Lecture "Vibrations & Phonons"

Dr. Giacomo Melani

Department of Chemistry, University of Zürich

6th African School on Electronic Structure Methods and Applications

Virtual school, 7/06/2021

ASESMA

Outline of this lecture:

- From the Born-Oppenheimer Approximation to Vibrations

- Vibrational Modes from the Harmonic Approximation

- Vibrational Modes in Periodic Systems

- Calculation of phonon band structures

- Limitations of static approaches

Back to the basics: the Born-Oppenheimer Approximation

- Electrons are much lighter than nuclei ($m_p/m_e \sim 2000$)

- Nuclei respond to changes in electronic density quite slowly

- Total wavefunction of the system can be factorized

- *Achtung!* This approximation fails in some cases (eg. photochemistry, molecule-metal scattering, …)

Back to the basics: the Born-Oppenheimer Approximation

- Electrons are much lighter than nuclei ($m_p/m_e \sim 2000$)

- Nuclei respond to changes in electronic density quite slowly

- Total wavefunction of the system can be factorized

- *Achtung!* This approximation fails in some cases (eg. photochemistry, molecule-metal scattering, …)

Necessary in most practical electronic structure calculations!

Back to the basics: the Born-Oppenheimer Approximation

$$\Psi_{tot}(\underline{r},\underline{R}) = \psi_{el}(\underline{r};\underline{R})\chi_{NU}(\underline{R}) \qquad E_{tot} = E_{el} + E_{Nu}$$

Back to the basics: the Born-Oppenheimer Approximation

$$\Psi_{tot}(\underline{r},\underline{R})=\psi_{el}(\underline{r};\underline{R})\chi_{NU}(\underline{R}) \qquad E_{tot}=E_{el}+E_{Nu}$$

$$\hat{H}_{el}\psi_{el}(\underline{r};\underline{R})=E_{el}\psi_{el}(\underline{r};\underline{R})$$

$$\hat{H}_{el}=-\frac{1}{2}\sum_{i}^{N}\nabla_{i}^{2}+\sum_{i}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}}-\sum_{i}^{N}\sum_{\alpha}^{M}\frac{Z_{\alpha}}{r_{i\alpha}}$$

ASESMA

Back to the basics: the Born-Oppenheimer Approximation

$$\Psi_{tot}(\underline{r},\underline{R}) = \psi_{el}(\underline{r};\underline{R})\,\chi_{NU}(\underline{R}) \qquad E_{tot} = E_{el} + E_{Nu}$$

$$\hat{H}_{el}\,\psi_{el}(\underline{r};\underline{R}) = E_{el}\,\psi_{el}(\underline{r};\underline{R})$$

$$\hat{H}_{Nu}\,\chi_{Nu}(\underline{R}) = E_{Nu}\,\chi_{Nu}(\underline{R})$$

$$\hat{H}_{el} = -\frac{1}{2}\sum_i^N \nabla_i^2 + \sum_i^N\sum_{j>i}^N \frac{1}{r_{ij}} - \sum_i^N\sum_\alpha^M \frac{Z_\alpha}{r_{i\alpha}}$$

$$\hat{H}_{Nu} = -\frac{1}{2}\sum_\alpha^M \nabla_\alpha^2 + \sum_\alpha^M\sum_{\beta>\alpha}^M \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} + E_{el} = -\frac{1}{2}\sum_\alpha^M \nabla_\alpha^2 + V_{el}(\underline{R})$$

ASESMA

Back to the basics: the Born-Oppenheimer Approximation

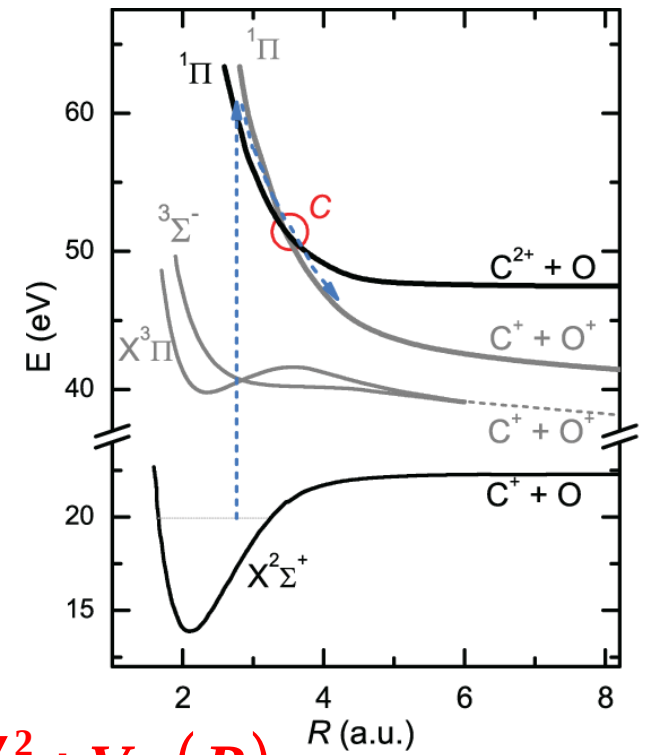$$\Psi_{tot}(\underline{r},\underline{R})=\psi_{el}(\underline{r};\underline{R})\chi_{NU}(\underline{R}) \qquad E_{tot}=E_{el}+E_{Nu}$$

$$\hat{H}_{el}\psi_{el}(\underline{r};\underline{R})=E_{el}\psi_{el}(\underline{r};\underline{R})$$

$$\hat{H}_{Nu}\chi_{Nu}(\underline{R})=E_{Nu}\chi_{Nu}(\underline{R})$$

$$\hat{H}_{el}=-\frac{1}{2}\sum_{i}^{N}\nabla_{i}^{2}+\sum_{i}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}}-\sum_{i}^{N}\sum_{\alpha}^{M}\frac{Z_{\alpha}}{r_{i\alpha}}$$

$$\hat{H}_{Nu}=-\frac{1}{2}\sum_{\alpha}^{M}\nabla_{\alpha}^{2}+\sum_{\alpha}^{M}\sum_{\beta>\alpha}^{M}\frac{Z_{\alpha}Z_{\beta}}{R_{\alpha\beta}}+E_{el}=-\frac{1}{2}\sum_{\alpha}^{M}\nabla_{\alpha}^{2}+V_{el}(\underline{R})$$

Towards vibrations: the Harmonic Approximation

- For small deviations of nuclear coordinate, we can expand the

  potential energy in a Taylor series:

Towards vibrations: the Harmonic Approximation

- For small deviations of nuclear coordinate, we can expand the potential energy in a Taylor series:

$$V(R) \approx V(R_0) + \left|\frac{\partial V}{\partial R}\right|_{R_0} \Delta R + \frac{1}{2!}\left|\frac{\partial^2 V}{\partial R^2}\right|_{R_0} \Delta R^2 + \frac{1}{3!}\left|\frac{\partial^3 V}{\partial R^3}\right|_{R_0} \Delta R^3 + \dots$$

University of Zurich UZH

Towards vibrations: the Harmonic Approximation

- For small deviations of nuclear coordinate, we can expand the potential energy in a Taylor series:

$$V(R) \approx V(R_0) + \left|\frac{\partial V}{\partial R}\right|_{R_0} \Delta R + \frac{1}{2!}\left|\frac{\partial^2 V}{\partial R^2}\right|_{R_0} \Delta R^2 + \frac{1}{3!}\left|\frac{\partial^3 V}{\partial R^3}\right|_{R_0} \Delta R^3 + \dots$$

