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$$

$n_1, n_2$  and  $n_3$  are the whole numbers  
 $\vec{a}, \vec{b}, \vec{c}$  are the primitive translation vectors

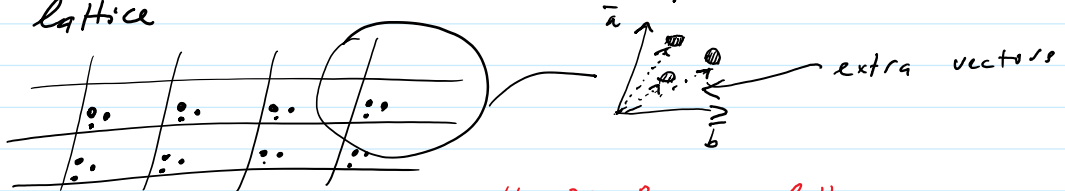
\* An elementary unit cell is the minimal box build upon the vectors  $\vec{a}, \vec{b}, \vec{c}$

\* All elementary unit cells have the same shape and the same volume  $\vec{a} \cdot (\vec{b} \times \vec{c})$

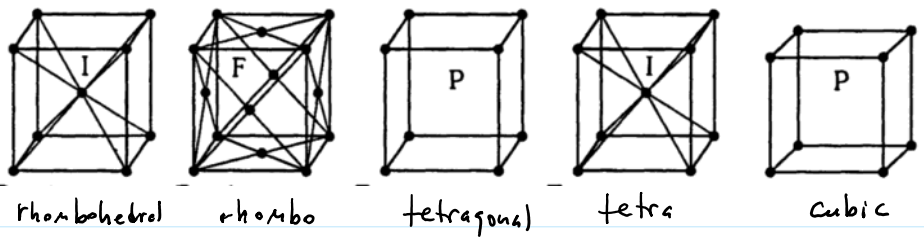
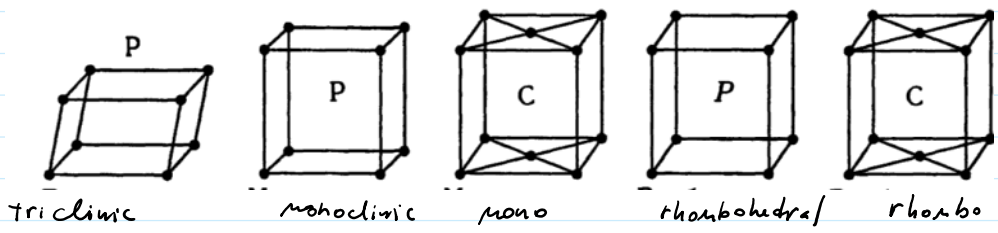
\* If atoms are ONLY at the vertices of the primitive lattice, then it's called primitive lattice

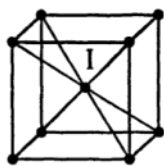
\* A Bravais lattice describes the position of vertices in space which coincide with atoms only for primitive unit cells.

\* To describe a crystal we need to have = lattice + basis  
 Basis is a sum of coordinates of atoms, distances between them and bond angles which will repeat at each vertex of the lattice

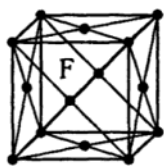


## 14 3D Bravais lattices





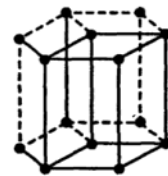
cubic



cubic



trigonal

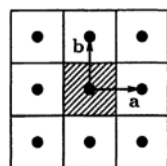


hexagonal

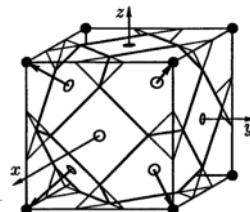
## Reciprocal Lattice

Consider a 2D Bravais lattice

- pick a lattice point
- draw  $\vec{a}$  and  $\vec{b}$
- draw planes through  $1/2$  distance



this cell (shaded) is called  $\rightarrow$  Wigner  
Zell



3D W-S cell for a body-centered lattice

Lets introduce vectors  $\vec{a}^*$ ,  $\vec{b}^*$ ,  $\vec{c}^*$  such as

$$e^{i(\vec{a} \cdot \vec{a}^*)} = 1$$

$$e^{i(\vec{b} \cdot \vec{b}^*)} = 1$$

$$e^{i(\vec{c} \cdot \vec{c}^*)} = 1$$

$$e^{i\alpha} = i \sin \alpha + \cos \alpha = 1$$

in the reciprocal space those vectors will create a new linear space which connects to the real space as:

$$\begin{aligned} \Downarrow \\ x = 0 \\ \Downarrow \\ a \perp \vec{a}^* \\ b \perp \vec{b}^* \\ c \perp \vec{c}^* \end{aligned}$$

$$\vec{a}^* = 2\pi \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

$$\vec{b}^* = 2\pi \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

$$\vec{c}^* = 2\pi \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

For any vector in the reciprocal space can be obtained as

$$\vec{g} = h_1 \vec{a}^* + h_2 \vec{b}^* + h_3 \vec{c}^*$$