# Phonon dispersion computations

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# Equations of Motion

$$m_k \ddot{q}_{\alpha\binom{A}{k}} = -\sum_{\beta,B,n} K_{\alpha\binom{A}{k}\beta\binom{B}{n}} q_{\beta\binom{B}{n}}$$

- To solve we make a plane-wave plus a periodic (Born – v. Karmen) assumption:

$$q_{\alpha\binom{A}{k}}(t) = \hat{q}_{\alpha k}(\omega, \boldsymbol{f}) e^{i(\boldsymbol{x}_A \cdot \boldsymbol{f} - \omega t)}$$

$$q_{\alpha\binom{N+1}{k}} = q_{\alpha\binom{1}{k}}$$

  - Assuming $N$ lattice cells in each coordinate direction.
  - $\boldsymbol{x}_A = \boldsymbol{F}\boldsymbol{X}_A$, if deformation.

# Implications of Periodicity

- Consider a fixed lattice direction $\boldsymbol{x}_A = A\boldsymbol{a}_1$. The periodic BC implies

$$e^{i(N+1)\boldsymbol{a}_1\cdot\boldsymbol{f}} = e^{i\boldsymbol{a}_1\cdot\boldsymbol{f}}$$

- Define the (dual) reciprocal vectors $\boldsymbol{b}_j$ via $\boldsymbol{b}_j \cdot \boldsymbol{a}_i = \delta_{ij}$; i.e. $\boldsymbol{b}_i = (\boldsymbol{a}_j \times \boldsymbol{a}_k)/[\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3]$, where $i, j, k$ are a cyclic permutation of $\{1, 2, 3\}$. If one expands $\boldsymbol{f}$ as $\boldsymbol{f} = f_1\boldsymbol{b}_1 + f_2\boldsymbol{b}_2 + f_3\boldsymbol{b}_3$, then

$$f_1 = \frac{2\pi n_1}{N} \qquad n_1 \in \mathbb{J}$$

- In general $\boldsymbol{f} \in \left(\frac{2\pi n_1}{N}, \frac{2\pi n_2}{N}, \frac{2\pi n_3}{N}\right)$ where $n_1, n_2, n_3 \in \mathbb{J}$.

# Restricted Wave Vector Range

- The unique (physically) distinct solutions only occur for

$$n_i \in \{0, 1, \cdots, N-1\}$$

  - Or any shifted set of integers of “length” $N$.
- This follows since adding $N$ to a wave vector index, say $2\pi n/N \to 2\pi(n+N)/N$, yields

$$e^{i2\pi(n+N)/N} = e^{i2\pi n} e^{i2\pi} = e^{i2\pi n}$$

# Eigen Equations

- Using our expansion in the equations of motion

$$-m_k\omega^2(\boldsymbol{f})\hat{q}_{\alpha k}(\omega,\boldsymbol{f})e^{i\boldsymbol{x}_A\cdot\boldsymbol{f}} = -\sum_{\beta,B,n} K_{\alpha\binom{A}{k}\beta\binom{B}{n}}\hat{q}_{\beta n}e^{i\boldsymbol{x}_B\cdot\boldsymbol{f}}$$

  - The sum over $B$ ranges over all cells in the crystal but effectively is restricted to just those that interact with the atom at $\binom{A}{k}$.

- Without loss of generality, let us focus on the cell $A = 1$ and assume $\boldsymbol{x}_A = \boldsymbol{0}$. Define the dynamical matrix

$$D_{\alpha k\beta n} = \sum_{B} K_{\alpha\binom{1}{k}\beta\binom{B}{n}}e^{i\boldsymbol{x}_B\cdot\boldsymbol{f}}$$