- If we generalize for a multidimensional, polyatomic case:

$$V(\underline{R}) \approx V(\underline{R_0}) + \sum_{\alpha}^{M}\sum_{\mu}^{3}\left|\frac{\partial V}{\partial R_{\mu,\alpha}}\right|_{\underline{R_0}} \Delta R_{\mu,\alpha} + \frac{1}{2}\sum_{\alpha,\beta}^{M}\sum_{\mu,\nu}^{3}\left|\frac{\partial^2 V}{\partial R_{\mu,\alpha}\partial R_{\nu,\beta}}\right|_{\underline{R_0}} \Delta R_{\mu,\alpha} \Delta R_{\nu,\beta}$$

$$\Delta R_{\mu,\alpha} = s_{\mu,\alpha}$$

ASESMA

Towards vibrations: the Harmonic Approximation

$$V(\underline{R}) \approx V(\underline{R}_0) + \sum_{\alpha}^{M} \sum_{\mu}^{3} \left| \frac{\partial V}{\partial R_{\mu,\alpha}} \right|_{\underline{R}_0} s_{\mu,\alpha} + \frac{1}{2} \sum_{\alpha,\beta}^{M} \sum_{\mu,\nu}^{3} \left| \frac{\partial^2 V}{\partial R_{\mu,\alpha} \partial R_{\nu,\beta}} \right|_{\underline{R}_0} s_{\mu,\alpha} s_{\nu,\beta}$$

Towards vibrations: the Harmonic Approximation

$$V(\underline{R}) \approx V(\underline{R}_0) + \sum_{\alpha}^{M} \sum_{\mu}^{3} \left. \cancel{\frac{\partial V}{\partial R_{\mu,\alpha}}} \right|_{\underline{R}_0} s_{\mu,\alpha} + \frac{1}{2} \sum_{\alpha,\beta}^{M} \sum_{\mu,\nu}^{3} \underbrace{\left. \frac{\partial^2 V}{\partial R_{\mu,\alpha} \partial R_{\nu,\beta}} \right|_{\underline{R}_0}}_{} s_{\mu,\alpha} s_{\nu,\beta}$$

= 0, because we are equilibrium position

= Φ, Hessian Matrix

Towards vibrations: the Harmonic Approximation

$$V(\underline{R}) \approx V(\underline{R}_0) + \sum_{\alpha}^{M}\sum_{\mu}^{3}\left.\frac{\partial V}{\partial R_{\mu,\alpha}}\right|_{\underline{R}_0} s_{\mu,\alpha} + \frac{1}{2}\sum_{\alpha,\beta}^{M}\sum_{\mu,\nu}^{3}\left.\frac{\partial^2 V}{\partial R_{\mu,\alpha}\partial R_{\nu,\beta}}\right|_{\underline{R}_0} s_{\mu,\alpha}s_{\nu,\beta}$$

= 0, because we are equilibrium position

= Φ, Hessian Matrix

$$\hat{H}_{Nu}(\underline{R}) = \frac{1}{2}\sum_{\alpha}^{M}\frac{1}{m_{\alpha}}\nabla^2_{\alpha} + V(\underline{R}_0) + \frac{1}{2}\sum_{\alpha,\beta}^{M}\sum_{\mu,\nu}^{3}\Phi^{\mu,\nu}_{\alpha,\beta}s_{\mu,\alpha}s_{\nu,\beta}$$

University of Zurich[UZH]

Towards vibrations: the Harmonic Approximation

$$V(\underline{R}) \approx V(\underline{R_0}) + \sum_\alpha^M \sum_\mu^3 \left. \frac{\partial V}{\partial R_{\mu,\alpha}} \right|_{\underline{R_0}} s_{\mu,\alpha} + \frac{1}{2} \sum_{\alpha,\beta}^M \sum_{\mu,\nu}^3 \left. \frac{\partial^2 V}{\partial R_{\mu,\alpha} \partial R_{\nu,\beta}} \right|_{\underline{R_0}} s_{\mu,\alpha} s_{\nu,\beta}$$

= 0, because we are equilibrium position

= Φ, Hessian Matrix

$$\hat{H}_{Nu}(\underline{R}) = \frac{1}{2} \sum_\alpha^M \frac{1}{m_\alpha} \nabla_\alpha^2 + V(\underline{R_0}) + \frac{1}{2} \sum_{\alpha,\beta}^M \sum_{\mu,\nu}^3 \Phi_{\alpha,\beta}^{\mu,\nu} s_{\mu,\alpha} s_{\nu,\beta}$$

Let's now consider the classical EOM for each α-nucleus:

$$F_{\alpha,\mu} = m_\alpha \frac{d^2 s_{\alpha,\mu}}{dt^2} = \sum_\beta^M \sum_\nu^3 \Phi_{\alpha,\beta}^{\mu,\nu} s_{\nu,\beta} \longrightarrow$$

Time-dependent ansatz (nuclei are not frozen!)

ASESMA

From vibrations to phonons: The case of periodic systems

$$F_{\alpha,\mu} = m_\alpha \frac{d^2 s_{\alpha,\mu}}{dt^2} = -\sum_\beta^M \sum_\nu^3 \Phi_{\alpha,\beta}^{\mu,\nu} s_{\nu,\beta} \longrightarrow$$

Time-dependent ansatz

$$s_{\mu,\alpha}(t) = u_{\alpha,\mu} e^{i\omega t}$$

From vibrations to phonons: The case of periodic systems

Time-dependent ansatz

$$F_{\alpha,\mu} = m_\alpha \frac{d^2 s_{\alpha,\mu}}{dt^2} = -\sum_\beta^M \sum_\nu^3 \Phi_{\alpha,\beta}^{\mu,\nu} s_{\nu,\beta} \longrightarrow \boxed{s_{\mu,\alpha}(t) = u_{\alpha,\mu} e^{i\omega t}}$$

$$m_\alpha \omega^2 u_{\alpha,\mu} = \sum_\beta^M \sum_\nu^3 \Phi_{\alpha,\beta}^{\mu,\nu} u_{\beta,\nu}$$

From vibrations to phonons: The case of periodic systems

$$F_{\alpha,\mu} = m_\alpha \frac{d^2 s_{\alpha,\mu}}{dt^2} = -\sum_\beta^M \sum_\nu^3 \Phi_{\alpha,\beta}^{\mu,\nu} s_{\nu,\beta}$$

Time-dependent ansatz

$$s_{\mu,\alpha}(t) = u_{\alpha,\mu} e^{i\omega t}$$

$$m_\alpha \omega^2 u_{\alpha,\mu} = \sum_\beta^M \sum_\nu^3 \Phi_{\alpha,\beta}^{\mu,\nu} u_{\beta,\nu}$$

$$u_{\alpha,\mu} = \frac{1}{\sqrt{m_\alpha}} c_{\alpha,\mu} e^{i q \underline{L}_n}$$

$\underline{L}_n$ is the Bravais lattice vector

From vibrations to phonons: The case of periodic systems

$$F_{\alpha,\mu} = m_\alpha \frac{d^2 s_{\alpha,\mu}}{dt^2} = -\sum_\beta^M \sum_\nu^3 \Phi_{\alpha,\beta}^{\mu,\nu} s_{\nu,\beta}$$

Time-dependent ansatz

$$s_{\mu,\alpha}(t) = u_{\alpha,\mu} e^{i\omega t}$$

$$m_\alpha \omega^2 u_{\alpha,\mu} = \sum_\beta^M \sum_\nu^3 \Phi_{\alpha,\beta}^{\mu,\nu} u_{\beta,\nu}$$

$$u_{\alpha,\mu} = \frac{1}{\sqrt{m_\alpha}} c_{\alpha,\mu} e^{iq \underline{L}_n}$$

$\underline{L}_n$ *is the Bravais lattice vector*

$$\omega^2 c_{\alpha,\mu} = \sum_\beta^M \sum_\nu^3 D_{\alpha,\beta}^{\mu,\nu}(q) c_{\beta,\nu}$$

$$\omega^2 \underline{c} = \underline{\underline{D}}(q) \underline{c}$$

From vibrations to phonons: The case of periodic systems

Time-dependent ansatz

$$F_{\alpha,\mu} = m_\alpha \frac{d^2 s_{\alpha,\mu}}{dt^2} = -\sum_\beta^M \sum_\nu^3 \Phi_{\alpha,\beta}^{\mu,\nu} s_{\nu,\beta} \longrightarrow \boxed{s_{\mu,\alpha}(t) = u_{\alpha,\mu} e^{i\omega t}}$$

$$m_\alpha \omega^2 u_{\alpha,\mu} = \sum_\beta^M \sum_\nu^3 \Phi_{\alpha,\beta}^{\mu,\nu} u_{\beta,\nu} \longrightarrow u_{\alpha,\mu} = \frac{1}{\sqrt{m_\alpha}} c_{\alpha,\mu} e^{i q \underline{L}_n} \quad \underline{L}_n \text{ is the Bravais lattice vector}$$

$$\omega^2 c_{\alpha,\mu} = \sum_\beta^M \sum_\nu^3 D_{\alpha,\beta}^{\mu,\nu}(q) c_{\beta,\nu} \implies \omega^2 \underline{c} = \underline{\underline{D}}(q) \underline{c}$$

Dynamical matrix

From vibrations to phonons: The case of periodic systems

Time-dependent ansatz

$$F_{\alpha,\mu} = m_\alpha \frac{d^2 s_{\alpha,\mu}}{dt^2} = -\sum_\beta^M \sum_\nu^3 \Phi_{\alpha,\beta}^{\mu,\nu} s_{\nu,\beta} \longrightarrow \boxed{s_{\mu,\alpha}(t) = u_{\alpha,\mu} e^{i\omega t}}$$

$$m_\alpha \omega^2 u_{\alpha,\mu} = \sum_\beta^M \sum_\nu^3 \Phi_{\alpha,\beta}^{\mu,\nu} u_{\beta,\nu} \longrightarrow u_{\alpha,\mu} = \frac{1}{\sqrt{m_\alpha}} c_{\alpha,\mu} e^{i q \underline{L}_n} \quad \underline{L}_n \text{ is the Bravais lattice vector}$$

$$\omega^2 c_{\alpha,\mu} = \sum_\beta^M \sum_\nu^3 D_{\alpha,\beta}^{\mu,\nu}(q) c_{\beta,\nu} \quad \Longrightarrow \quad \omega^2 \underline{c} = \underline{\underline{D}}(q) \underline{c}$$

Dynamical matrix

Two different ways to compute it:
- finite differences
- linear response (DFPT)*

From vibrations to phonons: The case of periodic systems

Time-dependent ansatz

$$F_{\alpha,\mu} = m_\alpha \frac{d^2 s_{\alpha,\mu}}{dt^2} = -\sum_\beta^M \sum_\nu^3 \Phi_{\alpha,\beta}^{\mu,\nu} s_{\nu,\beta} \longrightarrow \boxed{s_{\mu,\alpha}(t) = u_{\alpha,\mu} e^{i\omega t}}$$

$$m_\alpha \omega^2 u_{\alpha,\mu} = \sum_\beta^M \sum_\nu^3 \Phi_{\alpha,\beta}^{\mu,\nu} u_{\beta,\nu} \longrightarrow u_{\alpha,\mu} = \frac{1}{\sqrt{m_\alpha}} c_{\alpha,\mu} e^{i q \underline{L}_n} \quad \underline{L}_n \text{ is the Bravais lattice vector}$$

$$\omega^2 c_{\alpha,\mu} = \sum_\beta^M \sum_\nu^3 \underbrace{D_{\alpha,\beta}^{\mu,\nu}(q)}_{} c_{\beta,\nu} \implies \omega^2 \underline{c} = \underline{\underline{D}}(q) \underline{c}$$

Dynamical matrix

Two different ways to compute it:
- *finite differences*
- *linear response (DFPT)**

*S. Baroni et al., Rev. Mod. Phys. 73, 515 (2001)

From vibrations to phonons: The case of periodic systems

Time-dependent ansatz

$$F_{\alpha,\mu} = m_\alpha \frac{d^2 s_{\alpha,\mu}}{dt^2} = -\sum_\beta^M \sum_\nu^3 \Phi_{\alpha,\beta}^{\mu,\nu} s_{\nu,\beta} \longrightarrow \boxed{s_{\mu,\alpha}(t) = u_{\alpha,\mu} e^{i\omega t}}$$

$$m_\alpha \omega^2 u_{\alpha,\mu} = \sum_\beta^M \sum_\nu^3 \Phi_{\alpha,\beta}^{\mu,\nu} u_{\beta,\nu} \longrightarrow u_{\alpha,\mu} = \frac{1}{\sqrt{m_\alpha}} c_{\alpha,\mu} e^{iq L_n}$$

$\underline{L}_n$ *is the Bravais lattice vector*

$$\omega^2 c_{\alpha,\mu} = \sum_\beta^M \sum_\nu^3 D_{\alpha,\beta}^{\mu,\nu}(q) c_{\beta,\nu} \implies \omega^2 \underline{c} = \underline{\underline{D}}(\underline{q}) \underline{c}$$

Solutions: phonon frequencies in $\underline{q}$-space!

