Methods

- Harmonic approximation
  - MD
  - frozen phonons
  - linear response
  - Taylor expansion of PES (MD, sampling)

Phonons are independent quasiparticles with ∞ lifetime.

- Structure & thermodynamics: quasiharmonic approximation (QHA)
  Gives structure $(\vec{a}_i, \vec{X}_s)$ at $T \geq 0$, $P \geq 0$ for many systems, but full implementation is computationally challenging for non-cubic crystals.

- Inclusion of anharmonicity
  - MD (SCAILD)
  - MD (TDEP)
  - perturbation (when small) (SCP)
  - stochastic methods (SSCHA)

Quantum?
+/−
−
+
+

Quantum consideration

$$PE = \frac{1}{2}\sum_{ij}\Phi_{ij}u_i u_j \Rightarrow \left[\sum_i \frac{p_i^2}{2M_i} + \frac{1}{2}\sum_{ij}\Phi_{ij}u_i u_j\right]\Psi = E\Psi$$

classical dynamical matrix

This can be diagonalised to "classical" normal modes: $\mathcal{D} = M^{-1/2}\Phi M^{-1/2}$,

$$PE = \frac{1}{2}u^T\Phi u = \frac{1}{2}u^T\left(M^{-1/2}\mathcal{D}M^{-1/2}\right)u = \frac{1}{2}u^T M^{-1/2}\left(\sum_\lambda \omega_\lambda^2 \gamma_\lambda \gamma_\lambda^T\right)M^{-1/2}u = \frac{1}{2}\sum_\lambda \omega_\lambda^2 y_\lambda^2$$

where $y_\lambda = M^{1/2}\gamma_\lambda^T u \equiv \sum_i \sqrt{M_i}\,\gamma_{\lambda i}u_i$ are normal modes (classical)

Momentum: $p_i = -i\hbar\frac{\partial}{\partial u_i} = -i\hbar\sum_\lambda \frac{\partial y_\lambda}{\partial u_i}\frac{\partial}{\partial y_\lambda} = -i\hbar\sum_\lambda \sqrt{M_i}\,\gamma_{\lambda i}\frac{\partial}{\partial y_\lambda} = \sum_\lambda \sqrt{M_i}\,\gamma_{\lambda i}\,p_\lambda$

Hence,

$$KE = \frac{1}{2}\sum_i \frac{1}{M_i}p_i^2 = \frac{1}{2}\sum_i \frac{1}{M_i}\sum_{\lambda\lambda'} M_i \gamma_{\lambda i}\gamma_{\lambda' i}\,p_\lambda p_{\lambda'} = \frac{1}{2}\sum_{\lambda\lambda'}\underbrace{\left(\sum_i \gamma_{\lambda i}\gamma_{\lambda' i}\right)}_{\delta_{\lambda\lambda'}} p_\lambda p_{\lambda'} = \frac{1}{2}\sum_\lambda p_\lambda^2$$

The Hamiltonian

$$\hat{H} = \sum_\lambda\left(\frac{1}{2}p_\lambda^2 + \frac{1}{2}\omega_\lambda^2 y_\lambda^2\right) \Rightarrow \text{sum of independent harmonic oscillators}$$

$$E = \sum_\lambda \hbar\omega_\lambda\left(n_\lambda + \frac{1}{2}\right), \quad \Psi = \prod_\lambda \psi_\lambda^{(n_\lambda)} \equiv \prod_\lambda |\{n_\lambda\}\rangle$$

$\hookrightarrow 0, 1, 2, \ldots$

Phonon's statistics

$\hat{H} = \sum_\lambda \hat{h}_\lambda$, $\hat{h}_\lambda = \hbar\omega_\lambda\left(\hat{n}_\lambda + \frac{1}{2}\right)$, $\hat{n}_\lambda |n_\lambda\rangle = n_\lambda |n_\lambda\rangle$, $\boxed{\hat{n}_\lambda = b_\lambda^\dagger b_\lambda}$

The free energy (Helmholtz) $\boxed{F = U - TS = -k_B T \ln Z}$

$\boxed{\beta = 1/k_B T}$

Z – statistical sum: $Z = Tr\left(e^{-\beta H}\right) = \prod_\lambda Z_\lambda$, $Z_\lambda = Tr\left(e^{-\beta h_\lambda}\right)$

$\downarrow \sum_n \langle n| \ldots |n\rangle$

for one oscillator

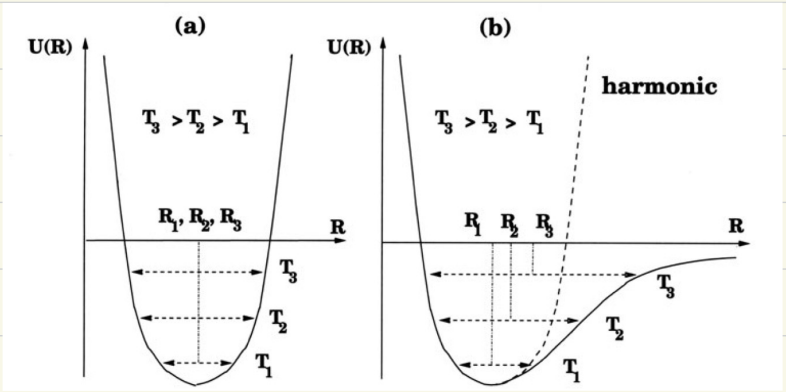
$$Z_\lambda = \sum_{n_\lambda=0}^{\infty} \langle n_\lambda | e^{-\beta h_\lambda} | n_\lambda \rangle = \sum_{n_\lambda=0}^{\infty} e^{-\beta\hbar\omega_\lambda\left(n_\lambda+\frac{1}{2}\right)} = \frac{e^{-\beta\hbar\omega_\lambda/2}}{1 - e^{-\beta\hbar\omega_\lambda}}$$

The free energy $F = -k_B T \ln\left(\prod_\lambda Z_\lambda\right) \Rightarrow$

$$\boxed{F = \sum_\lambda \left[\frac{\hbar\omega_\lambda}{2} + k_B T \ln\left(1 - e^{-\beta\hbar\omega_\lambda}\right)\right] \equiv F(T)}$$

($\frac{\hbar\omega_\lambda}{2}$: zero point energy)

Quasiharmonic approximation



harmonic anharmonic

At $T > 0$ crystals expand. Approximately ($P = 0$):

$F = U_{DFT}(V) + F_{vibr}(V, T)$

$\min_V F \rightarrow$ structure for the given $T \rightarrow \left(\frac{\partial F}{\partial V}\right)_T = 0$

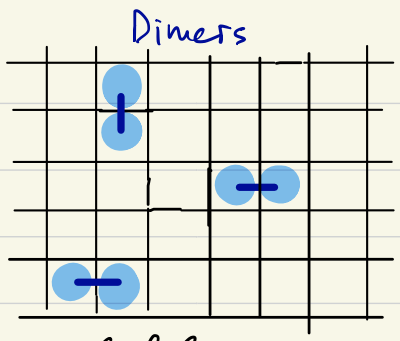
At $P > 0$ one has to use $G = F + PV$

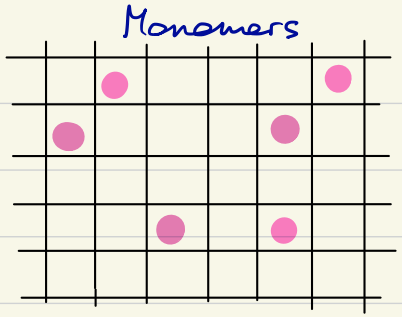
$\min_V G \rightarrow$ structure for the given T

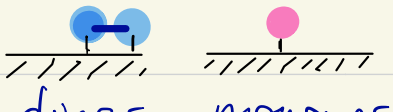
$$\boxed{\left(\frac{\partial F}{\partial V}\right)_T = -P}$$

Configurational entropy

Which structure is more energetically favourable?







$N \ll M$

but still $\gg 1$

M – total number of sites available; N – number of species.

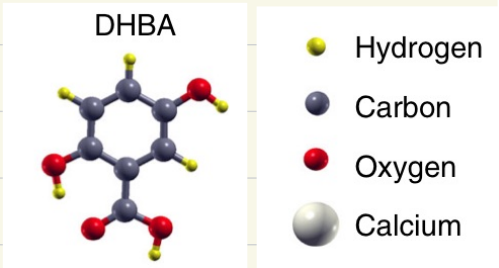
$\ln N! \simeq N \ln N - N$

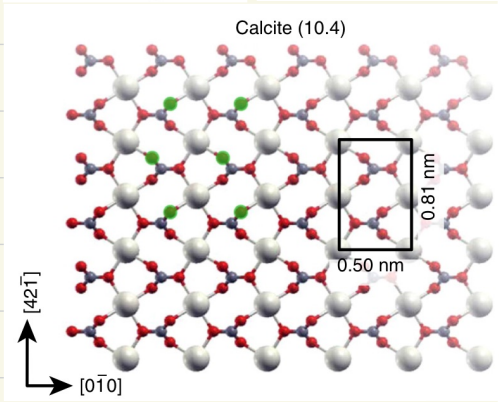
$$\Delta S = k_B \ln \frac{M!}{N!(M-N)!} = N k_B \left[\ln \frac{1-\theta}{\theta} - \frac{1}{\theta} \ln(1-\theta) \right], \text{ where } \theta = \frac{N}{M} \text{ coverage.}$$

