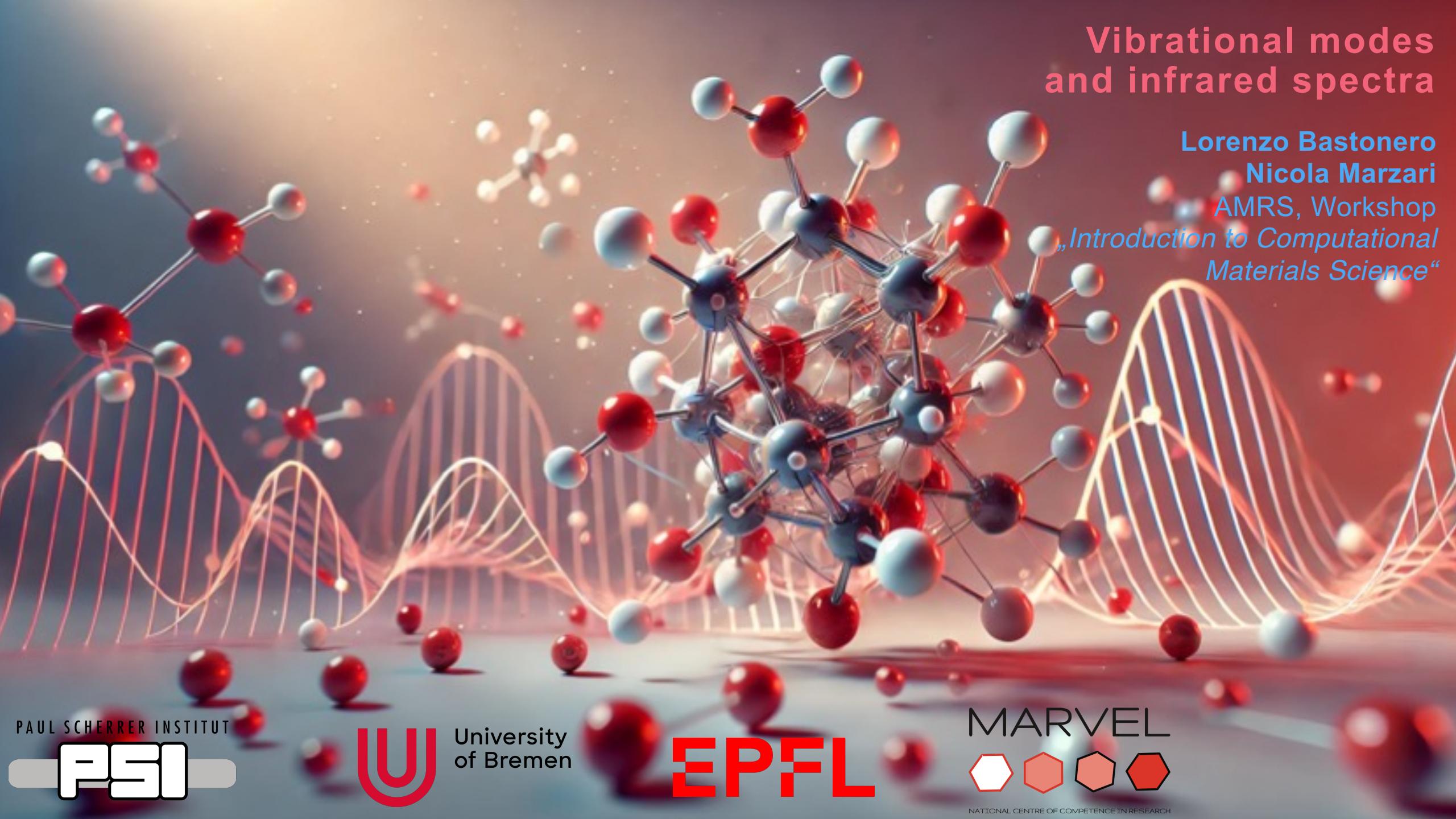


`osscar-quantum-mechanics.materialscloud.io`

`github.com/MosaicGroupCMU/African-MRS-Tutorials`



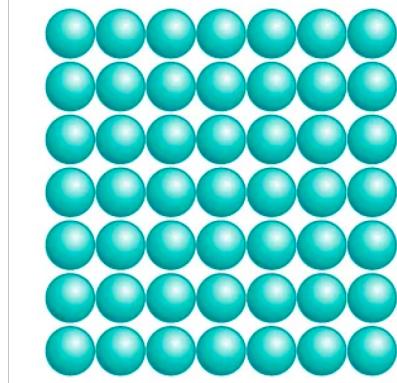
Vibrational modes and infrared spectra

Lorenzo Bastonero
Nicola Marzari

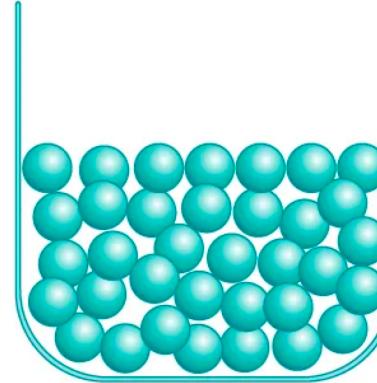
AMRS, Workshop

*„Introduction to Computational
Materials Science“*

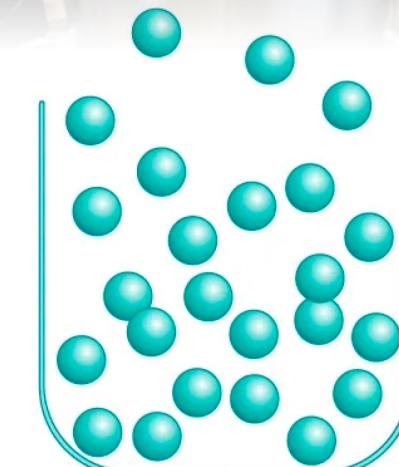
Solid



Liquid

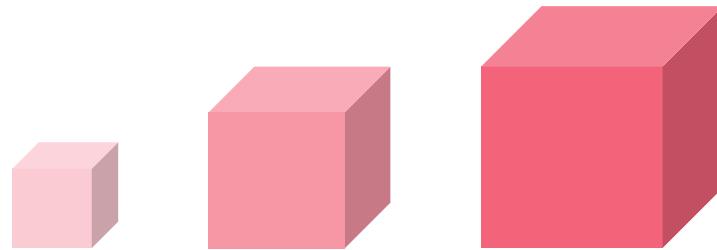


Gas

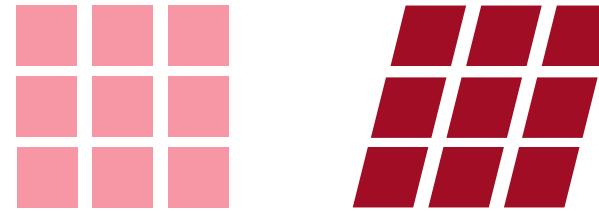


From DFT $E[\rho; \{R\}] \equiv E(\{R\})$

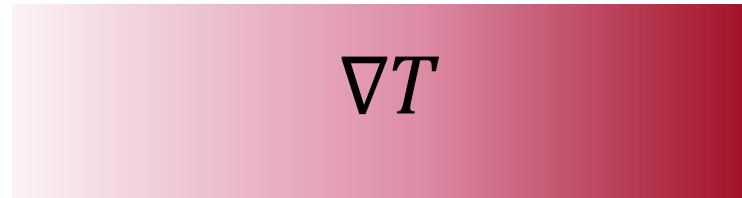
What $E(\{R\})$ controls?



