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Anharmonic phonon theory in condensed matter physics *with applications based on DFT*

Terumasa Tadano

National Institute for Materials Science, Tsukuba, Japan

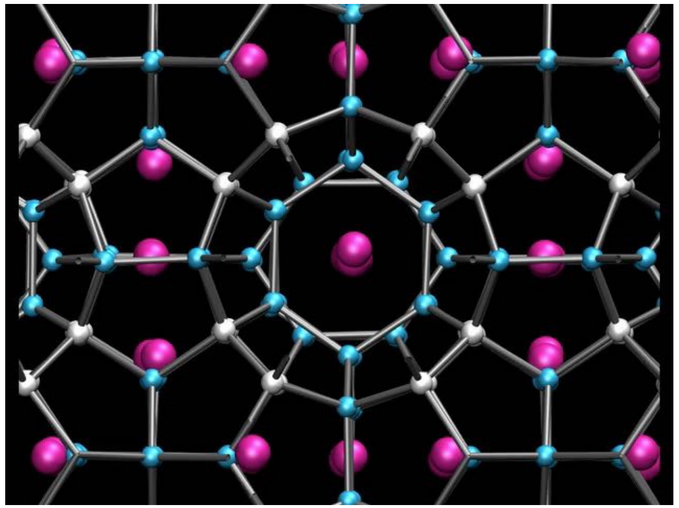
E-mail: TADANO.Terumasa@nims.go.jp

Outline

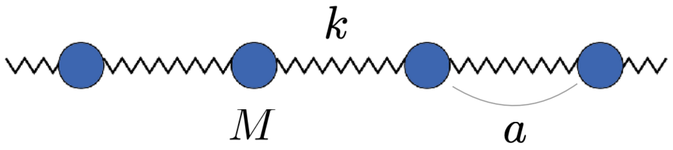
1. Introduction
2. History of anharmonic phonon theory
3. Perturbative expansion method and applications to thermal transport
4. Self-consistent phonon theory and applications to phase transition
5. Summary & outlook

What is phonon?

Quantum description of lattice vibration



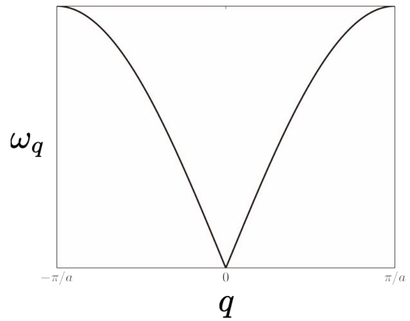
1D chain



Interaction $$V = \sum_i \frac{1}{2} k (u_i - u_{i-1})^2$$

displacement

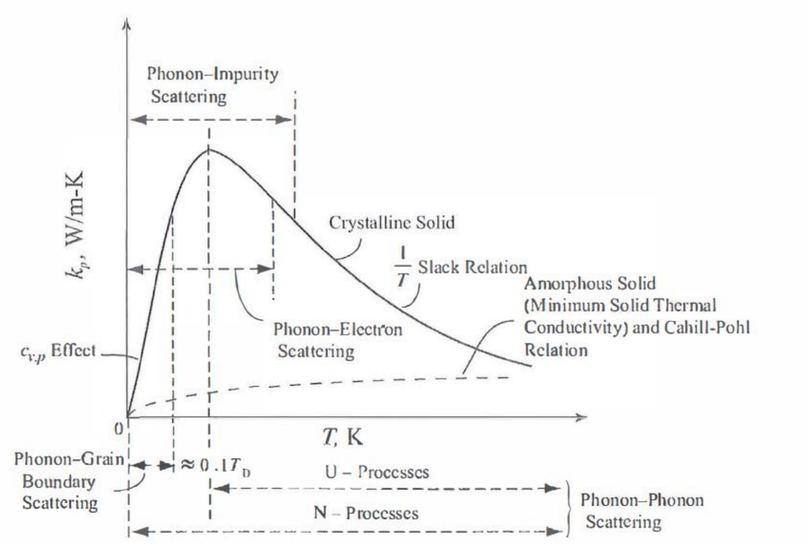
Eq. of motion $$M\ddot{u}_i = -k(2u_i - u_{i-1} - u_{i+1})$$



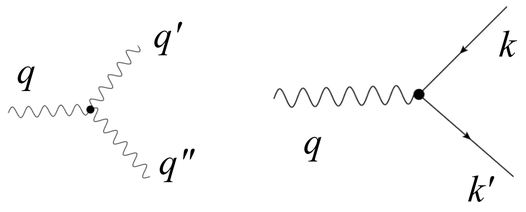
Phonon dispersion (1D)

Why/when is phonon important?

Thermal conductivity



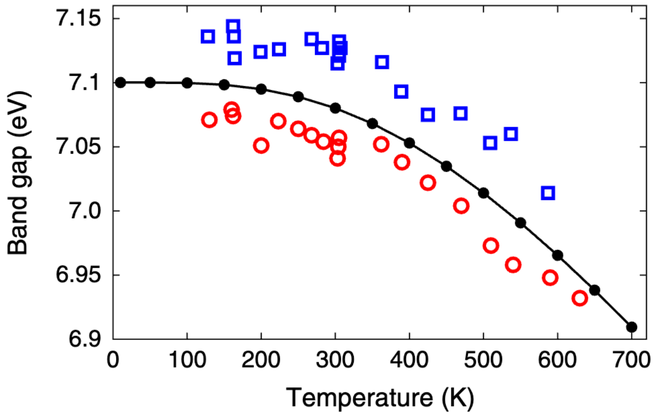
R. Berman. Thermal conduction in Solids.

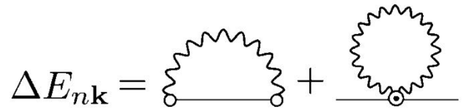


Phonon-phonon cattering

Phonon-electron cattering

Band-gap renormalization

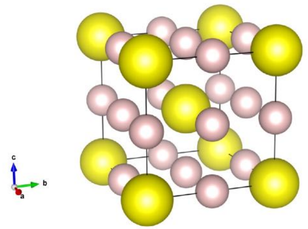




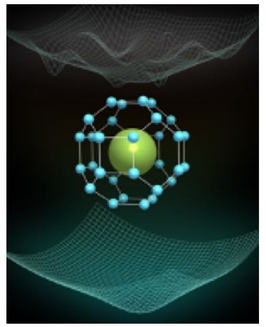
PRL 105, 265501 (2010)

Electron-phonon interaction

Superconductivity



H_3S



LaH_{10}

Other phenomena include

- thermal expansion
- structural phase transition

Non-interacting picture

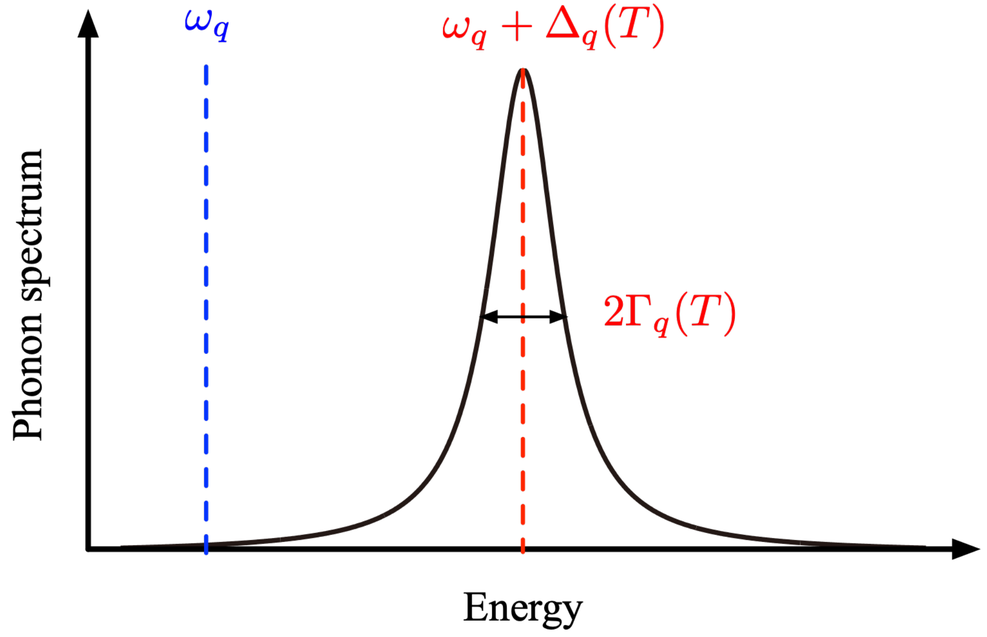
Hamiltonian of non-interacting phonon (harmonic approximation)

$$\hat{H}_0 = \sum_q \hbar\omega_q \left(\hat{b}_q^\dagger \hat{b}_q + \frac{1}{2}\right)$$

✗ Phonon is non-interacting
→ **infinite** lifetime
→ **infinite** thermal conductivity

✗ Phonon is temperature-independent
→ **no** displacive structural phase transition

✗ Phonon is volume-independent
→ **no** thermal expansion



Non-interacting picture

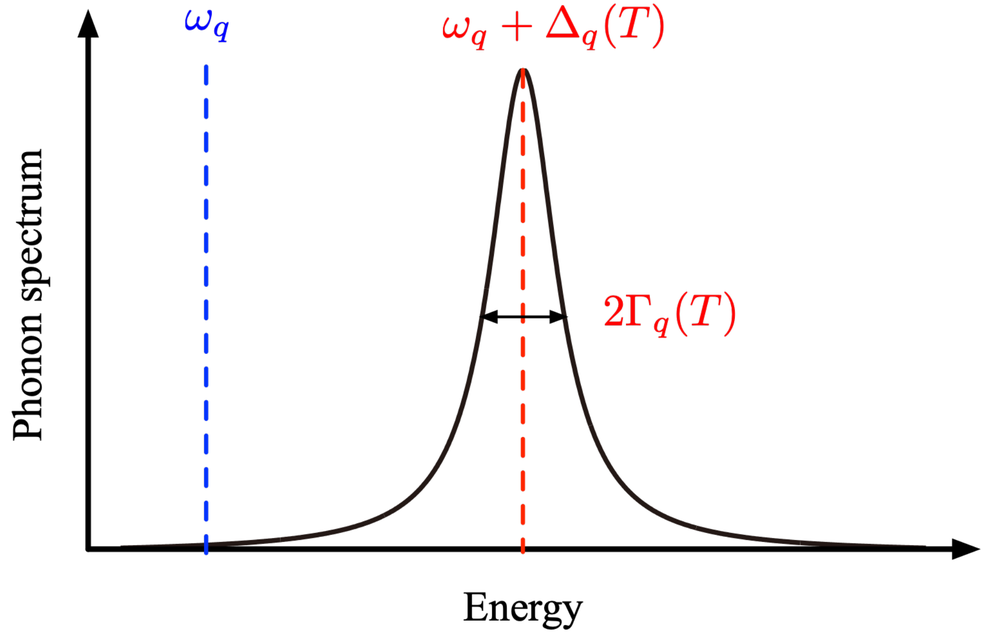
Hamiltonian of non-interacting phonon (quasi-harmonic approximation)

$$\hat{H}_0 = \sum_q \hbar\omega_q(V)\left(\hat{b}_q^\dagger \hat{b}_q + \frac{1}{2}\right)$$

✗ Phonon is non-interacting
→ **infinite** lifetime
→ **infinite** thermal conductivity

✗ Phonon is temperature-independent
→ **no** displacive structural phase transition

✗ Phonon is volume-dependent
→ **finite** thermal expansion



Many-body problem of phonons

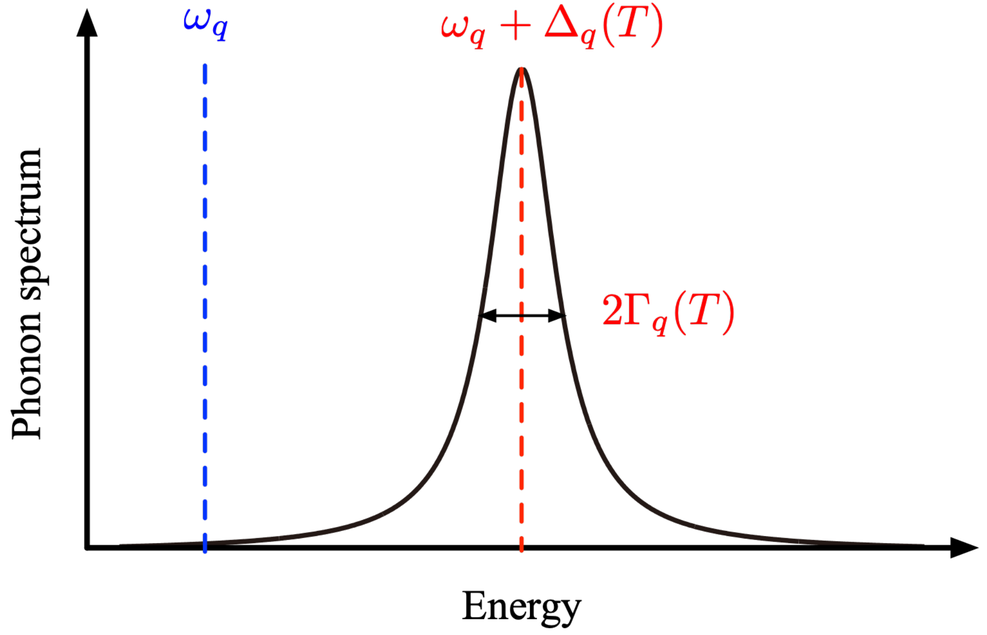
Phonon Hamiltonian with interaction terms (**anharmonicity**)

$$\hat{H} = \sum_q \hbar\omega_q \left(\hat{b}_q^\dagger \hat{b}_q + \frac{1}{2}\right) + \hat{U}_3 + \hat{U}_4 + \cdots$$

✓ Phonon is interacting via anharmonicity
→ finite lifetime
→ finite thermal conductivity

✓ Phonon is volume-dependent
→ finite thermal expansion

✓ Phonon is temperature-dependent
→ explains structural phase transition



How to solve the many-body problem?

$$\hat{H} = \sum_q \hbar\omega_q \left(\hat{b}_q^\dagger \hat{b}_q + \frac{1}{2}\right) + \hat{U}_3 + \hat{U}_4 + \cdots$$

- **Perturbative expansion**

$$\hat{H} = \hat{H}_0 + \hat{U}_3 + \hat{U}_4 + \cdots$$

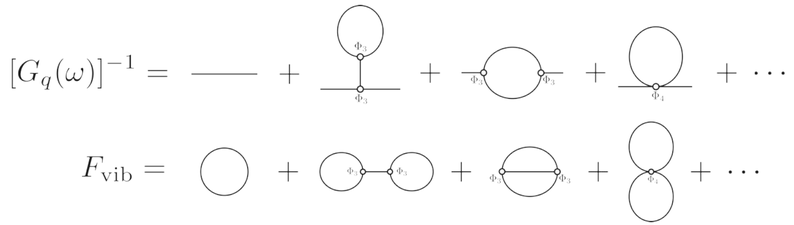
perturbation

Dyson equation

$$[G(\omega)]^{-1} = [G_0(\omega)]^{-1} - \Sigma(\omega)$$

Free energy expansion (cumulant)

$$F = F_0 + F_1 + F_2 + \cdots$$



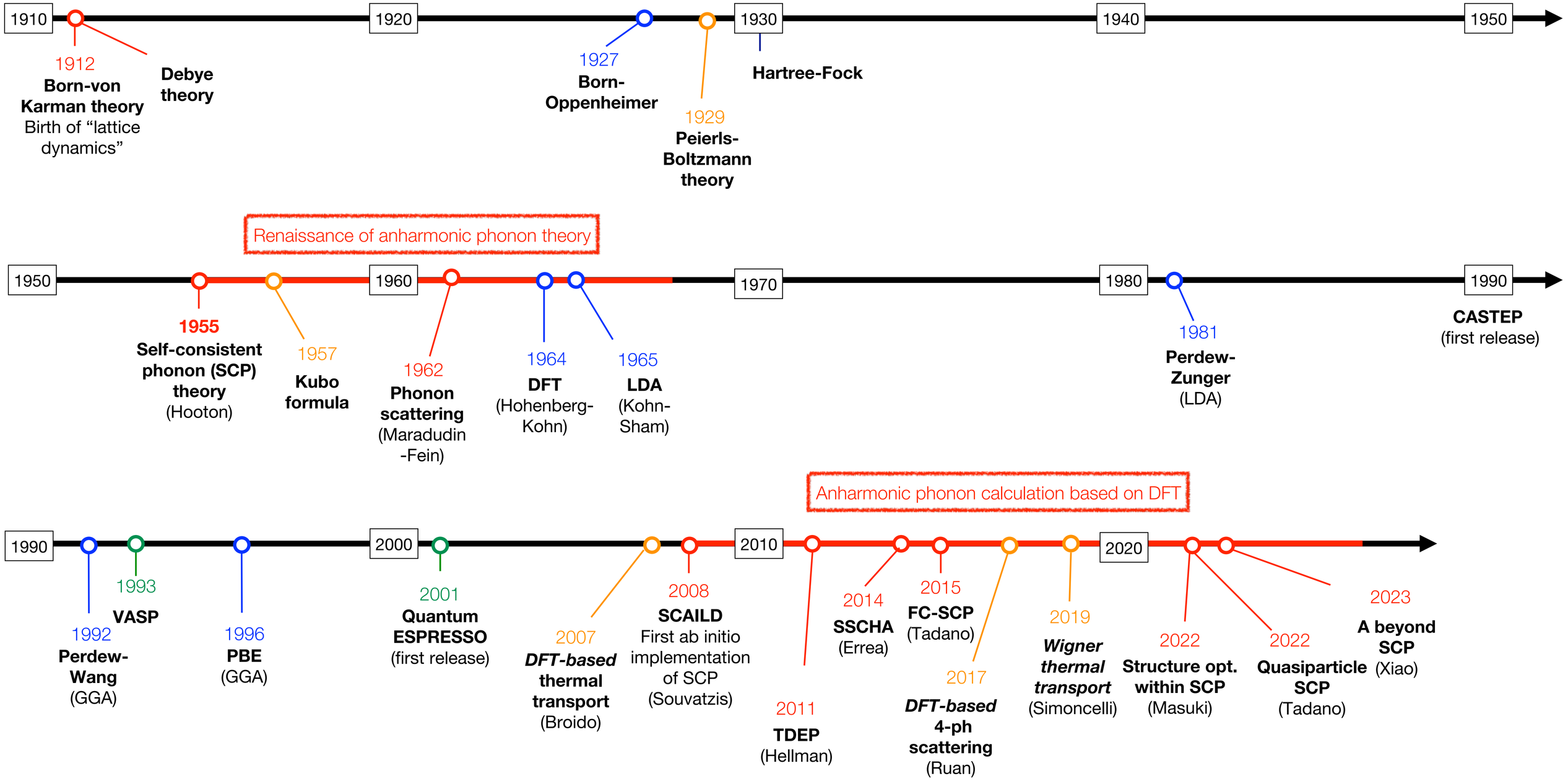
- **Variational approach (self-consistent phonon)**

$$\begin{aligned}\hat{H} &= \hat{H}_0 + \hat{U}_3 + \hat{U}_4 + \cdots \\ &= \hat{\mathcal{H}}_0 + (\hat{H}_0 - \hat{\mathcal{H}}_0 + \hat{U}_3 + \hat{U}_4 + \cdots)\end{aligned}$$

Find a good one-body approximation
based on the free-energy minimization

- Monte Carlo or Molecular dynamics (if classical)

History of many-body phonon theory (and others)



Perturbation theory

$$\hat{H} = \sum_q \hbar\omega_q \left(\hat{b}_q^\dagger \hat{b}_q + \frac{1}{2}\right) + \hat{U}_3 + \hat{U}_4 + \cdots$$

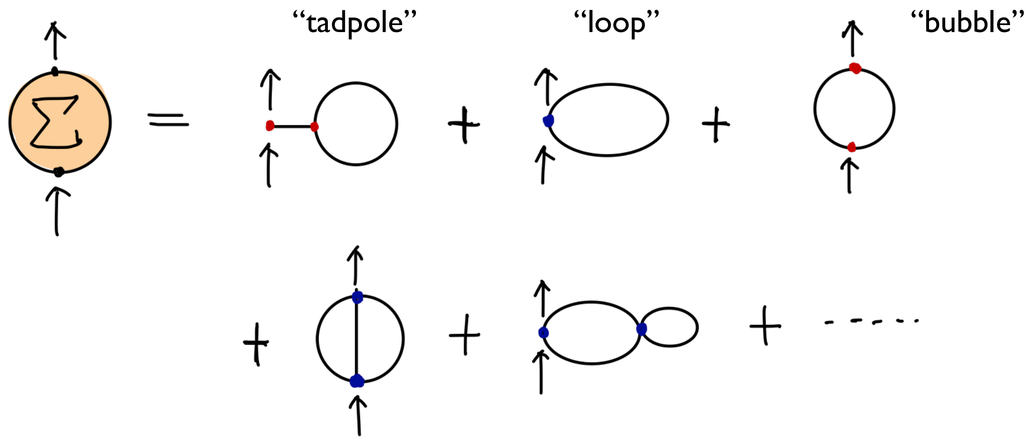
perturbation H'

$$\hat{U}_n = \frac{1}{n!} \sum_q V(q_1; \ldots; q_n) \hat{A}_{q_1} \cdots \hat{A}_{q_n} \qquad \hat{A}_q = \hat{b}_q + \hat{b}_{-q}^\dagger$$

