Lattice vibrations, phonons, and the speed of sound

Assume Hamiltonian of ionic degrees of freedom looks like

$$H = \underbrace{\sum_{R_i} \frac{\vec{P}_i^2}{2M}}_{\text{kinetic}} + \underbrace{U_{ion}(\{\vec{R}_i\})}_{\text{potential due to ion-ion interactions}}$$

ions at positions $\vec{R}_i$, momentum $\vec{P}_i$, mass M

Write $\vec{R}_i = \vec{R}_i^{\,0} + \vec{u}_i$

$\vec{R}_i^{\,0}$: position in periodic BL

$\vec{u}_i$: small displacement due to elastic distortions

If $\vec{u}_i$ is small, expand U_{ion} about the BL positions $\vec{R}_i^{\,0}$. Since the positions $\vec{R}_i^{\,0}$ are assumed to be positions of mechanical equilibrium, the linear term in the expansion must vanish, and the quadratic term is the leading order term.

$$U_{ion}(\{\vec{u}_i\}) = U_{ion}^{0} + \frac{1}{2} \sum_{\substack{i\alpha \\ j\beta}} u_{i\alpha} \, \mathbb{D}_{ij}^{\alpha\beta} \, u_{j\beta}$$

i, j label BL sites

α, β label components x, y, z of the displacement

$$\mathbb{D}_{ij}^{\alpha\beta} = \left. \frac{\partial^2 U_{ion}}{\partial u_{i\alpha} \, \partial u_{j\beta}} \right|_{\{\vec{R}_i^{\,0}\}}$$ is the <u>dynamical matrix</u>

The classical equations of motion for the ions are then

$$M \ddot{\vec{u}}_i = -\frac{\partial U_{ion}}{\partial \vec{u}_i} \Rightarrow M \ddot{u}_{i\alpha} = -\sum_{j\beta} D_{ij}^{\alpha\beta} u_{j\beta}$$

Now by translational invariance of the Bravais lattice $D_{ij}^{\alpha\beta}$ depends only on $\vec{R}_i^{\,0} - \vec{R}_j^{\,0}$.

We can define the Fourier transforms

$$\vec{u}_i(t) = \int_{q \in 1^{st} BZ} d^3q \int_{-\infty}^{\infty} d\omega \; e^{i \vec{q} \cdot \vec{R}_i^{\,0}} e^{-i\omega t} \vec{u}(\vec{q}, \omega)$$

$$D_{ij}^{\alpha\beta} = \int_{q \in 1^{st} BZ} d^3q \; e^{i \vec{q} \cdot (\vec{R}_i^{\,0} - \vec{R}_j^{\,0})} D^{\alpha\beta}(\vec{q})$$

Note: in defining Fourier transform of a function that exists only on the discrete sites of a B.L., the only wave vectors we need to consider are those $\vec{q}$ in the 1^{st} BZ. This is because any wavevector $\vec{k}$ can always be written as $\vec{k} = \vec{q} + \vec{K}$ with $\vec{K}$ a unique R.L. vector and $\vec{q}$ in the 1^{st} BZ. Then the plane wave factor would be

$$e^{i \vec{k} \cdot \vec{R}_i^{\,0}} = e^{i (\vec{q} + \vec{K}) \cdot \vec{R}_i^{\,0}} = e^{i \vec{q} \cdot \vec{R}_i^{\,0}} \quad \text{since } e^{i \vec{K} \cdot \vec{R}_i^{\,0}} = 1$$

so we still only get oscillations at $\vec{q}$ in 1^{st} BZ

Substitute these into the equation of motion

$$\int\limits_{q \text{ in } 1^{st} BZ} d^3q \int_{-\infty}^{\infty} d\omega\, e^{i\vec{q}\cdot\vec{R}_i^0} e^{-i\omega t} (-\omega^2) M \vec{u}(\vec{q},\omega)$$

$$= -\int\limits_{q\in 1^{st}BZ} d^3q \int\limits_{q'\in 1^{st}BZ} d^3q' \int_{-\infty}^{\infty} d\omega \sum_j e^{i\vec{q}\cdot(\vec{R}_i^0-\vec{R}_j^0)} e^{i\vec{q}'\cdot\vec{R}_j^0} e^{-i\omega t}\, \overleftrightarrow{D}(q) \cdot \vec{u}(\vec{q}',\omega)$$