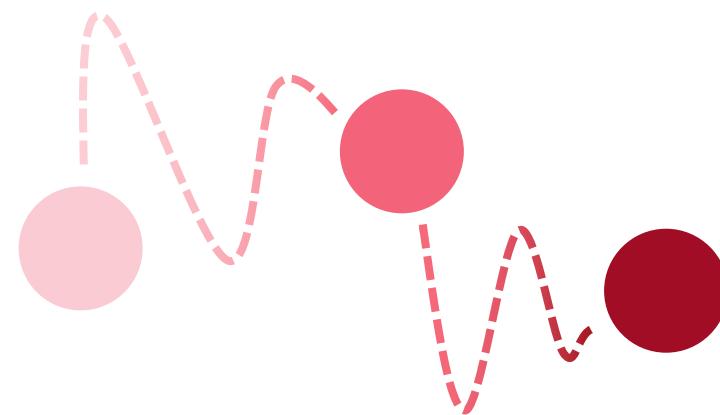
Thermal expansion



Phase transition & Dynamical stability



Heat transport

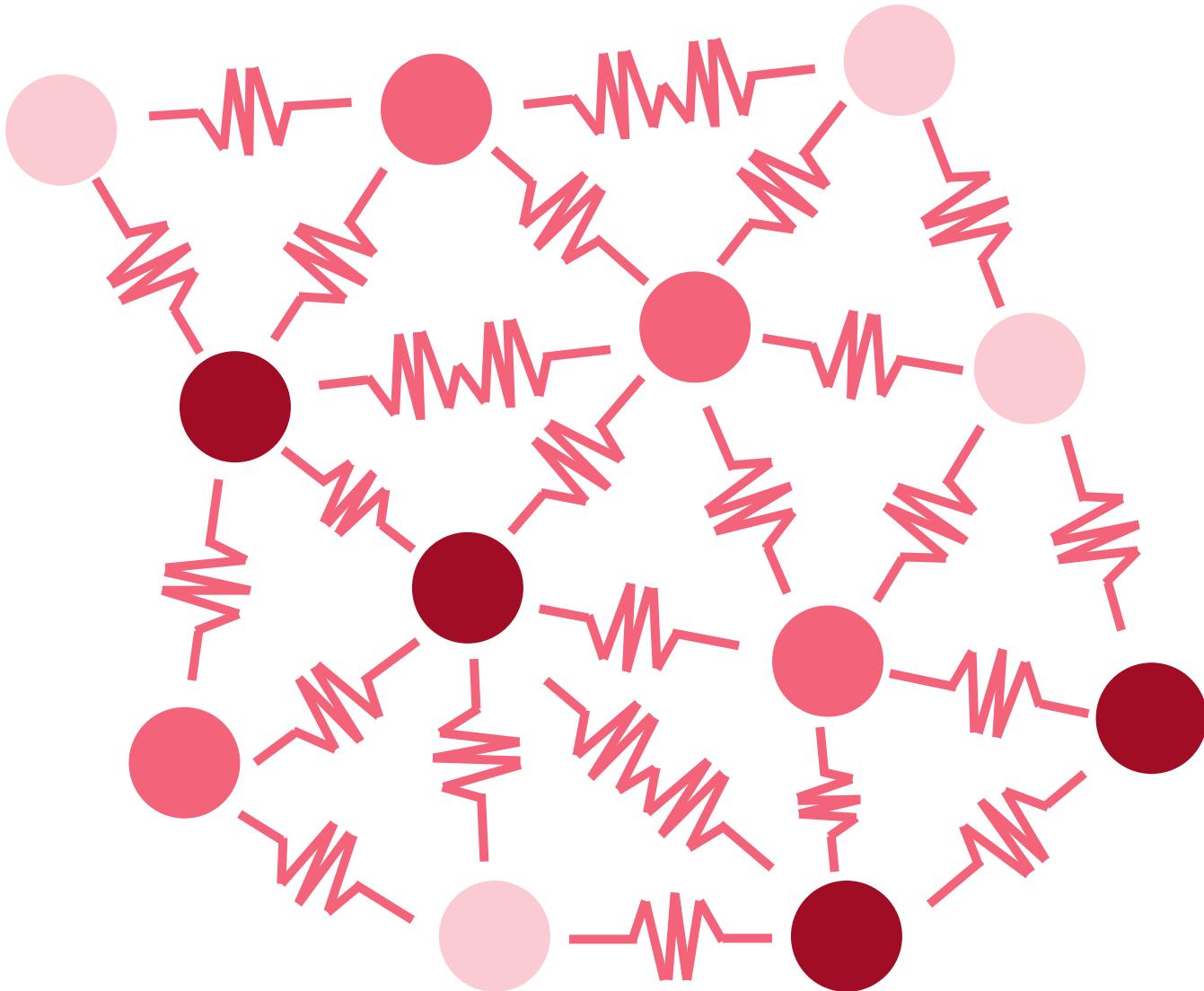


Transport coefficients



How can we study $E(\{R\})$?

Atomic interactions as springs



The harmonic approximation

$$E(d) \approx E(d_{eq}) + \frac{\partial E}{\partial d}(d - d_{eq}) + \frac{1}{2} \frac{\partial^2 E}{\partial d^2}(d - d_{eq})^2 + \dots$$

constant $= 0$

$k = \text{force const.}$

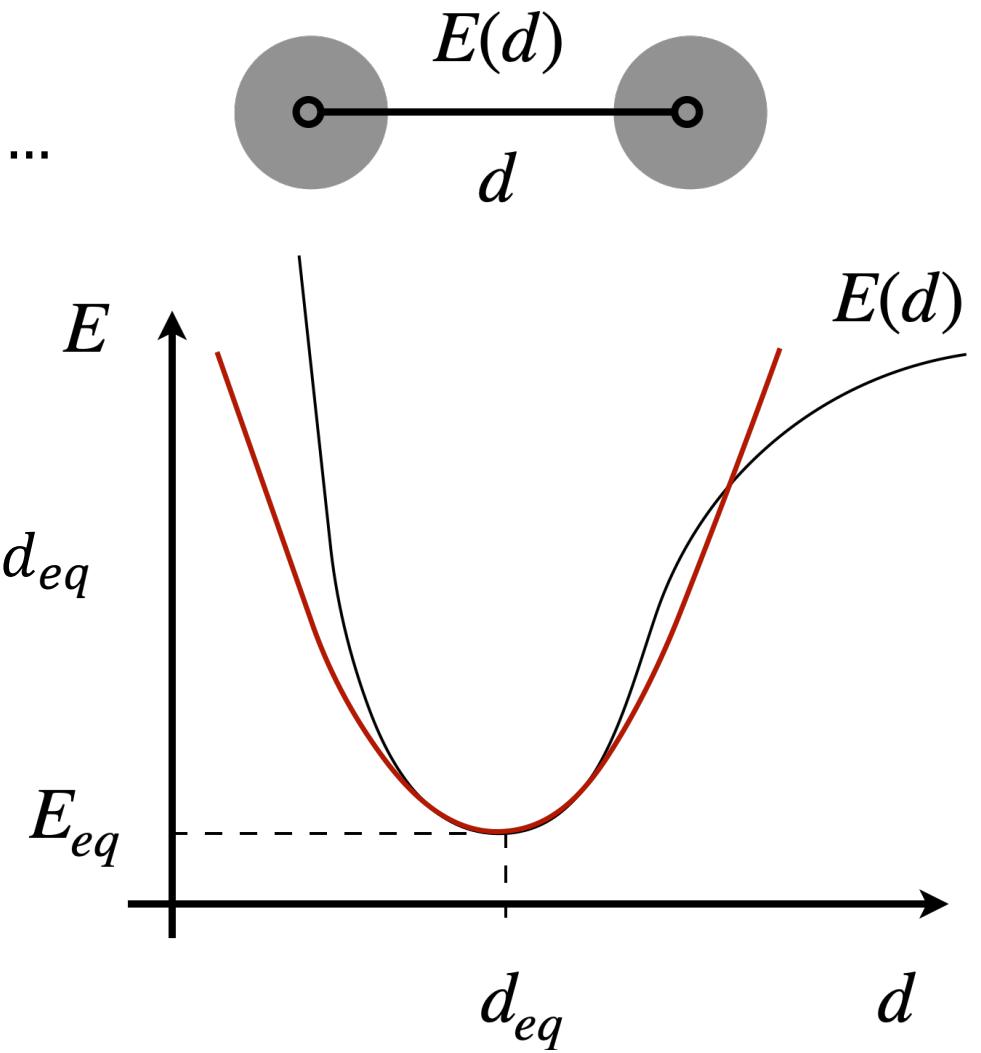
$$F = m a = m \frac{\partial^2 d}{\partial t^2}$$

