Lattice Vibrations

1. An 1d lattice of masses connected by springs:

\[ K \]
\[ m \quad m \quad m \quad m \]
\[ K \quad a \quad \rightarrow \]

\[ u_n = \text{displacement of } n^{th} \text{ mass from equilibrium} \]

Thus
\[ m \ddot{u}_n = -K(u_n - u_{n-1}) + K(u_{n+1} - u_n) \]
\[ = -K(2u_n - u_{n+1} - u_{n-1}) \]

Try solution
\[ u_n = \text{Re} \left\{ u_0 e^{-i\omega t} \right\} \]

Look for traveling wave:
\[ u_0 = u_0 e^{ikna} \]
\[ na = \text{equilibrium position of } n^{th} \text{ atom.} \]

\[ \text{Re} \left\{ m (-\omega^2) u_0 e^{ikna-i\omega t} \right\} \]
\[ = \text{Re} \left\{ -K \left[ 2e^{ik(n+1)a} - e^{ik(n-1)a} \right] \right\} \]
or \[ m \omega^2 u_0 = 2Ku_0 \left( 2e^{ika} - e^{-ika} \right) \]

\[ = 2Ku_0 \left( 1 - \cos ka \right) \]

If \( u_0 \neq 0 \) we must have

\[ \omega^2(k) = 2 \frac{K}{m} \left( 1 - \cos ka \right) \]

with \( u_n = \text{Re} \{ u_{0e} e^{ika - iwT} \} \)

Comments:

(a) \( k \) and \( k + \frac{2\pi}{a} \) are equivalent with \( l = 0, \pm 1, \pm 2, \ldots \)

so just consider the first Brillouin zone:

\[-\frac{\pi}{a} < k \leq \frac{\pi}{a}.

(b) Can take \( \omega = +\sqrt{2 \frac{K}{m} (1 - \cos ka)} \)

since - solution is actually equivalent to

\(-k\).

Proof: We have \( u_n = |u_0| \cos (kna - \omega T) + \phi \)

where \( u_0 = u_0 e^{i\phi} \)
If we have a negative solution for \( \omega \), then we would have

\[
\omega + \omega_n = \Re \left[ \frac{U_0 e^{-i\phi}}{-ikna - i\omega t} \right]
\]

which is a wave propagating in \(-k\) direction.

or \( u_n = \Re \left[ U_0 e^{-i\phi} e^{-ikna - i\omega t} \right] \)

which is a wave with \( +\omega, -k \).

(c). Long-wavelength limit:

\[
\omega \sim \sqrt{\frac{k}{m}} (Na) = \alpha c k \quad c = \text{speed of sound}
\]

so this is a sound wave.

Number of modes: Imposing periodic B.C. (which is equiv. to these Born- von Karman B.C. for this case)

\[
\begin{align*}
N + 1 &= N' \\
\Rightarrow & \quad e^{i k Na} = 1
\end{align*}
\]

\[
k = \frac{2\pi l a}{Na} \quad l = 0, 1, ...
\]

Exactly spacing is \( \frac{2\pi}{Na} \)

\[
= \Delta k \quad \# \text{of modes in 1st B.Z.}
\]

\[
= \left( \frac{2\pi}{a} \right) \frac{2\pi}{Na} = N
\]
Thus: What?

$N$ degrees of freedom, $N$ modes.

$L_k$ is just ordinary translation ($k=0$)

Maximum $w$ is at $k=\pi/a$ where $w = 2\sqrt{\frac{k}{m}}$

Alternate derivation: From Hamilton's equations

$$H = \sum_{n=1}^{N} \frac{p_n^2}{2m} + \frac{1}{2} K \sum_{n=1}^{N} \frac{(u_{n+1} - u_n)^2}{m^2}$$

with $u_{N+1} \equiv u_1$.

$$\dot{p}_n = -\frac{\partial H}{\partial u_n} \quad \dot{u}_n = +\frac{\partial H}{\partial p_n} = \frac{p_n}{m}$$

$$\dot{p}_n = -K \left[ (u_n - u_{n+1}) + (u_n - u_{n-1}) \right] = \ddot{u}_n \quad m$$

So $\ddot{u}_n = -\frac{K}{m} (2u_n - u_{n-1} - u_{n+1})$ as before.
Why do we have this same kind of structure to solutions? Periodic Hamiltonian
(translationally invariant)

