ACOUSTIC. PHONONS

Energetic spectrum of acoustic phonons

As you recall there can be only 3 waves in a crystal, so for any specific direction \( E \) there will be 3 dispersion curves (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 \( w = w(E) \) for each branch \( i \).

Dispersion curves of Al in [110]

Note: \( w \) depends on \( E \) is a periodic function with the period defined by the size of the Brillouin zone — which is an area which is symmetric wrt to \( E = 0 \). For a chain of size \( a = 2\pi a \)

For 2D \( (k_x, k_y) = \frac{2\pi}{a} \). In general the shape in 3D is defined by symmetry of a crystalline lattice.

\[ \frac{2\pi}{a} \leq k \leq \frac{2\pi}{a} \]

It contains all possible values of \( k \). So once you have this for 1 BZ, you have it determined for the whole crystal. \( \Rightarrow w(E) = w(\vec{E} + n\vec{g}) \), where \( \vec{g} \) is the crystal momentum, where \( n = 1, 2, 3, \ldots \)

Consider the case of a square lattice of size \( a \)

1) The closest points to \( E = 0 \) 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 further ones are the corners of the cube.

To determine the shape of the phonon curves consider e.g. [010] for \( w_1, w_2 \) and \( w_3 \) and \( k_2 = 0 \)

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 farthest 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 \( w(x) = c_{n+1} \) for \( t = 1, 2, 3 \). Those surfaces define a very important quantity \( D(w) = \frac{dN}{dw} \).

The spectral density of phonons is \( \# \) of phonons in the interval of freq. \( dw \)

\[ h(w) = h_{11} + h_{11} + h_{12} \rightarrow D(w) = \sum_{i=1}^{3} \frac{d h_{i}(c_{w})}{dw} = \sum_{i=1}^{3} D_{i}(w) \]

Clearly \( \int_{0}^{w} D(c_{w}) dw = \text{total number of allowed states in the } BZ. \)

For example, single atom x 141:

\[ \rho \rightarrow \frac{2\pi}{L_{x}} \frac{2\pi}{L_{y}} \frac{2\pi}{L_{z}} \quad x = \pm 1, \pm 2, \ldots \]

All allowed values of \( k \) must be inside with volume \( (2\pi)^{3} \)

The elementary volume available for 1 state:

\[ \frac{(2\pi)^{3}}{V} = \frac{(2\pi)^{3}}{V} = \frac{(2\pi)^{3}}{V} \]

The total number of acoustic waves is \( 3N \)

which is true for any single atom lattice.

Let's calculate \( D_{i}(w) = \frac{dN}{dw} \) we need to calculate the change of \( dw \) for \( dN \). Consider 2 surfaces \( \omega_{i}(x) = c_{n+1} \) and \( \omega + \omega_{0}(x) = c_{n+1} \)

The volume for the arc \( ds \) is \( ds \cdot ds \). The total volume between \( \omega \) and \( \omega + dw \)

\[ \Delta = \int_{C_{w}} ds \quad ds = \int_{C_{w}} \frac{ds}{V_{w}} \frac{dV}{V_{w}(x)} = dw \int_{C_{w}} \frac{ds}{V_{w}(x)} \]

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

\[ dN = \frac{\Delta}{(2\pi)^{3}/V} = V dw \int_{C_{w}} \frac{ds}{V_{w}(x)} \Rightarrow \]

\[ D(w) = \frac{dN}{dw} = \frac{V}{(2\pi)^{3}} \int_{C_{w}} \frac{ds}{V_{w}(x)} \] the integration is along the cease surface for each branch \( i \).

Because each branch has \( \rho \) we get the result for 3D

\[ D_{i}(w) = \begin{cases} \frac{V}{(2\pi)^{3}} \int_{C_{w}} \frac{ds}{V_{w}} & \text{for } \omega \leq \omega_{0} \text{ max} \\ 0 & \omega > \omega_{0} \text{ max} \end{cases} \]

The value of \( \omega_{0} \) is determined for: \( \int_{0}^{\omega_{0}} D_{i}(w) dw = \int_{0}^{\omega_{0}} D_{i}(w) dw = N \)

\[ D(\omega) = \int_{0}^{\omega_{0}} D_{i}(w) dw = \int_{0}^{\omega_{0}} D_{i}(w) dw = N \]
The value of $\omega_{\text{max}}$ is determined from:

$$D_i(\omega) = \int_0^{\infty} D_i(\omega) \, d\omega = \int_0^{\infty} \frac{d\omega}{\sqrt{\omega}}$$

and $D_i^{\text{2D}}(\omega) = \int_0^{\infty} \frac{d\omega}{\sqrt{\omega}}$, element of line of constant $\omega$ for the branch of spectrum.

