first-principles description of second-order phase transitions & temperature-dependent anharmonic phonons

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outline

-second-order phase transitions and phonon softening

-free-energy with self-consistent harmonic approximation (SCHA)

-curvature of free-energy and its stochastic evaluation suitable for first-principles calculations

-applications to CDW in bulk and monolayer NbS_2 and $NbSe_2$

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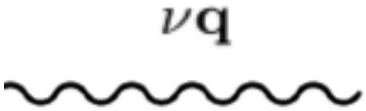
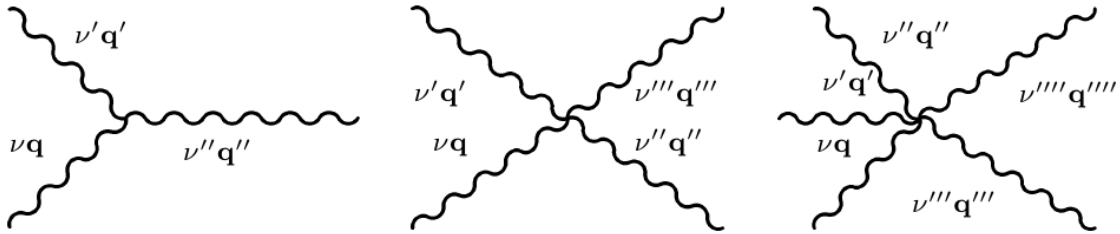
harmonic approximation



Potential is truncated at second order
phonons well-defined quasiparticles with infinite lifetime

weak anharmonicity

Higher order terms of the potential are considered, phonons interact *in a perturbative manner*:



strong anharmonicity beyond the perturbative approach

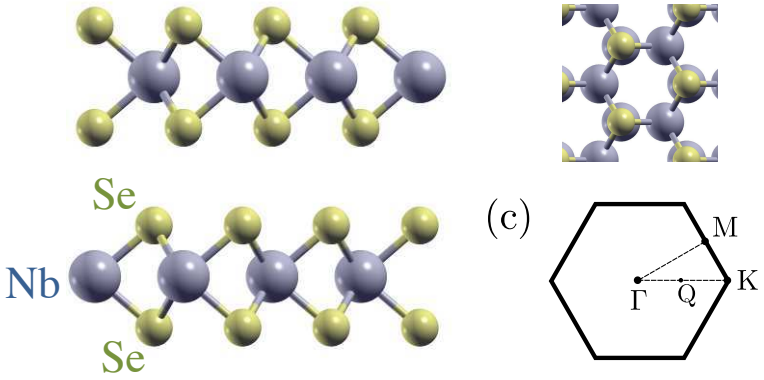
for large fluctuations from equilibrium at **high temperature** or with **zero-point quantum motion** (e.g. with H)

close to a dynamical instability, e.g. near a second-order phase transition like a **ferroelectric** of a **charge density wave** (CDW) transition

softening of a phonon modes at the CDW transition:

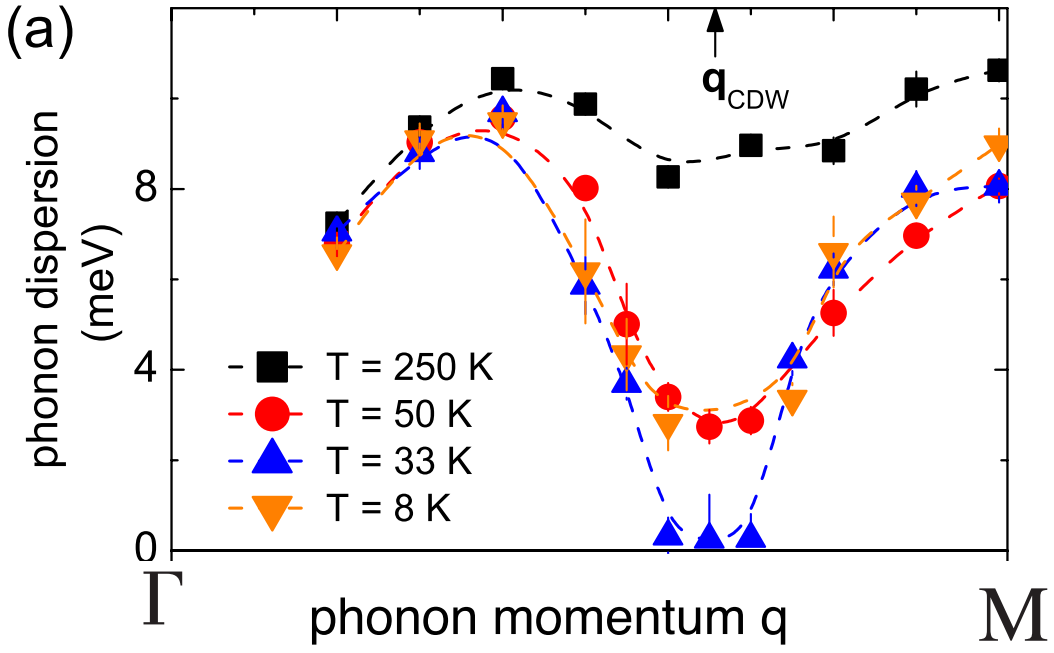
2H-$NbSe_2$ Inelastic X-Ray scattering (IXS)

[Weber *et al.* PRL 107, 107403 (2011)]

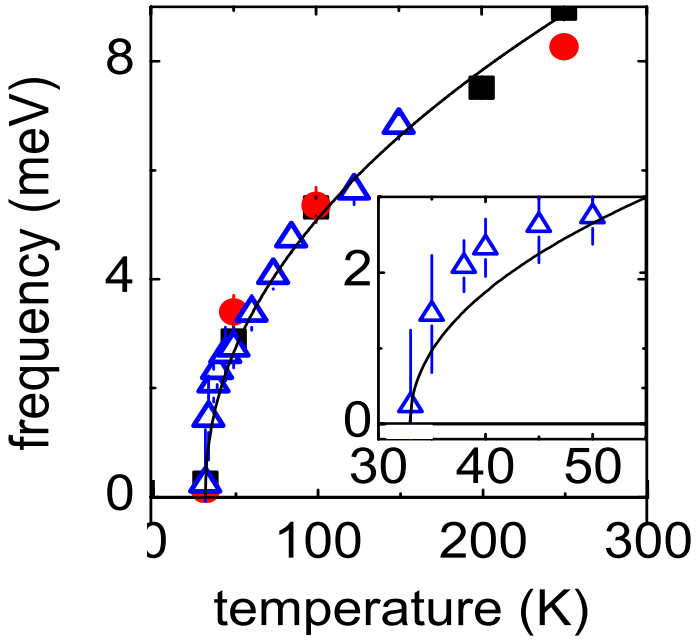


CDW transition temperature, $T_c \sim 33$ K

for $T<T_c$ a superstructure appears with periodicity close to a (3x3x1) reconstruction



frequency at q_{CDW}



our goal: description of phonons in strong anharmonic regimes using a first principles approach

Self Consistent Harmonic Approximation (SCHA)

[D. J. Hooton, Philos. Mag. 46, 522 (1955)]

- even in the strong non-perturbative regime (e.g. CDW, ferroelectrics) phonons still exist and can be measured!

- Same philosophy of the Hatree-Fock approximation, *effective non-interacting electrons* that minimizes the total-energy *with the exact e-e interaction*

- *Effective harmonic (non-interacting) phonons* that minimize the Free-energy with the *exact (anharmonic to all orders) potential*

free energy functional: variational principle

$$F_H = U - TS = \min_{\rho,\mathrm{tr}[\rho]=1} \left\{ \mathrm{tr}\left[H\rho\right] + k_\mathrm{B} T \mathrm{tr}\left[\rho \ln(\rho)\right] \right\}$$

ρ = ionic (n-body) density matrix $\qquad H = \frac{1}{2m} P^2 + V(\mathbf{R})$

free energy functional: variational principle

$$F_H = U - TS = \min_{\rho,\mathrm{tr}[\rho]=1} \left\{ \mathrm{tr}\left[H\rho\right] + k_\mathrm{B}T\,\mathrm{tr}\left[\rho\ln(\rho)\right] \right\}$$

ρ = ionic (n-body) density matrix $\qquad H = \frac{1}{2m}P^2 + V(\mathbf{R})$

At the minimum the density matrix is:

$$\rho = \exp\left(-\frac{H}{k_\mathrm{B}T}\right)Z^{-1} \qquad Z = \mathrm{tr}\left[\exp\left(-\frac{H}{k_\mathrm{B}T}\right)\right]$$

free energy functional: variational principle

$$F_H = U - TS = \min_{\rho,\mathrm{tr}[\rho]=1} \left\{ \mathrm{tr}\left[H\rho\right] + k_\mathrm{B}T\mathrm{tr}\left[\rho\ln(\rho)\right] \right\}$$

We define a functional of a trial Hamiltonian $\tilde{H}$

$$\tilde{F}_H[\tilde{H}] = \left\{ \mathrm{tr}\left[H\tilde{\rho}\right] + k_\mathrm{B}T\mathrm{tr}\left[\tilde{\rho}\ln(\tilde{\rho})\right] \right\} \quad \tilde{\rho} = \exp\left(-\frac{\tilde{H}}{k_\mathrm{B}T}\right)\tilde{Z}^{-1}$$

variational principle (Gibbs-Bogolugov inequality)

$$\tilde{F}_H[\tilde{H}] \geq F_H$$

where the equality holds for $H = \tilde{H}$

Self Consistent Harmonic Approximation

$$\tilde{F}_H[\tilde{H}] = \left\{ \mathrm{tr}\left[H\tilde{\rho} \right] + k_B T \mathrm{tr}\left[\tilde{\rho} \ln(\tilde{\rho}) \right] \right\} \qquad \tilde{\rho} = \exp\left(-\frac{\tilde{H}}{k_B T} \right) \tilde{Z}^{-1}$$

the SCHA uses a generic trial Harmonic Hamiltonian:

$$\tilde{H} = \frac{1}{2m} P^2 + \frac{1}{2} (\mathbf{R} - \mathbf{R}_c) \vec{\mathbf{D}} (\mathbf{R} - \mathbf{R}_c)$$

the free energy functional is minimized with respect to the parameters $(\mathbf{R}_c; \vec{\mathbf{D}})$

at the minimum:

$(\mathbf{R}_c; \vec{\mathbf{D}})$ is the **best** self-consistent harmonic potential

$\tilde{F}_H[\tilde{H}]$ is the SCHA Free energy

Self Consistent Harmonic Approximation

SCHA applied so far to crystals of noble gasses: ion-ion total energy and forces can be obtained by fast empirical potentials

Ab-initio (from DFT or quantum Monte-Carlo) total energy and forces are computational much more demanding

We implemented the Self Consistent Harmonic Approximation, with a **stochastic** scheme that **minimizes number of calls to the ab-initio total-energy-and-forces engine:**

Errea, Calandra, Mauri, PRL 111, 177002 (2013), PRB 89, 064302 (2014), Monacelli, Errea, Calandra, Mauri PRB 98, 024106 (2018)

meaning of the auxiliary harmonic Hamiltonian:

$$\tilde{H} = \frac{1}{2m} P^2 + \frac{1}{2} (\mathbf{R} - \mathbf{R}_c) \overleftrightarrow{\mathbf{D}} (\mathbf{R} - \mathbf{R}_c)$$

direct access to phonon instabilities (phase transitions)?

