Phonons and Electron-Phonon Couplings

Qijing Zheng

Department of Physics

University of Science and Technology of China
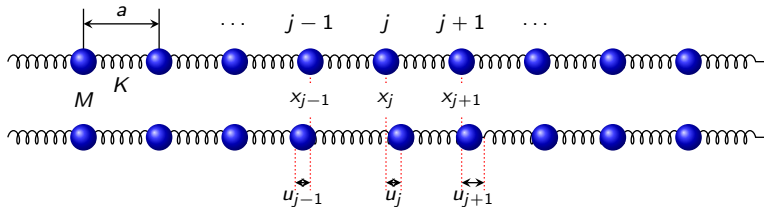
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A 1D chain of N equally spaced atoms at $R_j(t) = x_j + u_j(t)$
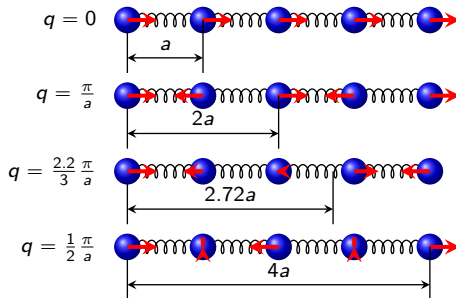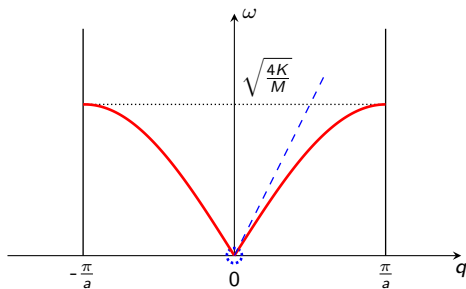

The Newton's Equation

$$M\frac{\mathrm{d}^2 u_j}{\mathrm{d}t^2} = K(u_{j+1} + u_{j-1} - 2u_j) \qquad j = 1, \ldots, N$$

Assume the solution has the form $u_j(t) = \frac{A_q}{\sqrt{M}}e^{i(qx_j - \omega t)}$, then [1]

$$\omega^2 = \frac{K}{M}(2 - e^{iqa} - e^{-iqa})$$

$$= \frac{2K}{M}(1 - \cos qa)$$

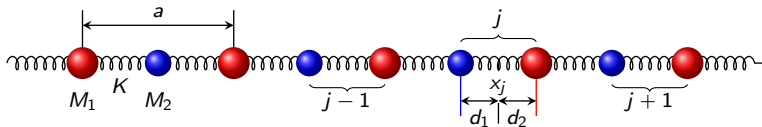$$\Rightarrow \quad \omega = \sqrt{\frac{4K}{M}}\left|\sin\frac{qa}{2}\right|$$

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[1] $u_j(t)$ here is complex. In practice, take the real part, i.e. $\mathrm{Re}[u_j(t)]$.

A 1D chain with 2 atoms in each unit: $R_s^j(t) = x_j + d_s + u_s^j(t); \quad s = 1, 2$

The Newton's Equation

$$M_1 \frac{\mathrm{d}^2 u_1^j}{\mathrm{d}t^2} = K(u_2^j + u_2^{j-1} - 2u_1^j)$$
$$M_2 \frac{\mathrm{d}^2 u_2^j}{\mathrm{d}t^2} = K(u_1^j + u_1^{j+1} - 2u_2^j)$$

$$\implies \quad \begin{cases} u_j^1(t) = \dfrac{A_q}{\sqrt{M_1}} e^{i(q x_j - \omega t)} \\[2mm] u_j^2(t) = \dfrac{B_q}{\sqrt{M_2}} e^{i(q x_j - \omega t)} \end{cases}$$

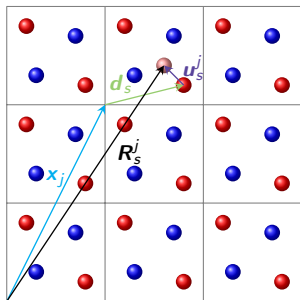We then have

$$\begin{pmatrix} \dfrac{2K}{M_1} & \dfrac{-K}{\sqrt{M_1 M_2}}(1 + e^{-iqa}) \\[4mm] \dfrac{-K}{\sqrt{M_1 M_2}}(1 + e^{iqa}) & \dfrac{2K}{M_2} \end{pmatrix} \begin{pmatrix} A_q \\[2mm] B_q \end{pmatrix} = \omega^2 \begin{pmatrix} A_q \\[2mm] B_q \end{pmatrix}$$

