PHONONS

The wave nature of light is the same as that which makes sound echo.
- Richard P. Feynman

THIS LECTURE

- Harmonic approximation
- Vibrational dynamics, periodicity, phonons
- Simple model example
- *Ab initio* results for bulk phonons
- *Ab initio* results for surface phonons and inelastic HAS

HARMONIC APPROXIMATION

- For small displacements $\left(T \lesssim \frac{1}{3} T_{\mathrm{melt}}\right)$, $E_0(\vec{r}_1, \vec{r}_2, \ldots)$ is in harmonic/linear:

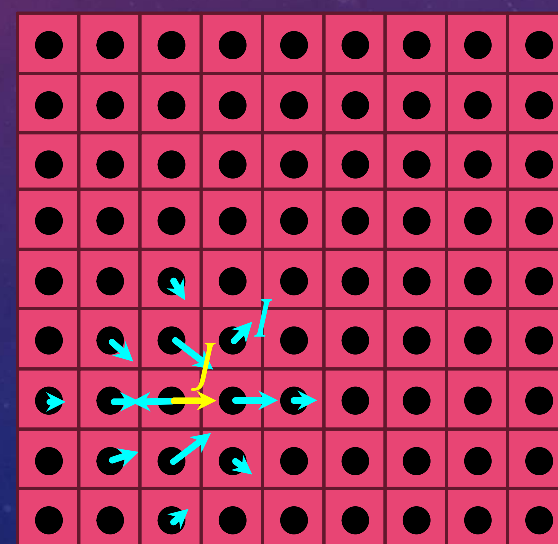
$$E_0(\vec{r}_1, \vec{r}_2, \ldots) = E_0 + \sum_I \cancel{\frac{\partial E_0}{\partial \vec{r}_I}} \cdot \delta\vec{r}_I + \frac{1}{2} \sum_{IJ} \delta\vec{r}_I \cdot \frac{\partial^2 E_0}{\partial \vec{r}_I \partial \vec{r}_J} \cdot \delta\vec{r}_J + \cdots$$

$$= E_0 + \frac{1}{2} \sum_{IJ} \delta\vec{r}_I \cdot K_{IJ} \cdot \delta\vec{r}_J$$

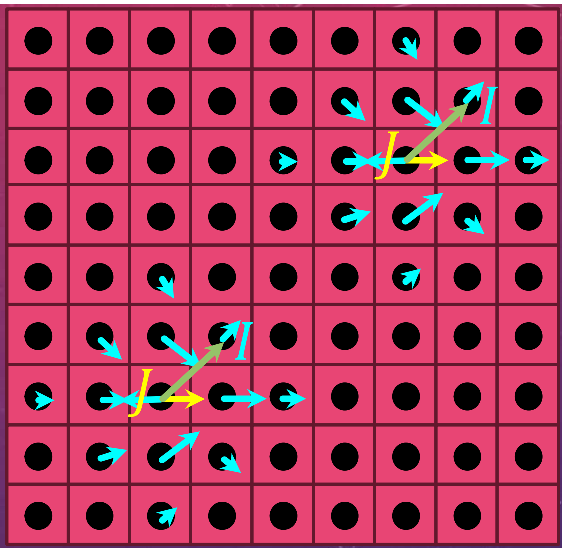
$$\vec{F}_I = -\frac{\partial E_0(\vec{r}_1, \vec{r}_2, \ldots)}{\partial \vec{r}_I} = -\sum_J K_{IJ} \delta\vec{r}_J$$

- K_{IJ}, the “spring-constant matrix” can be computed from

For all J: ↻ $K_{IJ} = -\frac{\vec{F}_I(\{\vec{r}_I + \hat{e}_J \cdot \Delta r\}) - \vec{F}_I(\{\vec{r}_I - \hat{e}_J \cdot \Delta r\})}{2 \cdot \Delta r}$



VIBRATIONAL DYNAMICS



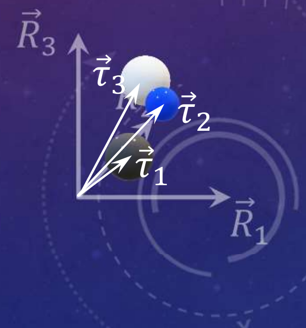
- Vibrational modes:

$$\vec{F}_I = M_I \ddot{\vec{r}}_I$$

$$-\sum_J K_{IJ} \cdot \delta\vec{r}_J = -M_I \omega^2 \vec{r}_I$$

$$\sum_J K_{IJ} \cdot \delta\vec{r}_J^{(\mathrm{v})} = M_I \omega_{(\mathrm{v})}^2 \cdot \delta\vec{r}_I^{(\mathrm{v})}$$ (eigenvalue problem)