$$F = -\frac{\partial E}{\partial d} = -k(d - d_{eq})$$

$$d(t) = A \sin(\omega t + \varphi) + d_{eq}$$

$$\omega = \sqrt{\frac{k}{m}}$$

oscillation frequency

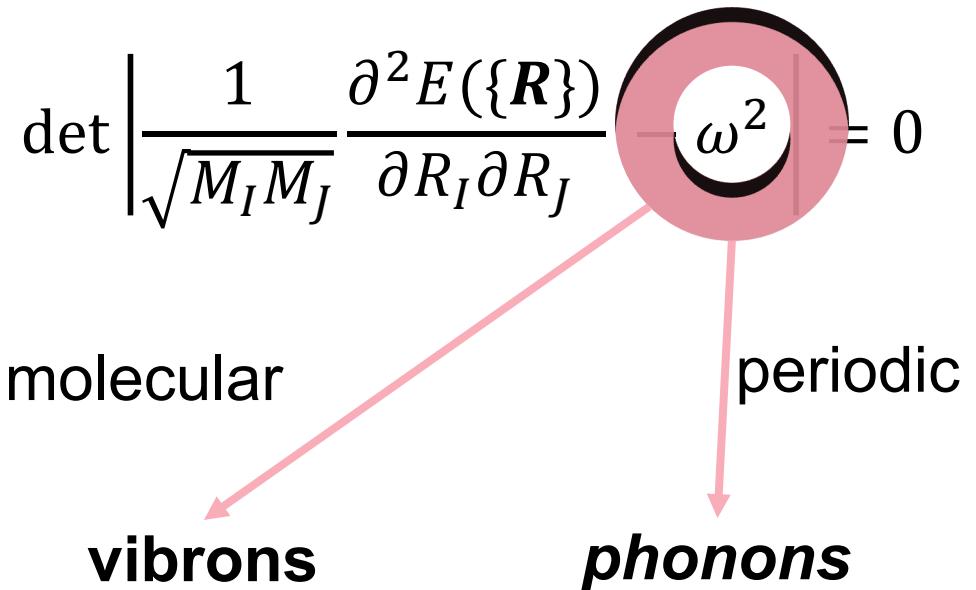
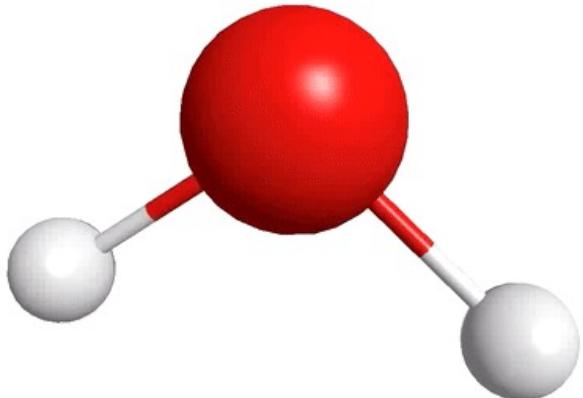


- Same approach as for the pendulum
- Small angle \leftrightarrow small (atomic) oscillations

Normal modes and vibrational frequencies

$$E(\{R\}) \approx \frac{1}{2} \sum_I \frac{\partial^2 E}{\partial R_I \partial R_J} (R_I - R_I^0)(R_J - R_J^0)$$

Interatomic Force Constant (IFC) matrix

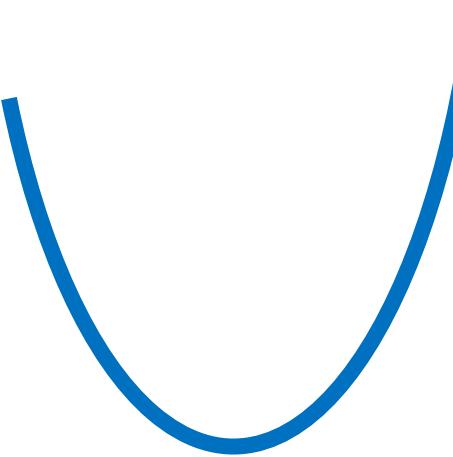


Number of frequencies
=

Number of degree of freedom

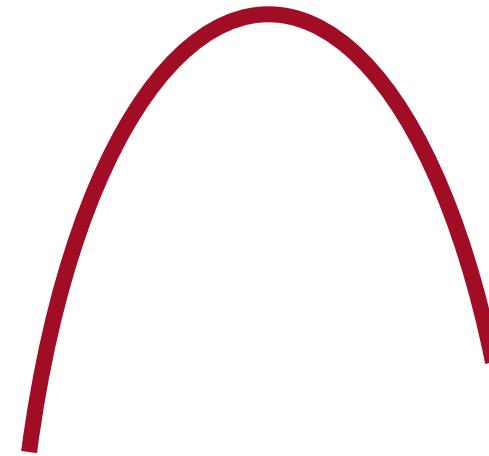
For water: (3 atoms) x (3 directions) – (3 translations) – (2 rotations) – (1 reflection/mirror) = 3 !

Dynamical stability



$$\omega^2 > 0$$

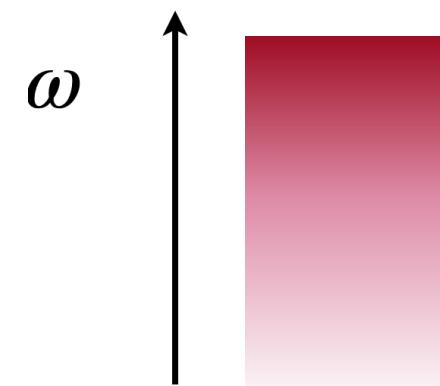
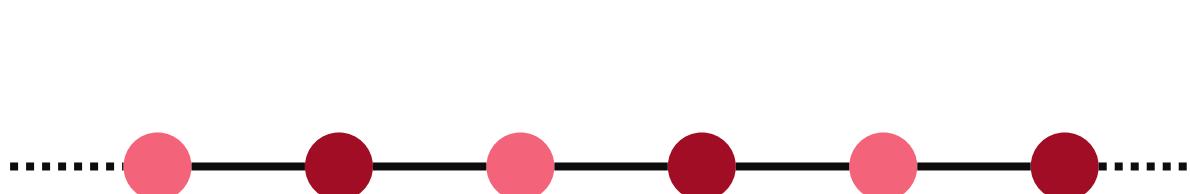
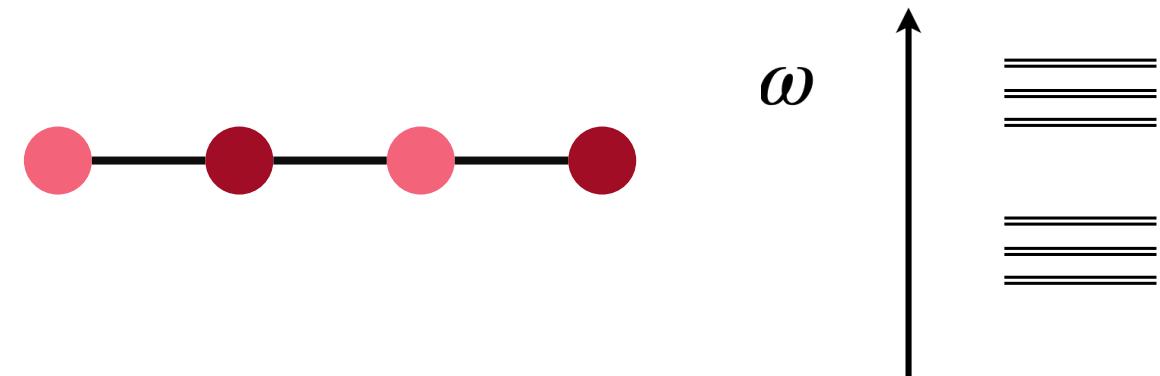
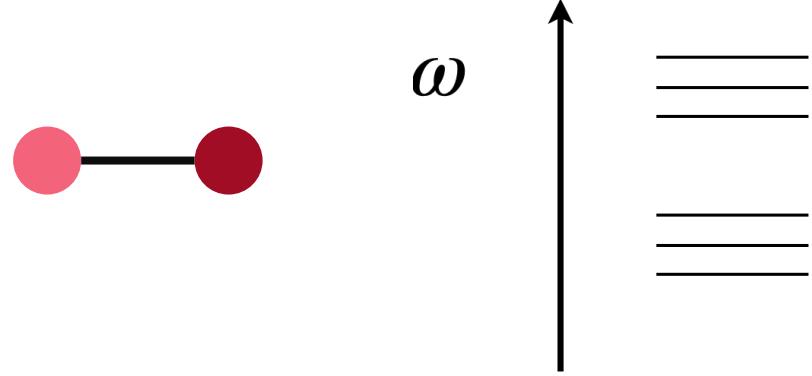
Stable