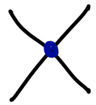
Dressed phonon Green's function

$$G_{q,q'}(\tau) = \left\langle T\tilde{A}_q(\tau)\tilde{A}_{q'}^\dagger(0) \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_0^\beta d\beta_1 \cdots \int_0^\beta d\beta_n \tilde{H}'(\beta_1) \cdots \tilde{H}'(\beta_n) \right\rangle_{0c}$$

Dyson eq. $[G(\omega)]^{-1} = [G_0(\omega)]^{-1} - \Sigma(\omega)$

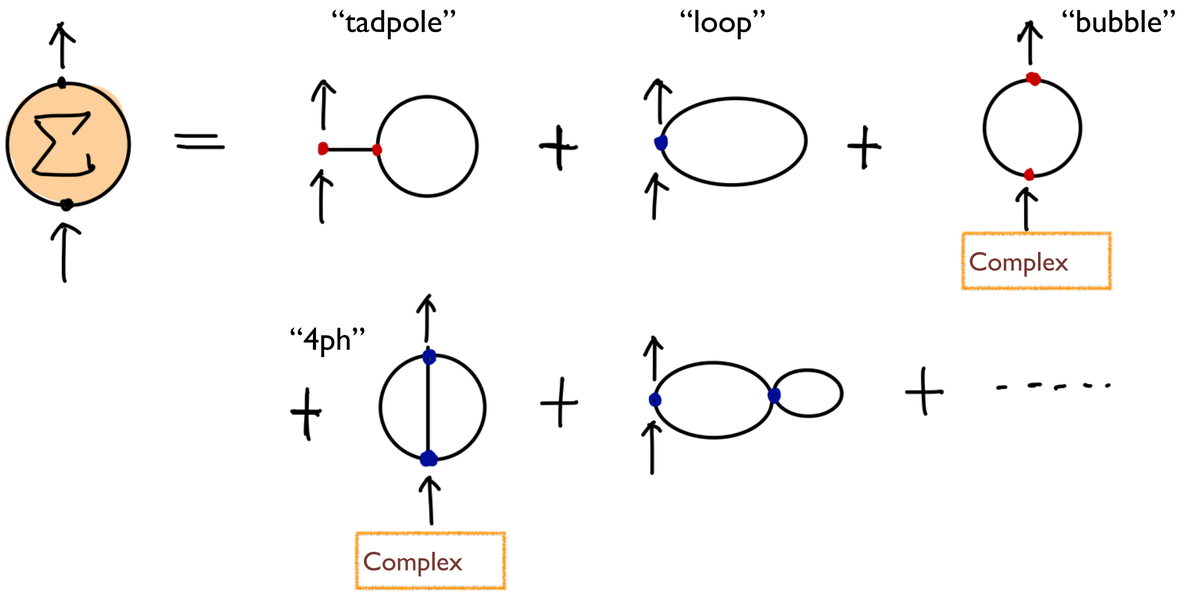


3-phonon interaction (cubic anharmonicity)

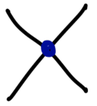


4-phonon interaction (quartic anharmonicity)

Anharmonic self-energies



3-phonon interaction (cubic anharmonicity)



4-phonon interaction (quartic anharmonicity)

$\mathrm{Re}\Sigma_q(\omega)$ ➡ eigen-energy shift

$\mathrm{Im}\Sigma_q(\omega)$ ➡ linewidth (inverse scattering rate)

Bubble self-energy

Phonon scattering by the three-phonon process

Linewidth

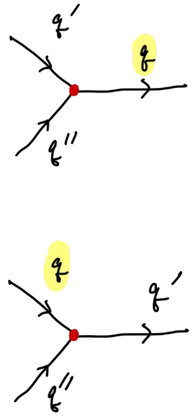
$$\Gamma_q(\omega) = \mathrm{Im}\left[\ \right]$$

$$= \frac{\pi}{2N}\sum_{q',q''}\frac{\hbar|\Phi_3(-q,q',q'')|^2}{8\omega_q\omega_{q'}\omega_{q''}}\Delta(-\boldsymbol{q}+\boldsymbol{q}'+\boldsymbol{q}'')$$

$$\times\left[(n_{q'}+n_{q''}+1)\delta(\omega_q-\omega_{q'}-\omega_{q''})\right.$$

$$\left.-2(n_{q'}-n_{q''})\delta(\omega_q-\omega_{q'}+\omega_{q''})\right]$$

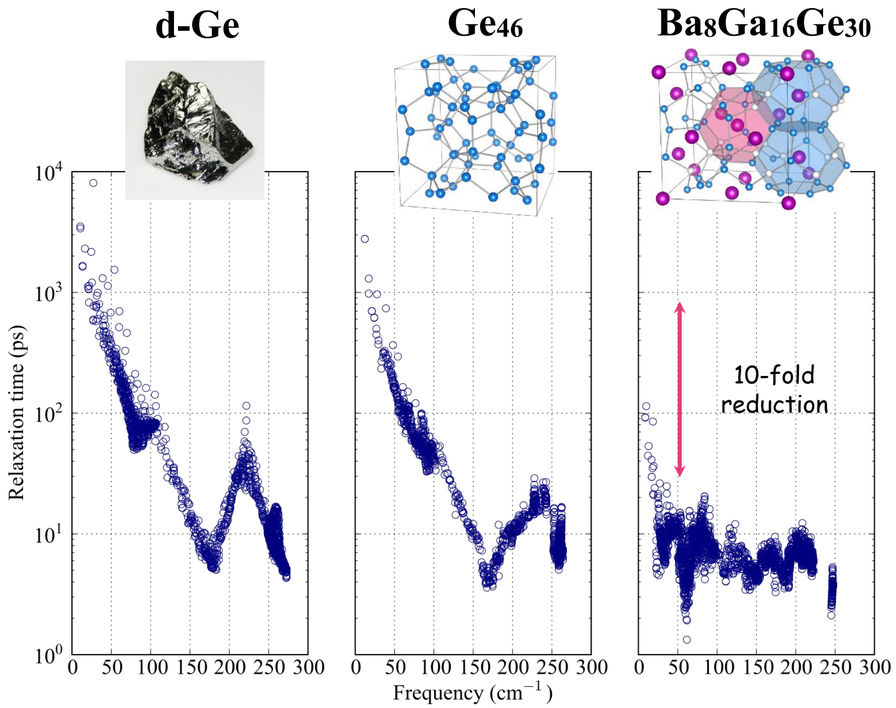
$$kT \gg \hbar\omega$$



Lifetime

$$\tau_q = \frac{\hbar}{2\Gamma_q(\omega_q)}$$

Maradudin and Fein, Phys. Rev. **128**, 2589 (1962).



10x larger phonon-phonon scattering rate of heat-carrying acoustic phonons induced by low-energy rattling guest modes in BGG

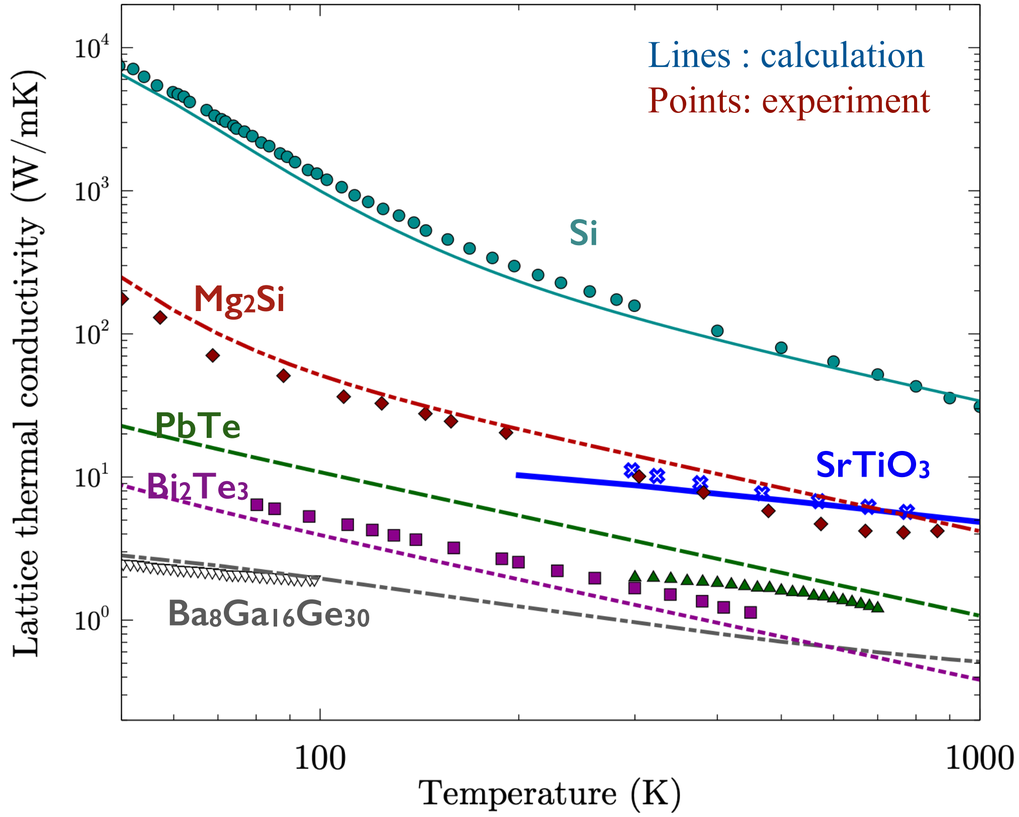
TT, Y. Gohda, and S. Tsuneyuki, PRL **114**, 095501 (2015).

Prediction of thermal conductivity

Boltzmann transport theory

$$\kappa_{\mathrm{ph}}^{\mu\nu} = \frac{1}{N_q V} \sum_q c_q(T) v_q^\mu v_q^\nu \tau_q(T)$$

Lifetime $\tau_q = \dfrac{\hbar}{2\Gamma_q(\omega_q)}$



Good agreement between theory and experiments

useful for computational discovery of novel thermal management materials

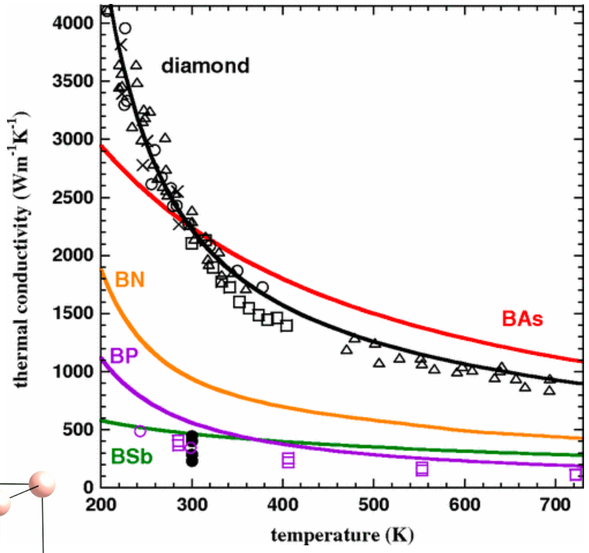
4-phonon scattering

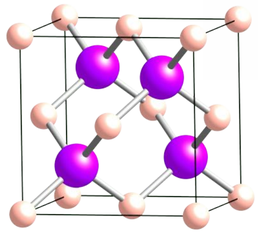
First theoretical prediction

Phys. Rev. Lett. **111**, 025901 (2013)

Boltzmann theory only with 3ph process

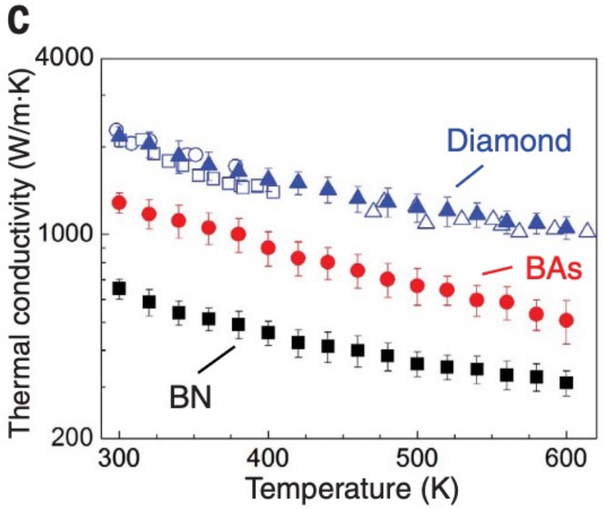
$$\tau_q = \frac{\hbar}{2\Gamma_q^{3\mathrm{ph}}(\omega_q)}$$

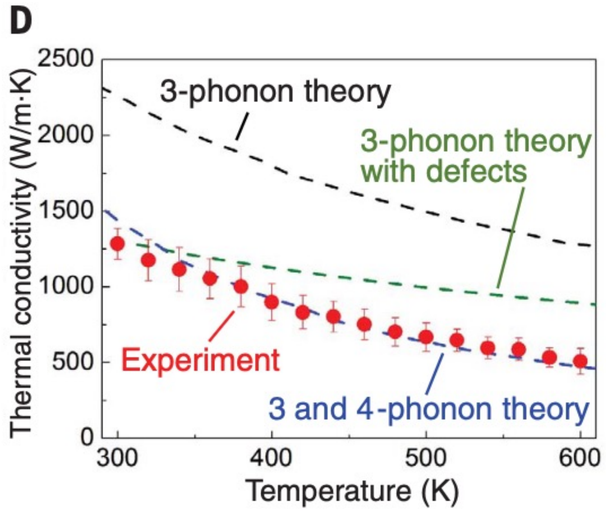




Experimental validation

Science **361**,575-578 (2018)





Boltzmann theory with 3ph & 4ph processes

Inclusion of 4ph scattering lead to better agreement with the experimental thermal conductivity

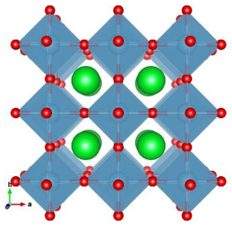
However, the same approach does not necessarily improve the prediction by Boltzmann+3ph in general cases.

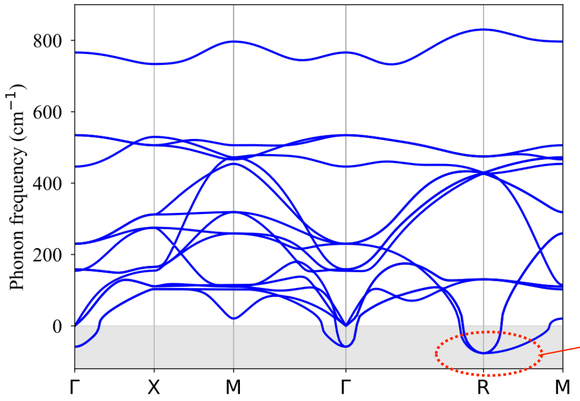
Limitation of the perturbation method

- Series expansion may not converge if the perturbation term $\hat{H}'$ is reasonably large.

  This can happen more likely for strongly anharmonic materials

- The non-interacting Hamiltonian $\hat{H}_0$ is ill-defined in many cases (high-symmetry phases of solids).





Phonon
(**Harmonic**)

$$\hat{H}_0 = \sum_q \hbar\omega_q \left(\hat{b}_q^\dagger \hat{b}_q + \frac{1}{2}\right)$$

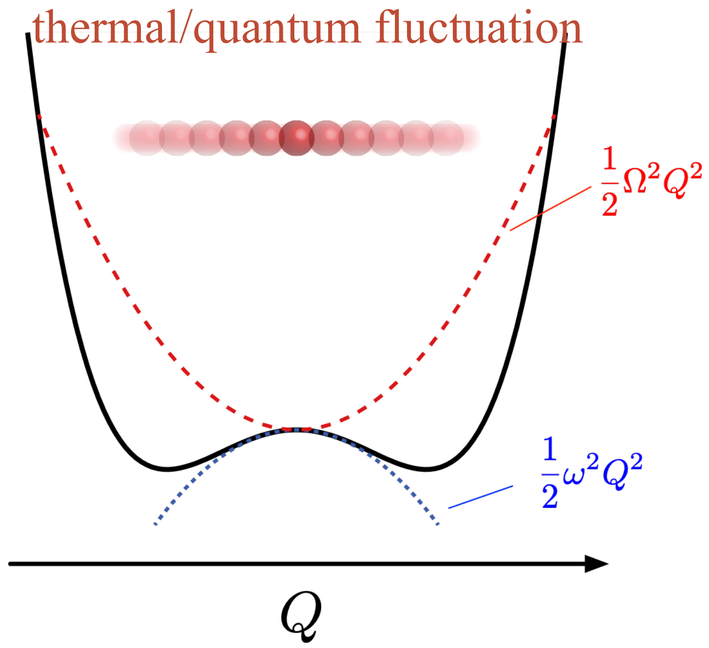
Frequency is pure imaginary
("imaginary phonon")

Need to construct a better one-body starting point

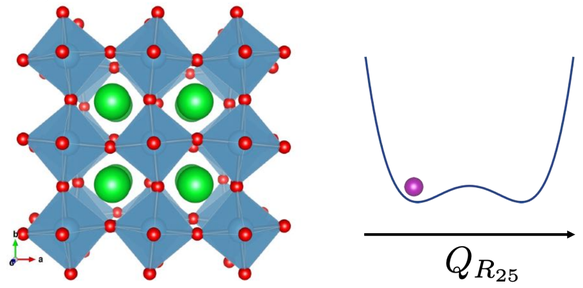
Anharmonic *renormalization* solves imaginary phonon problem

***Effective* harmonic force constant at finite temperature**

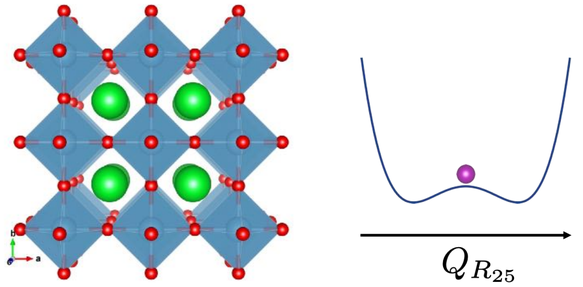
$$\tilde{\Phi}_{ij}(T) = \Phi_{ij} + \frac{1}{4}\sum_{kl}\Phi_{ijkl}\langle u_k u_l \rangle$$



$SrTiO_3$ tetragonal (T < 105 K)



$SrTiO_3$ cubic (T > 105 K)



Self-consistent phonon theory:

Stochastic implementation : Errea *et al.,* PRB 2014

Deterministic implementation: TT and S. Tsuneyuki, PRB 2015

Effective force constant from MD: Hellman *et al.*, PRB 2011

Self-consistent phonon (SC1) theory

N. R. Werthamer, Phys. Rev. B **1**, 572 (1970)

$\hat{H}$: Exact Hamiltonian of the interacting phonon system with full anharmonicity.