$$\boxed{\omega = \omega_i(\underline{q}), i = 1, 2, \ldots, 3M}$$

From vibrations to phonons: The case of periodic systems
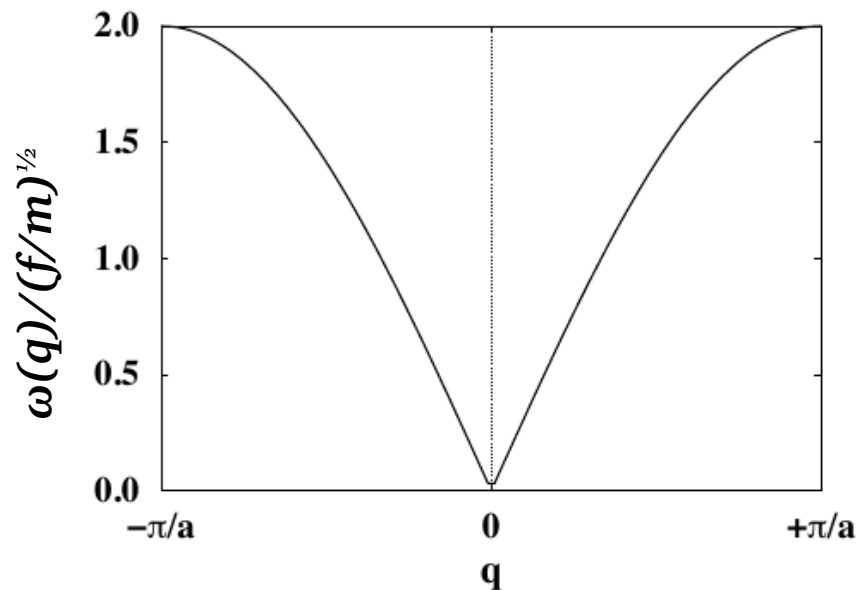
- Linear chain with one atom per unit cell:
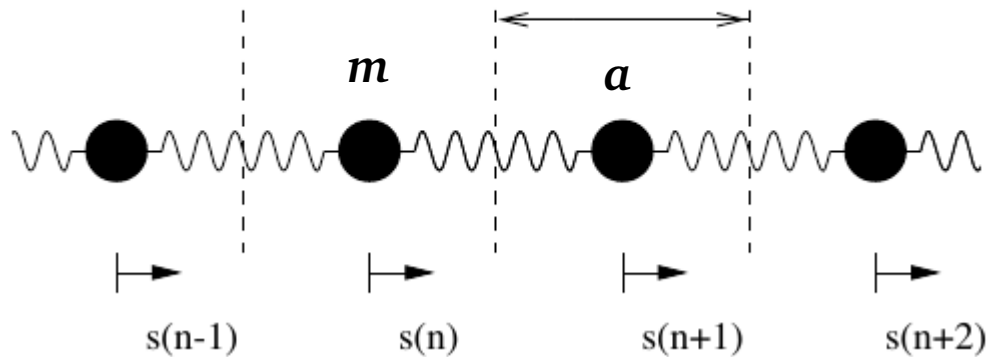
From vibrations to phonons: The case of periodic systems
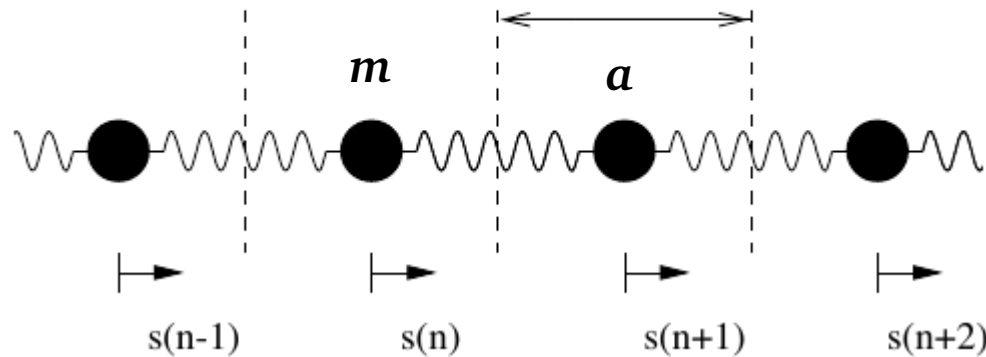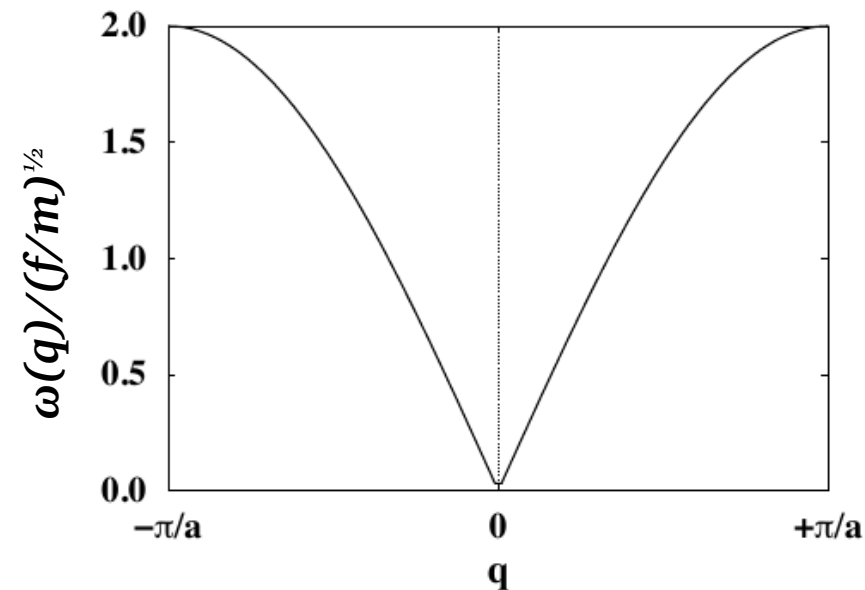
- Linear chain with one atom per unit cell:
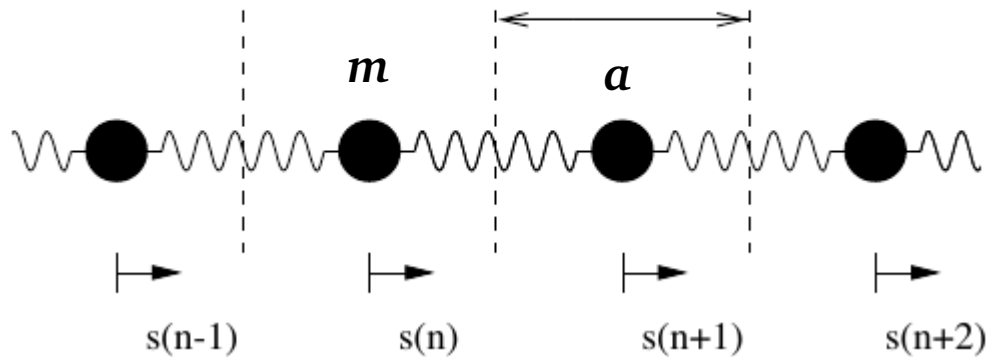
$$D(q) = \frac{f}{m}\left(2 - e^{iqa} - e^{-iqa}\right)$$

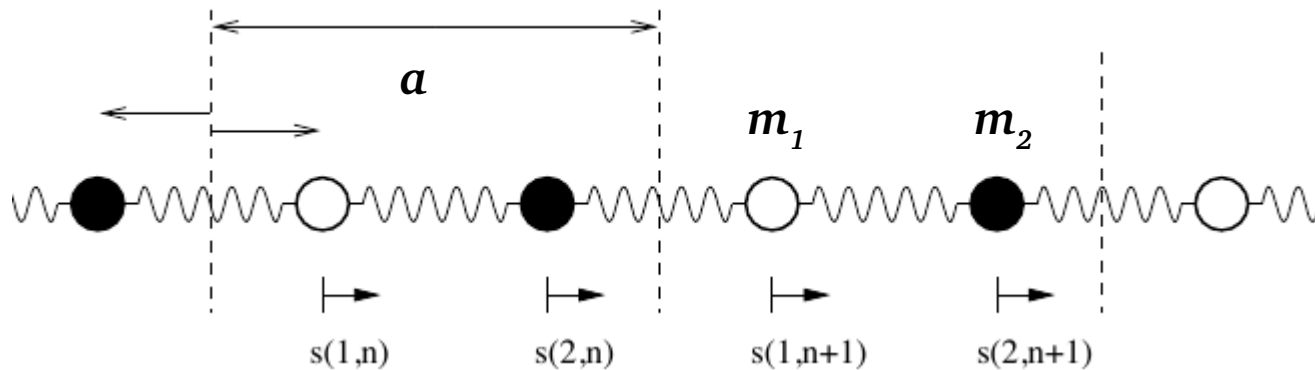$$\omega(q) = 2\sqrt{\frac{f}{m}}\left|\sin\left(\frac{qa}{2}\right)\right|$$

