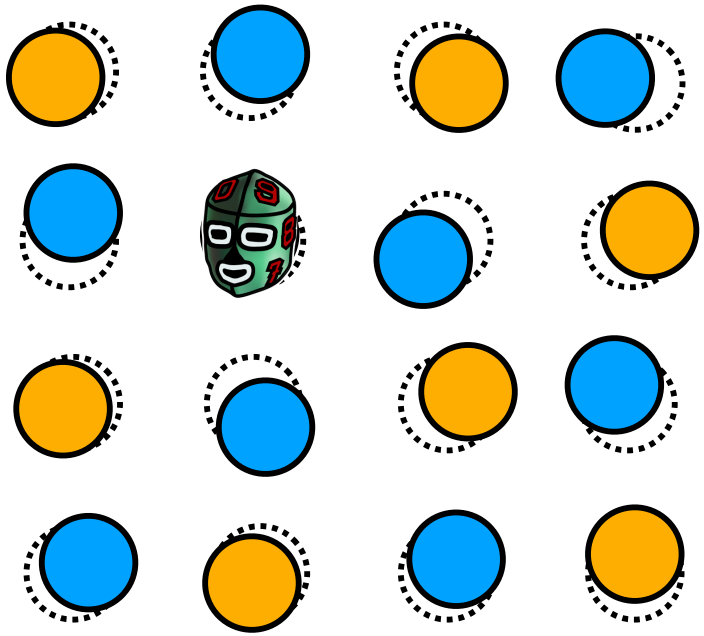
Anharmonic phonons with TDEP + SIESTA



Matthieu Verstraete
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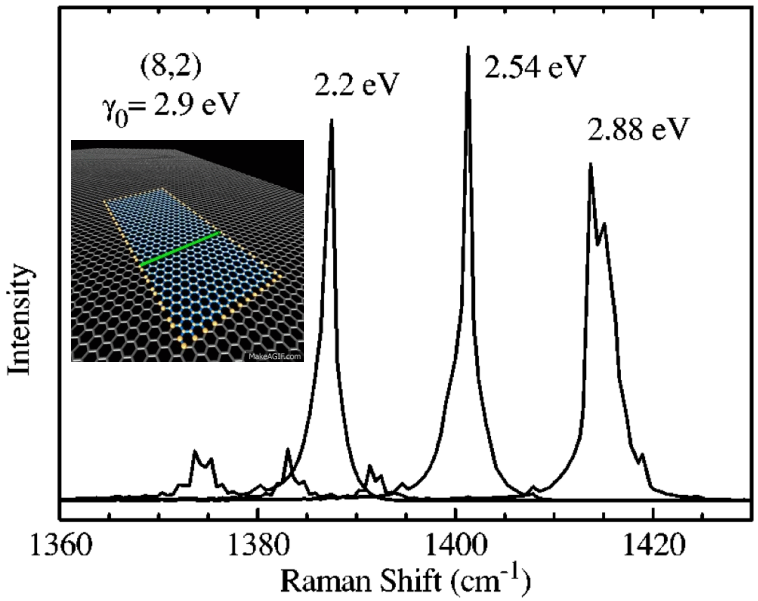
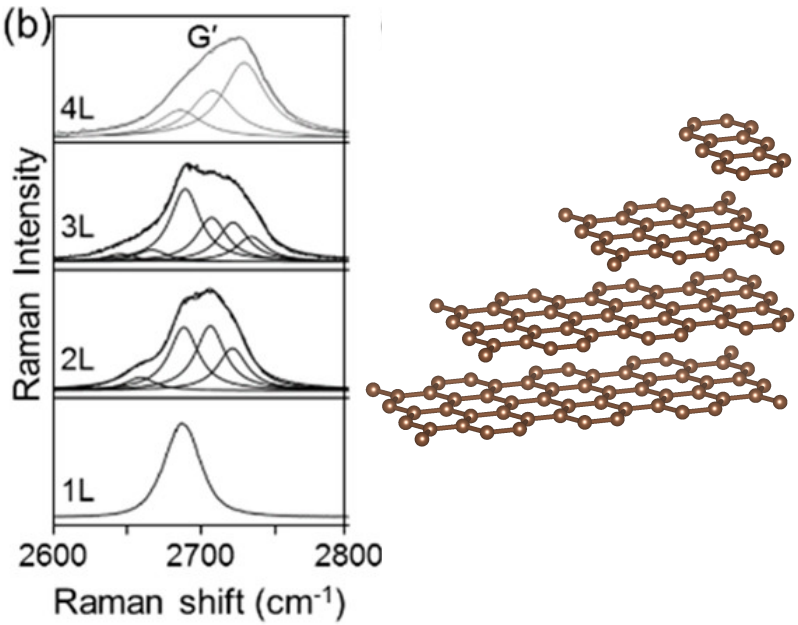
Vibrational spectroscopy

Its many uses in science…



J. Maultzsch PRB **64**, 121407(R) (2001)

Chirality of nanotubes



LM Malard et al. Phys. Rep **473**, 51 (2009)

Thickness of 2D materials

Vibrational spectroscopy

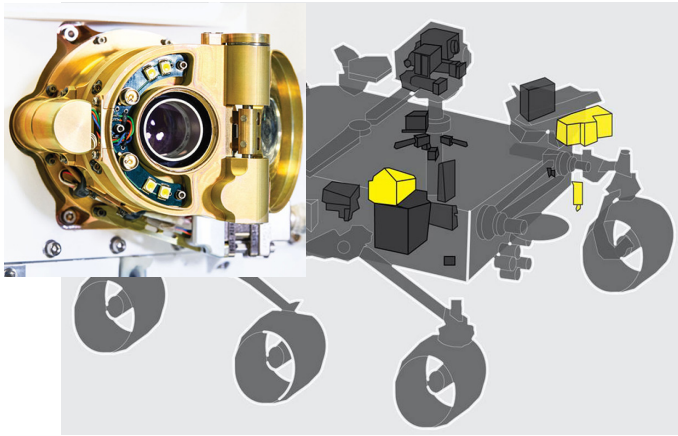
… and beyond

Raman for acrylamide:
A case study with potato chips
Zhi-hao Ye et al. Food Chemistry **403**, 134377, (2023)

Find toxins

Biological Raman sound (908devices.com)

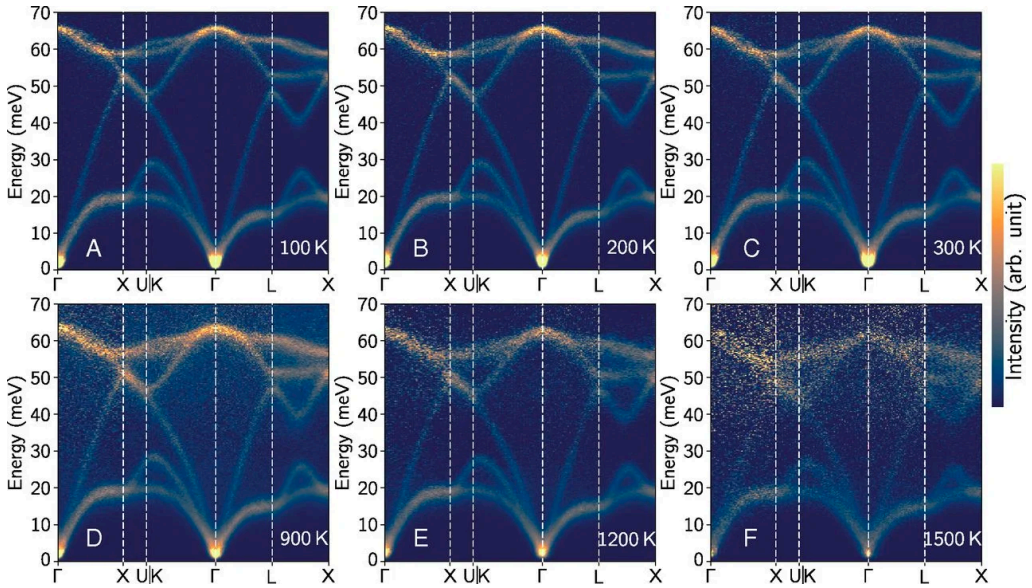
Quantify biostuff



Perseverance rover (mars.nasa.gov/mars2020)