Density operator: $\hat{\rho}_H = \dfrac{\exp(-\beta\hat{H})}{\mathrm{tr}[\exp(-\beta\hat{H})]}$

Exact free energy: $F_H = \mathrm{tr}(\hat{\rho}_H\hat{H}) + \dfrac{1}{\beta}\mathrm{tr}(\hat{\rho}_H \ln\hat{\rho}_H)$ infeasible to calculate

$\hat{\mathcal{H}}_0$: Effective one-body Hamiltonian of the interacting phonon system $\hat{\mathcal{H}}_0 = \sum_q \hbar\Omega_q\left(\hat{b}_q^\dagger\hat{b}_q + \dfrac{1}{2}\right)$

Density operator: $\hat{\rho}_{\mathcal{H}_0} = \dfrac{\exp(-\beta\hat{\mathcal{H}}_0)}{\mathrm{tr}[\exp(-\beta\hat{\mathcal{H}}_0)]}$

Approximated free energy: $F_H(\hat{\mathcal{H}}_0) = \mathrm{tr}(\hat{\rho}_{\mathcal{H}_0}\hat{H}) + \dfrac{1}{\beta}\mathrm{tr}(\hat{\rho}_{\mathcal{H}_0} \ln\hat{\rho}_{\mathcal{H}_0})$ computation is feasible

Feynmann–Gibbs–Bogoliubov inequality: $F_H \le F_H(\hat{\mathcal{H}}_0)$

SC1 free energy and SC1 frequency

Feynmann–Gibbs–Bogoliubov inequality: $F_H \leq F_H(\hat{\mathcal{H}}_0)$

SC1 vibrational free energy

$$F_H(\hat{\mathcal{H}}_0) = \mathrm{tr}(\hat{\rho}_{\mathcal{H}_0}\hat{H}) + \frac{1}{\beta}\mathrm{tr}(\hat{\rho}_{\mathcal{H}_0}\ln\hat{\rho}_{\mathcal{H}_0})$$

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{U}_2 + \hat{U}_3 + \hat{U}_4 + \hat{U}_5 + \hat{U}_6 + \cdots \\ &= \hat{\mathcal{H}}_0 + (\hat{U}_2 - \hat{\mathcal{U}}_2 + \hat{U}_3 + \hat{U}_4 + \hat{U}_5 + \hat{U}_6 + \cdots)\end{aligned}$$

$$\begin{aligned}\mathrm{tr}(\hat{\rho}_{\mathcal{H}_0}\hat{H}) = \mathrm{tr}(\hat{\rho}_{\mathcal{H}_0}\hat{\mathcal{H}}_0) + \mathrm{tr}(\hat{\rho}_{\mathcal{H}_0}(\hat{U}_2 - \hat{\mathcal{U}}_2)) \\ + \mathrm{tr}(\hat{\rho}_{\mathcal{H}_0}\hat{U}_4) + \mathrm{tr}(\hat{\rho}_{\mathcal{H}_0}\hat{U}_6) + \cdots\end{aligned}$$

even-term anharmonicity

SC1 frequency

$$\nabla_{\Omega_q} F_H(\hat{\mathcal{H}}_0) = 0$$

$$\begin{aligned}\Omega_q^2 = \omega_q^2 &+ \frac{1}{2}\sum_{q'}\Phi_4(-q,q;-q',q')\alpha_{q'} \\ &+ \frac{1}{8}\sum_{q'q''}\Phi_6(-q,q;-q',q';-q'',q'')\alpha_{q'}\alpha_{q''} \\ &+ \cdots\end{aligned}$$

anharmonic force constants

$$\alpha_q = \frac{\hbar(2n_q+1)}{2\Omega_q}$$

mean-square displacement

A diagrammatic view of SC1 theory

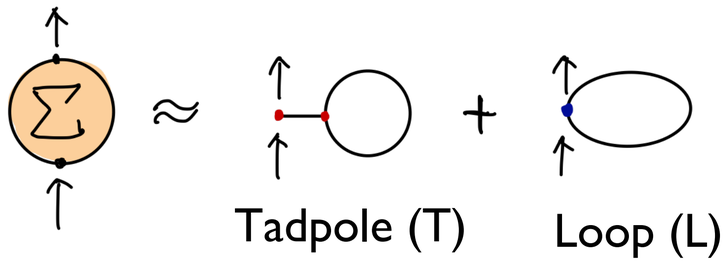
The self-consistent phonon (SC1) equation is obtained via $\nabla_{\Omega_q} F_H(\hat{\mathcal{H}}_0) = 0$

"Hatree-Fock" theory for phonons

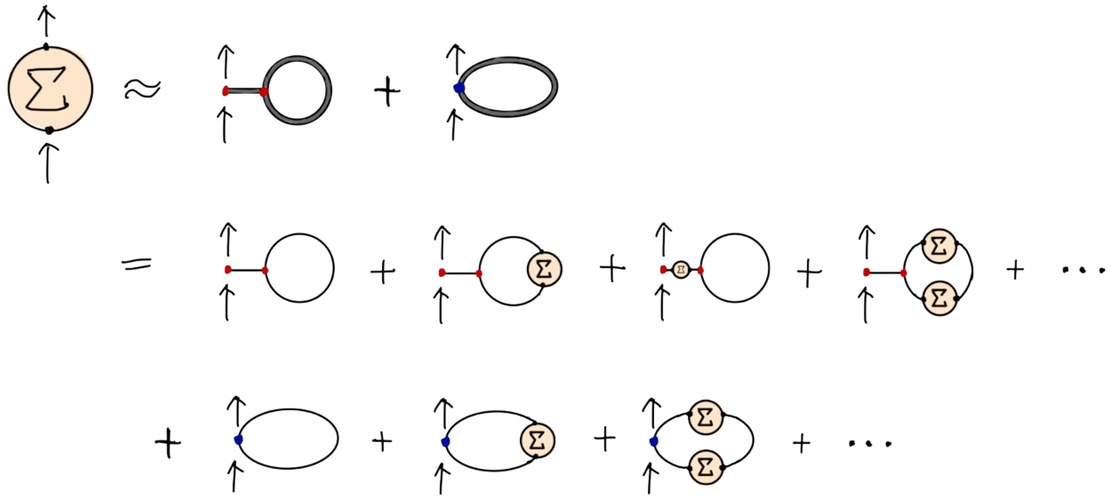
A diagrammatic representation of the SC1 theory:

$$\{G_q(\omega)\}^{-1} = \{G_q^0(\omega)\}^{-1} - \Sigma_q^{\mathrm{T}}[G] - \Sigma_q^{\mathrm{L}}[G]$$

Self-energy in perturbation theory



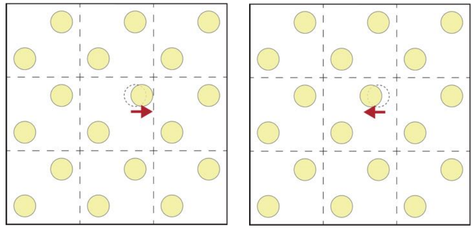
Self-energy in self-consistent phonon theory



Force constant calculation: A brute-force approach

$$\Phi_{ij} = \frac{\partial^2 V}{\partial u_i \partial u_j} = -\frac{\partial F_j}{\partial u_i} \approx -\frac{[F_j(u_i = h) - F_j(u_i = -h)]}{2h}$$

2 patterns

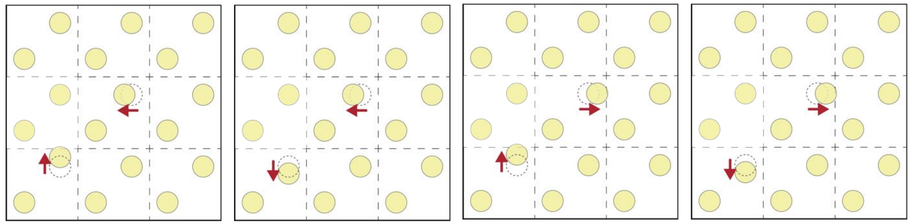


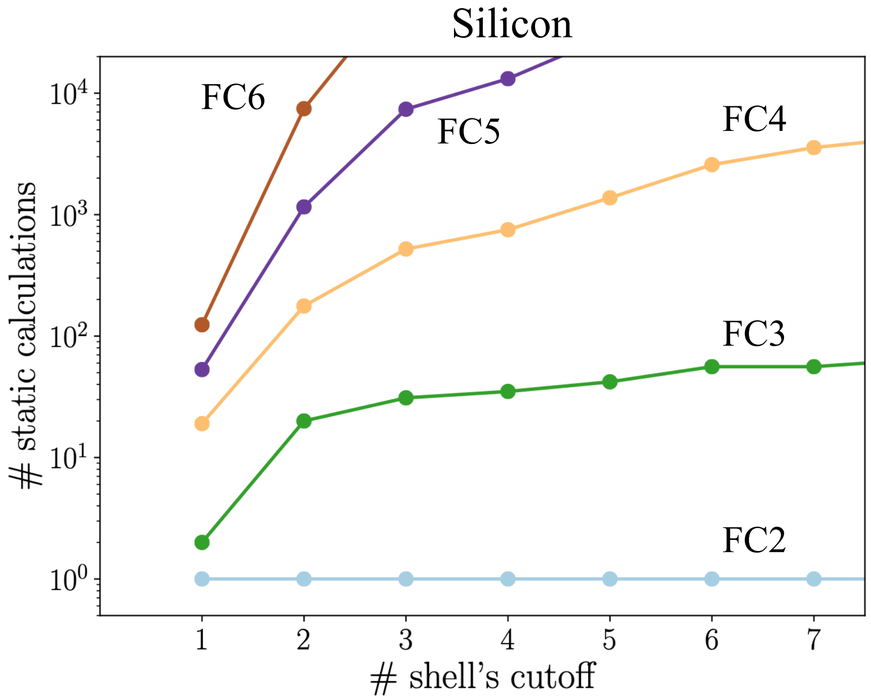
$$\Phi_{ijk} = \frac{\partial^3 V}{\partial u_i \partial u_j \partial u_k} = -\frac{\partial F_k}{\partial u_i \partial u_j}$$

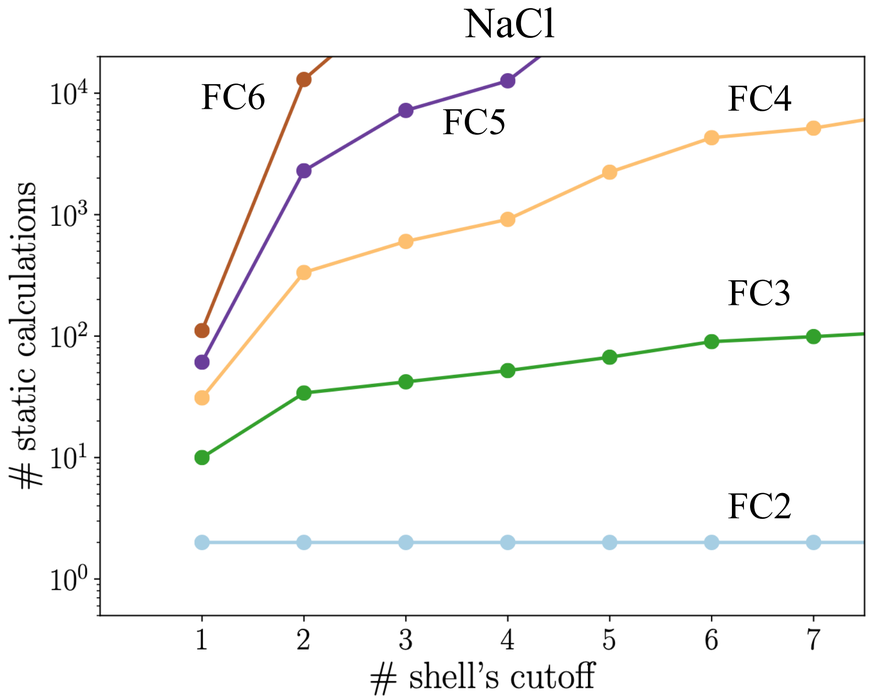
$$\approx -\frac{1}{4h^2}\,[F_k(u_i = h, u_j = h) - F_k(u_i = h, u_j = -h)$$

$$-F_k(u_i = -h, u_j = h) + F_k(u_i = -h, u_j = -h)]$$

4 patterns







Force constants from sparse modeling

$$V_{\mathrm{ALM}} = V_2 + V_3 + V_4 + \cdots$$
$$= \frac{1}{2}\sum_{i,j} \Phi_{ij} u_i u_j + \frac{1}{3!}\sum_{i,j,k} \Phi_{ijk} u_i u_j u_k + \frac{1}{4!}\sum_{i,j,k,\ell} \Phi_{ijk\ell} u_i u_j u_k u_\ell + \cdots$$

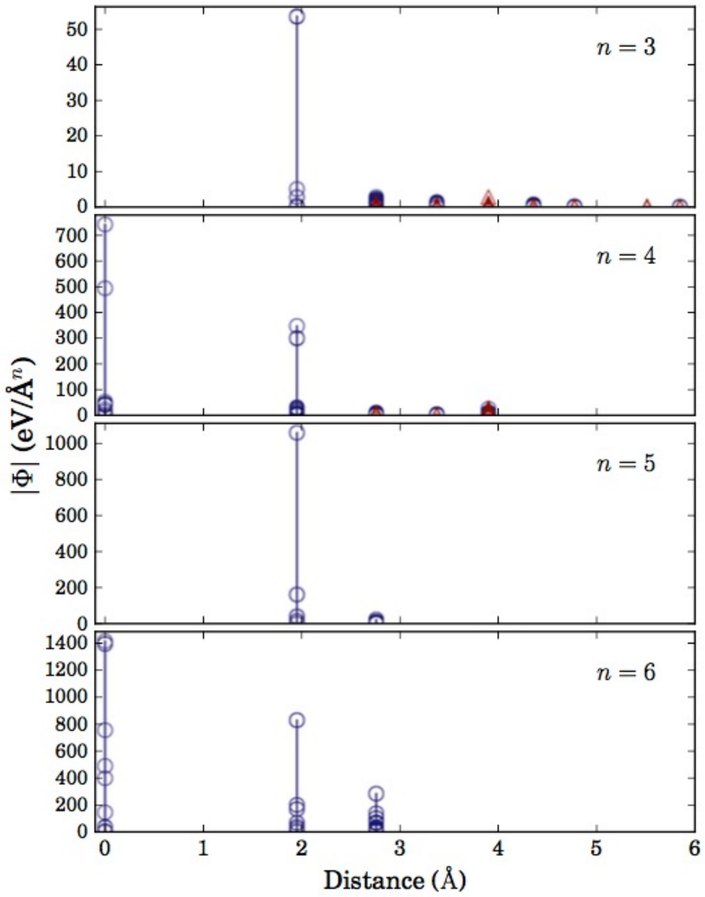
parameters

basis

$$= \boldsymbol{b} \cdot \boldsymbol{\Phi}$$

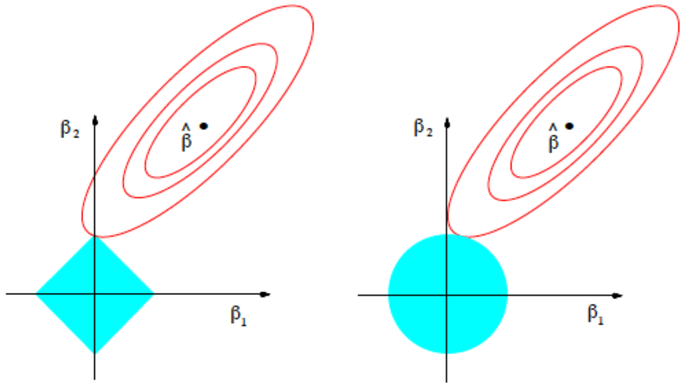
$$\boldsymbol{\Phi} = \left[\Phi_1, \Phi_2, \ldots, \Phi_M\right]^T$$ M: The number of independent parameters

$$\boldsymbol{F}_{\mathrm{ALM}} = -\frac{\partial V_{\mathrm{ALM}}}{\partial \boldsymbol{u}} = -\frac{\partial \boldsymbol{b}^T}{\partial \boldsymbol{u}}\boldsymbol{\Phi} = A\boldsymbol{\Phi}$$



Shrinkage

$$\tilde{\boldsymbol{\Phi}} = \arg\min_{\boldsymbol{\Phi}} \|A\boldsymbol{\Phi} - \boldsymbol{F}^{\mathrm{DFT}}\|^2 + \alpha|\boldsymbol{\Phi}|^p$$

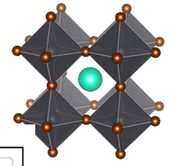


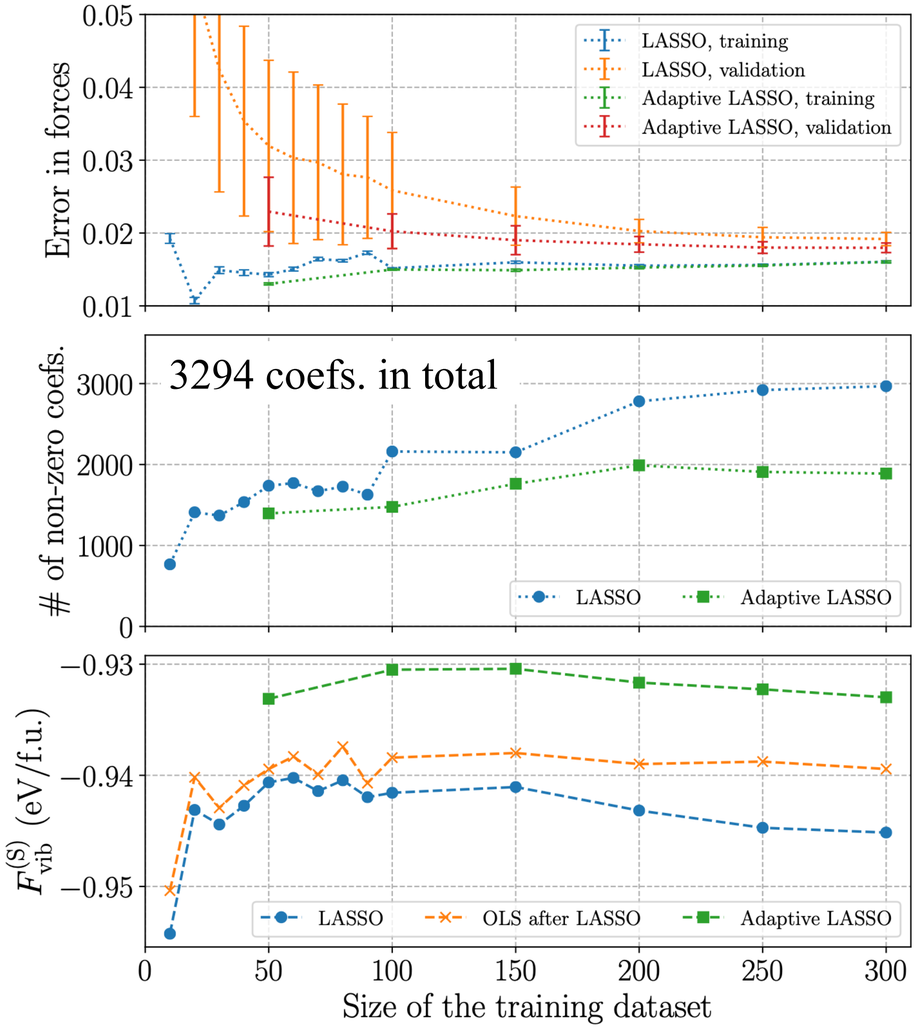
p=1: LASSO

p=2: ridge regression

Benchmark: Efficiency of sparse modeling

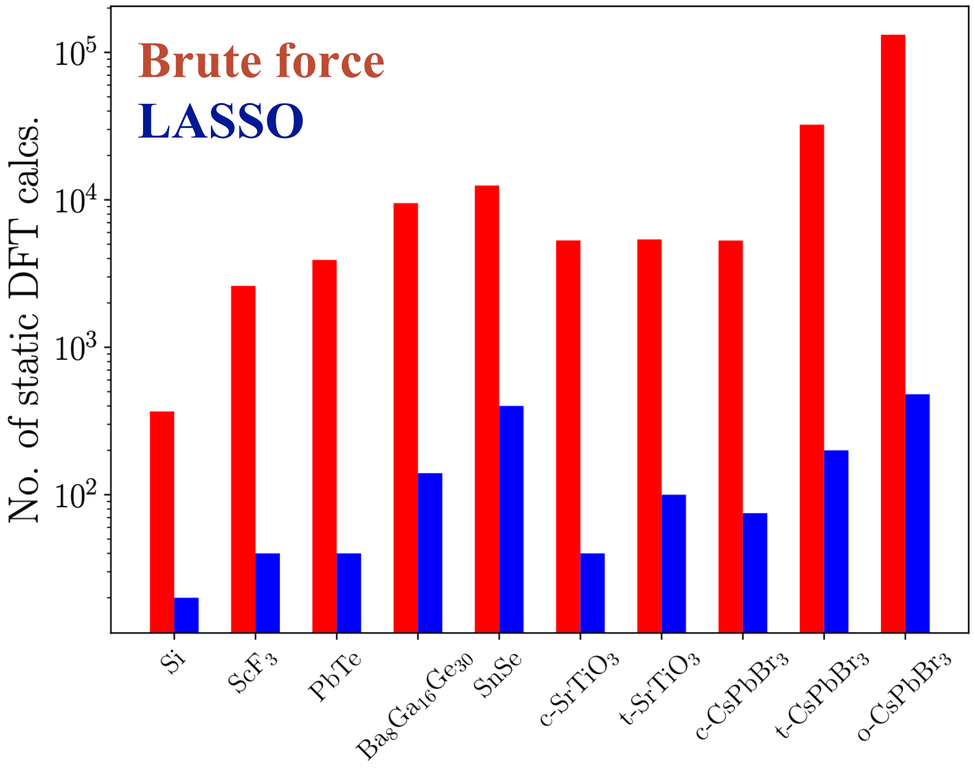
Result for cubic $CsPbBr_3$



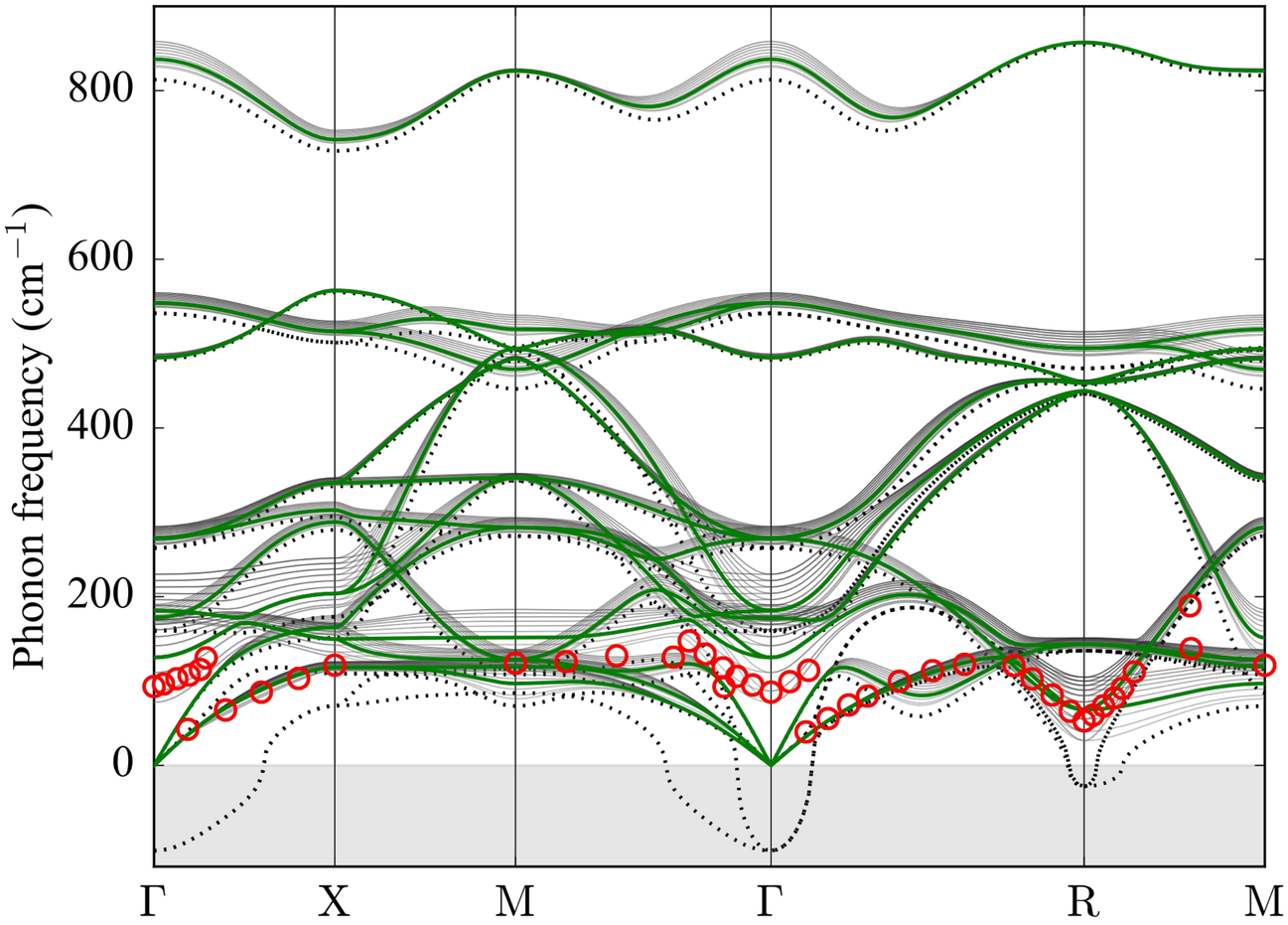


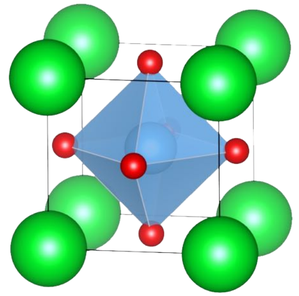
✓Adaptive LASSO gives more sparse solution

✓50 structure snapshots is enough to reach convergence of F_{vib} within 1 meV/atom error



Temperature dependent phonon in cubic $SrTiO_3$





Green line:
SCP result@300K

Red circle:
INS result@300 K

- ☑ HSE hybrid functional
- ☑ Anharmonic stabilization of soft modes

TT and S. Tsuneyuki, J. Phys. Soc. Jpn. **87**, 041015 (2018)

First-principles implementation of SCP (SC1)

How to update Φ (*effective* 2nd-order force constants)?