Two atoms per primitive cell:

\[
\begin{align*}
& \begin{array}{cccc}
  \text{M} & \text{M} & \text{M} \\
  m & m & m
\end{array} \\
\end{align*}
\]

\[
\begin{align*}
\ll a \rr & \ll a \rr \\
\end{align*}
\]

\[
H = \sum_{n=1}^{N} \left( \frac{p_{n1}^2 + p_{n2}^2}{2m} \right) + \sum_{n=1}^{N} \left[ \frac{1}{2} K (u_{n1} - u_{n2})^2 \\
& \quad + \frac{1}{2} G (u_{n2} - u_{n+1,1})^2 \right]
\]

with \( u_{n+1, i} = u_{i, j} \)

\[
\begin{align*}
& \dot{u}_{n1} = \frac{\partial H}{\partial p_{n1}} = \frac{p_{n1}}{m} \\
& \dot{u}_{n2} = \frac{\partial H}{\partial p_{n2}} = \frac{p_{n2}}{m} \\
& \dot{p}_{n1} = -\frac{\partial H}{\partial u_{n1}} = -K (u_{n1} - u_{n2}) - G (u_{n1} - u_{n+1,2}) = m \ddot{u}_{n1} \\
& \dot{p}_{n2} = -\frac{\partial H}{\partial u_{n2}} = -G (u_{n2} - u_{n+1,1}) - K (u_{n2} - u_{n1}) = m \ddot{u}_{n2}
\end{align*}
\]

Now write \( u_{n1} = \text{Re} \left( u_{1} e^{i2kna - i\omega t} \right) \)

\[
\begin{align*}
u_{n2} &= \text{Re} \left( u_{2} e^{i2kna - i\omega t} \right)
\end{align*}
\]
So \(-m\omega^2 u_1 e^{2ikna} = -(K+G)u_1 e^{2ikna} + \left[K e^{2ikna} + Ge^{2ik(n-1)a}\right] u_2\)

and \(-m\omega^2 u_2 e^{2ikna} = -(K+G)u_2 e^{2ikna} + \left[K e^{2ikna} + Ge^{2ik(n+1)a}\right] u_1\)

or, on canceling out the factors of \(e^{2ikna}\) and rearranging, we get

\[(K+G-m\omega^2)u_1 - (K+G e^{-2ika})u_2 = 0\]

\[-(K+G e^{2ika})u_1 + (K+G - m\omega^2)u_2 = 0\]

Nontrivial solution if

\[\det \begin{vmatrix} K+G-m\omega^2 & -(K+G e^{-2ika}) \\ -(K+G e^{2ika}) & K+G - m\omega^2 \end{vmatrix} = 0\]

or \((m\omega^2 - (K+G))^2 - \left[K^2 + G^2 + \frac{2\pi}{2} K G \cos(2ka)\right] = 0\)

\[\omega^2 = \frac{(K+G)^4}{m^2} \pm \frac{1}{m} \sqrt{K^2 + G^2 + 2KG \cos 2ka}\]

\[\text{here?}\]
In this case, we have
\[-\frac{\pi}{2a} < k < \frac{\pi}{2a}\]

Sewall
Some special values: \(2ka << 1\)
\[
\cos 2ka \approx 1 - 2k^2a^2
\]
\[
\sqrt{K^2 + G^2 + 2KG - 4KGk^2a^2}
\]
\[
\approx \sqrt{(K+G)^2 - 4KGk^2a^2} = \sqrt{\left(K+G\right)^2 - \frac{4KGk^2a^2}{(K+G)^2}}
\]
\[
\approx (K+G) \left[ 1 - \frac{2KGk^2a^2}{(K+G)^2} \right]
\]

So the two vertical modes branches have values
\[
\omega \approx \frac{K+G}{m} \pm \left[ \frac{K+G}{m} - \frac{2KGk^2a^2}{m(K+G)} \right]
\]
\[
\approx \frac{2(K+G)}{m} + \frac{2KGk^2a^2}{m(K+G)}
\]

Graph looks as below:

- \(\omega\)
- \(k\)
- \(K > G\)
Note that: there is a split in the bands.
There are $N$ k vectors (if $2N$ atoms),

two modes per k vector.

