Lecture 3:

Second-order phase transitions in the SSCHA

Raffaello Bianco

Self-Consistent Harmonic Approximation

The exact system:

$$H = K + V(R)$$

$$\rho \propto \exp(-\beta H)$$

Free Energy

$$F = \mathrm{Tr}[\rho H] + \frac{1}{\beta}\mathrm{Tr}[\rho \ln \rho]$$

Self-Consistent Harmonic Approximation

The exact system:

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The harmonic trial system:

$$H_{\mathcal{R},\Phi} = K + \frac{1}{2}(R - \mathcal{R}) \cdot \Phi \cdot (R - \mathcal{R})$$

$$\rho_{\mathcal{R},\Phi} \propto \exp(-\beta H_{\mathcal{R},\Phi})$$

Free Energy

$$F = \mathrm{Tr}[\rho H] + \frac{1}{\beta}\mathrm{Tr}[\rho \ln \rho]$$

Trial variabiles:

$\mathcal{R}$ — **Quadratic potential centroid (average atomic configuration)**

Φ — **Quadratic potential amplitude (positive definite) (related to the amplitude of the trial ground-state wfc)**

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$$\rho_{\mathcal{R},\Phi} \propto \exp(-\beta H_{\mathcal{R},\Phi})$$

$$\boxed{\rho \to \rho_{\mathcal{R},\Phi}}$$

Free Energy

$$F = \mathrm{Tr}[\rho H] + \frac{1}{\beta}\mathrm{Tr}[\rho \ln \rho]$$

Free Energy Functional

$$\mathcal{F}(\mathcal{R},\Phi) = \mathrm{Tr}[\rho_{\mathcal{R},\Phi} H] + \frac{1}{\beta}\mathrm{Tr}[\rho_{\mathcal{R},\Phi} \ln \rho_{\mathcal{R},\Phi}]$$

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Free Energy

$$F = \mathrm{Tr}[\rho H] + \frac{1}{\beta}\mathrm{Tr}[\rho \ln \rho]$$

$$\boxed{\rho \rightarrow \rho_{\mathcal{R},\Phi}}$$

Free Energy Functional

$$\mathcal{F}(\mathcal{R},\Phi) = \mathrm{Tr}[\rho_{\mathcal{R},\Phi} H] + \frac{1}{\beta}\mathrm{Tr}[\rho_{\mathcal{R},\Phi} \ln \rho_{\mathcal{R},\Phi}]$$

$$\mathcal{F}(\mathcal{R},\Phi) \xrightarrow{\text{Minim. w.r.t } (\mathcal{R},\Phi)} \mathcal{F}(\mathcal{R}^{\mathrm{MIN}},\Phi^{\mathrm{MIN}}) \simeq F$$

Self-Consistent Harmonic Approximation

The exact system:

$$H = K + V(R)$$

$$\rho \propto \exp(-\beta H)$$

The harmonic trial system:

$$H_{\mathcal{R},\Phi} = K + \frac{1}{2}(R - \mathcal{R}) \cdot \Phi \cdot (R - \mathcal{R})$$

$$\rho_{\mathcal{R},\Phi} \propto \exp(-\beta H_{\mathcal{R},\Phi})$$

Free energy estimate

$$F \simeq \mathcal{F}(\mathcal{R}^{\mathrm{MIN}}, \Phi^{\mathrm{MIN}})$$

SCHA effective harmonic Hamiltonian

$$H^{\mathrm{SCHA}} = K + \frac{1}{2}(R - \mathcal{R}^{\mathrm{MIN}}) \cdot \Phi^{\mathrm{MIN}} \cdot (R - \mathcal{R}^{\mathrm{MIN}})$$

Self-Consistent Harmonic Approximation

The exact system:

$$H = T + V^{\text{N-N}}(R)$$

$$\rho \propto \exp(-\beta H)$$

The harmonic trial system:

$$H_{\mathcal{R},\varPhi} = T + \frac{1}{2}(R-\mathcal{R})\cdot\varPhi\cdot(R-\mathcal{R})$$

$$\rho_{\mathcal{R},\varPhi} \propto \exp(-\beta H_{\mathcal{R},\varPhi})$$

Free energy estimate

$$F \simeq \mathcal{F}(\mathcal{R}^{\text{MIN}}, \varPhi^{\text{MIN}})$$

Physical meaning?

SCHA effective harmonic Hamiltonian

$$H^{\text{SCHA}} = K + \frac{1}{2}(R-\mathcal{R}^{\text{MIN}})\cdot\varPhi^{\text{MIN}}\cdot(R-\mathcal{R}^{\text{MIN}})$$

$$\mathcal{R}^{\mathrm{MIN}} = \mathcal{R}_{\mathrm{eq}}$$

Average configuration of the atoms at equilibrium

Physical meaning?

SCHA effective harmonic Hamiltonian

$$H^{\mathrm{SCHA}} = K + \frac{1}{2}(R - \mathcal{R}^{\mathrm{MIN}}) \cdot \Phi^{\mathrm{MIN}} \cdot (R - \mathcal{R}^{\mathrm{MIN}})$$

$$\Phi^{\mathrm{MIN}} = \Phi$$

$$D^{(\mathrm{SCHA})} = \frac{\Phi}{\sqrt{MM}}$$

NOT generalized/effective "dynamical matrix"

NOT generalized/effective "phonons"

Physical meaning?

SCHA effective harmonic Hamiltonian

$$H^{\mathrm{SCHA}} = K + \frac{1}{2}(R - \mathcal{R}^{\mathrm{MIN}}) \cdot \Phi^{\mathrm{MIN}} \cdot (R - \mathcal{R}^{\mathrm{MIN}})$$

$$\mathit{\Phi}^{\mathrm{MIN}} = \Phi$$

$$D^{(\mathrm{SCHA})} = \frac{\Phi}{\sqrt{MM}}$$

NOT generalized/effective "dynamical matrix"

NOT generalized/effective "phonons"

$$\underbrace{D^{(\mathrm{SCHA})}\ \textbf{Positive definite} \ \Rightarrow \ \textbf{NO imaginary frequencies}}_{\textbf{NO structural instability}}$$

Physical meaning?

SCHA effective harmonic Hamiltonian

$$H^{\mathrm{SCHA}} = K + \frac{1}{2}(R - \mathcal{R}^{\mathrm{MIN}}) \cdot \mathit{\Phi}^{\mathrm{MIN}} \cdot (R - \mathcal{R}^{\mathrm{MIN}})$$

Fundamental concept:

Positional free energy

(free energy as a function of average atomic config.)

$$F(\mathcal{R}) = \min_{\Phi} \mathcal{F}(\mathcal{R}, \Phi)$$

Of course...

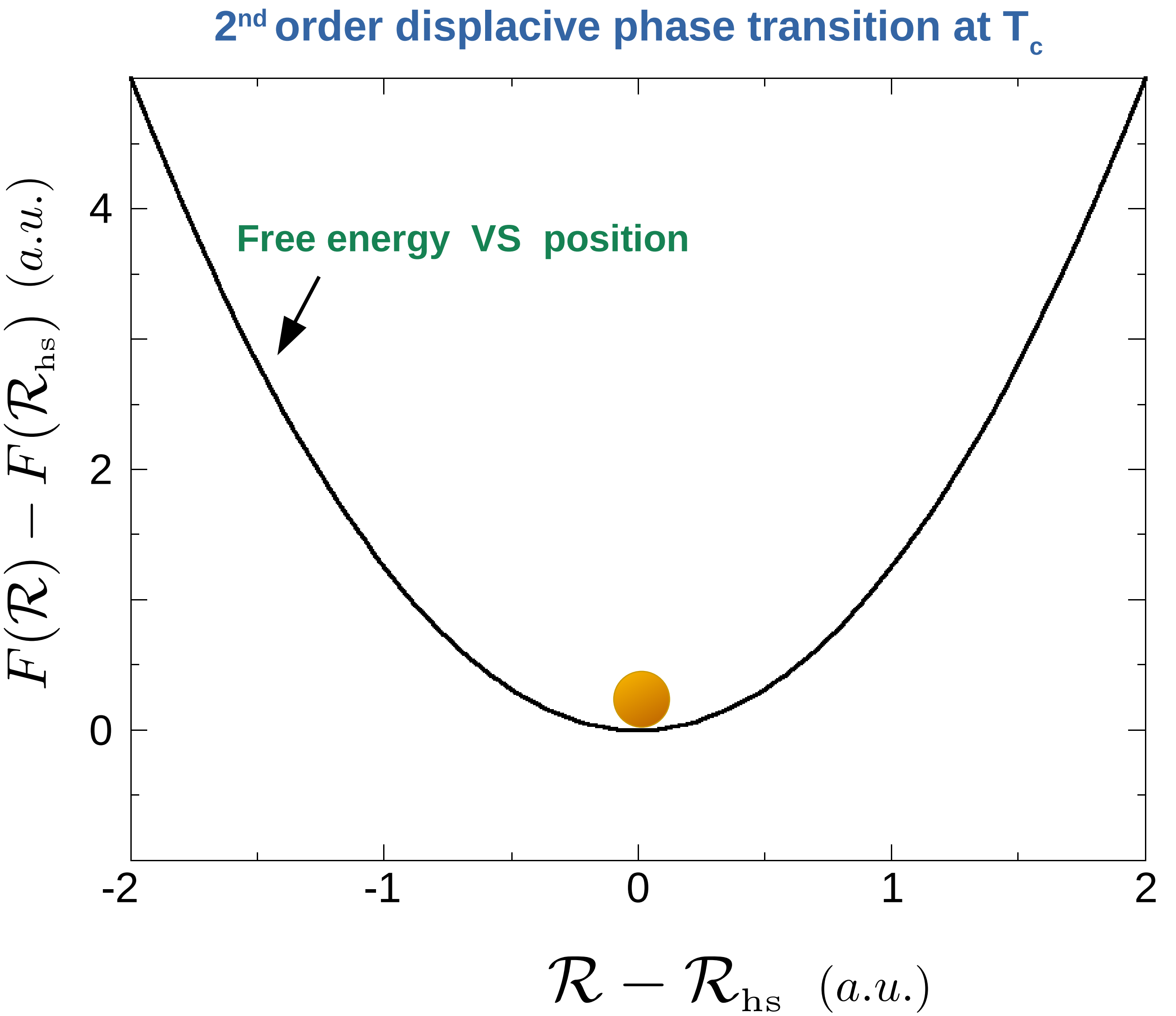
$$F = \min_{\mathcal{R}} F(\mathcal{R}) = F(\mathcal{R}_{\mathrm{eq}})$$

Physical meaning?

SCHA effective harmonic Hamiltonian

$$H^{\mathrm{SCHA}} = K + \frac{1}{2}(R - \mathcal{R}^{\mathrm{MIN}}) \cdot \Phi^{\mathrm{MIN}} \cdot (R - \mathcal{R}^{\mathrm{MIN}})$$

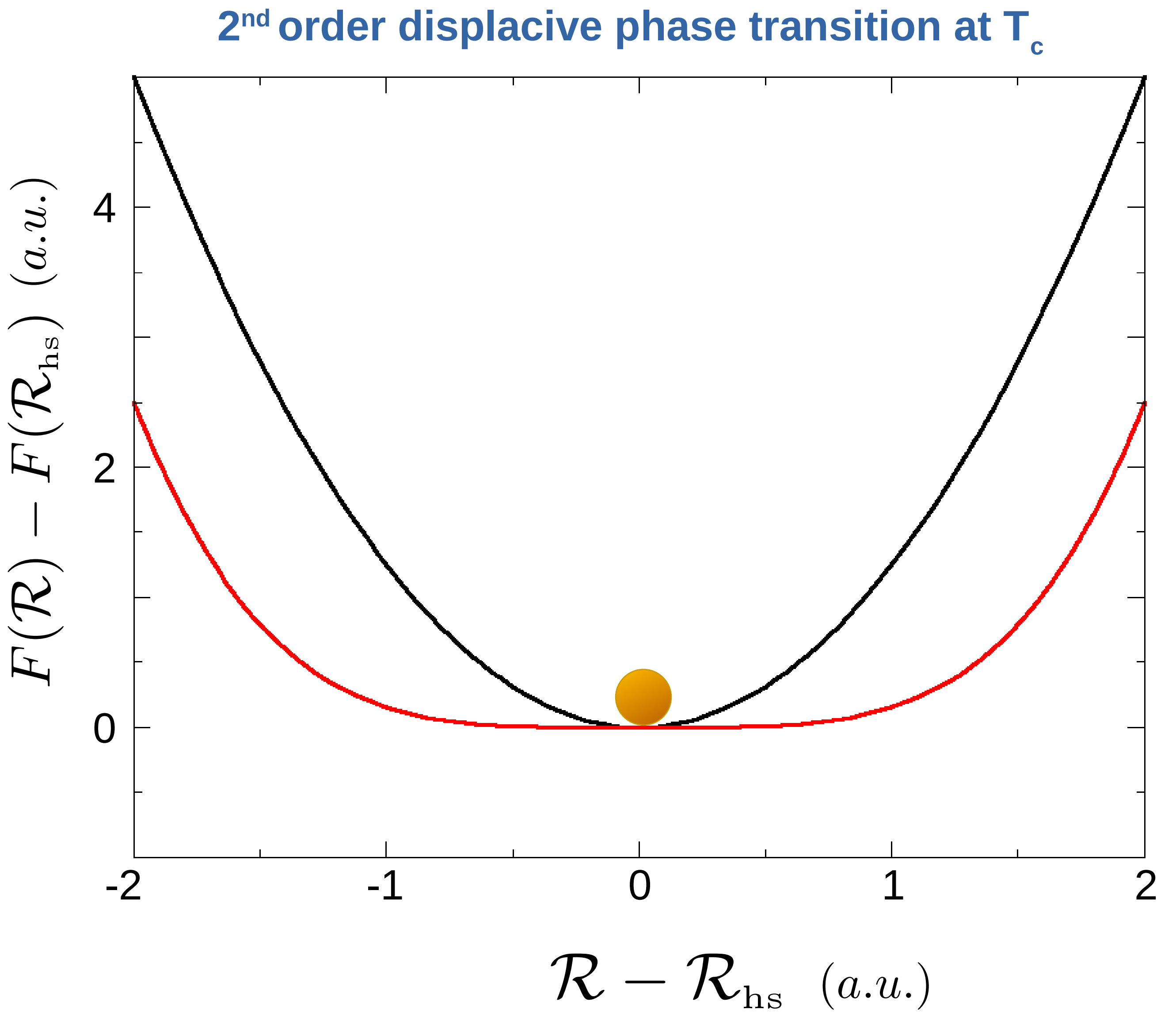
2^{nd} order displacive phase transitions: Landau picture



