Lecture 2

Free-Energy Hessian and Structural Phase Transitions within SSCHA

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SSCHA

Stochastic Self-Consistent Harmonic Approximation

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Self-Consistent Harmonic Approximation

The exact system:

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

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

The harmonic trial system:

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

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

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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Free Energy

Condition necessary so that $\rho_{\mathcal{R},\Phi}$ can be normalized

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

Free Energy

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

Free Energy Functional

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

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

Self-Consistent Harmonic Approximation

The exact system:

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

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:

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

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

Free energy estimate

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

Physical meaning?

SCHA effective harmonic Hamiltonian

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

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

Average configuration of the atoms at equilibrium

In general, different from the PES mininum, i.e. different from the classical eq. conf.

SCHA effective harmonic Hamiltonian

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

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

$$\Phi^{\mathrm{MIN}} = \Phi$$ **SCHA FC**

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

NOT generalized/effective "dynamical matrix"

NOT generalized/effective "phonons"

Physical meaning?

SCHA effective harmonic Hamiltonian

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

$$\Phi^{\mathrm{MIN}} = \Phi$$ **SCHA FC**

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

NOT generalized/effective "dynamical matrix"

NOT generalized/effective "phonons"

$D^{(\mathrm{SCHA})}$ **Positive definite** ➡ **NO imaginary frequencies**

NO structural instability

Physical meaning?

SCHA effective harmonic Hamiltonian

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

The SSCHA minimization

At the end of the minimization we have:

- **Free energy**
- **Relaxed internal coordinates**
- **The SCHA force constants/dynamical matrix**

The SSCHA minimization

At the end of the minimization we have:

- **Free energy**
- **Relaxed internal coordinates**
- **The SCHA force constants/dynamical matrix**

Questions to address

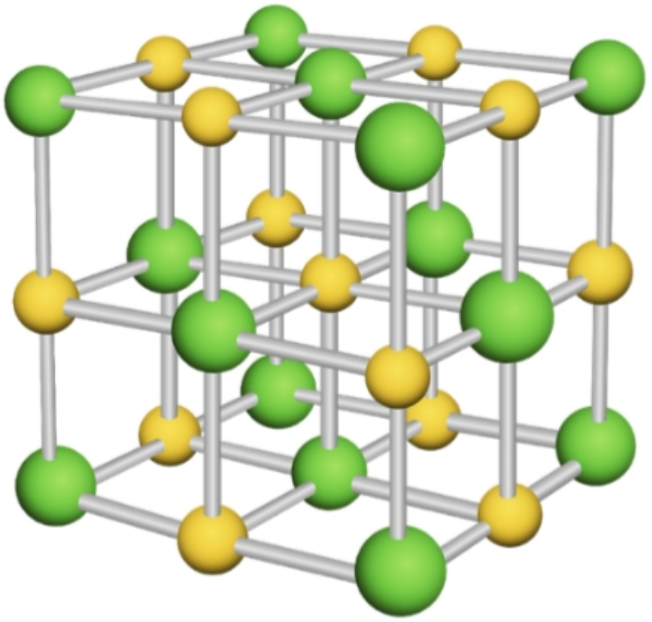
- **What is the meaning of the SCHA force constant Φ ?**
- **What is the meaning of the SCHA frequencies? (i.e. the frequencies of $D^{(\mathrm{SCHA})} = \Phi / \sqrt{MM}$)**
- **Within the SCHA framework, what does characterize a structural instability?**

The ferroelectric phase transition in SnTe

Sn Te

High-temperature: **High-symmetry phase**

α-phase ($Fm\bar{3}m$ structure)



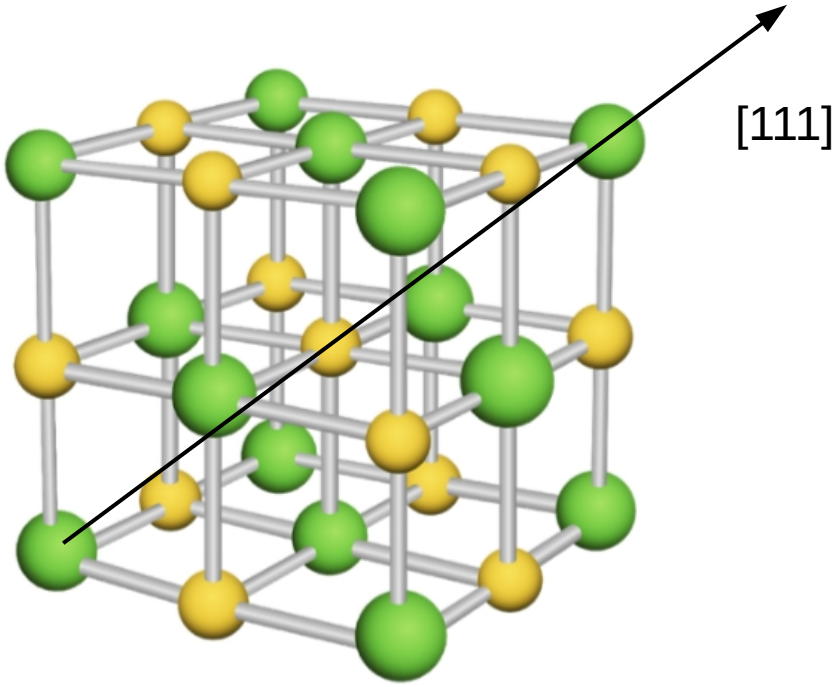
The ferroelectric phase transition in SnTe

Sn Te

On lowering temperature, at Tc ~ 100 K:

Rhombohedral phase transition

α-phase ($Fm\bar{3}m$ structure) → β-phase (R3m structure)



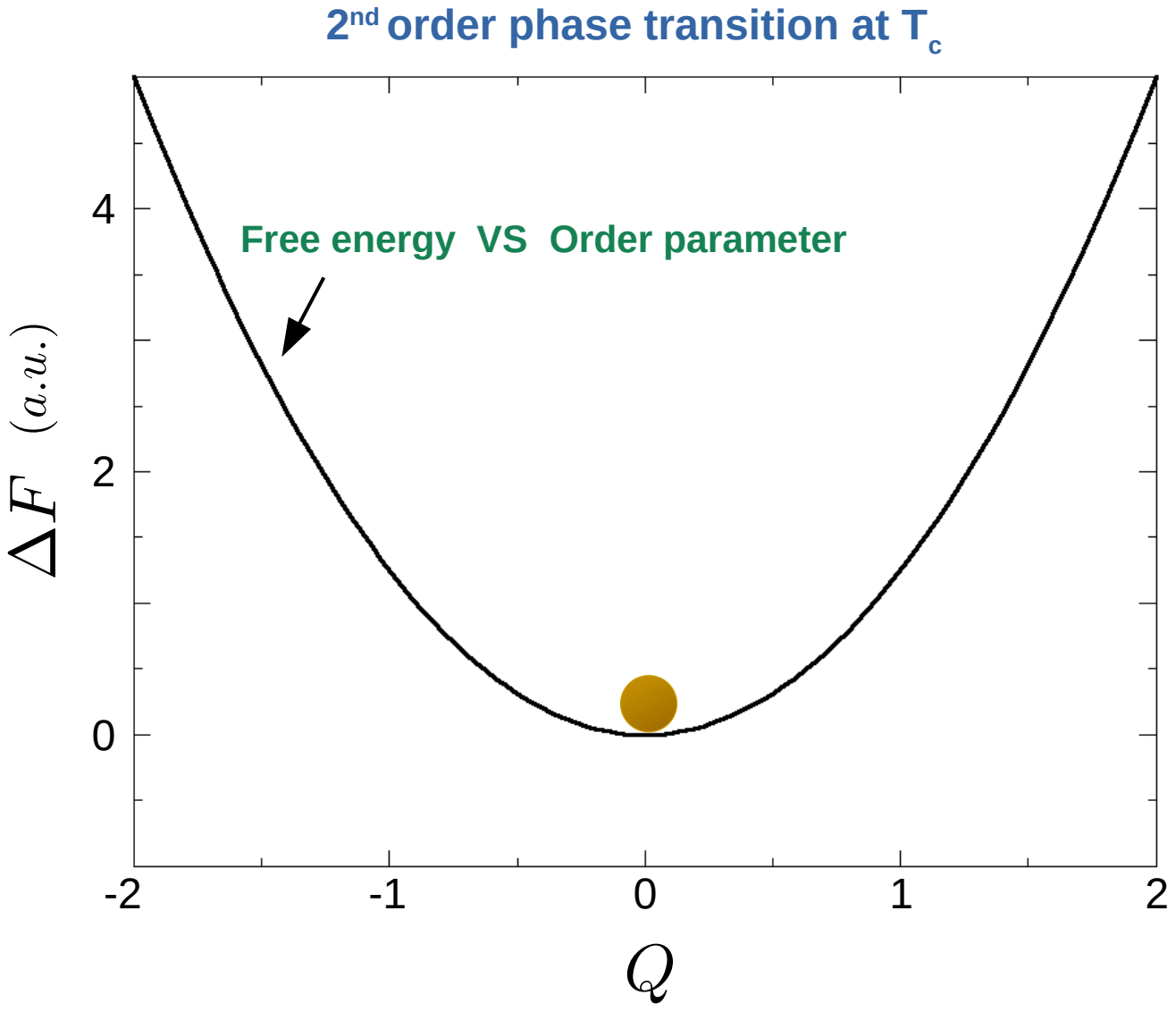
Order parameter:

relative change of the Sn–Te separation along the polar direction [111] w.r.t. the high-symmetry phase distance

$$Q = \frac{d_{SnTe}^{[111]} - d_{SnTe}^{(0)[111]}}{d_{SnTe}^{(0)[111]}}$$

The ferroelectric phase transition in SnTe is a second-order phase transition

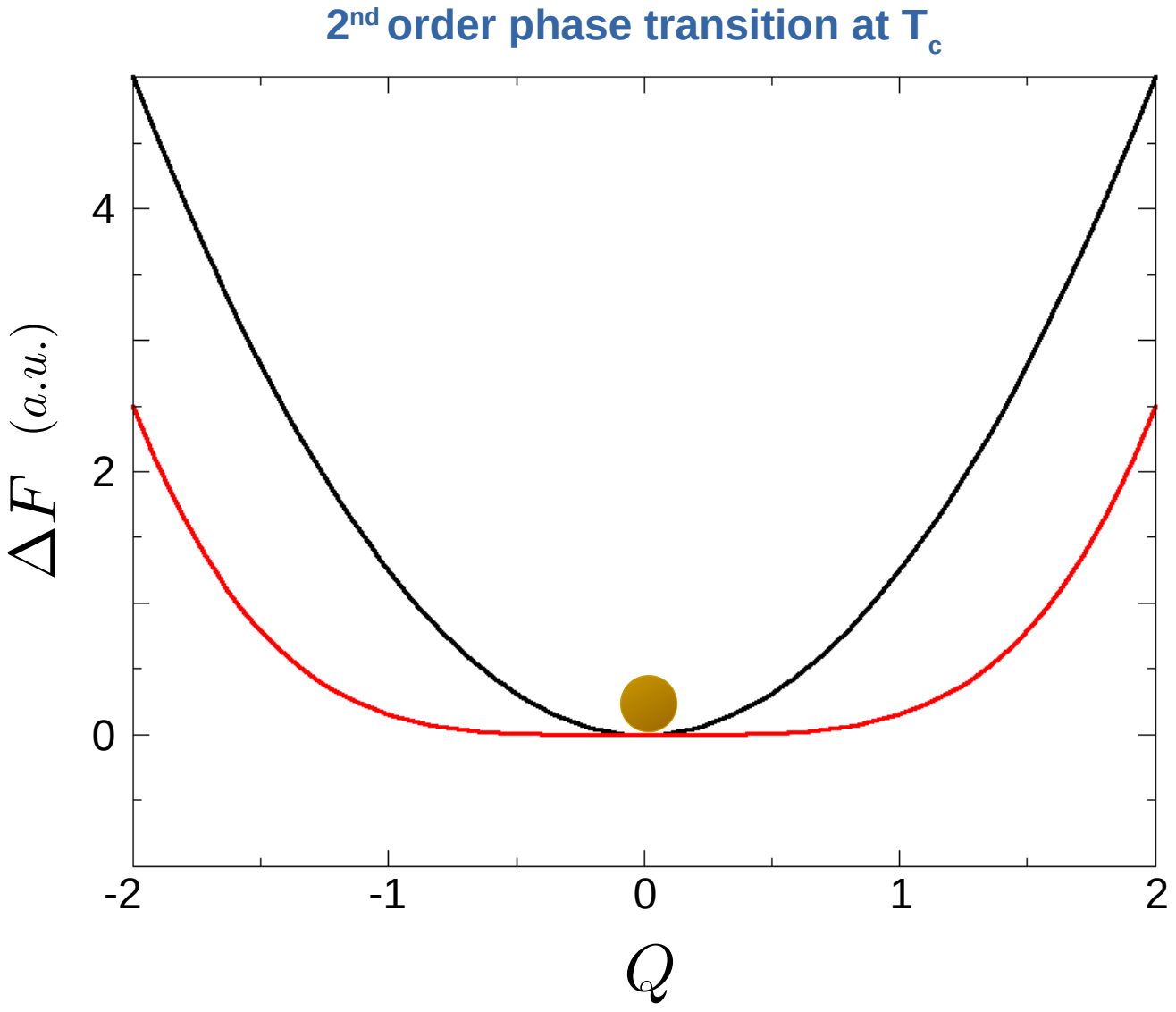
2nd order phase transitions: Landau picture



T > T_c

System in equilibrium in the high-symmetry configuration (Q=0)

2nd order phase transitions: Landau picture



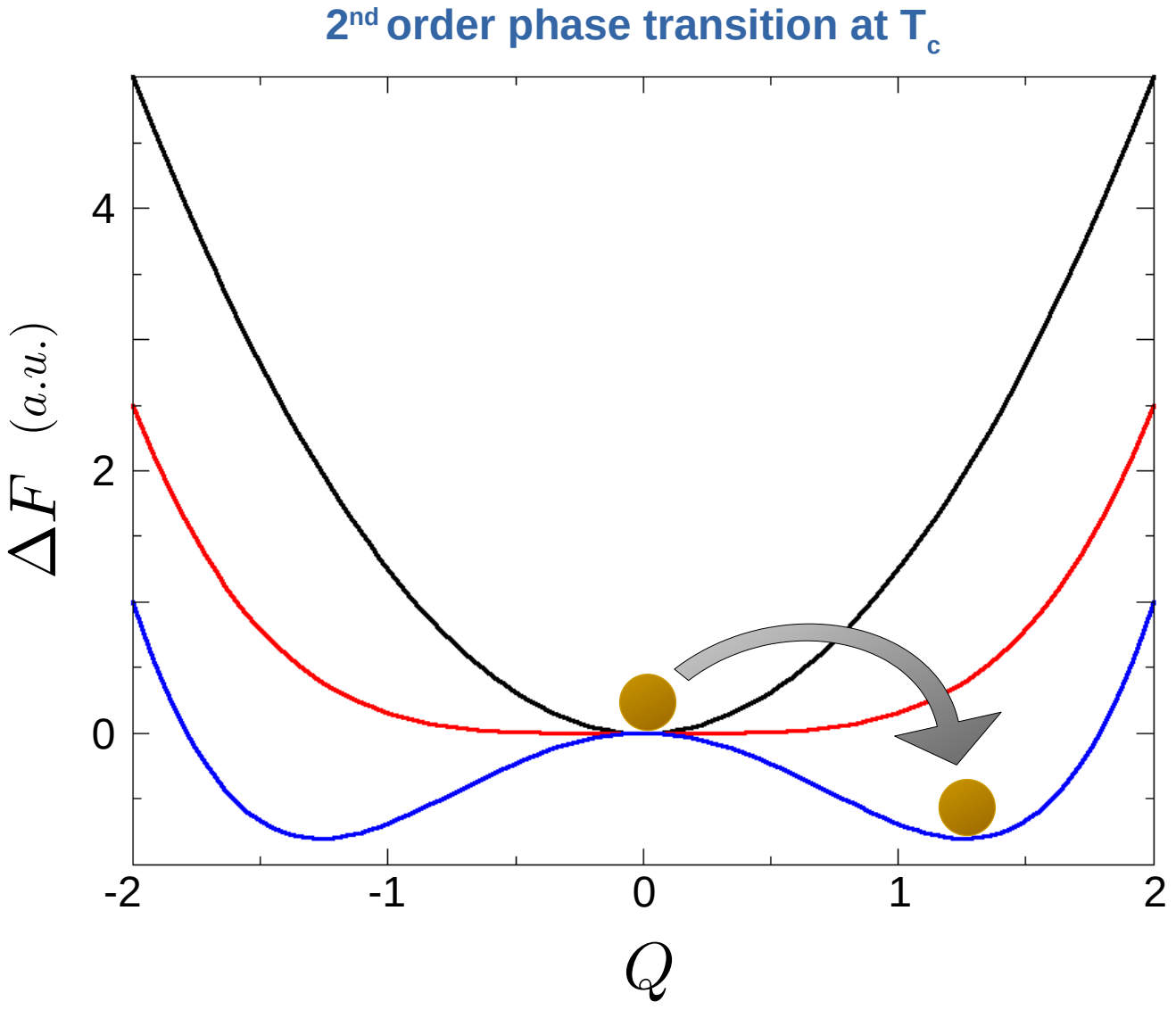
T > T_c

System in equilibrium in the high-symmetry configuration (Q=0)

T = T_c

Instability appears

2nd order phase transitions: Landau picture



T > T_c

System in equilibrium in the high-symmetry configuration (Q=0)

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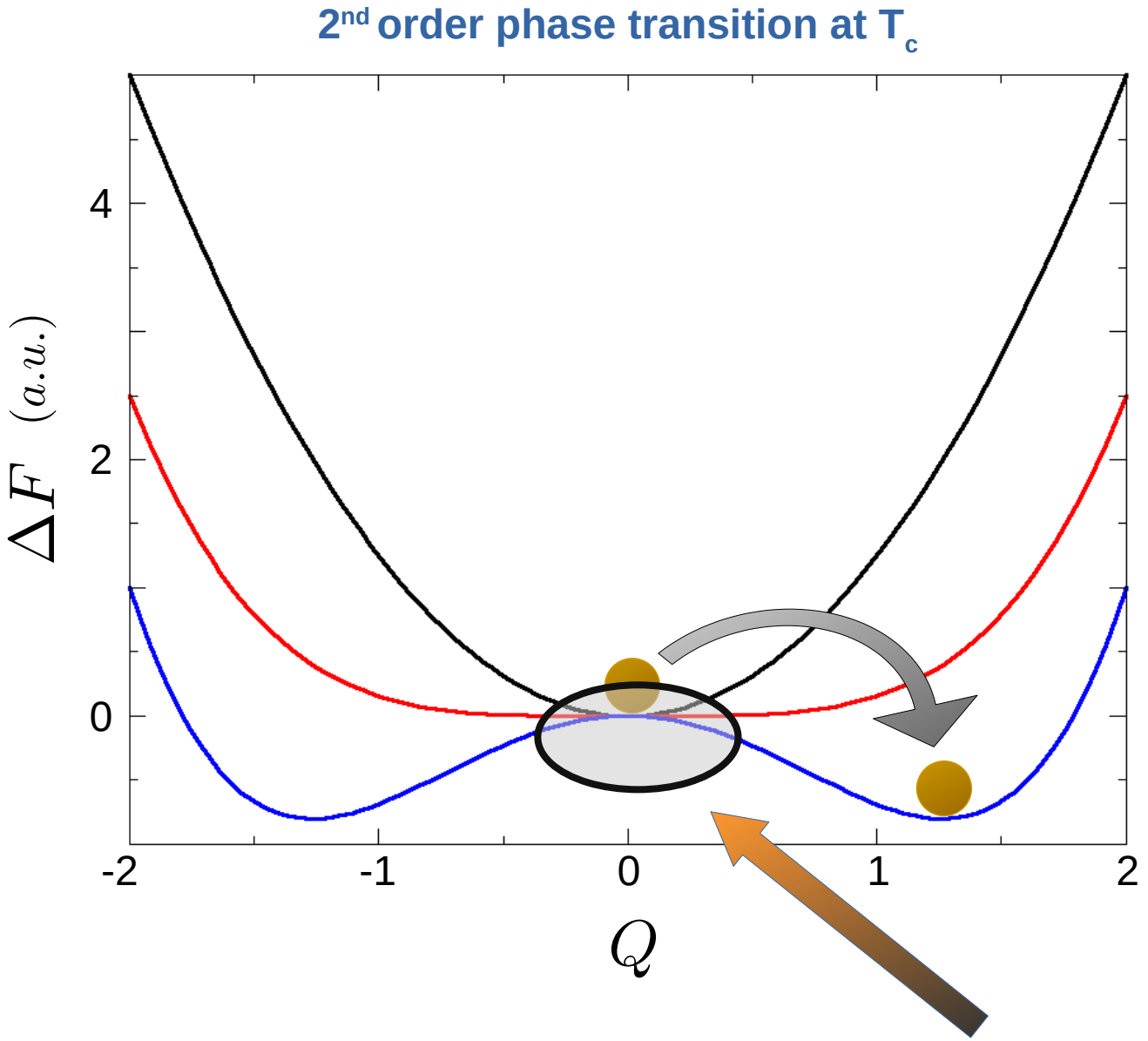
Instability appears