"Acoustic" branch: $\omega \propto |k|$
at small $|k|$

"Optic" branch: $\omega \rightarrow \text{const as } |k| \rightarrow 0$.

Typical frequencies: At zero frequency,

$\hbar \omega_0 \approx k_B T$ with $T \sim 300 K$

(not atypical of most actual solids)
Lattice Vibrations in 3d

(i). 1 atom per primitive cell

Let \( \vec{x}_i \) = position of \( i \)th atom
\[ \vec{x}_i = \vec{R}_i + \vec{u}_i \]
\( \vec{R}_i \) = Bravais lattice vector

Potential energy is
\[ U = U(\{\vec{x}_i\}) \]

and
\[ H = \sum_{i=1}^{N} \frac{p_i^2}{2M} + U(\{\vec{x}_i\}) \]

Taylor expand potential energy:
\[ U(\{\vec{x}_i\}) = \sum_{i=1}^{N} \frac{\partial U}{\partial \vec{x}_i} u_i + \sum_{i=1}^{N} \sum_{a=1}^{3} \frac{\partial^2 U}{\partial x_i^a \partial x_j^a} u_i u_j \]
\[ (\vec{U}_i = 0) \]
\[ + \frac{1}{2} \sum_{i=1}^{N} \sum_{a=1}^{3} \sum_{j=1}^{N} \sum_{\beta=1}^{3} \frac{\partial^2 U}{\partial x_i^a \partial x_j^\beta} u_i u_j u_{i\beta} \]

Now \( \left( \frac{\partial U}{\partial u_{i\alpha}} \right)_0 = 0 \) since otherwise crystal would not be stable at its actual equilibrium lattice sites.
(c). \( D_{\alpha \beta} (\hat{R}_i - \hat{R}_j) = D_{\beta \alpha} (\hat{R}_j - \hat{R}_i) \)

because Bravais lattice has inversion symmetry.

Therefore, if we make a displacement \( \vec{u}(\hat{R}_i) \) or \( -\vec{u}(-\hat{R}_i) \),

give the same change in energy.

\( \Delta U \) in case I is

\[
\Delta U = \frac{1}{2} \sum_{i \alpha \beta} D_{\alpha \beta} (\hat{R}_i - \hat{R}_j) \frac{\partial \phi}{\partial \alpha} \frac{\partial \phi}{\partial \beta} \]

and in case II it is

\[
\Delta U = \frac{1}{2} \sum_{i \alpha \beta} D_{\alpha \beta} (\hat{R}_j - \hat{R}_i) \frac{\partial \phi}{\partial \alpha} \frac{\partial \phi}{\partial \beta} \]
and we give the second coefficient a name:

\[ \left( \frac{\partial^2 U}{\partial u_i \partial u_j} \right) = D_{ij}(\hat{R}_i, \hat{R}_j) \] 

so-called dynamical matrix 

\[ (3N \times 3N) \]

Properties:

(a) \( D_{ij}(\hat{R}_i, \hat{R}_j) = D_{ji}(\hat{R}_i, \hat{R}_j) \) if crystal is periodic.

Since the change of energy when two atoms are moved only depends on how far they are apart, not on their absolute separated positions.

(b) \( D_{ij}(\hat{R}_1 - \hat{R}_j) = D_{ji}(\hat{R}_1 - \hat{R}_j) \)

because of symmetry of second derivatives.

Thus, through second order, we have

\[ H = \sum_i \frac{\hat{p}_{id}^2}{2M} + \frac{1}{2} \sum_i \sum_j D_{ij}(\hat{R}_1 - \hat{R}_j) \hat{u}_{id} \hat{u}_{jd} + \text{const.} \]

Now, try to look for traveling-wave solutions, as in 1d, to the eqs. of motion.