- Translational symmetry:
  - Each atom at location $\vec{r}_I = \vec{R}_I + \vec{\tau}_{n_I}$
  - $K_{IJ} = K_{\vec{R}_I,n_I;\vec{R}_J,n_J} = K_{\vec{R}_J-\vec{R}_I,n_I;\vec{0},n_J}$, $M_I = M_{\vec{R}_I,n_I} = M_{n_I}$
  - $\delta\vec{r}_I = \delta\vec{r}_{\vec{R},n} = e^{i\vec{q}\cdot\vec{R}}\vec{\mathcal{E}}_n$ (like Bloch's Theorem: envelope × "polarization")



- Reduced problem:
  - $\sum_m D_{nm}(\vec{q}) \cdot \vec{\mathcal{E}}_m^{(\nu\vec{q})} = M_n \omega_{(\nu q)}^2 \cdot \vec{\mathcal{E}}_n^{(\nu\vec{q})}$
  - Dynamical matrix $D_{nm}(\vec{q}) \equiv \sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}} K_{\vec{R},n;\vec{0},m}$ (eigenvalue problem)
  - Phonon modes: Frequencies $\omega_{(\nu\vec{q})}$, displacements/polarization $\mathcal{E}_m^{(\nu\vec{q})}$

VIBRATIONAL DYNAMICS: 1D EXAMPLE

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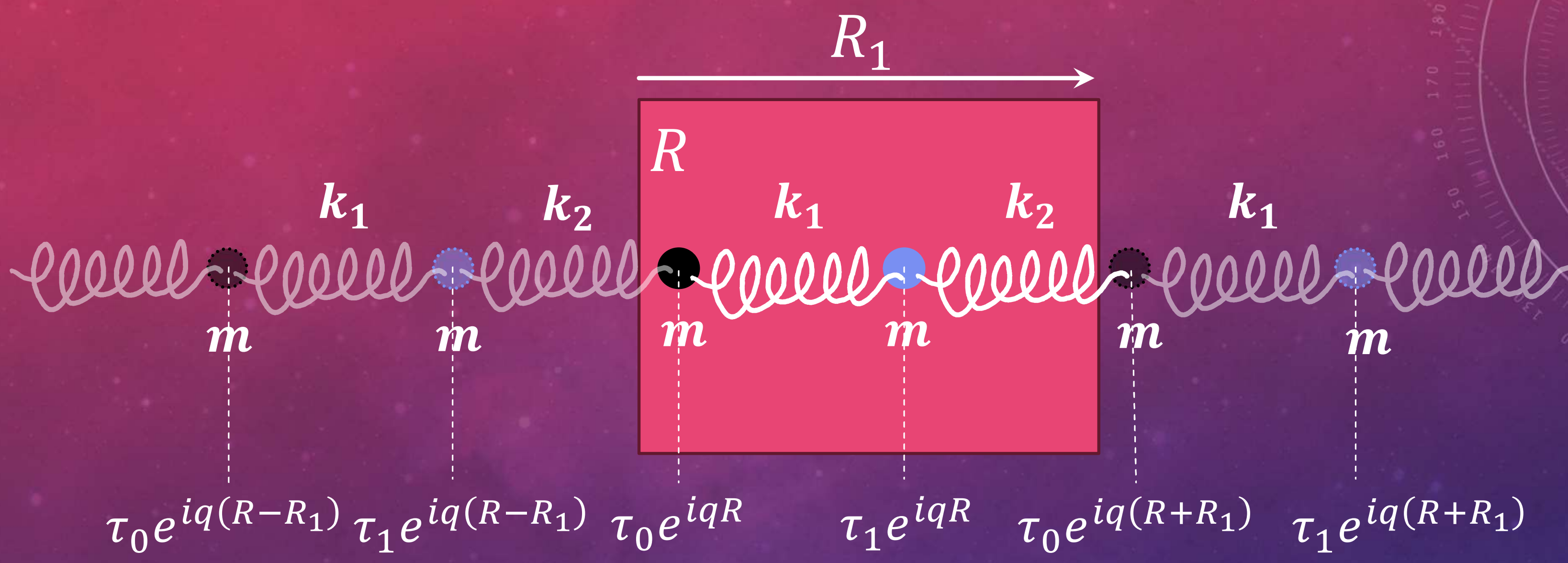


$ma = F$:

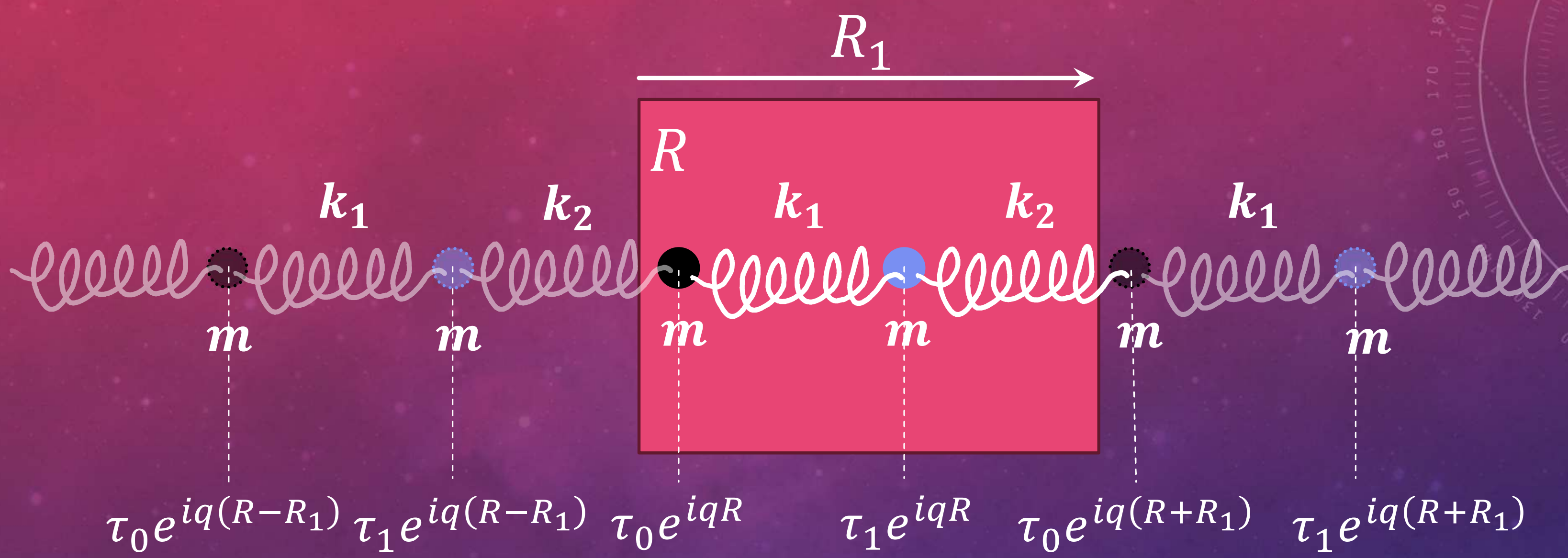
Expand

$$-m\omega^2\tau_0 e^{iqR} = k_1\left(\tau_1 e^{iqR} - \tau_0 e^{iqR}\right) - k_2\left(\tau_0 e^{iqR} - \tau_1 e^{iq(R-R_1)}\right)$$

$$-m\omega^2\tau_1 e^{iqR} = k_2\left(\tau_0 e^{iq(R+R_1)} - \tau_1 e^{iqR}\right) - k_1\left(\tau_1 e^{iqR} - \tau_0 e^{iqR}\right)$$

Expand

VIBRATIONAL DYNAMICS: 1D EXAMPLE



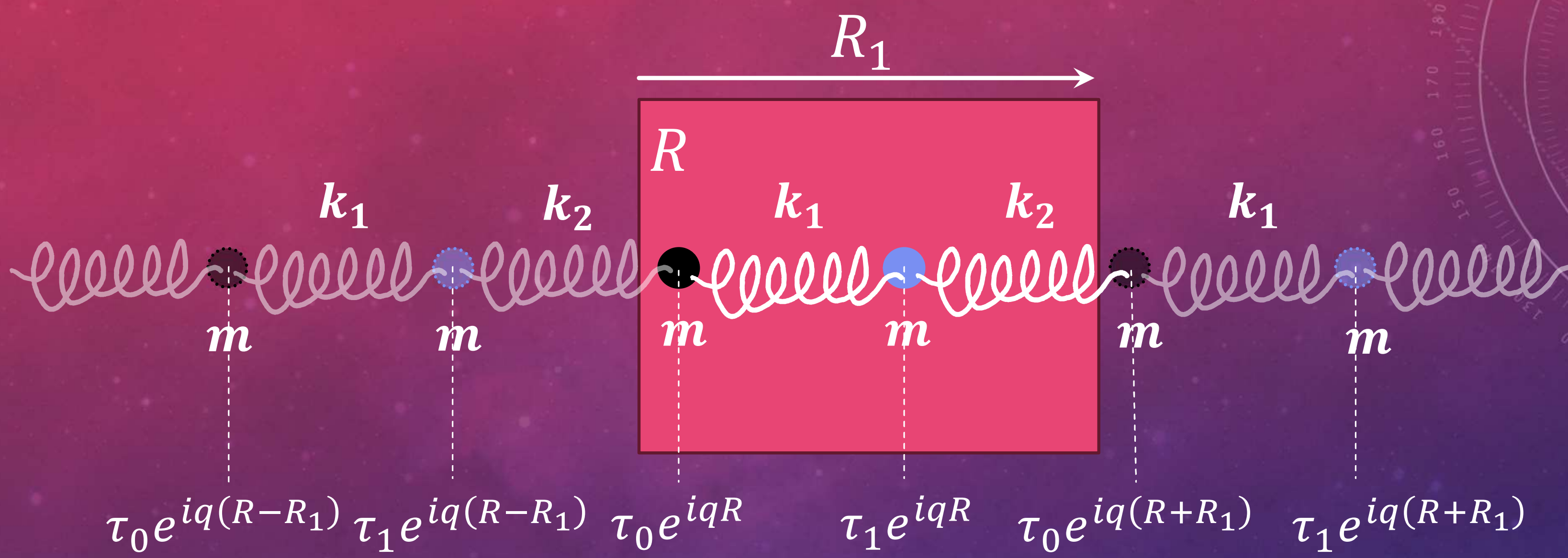
$ma = F$:

Cancel

$$-m\omega^2\tau_0 \cancel{e^{iqR}} = k_1\left(\tau_1 \cancel{e^{iqR}} - \tau_0 \cancel{e^{iqR}}\right) - k_2\left(\tau_0 \cancel{e^{iqR}} - \tau_1 \cancel{e^{iqR}} e^{-iqR_1}\right)$$

$$-m\omega^2\tau_1 \cancel{e^{iqR}} = k_2\left(\tau_0 \cancel{e^{iqR}} e^{iqR_1} - \tau_1 \cancel{e^{iqR}}\right) - k_1\left(\tau_1 \cancel{e^{iqR}} - \tau_0 \cancel{e^{iqR}}\right)$$

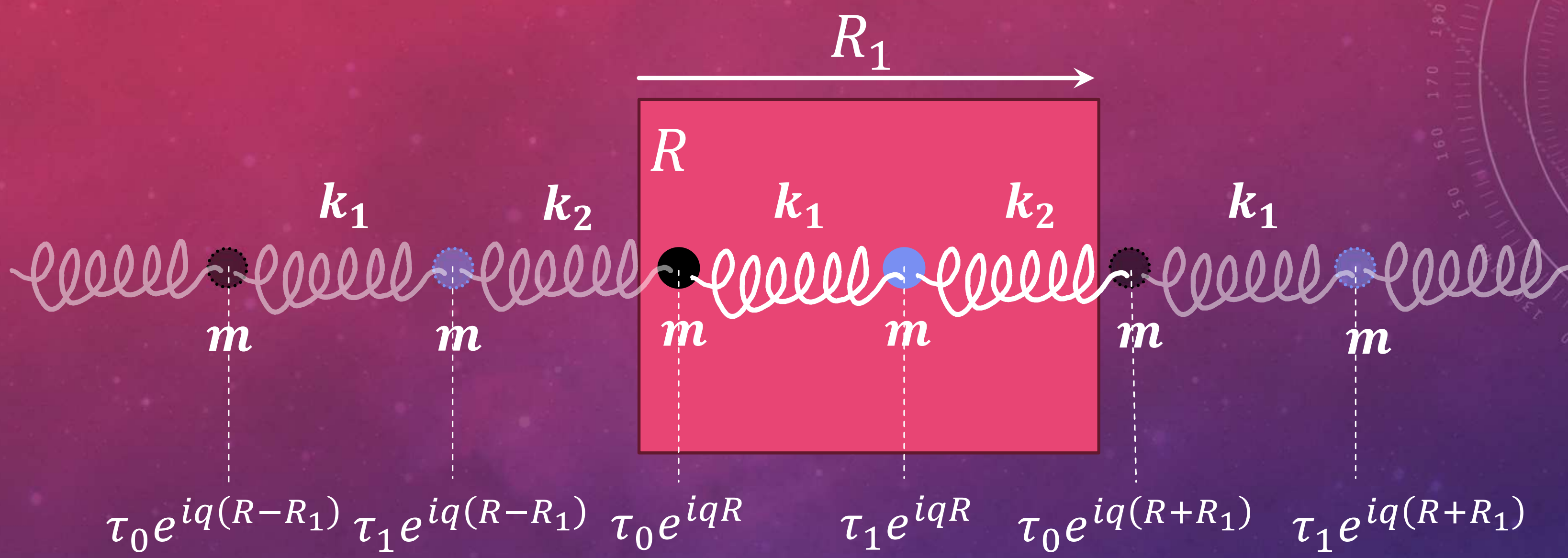
VIBRATIONAL DYNAMICS: 1D EXAMPLE



$ma = F$:

$$-m\omega^2\tau_0 = k_1(\tau_1 - \tau_0) - k_2\left(\tau_0 - \tau_1 e^{-iqR_1}\right)$$
$$-m\omega^2\tau_1 = k_2\left(\tau_0 e^{iqR_1} - \tau_1\right) - k_1(\tau_1 - \tau_0)$$

