Phonons and Electron-Phonon Couplings

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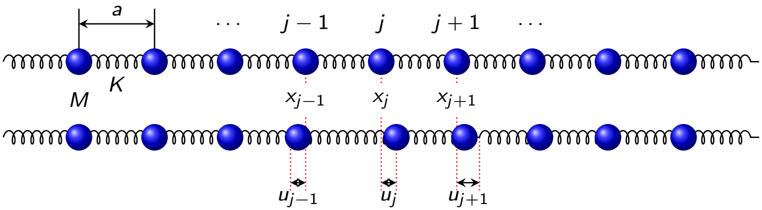
Outline

1. Lattice Dynamics
   - 1D Atomic Chain
   - 3D Lattice
   - How to calculate the dynamical matrix

A 1D chain of N equally spaced atoms at $R_j(t) = x_j + u_j(t)$



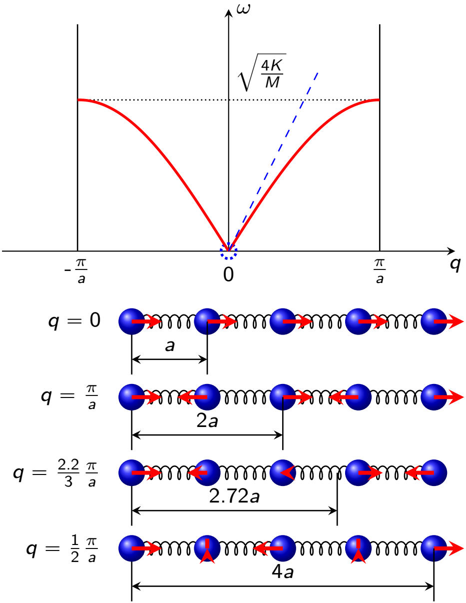
The Newton's Equation

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

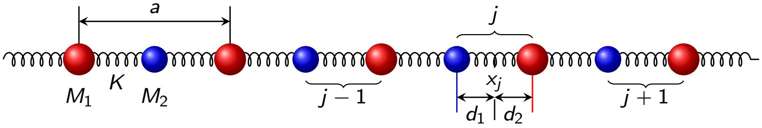
Assume the solution has the form $u_j(t) = \frac{A_q}{\sqrt{M}} e^{i(q x_j - \omega t)}$, then [1]

$$\begin{aligned}\omega^2 &= \frac{K}{M}(2 - e^{iqa} - e^{-iqa}) \\ &= \frac{2K}{M}(1 - \cos qa) \\ \Rightarrow \quad \omega &= \sqrt{\frac{4K}{M}}\left|\sin\frac{qa}{2}\right|\end{aligned}$$

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


ω
$\sqrt{\frac{4K}{M}}$
$-\frac{\pi}{a}$
0
$\frac{\pi}{a}$
q
$q = 0$
a
$q = \frac{\pi}{a}$
$2a$
$q = \frac{2.2}{3}\frac{\pi}{a}$
$2.72a$
$q = \frac{1}{2}\frac{\pi}{a}$
$4a$

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



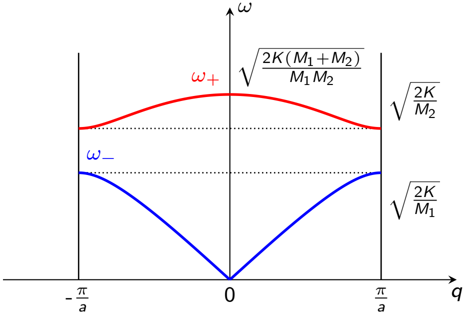
The Newton's Equation

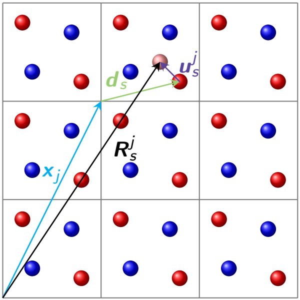
$$\begin{aligned} M_1 \frac{\mathrm{d}^2 u_1^j}{\mathrm{d}t^2} &= K(u_2^j + u_2^{j-1} - 2u_1^j) \\ M_2 \frac{\mathrm{d}^2 u_2^j}{\mathrm{d}t^2} &= K(u_1^j + u_1^{j+1} - 2u_2^j) \end{aligned} \quad \Longrightarrow \quad \begin{cases} u_j^1(t) = \dfrac{A_q}{\sqrt{M_1}} e^{i(qx_j - \omega t)} \\ u_j^2(t) = \dfrac{B_q}{\sqrt{M_2}} e^{i(qx_j - \omega t)} \end{cases}$$