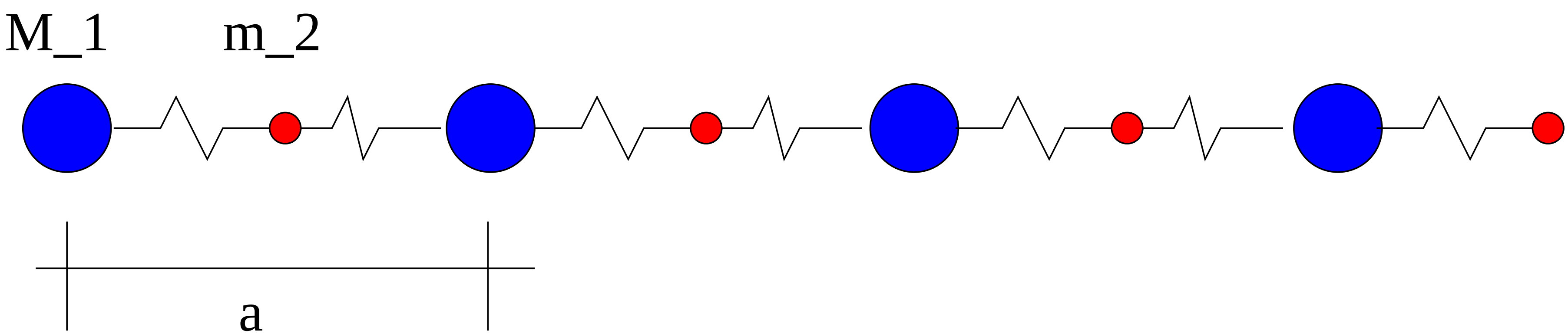
# Phonon Spectra Equation

- We are now left with the eigenproblem

$$\left| D_{(\alpha k)(\beta n)}(\boldsymbol{f}) - m_k \omega^2(\boldsymbol{f}) I_{(\alpha k)(\beta n)} \right| = 0$$

  - This is a $3s \times 3s$ eigenvalue problem that needs to be solved for each acceptable $\boldsymbol{f}$ of which there are $N^3 = N_c$.
  - By symmetry considerations one can greatly reduce the number of needed computations.
  - All the binding energy of the crystal is hidden inside the dynamical matrix which contains the crystal stiffness.
  - The result is valid for full finite deformation states as long as the stiffness is computed with respect to the deformed (Cauchy-Born) lattice positions (with basis relaxation).

# 1D example with 2 atom basis




- 2 atom basis $s = 2$
- 1 dof per atom
- $N$ lattice cells

# Equations in 1D

- In 1D we can drop the $\alpha, \beta$ subscripts to give:

$$m_k \ddot{q}_{\binom{A}{k}} = -\sum_{B,n} K_{\binom{A}{k}\binom{B}{n}} q_{\binom{B}{n}}$$

- The corresponding Ansatz is:

$$q_{\binom{A}{k}}(t) = \hat{q}_k(\omega, f) e^{i(x_A f - \omega t)}$$

where $x_A = (A-1)a$ and by the Born – v. Karmen conditions $f = 2\pi n / aN$.

# Dynamical Matrix

- The dynamical matrix in this setting will be

$$D_{kn}(f) = \sum_{B} e^{ix_B f} K_{\binom{1}{k}\binom{B}{n}}$$

- To compute let us assume that $\phi(l_b) = \frac{1}{2}C(l_b - l_o)^2$ and that interactions only occur with respect to neighboring atoms (nearest neighbor approximation).

# Stiffness and Dynamical Matrix

- Potential Energy (skip self interaction terms)

$$V = \frac{1}{2} \sum_{A,B,k,n} \phi(|r_{\binom{A}{k}} - r_{\binom{B}{n}}|)$$

# Stiffness and Dynamical Matrix

- Forces

$$\frac{\partial V}{\partial r_{\binom{C}{m}}} = \frac{1}{2}\sum_{A,B,k,n} \phi'(|r_{\binom{A}{k}} - r_{\binom{B}{n}}|)\frac{r_{\binom{A}{k}} - r_{\binom{B}{n}}}{|r_{\binom{A}{k}} - r_{\binom{B}{n}}|}$$

$$[\delta_{AC}\delta_{km} - \delta_{BC}\delta_{mn}]$$

$$= \sum_{B,n} \phi'(|r_{\binom{C}{m}} - r_{\binom{B}{n}}|)\frac{r_{\binom{C}{m}} - r_{\binom{B}{n}}}{|r_{\binom{C}{m}} - r_{\binom{B}{n}}|}$$

