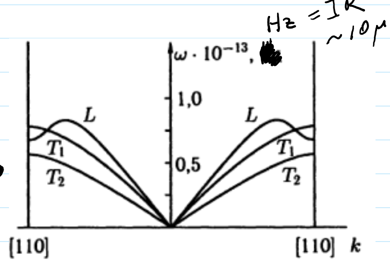
ACOUSTIC. PHONONS

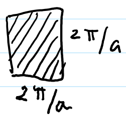
# Energetic spectrum of acoustic phonons

1 

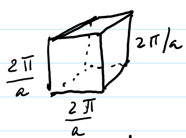

Dispersion curves of Al in [110]

As you recall there can be only 3 waves in a crystal, so for any specific direction $\bar{k}$ there will be 3 dispersion curves $\omega(\bar{k})$ 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 $\omega = \omega_i(k)$ for each branch $i$.

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

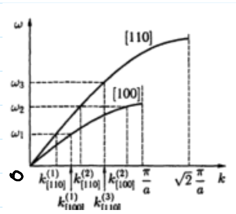
For 2D square lattice $(k_x, k_y)$ = 

. In general the shape in 3D is defined by symmetry of a crystalline lattice.

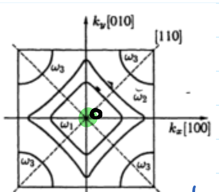


← it contains all possible values of $k$, So once you have this for 1 BZ, you have it determined for the whole crystal. ⇒ $\omega(\bar{k}) = \omega(\bar{k} + n\bar{g})$, where $\bar{g}$ is the crystal momentum.
where $n = 1, 2, 3, \ldots$

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




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

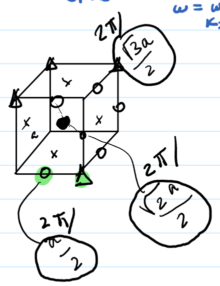



Cross-section of $\omega = \omega(k)$, $k_z = 0$

1) The closest points to $k=0$ are the points located to the center of the cube faces. ×

2) next are the center of the edges of the cube ○

3) and the furthe ones are the corners of the cube △




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

5 Note for small $k$ all branches are linear in all directions. However depending on the 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

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

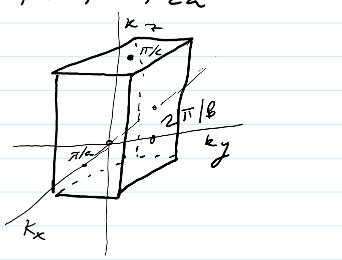
= SPECTRAL DENSITY OF PHONONS = # of phonons in the interval of freq. $d\omega$

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

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

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

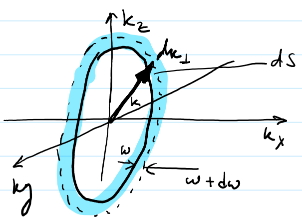
All allowed values of $k$ must be inside the 1st BZ with volume $= \frac{(2\pi)^3}{(abc)} = V_{BZ}$




The elementary volume available for 1 state: $\frac{(2\pi)^3}{(L_x L_y L_z)} = \frac{(2\pi)^3}{V}$ : the total # of states $\frac{(2\pi)^3}{(abc)} \Big/ \frac{(2\pi)^3}{V} \Rightarrow \frac{V}{\underbrace{(abc)}_{\text{size of unit cell}}} = N$

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

2 Lets calculate $D_i(\omega) = dn_i/d\omega$ we need to calculate the change of $dn_i$ for $d\omega$. Consider 2 surfaces $\omega_i(k) = const$ and $d\omega + \omega_i(k) = const$




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

$$\Delta = \int_{S(\omega)} ds\, dk = \int_{S(\omega)} \frac{d\omega_i\, ds}{|v_g(k)|} = d\omega \int_{S(\omega)} \frac{ds}{|v_g(k)|}$$

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

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

$$D(\omega) = \frac{dn_i}{d\omega} = \frac{V}{(2\pi)^3} \int \frac{ds}{|v_{g_i}(k)|}$$ , the integration is along the close surface for each branch $i$

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

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

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

$\cancel{D_i^{2D}(\omega) = \int \frac{S}{(2\pi)^2} \oint \frac{dl}{v_g}}$

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

$$D_i^{2D}(\omega) = \begin{cases} \frac{S}{(2\pi)^2} \oint_{\ell(\omega_i)} \frac{d\ell}{|v_{g_i}(k)|} \\ 0 \end{cases} \quad \text{and} \quad D_i^{1D}(\omega) = \begin{cases} \frac{L}{2\pi}\frac{1}{v_g} \\ 0 \end{cases}$$

