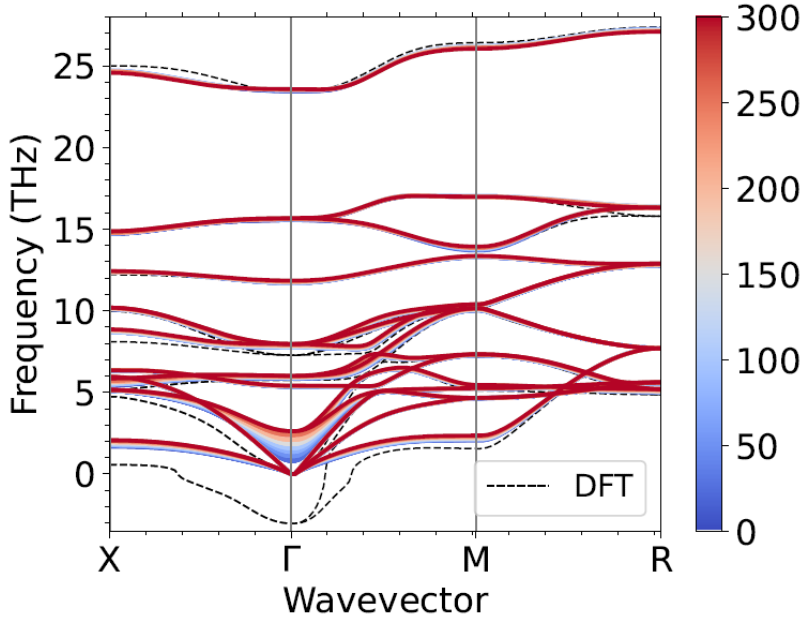
# SPONTANEOUS SYMMETRY BREAKING IN CRYSTALLINE MATERIALS: CALCULATING COLLECTIVE MODES FROM FIRST PRINCIPLES





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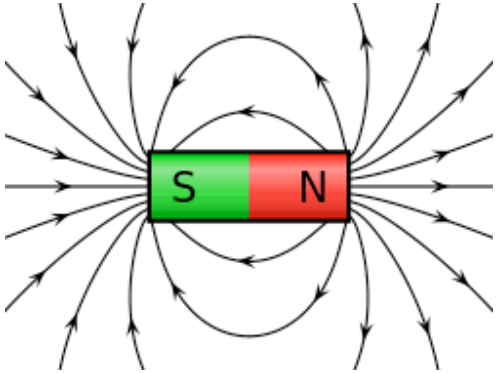
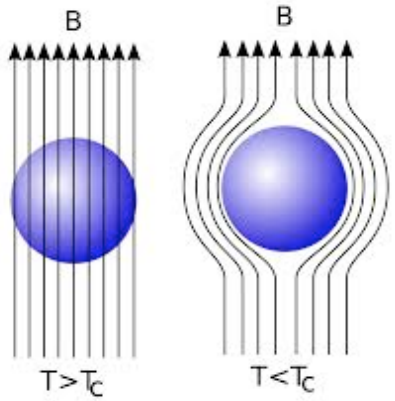
M. Norman (Argonne)
N. Mingo (CEA Grenoble)
A. Van Roekeghem (CEA Grenoble)
D. Juraschek (Tel Aviv Univ.)
P. Narang (UCLA)

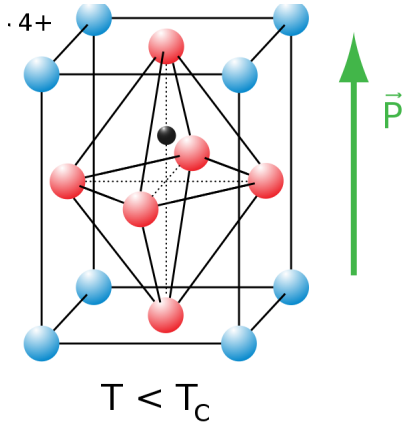
# Spontaneous symmetry breaking



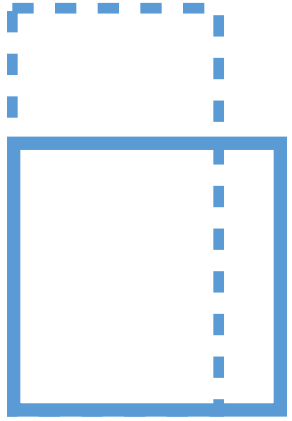

Magnetism




Superconductivity




Ferroelectricity



Ferroelasticity

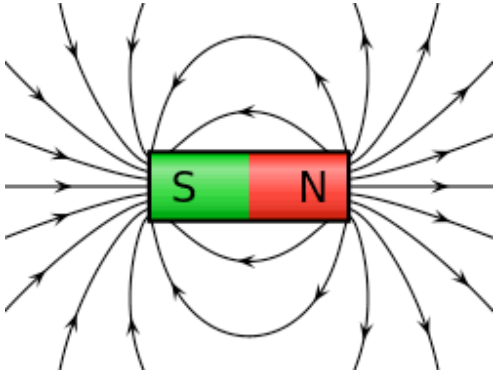
**Electronic**

Broken symmetries in the electronic system

**Structural**

Broken crystal symmetries

# Spontaneous symmetry breaking

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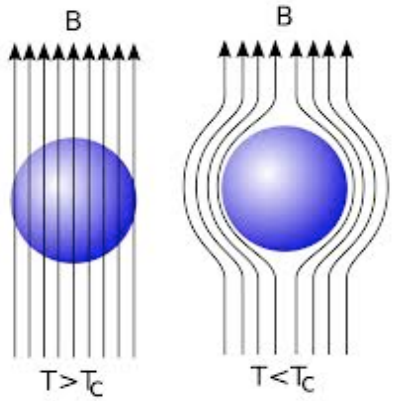


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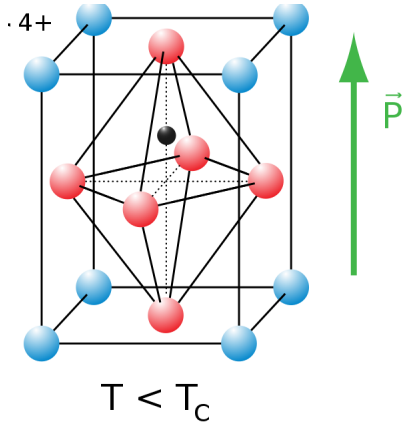
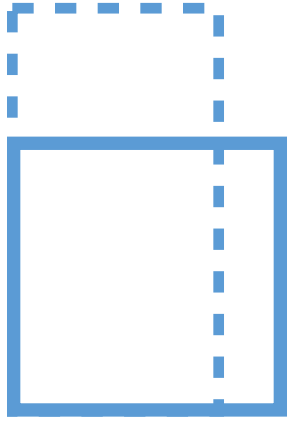



Ferroelectricity



Ferroelasticity

**Electronic**

Broken symmetries in the electronic system

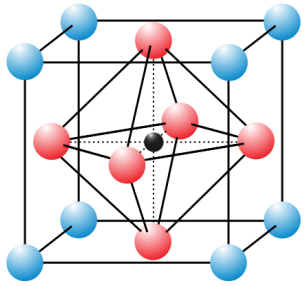
**Structural**

Broken crystal symmetries

# Collective phonon modes as remnants of broken symmetries

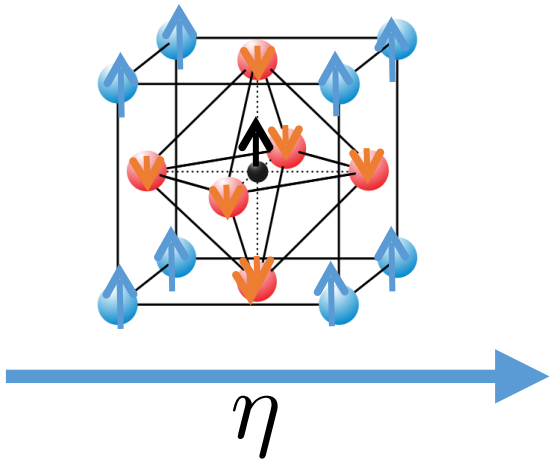
# Structural phase transitions

High-symmetry



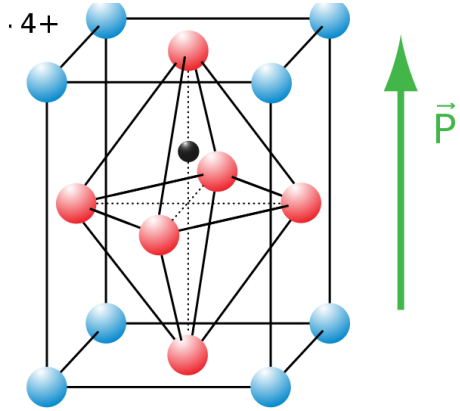
$T > T_C$

Space group G




G is a subgroup G’

Low symmetry

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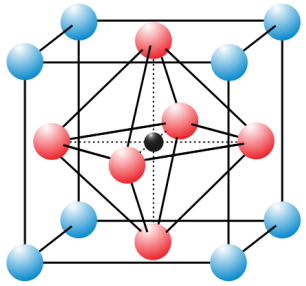
Space group G’

$\eta$ is the amplitude of a symmetry-adapted displacement pattern (belong to irreducible representation)

# Structural phase transitions

High-symmetry



T > $T_C$

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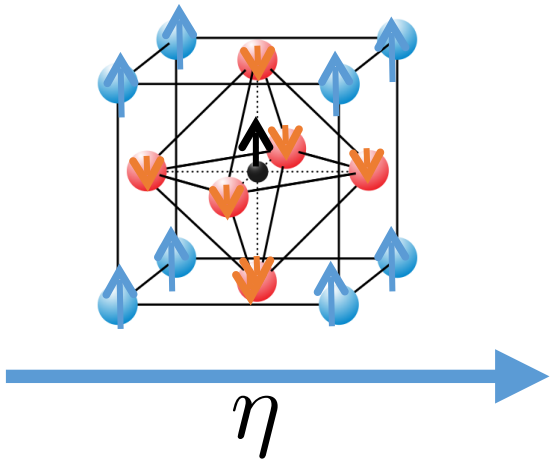


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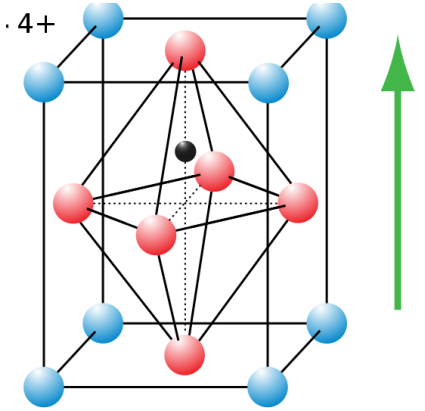
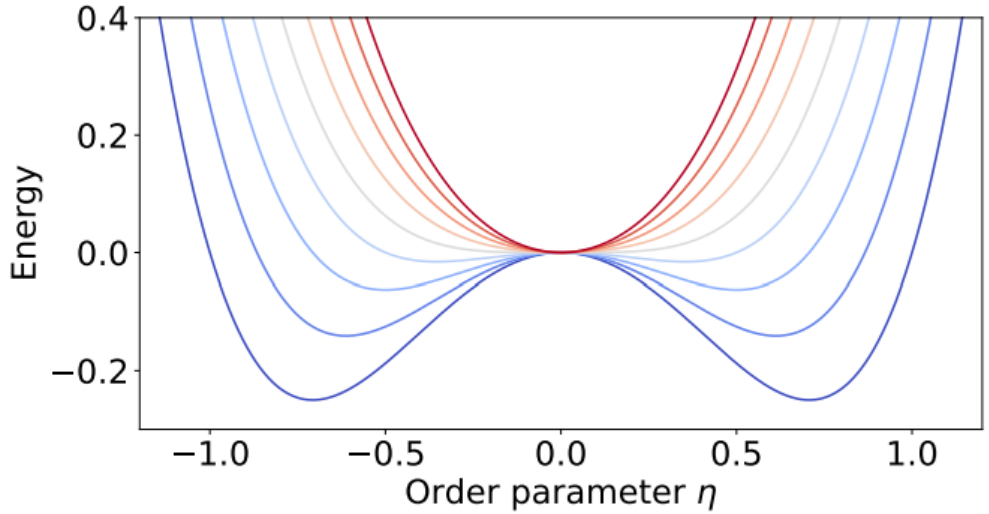



T < $T_C$

Space group G'

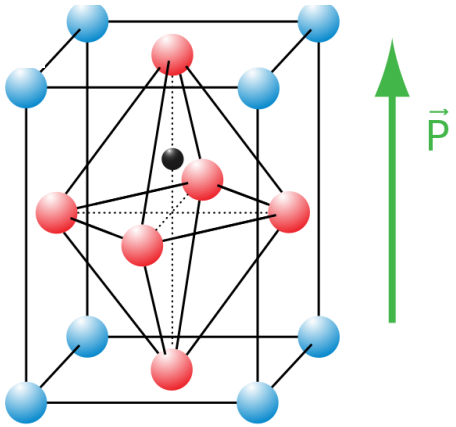
Free energy

$$F(T) = \frac{a_0\left(\frac{T-T_C}{T_C}\right)}{2}\eta^2 + \frac{b}{4}\eta^4 + \ldots - \eta H$$




$\eta$ is the amplitude of a symmetry-adapted displacement pattern (belong to irreducible representation)

# The soft mode (1D)

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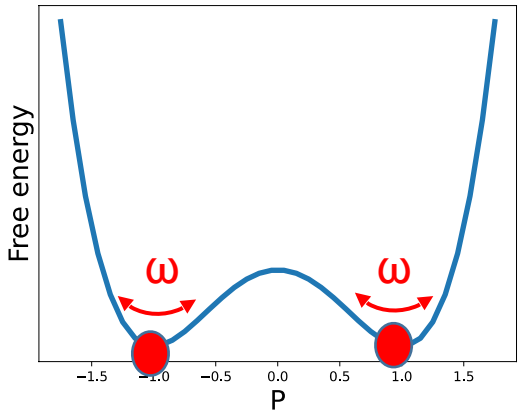
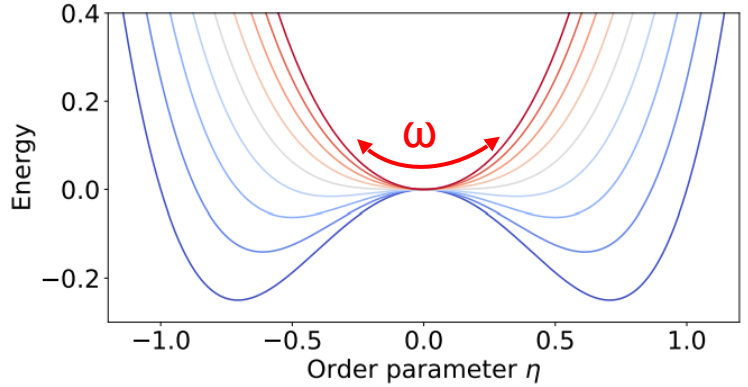
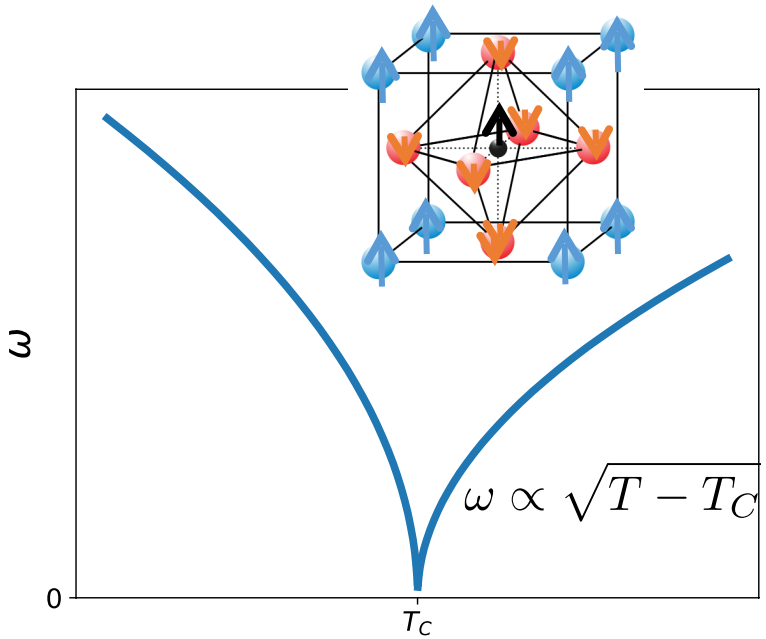
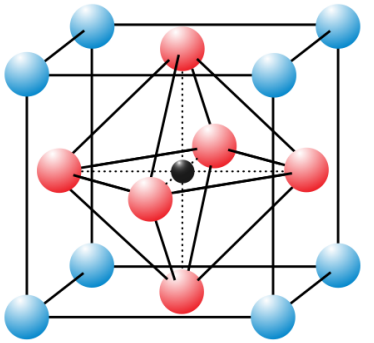