$T > T_c$

System in equilibrium at $\mathcal{R}_{\mathrm{hs}}$

2^{nd} order displacive phase transitions: Landau picture



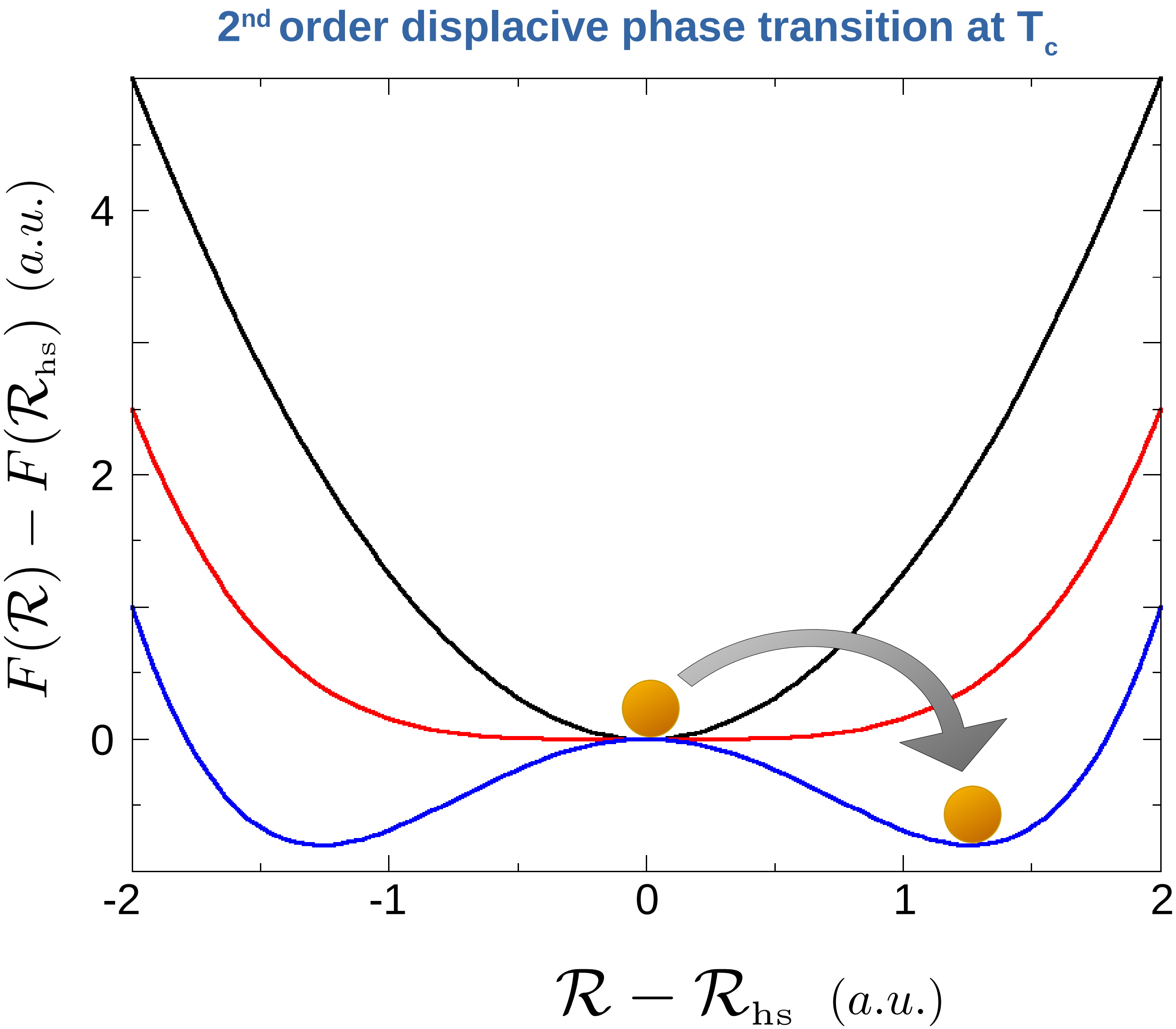
$T > T_c$

System in equilibrium at $\mathcal{R}_{\mathrm{hs}}$

$T = T_c$

Instability appears

2^{nd} order displacive phase transitions: Landau picture



$T > T_c$

System in equilibrium at $\mathcal{R}_{\mathrm{hs}}$

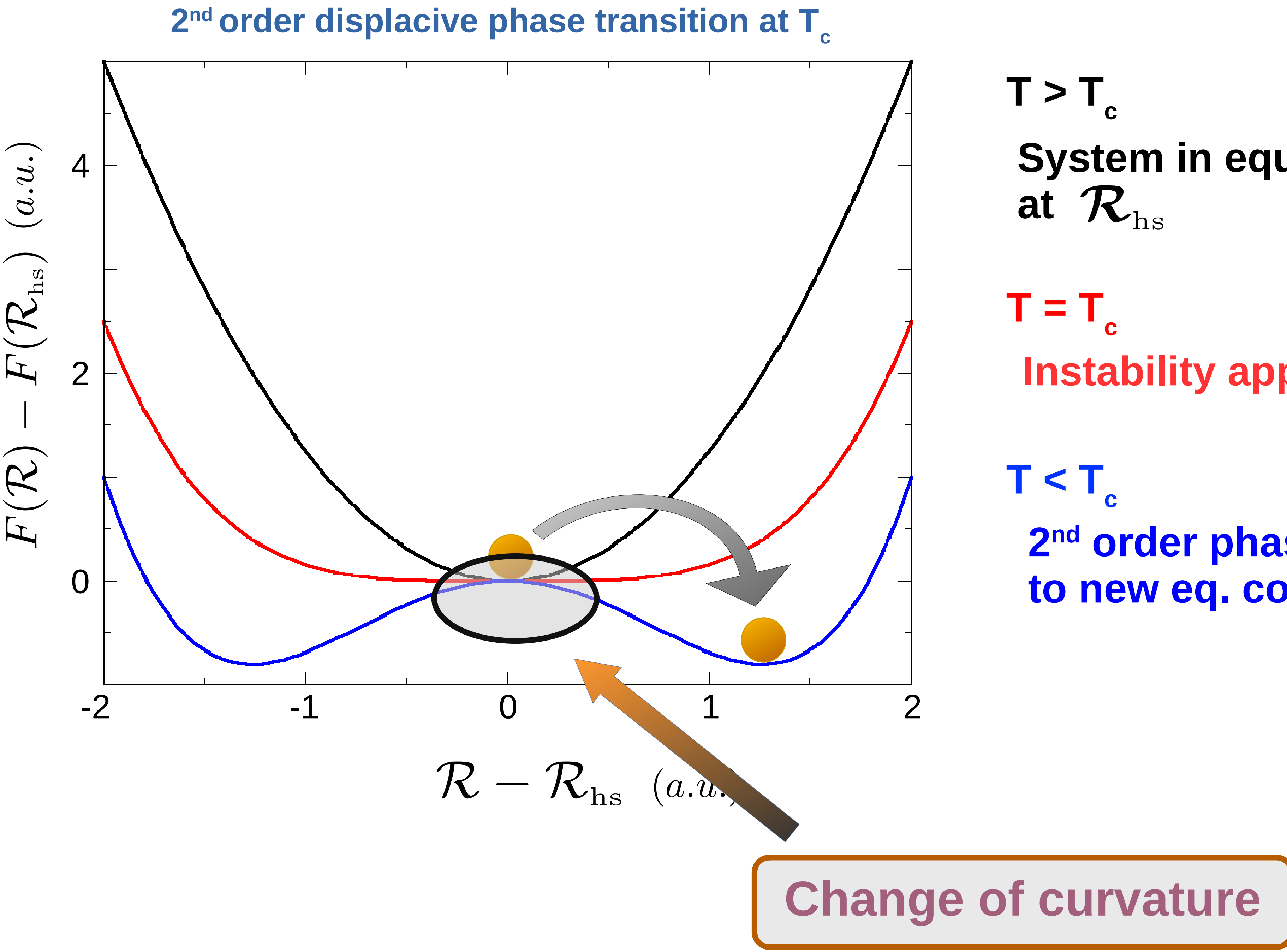
$T = T_c$

Instability appears

$T < T_c$

2^{nd} order phase trans. to new eq. config.

2^{nd} order displacive phase transitions: Landau picture



T > T_c

System in equilibrium at $\mathcal{R}_{\text{hs}}$

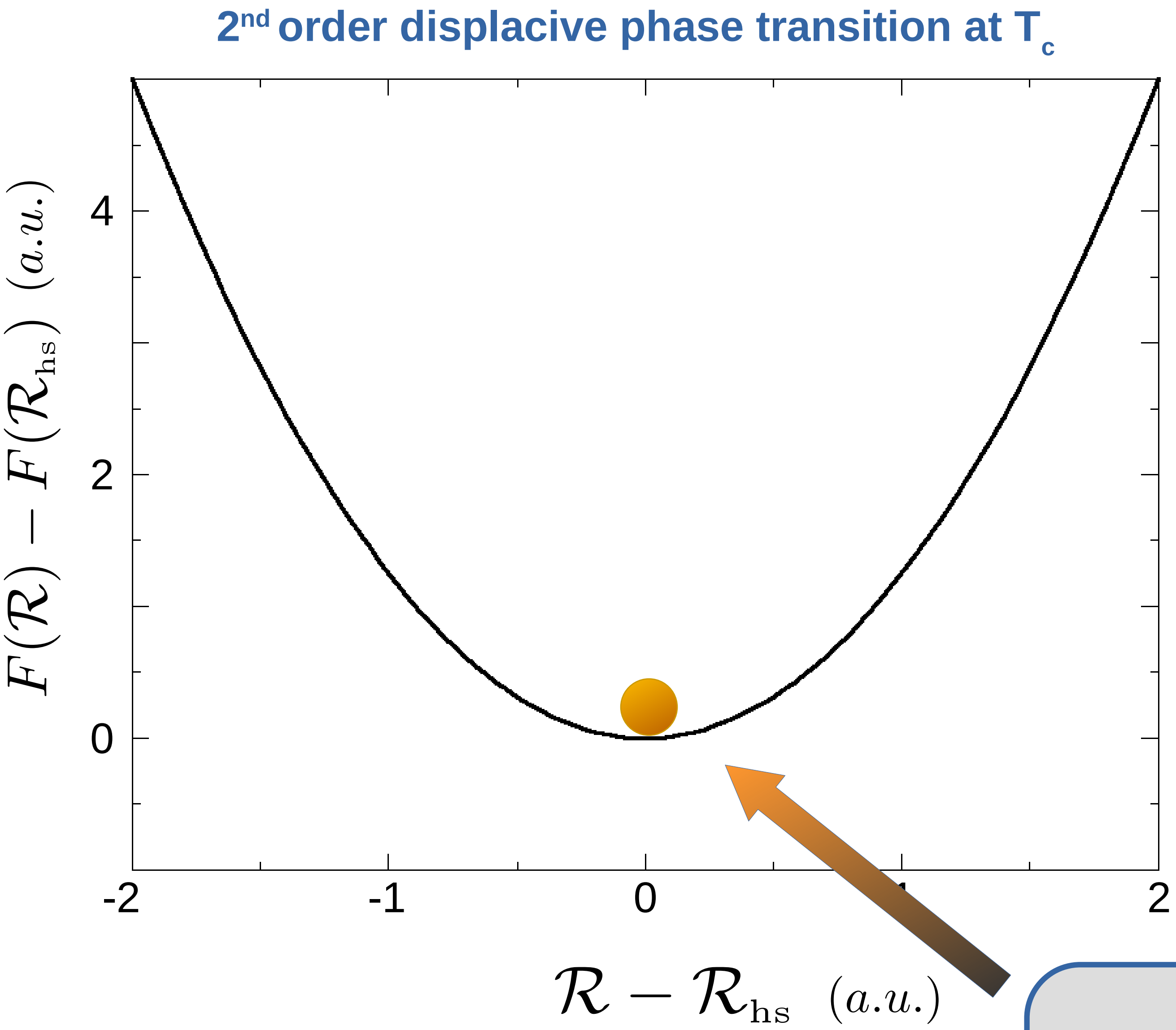
T = T_c

Instability appears

T < T_c

2^{nd} order phase trans. to new eq. config.

2^{nd} order displacive phase transitions: Landau picture



$T > T_c$

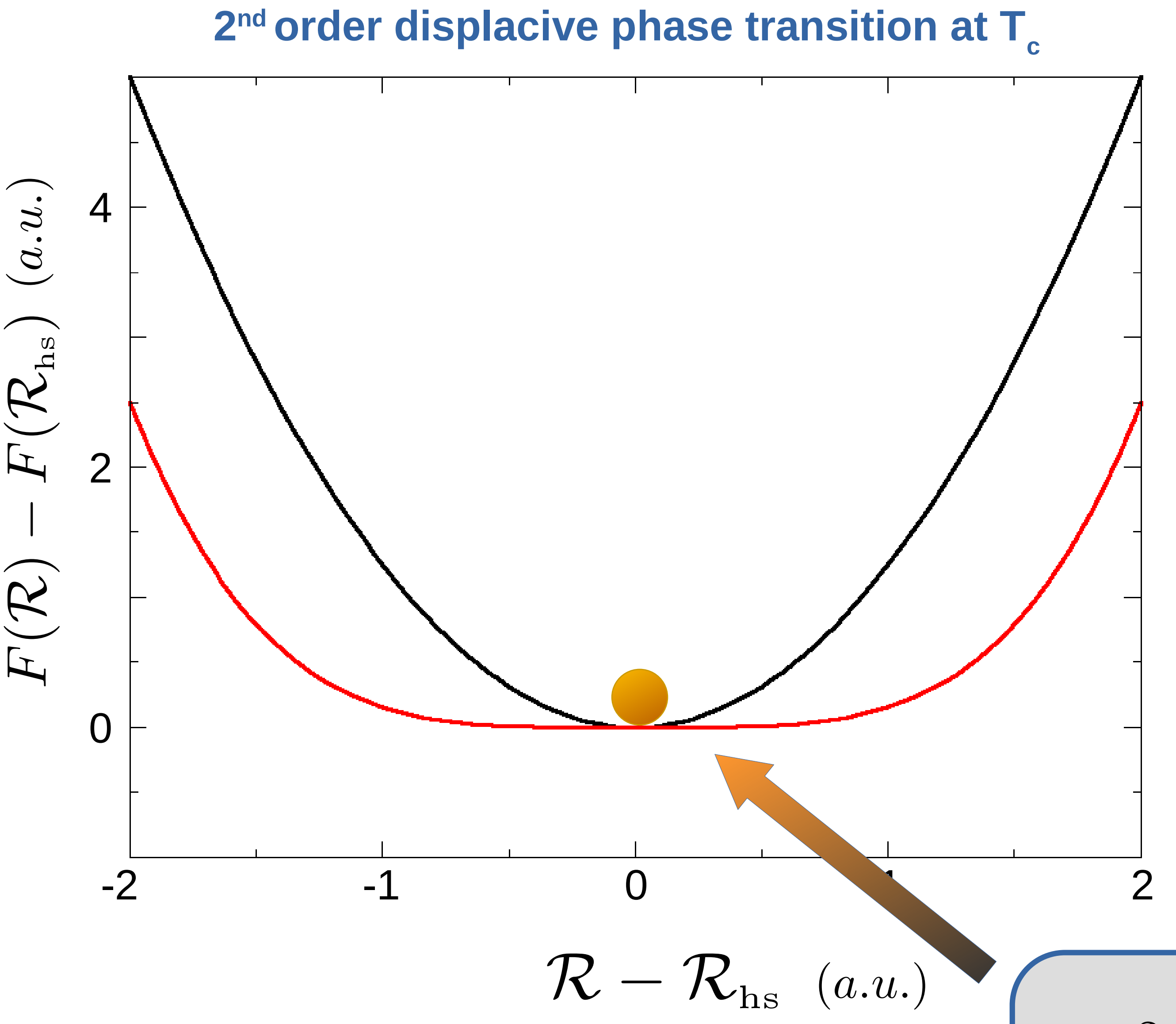
System in equilibrium at $\mathcal{R}_{\rm hs}$

Free energy Hessian in $\mathcal{R}_{\rm hs}$

$$\left.\frac{\partial^2 F}{\partial\mathcal{R}\partial\mathcal{R}}\right|_{\mathcal{R}_{\rm hs}}$$

Positive eigenvalues

2^{nd} order displacive phase transitions: Landau picture



$T > T_c$

System in equilibrium at $\mathcal{R}_{\mathrm{hs}}$

$T = T_c$

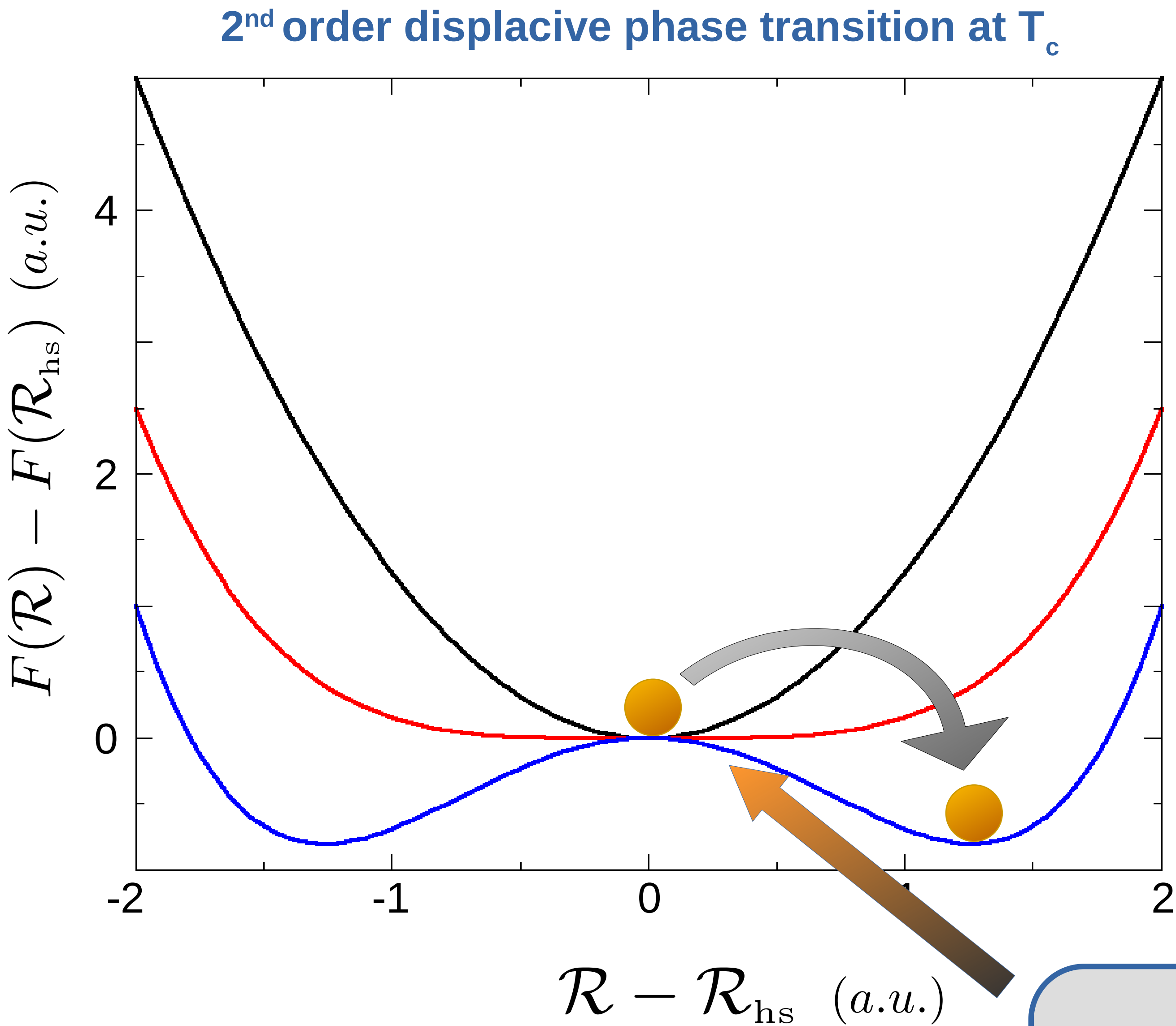
Instability appears

Free energy Hessian in $\mathcal{R}_{\mathrm{hs}}$

$$\left.\frac{\partial^2 F}{\partial \mathcal{R} \partial \mathcal{R}}\right|_{\mathcal{R}_{\mathrm{hs}}}$$

Null eigenvalue (along instability mode)

2^{nd} order displacive phase transitions: Landau picture



$T > T_c$

System in equilibrium at $\mathcal{R}_{\mathrm{hs}}$

$T = T_c$

Instability appears

$T < T_c$

2^{nd} order phase trans. to new eq. config.