Identify minerals on mars

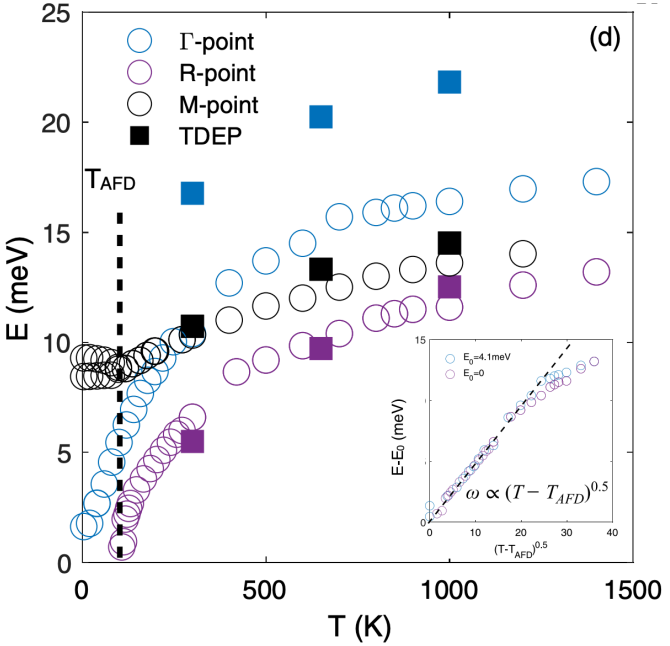
Thermal evolution of materials



Phonons in silicon

D.S. Kim Proc. Natl. Acad. Sci. U.S.A. **115** 9 (2018)

Explain anomalous expansion



Soft mode in $SrTiO_3$

B. Fauqué Phys. Rev. B **106**, L140301 (2022)

Follow phase transitions

Overview:

- Quick review of harmonic vibrations
- Anharmonicity
- TDEP methods
- Outputs and observables
- Tutorial / demonstration with SIESTA

Quick review of harmonic vibrations

Setting up the problem

Quantum system composed of Electrons + nuclei

Born-Oppenheimer approximation

For a configuration $\mathbf{R}$ -> we can assign an energy $V(\mathbf{R})$ using e.g. DFT

The ion's point of view

The ionic Hamiltonian

$$H = \frac{1}{2}\sum_i \frac{\mathbf{p}_i^2}{M_i} + V(\mathbf{R})$$

Problem :

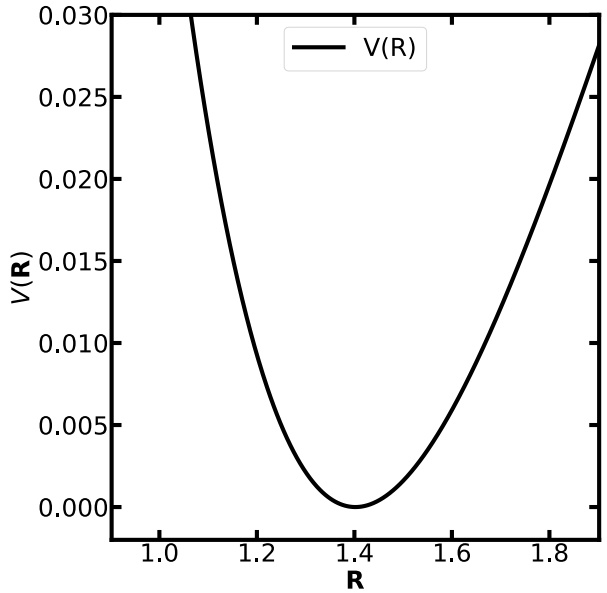
$V(\mathbf{R})$ is a many-body function

Still can not be solved exactly !

Intuitive observation :