# Stiffness and Dynamical Matrix

- The stiffness

$$\frac{\partial^2 V}{\partial r_{\binom{C}{m}} \partial r_{\binom{D}{p}}} = \sum_{B,n} \phi''(|r_{\binom{C}{m}} - r_{\binom{B}{n}}|) \frac{r_{\binom{C}{m}} - r_{\binom{B}{n}}}{|r_{\binom{C}{m}} - r_{\binom{B}{n}}|}$$

$$\frac{r_{\binom{C}{m}} - r_{\binom{B}{n}}}{|r_{\binom{C}{m}} - r_{\binom{B}{n}}|} [\delta_{CD}\delta_{mp} - \delta_{BD}\delta_{np}]$$

$$+ \quad \phi'(|r_{\binom{C}{m}} - r_{\binom{B}{n}}|) \frac{\partial}{\partial r_{\binom{D}{p}}} \frac{r_{\binom{C}{m}} - r_{\binom{B}{n}}}{|r_{\binom{C}{m}} - r_{\binom{B}{n}}|}$$

$$= \sum_{B,n} \phi''(|r_{\binom{C}{m}} - r_{\binom{B}{n}}|) [\delta_{CD}\delta_{mp} - \delta_{BD}\delta_{np}]$$

# Stiffness and Dynamical Matrix

- The Dynamical matrix

$$
\begin{aligned}
D_{mp} &= \sum_{D} e^{ix_D f} \left\{ \sum_{B,n} \phi''(|x_{\binom{1}{m}} - x_{\binom{B}{n}}|)[\delta_{1D}\delta_{mp} - \delta_{BD}\delta_{np}] \right\} \\
