

# Phonons and Electron-Phonon Couplings

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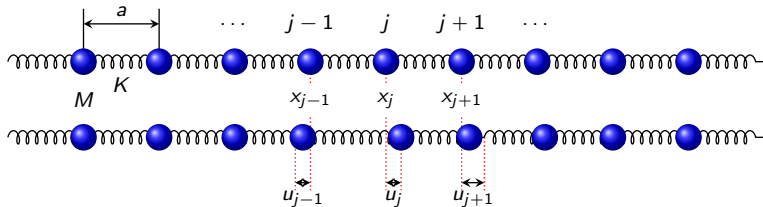


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- 1 Lattice Dynamics
  - 1D Atomic Chain
  - 3D Lattice

# 1D Chain of Atoms — 1 Atom per Unit

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



The Newton's Equation

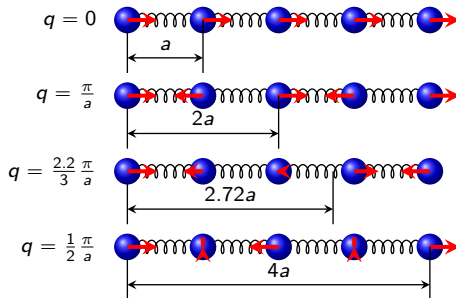
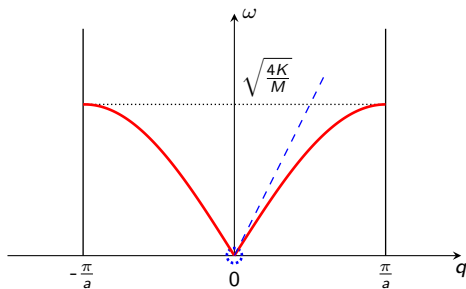
$$M \frac{d^2 u_j}{dt^2} = K(u_{j+1} + u_{j-1} - 2u_j) \quad j = 1, \dots, N$$

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

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

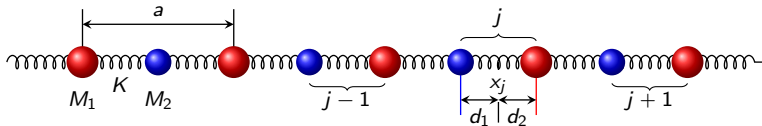
<sup>1</sup> $u_j(t)$  here is complex. In practice, take the real part, i.e.  $\text{Re}[u_j(t)]$ .

# 1D Chain of Atoms



# 1D Chain of Atoms — 2 Atoms per Unit

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



The Newton's Equation

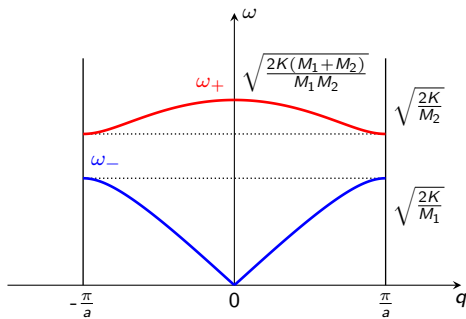
$$\begin{aligned} M_1 \frac{d^2 u_1^j}{dt^2} &= K(u_2^j + u_2^{j-1} - 2u_1^j) \\ M_2 \frac{d^2 u_2^j}{dt^2} &= K(u_1^j + u_1^{j+1} - 2u_2^j) \end{aligned} \quad \Rightarrow \quad \begin{cases} u_1^j(t) = \frac{A_q}{\sqrt{M_1}} e^{i(qx_j - \omega t)} \\ u_2^j(t) = \frac{B_q}{\sqrt{M_2}} e^{i(qx_j - \omega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

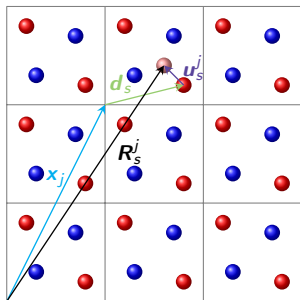
We then have

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

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

# 1D Chain of Atoms





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

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

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

The total energy can be written as

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

- The expression is exact if we take all the orders in the expansion.
- All the derivatives are taken at the equilibrium positions  $\{\mathbf{r}_s^j\}$ , 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  $j$

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

The ansatz of the solution

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

Substitute Eq. 2 into Eq. 1

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

In matrix form

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

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

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

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

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

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

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

## The Dynamical Matrix

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

- $D_{s\alpha,t\beta}(\mathbf{q})$  can be seen as the second derivative of  $E_{\text{tot}}^0$  with respect to the amplitude of a lattice distortion of definite wave vector  $\mathbf{q}$
- Dynamical matrix is Hermitian

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

## PROOF

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

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

# How to Calculate the Dynamical Matrix I

The definition of the dynamical matrix

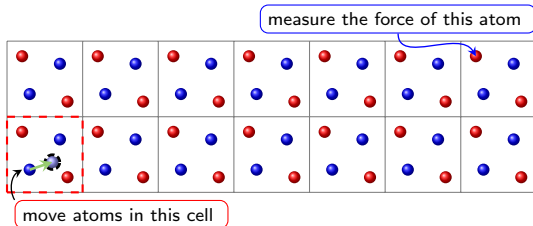
$$D_{s\alpha,t\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_{l=-\infty}^{\infty} C_{s\alpha,t\beta}^{0,l} e^{i\mathbf{q}\cdot\mathbf{x}_l} \approx \frac{1}{\sqrt{M_s M_t}} \sum_{|l| < l_{\text{cut}}} C_{s\alpha,t\beta}^{0,l} e^{i\mathbf{q}\cdot\mathbf{x}_l} \quad (6)$$

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

IFC by finite-difference:

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

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

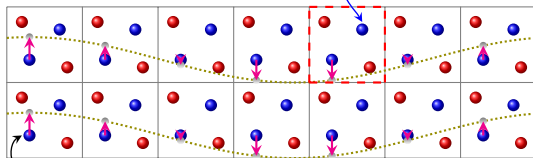


- Supercell must be large enough so that IFC is negligible at the cell boundary.
- Movements done **only** in one primitive cell.
- $3 \times N_a \times 2$  movements, i.e. move by  $\pm \Delta$  in x/y/z directions for each atom in the primitive cell.
- Symmetry can be adopted to reduce the number of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

# How to Calculate the Dynamical Matrix II

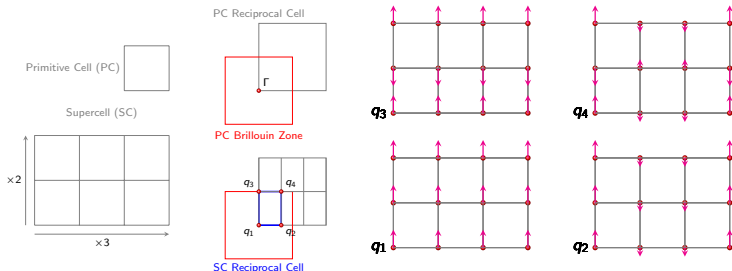
Dynamical matrix:

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



move atom  $s$  in cell  $l$  by  $\Delta_{s,\mathbf{q}} e^{-i\mathbf{q}\cdot\mathbf{x}_l}$

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



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

Thank you!