SCHA probability distribution

observable that depends just on positions

$$\tilde{H} = \frac{1}{2m} P^2 + \frac{1}{2}(\mathbf{R} - \mathbf{R}_c)\overleftrightarrow{\mathbf{D}}(\mathbf{R} - \mathbf{R}_c)$$

$$\langle O(\mathbf{R}) \rangle_{(\mathbf{R}_c; \overleftrightarrow{\mathbf{D}})} = \mathrm{tr}[O(\mathbf{R})\tilde{\rho}] = \int dR\, O(\mathbf{R}) p(\mathbf{R})_{(\mathbf{R}_c; \overleftrightarrow{\mathbf{D}})}$$

analytic function of $\overleftrightarrow{\mathrm{D}}$ and T

$$p(\mathbf{R})_{(\mathbf{R}_c; \overleftrightarrow{\mathbf{D}})} = \langle \mathbf{R} | \tilde{\rho} | \mathbf{R} \rangle = a \exp[-(\mathbf{R} - \mathbf{R}_c) \cdot \overleftrightarrow{\mathbf{B}} \cdot (\mathbf{R} - \mathbf{R}_c)]$$

SCHA probability distribution

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analytic function of $\overleftrightarrow{\mathrm{D}}$ and T

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$$\langle \mathbf{R} \rangle_{(\mathbf{R}_c; \overleftrightarrow{\mathbf{D}})} = \mathbf{R}_c \quad = \text{quantum centroid of the nuclei}$$

SCHA probability distribution

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$$\tilde{H} = \frac{1}{2m}P^2 + \frac{1}{2}(\mathbf{R}-\mathbf{R}_c)\vec{\vec{\mathbf{D}}}(\mathbf{R}-\mathbf{R}_c)$$

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$$\langle \mathbf{R}\rangle_{(\mathbf{R}_c;\overleftrightarrow{\mathbf{D}})} = \mathbf{R}_c$$ = quantum centroid of the nuclei

$p(\mathbf{R})_{(\mathbf{R}_c;\overleftrightarrow{\mathbf{D}})}$ bounded distribution if $\overleftrightarrow{\mathbf{B}}$ and $\overleftrightarrow{\mathbf{D}}$ positive definite

$\overleftrightarrow{\mathbf{D}}$ no physical phonons (no softening at the phase transition)!

free energy – dependence on centroids

[Bianco, Errea, Paulatto, Calandra, Mauri, PRB 96, 014111 (2017)]

$$\tilde{F}_H[\tilde{H}] = \left\{ \mathrm{tr}\left[H\tilde{\rho} \right] + k_\mathrm{B} T \mathrm{tr}\left[\tilde{\rho} \ln(\tilde{\rho}) \right] \right\} \qquad \tilde{\rho} = \exp\left(-\frac{\tilde{H}}{k_\mathrm{B} T} \right) \tilde{Z}^{-1}$$

$\mathbf{R}_\mathbf{c}$ = centroid = order parameter of phase transition

$$F(\mathbf{R}_\mathrm{c}) = \min_{\overleftrightarrow{\mathbf{D}}} \tilde{F}_H[\tilde{H}_{(\mathbf{R}_\mathrm{c};\overleftrightarrow{\mathbf{D}})}]$$

stable equilibrium structure

$$\frac{\partial F(\mathbf{R}_\mathrm{c})}{\partial \mathbf{R}_\mathrm{c}} = \mathbf{0} \qquad \frac{\partial^2 F(\mathbf{R}_\mathrm{c})}{\partial \mathbf{R}_\mathrm{c} \partial \mathbf{R}_\mathrm{c}} \text{ positive definite}$$

at phase transition $\dfrac{\partial^2 F(\mathbf{R}_\mathrm{c})}{\partial \mathbf{R}_\mathrm{c} \partial \mathbf{R}_\mathrm{c}}$ acquires a negative eigenvalue

free energy – curvature

[Bianco, Errea, Paulatto, Calandra, Mauri, PRB 96, 014111 (2017)]

The auxiliary matrix that minimizes for a given $\mathbf{R}_c$ the SCHA free energy obeys to the self-consistent equation:

$$\overleftrightarrow{\mathbf{D}} = \left\langle \frac{\partial^2 V(\mathbf{R})}{\partial \mathbf{R} \partial \mathbf{R}} \right\rangle_{(\mathbf{R}_c; \overleftrightarrow{\mathbf{D}})}$$

free energy – curvature

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exact SCHA free-energy curvature:

rank-4 tensor, analytic function of $\overleftrightarrow{\mathbf{D}}$ and T

$$\frac{\partial^2 F(\mathbf{R}_c)}{\partial \mathbf{R}_c \partial \mathbf{R}_c} = \overleftrightarrow{\mathbf{D}} + \overset{(3)}{\mathbf{D}} : \overleftrightarrow{\mathbf{\Lambda}} : \left(\overleftrightarrow{\mathbf{1}} - \overset{(4)}{\mathbf{D}} : \overleftrightarrow{\mathbf{\Lambda}} \right)^{-1} : \overset{(3)}{\mathbf{D}}$$

rank-3 tensor

$$\overset{(3)}{\mathbf{D}} = \left\langle \frac{\partial^3 V(\mathbf{R})}{\partial \mathbf{R} \partial \mathbf{R} \partial \mathbf{R}} \right\rangle_{(\mathbf{R}_c; \overleftrightarrow{\mathbf{D}})}$$

rank-4 tensor

$$\overset{(4)}{\mathbf{D}} = \left\langle \frac{\partial^4 V(\mathbf{R})}{\partial \mathbf{R} \partial \mathbf{R} \partial \mathbf{R} \partial \mathbf{R}} \right\rangle_{(\mathbf{R}_c; \overleftrightarrow{\mathbf{D}})}$$

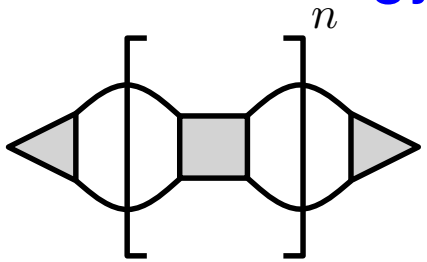
free energy – curvature - diagrams

[Bianco, Errea, Paulatto, Calandra, Mauri, PRB 96, 014111 (2017)]

exact SCHA free-energy curvature:

static self-energy (real quantity)

$$\frac{\partial^2 F(\mathbf{R}_c)}{\partial \mathbf{R}_c \partial \mathbf{R}_c} = \overleftrightarrow{\mathbf{D}} + \sum_{n=0}^{\infty}$$



—— phonon Green function with the auxiliary Hamiltonian

$$\tilde{H} = \frac{1}{2m} P^2 + \frac{1}{2}(\mathbf{R} - \mathbf{R}_c)\vec{\mathbf{D}}(\mathbf{R} - \mathbf{R}_c)$$

 $= \overset{(3)}{\mathbf{D}} /3!$

 $= \overset{(4)}{\mathbf{D}} /4!$

$$\overleftrightarrow{\mathbf{D}} = \langle \frac{\partial^2 V(\mathbf{R})}{\partial \mathbf{R} \partial \mathbf{R}} \rangle_{(\mathbf{R}_c; \overleftrightarrow{\mathbf{D}})} \qquad \overset{(3)}{\mathbf{D}} = \langle \frac{\partial^3 V(\mathbf{R})}{\partial \mathbf{R} \partial \mathbf{R} \partial \mathbf{R}} \rangle_{(\mathbf{R}_c; \overleftrightarrow{\mathbf{D}})} \qquad \overset{(4)}{\mathbf{D}} = \langle \frac{\partial^4 V(\mathbf{R})}{\partial \mathbf{R} \partial \mathbf{R} \partial \mathbf{R} \partial \mathbf{R}} \rangle_{(\mathbf{R}_c; \overleftrightarrow{\mathbf{D}})}$$

CDW in bulk and monolayer TMDs: NbS_2 $NbSe_2$

$T<T_{CDW}$: CDW (low symmetry phase)

$T=T_{CDW}$: second order phase transition

$T> T_{CDW}$: CDW melting (high symmetry phase)

The CDW melting has an electronic origin (thermal excitations of electrons) or is ruled by quantum and thermal anharmonic fluctuations of nuclei?

bulk and monolayer NbS_2

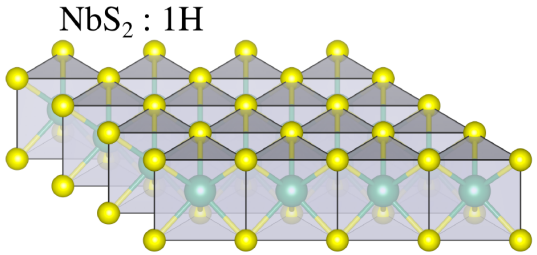
Expt:

BULK: no CDW but strong dependence of phonon on T

MONOLAYERS: CWD in on graphene substrate but not on Au

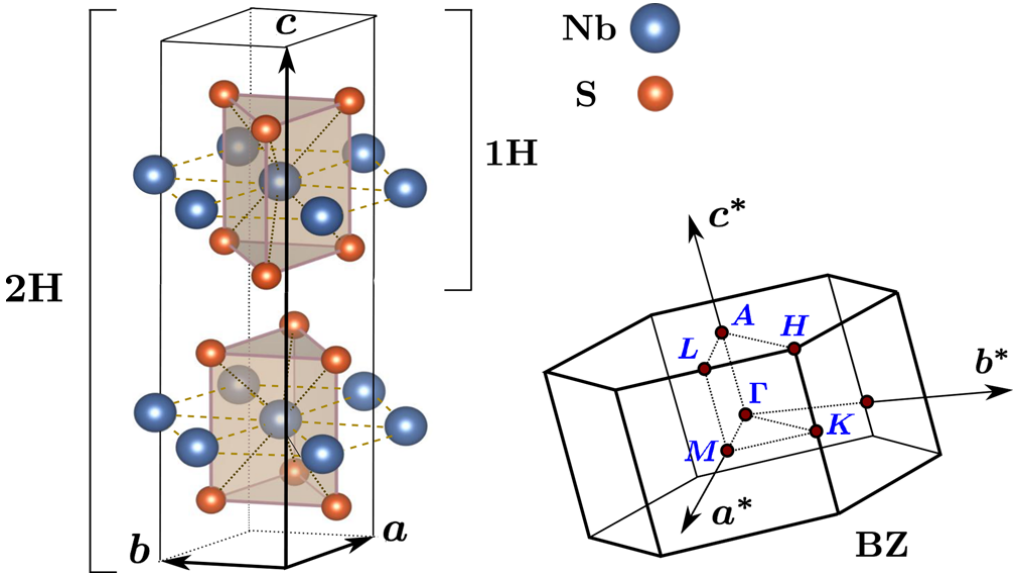
CDW in bulk and monolayer TMDs: NbS_2 or $NbSe_2$