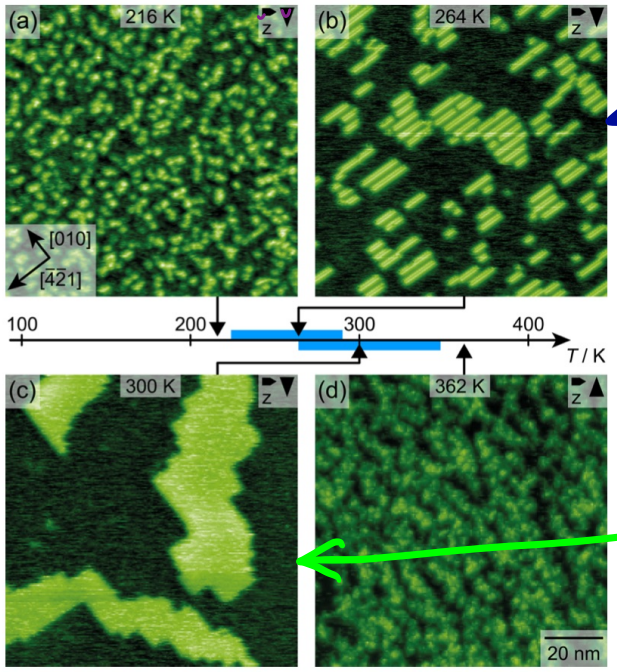
$\theta_D = \theta_M / 2$

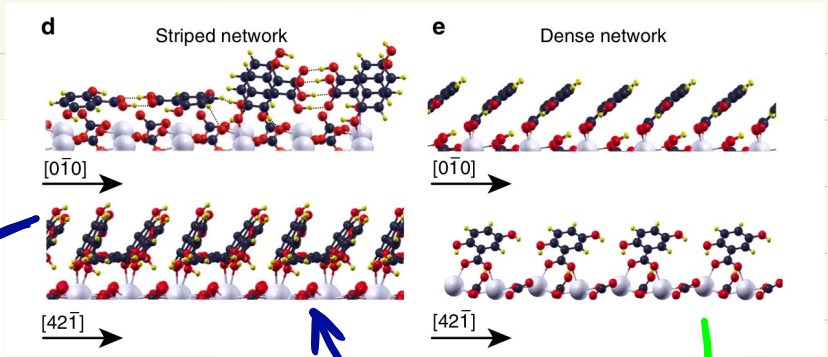
Free energy per species:

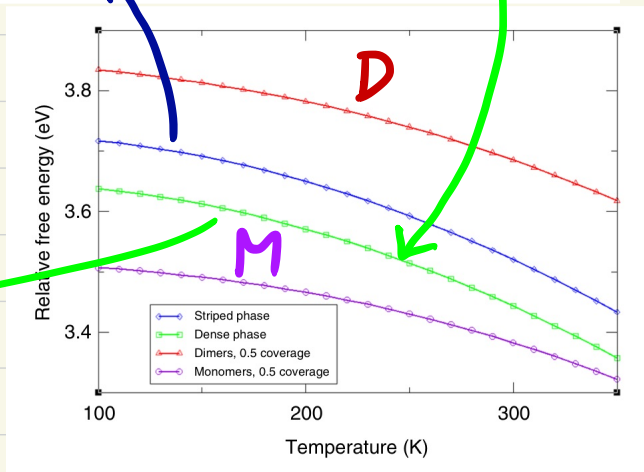
$$F = \Delta U_{DFT} + \Delta F_{vibr} - k_B T \left[\ln \frac{1-\theta}{\theta} - \frac{1}{\theta} \ln(1-\theta) \right]$$





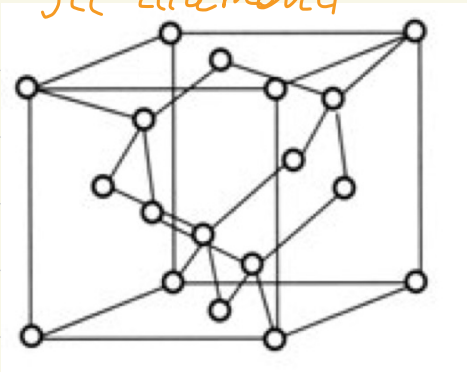






C. Paris et al. – Comm. Chem. 1 66 (2018)

fcc diamond

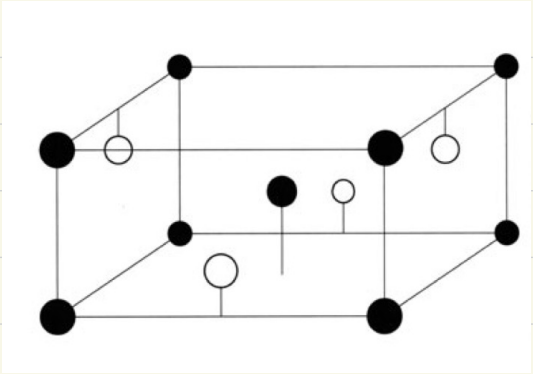


α - Sn (gray tin)

(T < Tc)

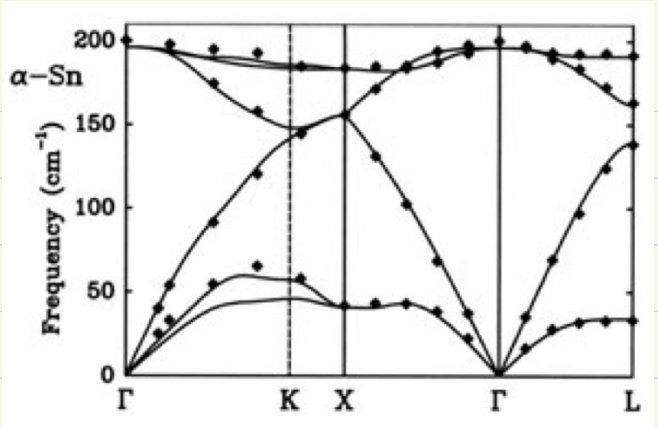
13°C ⟹

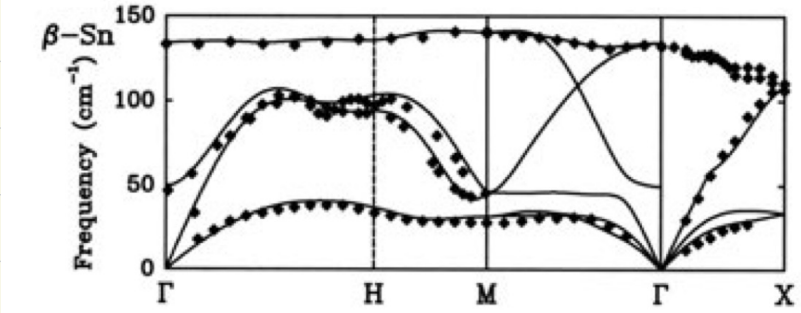
body-centred tetragonal (bct)



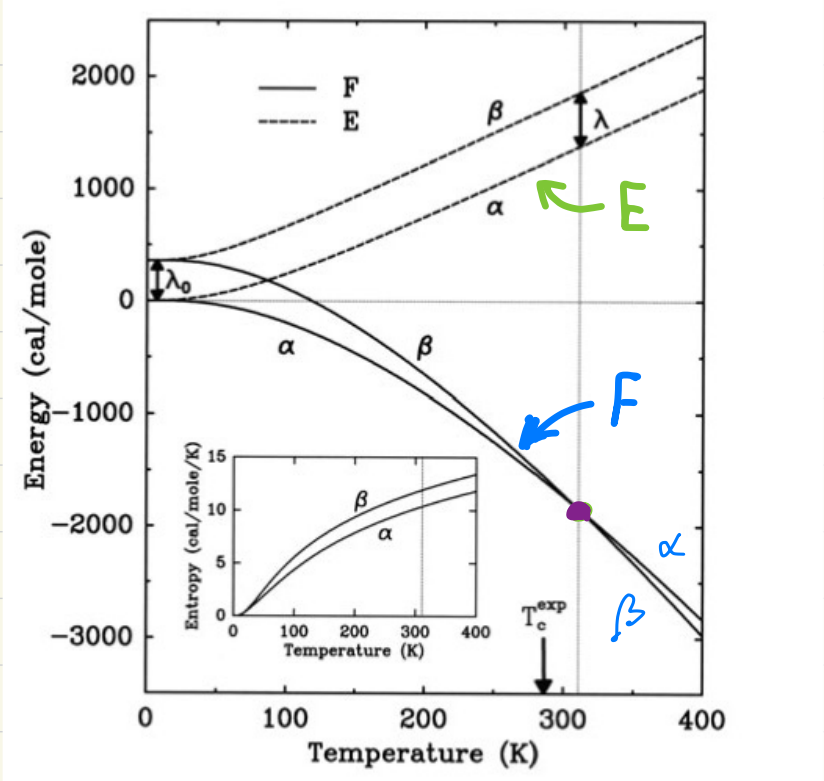
β - Sn (white tin)

(T > Tc)





$F = E - TS$ (naive QH approximation)

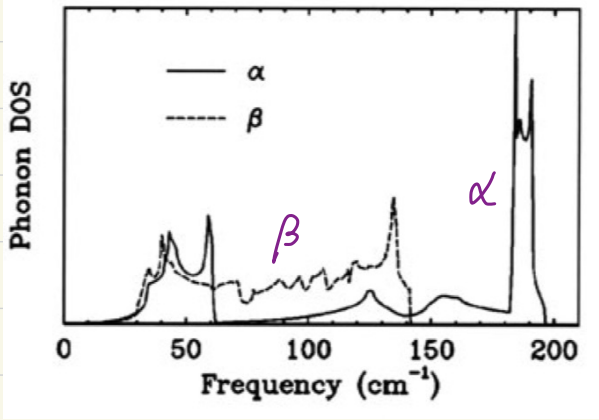


The phase transition is driven by phonons

$S_\beta - S_\alpha \simeq k_B \ln \frac{\omega_\alpha}{\omega_\beta}$

(Einstein model)