$$\implies \quad \omega_\pm^2 = \frac{K}{M_1 M_2} \left((M_1 + M_2) \pm \sqrt{M_1^2 + M_2^2 + 2M_1 M_2 \cos qa} \right)$$
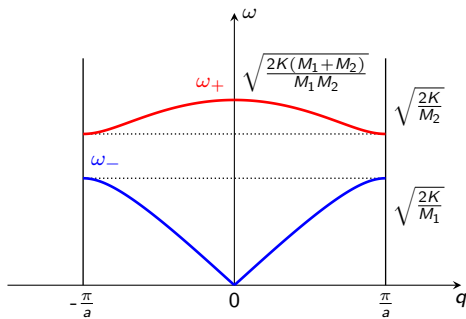
- x_j: the position of unit cell j
- d_s: the equilibrum position of the atom s in the cell
- u_s^j: displacement from the equilibrum positon for the atom s in the cell j
- R_s^j: the position of the atom s in the cell j

$$\boldsymbol{R}_s^j(t) = \boldsymbol{x}_j + \boldsymbol{d}_s + \boldsymbol{u}_s^j(t)$$
$$= \boldsymbol{r}_s^j + \boldsymbol{u}_s^j(t)$$
$$R_{s\alpha}^j(t) = r_{s\alpha}^j + u_{s\alpha}^j(t) \quad (\alpha = x, y, z)$$

The total energy can be written as

$$E_{\text{tot}}\left(\{\boldsymbol{R}_s^j(t)\}\right) = E_{\text{tot}}^0\left(\{\boldsymbol{r}_s^j\}\right) + \sum_{js\alpha} \frac{\partial E_{\text{tot}}^0}{\partial u_{s\alpha}^j} u_{s\alpha}^j + \frac{1}{2} \sum_{\substack{js\alpha \\ kt\beta}} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} u_{s\alpha}^j u_{t\beta}^k + \dots$$

- The expression is exact if we take all the orders in the expansion.
- All the derivatives are taken at the equilibrium positions $\{\boldsymbol{r}_s^j\}$, i.e. $\frac{\partial E_{\text{tot}}^0}{\partial u_{s\alpha}^j} = 0$.
- Harmonic approximation: truncated at *second* order.

Within the harmonic approximation, the Newton's equation for the atom s in cell j

$$M_s \frac{\mathrm{d}^2 u_{s\alpha}^j(t)}{\mathrm{d}t^2} = -\frac{\partial E_{\text{tot}}}{\partial u_{s\alpha}^j} = -\sum_{kt\beta} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} u_{t\beta}^k = -\sum_{kt\beta} C_{s\alpha, t\beta}^{j,k} u_{t\beta}^k \tag{1}$$

The ansatz of the solution

$$u_{s\alpha}^j(t) = \frac{\eta_\alpha^s(\boldsymbol{q})}{\sqrt{M_s}} e^{i\boldsymbol{q}\boldsymbol{x}_j} e^{-i\omega t} \tag{2}$$

Substitute Eq. 2 into Eq. 1

$$\omega^2(\boldsymbol{q})\, \eta_\alpha^s = \sum_{t\beta} \left[\sum_k \frac{1}{\sqrt{M_s M_t}} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} e^{i\boldsymbol{q}(\boldsymbol{x}_k - \boldsymbol{x}_j)} \right] \eta_\beta^t = \sum_{t\beta} D_{s\alpha, t\beta}(\boldsymbol{q})\, \eta_\beta^t$$

In matrix form

$$\underbrace{\begin{pmatrix} \ddots & & \\ & D_{s\alpha, t\beta}(\boldsymbol{q}) & \\ & & \ddots \end{pmatrix}}_{3N_a \times 3N_a} \begin{pmatrix} \vdots \\ \eta_\beta^t(\boldsymbol{q}) \\ \vdots \end{pmatrix} = \omega^2(\boldsymbol{q}) \underbrace{\begin{pmatrix} \vdots \\ \eta_\beta^t(\boldsymbol{q}) \\ \vdots \end{pmatrix}}_{3N_a}$$

where N_a is the number of atoms in a cell.