monolayer: 1H



Trigonal prismatic coordination

bulk: 2H

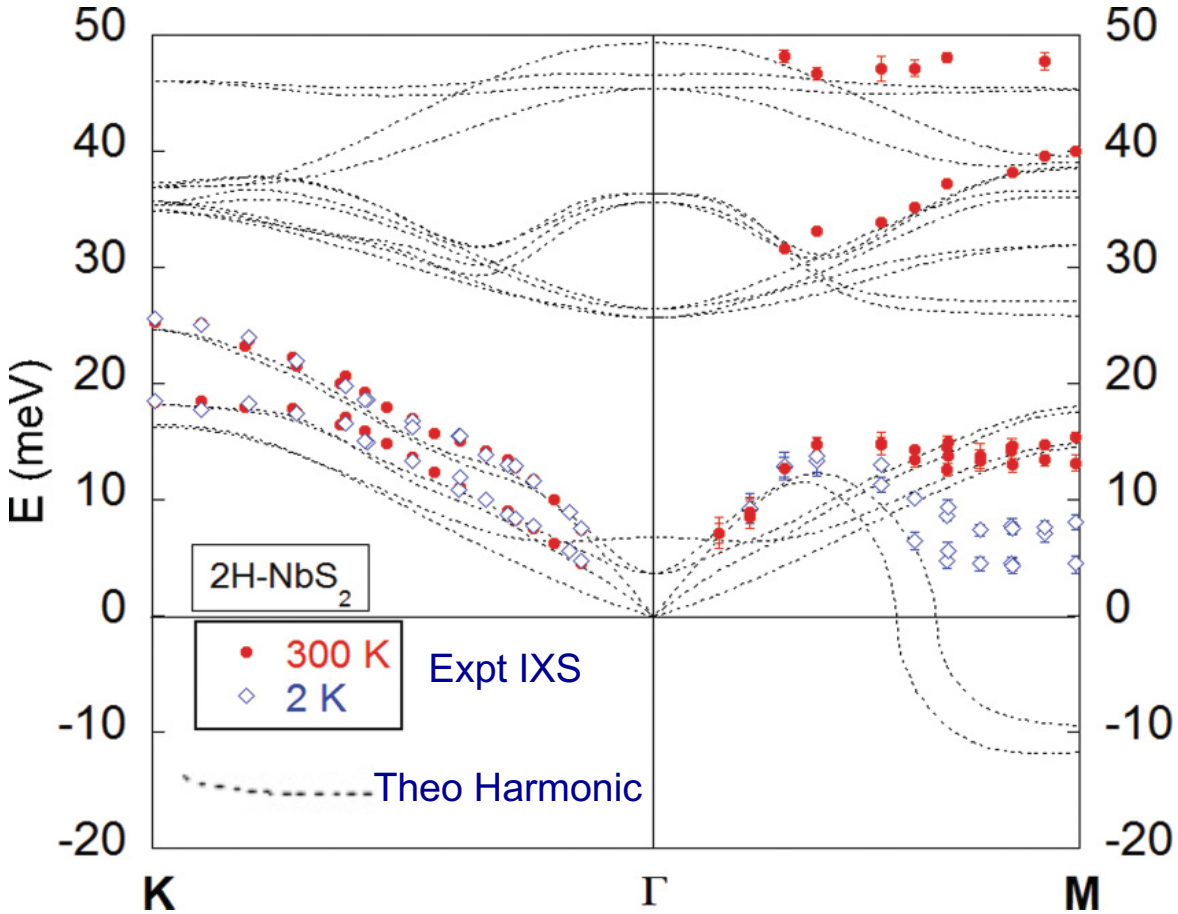


experiment on bulk NbS_2: no CWD (incipient CDW)

[Leroux et al., Phys. Rev. B 86, 155125 (2012)]

Harmonic DFT calculations suggest 2x2 CDW, while no CDW is present in bulk.

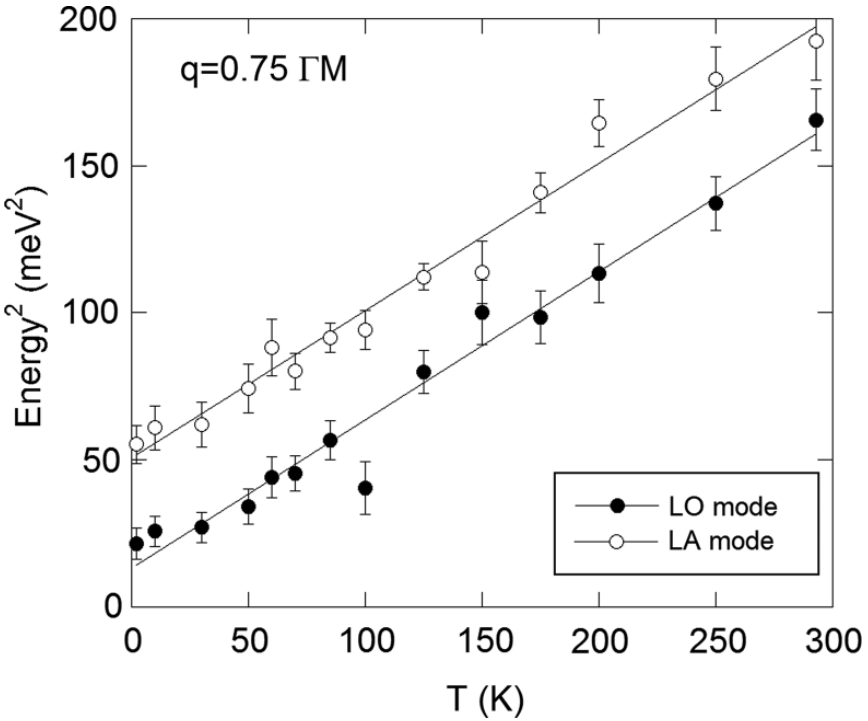
Incipient CDW: Strongly temperature dependent IXS phonon spectra.



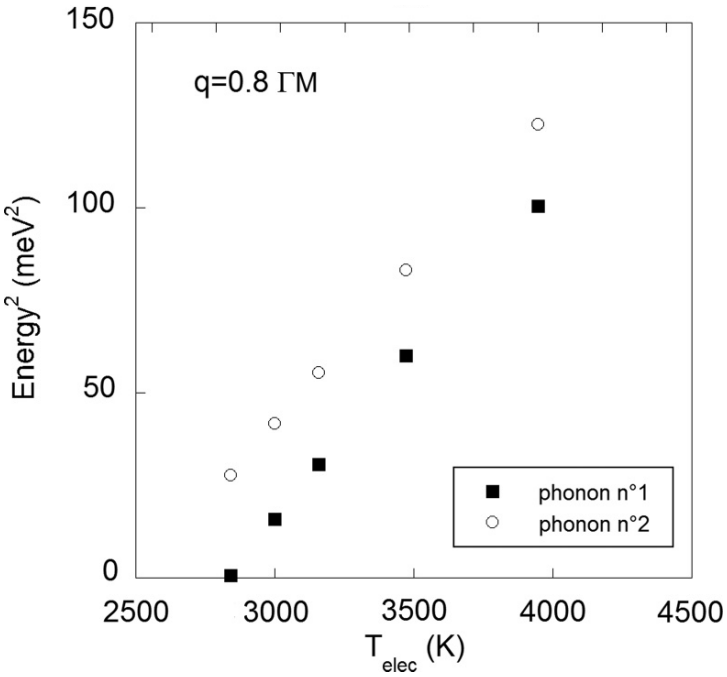
bulk NbS_2: temperature dependence

[Leroux et al., Phys. Rev. B 86, 155125 (2012)]

experiment IXS



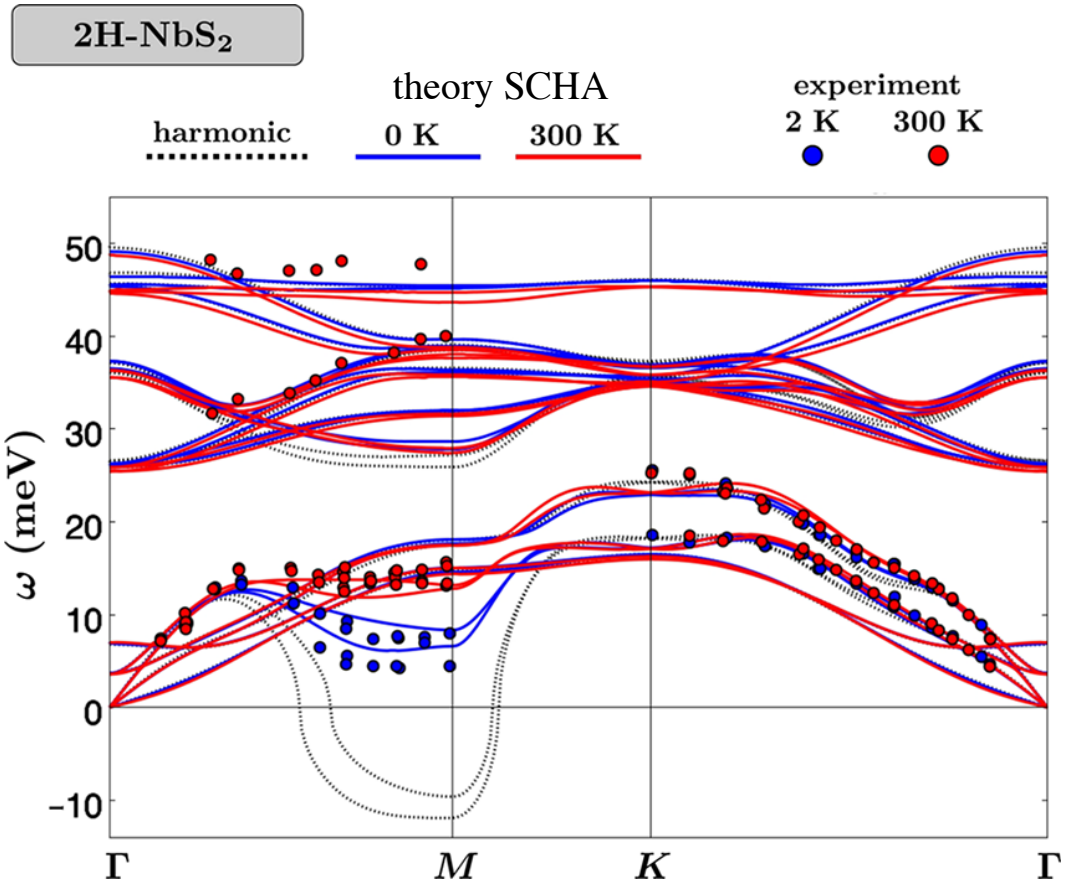
harmonic theory at finite electronic temperature



the electronic temperature has no role in the phonon hardening!