Free energy Hessian in $\mathcal{R}_{\mathrm{hs}}$

$$\left.\frac{\partial^2 F}{\partial \mathcal{R} \partial \mathcal{R}}\right|_{\mathcal{R}_{\mathrm{hs}}}$$

Negative eigenvalue (along instability mode)

Free energy Hessian & 2nd order phase transitions

Free energy Hessian

Generalization of the harmonic dynamical matrix

$$\left.\frac{1}{\sqrt{MM}}\frac{\partial^2 V}{\partial R \partial R}\right|_{R_{\mathrm{eq}}} \Rightarrow \left.\frac{1}{\sqrt{MM}}\frac{\partial^2 F}{\partial \mathcal{R} \partial \mathcal{R}}\right|_{\mathcal{R}_{\mathrm{eq}}}$$

$$D^{(\mathrm{Harm})} \qquad\qquad D^{(\mathrm{F})}$$

$F - F_{eq}$ (a.u.)

4

2

0

$$\left.\frac{}{\partial R \partial R}\right|_{R_{\mathrm{eq}}}$$

...envalue (along instability mode)

Generalization of the harmonic dynamical matrix

$$\left.\frac{1}{\sqrt{MM}}\,\frac{\partial^2 V}{\partial R \partial R}\right|_{R_{\mathrm{eq}}} \Rightarrow \left.\frac{1}{\sqrt{MM}}\,\frac{\partial^2 F}{\partial \mathcal{R} \partial \mathcal{R}}\right|_{\mathcal{R}_{\mathrm{eq}}}$$

$$D^{(\mathrm{Harm})} \qquad\qquad D^{(\mathrm{F})}$$

$$F = E - TS$$

Generalization of the harmonic dynamical matrix

$$\left.\frac{1}{\sqrt{MM}}\frac{\partial^2 V}{\partial R \partial R}\right|_{R_{\mathrm{eq}}} \quad \Longrightarrow \quad \left.\frac{1}{\sqrt{MM}}\frac{\partial^2 F}{\partial \mathcal{R} \partial \mathcal{R}}\right|_{\mathcal{R}_{\mathrm{eq}}}$$

$$D^{(\mathrm{Harm})} \qquad\qquad D^{(\mathrm{F})}$$

$$F = E - TS$$

- $V \Longrightarrow E = \langle K \rangle + \langle V \rangle$

Quantum nature of nuclei taken into account

Generalization of the harmonic dynamical matrix

$$\frac{1}{\sqrt{MM}} \frac{\partial^2 V}{\partial R \partial R}\bigg|_{R_{\mathrm{eq}}} \Longrightarrow \frac{1}{\sqrt{MM}} \frac{\partial^2 F}{\partial \mathcal{R} \partial \mathcal{R}}\bigg|_{\mathcal{R}_{\mathrm{eq}}}$$

$$D^{(\mathrm{Harm})} \qquad\qquad D^{(\mathrm{F})}$$

$$F = E - TS$$

- $V \Longrightarrow E = \langle K \rangle + \langle V \rangle$
- $E \Longrightarrow E - TS$

Thermal fluctuations taken into account

Free energy Hessian & 2nd order phase transitions

Free energy Hessian

Generalization of the harmonic dynamical matrix

$$\boxed{\frac{1}{\sqrt{MM}}\left.\frac{\partial^2 V}{\partial R \partial R}\right|_{R_{\text{eq}}}} \Rightarrow \boxed{\frac{1}{\sqrt{MM}}\left.\frac{\partial^2 F}{\partial \mathcal{R} \partial \mathcal{R}}\right|_{\mathcal{R}_{\text{eq}}}}$$

$$D^{(\text{Harm})} \qquad\qquad D^{(\text{F})}$$

Quantum, thermal, anharmonic effects included

How to study displacive second-order phase transitions

- **Compute**

$$D^{(\mathrm{F})} = \frac{1}{\sqrt{MM}} \left. \frac{\partial^2 F}{\partial \mathcal{R} \partial \mathcal{R}} \right|_{R_{\mathrm{hs}}}$$

as a function T

- **Go from real to reciprocal space (Fourier transform) and diagonalize:**

generalized phonon dispersion $\boldsymbol{\omega_\mu(q)}$
as a function of *T*

- **Displacive second-order phase transition characterization:**

  - **Critical value T_c**
    (temperature at which phonon goes imaginary)

  - **Displacement pattern**
    (imaginary-phonon eigenmode)

…not only temperature!

- **Analogous approach works more in general for the Gibbs free energy:**

$$\frac{1}{\sqrt{MM}} \frac{\partial^2 G}{\partial \mathcal{R} \partial \mathcal{R}}\bigg|_{R_{\mathrm{hs}}} \qquad G = E - TS + PV$$

- **Generalized phonon dispersion $\boldsymbol{\omega_\mu(q)}$**
  (as a function of *T or P*)

- **Displacive second-order phase transition:**

- **Critical value of external parameter (*T_c* or *P_c*)**
  (phonon goes imaginary)

- **Displacement pattern**
  (imaginary-phonon eigenmode)

Temperature-dependent harmonic free-energy Hessian

An **approach sometimes used**
to estimate T_c of 2^{nd} order phase transitions:

Harmonic phonon dispersion as a function of temperature
(computed with Fermi-Dirac electron smearing)

Temperature-dependent harmonic free-energy Hessian

An **approach sometimes used**
to estimate T_c of 2nd order phase transitions:

Harmonic phonon dispersion as a function of temperature
(computed with Fermi-Dirac electron smearing)

- **This approach discards:**

  Quantum nature of nuclei

  Nuclei contribution to entropy
  (only electron entropy is included)

This typically leads to significant errors...an example will be shown later

SCHA Free energy Hessian

$$\frac{\partial^2 F}{\partial\mathcal{R}\partial\mathcal{R}} = \Phi + \overset{(3)}{\Phi} : \Lambda : \left[\mathbb{1} - \Lambda : \overset{(4)}{\Phi}\right]^{-1} : \overset{(3)}{\Phi}$$

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SCHA matrix

$$\left\langle \frac{\partial^2 V}{\partial R \partial R} \right\rangle_{\rho_\Phi}$$

$$\langle \mathcal{O}(R) \rangle_{\rho_\Phi} = \int dR \, \mathcal{O}(R) \overbrace{\rho_\Phi(R)}^{\text{density matrix of } H^{\mathrm{SCHA}} = K + \frac{1}{2}(R - \mathcal{R}) \cdot \Phi \cdot (R - \mathcal{R})}$$

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SCHA matrix

$$\left\langle \frac{\partial^2 V}{\partial R \partial R} \right\rangle_{\rho_\Phi}$$

Self-Consistent Harmonic Approximation

density matrix of $H^{\mathrm{SCHA}} = K + \frac{1}{2}(R - \mathcal{R}) \cdot \Phi \cdot (R - \mathcal{R})$

$$\langle \mathcal{O}(R) \rangle_{\rho_\Phi} = \int dR\, \mathcal{O}(R) \overbrace{\rho_\Phi(R)}$$

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$$\left\langle \frac{\partial^3 V}{\partial R \partial R \partial R} \right\rangle_{\rho_\Phi}$$

$$\left\langle \frac{\partial^4 V}{\partial R \partial R \partial R \partial R} \right\rangle_{\rho_\Phi}$$

density matrix of $H^{\mathrm{SCHA}} = K + \frac{1}{2}(R - \mathcal{R}) \cdot \Phi \cdot (R - \mathcal{R})$

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SCHA matrix

$$\left\langle \frac{\partial^2 V}{\partial R \partial R} \right\rangle_{\rho_\Phi}$$

Computed from the SCHA matrix

$$\left. \begin{array}{l} \text{Frequencies } \omega_\mu \\ \text{Eigenmodes } e_\mu^a \end{array} \text{ of } \frac{\Phi}{\sqrt{MM}} \right\} \longrightarrow \Lambda$$

$$\langle \mathcal{O}(R) \rangle_{\rho_\Phi} = \int dR\, \mathcal{O}(R) \overbrace{\rho_\Phi(R)}^{\text{density matrix of } H^{\text{SCHA}} = K + \frac{1}{2}(R - \mathcal{R}) \cdot \Phi \cdot (R - \mathcal{R})}$$

SCHA Free energy Hessian

$$\frac{\partial^2 F}{\partial \mathcal{R}\partial \mathcal{R}} = \boxed{\Phi} + \overset{(3)}{\Phi} : \boxed{\Lambda} : \left[\mathbb{1} - \boxed{\Lambda} : \overset{(4)}{\Phi}\right]^{-1} : \overset{(3)}{\Phi}$$

SCHA matrix

$$\left\langle \frac{\partial^2 V}{\partial R \partial R} \right\rangle_{\rho_\Phi}$$

Computed from the SCHA matrix

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$$\Lambda^{abcd} = \sum_{\mu\nu} \mathcal{F}(\omega_\mu, \omega_\nu)\, e_\mu^a e_\nu^b e_\mu^c e_\nu^d$$

SCHA Free energy Hessian

$$\frac{\partial^2 F}{\partial \mathcal{R} \partial \mathcal{R}} = \boxed{\Phi} + \overset{(3)}{\Phi} : \boxed{\Lambda} : \left[\mathbb{1} - \boxed{\Lambda} : \overset{(4)}{\Phi} \right]^{-1} : \overset{(3)}{\Phi}$$

SCHA matrix

$$\left\langle \frac{\partial^2 V}{\partial R \partial R} \right\rangle_{\rho_\Phi}$$

Computed from the SCHA matrix

$$\left.\begin{array}{l} \text{Frequencies } \omega_\mu \\ \text{Eigenmodes } \mathrm{e}_\mu^a \end{array} \text{ of } \frac{\Phi}{\sqrt{MM}} \right\} \longrightarrow \Lambda$$

$$\Lambda^{abcd} = \sum_{\mu\nu} \mathcal{F}(\omega_\mu, \omega_\nu)\, e_\mu^a e_\nu^b e_\mu^c e_\nu^d$$

$$n_\mu = \frac{1}{e^{\beta\omega_\mu} - 1}$$

$$\mathcal{F}(\omega_\mu, \omega_\nu) = \frac{\hbar}{4\omega_\nu\omega_\mu} \left[\frac{(\omega_\mu - \omega_\nu)(n_\mu - n_\nu)}{(\omega_\mu - \omega_\nu)^2} - \frac{(\omega_\mu + \omega_\nu)(1 + n_\mu + n_\nu)}{(\omega_\mu + \omega_\nu)^2} \right]$$

SCHA Free energy Hessian

$$\frac{\partial^2 F}{\partial \mathcal{R} \partial \mathcal{R}} = \boxed{\Phi} + \boxed{\overset{(3)}{\Phi}} : \Lambda : \left[\mathbb{1} - \Lambda : \boxed{\overset{(4)}{\Phi}} \right]^{-1} : \boxed{\overset{(3)}{\Phi}}$$

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$$\left\langle \frac{\partial^3 V}{\partial R \partial R \partial R} \right\rangle_{\rho_\Phi}$$

$$\left\langle \frac{\partial^4 V}{\partial R \partial R \partial R \partial R} \right\rangle_{\rho_\Phi}$$

$$H^{\mathrm{SCHA}} = K + \frac{1}{2}(R - \mathcal{R}) \cdot \Phi \cdot (R - \mathcal{R})$$

$$\langle \mathcal{O}(R) \rangle_{\rho_\Phi} = \int dR\, \mathcal{O}(R) \overbrace{\rho_\Phi(R)}^{\text{density matrix of}}$$

SCHA Free energy Hessian

$$\frac{\partial^2 F}{\partial \mathcal{R} \partial \mathcal{R}} = \boxed{\Phi} + \boxed{\overset{(3)}{\Phi}} : \Lambda : \left[\mathbb{1} - \Lambda : \boxed{\overset{(4)}{\Phi}} \right]^{-1} : \boxed{\overset{(3)}{\Phi}}$$

SCHA matrix

$$\left\langle \frac{\partial^2 V}{\partial R \partial R} \right\rangle_{\rho_\Phi}$$

$$\left\langle \frac{\partial^3 V}{\partial R \partial R \partial R} \right\rangle_{\rho_\Phi} \qquad \left\langle \frac{\partial^4 V}{\partial R \partial R \partial R \partial R} \right\rangle_{\rho_\Phi}$$

How to compute them?

(direct stochastic approach ruled out)

de

$$\langle \mathcal{O}(R) \rangle_{\rho_\Phi} = \int dR \, \mathcal{O}(R) \rho_\Phi(R)$$

High-order FCs: stochastic approach

$$\left\langle \frac{\partial^3 V}{\partial R \partial R \partial R} \right\rangle_{\rho_\Phi} = \int \frac{\partial^3 V}{\partial R \partial R \partial R} \, \rho_\Phi(R) \, dR$$

$$\left\langle \frac{\partial^4 V}{\partial R \partial R \partial R \partial R} \right\rangle_{\rho_\Phi} = \int \frac{\partial^4 V}{\partial R \partial R \partial R \partial R} \, \rho_\Phi(R) \, dR$$

High-order FCs: stochastic approach

$$\left\langle \frac{\partial^3 V}{\partial R \partial R \partial R} \right\rangle_{\rho_\Phi} = \int \frac{\partial^3 V}{\partial R \partial R \partial R} \boxed{\rho_\Phi(R)} \, dR$$

normal distribution

$$\left\langle \frac{\partial^4 V}{\partial R \partial R \partial R \partial R} \right\rangle_{\rho_\Phi} = \int \frac{\partial^4 V}{\partial R \partial R \partial R \partial R} \boxed{\rho_\Phi(R)} \, dR$$

With integration by parts ...