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

$$\sigma_{i,j} = \sigma_{j,i} \text{ and } \upsilon_{i,j} \text{ independent of } x$$

In this model we have $\omega_{\text{ill}} = \sigma_{\text{ill}} \text{ and } \omega_{\text{ill}} = \upsilon_{\text{ill}} \text{ for } \text{ill}$.

The surface of constant $\omega$ are spheres: double degenerate of radius $k_{\text{ill}} = \frac{\omega_{\text{ill}}}{\upsilon_{\text{ill}}}$.\n\n$$D_i(\omega) = \int_0^{\infty} \frac{d\omega}{\upsilon_{\text{ill}}} \frac{\omega}{(2\pi)^3} = \frac{V}{\upsilon_{\text{ill}}} \frac{\omega}{(2\pi)^3} = \frac{\sqrt{\omega^2}}{2 \pi^2 \upsilon_{\text{ill}}^3}$$

The total $D(\omega) = \sum_i D_i(\omega)$. The $\omega_{\text{max}}$ is determined by

$$\text{from } \int_0^{\omega_{\text{max}}} D_i(\omega) \, d\omega = N \text{ or } \frac{V}{(2\pi)^3} \omega_{\text{max}}^3 = N$$

Spectral distribution of $D_{\text{ill}}$ and $D_{i,1}$ and $D_{i,2}$

$$\omega_{\text{max}} = \frac{\omega_{\text{ill}}^3}{(2\pi)^3}$$

Derive $\omega_{\text{max}}$ for the 2D and 1D cases.

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

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

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

$$D(\omega) = \begin{bmatrix} A & E \end{bmatrix}$$
Van Hove Singularities

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

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

\[
\frac{\partial^2}{\partial \omega^2} \Omega(\omega) = 0 \quad \Rightarrow \quad D_{\text{vH}}(\omega) = \left( \frac{\nu}{(2\pi)^3} \right) \int \frac{d^3 \mathbf{k}}{\hbar^3} \left| \frac{\partial S(\mathbf{k})}{\partial \omega} \right| \to \infty
\]

There are four kinds of critical points in the BZ:

- 2 points - \( \text{MIN and MAX} \) \( \text{(in} \overline{\text{BZ}} \text{corresponding}) \)
- 2 points - saddle

The Van Hove singularities.

Let me illustrate this phenomenon in 3D system:

We use a Taylor expansion in the vicinity of a singularity \( k_0 \) or \( \omega(k_0) = \omega_0 + a_1 (k_1 - k_1^0)^2 + a_2 (k_1 - k_1^0)^2 + a_3 (k_1 - k_1^0)^2 \)

We do not have any linear terms since at \( k = k_0 \), \( \partial \Omega(\omega) = 0 \)

\( a_1, a_2 > 0 \) for local min, \( a_2 < 0 \) for local max.

As you noticed, \( \omega(k) = \text{const} \Rightarrow \text{an ellipsoid in the BZ with axes} k, \Omega \).

For min:

\[
a = \left[ \frac{\omega_0}{a_1} \right] \quad \text{for min}
\]

For max:

\[
a = \left[ \frac{\omega - \omega_0}{a_1} \right] \quad \text{for max}
\]

The volume \( V_\omega \) in the BZ limited by this surface at the vicinity of min and max:

\[
V_\omega = \frac{4}{3} \pi a b c = \frac{4}{3} \pi \left( \omega - \omega_0 \right)^{3/2} \left( 1 \right) \frac{\omega}{\sqrt{1 + d_1 + d_2 + 11d_3^2}}
\]
\[ \Omega = \frac{h}{3} abc \frac{\sqrt{1 - \omega_0^2/\omega^2}}{\sqrt{1 - \omega_0^2/\omega^2}} \]

The number of phonon states \( N \) inside of this ellipsoid

\[ N = \frac{\sqrt{\Omega}}{(2\pi)^3} \Rightarrow d^3k \frac{dN}{d\omega} = \frac{\sqrt{1 - \omega_0^2/\omega^2}}{(2\pi)^2} \]

As you see, \( d^3k \) around singularity is still analytical. But

\[ d^3k \frac{d\omega}{d\omega} \to \infty \]

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 \( k' \)

Repeat this calculation for 2D and 1D

**Statistics of Acoustic Phonons**

(May be 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 (why? they are bosons!)