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

## DEBYE MODEL OF PHONONS

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 $\bar{k}$

In this model we have $\omega_{\parallel} = v_{\parallel}|k|$ $\quad v_{\perp} = v_{\perp}|k|$

double degenerate

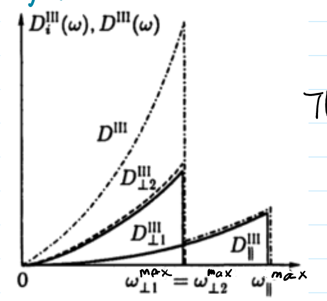
The surface of const freq. are spheres: of radius $k_{\parallel} = \frac{\omega_{\parallel}}{v_{\parallel}}$, $k_{\perp} = \frac{\omega_{\perp}}{v_{\perp}}$ $\Rightarrow$ $|v_g| = \text{const}$ $\Rightarrow$

$$D_i^{3D}(\omega) = \begin{cases} \frac{V}{(2\pi)^3} \cdot \frac{1}{|v_{g_i}|} \oint ds \\ 0 \end{cases} = \frac{V}{(2\pi)^3} \frac{4\pi}{|v_i|^3}\omega^2 = \boxed{\frac{V\omega^2}{2\pi^2 |v_i|^3}}$$

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

$k_i$

**Debye Model:**




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

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

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

or $\omega_i^{max} = |v_i|\left(6\pi^2 \frac{N}{V}\right)^{1/3}$

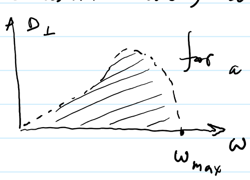
$n$ = density o phonon modes

$\omega_{\parallel}^{max} > \omega_{\perp 1}^m = \omega_{\perp 2}^m$

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

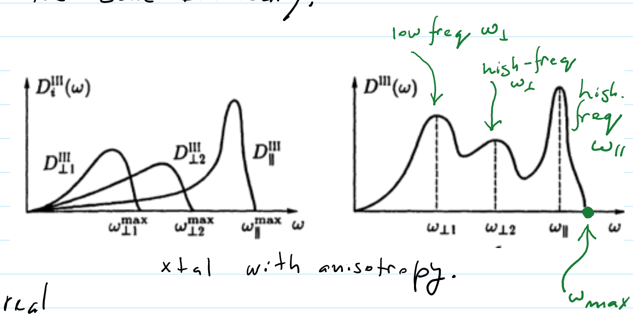
Note: Debye model is the only model with an analytical result.

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



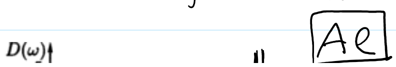

for a real xtal

no anisotropy



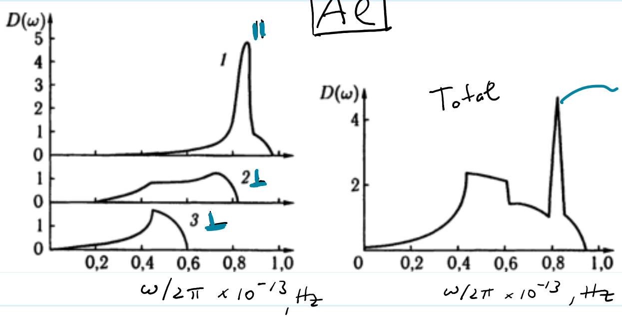

xtal with anisotropy.

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



calculation for Ae based on DFT.

$\boxed{Ae}$




? why is it so sharp?

## VAN Hove Singularities

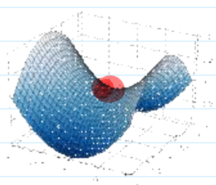
if you compare the Debye model and DFT you notice that we have a very similar behaviour. But in DFT we see many sharp features. Why?
The reason for kind of behavior is that we have those "spikes" when we reach the frequencies corresponding to ω in the BZ with some critical points, meaning that at those points

$$v_g = \nabla_k \omega(k) = 0 \quad \Rightarrow \quad D_i(\omega) = \frac{V}{(2\pi)^3} \oint_{S(\omega_i)} \frac{dS}{|v_{g,i}(k)|} \to \infty$$