The classical Hamiltonian equations of motion are:

\[ \dot{u}_{id} = \frac{\partial H}{\partial \hat{p}_{id}} \quad \hat{p}_{id} = -\frac{\partial H}{\partial u_{id}} \]
Inversion symmetry of Bravais lattice:

\[ \Delta U = \frac{1}{2} \sum_{i \neq j} D_{\alpha \beta} (\vec{R}_i - \vec{R}_j) U_{i \alpha} \bar{U}_{j \beta} \]

This should be the same change in energy if we make the replacement

\[ U_{i \alpha} \rightarrow -U_{i \alpha} \]

i.e. 

\[ U_{\alpha} (\vec{R}_i) \rightarrow -U_{\alpha} (-\vec{R}_i) \]

In the case when we have this displacement, then

\[ \Delta U = \frac{1}{2} \sum_{i \neq j} D_{\alpha \beta} (\vec{R}_i - \vec{R}_j) U_{\alpha} (\vec{R}_i) \bar{U}_{\beta} (\vec{R}_j) \]

Now sum over \( \vec{R}_i = \vec{R} \) and \( \vec{R}_j = \vec{R}' \) and we get

\[ \Delta U = \frac{1}{2} \sum_{i \neq j} D_{\alpha \beta} (\vec{R}' - \vec{R}) U_{\alpha} (\vec{R}) \bar{U}_{\beta} (\vec{R}) \]

which can be true for a general displacement only if \( D_{\alpha \beta} (\vec{R} - \vec{R}') = D_{\alpha \beta} (\vec{R}' - \vec{R}) \)

Q.E.D.
Writing these out, we get
\[ \vec{v}_{ia} = \frac{\vec{p}_{ia}}{M} \]
\[ \dot{\vec{p}}_{ia} = -\sum_{j} D_{\alpha \beta}(\vec{R}_i - \vec{R}_j) \vec{v}_{j \beta} = M \ddot{\vec{u}}_{ia} \]

Again, try solutions as in 1d:
\[ \vec{v}_{ia}(t) = \text{Re} \left\{ \vec{u}_{0a} e^{i \kappa \vec{R}_i - i\omega t} \right\} \]

where \( \vec{u}_{0a} \) is a complex number.
\[ \vec{u}_{0a} = \text{Re} \left\{ -\omega \vec{u}_{0a} e^{i \kappa \vec{R}_i - i\omega t} \right\} \]

Traveling wave in the \( \vec{k} \) direction:
\[ \text{Re} \left\{ \omega \vec{u}_{0a} e^{i \kappa \vec{R}_i - i\omega t} \right\} = \text{Re} \left\{ \sum_{j} D_{\alpha \beta}(\vec{R}_i - \vec{R}_j) e^{i \kappa \vec{R}_j - i\omega t} \vec{u}_{0\beta} \right\} \]

or
\[ \omega \vec{u}_{0a} e^{i \kappa \vec{R}_i - i\omega t} = \sum_{j} D_{\alpha \beta}(\vec{R}_i - \vec{R}_j) e^{i \kappa \vec{R}_j - i\omega t} \vec{u}_{0\beta} \]

\[ \omega \vec{u}_{0a} = \sum_{j} D_{\alpha \beta}(\vec{R}_i - \vec{R}_j) e^{-i \kappa (\vec{R}_i - \vec{R}_j)} \vec{u}_{0\beta} \]

Now, what to do about this sum?

Suppose we have an array of infinite periodic solid.

Then, we can just sum over \( \vec{R}_{ik} = \vec{R}_i - \vec{R}_j \) instead of \( \vec{R}_j \) and the eqs. of motion become
\[ M \omega^2 \psi_{0\alpha} = \sum_{\beta} D_{\alpha \beta}(\vec{R}_l) e^{-i \vec{k} \cdot \vec{R}_l} \psi_{0\beta} \]

\[ = \sum_{\beta} D_{\alpha \beta}(\vec{0}) \psi_{0\beta} \]

where \[ D_{\alpha \beta}(\vec{R}_l) = \sum_{l} D_{\alpha \beta}(\vec{R}_l) e^{-i \vec{k} \cdot \vec{R}_l} \]

\[ (\text{incl. } \vec{R}_l = \vec{0}) \]

and \[ D_{\alpha \beta}(\vec{R}_l) = \begin{pmatrix} \frac{\partial^2 U}{\partial \psi_{0\alpha} \partial \psi_{0\beta}} \\ \frac{\partial^2 U}{\partial \psi_{0\alpha} \partial \psi_{0\beta}} \end{pmatrix} \]

Note that \( 3N \) eqs. have shrunk to just 3 (because of periodicity).