↑ matrix product over coordinates

Do the ~~integral~~ summation

$$\sum_j e^{i(\vec{q}'-\vec{q})\cdot\vec{R}_j^0} = \delta(\vec{q}-\vec{q}')$$

Follows since $\{\vec{R}_j^0 + \vec{R}_0^0\} = \{\vec{R}_j^0\}$ since BL is closed under translation by any BL vector $\vec{R}_0^0$

$$\Rightarrow \sum_{R_j^0} e^{i(\vec{q}'-\vec{q})\cdot\vec{R}_j^0} = \sum_{R_j^0} e^{i(\vec{q}'-\vec{q})\cdot(\vec{R}_j^0+\vec{R}_0^0)}$$

$$= e^{i(\vec{q}'-\vec{q})\cdot\vec{R}_0^0} \sum_{R_j^0} e^{i(\vec{q}'-\vec{q})\cdot\vec{R}_j^0}$$

$$\Rightarrow e^{i(\vec{q}'-\vec{q})\cdot\vec{R}_0^0} = 1 \text{ for any } \vec{R}_0^0 \text{ in BL}$$

$$\Rightarrow \vec{q}'-\vec{q} = \vec{K} \text{ in R.L.}$$

But since $\vec{q}, \vec{q}'$ both in 1^{st} BZ $\Rightarrow \vec{K}=0$ and

$\vec{q} = \vec{q}'$ or the sum must vanish

$$\int_{1^{st}BZ} d^3q \int d\omega\, e^{i(\vec{q}\cdot\vec{R}_i^0 - \omega t)} (-\omega^2) M\, \vec{u}(\vec{q},\omega)$$

$$= -\int_{1^{st}BZ} d^3q\, d\omega\, e^{i(\vec{q}\cdot\vec{R}_i^0 - \omega t)} \overleftrightarrow{D}(\vec{q}) \cdot \vec{u}(\vec{q},\omega)$$

equate Fourier amplitudes to get

$$+\omega^2 M\, \vec{u}(\vec{q},\omega) = \overleftrightarrow{D}(\vec{q}) \cdot \vec{u}(\vec{q},\omega)$$

If the eigenvectors and eigenvalues of $\overleftrightarrow{D}(\vec{q})$ are $\vec{\epsilon}_1(\vec{q}), \vec{\epsilon}_2(q), \vec{\epsilon}_3(q)$ and $\lambda_1(\vec{q}), \lambda_2(\vec{q}), \lambda_3(\vec{q})$

Then

$$+\omega_s^2 M = \lambda_s(\vec{q}) \qquad s = 1, 2, 3$$

$$\omega_s = \sqrt{\frac{\lambda_s(\vec{q})}{M}}$$

dispersion relation for elastic vibrations at wave vector $\vec{q}$, polarization $\vec{\epsilon}_s(\vec{q})$

We expect that in the <u>long wave length limit</u> we can expand

$$\overleftrightarrow{D}(q) = \sum_i e^{-i\vec{q}\cdot\vec{R}_i} \overleftrightarrow{D}(\vec{R}_i)$$

$$\simeq \sum_i \left\{ 1 - i\vec{q}\cdot\vec{R}_i - \tfrac{1}{2}(\vec{q}\cdot\vec{R}_i)^2 \right\} \overleftrightarrow{D}(\vec{R})$$

$\sum_i \overleftrightarrow{D}(\vec{R}_i) = 0$ because if all $\vec{u}_i = \vec{u}_0$ a uniform displacement, then net force on ion i must vanish

$\sum_i \vec{R}_i \overleftrightarrow{D}(\vec{R}_i) = 0$ by inversion symmetry $\vec{R}_i \to -\vec{R}_i$
$\overleftrightarrow{D}(\vec{R}_i) = \overleftrightarrow{D}(-\vec{R}_i)$

so

$$\overleftrightarrow{D}(q) \simeq -\frac{q^2}{2} \sum_{\vec{R}_i} (\hat{q}\cdot\vec{R}_i)^2 \overleftrightarrow{D}(\vec{R})$$

we assume this sum converges

$\Rightarrow \overleftrightarrow{D}(q) \propto q^2$

so $\lambda_s(\vec{q}) \propto q^2$ or $\lambda_s(\vec{q}) = A_s q^2$
~~for~~ small $\vec{q}$

$\Rightarrow \omega_s = \sqrt{\frac{A_s}{M}}\,|\vec{q}|$ with

$c_s = \sqrt{A_s/M}$ the speed of sound ~~for~~ for polarization s.