We then have

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

$$\Longrightarrow \quad \omega_\pm^2 = \frac{K}{M_1 M_2} \left((M_1 + M_2) \pm \sqrt{M_1^2 + M_2^2 + 2M_1 M_2 \cos qa} \right)$$


ω
ω_+
$\sqrt{\frac{2K(M_1+M_2)}{M_1M_2}}$
$\sqrt{\frac{2K}{M_2}}$
ω_-
$\sqrt{\frac{2K}{M_1}}$
$-\frac{\pi}{a}$
0
$\frac{\pi}{a}$
q



- $\boldsymbol{x}_j$: the position of unit cell j
- $\boldsymbol{d}_s$: the equilibrum position of the atom s in the cell
- $\boldsymbol{u}_s^j$: displacement from the equilibrum positon for the atom s in the cell j
- $\boldsymbol{R}_s^j$: the position of the atom s in the cell j

$$\begin{aligned}\boldsymbol{R}_s^j(t) &= \boldsymbol{x}_j + \boldsymbol{d}_s + \boldsymbol{u}_s^j(t) \\ &= \boldsymbol{r}_s^j + \boldsymbol{u}_s^j(t)\end{aligned}$$

$$R_{s\alpha}^j(t) = r_{s\alpha}^j + u_{s\alpha}^j(t) \quad (\alpha = x, y, z)$$

The total energy can be written as

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

- 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

$$M_s \frac{\mathrm{d}^2 u^j_{s\alpha}(t)}{\mathrm{d}t^2} = -\frac{\partial E_{\mathrm{tot}}}{\partial u^j_{s\alpha}} = -\sum_{kt\beta} \frac{\partial^2 E^0_{\mathrm{tot}}}{\partial u^j_{s\alpha} \partial u^k_{t\beta}} u^k_{t\beta} = -\sum_{kt\beta} C^{j,k}_{s\alpha,t\beta}\, u^k_{t\beta} \tag{1}$$

The ansatz of the solution

$$u^j_{s\alpha}(t) = \frac{\eta^\sigma_{s\alpha}(\boldsymbol{q})}{\sqrt{M_s}}\, e^{i\boldsymbol{q}\boldsymbol{x}_j}\, e^{-i\omega_\sigma t} \tag{2}$$

Substitute Eq. 2 into Eq. 1

$$\omega^2_\sigma(\boldsymbol{q})\, \eta^\sigma_{s\alpha} = \sum_{t\beta} \left[\sum_k \frac{1}{\sqrt{M_s M_t}} \frac{\partial^2 E^0_{\mathrm{tot}}}{\partial u^j_{s\alpha} \partial u^k_{t\beta}}\, e^{i\boldsymbol{q}(\boldsymbol{x}_k - \boldsymbol{x}_j)} \right] \eta^\sigma_{t\beta} = \sum_{t\beta} D_{s\alpha,t\beta}(\boldsymbol{q})\, \eta^\sigma_{t\beta}$$

In matrix form

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

where $\sigma = 1, \ldots, 3N_a$ and N_a is the number of atoms in the *primitive cell*.