$$\omega^2 < 0$$

Unstable

Vibrations in solids

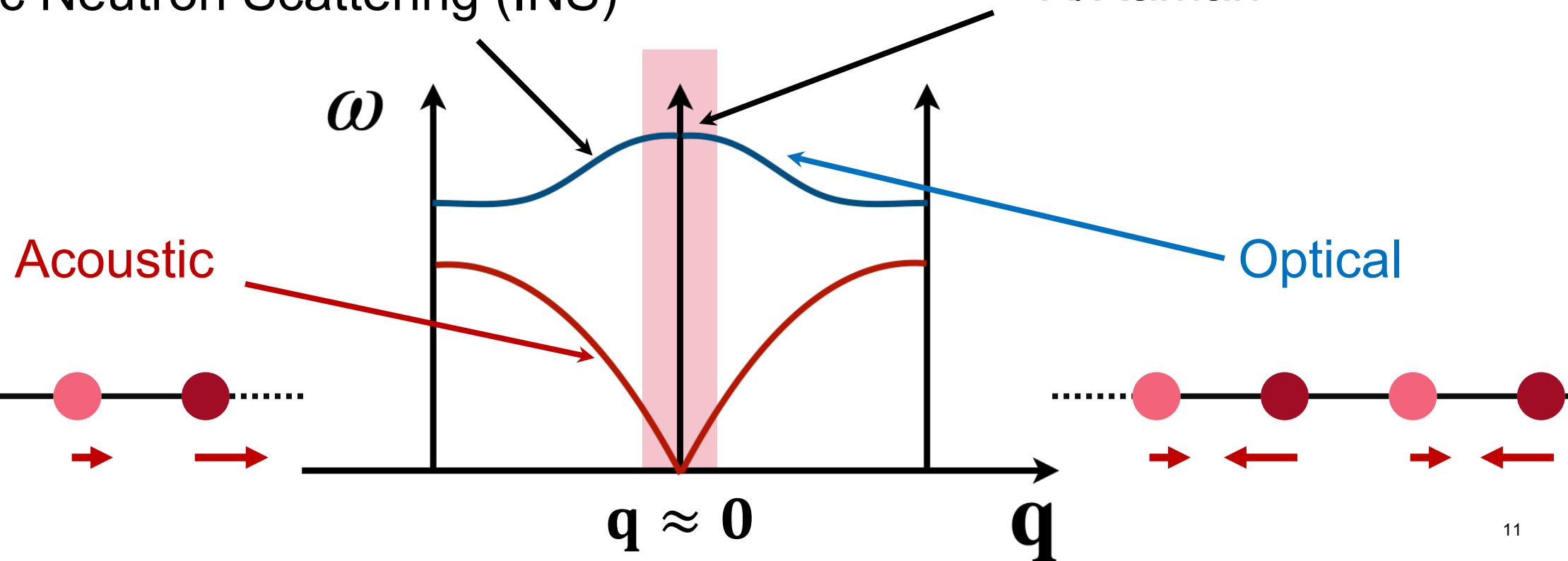


Phonon dispersion

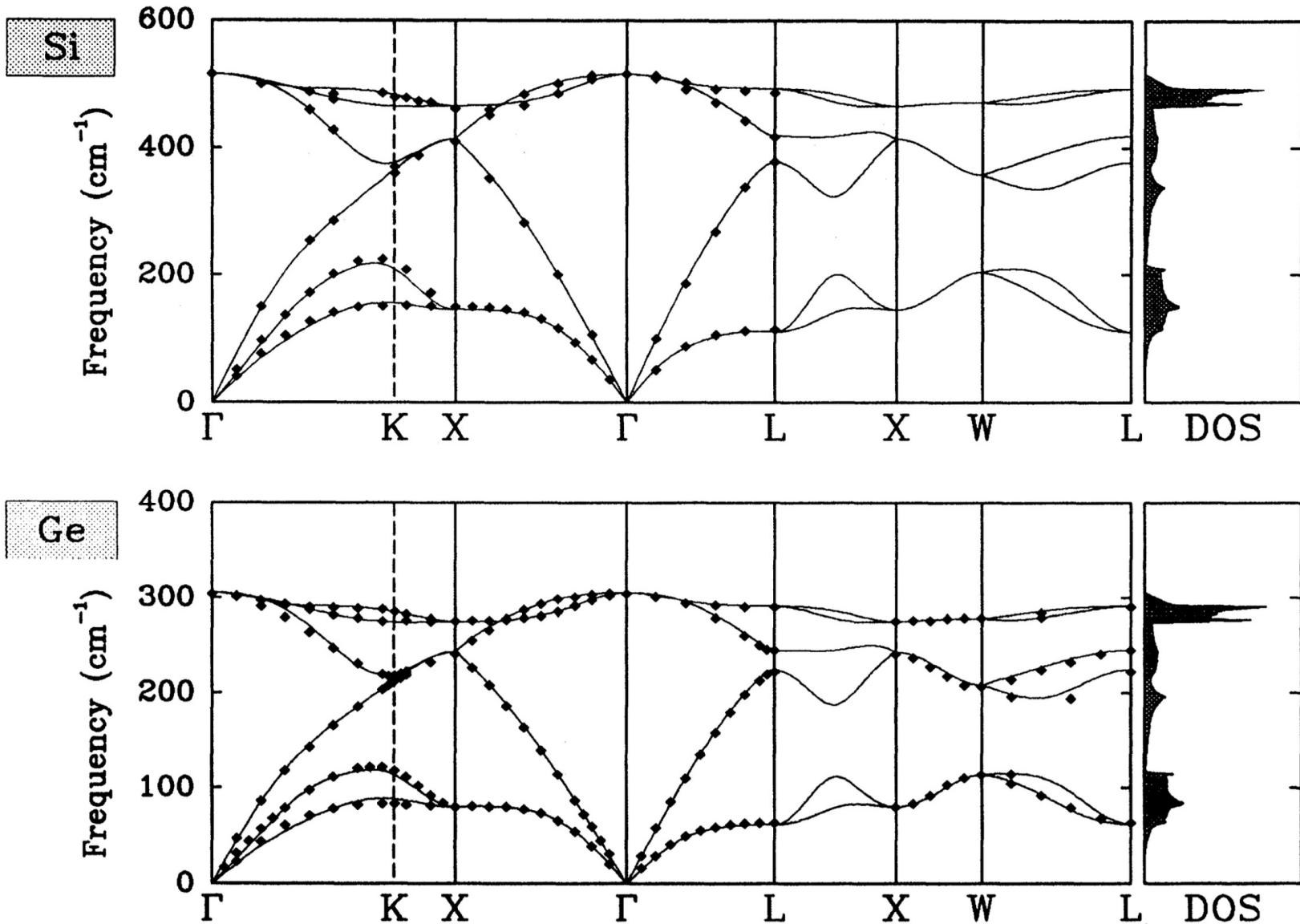
Dynamical matrix

$$D_{IJ}(\mathbf{q}) = \sum_R e^{i\mathbf{q}\cdot\mathbf{R}} \frac{1}{\sqrt{M_I M_J}} \frac{\partial^2 E}{\partial R_I \partial R_J} \rightarrow \det[D(\mathbf{q}) - \omega^2(\mathbf{q})] = 0$$

Inelastic Neutron Scattering (INS)



Examples: Si and Ge



How to compute phonons?