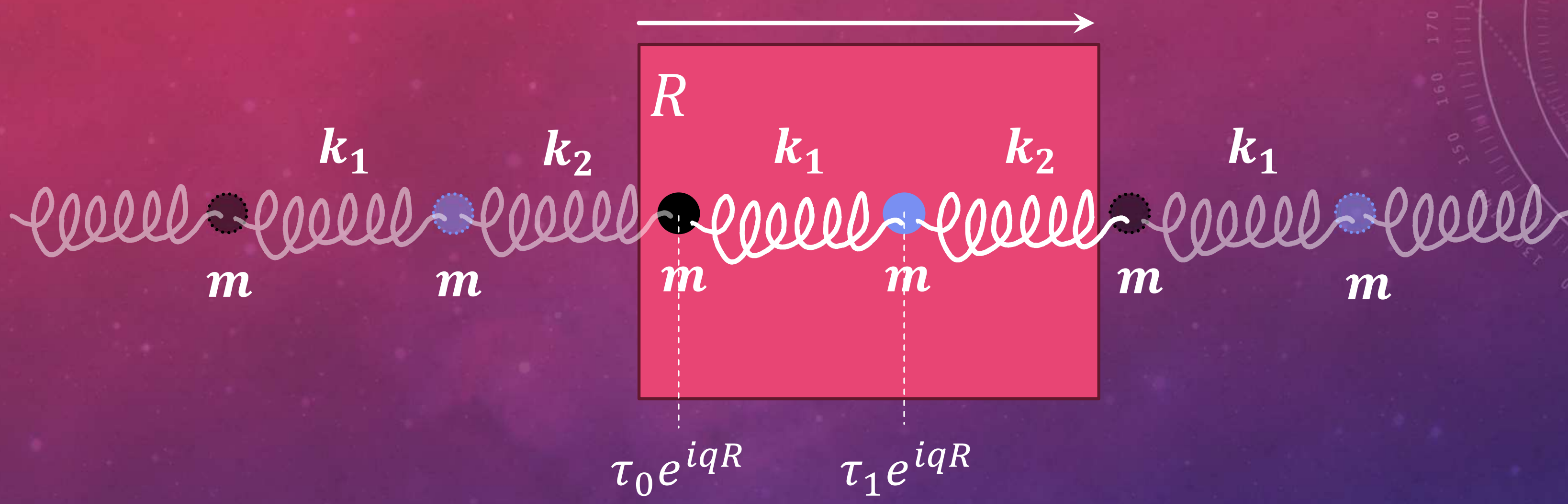
VIBRATIONAL DYNAMICS: 1D EXAMPLE



$ma = F$:

$$-m\omega^2 \begin{pmatrix} \tau_0 \\ \tau_1 \end{pmatrix} = -\overbrace{\begin{pmatrix} k_1 + k_2 & -\left(k_1 + k_2 e^{-iqR_1}\right) \\ -\left(k_1 + k_2 e^{iqR_1}\right) & k_1 + k_2 \end{pmatrix}}^{D(q)} \begin{pmatrix} \tau_0 \\ \tau_1 \end{pmatrix}$$