&= \sum_{B,n} \phi''(|x_{\binom{1}{m}} - x_{\binom{B}{n}}|)\delta_{mp} e^{i\cdot 0} \\
&- \sum_{D} e^{ix_D f} \phi''(|x_{\binom{1}{m}} - x_{\binom{D}{p}}|)
\end{aligned}
$$

# Stiffness and Dynamical Matrix

- The Dynamical matrix

$$D_{mp} = \begin{bmatrix} 2C & 0 \\ 0 & 2C \end{bmatrix} - \begin{bmatrix} 0 & C \\ 0 & 0 \end{bmatrix} e^{-iaf} - \begin{bmatrix} 0 & C \\ C & 0 \end{bmatrix} e^{i \cdot 0} - \begin{bmatrix} 0 & 0 \\ C & 0 \end{bmatrix} e^{iaf}$$

# Stiffness and Dynamical Matrix

- The Dynamical matrix

$$D_{mp} = C \begin{bmatrix} 2 & -(1 + e^{-iaf}) \\ -(1 + e^{iaf}) & 2 \end{bmatrix}$$

# Final eigencompuation

- Eigenvalue problem

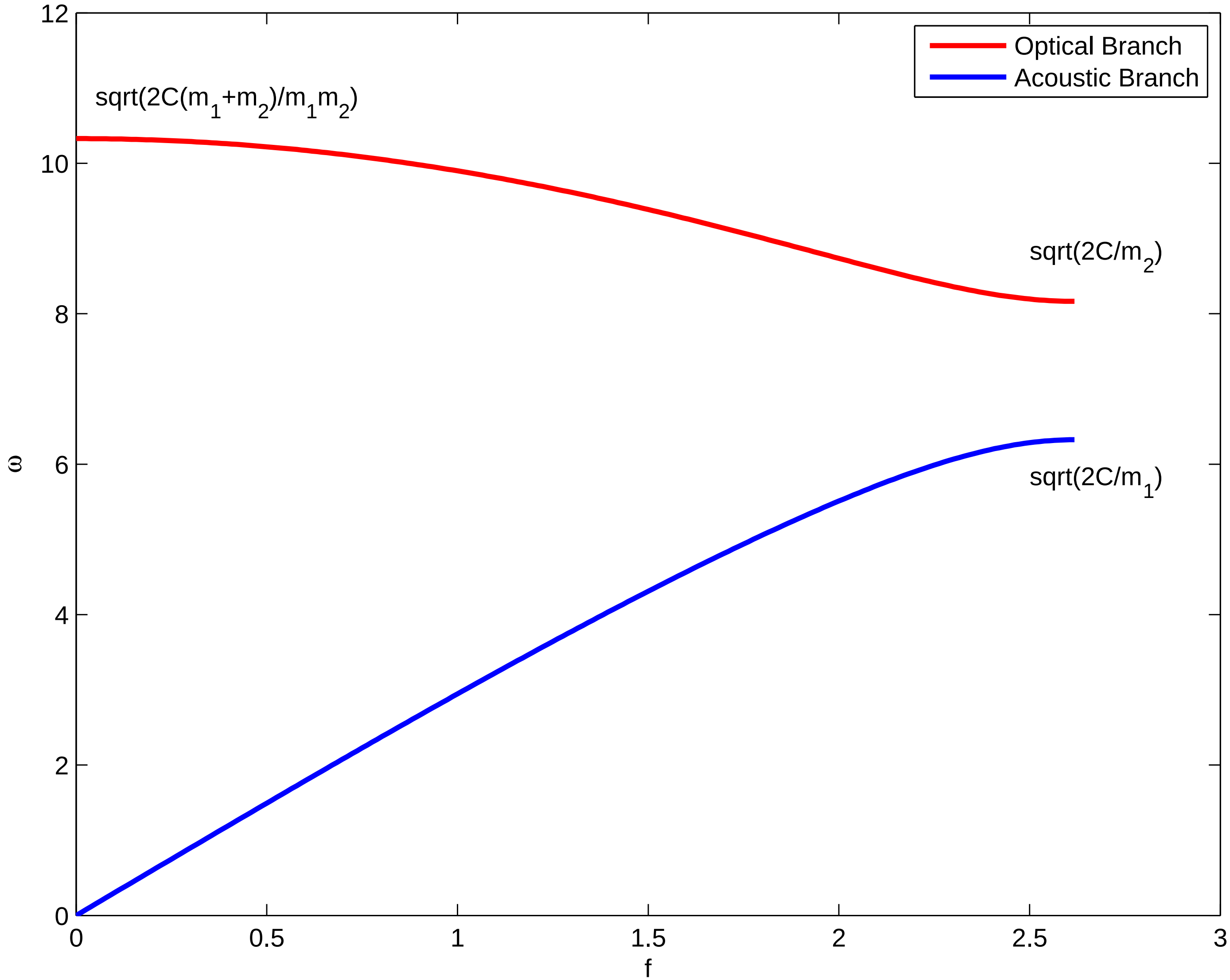
$$\left| C \begin{bmatrix} 2 & -(1+e^{-iaf}) \\ -(1+e^{iaf}) & 2 \end{bmatrix} - \omega^2(f) \begin{bmatrix} m_1 & 0 \\ 0 & m_2 \end{bmatrix} \right| = 0$$