Rewriting these equations:

\[ \sum_{\beta} \left[ D_{\alpha \beta}(\vec{R}_l) - M \omega^2 \delta_{\alpha \beta} \right] \psi_{0\beta} = 0 \]

\( D_{\alpha \beta}(\vec{R}_l) \) also called dynamical matrix.

Comments:

(a). \[ D_{\beta \alpha}(\vec{R}_l) = \sum_{l} D_{\beta \alpha}(\vec{R}_l) e^{-i \vec{k} \cdot \vec{R}_l} \]

\[ = \sum_{l} D_{\beta \alpha}(-\vec{R}_l) e^{-i \vec{k} \cdot \vec{R}_l} \]

because of symm. already mentioned.
\[ \sum_{l'} D_{l'p}(\vec{R}_{l'}) e^{ik \cdot \vec{R}_{l'}} \quad \vec{R}_{l'} = -\vec{R}_l \]

\[ = D_{l'p}(\vec{k}) \quad \text{since all the } D_{l'p}(\vec{R}_{l'})'s \text{ are real.} \]

So \( D_{l'p}(\vec{k}) \) is Hermitian

Also, we have

\[ D_{l'p}(\vec{k}) = \sum_{l} D_{l'p}(\vec{R}_l) e^{ik \cdot \vec{R}_l} \]

\[ = \sum_{l} D_{l'p}(\vec{R}_l) e^{-ik \cdot \vec{R}_l} \]

\[ = \sum_{l} D_{l'p}(\vec{R}_l) e^{ik \cdot \vec{R}_l} \]

\[ = \frac{1}{2} \sum_{l} D_{l'p}(\vec{R}_l) \cos k \cdot \vec{R}_l \quad \text{so } D_{l'p}(\vec{k}) \text{ is real} \]

Allowed eigenvalues thus determined by

\[ \det \left| D_{l'p}(\vec{k}) - M \omega^2(\vec{r}) \delta_{l'l''} \right| = 0 \]

3 allowed solutions

Comments: different solutions have different polarizations.

Since \( D_{l'p}(\vec{k}) \) is Hermitian, the eigenvectors \( \vec{u}_{l'p}(\vec{k}) \) corresponding different \( p \) are orthogonal.

Let unit vectors \( \vec{e}_s \)

\[ \vec{u}_{l'p}(\vec{k}) \cdot \vec{e}_s = 5 \quad \text{if } \vec{e}_s \text{ are normalized} \]
Transverse mode: \[ \hat{L}_k \]
Longitudinal mode: \[ \hat{L}_k \]

In general, can have both, i.e. modes are neither purely longitudinal nor purely transverse.

Isotope effect: modes satisfy \( w(x) \propto \sqrt{M} \).

Long wavelength dynamical matrix:

We have \( D_{\alpha \beta} (\hat{L}_k) = \sum_l D_{\alpha \beta} (\hat{R}_l) e^{-i k \cdot \hat{R}_l} \)

Now the long wavelength limit is

\[ \sum_l D_{\alpha \beta} (\hat{R}_l) \cdot = \sum_l \left( \frac{\partial^2 U}{\partial \nu_0 \partial \nu_0} \right) \]

Now

But now consider what this second derivative means. Let us move each atom by a distance \( \hat{\nu}_0 = \tilde{\nu}_0 \). According to the Taylor expansion, the potential energy, to second order, changes by

\[ \Delta U = \frac{1}{2} \sum_{\alpha \beta} \sum_{\alpha \beta} \sum_{\alpha \beta} D_{\alpha \beta} (\tilde{\nu}_0 - \hat{\nu}_0) u_{\alpha \alpha} u_{\beta \beta} \]

= 0 since a uniform shift cannot change the energy.
\[ \Delta U = N \sum \sum D_{\alpha \beta}(\mathbf{R}_n) U_{\alpha \alpha} U_{\beta \beta} = 0 \]

for any \( U_{\alpha \alpha} \). This is only possible if \( D_{\alpha \beta}(\mathbf{k} = 0) = \sum \sum D_{\alpha \beta}(\mathbf{R}_n) = 0 \) for any \( \alpha, \beta \).