The Interatomic Force Constants (IFC)

$$\frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} = C_{s\alpha,t\beta}^{j,k}$$

- Symmetric because partial differentiation is commutative

$$\frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} = \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{t\beta}^k \partial u_{s\alpha}^j} \quad \Rightarrow \quad C_{s\alpha,t\beta}^{j,k} = C_{t\beta,s\alpha}^{k,j} \tag{3}$$

- Translation invariance, depend on the difference between j and k

$$\frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} = \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^0 \partial u_{t\beta}^{(k-j)}} \quad \Rightarrow \quad C_{s\alpha,t\beta}^{j,k} = C_{s\alpha,t\beta}^{0,k-j} \tag{4}$$

- Acoustic Sum Rule (ASR): if we displace the whole solid by an arbitrary uniform displacement, the forces acting on the atoms must be zero.

$$F_{s\alpha}^j = -\sum_\beta \left[\sum_{kt} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} \right] \delta_\beta = 0 \quad \Rightarrow \quad \sum_{kt} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} = 0 \tag{5}$$

The Dynamical Matrix

$$D_{s\alpha,t\beta}(\boldsymbol{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_l \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^0 \partial u_{t\beta}^l} e^{i\boldsymbol{q}\boldsymbol{x}_l} = \frac{1}{\sqrt{M_s M_t}} \sum_l C_{s\alpha,t\beta}^{0,l} e^{i\boldsymbol{q}\boldsymbol{x}_l}$$

- If we define the distortion pattern $\boldsymbol{u}_s^l(\boldsymbol{q}) = \boldsymbol{v}_s(\boldsymbol{q}) e^{i\boldsymbol{q}\boldsymbol{x}_l}$

$$D_{s\alpha,t\beta}(\boldsymbol{q}) = \frac{1}{N} \frac{1}{\sqrt{M_s M_t}} \frac{\partial^2 E_{\text{tot}}^0}{\partial v_{s\alpha}^*(\boldsymbol{q}) \partial v_{t\beta}(\boldsymbol{q})}$$

- Dynamical matrix is Hermitian

$$D_{s\alpha,t\beta}(\boldsymbol{q}) = D_{t\beta,s\alpha}^*(\boldsymbol{q})$$

PROOF

$$D_{s\alpha,t\beta}(\boldsymbol{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_l C_{s\alpha,t\beta}^{0,l} e^{i\boldsymbol{q}\boldsymbol{x}_l}$$

$$= \frac{1}{\sqrt{M_s M_t}} \sum_l C_{s\alpha,t\beta}^{-l,0} e^{i\boldsymbol{q}\boldsymbol{x}_l}$$

$$= \frac{1}{\sqrt{M_s M_t}} \sum_l C_{t\beta,s\alpha}^{0,-l} e^{i\boldsymbol{q}\boldsymbol{x}_l}$$

$$D_{s\alpha,t\beta}^*(\boldsymbol{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_l C_{t\beta,s\alpha}^{0,-l} e^{-i\boldsymbol{q}\boldsymbol{x}_l}$$

$$= \frac{1}{\sqrt{M_s M_t}} \sum_l C_{t\beta,s\alpha}^{0,l} e^{i\boldsymbol{q}\boldsymbol{x}_l}$$

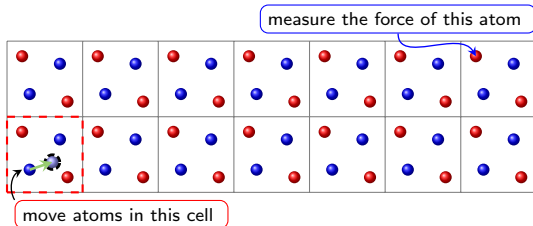$$= D_{t\beta,s\alpha}(\boldsymbol{q})$$

The definition of the dynamical matrix

$$D_{s\alpha,t\beta}(\boldsymbol{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_{l=-\infty}^{\infty} C_{s\alpha,t\beta}^{0,l} \, e^{i\boldsymbol{q}\boldsymbol{x}_l} \approx \frac{1}{\sqrt{M_s M_t}} \sum_{|l|<l_{\text{cut}}} C_{s\alpha,t\beta}^{0,l} \, e^{i\boldsymbol{q}\boldsymbol{x}_l} \qquad (6)$$

❶ Finite-difference and supercell approach —— Frozen phonon method

IFC by finite-difference:

$$\frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^0 \, \partial u_{t\beta}^l} = \frac{\partial F_{t\beta}^l}{\partial u_{s\alpha}^0}$$