$\omega_s = c_s q$ for small $\vec{q}$

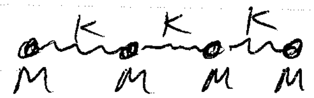
Also at small $\vec{q}$ we expect the spatial orientation of the B.L. to get "averaged over" and so the only directions of $\vec{q}$ and $\perp$ to $\vec{q}$. We thus expect the polarization vectors to become as $\vec{q} \to 0$

$\vec{\epsilon}_1(\vec{q}) = \hat{q}$ longitudinal sound mode, speed c_ℓ

$\left.\begin{matrix}\vec{\epsilon}_2(\vec{q})\\ \vec{\epsilon}_3(\vec{q})\end{matrix}\right\} \perp \hat{q}$ transverse sound modes, speed c_{t1}, c_{t2}

Exaple

1D chain of ions connected by springs



nearest neighbor interaction only

$\frac{1}{2}K(u_i-u_{i+1})^2$

u_i = displacement of ion i

$$M\ddot{u}_i = -K(u_i-u_{i+1}) - K(u_i-u_{i-1})$$

integer n

Assume $u_n(t) = u_0 e^{i(kR_n-\omega t)}$ $\quad R_n = an$

Substitute in and cancel common factors of $e^{i(kR_n-\omega t)}$

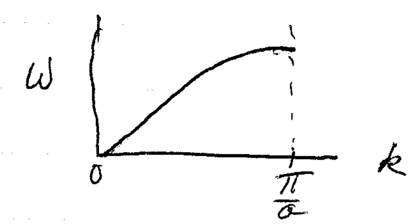
$$-\omega^2 M u_0 = -K(u_0 - u_0 e^{ika}) - K(u_0 - u_0 e^{-ika})$$

$$\Rightarrow -\omega^2 M = -K(1-e^{ika} + 1 - e^{-ika})$$
$$= -2K(1-\cos ka)$$

$$\omega = \sqrt{\frac{2K}{M}(1-\cos ka)}$$

use $\frac{1-\cos ka}{2} = \sin^2(\frac{ka}{2})$

$$\omega = \sqrt{\frac{K}{M}}\, 2\left|\sin\left(\frac{ka}{2}\right)\right|$$



at small $ka \ll 1$, $\sin ka \simeq ka$

$$\omega \simeq \sqrt{\frac{K}{M}}\, ka \quad \Rightarrow \text{speed of sound}$$

$$c = \sqrt{\frac{K}{M}}\, a$$

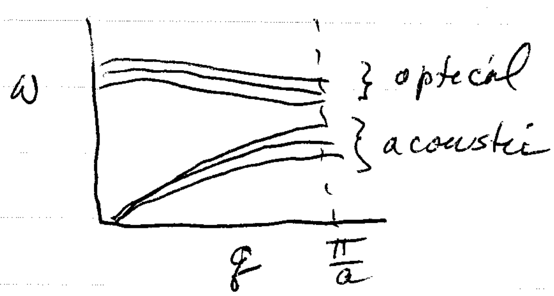
Previous discussion assumed monatomic B.L. When have BL with basis, the dynamic matrix must acquire an additional index that labels the n atoms in the basis at any BL site R_i

$\Rightarrow$ 3 modes for each atom in primitive cell of BL

$\Rightarrow$ $3n$ elastic modes

of these, 3 are acoustic modes as before – one longitudinal, two transverse – with $\omega_s \simeq c_s q$ as $q \to 0$.

The $3(n-1)$ remaining modes are "optical" modes where $\omega_s(q) \to$ const as $q \to 0$.



see A+M chpt 22 and problem #1 on Problem Set 6

optical modes correspond to "internal" vibrations of the atoms within a primitive cell of the BL ~~with respect to each other~~

acoustic modes correspond to motions of the primitive cell as a whole.