Rewrite, then:

\[ D_{\alpha \beta}(\mathbf{k}) = \frac{1}{2} \sum \sum D_{\alpha \beta}(\mathbf{R}_k) \left( e^{i \mathbf{k} \cdot \mathbf{R}_k} e^{-i \mathbf{k} \cdot \mathbf{R}_k} \right) \]

\[ = \frac{1}{2} \sum \sum D_{\alpha \beta}(\mathbf{R}_k) \left( e^{i \mathbf{k} \cdot \mathbf{R}_k} + e^{-i \mathbf{k} \cdot \mathbf{R}_k} \cos \mathbf{k} \cdot \mathbf{R}_k \right) \]

\[ = \frac{1}{2} \sum \sum D_{\alpha \beta}(\mathbf{R}_k) \left( \sin^2 \left( \frac{\mathbf{k} \cdot \mathbf{R}_k}{2} \right) \right) \]

Small \( \mathbf{k} \):

\[ D_{\alpha \beta}(\mathbf{k}) \approx -\frac{1}{2} \sum \sum k_{i k} k_{j \beta} \sum \frac{D_{\alpha \beta}(\mathbf{R}_n) \mathbf{R}_{i k} \mathbf{R}_{j \beta}}{2} \]

So all the \( \omega_{n s}(\mathbf{k}) \) satisfy, at small \( \mathbf{k} \):

\[ \omega_{n s}(\mathbf{k}) \approx \sum \sum \sum K_{i j ; s} \]

\( \omega \) quadratic in \( k_i \)'s. (acoustic modes)
Typical graph:

\[ W \]

(k, B.Z. face)

(in some direction)

# Need only consider \( \mathbf{k} \) in 1st B.Z. because \( \mathbf{k} \) and \( \mathbf{k} + \mathbf{K} \) are equivalent.

If \( N \) atoms, \( 3N \) modes

\( N \) \( \mathbf{k} \)-vectors.

Long-wavelength modes

Allowed \( \mathbf{k} \)-vectors are those permitted by Born-von Karman boundary conditions.
More than one atom per primitive cell

\[ H = \sum_{l=1}^{N} \sum_{i=1}^{m_3} \sum_{\xi=1}^{2} \frac{e^{2}}{2}\sum_{l'=1}^{N} \sum_{i=1}^{m_3} \sum_{\xi=1}^{2} \sum_{\alpha=1}^{3} \sum_{\beta=1}^{3} \sum_{\gamma=1}^{3} \sum_{\delta=1}^{3} \sum_{\epsilon=1}^{3} \sum_{\zeta=1}^{3} \frac{D(\mathbf{R}_l - \mathbf{R}_{l'})}{\varepsilon_{\alpha\beta\gamma\delta\epsilon\zeta}} \]

\[ + \frac{1}{2} \sum_{l=1}^{N} \sum_{i=1}^{m_3} \sum_{\xi=1}^{2} \sum_{l'=1}^{N} \sum_{i=1}^{m_3} \sum_{\xi=1}^{2} \sum_{\alpha=1}^{3} \sum_{\beta=1}^{3} \sum_{\gamma=1}^{3} \sum_{\delta=1}^{3} \sum_{\epsilon=1}^{3} \sum_{\zeta=1}^{3} \frac{u_{\alpha\beta}(\mathbf{R}_l) u_{\gamma\delta}(\mathbf{R}_{l'})}{\varepsilon_{\alpha\beta\gamma\delta\epsilon\zeta}} \]

\[ i \] labels atoms within primitive cell.

Again we write down equations of motion using

\[ \dot{\mathbf{p}}_{\mathbf{r}_{\mathbf{l}x}} = - \frac{\partial H}{\partial \mathbf{r}_{\mathbf{l}x}} \quad \dot{\mathbf{u}}_{\mathbf{r}_{\mathbf{l}x}} = \frac{\partial H}{\partial \mathbf{u}_{\mathbf{r}_{\mathbf{l}x}}} = \mathbf{M}^{-1}_{\mathbf{l}x} \mathbf{p}_{\mathbf{l}x} \]

\[ = \mathbf{M}_{\mathbf{l}x} \mathbf{u}_{\mathbf{l}x} \]