* **Stochastic methods**
  - SSCHA http://sscha.eu
  - QSCAILD https://github.com/vanroeke/qscaild
  - HiPhive https://hiphive.materialsmodeling.org
  - Phonopy https://phonopy.github.io/

Stochastically displace atoms in a supercell and update Φ so as to minimize $\nabla_\Phi F_H(\hat{\mathcal{H}}_0)$

Pros.
- **Full** anharmonicity (at the mean-field level)
- **No** explicit computation of anharmonic force constants

Cons.
- More expensive computationally

* **Force constant based approach (FC-SCP)**
  - ALAMODE https://alamode.readthedocs.io/

From $\nabla_\Phi F_H(\hat{\mathcal{H}}_0) = 0$, derive the self-consistent equation analytically. The Taylor series is truncated.

$$\langle \hat{H} - \hat{\mathcal{H}}_0 \rangle = \langle \hat{U}_0 - \hat{\mathcal{U}}_0 + \hat{U}_3 + \hat{U}_4 + \ldots \rangle_0$$
$$\approx \langle \hat{U}_0 - \hat{\mathcal{U}}_0 + \hat{U}_4 \rangle_0$$

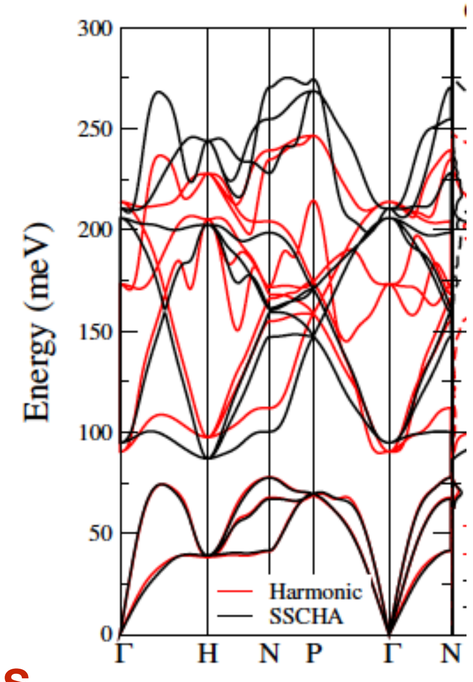
Pros.
- More efficient particularly for scanning temperature
- Faster convergence

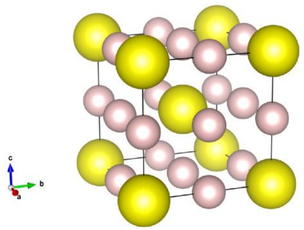
Cons.
- Omit higher-order anharmonicity
- Requires anharmonic force constants as input

Consistency between two approaches

Stochastic method (SSCHA)

I. Errea et al., Phys. Rev. B **89**, 064302 (2014).





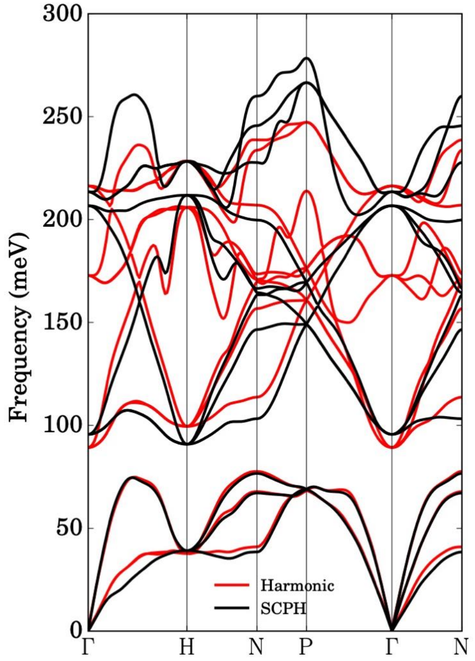
H_3S

H_3S

Phys. Rev. Lett. **114**, 157004 (2015)

Force-constant based approach (FC-SCP)

TT and S. Tsuneyuki, Phys. Rev. B **92**, 054301 (2015).

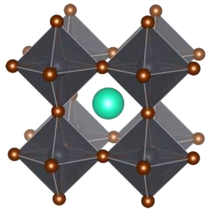


H_3S

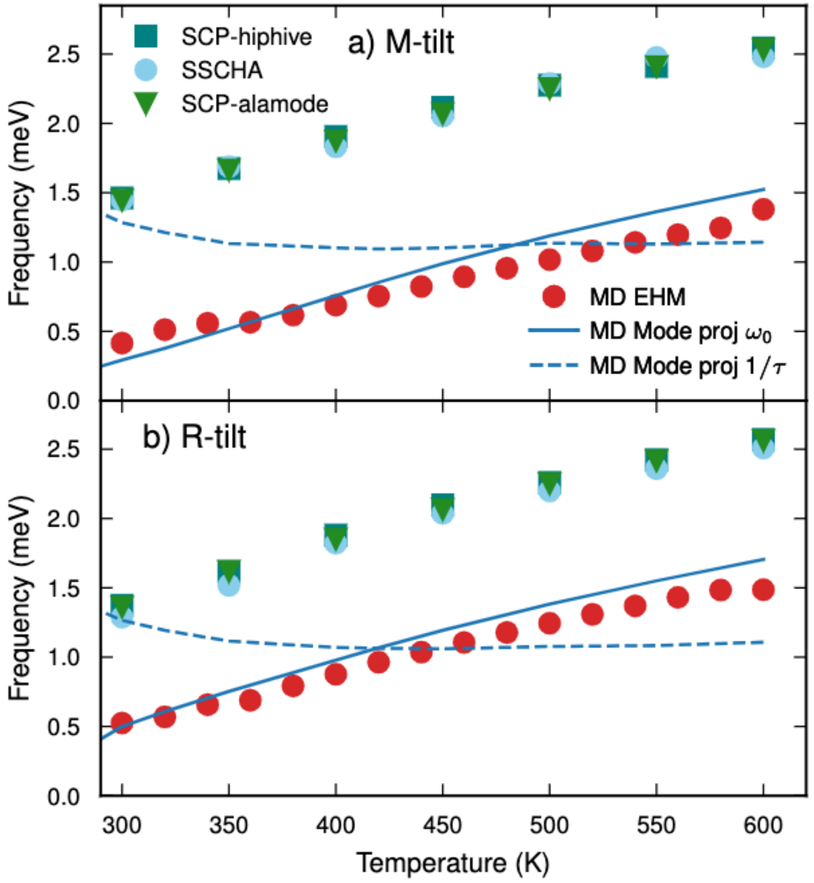
Phys. Rev. B. **93**, 094525 (2016).

Another comparison on anharmonic solid

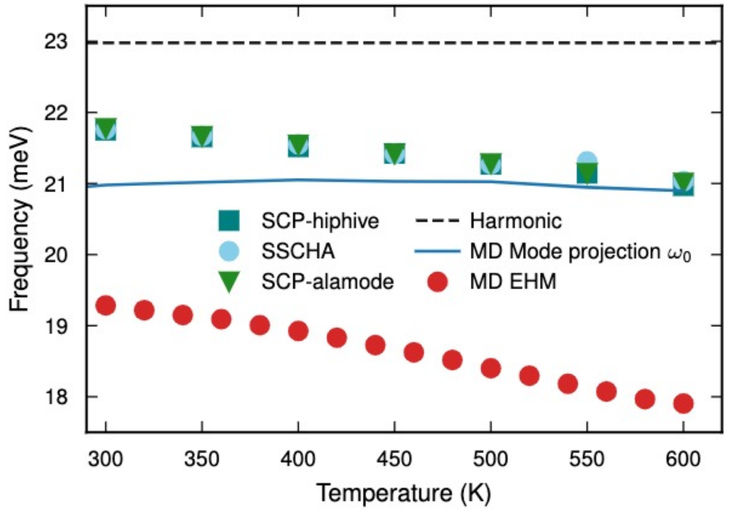
$CsPbBr_3$



Soft phonon frequency



High-energy phonon frequency



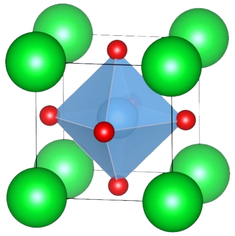
MD EHM = TDEP法

$$\tilde{\mathbf{\Phi}}^{(2)}_{\mathrm{TDEP}} = \arg\min_{\mathbf{\Phi}^{(2)}} \left\langle \sum_i (F_i^{\mathrm{har}} - F_i^{\mathrm{DFT}})^2 \right\rangle_H$$

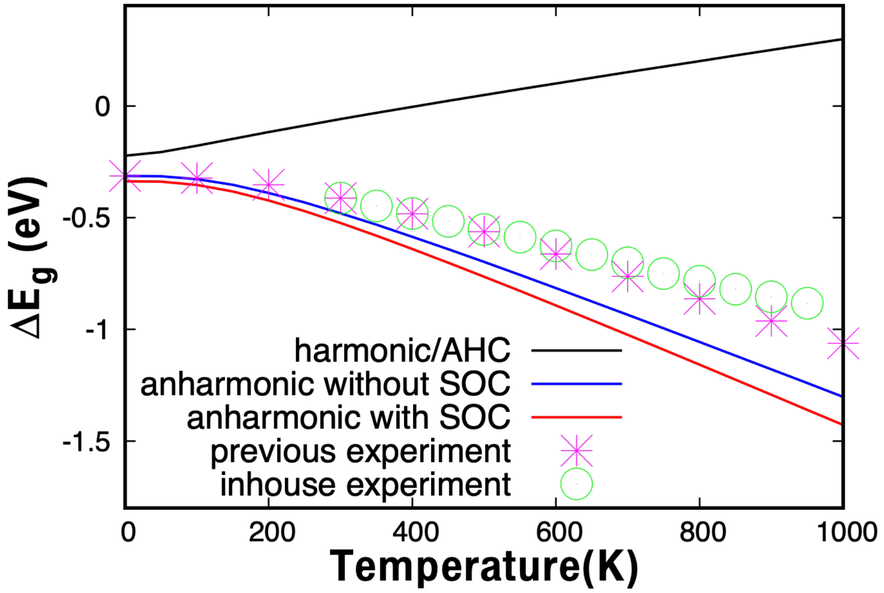
- Does not satisfy the variational principles. Looks heuristic.

E. Fransson, P. Rosander, F. Eriksson, J. M. Rahm, TT, and P. Erhart, Commun. Phys. **6**, 1 (2023).

Application to el-ph problem: band-gap renormalization



cubic
$SrTiO_3$



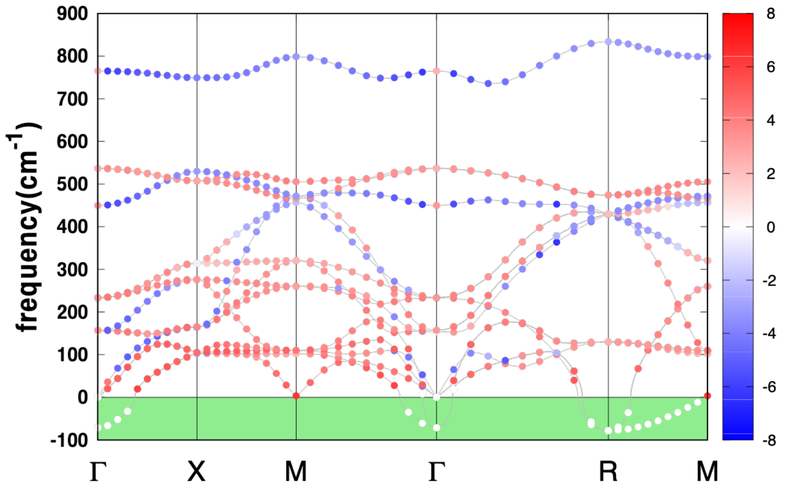
Allen–Heine–Cardona (AHC) theory

$$\Delta\epsilon_g(T) = \frac{1}{N_q}\sum_{\boldsymbol{q},\nu}\frac{a^{(2)}_{\boldsymbol{q}\nu;\boldsymbol{q}\nu}}{\omega_{\boldsymbol{q}\nu}}\left[\frac{1}{2}+n_{\boldsymbol{q}\nu}(T)\right]$$

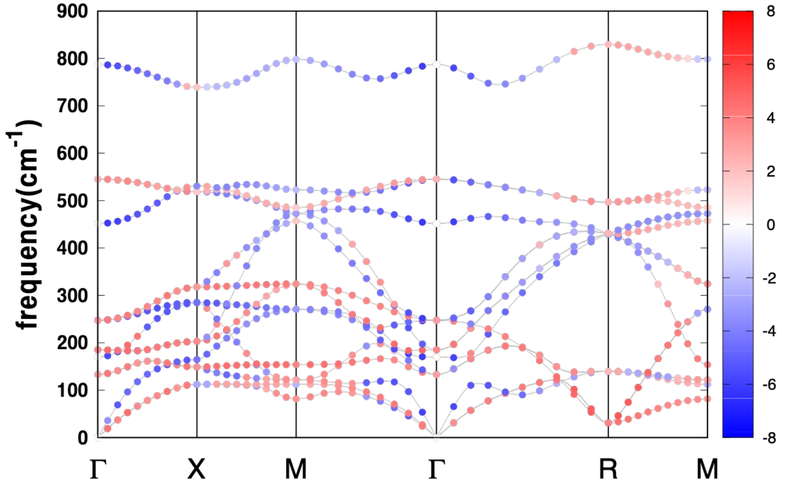
Finite difference method using non-diagonal supercell

Monserrat, J Phys Condens Matter **30**, 083001 (2018).

Harmonic

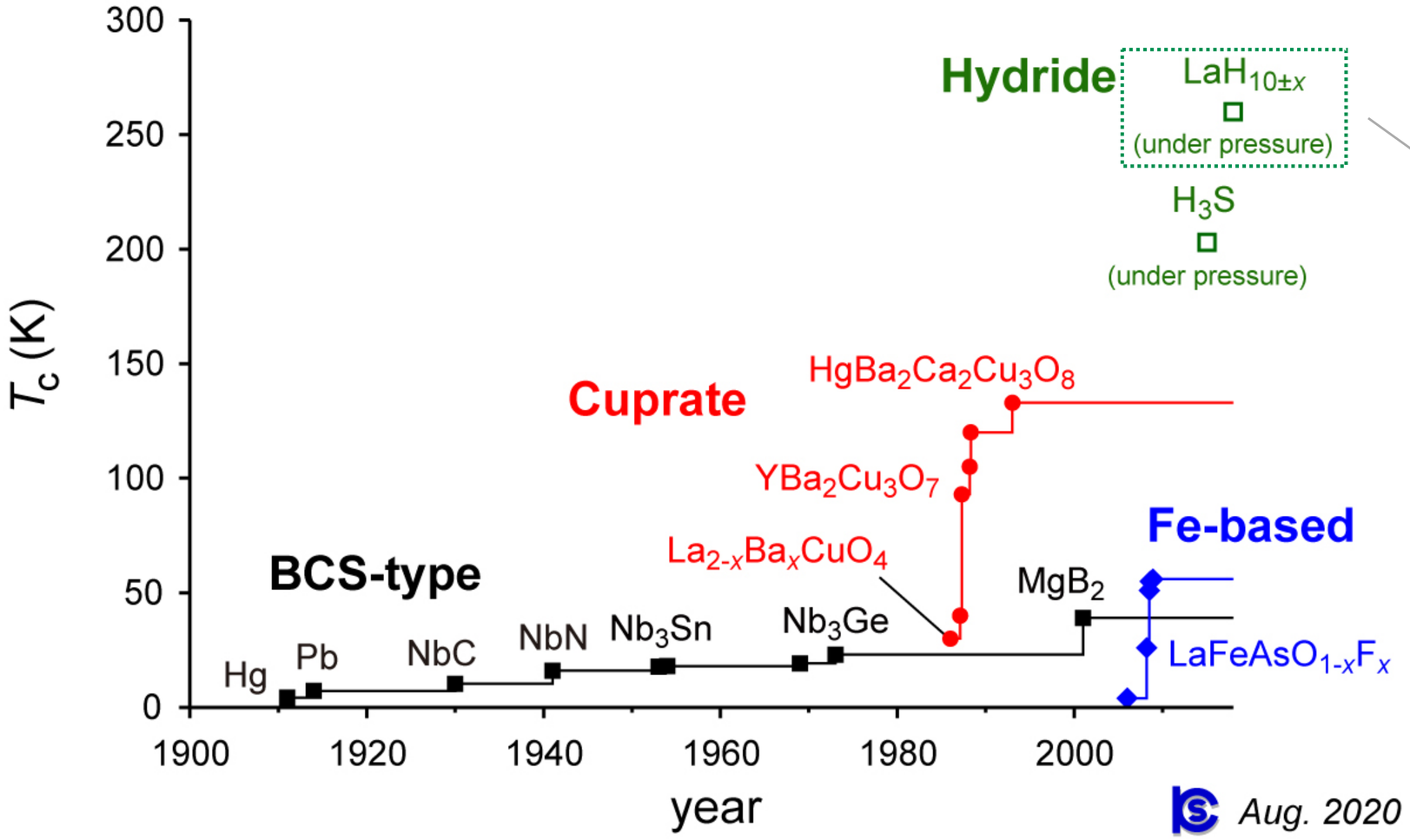


Anharmonic

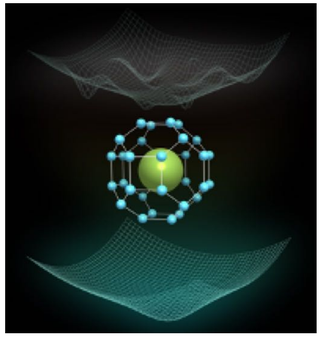


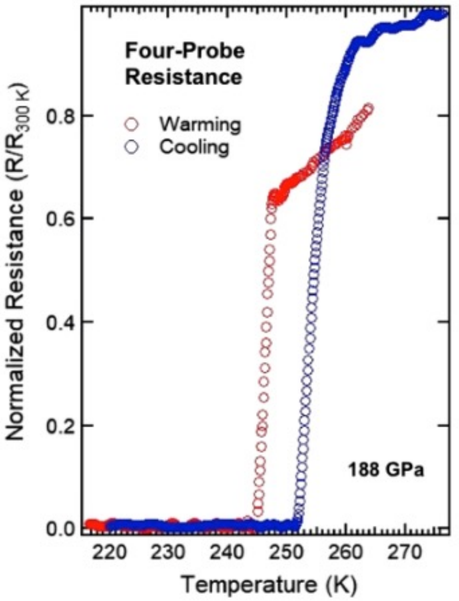
Y. Wu, TT *et al.*, J. Phys. Chem. Lett. **11**, 2518 (2020).

History of superconducting T_c record



Somayazulu *et al.*,
PRL **122**, 027001 (2019).

