Phonons in crystals

Position of an atom:

$$\vec{R}_{j\vec{n}} = \underbrace{\vec{n} + \vec{\rho}_j}_{\text{equilibrium position, } \vec{R}^{(0)}_{\vec{n}j}} + \underbrace{\vec{u}_{j\vec{n}}}_{\text{displacement}}$$

$\vec{n} = n_1 \cdot \vec{a}_1 + n_2 \cdot \vec{a}_2 + n_3 \cdot \vec{a}_3$ - lattice

$\vec{\rho}_j$ - basis $(j = 1, 2, \dots, g)$

α, β = three perpendicular directions (x, y, z).

$d = 3$ - dimensions

Equation of motion for each atom (Newton's law):

$$M_j \ddot{u}^{\alpha}_{j\vec{n}} = - \sum_{j_1 \vec{n}_1} A^{\alpha\ \beta}_{\substack{j\ j_1 \\ \vec{n}\ \vec{n}_1}} u^{\beta}_{j_1 \vec{n}_1} \qquad (\sim 10^{23} \text{ equations}) \qquad (1)$$

note: sum over β.

$$A^{\alpha\ \beta}_{\substack{j\ j_1 \\ \vec{n}\ n_1}} = \left(\frac{\partial^2 U}{\partial R^{\alpha}_{j\vec{n}} \, \partial R^{\beta}_{j_1 n_1}} \right)_0 \leftarrow \text{in equilibrium}$$

To achieve a translational symmetry for a finite crystal, let us use periodic boundary condition:

In this case, A can only depend on difference $\vec{n} - \vec{n}_1$: $A^{\alpha\beta}_{\substack{j\ j_1 \\ \vec{n}\ \vec{n}_1}} = A^{\alpha\beta}_{jj_1}(\vec{n} - \vec{n}_1)$.

The solutions for two crystals (one shifted by $\vec{n}_1$ withe respect to the other) can only differ by a phase: $u^{\alpha}_{j(\vec{n}+\vec{n}_1)} = \underset{\text{phase}}{(\dots)} u^{\alpha}_{j\vec{n}}$.

Therefore, we are looking for a solution in a form: $u^{\alpha}_{j\vec{n}} = V^{\alpha}_j e^{i\vec{f}\vec{n}} e^{-i\omega t}$, (2)

where $\vec{f}$ is a vector, such as $\vec{f}\vec{n} \in \mathbb{R}$

Substituting (2) in (1): $M_j V^{\alpha}_j e^{i\vec{f}\vec{n}} (-\omega^2 e^{-i\omega t}) = - \sum_{j_1 \vec{n}_1} A^{\alpha\beta}_{jj_1}(\vec{n} - \vec{n}_1) V^{\beta}_{j_1} e^{i\vec{f}\vec{n}_1} e^{-i\omega t}$

$$M_j \omega^2 V^{\alpha}_j = \sum_{j_1} \cdot \underbrace{\sum_{\vec{n}_1} A^{\alpha\beta}_{jj_1}(\vec{n} - \vec{n}_1) e^{-i\vec{f}(\vec{n} - \vec{n}_1)}}_{\text{does not depend on } \vec{n}} \cdot V^{\beta}_{j_1}$$

$\Rightarrow$ we can chose $\vec{n} = 0$.

$$M_j \omega^2 V^{\alpha}_j = \sum_{j_1} \sum_{\vec{n}} A^{\alpha\beta}_{jj_1}(\vec{n}) e^{-i\vec{f}\vec{n}} \cdot V^{\beta}_{j_1} \quad (3) \qquad dg \sim 10 \text{ equations}$$

Normalization: $V_j^\alpha = \ell_j^\alpha \cdot \frac{1}{\sqrt{M_j}}$ (4)

$$C_{jj'}^{\alpha\beta} = \frac{1}{\sqrt{M_j M_{j'}}} \cdot \sum_{\vec{n}} A_{jj'}^{\alpha\beta}(\vec{n}) e^{-i\vec{f}\vec{n}} \quad (5)$$