T < T_c

2nd order phase trans. to new eq. config. with lower symmetry (Q ≠ 0)

2nd order phase transitions: Landau picture



T > T_c

System in equilibrium in the high-symmetry configuration (Q=0)

T = T_c

Instability appears

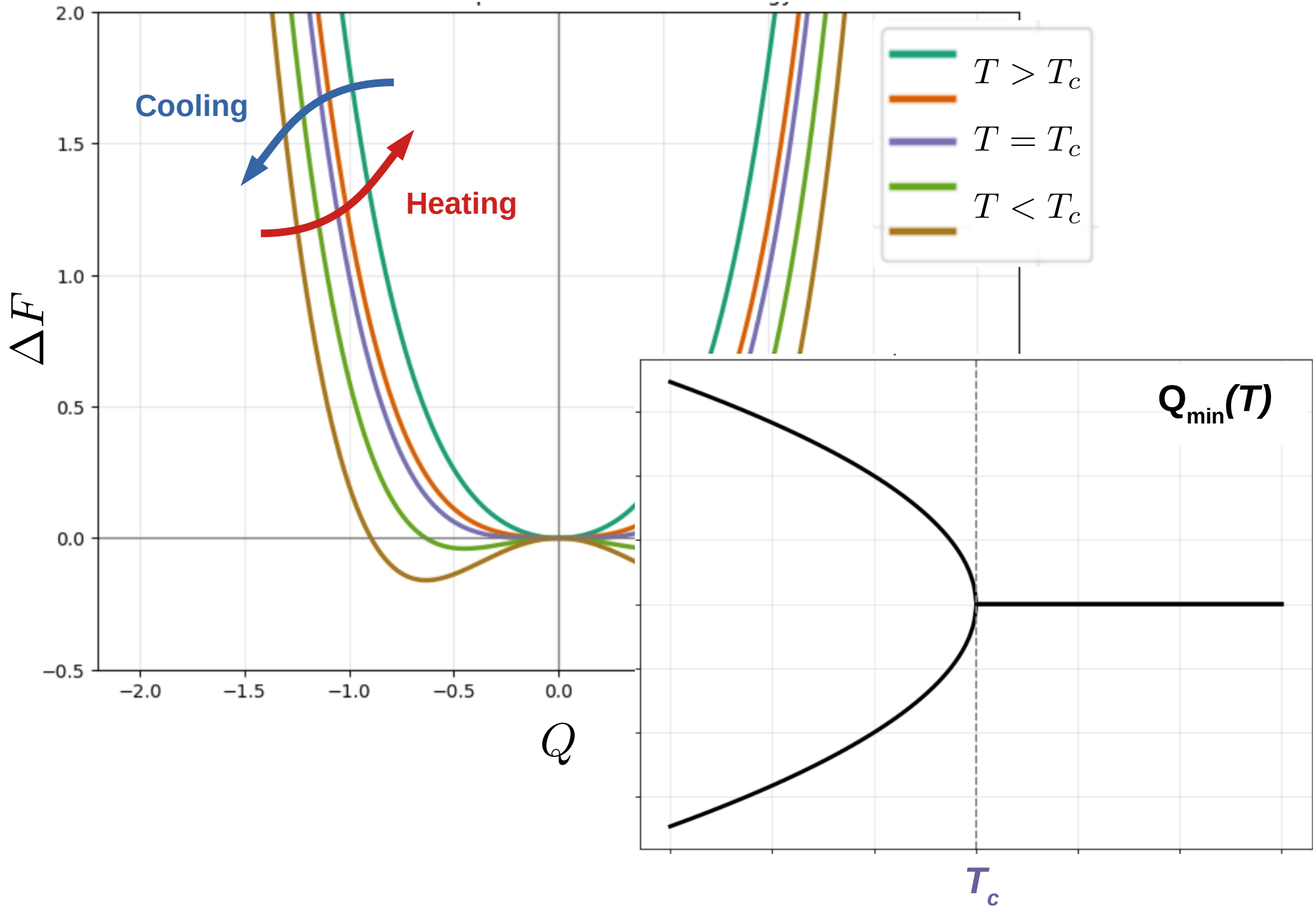
T < T_c

2nd order phase trans. to new eq. config. with lower symmetry (Q ≠ 0)

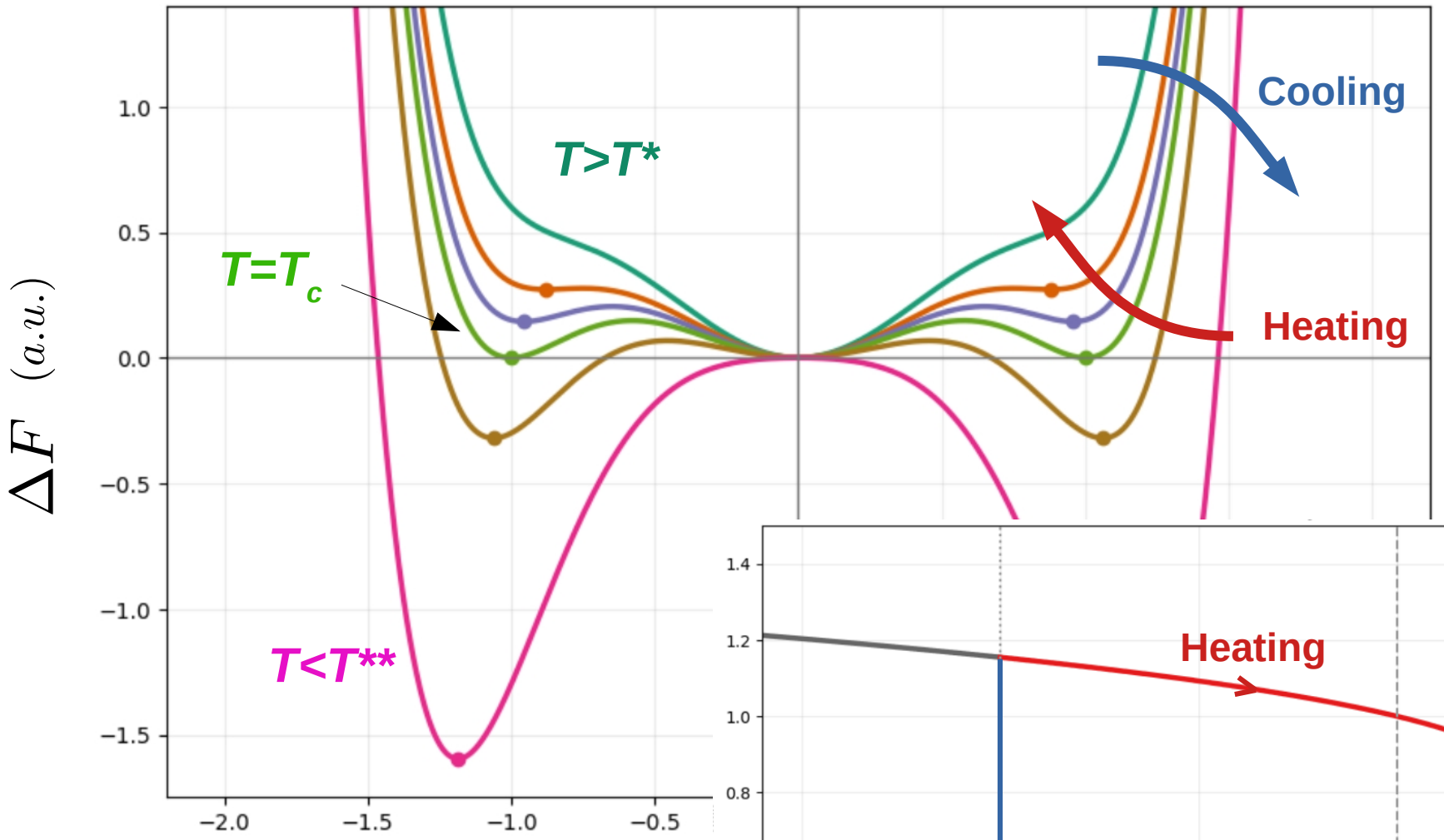
Change of curvature

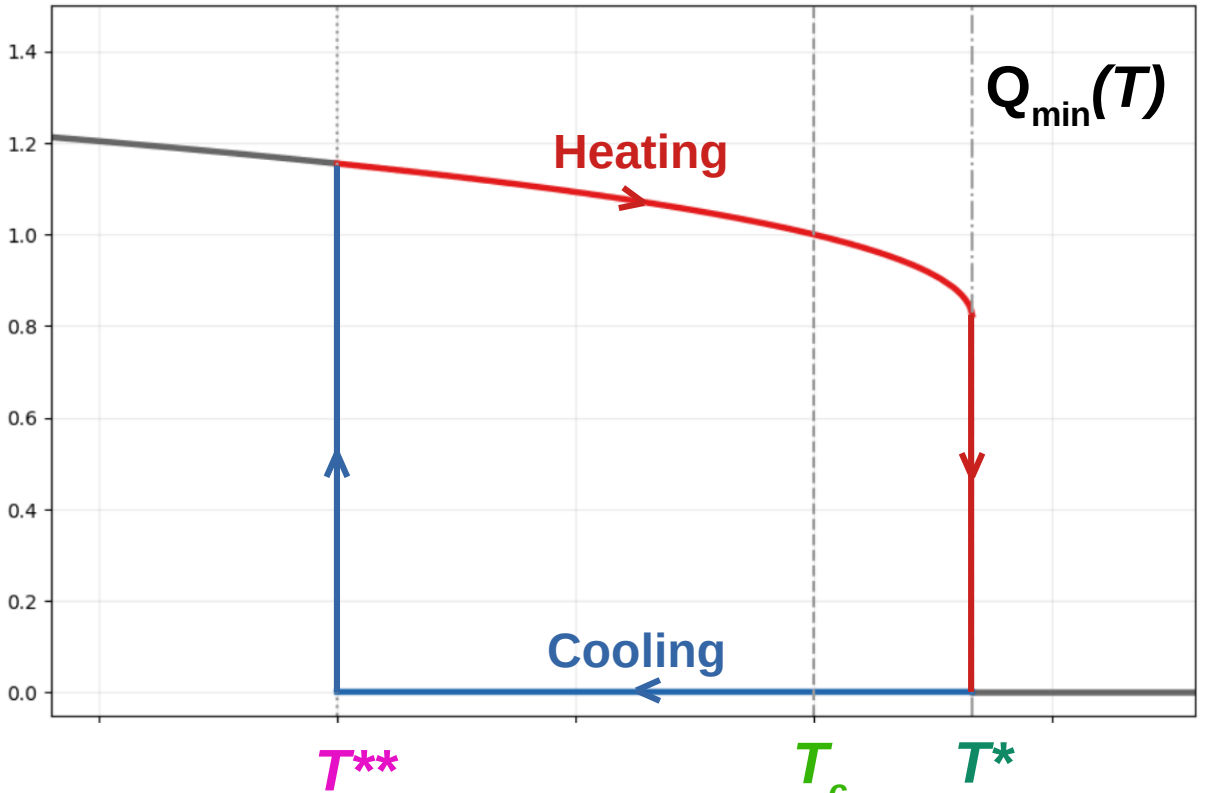
$\partial^2 F / \partial Q^2$ **changes sign**

2nd order phase transitions are continuous phase transitions



1st order phase transitions: Landau picture

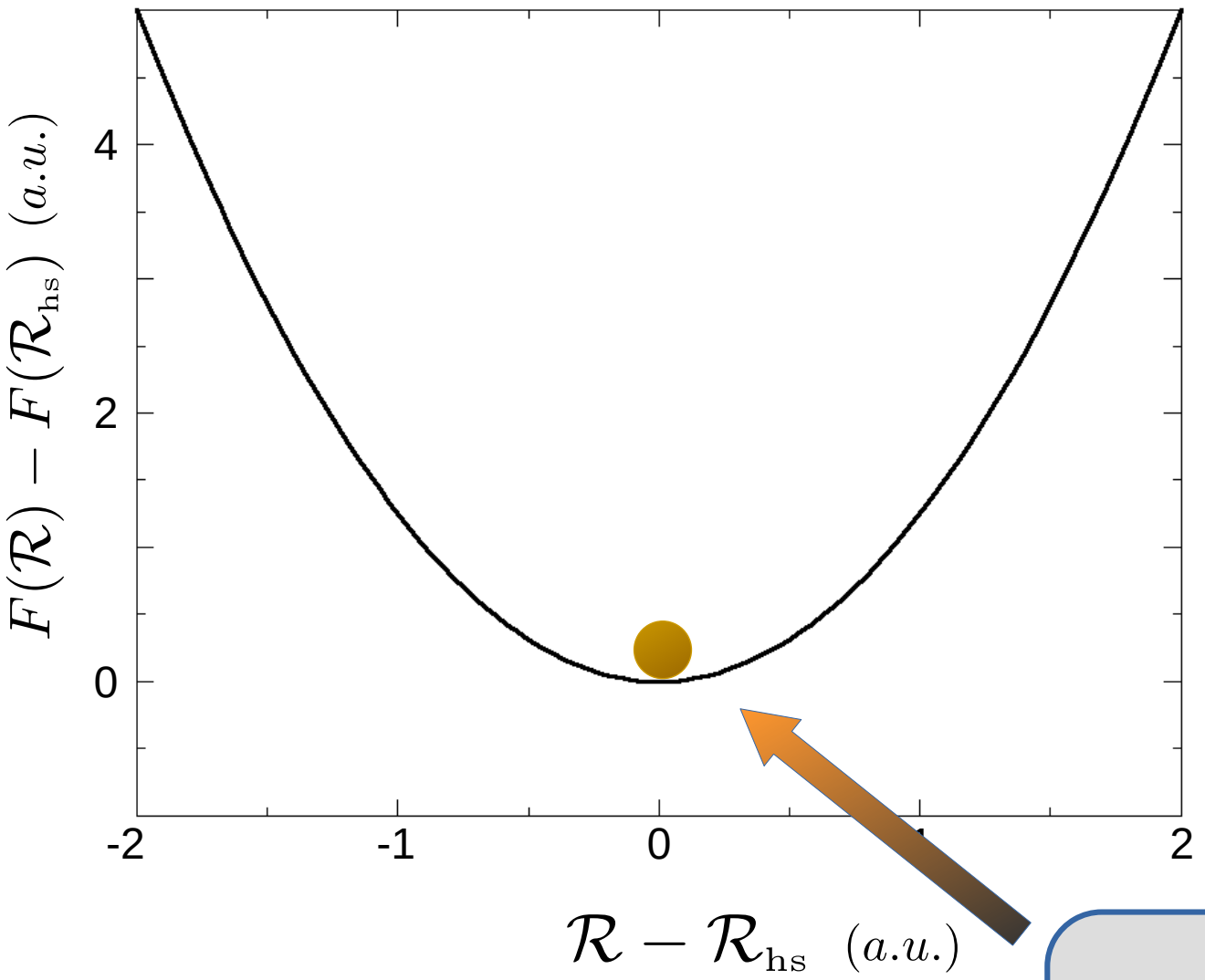




First-order transitions are characterized by competing free-energy minima and generally cannot be identified solely from the Hessian

2nd order displacive phase transitions: Landau picture

2nd order displacive phase transition at T_c



$T > T_c$

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

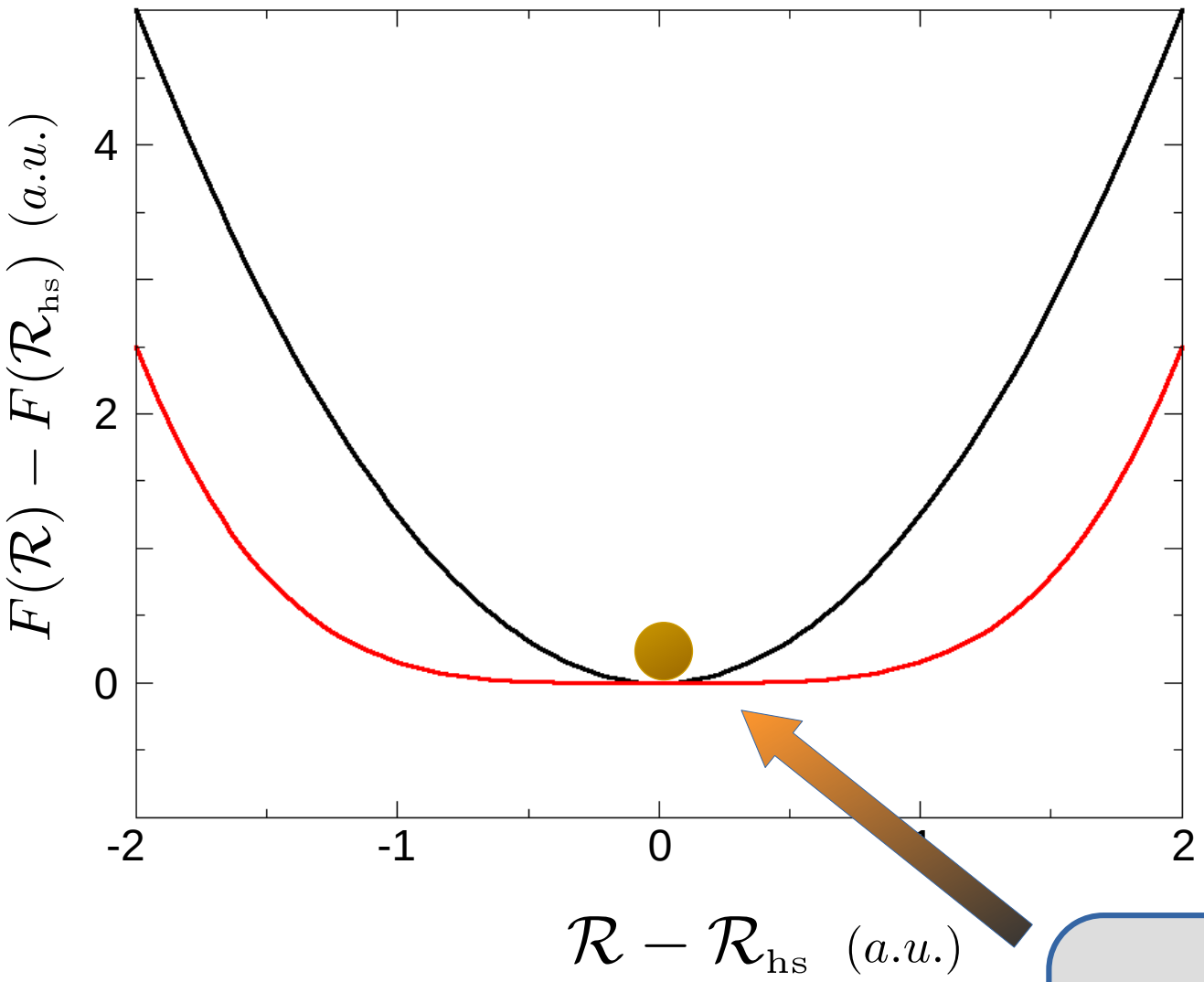
Free energy Hessian in $\mathcal{R}_{\rm hs}$