$\varepsilon = (T - T_C/T_C)$



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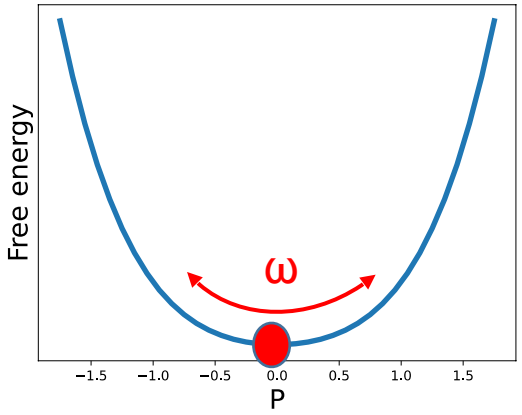


# Spontaneous breaking of a continuous symmetry

**Multi-component order parameters**

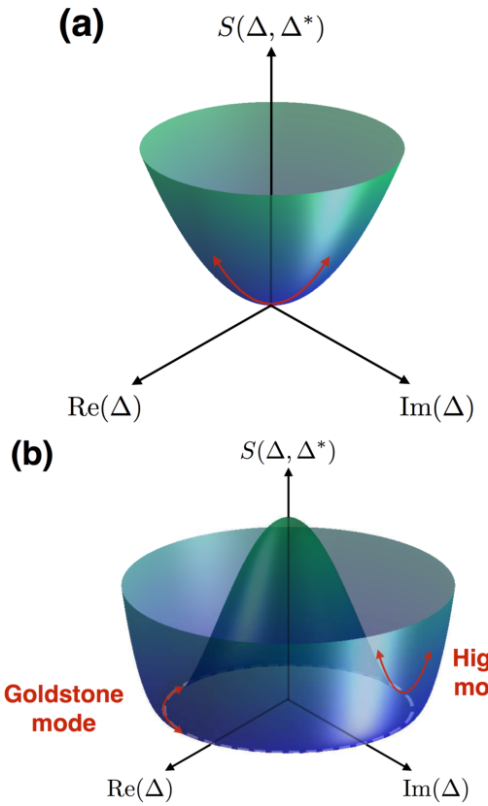
$$F(T) = \frac{a_0(\frac{T-T_c}{T_c})}{2}(\eta_1^2 + \eta_2^2) + b(\eta_1^2 + \eta_2^2)^2 + c\eta_1^2\eta_2^2 + \mathcal{O}(\eta_1^5, \eta_2^5)$$

Anisotropy

Phase transition from discrete symmetry to discrete symmetry

**“dangerous irrelevance”** of the anisotropy at Tc.

Breaking of a n-dimensional continuous symmetry leads to 1 amplitude (Higgs) modes and n-1 massless phase (Goldstone) modes




T>Tc

T<Tc

G. Bruun, Phys. Rev. A 90, 023621 (2014)

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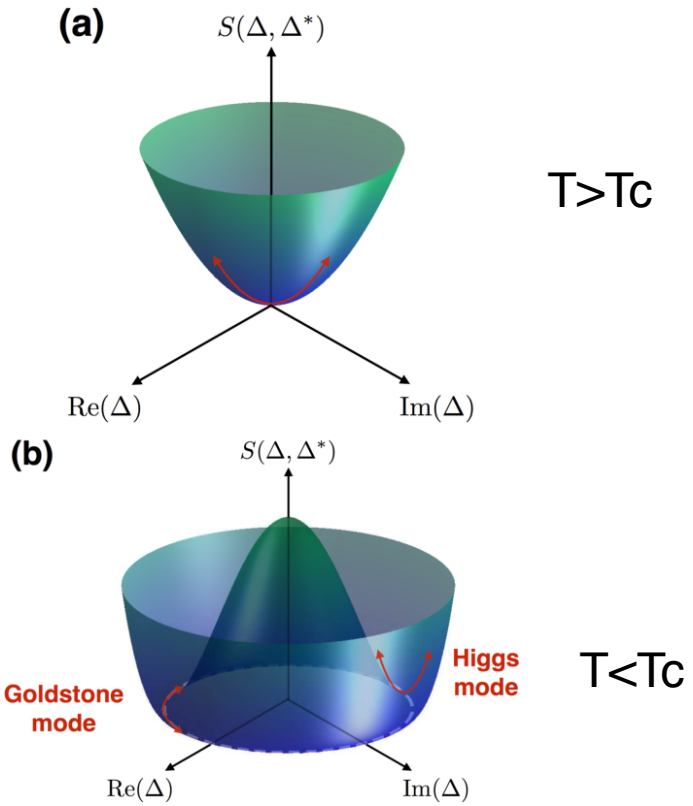



T>Tc

T<Tc

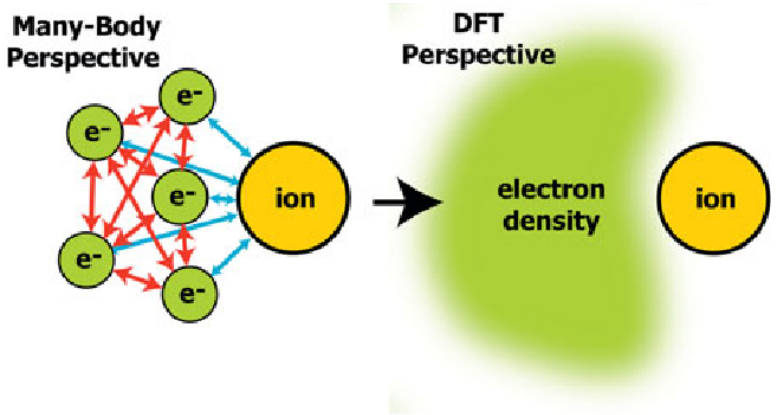
G. Bruun, Phys. Rev. A 90, 023621 (2014)

**Are these kind of modes realised in crystalline systems?**

# Density functional theory

Many-body Hamiltonian

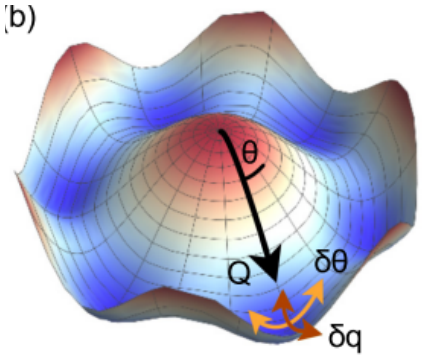
$$\hat{H}\Psi = \left[\hat{T} + \hat{V} + \hat{U}\right]\Psi = \left[\sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m_i}\nabla_i^2\right) + \sum_{i=1}^{N} V(\mathbf{r}_i) + \sum_{i<j}^{N} U(\mathbf{r}_i, \mathbf{r}_j)\right]\Psi = E\Psi,$$



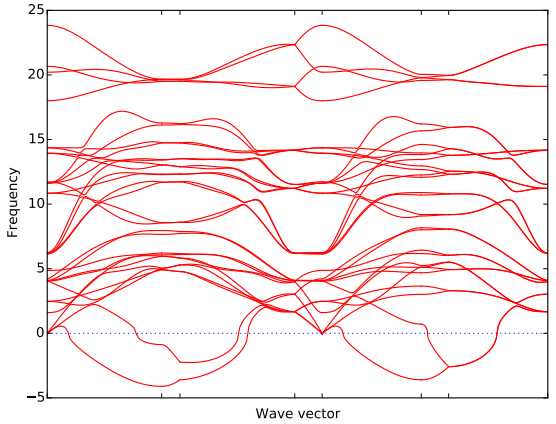

Density functional

$$E[n] = T[n] + U[n] + \int V(\mathbf{r})n(\mathbf{r})\,\mathrm{d}^3\mathbf{r}$$

In particular: Calculation of energy landscapes




Calculation of phonons



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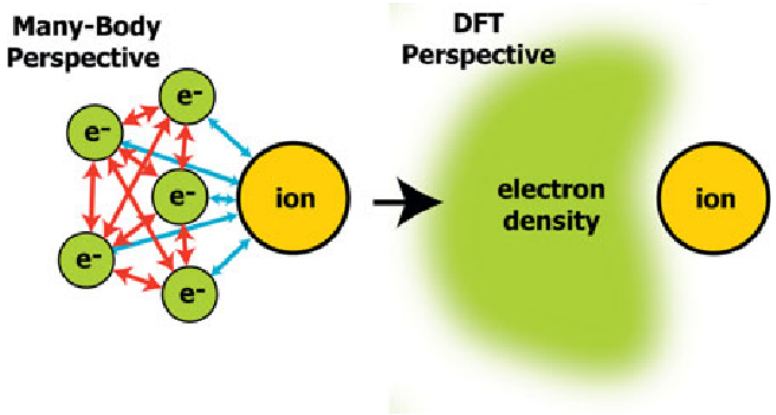


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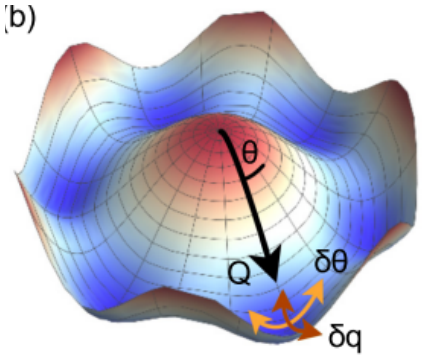
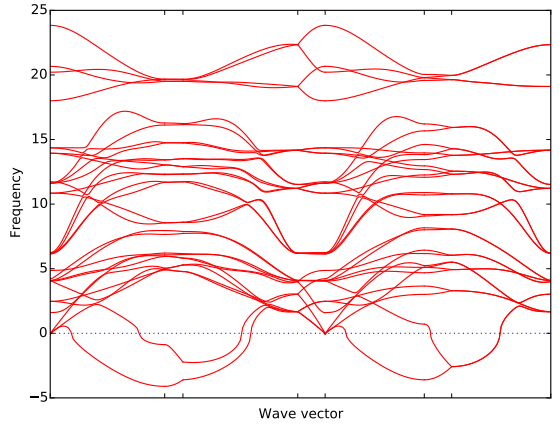



Calculation of phonons

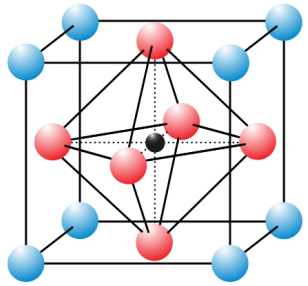



Only at 0K!

# Identification of an order parameter/soft mode

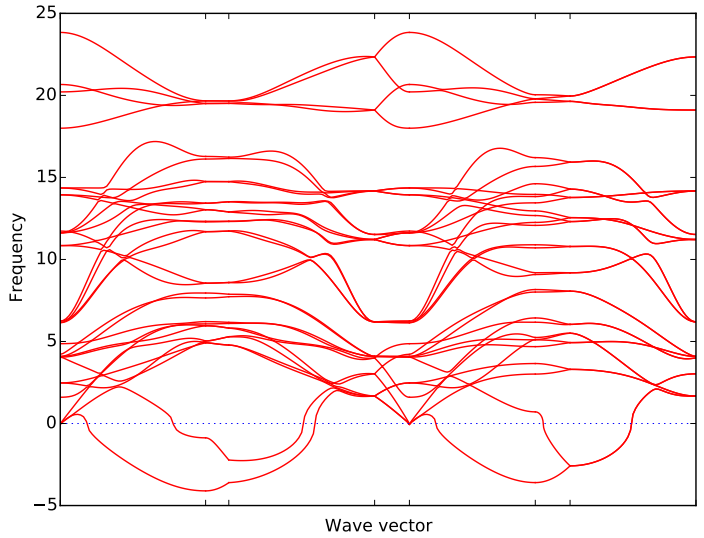
## Identification of the order parameter

High symmetry structure:



$T > T_c$

$$\Phi_{ij} = \frac{\partial^2 E}{\partial u_i \partial u_j}$$



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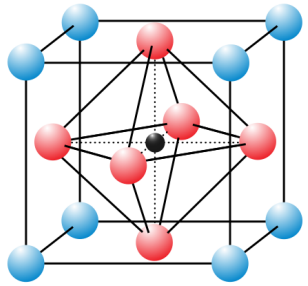

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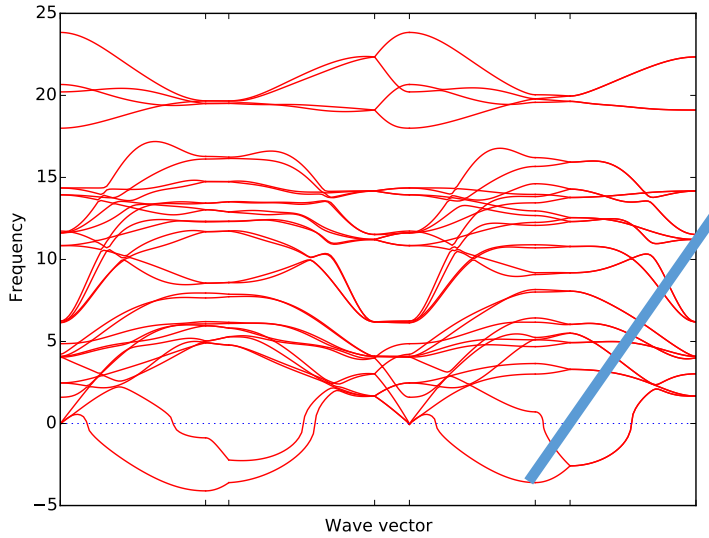


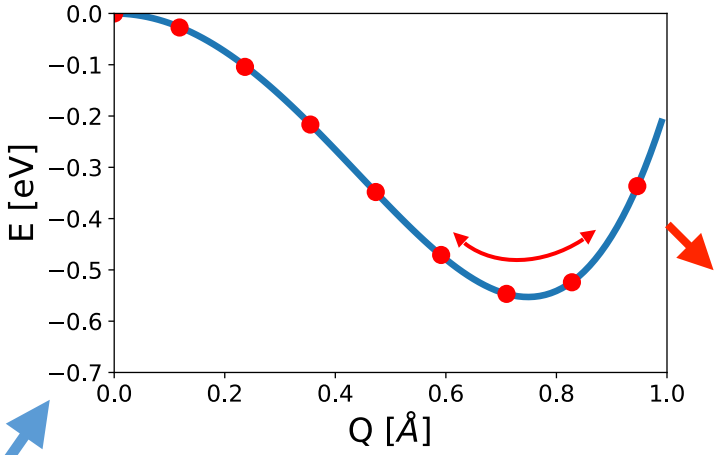


$$F(T) = \frac{a_0\left(\frac{T-T_C}{T_C}\right)}{2}\eta^2 + \frac{b}{4}\eta^4$$

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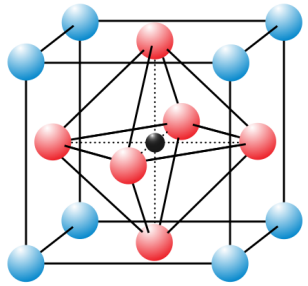

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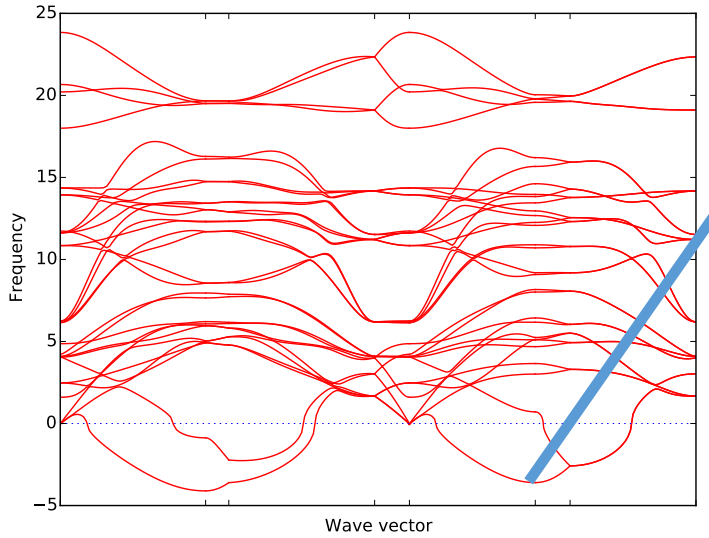