Frozen phonons
(finite displacements)

$$\frac{\partial^2 E}{\partial R_I \partial R_J} = - \frac{\partial F_I}{\partial R_J}$$

Linear response (DFPT)

$$H = H_0 + \lambda H_1$$
$$\rho = \rho_0 + \Delta \rho$$

$$\frac{\partial f}{\partial x} \approx \frac{f(x_0 + \Delta x) - f(x_0)}{\Delta x} + O(\Delta x)$$

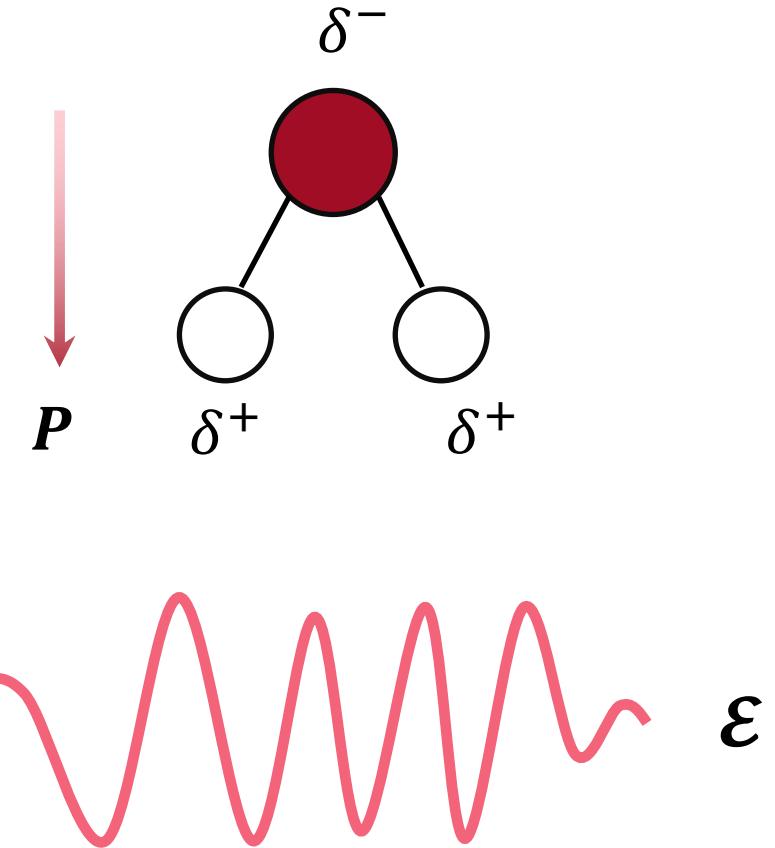
$$\frac{\partial^2 E}{\partial R_I \partial R_J}$$



To compute in supercell

- New set of self-consistent equations
- To solve in primitive cell for each \mathbf{q}
- Calculates $D(\mathbf{q})$

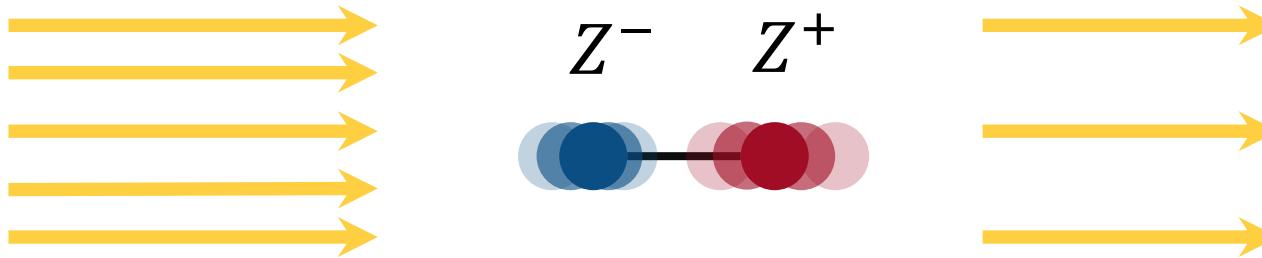
Interaction with light



Electromagnetic range where ions respond: 0– 10^{12} Hz

$E(\{R\}, \mathcal{E})$

Infrared absorption



Oscillator strength

$$I_{IR} \propto \frac{|Z^+ - Z^-|^2}{\omega}$$

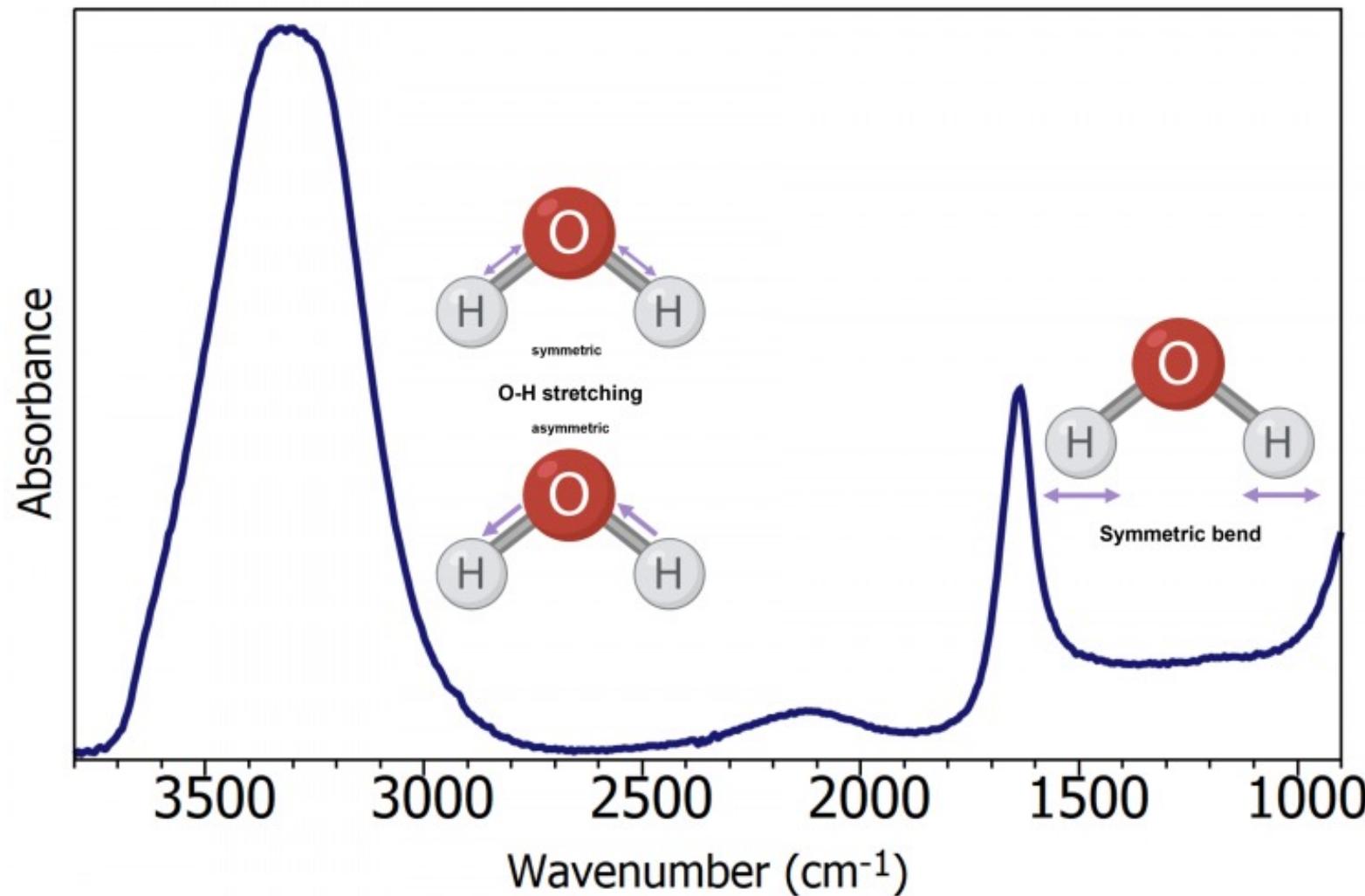
$$I_{IR}^n = \frac{1}{\omega^n} \left| \sum_{jI} Z_{I,ij}^* \frac{e_{jI}^n}{\sqrt{M_I}} \right|^2$$

Born effective charges

$$Z_{I,ij}^* = \Omega \frac{\partial \mathbf{P}_i}{\partial \mathbf{R}_j^I} = \frac{\partial \mathbf{F}_j^I}{\partial \mathcal{E}_i} = - \frac{\partial^2 E(\mathcal{E}, \{\mathbf{R}\})}{\partial \mathcal{E}_i \partial \mathbf{R}_j^I}$$