So the total number of phonons is really defined by the thermal equilibrium condition:

\[ \frac{2F}{\partial N} = 0 \quad \text{but} \quad \frac{2F}{\partial N} = \mu \equiv \text{chem. potential} \Rightarrow \]

Chem. potential of phonons is ZERO.

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

\[ E_{\omega} = \hbar \omega \left( h + \frac{1}{2} \right) \quad \hbar = 0, 1, 2 \ldots \]

From Gibbs distribution, the probability that oscillator with \( \omega \) is in the state \( h + \frac{1}{2} \) has energy \( E_{\omega} \):

\[ W_h = \frac{1}{Z} e^{-E_{\omega}/k_B T} \Rightarrow \mu \text{ is from } \sum_{h=0}^{\infty} W_h = 1 \]

\[ \mu = \frac{1}{Z} \left[ 1 - e^{-\mu/2 k_B T} \right] e^{\mu/2 k_B T} \Rightarrow \]

\[ \frac{1}{Z} = \sum_{h} e^{-E_{\omega}/k_B T} \]

Geometric series
\[ W_{\gamma} \equiv \left[ 1 - e^{-\frac{\hbar \omega_{\gamma}}{k_B T}} \right] e^{-\frac{\hbar \omega_{\gamma}}{k_B T}} \]

Now lets calculate the average number of phonons:
\[ n_{\gamma}^{av} = \sum_{\eta = 0}^{\infty} n_{\gamma} W_{\eta} \]

\[ \sum_{\eta = 0}^{\infty} n_{\gamma} e^{-\frac{\hbar \omega_{\gamma}}{k_B T}} = \sum_{\eta = 0}^{\infty} e^{-\eta x} = \frac{d}{dx} \left( \sum_{\eta = 0}^{\infty} e^{-\eta x} \right) = \frac{d}{dx} \left( \frac{1}{1 - e^{-x}} \right) \]

thus we end up:
\[ n_{\gamma}^{av} = \left[ 1 - e^{-x} \right] e^{-x} = \frac{1}{(1 - e^{-x})^2} = \frac{1}{e^{\hbar \omega_{\gamma}/k_B T} - 1} \]

\[ n_{\gamma}^{av} = \frac{1}{e^{\hbar \omega_{\gamma}/k_B T} - 1} \]

Next we can calculate the average energy of the excited oscillator with freq. \( \omega_{\gamma} \) at given \( T \), i.e. the energy of the \( \omega_{\gamma} \) phonon mode.
\[ E_{\gamma}^{av} = \sum_{\eta = 0}^{\infty} E_{\eta} W_{\eta} = \frac{\hbar \omega_{\gamma}}{2} + \hbar \omega_{\gamma} \sum_{\eta = 0}^{\infty} n_{\gamma} W_{\eta} \]

inserting \( W_{\eta} \) from above we get:
\[ E_{\gamma}^{av} = \frac{\hbar \omega_{\gamma}}{2} + \frac{\hbar \omega_{\gamma}}{2} \frac{1}{e^{\hbar \omega_{\gamma}/k_B T} - 1} = \frac{\hbar \omega_{\gamma}}{2} \left( 1 + \frac{1}{e^{\hbar \omega_{\gamma}/k_B T} - 1} \right) \]

For low \( T \): \( T \ll \hbar \omega_{\gamma}/k_B \)
\[ n_{\gamma}^{av} \text{ and } E_{\gamma}^{av} \text{ are very small} \Rightarrow n_{\gamma}^{av} = e^{-\frac{\hbar \omega_{\gamma}}{k_B T}} \]
\[ E_{\gamma}^{av} = \hbar \omega_{\gamma} e^{-\frac{\hbar \omega_{\gamma}}{k_B T}} \]

In high \( T \): \( \hbar \omega_{\gamma} \) both grow as \( T \)
\[ n_{\gamma}^{av} \sim k_B T \]
Recall the number of modes or waves with freq. \( \omega \) in each branch of acoustic phonons = \( N \) atoms in lattice. And the total number = \( sN \). But the number of phonons in each mode with freq. \( \omega \) is unlimited and is determined only by \( T \). Also remember for each mode we have max freq. \( \omega_{\text{max}} \) so we end up with some characteristic \( T^* \):

\[
\frac{\hbar \omega_{\text{max}}}{k_B}, \quad \text{meaning the probability of excitation of one phonon with max } \omega_{\text{max}} = 0.272
\]

two = 0.086

three = 0.232

But at \( T > T^* \) we excite ALL modes from \( \omega_{\text{min}} \) to \( \omega_{\text{max}} \) 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 temperature when energy of thermal oscillations of lattice \( \approx E_{\text{av}} \) of high frequency phonon modes.