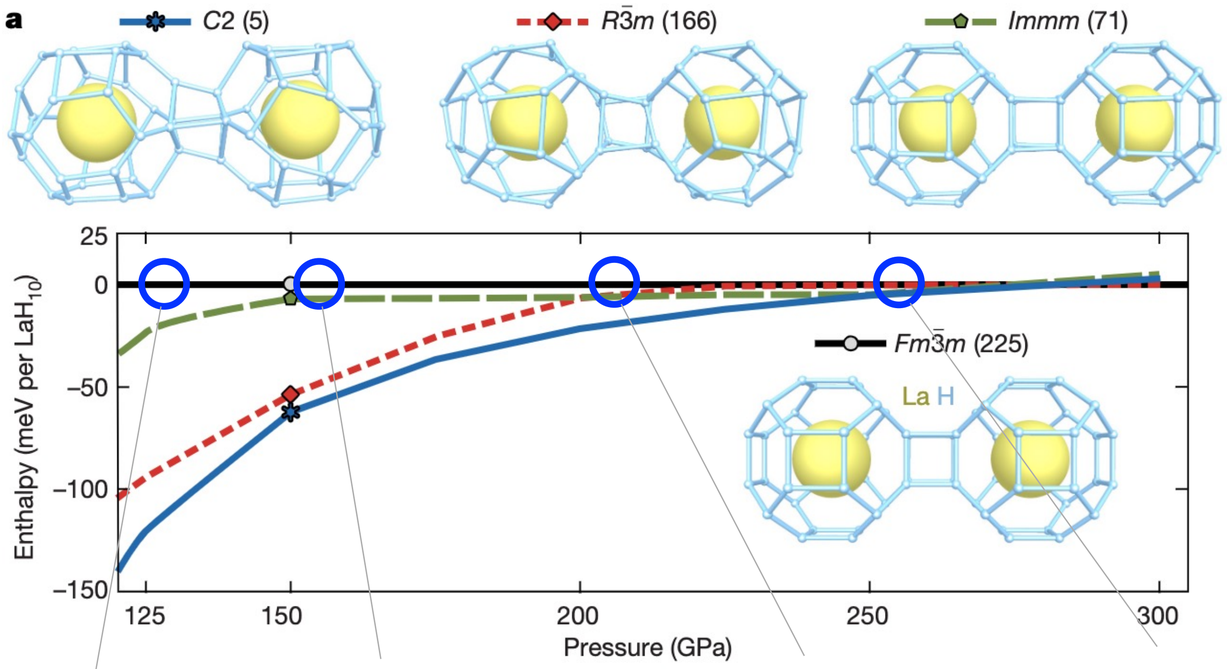


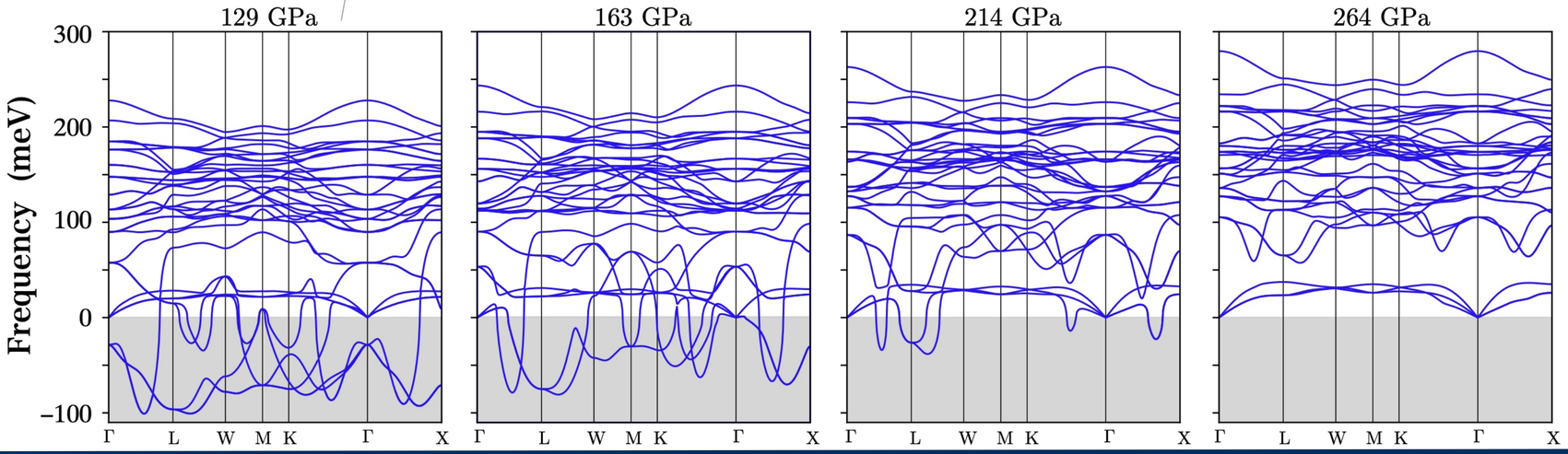


p =180 GPa!

https://kittaka.r.chuo-u.ac.jp/contents/others/tc-history/index.html

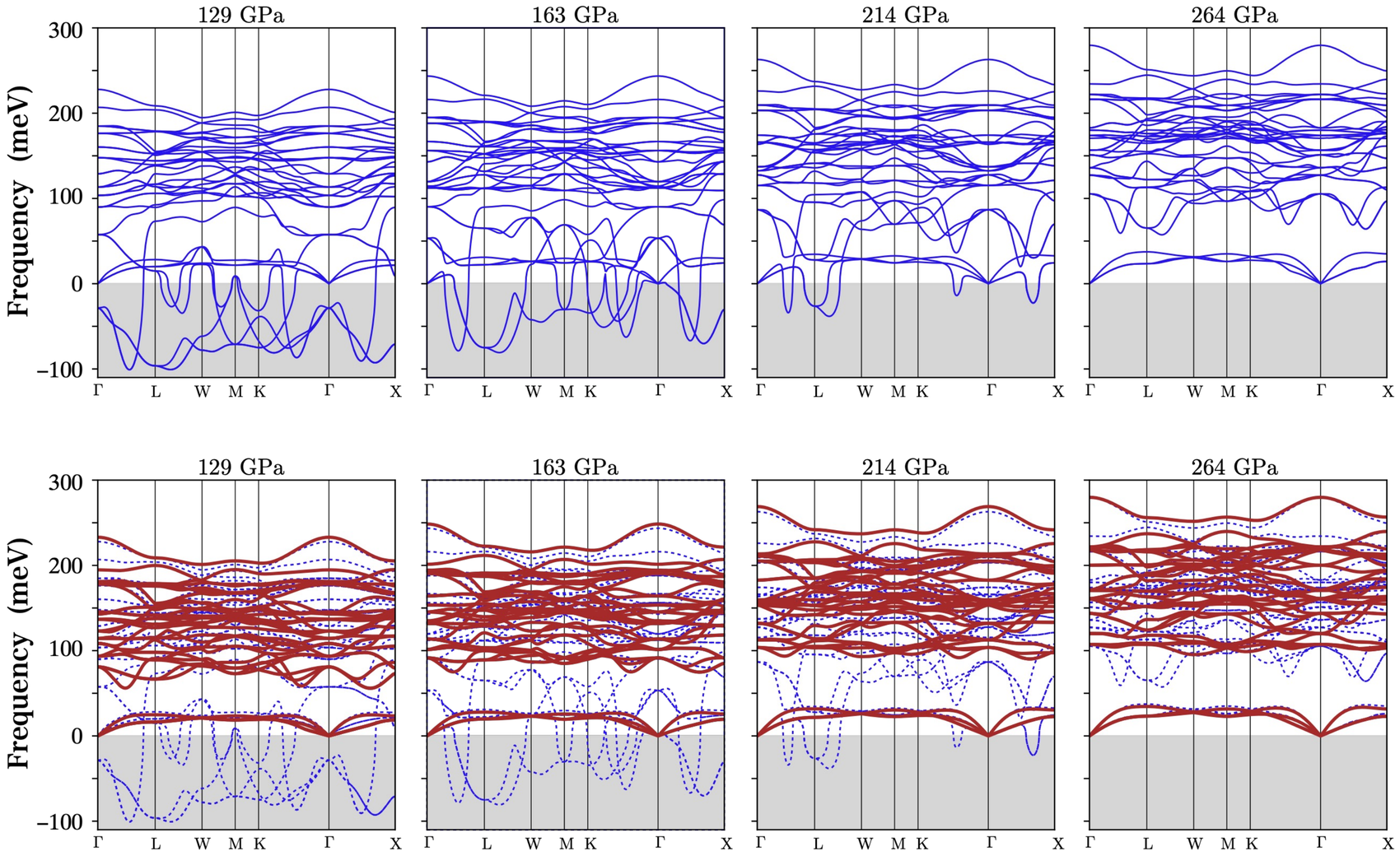
Distortion and phonon instability in $Fm\bar{3}m$-LaH_{10}





$Fm\bar{3}m$-LaH_{10} distorts into a lower-symmetry structure below ~250 GPa when atoms are treated as classical particles.

Stabilization of $Fm\bar{3}m$-LaH_{10} by anharmonic renormalization



Classical particle
(at absolute rest)

No anharmonic renormalization

Quantum fluctuation
(> 10% of interatomic distance)

Large anharmonic renormalization

Nature **578**, 66-69 (2020)

T_c calculated with renormalized phonon

DFT for superconductors (SCDFT)

$$\Delta(\xi) = -\mathcal{Z}(\xi)\Delta(\xi) - \frac{1}{2}\int d\xi' N(\xi')\mathcal{K}(\xi,\xi')\frac{\tanh\left[\frac{\beta E(\xi)}{2}\right]}{E(\xi)}\Delta(\xi')$$

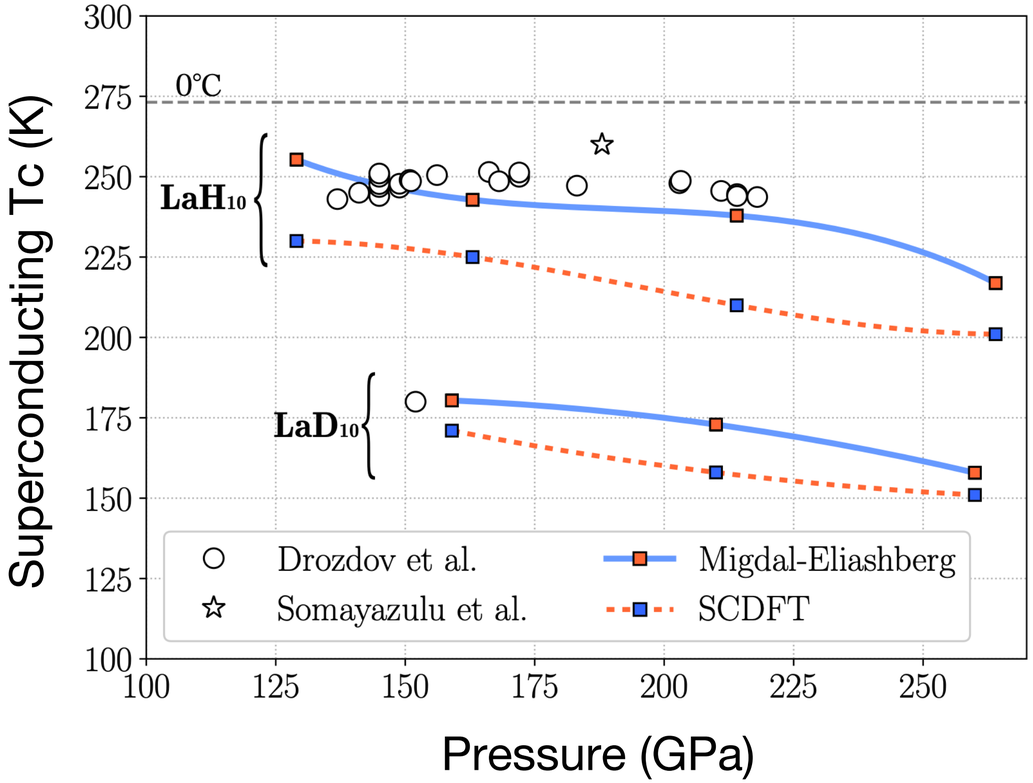
Marques *et al.*, PRB **72**, 024545 (2005).

Sanna *et al.,* JPSJ **87**, 041012 (2018).
Sanna *et al.,* PRL **125**, 057001 (2020).

Migdal–Eliashberg Theory

$$\Delta_{n\boldsymbol{k}}(\mathrm{i}\omega_i) = -\frac{1}{N_q\beta}\sum_{\mu,m\boldsymbol{q}}\left\{V^{\mathrm{ph}}_{nm}(\boldsymbol{q},\mathrm{i}\omega_\mu) + V^{\mathrm{c}}_{nm}(\boldsymbol{q},\mathrm{i}\omega_\mu)\right\}$$
$$\times G_{m\boldsymbol{k}+\boldsymbol{q}}(\mathrm{i}\omega_\mu + \mathrm{i}\omega_i)G_{m-\boldsymbol{k}-\boldsymbol{q}}(-\mathrm{i}\omega_\mu - \mathrm{i}\omega_i)\Delta_{m\boldsymbol{q}}(\mathrm{i}\omega_\mu + \mathrm{i}\omega_i),$$
$$\Sigma_{n\boldsymbol{k}}(\mathrm{i}\omega_i) = -\frac{1}{N_q\beta}\sum_{\mu,m\boldsymbol{q}} V^{\mathrm{ph}}_{nm}(\boldsymbol{q},\mathrm{i}\omega_\mu)G_{m\boldsymbol{k}+\boldsymbol{q}}(\mathrm{i}\omega_\mu + \mathrm{i}\omega_i).$$

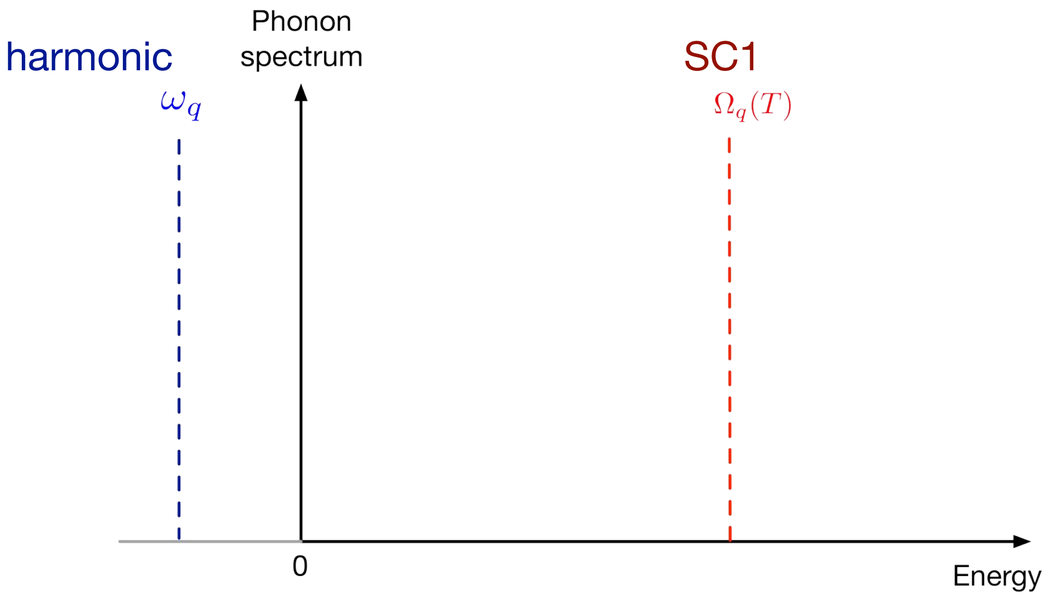
Sano *et al.,* PRB **93**, 094525 (2016).

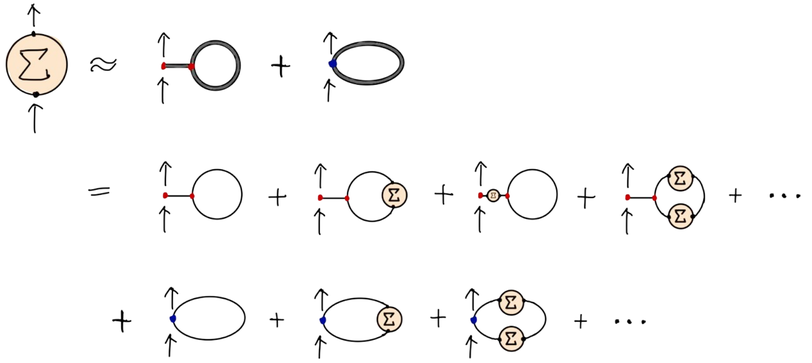


Nature **578**, 66-69 (2020)

Phonon linewidth from first principles

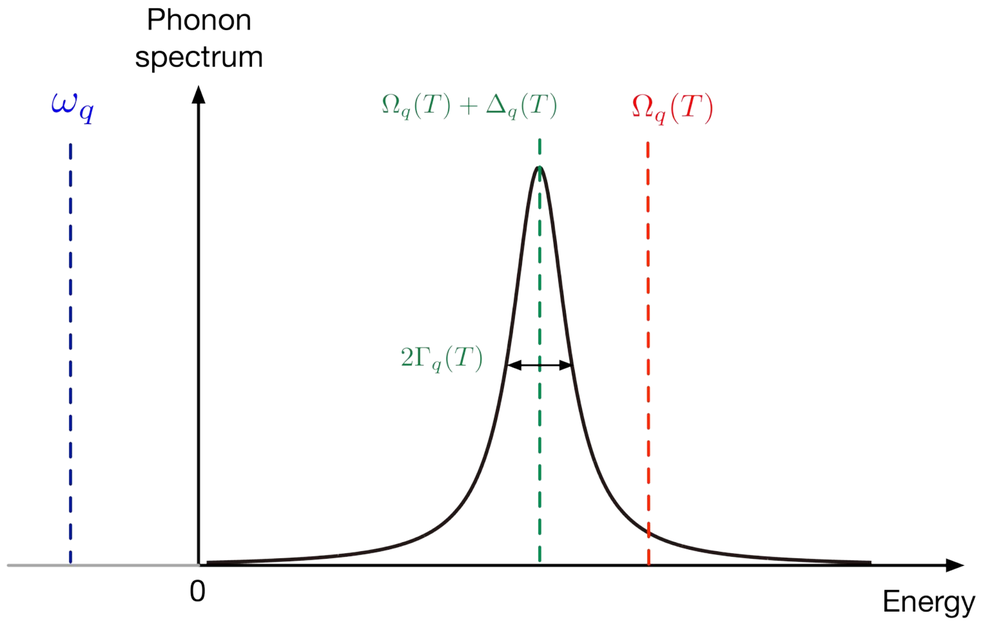
SC1 is still one-body (infinite lifetime)



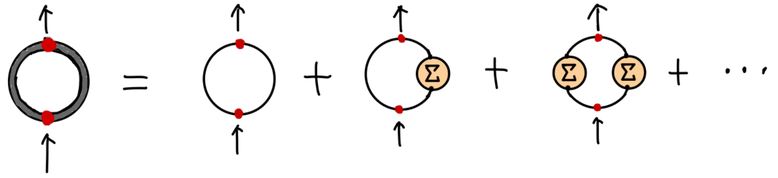


4th-order anharmonicity

SC1 + Bubble gives finite line width



“bubble” self-energy

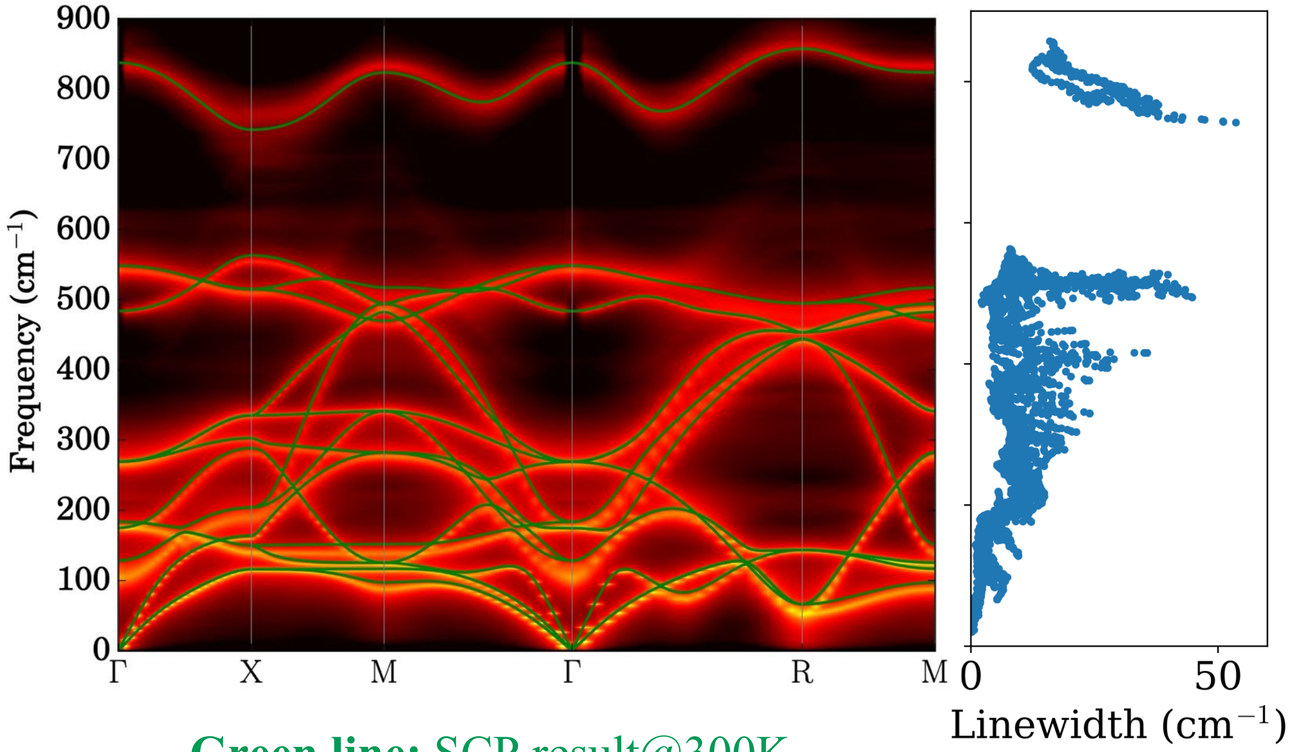


3rd-order anharmonicity

$SrTiO_3$: phonon linewidth & thermal conductivity

Phonon spectral function

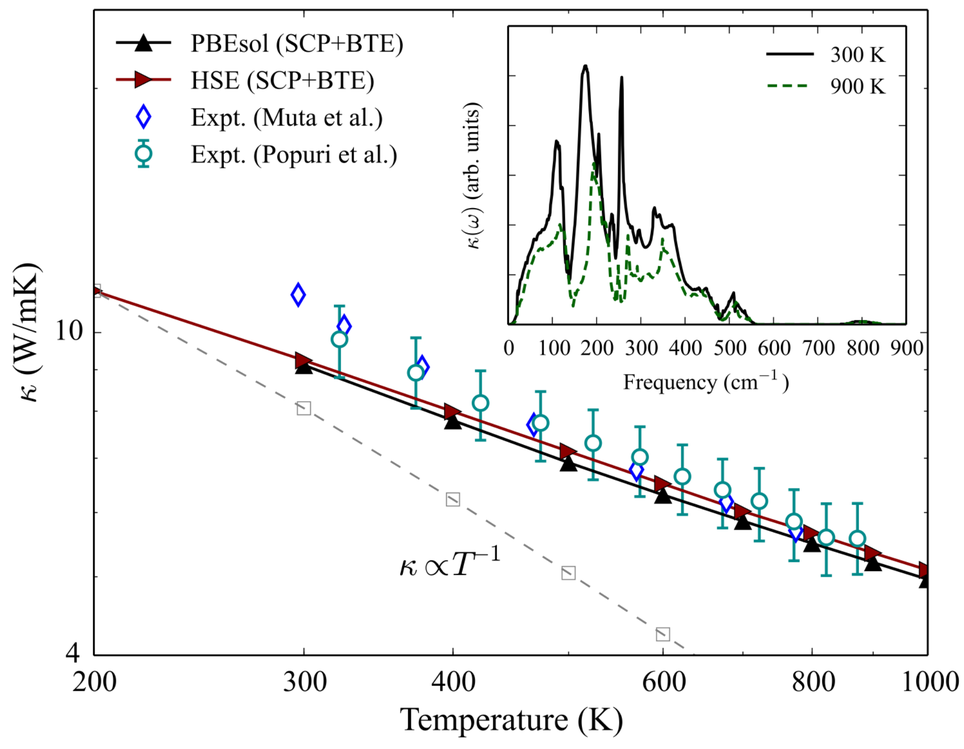
$$A_q(\omega) = \frac{1}{\pi} \frac{4\Omega_q^2 \Gamma_q^{(\mathrm{B})}(\omega)}{\{\omega^2 - \Omega_q^2 - 2\Omega_q \Delta_q^{(\mathrm{B})}(\omega)\}^2 + \{2\Omega_q \Gamma_q^{(\mathrm{B})}(\omega)\}^2}$$