- Solutions

$$\omega^2(f) = \frac{C(m_1+m_2)}{m_1 m_2} \left[ 1 \pm \sqrt{1 - \frac{2m_1 m_2(1-\cos(fa))}{(m_1+m_2)^2}} \right]$$

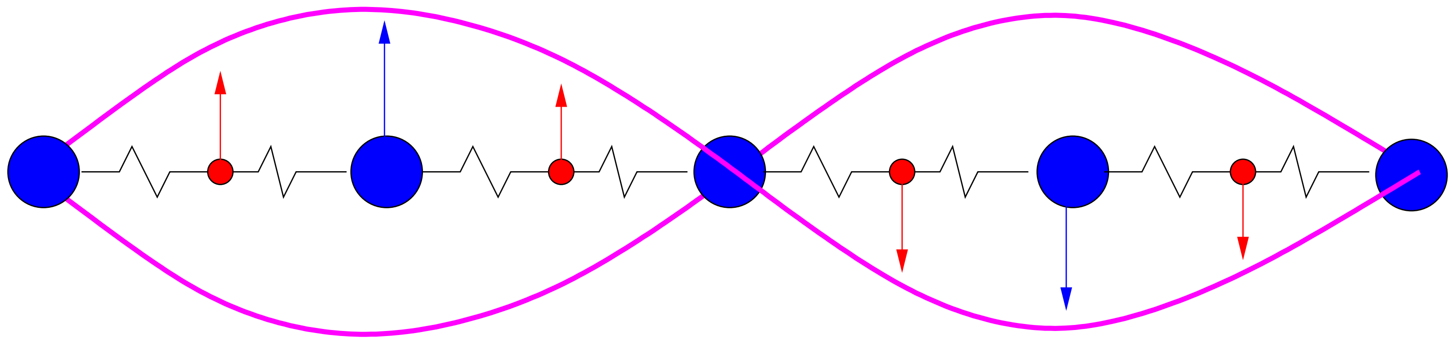
# Dispersion Curves

$a = 1.2$, $m_1 = 50$, $m_2 = 30$, $C = 1000$

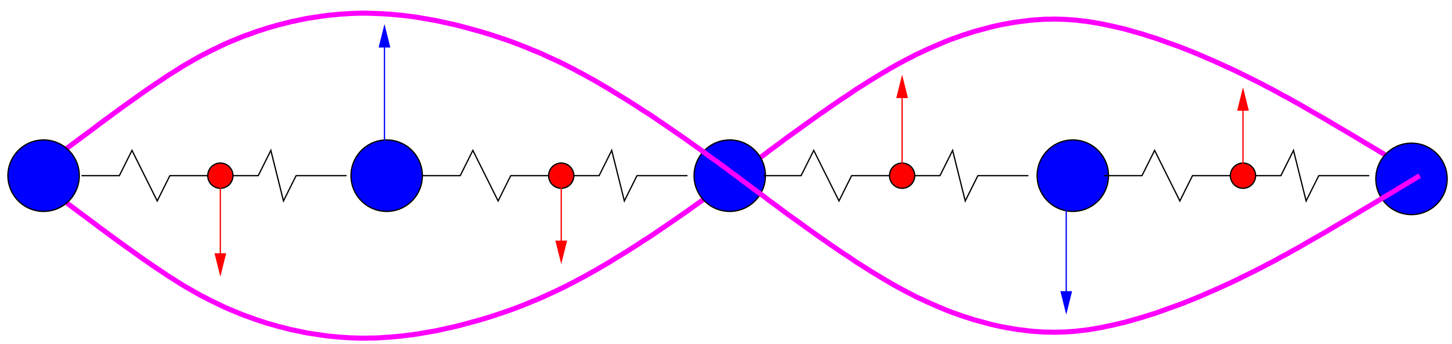


# Branches

- Acoustic branch eigenvector $f = \frac{\pi}{2a} \longrightarrow \lambda = \frac{2\pi}{f} = 4a$



- Optical branch eigenvector $f = \frac{\pi}{2a} \longrightarrow \lambda = \frac{2\pi}{f} = 4a$



# Remarks

- Per space dimension, $d$, one has 1 acoustic branch ([P,SV,SH] in 3D).
- $(s-1)\cdot d$ optical branches.
- $s \cdot d$ branches in total
- Continuous curves are shown but they are really discrete.
- Slopes correspond to the group velocities $d\omega/df$ which govern the velocity of energy transport.

# Multi-D Case

- The potential depends on $V(\boldsymbol{F}\boldsymbol{X}_A + \boldsymbol{b}_k + \boldsymbol{q}_{\binom{A}{k}})$ where the $\boldsymbol{b}_k$ need to be found by minimizing the crystal energy for the given deformation state.
- Assuming such, as well as pair potentials, and noting

$$\boldsymbol{r}_{\binom{A}{k}} = \underbrace{\overbrace{\boldsymbol{F}\boldsymbol{X}_A}^{\boldsymbol{x}_A} + \boldsymbol{b}_k}_{\boldsymbol{x}_{\binom{A}{k}}} + \boldsymbol{q}_{\binom{A}{k}},$$ gives

$$V = \frac{1}{2}\sum_{A,B,k,n} \phi(\|\boldsymbol{r}_{\binom{A}{k}} - \boldsymbol{r}_{\binom{B}{n}}\|)$$

# Forces

$$\frac{\partial V}{\partial \boldsymbol{r}_{\binom{C}{m}}} = \frac{1}{2}\sum_{A,B,k,n} \phi'\left(\left\|\boldsymbol{r}_{\binom{A}{k}} - \boldsymbol{r}_{\binom{B}{n}}\right\|\right)\frac{\boldsymbol{r}_{\binom{A}{k}} - \boldsymbol{r}_{\binom{B}{n}}}{\left\|\boldsymbol{r}_{\binom{A}{k}} - \boldsymbol{r}_{\binom{B}{n}}\right\|}$$

$$[\delta_{AC}\delta_{km} - \delta_{BC}\delta_{mn}]$$

$$= \sum_{B,n} \phi'\left(\left\|\boldsymbol{r}_{\binom{C}{m}} - \boldsymbol{r}_{\binom{B}{n}}\right\|\right)\frac{\boldsymbol{r}_{\binom{C}{m}} - \boldsymbol{r}_{\binom{B}{n}}}{\left\|\boldsymbol{r}_{\binom{C}{m}} - \boldsymbol{r}_{\binom{B}{n}}\right\|}$$