The Interatomic Force Constants (IFC)

$$\frac{\partial^2 E^0_{\text{tot}}}{\partial u^j_{s\alpha} \partial u^k_{t\beta}} = C^{j,k}_{s\alpha,t\beta}$$

- Symmetric because partial differentiation is commutative

$$\frac{\partial^2 E^0_{\text{tot}}}{\partial u^j_{s\alpha} \partial u^k_{t\beta}} = \frac{\partial^2 E^0_{\text{tot}}}{\partial u^k_{t\beta} \partial u^j_{s\alpha}} \quad \Rightarrow \quad C^{j,k}_{s\alpha,t\beta} = C^{k,j}_{t\beta,s\alpha} \tag{3}$$

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

$$\frac{\partial^2 E^0_{\text{tot}}}{\partial u^j_{s\alpha} \partial u^k_{t\beta}} = \frac{\partial^2 E^0_{\text{tot}}}{\partial u^0_{s\alpha} \partial u^{(k-j)}_{t\beta}} \quad \Rightarrow \quad C^{j,k}_{s\alpha,t\beta} = C^{0,k-j}_{s\alpha,t\beta} \tag{4}$$

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

$$F^j_{s\alpha} = -\sum_\beta \left[\sum_{kt} \frac{\partial^2 E^0_{\text{tot}}}{\partial u^j_{s\alpha} \partial u^k_{t\beta}} \right] \delta_\beta = 0 \qquad \Rightarrow \qquad \sum_{kt} \frac{\partial^2 E^0_{\text{tot}}}{\partial u^j_{s\alpha} \partial u^k_{t\beta}} = 0 \tag{5}$$

The Dynamical Matrix

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

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

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

- Dynamical matrix is Hermitian

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

Proof

$$\begin{aligned} D_{s\alpha,t\beta}(\boldsymbol{q}) &= \frac{1}{\sqrt{M_s M_t}} \sum_l C^{0,l}_{s\alpha,t\beta}\, e^{i\boldsymbol{q}\boldsymbol{x}_l} \\ &= \frac{1}{\sqrt{M_s M_t}} \sum_l C^{-l,0}_{s\alpha,t\beta}\, e^{i\boldsymbol{q}\boldsymbol{x}_l} \\ &= \frac{1}{\sqrt{M_s M_t}} \sum_l C^{0,-l}_{t\beta,s\alpha}\, e^{i\boldsymbol{q}\boldsymbol{x}_l} \end{aligned}$$

$$\begin{aligned} D^*_{s\alpha,t\beta}(\boldsymbol{q}) &= \frac{1}{\sqrt{M_s M_t}} \sum_l C^{0,-l}_{t\beta,s\alpha}\, e^{-i\boldsymbol{q}\boldsymbol{x}_l} \\ &= \frac{1}{\sqrt{M_s M_t}} \sum_l C^{0,l}_{t\beta,s\alpha}\, e^{i\boldsymbol{q}\boldsymbol{x}_l} \\ &= D_{t\beta,s\alpha}(\boldsymbol{q}) \end{aligned}$$

The eigenvectors $\boldsymbol{\eta}^{\sigma}(\boldsymbol{q})$ of the Hermitian matrix $D_{s\alpha,t\beta}(\boldsymbol{q})$ are called the phonon polarization vector.

- The polarization vector is *cell-periodic*.

$$u^{j}_{s\alpha}(t) = \frac{\eta^{\sigma}_{s\alpha}(\boldsymbol{q})}{\sqrt{M_s}}\, e^{i\boldsymbol{q}\boldsymbol{x}_j}\, e^{-i\omega_\sigma t}$$

  So the solution is a cell-periodic part multiply by $e^{i\boldsymbol{q}\boldsymbol{x}}$ — Bloch's theorem.

- Orthogonalization relation:

$$\sum_{s\alpha} \eta^{\sigma'}_{s\alpha}(\boldsymbol{q})\, \eta^{\sigma}_{s\alpha}(\boldsymbol{q}) = \delta_{\sigma\sigma'}; \qquad \sum_{\sigma} \eta^{\sigma}_{s\alpha}(\boldsymbol{q})\, \eta^{\sigma}_{t\beta}(\boldsymbol{q}) = \delta_{st}\,\delta_{\alpha\beta}$$

- Relation to phonon displacemoment — direction and amplitude of the vibration.

$$\xi^{\sigma}_{s\alpha} = \frac{1}{\sqrt{M_s}}\, \eta^{\sigma}_{s\alpha}(\boldsymbol{q})$$