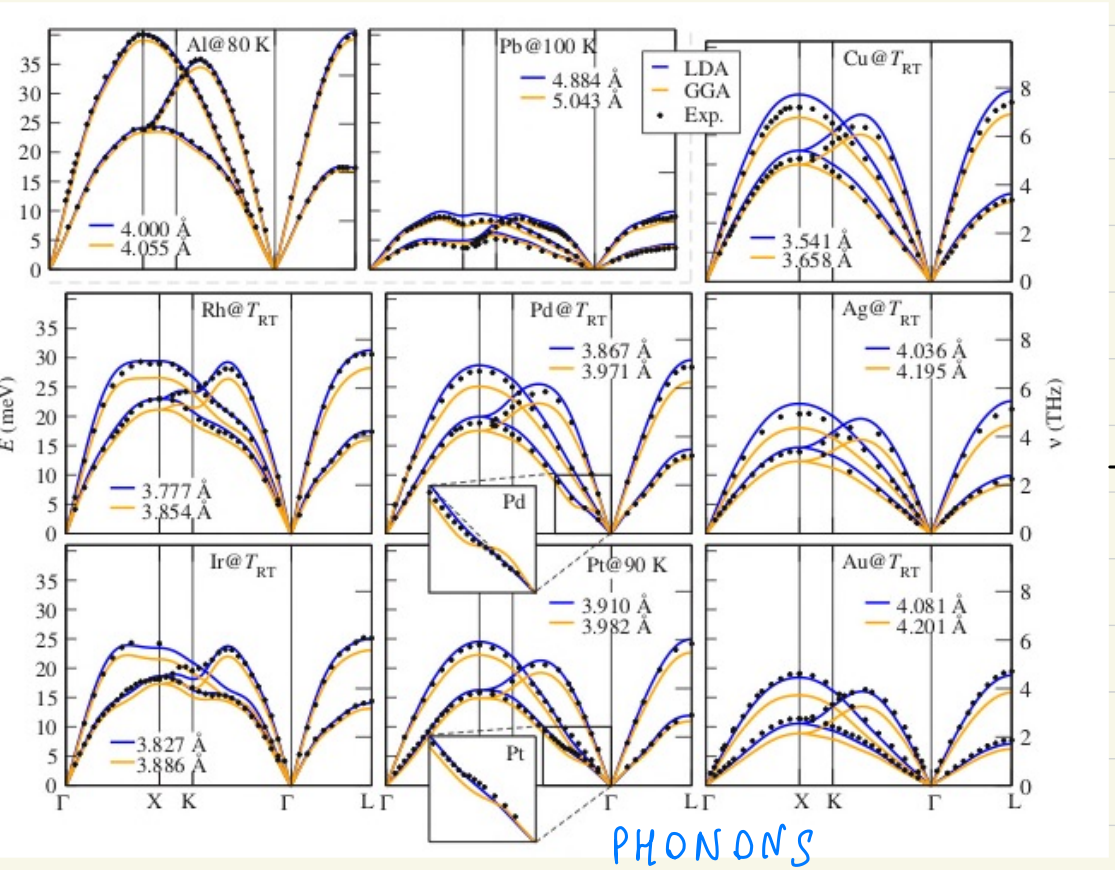
$\omega_\alpha >> \omega_\beta \Rightarrow S_\beta - S_\alpha > 0$



[193] P. Pavone. Old and new aspects in lattice-dynamical theory. *J. Phys.: Condens. Matter*, 13:7593–7610, 2001.

Thermal expansion of simple metals

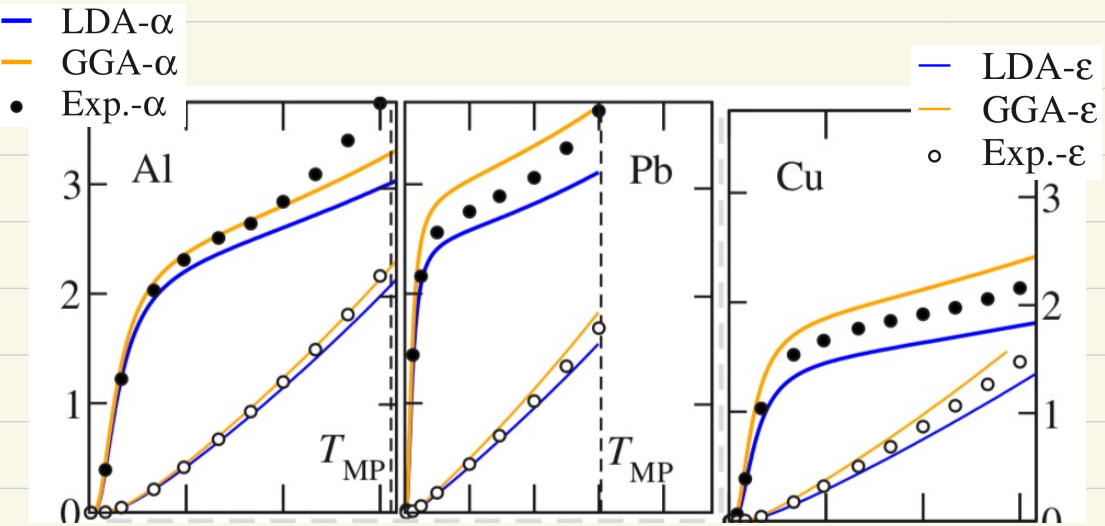
$F = F_{el} + f_{QH} \; (+ f_{AH} + f_{defects})$



PHONONS

- Large cutoffs
- Large k-points meshes (up to 4×4×4)
- Large supercells (up to 5×5×5)
- LDA vs. GGA compared

- DFT first used for various values of the volume V.
- For each V phonons were calculated
- Frequences ω_{kj} for non-exact k points were interpolated across the BZ using a Fourier method (?)
- Free energy $f(V,T)$ calculated
- $P = -\left(\frac{\partial F}{\partial V}\right)_T$ solved to get $V_{eq}(P,T)$



EXPANSION

$$\alpha(T) = \frac{a(T) - a(T_{ref})}{a(T_{ref})}$$

$$\varepsilon(T) = \frac{1}{a(T)} \frac{da(T)}{dT}$$

B. Grabowski et al. – PRB 76 024309 (2007)

Self-Consistent Ab Initio Lattice Dynamics (SCAILD)

- Using HA formulae (monoatomic):

$$\mathcal{D}_{ss'}(k) = \frac{1}{M}\sum_{L} \Phi_{ss'}(L)\, e^{-ikL} \quad , \quad \mathcal{D}(k)\, e_{jk} = \omega^2_{jk}\, e_{jk}$$

Displacements: $$u_L = \frac{1}{\sqrt{MN}} \sum_{kj} Q_{kj}\, e_{kj}\, e^{ikL}$$

Q_{kj} ← normal coordinates (operators)

- Operators Q_{kj} are replaced by numbers via (high T)

$$\frac{Q_{kj}}{\sqrt{M}} \to \sqrt{\frac{\langle Q^\dagger_{kj} Q_{kj}\rangle}{M}} \quad , \quad \langle Q^\dagger_{kj} Q_{kj}\rangle = \frac{\hbar}{2\omega_{kj}}(1 + 2n_{kj})$$

$[e^{\beta\hbar\omega_{kj}} - 1]^{-1}$

allowing to relate FT of atomic forces to the displacements:

$$f_{k\alpha} = -\sum_{j} M\, \omega^2_{kj}\, A_{kj}\, e_{kj\alpha} \quad , \quad A_{kj} = \pm\sqrt{\frac{\langle Q^\dagger_{kj} Q_{kj}\rangle}{M}}$$

real numbers

$$\omega^2_{kj} = -\frac{1}{M}\frac{f_k \cdot e_{kj}}{A_{kj}}$$

Comp. Mat. 44 888 (2009)

- Algorithm:

$$\omega_{kj}^{(0)} \rightarrow U_{L\alpha} \xrightarrow{\text{DFT}} f_{L\alpha} \xrightarrow{(A_{kj})} f_{k\alpha} \rightarrow \omega_{kj}^{(1)} \rightarrow \dots$$

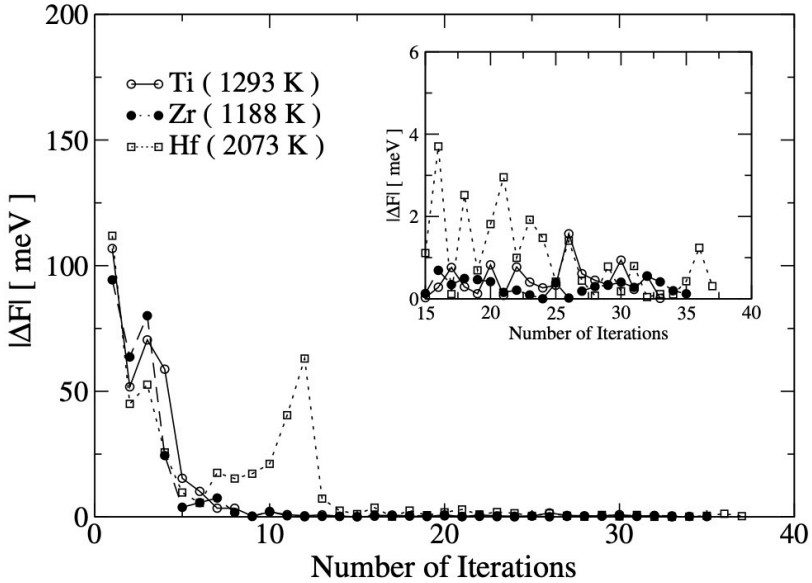
($\pm$ sign at random)

- Depends on T (via $A_{kj} \sim \sqrt{\langle Q_{kj}^{\dagger} Q_{kj} \rangle}$)
- Quantum effects are also somewhat included because of $\langle Q_{kj}^{\dagger} Q_{kj} \rangle$
- AH is effectively included through the SC procedure.
- Free energy can also be calculated via the QHA formula:

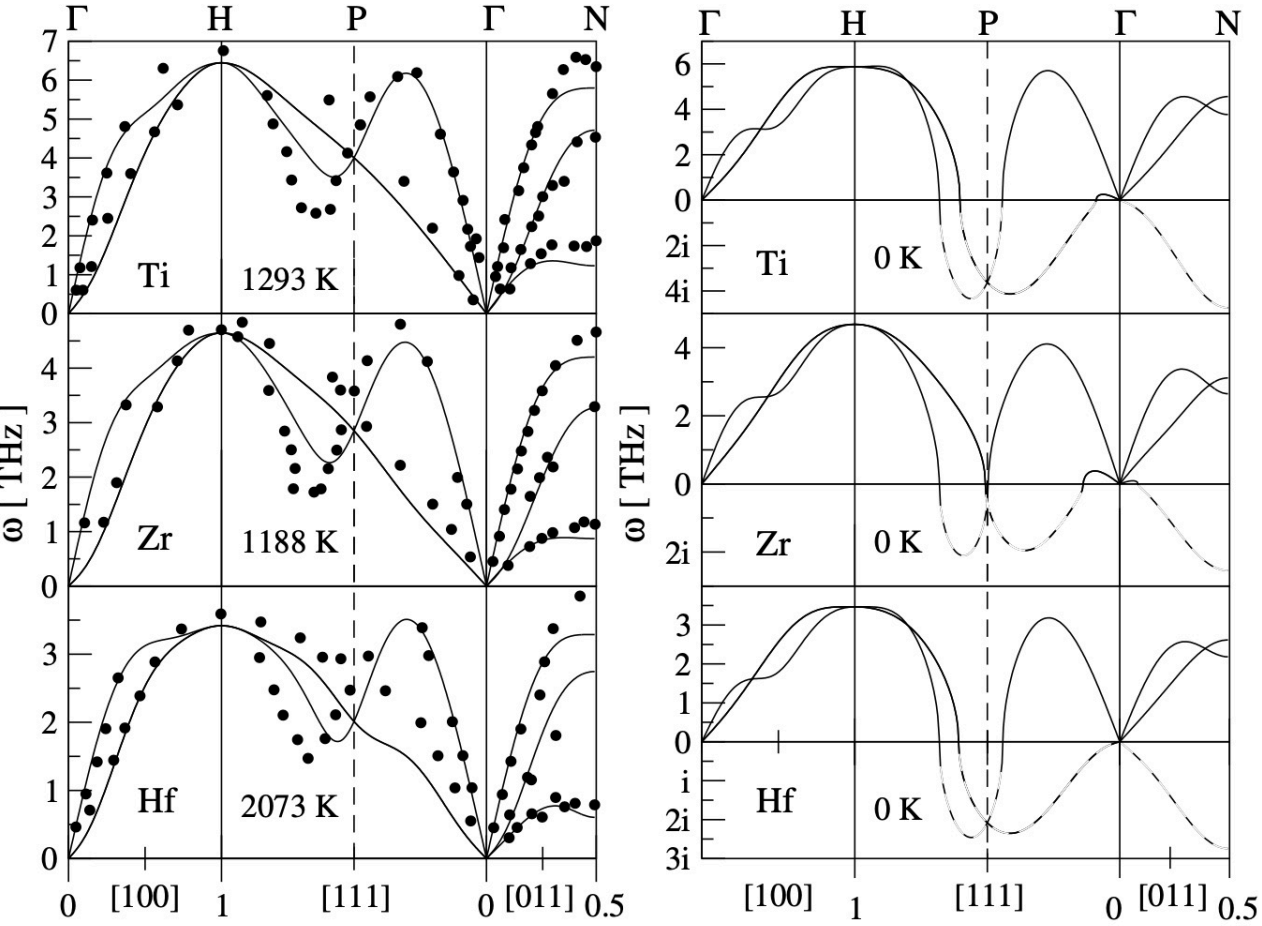
$$F = \int_0^{\infty} g(\omega) \left[\frac{\hbar\omega}{2} + \frac{1}{\beta} \ln\left(1 - e^{-\beta\hbar\omega}\right) \right] d\omega$$

($g(\omega)$: DOS; the bracketed term: QHA)

Convergence



Phonons



bcc phase of Ti, Zr, Hf: stable at $T > 0$ K

Phase transition

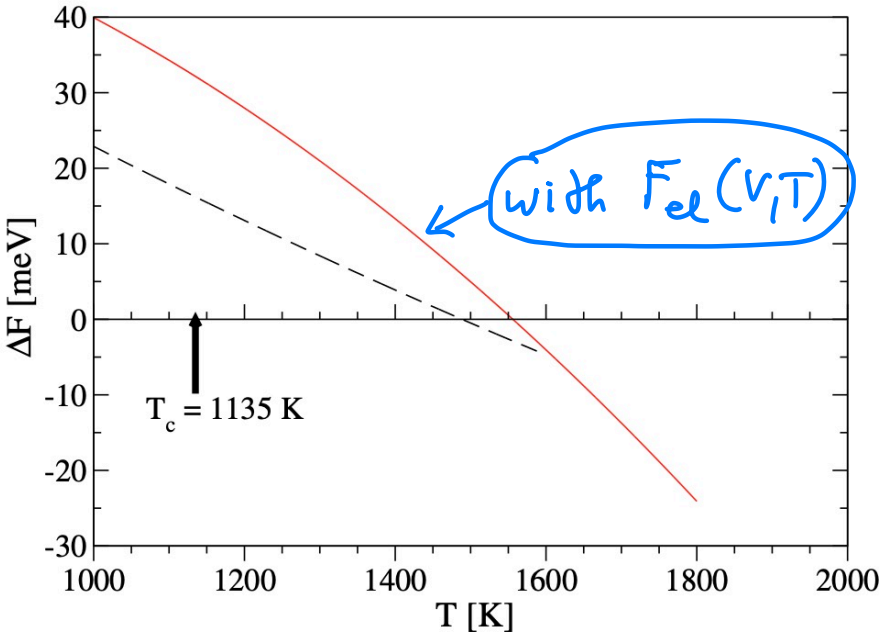
hcp (α) — 1135 K — bcc (β) — T

4x4x4 – bcc

4x4x3 – hcp, c/a ← constant

$F(V,T)$ for both phases

$F = E(V) + f_{ph}(V,T) + F_{el}(V,T)$



T-dependent Effective Potential (TDEP) method

PHYSICAL REVIEW B **84**, 180301(R) (2011)

Lattice dynamics of anharmonic solids from first principles

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(Received 10 August 2011; revised manuscript received 25 October 2011; published 14 November 2011)

PHYSICAL REVIEW B **87**, 104111 (2013)

Temperature dependent effective potential method for accurate free energy calculations of solids

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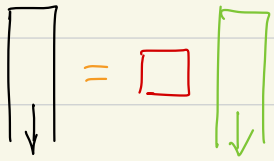
(Received 10 December 2012; published 25 March 2013)

- ab initio
- includes anharmonicity
- finite T
- can be extended to any lattices (e.g. non cubic)

- $U(t) = U_0(T) + \frac{1}{2} u_t^T \Phi u_t$ ← a model PE
  - u_t → displacements
  - Φ → force constant matrix

- NPT first
- NVT next

MD (NVT): u_t and forces f_t $\Rightarrow$ $f_t = -\Phi u_t$



- The "best" least square fit to Φ:

$$\min_{\Phi} \Delta F = \frac{1}{N_t} \sum_t \left| F_t^{MD} - \left(-\Phi u_t^{MD} \right) \right|^2$$

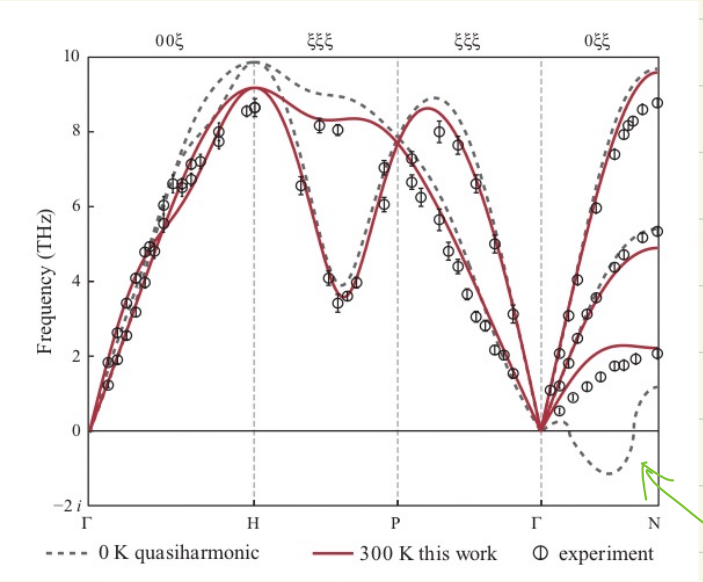
The force constant matrix is obtained via the pseudoinverse: $\Phi = -u^+ f$

- free energy follows from vibrational frequences due to Φ: to avoid double counting!

$$\mathcal{F} = U_0 + \mathcal{F}_{vib}$$ with $$U_0 = \left\langle U_{MD}(t) - \frac{1}{2} \sum_{ij} \Phi_{ij} u_i(t) u_j(t) \right\rangle$$

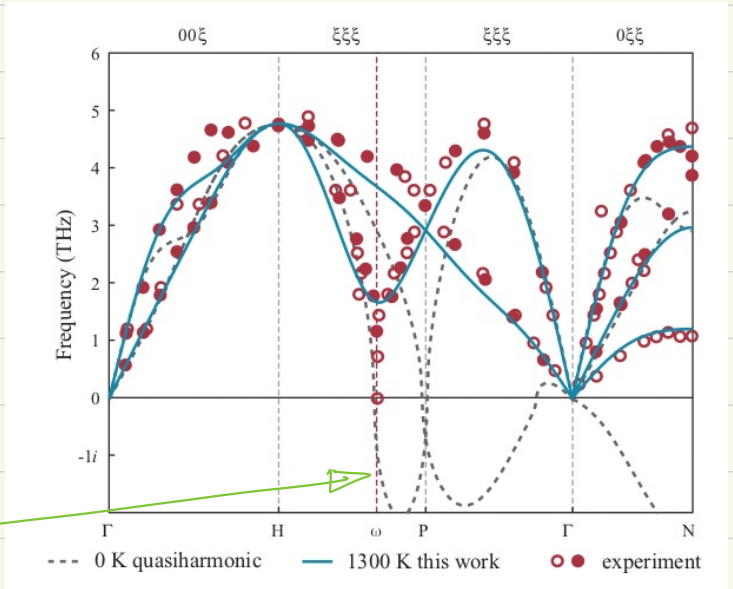
$\mathcal{F}$: free energy

$U_{MD}(t)$: exact PE at time t (T dependent!)