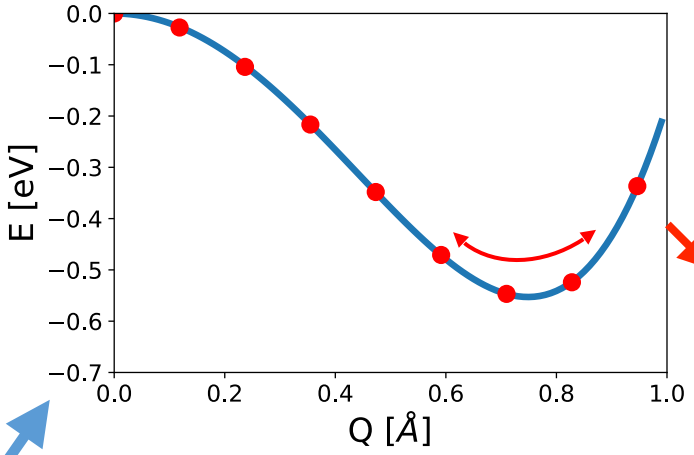


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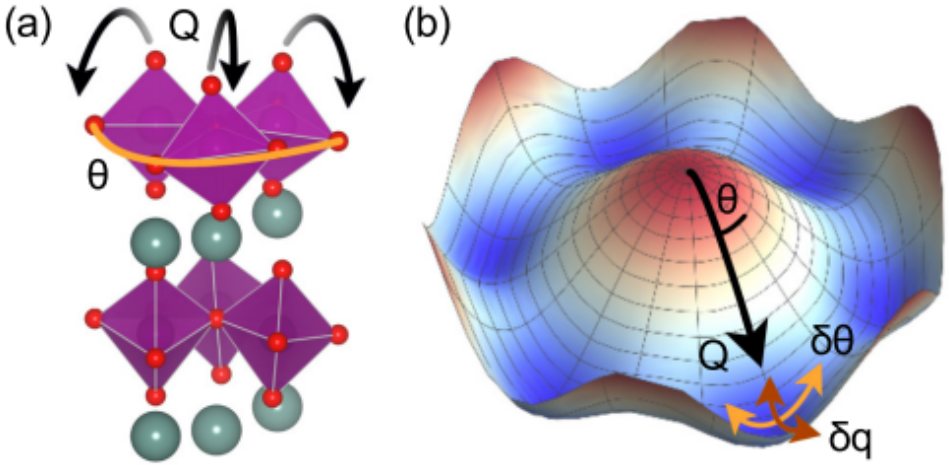
$$\phi_{ii} = \left.\frac{\partial^2 F}{\partial \eta^2}\right|_{\eta=\langle\eta(T)\rangle}$$

Order parameters
Temperature dependent

$$\Phi(T) = \begin{bmatrix} \phi_{11} & \phi_{12} & \phi_{13} & 0 & 0 & \dots & 0 \\ \phi_{21} & \phi_{22} & \phi_{23} & 0 & 0 & \dots & 0 \\ \phi_{31} & \phi_{32} & \phi_{33} & 0 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \alpha_4 & 0 & \dots & 0 \\ 0 & 0 & 0 & \vdots & \vdots & \ddots & \vdots \\ & & & 0 & 0 & \dots & \alpha_{3N} \end{bmatrix}$$

Rest of the modes
Temperature independent

# Phonon analogues of Higgs and Goldstone modes





Nicola Spaldin

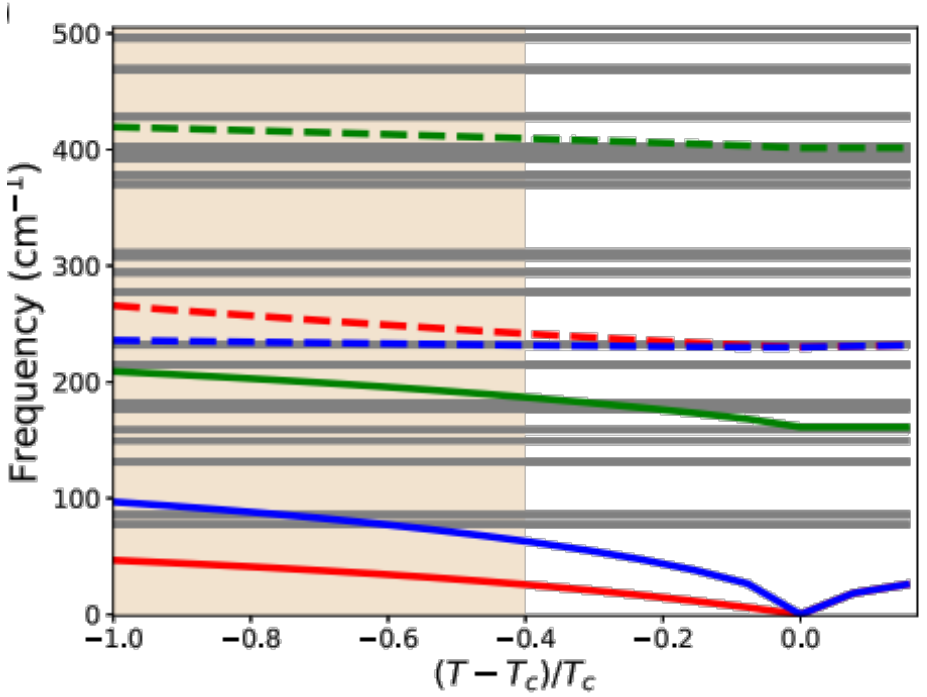

Dirk Van der Marel

Landau free energy, scaled using $a = a_0\left(\frac{T - T_c}{T_c}\right)$

$$F = \frac{a}{2}Q^2 + \frac{b}{4}Q^4 + \frac{1}{6}(c + c'\cos 6\theta)Q^6 - gQ^3P\cos 3\theta + \frac{g}{2}Q^2P^2 + \frac{a_p}{2}P^2.$$

Artyukhin et al, Nat. Mater (2012)

Calculated at 0K by calculating the change of energy when displacing along the order parameter




Higgs-like

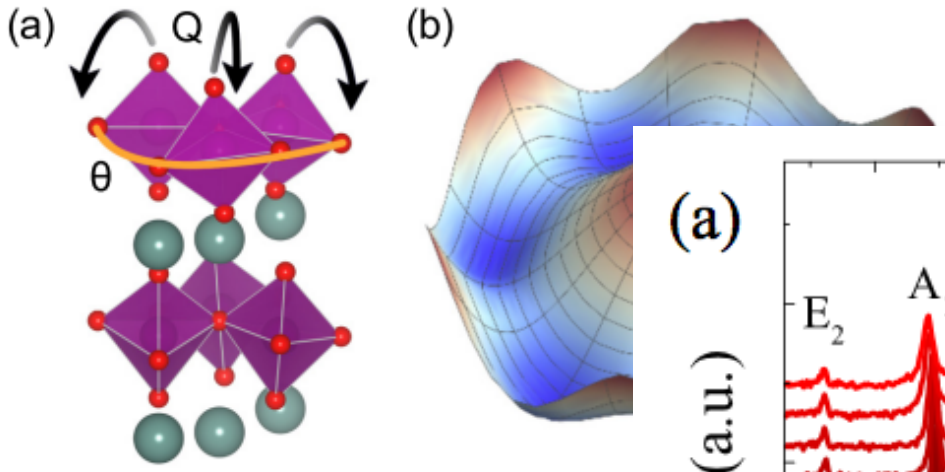
Goldstone-like

QNM et al., Phys Rev B 102 (1), 014102 (2020)

# Phonon analogues of Higgs and Goldstone modes


Nicola Spaldin

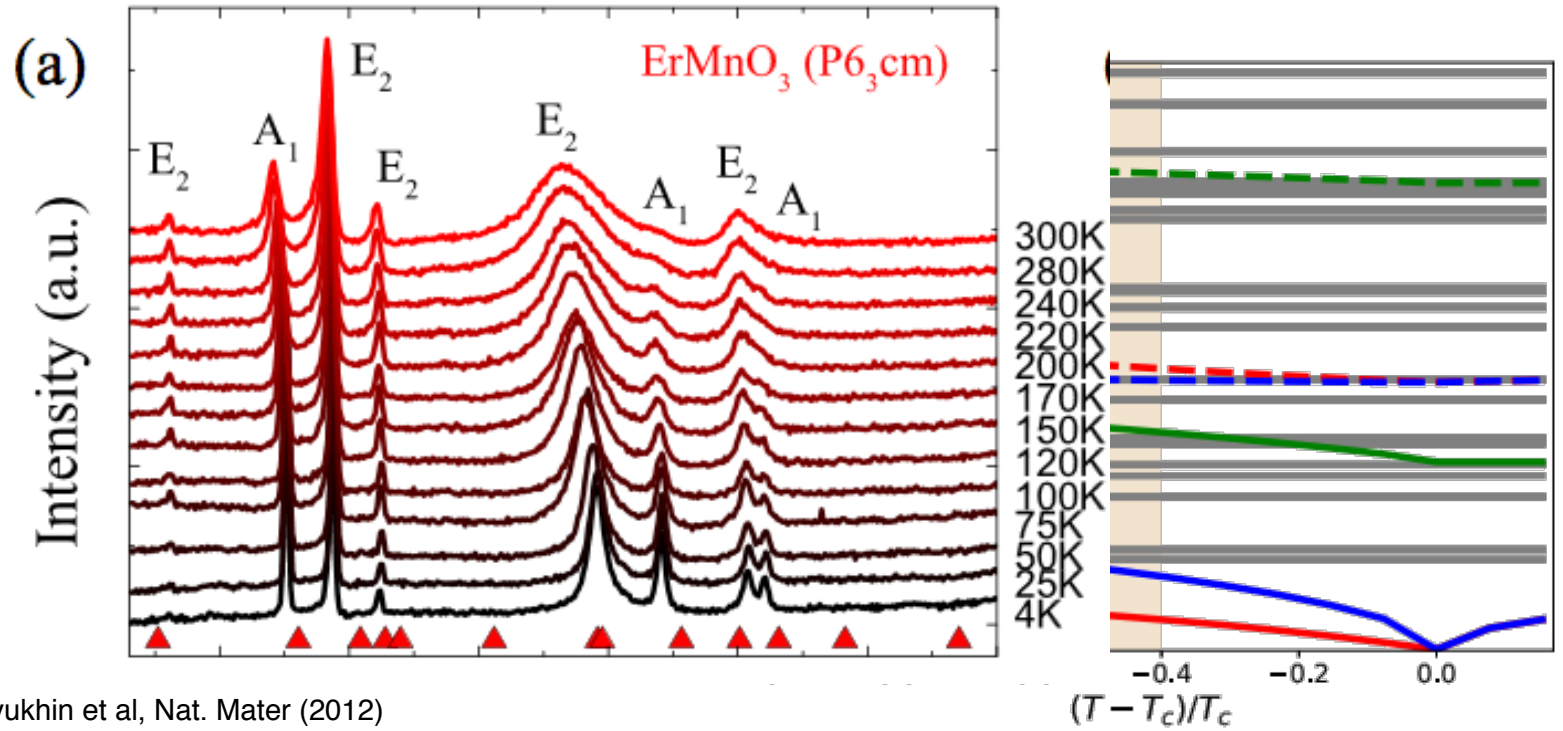

Dirk Van der Marel




Landau free energy, scaled

$$F = \frac{a}{2}Q^2 + \frac{b}{4}Q^4 + \frac{1}{6}(c + c'$$

$$- gQ^3P\cos 3\theta + \frac{g}{2}Q^2P$$

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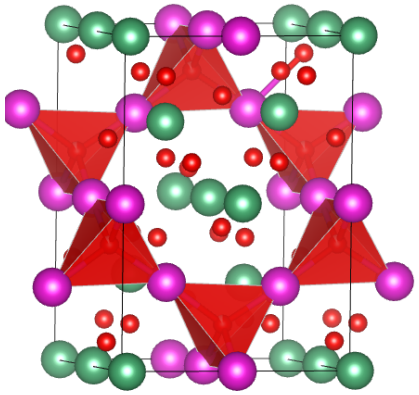
QNM et al., Phys Rev B 102 (1), 014102 (2020)

# Spontaneous symmetry breaking in $Cd_2Nb_2O_7$



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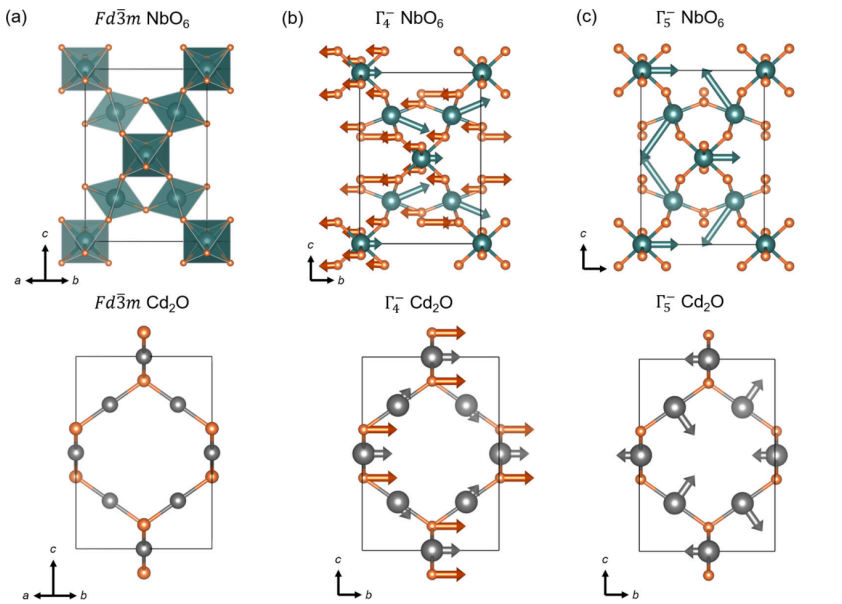
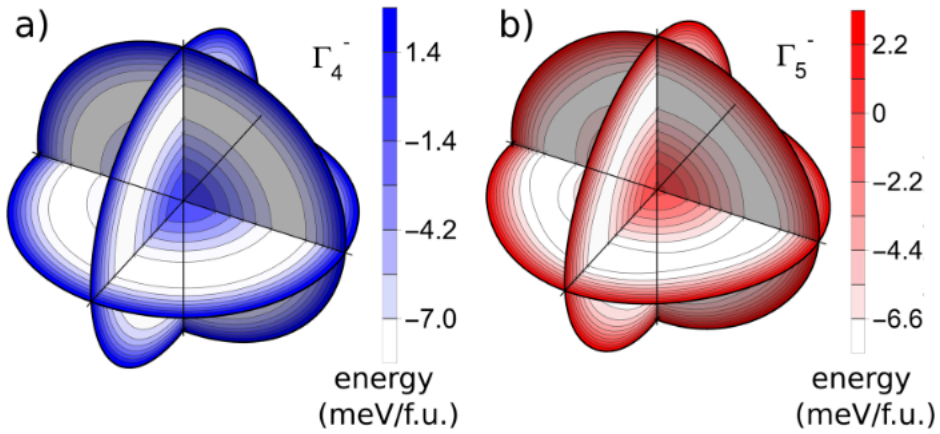
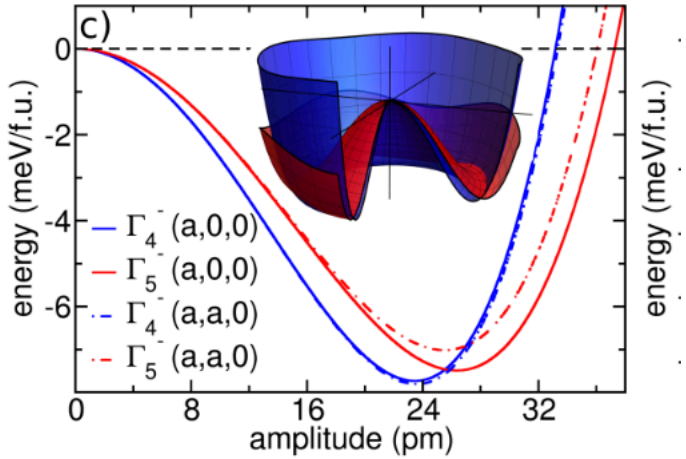



James Rondinelli

Mike Norman

Calculated energy landscape



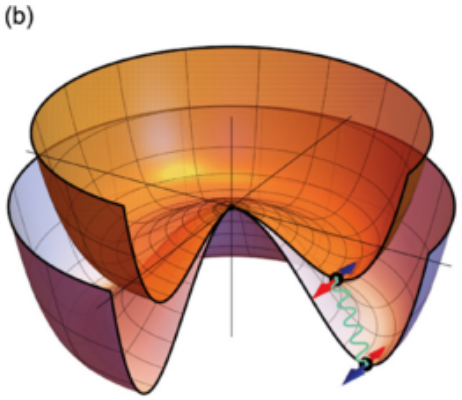

Hickox-Young, QNM et al, Phys. Rev. Research 4 (3), 033187 (2022)

# Leggett modes in the pyrochlore $Cd_2Nb_2O_7$

Coexistence of ferroelectric and anti-polar distortions
2 different soft modes of dimension 3:
Reduce force constant matrix into 6x6 matrix
Anharmonic coupling -> Leggett's mode