Green line: SCP result@300K

Boltzmann transport theory

$$\kappa_{\mathrm{ph}}^{\mu\nu} = \frac{1}{N_q V} \sum_q c_q(T) v_q^{\mu}(T) v_q^{\nu}(T) \tilde{\tau}_q(T)$$



TT and S. Tsuneyuki, J. Phys. Soc. Jpn. **87**, 041015 (2018)

Quasiparticle approximation

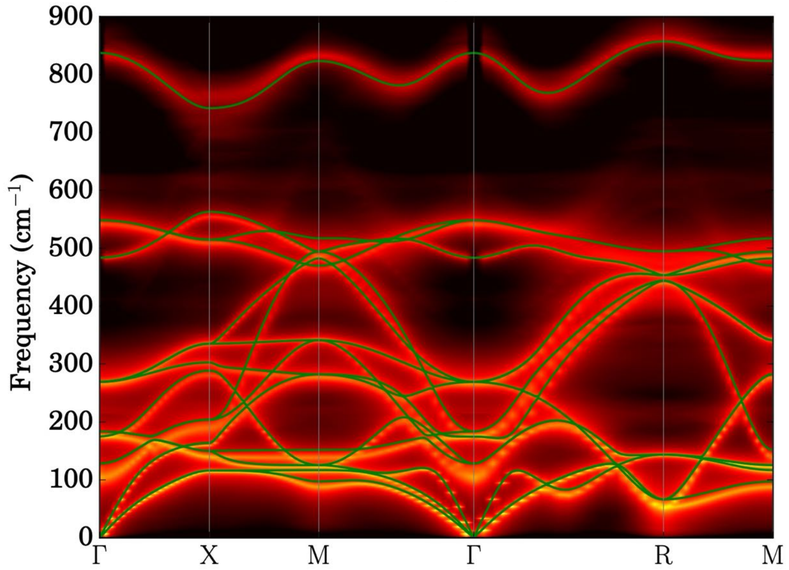
$$\{G_q(\omega)\}^{-1} = \{G_q^{\mathrm{S}}(\omega)\}^{-1} - \Sigma_q^{\mathrm{B}}[G^{\mathrm{S}}, \Phi_3^{\mathrm{S}}](\omega = \omega_0)$$

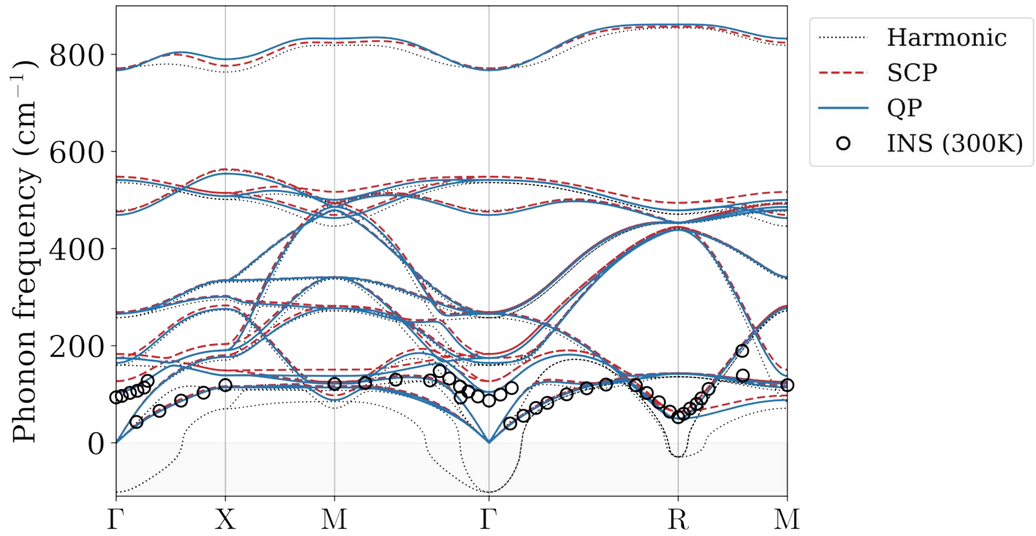
Quasiparticle (QP) approx.

$$\Omega_{\boldsymbol{q}\nu}^2 = (\omega_{\boldsymbol{q}\nu}^{\mathrm{S}})^2 - 2\omega_{\boldsymbol{q}\nu}^{\mathrm{S}} \mathrm{Re}\Sigma_{\boldsymbol{q}\nu}^{\mathrm{B}}[G^{\mathrm{S}}, \Phi_3](\Omega_{\boldsymbol{q}\nu})$$

$SrTiO_3$

$$A_q(\omega) = \frac{1}{\pi}|\mathrm{Im}G_q(\omega)|$$





- Full-frequency dependence
- (often) inconvenient for el-ph calculation

- Better one-body approximation
- Dropped frequency dependence

TT and W. Saidi, Phys. Rev. Lett. **129**, 185901 (2022)

Quasiparticle approximation

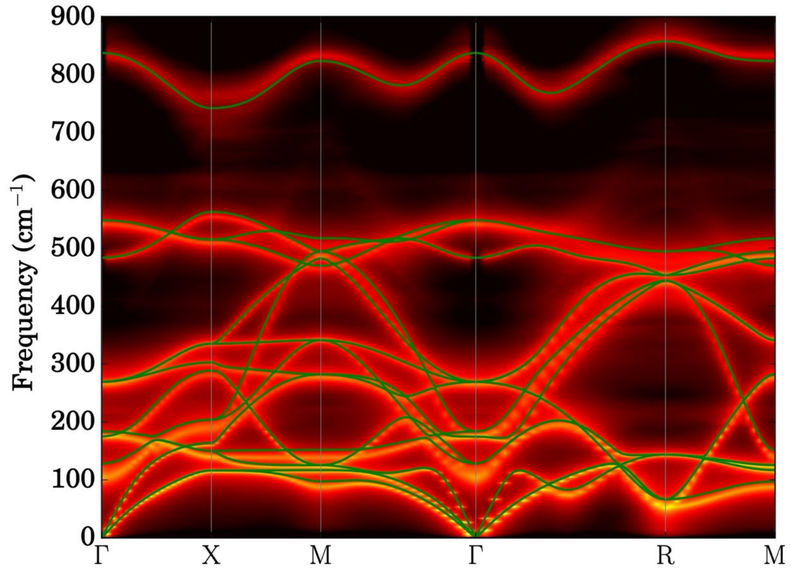
$$\{G_q(\omega)\}^{-1} = \{G_q^{\mathrm{S}}(\omega)\}^{-1} - \Sigma_q^{\mathrm{B}}[G^{\mathrm{S}}, \Phi_3^{\mathrm{S}}](\omega = \omega_0)$$

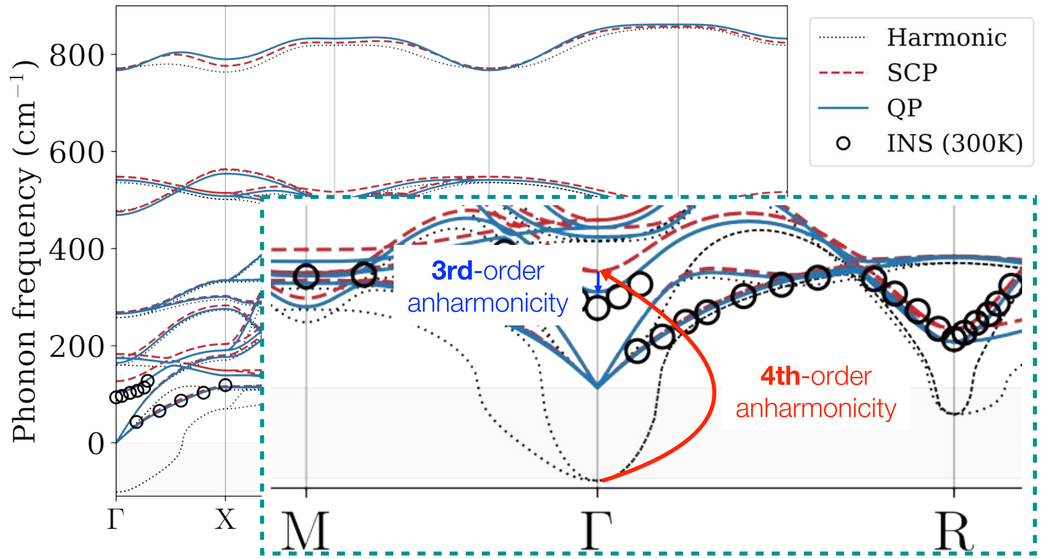
Quasiparticle (QP) approx.

$$\Omega_{\boldsymbol{q}\nu}^2 = (\omega_{\boldsymbol{q}\nu}^{\mathrm{S}})^2 - 2\omega_{\boldsymbol{q}\nu}^{\mathrm{S}} \mathrm{Re}\Sigma_{\boldsymbol{q}\nu}^{\mathrm{B}}[G^{\mathrm{S}}, \Phi_3](\Omega_{\boldsymbol{q}\nu})$$

$SrTiO_3$

$$A_q(\omega) = \frac{1}{\pi}|\mathrm{Im}G_q(\omega)|$$





- Full-frequency dependence
- (often) inconvenient for el-ph calculation

- Better one-body approximation
- Dropped frequency dependence

TT and W. Saidi, Phys. Rev. Lett. **129**, 185901 (2022)

*GW*A and SCP: A comparison

	GWA	**SCP**
starting (unperturbed) G_0	Kohn–Sham (DFT)	SC1 (Hartree–Fock for phonons)
Interaction	*Screened* Coulomb W	*Renormalized* anharmonicity Φ_3
Self-energy	$\Sigma = iGW$	$\Sigma = \Sigma^{\mathrm{B}}[G^{\mathrm{S}}, \Phi_3^{\mathrm{S}}]$
QP approx. (“one-shot”)	$\epsilon_{n\boldsymbol{k}} = \epsilon_{n\boldsymbol{k}}^{\mathrm{KS}} + \mathrm{Re}\,\langle \varphi_{n\boldsymbol{k}}^{\mathrm{KS}} \vert \Sigma^{\mathrm{GW}}(\epsilon_{n\boldsymbol{k}}) - v^{\mathrm{xc}} \vert \varphi_{n\boldsymbol{k}}^{\mathrm{KS}} \rangle$	$\Omega_{\boldsymbol{q}\nu}^2 = (\omega_{\boldsymbol{q}\nu}^{\mathrm{S}})^2 - 2\omega_{\boldsymbol{q}\nu}^{\mathrm{S}} \mathrm{Re}\Sigma_{\boldsymbol{q}\nu}^{\mathrm{B}}[G^{\mathrm{S}}, \Phi_3](\Omega_{\boldsymbol{q}\nu})$
Beyond one-shot	QS*GW*, sc*GW*	QS*GW*-like treatment, another approach (e.g., PRB **107**, 094303 (2023))

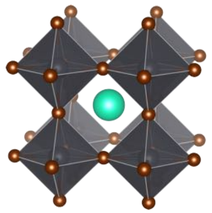
But, accurate prediction of Tc is challenging

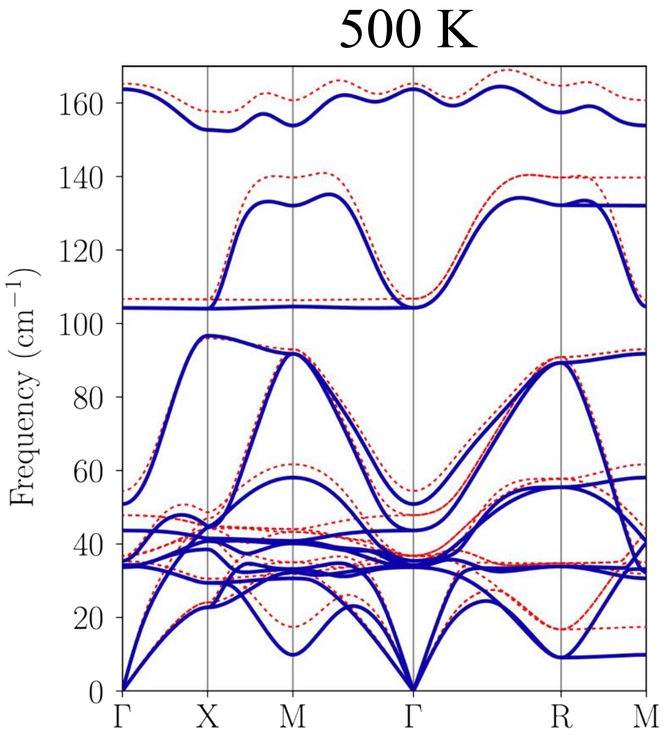
$$\{G_q(\omega)\}^{-1} = \{G_q^{\mathrm{S}}(\omega)\}^{-1} - \Sigma_q^{\mathrm{B}}[G^{\mathrm{S}}, \Phi_3^{\mathrm{S}}](\omega = \omega_0)$$

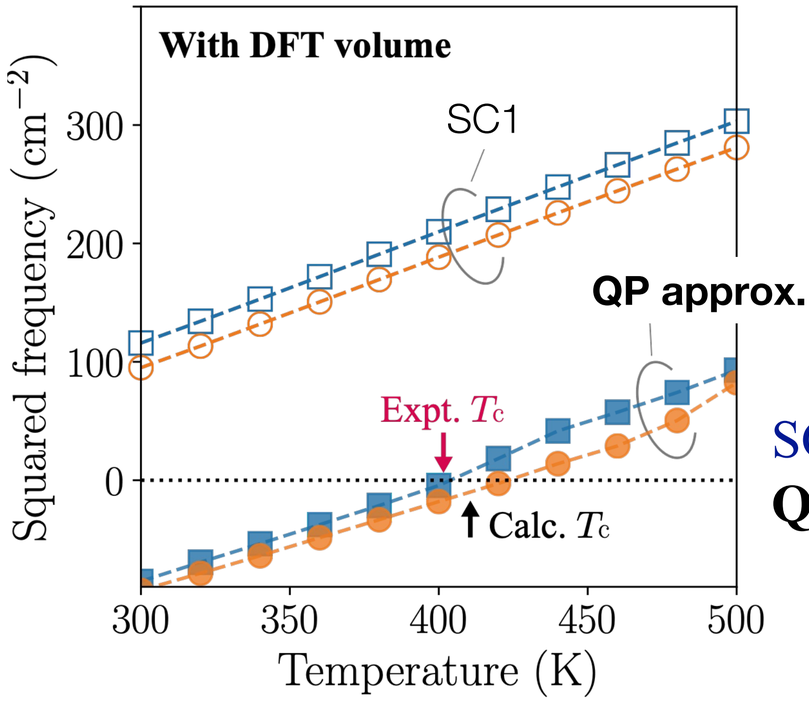
Quasiparticle (QP) approx.

$$\Omega_{\boldsymbol{q}\nu}^2 = (\omega_{\boldsymbol{q}\nu}^{\mathrm{S}})^2 - 2\omega_{\boldsymbol{q}\nu}^{\mathrm{S}} \mathrm{Re}\Sigma_{\boldsymbol{q}\nu}^{\mathrm{B}}[G^{\mathrm{S}}, \Phi_3](\Omega_{\boldsymbol{q}\nu})$$

$CsPbBr_3$





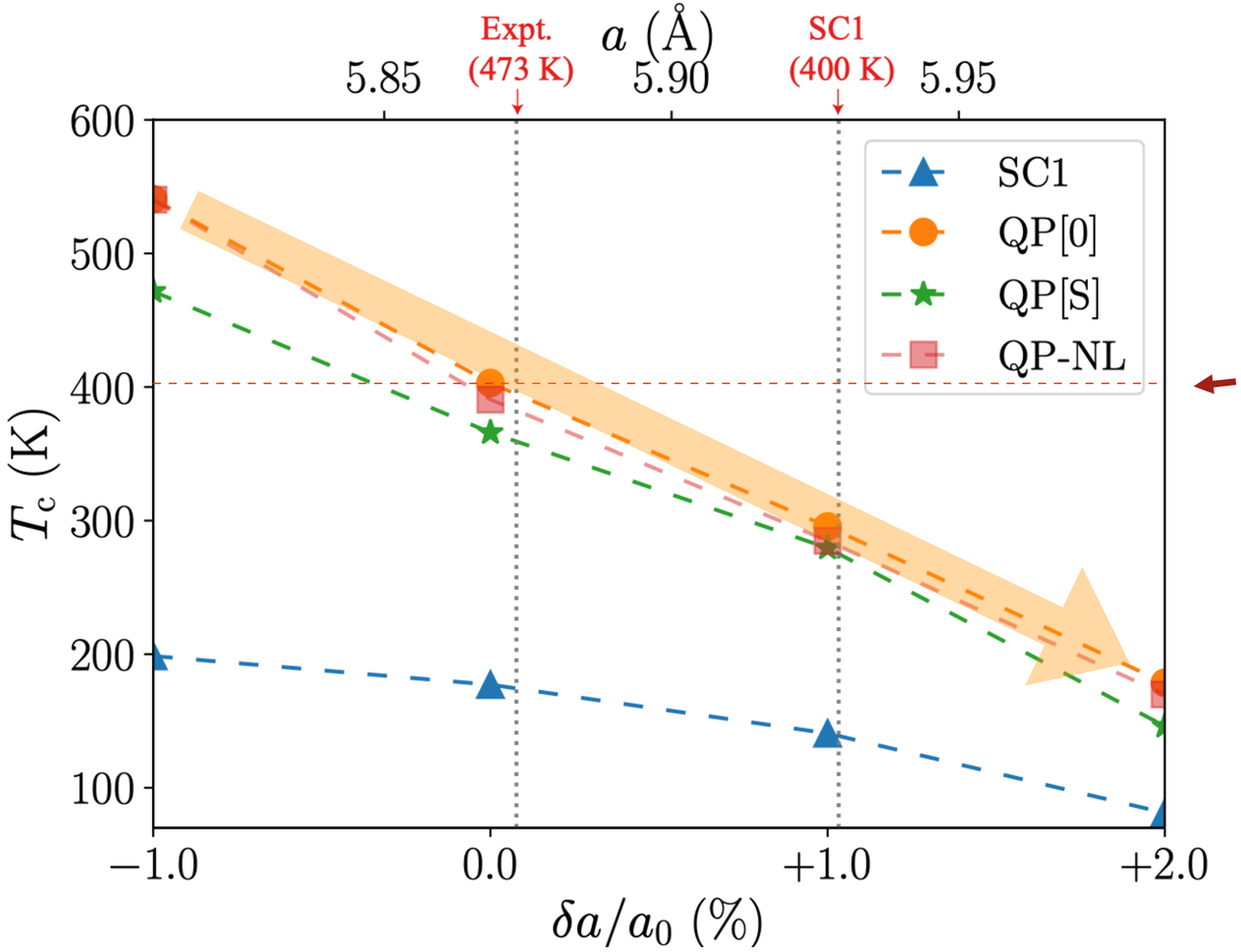


SCP theory: T_c = 198 K

QP approx.: T_c =**423** K

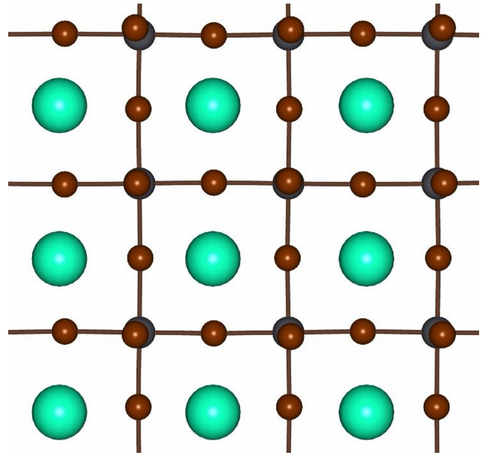
Expt.: T_c = 403 K

Influence of lattice parameter



Expt. T_c (403 K)