VIBRATIONAL DYNAMICS: 1D EXAMPLE

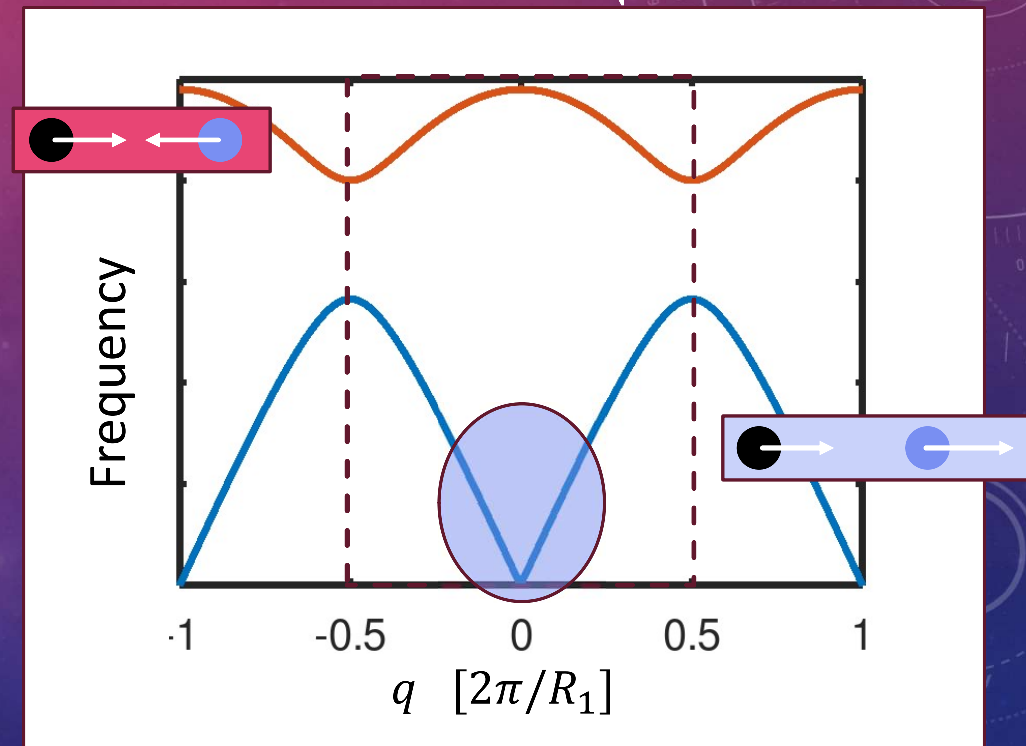


$$-D(q) = e^{-iq(-R_1)}\begin{pmatrix} 0 & 0 \\ k_2 & 0 \end{pmatrix} + \begin{pmatrix} -(k_1+k_2) & k_1 \\ k_1 & -(k_1+k_2) \end{pmatrix} + e^{-iq(+R_1)}\begin{pmatrix} 0 & k_2 \\ 0 & 0 \end{pmatrix}$$

VIBRATIONAL DYNAMICS: 1D EXAMPLE

- Results periodic in q …
  - because e^{iqR_1}, $D(q)$ are periodic
- Relevant range is [-0.5 0.5]
  - "Brillouin zone"
- Two "bands" (—,—)
  - because two degrees of freedom
- Lower band is ≈linear, $\omega = c\ q$
  - Corresponds to <u>acoustic</u> waves
- Higher band has non-zero ω
  - Corresponds to <u>optical</u> activity
- Displacements <u>longitudinal</u>
  - 1 LA and 1 LO mode

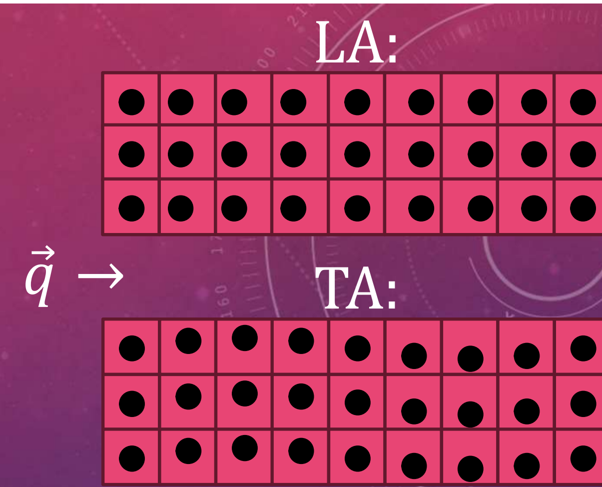
$$D(q)\vec{\mathcal{E}} = m\omega^2\vec{\mathcal{E}} \Rightarrow \omega = \sqrt{\mathrm{eig}\left(D(q)\right)/m}$$