It enters all interesting thermodynamic parameters.

Only for 1D chain: \( T_D = \frac{\hbar \omega_{\text{max}}}{k_B} = \Theta_D / k_B \) so in this case the \( \omega_{\text{max}} = \omega_0 \).

In real 3D crystals we have 3 different branches so we need to think of \( \Theta_{D1}, \Theta_{D2}, \Theta_{D3} \) so we have to average over these frequencies.

Debye suggested to approximate it by:

\[
\Theta_D (\omega) = \frac{V \omega^2}{2 \pi^2 5^3 \omega_i^3} \quad \text{for } \omega < \omega_{\text{max}}
\]
and assume that \( u_{a,i} = \text{const} \), for each branch. For even simple cubic lattice we have a complication since \( u_{11}, a \) and \( u_{11}, a \) depend on \( k \). That is, we have the notion of an average speed of sound is very uncertain.

For small \( k \), \( u_{a}(k) \) is linear and we can approximate it as
\[
|k_{i}(w)|^2 = k_{x}^2 + k_{y}^2 + k_{z}^2 \quad \text{and} \quad u_{i,a} = \frac{\omega}{k_{i}(w)}
\]
and since \( u_{i,a} = \text{const} \)
\[
\overline{\omega}_{i}^{\text{max}} = u_{i,a} \left( \frac{6\pi^2 N}{V} \right)^{1/3}
\]
and from \( \bar{\Theta}_{11} = \hbar \omega_{11} \) etc. we can calculate \( \bar{\Theta}_{D} \).

Also Debye approximated \( D_{\omega} \) by the parabolic dependence
\[
D_{\omega}^{3D}(w) = \int \frac{U_{\omega}^2}{2\pi V_{a}^3}
\]
so we can find \( \overline{\omega}_{\text{max}} \) from
\[
\int_{0}^{\overline{\omega}_{\text{max}}} D_{\omega}(w) \, dw = 3N \quad \text{where} \quad D_{\omega} = \sum_{i=1}^{2} D_{\omega}^{3D}(w) = \frac{V_{a}}{2\pi^2} \left( \frac{1}{V_{a,1}} + \frac{1}{V_{a,1}^3} + \frac{1}{V_{a,2}^3} \right) \Rightarrow \overline{\omega} = \frac{V_{a}}{6\pi^2 N} \left( \frac{6\pi^2 N}{V} \right)^{1/3}
\]
where \( \frac{3}{V_{a}} \)

and thus \( \bar{\Theta}_{D} = \hbar \overline{\omega}_{\text{max}} \).

To summarize, the physical meaning of \( \bar{\Theta}_{D} \) is to characterize the energy state of a crystal by separating the temperature scale into 2 regions:

1) \( k\hbar T \ll \bar{\Theta}_{D} \) we get only long wavelength excitations with \( \hbar \omega \ll \bar{\Theta}_{D} \)

2) \( k\hbar T \gg \bar{\Theta}_{D} \) we have all possible excitations including those with \( \hbar \omega \sim \bar{\Theta}_{D} \) and no more modes.
THE END OF PHONONS THERE!
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 \( \text{OPTICAL PHONONS (OP)} \).

The key distinction for OPs is the fact that near neighbours oscillate \text{\underline{OUT OF PHASE}}.

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

Thus for any given \( k \), \( \leftarrow \frac{2 \pi}{\lambda} \), we have 2 waves for the same \( k \) - acoustic and optical.

Note: since \( m, n \) are out of phase the frequency for OPs is close to the \( v_{\text{acoustic}} \) and is almost independent of \( k \).

So in general we have 6 branches:

\( W_{1,1}^{+}, W_{1,1}^{-}, W_{1,2}^{+}, W_{1,2}^{-}, W_{2,3}^{+}, W_{2,3}^{-} \)

\text{\underline{DISPERSION OF OPs}}

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

\[ \begin{align*}
M & \quad 2 \hbar c_2 = \beta_1 \left( \frac{\hbar c_2}{2} \right. \\
M & \quad \left. \frac{\hbar c_2}{2} + \frac{\hbar c_2}{2} \right) = \beta_1 \left( \frac{\hbar c_2}{2} + \frac{\hbar c_2}{2} - 2 \frac{\hbar c_2}{2} \right).
\end{align*} \]

we search for a solution in the form:

\[ e^{i(w + (2n + 1)k)a} \]

\[ \begin{align*}
\frac{\hbar c_2}{2} = \beta_1 \left( \frac{\hbar c_2}{2} + \frac{\hbar c_2}{2} - 2 \frac{\hbar c_2}{2} \right) \\
\frac{\hbar c_2}{2} = \beta_1 \left( \frac{\hbar c_2}{2} + \frac{\hbar c_2}{2} - 2 \frac{\hbar c_2}{2} \right).
\end{align*} \]

