## Appendix E (Optional)

### Monatomic Crystals in 3D: General Formalism

1 atom/basis (To illustrate the formalism)

Direct lattice: $\{\vec{R}\}$

Each atom belongs to a primitive cell labelled by a lattice vector $\vec{R}$.

$\vec{u}(\vec{R}) = (u_x(\vec{R}), u_y(\vec{R}), u_z(\vec{R}))$ = displacement of atom whose equilibrium position is at $\vec{R}$

- Generally speaking, the potential energy $V$ of the system is

$$V = V(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) \quad \text{function of positions of all } N \text{ atoms}$$

$$\equiv V(\{\vec{r}_i\})$$

$$= V(\{\vec{R}_i + \vec{u}(\vec{R}_i)\})$$

$$= V(\{\vec{R}_i\}) + \text{first order term} + \frac{1}{2}\sum_{\substack{\alpha,\beta \\ \vec{R}_i,\vec{R}_j \\ x,y,z \\ x,y,z}} \frac{\partial^2 V}{\partial u_\alpha(\vec{R}_i)\partial u_\beta(\vec{R}_j)} u_\alpha(\vec{R}_i) u_\beta(\vec{R}_j) + \text{higher order terms}$$

$V(\{\vec{R}_i\})$: minimum of $V$ (a number); first order term: 0; $\Phi_{\alpha\beta}(\vec{R}_i|\vec{R}_j)$: spring constant; harmonic term; anharmonic terms (neglected)

$$\cong V(\{\vec{R}_i\}) + \frac{1}{2}\sum_{\alpha,\beta}\sum_{\vec{R}_i,\vec{R}_j} \Phi_{\alpha\beta}(\vec{R}_i|\vec{R}_j)\, u_\alpha(\vec{R}_i)\, u_\beta(\vec{R}_j)$$



- Thus, not restricting to nearest neighboring interaction only, the $\alpha$-th component of the force on atom at $\vec{R}''$ due to the displacement $\vec{u}(\vec{R}')$ of the atom at $\vec{R}'$ is:

$$-\sum_{\beta=x,y,z} \Phi_{\alpha\beta}(\vec{R}''|\vec{R}')\, u_\beta(\vec{R}')$$

[$\vec{R}''$, $\vec{R}'$ need not be neighboring lattice pts.]

Equation of motion:

$$m\frac{d^2 u_\alpha(\vec{R}'')}{dt^2} = -\sum_{\vec{R}'}\sum_{\beta=x,y,z} \Phi_{\alpha\beta}(\vec{R}''|\vec{R}')\, u_\beta(\vec{R}') \qquad \alpha = x,y,z$$

Big Matrix

- Normal mode solution: $\vec{u}(\vec{R}'') = \vec{A}\, e^{i\vec{q}\cdot\vec{R}''} e^{-i\omega t}$ ($\vec{A}$: amplitude)

$$-m\omega^2 A_\alpha e^{i\vec{q}\cdot\vec{R}''} = -\sum_{\vec{R}'}\sum_{\beta} \Phi_{\alpha\beta}(\vec{R}''|\vec{R}')\, A_\beta e^{i\vec{q}\cdot\vec{R}'}$$

$$\Rightarrow \sum_\beta \underbrace{\left(\frac{1}{m}\sum_{\vec{R}'} \Phi_{\alpha\beta}(\vec{R}''|\vec{R}')\, e^{-i\vec{q}\cdot(\vec{R}''-\vec{R}')}\right)}_{\equiv D_{\alpha\beta}(\vec{q})} A_\beta = \omega^2 A_\alpha$$

$$\Rightarrow \boxed{\sum_\beta D_{\alpha\beta}(\vec{q}) = \omega^2 A_\alpha} \qquad (\alpha,\beta = x,y,z)$$

reduced to many $3\times 3$ matrix problems

Thus, $\begin{pmatrix} D_{xx}(\vec{q}) & D_{xy}(\vec{q}) & D_{xz}(\vec{q}) \\ D_{yx}(\vec{q}) & D_{yy}(\vec{q}) & D_{yz}(\vec{q}) \\ D_{zx}(\vec{q}) & D_{yz}(\vec{q}) & D_{zz}(\vec{q}) \end{pmatrix} \begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix} = \omega^2 \begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix}$

$\begin{cases} \vec{q} \in 1^{st}\ B.Z. \Rightarrow N \text{ values of } \vec{q}\text{'s} \\ \text{Each } \vec{q}, \text{ a } 3\times 3 \text{ eigenvalue problem} \Rightarrow 3 \text{ eigenfrequencies} \end{cases}$

↳ 3 branches and a total of $3N$ normal modes (as expected)

- Original problem (not invoking periodicity): $3N \times 3N$ problem
- Invoking periodicity: $\begin{cases} N \ (3\times 3)\text{-problems} \\ \text{one for each } \vec{q} \end{cases}$

$$D_{\alpha\beta}(\vec{q}) = \frac{1}{m}\sum_{\vec{R}''} \Phi_{\alpha\beta}(\vec{R}''|\vec{R}')\, e^{i\vec{q}\cdot(\vec{R}'-\vec{R}'')}$$

$$= \frac{1}{m}\sum_{\vec{R}} \Phi_{\alpha\beta}(\vec{R}''|\vec{R}''+\vec{R})\, e^{i\vec{q}\cdot\vec{R}}$$

$$= \frac{1}{m}\sum_{\vec{R}} \Phi_{\alpha\beta}(\vec{0}|\vec{R})\, e^{i\vec{q}\cdot\vec{R}}$$

↙ interaction should depend only on separation between atoms (due to periodicity)

$\overleftrightarrow{D}$ = Dynamical matrix

- Fitting experimental data with calculations (which require $\Phi$ and thus $V$) is a way to extract information about $V(\{\vec{r}_{ij}\})$ and thus interatomic forces.