Vibration eigenvector

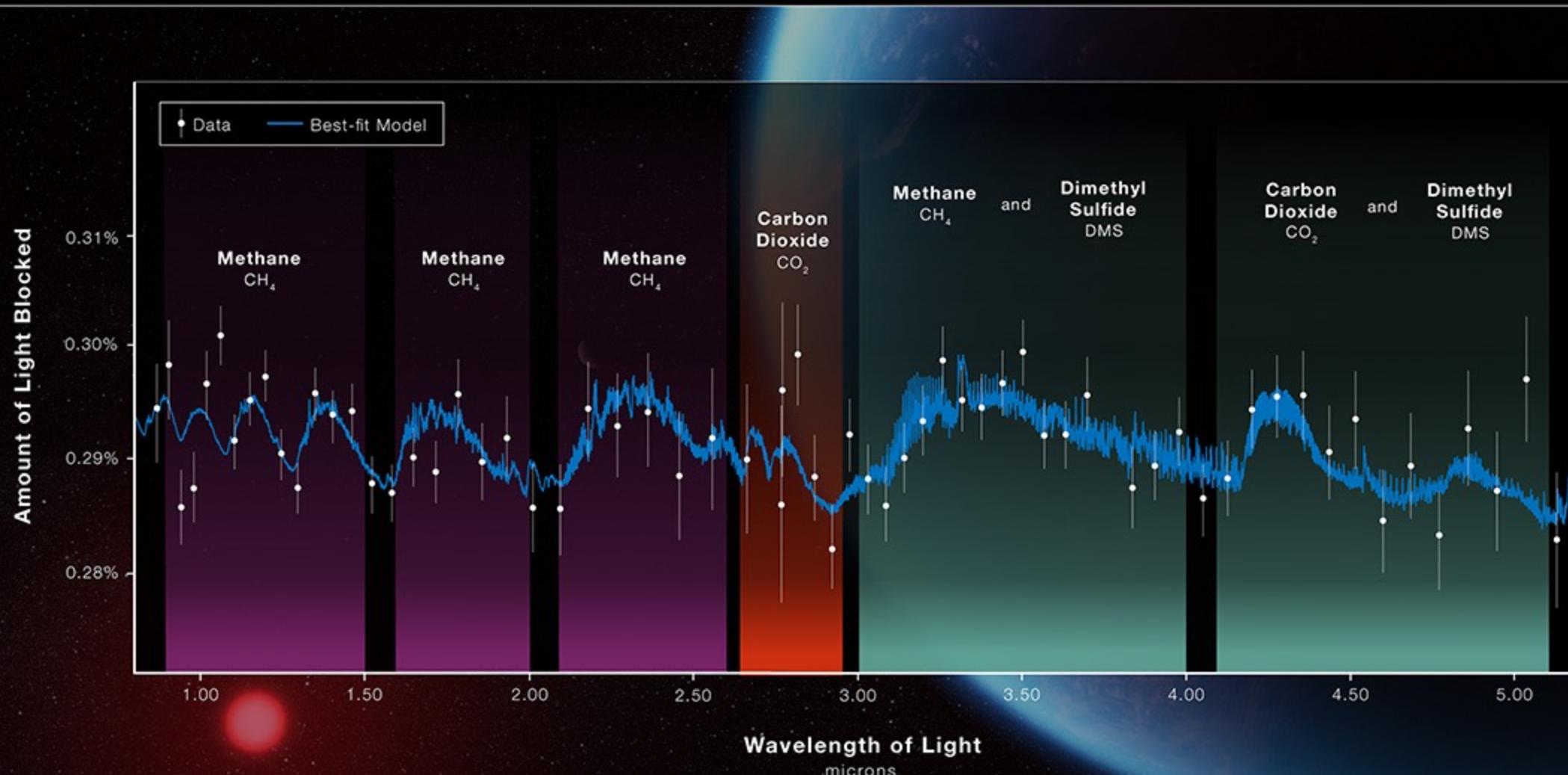
Example: water



EXOPLANET K2-18 b

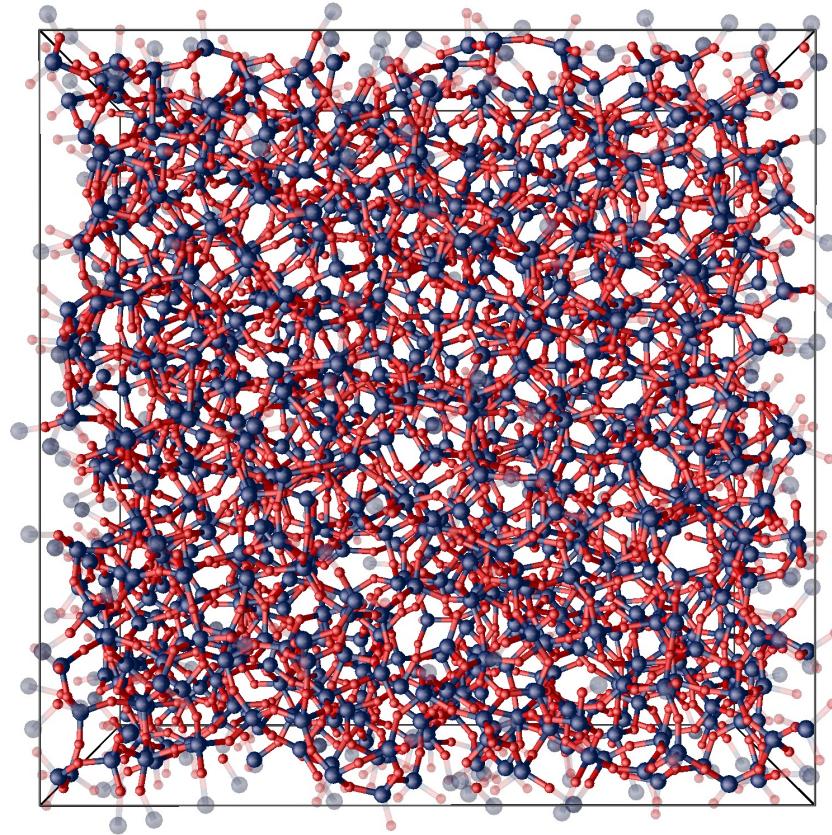
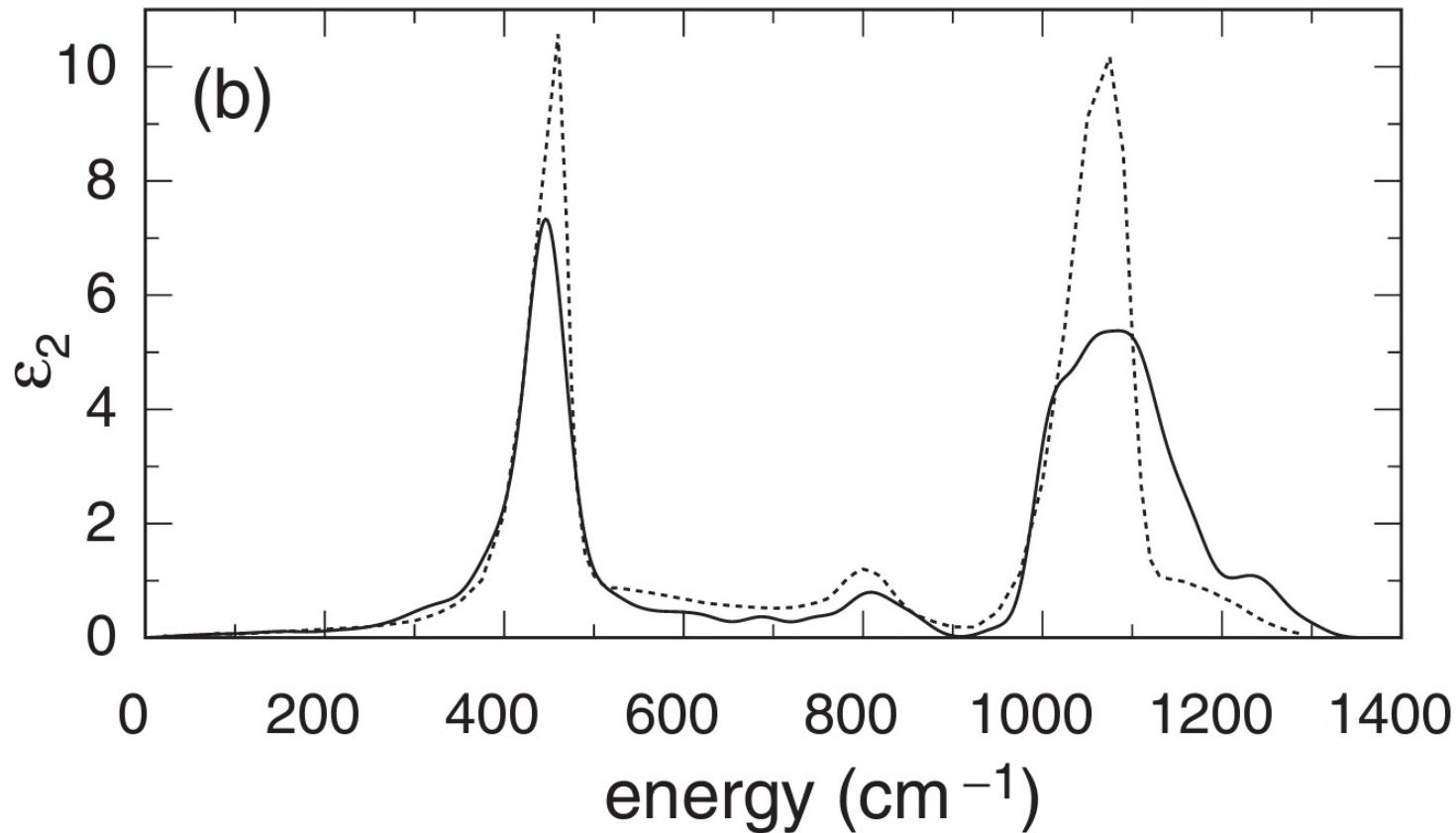
ATMOSPHERE COMPOSITION