High-order FCs: stochastic approach

$$\left\langle \frac{\partial^3 V}{\partial R \partial R \partial R} \right\rangle_{\rho_\Phi} = \int \boxed{\overset{(3)}{\mathbb{G}}(R, V(R), \mathrm{f}(R))} \rho_\Phi(R)\, dR$$

$$\left\langle \frac{\partial^4 V}{\partial R \partial R \partial R \partial R} \right\rangle_{\rho_\Phi} = \int \boxed{\overset{(4)}{\mathbb{G}}(R, V(R), \mathrm{f}(R))} \rho_\Phi(R)\, dR$$

Forces $\mathrm{f} = -\partial V / \partial R$

Linear functions $\left\{ \begin{array}{l} \boxed{\overset{(3)}{\mathbb{G}}(R, V, \mathrm{f})} \\ \boxed{\overset{(4)}{\mathbb{G}}(R, V, \mathrm{f})} \end{array} \right.$

High-order FCs: stochastic approach

$$\left\langle \frac{\partial^3 V}{\partial R \partial R \partial R} \right\rangle_{\rho_\Phi} = \left\langle \overset{(3)}{\mathbb{G}}(R, V(R), \mathrm{f}(R)) \right\rangle_{\rho_\Phi}$$

$$\left\langle \frac{\partial^4 V}{\partial R \partial R \partial R \partial R} \right\rangle_{\rho_\Phi} = \left\langle \overset{(4)}{\mathbb{G}}(R, V(R), \mathrm{f}(R)) \right\rangle_{\rho_\Phi}$$

Stochastic approach suited

High-order FCs: stochastic approach

$$\left\langle \frac{\partial^3 V}{\partial R \partial R \partial R} \right\rangle_{\rho_\Phi} = \left\langle \overset{(3)}{\mathbb{G}}(R, V(R), \mathrm{f}(R)) \right\rangle_{\rho_\Phi}$$

$$\left\langle \frac{\partial^4 V}{\partial R \partial R \partial R \partial R} \right\rangle_{\rho_\Phi} = \left\langle \overset{(4)}{\mathbb{G}}(R, V(R), \mathrm{f}(R)) \right\rangle_{\rho_\Phi}$$

Stochastic approach suited

Population $\{R_{\mathcal{I}}\}_{\mathcal{I}=1}^{\mathcal{N}}$ **generated according to** $\rho_\Phi(R)$

High-order FCs: stochastic approach

$$\left\langle \frac{\partial^3 V}{\partial R \partial R \partial R} \right\rangle_{\rho_\Phi} = \left\langle \overset{(3)}{\mathbb{G}}(R, V(R), \mathrm{f}(R)) \right\rangle_{\rho_\Phi}$$

$$\left\langle \frac{\partial^4 V}{\partial R \partial R \partial R \partial R} \right\rangle_{\rho_\Phi} = \left\langle \overset{(4)}{\mathbb{G}}(R, V(R), \mathrm{f}(R)) \right\rangle_{\rho_\Phi}$$

Stochastic approach suited

Population $\{R_{\mathcal{I}}\}_{\mathcal{I}=1}^{\mathcal{N}}$ generated according to $\rho_\Phi(R)$

↓

Compute total energy $\{V(R_{\mathcal{I}})\}_{\mathcal{I}=1}^{\mathcal{N}}$ and forces $\{\mathrm{f}(R_{\mathcal{I}})\}_{\mathcal{I}=1}^{\mathcal{N}}$

High-order FCs: stochastic approach

$$\left\langle \frac{\partial^3 V}{\partial R \partial R \partial R} \right\rangle_{\rho_\Phi} = \left\langle \overset{(3)}{\mathbb{G}}(R, V(R), \mathrm{f}(R)) \right\rangle_{\rho_\Phi}$$

$$\left\langle \frac{\partial^4 V}{\partial R \partial R \partial R \partial R} \right\rangle_{\rho_\Phi} = \left\langle \overset{(4)}{\mathbb{G}}(R, V(R), \mathrm{f}(R)) \right\rangle_{\rho_\Phi}$$

Stochastic approach suited

Population $\{R_\mathcal{I}\}_{\mathcal{I}=1}^{\mathcal{N}}$ generated according to $\rho_\Phi(R)$

↓

Compute total energy $\{V(R_\mathcal{I})\}_{\mathcal{I}=1}^{\mathcal{N}}$ and forces $\{\mathrm{f}(R_\mathcal{I})\}_{\mathcal{I}=1}^{\mathcal{N}}$

↓

$$\left\langle \mathbb{G}(R, V(R), \mathrm{f}(R)) \right\rangle_{\rho_\Phi} \simeq \frac{1}{\mathcal{N}} \sum_{\mathcal{I}=1}^{\mathcal{N}} \mathbb{G}(R_\mathcal{I}, V(R_\mathcal{I}), \mathrm{f}(R_\mathcal{I}))$$

Exploiting lattice-translation symmetry...

$$D^{(\mathrm{F})} = \frac{1}{\sqrt{MM}} \; \frac{\partial^2 F}{\partial \mathcal{R} \partial \mathcal{R}} \bigg|_{\mathcal{R}_{\mathrm{eq}}} \xrightarrow{\textbf{Fourier trans.}} D^{(\mathrm{F})}(\boldsymbol{q}) = \frac{1}{\sqrt{MM}} \frac{\partial^2 F}{\partial \mathcal{R}(-\boldsymbol{q}) \partial \mathcal{R}(\boldsymbol{q})} \bigg|_{\mathcal{R}_{\mathrm{eq}}}$$

Exploiting lattice-translation symmetry...

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But we can use **Fourier interpolation** and write it for any **q** point of the Brillouin zone

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$$\boxed{\delta_{\mu\nu}\, \omega^2_{\nu}(\boldsymbol{q})}$$

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Integration on a fine **k** grid of $N_{\mathbf{k}}$ points (towards convergence)

Exploiting lattice-translation symmetry...

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Pseudomomentum conservation

Exploiting lattice-translation symmetry...

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$$\overset{(3)}{D} = \frac{\overset{(3)}{\Phi}}{\sqrt{MMM}} \xrightarrow{\textbf{Fourier trans.}} \overset{(3)}{D}(\boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3) \quad \textbf{(after centering)}$$

Free Energy Hessian: a tool to characterize 2nd order displacive phase transitions

- Compute and diagonalize $D^{(\mathrm{F})}(\boldsymbol{q})$

  as a function of external parameter (e.g. *T* or *P*)

- Generalized phonon dispersion
  (as a function of *T, P,* ...)

- Displacive second-order phase transition:

  - Critical value of external parameter (e.g. T_c or P_c)
    (phonon goes imaginary)

  - Displacement pattern of
    (imaginary-phonon eigenmode)

Some examples...

Low dimensionality effects on CDW

Stronger fluctuations
from finite temperature

VS

Reduced screening
Stronger electron-phonon coupling

Long-range CDW order

Disfavored

Favored

	1H-$TaSe_2$	1H-TaS_2	1H-$NbSe_2$	1H-NbS_2
CDW mono w.r.t. bulk	Unchanged	Vanishes	Controversial	Controversial

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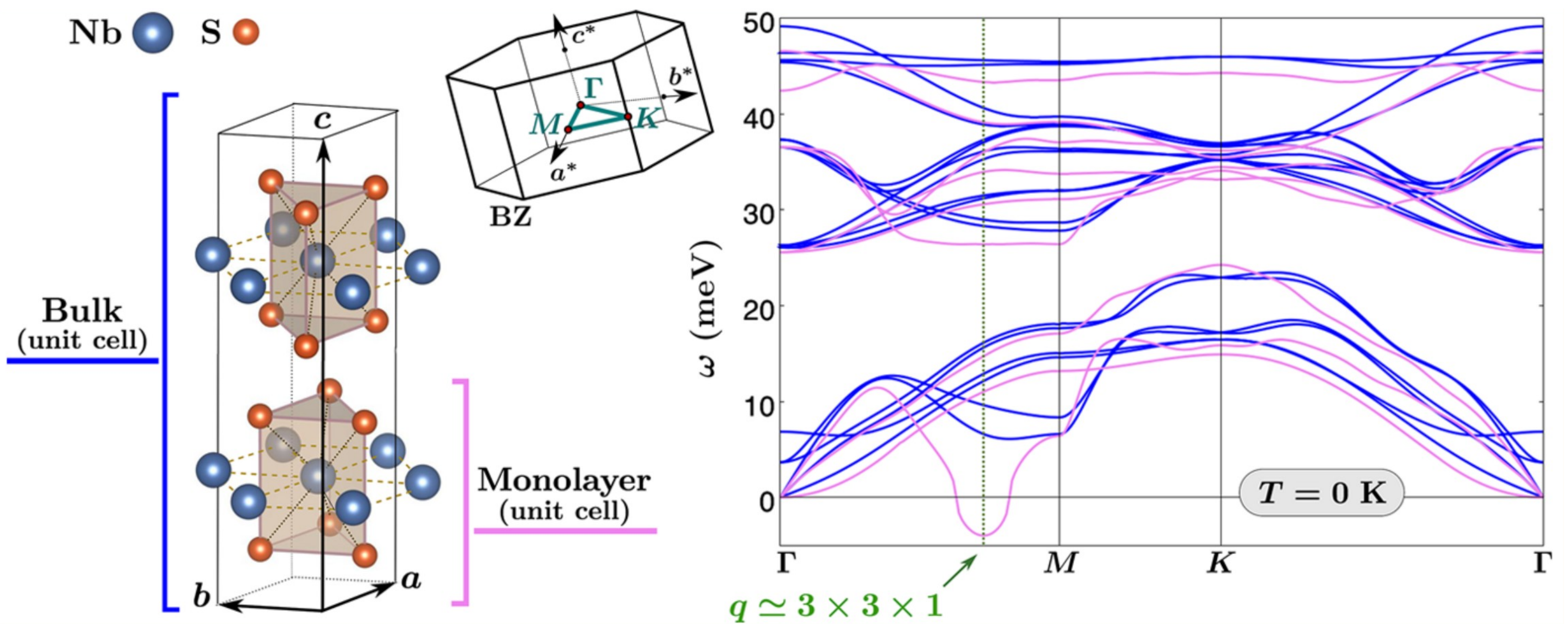
CDW mono w.r.t. bulk	Unchanged	Vanishes	Controversial	Controversial

NbS_2

Phonon dispersion including quantum anharmonic effects



Bulk: No CDW instability

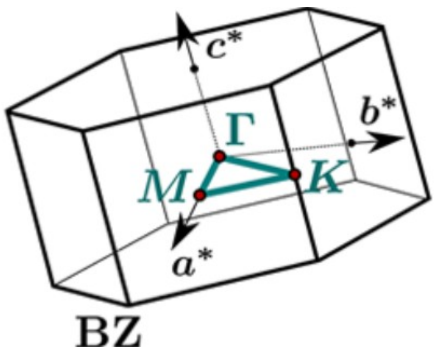
Suspended monolayer: 3x3 CDW distortion

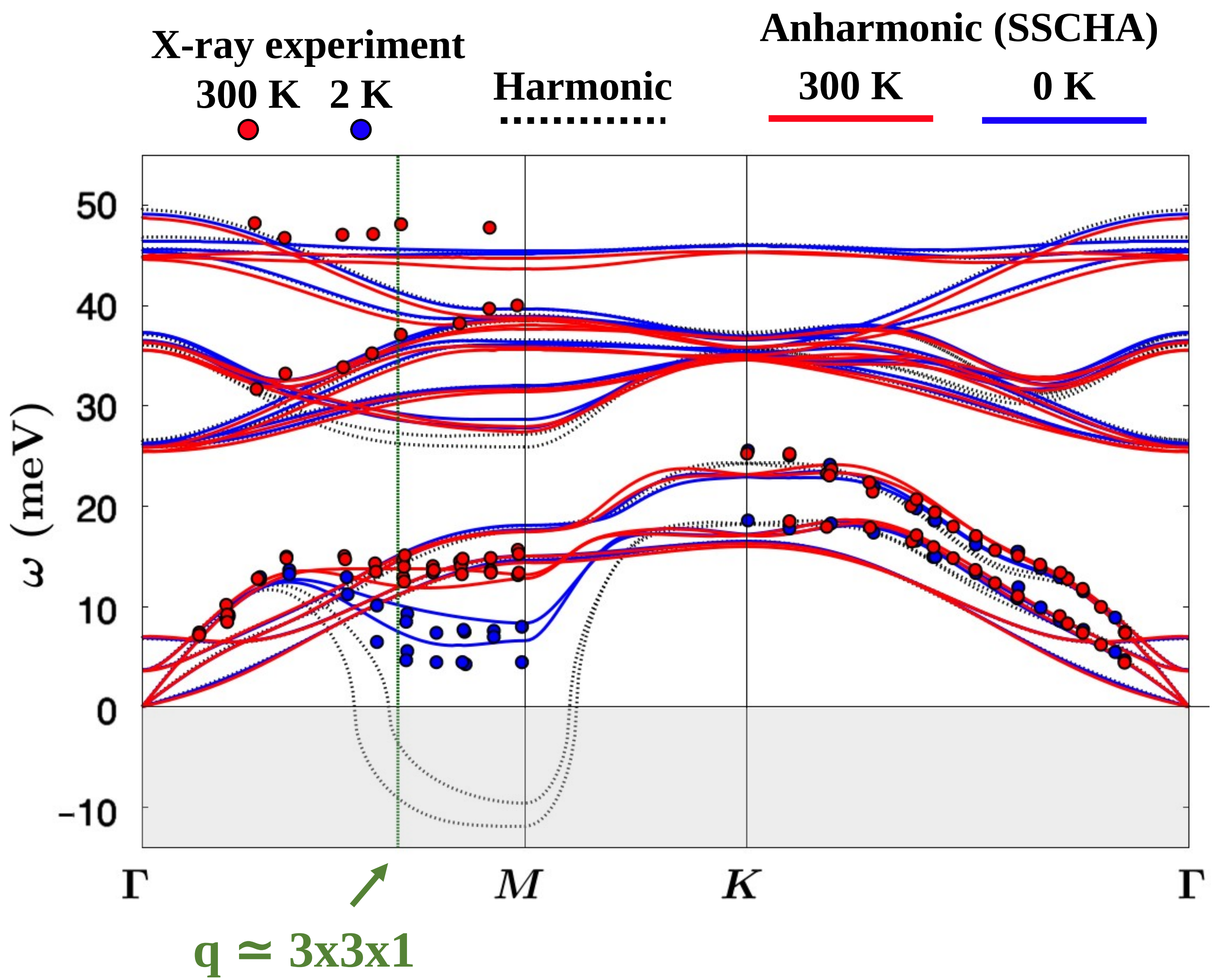
! **Quantum anharmonic effects are relevant...**

NbS_2: bulk

Harmonic dispersion:

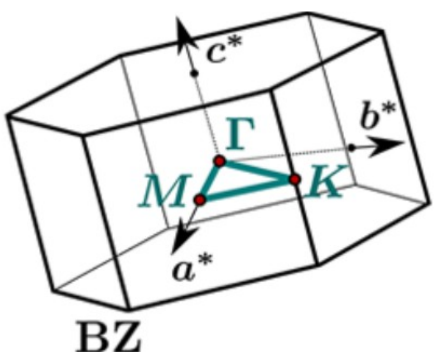
- No temperature dependence
- Wrong instability