bulk NbS_2: anharmonic temperature dependence

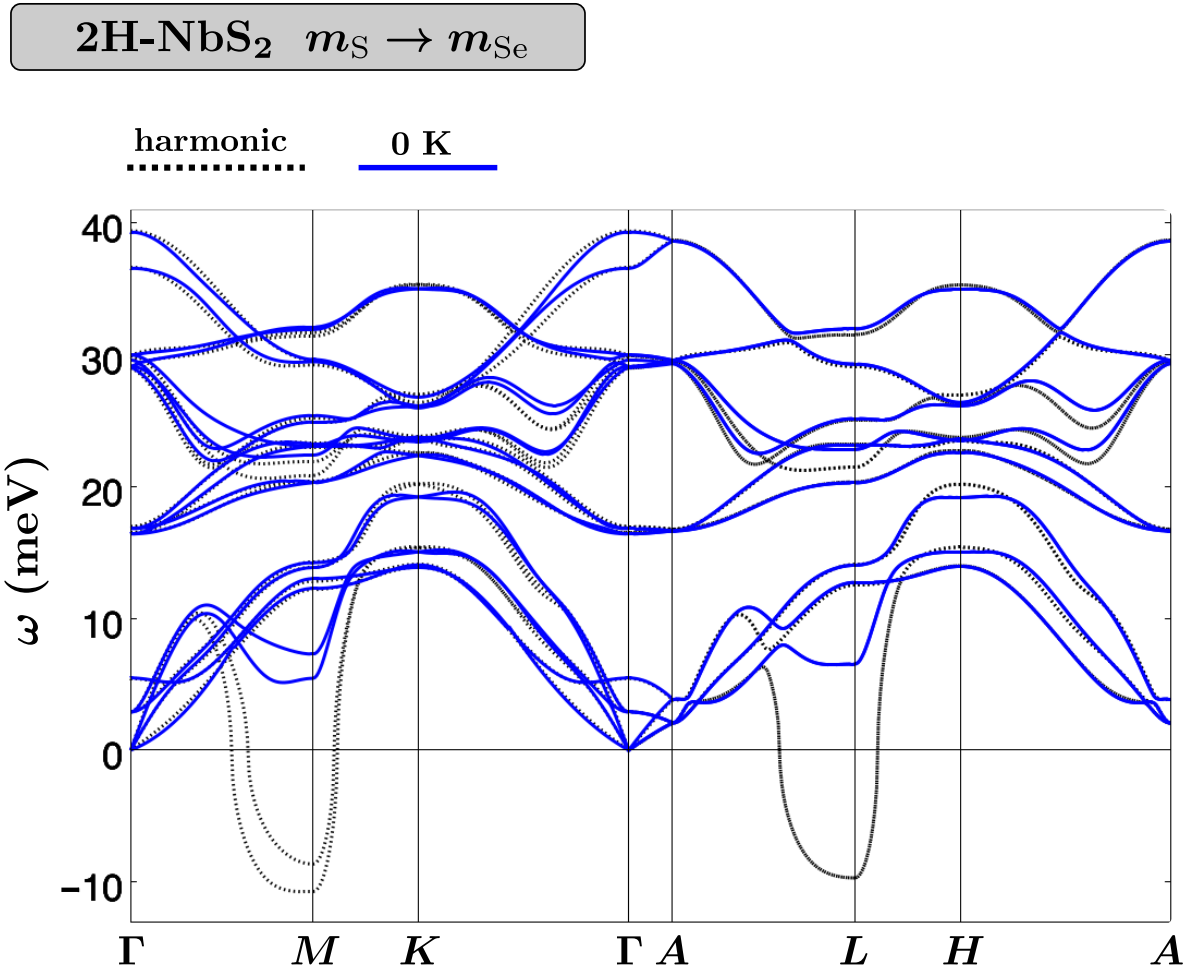
[Bianco, Errea, Monacelli, Calandra, Mauri, Nano Lett. 19, 3098 (2019)]



- SCHA reproduces the experiments
- Quantum fluctuation melt the “harmonic CDW” and thermal fluctuation explain the hardening with T

Why CDW $NbSe_2$ but not in NbS_2: isotope effect? (lighter S atom larger zero-point fluctuations)

[Bianco, Errea, Monacelli, Calandra, Mauri, Nano Lett. 19, 3098 (2019)]



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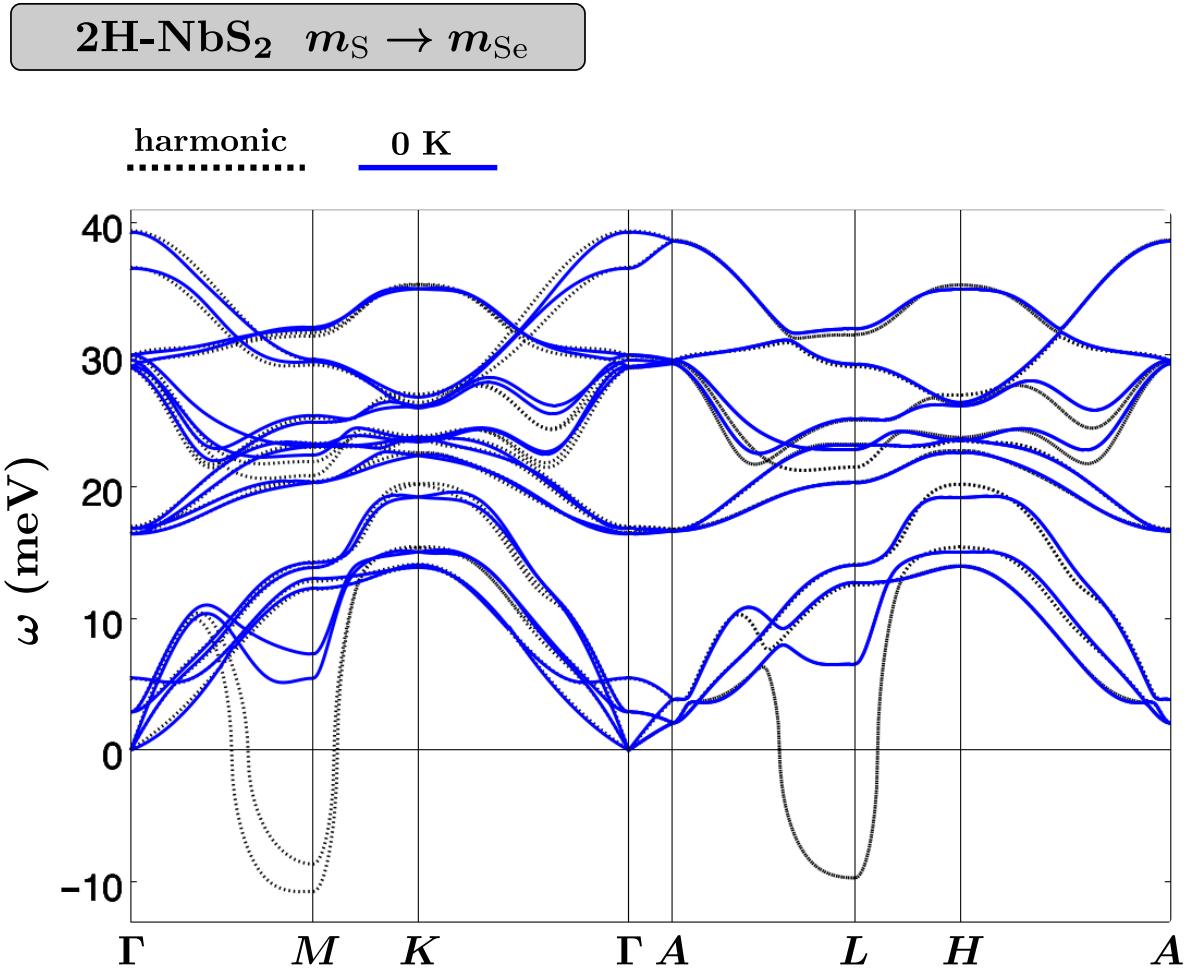
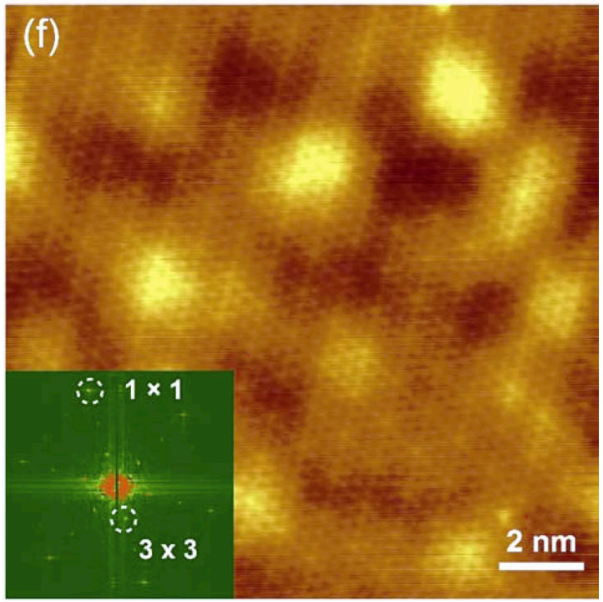


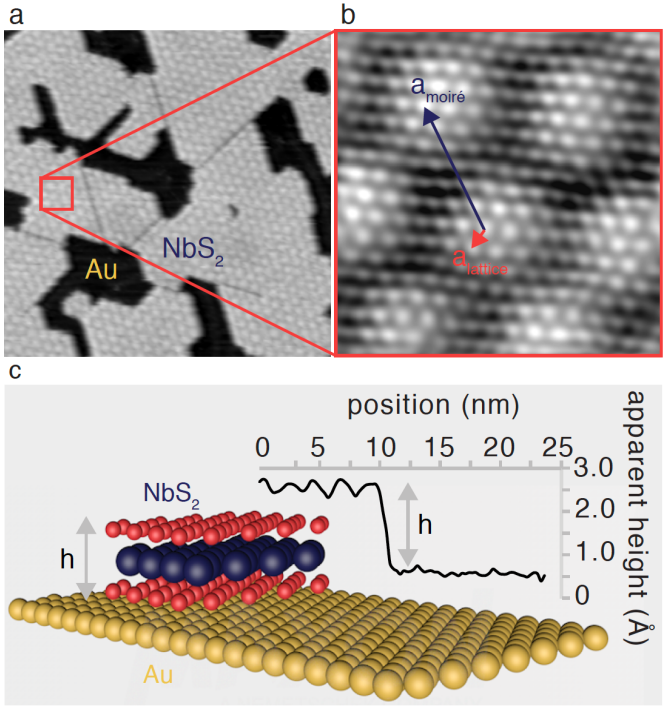
NO !

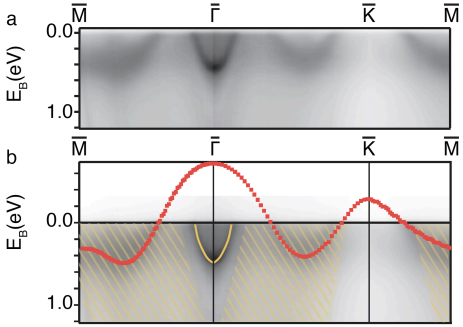
monolayer NbS_2 on different substrates: experiments

3x3 Charge CDW on graphene/6HSiC(0001) no CDW on Au(111)



FFT of STM





Au band at E_F , substantial charge transfer

Strong sensitivity of the CDW to environmental conditions.