At "reasonable" temperatures the system should be close to the ground-state

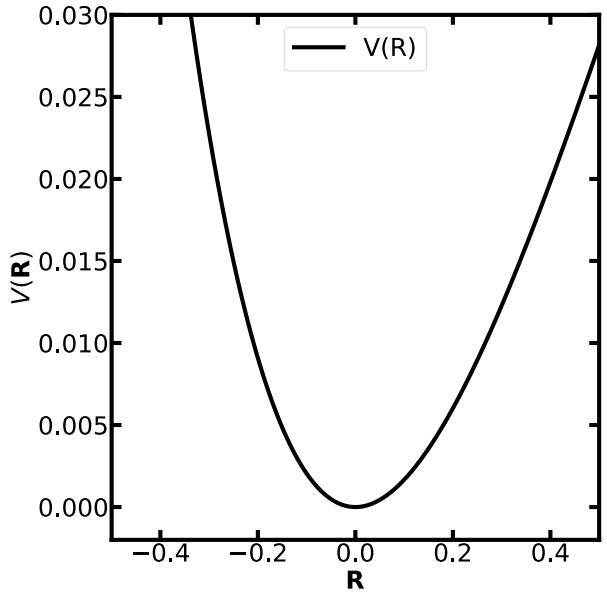
Simplifying the problem



The potential energy

$$V(R)$$

Simplifying the problem



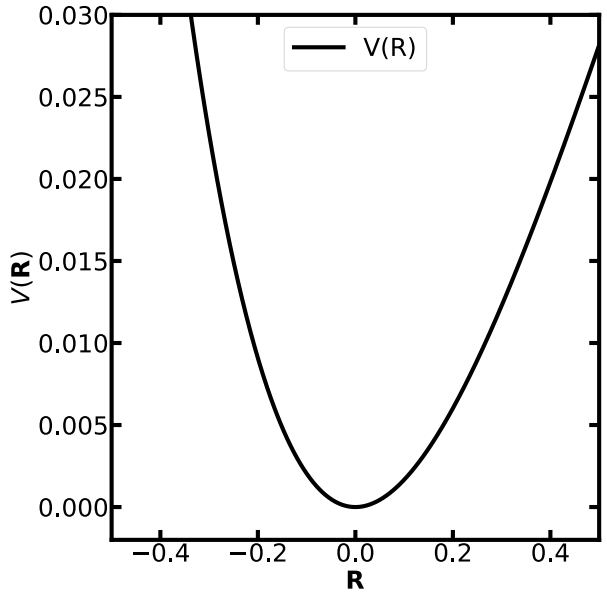
The potential energy

$$V(R)$$

Change of variable

$$R \rightarrow u = R - R_0$$

Simplifying the problem



The potential energy

$$V(R)$$

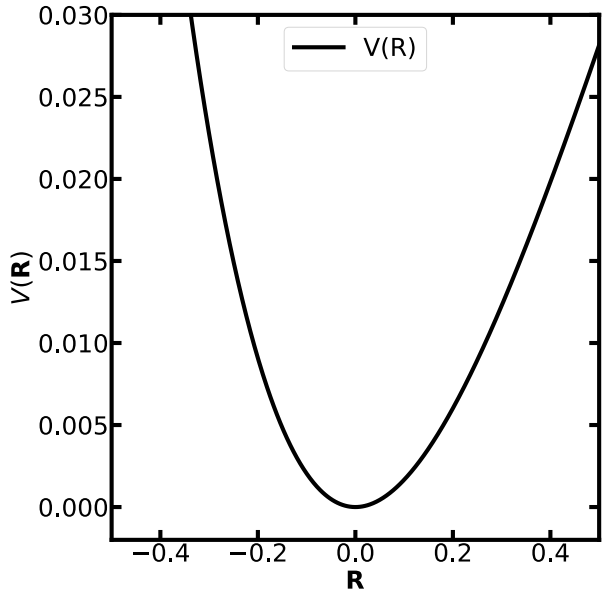
Change of variable

$$R \rightarrow u = R - R_0$$

Taylor expansion

$$V(R) \approx V(R_0) + \left.\frac{\partial V(R)}{\partial R}\right|_{R_0} u$$

Simplifying the problem



The potential energy

$$V(R)$$

Change of variable

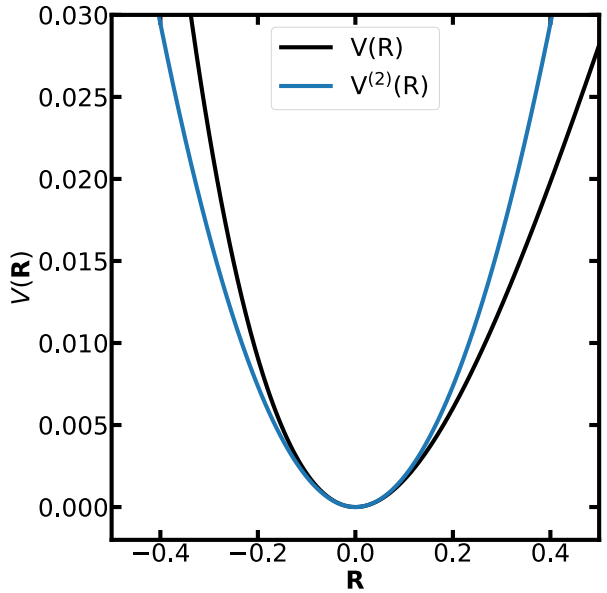
$$R \rightarrow u = R - R_0$$

Taylor expansion

$$V(R) \approx V(R_0) + \frac{\partial V(R)}{\partial R}\bigg|_{R_0} u$$

= constant = 0

Simplifying the problem



The potential energy

$$V(R)$$

Change of variable

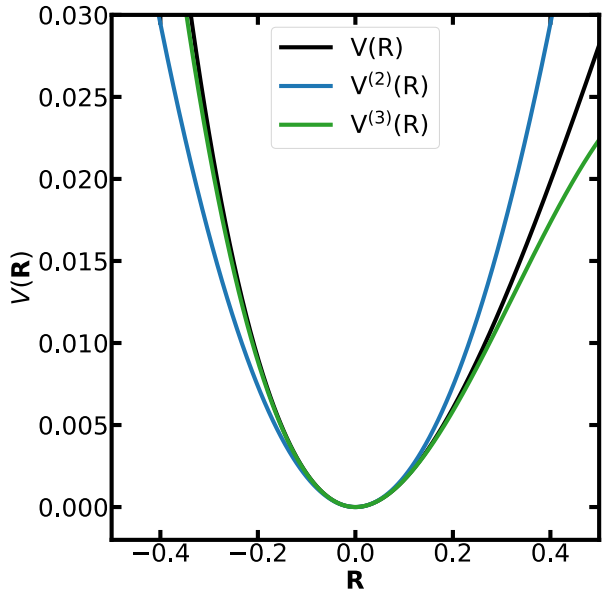
$$R \rightarrow u = R - R_0$$

Taylor expansion

$$V(R) \approx V(R_0) + \cancel{\frac{\partial V(R)}{\partial R}}\Big|_{R_0} u + \frac{1}{2}\frac{\partial^2 V(R)}{\partial R^2}\Big|_{R_0} u^2$$

= constant = 0

Simplifying the problem



The potential energy

$$V(R)$$

Change of variable

$$R \rightarrow u = R - R_0$$

Taylor expansion

$$V(R) = V(R_0) + \frac{\partial V(R)}{\partial R}\Big|_{R_0} u + \frac{1}{2}\frac{\partial^2 V(R)}{\partial R^2}\Big|_{R_0} u^2 + \frac{1}{3!}\frac{\partial^3 V(R)}{\partial R^3}\Big|_{R_0} u^3 + \dots$$

$V(R_0)$ = constant; $\frac{\partial V(R)}{\partial R}\Big|_{R_0}$ = 0

And for solids ?

Crystalline solids -> periodic repetition of a unit cell

I can define my atomic positions by indexing:

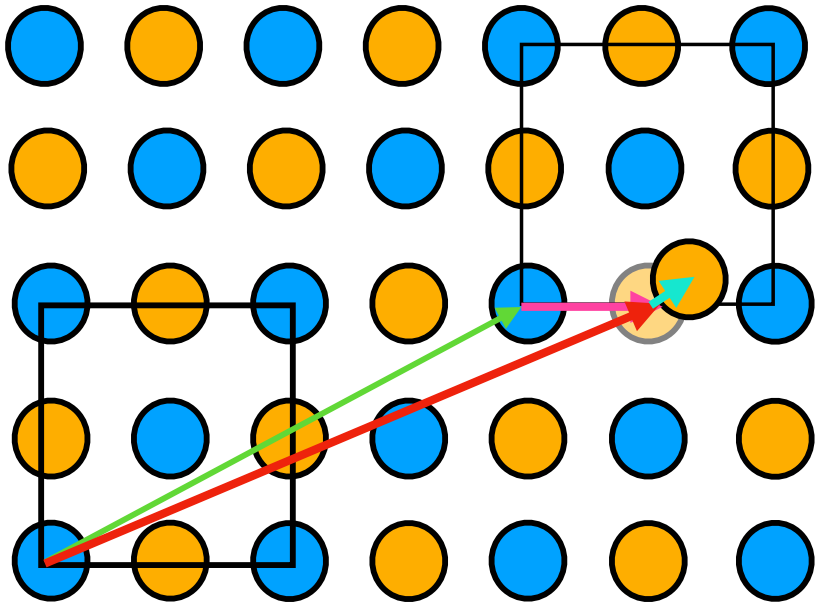
The atom in the unit cell τ_κ

The lattice vector $\mathbf{R}_l$

$$\mathbf{R}_\mu^\kappa = \mathbf{R}_\mu + \tau_\kappa$$

We can still define displacements

$$\mathbf{u}_\mu^\kappa = \mathbf{R}_\mu + \tau_\kappa - \mathbf{R}_{\mu,0}^\kappa$$



Generalized form for V

$$V(\mathbf{R}) = \frac{1}{2}\frac{\partial^2 V(R)}{\partial R^2}\Big|_{R_0} u^2 + \frac{1}{3!}\frac{\partial^3 V(R)}{\partial R^3}\Big|_{R_0} u^3 + \dots$$