bcc Li

Instability at T=0K



bcc Zr

Self-consistent phonons (SCP)

$$H = \sum_k \frac{\hat{p}_k^2}{2m_k} + V(u) \qquad V(u) = \underbrace{\frac{1}{2} u^T \Phi u}_{\text{HA}} + \underbrace{\sum_{n=3}^{\infty} \sum_{q_1 \dots q_n} V_{q_1 \dots q_n} u_{q_1} \dots u_{q_n}}_{\text{AH}}$$

For periodic crystal:

$$AH = \sum_n V_n, \quad V_n = \frac{1}{n!} \sum_{\{q\}} \Delta(q_1 + \dots + q_n) V(q_1, \dots, q_n) (b_{q_1} + b^+_{-q_1}) \dots (b_{q_n} + b^+_{-q_n})$$

$q \equiv (q_j)$

Use many-body perturbation theory. Define the phonon GF:

$$D_{kk'}(\tau, \tau') = -\frac{i}{\hbar} \left[\langle \hat{T} \varrho_k(\tau) \varrho_{k'}(\tau') \rangle - \langle \varrho_k(\tau) \rangle \langle \varrho_{k'}(\tau') \rangle \right], \quad \underbrace{\varrho_k = \sqrt{m_k} u_k}_{\text{massless displ.}}$$

It satisfies the Dyson equation:

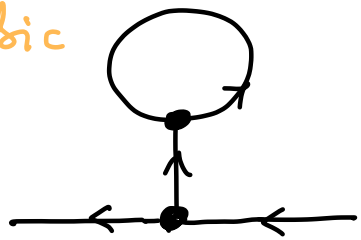
$$D(\tau_1, \tau') = D^0(\tau_1, \tau') + \int d\tau_1 d\tau_2 \, D^0(\tau_1, \tau_1) \underbrace{\Sigma(\tau_1, \tau_2)}_{\text{self-energy}} D(\tau_2, \tau')$$

D: full GF; D^0: HGF

Self-energy $\Sigma \equiv \Sigma[D]$ Needs to be calculated self-consistently.

Examples of cubic & quartic diagrams:

cubic



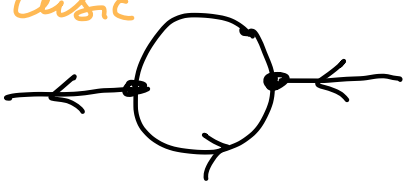
"tadpole"

$$\Sigma(q) = -\frac{1}{\hbar}\sum_{k_j} V(-q,q,0_j)\,V(0_j,k,-k)\,\frac{2n_{k_j}+1}{\omega_{0j}}$$

Bose

It is real → gives the AH shift of ω_q

cubic

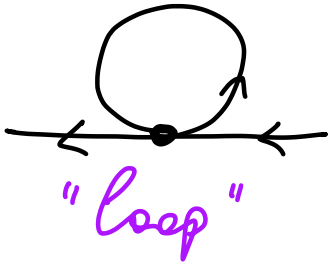


"bubble"

$$\Sigma(q,\omega) = \frac{1}{2\hbar}\sum_{q_1 q_2}\sum_{\pm} |V(-q,q_1,q_2)|^2\left[\frac{n_1+n_2+1}{\pm\omega^+ + \omega_{q_1}+\omega_{q_2}} - \frac{n_1-n_2}{\pm\omega^+ + \omega_{q_1}-\omega_{q_2}}\right]$$

It is imaginary → accounts for phonon's lifetime via $\mathrm{Im}\,\Sigma(q,\omega)$

quartic



"loop"

$$\Sigma(q) = -\sum_{q_1} V(q,-q,q_1,-q_1)\,\frac{2n_1+1}{2}$$

Also real → shift

The renormalised phonons are found from (mapping to a fictitious harmonic system)

$$\det\left[D^r(q,\omega)^{-1} - \Sigma(q,\omega)\right] = 0$$

- ## Calculation of IFCs

Taylor method: $V(u) = \frac{1}{2} u^T \Phi u + \sum_{n=3}^{N} \sum_{q_1 \dots q_n} \Phi_{q_1 \dots q_n} u_{q_1} \dots u_{q_n}$

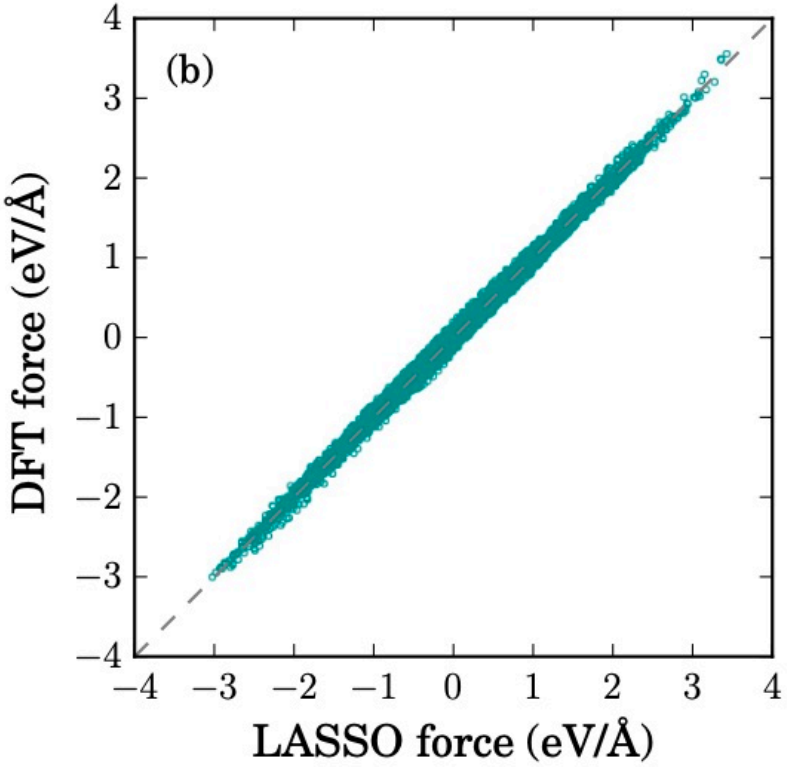
gives the atomic forces $f(u) = -\partial V(u)/\partial u$

The unknown coefficients $\Phi_{q_1 \dots q_n}$ are obtained from DFT forces using either the pseudoinverse : $\boxed{f = \Phi u}$, $\boxed{\Phi = u^+ f}$

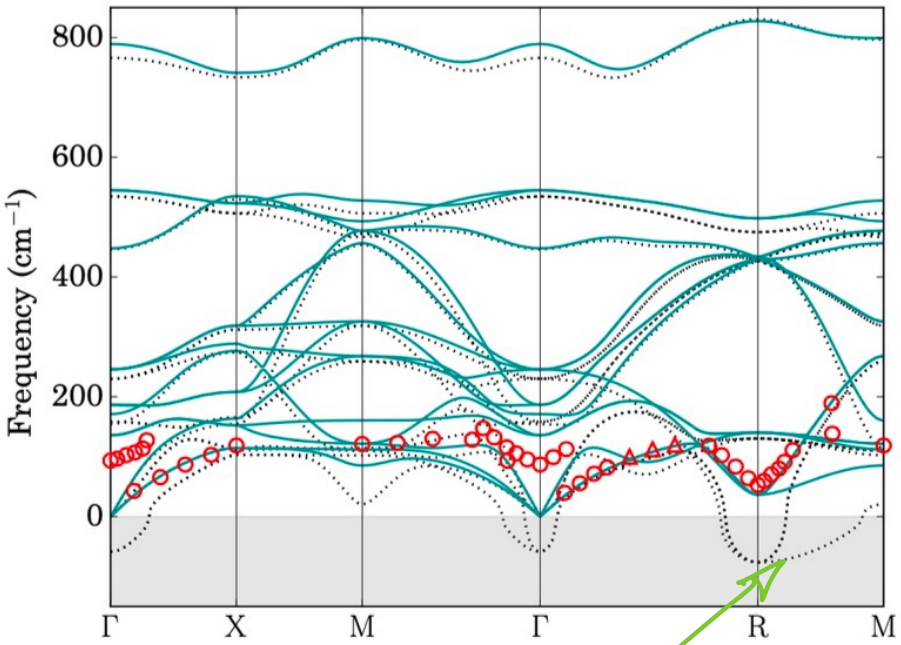
[equivalent to solving the least-square problem $\min_{\Phi} \| \Phi u - f \|$] or advanced regression algorithm (LASSO)

$\min_{\Phi} \| \Phi u - f \| + \lambda \| \Phi \|$ (to avoid overfitting)

λ → select the best using a testing set



Renormalised Phonons Ω_q



high T phase
of perovskite $SrTiO_3$

Only <u>bubble</u> diagram was used (self-consistently)

PRB <u>92</u> 054301 (2015)

Lattice Thermal Conductivity

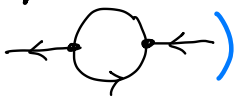
$$\kappa^L_{\alpha\beta}(T) = \frac{1}{v_c N}\sum_q c_q(T)\, v_\alpha(q) v_\beta(q) \tau_q$$