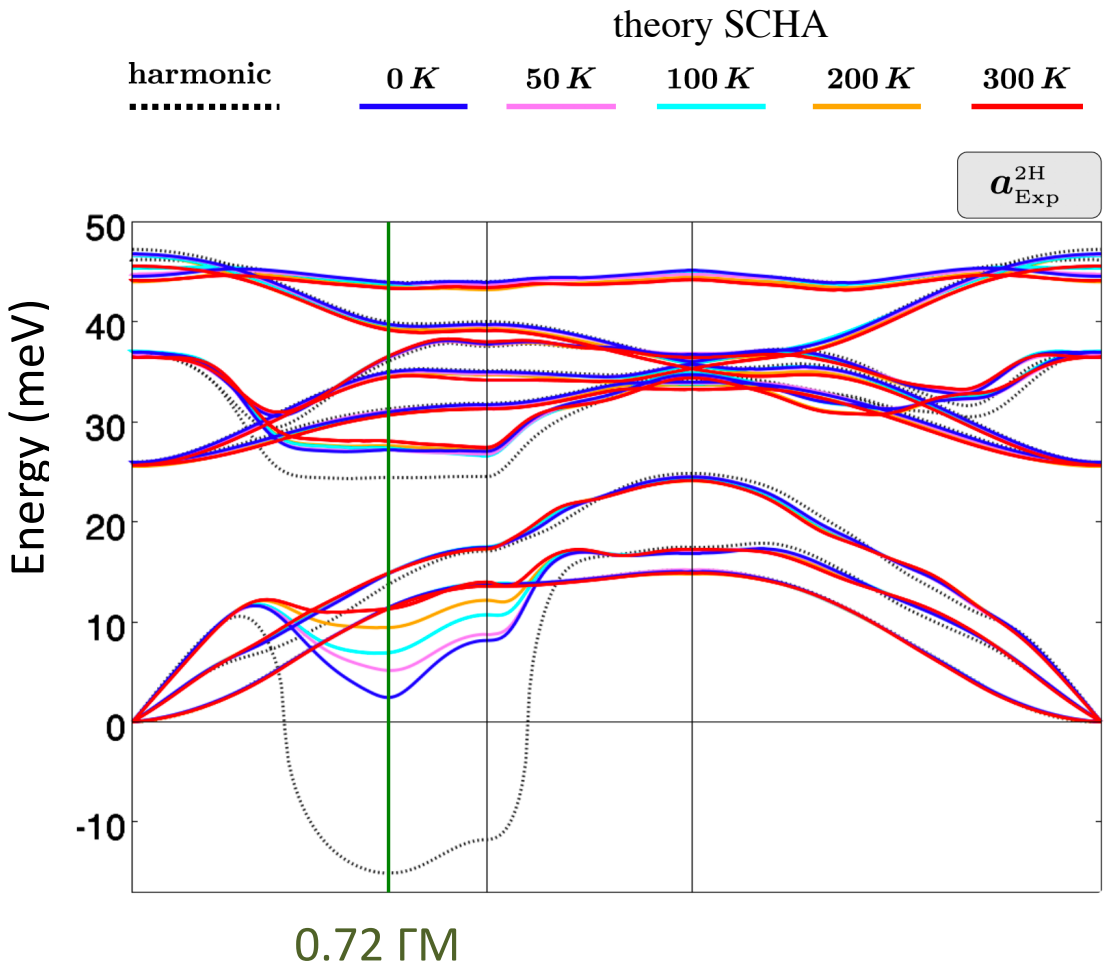
Lin *et al.*, Nano Research 11, 4722 (2018)

Stan *et al.*, arXiv:1901.03552 (2019)

monolayer NbS_2: theory SCHA

[Bianco, Errea, Monacelli, Calandra, Mauri, Nano Lett. 19, 3098 (2019)]

At the expt. lattice parameter, no CDW instability but the soft-mode 20% softer than in the bulk

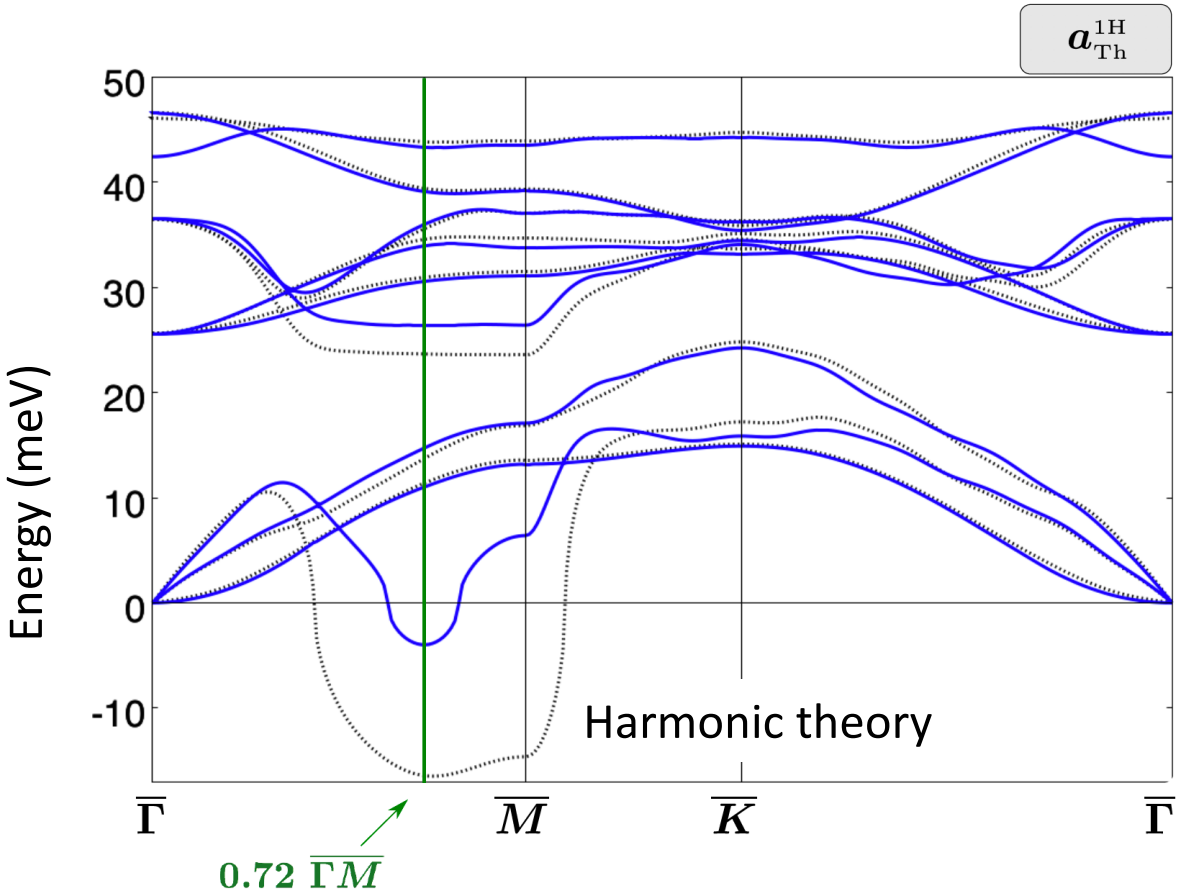


Sensitivity to strain ?

monolayer NbS_2: theory SCHA

[Bianco, Errea, Monacelli, Calandra, Mauri, Nano Lett. 19, 3098 (2019)]

By expanding the lattice parameter by 0.5% we find a 3x3 CDW instability



Anharmonic SCHA theory at T=0 K

Extreme sensitivity to environmental conditions.

Quantum enhancement of CDW in the 2D limit.

bulk and monolayer $NbSe_2$

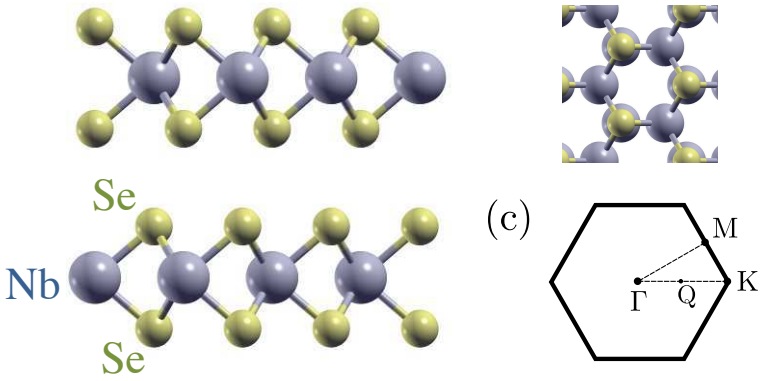
Expt:

BULK: CDW with T_c= 33 K

MONOLAYERS: CWD in one expt. Tc ~ 35 K in an other Tc ~ 145 K

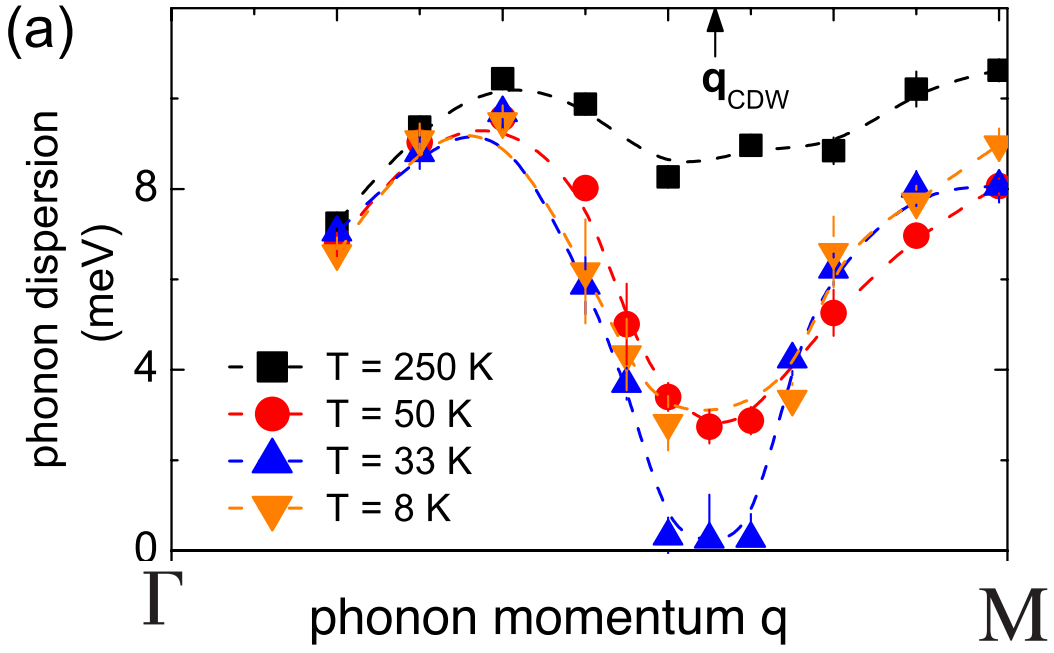
experiment on bulk $NbSe_2$ Inelastic X-Ray scattering (IXS)

[Weber *et al.* PRL 107, 107403 (2011)]

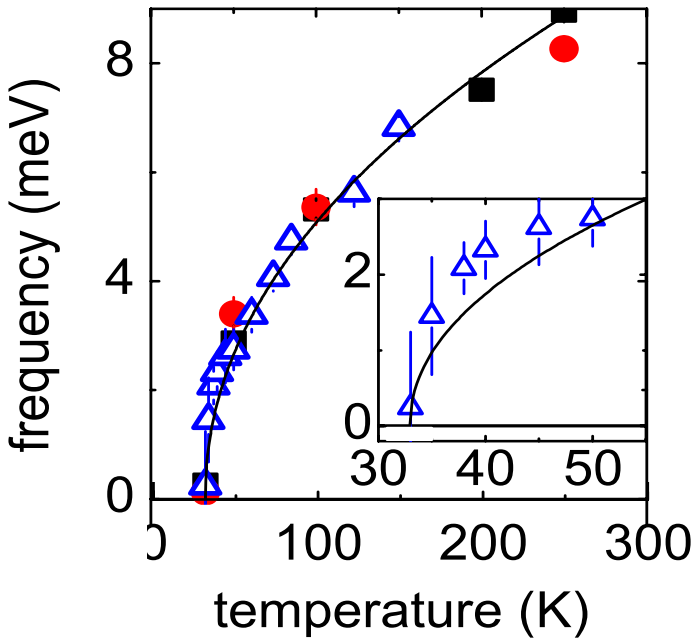


CDW transition temperature, $T_c \sim 33$ K

for $T<T_c$ a superstructure appears with periodicity close to a (3x3x1) reconstruction