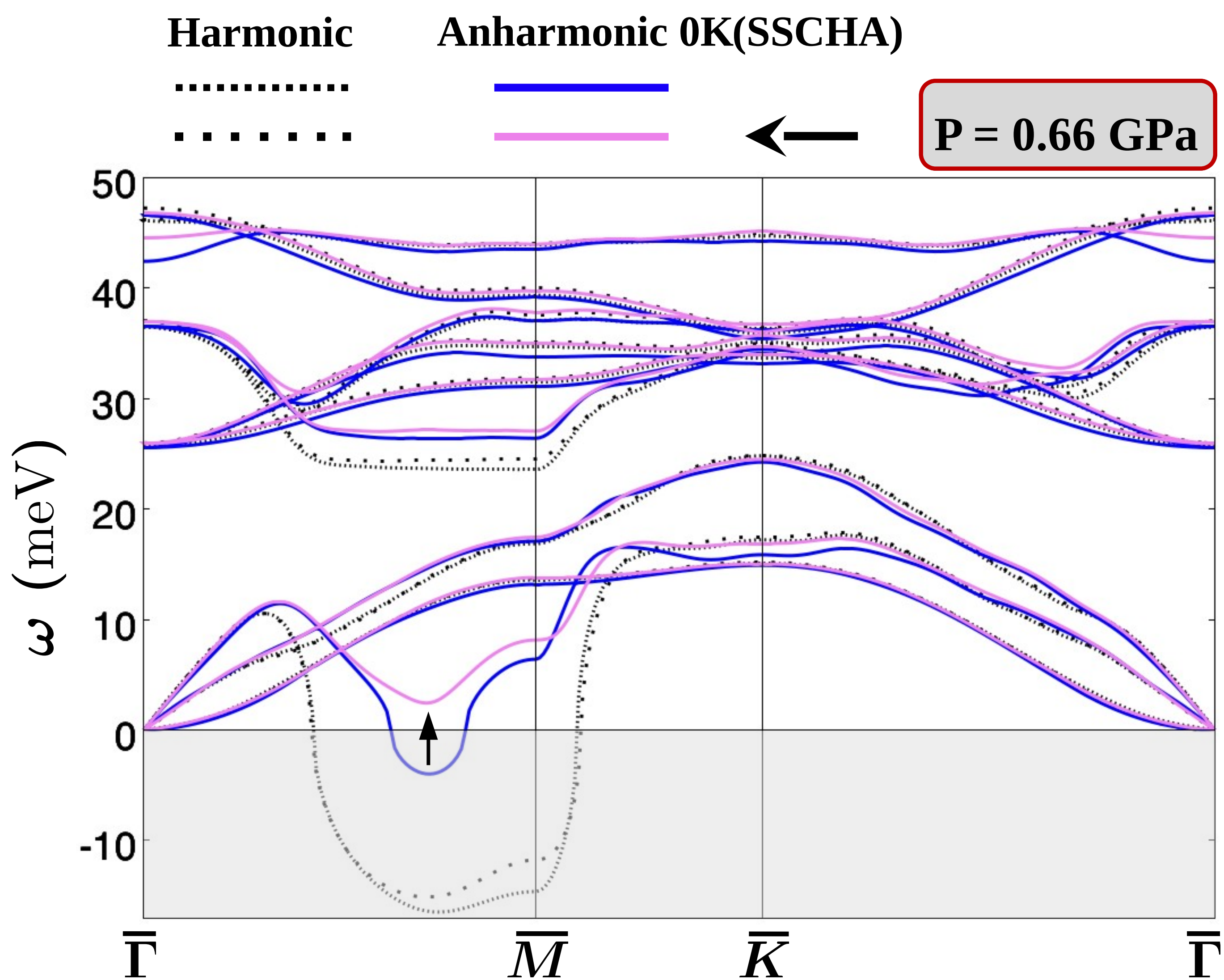




NbS_2: monolayer

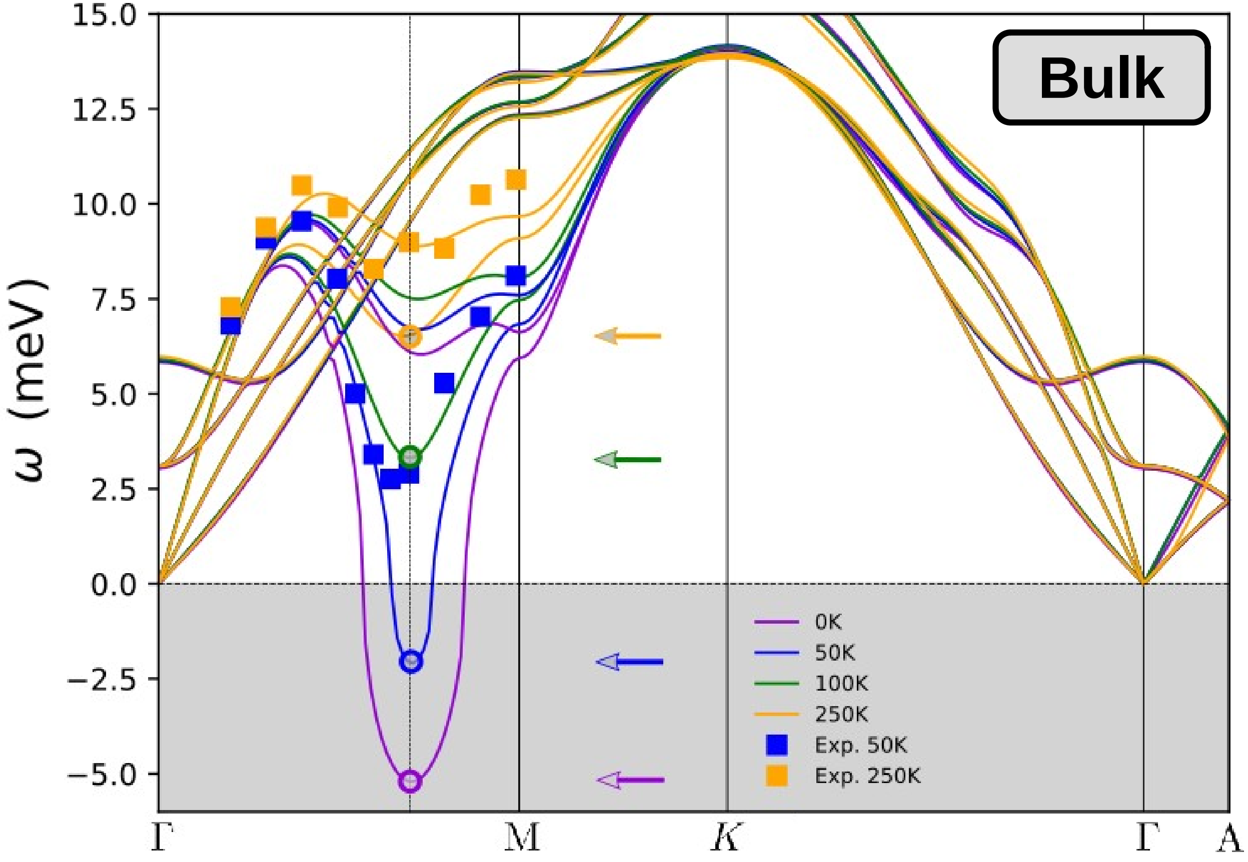
- **Structure compressed less than 0.5%** **(still compatible with exp. Estimates)** → **No CDW**
- **No effect at harmonic level**

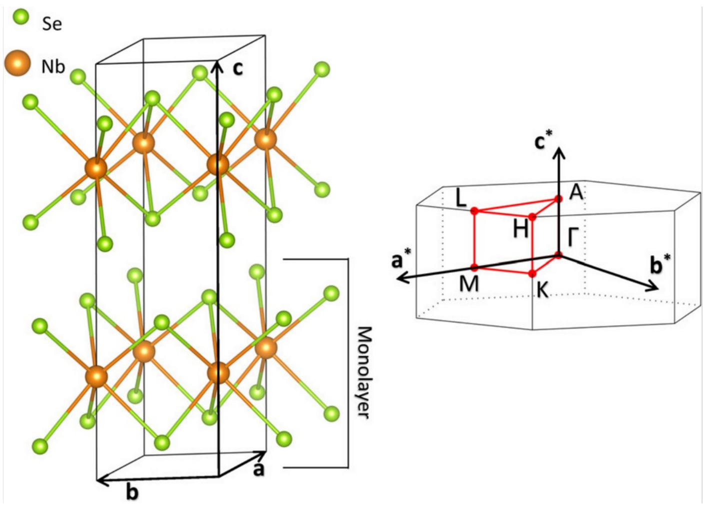




$NbSe_2$

SCHA phonon dispersion as a function of *T*





R. Bianco *et al.*, PRL 125, 106101 (2020)

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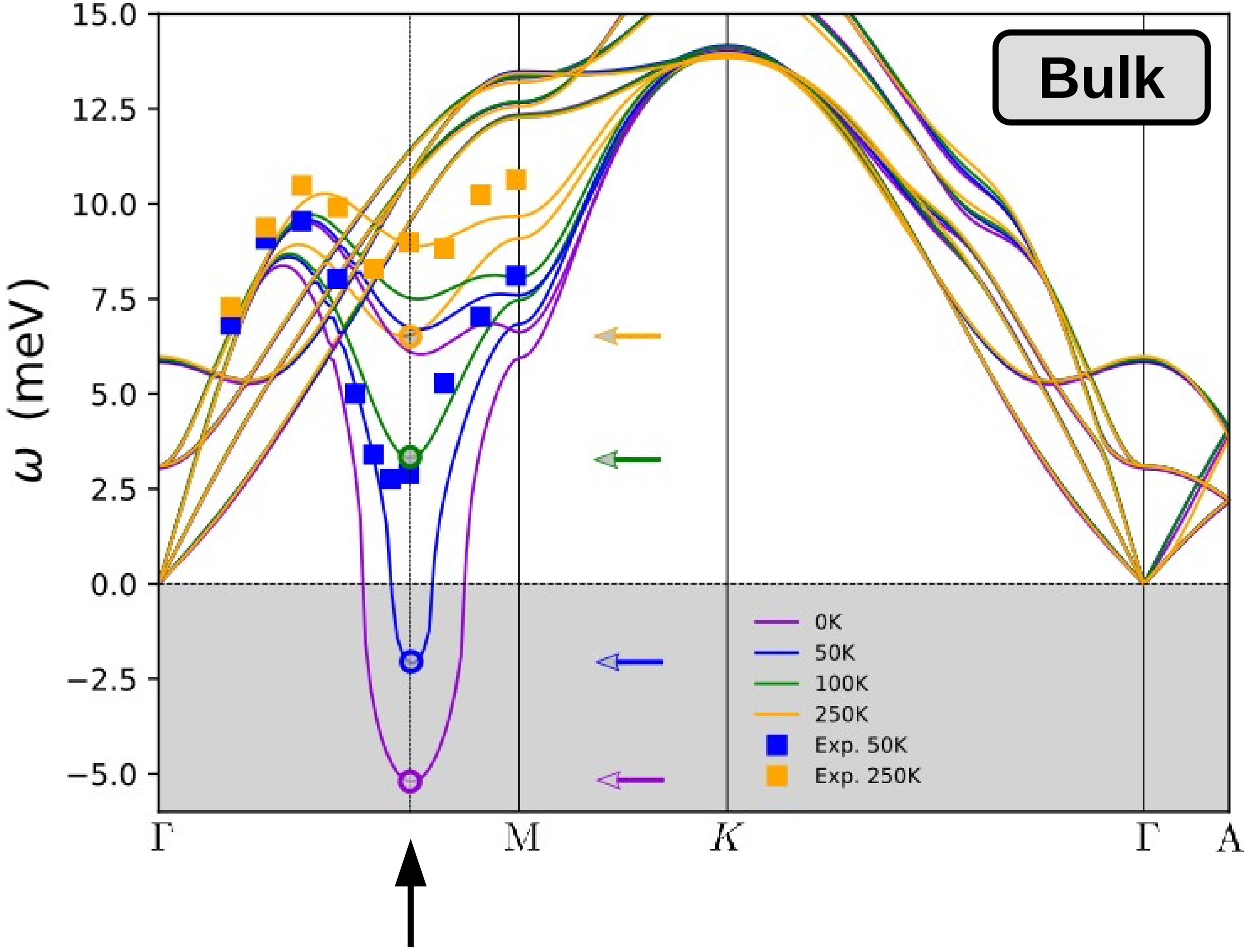
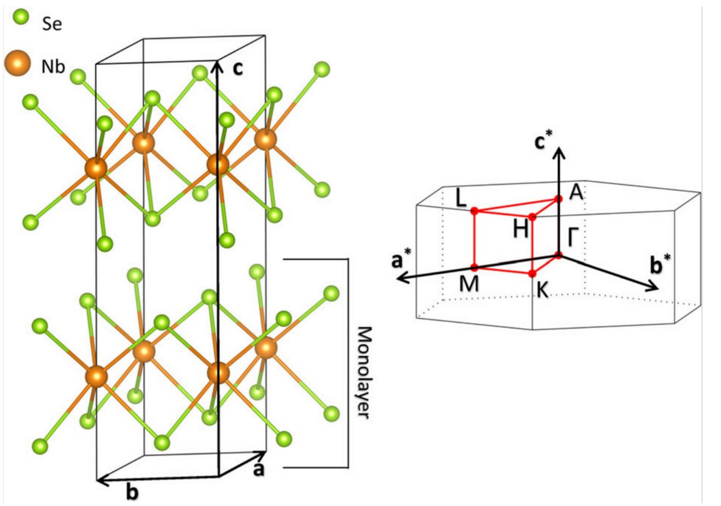




Phonon softening at the correct CDW spatial modulation (3x3x1)

Harmonic calculation reproduces the correct CDW spatial modulation too, but wrong T_c ...

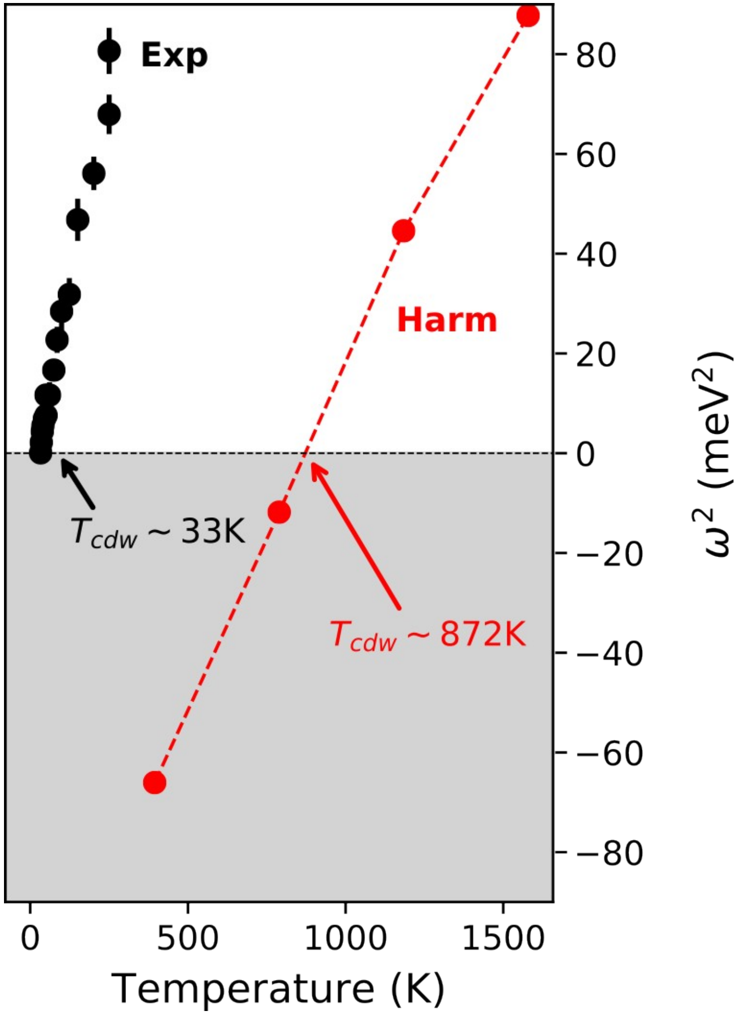
R. Bianco *et al.*, PRL 125, 106101 (2020)

Softening of $\omega^2(T)$ for q=3x3

Harmonic approximation:

Electronic temperature only

Nuclei contribution to entropy neglected



R. Bianco *et al.*, PRL 125, 106101 (2020)

Softening of $\omega^2(T)$ for q=3x3

Harmonic approximation:

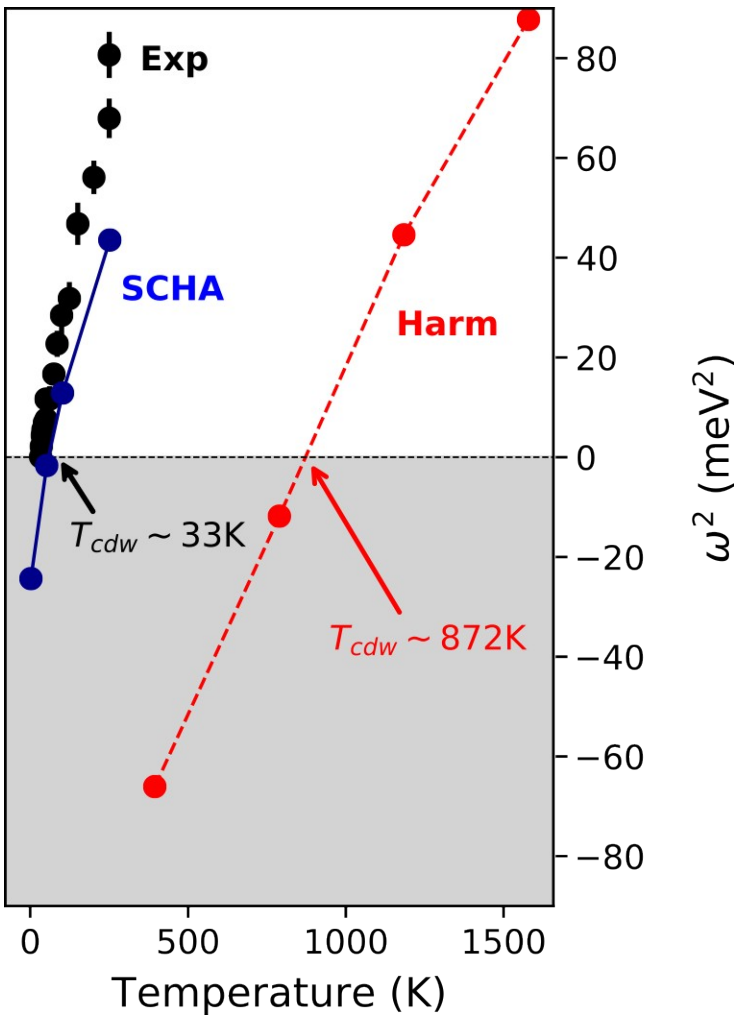
Electronic temperature only

Nuclei contribution to entropy neglected

SCHA approximation:

Nuclei and electronic temperature

Nuclei and electronic contribution to entropy



R. Bianco *et al.*, PRL 125, 106101 (2020)

$NbSe_2$

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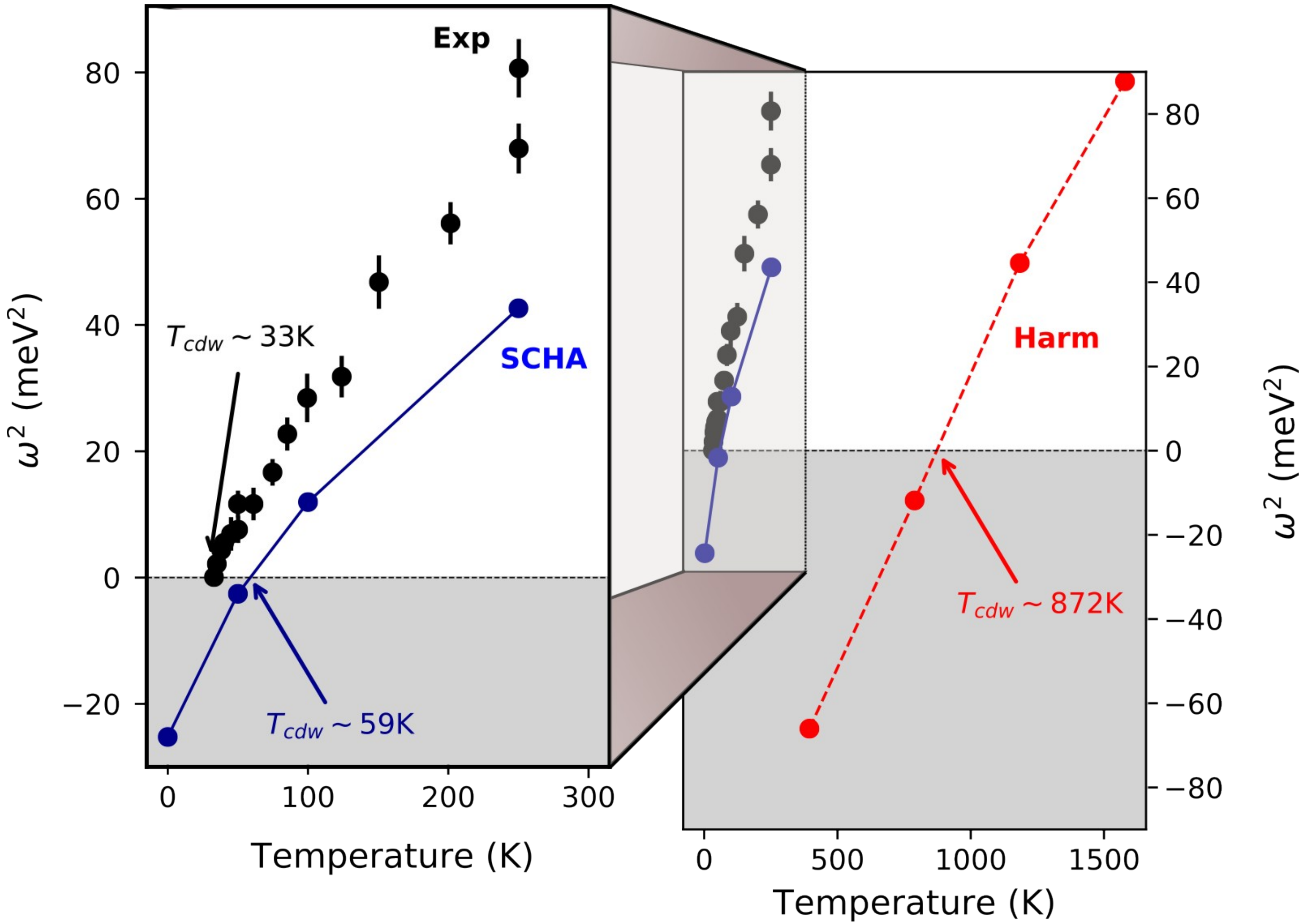

R. Bianco *et al.*, PRL 125, 106101 (2020)

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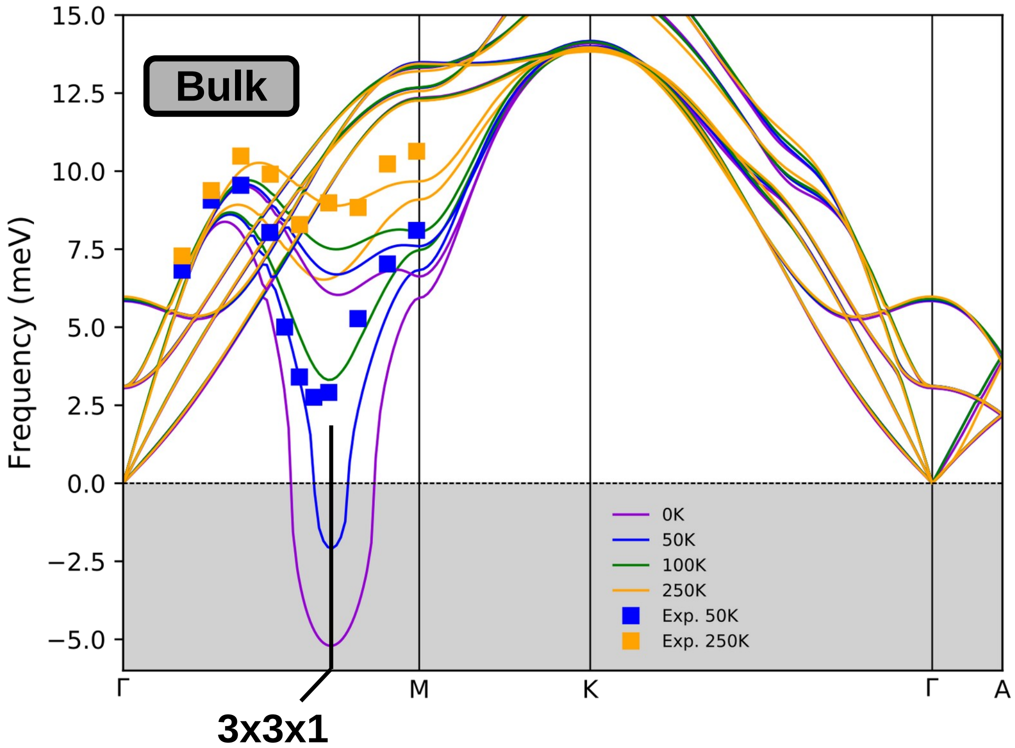
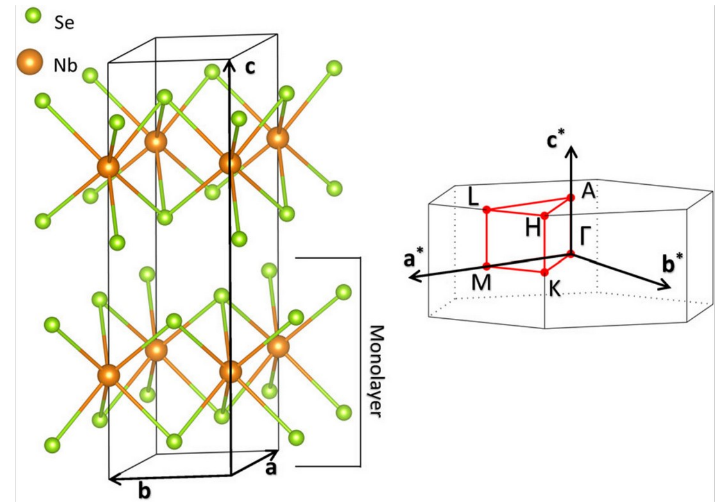
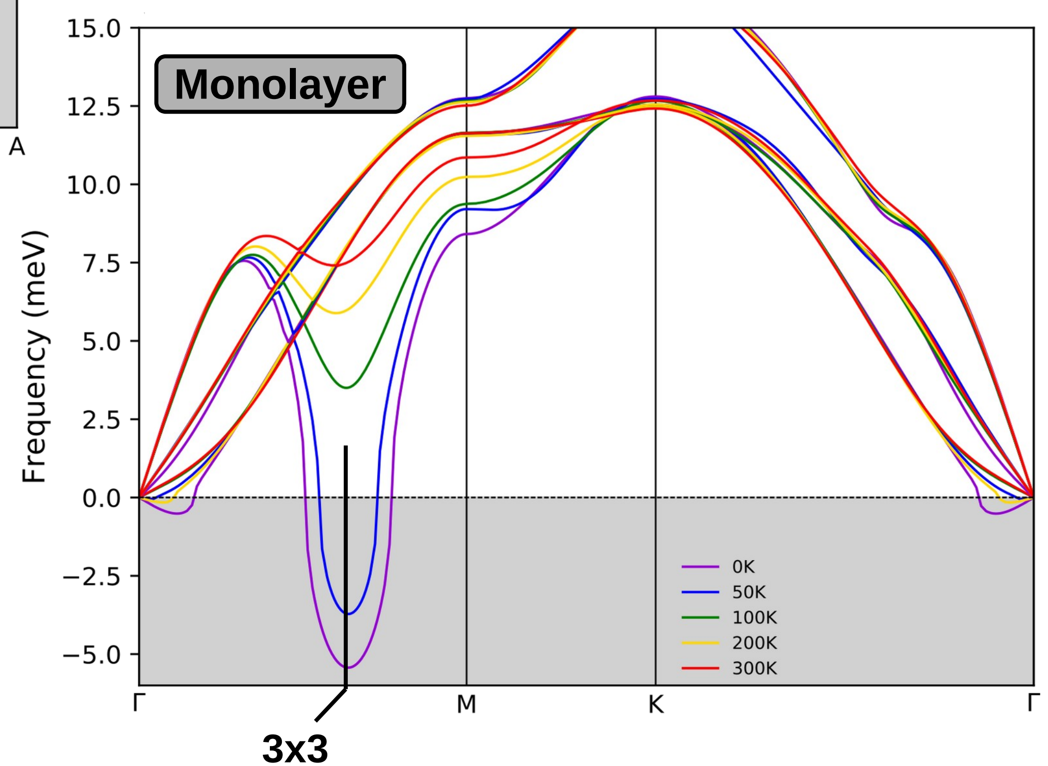




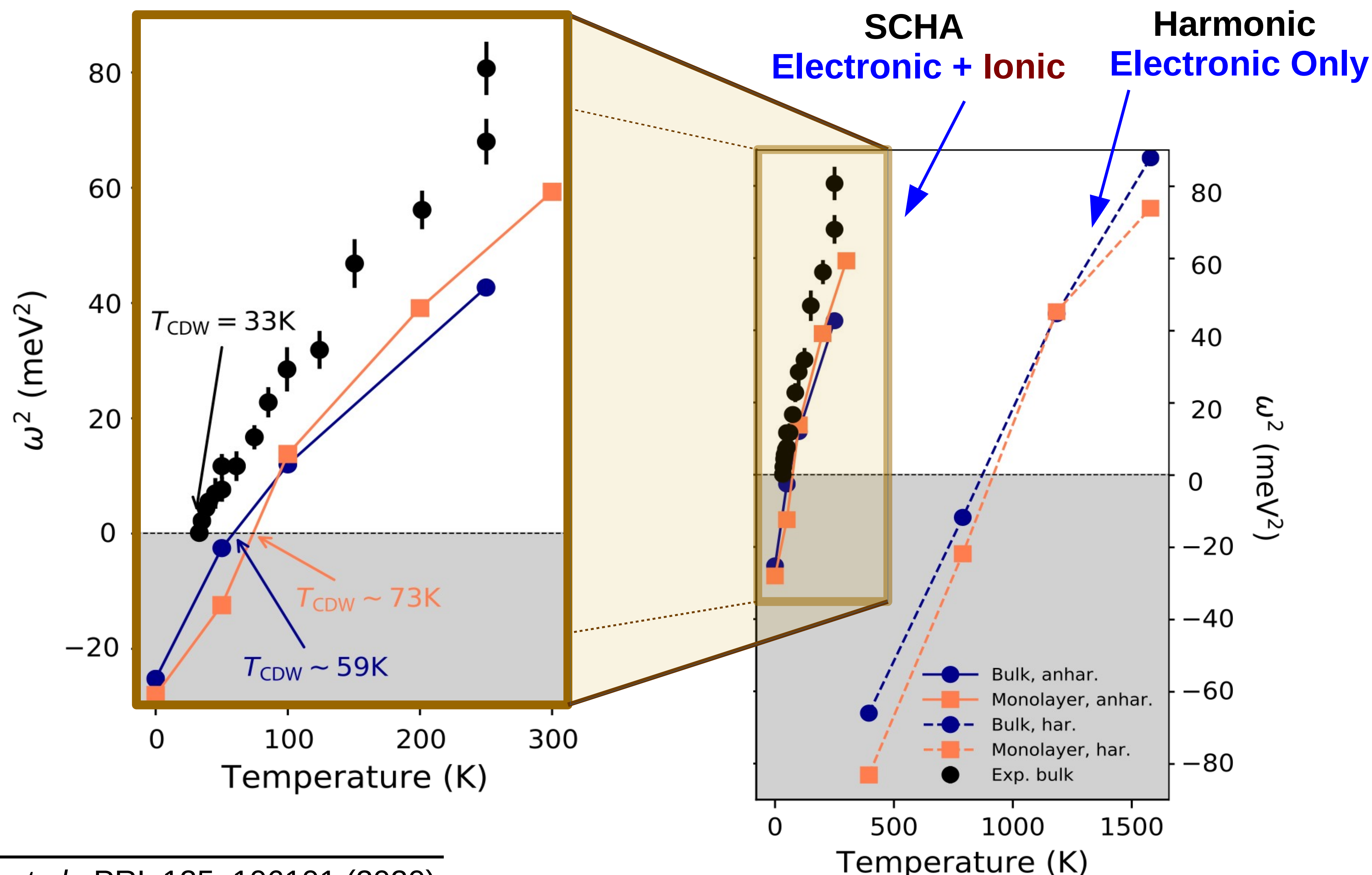


R. Bianco *et al.*, PRL 125, 106101 (2020)

$NbSe_2$: bulk and monolayer

Softening of $\omega^2(T)$ for q=3x3

- ● **Bulk Exp.**
- ● **Bulk Th.**
- ■ **Monolayer Th.**



R. Bianco *et al.*, PRL 125, 106101 (2020)

$NbSe_2$: bulk and monolayer

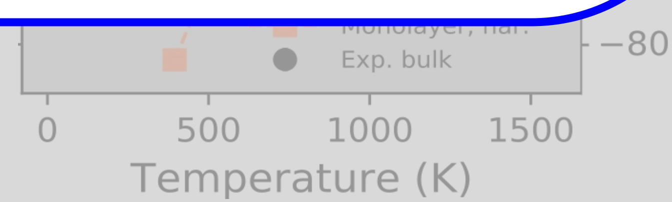
Softening of $\omega^2(T)$ for q=3x3

- Bulk Exp.
- Bulk Th.