BTE RTA

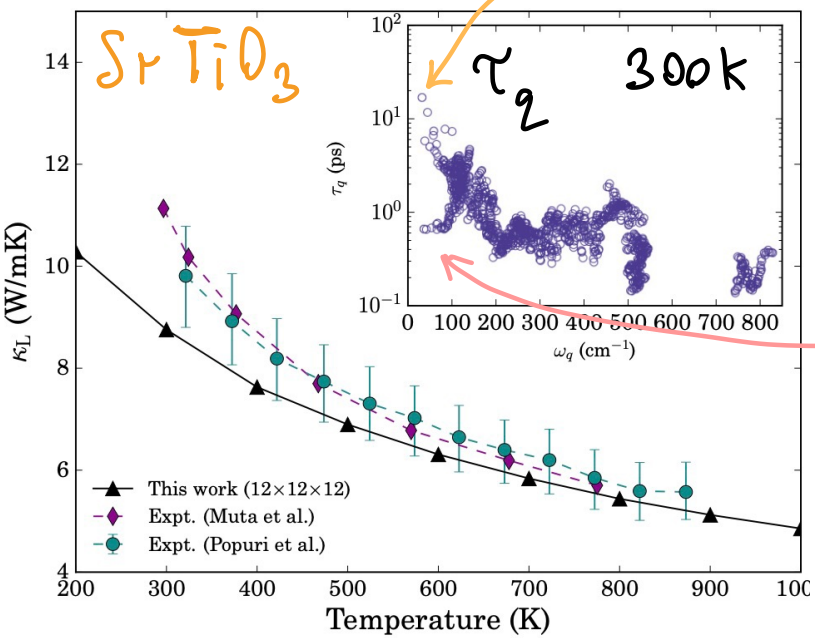
$v_\alpha(q) = \partial\Omega_q / \partial q_\alpha$ group velocity

Phonon lifetime $\frac{1}{\tau_q} = 2\Gamma_q(\Omega_q) \sim \mathrm{Im}\,\Sigma_q(\Omega_q)$

$$\Gamma_q(\omega) = \frac{\pi}{2N}\sum_{q'q''} \frac{\hbar|V(-q,q',q'')|^2}{8\Omega_q\Omega_{q'}\Omega_{q''}}\Big[(n_{q'}+n_{q''}+1)\times\delta(\omega-\Omega_{q'}-\Omega_{q''}) - 2(n_{q'}-n_{q''})\delta(\omega-\Omega_{q'}+\Omega_{q''})\Big]$$

(cubic bubble )

acoustic modes ($\tau_q \sim \omega^{-2}$)



optical around R point (severe AH)

Stochastic Self-Consistent Harmonic Approximation (SSCHA)

- **Free energy** $F_H[\rho_H] = -\frac{1}{\beta}\ln Z = \underbrace{\mathrm{Tr}(\rho_H H)}_{U=\langle H\rangle_{\rho_H}} - \frac{1}{\beta}\underbrace{\mathrm{Tr}(\rho_H \ln \rho_H)}_{S=\langle k_B \ln \rho_H\rangle_{\rho_H}} \equiv U - TS$

$\rho_H = \frac{1}{Z} e^{-\beta H}$, $Z = \mathrm{Tr}(e^{-\beta H})$ ← DM ($\mu = 0$ for phonons)

$H = K + V(R)$ ← exact Hamiltonian for atoms (BO)

It is a complicated quantity to calculate due to difficult $V(R)$

[can be done via diagrammatics if anharmonic terms a weak]

- **Gibbs - Bogoliubov inequality:** $\boxed{F_H[\rho_H] \le F_H[\rho_{\mathcal{H}}]}$, $\forall\ \mathcal{H} = K + \underbrace{\mathcal{V}}_{\text{trial Hamiltonian}}$

$$\tilde{F}[\rho_{\mathcal{H}}] \equiv F_H[\rho_{\mathcal{H}}] = \underbrace{F_{\mathcal{H}}[\rho_{\mathcal{H}}]}_{\mathrm{Tr}(\rho_{\mathcal{H}}\mathcal{H}) - \frac{1}{\beta}\mathrm{Tr}(\rho_{\mathcal{H}}\ln\rho_{\mathcal{H}})} + \int dR\,(V(R) - \mathcal{V}(R))\,\rho_{\mathcal{H}}(R)$$

R - all degrees of freedom (cell, atomic positions)

Main Refs: PRB 89, 064302 (2014); 96, 014111 (2017); J. Phys. Cond. M. 33, 363001 (2021)

Auxiliary Harmonic potential $\mathcal{V}$ ← the main (and clever) idea!

$$\mathcal{V} = \frac{1}{2}\sum_{ab} \Phi_{ab} u_a u_b \,, \quad u_a = R_a - R_{a} \,, \quad R_a = \langle R_a \rangle_{\tilde{\rho}}$$

$$\rho_{ge} \equiv \tilde{\rho} = \frac{1}{\mathcal{Z}} e^{-\beta \mathcal{H}} \,, \quad \mathcal{Z} = \mathrm{Tr}\left(e^{-\beta \mathcal{H}}\right)$$

Why is it clever?

1. $$F_{ge}[\tilde{\rho}] = \sum_{\mu} \left(\frac{\hbar\omega_\mu}{2} + \frac{1}{\beta} \ln\left(1 - e^{-\beta\hbar\omega_\mu}\right) \right)$$ ← harmonic

$$\mathcal{D} = M^{-1/2} \Phi M^{-1/2} \,, \quad \mathcal{D}\, e_\mu = \omega_\mu^2 e_\mu$$

2. DM $\tilde{\rho}$ is available analytically in the coordinate representation:

$$\langle u|\tilde{\rho}|u\rangle = \frac{1}{\sqrt{\det(2\pi\Psi)}} \exp\left(-\frac{1}{2}\sum_{ab} u_a \Psi^{-1}_{ab} u_b\right), \quad \int \langle u|\tilde{\rho}|u\rangle \, du = 1$$

$$\Psi_{ab} = \langle u_a u_b \rangle_{\tilde{\rho}} = \frac{\hbar}{2\sqrt{m_a m_b}} \sum_{\mu} \frac{2n_\mu + 1}{\omega_\mu} e_{\mu a} e_{\mu b}$$

$u = \underbrace{R - R_2}_{\text{displacement}}$

It is a multivariable Gaussian!

- The idea is to optimise $\mathcal{F}[\tilde{\rho}]$ with respect to R and Φ.
- The derivation is based on transferring all variables from $\tilde{\rho}$ into the observable that is to be averaged:

a product of Gaussians

$$\langle \mathcal{O}(R) \rangle_{\tilde{\rho}} = \int \mathcal{O}(R+u) \langle u|\tilde{\rho}|u\rangle \, du = \int \mathcal{O}(R+Ly) \left[\prod_\lambda \frac{e^{-\frac{1}{2}y_\lambda^2}}{\sqrt{2\pi}} dy_\lambda \right]$$

$$u_a = \sum_\lambda L_{a\lambda} y_\lambda \,, \quad L_{a\lambda} = \frac{\xi_\lambda}{\sqrt{m_a}} e_{\lambda a} \,, \quad \xi_\lambda = \frac{\hbar}{2\omega_\lambda}(1+2n_\lambda)$$

$$\hookrightarrow [e^{\beta\hbar\omega_\lambda} - 1]^{-1}$$

- Then, the required gradients are given by averages:

$$\frac{\partial \mathcal{F}}{\partial R_a} = \int \left(\frac{\partial V}{\partial R_a} \right)_R \langle u|\tilde{\rho}|u\rangle \, du \equiv \left\langle \frac{\partial V}{\partial R_a} \right\rangle_{\tilde{\rho}}$$

atomic force

$$\frac{\partial \mathcal{F}}{\partial \Phi_{ab}} = \frac{1}{2} \sum_{cd} \left\{ \left\langle \frac{\partial^2 V}{\partial R_c \partial R_d} \right\rangle_{\tilde{\rho}} - \Phi_{cd} \right\} \Lambda_{abcd} \,,$$

average Hessian

actual expressions are somewhat different for precision

where

$$\Lambda_{abcd} = \sum_{\nu\mu} A_{\mu\nu} \frac{e_{\nu a}}{\sqrt{m_a}} \frac{e_{\mu b}}{\sqrt{m_b}} \frac{e_{\nu c}}{\sqrt{m_c}} \frac{e_{\mu d}}{\sqrt{m_d}} \,, \quad A_{\mu\nu} = \frac{\hbar}{2\omega_\mu \omega_\nu} \begin{cases} \dfrac{dn_\nu}{d\omega_\nu} - \dfrac{2n_\nu+1}{2\omega_\nu} \,, & \omega_\nu = \omega_\mu \\ \dfrac{n_\mu - n_\nu}{\omega_\mu - \omega_\nu} - \dfrac{n_\mu + n_\nu + 1}{\omega_\mu + \omega_\nu} \,, & \omega_\nu \neq \omega_\mu \end{cases}$$

depends on $\{e_\nu, \omega_\nu\}$ from Φ.