- At some high-symmetry $\boldsymbol{q}$-path

$$\begin{cases} \boldsymbol{q} \parallel \eta(\boldsymbol{q}) & \text{Longitudinal Wave} \\ \boldsymbol{q} \perp \eta(\boldsymbol{q}) & \text{Transverse Wave} \end{cases}$$

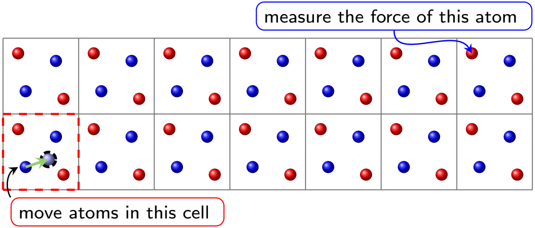
The definition of the dynamical matrix

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

1. Finite-difference and supercell approach — Frozen phonon method

IFC by finite-difference:

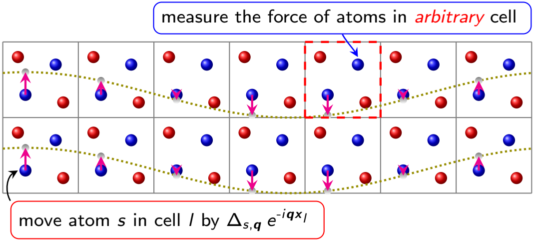
$$\frac{\partial^2 E^0_{\text{tot}}}{\partial u^0_{s\alpha}\,\partial u^l_{t\beta}} = \frac{\partial F^l_{t\beta}}{\partial u^0_{s\alpha}} \approx \frac{F^l_{t\beta}(\Delta_{s\alpha}) - F^l_{t\beta}(\text{-}\Delta_{s\alpha})}{2\Delta_{s\alpha}}$$



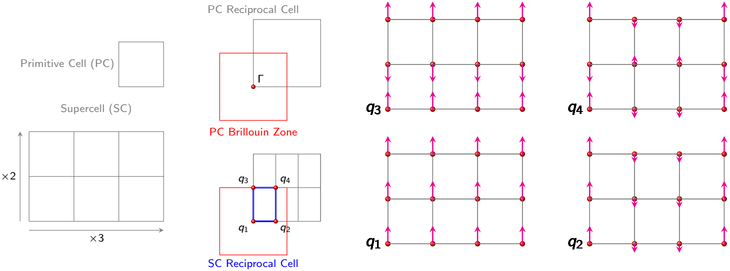
- Supercell must be large enough so that IFC is negligible at the cell boundary.
- Movements done *only* in one primitive cell.
- $3 \times N_a \times 2$ movements, i.e. move by $\pm\Delta$ in $x/y/z$ directions for each atom in the primitive cell.
- Symmetry can be adopted to reduce the number of movements.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

Dynamical matrix:

$$D_{s\alpha,t\beta}(\boldsymbol{q}) \approx \frac{1}{\sqrt{M_s M_t}} \times \frac{F^l_{t\beta}(\Delta_{s,\boldsymbol{q}}) - F^l_{t\beta}(-\Delta_{s,\boldsymbol{q}})}{2\Delta_{s,\boldsymbol{q}}}$$



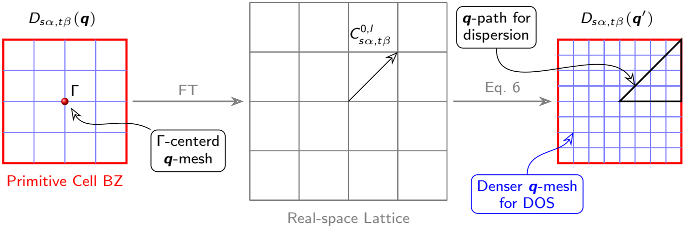
- Can only obtain dynamical matrix at certain $\boldsymbol{q}$.



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

How to Calculate the Dynamical Matrix III

2. Lineare response approach — density functional perturbation theory
   - Can calculate $D_{s\alpha,t\beta}(\boldsymbol{q})$ at *arbitrary* $\boldsymbol{q}$ using 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

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

Thank you!