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

Positive eigenvalues

2nd order displacive phase transitions: Landau picture

2nd order displacive phase transition at T_c



$T > T_c$

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

$T = T_c$

Instability appears

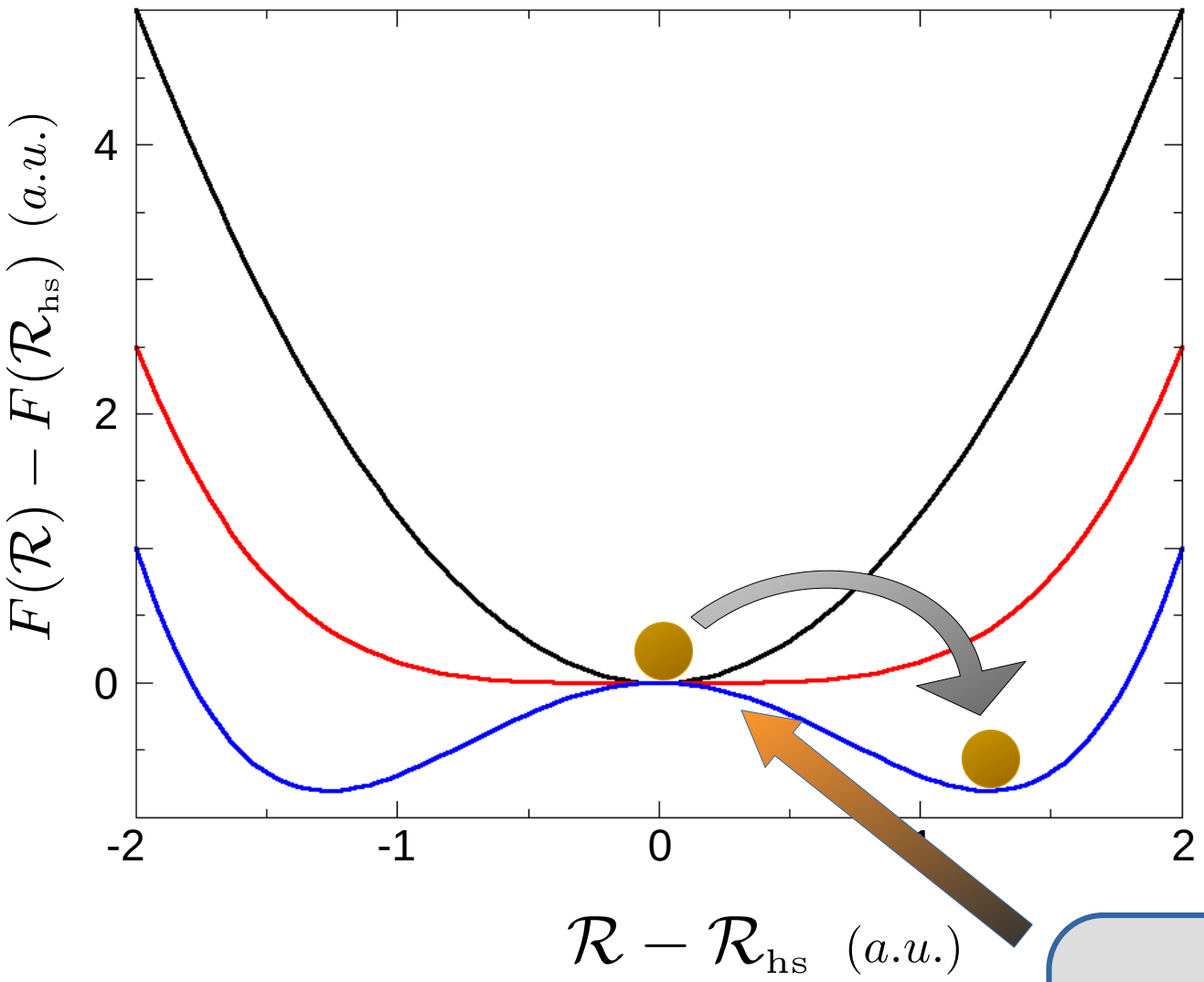
Free energy Hessian in $\mathcal{R}_{\rm hs}$

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

Null eigenvalue (along instability mode)

2nd order displacive phase transitions: Landau picture

2nd order displacive phase transition at T_c



$T > T_c$

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

$T = T_c$

Instability appears

$T < T_c$

2nd order phase trans. to new eq. config.

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

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

Negative eigenvalue (along instability mode)

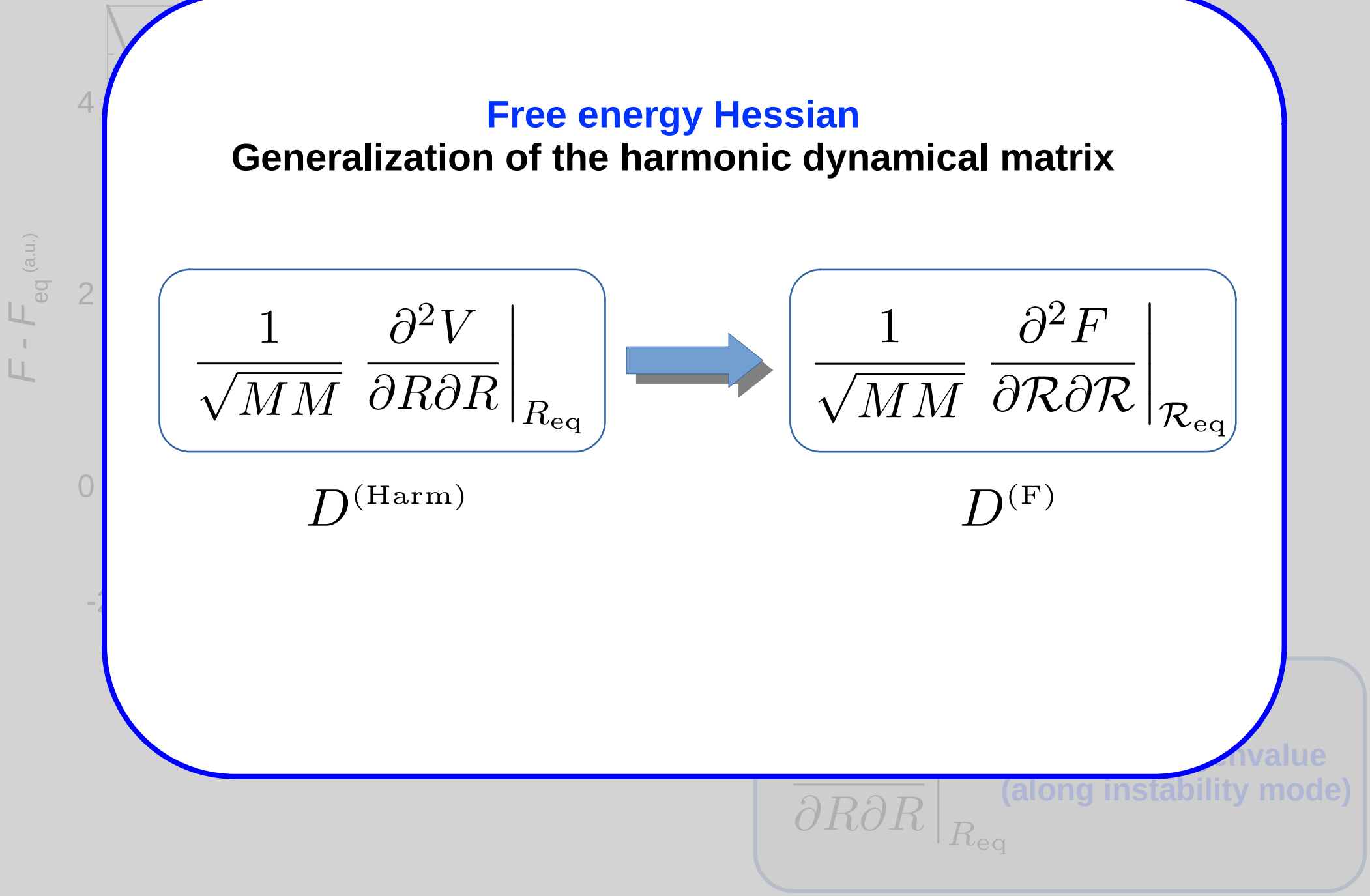
Free energy Hessian & 2nd order phase transitions

Free energy Hessian

Generalization of the harmonic dynamical matrix

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

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



Generalization of the harmonic dynamical matrix

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

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

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

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

$$F = E - TS$$

Generalization of the harmonic dynamical matrix

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

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

$$F = E - TS$$

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

Quantum nature of nuclei taken into account

Generalization of the harmonic dynamical matrix

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

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

$$F = E - TS$$

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

Thermal fluctuations taken into account

Free energy Hessian & 2nd order phase transitions

Free energy Hessian

Generalization of the harmonic dynamical matrix

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

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

Quantum, thermal, anharmonic effects included

$$\left.\frac{\partial^2 V}{\partial R \partial R}\right|_{R_{\mathrm{eq}}}$$

nvalue
(along instability mode)

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 $\omega_\mu(q)$ 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:**

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

- **Generalized phonon dispersion $\omega_\mu(q)$ (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

The positional SCHA free energy

Free energy as a function of average atomic config. $\mathcal{R}$

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

The positional SCHA free energy

Free energy as a function of average atomic config. $\mathcal{R}$

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

Positional SCHA matrix

The positional SCHA free energy

Free energy as a function of average atomic config. $\mathcal{R}$

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

Positional SCHA matrix

Of course...

$$F = F(\mathcal{R}_{\mathrm{eq}})$$ **SCHA free energy**

$$\Phi_{\mathrm{MIN}} = \Phi(\mathcal{R}_{\mathrm{eq}})$$ **SCHA force constant**

The positional free energy

It can be demonstrated that

For any fixed $\mathcal{R}$

$$\left\langle \frac{\partial^2 V}{\partial R \partial R} \right\rangle_{\rho_{\mathcal{R},\Phi(\mathcal{R})}} = \Phi(\mathcal{R})$$

The positional free energy

It can be demonstrated that

For any fixed $\mathcal{R}$

$$\left\langle \frac{\partial^2 V}{\partial R \partial R} \right\rangle_{\rho_{\mathcal{R}}, \Phi(\mathcal{R})} = \Phi(\mathcal{R})$$

Hence the "*self-consistent harmonic approx.*" name

The positional free energy

It can be demonstrated that

In particular for $\mathcal{R}_{\mathrm{eq}}$

$$\left\langle \frac{\partial^2 V}{\partial R \partial R} \right\rangle_{\rho_{\mathcal{R}_{\mathrm{eq}}}, \Phi_{\mathrm{MIN}}} = \Phi_{\mathrm{MIN}}$$

Characterizing structural phase transitions from the free energy

Knowing $F(\mathcal{R})$ allows us to study structural phase transitions

- **First-order transitions:**

  competing free-energy minima

- **Second-order transitions:**

  free-energy Hessian

$$\frac{\partial^2 F}{\partial \mathcal{R} \partial \mathcal{R}}$$

Direct finite-difference evaluation is impractical (computational cost, stochastic noise, ...)

Fortunately, an analytical expression exists

SCHA Free energy Hessian

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

R. Bianco *et al., Phys. Rev. B 96, 014111 (2017)*

SCHA Free energy Hessian

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

SCHA FC matrix

$$\left\langle \frac{\partial^2 V}{\partial R \partial R} \right\rangle_{\rho_{\mathcal{R}_{\mathrm{eq}},\Phi}}$$

density matrix of

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

SCHA Free energy Hessian

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

SCHA FC matrix

$$\left\langle \frac{\partial^2 V}{\partial R \partial R} \right\rangle_{\rho_{\mathcal{R}_{\mathrm{eq}}, \Phi}}$$

Self-Consistent Harmonic Approximation

SCHA Free energy Hessian

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SCHA FC matrix

$$\left\langle \frac{\partial^2 V}{\partial R \partial R} \right\rangle_{\rho_{\mathcal{R}_{\mathrm{eq}},\Phi}}$$

$$\left\langle \frac{\partial^3 V}{\partial R \partial R \partial R} \right\rangle_{\rho_{\mathcal{R}_{\mathrm{eq}},\Phi}}$$

$$\left\langle \frac{\partial^4 V}{\partial R \partial R \partial R \partial R} \right\rangle_{\rho_{\mathcal{R}_{\mathrm{eq}},\Phi}}$$

SCHA Free energy Hessian

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SCHA FC matrix

$$\left\langle \frac{\partial^2 V}{\partial R \partial R} \right\rangle_{\rho_{\mathcal{R}_{\mathrm{eq}},\Phi}}$$

Computed from the SCHA dyn. matrix

Frequencies ω_μ

Eigenmodes e_μ^a

of $\dfrac{\Phi}{\sqrt{MM}}$ $\longrightarrow$ Λ

SCHA Free energy Hessian

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

SCHA FC matrix

$$\left\langle \frac{\partial^2 V}{\partial R \partial R} \right\rangle_{\rho_{\mathcal{R}_{\mathrm{eq}},\Phi}}$$

Computed from the SCHA dyn. matrix

Frequencies ω_μ

Eigenmodes e_μ^a

of $\dfrac{\Phi}{\sqrt{MM}}$ $\longrightarrow$ Λ

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

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

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

SCHA Free energy Hessian

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

SCHA FC matrix

$$\left\langle \frac{\partial^2 V}{\partial R \partial R} \right\rangle_{\rho_{\mathcal{R}_{\mathrm{eq}},\Phi}}$$

$$\left\langle \frac{\partial^3 V}{\partial R \partial R \partial R} \right\rangle_{\rho_{\mathcal{R}_{\mathrm{eq}},\Phi}}$$

$$\left\langle \frac{\partial^4 V}{\partial R \partial R \partial R \partial R} \right\rangle_{\rho_{\mathcal{R}_{\mathrm{eq}},\Phi}}$$

SCHA Free energy Hessian

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

How to compute them?

(direct stochastic approach ruled out)

SCHA FC matrix

$$\left\langle \frac{\partial^2 V}{\partial R \partial R} \right\rangle_{\rho_{\mathcal{R}_{\mathrm{eq}},\Phi}}$$

$$\left\langle \frac{\partial^3 V}{\partial R \partial R \partial R} \right\rangle_{\rho_{\mathcal{R}_{\mathrm{eq}},\Phi}}$$

$$\left\langle \frac{\partial^4 V}{\partial R \partial R \partial R \partial R} \right\rangle_{\rho_{\mathcal{R}_{\mathrm{eq}},\Phi}}$$

High-order FCs: stochastic approach

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

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normal distribution

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

With integration by parts ...

High-order FCs: stochastic approach

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

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

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

Linear functions

- $\overset{(3)}{\mathbb{G}}(R, V, \mathrm{f})$
- $\overset{(4)}{\mathbb{G}}(R, V, \mathrm{f})$

High-order FCs: stochastic approach

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

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Stochastic approach suited

High-order FCs: stochastic approach

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Stochastic approach suited

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

High-order FCs: stochastic approach

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

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

↓

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

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↓

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

↓

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

Free energy Hessian: Diagrammatic Expression

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

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$$= \Phi + \overset{(3)}{\Phi} : \Lambda : \overset{(3)}{\Phi}$$

$$+ \overset{(3)}{\Phi} : \Lambda : \overset{(4)}{\Phi} : \Lambda : \overset{(3)}{\Phi}$$

$$+ \overset{(3)}{\Phi} : \Lambda : \overset{(4)}{\Phi} : \Lambda : \overset{(4)}{\Phi} : \Lambda : \overset{(3)}{\Phi}$$

$$+ \ldots$$

Free energy Hessian: Diagrammatic Expression

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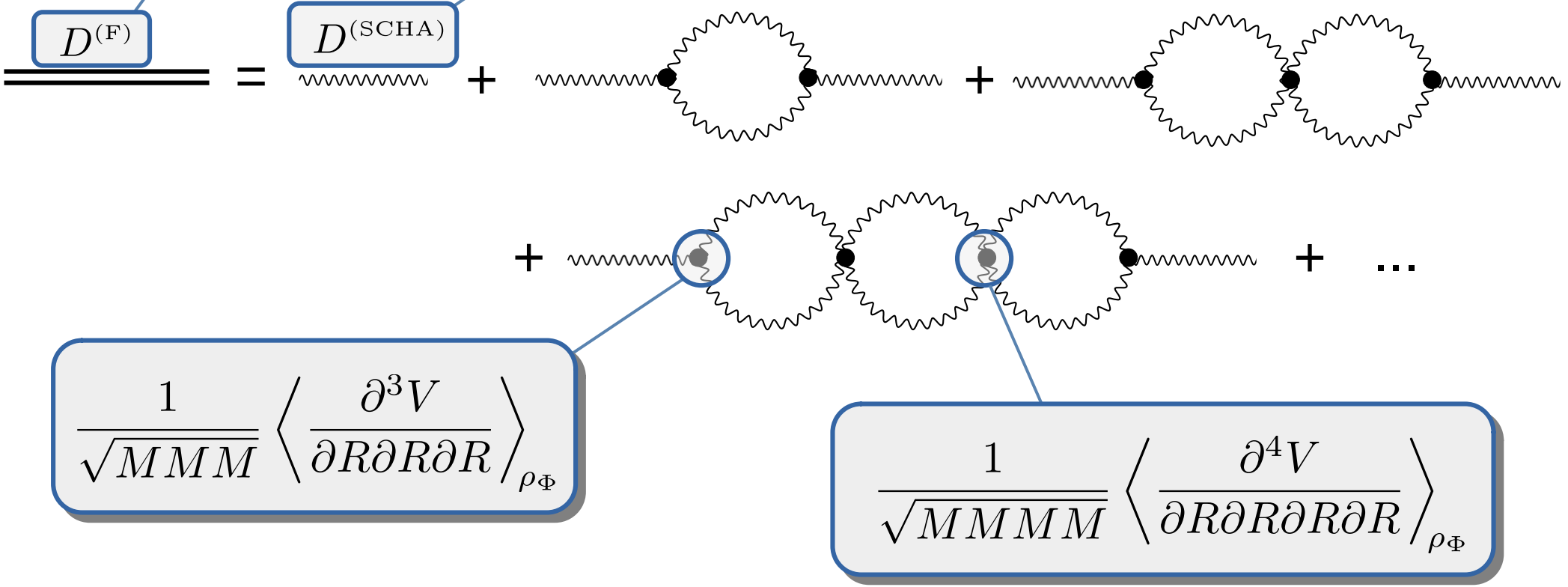
$$+ \overset{(3)}{\Phi} : \Lambda : \overset{(4)}{\Phi} : \Lambda : \overset{(4)}{\Phi} : \Lambda : \overset{(3)}{\Phi} + \dots$$

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

$\frac{\Phi}{\sqrt{MM}}$



$\frac{1}{\sqrt{MMM}} \left\langle \frac{\partial^3 V}{\partial R \partial R \partial R} \right\rangle_{\rho_\Phi}$

$\frac{1}{\sqrt{MMMM}} \left\langle \frac{\partial^4 V}{\partial R \partial R \partial R \partial R} \right\rangle_{\rho_\Phi}$

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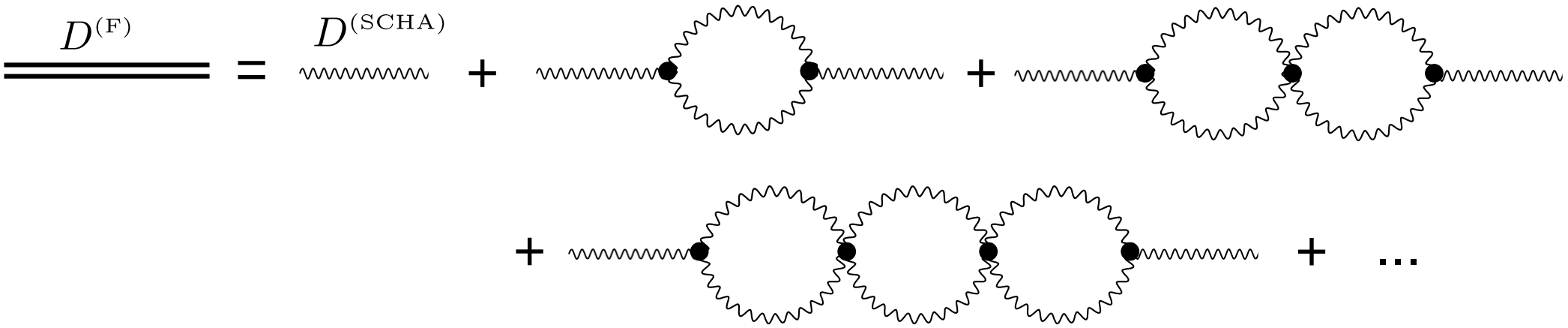

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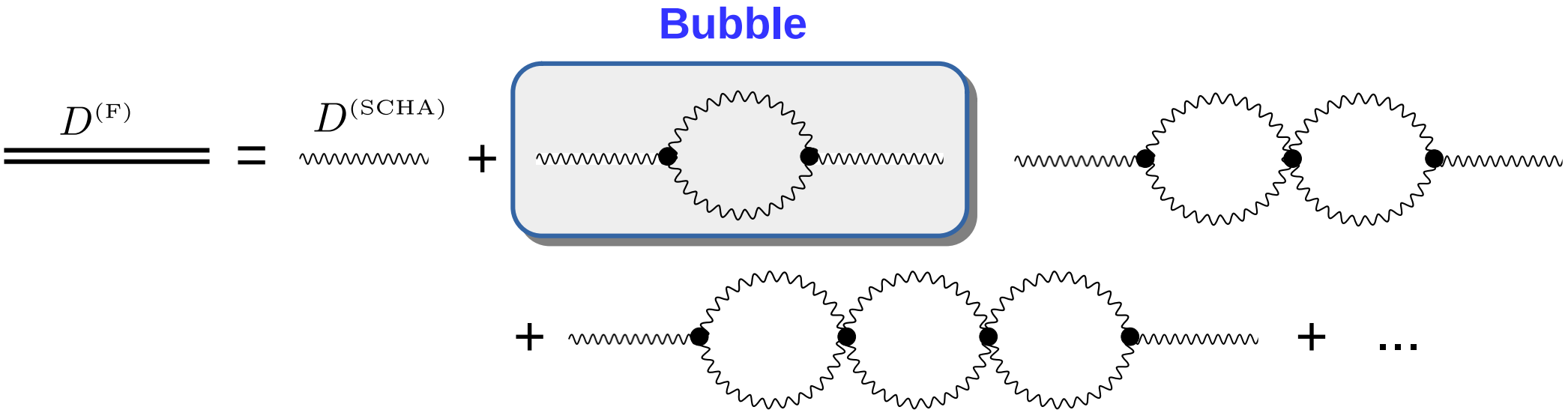
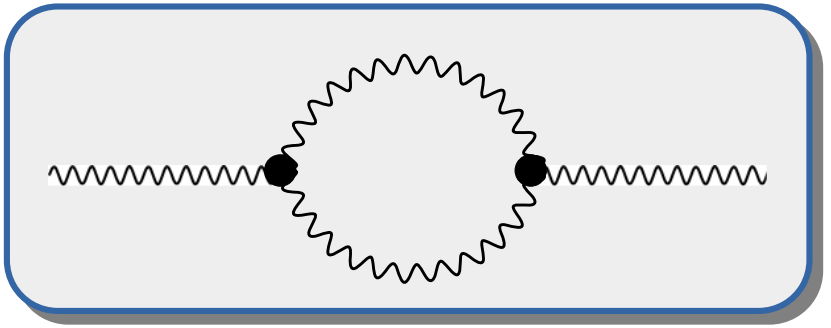


Free energy Hessian: Bubble approximation

$$\frac{\partial^2 F}{\partial R \partial R} \simeq \Phi + \overset{(3)}{\Phi} : \Lambda : \overset{(3)}{\Phi}$$

Bubble

$D^{(\mathrm{F})}$ $\simeq$ $D^{(\mathrm{SCHA})}$ +



Exploiting lattice-translation symmetry...

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

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At this level, $D^{(\mathrm{F})}(\boldsymbol{q})$ is defined only on a **q**-grid commensurate with the used supercell

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

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In the SCHA modes basis set is (discarding 4th order derivative terms...):

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

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

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Pseudomomentum conservation

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

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

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

  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...

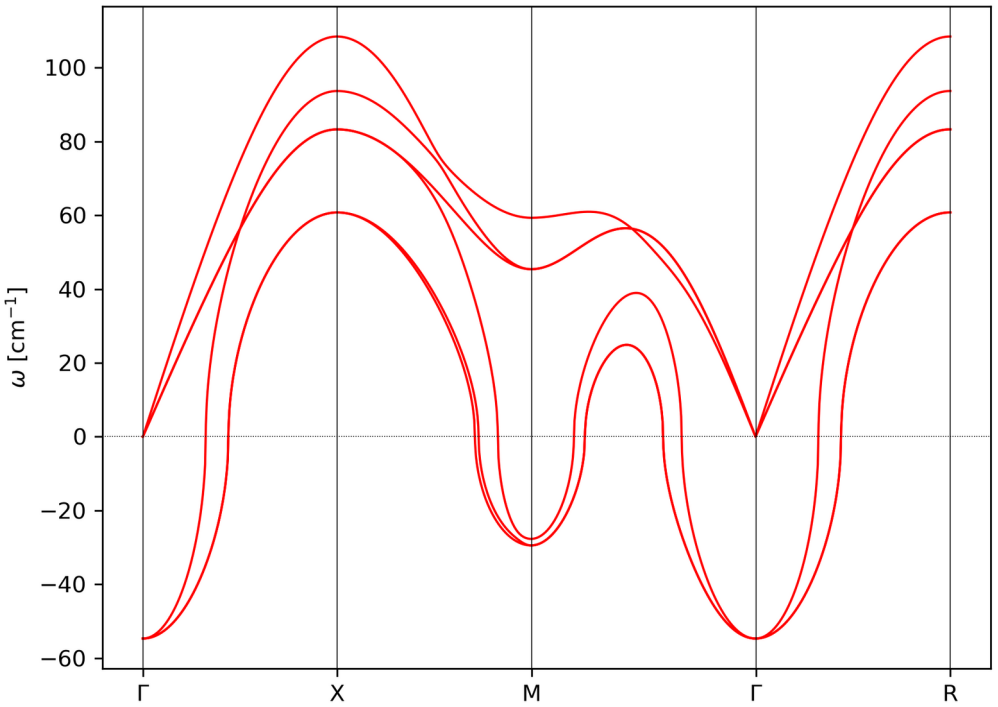
The ferroelectric transition in SnTe

In the hands-on session we will study this second-order phase transition within SSCHA employing a force field

$$V(R) = \frac{1}{2}\sum_{ab}\phi_{ab}\,u_a u_b + \frac{1}{3!}\sum_{abc}\overset{(3)}{\phi}_{abc}\,u_a u_b u_c + \frac{1}{4!}\sum_{abcd}\overset{(4)}{\phi}_{abcd}\,u_a u_b u_c u_d$$

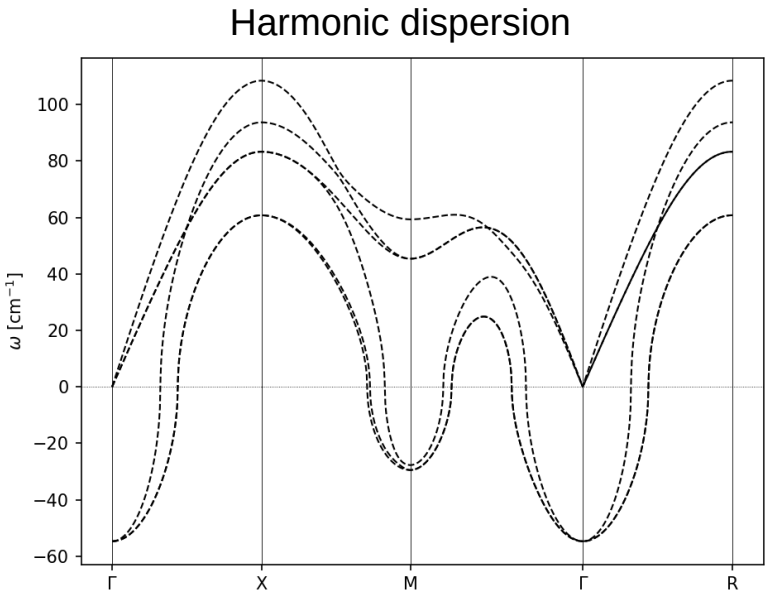
$$u^a = (R^a - R^a_{\mathrm{hs}})$$

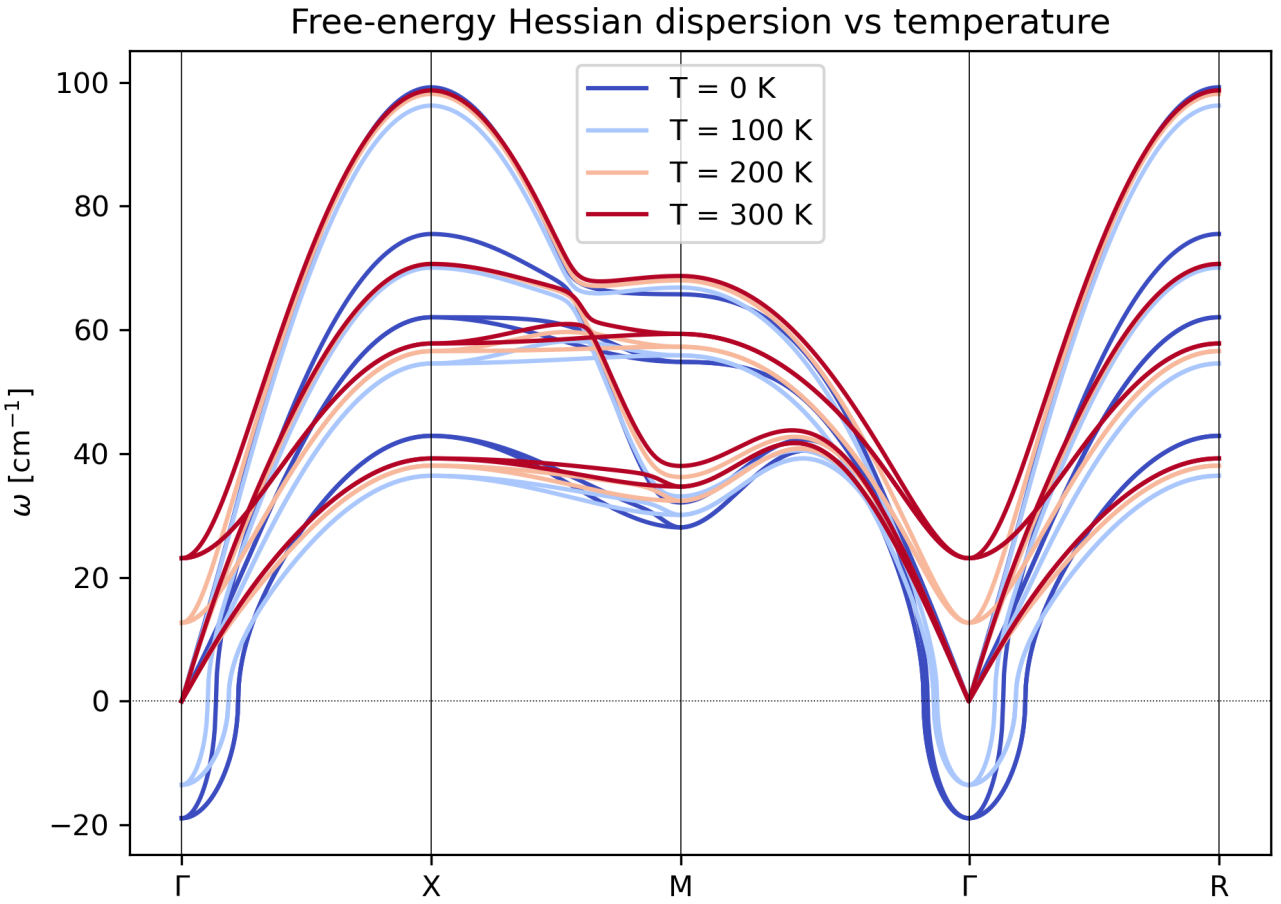
Harmonic phonons



Y. Chen, X. Ai, and C. A. Marianetti, Phys. Rev. Lett.,113, 105501 (2014)

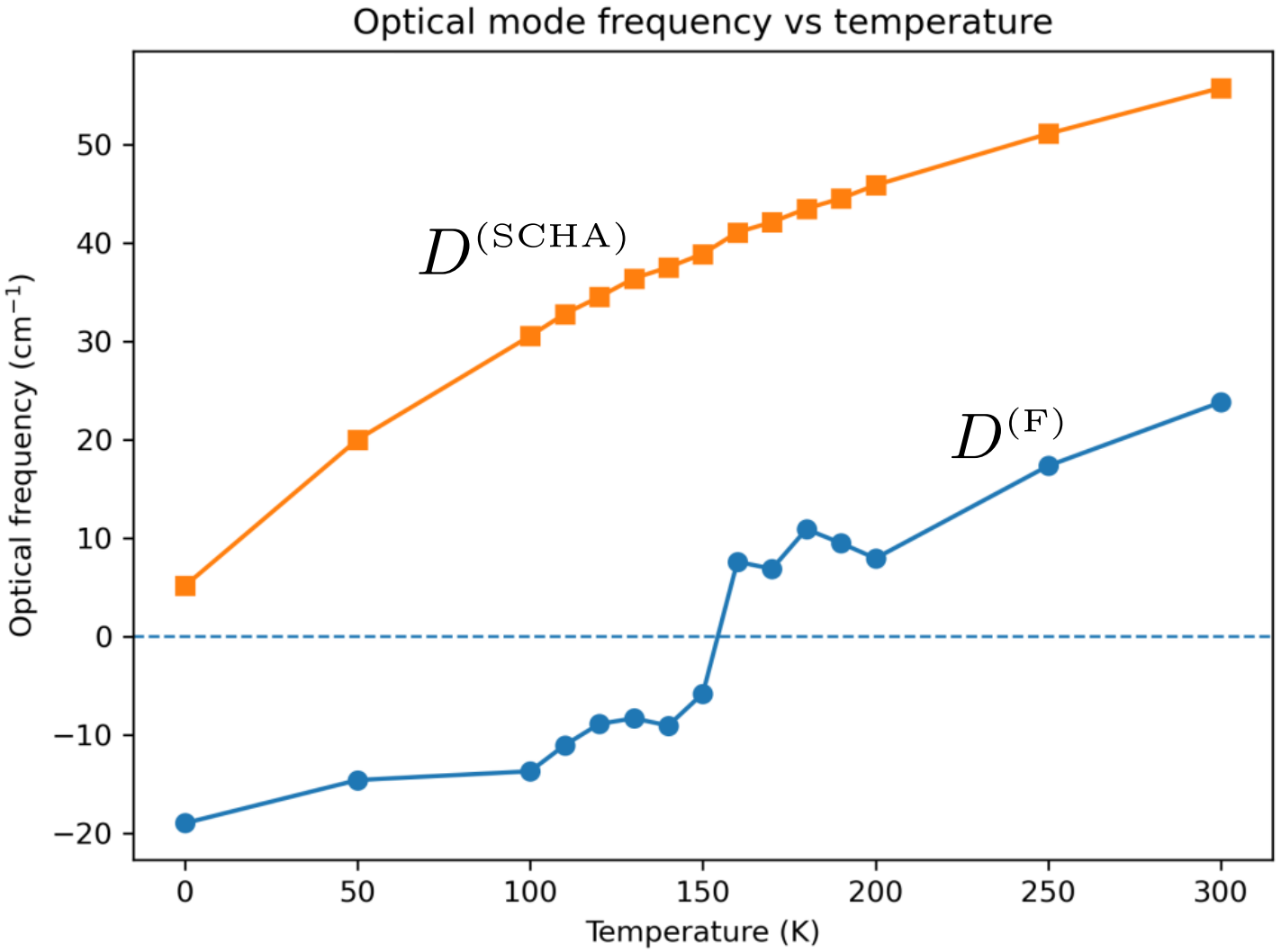
The ferroelectric transition in SnTe





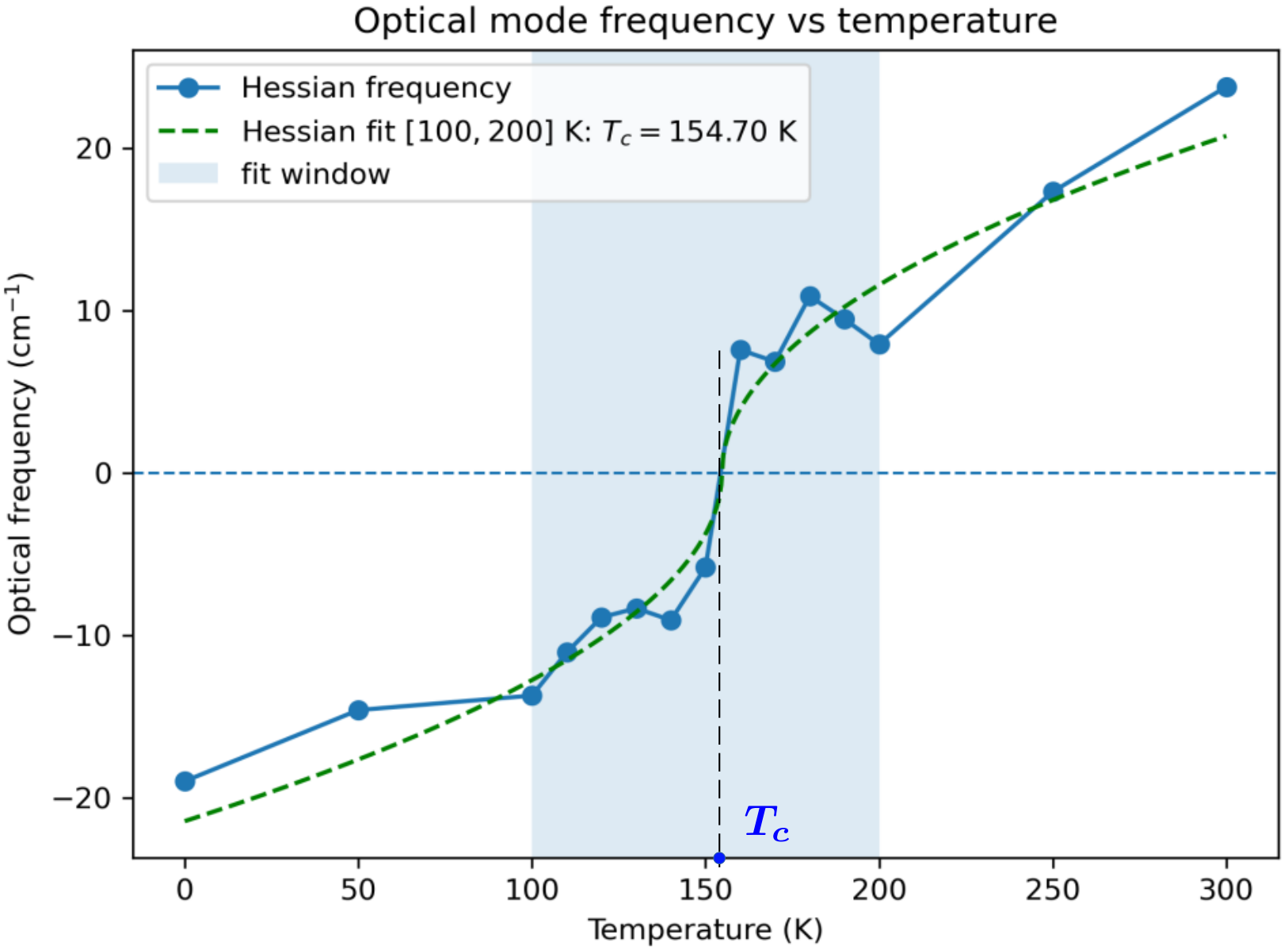
100 K ≤ T_c ≤ 200 K

The ferroelectric transition in SnTe



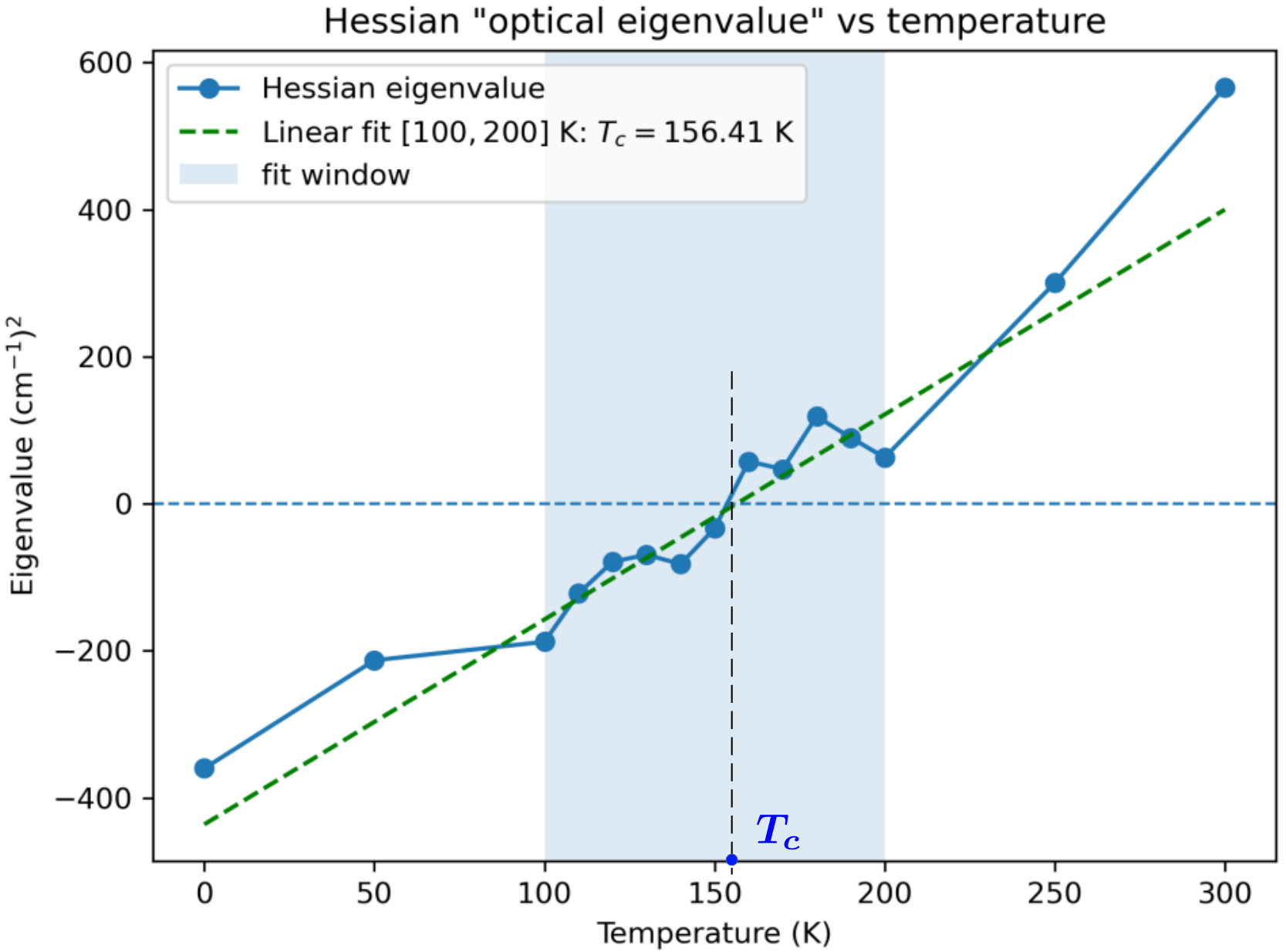
The ferroelectric transition in SnTe

Mean-field description of a 2nd order phase transition $\omega(T) \propto \sqrt{T - T_c}$



The ferroelectric transition in SnTe

Mean-field description of a 2nd order phase transition $\omega^2(T) \propto T - T_c$



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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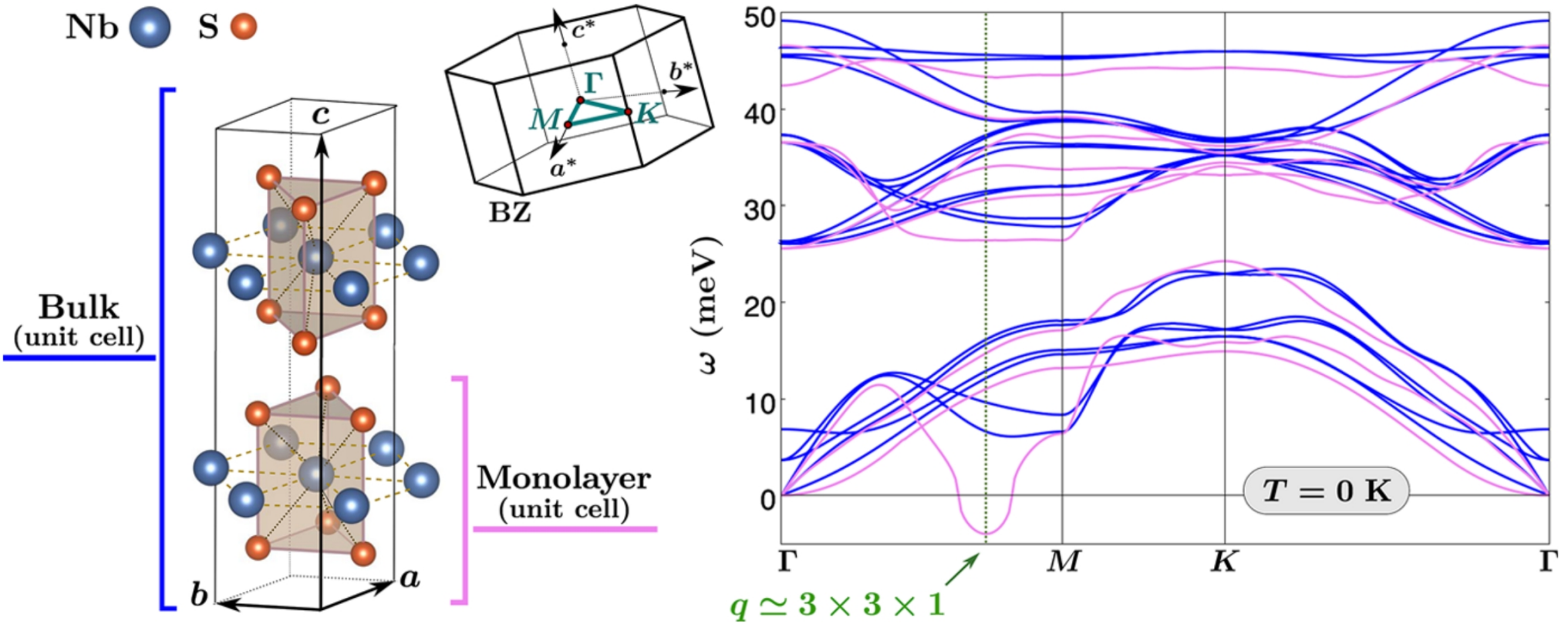
NbS_2

Phonon dispersion including quantum anharmonic effects



Bulk: **No CDW instability**

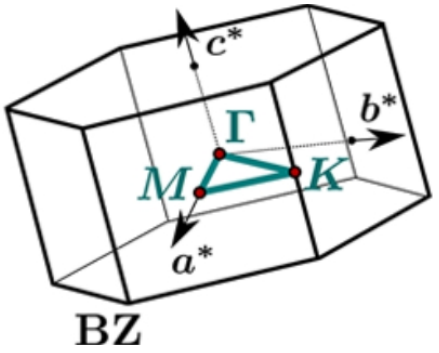
Suspended monolayer: **3x3 CDW distortion**

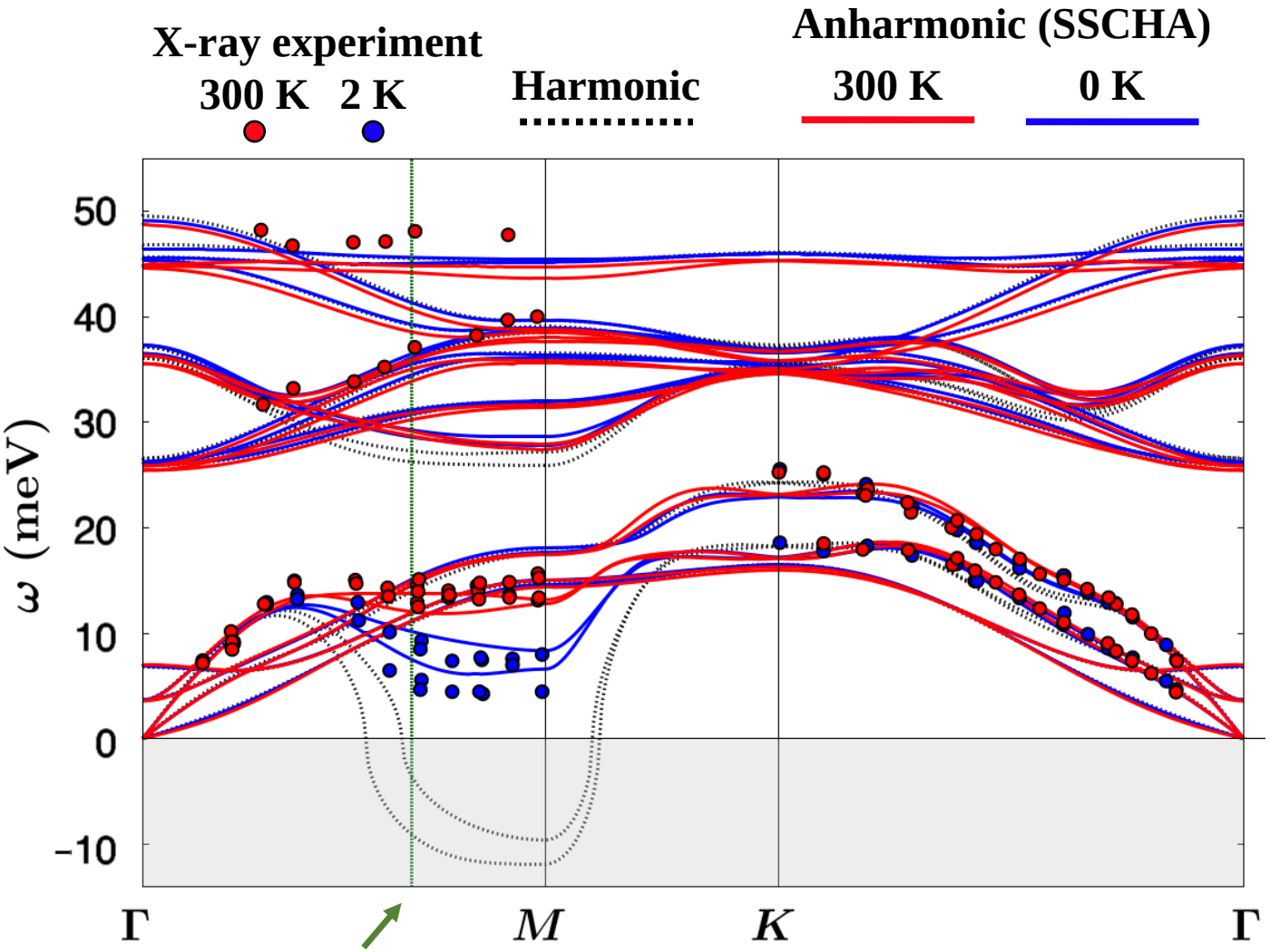
! **Quantum anharmonic effects are relevant...**

NbS_2: bulk

Harmonic dispersion:

- **No temperature dependence**
- **Wrong instability**

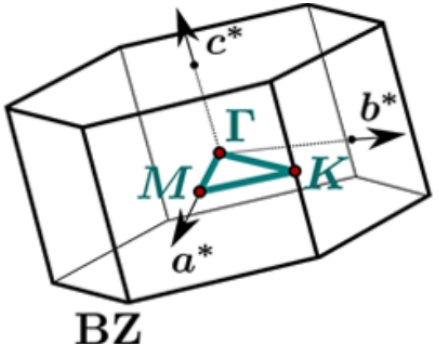


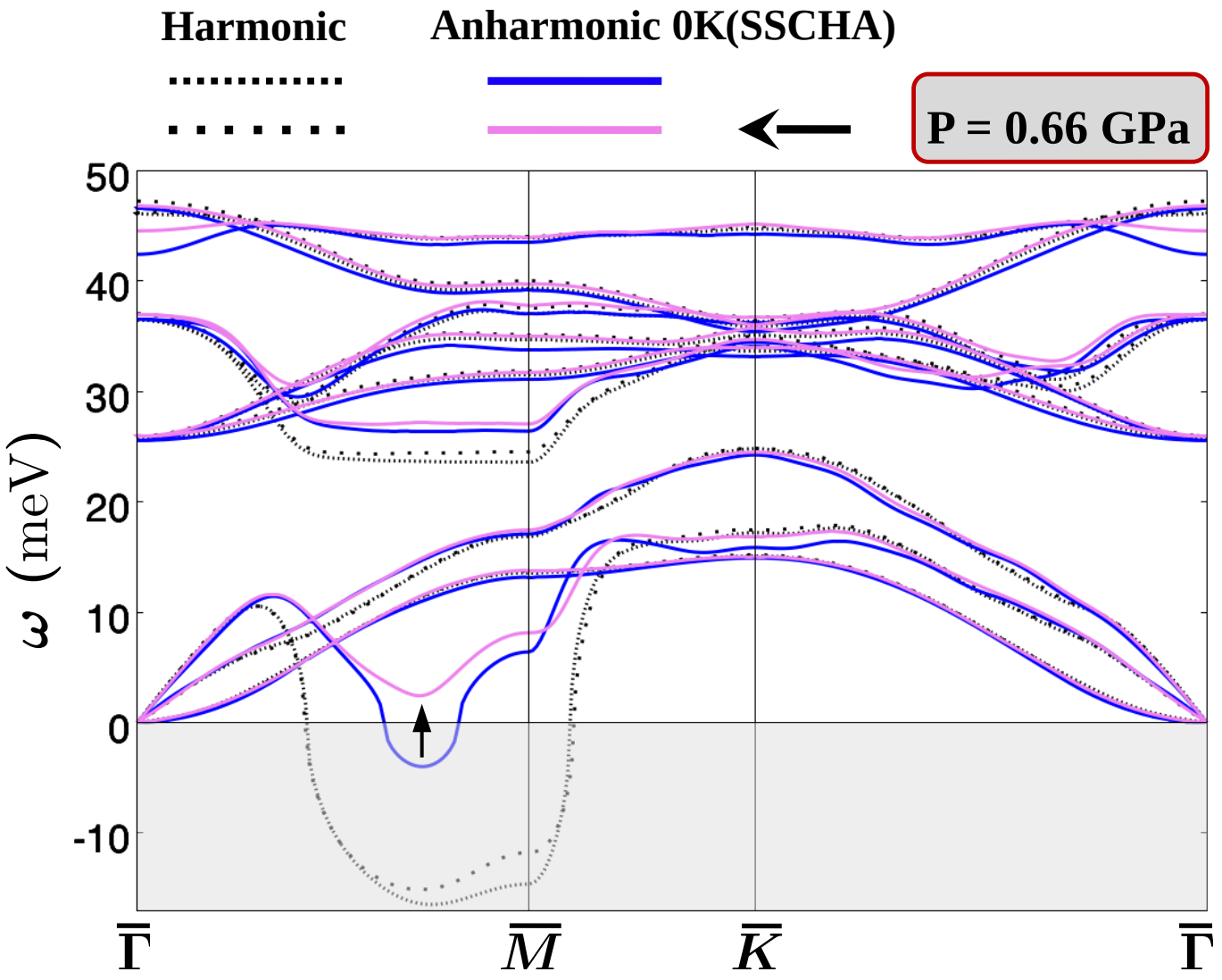


q ≃ 3x3x1

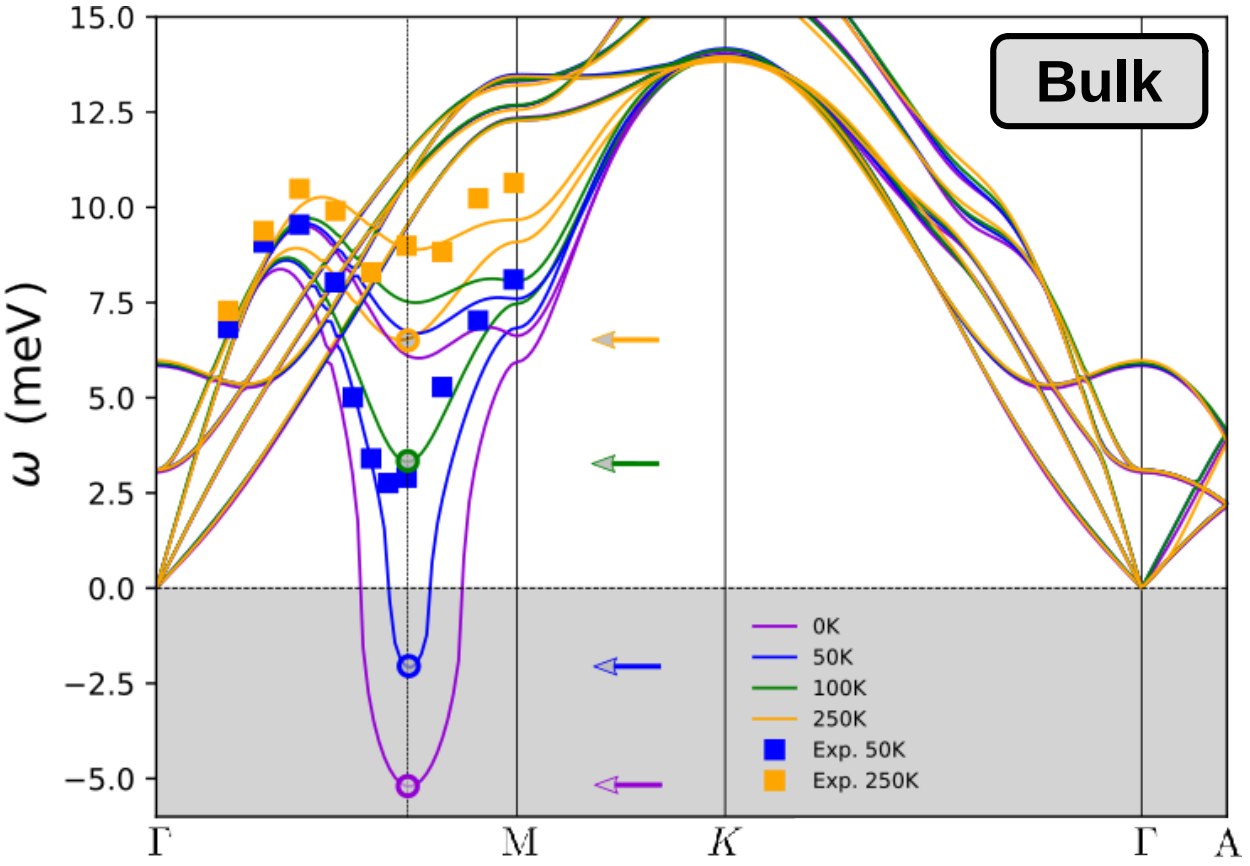
NbS_2: monolayer

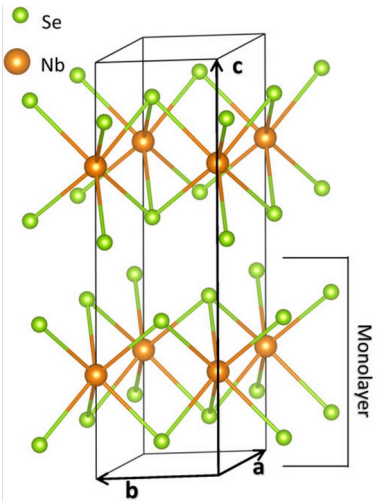
- **Structure compressed less than 0.5%**
  (still compatible with exp. Estimates) → **No CDW**
- **No effect at harmonic level**

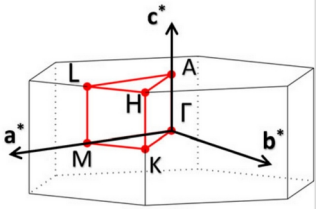




SCHA phonon dispersion as a function of *T*

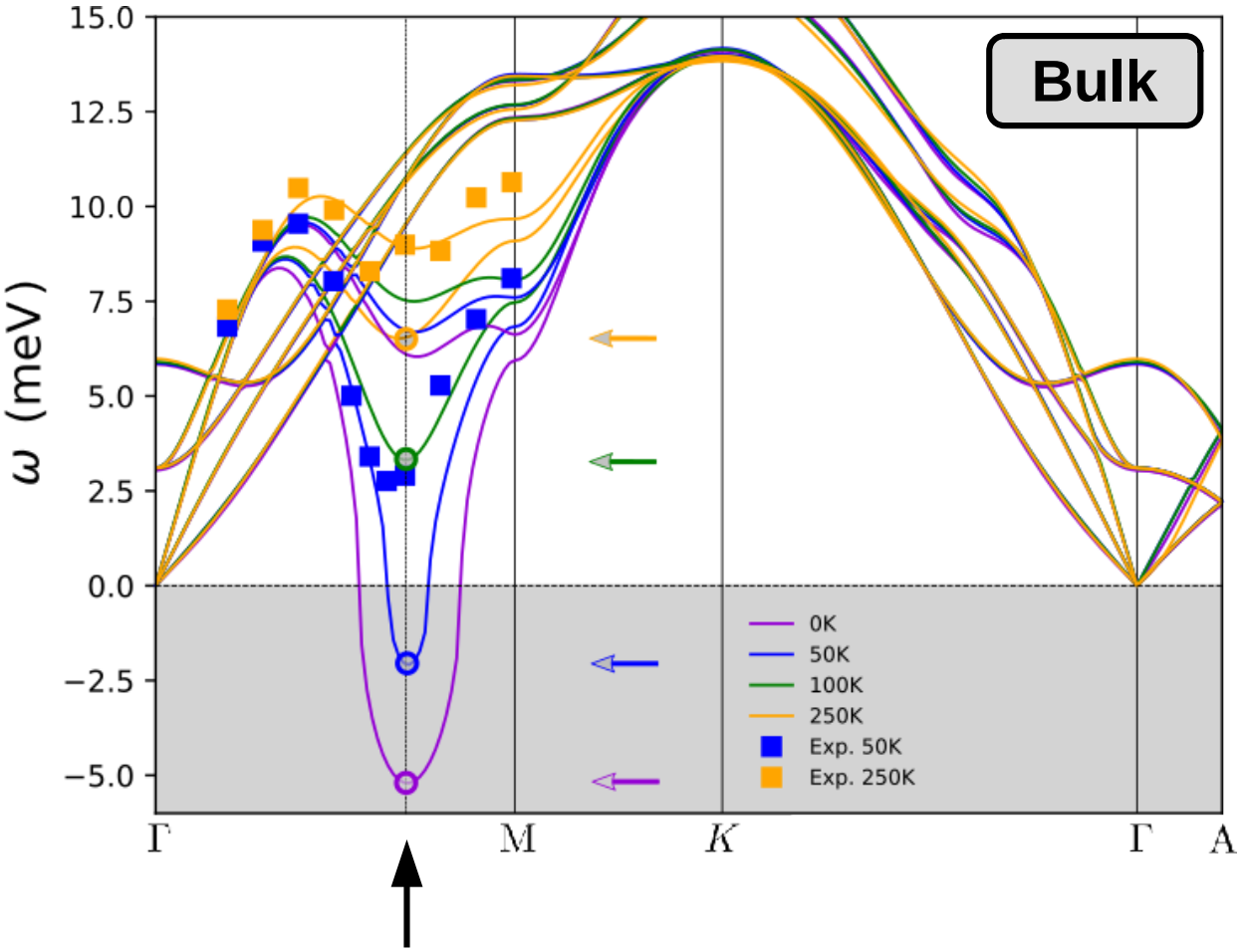


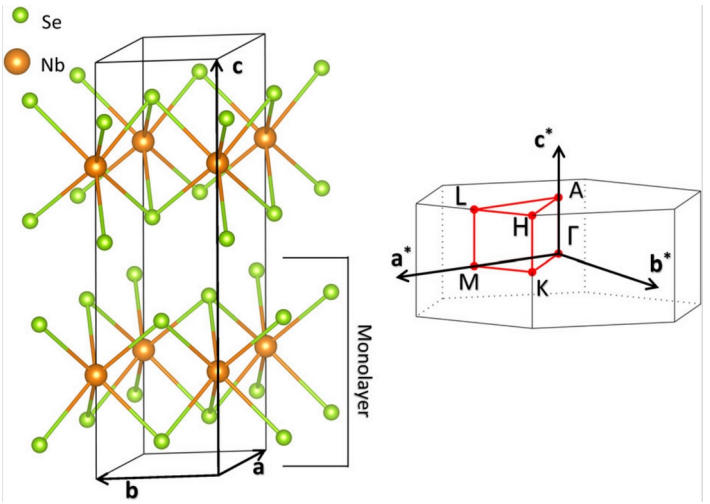




R. Bianco *et al.*, PRL 125, 106101 (2020)

SCHA phonon dispersion as a function of *T*





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

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

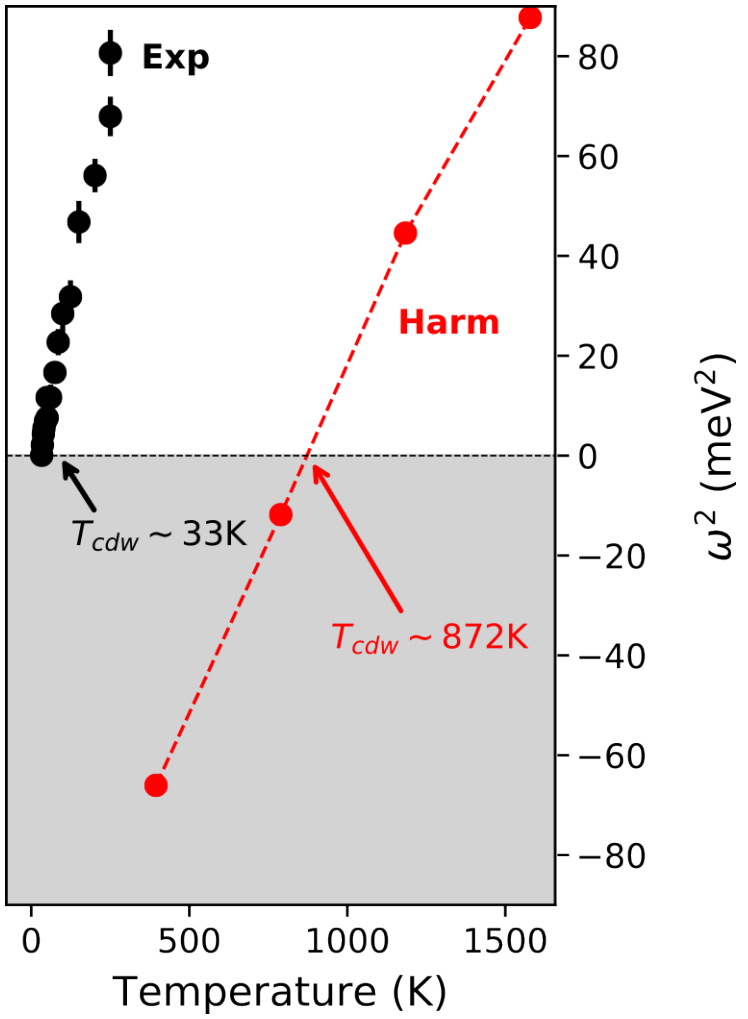
R. Bianco *et al.*, PRL 125, 106101 (2020)

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:

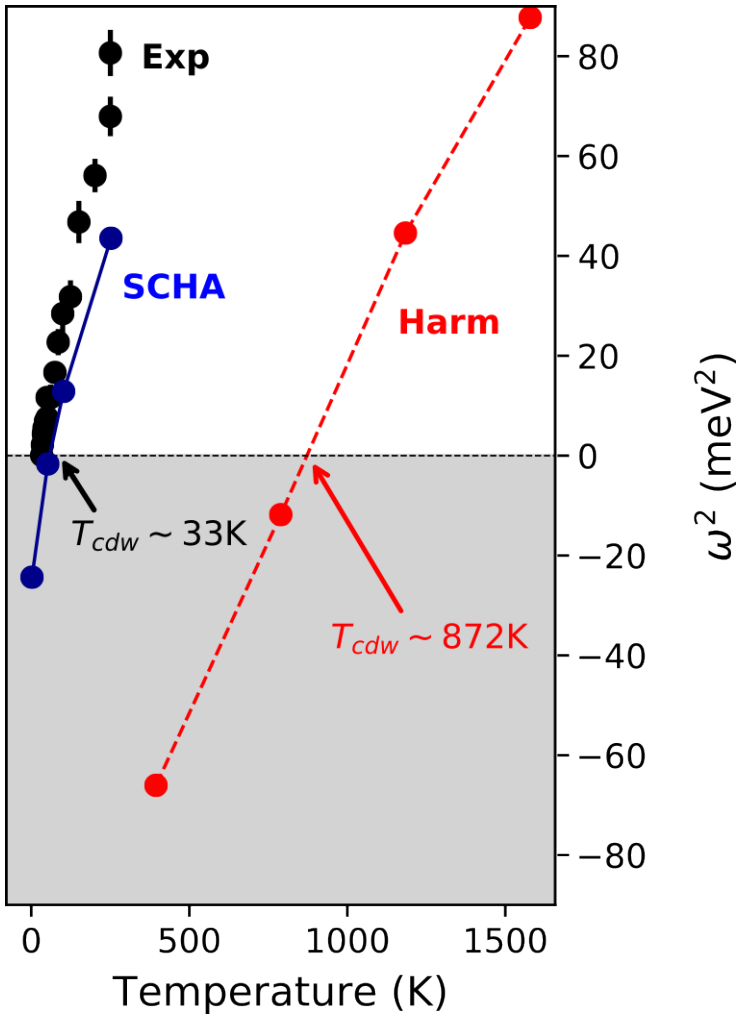
Electronic temperature only

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)

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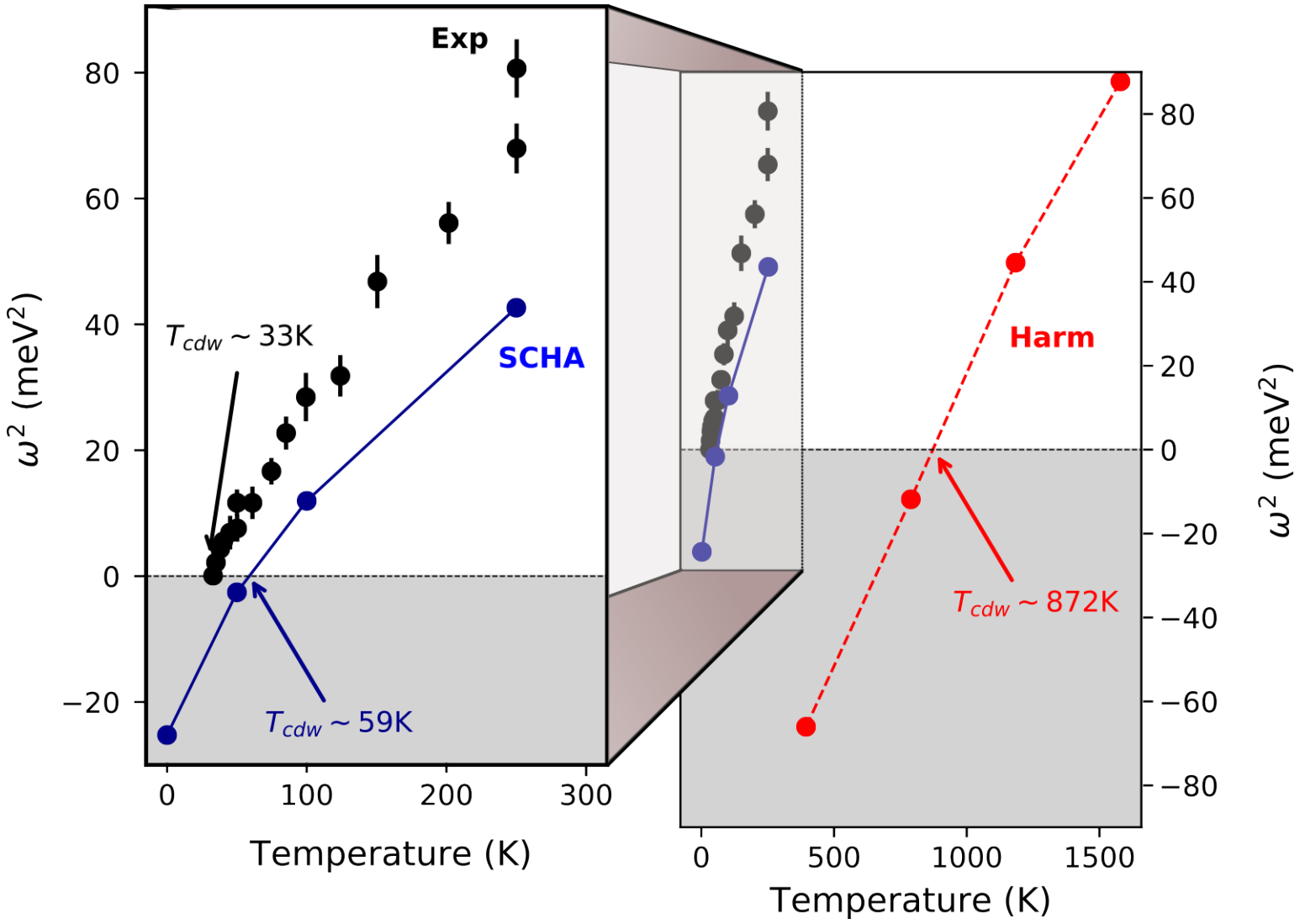
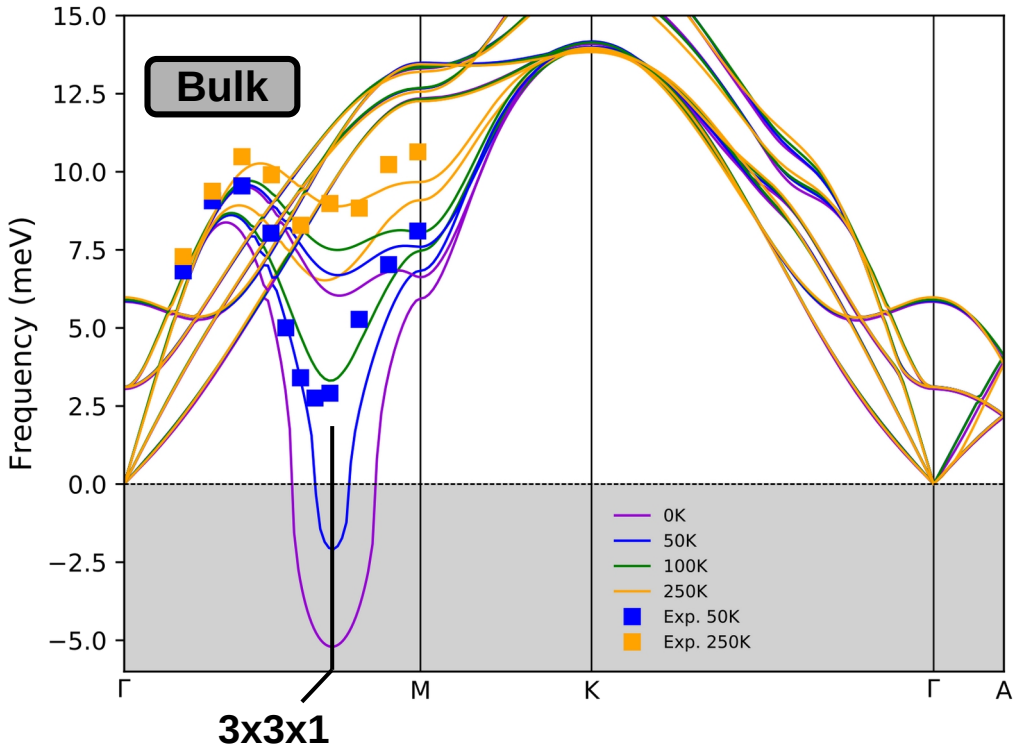
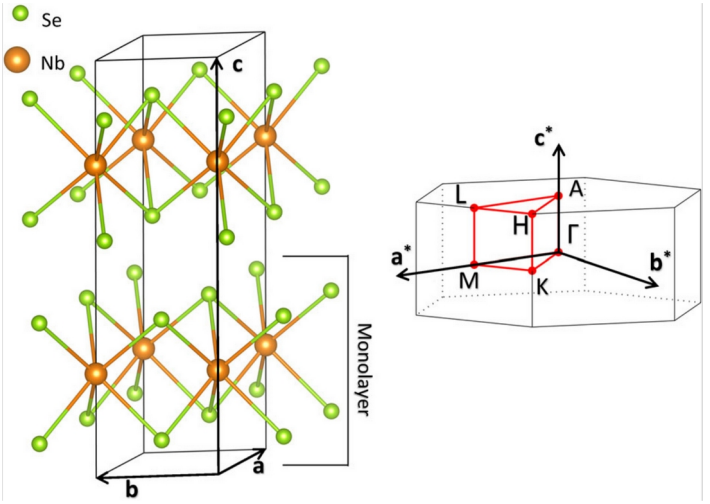
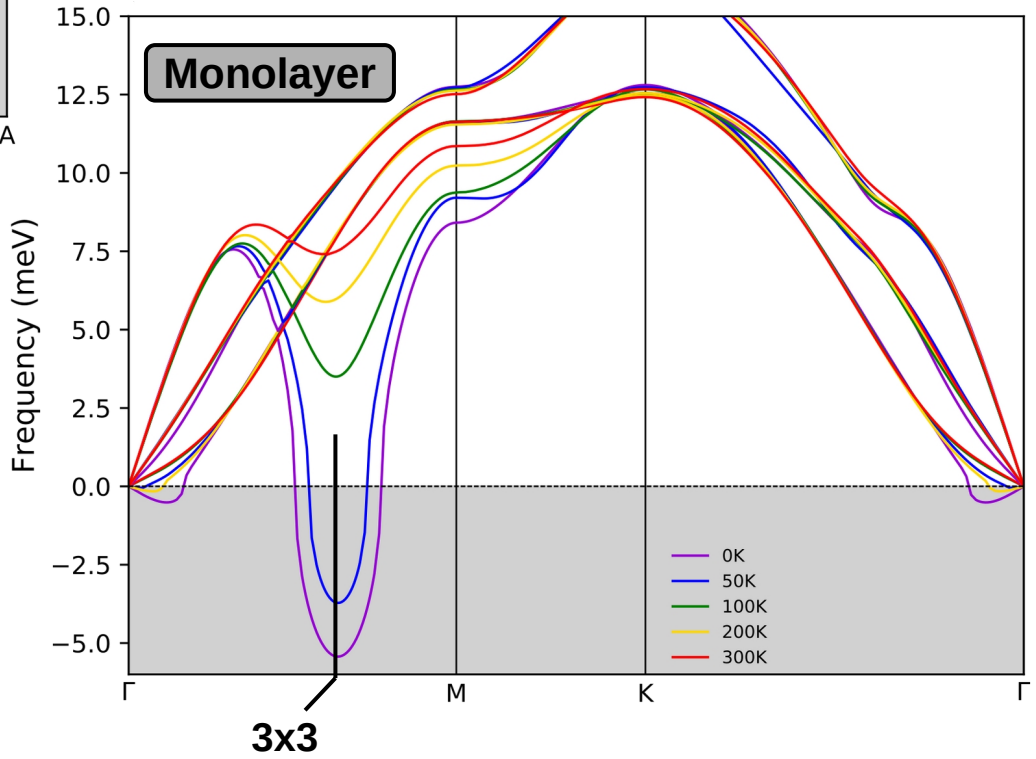


R. Bianco *et al.*, PRL 125, 106101 (2020)

SSCHA phonon dispersion as a function of *T*





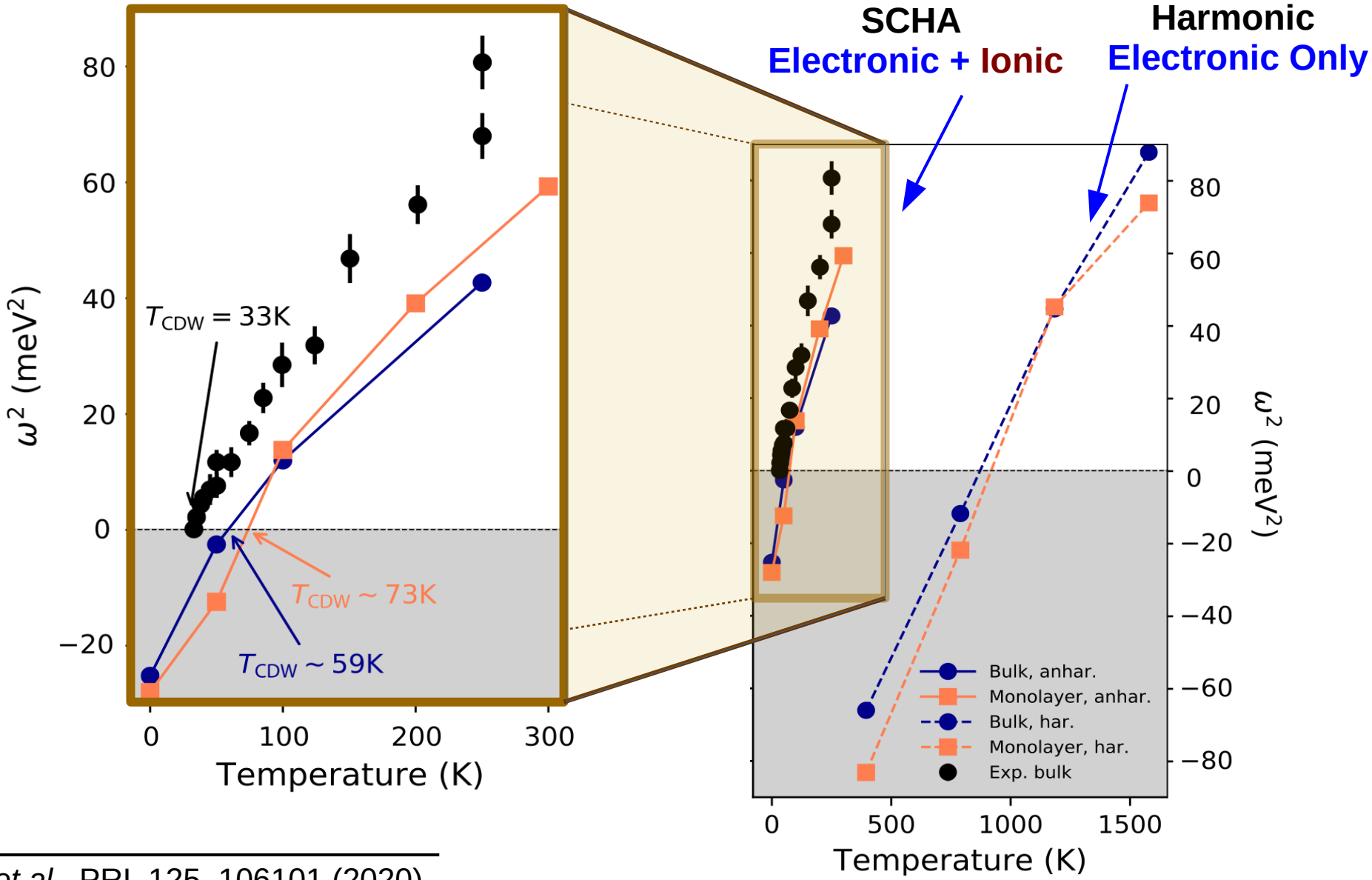


R. Bianco *et al.*, PRL 125, 106101 (2020)

$NbSe_2$: 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)

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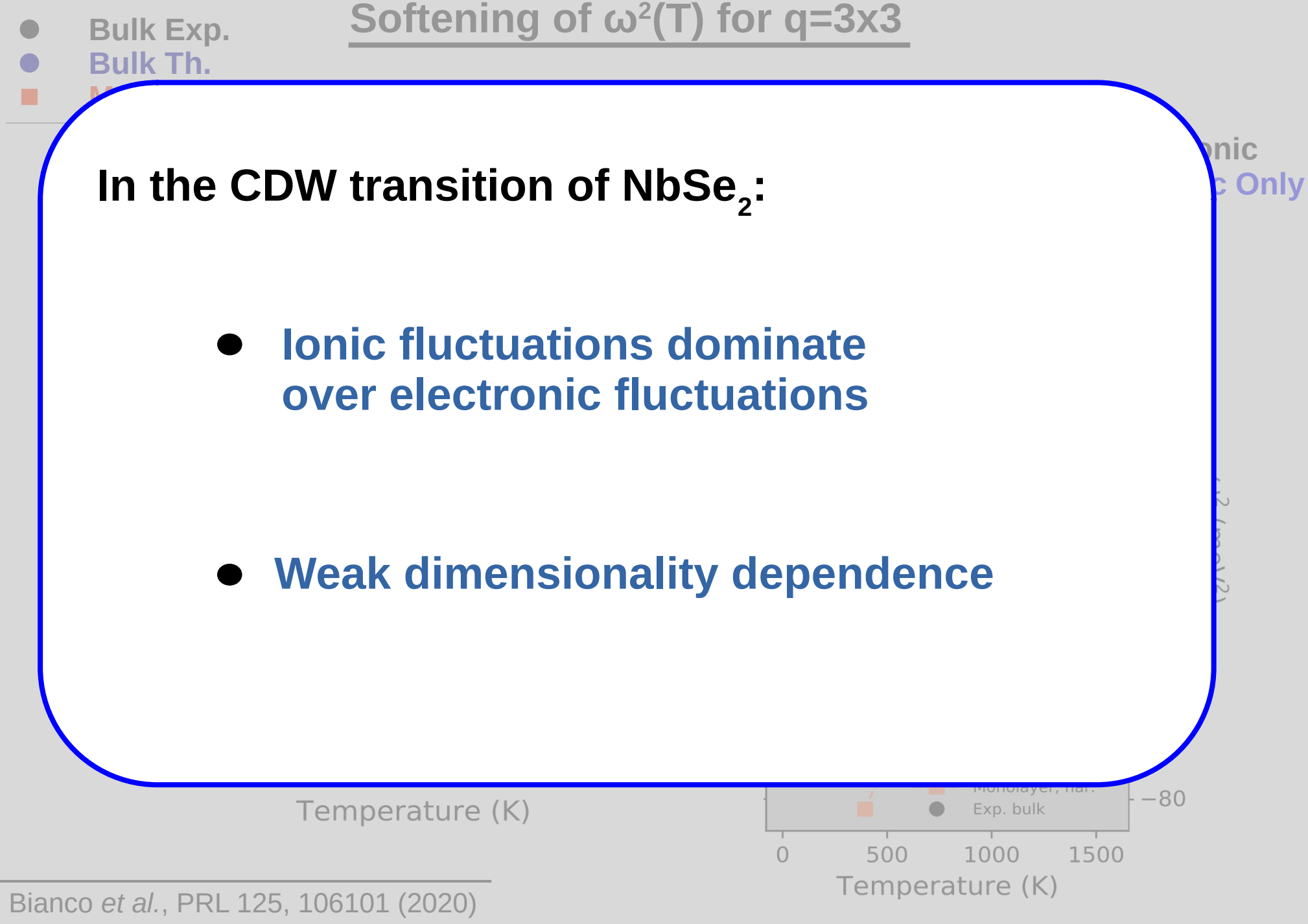
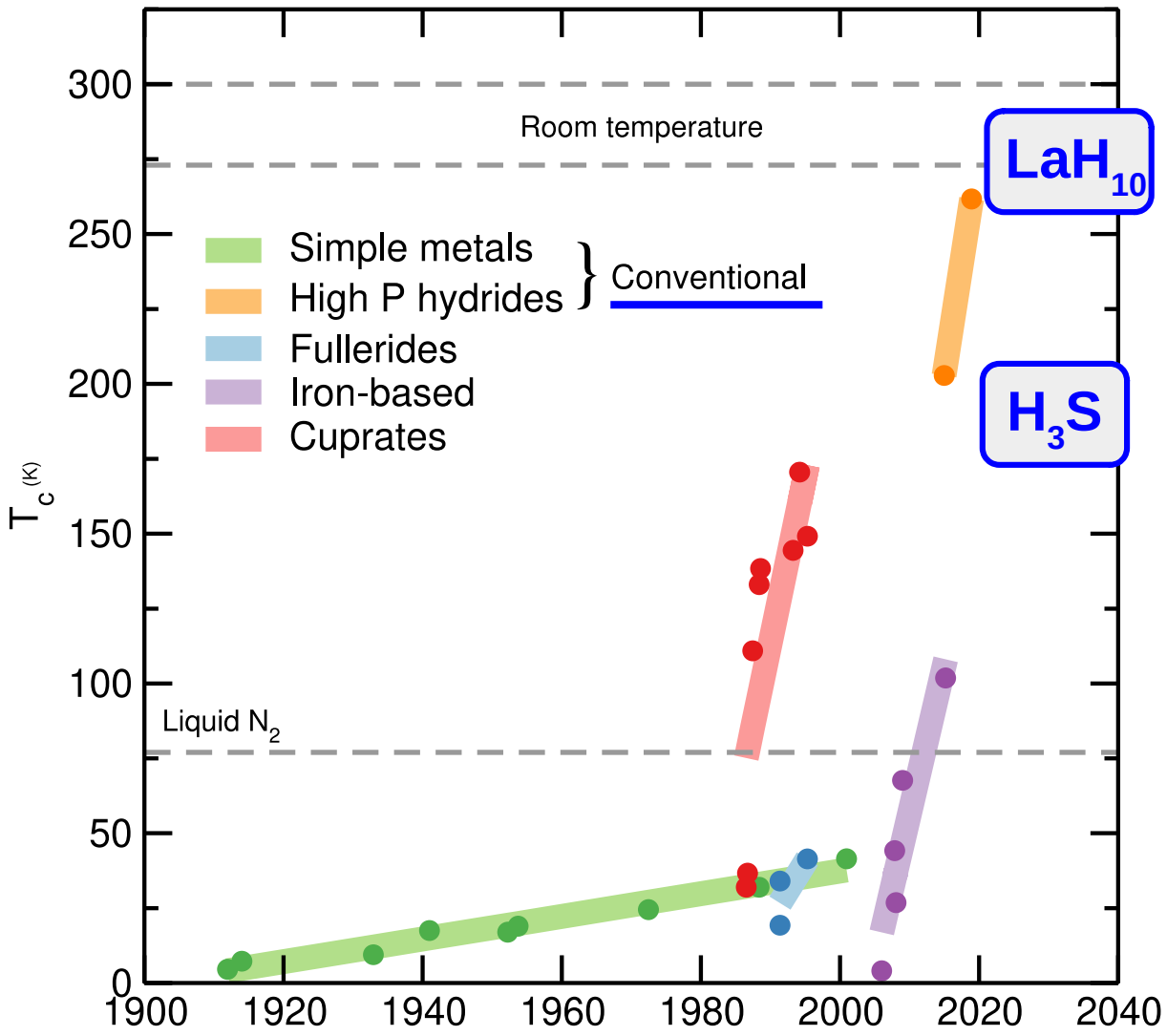


In the CDW transition of $NbSe_2$:

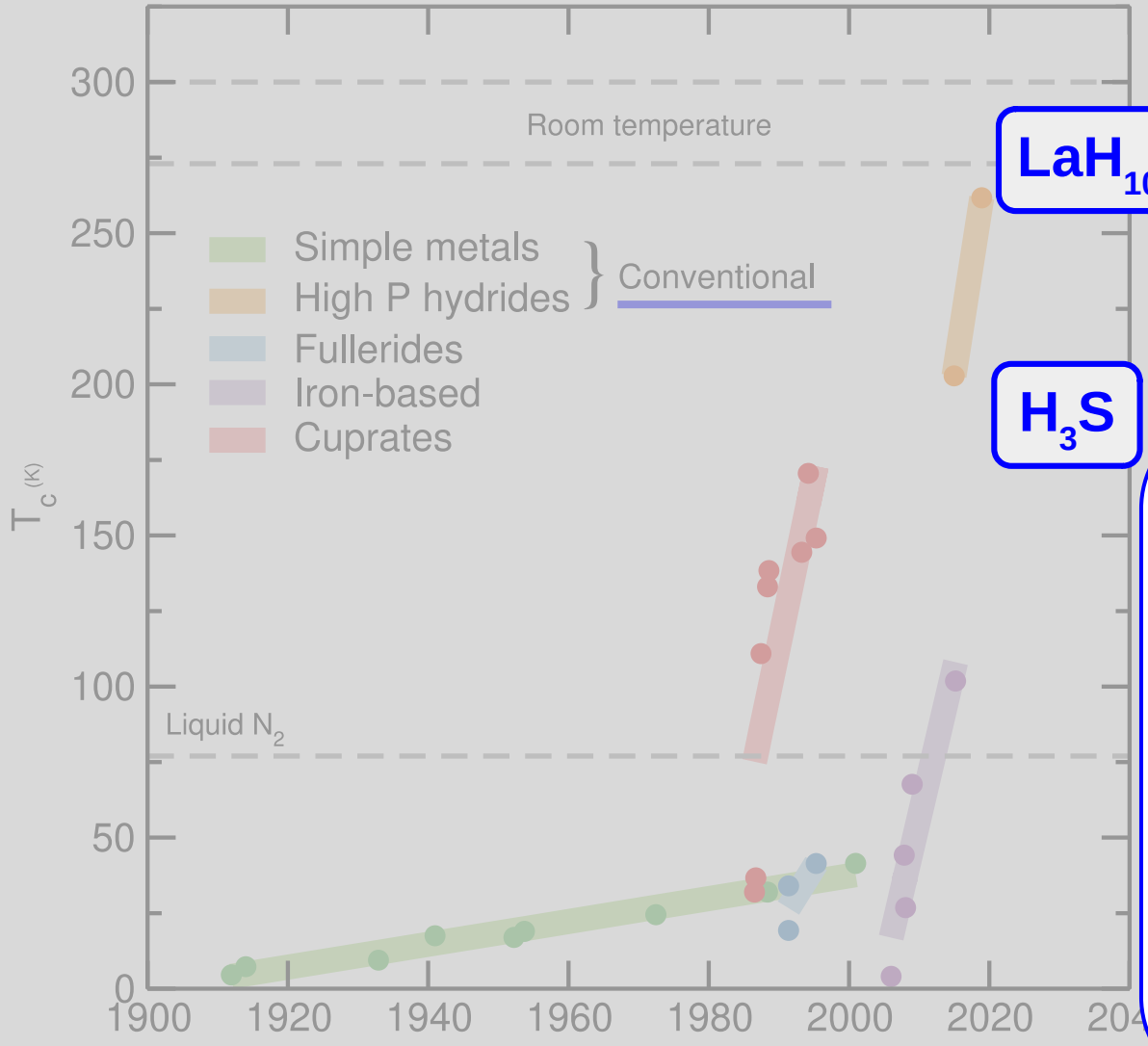
- **Ionic fluctuations dominate over electronic fluctuations**
- **Weak dimensionality dependence**

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

Superconductivity: the T_c history



Superconductivity: the T_c history

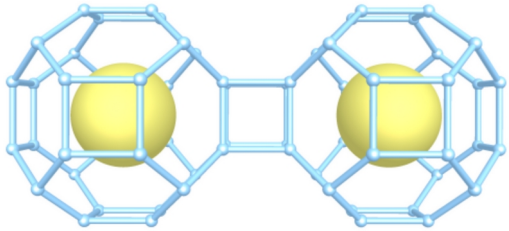


LaH_{10}

H_3S

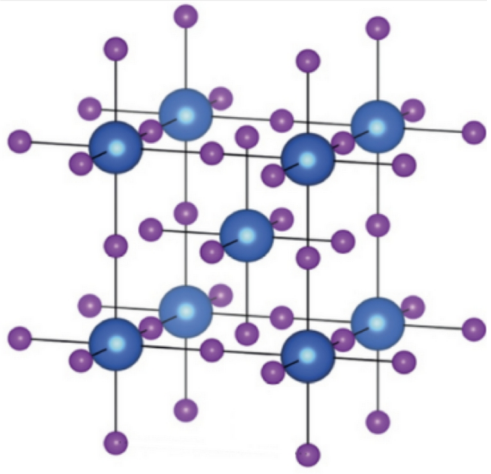
(P≃140 GPa) $Fm\bar{3}m$

LaH



(P≃150 GPa) $Im\bar{3}m$

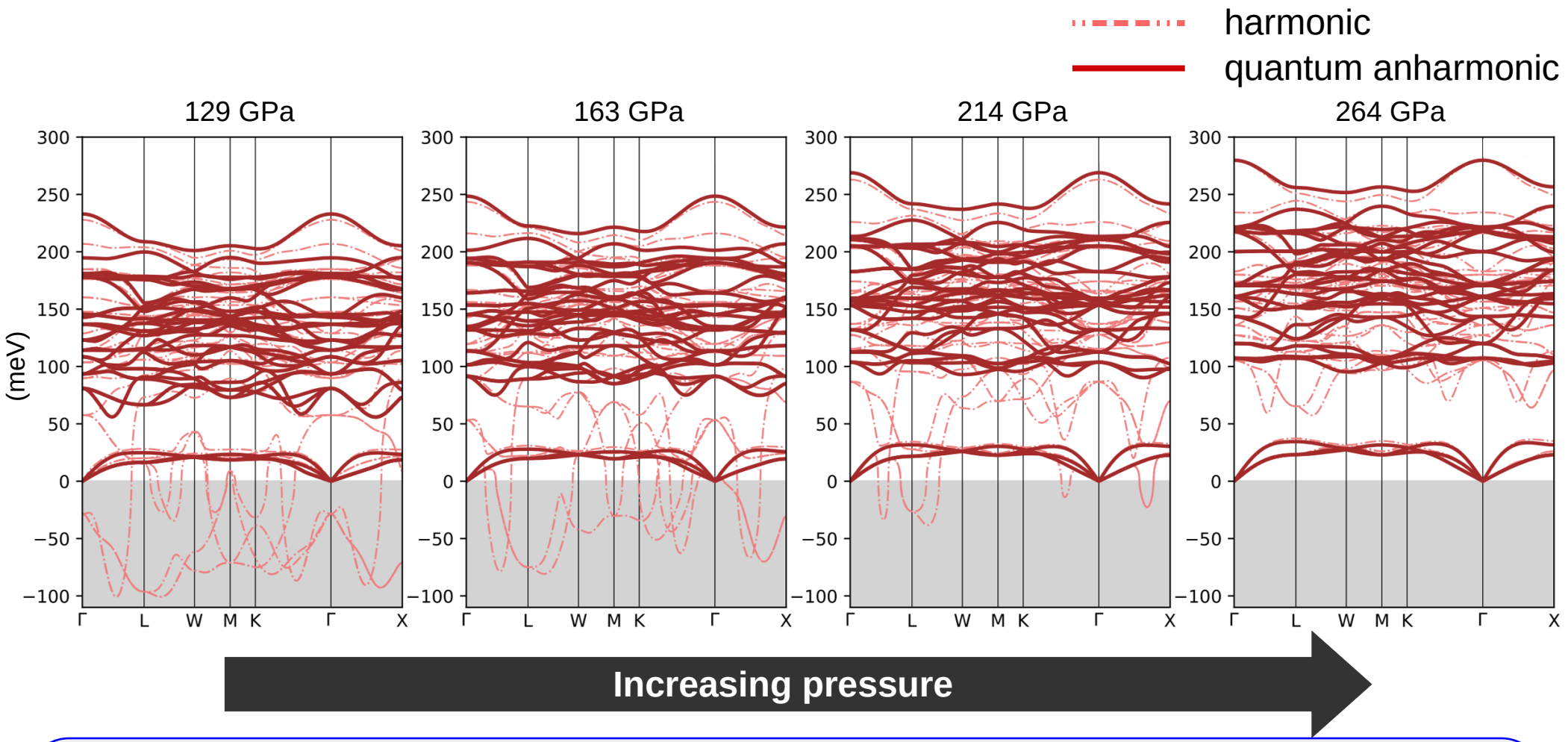
H_3S



!

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)

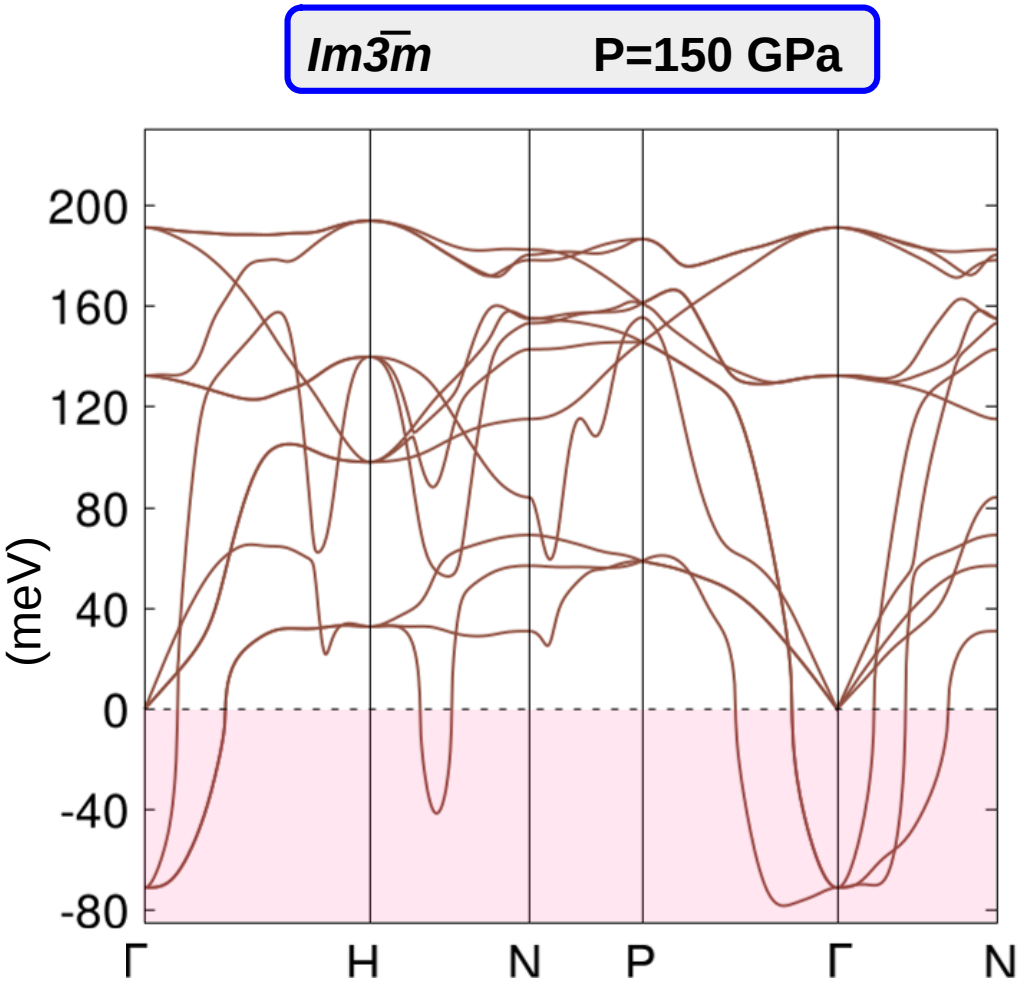
H_3S: the $Im\bar{3}m$ phase

Quantum anharmonic effects
neglected

⬇

High-symmetry phase
unstable

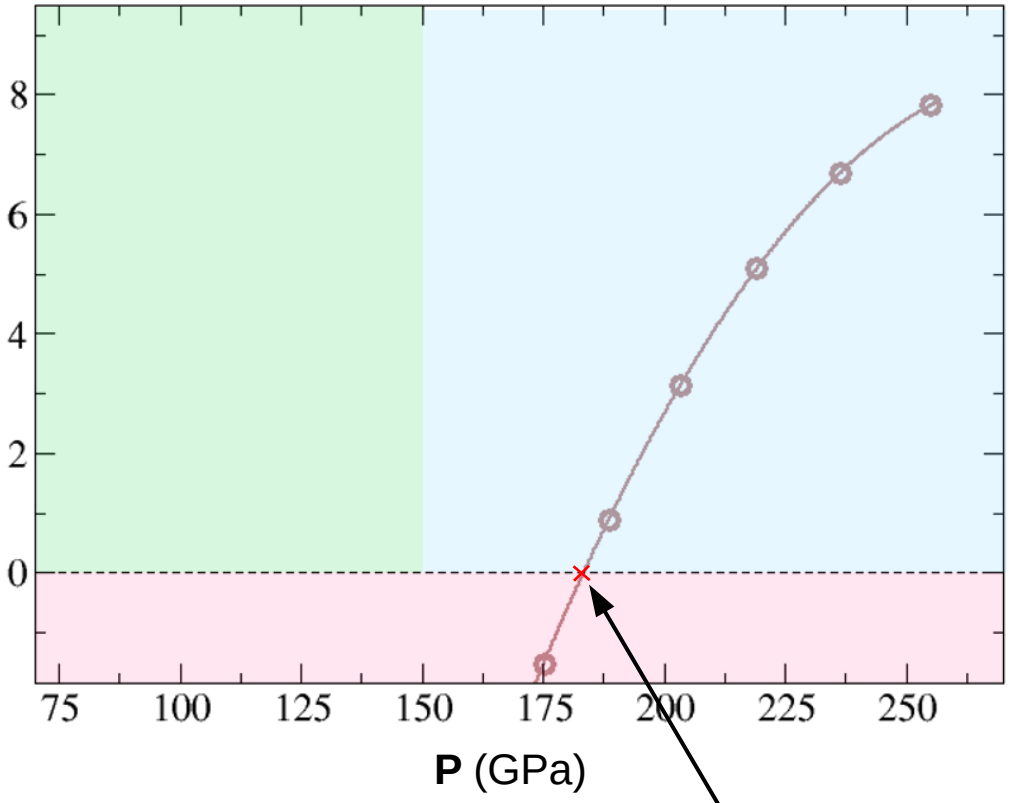
Harmonic phonons (classical)



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

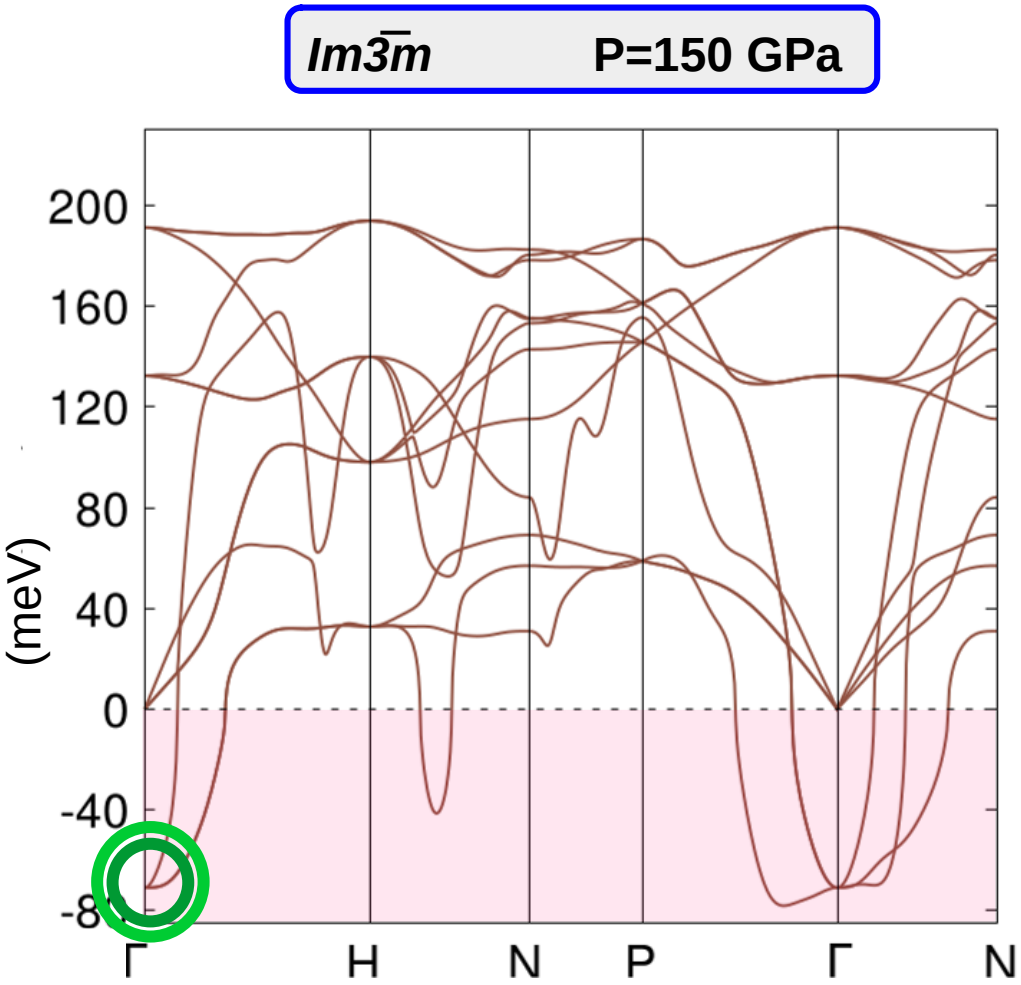
H_3S: the $Im\bar{3}m$ phase

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



P_c = 173 GPa

Harmonic phonons (classical)



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

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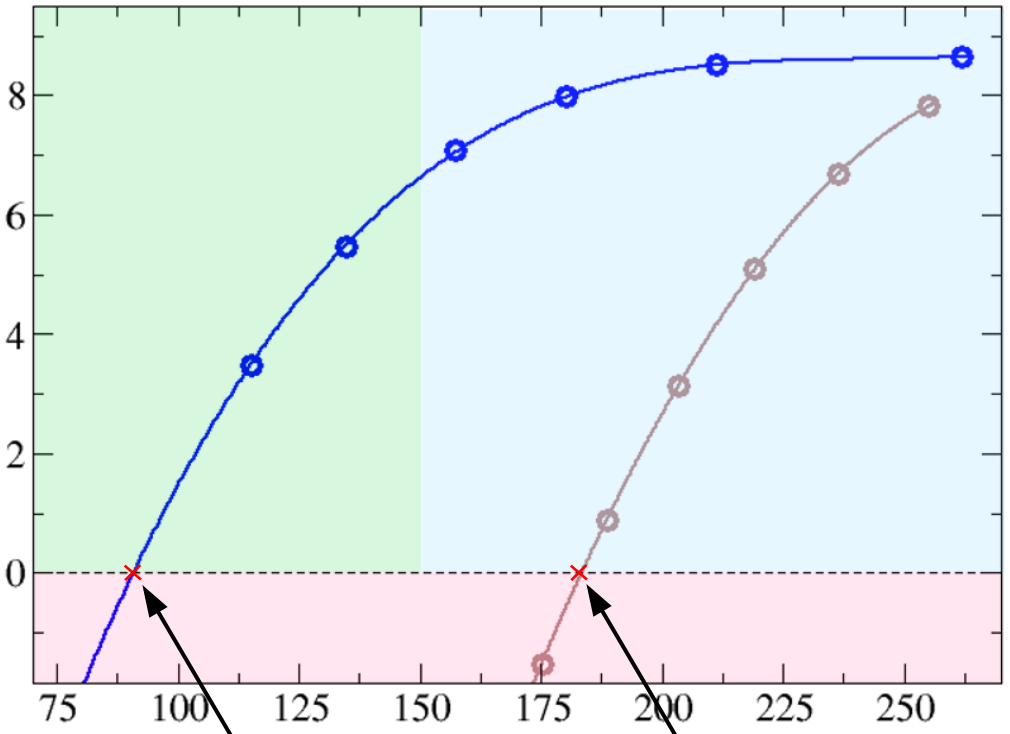
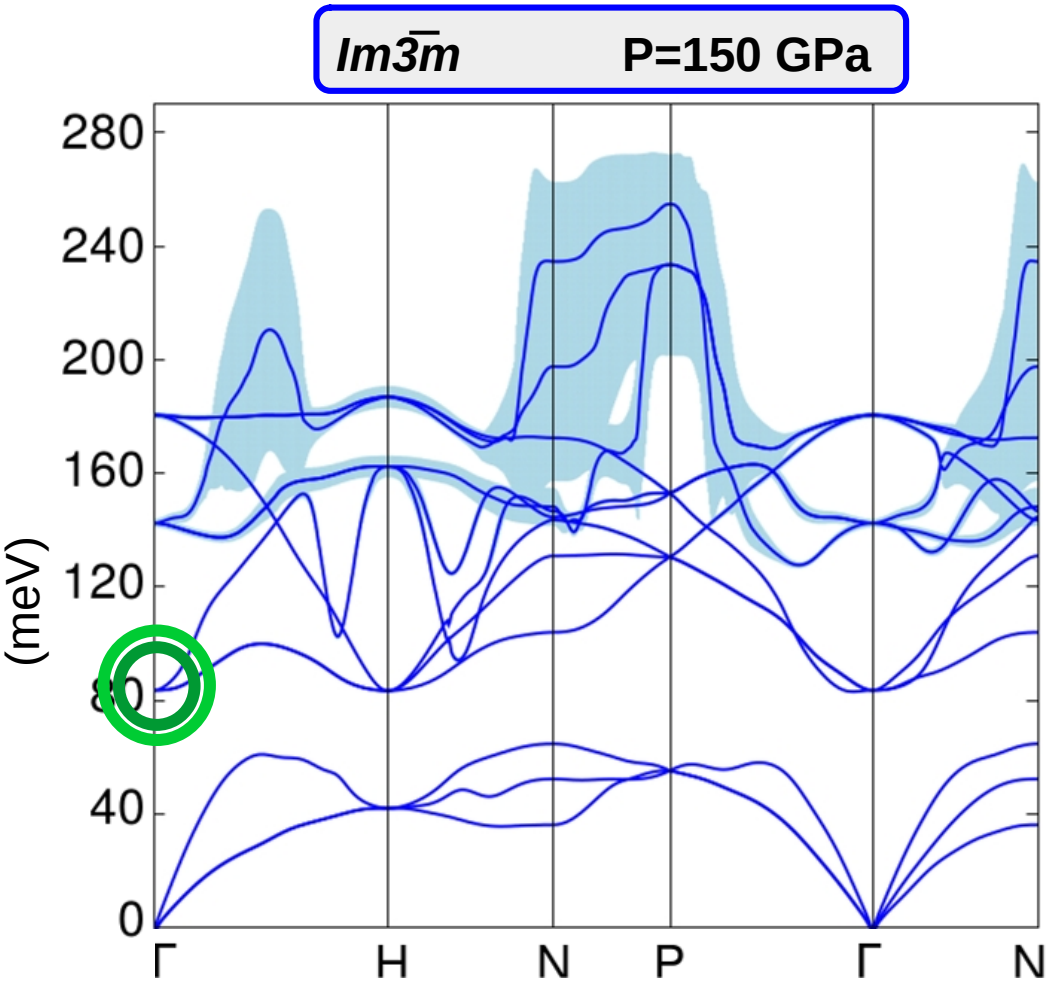


P_c = 91 GPa

P_c = 173 GPa

Harmonic phonons (classical)

Quantum anharmonic phonons



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

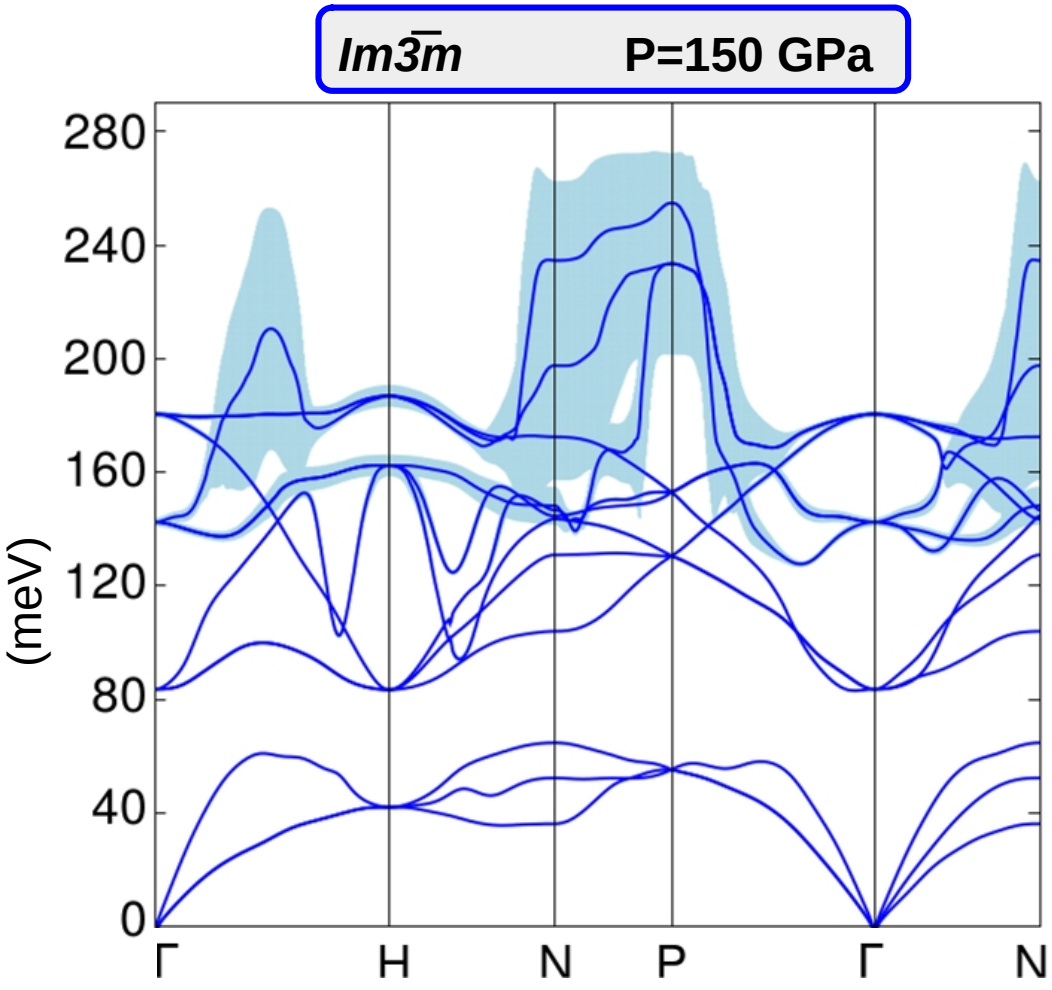
H_3S: the $Im\bar{3}m$ phase

Quantum anharmonic effects
included

⬇

High-symmetry phase
stable

Quantum anharmonic phonons



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

To summerize...

The SSCHA is a variational method
based on the thermodynamic free energy

The SSCHA can deal with strong anharmonicity
in the non-perturbative regime

The SSCHA can relax structures, both internal and cell parameters,
in the quantum and anharmonic energy landscape

The SSCHA gives a quantum & anharmonic generalization of
the harmonic dynamical matrix through the Free energy Hessian.
This allows to compute critical parameters of
displacive second order phase transitions

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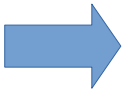
… are we done?

Need for a dynamic theory

Generalized dynamical matrix

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



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

Need for a dynamic theory

Generalized dynamical matrix

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

!

“Static” phonon theory

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

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

!

"Static" phonon theory

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The spectrum of $D^{(\mathrm{F})}$ describes vibrational excitations with infinite lifetime

A dynamic theory needs to be introduced….