- The average Hessian can also be expressed via averages of atomic forces:

$$\left\langle \frac{\partial^2 V}{\partial R_c \partial R_d} \right\rangle_{\tilde{\rho}} = \sum_m \psi_{mc}^{-1} \left\langle u_m \underbrace{\frac{\partial V}{\partial R_d}}_{\text{atomic force}} \right\rangle_{\tilde{\rho}}$$

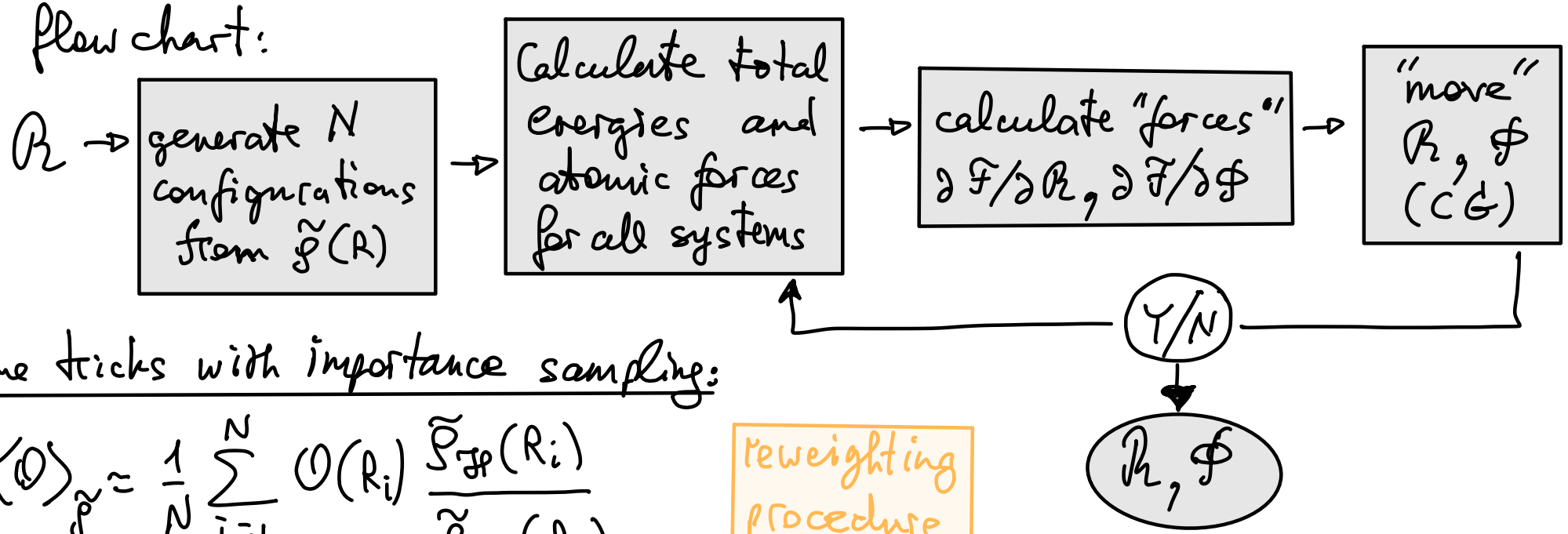
actual expressions are somewhat different for precision

- Averages are calculated using MC method based on the Gaussian distribution:

$$\langle O(R) \rangle_{\tilde{\rho}} = \int O(R)\,\tilde{\rho}(R)\,dR \simeq \frac{1}{N} \sum_{i=1}^{N} O(R_i)$$

R_i → sampled using $\tilde{\rho}(R) = \langle u | \tilde{\rho} | u \rangle$ (Gaussian!)

- The flowchart:



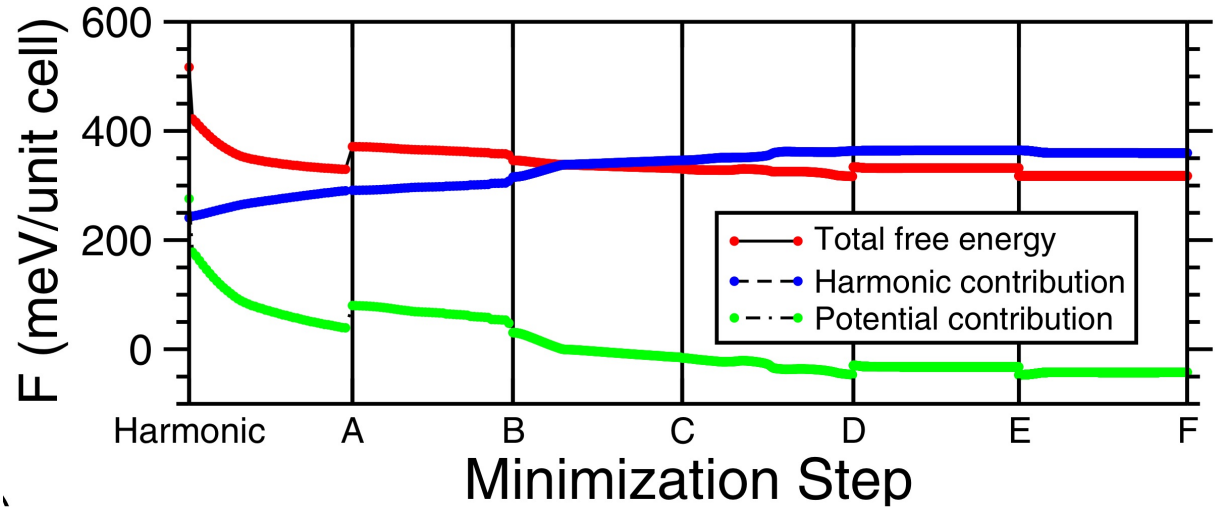
- Some tricks with importance sampling:

$$\langle O \rangle_{\tilde{\rho}} \simeq \frac{1}{N} \sum_{i=1}^{N} O(R_i) \frac{\tilde{\rho}_{\mathrm{FF}}(R_i)}{\tilde{\rho}_{\mathrm{FF}_0}(R_i)}$$

reweighting procedure

So no new configurations are needed! The same for different T.

- **PtH** at $P = 100$ GPa, $T = 0$ K; hcp structure ($a = 5.12$ Å, $c = 8.65$ Å)



$\tilde{F} = F_{\tilde{\rho}} + \int dR \, (V(R) - \mathcal{V}(R)) \, \rho_{\tilde{\rho}}(R)$

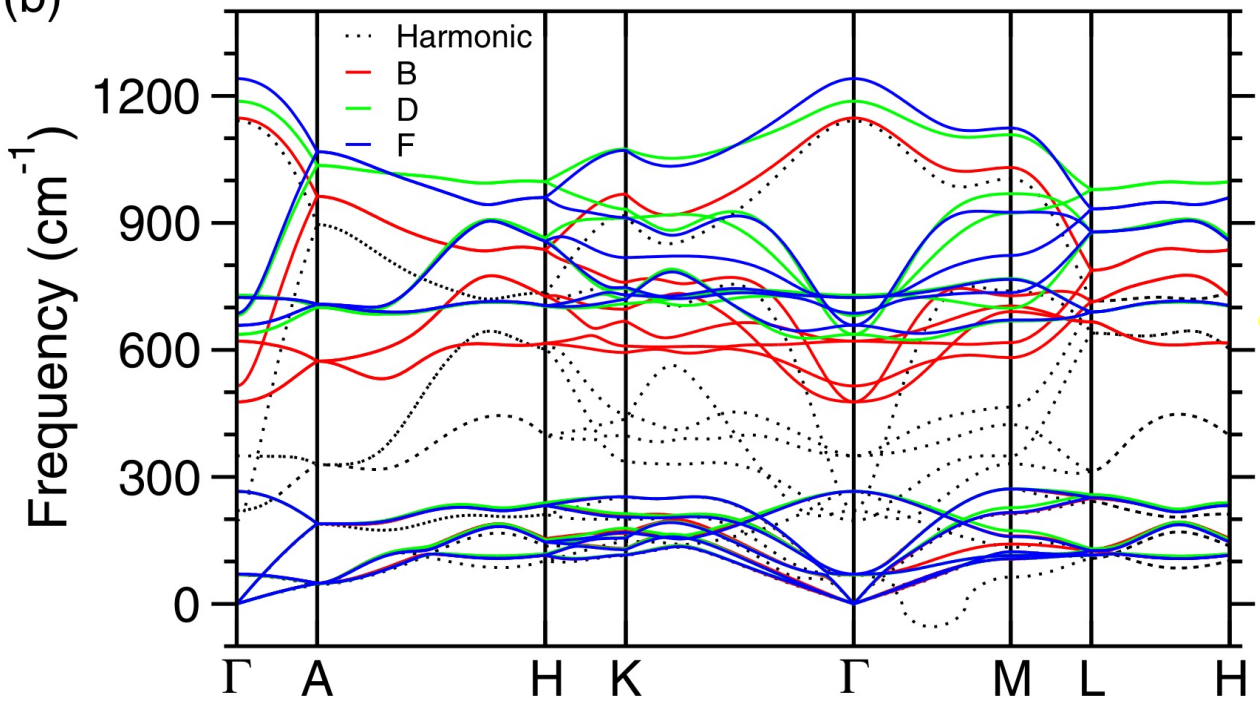
Both contributions are important

Started from 20 configurations, sampled from $\rho_{\tilde{\rho}_0}(R)$.

A – new configurations.

E → added 380 more to improve precision → 400 in all.

(b)



- **Phonons** [PRB 89, 064302 (2014)]

from $\Phi = (\Phi_{ab})$ after CG (at the minimum of $\tilde{F}$)

$$\Phi_{cd} = \left\langle \frac{\partial^2 V}{\partial R_c \partial R_d} \right\rangle_{\tilde{\rho}}$$

SCF condition

Imaginary frequencies around Γ disappeared. Shift of optical modes ↑.