From vibrations to phonons: The case of periodic systems

- Linear chain with one atom per unit cell:

$$D(q) = \frac{f}{m}\left(2 - e^{iqa} - e^{-iqa}\right)$$

$$\omega(q) = 2\sqrt{\frac{f}{m}}\left|\sin\left(\frac{qa}{2}\right)\right|$$

Acoustic branches:

- *For $q \to 0$, $\omega \approx aq(f/m)^{1/2}$: sound wave;*
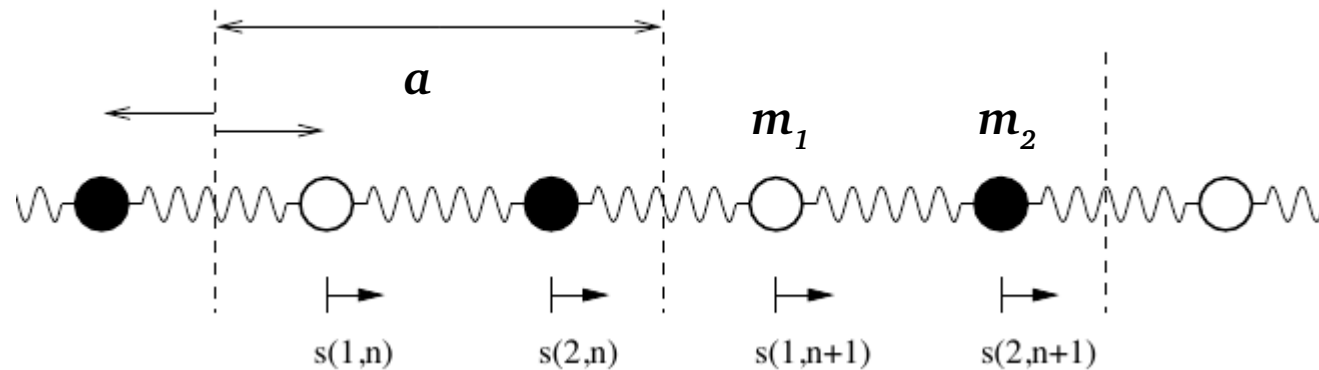- *Notable exceptions for some materials: graphene has a parabolic dispersion around Γ-point*

From vibrations to phonons: The case of periodic systems

- Linear chain with two different atoms per unit cell:

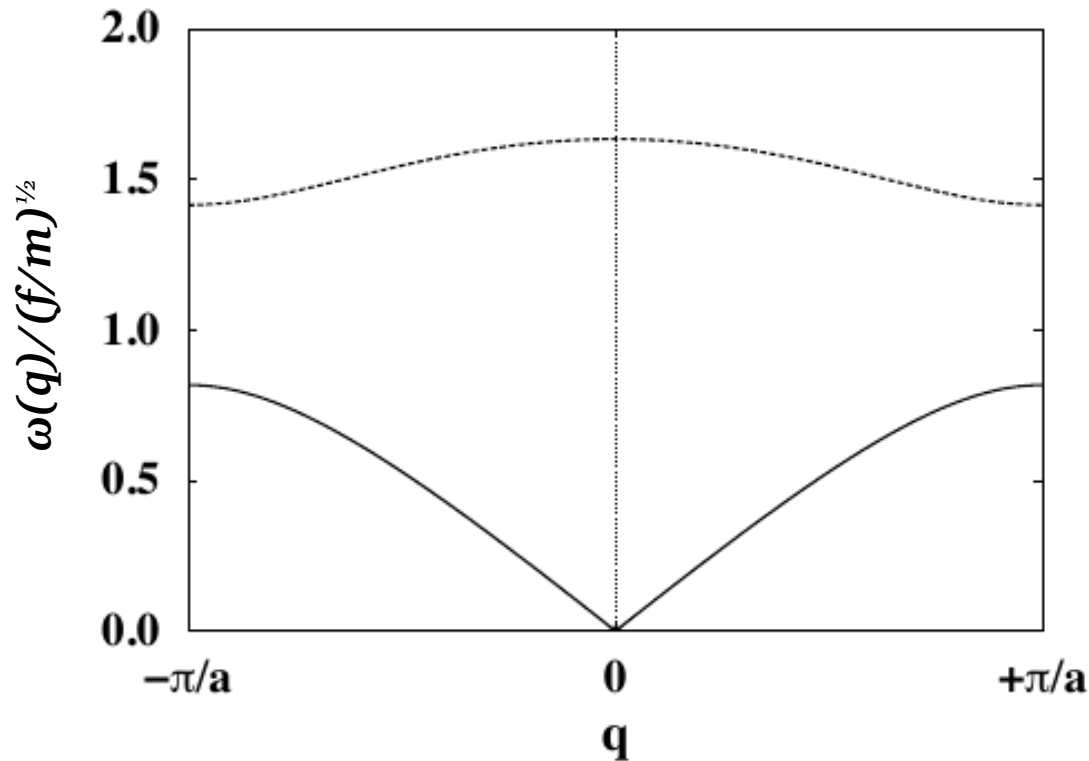# From vibrations to phonons: The case of periodic systems

- Linear chain with two different atoms per unit cell:

$$\omega(q)^2_{1,2} = f\left(\frac{1}{m_1} + \frac{1}{m_2}\right) \pm f\sqrt{\left(\frac{1}{m_1} + \frac{1}{m_2}\right)^2 - \frac{4}{m_1 m_2}\sin^2\left(\frac{qa}{2}\right)}$$

From vibrations to phonons: The case of periodic systems

- Linear chain with two different atoms per unit cell:

Optical branches:

- *Both atoms in the unit cell vibrate against each other;*
- *In ionic crystals these modes can be coupled to electromagnetic radiation*
- *At the borders of the BZ we have a gap opening between acoustic and optical branches.*

Statistical mechanics of phonons:

- The solution of the nuclear Hamiltonian for the lattice gives:

$$E^{vib} = \sum_i^{3M} \sum_q \hbar \omega_i(q) \left[n_i(q) + \frac{1}{2} \right]$$

Statistical mechanics of phonons:

- The solution of the nuclear Hamiltonian for the lattice gives:

$$E^{vib} = \sum_i^{3M} \sum_q \hbar \omega_i(q) \left[n_i(q) + \frac{1}{2} \right]$$

- Phonons are bosons, with occupation number:

$$n_i(q) = \left[e^{\frac{\hbar \omega_i(q)}{k_B T}} - 1 \right]^{-1}$$

→ *Occupation is not restricted to 0 or 1, like in the Fermi-Dirac statistics*

ASESMA

Statistical mechanics of phonons:

- The solution of the nuclear Hamiltonian for the lattice gives:

$$E^{vib} = \sum_i^{3M} \sum_q \hbar\omega_i(q)\left[n_i(q) + \frac{1}{2}\right]$$

- Phonons are bosons, with occupation number:

$$n_i(q) = \left[e^{\frac{\hbar\omega_i(q)}{k_B T}} - 1\right]^{-1}$$

Occupation is not restricted to 0 or 1, like in the Fermi-Dirac statistics

- At finite temperature, the average energy per phonon is:

$$\langle E \rangle_i(T, \omega(q)) = \hbar\omega_i(q)\left[\frac{1}{e^{\frac{\hbar\omega_i(q)}{k_B T}} - 1} + \frac{1}{2}\right]$$

ASESMA

Statistical mechanics of phonons:

- Summing over all modes we get the phonon Density of States:

$$g(\omega) = \frac{1}{(2\pi)^3} \sum_i^{3M} \int d\boldsymbol{q}\, \delta\big(\omega - \omega_i(\boldsymbol{q})\big)$$

Statistical mechanics of phonons:

- Summing over all modes we get the phonon Density of States:

$$g(\omega) = \frac{1}{(2\pi)^3} \sum_i^{3M} \int d\boldsymbol{q}\, \delta(\omega - \omega_i(\boldsymbol{q}))$$
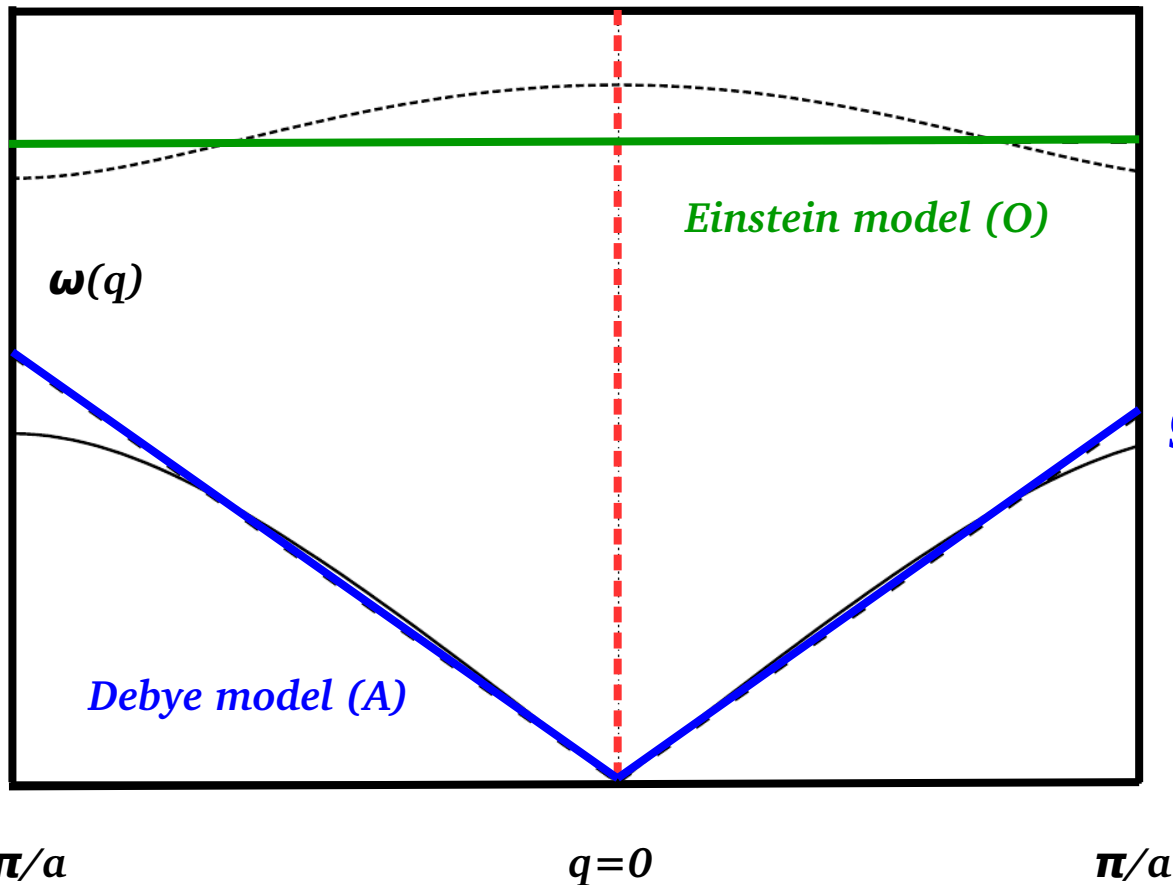
- We can then re-express the lattice vibrational energy:

$$E^{vib}(T) = V \int_0^\infty d\omega\, g(\omega) \left[\frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} + \frac{1}{2} \right] \hbar\omega$$

Statistical mechanics of phonons:

- Summing over all modes we get the phonon Density of States:

$$g(\omega) = \frac{1}{(2\pi)^3} \sum_i^{3M} \int d\boldsymbol{q} \, \delta(\omega - \omega_i(\boldsymbol{q}))$$

- We can then re-express the lattice vibrational energy:

$$E^{vib}(T) = V \int_0^\infty d\omega \, g(\omega) \left[\frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} + \frac{1}{2} \right] \hbar\omega$$

- And even define other thermodynamic quantities:

$$c_V^{vib}(T) = \frac{1}{V} \left| \frac{\partial E^{vib}(T)}{\partial T} \right|_V = \frac{\partial}{\partial T} \int_0^\infty d\omega \, g(\omega) \left[\frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} + \frac{1}{2} \right] \hbar\omega$$
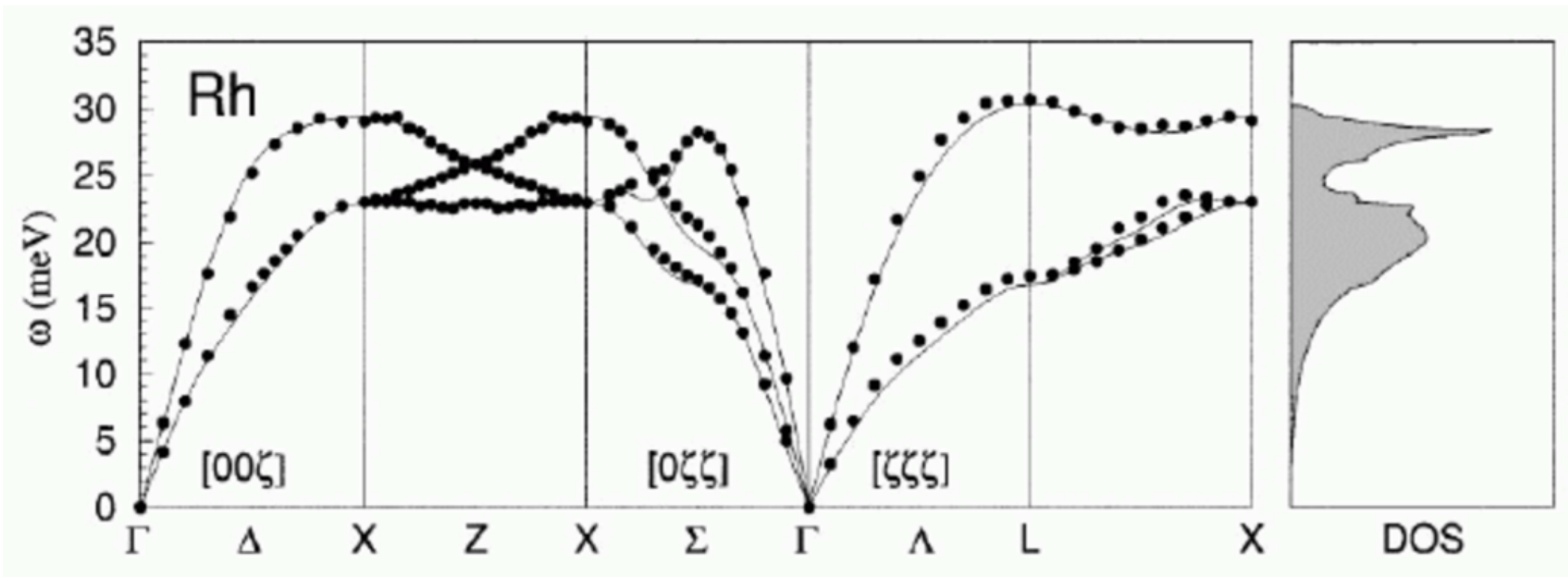
Statistical mechanics of phonons:

- Simple models can be used to approximate phonon bands:
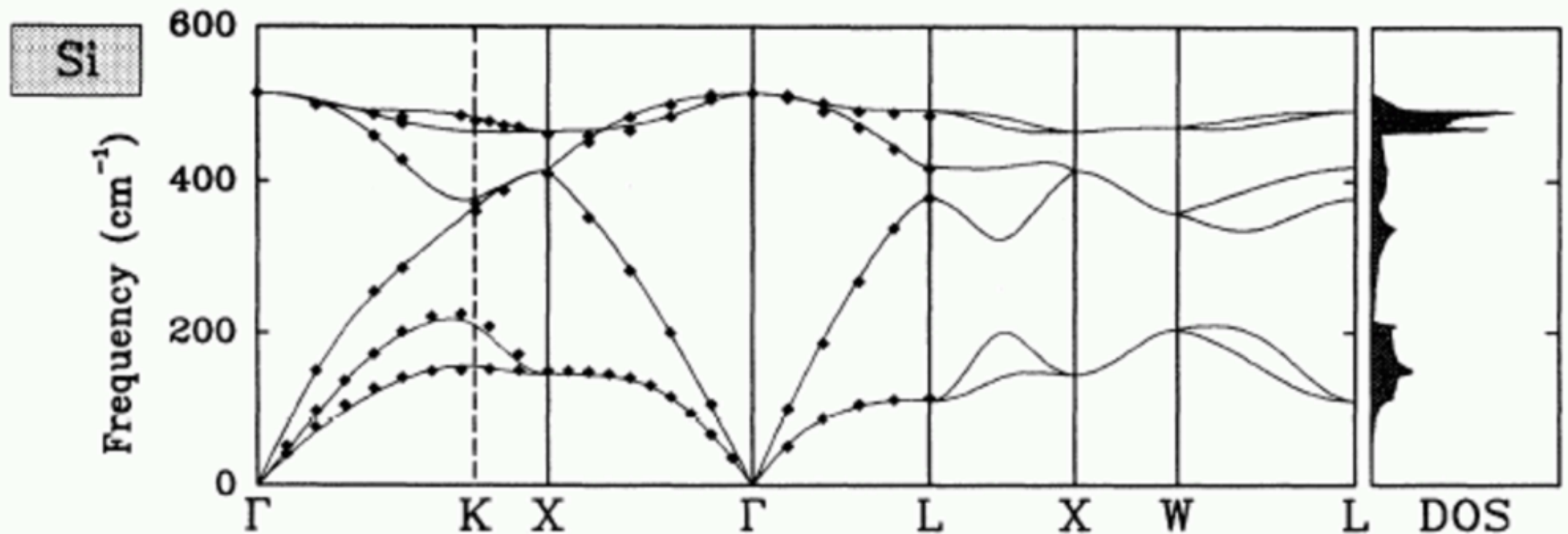
$$g_E(\omega) = \frac{3M}{V}\delta(\omega - \omega_E)$$

Einstein model (O)

$\omega(q)$

$$g(\omega) = \frac{3}{(2\pi)^3}\int dq^3\,\delta(\omega - v_g|q|)$$

Debye model (A)

$-\pi/a$ $q=0$ π/a

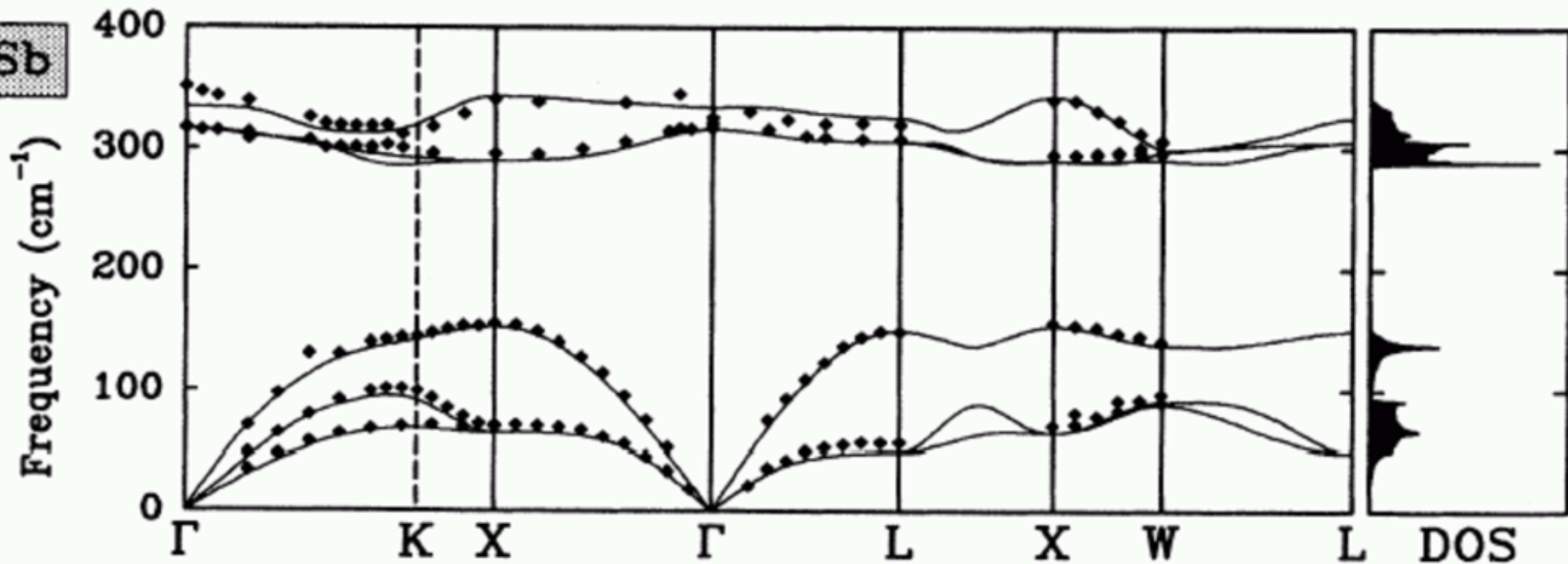# Calculation of phonon dispersion curves: A few examples

DFT-LDA vs experimental curves for bulk fcc Rhodium
(from R. Heid et al. Physica B, 263, 432 (1990))

# Calculation of phonon dispersion curves: A few examples

DFT-LDA vs experimental curves for bulk Silicon
(from P. Giannozzi et al. Phys. Rev. B, 43, 7231 (1991))

# Calculation of phonon dispersion curves: A few examples

DFT-LDA vs experimental curves for bulk AlSb (same crystal structure as Si) (also from P. Giannozzi et al. Phys. Rev. B, 43, 7231 (1991))

Limitations of this approaches to get phonons:
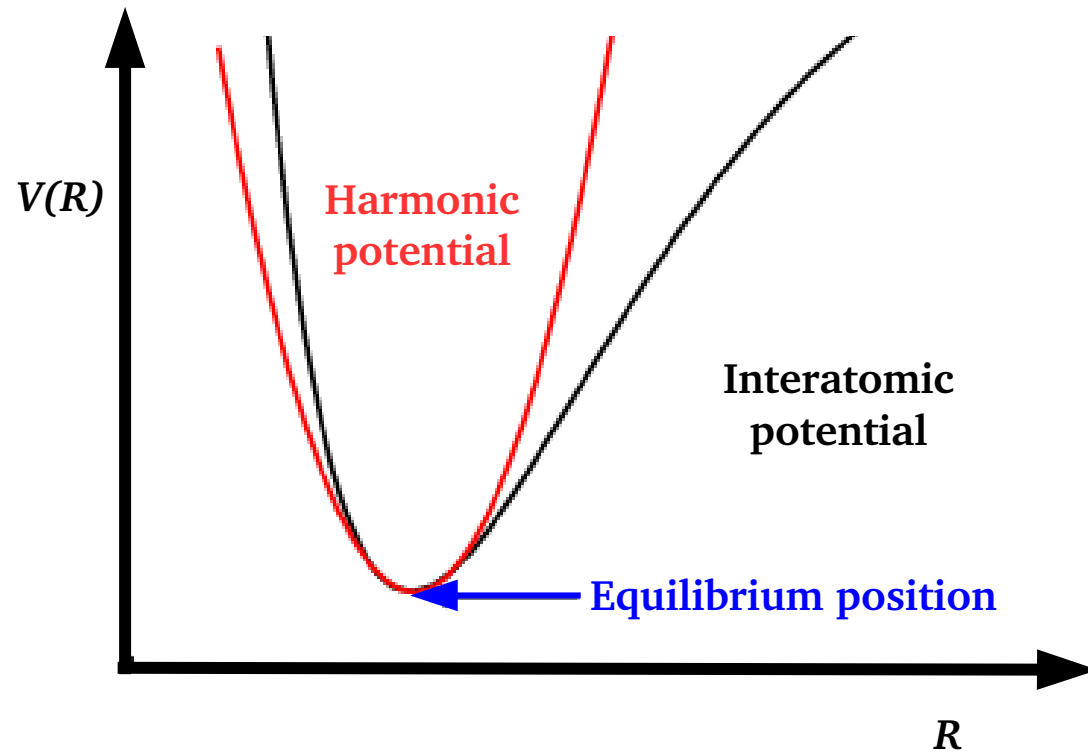
- The harmonic approximation is only valid for small deviations from the equilibrium structure.
- Each mode is treated as independent from the others (i.e. no couplings).
- At high temperature, anharmonicity becomes important.
- For structures with many possible quasi-degenerate minima, imaginary modes can appear.
- Not suitable for non-equilibrium properties (like heat transport) or dynamical processes.

Limitations of this approaches to get phonons:
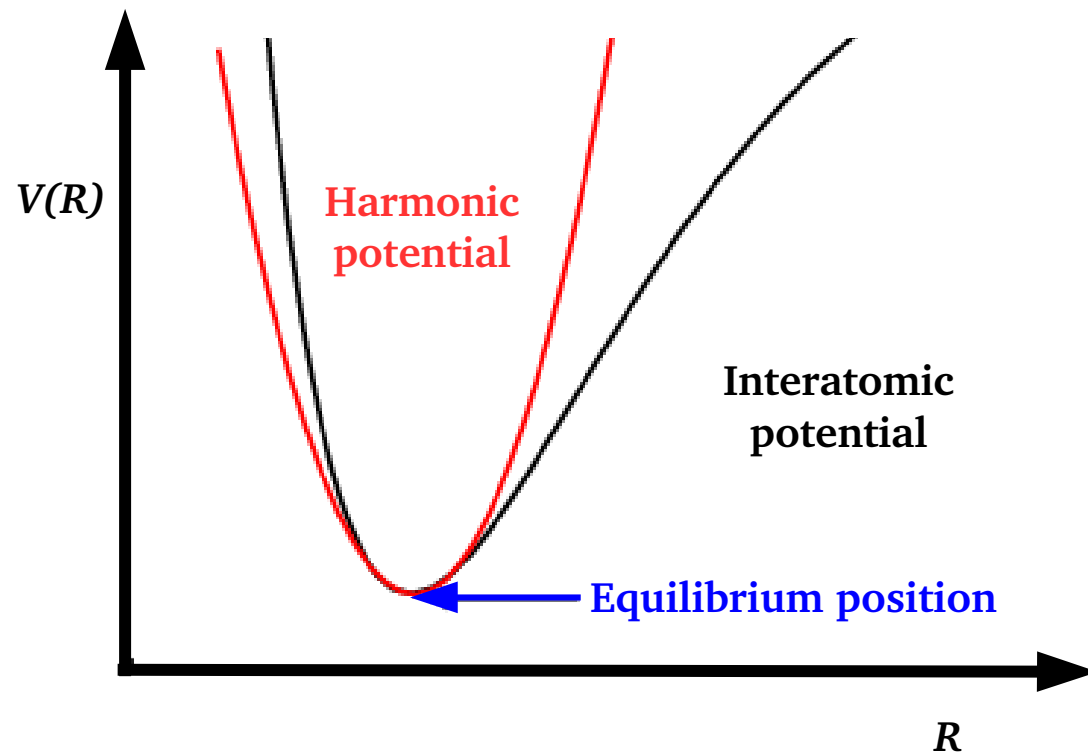
$V(R)$

Harmonic potential

Interatomic potential

Equilibrium position

R

- The harmonic approximation is only valid for small deviations from the equilibrium structure.
- Each mode is treated as independent from the others (i.e. no couplings).
- At high temperature, anharmonicity becomes important.
- For structures with many possible quasi-degenerate minima, imaginary modes can appear.
- Not suitable for non-equilibrium properties (like heat transport) or dynamical processes.

For everything related to motion, we need MOLECULAR DYNAMICS (→ tomorrow!)

Thank you very much for your attention!