In the CDW transition of $NbSe_2$:

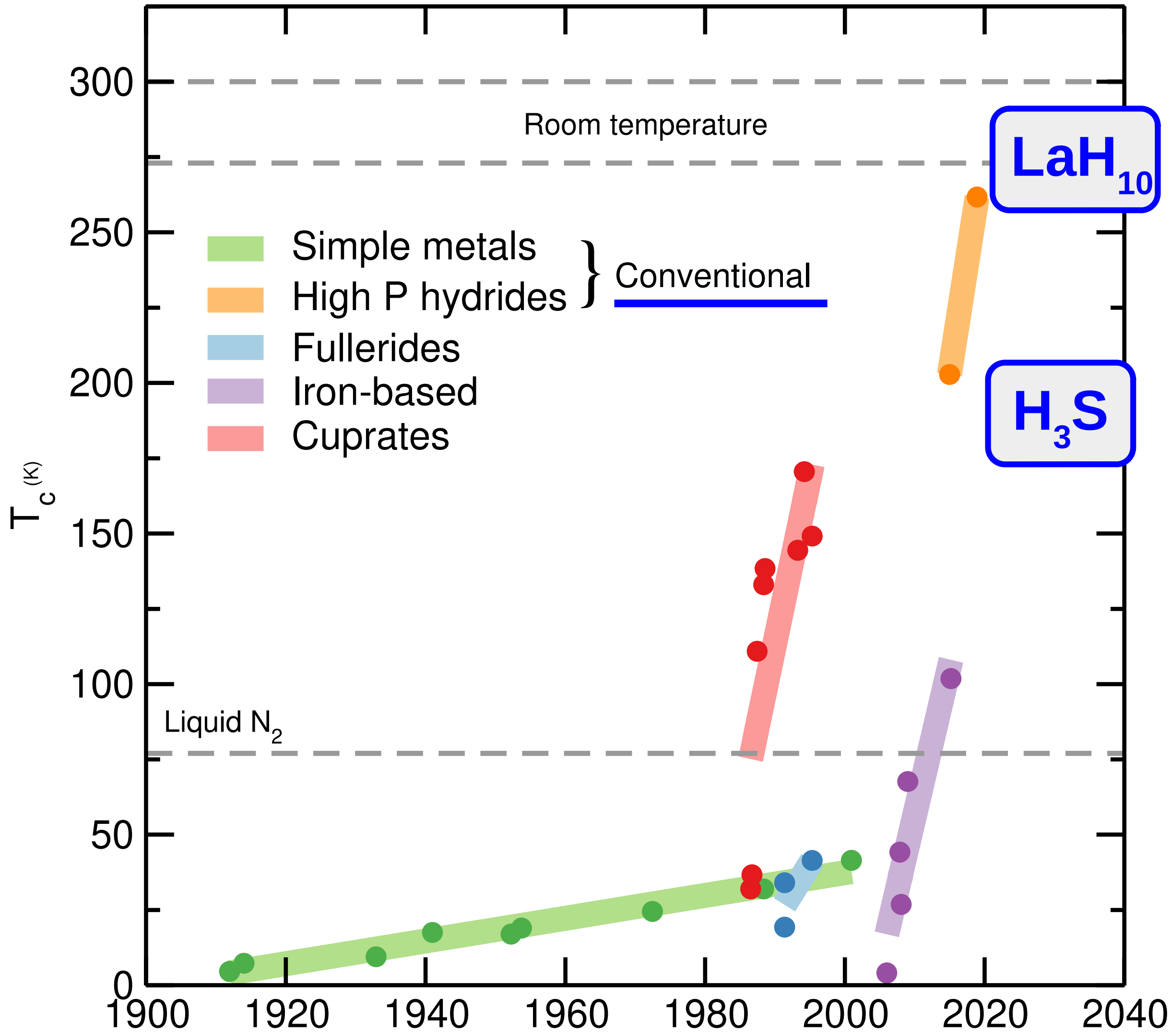
- **Ionic fluctuations dominate over electronic fluctuations**
- **Weak dimensionality dependence**

Temperature (K)



R. Bianco *et al.*, PRL 125, 106101 (2020)

Superconductivity: the T_c history



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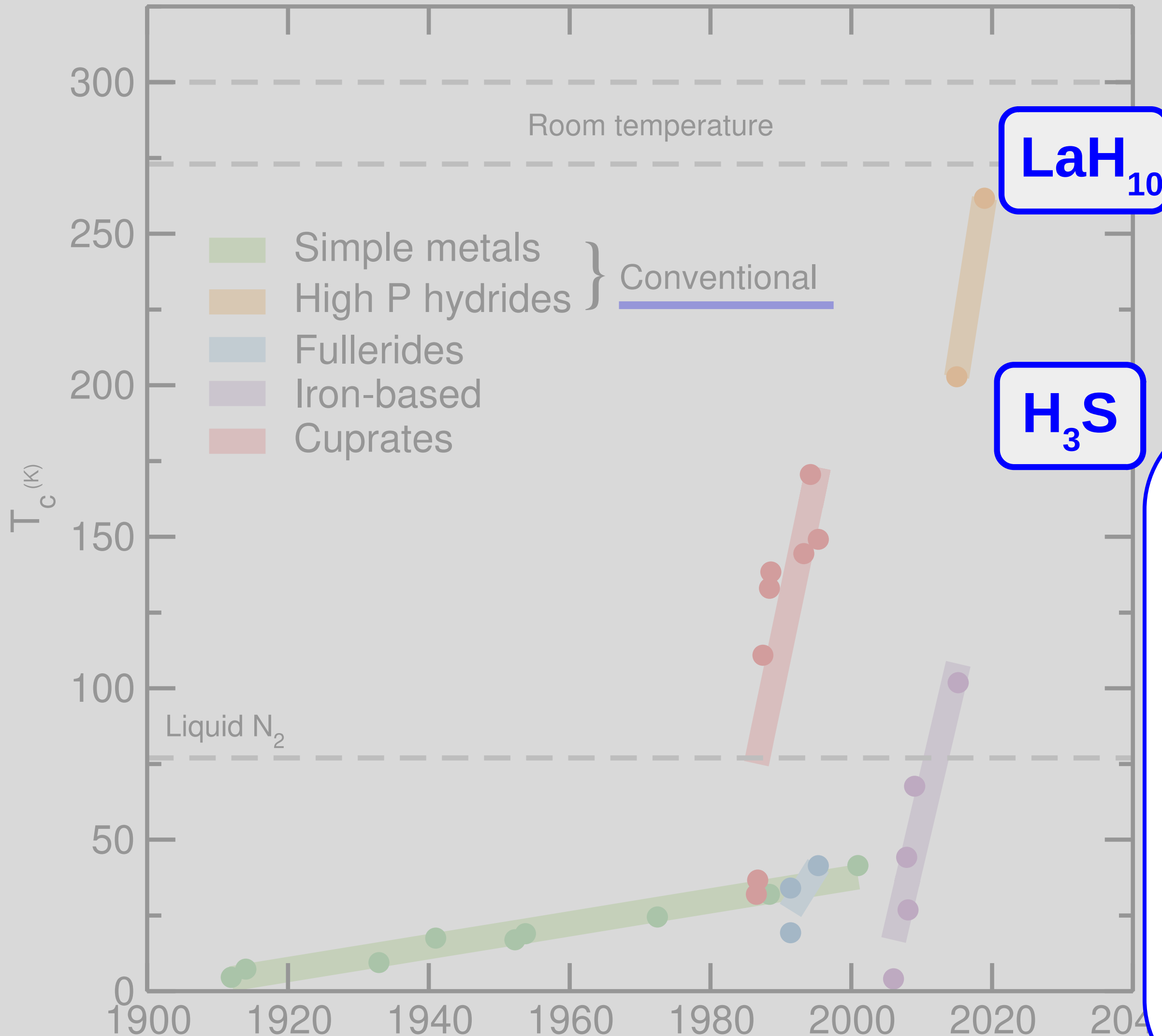
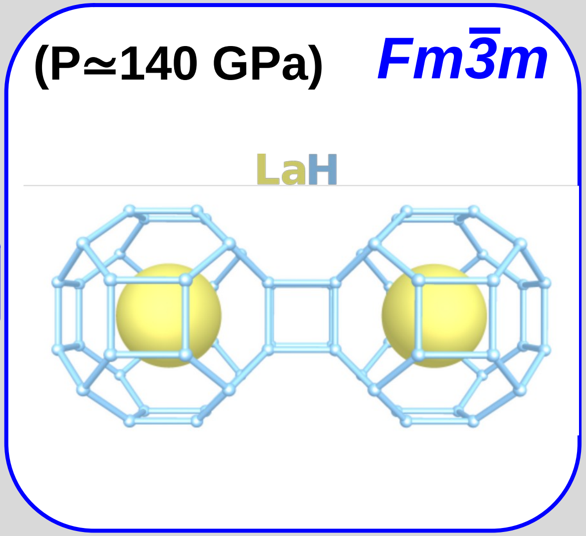
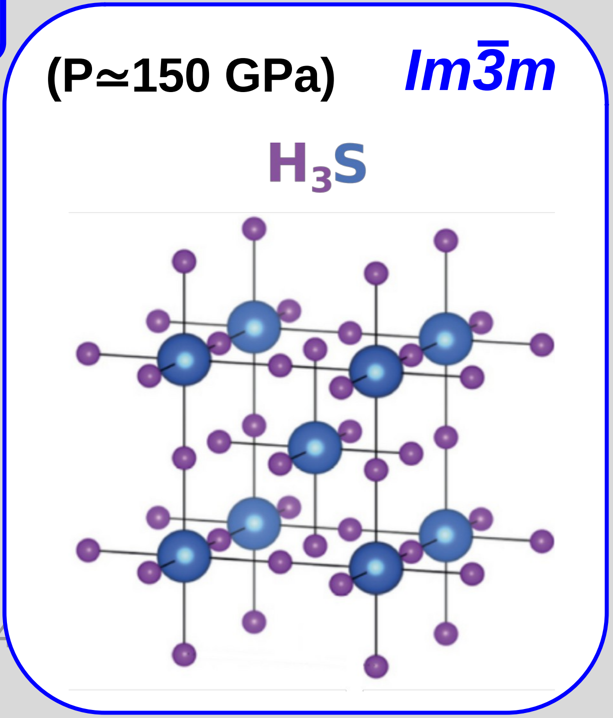


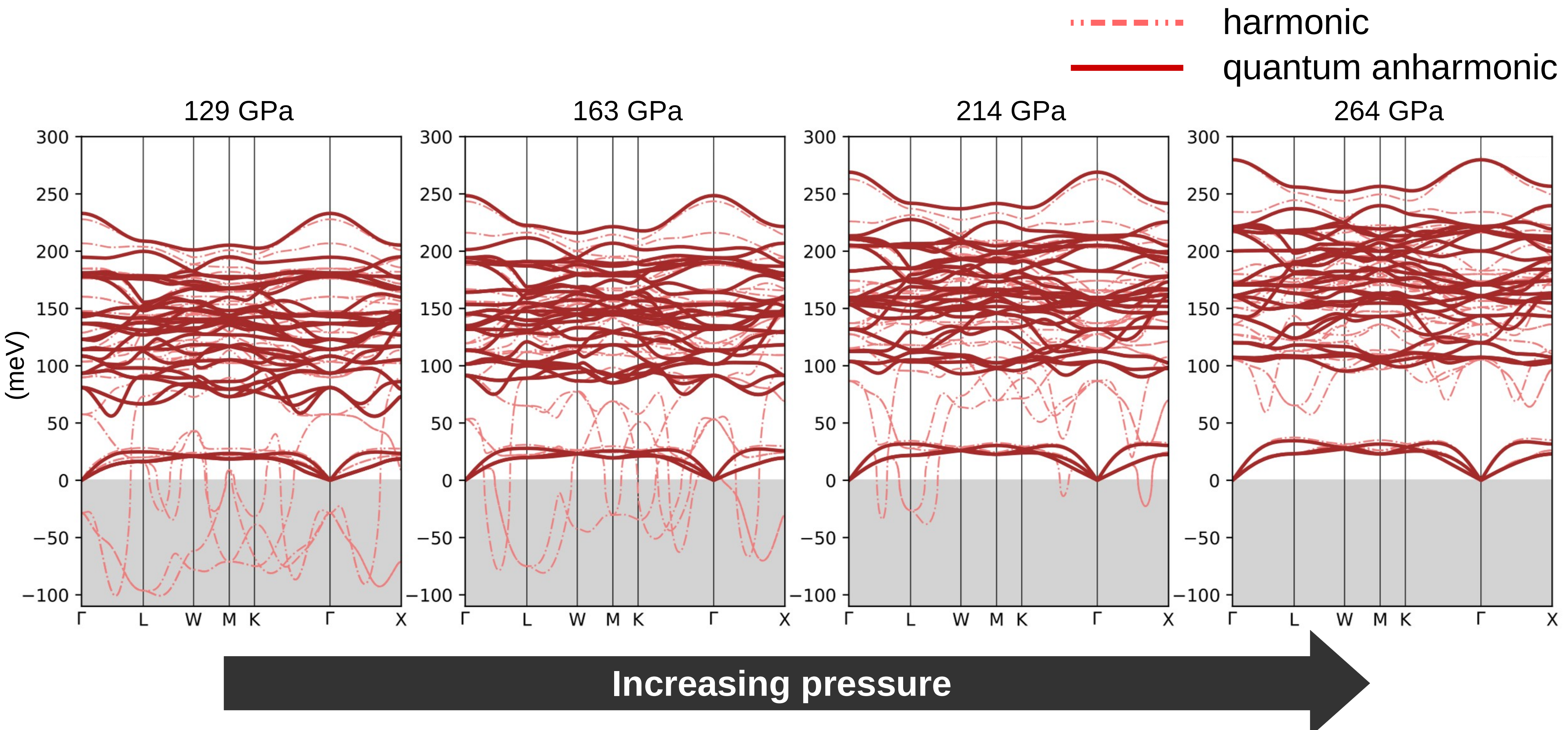




!

Protons have large zero-point energy:
the quantum nature of hydrogen cannot be neglected

LaH_{10} Phonon dispersion in the $Fm\bar{3}m$ phase



At harmonic level:

the structure becomes stable only above 220-250 GPa

below this pressure, large instabilities in several regions of the Brillouin zone

Errea et al., Nature 578, 66 (2020)

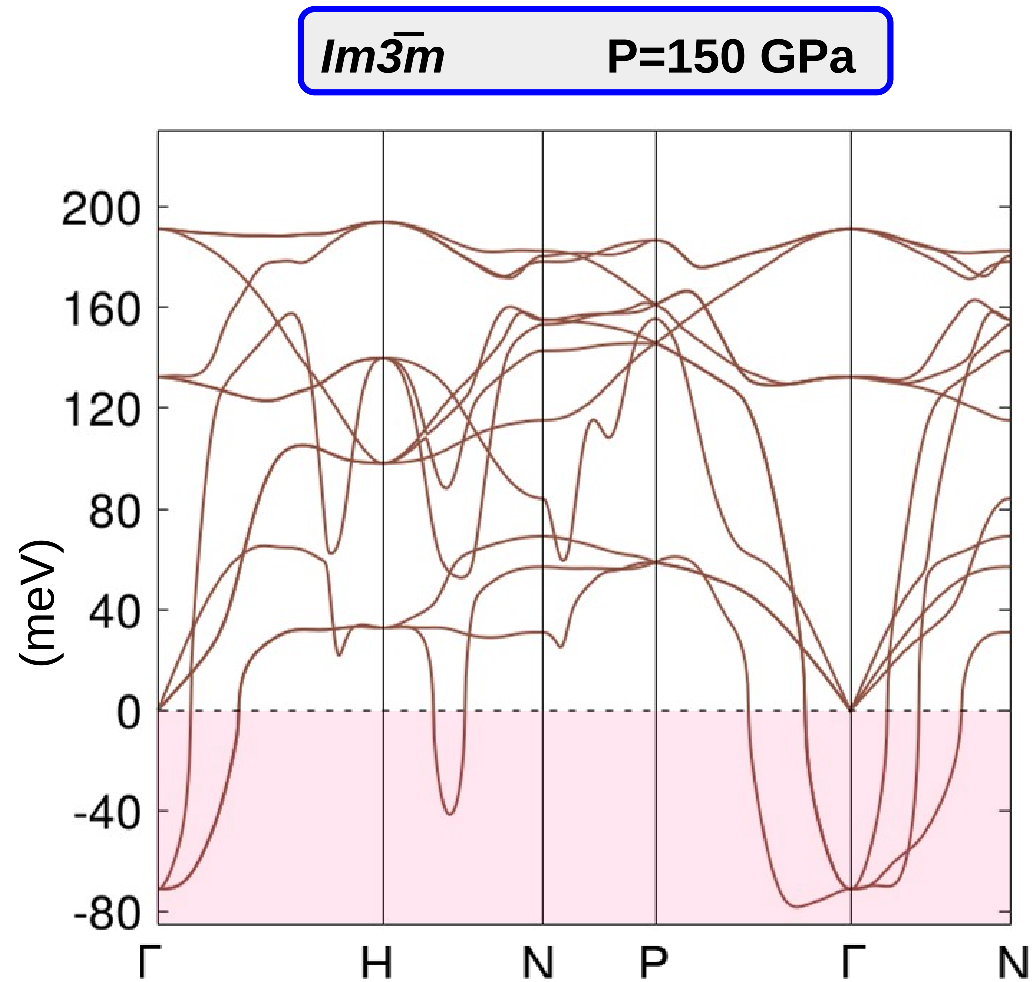
H_3S: the Im$\bar{3}$m phase

Harmonic phonons (classical)