(4), (5) → (3): $\omega^2 \ell_j^\alpha = \sum_{j'} C_{jj'}^{\alpha\beta}(\vec{f}) \cdot \ell_{j'}^\beta$

$$\sum_{j'} \left[\omega^2 \delta^{\alpha\beta} \delta_{jj'} - C_{jj'}^{\alpha\beta}(\vec{f})\right] \cdot \ell_{j'}^\beta = 0 \quad (6)$$ system of $d \cdot j$ equations

The linear system of equations has non-zero solutions when

$\det \| \omega^2 \delta^{\alpha\beta} \delta_{jj'} - C_{jj'}^{\alpha\beta}(\vec{f}) \| = 0$ (7)

From (7), we can find $\omega_s^2(\vec{f})$, for which $\ell_{j,s}^\beta$ are non-zero.
$s = 1, \dots, d \cdot g$.

Let us prove some important properties of $\hat{C}$, ℓ_s and ω_s.

1) $\hat{C}$ is Hermitian, i.e. $\hat{C}^+ = \hat{C}$

$$C_{jj'}^{*\alpha\beta}(\vec{f}) \underset{(5)}{=} \frac{1}{\sqrt{M_j M_{j'}}} \cdot \sum_{\vec{n}} A_{jj'}^{\alpha\beta}(\vec{n}) e^{i\vec{f}\vec{n}} \underset{\vec{n} \to -\vec{n}}{=} \frac{1}{\sqrt{M_j M_{j'}}} \sum_{\vec{n}} A_{jj'}^{\alpha\beta}(\vec{n}) e^{-i\vec{f}\vec{n}} = C_{j'j}^{\beta\alpha}(\vec{f}) \quad (8)$$

$$A_{jj'}^{\alpha\beta}(-\vec{n}) = A_{j'j}^{\beta\alpha}(\vec{n})$$

2) $C_{jj'}^{*\alpha\beta}(-\vec{f}) = C_{jj'}^{\alpha\beta}(\vec{f})$ (9) (follows from (5))

3) $\ell_{js}^\alpha(\vec{f}) = \ell_{js}^{*\alpha}(-\vec{f})$

$$\omega^2 \ell_j^\alpha = \sum_{j'} C_{jj'}^{\alpha\beta}(\vec{f}) \ell_{j'}^\beta \underset{(9)}{\Rightarrow} \omega_s^2(-\vec{f}) \ell_{js}^{*\alpha}(-\vec{f}) = \sum_{j'} C_{jj'}^{\alpha\beta}(\vec{f}) \cdot \ell_{j'}^{*\beta}(-\vec{f})$$

$\Rightarrow \det \| \omega_s^2(-\vec{f}) \delta^{\alpha\beta} \delta_{jj'} - C_{jj'}^{\alpha\beta}(\vec{f}) \| = 0$ - the same characteristic equation as (7)

$\Rightarrow \omega_s^2(-\vec{f}) = \omega_s^2(\vec{f})$ (10)

and $\ell_{js}^\alpha(\vec{f}) = \ell_{js}^{*\alpha}(-\vec{f})$ (11)

4) $\ell^{\alpha}_{js}(\vec{f})$ form a complete orthonormal basis

$$\omega_s^2(\vec{f})\cdot \ell^{\alpha}_{js}(\vec{f}) = \sum_{j'} C^{\alpha\beta}_{jj'}(\vec{f})\cdot \ell^{\beta}_{j's}(\vec{f}) \quad \Big| \cdot \ell^{*\alpha}_{js_1}(\vec{f}),\ \sum_j$$

$$\omega_s^2(\vec{f})\cdot \sum_j \ell^{*\alpha}_{js_1}(\vec{f})\cdot \ell^{\alpha}_{js}(\vec{f}) = \sum_{jj'} \ell^{*\alpha}_{js_1}(\vec{f})\cdot C^{\alpha\beta}_{jj'}(\vec{f})\cdot \ell^{\beta}_{j's}(\vec{f}) \qquad (12)$$