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 $k_0$
or $\omega(k) = \omega_0 + a_x(k_x - k_{0x})^2 + a_y(k_y - k_{0y})^2 + a_z(k_z - k_{0z})^2$
we do not have any linear terms since at $k = k_0$ $\nabla_k \omega(k) = 0$

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

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

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

$$a = \sqrt{\frac{\omega - \omega_0}{-\alpha_x}} \quad \dots \quad \text{for max}$$

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

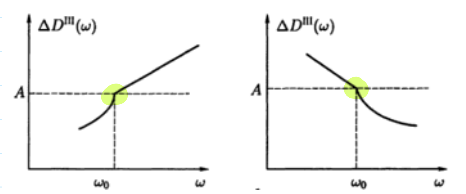
$$\cancel{\Omega_\omega = \frac{4}{3}\pi abc = \frac{4}{3}\pi \frac{|\omega - \omega_0|^{3/2}}{\sqrt{|\alpha_x||\alpha_y||\alpha_z|}}}$$

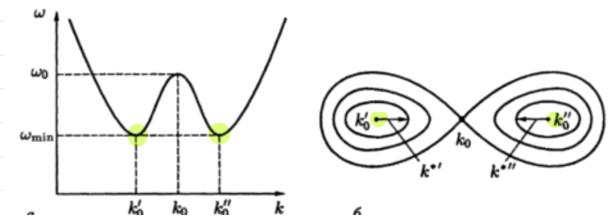
$$\Omega_\omega = \frac{4}{3}\pi\, abc = \frac{4}{3}\pi \frac{|\omega-\omega_0|^{3/2}}{\sqrt{|\alpha_x||\alpha_y||\alpha_z|}}$$

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 $\frac{d\,\Delta D^{3D}}{d\omega} \to \infty$. For example, the presence of a saddle point in the phonon spectrum means that in the BZ there are 2 local minima at $K_0'$ and $K_0''$




Repeat this calculation For 2D and 1D

## STATISTICS OF ACOUSTIC PHONONS

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:

$$E^{q}_{n_q} = \hbar\omega_q\left(n_q + \tfrac{1}{2}\right) \qquad n_q = 0, 1, 2 \ldots$$

(note $q = \kappa$ from previous lecture)

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

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

$$A_q = \frac{1}{\sum e^{-(E^q_{n_q}/k_B T)}} = \left[1 - e^{\hbar\omega_q/k_B T}\right] e^{\hbar\omega_q/2k_B T} \Rightarrow$$

geometric series

geometric series

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

Now lets calculate the average number of phonons:

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

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

thus we end up: $n_q^{av} = \dfrac{[1-e^{-x}]e^{-x}}{(1-e^{-x})^2} = \dfrac{1}{e^{\hbar\omega_q/k_BT}-1}$

$$\boxed{n_q^{av} = \frac{1}{e^{-\hbar\omega_q/k_BT}-1}}$$

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.

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

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

$$E_q^{av} = \frac{\hbar\omega_q}{2} + n_q^{av}\hbar\omega_q = \underset{\uparrow \text{ "0" oscillations}}{\frac{\hbar\omega_q}{2}} + \underset{\uparrow \text{ the average thermal energy due to phonons.}}{\frac{\hbar\omega_q}{e^{-\hbar\omega_q/k_BT}-1}} =$$

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

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

$n_q^{av}$ and $U_q^{av}$ are very small $\Rightarrow n_q^{av} \simeq e^{-\hbar\omega/k_BT}$

$$U_q^{av} \simeq \hbar\omega_q e^{-\hbar\omega_q/k_BT}$$

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

$$n_q^{av} \simeq k_BT/\hbar\omega_q$$

$$U_q^{av} \simeq k_B T.$$

Recall the number of modes, or waves with freq. $\omega_q$ in each branch of acoustic phonons $= N$ atoms in lattice. And the total number $= 3N$ for 3 branches, $(2\perp + 1\parallel)$

But the number of phonons in each mode with freq. $\omega_q$ 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.

Before $T^*$: we excite modes with higher and higher $\omega_k$ but for $T > T^*$ we populate each mode with more and more phonons.

* But at $T > T^*$ we excite ALL modes from $\omega^{min}$ to $\omega^{max}$ in the given 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 temperature when energy of thermal oscillations of lattice $\approx E_{hq}^{av}$ 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 $\Theta_{D\parallel}, \Theta_{D\perp}, \Theta_{D\perp,2}$ so we have to average over these 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 $v_{a,i} = const$, for each branch
For even simple cubic lattice we have a complication since $v_{\parallel,a}$ and $v_{\perp,a}$ depend on $\bar{k}$. That is we the notion of an average speed of sound is very uncertain.

For small $k$, $\omega(k)$ is linear and we can approximate it

$$|k_i(\omega)|^2 = k_x^2 + k_y^2 + k_z^2 \quad \text{and} \quad v_{i,a} = \frac{\omega}{k_i(\omega)}$$

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

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

and from $\bar{\theta}_{D,\parallel} = \hbar\omega_{\parallel}^{max}$ 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 $\bar{\omega}^{max}$ from

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

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

where $\frac{3}{\bar{v}_a^3}$

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

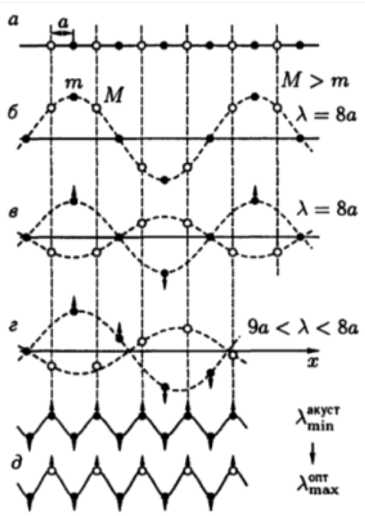
To summarize, the physical meaning of $\theta_D$ is to characterize the energy state of a crystall by separating the temperature scale into 2 regions:

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

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

# OPTICAL PHONONS

Wednesday, September 12, 2018 9:39 PM




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 $k_q = 2\pi/\lambda_q$ we have 2 waves for the same $k_q$ – acoustic and optical.

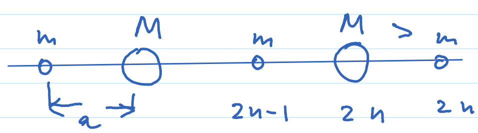
Note: since nn are out of phase the frequency for OPs is close to the $\omega_{acoustic}^{max}$ and is almost independent of k.

So in general we have 6 branches:

$$\boxed{\omega_{\parallel}^{a},\ \omega_{\perp,1}^{a}\quad \omega_{\perp,2}^{a}\ \text{ and }\ \omega_{1,2,3}^{o}}$$

## DISPERSION OF OPs.

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




equation of motion is given by

$$\begin{cases} M\dfrac{\partial^2 \xi_{2n}}{\partial t^2} = \beta_1\left(\xi_{2n+1} + \xi_{2n-1} - 2\xi_{2n}\right) \\[2ex] m\dfrac{\partial^2 \xi_{n+1}}{\partial t^2} = \beta_1\left(\xi_{2n+2} + \xi_{2n} - 2\xi_{2n+1}\right) \end{cases}$$

we search for a solution in the form:

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

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

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

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

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

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

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

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

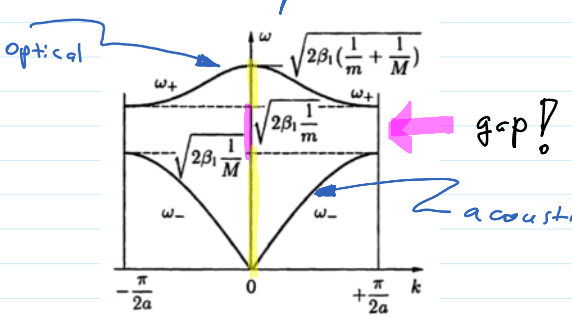
First consider $\omega_-(k)$ we have $v_a^{\parallel} = \frac{\partial\omega_-}{\partial k} = a\sqrt{\frac{2\beta_1}{M+m}}$

But we also have another branch: $\omega_+(k)$, to understand its phys. meaning lets take the ratio:

$\frac{\mu}{\eta}$ (just plug $\omega_+$ or $\omega_-$ in

$\frac{\mu}{\eta} = -\frac{M}{m}$ 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 $k=0$

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

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

The spectrum of allowed oscillations is confined into:

$0 < \omega < \sqrt{\frac{2\beta_1}{M}}$ — acoustic

and also we have a GAP!

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

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

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

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

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

The allowe wave numbers can be found from

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

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

for each $k_q$ we have $\lambda_q = \frac{2\pi}{k_q}$ $\quad 4a < \lambda_q < L$

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

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

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

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

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

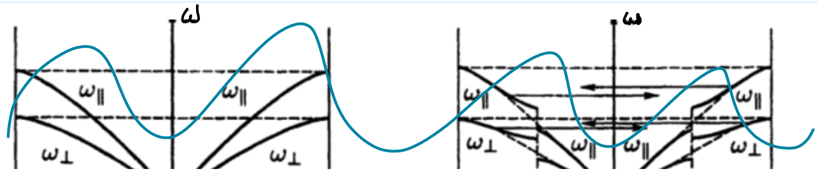
## A Physical meaning of the gap.

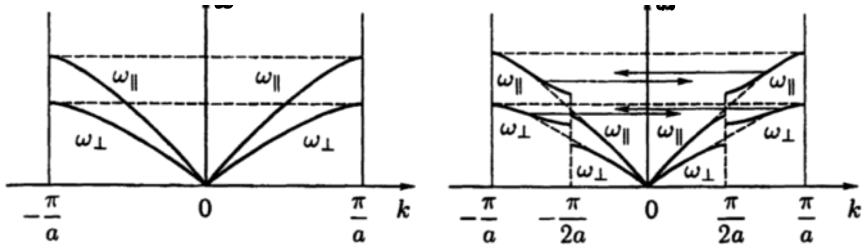
For $m \to M$ the waves will experience Bragg reflection at $k = \pm\pi/a$ and $\partial\omega/\partial k = 0$.

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

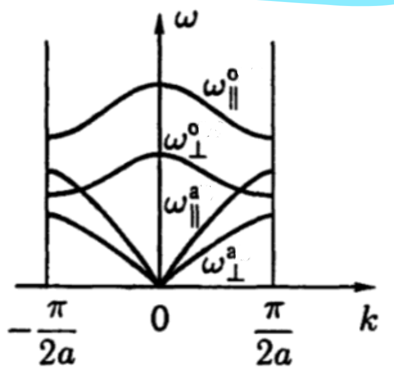
$\omega(k)$ splits into 2 branches seperated by the gap.






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 $\omega_i^o(k)$ $\quad \omega_\parallel^o(k)$, $\omega_{\perp,1,2}^o(k)$

It's hard to plot the isoenergetic surfaces of optical phonons b/c there are no linear k part of the spectrum for OPs. for small ks.

## STATISTICS OF OPs.

OPs are bosons. But they are special since their minimal energy ~ max energy of acoustic phonons. ~ $kT_D = \Theta_D$

Below $T_D$ the number of OPs gets very small.

Total number of modes : $= N$

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 $T \sim T_D \approx 100\%$. 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 $T \sim T_D/2$ the # of OPs $\sim 10\%$

$\sim T_D/3$ $\sim 5\%$

$T_D/50$ $\sim 10^{-20} N$

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

SPECTRAL DENSITY OF OPs

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

Dispersion of OP: For OPs $\frac{\partial \omega}{\partial k}$ is small and typically if $|k| \to 0$ $|k| \to k^{max}$

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?!)

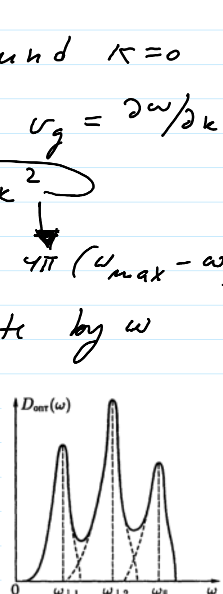
but lets assume for $k=0$ $\omega = \omega_{max}$ and also lets assume the isoenergy surface is a sphere around $k=0$ with $V = 4\pi k^3/3$, for small $k$, long $\lambda$ $v_g = \partial\omega/\partial k \sim 0$

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

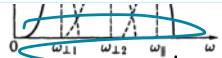
then the volume limited by $\omega = const \sim 4\pi(\omega_{max} - \omega)^{3/2} / 3\alpha^{3/2}$

If we devide it by $(2\pi)^3/V$ and diffirentiate by $\omega$

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




very narrow
Compared to accoustic phonons




~~very narrow compared to acoustic phonons.~~

# PHONON CONTRIBUTION TO THERMODYNAMICS OBSERVABLES

Thermal energy $U^{3D}$ at given $T$ is $\Sigma$ of $\bar{E}_q = \frac{\hbar\omega_q}{2} +$
$$+\bar{U}_q = \frac{\hbar\omega_q}{2} + \frac{\hbar\omega_q}{e^{(\hbar\omega_q/k_BT)}-1}$$

with $\bar{n}_q$ (per mode) $= \dfrac{1}{e^{\hbar\omega_q/k_BT}-1}$

number of phonons in the mode $\omega_q$

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

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

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

**Physics:** for $T \ll T_D$ we have ~~no~~ optical phonons, and some long $\lambda$ acoustic phonons. We can think that the volume limited by the surface of const $\omega$ $\omega_q = \omega, (q)$ $\sim |\bar{q}|^3$. Also, for small $\bar{q}$s $\omega_q \sim |q| \le k_BT/\hbar$ and hence $\omega_q \sim T^3$

In short, if the density of wavector states inside BZ is constant hence the number of # of excited mods at $T \sim T^3$

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

Then $\bar{U}^{3D} \sim (k_BT) \cdot T^3 \sim T^4$.

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 $\bar{U}^{3D}_{acoustic} \sim 3Nk_BT$

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

## Debye THEORY

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

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

Let us introduce $T_D = \theta_D / k_B = \hbar\omega^m / k_B$, and recal $\bar{\omega}^m = \bar{v}_a \left(\frac{6\pi^2 N}{V}\right)^{1/3}$

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

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

Riman 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 $e^x \sim 1 + x + \ldots$

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

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

Works very well for many metals from e.g. Al to Cu up to their melting points.

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

## THERMAL CONDUCTIVITY

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

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

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

$$\chi_{ph} = \frac{1}{3} C_{ph} v_a \ell_{ph} = \frac{1}{3} C_{ph} v_a^3 \tau_{ph}$$

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

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

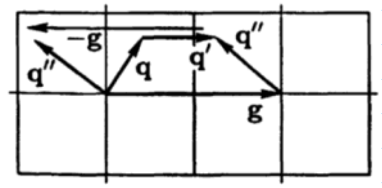
A. NORMAL SCATTERING PROCESSES (N-process)

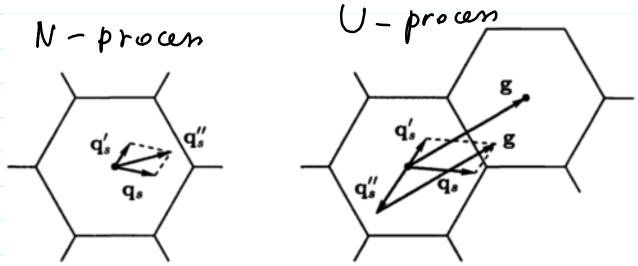
Remember heat flow is a directional motion of phonons then scattering means ph-ph interaction when the phonon after the collision gets out of the stream. Meaning, large changes in $\bar{k}$. For small angle scattering there is no relaxation.

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 $q_s + q_s' = q_s'' + g$




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

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

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 calle U - processes ( Unclapp - 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 cosider 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 wave length phonons can participate.

And the number of highly excited phonons with $q \sim g$ drops exponentially, and below $T < T_D$ $\nu_{p-p}^U$ sharply decreasses. This can only be seen experimentally for dielectics 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 $T$, $\nu$ goes down and $\ell_{ph}$ 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 $\lambda_{ph}$. Lets consider a very simple model of diffuse scattering. In this case

$\nu_{ph-s} = \frac{1}{\tau} = v$ and almost const with $T$. 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 $C(T) = const(T)$ and $\nu_{ph-ph} \sim T$ we conclude for $T \geqslant T_D$

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

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

$$\nu^U_{ph-ph} \sim T^{\xi} e^{-\alpha T_D / T}$$

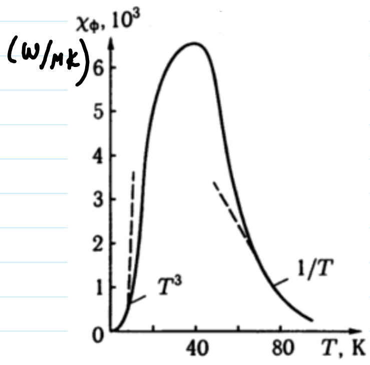
where $1 \lesssim \xi < 3$ (no proof here)

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

and $C_{lattice} = C(T)$ we get

$$W_{ph} \sim \frac{1}{C(T)\, v_a^2} T^{\xi} e^{-\alpha T_D/T} \qquad 1 < \xi < 3$$

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




$\chi_{ph}$ for $Al_2O_3$ (sapphire)

~~SURFACE PHONONS~~

~~{Possibly the story of SC in FeSe monolayer)~~

THE END OF PHONON THEME!