NIRISS and NIRSpec (G395H)



WEBB
SPACE TELESCOPE

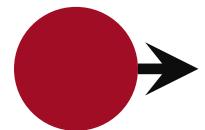
Example: amorphous silica (SiO_2)



Nature of the interactions

Short range
(homopolar semiconductors, metals)

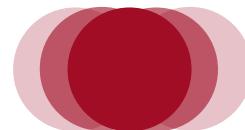
$$Z \approx 0$$



$$\frac{\Delta F}{\Delta R^+} \approx 0$$

• • •

$$Z \approx 0$$



Long range
(polar semiconductors)

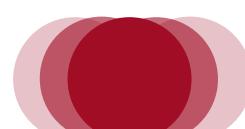
$$Z^-$$



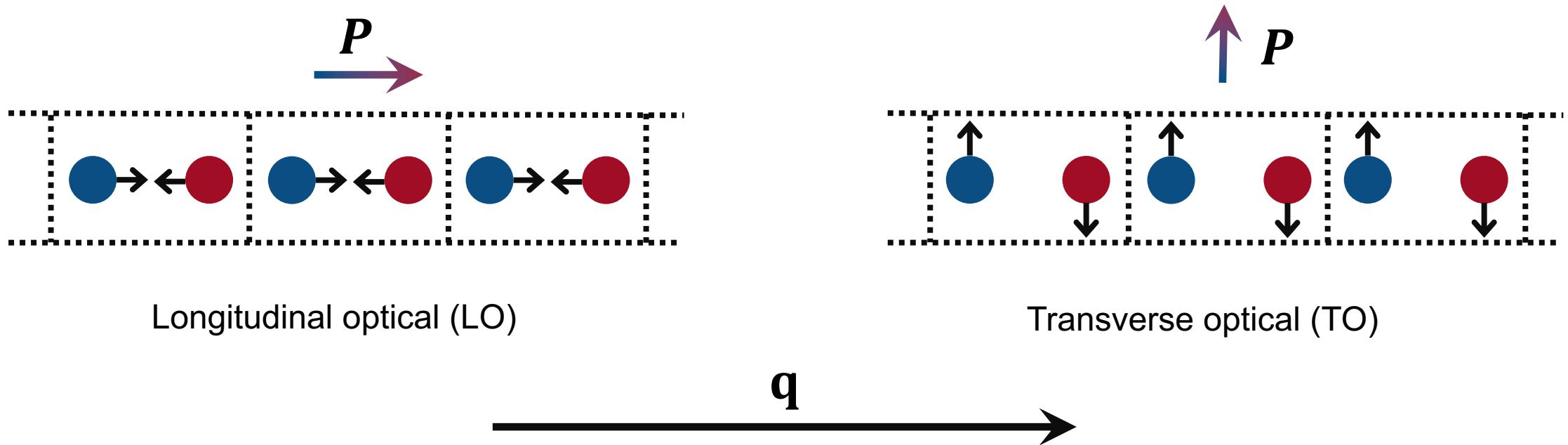
$$\frac{\Delta F}{\Delta R^+} \neq 0$$

• • •

$$Z^+$$

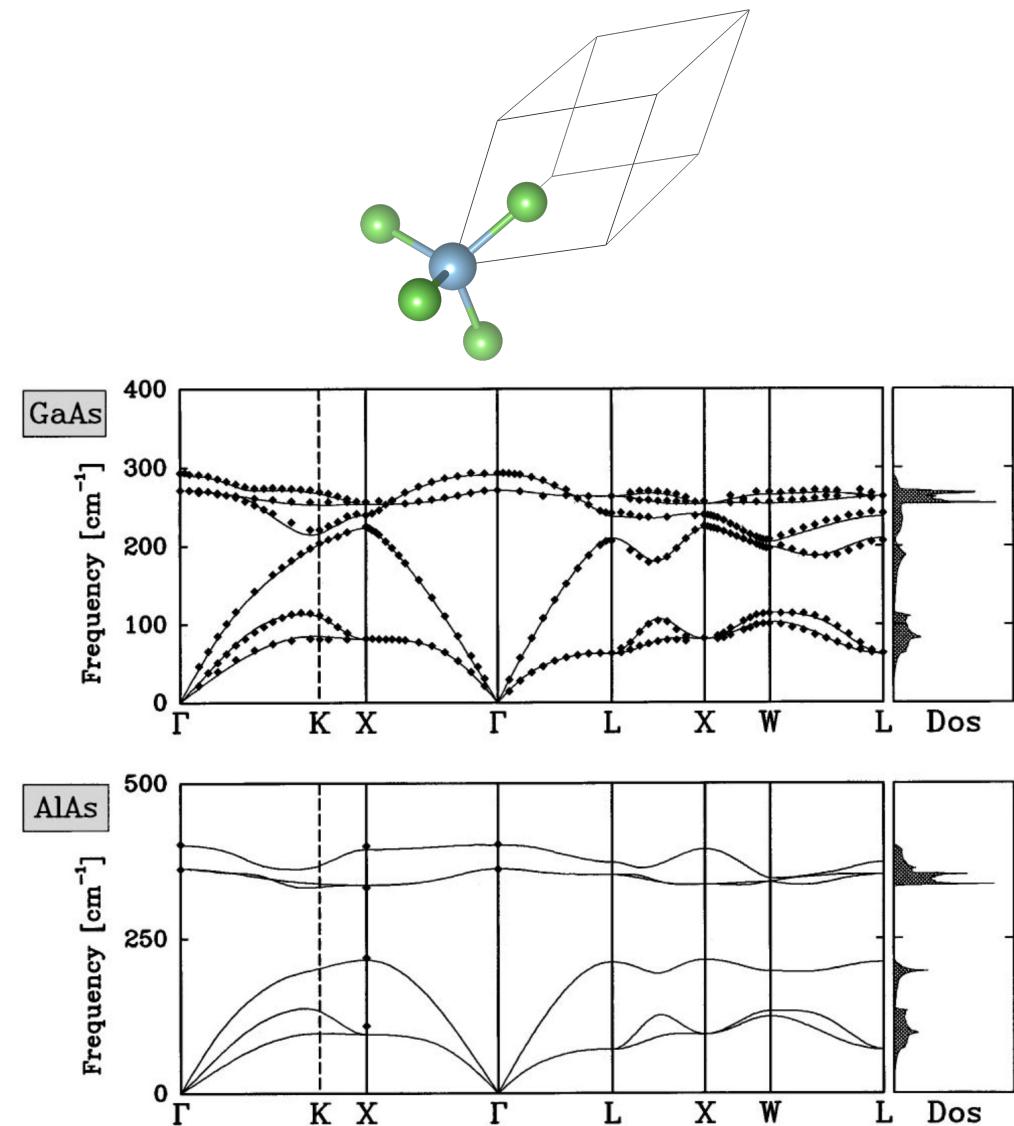
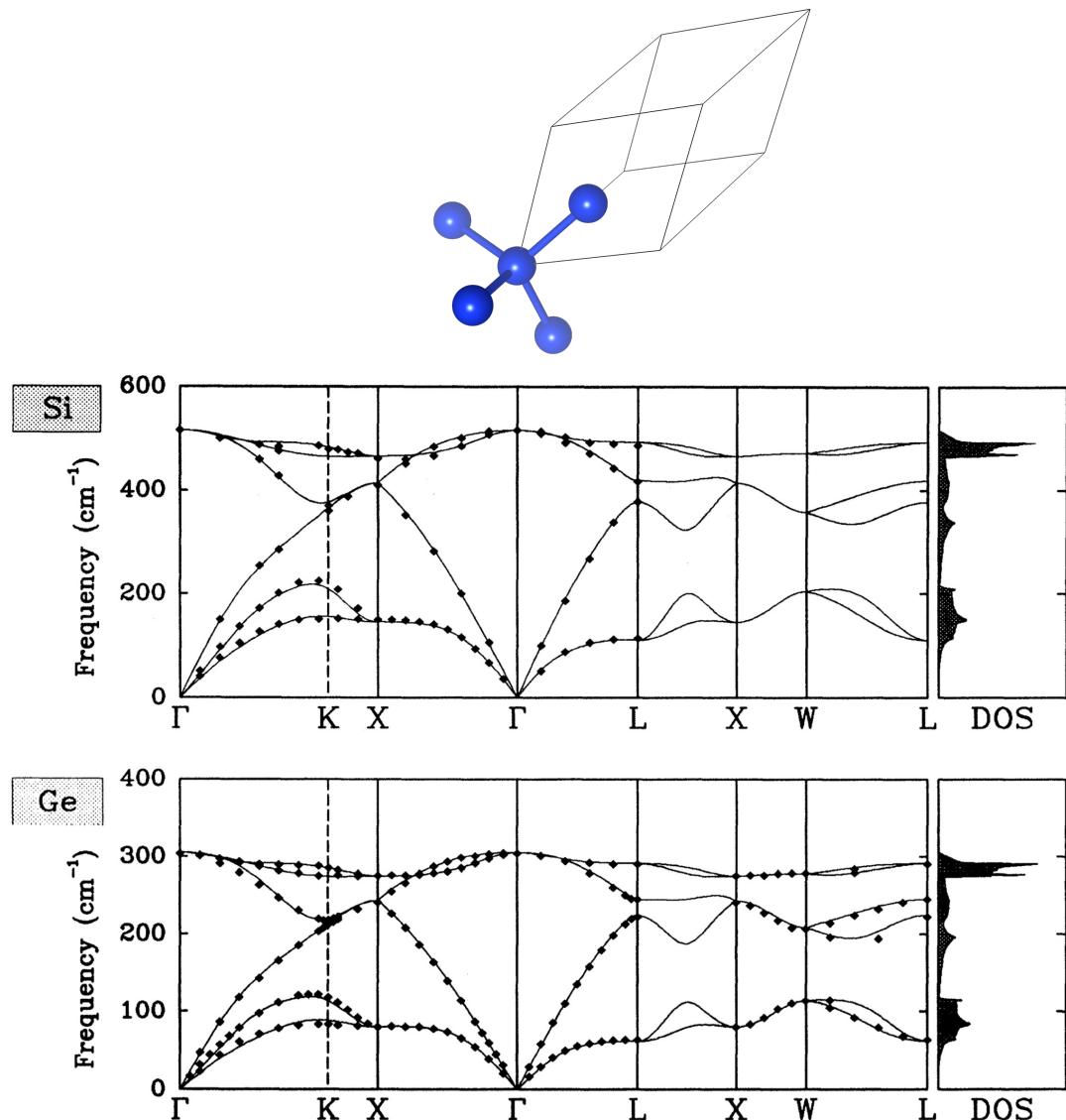