From 1D to 3 N_{at} dimensions

$$V(\mathbf{R}) = \frac{1}{2}\sum_{l\kappa}\sum_{m\mu}\Phi^{m\mu}_{l\kappa} u^{\kappa}_{l} u^{\mu}_{m} + \frac{1}{3!}\sum_{l\kappa}\sum_{m\mu}\sum_{n\nu}\Phi^{\kappa\mu\nu}_{lmn} u^{\kappa}_{l} u^{\mu}_{m} u^{\nu}_{n} + \dots$$

$\Phi^{(n)}$ are the Interatomic Force Constants (IFC)

The harmonic approximation

Simplifying the problem for real this time

$$V(R) \approx V_0(\mathbf{u}) = \frac{1}{2} \sum_{l\kappa} \sum_{m\mu} \Phi^{m\mu}_{l\kappa} u^{\kappa}_{l} u^{\mu}_{m}$$

The ionic Hamiltonian in the harmonic approximation

$$H_0 = \frac{1}{2} \sum_{i} \frac{\mathbf{p}_i^2}{M_i} + V_0(\mathbf{R})$$

can be solved exactly ! (quantum or classical)

The harmonic solution

Newton's equation of motion

$$M_\kappa \, \ddot{\mathbf{u}}_{l\kappa} = -\sum_{m\mu} \mathbf{\Phi}^{m\mu}_{l\kappa} \mathbf{u}^{\mu}_{m}$$

Ansatz : plane-waves

$$\mathbf{u}^{\kappa}_{l}(t) = \frac{1}{\sqrt{M_\kappa}} \sum_{\lambda,\mathbf{q}} A_\lambda \boldsymbol{\varepsilon}^{\lambda}(\mathbf{q}) e^{i(\mathbf{q}\mathbf{R}_l - \Omega_\lambda(\mathbf{q})t)}$$

Solve eigenvalue equation of Dynamical Matrix

$$\Omega^2_\lambda(\mathbf{q}) \, \boldsymbol{\varepsilon}^{\lambda}(\mathbf{q}) \; = \; \overline{D}(\mathbf{q}) \, \boldsymbol{\varepsilon}^{\lambda}(\mathbf{q})$$

$$\overline{D}_{\mu\kappa}(\mathbf{q}) = \sum_{m} \frac{\mathbf{\Phi}^{m\mu}_{0\kappa}}{\sqrt{\mathbf{M}_\mu \mathbf{M}_\kappa}} \, e^{i\mathbf{q}\mathbf{R}_m}$$

Quantum harmonic oscillators

So far we have a classical solution

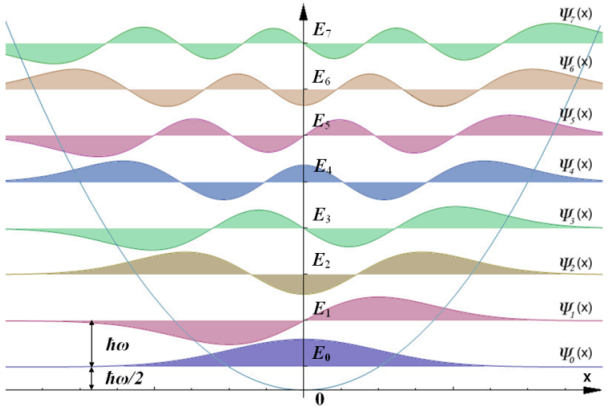
Introduce creation and annihilation operators

$$\hat{a}^{\dagger}_{\lambda}(\mathbf{q}) = \frac{1}{\sqrt{2N\hbar}} \sum_{l,\kappa} \boldsymbol{\varepsilon}_{\lambda}(\mathbf{q}) e^{i\mathbf{q}\mathbf{R}_l} \left(\sqrt{M_{\kappa}\Omega_{\lambda}(\mathbf{q})}\hat{u}^{\kappa}_{l} - i\frac{\hat{p}^{\kappa}_{l}}{\sqrt{M_{\kappa}\Omega_{\lambda}(\mathbf{q})}} \right)$$

Up a level

$$\hat{a}_{\lambda}(\mathbf{q}) = \frac{1}{\sqrt{2N\hbar}} \sum_{l,\kappa} \boldsymbol{\varepsilon}_{\lambda}(\mathbf{q}) e^{i\mathbf{q}\mathbf{R}_l} \left(\sqrt{M_{\kappa}\Omega_{\lambda}(\mathbf{q})}\hat{u}^{\kappa}_{l} + i\frac{\hat{p}^{\kappa}_{l}}{\sqrt{M_{\kappa}\Omega_{\lambda}(\mathbf{q})}} \right)$$

Down a level



We can now rewrite the Hamiltonian

$$\hat{H}_0 = \sum_{\lambda\mathbf{q}} \left(\hat{a}^{\dagger}_{\lambda}(\mathbf{q})\hat{a}_{\lambda}(\mathbf{q}) + \frac{1}{2} \right) \hbar\Omega_{\lambda}(\mathbf{q})$$

Superposition of atomic quantum harmonic oscillators = phonons !

What is a phonon ?

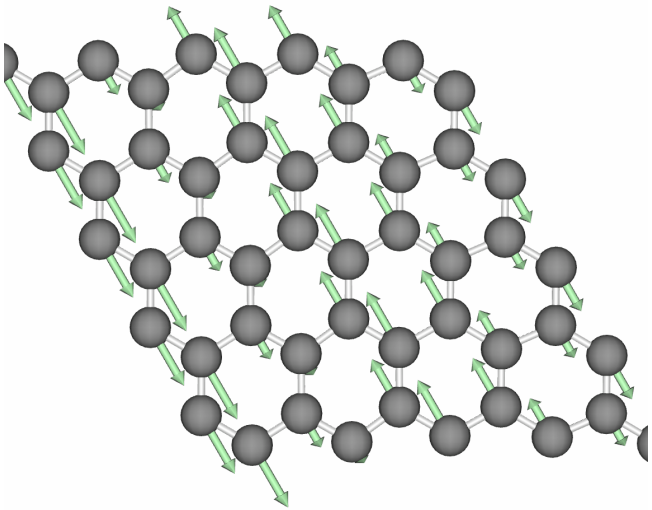
Let's rewrite the displacements

$$\hat{u}_l^{\kappa}(t) = \sum_{\lambda \mathbf{q}} \hat{A}_{\lambda}(\mathbf{q}, t)\, \boldsymbol{\varepsilon}_{\lambda}^{l,\kappa}(\mathbf{q})$$

Amplitude

Eigenvector :

Pattern of displacements



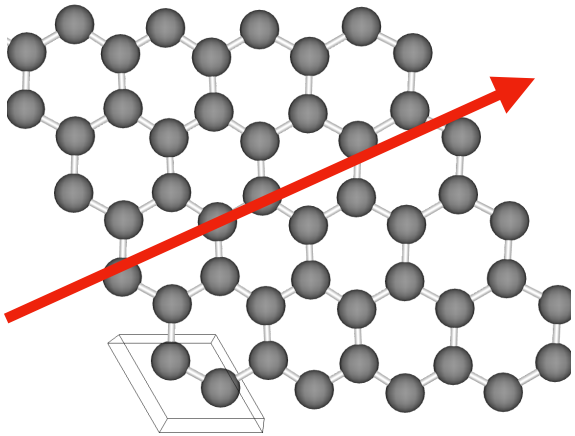
henriquemiranda.github.io/phononwebsite

Phonons are "quasi"particles:
collective excitations of an existing medium

= Wave of displacements

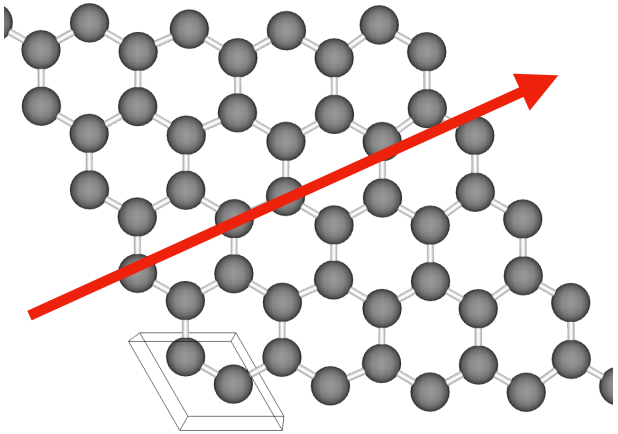
= Quantum particles of vibration or sound