$s_1 \neq s$: $$\omega_{s_1}^2(\vec{f})\cdot \ell^{*\alpha}_{js_1}(\vec{f}) = \sum_{j'} C^{*\alpha\beta}_{jj'}(\vec{f})\,\ell^{*\beta}_{j's_1}(\vec{f}) \underset{(8)}{=} \sum_{j'} C^{\beta\alpha}_{j'j}(\vec{f})\,\ell^{*\beta}_{j's_1}(\vec{f}) \quad \Big| \cdot \ell^{\alpha}_{js}(\vec{f}),\ \sum_j$$

$$\omega_{s_1}^2(\vec{f})\cdot \sum_j \ell^{*\alpha}_{js_1}(\vec{f})\,\ell^{\alpha}_{js}(\vec{f}) = \sum_{jj'} \ell^{*\beta}_{j's_1}(\vec{f})\cdot C^{\beta\alpha}_{j'j}(\vec{f})\cdot \ell^{\alpha}_{js}(\vec{f})$$

$$\underset{\substack{\alpha \rightleftarrows \beta \\ j' \rightleftarrows j}}{=} \sum_{jj'} \ell^{*\alpha}_{js_1}(\vec{f})\, C^{\alpha\beta}_{jj'}(\vec{f})\cdot \ell^{\beta}_{j's}(\vec{f}) \qquad (13)$$

(12)-(13) $$\left[\omega_s^2(\vec{f}) - \omega_{s_1}^2(\vec{f})\right]\cdot \sum_j \ell^{*\alpha}_{js_1}(\vec{f})\,\ell^{\alpha}_{js}(\vec{f}) = 0$$

if $s_1 \neq s$: $\Rightarrow \omega_s^2(\vec{f}) \neq \omega_{s_1}^2(\vec{f}) \Rightarrow \sum_j \ell^{*\alpha}_{js_1}(\vec{f})\,\ell^{\alpha}_{js}(\vec{f}) = 0$ (14) - orthogonality

if $s_1 = s$: we can always normilize ℓ^{α}_{js} so that $\sum_j \ell^{*\alpha}_{js}(\vec{f})\cdot \ell^{\alpha}_{js}(\vec{f}) = 1$ (15)

(14);(15) $$\sum_j \ell^{*\alpha}_{js_1}(\vec{f})\,\ell^{\alpha}_{js}(\vec{f}) = \delta_{ss_1} \qquad (16) \qquad \Big| \cdot \ell^{\beta}_{j's_1}(\vec{f}),\ \sum_{s_1}$$

$$\sum_j \left[\sum_{s_1} \ell^{*\alpha}_{js_1}(\vec{f})\,\ell^{\beta}_{j's_1}(\vec{f})\right] \ell^{\alpha}_{js}(\vec{f}) = \sum_{s_1} \delta_{ss_1}\,\ell^{\beta}_{j's_1}(\vec{f}) = \ell^{\beta}_{j's}(\vec{f})$$

$$\Rightarrow \sum_{s_1} \ell^{*\alpha}_{js_1}(\vec{f})\,\ell^{\beta}_{j's_1}(\vec{f}) = \delta^{\alpha\beta}\delta_{jj'} \qquad (17)$$

To summarize, we are solving $\omega^2(\vec{f})\,\ell^{\alpha}_{j}(\vec{f}) = \sum_{j'} C^{\alpha\beta}_{jj'}(\vec{f})\cdot \ell^{\beta}_{j'}(\vec{f})$

$\omega_s^2(\vec{f})\,\vec{\ell}_s(\vec{f}) = \hat{C}(\vec{f})\cdot\vec{\ell}_s(\vec{f})$ ← a Sturm-Liouville problem

$\hat{C}(\vec{f})$ - Hermit-conjugate operator

$\omega_s^2 \in \mathbb{R}$ - real eigenvalues

$\hat{\vec{\ell}}_s(\vec{f})$ - orthonormal basis

So far, we always considered $\vec{f}$ to be fixed.
Now let us investigate the solutions as a function of $\vec{f}$.
First, let us consider $\vec{f} \to 0$.