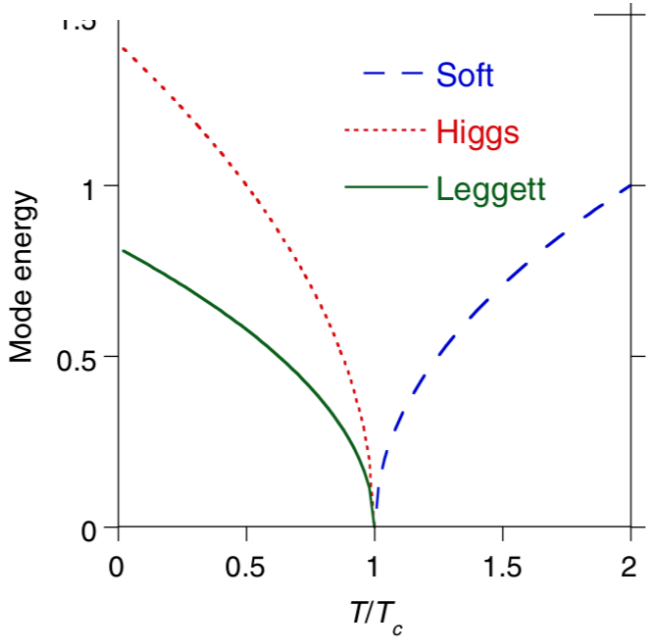
A.J. Leggett, Prog. Theor. Phys. 36, 901 (1966)

$$F = \frac{\alpha_4}{2}(a^2+b^2) + \frac{\alpha_5}{2}(c^2+d^2) + \frac{\beta_4}{4}(a^2+b^2)^2 + \frac{\gamma_4}{4}(a^4+b^4) + \frac{\beta_5}{4}(c^2+d^2)^2 + \frac{\gamma_5}{4}(c^4+d^4) + \frac{\delta}{2}(a^2+b^2)(c^2+d^2) + \epsilon_1(ab)(ad-bc) + \frac{\epsilon_2}{2}(a^2c^2+b^2d^2) + \epsilon_3(abcd) + \epsilon_4(cd)(ad-bc).$$




$$\Phi = \begin{bmatrix} H_{\mathbf{q}} & M & 0 & 0 \\ M & H_{\mathbf{r}} & 0 & 0 \\ 0 & 0 & G_{\mathbf{q}} & L \\ 0 & 0 & L & G_{\mathbf{r}} \end{bmatrix}$$

Anharmonicity + Coupling between Goldstone-like modes

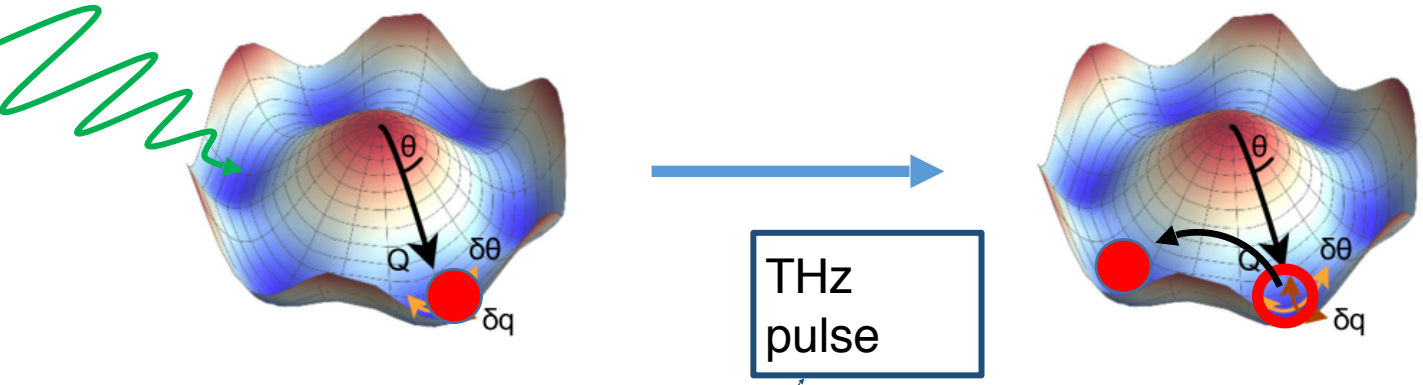



Energy landscape shows two independent soft modes

QNM et al, Phys. Rev. X 12, 011024 (2022)

# THz control of order parameters

- Idea: Use THz radiation to control the phase of the material:
- Phase fluctuations can be induced by pumping the Higgs mode, BUT no deterministic control of the phase (yet)

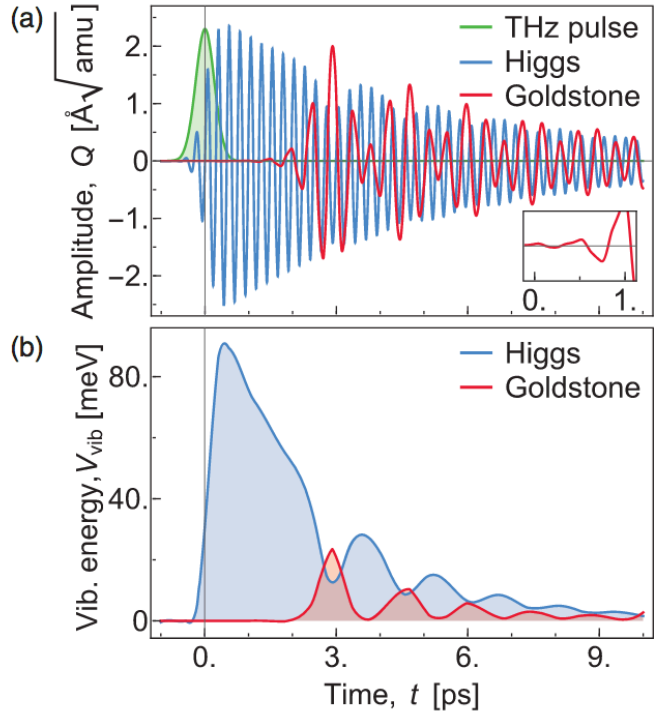



Theory: phononic equations of motion

$$\ddot{Q}_i + \kappa_i \dot{Q}_i + \frac{\partial V}{\partial Q_i} - Z_i E(t) = 0,$$

$$V(Q_A, Q_B) = \frac{{\omega_A}^2}{2} Q^2_{\omega_A} + \frac{{\omega_B}^2}{2} Q^2_{\omega_B} + c Q^3_{\omega_A} + d Q_A Q^2_B$$

Dominik Juraschek  Prineha Narang

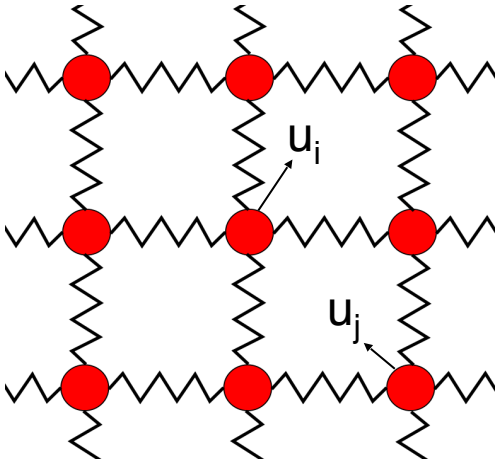


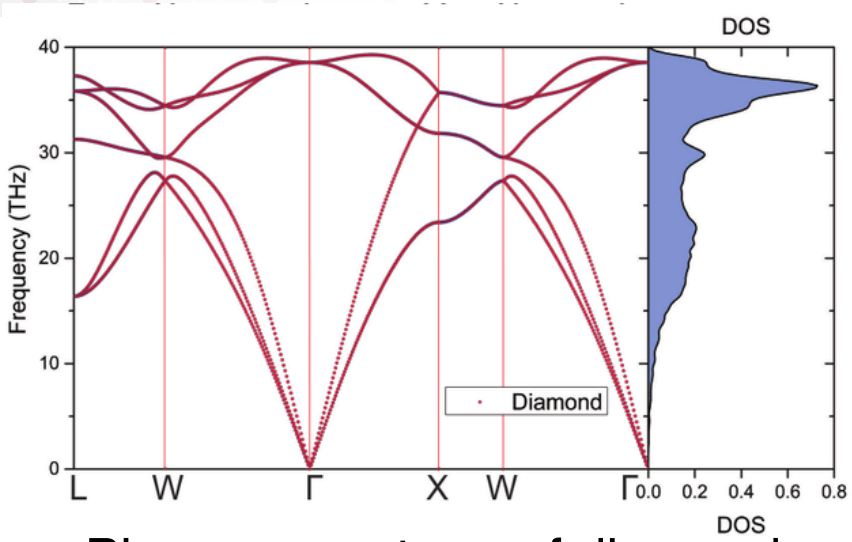

D. Juraschek, QNM, P. Narang
Phys. Rev. Lett. 124, 117401 (2020)

# Anharmonic ab initio lattice dynamics

# Thermal activation of the vibrational spectrum

Vibrational spectrum




Phonon spectrum of diamond

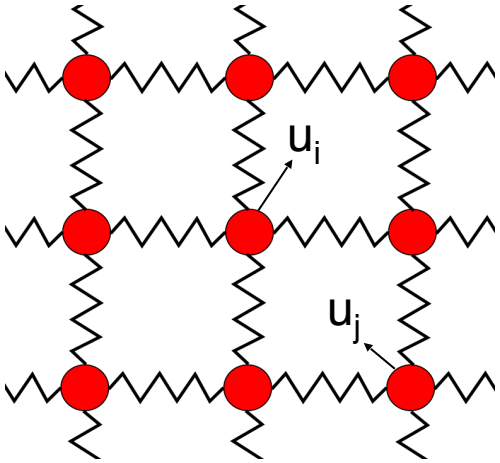
S. Yue et al, Review B. 95. 085207 (2017)

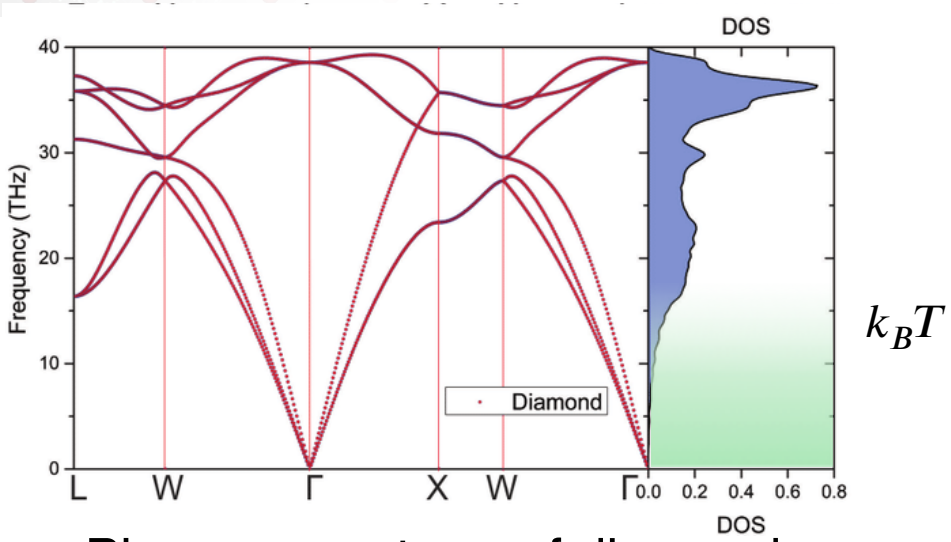
Anharmonic interactions of thermally active and zero-point phonons change the phonon spectrum!

→ We can include thermal displacements of the atoms in calculation of the force constants

# Thermal activation of the vibrational spectrum

Vibrational spectrum




$k_B T$

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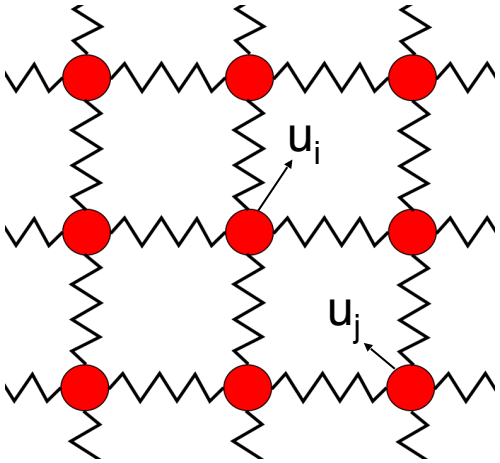


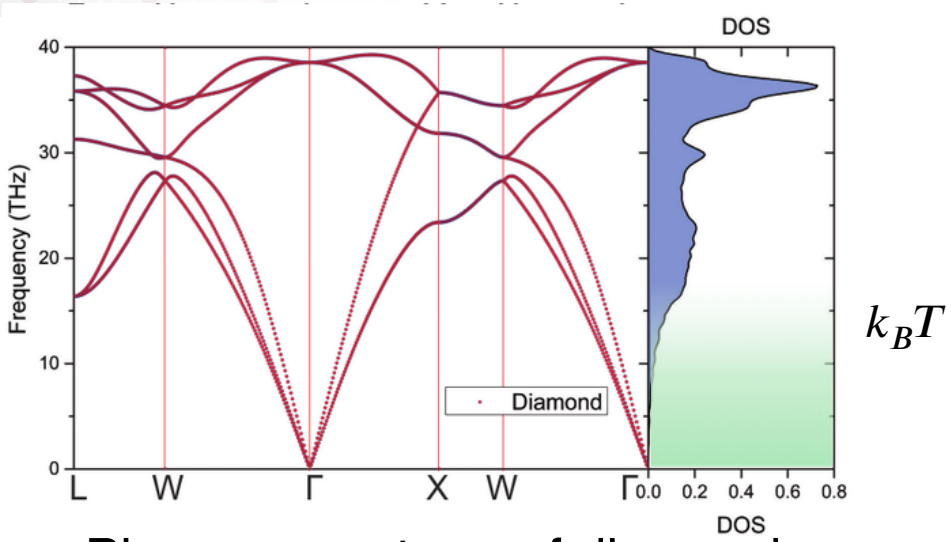


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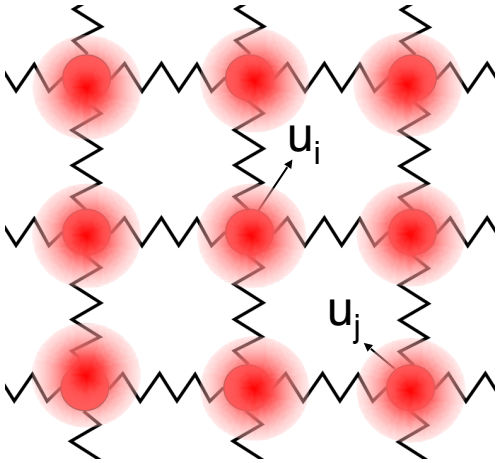


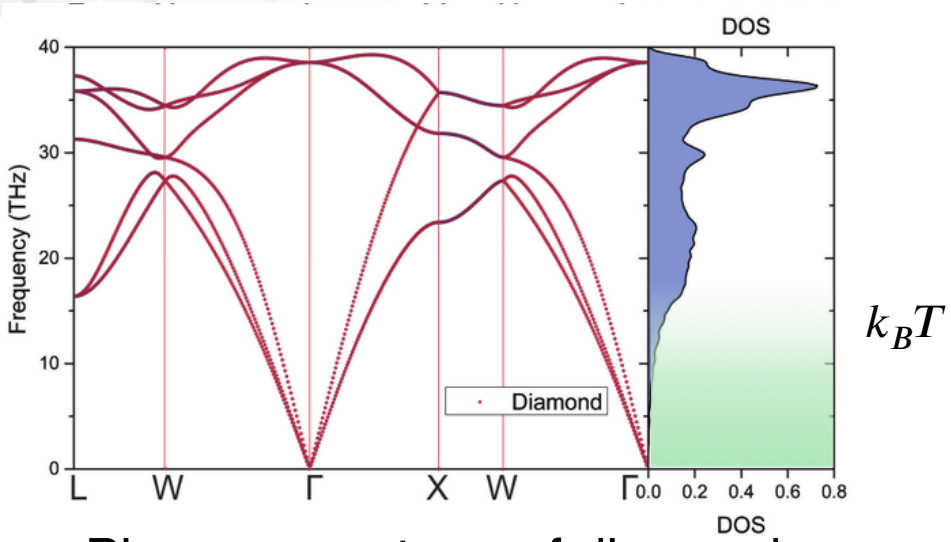


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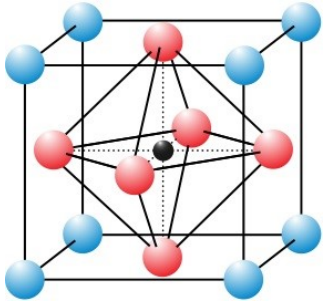
# The QSCAILD program

