Lattice vibrations, phonons, and the speed of sound

Assume Hamiltonian of ionic degrees of freedom looks like

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

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 $\mathcal{U}_{ion}$ 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.

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

i, j label BL sites

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

$$\mathbb{D}_{ij}^{\alpha\beta} \equiv \left. \frac{\partial^2 \mathcal{U}_{ion}}{\partial u_{i\alpha} \partial u_{j\beta}} \right|_{\{\vec{R}_i^{\,0}\}}$$ 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 $\vec{R}_i^{\,o} - \vec{R}_j^{\,o}$.

We can define the Fourier transforms

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

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

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

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

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

Substitute these into the equation of motion

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

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

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 $\vec{R}_0^0$

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

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

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

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

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 $\vec{\epsilon}_1(\vec{q}), \vec{\epsilon}_2(\vec{q}), \vec{\epsilon}_3(\vec{q})$ 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

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

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

$\sum_i \overleftrightarrow{D}(\vec{R}_i) = 0$ 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 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 then expect the polarization vectors to become as $\vec{q} \to 0$

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

$\left.\begin{array}{l}\vec{\epsilon}_2(\vec{q}) \\ \vec{\epsilon}_3(\vec{q})\end{array}\right\} \perp \hat{q}$ transverse sound modes, speed c_{t_1}, c_{t_2}