- In later studies they changed their view: **phonons from the Hessian of $\mathcal{F}(R)$:**

PRB 96 014111 (2017)

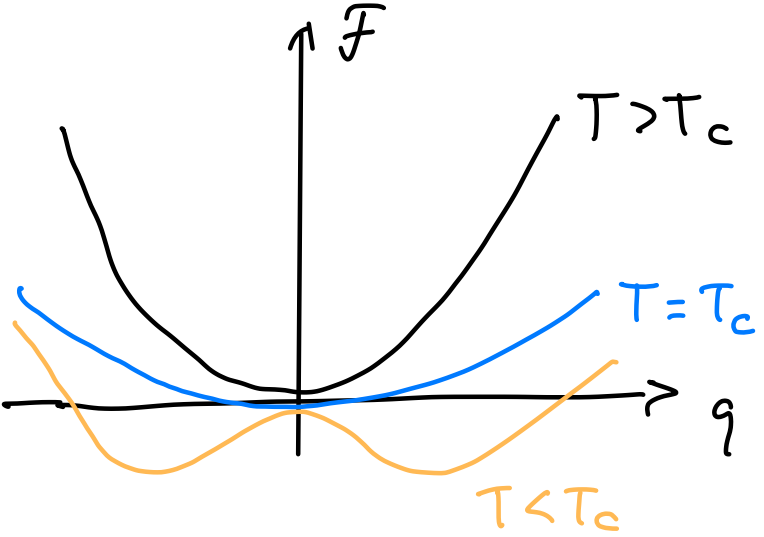
$$\frac{\partial^2 \mathcal{F}}{\partial R \partial R} = \Phi + \Phi^{(3)} \Lambda \Phi^{(3)} + \Phi^{(3)} \Lambda \textcircled{H} \Lambda \Phi^{(3)}$$

$$\Phi^{(3)} \equiv (\Phi_{abc}), \quad \Phi_{abc} = \left\langle \frac{\partial^3 V}{\partial R_a \partial R_b \partial R_c} \right\rangle_{\tilde{\rho}}$$

$$\textcircled{H} = \left[\mathbb{1} - \Phi^{(4)} \Lambda \right]^{-1} \Phi^{(4)}, \quad \Phi^{(4)} = (\Phi_{abcd}), \quad \Phi_{abcd} = \left\langle \frac{\partial^4 V}{\partial R_a \partial R_b \partial R_c \partial R_d} \right\rangle_{\tilde{\rho}}$$

Here all are matrices w.r.t. double indices: $\Lambda_{abcd} \equiv \Lambda_{AB}$, $A=(ab)$, $B=(cd)$

- 2nd order phase transition



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

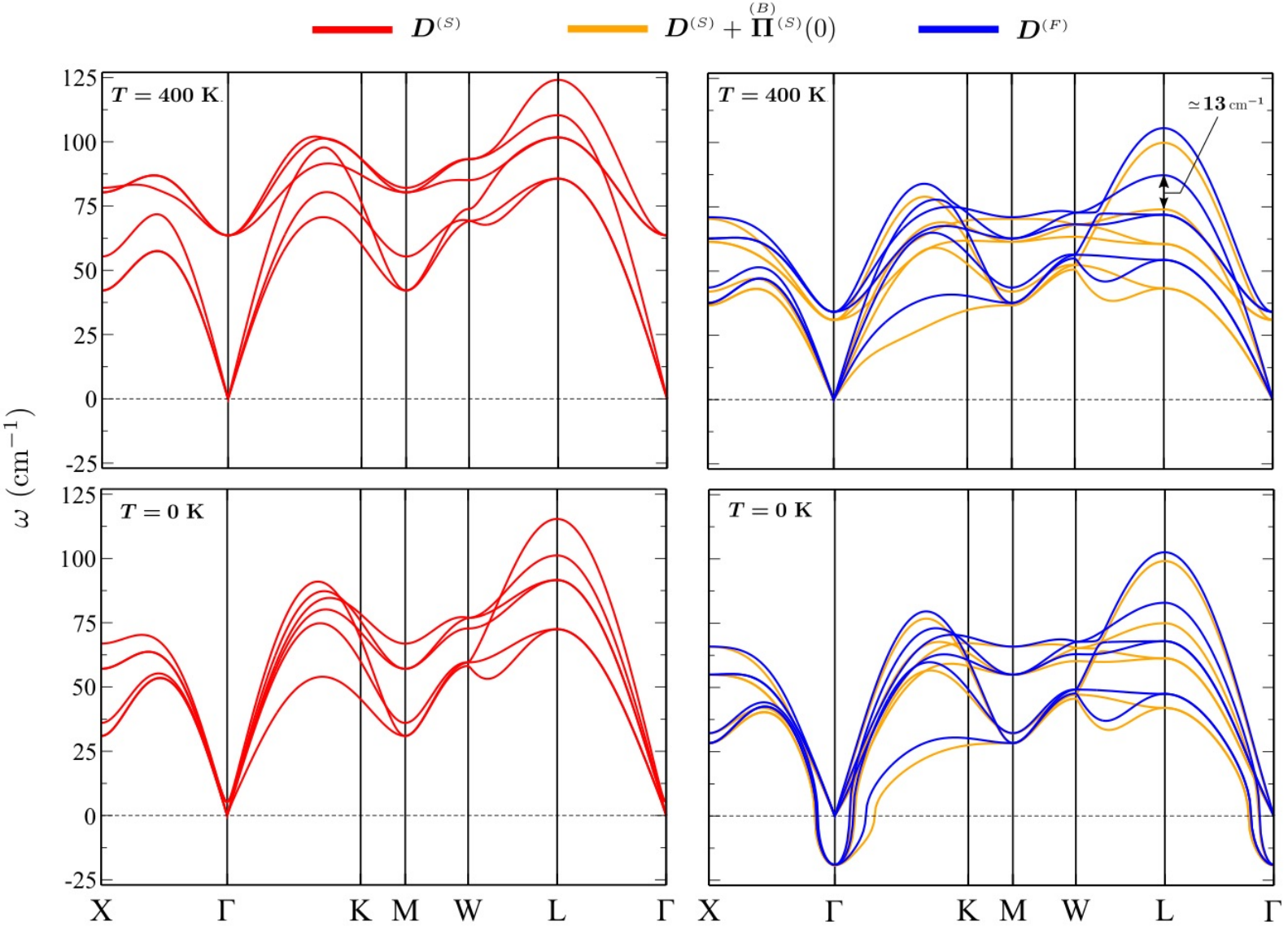
There must be a soft mode!

Φ_{abc}, Φ_{abcd} – via R_i forces in $\langle \dots \rangle_{\tilde{\rho}}$

$$\Phi_{abc} = -\sum_{pq} \Psi^{-1}_{ap} \Psi^{-1}_{bq} \langle u_p u_q ff_c \rangle_{\tilde{\rho}}$$

$$\Phi_{abcd} = -\sum_{pqr} \Psi^{-1}_{ap} \Psi^{-1}_{bq} \Psi^{-1}_{cr} \langle u_p u_q u_r ff_c \rangle_{\tilde{\rho}}$$

ff_c – basically, an atomic force.



$T > T_c$

$T < T_c$

using Φ_{ab} only (positive definite)

using $\dfrac{\partial^2 F}{\partial R \partial R}$

there are imaginary phonons $T < T_c$

Crystal structure prediction

Homogeneous strain: $R \to R' = (\mathbb{1} + \varepsilon) R$

$$F = \mathcal{F} + \langle V(R) - \mathcal{V}(R) \rangle$$

$$\frac{\partial F}{\partial \varepsilon} = \left\langle \frac{\partial V}{\partial \varepsilon} \right\rangle - \left\langle \frac{\partial \mathcal{V}}{\partial \varepsilon} \right\rangle$$

→ ordinary stress

contribution due to AH

Stress tensor:

$$\sigma_{\alpha\beta} = -\frac{1}{v_c} \frac{\partial F}{\partial \varepsilon_{\alpha\beta}}$$

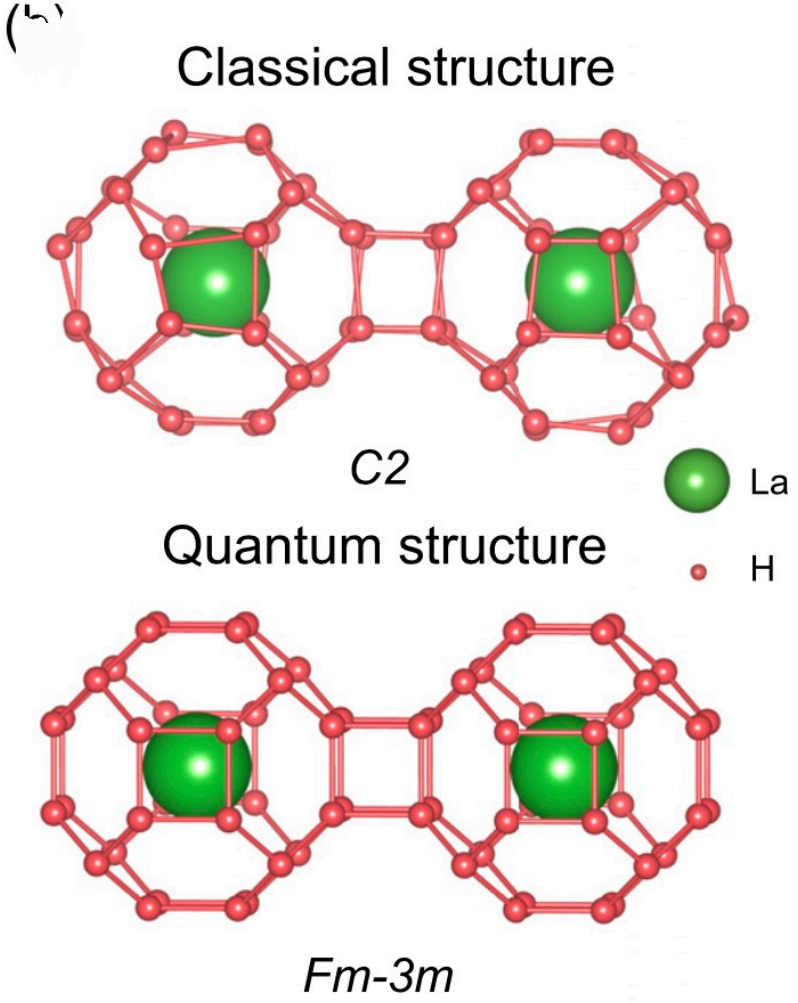
$$= \sigma_{\alpha\beta}^{(BO)} - \frac{1}{2v_c} \sum_a \left(u_{a\alpha} f_{a\beta} + u_{a\beta} f_{a\alpha} \right)$$

$\sigma_{\alpha\beta}^{(BO)}$: DFT code

$\frac{1}{2v_c} \sum_a \left(u_{a\alpha} f_{a\beta} + u_{a\beta} f_{a\alpha} \right)$: due to AH + quantum

$$f_{a\alpha} = -\sum_{b\beta} \Phi_{a\alpha, b\beta} u_{b\beta}$$ – fictitious force

LaH_{10}



C2 – minimises V

Fm3m – minimises F

J. Phys. Cond. M. 33 363001 (21)