Python-based inhouse code
Easy to use, fully compatible with phonopy
Works with VASP, but can easily be adapted for any dft code
Freely available: https://github.com/vanroeke/qscaild
Compatible for the use with almaBTE for thermal transport

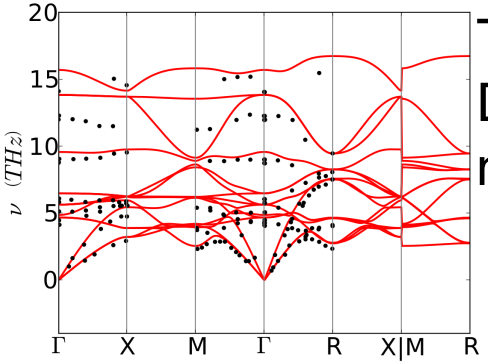
Ambroise van Roekeghem

Natalio Mingo

# Simplified schematic



Atomic positions, symmetries




Thermal Displacement matrix

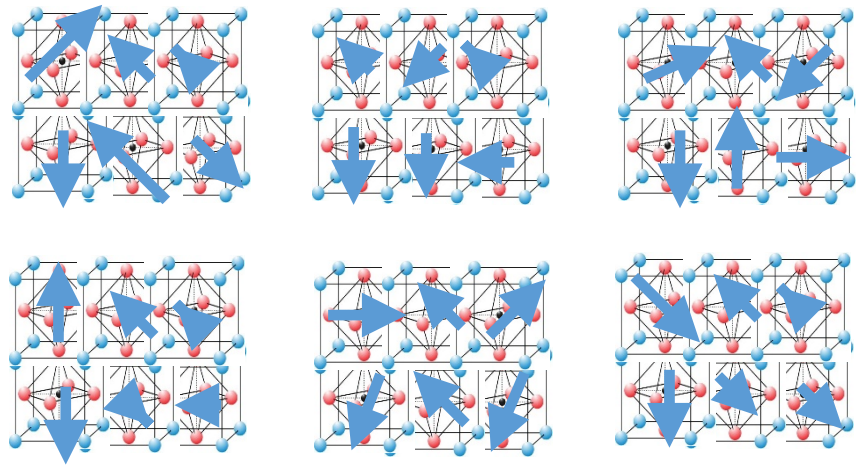
Best fit force constants

$$F_i^\alpha = \sum_{j\beta} \Phi_{ij}^{\alpha\beta} u_j^\beta + \frac{1}{2} \sum_{jk\beta\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_j^\beta u_k^\gamma$$

Including LO/TO splitting

Self-consistent cycle

N configurations with random displacements
Weighted by quantum statistics



Computationally heavy!

# Overcoming the bottleneck using machine learning

## Machine-learning interatomic potentials

DFT training set: energies, forces, stresses

↓

Effective potentials

↓

Neural network | Regression

↓

Predict energies and forces of a new configuration

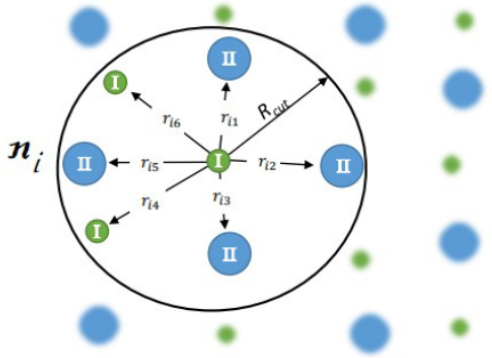
- Combines speed of empirical potentials with accuracy of DFT
- Enables calculation of large cells
- Ideal in combination MD or stochastic methods

## Moment tensor potential

$$M_{\mu,\nu}(\mathrm{n}_i) = \sum_j f_\mu(|r_{ij}|, z_i, z_j)\, \underbrace{r_{ij} \otimes \ldots \otimes r_{ij}}_{\nu \text{ times}},$$

**Radial: depends on relative distances and types of atoms**

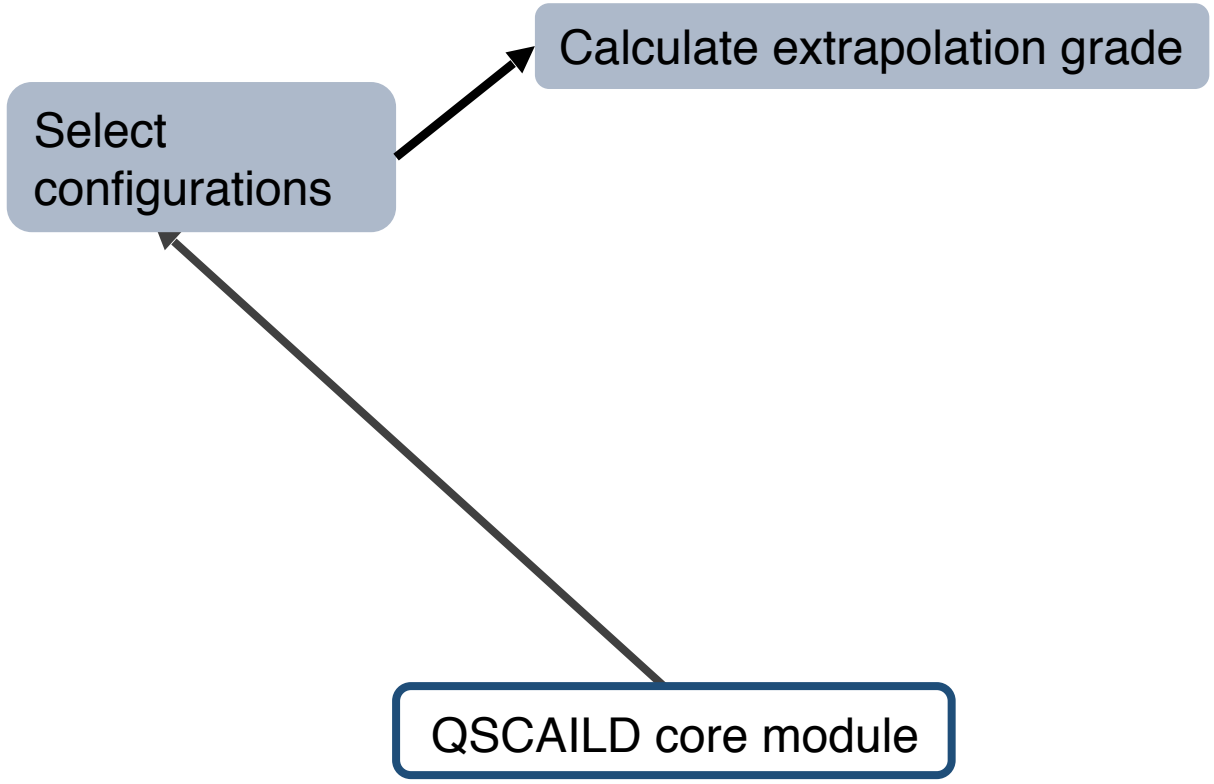
**Angular: tensor resembling moments of inertia**




INovikov et al, Mach. Learn.: Sci. Technol. 2 025002 (2021)

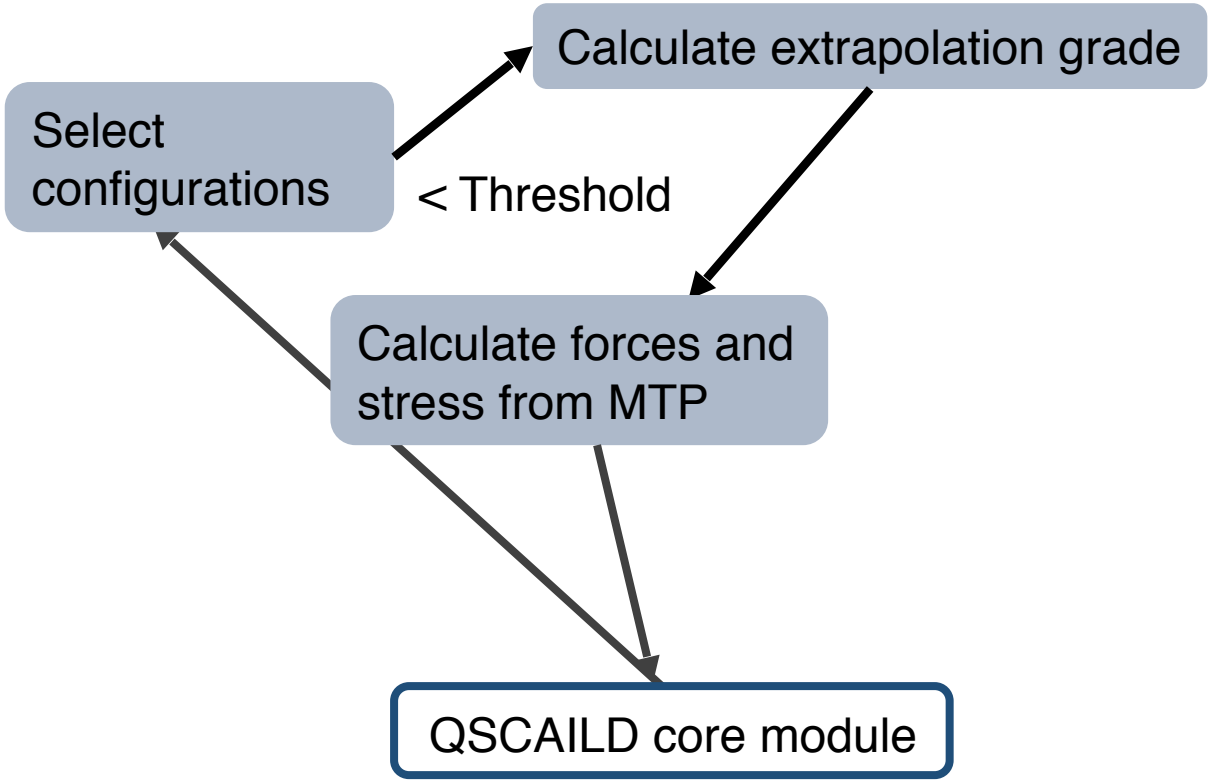
# Implementation of an active learning mechanism

On-the-fly active learning scheme



# Implementation of an active learning mechanism

On-the-fly active learning scheme



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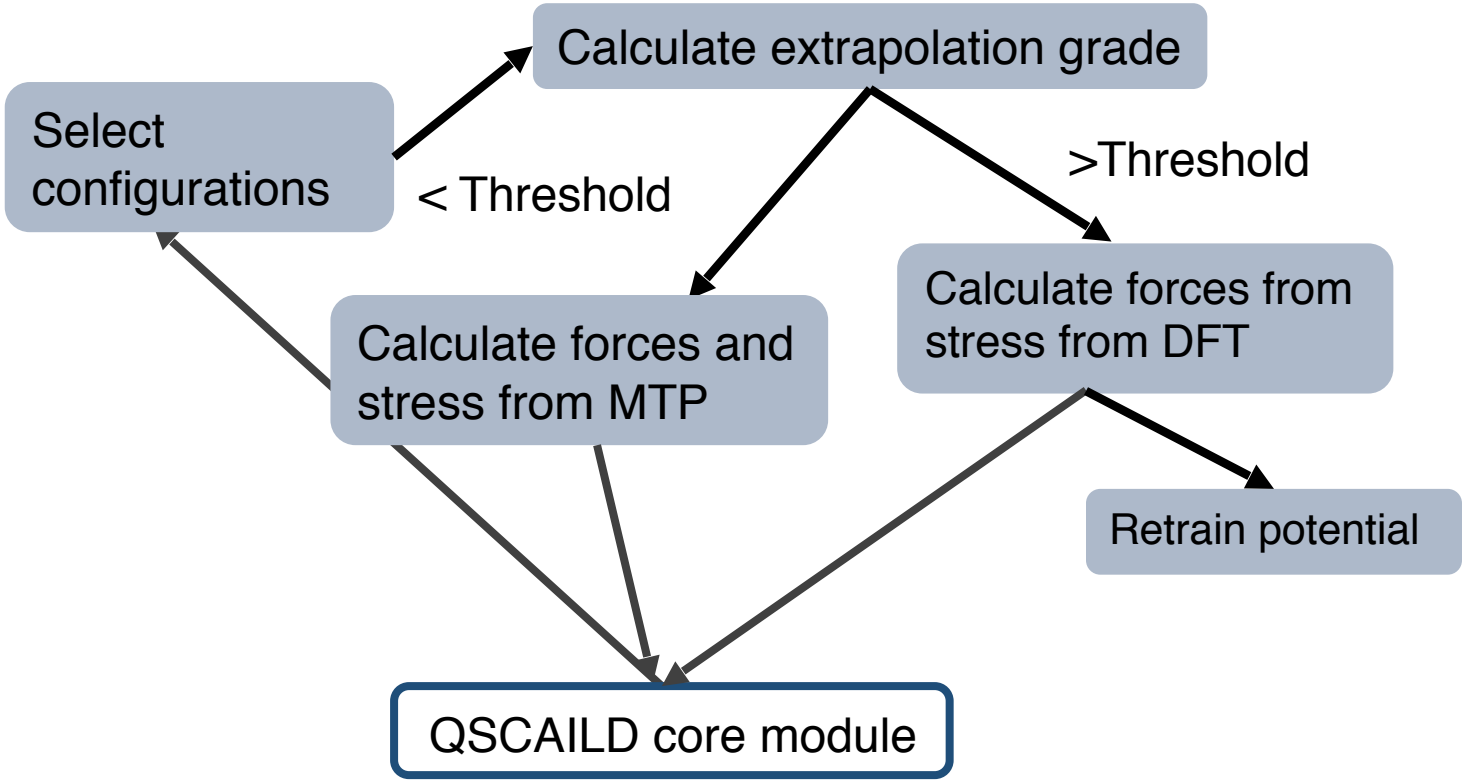


# Quantum paraelectricity in $KTaO_3$ (KTO)

Ferroelectric soft mode → Curie-Weiss behavior of the dielectric constant

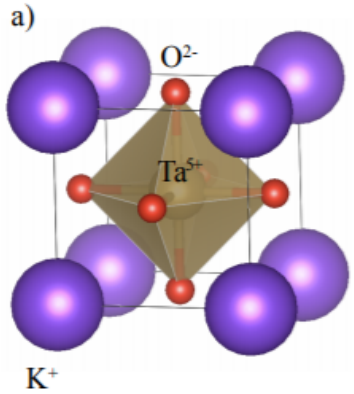
No ferroelectric phase transition, not even at 0 K