AFD mode



$$\frac{\partial T_c}{\partial a} \sim -2 \times 10^3 \ \mathrm{K} \cdot \mathrm{Å}^{-1}$$

TT and W. Saidi, Phys. Rev. Lett. **129**, 185901 (2022)

Structure optimization at finite temperatures

Self-consistent phonon (SC1) theory

- ☑ Able to compute renormalized phonons at finite temperatures
- ☐ Able to compute crystal structures at finite temperatures

R. Masuki, TT *et al.*, Phys. Rev. B **106**, 224104 (2022)

R. Masuki, TT *et al.*, Phys. Rev. B **107**, 134119 (2023)

Ryota Masuki
(Univ. Tokyo)

SC1 free energy and SC1 frequency

Feynmann–Gibbs–Bogoliubov inequality: $F_H \leq F_H(\hat{\mathcal{H}}_0)$

SC1 vibrational free energy

$$F_H(\hat{\mathcal{H}}_0) = \mathrm{tr}(\hat{\rho}_{\mathcal{H}_0}\hat{H}) + \frac{1}{\beta}\mathrm{tr}(\hat{\rho}_{\mathcal{H}_0}\ln\hat{\rho}_{\mathcal{H}_0})$$

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{U}_2 + \hat{U}_3 + \hat{U}_4 + \hat{U}_5 + \hat{U}_6 + \cdots \\ &= \hat{\mathcal{H}}_0 + (\hat{U}_2 - \hat{\mathcal{U}}_2 + \hat{U}_3 + \hat{U}_4 + \hat{U}_5 + \hat{U}_6 + \cdots)\end{aligned}$$

$$\begin{aligned}\mathrm{tr}(\hat{\rho}_{\mathcal{H}_0}\hat{H}) = \mathrm{tr}(\hat{\rho}_{\mathcal{H}_0}\hat{\mathcal{H}}_0) + \mathrm{tr}(\hat{\rho}_{\mathcal{H}_0}(\hat{U}_2 - \hat{\mathcal{U}}_2)) \\ + \mathrm{tr}(\hat{\rho}_{\mathcal{H}_0}\hat{U}_4) + \mathrm{tr}(\hat{\rho}_{\mathcal{H}_0}\hat{U}_6) + \cdots\end{aligned}$$

even-term anharmonicity

SC1 frequency

$$\nabla_{\Omega_q} F_H(\hat{\mathcal{H}}_0) = 0$$

$$\begin{aligned}\Omega_q^2 = \omega_q^2 &+ \frac{1}{2}\sum_{q'}\Phi_4(-q,q;-q',q')\alpha_{q'} \\ &+ \frac{1}{8}\sum_{q'q''}\Phi_6(-q,q;-q',q';-q'',q'')\alpha_{q'}\alpha_{q''} \\ &+ \cdots\end{aligned}$$

anharmonic force constants

$$\alpha_q = \frac{\hbar(2n_q+1)}{2\Omega_q}$$

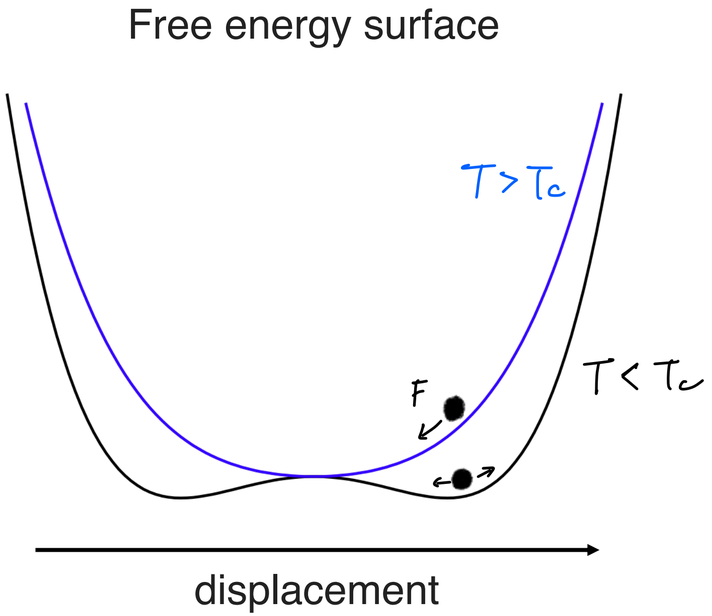
mean-square displacement

Atomic force at finite temperature

SC1 free energy $F_{\mathrm{SC1}} = \min_{\mathcal{H}_0} F_H(\hat{\mathcal{H}}_0)$

Atomic force $\boldsymbol{F}_\alpha = -\frac{\partial E_{\mathrm{BO}}}{\partial \boldsymbol{R}_\alpha} - \frac{\partial F_{\mathrm{SC1}}}{\partial \boldsymbol{R}_\alpha}$

DFT force — SC1 correction



$$\frac{\partial F_{\mathrm{SC1}}}{\partial \boldsymbol{R}_\alpha} = \sum_\nu \sqrt{M_\alpha}\boldsymbol{e}(\alpha, 0\nu)\frac{\partial F_{\mathrm{SC1}}}{\partial q_\nu^{(0)}}$$

$$= \sum_\nu \sqrt{M_\alpha}\boldsymbol{e}(\alpha, 0\nu)\left[\frac{1}{2}\sum_q \Phi_3(-q;q;0\nu)\alpha_q + \frac{1}{8}\sum_{qq'}\Phi_5(-q;q;-q';q';0\nu)\alpha_q\alpha_{q'} + \cdots\right]$$

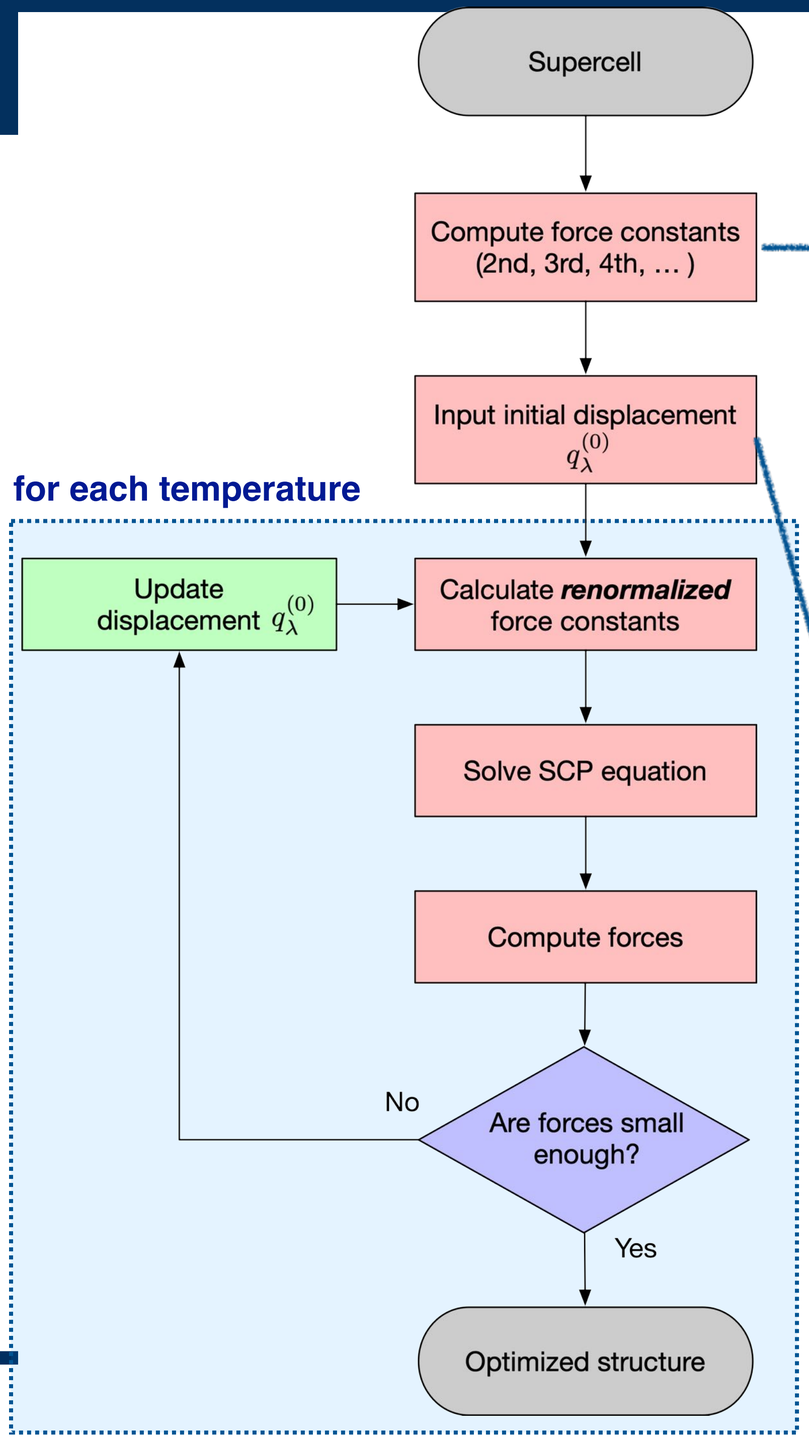
odd-term anharmonicity

See also stochastic implementation (SSCHA): Monacelli et al., *Phys Rev B* **98**, 024106 (2018).

DFT and SC1: A comparison

	DFT (0 K)	**SC1** (finite temperature)
What to minimize	Enthalpy $H = U_0 + pV$	Free energy $G = U_0 + F_{\mathrm{SC1}} + pV$
Forces	$\boldsymbol{F}_\alpha = -\dfrac{\partial E_{\mathrm{BO}}}{\partial \boldsymbol{R}_\alpha}$	$\boldsymbol{F}_\alpha = -\dfrac{\partial E_{\mathrm{BO}}}{\partial \boldsymbol{R}_\alpha} - \dfrac{\partial F_{\mathrm{SC1}}}{\partial \boldsymbol{R}_\alpha}$
Stress tensor	$\sigma_{\alpha\beta} = \dfrac{1}{\Omega_0}\dfrac{\partial U_0}{\partial \epsilon_{\alpha\beta}}$	$\sigma_{\alpha\beta} = \dfrac{1}{\Omega_0}\dfrac{\partial U_0}{\partial \epsilon_{\alpha\beta}} + \dfrac{1}{\Omega_0}\dfrac{\partial F_{\mathrm{SC1}}}{\partial \epsilon_{\alpha\beta}}$

Computational workflow



$$E_{\mathrm{BO}} - U_0 = U_2 + U_3 + U_4 + \cdots$$
$$= \frac{1}{2}\sum_{i,j}\Phi_{ij}u_iu_j + \frac{1}{3!}\sum_{i,j,k}\Phi_{ijk}u_iu_ju_k + \frac{1}{4!}\sum_{i,j,k,\ell}\Phi_{ijk\ell}u_iu_ju_ku_\ell + \cdots$$
$$= \boldsymbol{b}\cdot\boldsymbol{\Phi}$$

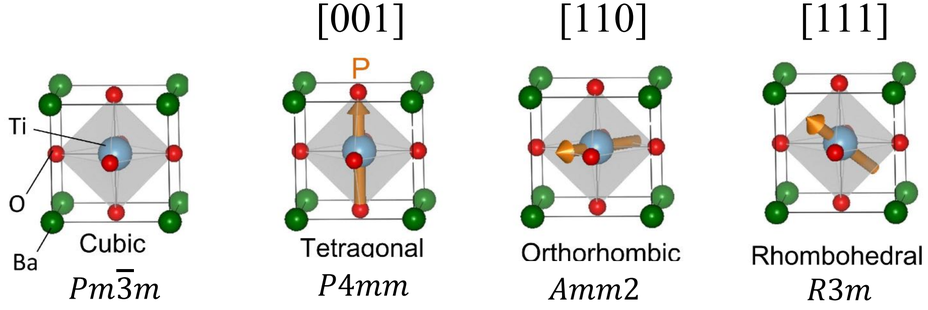
parameters

basis

* Generate displacement-force dataset using DFT calculation (~ 100 training snapshots)
* Estimate force constants using compressive sensing (linear regression)

adaptive LASSO $\quad \tilde{\boldsymbol{\Phi}}_{\mathrm{ada-LASSO}} = \arg\min_{\boldsymbol{\Phi}} \|A\boldsymbol{\Phi} - \boldsymbol{F}^{\mathrm{DFT}}\|_2^2 + \lambda\sum_i w_i|\Phi_i|$

F. Zhou, W. Nielson, Y. Xia, V. Ozoliņš, *PRL* **113**, 185501 (2014).
TT and Tsuneyuki, *PRB* **92**, 054301 (2015)



* initial displacement works as a small perturbation that breaks the symmetry

Figures from J. Fujioka. *et al, Sci Rep* **5**, 13207 (2015).

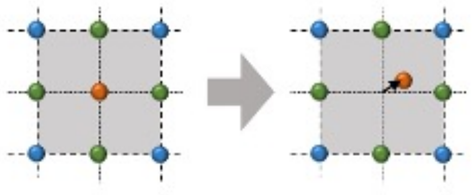
“Renormalization” of force constants

***n*th-order IFC**
in a **displaced** structure

***n*th-, (*n*+1)th-, … order IFC**
in the **reference** structure

$$\tilde{\Phi}_n^{(\xi)}(q_1;q_2;\ldots;q_n) = \tilde{\Phi}_n^{(0)}(q_1;q_2;\ldots;q_n) + \sum_{j_1} \tilde{\Phi}_{n+1}^{(0)}(q_1;q_2;\ldots;q_n;\mathbf{0}j_1) \times \xi_{j_1} + \frac{1}{2}\sum_{j_1 j_2} \tilde{\Phi}_{n+2}^{(0)}(q_1;q_2;\ldots;q_n;\mathbf{0}j_1;\mathbf{0}j_2) \times \xi_{j_1}\xi_{j_2} + \cdots$$

Normal mode displacement (**variable**)

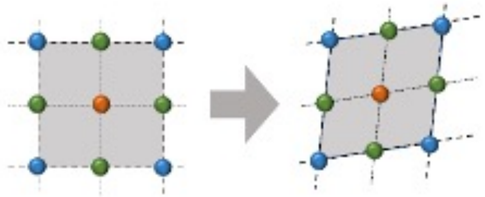


***n*th-order IFC**
in a **distorted** lattice

$$\Phi_{\mu_1\ldots\mu_n}^{(u_{\mu\nu})}(R_1\alpha_1;\ldots;R_n\alpha_n) = \Phi_{\mu_1\ldots\mu_n}^{(0)}(R_1\alpha_1;\ldots;R_n\alpha_n) + \sum_{R'_1\alpha'_1\mu'_1\nu'_1} \Phi_{\mu_1\ldots\mu_n\mu'_1}^{(0)}(R_1\alpha_1;\ldots;R_n\alpha_n;R'_1\alpha'_1) \times u_{\mu'_1\nu'_1} R'_{1\alpha'_1\nu'_1} + \frac{1}{2}\sum_{R'_1\alpha'_1\mu'_1\nu'_1}\sum_{R'_2\alpha'_2\mu'_2\nu'_2} \Phi_{\mu_1\ldots\mu_n\mu'_1\mu'_2}^{(0)}(R_1\alpha_1;\ldots;R_n\alpha_n;R'_1\alpha'_1;R'_2\alpha'_2) \times u_{\mu'_1\nu'_1} R'_{1\alpha'_1\nu'_1} u_{\mu'_2\nu'_2} R'_{2\alpha'_2\nu'_2} + \cdots$$

Strain tensor (**variable**)

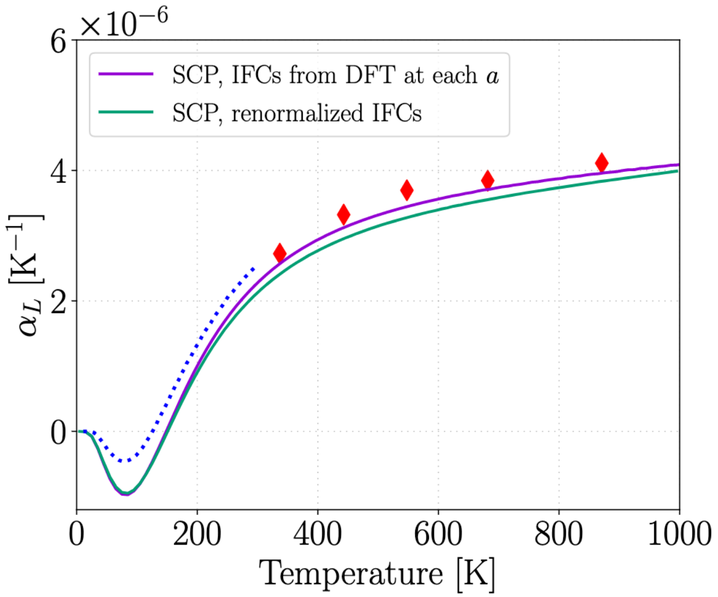
Cartesian coordinate



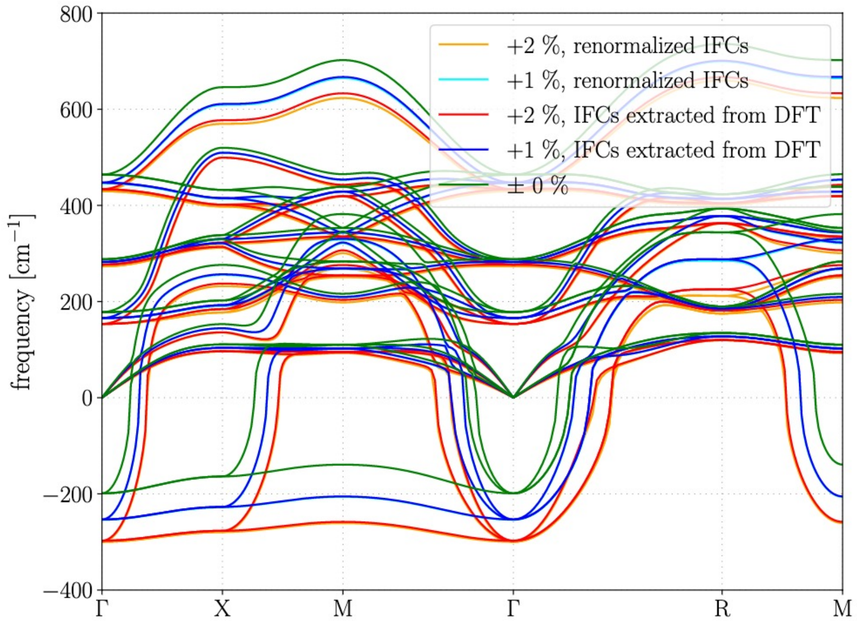
R. Masuki, TT *et al.*, Phys. Rev. B **106**, 224104 (2022)

How good is “renormalization”?

Thermal expansion of Si



Harmonic phonon of $BaTiO_3$



purple: compute harmonic and anharmonic IFCs for **14 different lattice constants**

green: compute harmonic and anharmonic IFCs for a_0 **only**. The IFCs at different lattice constants are estimated by “renormalization”.

✓ Good agreement between the renormalization technique and full DFT calculation.