Types of phonons



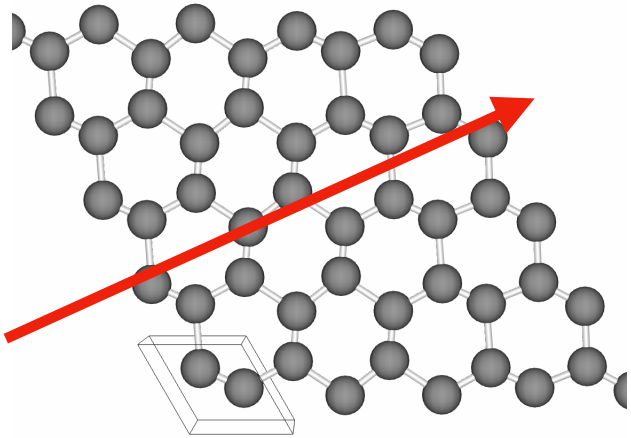
LA

Longitudinal acoustic



TA

Transverse acoustic



TO

Transverse optic

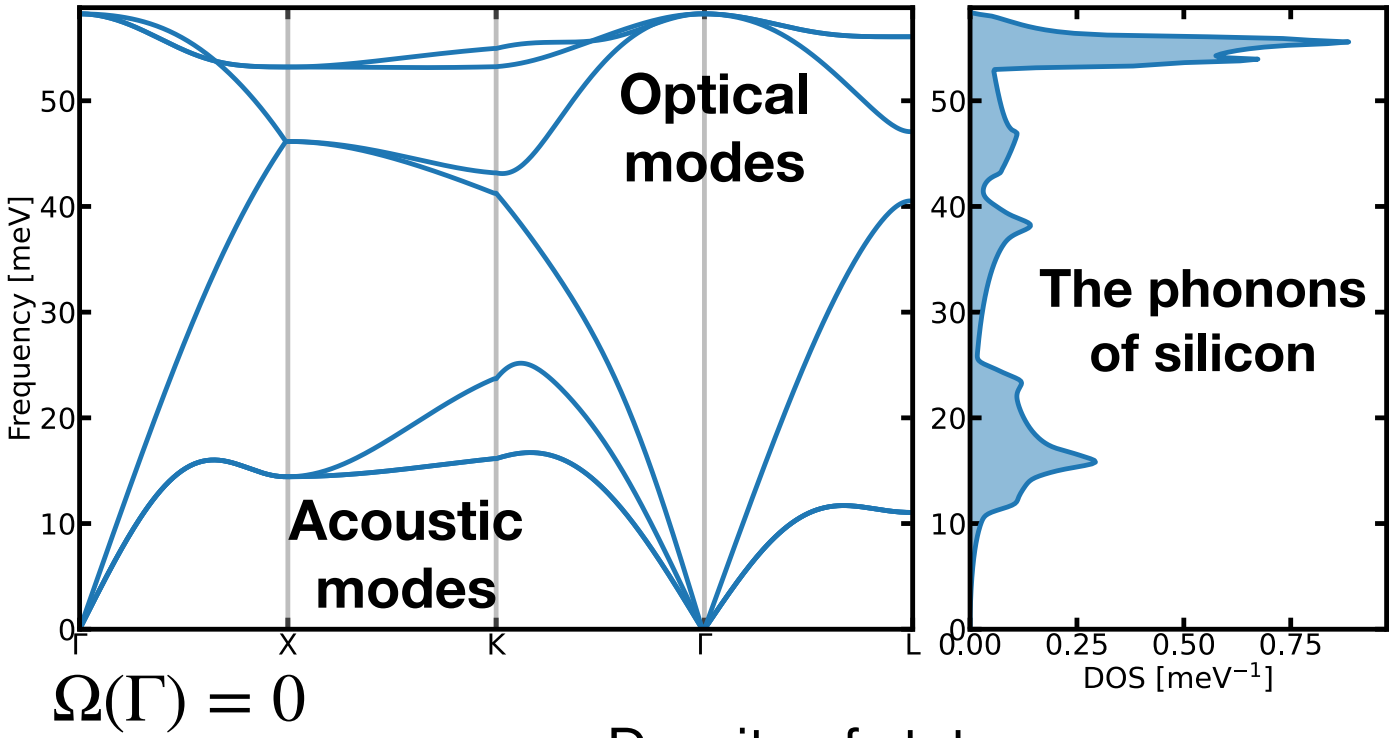
https://henriquemiranda.github.io/phononwebsite

The phonon dispersion

Optical modes at Γ related to:
- interaction with photons
- IR / Raman spectroscopy…

Linear disperson at Γ to:
- speed of sound
- elastic constants

Vibrational spectrum
= ideal delta of energy



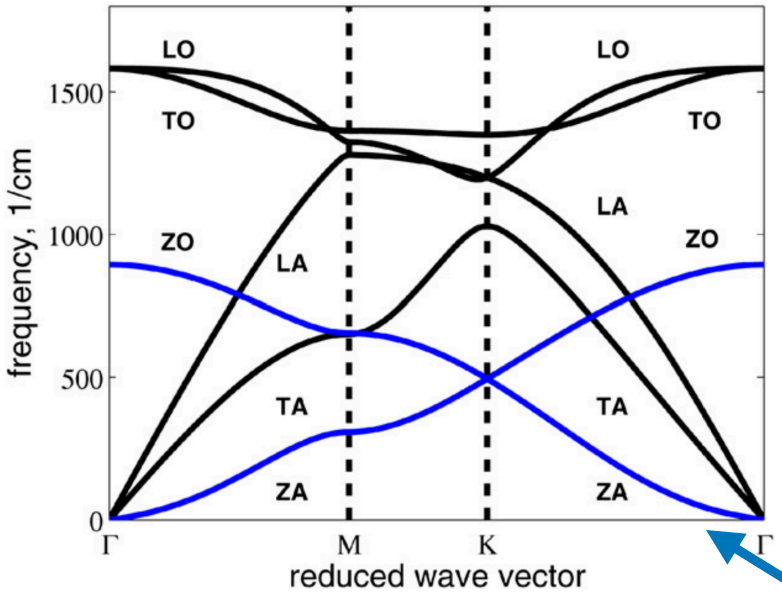
$$\Omega(\Gamma) = 0$$

Density of states :

$$g(\omega) = \sum_{\mathbf{q},\lambda} \delta(\omega - \Omega_\lambda(\mathbf{q}))$$

The harmonic approximation

Phonons in 2D materials

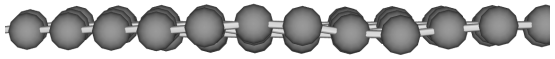


Phonons of graphene

L.A. Falkovsky, Physics Letters A 372 (2008)