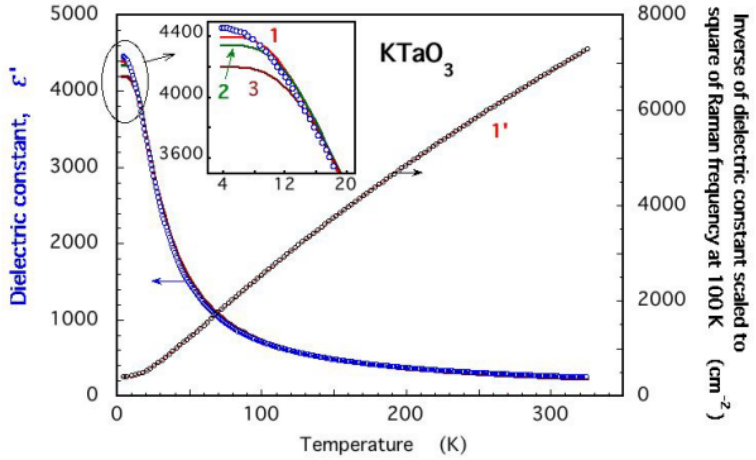
At low T, dielectric constant flattens

→ Barrett law

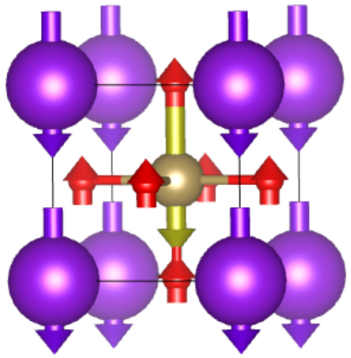
On the verge of becoming ferroelectric

→ small perturbations can induce ferroelectric phase

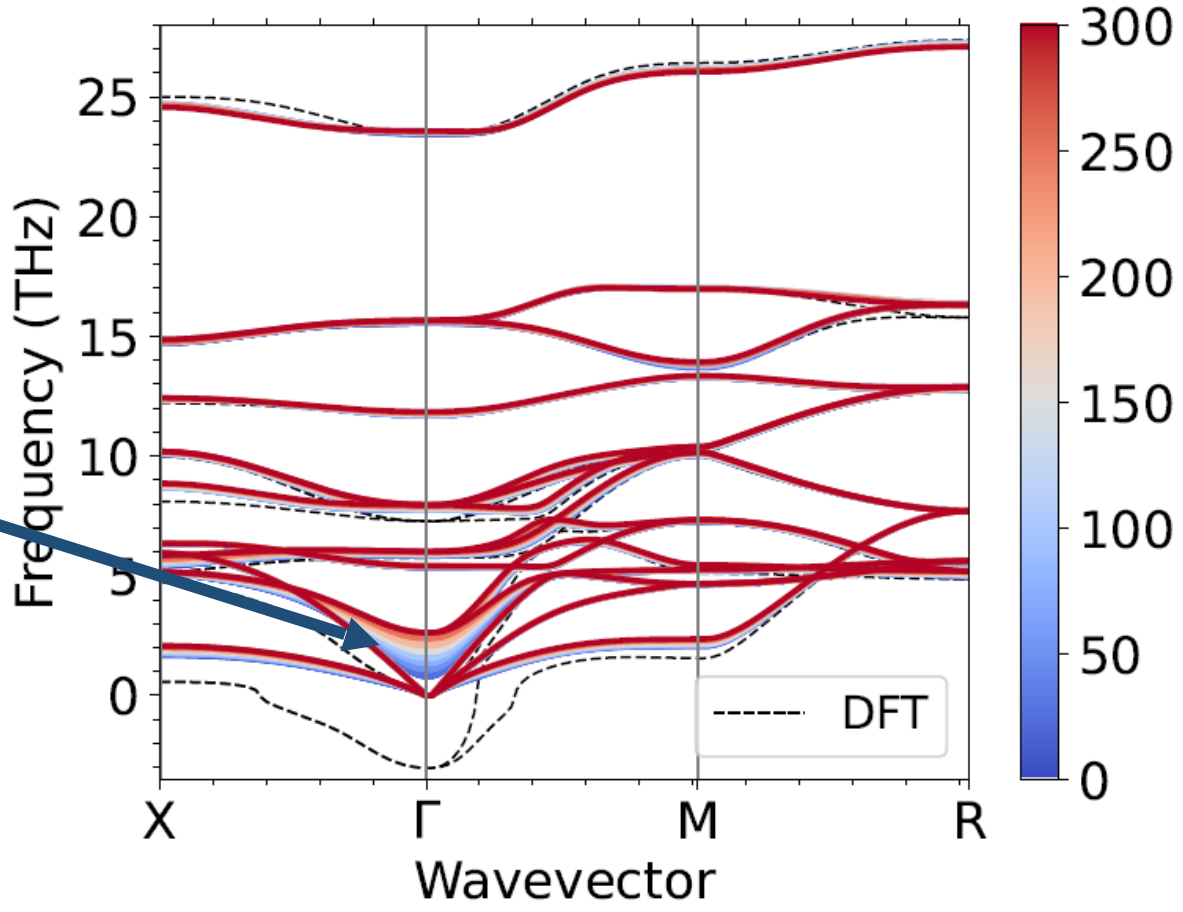


# Temperature dependent phonon band structure of $KTaO_3$



Crystal structure and softmode of $KTaO_3$




Meier et al, arXiv:2206.08296

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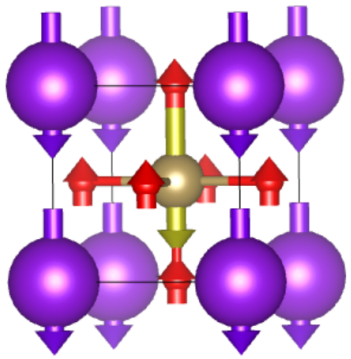

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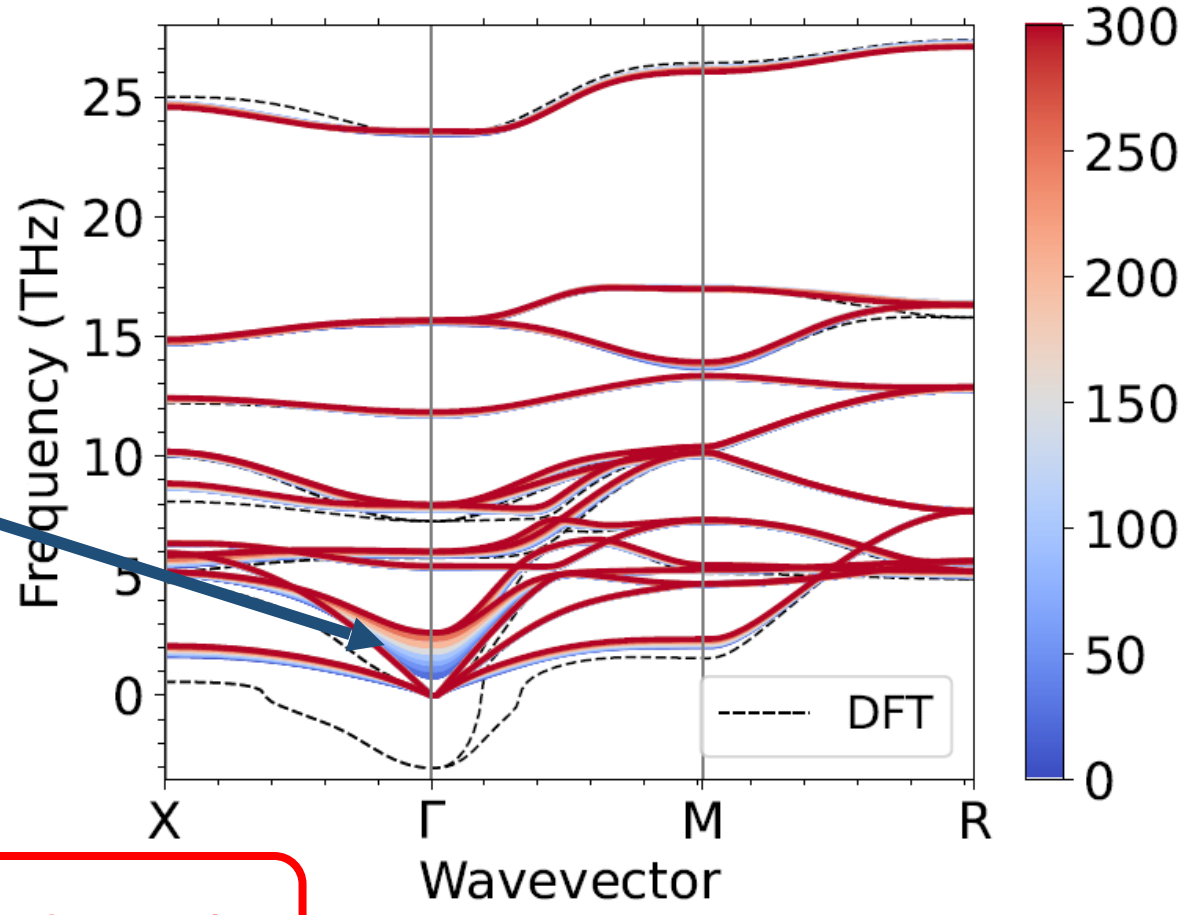
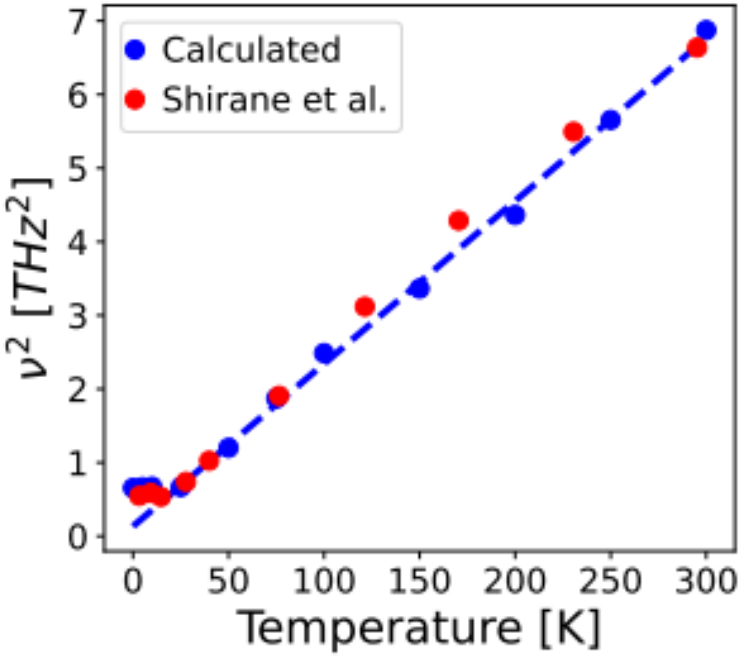



Strong anharmonic softening in a polar zero-point mode

Meier et al, arXiv:2206.08296

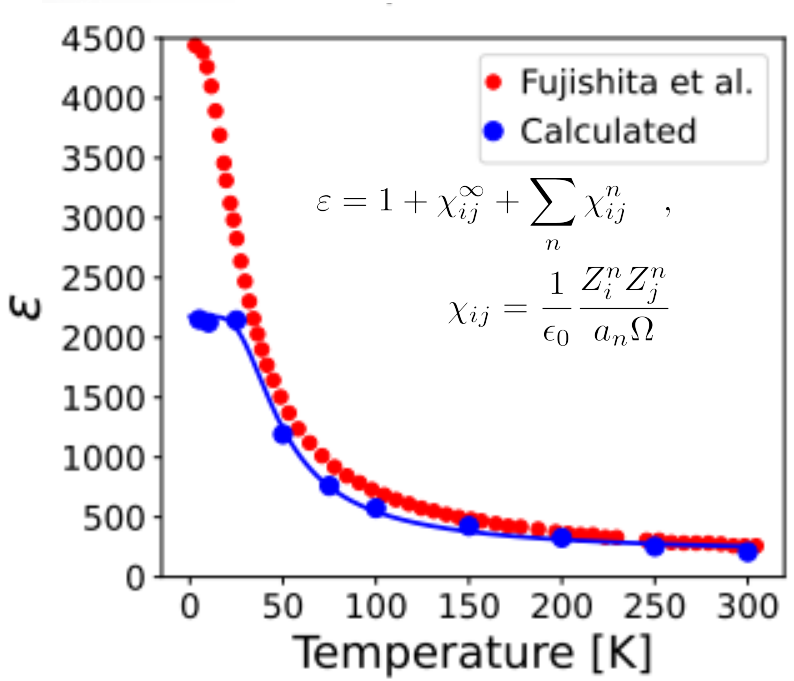
# Phonon frequencies and dielectric constants of $KTaO_3$




Excellent agreement of temperature dependent phonon frequencies with experiment

Small difference in temperature of saturation

G. Shirane, R. Nathans, and V. J. Minkiewicz
Phys. Rev. 157, 396 (1967)



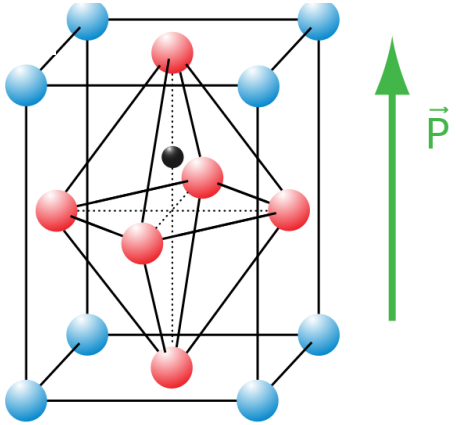

Temperature dependent dielectric constant compared to experiment, excellent agreement up to 25K
and observation of a Barrett law

Fujishita et al, J. Phys. Soc. Jpn. 85, 074703 (2016)
J. Barrett, Phys. Rev. 86, 118 (1952)

Q.N.M et al, arXiv:2206.08296

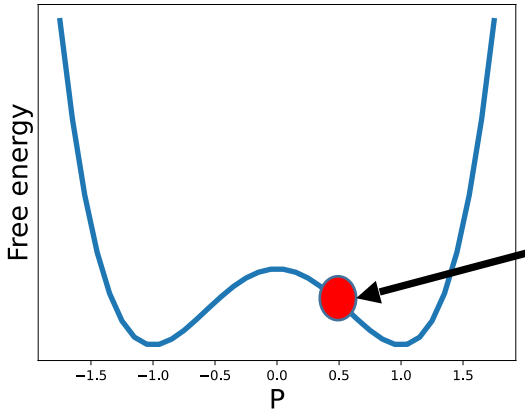
# In the low-symmetry phase, the structure is temperature dependent

- Amplitude of polarization depends on temperature



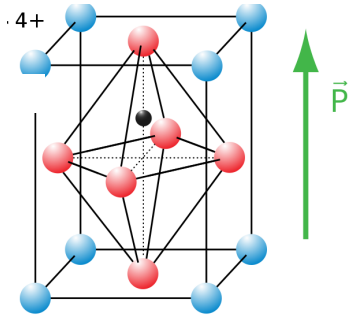

We get a non-zero average force on the atoms

$$F_i^\alpha = \sum_{j\beta} \Phi_{ij}^{\alpha\beta} u_j^\beta + \frac{1}{2} \sum_{jk\beta\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_j^\beta u_k^\gamma + \mathcal{F}_i^\alpha$$



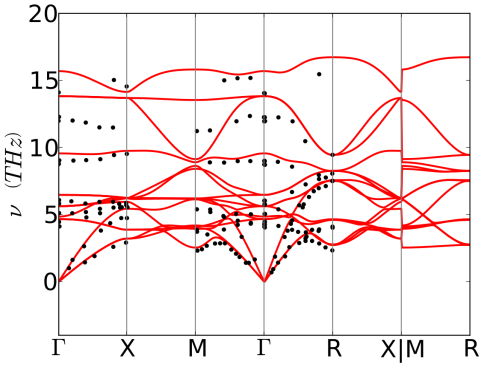

Input structure might not be at the minimum for a given temperature!

# Workflow of temperature dependent relaxation in QSCAILD



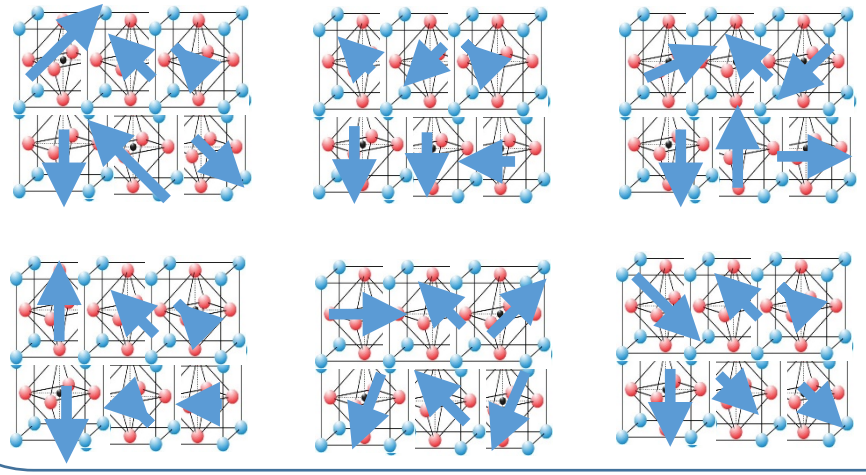

$T < T_C$

Atomic positions, symmetries




Thermal Displacement matrix

N configurations with random displacements
Weighted by quantum statistics



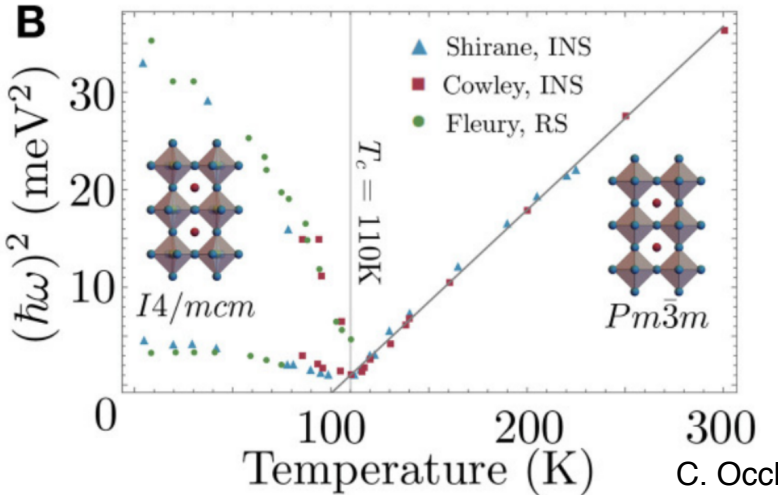
Self-consistent cycle

Force constants

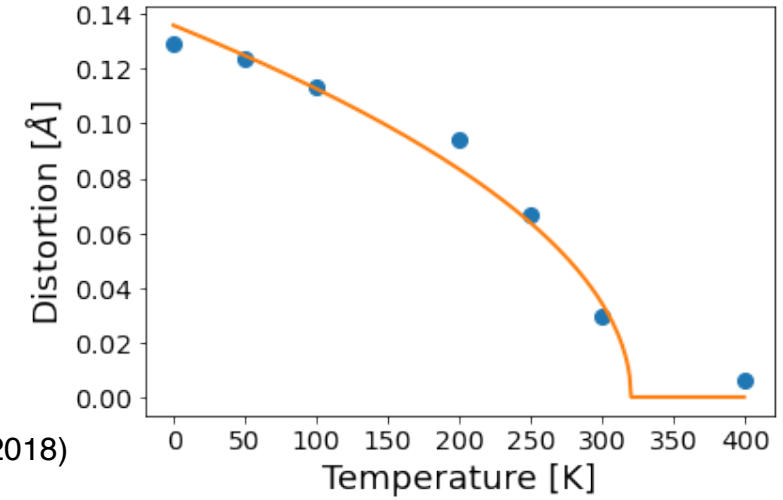
$$F_i^\alpha = \sum_{j\beta} \Phi_{ij}^{\alpha\beta} u_j^\beta + \frac{1}{2} \sum_{jk\beta\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_j^\beta u_k^\gamma$$

Symmetrized average forces $\mathcal{F}_i^\alpha$

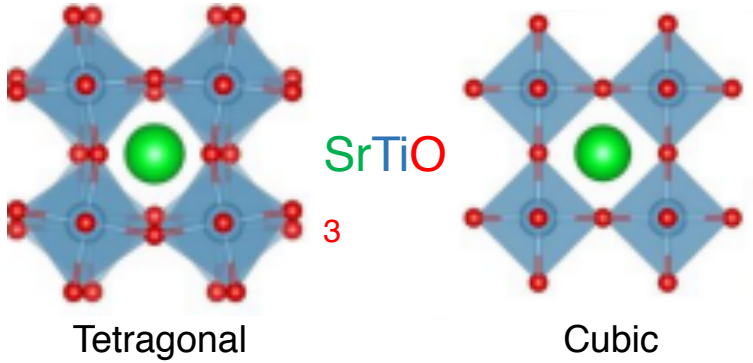
# Cubic to tetragonal transition in SrTiO3



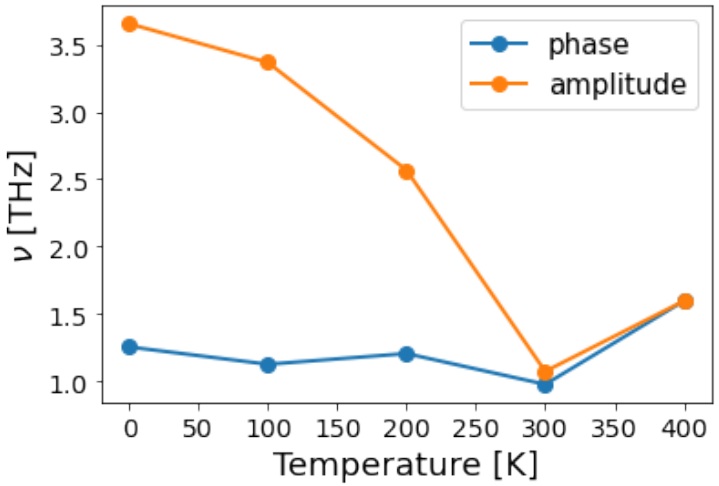

C. Occhialini et al, Front. Chem 20 (2018)




Cubic to tetragonal transition in STO



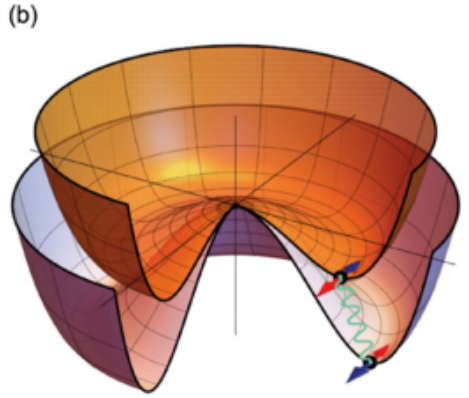

Rotational mode

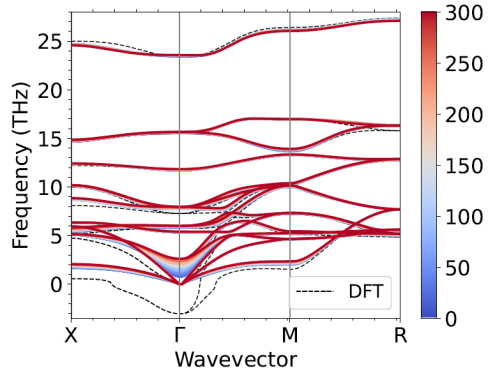



Meier et al, in preparation

# Conclusion

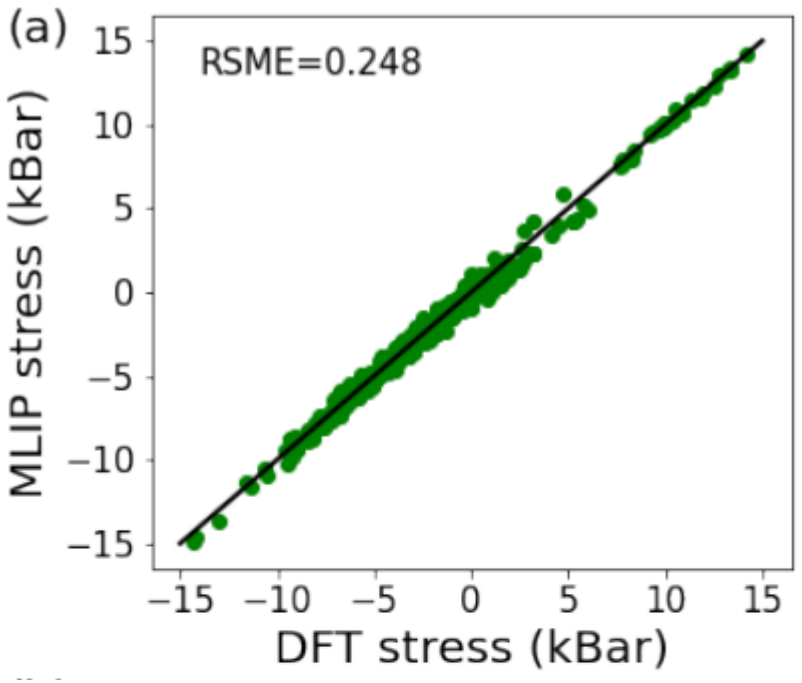
- Soft phonon modes are used to describe structural phase transitions
- Hard to calculate because DFT is only at zero temperature
- Showed phenomenological as well as ab initio treatment
- Machine learning potentials allow us to calculate temperature-dependent phonon modes and structure for a reasonable computational cost

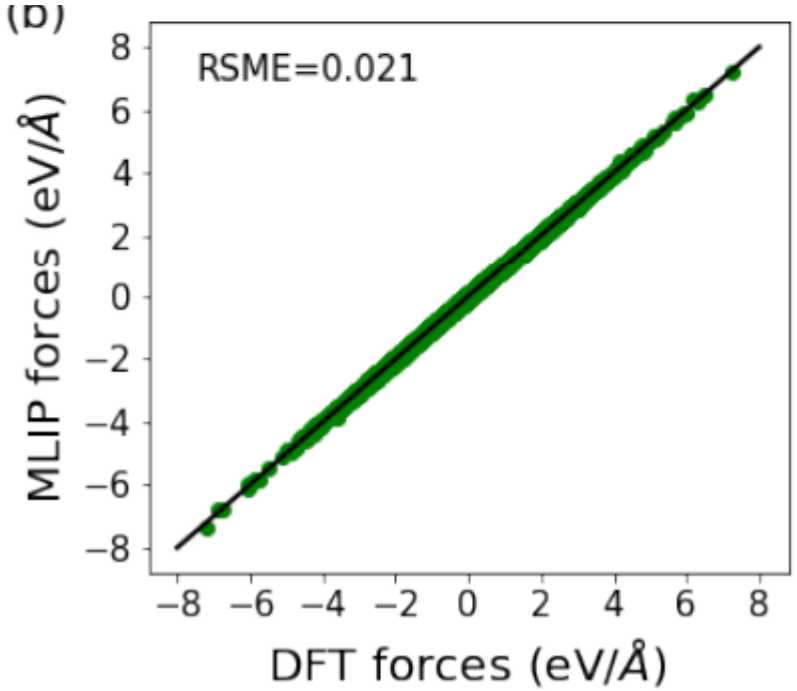


# QSCAILD + Machine learning

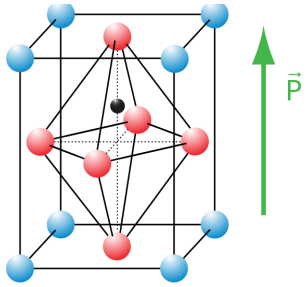
- Allows us to overcome the bottleneck -> enourmous speedup, reduction of cpu hours
- Training of a machine-learned potential while running the calculation
- Almost zero loss of accuracy
- Hi

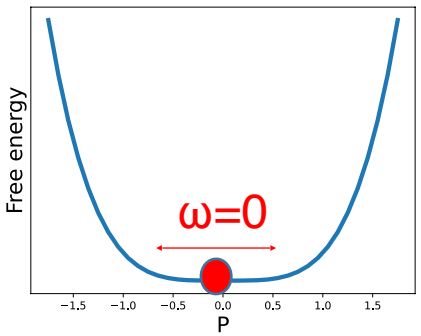


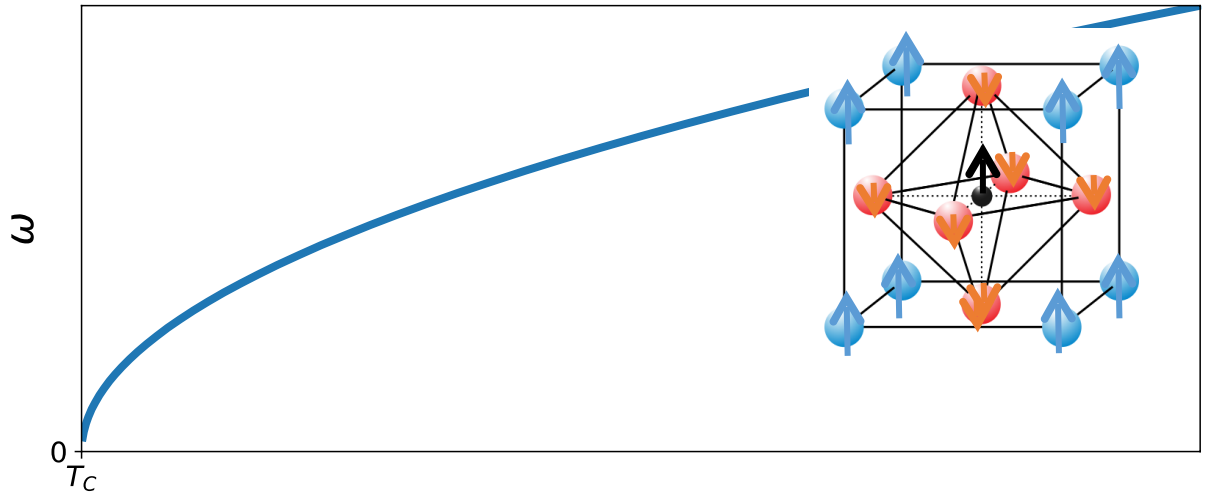
# Phonons

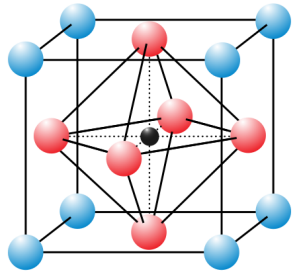
A soft mode is a mode that “condenses” at a structural phase transition

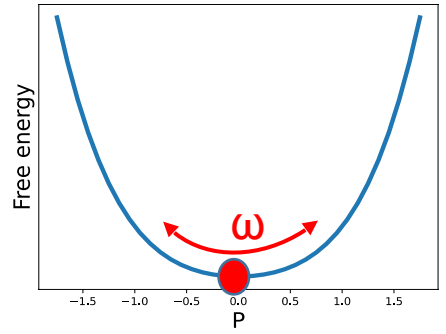



(phonon frequency)$^2$ ~ curvature of the free energy

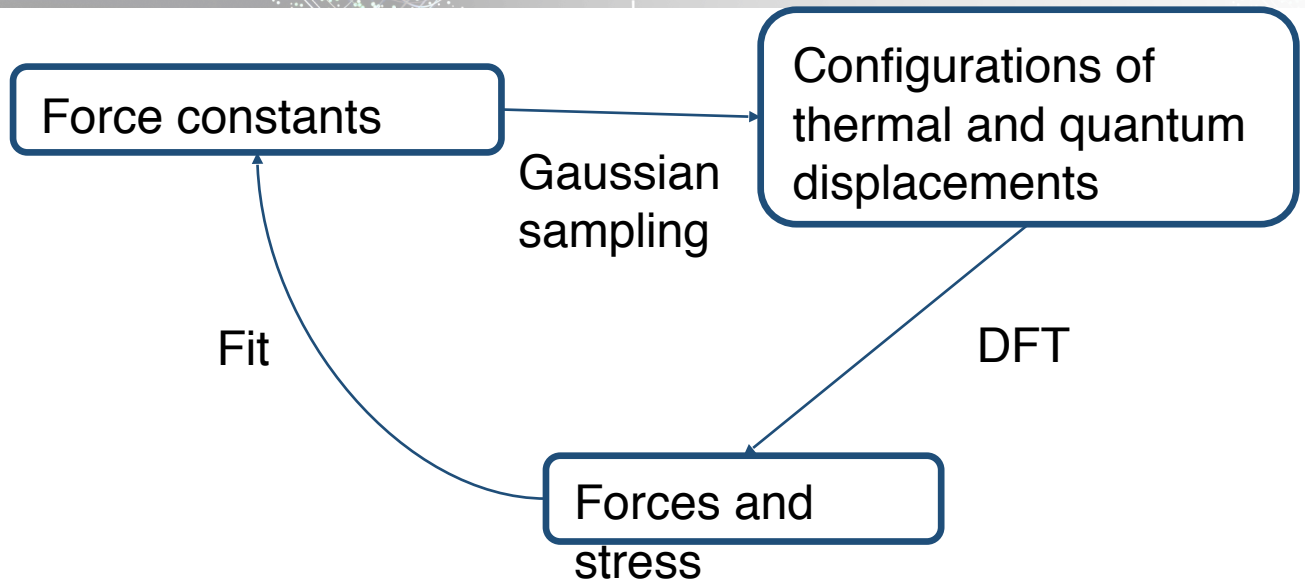


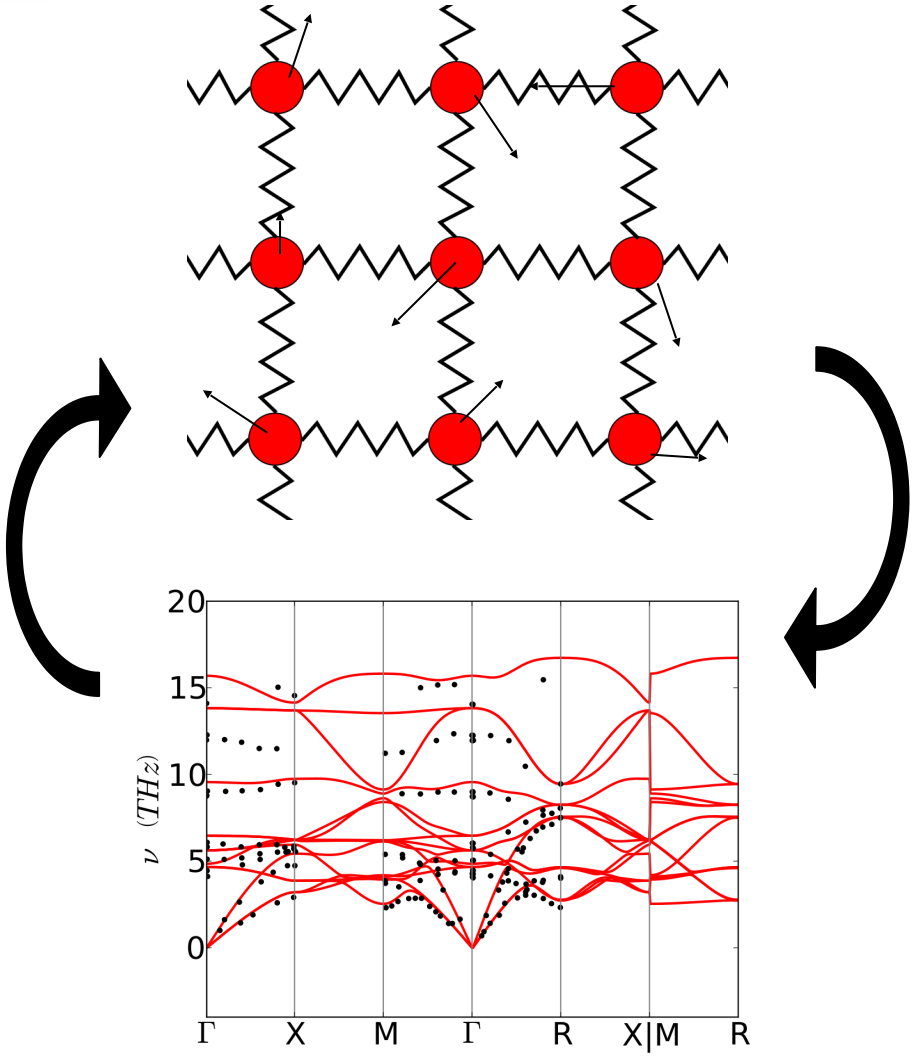




Eigenvector pattern corresponds to the spontaneous polarization

# Quantum self-consistent lattice dynamics (QSCAILD)




## Sampling

Quantum covariance matrix

$$\Sigma_{i\alpha,j\beta} = \frac{\hbar}{2\sqrt{M_i M_j}} \sum_m \omega_m^{-1} \left(1 + 2n_B\left(\omega_m; T\right)\right) \epsilon_{mi\alpha} \epsilon^*_{mj\beta}$$