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\frac{\hbar c_2}{2} = \beta_1 \left( \frac{\hbar c_2}{2} + \frac{\hbar c_2}{2} - 2 \frac{\hbar c_2}{2} \right). \\
\end{align*} \]
\[
\begin{align*}
- M \mu \omega^2 &= \beta_1 \eta \left( e^{i\omega t} + e^{-i\omega t} \right) - 2\beta_1 \eta x \\
- \omega \eta \omega^2 &= \beta_1 \mu \left[ e^{i\omega t} + e^{-i\omega t} \right] - 2\beta_1 \eta \\
\begin{vmatrix} 2(\beta_1 - \omega^2 m) & (-2\beta_1 \cos \kappa) \\
(-2\beta_1 \cos \kappa) & (2\beta_1 - \omega^2 m) \end{vmatrix} &= 0 \\
\omega^2 &= \beta_1 \left( \frac{1}{m} + \frac{1}{M} \right) \pm \beta_1 \sqrt{\left( \frac{1}{m} + \frac{1}{M} \right)^2 - \frac{4\beta_1^2 \kappa^2}{mM}}
\end{align*}
\]

Notice \( \omega^2 \) is independent of \( \eta \).

Consider \( \omega_+ \), \( \omega_- \) for \( \kappa = 0 \):
\[\omega_+ \sim \sqrt{2\beta_1 \left( \frac{1}{m} + \frac{1}{M} \right)} \quad \omega_- \sim \left( \frac{2\beta_1}{M+m} \right)^{1/2} \]

First consider \( \omega_- (\omega) \) we have \( \omega_-'' = \frac{2\omega_-'}{\omega_-} = a \sqrt{2\beta_1} \)

But we also have another branch: \( \omega_+ (\omega) \), to understand its physics, meaning let's take the ratio:
\[\frac{\omega_+}{\omega_-} \]

which is \( M\omega_+ + m\omega_- = 0 \) which means the amplitude of the center of gravity motion = 0 (for \( \kappa = 0 \))
i.e., the atoms move in antiphase.

Let's plot these two branches:

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

for \( k = 0 \):
\[\omega_+ = \sqrt{2\beta_1 \left( \frac{1}{m} + \frac{1}{M} \right)} \quad \text{and} \quad 2\omega_-'' = 0 \quad a + k = 0 \]

such that \( k = \frac{\pi}{2a} \)
\[\omega_{+\min} = \sqrt{2\beta_1} \]

and for \( k = \frac{\pi}{2a} \), \( 2\omega_-'' = 0 \)

\[\text{The spectrum of allowed oscillations is confined into:}\]
\[0 < \omega < \sqrt{\frac{2\beta_1}{m}} \quad \text{--- acoustic}
\]
\[\sqrt{\frac{2\beta_1}{m}} < \omega < \sqrt{2\beta_1 \left( \frac{1}{m} + \frac{1}{M} \right)} \quad \text{--- optical}\]

Note, for \( M \gg m \) the spectrum of optical phonons is very narrow.
\[\omega_{+\max} = \sqrt{2\beta_1 \left( \frac{1}{m} + \frac{1}{M} \right)} \approx \left( 1 + \frac{m}{2M} \right)^{1/2} \sqrt{2\beta_1} - \sqrt{\frac{2\beta_1}{m}}\]
\[ \omega_{\text{max}} = \sqrt{2} \beta I \left( \frac{1}{m} + \frac{1}{M} \right) \approx \left( 1 + \frac{m}{2M} \right) \sqrt{2} \beta I \frac{1}{M} - \sqrt{2} \beta I \frac{1}{m} \]

* 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

\[ \xi_{2n} = \xi_{2n+N} \text{ or } \xi_{2n+1} = \xi_{2n+1+N} \text{ (periodic boundary cond.)} \]

\[ k_n = 2\pi \frac{n}{N} = 2\pi \frac{q}{L} \quad q = \pm 1, \pm 2, \ldots \pm \frac{N}{2} \]

For each \( k_n \) we have \( \lambda_n = \frac{2\pi}{k_n} \quad 4a < \lambda_n < L \)

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

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

The discrete spectrum of \( \omega_n \) is defined by the set of \( k_n \) from \( \pm \frac{\pi}{2a} \) which is the BZ for the di-atomic chain.