2D → no repetition in Z direction

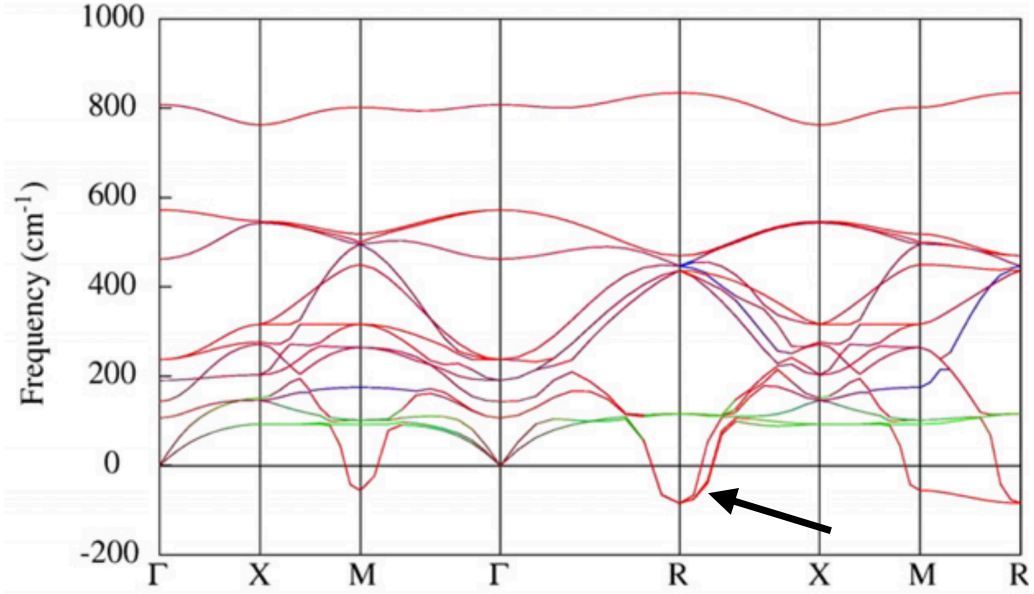
Some phonons have vibrations out of plane → flexural modes



Close to Γ for flexural acoustic → Quadratic dispersion

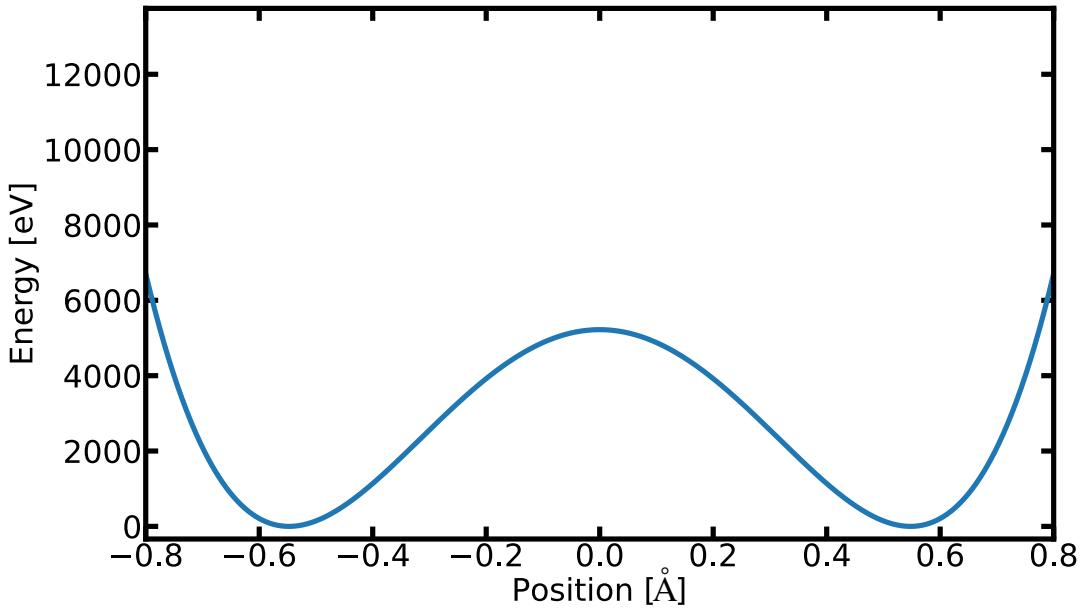
Harmonic instabilities

$\Omega^2 < 0 \rightarrow \Omega \in \Im$: **Imaginary modes -> informations on stability**



Phonons of cubic $SrTiO_3$

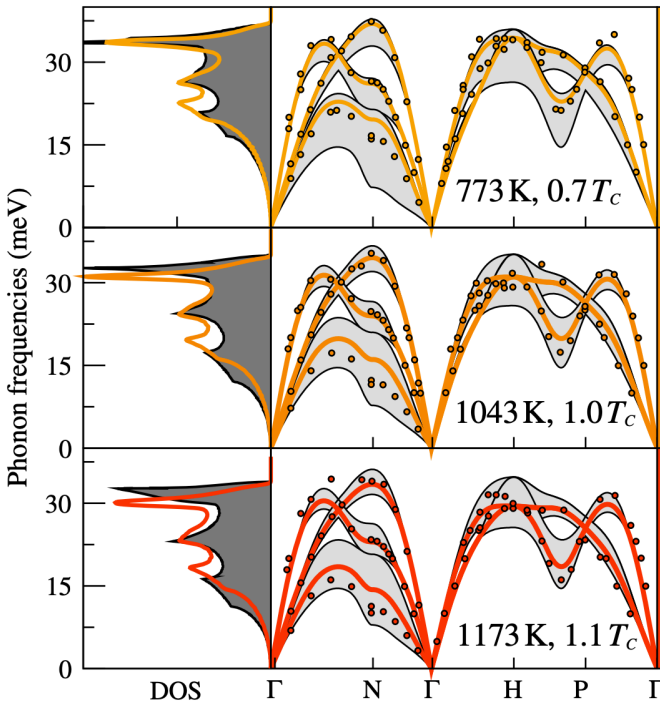
Y. Xie et al, J. Phys.: Condens. Matter **20** 215215 (2008)



$\Omega^2_\lambda(\mathbf{q}) \rightarrow$ curvature of potential energy surface

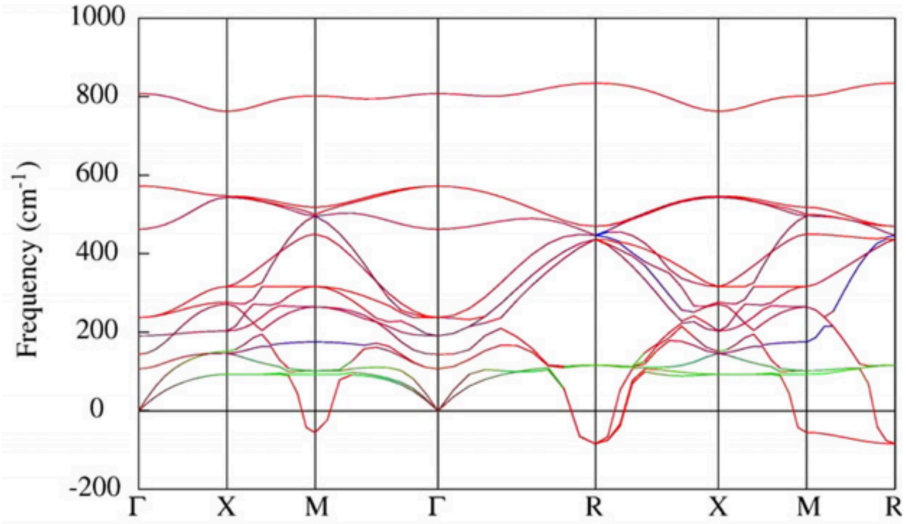
Some applications of the harmonic approximation

DFPT and Finite difference



Phonons in Fe through the magnetic phase transition
Finite-differences

F. Körmann et al, Phys. Rev. Lett. 113, 165503 (2014)



Phonons of cubic $SrTiO_3$
Finite-differences

Y. Xie et al, J. Phys.: Condens. Matter **20** 215215 (2008)

DFPT and Finite difference

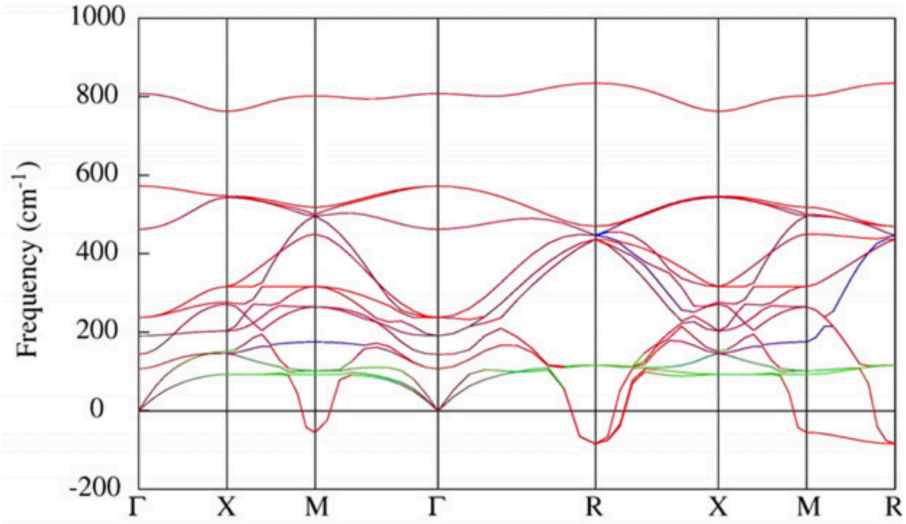
Problem :

This phase (cubic) is observed at room temperature

Something is happening to these imaginary modes with temperature !

Harmonic approximation → 0K

→ limitation



Phonons of cubic $SrTiO_3$
Finite-differences

Y. Xie et al, J. Phys.: Condens. Matter **20** 215215 (2008)

Anharmonicity

Anharmonicity

Let's go back to the beginning (real space):

The Taylor expansion

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

Harmonic contribution | Anharmonic Contribution

Phonon picture

Harmonic

Gas of non-interacting quasiparticles

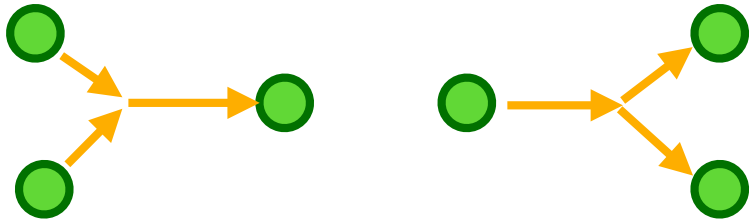
Phonon created → Nothing to stop it

Infinite lifetime

No frequency evolution

Anharmonic

Phonon-phonon interaction



Phonon scattered by or created with other phonons

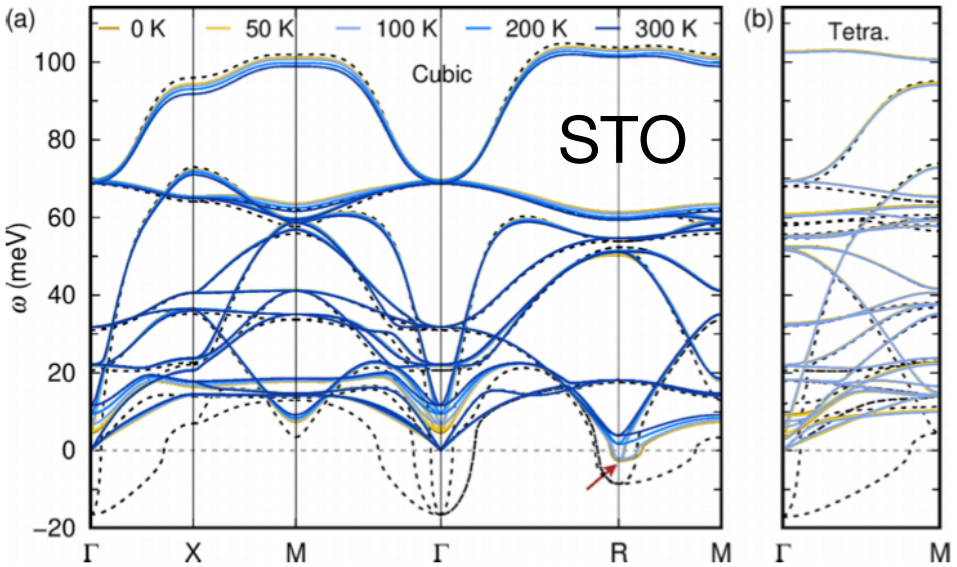
Finite lifetime

Renormalized frequencies

Observable consequences

- Thermal expansion (can be approximated with QHA though)
- Broadening of vibrational spectra (delta peaks in harmonic approx.)
- Heat transport (κ diverges in harmonic approximation)

- Evolution of frequencies in temperature
- Temperature stabilization: frequencies go from imaginary to real



Verdi Phys. Rev. Mater **7** L030801 (2023)

The two roads to anharmonicity

Many ways to go beyond harmonic theory. Most common are:

"Naive" perturbation theory

- T=0K Harmonic + small perturbation
- Adding $\Phi^{(3)}$, $\Phi^{(4)}$, …
- Series not always nicely convergent
- 0 K often a bad starting point

Non-perturbative approach

- Forget 0K harmonic approximation
- Recalculate $\Phi^{(2)}(T)$ for each T
- Finite Temperature Linear-response
- Add perturbation of **residual** $\Phi^{(3)}(T)$

Self-consistent harmonic approximation

Gibbs-Bogoliubov inequality

$$\mathcal{F} > \widetilde{\mathcal{F}}_0 + \langle V(R) - \widetilde{V}_0(R) \rangle_0$$

Average generated using $\widetilde{V}_0(R, T)$

Minimize the right hand term using model $\widetilde{\Phi}$

$$\widetilde{V}_0(R, T) \approx \frac{1}{2} \widetilde{\Phi}^{(2)}(T) u^2$$

Self-consistent cycle: (harmonic) sampling comes from $\widetilde{\Phi}$…

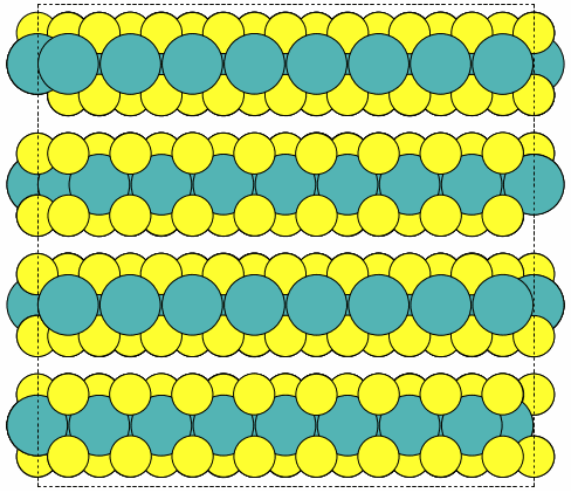
a.k.a. **sTDEP**, sSCHA, SCP…

The TDEP method

The MD-TDEP method

Idea: sample real canonical ensemble

- Perform MD sampling of trajectories (~250 atoms)
- Extract configurations (u_i, F_i, σ_i)
- Fit force constants to observed "exact" F



$$F^{m\mu}(\mathbf{R}) = \sum_{l\kappa} \Phi^{m\mu}_{l\kappa} u^{\kappa}_{l} + \frac{1}{2!} \sum_{l\kappa} \sum_{n\nu} \Phi^{\kappa\mu\nu}_{lmn} u^{\kappa}_{l} u^{\nu}_{n} + \dots$$

The MD-TDEP method

- Exploit symmetries, permutations … → only irreducible Φ
- Least square fit of $\Phi^{(2)}$, then to residual for $\Phi^{(3)}$, and even $\Phi^{(4)}$

$$\begin{pmatrix} u_1^1 & u_2^1 & \dots \\ u_1^2 & u_2^2 & \dots \\ u_1^3 & u_2^3 & \dots \\ \vdots & & \end{pmatrix} \begin{pmatrix} \Phi_1^{(2)} \\ \Phi_2^{(2)} \\ \Phi_3^{(2)} \\ \vdots \end{pmatrix} = \begin{pmatrix} F_1^{DFT} \\ F_2^{DFT} \\ F_3^{DFT} \\ \vdots \end{pmatrix} \qquad \begin{pmatrix} u_1^1 u_2^1 & \dots \\ u_1^2 u_2^2 & \dots \\ u_1^3 u_2^3 & \dots \\ \vdots & \end{pmatrix} \begin{pmatrix} \Phi_{12}^{(3)} \\ \Phi_{13}^{(3)} \\ \Phi_{23}^{(3)} \\ \vdots \end{pmatrix} = \begin{pmatrix} F_1^{DFT} - F_1^{harm} \\ F_2^{DFT} - F_2^{harm} \\ F_3^{DFT} - F_3^{harm} \\ \vdots \end{pmatrix}$$

- + Impose Huang invariances, translational/rotational sum rules

The MD-TDEP method

Advantages

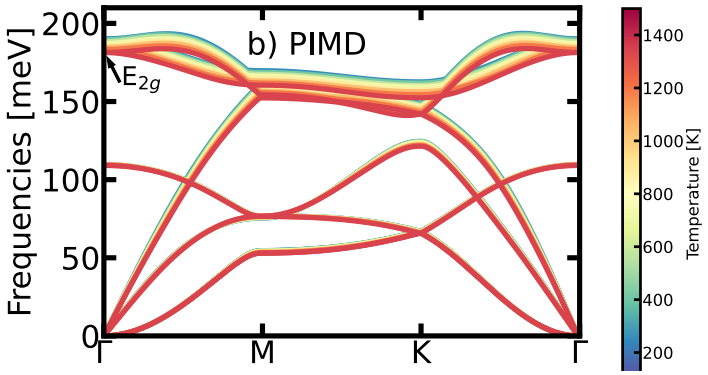
- The real canonical ensemble
- Just converge #configurations
- No self consistency
- Minimizes higher order Φ
- Justifies perturbation theory
- Least Means Squared robust to noise

Issues

- Requires full AIMD
- -> use SIESTA… or Machine Learning
- Or both
- Quantum nuclear effects require PIMD

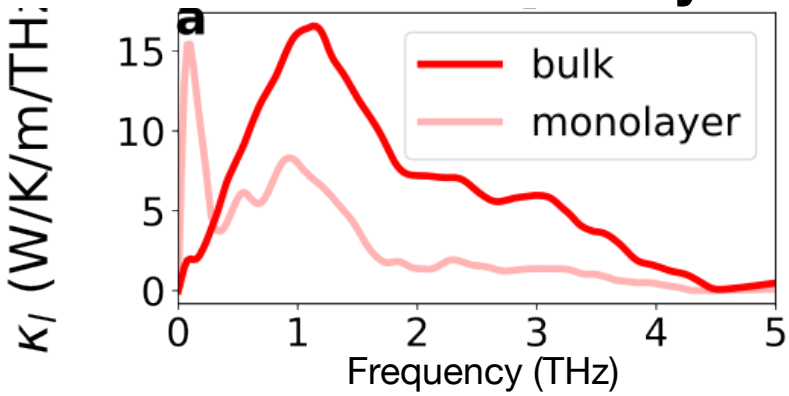
TDEP outputs

T-dependent phonons



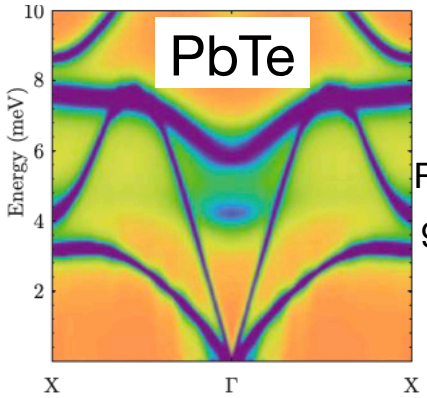
Castellano et al. J Chem Phys 159 234501 (2023)

Thermal conductivity



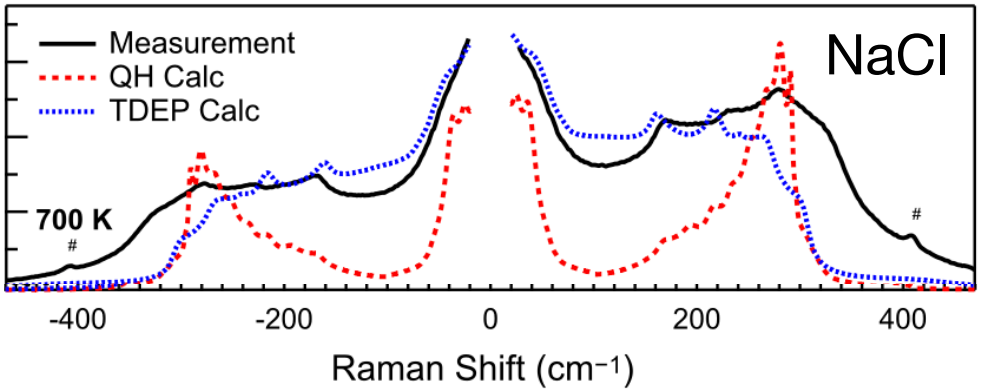
R Farris et al PRB 109 125422 (2024)

Phonon spectral function



Romero et al. PRB 91 214310 (2015)

T-dependent spectra



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TDEP Docs & Links

- Central web site https://github.com/tdep-developers/
- Source code, tutorials, documentation for executables
- MLIPs provided to run quickly
- Any DFT code will do
- Choose between sTDEP and MD-TDEP sampling

Hellman et al. PRB 84 180301 (2011)
Hellman et al. PRB 87 104111 (2013)
Knoop et al. J Open Source Software 94 6150 (2024)
Castellano et al. J Chem Phys 159 234501 (2023)

Questions?

Demonstration

Tutorial