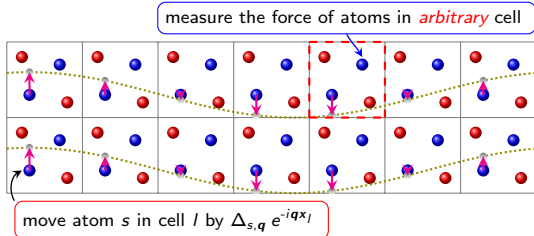$$\approx \frac{F_{t\beta}^l(\Delta_{s\alpha}) - F_{t\beta}^l(-\Delta_{s\alpha})}{2\Delta_{s\alpha}}$$

measure the force of this atom

move atoms in this cell

- Supercell must be large enough so that IFC is negligible at the cell boundary.
- Movements done *only* in one primitive cell.
- $3 \times N_a \times 2$ movements, i.e. move by $\pm\Delta$ in $x/y/z$ directions for each atom in the primitive cell.
- Symmetry can be adopted to reduce the number of movements.
- The dynamical matrix can then be obtained at arbitrary $\boldsymbol{q}$ by Eq. 6.
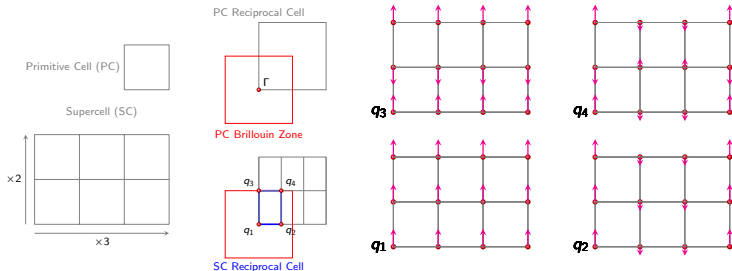
measure the force of atoms in *arbitrary* cell

Dynamical matrix:

$$D_{s\alpha,t\beta}(\boldsymbol{q}) \approx \frac{1}{\sqrt{M_s M_t}}$$

$$\times \frac{F_{t\beta}^l(\Delta_{s,\boldsymbol{q}}) - F_{t\beta}^l(-\Delta_{s,\boldsymbol{q}})}{2\Delta_{s,\boldsymbol{q}}}$$

move atom s in cell l by $\Delta_{s,\boldsymbol{q}} \, e^{-i\boldsymbol{q}x_l}$

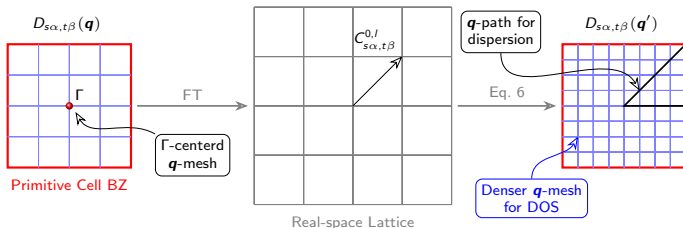- Can only obtain dynamical matrix at certain $\boldsymbol{q}$.

- $D_{s\alpha,t\beta}(\boldsymbol{q}) \xrightarrow{\text{FT}} C_{s\alpha,t\beta}^{0,l} \xrightarrow{\text{Eq. 6}} D_{s\alpha,t\beta}(\boldsymbol{k})$

② Lineare response theory — density functional perturbation theory

- Can calculate $D_{s\alpha,t\beta}(\boldsymbol{q})$ at *arbitrary* $\boldsymbol{q}$ with a *primitive cell*.
- $D_{s\alpha,t\beta}(\boldsymbol{q})$ is periodic in reciprocal space: $D_{s\alpha,t\beta}(\boldsymbol{q} + \boldsymbol{G}) = D_{s\alpha,t\beta}(\boldsymbol{q})$

- In practice, first calculate the dynamical matrix with a small $\boldsymbol{q}$-mesh, then perform the FT to get the IFC in real space. Finally, dynamical matrix at arbitrary $\boldsymbol{q}$ can be obtained.
- Fails in metal with Kohn anomalies or in polar semiconductors where the dynamical matrix is non-analytic for $\boldsymbol{q} \to 0$.

③ Codes: `Phonopy, PHON, YPHON, PhonTS, ShengBTE, ALM, ALAMODE, Quantum Espresso, Abinit...`

The Nonanalytic part of the Dynamical Matrix

$$D_{s\alpha,t\beta}^{\mathsf{na}}(\boldsymbol{q}) = \frac{1}{\sqrt{M_s M_t}} \frac{4\pi e^2}{\Omega} \frac{\left(\sum_{\gamma} q_{\gamma} Z_s^{*\gamma\alpha}\right)\left(\sum_{\mu} q_{\mu} Z_t^{*\mu\beta}\right)}{\sum_{\gamma\mu} q_{\gamma} \epsilon_{\infty}^{\gamma\mu} q_{\mu}}$$

Thank you!