For acoustic and optical branches for each \( \omega_n \) there are 2 waves with \( k_n \) and \(-k_n \) and symmetric around \( k=0 \).

**Problem:** What happens with \( \omega_n(k) \) 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 \( k = \pm \frac{\pi}{a} \) and \( \omega / 2k = 0 \).

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 \( k \neq \pm \frac{\pi}{2a} \) \( \omega_n(k) \) should stay unchanged and

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

\( \omega(k) \) splits into 2 branches separated by the gap.
1D chain: what happen when we double the period of the chain

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

Some connects about 3D:
1) for us in general there are very different branches
2) b/c of the anisotropy of a crystal there are no strict \( \omega_{||} \) and \( \omega_{\bot} \) except when polarization of light is along high symmetry axes of the crystal.
3) For different directions of \( \mathbf{k} \) in the \( \mathbf{BZ} \) there are different sets of \( \omega_0^0 \mathbf{e}_1 \), \( \omega_0^1 \mathbf{e}_2 \), \( \omega_0^2 \mathbf{e}_3 \)

It’s hard to plot the iso-energetic surfaces of optical phonons b/c there are no dense a part of the spectrum for OPs. for small \( \mathbf{k} \).

STATISTICS OF OPs.

OPs are bosons. But they are special since their minimal energy \( \sim \) max energy of acoustic phonons. \( \sim kT_0 = \Theta_0 \)
Below To 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: \( 3N/2 + 5N/2 = 3N \)
Again, the total number of OPs is unlimited within each mode

**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 \( \omega \).

For \( T \sim T_0/2 \) the # of OPs \( \sim 10\% \)
\[
\sim T_0/3 \sim 5\%
\sim T_0/50 \sim 0.2\%
\sim 10^{-2}\% \]

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 \( > \omega \)
For OPs \( \omega \) is small and typically if \( |k| \rightarrow 0 \) \( |k| \rightarrow k_{max} \)
That’s why \( D^0_\omega (\omega) \) has narrow peaks.

It is hard to tell what’s \( D^0_\omega (\omega) \) 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 \( V = \frac{4\pi\kappa^3}{3} \), for small \( \kappa \), long \( \lambda \), \( \nu_3 = 2\omega/\kappa \sim 0 \)

So we can assume that \( (\omega_{max} - \omega) = \Delta k^2 \)
then the volume limited by \( \omega = const \sim \frac{4\pi}{3} (\omega_{max} - \omega)^{3/2} \)
If we divide it by \( (2\pi)^3/\nu \) and differentiate by \( \omega \)
we get

\[
D^0_\omega (\omega) \rightarrow \frac{V \sqrt{\omega_{max} - \omega}}{16\pi^2 \kappa^{3/2}}
\]
PHONON CONTRIBUTION TO THERMODYNAMICS OBSERVABLES

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

with $\bar{E}_g$ (per mode) $= \frac{1}{e^{(\frac{\hbar w_g}{k_B T})} - 1}$

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

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

$D(\omega)$ 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 optical phonons, and some model for $T \gg T_D$, we have acoustic phonons. We can think that the volume limited by the surface of counter $\omega_g = \omega_g(\varphi)$

$\sim \varphi^2$. Also, for small $\varphi$, $\omega_g \sim |\varphi| \leq k_B T/\hbar$

and hence $\omega_g \sim T^3$

In short, if the density of wavevector states inside $BZ$ is constant as $T$ increases, hence the number of # of excited modes $\sim T^3$

The average energy of each mode $g$ with $\omega_g < k_B T$ $\sim k_B T$

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

Now, for $T \gg T_D$ # of acoustic phonons is independent of $T$ and $= 3N$ in the $BZ$. The energy of each changes $\sim T$. Therefore $U^{3D}_{\text{acoustic}} \sim 3N k_B T$
But we need to take into account OPs, which contribute to growth exponentially with $T \gg T_D$. 