Long-wavelength vibrations in polar materials



Coupling with macroscopic electric field \rightarrow frequency shift (or splitting): $\omega_{LO} = \sqrt{\omega_{TO}^2 + \frac{1}{M} \frac{4\pi Z^*}{\Omega} \frac{Z^*}{\epsilon^\infty}}$

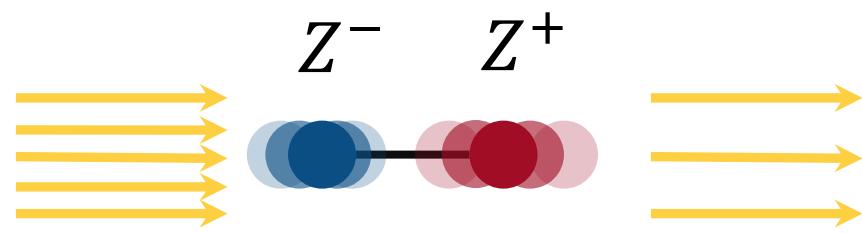
Examples: GaAs and AlAs



Summary

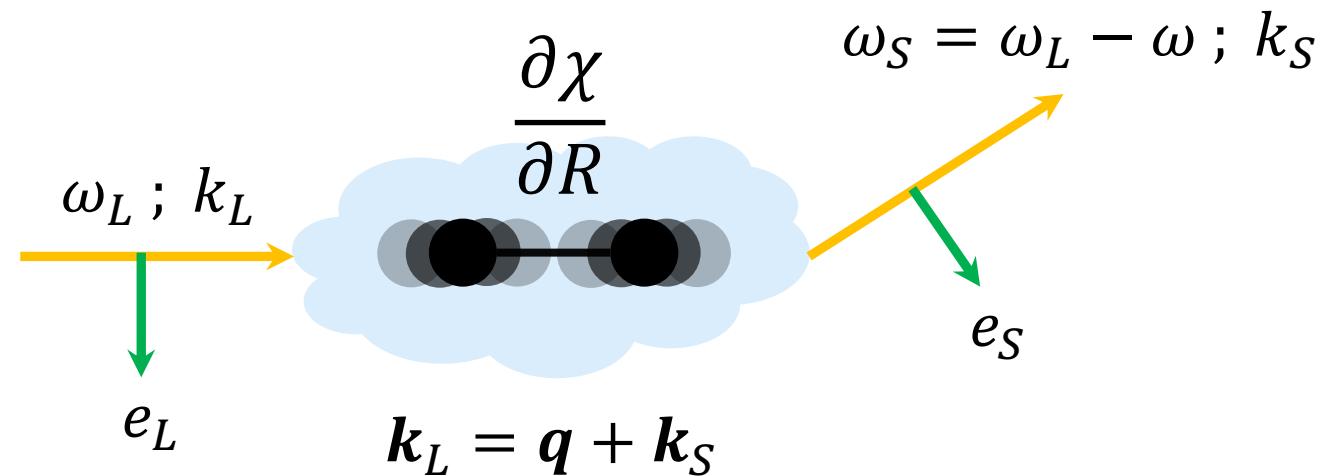
- The potential energy surface $E(\{R\})$ is responsible for many different observables.
- The **harmonic approximation** provides information on the **dynamics** and **stability** of the system.
- In **solids**, there are infinite frequencies described in Fourier space by a **phonon dispersion**.
- The **vibrational modes** can be **observed** using interaction **with light (IR)**.
- **Vibrational modes and IR absorption** can be computed **using DFT** coupled with more advanced techniques (finite differences, DFPT).

How to compute infrared intensities?



$$I_{IR} \propto \frac{|Z^+ - Z^-|^2}{\omega}$$

$$Z_{I,ij}^* = \Omega \frac{\partial \mathbf{P}_i}{\partial \mathbf{R}_j^I} = - \frac{\partial^2 E(\boldsymbol{\varepsilon}, \mathbf{R})}{\partial \boldsymbol{\varepsilon}_i \partial \mathbf{R}_j^I}$$



$$I_{Raman}^{Placzek} \propto \frac{(\omega_L - \omega)^4}{\omega} \left| e_L \frac{\partial \chi}{\partial \mathbf{R}} e_S \right|^2 (n + 1)$$

$$\frac{\partial \chi_{ij}}{\partial \mathbf{R}_k^I} = - \frac{1}{\Omega} \frac{\partial^3 E(\boldsymbol{\varepsilon}, \mathbf{R})}{\partial \boldsymbol{\varepsilon}_i \partial \boldsymbol{\varepsilon}_j \partial \mathbf{R}_k^I}$$

Long-wavelength vibrations in polar materials

$$D(\mathbf{q} \rightarrow \mathbf{0}) = D(\mathbf{q} = \mathbf{0}) + D^{NAC}(\mathbf{q})$$

$$D_{ij,IJ}^{NAC}(\mathbf{q}) = \frac{1}{\sqrt{M_I M_J}} \frac{4\pi}{\Omega} \frac{(Z^* \cdot \mathbf{q})_{iI} (Z^* \cdot \mathbf{q})_{jJ}}{\mathbf{q} \cdot \epsilon^\infty \cdot \mathbf{q}}$$