Quantum anharmonic effects
neglected

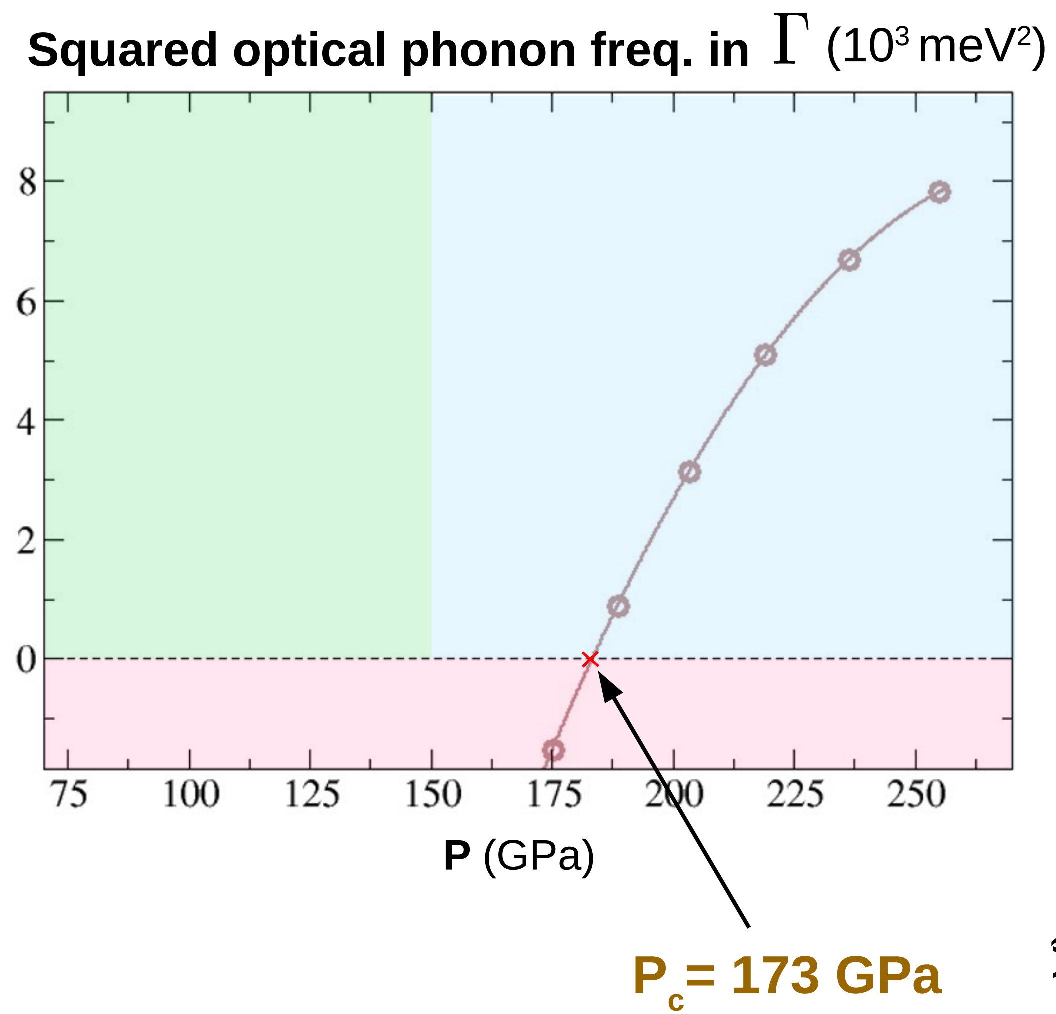
⬇

High-symmetry phase
unstable

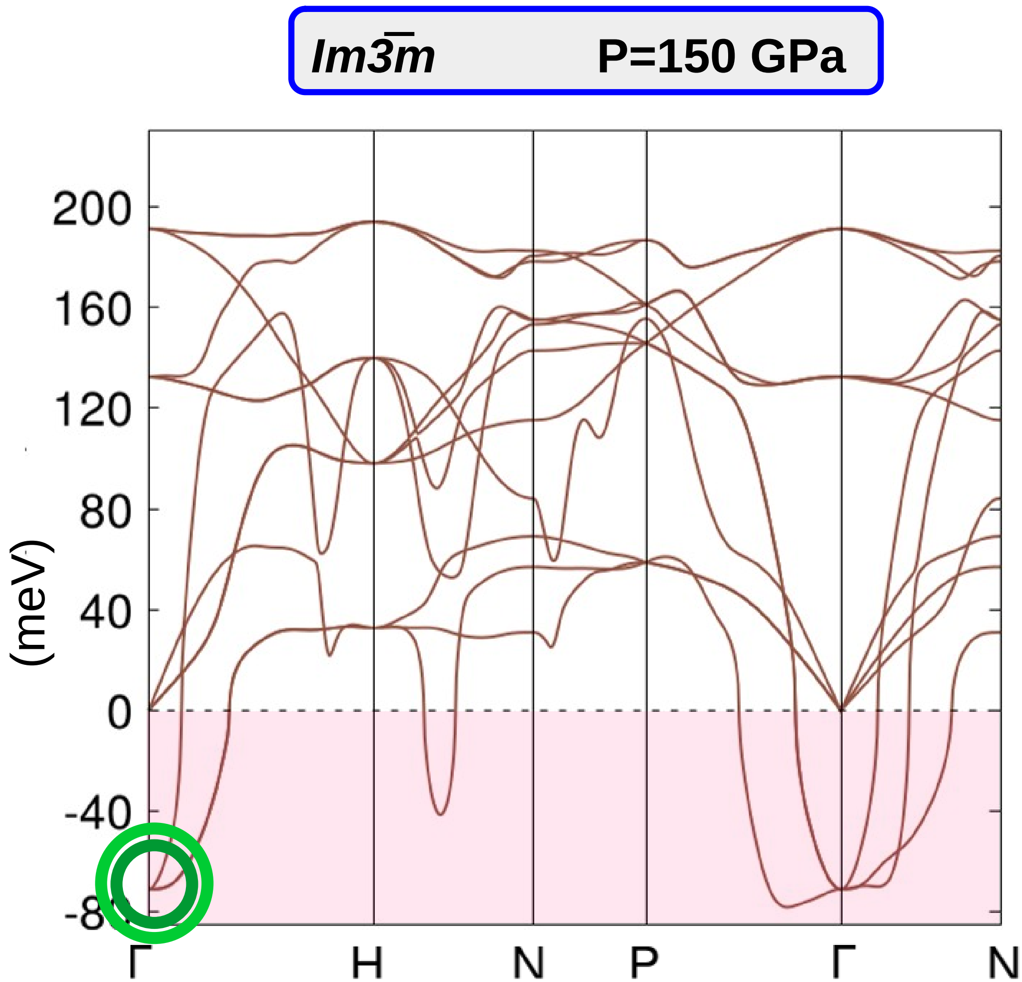


R. Bianco *et al.*, Physical Review B 97, 2018

H_3S: the $Im\bar{3}m$ phase



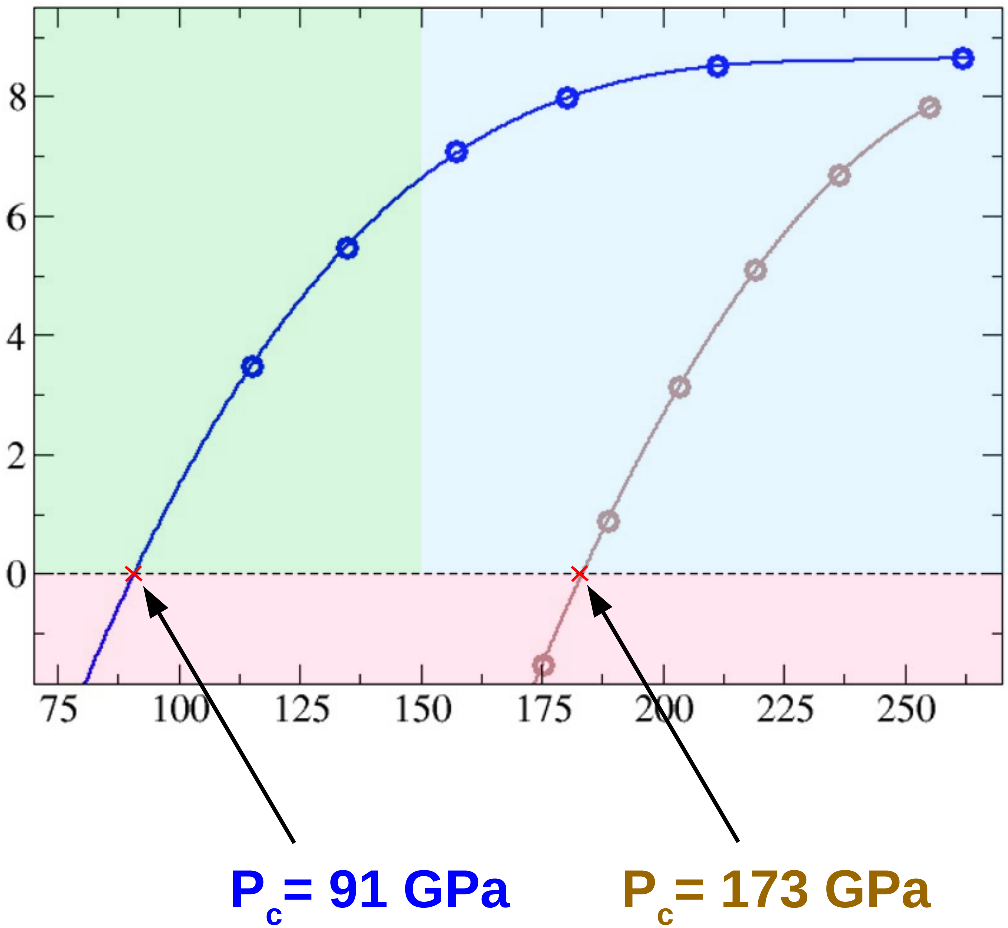
Harmonic phonons (classical)



R. Bianco *et al.*, Physical Review B 97, 2018

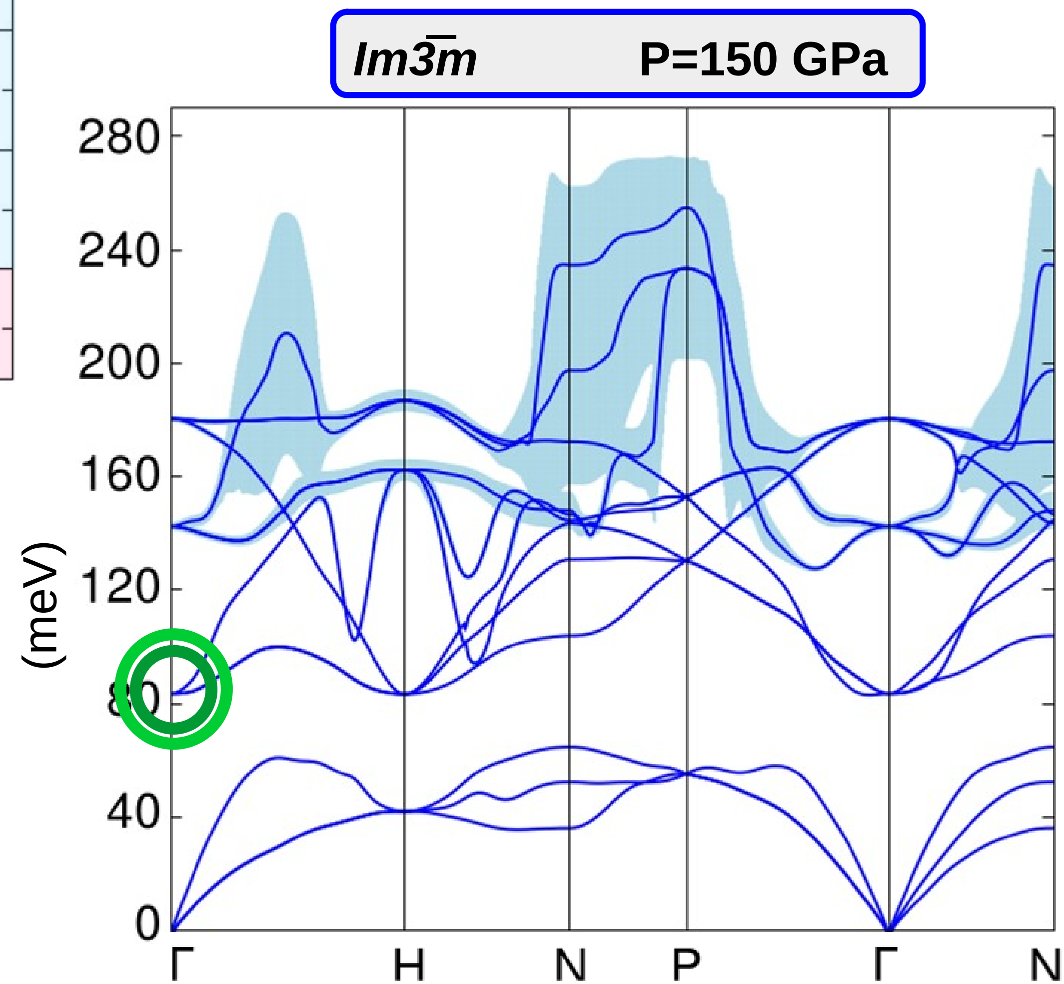
H_3S: the $Im\bar{3}m$ phase

Squared optical phonon freq. in Γ (10^3 meV^2)



Harmonic phonons (classical)

Quantum anharmonic phonons



R. Bianco *et al.*, **Physical Review B 97, 2018**

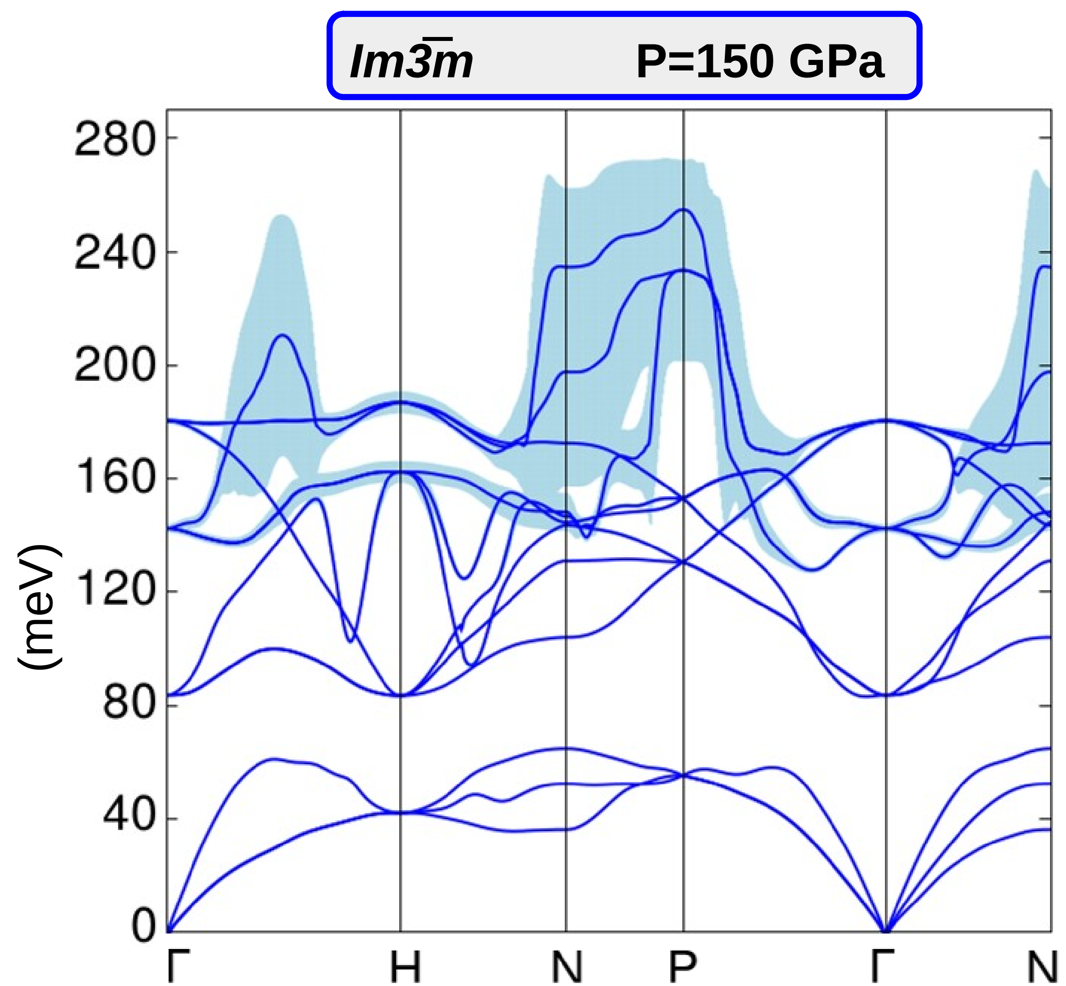
H_3S: the Im$\bar{3}$m phase

Quantum anharmonic effects
included

⬇

High-symmetry phase
stable

Quantum anharmonic phonons



R. Bianco *et al.*, Physical Review B 97, 2018

A sneak peek of Lecture 4

$$D^{(\mathrm{F})} = \frac{1}{\sqrt{MM}} \left. \frac{\partial^2 F}{\partial \mathcal{R} \partial \mathcal{R}} \right|_{\mathcal{R}_{\mathrm{eq}}}$$

Generalized phonon dispersion (as a function of *T*, *P*, ...)

A sneak peek of Lecture 4

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"Static" phonon theory

- **Infinite lifetime**
- **No phonon damping**

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"Static" phonon theory

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A dynamic theory needs to be introduced….