Eq. (3): $$\omega_s^2(\vec{f}\to 0)\cdot M_j \cdot V_j^\alpha = \sum_{j_1}\sum_{\vec{n}} A_{jj_1}^{\alpha\beta}(\vec{n})\cdot \underbrace{e^{-i\vec{f}\vec{n}}}_{\substack{=1\\ \text{for } \vec{f}\to 0}}\cdot V_{j_1}^\beta \quad , \quad \Big| \sum_j$$

$$\omega_s^2(\vec{f}\to 0)\cdot \sum_j M_j \cdot V_j^\alpha = \sum_{j_1} V_{j_1}^\beta \cdot \underbrace{\sum_{j\,\vec{n}} A_{jj_1}^{\alpha\beta}(\vec{n})}_{=0,\ \text{see below}} = 0.$$

Total force acting on a crystal is zero:

$$F^\alpha = \sum_{j\vec{n}} M_j\, \ddot{u}_{j\vec{n}}^\alpha \underset{(1)}{=} -\sum_{j_1\vec{n}_1}\Big(\sum_{j\vec{n}} A_{j\,j_1}^{\alpha\beta}(\vec{n}-\vec{n}_1)\, u_{j_1\vec{n}_1}^\beta = 0 \;\Rightarrow\; \sum_{j\vec{n}} A_{j\,j_1}^{\alpha\beta}(\vec{n}) = 0 \quad (18)$$

for any u

$$\omega_s^2(\vec{f}\to 0)\cdot \sum_j M_j V_j^\alpha = 0 \quad (19)$$

Condition (19) is possible, if a) $\sum_j M_j V_j^\alpha = 0$ and $\omega_s(\vec{f}\to 0)\neq 0$ ← optic branch
↑ center of mass of a unit cell is constant.

b) $\sum_j M_j V_j^\alpha \neq 0$ and $\omega_s(\vec{f}\to 0) = 0$ ← acoustic branch.

Eq. (3): $\underbrace{\omega_s^2(f\to 0)}_{\to 0}\cdot M_j \cdot V_j^\alpha = \sum_{\vec{n} j_1} A_{jj_1}^{\alpha\beta}(\vec{n})\cdot V_{j_1}^\beta = 0$

together with (18) $\sum_{\vec{n} j} A_{jj_1}^{\alpha\beta}(\vec{n}) = 0$

$\Big\} \Rightarrow V_{j_1}^\beta = \text{const}.$

i.e. for an acoustic branch, all atoms in a unit cell are displaced by the same value ($V_{j_1}^\beta = V^\beta$)

There are $d=3$ independent displacements, i.e. $d=3$ acoustic branches. The remaining $d\cdot g - d = 3g-3$ are optic branches.

It can be shown that the conservation laws for interaction between a crystal and electromagnetic waves can be fulfilled only for optic branches.

For acoustic branches:

Eq. (10) $\omega_s^2(\vec{f}) = \omega_s^2(-\vec{f})$ - even function.

Taylor expansion at $f \approx 0$:

$$\omega_s^2(\vec{f} \sim 0) \simeq 0 + \gamma_s^{\alpha\beta} f^\alpha f^\beta + \dots \simeq (\gamma_s^{\alpha\beta} \cdot n_f^\alpha n_f^\beta) f^2 = C_s^2(\vec{n}_f) \cdot f^2$$

$s = 1, \dots, d$

$$\gamma_s^{\alpha\beta} = \frac{1}{2}\left(\frac{\partial^2 \omega_s^2(\vec{f})}{\partial f^\alpha \partial f^\beta}\right)$$

unit vectors in the direction $\vec{f}$, $\vec{n} \uparrow\uparrow \vec{f}$

$$\omega_s(\vec{f} \sim 0) \simeq C_s(\vec{n}_f) \cdot |\vec{f}|.$$

$C_s(\vec{n}_f)$ - speed of sound. $(s = 1, \dots, d)$

It is different for different directions and for different acoustic branches.

For optic branches:

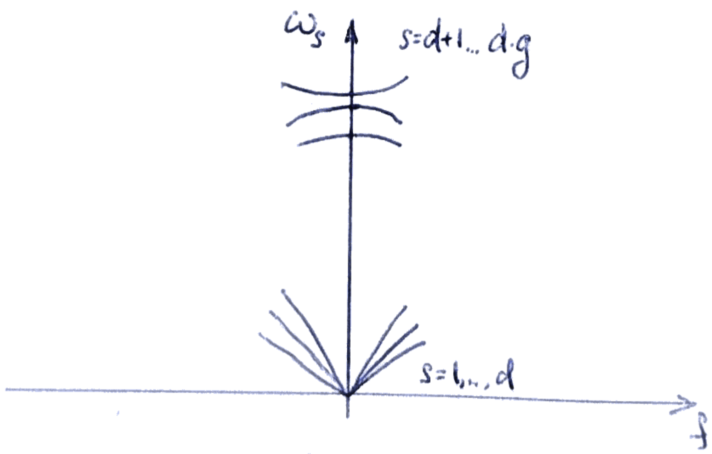
Eq (10): $\omega_s^2(\vec{f}) = \omega_s^2(-\vec{f})$ - even function.