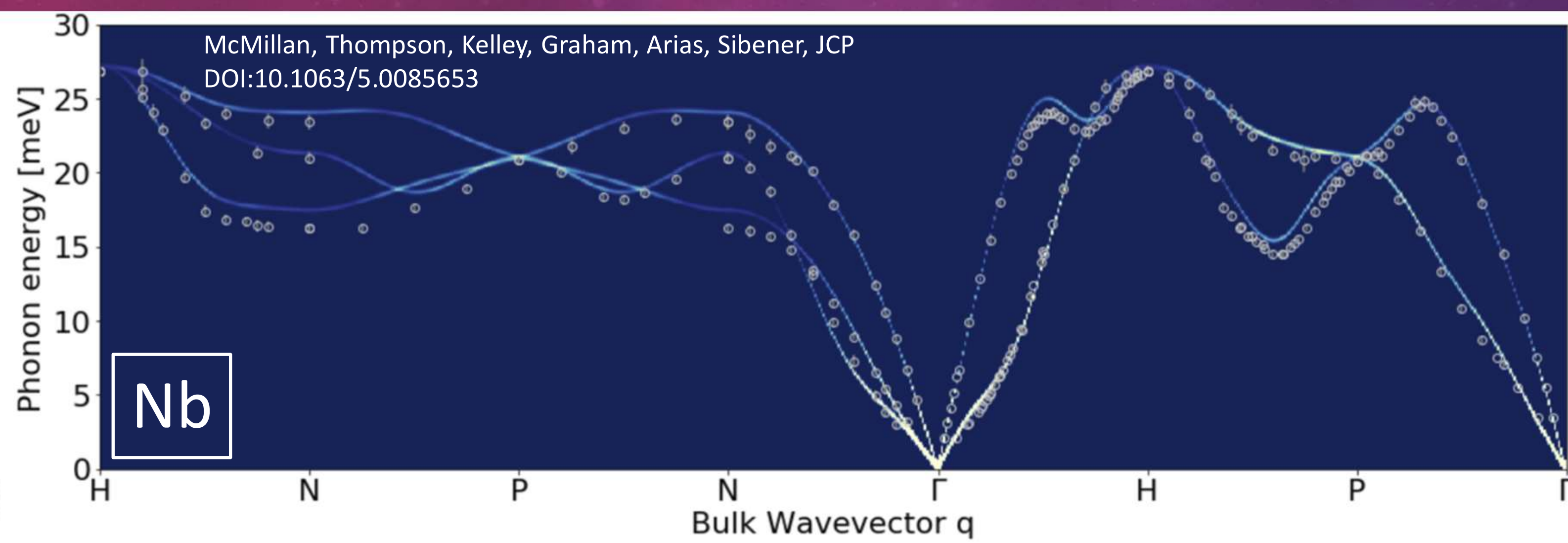


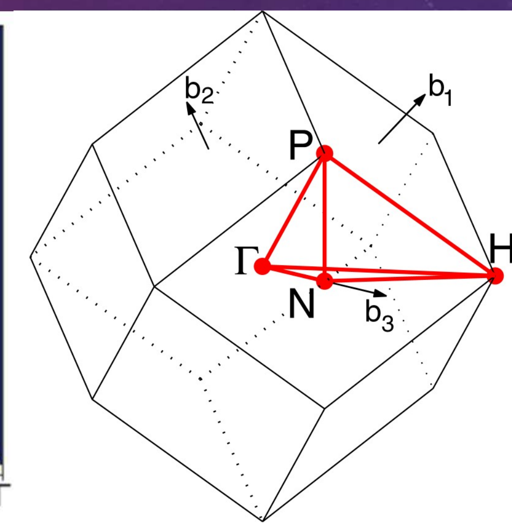
PHONON MODES I

BCC Nb:

- 1 atom/cell ⇒ acoustic modes only
- 3 D of F / unit cell ⇒ 3 bands
- 1 longitudinal (LA) and 2 transverse (TA) bands



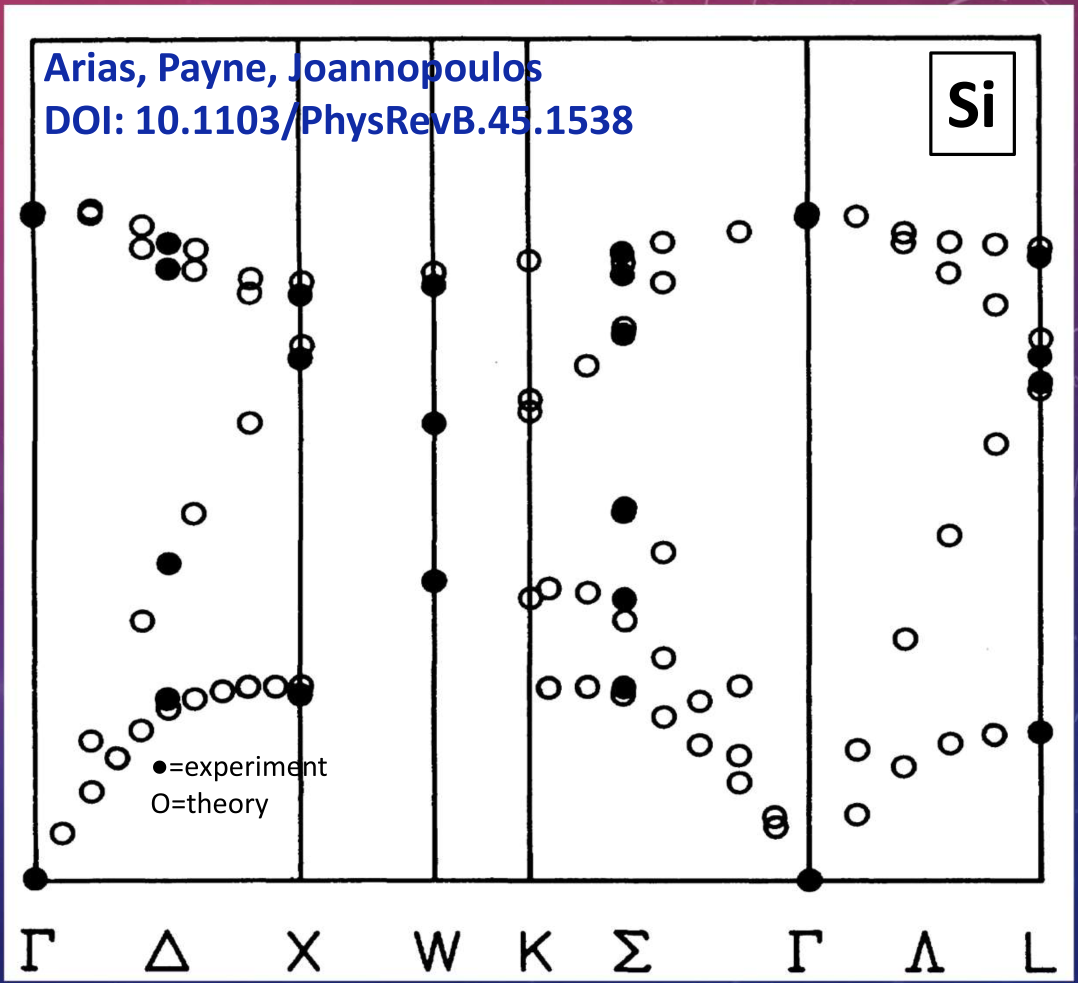




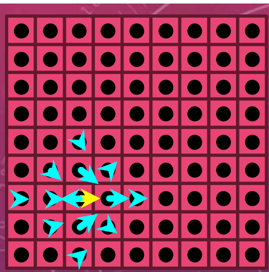
PHONON MODES I: BULK PHONONS

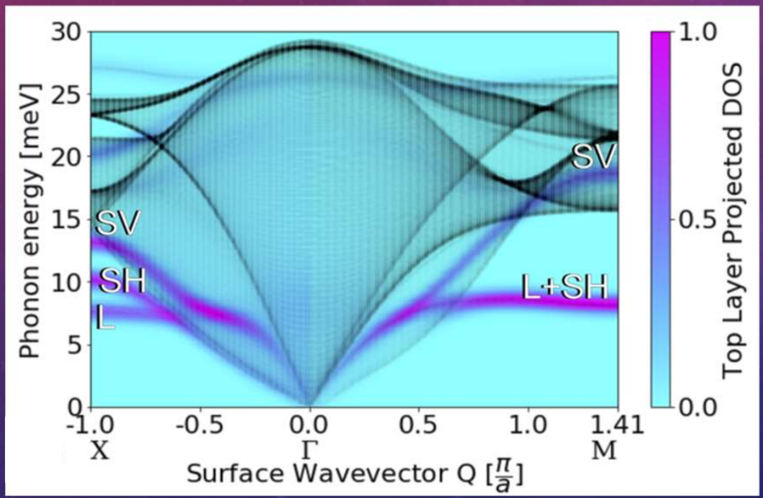
Si:

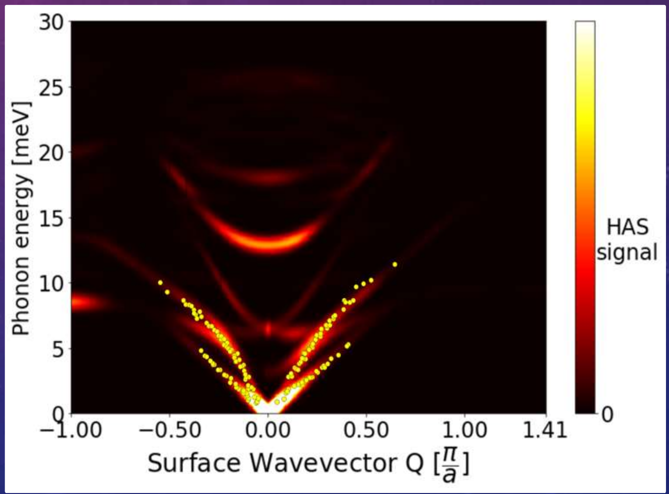
- 2 atoms/cell ⇒ A <u>and</u> O modes
- 6 D of F / unit cell ⇒ 6 bands
- 1 LA and 2 TA bands
- 1 LO and 2 TO bands



PHONON MODES II: QUANTIZED SURFACE PHONONS







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THANK YOU!

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