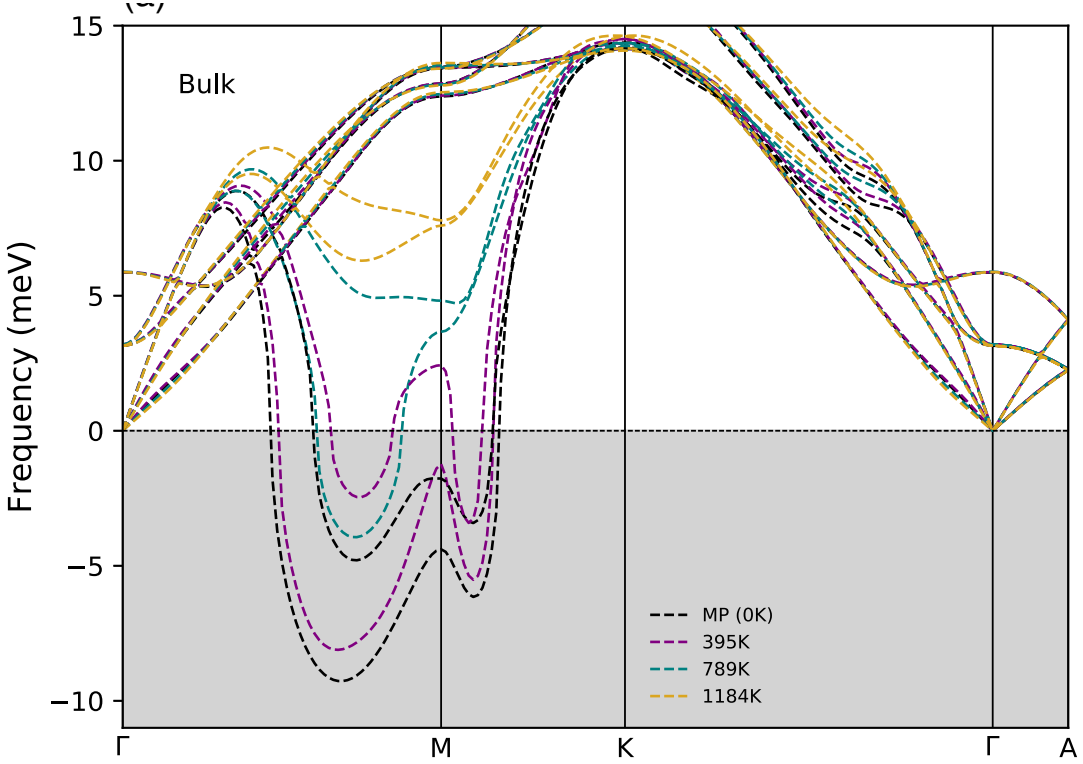
frequency at q_{CDW}

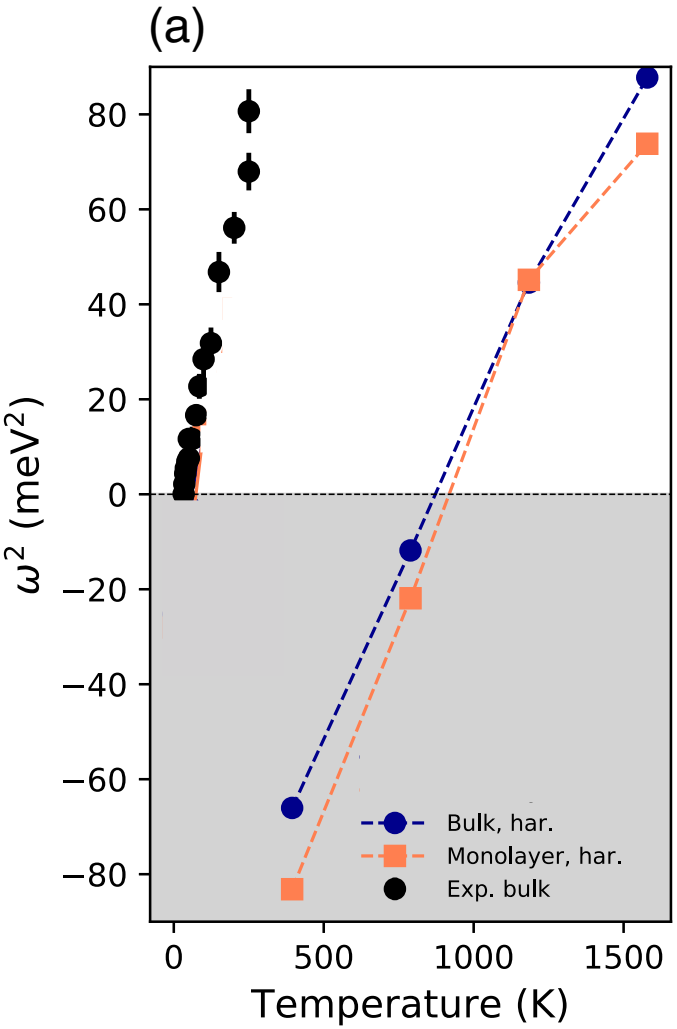


$NbSe_2$: role of electronic temperature

[Bianco, Monacelli, Calandra, Mauri, Errea, Phys. Rev. Lett. 125,106101 (2020)]

harmonic theory at finite electronic temperature



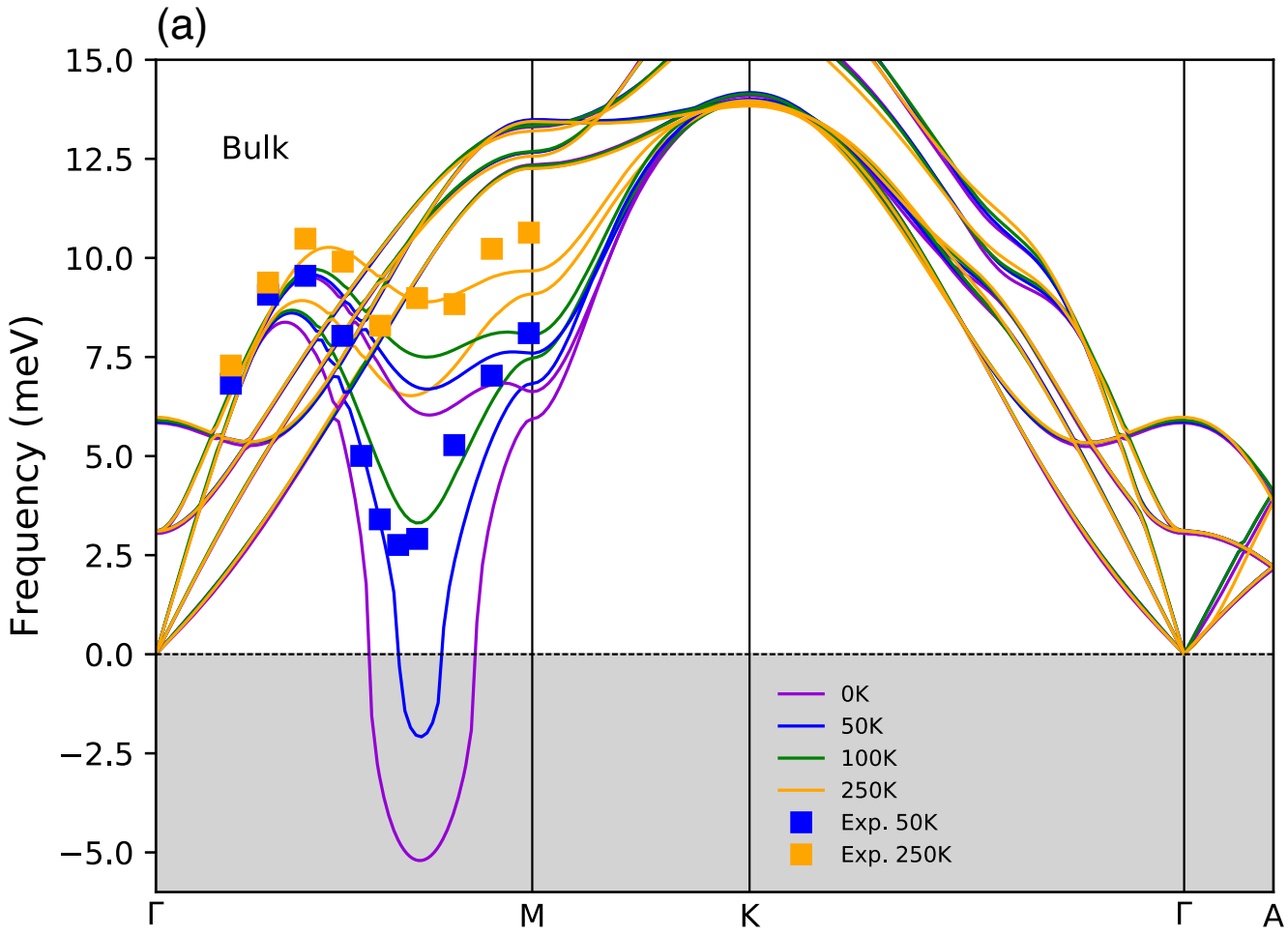


the electronic temperature has no role in the phonon hardening!

$NbSe_2$: role of anharmonic nuclear fluctuations

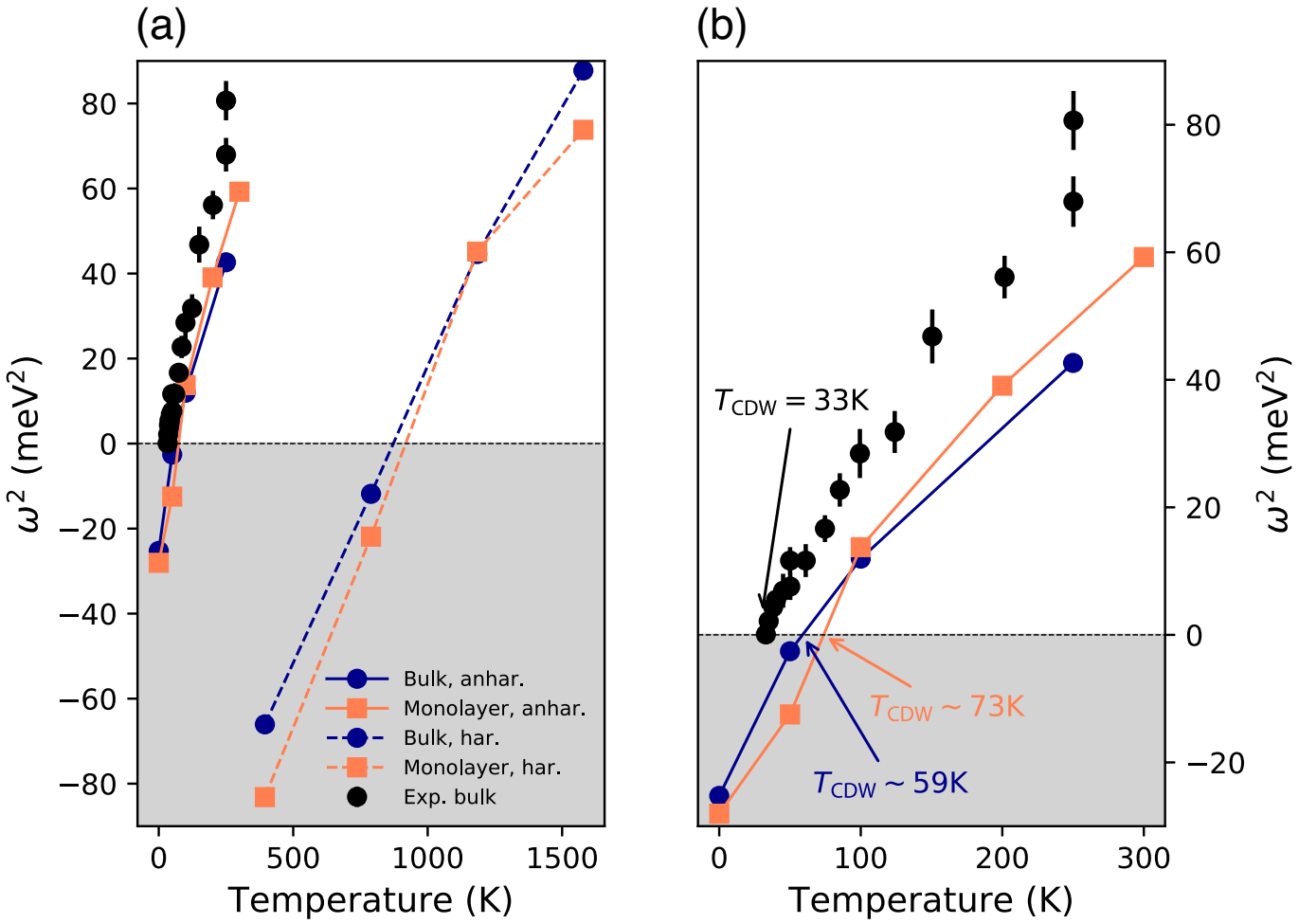
[Bianco, Monacelli, Calandra, Mauri, Errea, Phys. Rev. Lett. 125,106101 (2020)]