Taylor expansion at $f \approx 0$

$$\omega_s^2(\vec{f} \sim 0) \approx \omega_{s0}^2 + \gamma_s^{\alpha\beta} \cdot f^\alpha \cdot f^\beta + \dots$$

$s = d+1, \dots, dg$

$$\omega_s(\vec{f} \sim 0) \approx \sqrt{\omega_{s0}^2 + \gamma_s^{\alpha\beta} \cdot n_f^\alpha n_f^\beta \cdot f^2} \approx \omega_{s0} + \frac{1}{2} \frac{\gamma_s^{\alpha\beta} n_f^\alpha n_f^\beta}{\omega_{s0}^2} \cdot f^2 = \omega_{s0} + \dots f^2$$



Now let us check, whether it is possible to find a vector $\vec{G}$ such, that $\hat{C}(\vec{f}+\vec{G}) = \hat{C}(\vec{f})$

Eq. (5): $$C_{jj'}^{\alpha\beta} = \frac{1}{\sqrt{M_j M_{j'}}} \cdot \sum_{\vec{n}} A_{jj'}^{\alpha\beta}(\vec{n})\, e^{-i\vec{f}\vec{n}}$$

$$\hat{C}(\vec{f}+\vec{G}) = \hat{C}(\vec{f}) \iff e^{-i(\vec{f}+\vec{G})\vec{n}} = e^{-i\vec{f}\vec{n}} \iff e^{-i\vec{G}\vec{n}} = 1 \iff \vec{G}\cdot\vec{n} = 2\pi\cdot p$$

If $\vec{n} = \sum_i n_i \vec{a}_i$, $\vec{G}\vec{n} = 2\pi p = \sum_i n_i(\vec{G}\vec{a}_i) \iff \vec{G}\cdot\vec{a}_i = 2\pi p_i$

Let us look for $\vec{G}$ in a form $\vec{G} = m_1\vec{b}_1 + m_2\cdot\vec{b}_2 + m_3\cdot\vec{b}_3 = \sum_j m_j \vec{b}_j$

where $\vec{b}_j\cdot\vec{a}_i = 2\pi\cdot\delta_{ji}$, i.e.

$$\vec{b}_1 = \frac{2\pi}{\Omega_0}[\vec{a}_2\times\vec{a}_3]$$
$$\vec{b}_2 = \frac{2\pi}{\Omega_0}[\vec{a}_3\times\vec{a}_1] \qquad (20)$$
$$\vec{b}_3 = \frac{2\pi}{\Omega_0}[\vec{a}_1\times\vec{a}_2]$$

where $\Omega_0 = \vec{a}_1[\vec{a}_2\times\vec{a}_3] = \vec{a}_2\cdot[\vec{a}_3\times\vec{a}_1] = \vec{a}_3\cdot[\vec{a}_1\times\vec{a}_2]$ - the volume of the unit cell in real space.

$$\left.\begin{array}{l}\hat{C}(\vec{f}+\vec{G}) = \hat{C}(\vec{f})\\ \vec{G} = \sum_j m_j \vec{b}_j\end{array}\right\} \Rightarrow -\frac{G_{min}^{\alpha}}{2} < f_\alpha \le \frac{G_{min}^{\alpha}}{2}$$

, where $G_{min}^{\alpha} = b_\alpha = (\vec{e}_\alpha, \vec{b}_\alpha)$ - projection of b_α onto the axis $\vec{e}_\alpha \parallel \vec{a}_\alpha$

For example, $b_1 = (\vec{e}_1\vec{b}_1) = \frac{2\pi}{\Omega_0}\vec{e}_1\vec{a}_1[\vec{a}_2\vec{a}_3]\cdot\frac{a_1}{a_1} = \frac{2\pi}{a_1}$

$$-\frac{\pi}{a_\alpha} < f_\alpha \le \frac{\pi}{a_\alpha} \qquad (21)$$

← size of the reciprocal unit cell along the direction

Periodic boundary condition: everything in the cell „1_α" is equivalent to the cell „$N_\alpha+1$"

$$u_{j\vec{n}_{1\alpha}}^{\alpha} = \frac{e_j^{\alpha}}{\sqrt{M_j}}\cdot e^{i\vec{f}\vec{n}_{1\alpha}-i\omega t}$$
$$|||$$
$$u_{j\vec{n}_{N_\alpha+1}}^{\alpha} = \frac{e_j^{\alpha}}{\sqrt{M_j}}\, e^{i\vec{f}\vec{n}_{N_\alpha+1}-i\omega t}$$

$$\Rightarrow e^{i\vec{f}\vec{n}_{1\alpha}} = e^{i\vec{f}\vec{n}_{N_\alpha+1}} = e^{i\vec{f}\vec{n}_{1\alpha}}\cdot e^{i\vec{f}\vec{n}_{N_\alpha}} \Rightarrow e^{i\vec{f}\vec{n}_{N_\alpha}} = 1$$

$$\Rightarrow f_\alpha a_\alpha N_\alpha = 2\pi p_\alpha \Rightarrow f_\alpha = \frac{2\pi}{a_\alpha}\cdot\frac{p_\alpha}{N_\alpha} \qquad (22)$$

where $-\frac{N_\alpha}{2} < p_\alpha \le \frac{N_\alpha}{2}$ (follows from (21))

In total, there are $\{\vec{f}\} = \{f_1\}\cdot\{f_2\}\cdot\{f_3\} = N_1\cdot N_2\cdot N_3 = N$ possible vectors $\vec{f}$ within the reciprocal unit cell. $\{s\}$ and $\{\vec{f}\}$ define $\omega_s^2(\vec{f})$ and $\vec{e}_{sj}(\vec{f})$ — $d\cdot g\cdot N$ possible sets in total.

The branch number s and the wavevector $\vec{f}$ define $\omega_s^2(\vec{f})$ and $\vec{l}_{sj}(\vec{f})$.
In total, there are dgN possible unique solutions.
$\{\vec{l}_{sj}(\vec{f})\}$ is a complete orthonormal basis. So any arbitrary real displacement $u^\alpha_{j\vec{n}}(t)$ can be represented as

$$u^\alpha_{j\vec{n}}(t) = \frac{1}{\sqrt{N}} \cdot \sum_{s,\vec{f}} \Big[Q_s(\vec{f}) \cdot \frac{l^\alpha_{js}(\vec{f})}{\sqrt{M_j}} \cdot e^{i\vec{f}\vec{n} - i\omega_s(\vec{f})t} + \underbrace{Q^*_s(\vec{f}) \cdot \frac{l^{*\alpha}_{js}(\vec{f})}{\sqrt{M_j}} e^{-i\vec{f}\vec{n} + i\omega_s(\vec{f})t}}_{\text{to guarantee that } u \text{ is real.}} \Big]$$

let us change $\vec{f} \to -\vec{f}$,

$$l^{*\alpha}_{js}(-\vec{f}) \underset{(11)}{=} l_{js}(\vec{f})$$

$$\omega_s(-\vec{f}) \underset{(10)}{=} \omega_s(\vec{f})$$

$$u^\alpha_{j\vec{n}}(t) = \frac{1}{\sqrt{N}} \cdot \sum_{s,\vec{f}} \Big[Q_s(\vec{f}) \cdot \frac{l^\alpha_{js}(\vec{f})}{\sqrt{M_j}} \cdot e^{i\vec{f}\vec{n} - i\omega_s(\vec{f})t} + Q^*_s(-\vec{f}) \frac{l^\alpha_{js}(\vec{f})}{\sqrt{M_j}} e^{i\vec{f}\vec{n} + i\omega_s(\vec{f})t} \Big]$$

Let us introduce a combined variable $\xi = \vec{f}, s$ $\quad (-\xi = -\vec{f}, s)$

$$u^\alpha_{j\vec{n}}(t) = \frac{1}{\sqrt{N M_j}} \cdot \sum_{\xi} l^\alpha_{js}(\vec{f}) \cdot e^{i\vec{f}\vec{n}} \cdot \Big[\underbrace{Q_s(\vec{f}) \cdot e^{-i\omega_s(\vec{f})t}}_{q_\xi} + \underbrace{Q^*_s(-\vec{f}) e^{i\omega_s(\vec{f})t}}_{q^*_{-\xi}} \Big]$$

$$= \frac{1}{\sqrt{N M_j}} \sum_{\xi} l^\alpha_{js}(\vec{f}) e^{i\vec{f}\vec{n}} (q_\xi + q^*_{-\xi}) \qquad (23)$$

Let us calculate the kinetic energy of atoms in a crystal

$$T = \sum_{j\vec n} \frac{M_j}{2} \left(\dot u^\alpha_{j\vec n}\, \dot u^\alpha_{j\vec n}\right) \underset{(23)}{=} \frac{1}{2} \sum_j \sum_{\vec n} M_j \frac{1}{(\sqrt{M_j N})^2} \sum_\xi l^\alpha_{j\xi}\, e^{i\vec f \vec n} (\dot q_\xi + \dot q^*_{-\xi}) \cdot$$

$$\cdot \sum_{\xi_1} l^\alpha_{j\xi_1}\, e^{i\vec f_1 \vec n} (\dot q_{\xi_1} + \dot q^*_{-\xi_1}) =$$

using lattice sum: $\sum_{\vec n} e^{i(\vec f + \vec f_1)\vec n} = N \cdot \delta_{\vec f_1, -\vec f}$ (24)

$$T = \frac{1}{2} \sum_j \sum_{\vec f} \cdot \sum_s l^\alpha_{js}(\vec f)\left(\dot q_s(\vec f) + \dot q^*_s(-\vec f)\right) \cdot \sum_{s_1} l^\alpha_{js_1}(-\vec f)\left(\dot q_{s_1}(-\vec f) + \dot q^*_{s_1}(\vec f)\right)$$

using orthogonality: $\sum_j l^\alpha_{js}(\vec f) \cdot l^\alpha_{js_1}(-\vec f) \underset{(11)}{=} \sum_j l^\alpha_{js}(\vec f) \cdot l^{*\alpha}_{js_1}(\vec f) \underset{(16)}{=} \delta_{ss_1}$

$$T = \frac{1}{2} \sum_{\vec f, s} \left[\dot q_s(\vec f) \cdot \dot q^*_s(-\vec f)\right]\left[\dot q_s(-\vec f) + \dot q^*_s(\vec f)\right] = \frac{1}{2} \sum_\xi (\dot q_\xi + \dot q^*_{-\xi})(\dot q_{-\xi} + \dot q^*_\xi) \qquad (24)$$

From the sum over atoms, we arrived to the sum over states.

Analogously, we can calculate the potential energy:

$$\Delta U = \frac{1}{2} \sum_{\substack{j\, j_1 \\ \vec n\, \vec n_1}} A^{\alpha\beta}_{jj_1}(\vec n - \vec n_1)\, u^\alpha_{j\vec n}\, u^\beta_{j_1\vec n_1} = -\frac{1}{2} \sum_{j\vec n} M_j \ddot u^\alpha_{j\vec n} u^\alpha_{j\vec n} = \dots = -\frac{1}{2} \sum_\xi (\ddot q_\xi + \ddot q^*_{-\xi})(q_{-\xi} + q^*_\xi) \qquad (25)$$

Equation of motion: $M_j \ddot u^\alpha_{j\vec n} = -\sum_{j_1\vec n_1} A^{\alpha\beta}_{jj_1}(\vec n - \vec n_1)\, u^\beta_{j_1\vec n_1}$

From eq. (23):

$$q_\xi = Q_s(\vec f) e^{-i\omega_s(\vec f)t} \Rightarrow \dot q_\xi = -i\omega_s(\vec f) \cdot q_\xi, \quad \ddot q_\xi = -\omega_s^2 q_\xi$$

$$q^*_\xi = Q^*_s(\vec f) e^{+i\omega_s(\vec f)t} \Rightarrow \dot q^*_\xi = i\omega_s(\vec f) \cdot q^*_\xi, \quad \ddot q^*_\xi = -\omega_s^2 q^*_\xi$$

Total energy:

$$E = T + \Delta U = \frac{1}{2}\sum_{\xi}(\dot{q}_\xi + \dot{q}^*_{-\xi})(\dot{q}_{-\xi} + \dot{q}^*_\xi) - (\ddot{q}_\xi + \ddot{q}^*_{-\xi})(q_{-\xi} + q^*_\xi)$$

$$= \frac{1}{2}\sum_{\xi}(-i\omega_\xi \cdot q_\xi + i\omega_\xi \cdot q^*_{-\xi})(-i\omega_\xi q_{-\xi} + i\omega_\xi q^*_\xi) - (-\omega_\xi^2 q_\xi - \omega_\xi^2 q^*_{-\xi})(q_{-\xi} + q^*_\xi)$$

$$= \frac{1}{2}\sum_{\xi}\omega_\xi^2 (q_\xi - q^*_{-\xi})(-q_{-\xi} + q^*_\xi) + \omega_\xi^2 (q_\xi + q^*_{-\xi})(q_{-\xi} + q^*_\xi)$$

$$= \sum_{\xi}\omega_\xi^2 (\underbrace{q^*_{-\xi} q_{-\xi}}_{\vec{\xi} \to -\vec{\xi}} + q_\xi q^*_\xi) = \sum_{\xi}\omega_\xi^2 (q^*_\xi q_\xi + q_\xi q^*_\xi) \ldots$$

This looks like a sum over $d \cdot g \cdot N$ harmonic oscillators. Indeed, introducing:

$$\begin{cases} q_\xi = \frac{1}{2}\left(x_\xi - \frac{p_\xi}{i\omega_\xi}\right) \\ q^*_\xi = \frac{1}{2}\left(x_\xi + \frac{p_\xi}{i\omega_\xi}\right) \end{cases} \quad (26) \quad \text{or} \quad \begin{cases} x_\xi = q_\xi + q^*_\xi \leftarrow \text{real} \\ p_\xi = (q^*_\xi - q_\xi) i\omega_\xi \leftarrow \text{real} \end{cases} \quad (27)$$

$$E = \sum_{\xi}\omega_\xi^2 \left[\frac{1}{4}\left(x_\xi^2 + \frac{p_\xi^2}{\omega_\xi^2}\right) + \frac{1}{4}\left(x_\xi^2 + \frac{p_\xi^2}{\omega_\xi^2}\right)\right] = \sum_{\xi}\underbrace{\left(\frac{\omega_\xi^2 \cdot x_\xi^2}{2} + \frac{p_\xi^2}{2 \cdot 1}\right)}_{\text{energy of an oscillator with a mass } m_\xi = 1} = \sum_{\xi} \mathcal{E}_\xi$$

For each oscillator:

$$\mathcal{E}_\xi = \frac{p_\xi^2}{2} + \frac{\omega_\xi^2 x_\xi^2}{2} \quad (28)$$

Moreover, from (23) and (27)

$$x_\xi = Q_s(\vec{f})e^{-i\omega_s(\vec{f})t} + Q_s^*(\vec{f})e^{+i\omega_s(\vec{f})t} \quad \overset{\text{real}}{=} A_\xi \cdot \cos(\omega_\xi t + \varphi_\xi)$$

$$\ddot{x}_\xi = -\omega_\xi^2 \cdot A_\xi \cdot \cos(\omega_\xi t + \varphi_\xi) = -\omega_\xi^2 \cdot x_\xi$$

$$p_\xi = -\omega_\xi \cdot A_\xi \cdot \sin(\omega_\xi t + \varphi_\xi) = \dot{x}_\xi$$

$$\dot{p}_\xi = -\omega_\xi^2 \cdot A_\xi \cdot \cos(\omega_\xi t + \varphi_\xi) = -\omega_\xi^2 \cdot x_\xi$$

n other words, p_ξ and x_ξ satisfy the Hamilton equations,

$$\dot{p}_\xi = -\frac{\partial \mathcal{E}_\xi}{\partial x_\xi} = -\omega_\xi^2 x_\xi$$

$$\dot{x}_\xi = -\frac{\partial \mathcal{E}_\xi}{\partial p_\xi} = p_\xi$$

$\Rightarrow$ p_ξ, x_ξ are canonically conjugate variables, and they can be directly quantised.