**Debye Theory**

For $P_3^D(\omega) = \frac{\hbar^2 V_a^2}{2\pi^2 U_v^2} \Rightarrow U_3^D = \frac{\hbar^2 V_a^2}{2\pi^2 U_v^2} \int_0^{\infty} \frac{\omega^3 d\omega}{e^{\frac{\hbar \omega}{k_B T}} - 1} = \frac{3\hbar V_a k_B T}{2\pi^2 k_B^2 V_a^3} \int_0^\infty \frac{x^n dx}{e^x - 1} \quad x_m = \frac{\hbar n}{k_B T}$

Let us introduce $T_D = \frac{T_D}{k_B} = \frac{\hbar}{\kappa_B}$, and recall $\overline{\omega}^n = \overline{\omega}(\frac{T_D}{N})^{\frac{1}{2}}$

$$U_3^D = \kappa_B N \left( \frac{T}{T_D} \right)^2 \int_0^{T_D} \frac{x^3 dx}{e^x - 1} \quad \text{for } T \ll T_D \quad \text{or } \quad T \gg T_D$$

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{6}{5} \left( \frac{\pi}{\sqrt{3}} \right)^5$$

$$\boxed{\overline{U}_D = \frac{3\pi^4 \kappa_B N T}{5 T_D^3} \quad T \ll T_D}$$

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

$$C_3^D = \frac{\partial U_3^D}{\partial T} = 12\pi^4 \kappa_B N \left( \frac{T}{T_D} \right)^3 = \frac{2 \pi^2 \kappa_B N \left( \frac{T}{T_D} \right)^3}{5}$$

It works very well for many solids if $T \ll T_D$

For high $T \gg T_D$, $x \ll 1$ everywhere $\overline{\rho} \sim 1 + x + \ldots$

and Thus

$$U_3^D \approx \frac{3\kappa_B N T}{T_D} \quad T \gg T_D$$

$$C_3^D = \frac{\partial U_3^D}{\partial T} = 3\kappa_B N$$

in general

$$C_3^D (T) = \frac{\partial U_3^D}{\partial T} = \kappa_B N \left( \frac{T}{T_D} \right)^3 \int_0^{T_D} \frac{x^2 dx}{e^x - 1}$$

Works very well for many metals, e.g., Al and 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 $\vec{q} \sim \nabla T$

In isotropic solid $\vec{q} = -\kappa \nabla T$

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 $\tau$.

Then $\kappa = \sqrt{\frac{C}{2}} \frac{1}{\tau}$, $\tau = \tau_{\text{relaxation}}$

We want apply it to our gas of phonons, where $\tau$

- is the average group velocity $\omega/k = v_g$

$\chi_{ph} = \frac{3}{2} C_{ph} v_g^2 R_{ph} = \frac{3}{2} C_{ph} v_g^2 T_{ph}$

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

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

$\kappa = \sum_i \tau_{i,ph}$ for several scattering mechanisms.

$$\Rightarrow \kappa_{ph} = \frac{1}{\chi_{ph}} = \frac{3}{C_{ph} \frac{1}{v_g^2} T_{ph}} = \frac{3 \tau_{ph}}{C_{ph} \frac{1}{v_g^2}}$$

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

**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 $\vec{v}_a$
Next, thermal resistance $W$ is determined by the so-called $U$-process $q_s + q_s' = q'' + g$

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

$w_s = u_q q_s$, $w_s' = u_q q_s'$, $w'' = u_q q''$

The energy carried by phonons

$\frac{1}{4} u_2 q_s + \frac{1}{2} u_2 q_s' = \frac{1}{4} u_2 (q_s + q_s')$

and after the interaction: $\frac{1}{4} u_2 q_s'' = \frac{1}{4} u_2 (q_s + q_s')$

In $N$-process $q_s + q_s' + q_s'' = 0 \Rightarrow 0$

The thermal resistance in $ph-ph$ mechanism of conductivity is defined only by the so-called $U$-processes (von Klappenberge).

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

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 $dp-p$ we need only consider the $U$-process.

At high $T$ $W_{dp-p} \sim 1$ and hence $W_{ph} \sim 1$

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

And the number of highly excited phonons with $g \sim g$

drops exponentially, and below $T < T_D$ $dp-p$ 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 mean $\sim$ size of a lattice constant at $T = T_0$, $\lambda_{ph} \approx 2a$, and the energy $k_B T \sim \frac{4\sqrt{\pi}}{\lambda_{ph}}$

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 $T$, $U$ 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

$$\nu_{ph-s} = \frac{1}{\lambda_{ph}} = \frac{U}{\nu_{ph-s}}$$

and almost constant with $T$. for $\nu_{ph} > d$

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

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

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

we conclude for $T > T_0$

$$\nu_{ph} \sim \frac{1}{\nu_{ph-s}} \sim T$$

and thus $\lambda_{ph} \sim \frac{1}{T}$

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

$$\nu_{ph} \sim \frac{T^3}{e^{-\frac{\lambda_{ph}}{T}}}$$

where $k_B T < e$ (no proof here)

and by ignoring $\nu_{ph}$-defect and $\nu_{ph}$-interface
\[ a_1 \text{ and } C_{\text{attice}} = C(T) \text{ we get} \]
\[ W_{\text{ph}} \sim \frac{T}{C(T) v_a^2} T^3 e^{-\frac{\omega_T}{T}} \quad 1 \leq \frac{T}{T_0} \leq 3 \]

For \( T < T_0 \), \( C \sim T^3 \) and \( W_{\text{ph}} \) goes rapidly down and only \( \text{v}_{\text{ph}} \)-inter 
face contribute.

![Graph](image)

\[ T_0 \text{ for } Al_2O_3 \text{ (sapphire)} \]

**SURFACE PHONONS**

*Possibly the story of SC in FeSe monolayer*
Surface phonons (SPs) are special acoustic waves. SPs can be of 2 kinds:

i) Vertical polarization \( \perp \) to the surface/interface (Rayleigh waves)

\[ \begin{align*}
\frac{\partial^2}{\partial x^2} \psi + \frac{1}{v^2} \frac{\partial^2}{\partial t^2} \psi &= 0 \\
\psi &= \text{on the surface} \ U_{\parallel}, \\
\psi &= \text{to the surface} \ U_{\perp}
\end{align*} \]

ii) Horizontally polarized along the surface

\( R \) waves are the only kind which can propagate on the surface

\[ \begin{align*}
\psi &= \text{inside, i.e. along } \mathbf{z}.
\end{align*} \]

Let's look for a solution \( \psi = A e^{i (\omega t - k_x x)} \)

since \( \omega < 0 \) we picked the sign for \( k_\perp \).

The true \( \psi = \bar{\psi}_{\parallel} + \bar{\psi}_{\perp} \) with \( \bar{\psi}_{\parallel} \) and \( \bar{\psi}_{\perp} \).

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

For SPs \( \psi \) is limited by the surface. The boundary condition for \( z = 0 \)

\[ \begin{align*}
\frac{\partial \bar{\psi}_{\parallel}}{\partial z} + \frac{\partial \bar{\psi}_{\perp}}{\partial z} &= 0 \\
\frac{\partial \bar{\psi}_{\parallel}}{\partial x} + \frac{\partial \bar{\psi}_{\perp}}{\partial x} &= 0
\end{align*} \]
A Bravais lattice is the infinite system of geometrical points which is created via translation of a single point line this:
\[ \mathbf{r} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} \]
where \( n_1, n_2, \) and \( n_3 \) are the whole numbers. \( \mathbf{a}, \mathbf{b}, \mathbf{c} \) are the primitive translation vectors.

An elementary unit cell is the minimal box built upon the vectors \( \mathbf{a}, \mathbf{b}, \mathbf{c} \).

All elementary unit cells have the same shape and the same volume: \( \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) \).

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 a 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.
Reciprocal Lattice

Consider a 2D Bravais lattice

- pick a lattice point
- draw \( \mathbf{a} \) and \( \mathbf{b} \)
- draw planes through \( \frac{1}{2} \) distance

This cell (shaded) is called Wigner-Seitz cell

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

```
\begin{align*}
\mathbf{e}^{i(\mathbf{a} \cdot \mathbf{a}^*)} &= 1 \\
\mathbf{e}^{i(\mathbf{b} \cdot \mathbf{b}^*)} &= 1 \\
\mathbf{e}^{i(\mathbf{c} \cdot \mathbf{c}^*)} &= 1 \\
\mathbf{e}^{i \xi \mathbf{a} \cdot \mathbf{x} + \alpha \mathbf{x}^*} &= 1
\end{align*}
```

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

\[
\begin{aligned}
\mathbf{a}^* &= 2\pi \frac{\mathbf{b} \cdot \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \\
\mathbf{b}^* &= 2\pi \frac{\mathbf{a} \cdot \mathbf{c}}{\mathbf{b} \cdot (\mathbf{a} \times \mathbf{c})} \\
\mathbf{c}^* &= 2\pi \frac{\mathbf{a} \cdot \mathbf{b}}{\mathbf{c} \cdot (\mathbf{a} \times \mathbf{b})}
\end{aligned}
\]

For any vector in the reciprocal space can be obtained as:

\[
\mathbf{g} = h_1 \mathbf{a}^* + h_2 \mathbf{b}^* + h_3 \mathbf{c}^*
\]