Probability of finding the system in a random configuration u

$$\rho(u) \propto \exp\left[-\frac{1}{2} u^T \Sigma^{-1} u\right]$$

A. Van Roekeghem et al, Comp. Phys. Commun, 107945 (2021)

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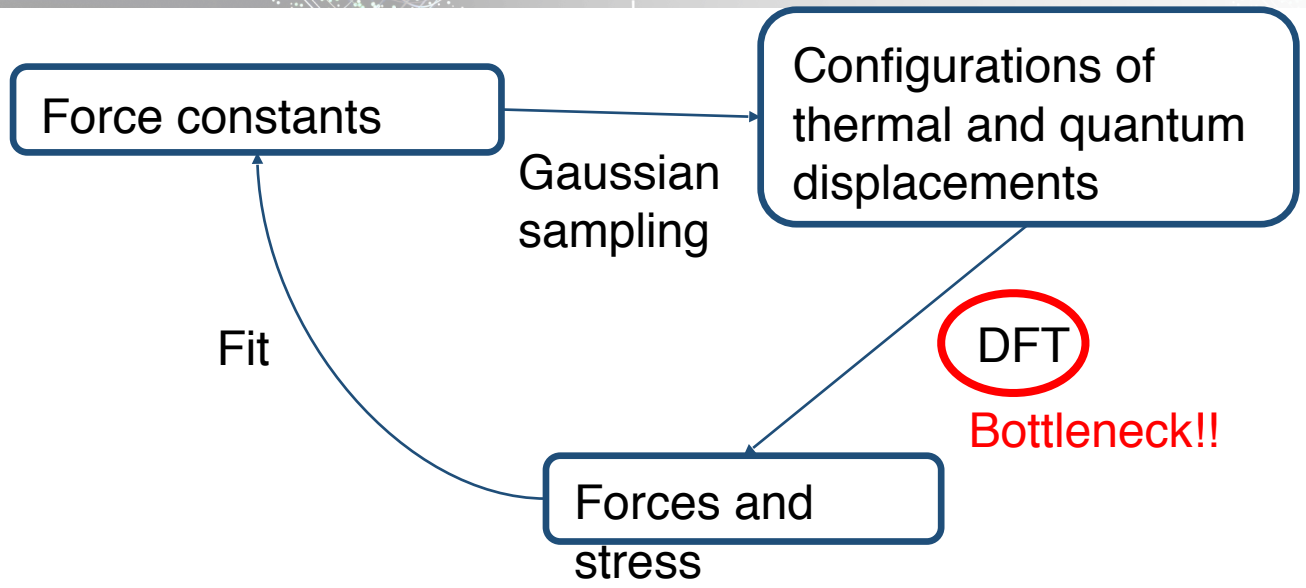


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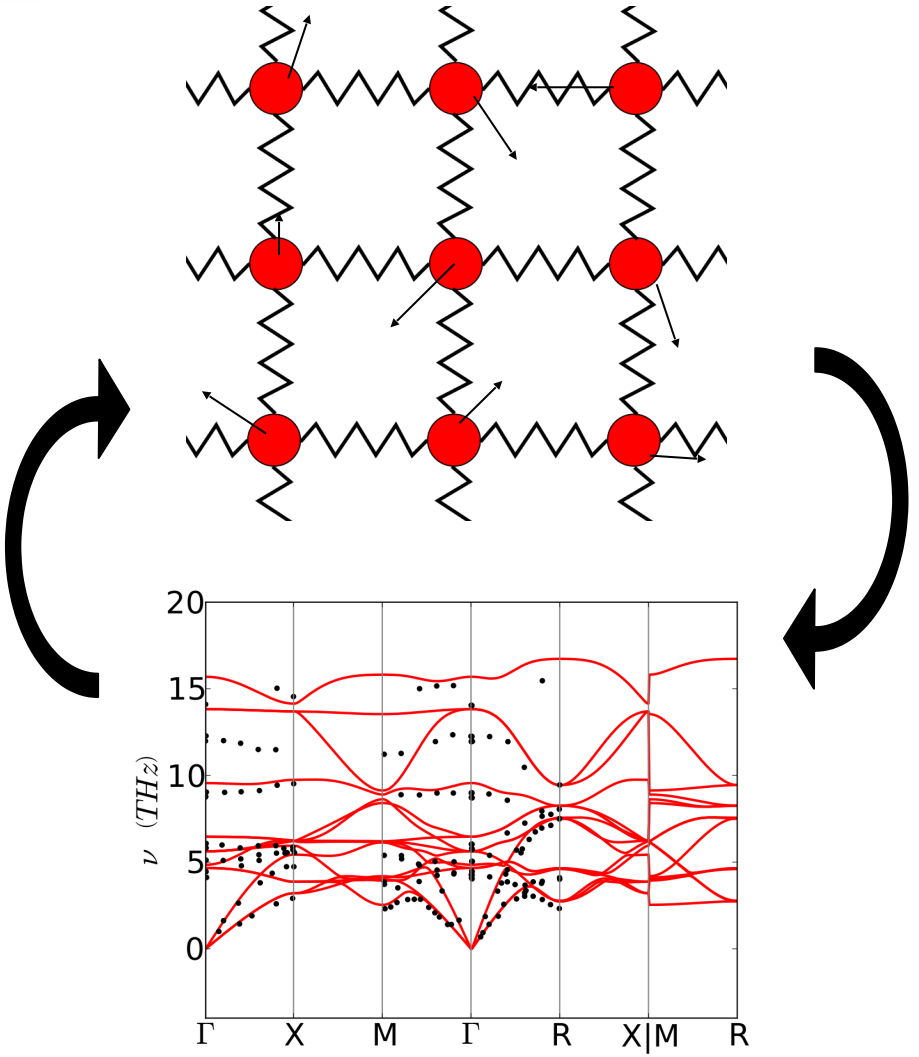
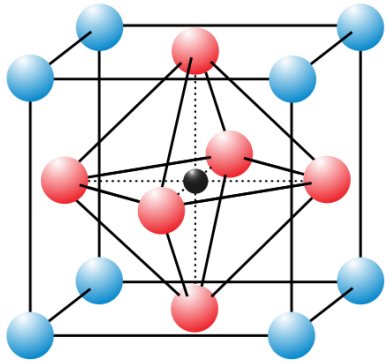
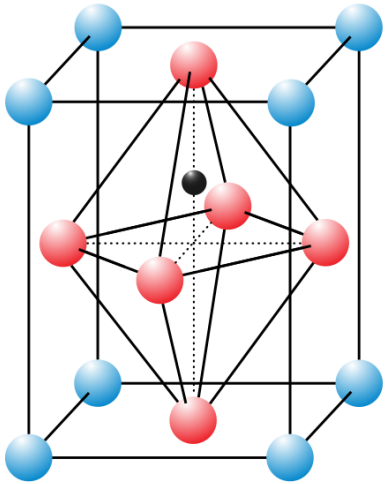


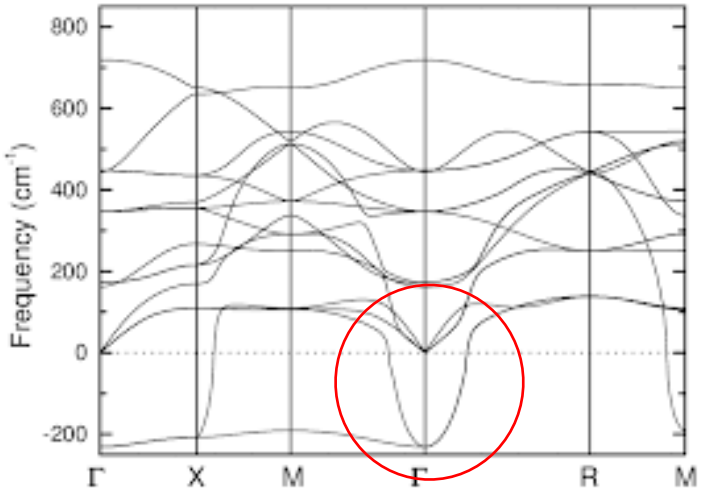

A. Van Roekeghem et al, Comp. Phys. Commun, 107945 (2021)

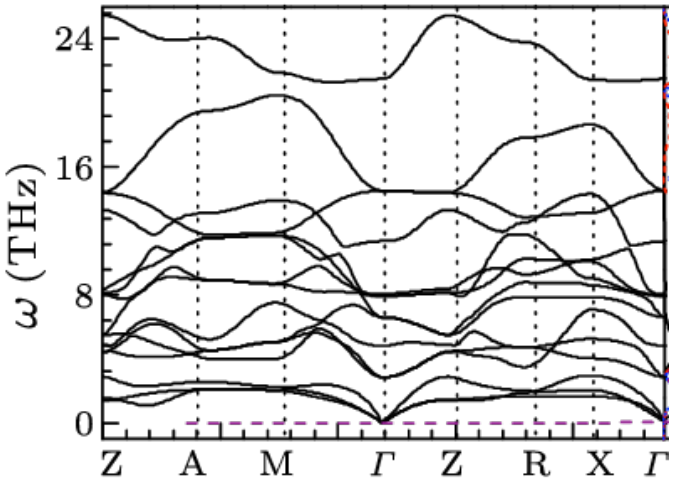
# Structural instabilities

When calculating the phonon spectrum from DFT:
Unstable modes in the parent structure!



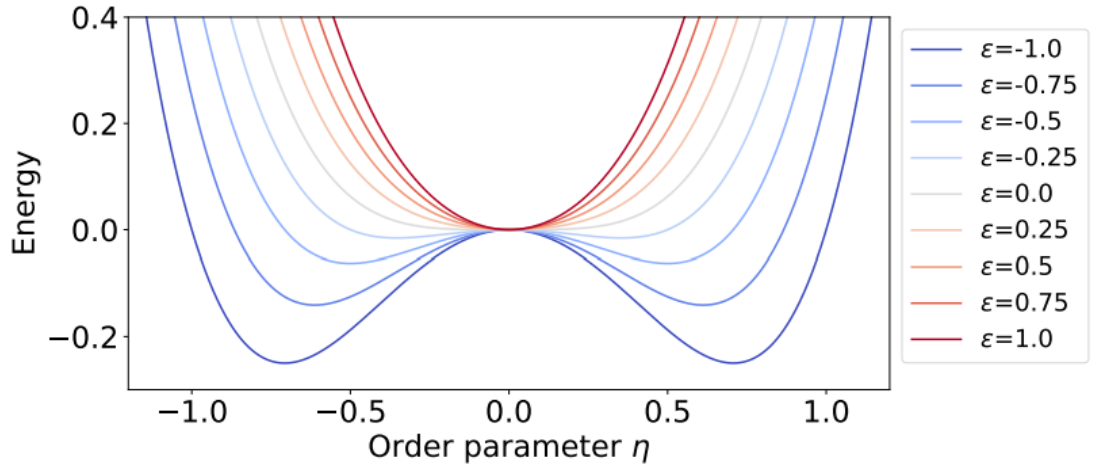




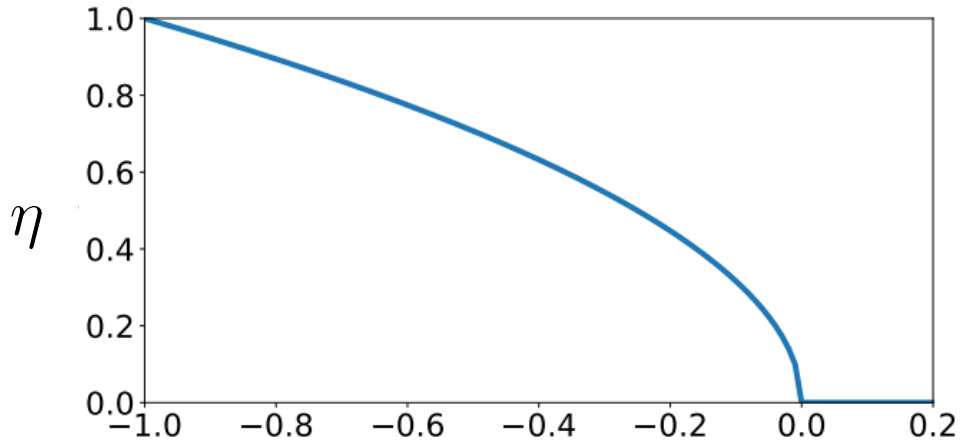

Unstable branches!

# Landau theory




$$F(T) = \frac{a_0\left(\frac{T-T_C}{T_C}\right)}{2}\eta^2 + \frac{b}{4}\eta^4 + ... - \eta H$$

Where H is the conjugate field of the order parameter




$$\epsilon = \frac{T - T_C}{T_C}$$

The order parameter $\eta$ is a property that is zero in the high-symmetry phase and non-zero in the low-symmetry phase

$\eta = \vec{P}, \vec{M}, \vec{\mathcal{E}}$, or an other quantity related to the phase transition

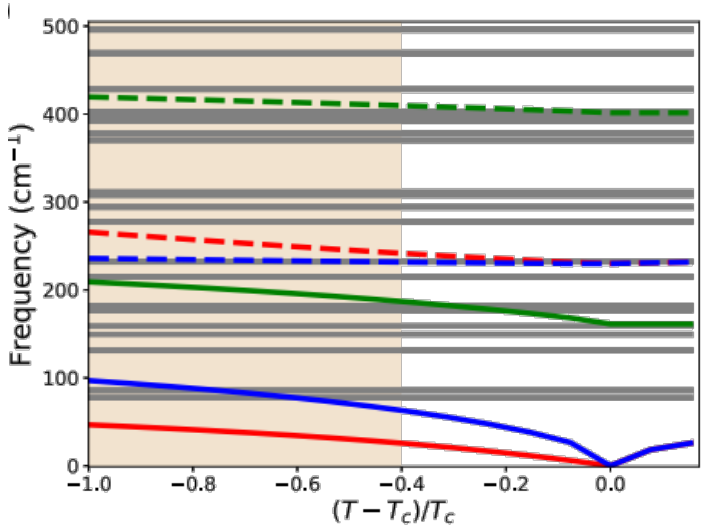
# Introduce anharmonicity using Landau expansion

Reducing the degrees of freedom in the force constant matrix in diagonal form:

$$\Phi(T) = \begin{bmatrix} \chi_{\delta q}^{-1}(T) & 0 & 0 & 0 & 0 & \dots & 0 \\ 0 & \chi_{\delta\theta}^{-1}(T) & 0 & 0 & 0 & \dots & 0 \\ 0 & 0 & \chi_{\delta p}^{-1}(T) & 0 & 0 & \dots & 0 \\ 0 & 0 & 0 & \alpha_4 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & 0 & \dots & \alpha_{3N} \end{bmatrix}$$

Order parameters
Temperature dependent

Rest of the modes
Temperature independent




Stable phonon spectrum

Calculate renormalized force constants
(Curvature around the minimum of the free energy)

$$\chi_{\delta q}^{-1}(T) = \frac{\partial^2 F}{\partial Q^2}\bigg|_{Q=\tilde{Q},\theta=0,P=\tilde{P}} = a(T) + 3b\tilde{Q}^2 - 5c\tilde{Q}^4 + d\tilde{P}^2 - 6g\tilde{Q}\tilde{P} - 4f\tilde{P}^3$$

$$\chi_{\delta\theta}^{-1}(T) = \frac{1}{Q^2}\frac{\partial^2 F}{\partial\theta^2}\bigg|_{Q=\tilde{Q},\theta=0,P=\tilde{P}} = -6\tilde{Q}^4 + 9g\tilde{Q}\tilde{P}$$

$$\chi_{\delta p}^{-1}(T) = \frac{\partial^2 F}{\partial P^2}\bigg|_{Q=\tilde{Q},\theta=0,P=\tilde{P}} = g'\tilde{Q}^2 + a_p$$