R. Masuki, TT *et al.*, Phys. Rev. B **106**, 224104 (2022)

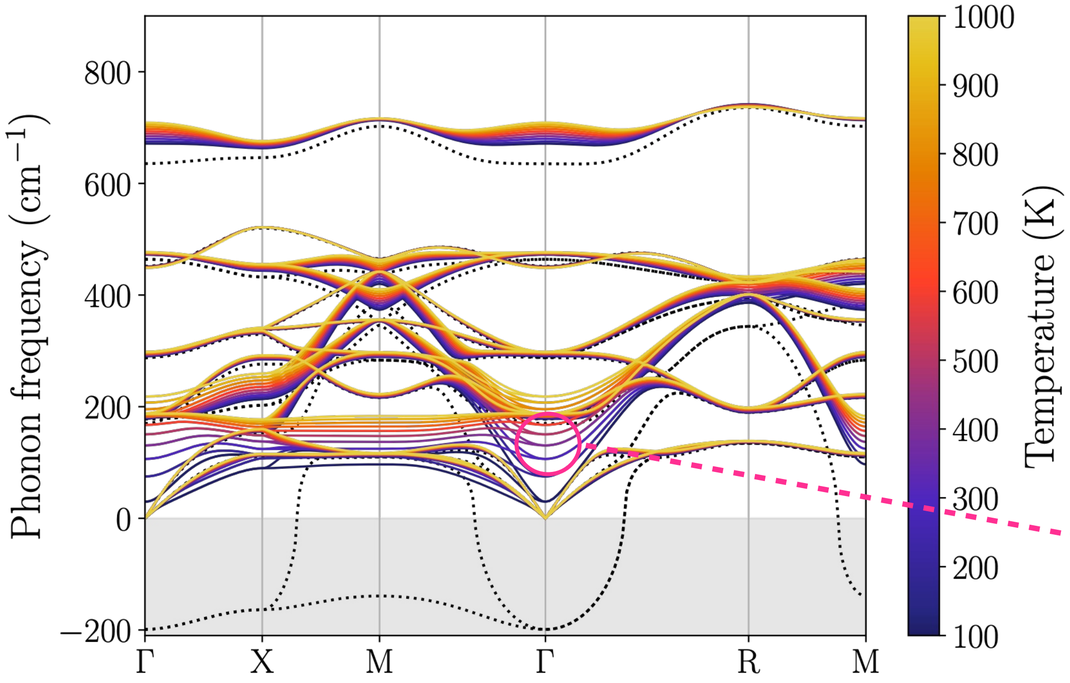
Application to consecutive transition in $BaTiO_3$

- VASP code for DFT (PAW)
- PBEsol xc functional
- 2x2x2 supercell for force constant calculation
- Truncate Taylor series at the fourth-order
- 80 training structures (80 static DFT calculations)

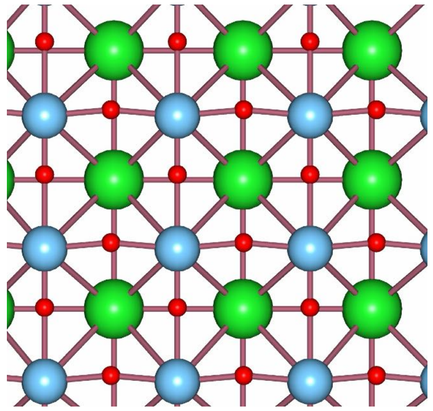
ALAMODE

https://alamode.readthedocs.io/

SC1 frequency for cubic $BaTiO_3$

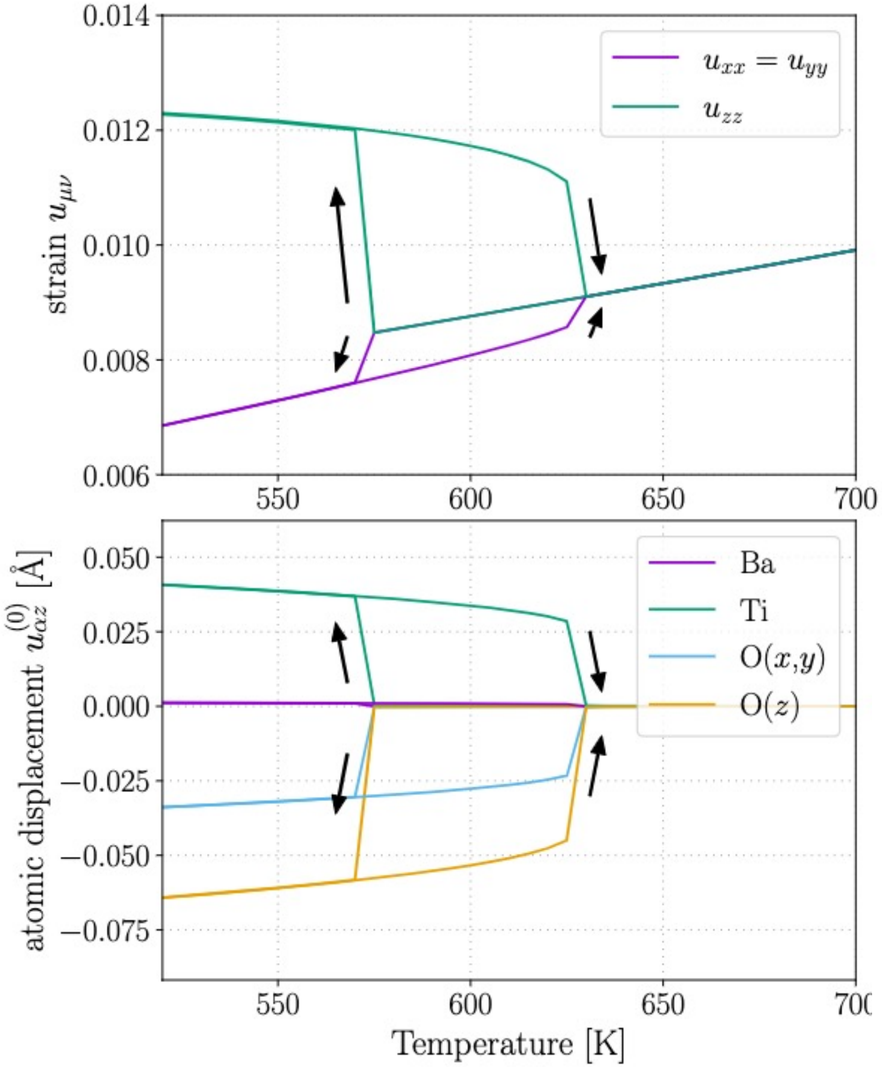


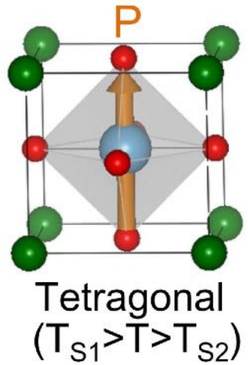
Ferroelectric soft mode



Cubic-to-Tetragonal transition

- Start the calculation with **small displacements along [001]**





✓ Succeeded in predicting structural phase transition with a temperature hysteresis

✓ Predicted T_c ~ **600** K Expt.: T_c ~ **393** K

✓ Overestimate T_c due to slightly larger (+0.01 Å) lattice constant by PBEsol

Previous theoretical studies:

- MC, effective Hamiltonian (no ZPE, LDA): **297** K [1]
- MC, effective Hamiltonian (ZPE, LDA) : **265** K [2]
- MD, DFT-fitted model potentials (PBEsol): **160–170** K [3]

[1] Zhong, Vanderbilt, Rabe, *PRL*1994.

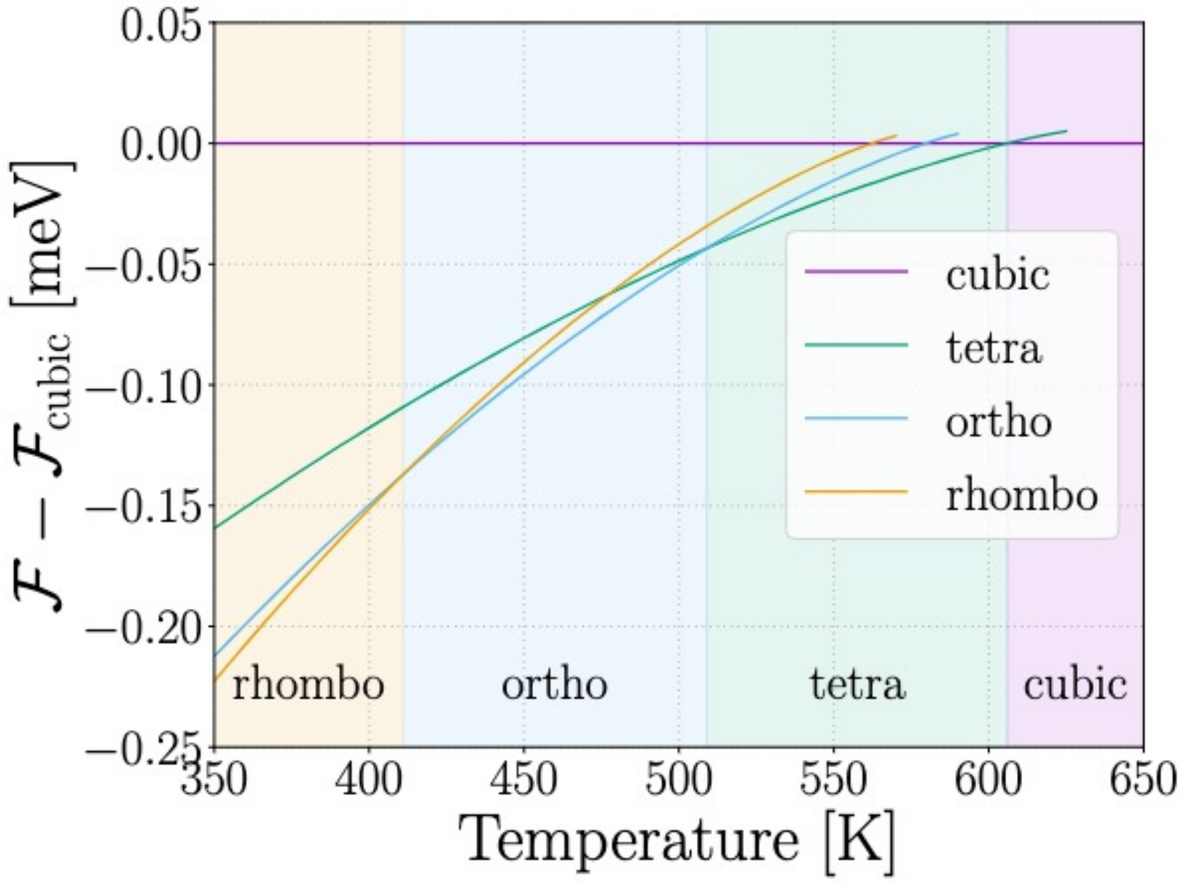
[2] Zhong, Vanderbilt, *PRB*1996.

[3] Qi, Liu, Grinberg, Rappe, *PRB*2016.

Successive phase transition

- Tetra.: small displacements along **[001]**
- Ortho.: small displacements along **[110]**
- Rhombo.: small displacements along **[111]**

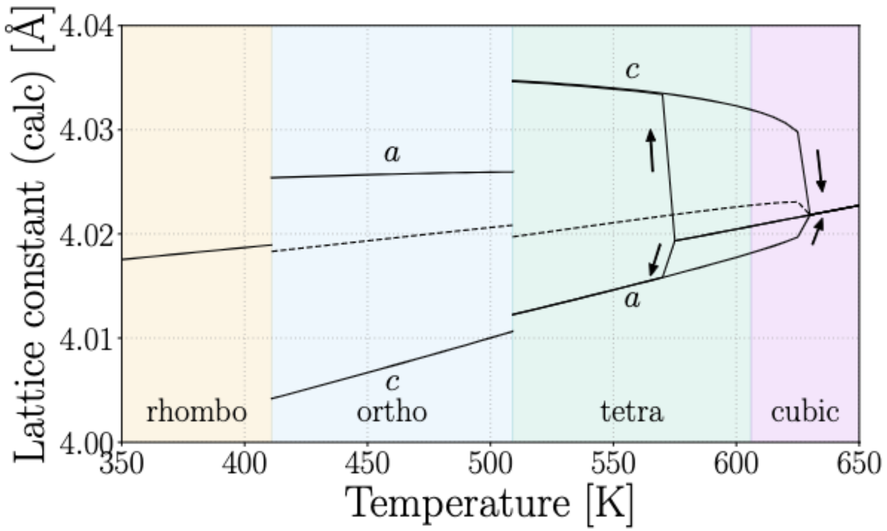
	our method [K]	experiment [K]
cubic-tetra	606	~390
tetra-ortho	509	~ 270
ortho-rhombo	411	~ 180

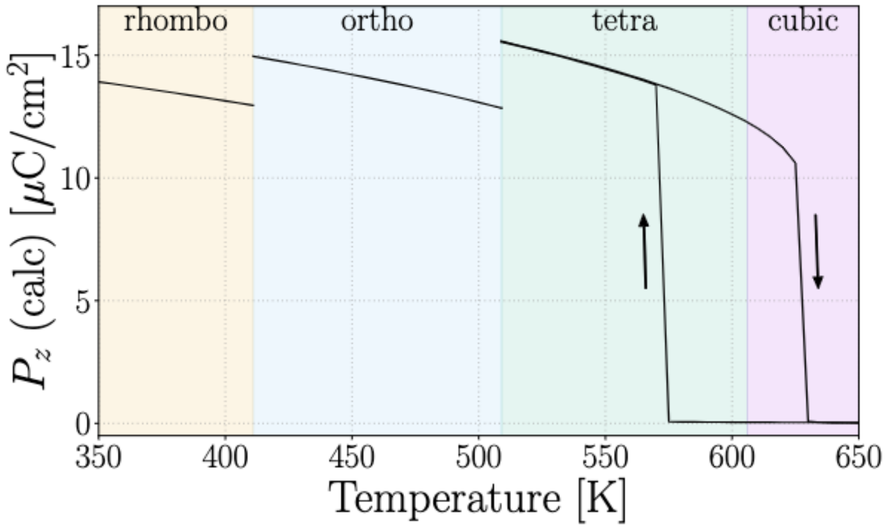


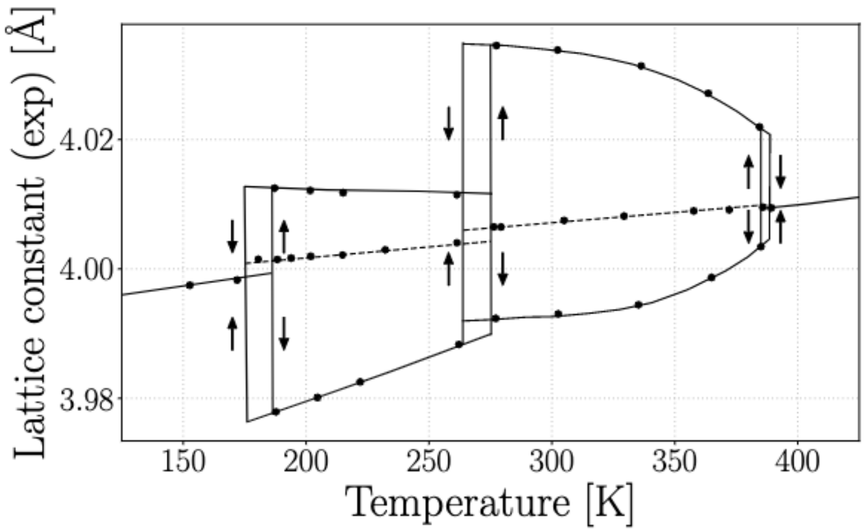
✓ Successive phase transition can be reproduced with the correct sequence

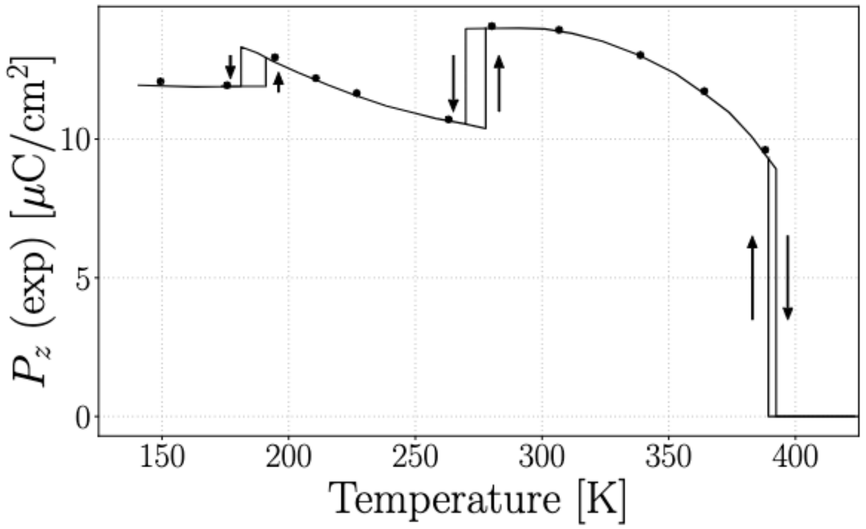
R. Masuki, TT et al., Phys. Rev. B **106**, 224104 (2022)

Lattice parameters and spontaneous polarization







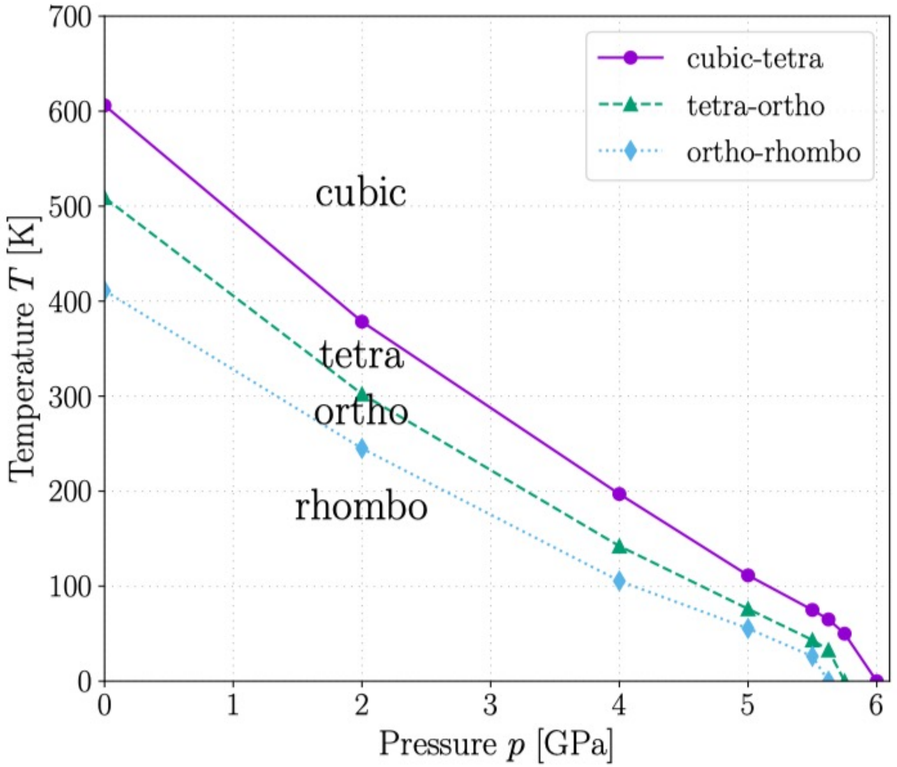


✓ Able to compute finite-temperature structural parameters and spontaneous polarization

R. Masuki, TT *et al.*, Phys. Rev. B **106**, 224104 (2022)

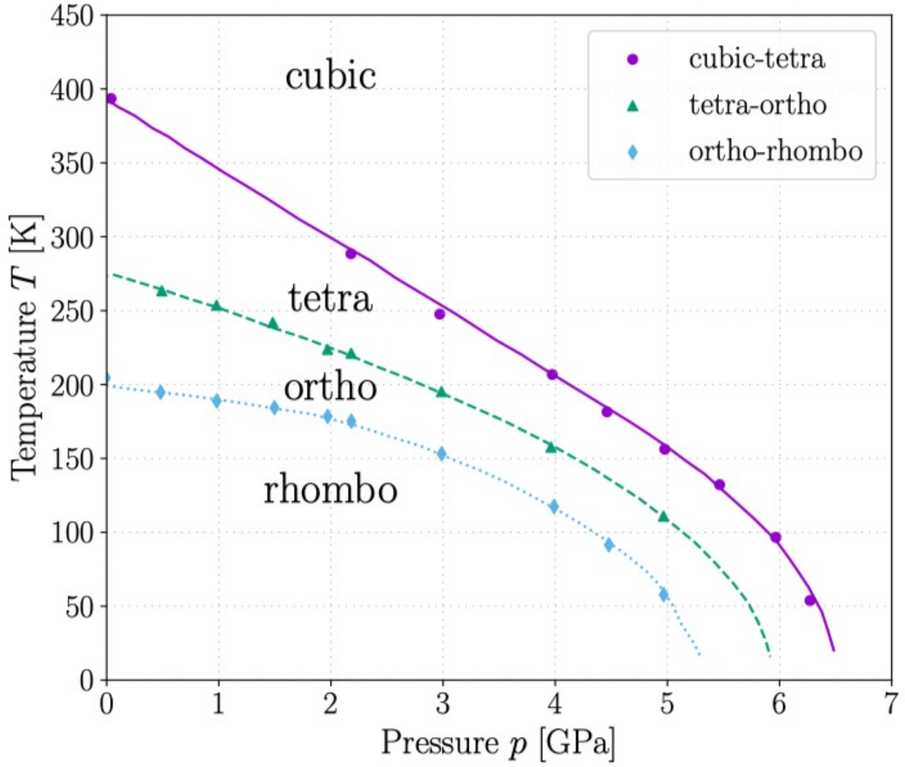
Finite temperature + finite pressure

Our method



Expt.

Phys. Rev. Lett. 78, 2397 (1997).

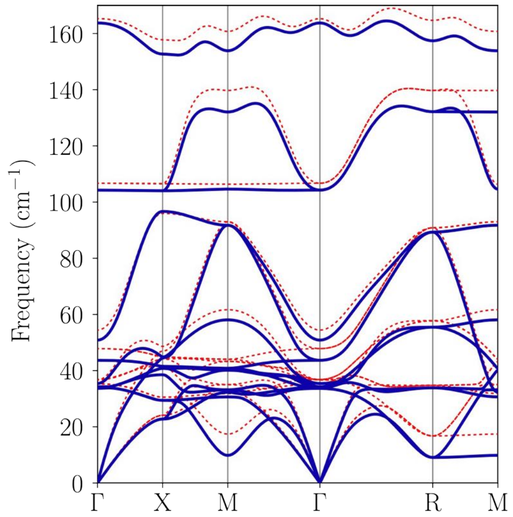


Comparison between SC1 and MD

	SC1	Molecular dynamics (MD)
Pros.	• Lower computational costs • Finite-temperature structures can be obtained deterministically • Phonons can be obtained simultaneously • Include zero-point motion	• Full anharmonicity • Able to simulate order-disorder transition
Cons.	• Approximate the atomic distribution by Gaussian assuming displacive transition • Anharmonicity is included at the mean-field level	• High computational cost • (usually) ignores the zero-point motion

Summary & perspective

- Perturbative expansion has been successful in predicting phonon-phonon scattering rates and thermal conductivity of various solids. **However, it may breakdown for strongly anharmonic solids.**



- Variational approach (Self-consistent phonon) is a powerful tool for obtaining a **better one-body description** of phonon. It even enables us to calculate **structures at finite temperatures.**

- **Future directions**

  More application studies

  Transport properties near the phase transition

  Higher-order anharmonicity (5th, …)

  Comparison to MD using machine-learning FF

ALAMODE