The equations of motion eventually become

\[ \mathbf{M}_{\mathbf{l}x} \mathbf{u}_{\mathbf{l}x} = - \sum_{j=1}^{n} \sum_{\beta=1}^{3} \sum_{i=1}^{m_3} \sum_{\alpha=1}^{3} \sum_{i=1}^{m_3} \sum_{\beta=1}^{3} \sum_{\gamma=1}^{3} \sum_{\delta=1}^{3} \sum_{\epsilon=1}^{3} \sum_{\zeta=1}^{3} \mathcal{D}_{\alpha\beta\gamma\delta\epsilon\zeta}(\mathbf{R}_l - \mathbf{R}_\beta) u_{\beta \alpha}(\mathbf{R}_\beta) \]

Make substitution

\[ \mathbf{v}_{\mathbf{l}x} = \mathbf{R}_{\beta} \left[ \mathbf{u}_{\mathbf{l}x} e^{i \mathbf{k} \cdot \mathbf{R}_{l} - i \omega t} \right] \]

Then we eventually get
\[ M_i \omega^2 \nu_{\text{die}} e^{ik \cdot \vec{R}_l - i \omega t} = \sum_{\delta \beta} \sum_{\ell' l} D_{\delta \beta, ij} (R_l - \vec{R}_{\ell'}) \nu_{\delta \beta} e^{ik \cdot \vec{R}_l - i \omega t} \]

or \[ \sum_{\delta \beta} \left( D_{\delta \beta, ij} (k) \nu_{\delta \beta} - M_i \omega^2 \delta_{\delta \beta} \delta_{ij} \right) \nu_{\delta \beta} = 0 \]

where \[ D_{\delta \beta, ij} (k) = \sum_{l l'} D_{\delta \beta; ij} (R_l - \vec{R}_{l'}) e^{-ik \cdot \vec{R}_l} \]

which is once again a Hermitian matrix.

This is a matrix (a Hermitian matrix) of dimension \( d n \times d n \), where \( d (= 3) = \) dimension

and \( n = \# \) of atoms in primitive cell.

Thus there are \( d n \) branches

and \( N d n \) modes for a \( d \times n \) system having \( N \) primitive cells.

There will be \( 3 \) acoustic branches,

and \( 3(n-1) \) optic branches

(in 3 dimensions)
A typical phonon spectrum (for \( n=2 \)) along a particular direction in \( k \)-space might look as below:

Why only three acoustic branches?

Because there are only three independent translations which produce no change in energy:

\[ \overrightarrow{\varepsilon} = \overrightarrow{\tilde{U}} \]

\( TA, LA \) \text{ transverse, longitudinal acoustic branches}

\( TO, LO \) \text{ optic branches.}

Usually, \( \omega_{LO} > \omega_{TO} \); \( \omega_{LA} > \omega_{TA} \).
Orthogonality of modes:

We have 3n amplitudes $U_{0,ix}$

$i=1, 2, \ldots, n; \alpha = 1, \ldots, 3$.

Let us write these as the displacement as

$$\hat{\mathbf{R}} = \sum_{i=1}^{n} k_i \mathbf{r}_i e^{-i \omega t}$$

$$\mathbf{R} = \varepsilon_s \sum_{i=1}^{3} \varepsilon_s^i(t) \mathbf{e}_i$$

$$\mathbf{R} = \varepsilon_s \sum_{i=1}^{3} \varepsilon_s^i(\mathbf{r}) e^{-i \omega t}$$

$$\mathbf{R} = \varepsilon_s \sum_{i=1}^{3} \varepsilon_s^i(\mathbf{r}) e^{-i \omega t}$$

Orthogonality relation is

$$\sum_i \varepsilon_s^i(\mathbf{r})^* \varepsilon_s^{i'}(\mathbf{r}) M_{ij} = \delta_{ss'}$$

Not so simple.

Finally, "canonical form" of Hamiltonian in terms of normal modes (1 atom per primitive cell)

We have

$$H = \frac{1}{2M} \sum_{\mathbf{R}} \left( \frac{\mathbf{P}^2}{2M} + \frac{1}{2} \sum_{\alpha \beta} \sum_{\mathbf{R}} \mathbf{D}_{\alpha \beta} (\mathbf{R} - \mathbf{R}') \mathbf{U}_{\alpha \beta} \mathbf{U}'_{\alpha \beta} \right)$$

Let us "diagonalize this quadratic form.

I will just quote the result for a classical crystal.