SCHA vs. experiment



$NbSe_2$: role of anharmonic nuclear fluctuations

[Bianco, Monacelli, Calandra, Mauri, Errea, Phys. Rev. Lett. 125,106101 (2020)]



- SCHA reproduces the experiments
- weak dependence on dimensionality

How to:

SSCHA

Stochastic Self-Consistent
Harmonic Approximation

Code (interfaced with Quantum-Espresso) available at: http://sscha.eu/

[*The Stochastic Self-Consistent Harmonic Approximation: Calculating Vibrational Properties of Materials with Full Quantum and Anharmonic Effects.* Monacelli, Bianco, Cherubini, Calandra, Errea, Mauri, arXiv:2103.03973 (2021)]

SCHA our approach

$$\tilde{F}_H[\tilde{H}] = \left\{ \mathrm{tr}\left[H\tilde{\rho} \right] + k_\mathrm{B} T \mathrm{tr}\left[\tilde{\rho} \ln(\tilde{\rho}) \right] \right\} \qquad \tilde{\rho} = \exp\left(-\frac{\tilde{H}}{k_\mathrm{B} T} \right) \tilde{Z}^{-1}$$

$$\tilde{H} = \frac{1}{2m} P^2 + \frac{1}{2} (\mathbf{R} - \mathbf{R}_\mathrm{c}) \overleftrightarrow{\mathbf{D}} (\mathbf{R} - \mathbf{R}_\mathrm{c})$$

conjugate gradient (CG) minimization of the functional with respect to the parameters $(\mathbf{R}_\mathrm{c}; \overleftrightarrow{\mathbf{D}})$ and eventually of the cell

minimization = trajectory in the parameter space

$$(\mathbf{R}_\mathrm{c}; \overleftrightarrow{\mathbf{D}})_0 \longrightarrow (\mathbf{R}_\mathrm{c}; \overleftrightarrow{\mathbf{D}})_1 \longrightarrow (\mathbf{R}_\mathrm{c}; \overleftrightarrow{\mathbf{D}})_2 \longrightarrow \cdots \longrightarrow (\mathbf{R}_\mathrm{c}; \overleftrightarrow{\mathbf{D}})_n$$

for the CG, we need the gradient of the functional

Gradients of the functional

DFT ab-initio forces

harmonic trial forces

$$\nabla_{\mathbf{R}_c} \tilde{F}_H[\tilde{H}] = -\int dR \left[\mathbf{f}(\mathbf{R}) - \tilde{\mathbf{f}}(\mathbf{R}) \right] \tilde{p}(\mathbf{R})$$

analytic function of $\mathbf{D}$ and T

$$\nabla_{\vec{\mathbf{D}}} \tilde{F}_H[\tilde{H}] = -\int dR \left[\mathbf{f}(\mathbf{R}) - \tilde{\mathbf{f}}(\mathbf{R}) \right] \cdot \nabla_{\vec{\mathbf{D}}} \overleftrightarrow{\mathbf{A}} \cdot [\mathbf{R} - \mathbf{R}_c] \tilde{p}(\mathbf{R})$$

probability distribution

analytic function of $\mathbf{D}$ and T

$$\tilde{p}(\mathbf{R}) = \langle \mathbf{R} | \tilde{\rho} | \mathbf{R} \rangle = a \exp\left[-(\mathbf{R} - \mathbf{R}_c) \cdot \overleftrightarrow{\mathbf{B}} \cdot (\mathbf{R} - \mathbf{R}_c) \right]$$

Gradients of the functional: important sampling

DFT ab-initio forces

$$\nabla \tilde{F}_H[\tilde{H}] = \int dR O\left[\mathbf{f}(\mathbf{R})\right] \tilde{p}(\mathbf{R})_{(\mathbf{R_c};\vec{\mathbf{D}})_0}$$

stochastic evaluation of the integrals:

$\left\{\mathbf{R}_I\right\}_{I=1,\ldots,N_c}$ N_c ionic configuration generated according to the probability of the initial distribution $p(\mathbf{R})_{(\mathbf{R_c};\vec{\mathbf{D}})_0}$

$$\nabla \tilde{F}_H[\tilde{H}] = \frac{1}{N_c}\sum_{I=1}^{N_c} O\left[\mathbf{f}(\mathbf{R}_I)\right]$$

Recycling the ab-initio forces for many steps of the conjugent gradient trajectory

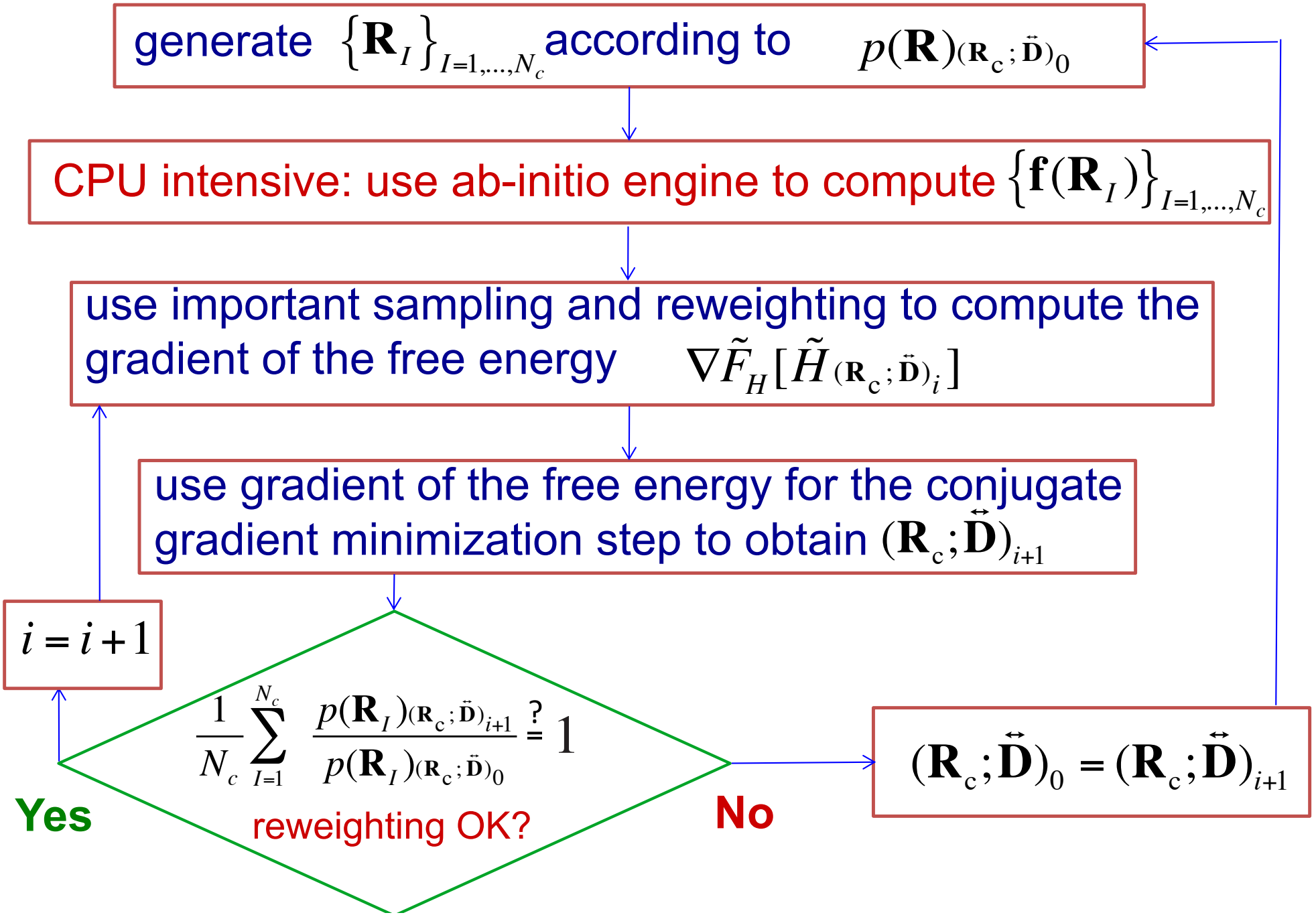
$$(\mathbf{R}_c;\vec{\vec{\mathbf{D}}})_0 \longrightarrow (\mathbf{R}_c;\vec{\vec{\mathbf{D}}})_1 \longrightarrow (\mathbf{R}_c;\vec{\vec{\mathbf{D}}})_2 \longrightarrow \cdots \longrightarrow (\mathbf{R}_c;\vec{\vec{\mathbf{D}}})_n$$

reweighting

$\{\mathbf{R}_I\}_{I=1,\ldots,N_c}$ N_c ionic configuration generated according to the probability of the initial distribution $p(\mathbf{R})_{(\mathbf{R}_c;\vec{\vec{\mathbf{D}}})_0}$

$$\nabla \tilde{F}_H[\tilde{H}_{[(\mathbf{R}_c;\vec{\vec{\mathbf{D}}})_i]}] = \frac{1}{N_c}\sum_{I=1}^{N_c} O[\mathbf{f}(\mathbf{R}_I)] \frac{p(\mathbf{R}_I)_{(\mathbf{R}_c;\vec{\vec{\mathbf{D}}})_i}}{p(\mathbf{R}_I)_{(\mathbf{R}_c;\vec{\vec{\mathbf{D}}})_0}}$$