# Stiffness

$$
\begin{aligned}
\frac{\partial^2 V}{\partial \boldsymbol{r}_{\binom{C}{m}} \partial \boldsymbol{r}_{\binom{D}{p}}} &= \sum_{B,n} \Bigg\{ \phi''(\|\boldsymbol{r}_{\binom{C}{m}} - \boldsymbol{r}_{\binom{B}{n}}\|) \frac{\boldsymbol{r}_{\binom{C}{m}} - \boldsymbol{r}_{\binom{B}{n}}}{\|\boldsymbol{r}_{\binom{C}{m}} - \boldsymbol{r}_{\binom{B}{n}}\|} \\
& \otimes \frac{\boldsymbol{r}_{\binom{C}{m}} - \boldsymbol{r}_{\binom{B}{n}}}{\|\boldsymbol{r}_{\binom{C}{m}} - \boldsymbol{r}_{\binom{B}{n}}\|} [\delta_{CD}\delta_{mp} - \delta_{BD}\delta_{np}] \\
&+ \phi'(\|\boldsymbol{r}_{\binom{C}{m}} - \boldsymbol{r}_{\binom{B}{n}}\|) \Bigg[ \frac{\mathbf{1}\delta_{DC}\delta_{mp} - \mathbf{1}\delta_{DB}\delta_{pn}}{\|\boldsymbol{r}_{\binom{C}{m}} - \boldsymbol{r}_{\binom{B}{n}}\|} \\
&- \frac{\left(\boldsymbol{r}_{\binom{C}{m}} - \boldsymbol{r}_{\binom{B}{n}}\right) \otimes \left(\boldsymbol{r}_{\binom{C}{m}} - \boldsymbol{r}_{\binom{B}{n}}\right)}{\|\boldsymbol{r}_{\binom{C}{m}} - \boldsymbol{r}_{\binom{B}{n}}\|^3} \\
& [\delta_{DC}\delta_{mp} - \delta_{BD}\delta_{pn}] \Bigg] \Bigg\}
\end{aligned}
$$

# Dynamical Matrix ($3 \times 3$ block)

$$\boldsymbol{D}_{mp}(\boldsymbol{f}) = \sum_{D} e^{i\boldsymbol{x}_D \cdot \boldsymbol{f}} \boldsymbol{K}_{\binom{1}{m}\binom{D}{p}}$$

$$= \delta_{mp} \sum_{B,n} \left\{ \phi''(\|\boldsymbol{\beta}\|) \frac{\boldsymbol{\beta} \otimes \boldsymbol{\beta}}{\|\boldsymbol{\beta}\|^2} + \phi'(\boldsymbol{\beta}) \left[ \frac{\mathbf{1}}{\|\boldsymbol{\beta}\|} - \frac{\boldsymbol{\beta} \otimes \boldsymbol{\beta}}{\|\boldsymbol{\beta}\|^3} \right] \right\}$$

$$+ \sum_{D} \left\{ e^{i\boldsymbol{x}_D \cdot \boldsymbol{f}} \left[ \phi'(\|\boldsymbol{v}\|) \left( \frac{\boldsymbol{v} \otimes \boldsymbol{v}}{\|\boldsymbol{v}\|^3} - \frac{\mathbf{1}}{\|\boldsymbol{v}\|} \right) - \phi''(\|\boldsymbol{v}\|) \frac{\boldsymbol{v} \otimes \boldsymbol{v}}{\|\boldsymbol{v}\|^2} \right] \right\}$$

$\boldsymbol{\beta} = \boldsymbol{x}_{\binom{1}{m}} - \boldsymbol{x}_{\binom{B}{n}}$ and $\boldsymbol{v} = \boldsymbol{x}_{\binom{1}{m}} - \boldsymbol{x}_{\binom{D}{p}}$

# Final Matrices

- Dynamical Matrix

$$\boldsymbol{D} = \begin{bmatrix} \boldsymbol{D}_{11} & \boldsymbol{D}_{12} & \cdots & \boldsymbol{D}_{1s} \\ \boldsymbol{D}_{21} & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ \boldsymbol{D}_{s1} & \cdots & \cdots & \boldsymbol{D}_{ss} \end{bmatrix}$$

- Mass Matrix

$$\boldsymbol{I} = \begin{bmatrix} m_1 \mathbf{1} & & & \\ & m_2 \mathbf{1} & & \\ & & \ddots & \\ & & & m_s \mathbf{1} \end{bmatrix}$$

# Remarks

- Self energy terms are to be skipped, i.e. when $\boldsymbol{v} = \mathbf{0}$ and $\boldsymbol{\beta} = \mathbf{0}$.
- Reasonable units for such computations are Åand eV. This implies force = eV/Å$\approx 1.6 \times 10^{-9}$ N.
- If mass is given in a.m.u. (grams per mole) then computed frequencies are in units of roughly $0.49$ THz.