practical recipe



example of minimization

PtH (0K, 100GPa): forces computed on a 2x2x1 hexagonal cell

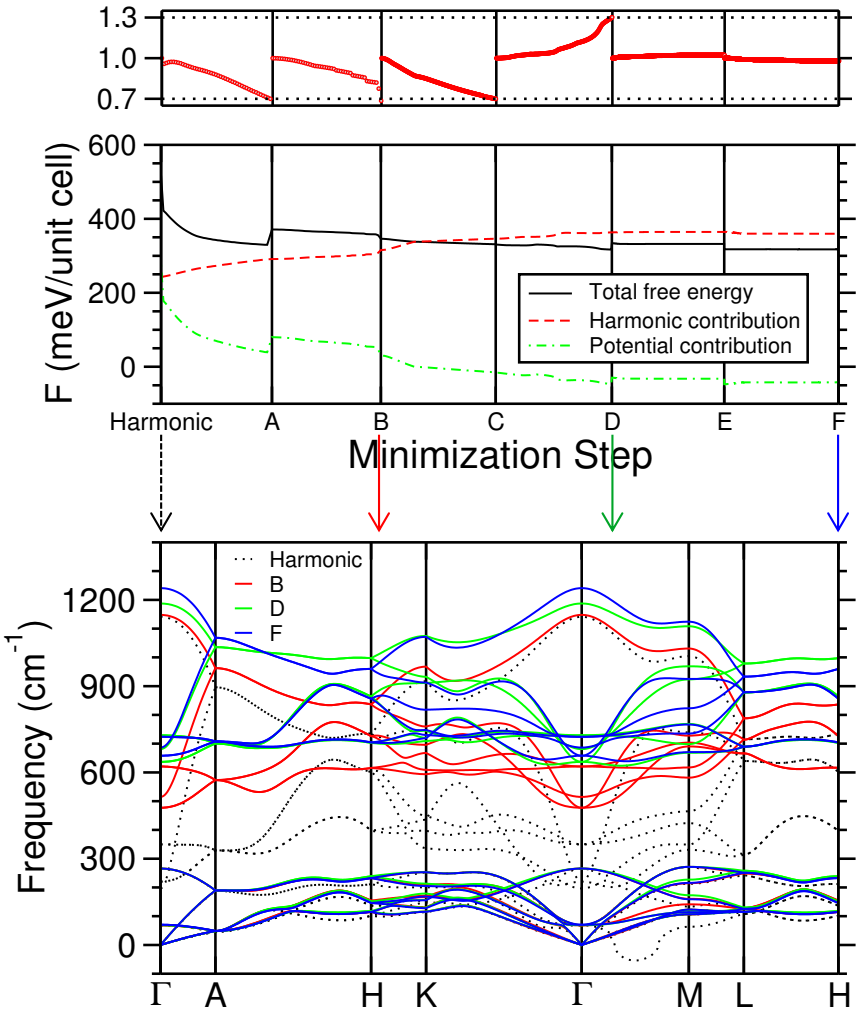
20 new force calculations (CPU intensive part) at Harmonic, A, B, C, D

380 new force calculations (CPU intensive part) at E

$$\frac{1}{N_c}\sum_{I=1}^{N_c}\frac{p(\mathbf{R}_I)_{(\mathrm{R_c};\vec{\mathbf{D}})_{i+1}}}{p(\mathbf{R}_I)_{(\mathrm{R_c};\vec{\mathbf{D}})_0}}$$

Free energy

$$\tilde{F}_H[\tilde{H}] = \tilde{F}_{\tilde{H}}[\tilde{H}] + \int dR\left[V(\mathbf{R}) - \tilde{V}(\mathbf{R})\right]\tilde{p}(\mathbf{R})$$



for free-energy curvature evaluation

[Bianco, Errea, Paulatto, Calandra, Mauri, PRB 96, 014111 (2017)]

$$\overset{(3)}{\mathbf{D}} = \left\langle \frac{\partial^3 V(\mathbf{R})}{\partial \mathbf{R} \partial \mathbf{R} \partial \mathbf{R}} \right\rangle_{(\mathbf{R}_c; \overleftrightarrow{\mathbf{D}})} \qquad \overset{(4)}{\mathbf{D}} = \left\langle \frac{\partial^4 V(\mathbf{R})}{\partial \mathbf{R} \partial \mathbf{R} \partial \mathbf{R} \partial \mathbf{R}} \right\rangle_{(\mathbf{R}_c; \overleftrightarrow{\mathbf{D}})}$$

DFT ab-initio forces

harmonic auxiliary forces

$$\overset{(3)}{\mathbf{D}} = -\int dR\, [\overleftrightarrow{\mathbf{B}} \cdot (\mathbf{R} - \mathbf{R}_c)][\overleftrightarrow{\mathbf{B}} \cdot (\mathbf{R} - \mathbf{R}_c)][\mathbf{f}(\mathbf{R}) - \tilde{\mathbf{f}}(\mathbf{R})] p(\mathbf{R})_{(\mathbf{R}_c; \overleftrightarrow{\mathbf{D}})}$$

$$\overset{(4)}{\mathbf{D}} = -\int dR\, [\overleftrightarrow{\mathbf{B}} \cdot (\mathbf{R} - \mathbf{R}_c)][\overleftrightarrow{\mathbf{B}} \cdot (\mathbf{R} - \mathbf{R}_c)][\overleftrightarrow{\mathbf{B}} \cdot (\mathbf{R} - \mathbf{R}_c)][\mathbf{f}(\mathbf{R}) - \tilde{\mathbf{f}}(\mathbf{R})] p(\mathbf{R})_{(\mathbf{R}_c; \overleftrightarrow{\mathbf{D}})}$$

$$p(\mathbf{R})_{(\mathbf{R}_c; \overleftrightarrow{\mathbf{D}})} = a \exp[-(\mathbf{R} - \mathbf{R}_c) \cdot \overleftrightarrow{\mathbf{B}} \cdot (\mathbf{R} - \mathbf{R}_c)]$$

stochastic evaluation with forces

[Bianco, Errea, Paulatto, Calandra, Mauri, PRB 96, 014111 (2017)]

$$\overset{(n)}{\mathbf{D}} = \int dR\, O[\mathbf{R}, \mathbf{f}(\mathbf{R}), (\mathbf{R}_\mathrm{c}; \overset{\leftrightarrow}{\mathbf{D}})] p(\mathbf{R})_{(\mathbf{R}_\mathrm{c}; \overset{\leftrightarrow}{\mathbf{D}})}$$

evaluation of the integrals with importance sampling:

$\{\mathbf{R}_I\}_{I=1,\ldots,N_c}$ N_c ionic configuration generated according to the probability distribution $p(\mathbf{R})_{(\mathbf{R}_\mathrm{c}; \vec{\mathbf{D}})}$

DFT ab-initio forces for configuration $\mathbf{R}_I$ (displaced from equilibrium)

$$\overset{(n)}{\mathbf{D}} = \frac{1}{N_\mathrm{c}} \sum_{I=1}^{N_\mathrm{c}} O[\mathbf{R}_I, \mathbf{f}(\mathbf{R}_I), (\mathbf{R}_\mathrm{c}; \overset{\leftrightarrow}{\mathbf{D}})]$$

our ab-initio stochastic SCHA: features

computational cost comparable or smaller that of ab-initio MD
(force/total energy calculation for ~ few 1000 configurations)

it includes thermal and quantum fluctuations

variational approach (it can deal with large anharmonicity)

access to stress tensor (full cell minimization)

direct access to Free Energy without thermodynamic integration
(first-order phase transition)

direct access to Free Energy curvature
(second-order phase transition)

Time-dependent SCHA: *spectroscopic properties and and time correlation functions with the inclusion of anharmonic quantum/thermal fluctuations*
(not available in path-integral Monte Carlo):
[Monacelli, Mauri, PRB 103, 104305 (2021)]

conclusions

- centroids (average atomic positions): order parameters in second-order structural phase transitions

- curvature of free energy changes sign at phase transitions

- we obtained an exact analytic formula for free-energy curvature

- in both $NbSe_2$ and NbS_2 the CDW instability is related to state within ~ 0.1 eV from the Fermi level, since an the electronic temperature of 1100 K affects the harmonic phonons.

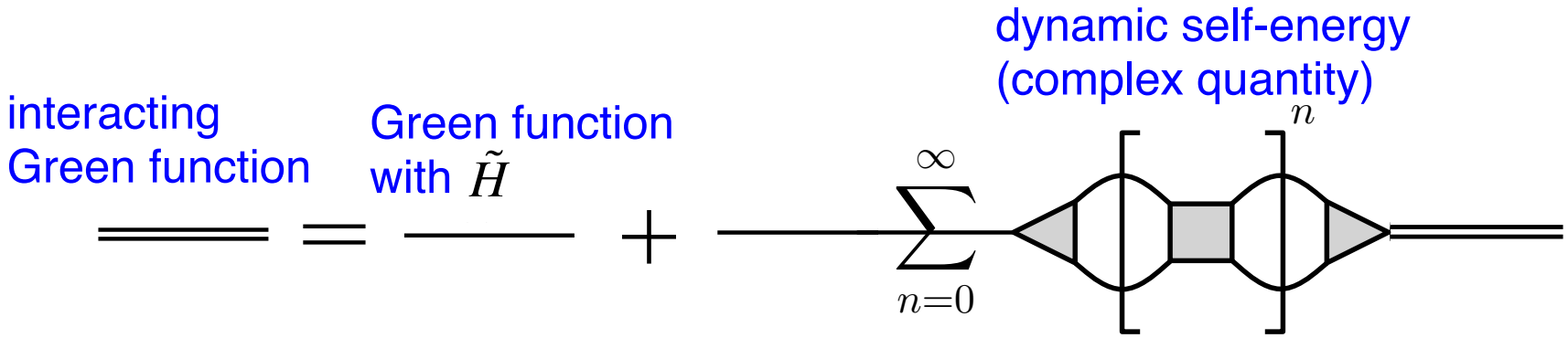
- however T_{CDW} and the temperature dependence of phonons are ruled by the anharmonic quantum and thermal fluctuation of the nuclei and not by the electronic temperature (electronic excitations)

- strong dependence in the monolayer of T_{CDW} on the environment: a small doping and/or strain has a big influence on it

Ansatz for physical phonons

[Bianco, Errea, Paulatto, Calandra, Mauri, PRB 96, 014111 (2017)]

Free-energy curvature is exact but computed for a static displacement of the centroids. Perfect for phase transition but in phonon measurements the atoms oscillate at finite frequency.



The Ansatz (Dyson equation) recovers:

- the free-energy curvature in the the static limit

Ansatz for physical phonons

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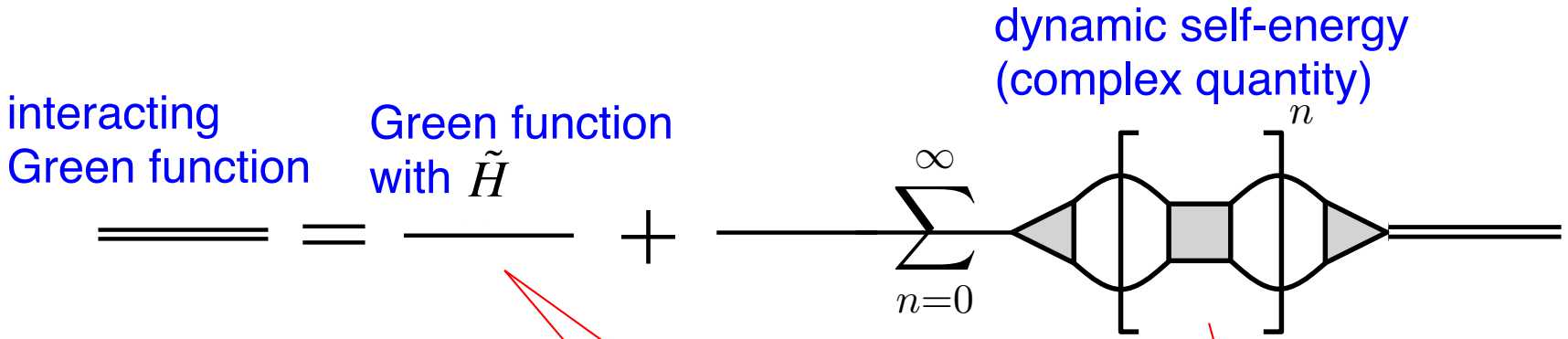

The Ansatz (Dyson equation) recovers:

- the free-energy curvature in the the static limit
- the perturbative expansion of the Green function in the weak anharmonicity limit: