35th Computational Materials Design (CMD) Workshop

Phonon anharmonicity from first principles

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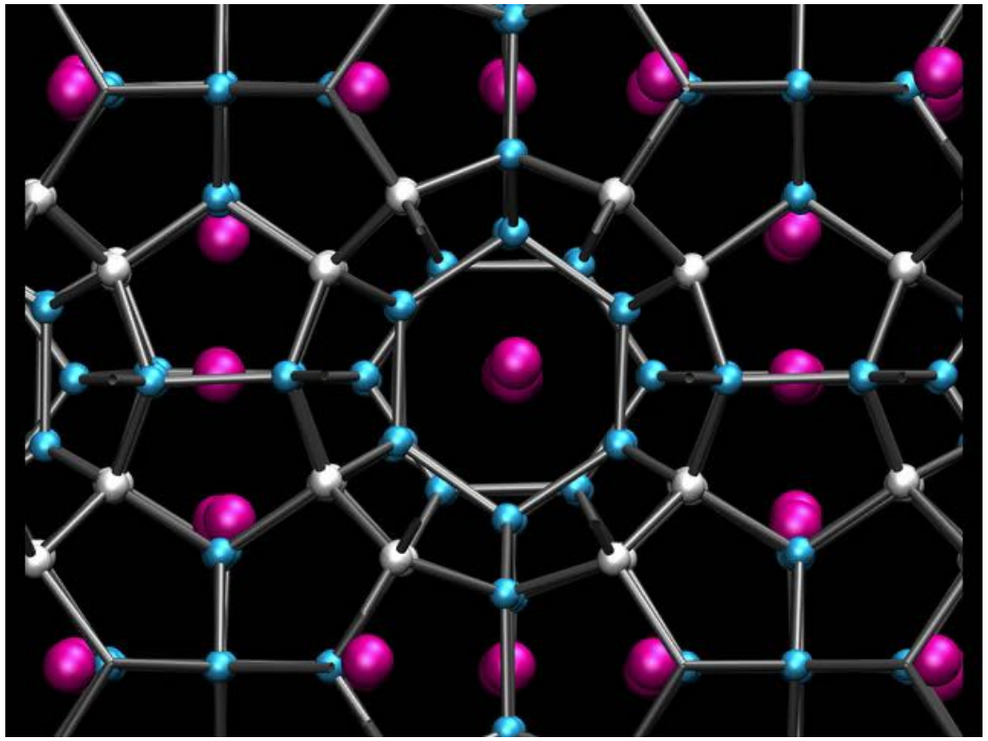
Outline

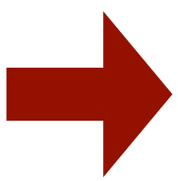
1. Introduction to phonon anharmonicity
2. Perturbative treatment of anharmonicity
3. Non-perturbative treatment of anharmonicity
4. Efficient calculation of anharmonic force constants
5. Applications
6. Summary

Phonon (lattice vibration)

- Density functional theory (DFT) is theory at absolute zero (T = 0 K)
- Lattice or molecular vibration affects physics at finite temperature.



How to treat lattice vibration in crystals?



***Ab initio* phonon calculation**

Ab initio molecular dynamics

Phonon physics

Phonon dispersion relation

- Raman, IR, INS, IXS measurements
- Dynamical stability

Thermodynamics & mechanics

- Vibrational entropy, Helmholtz free energy, …
- Lattice constant, elastic constants at finite temperature
- Phase transformation at finite temperature

Transport

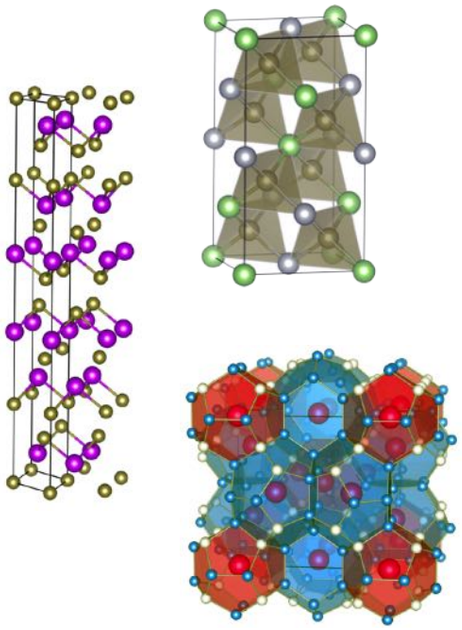
- Phonon thermal transport
- Scattering of electrons by el-ph coupling
- Phonon-mediated superconductivity

Dielectrics

- Dielectric constant
- Band-gap renormalization by phonons

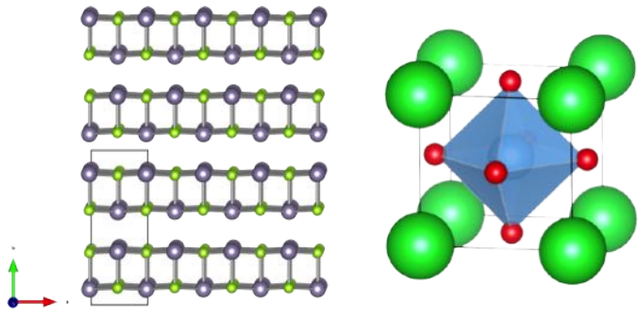
Lattice vibration in energy materials

Thermal conductivity



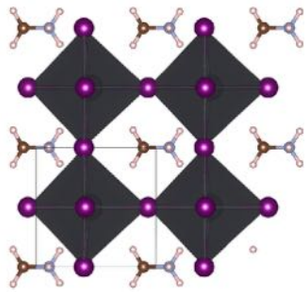
Thermoelectric materials

Structural phase transition

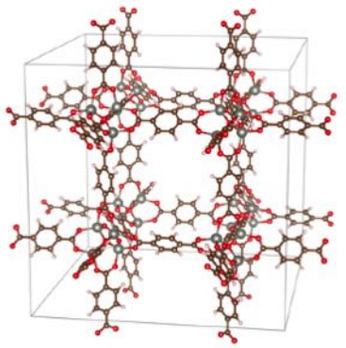


(Piezo, ferro)electric materials

Thermal stability



Photovoltaic materials

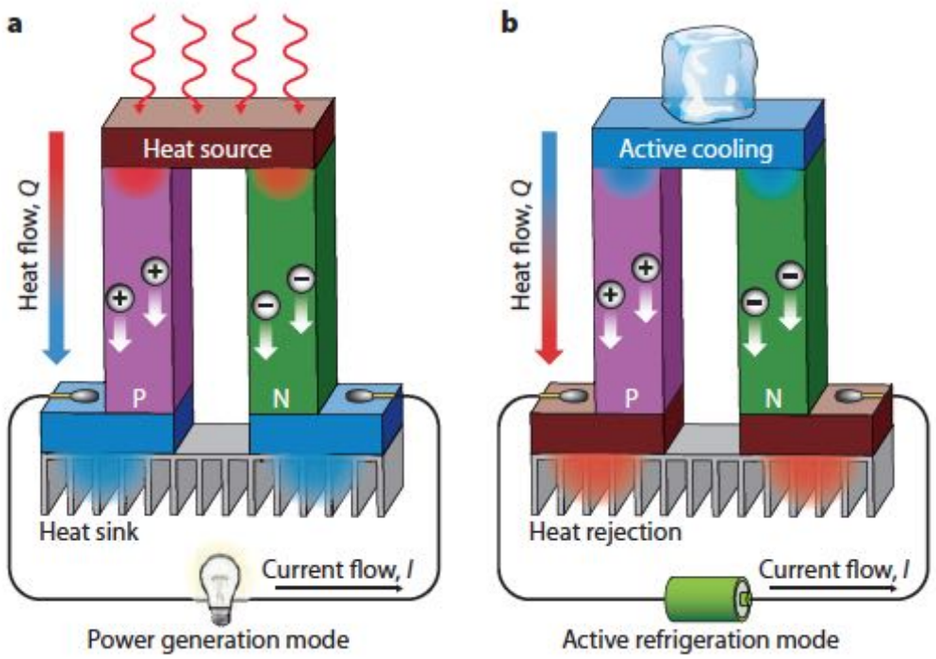


MOF

Electron-phonon coupling

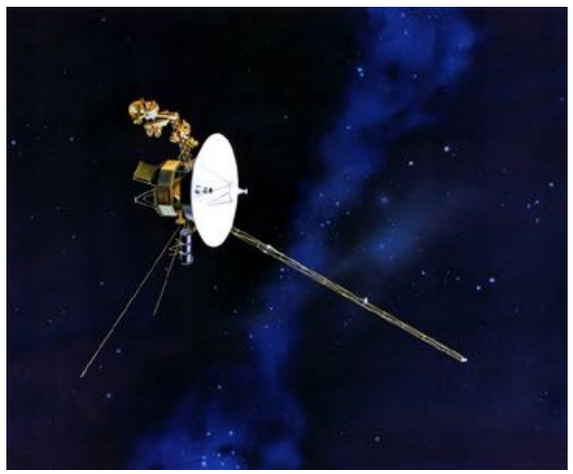
- Quantitative prediction & robust understanding of thermophysical properties is desired.
- Challenging due to **anharmonic effects**

Thermoelectric (TE) materials



J.-F. Li et al., NPG Asia Mater **2**, *152 (2010).*

- Thermoelectric (TE) devices efficiently convert a temperature difference to an electrical potential, and vice versa.
- Electrical power generation (Seebeck effect)
- Cooling (Peltier effect)
- About 60% of energy is lost as heat



NASA Voyager

BMW 530i

Thermoelectric figure of merit

For high energy efficiency, new and abundant materials that possess high figure-of-merit are necessary

Figure of merit

$$ZT = \sigma S^2 T / (\kappa_c + \kappa_L)$$

Electrical conductivity
> 10^3 / (Ω·m)

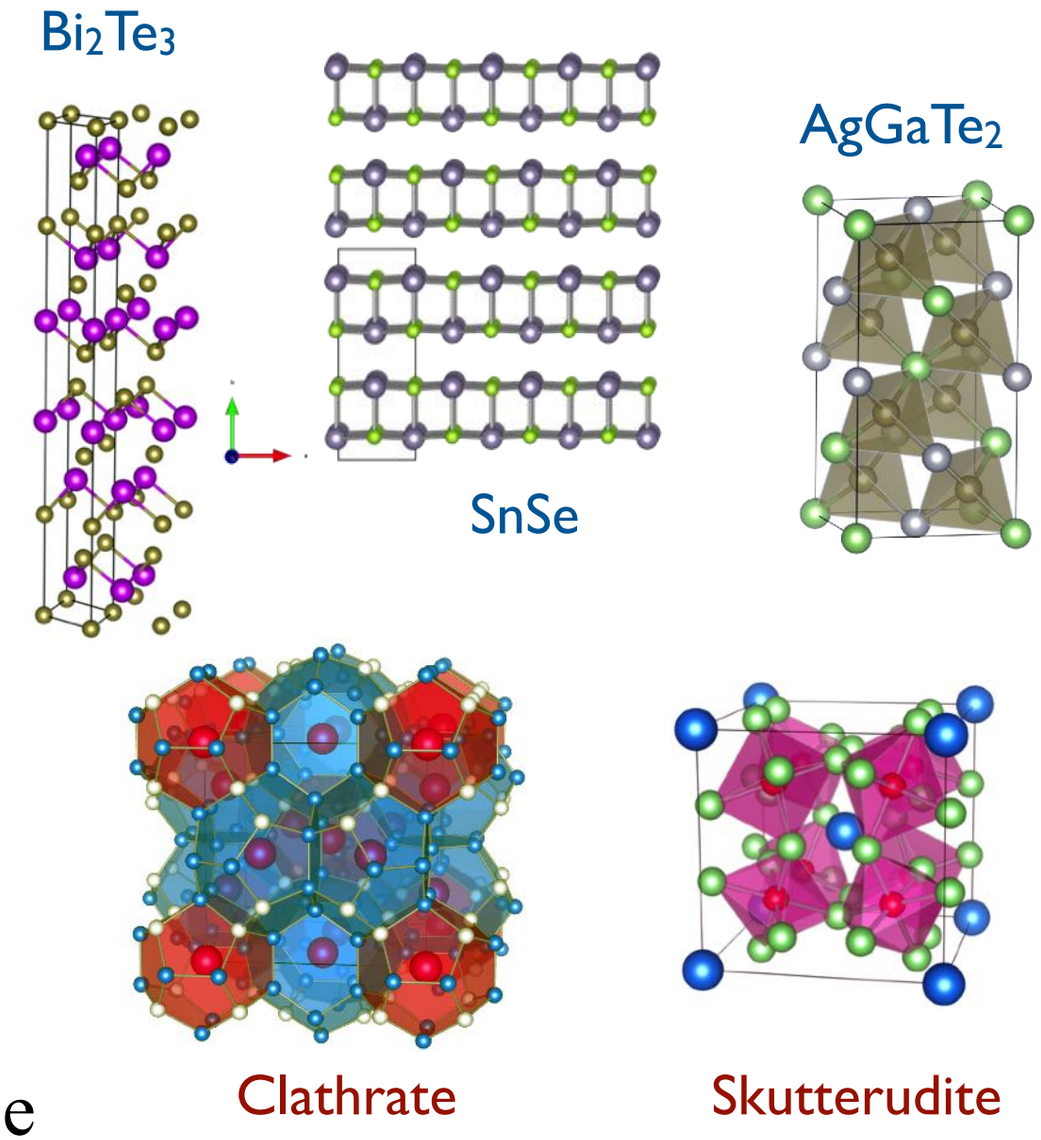
Seebeck coefficient
> 100 μV/K

Lattice Thermal Conductivity (LTC) < 1.0 W/mK

$ZT > 1$ is necessary, $ZT > 2$ or higher is desired.
Design principle looks simple but realizing higher ZT is challenging.

Strong anharmonicity in thermoelectric materials

- **Chalcolagenide TE materials**
  - PbTe, Bi_2Te_3, SnSe, $AgGaTe_2$, Cu_2Se, …
  - Lone pair
- **Host-guest structures**
  - Clathrates, Skutterudites, Pyrochrore
  - "Rattling" guest



Large atomic displacement factor

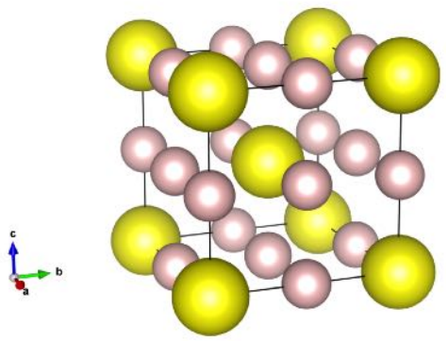
- Strong anharmonicity
- Ultralow κ_L & its unusual T-dependence

Large atomic displacement → Strong anharmonicity → Breakdown of harmonic approx.

Strong anharmonicity in other materials

High-Tc superconductors

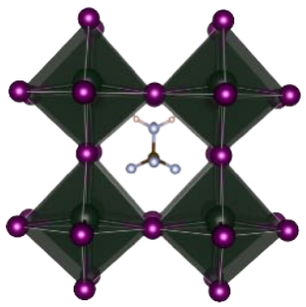
H_3S

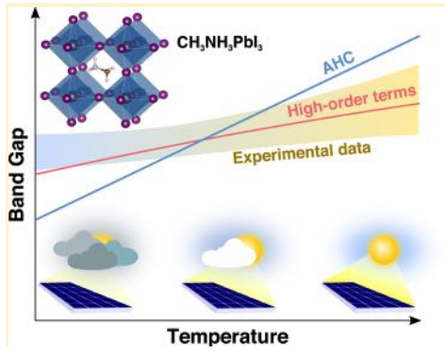


Nature **525**, 73 (2015).

Perovskite solar cell

$MAPbI_3$

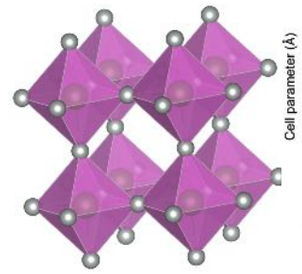


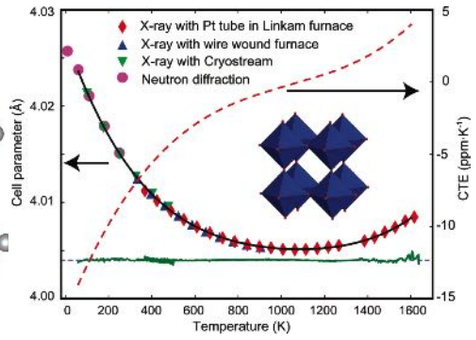


J. Phys. Chem. Lett. **7**, 5247 (2016).

Negative thermal expansion

ScF_3

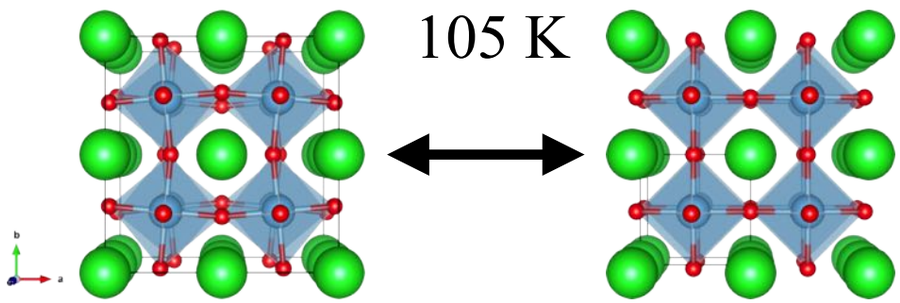




JACS **132**, 15496 (2010).

Structural phase transition

$SrTiO_3$



Tetragonal Cubic

Anharmonicity affects many properties

- Thermodynamical stability
- Optical properties
- Transport properties
- Elastic properties

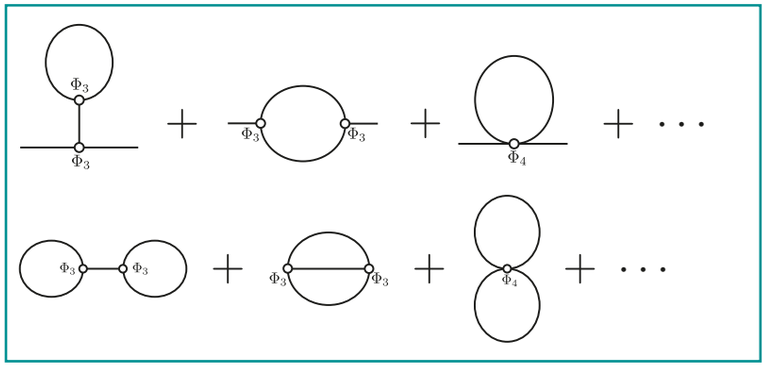
How to include anharmonic effects?

Many-body theory

- ✓ Quantum statistics
- ✓ Thermodynamic limit is accessible
- ✗ Anharmonic effects are included only partially
- ✗ **Requires anharmonic coupling constants**

$$[G_q(\omega)]^{-1} = \text{——} + \text{anharmonic correction}$$

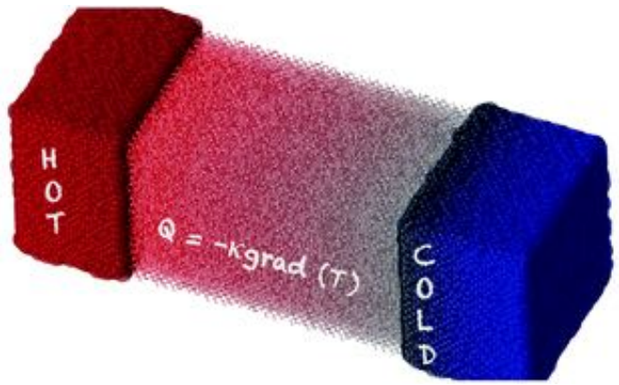
$$F_{\text{vib}} = \text{◯} + \text{anharmonic correction}$$



Molecular Dynamics (MD) methods

- ✓ Full anharmonicity
- ✓ (Dynamical) disorders
- ✗ Classical statistics
- ✗ Long-time & large-scale simulation is necessary
- ✗ DFT-MD is **very costly**

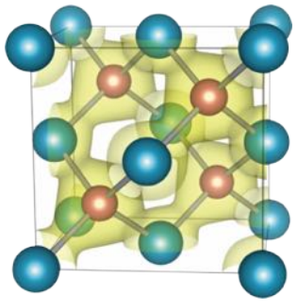
$$M_I \ddot{\boldsymbol{R}}_I = \boldsymbol{F}_I$$



Y. He *et al.*, Phys. Chem. Chem. Phys. **14**, 16209 (2012).

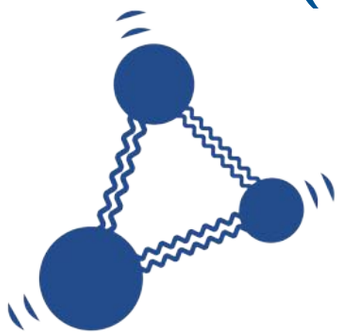
Outline of our approach

DFT calculation

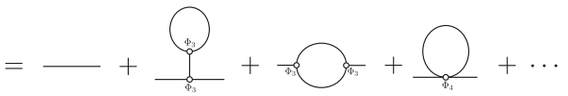


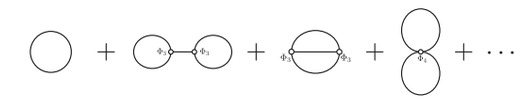
compressive sensing

Anharmonic lattice model (ALM)



Many-body theory

$$[G_q(\omega)]^{-1} =$$ 

$$F_{\mathrm{vib}} =$$ 

Molecular dynamics (DFT, Machine learning FF)

Thermal properties

- Phonons at finite temperature
- Vibrational free-energy (beyond QHA)
- Structural phase transition
- Thermal conductivity
- Thermal expansion
- …

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1. Introduction to phonon anharmonicity
2. Perturbative treatment of anharmonicity
3. Non-perturbative treatment of anharmonicity
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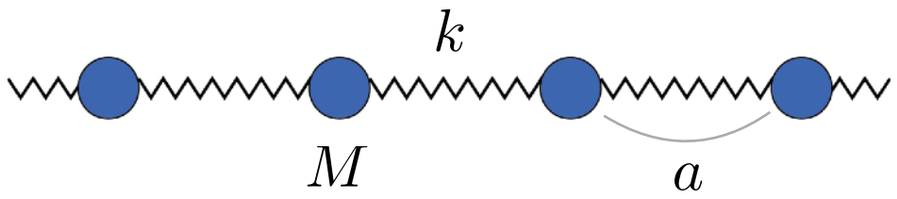
Phonons (harmonic)

Linear chain

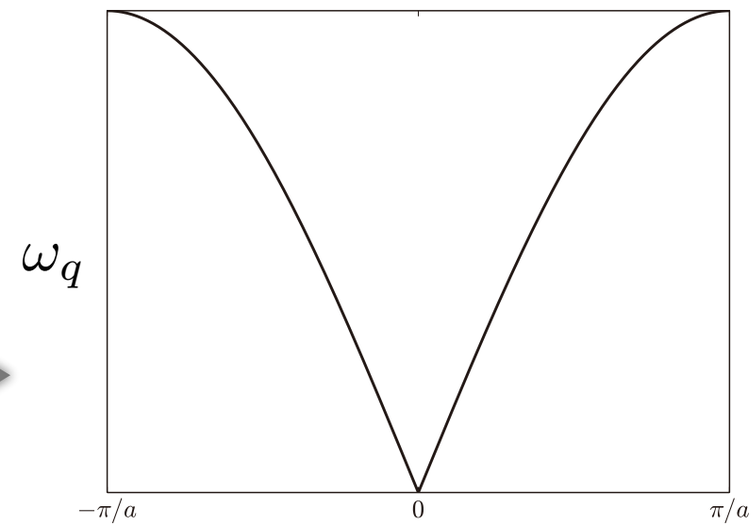


dispersion relation $\omega_q = 2\sqrt{\frac{k}{M}}|\sin\frac{1}{2}qa|$

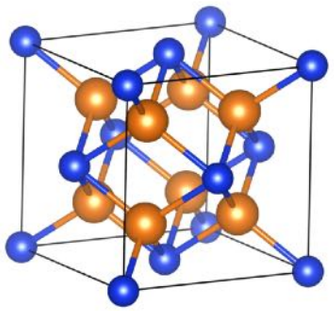
potential energy $V = \sum_i \frac{1}{2}k(u_i - u_{i-1})^2$

displacement

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



Generalization to 3D

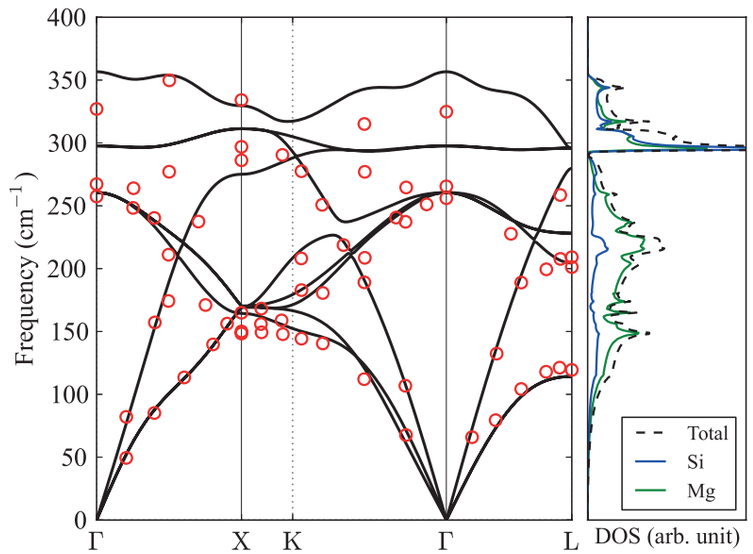


potential energy $V = \sum_{i,j} \frac{1}{2}\Phi_{ij}u_i u_j$

Harmonic force constants

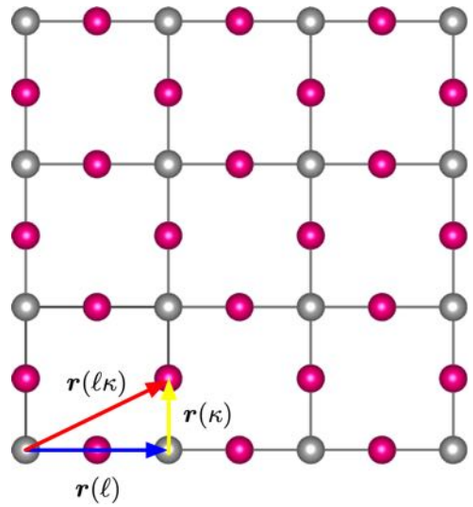
Eq. of motion $M_i u_i = -\sum_j \Phi_{i,j}u_j$

dispersion relation



Taylor expansion of potential energy surface

$$
\begin{aligned}
U - U_0 &= U_2 + U_3 + U_4 + \cdots \\
&= \frac{1}{2} \sum_{\{\ell,\kappa,\mu\}} \Phi_{\mu_1\mu_2}(\ell_1\kappa_1;\ell_2\kappa_2) \times u_{\mu_1}(\ell_1\kappa_1) u_{\mu_2}(\ell_2\kappa_2) \\
&+ \frac{1}{3!} \sum_{\{\ell,\kappa,\mu\}} \Phi_{\mu_1\mu_2\mu_3}(\ell_1\kappa_1;\ell_2\kappa_2;\ell_3\kappa_3) \times u_{\mu_1}(\ell_1\kappa_1) u_{\mu_2}(\ell_2\kappa_2) u_{\mu_3}(\ell_3\kappa_3) \\
&+ \frac{1}{4!} \sum_{\{\ell,\kappa,\mu\}} \Phi_{\mu_1\mu_2\mu_3\mu_4}(\ell_1\kappa_1;\ell_2\kappa_2;\ell_3\kappa_3;\ell_4\kappa_4) \times u_{\mu_1}(\ell_1\kappa_1) u_{\mu_2}(\ell_2\kappa_2) u_{\mu_3}(\ell_3\kappa_3) u_{\mu_4}(\ell_4\kappa_4) + \cdots
\end{aligned}
$$



$\boldsymbol{u}(\ell\kappa) = \boldsymbol{R}(\ell\kappa) - \boldsymbol{R}^0(\ell\kappa)$ is atomic displacement from the equilibrium position $\boldsymbol{R}^0(\ell\kappa)$

n th-order interatomic force constant (IFC):

$$
\Phi_{\mu_1\ldots\mu_n}(\ell_1\kappa_1;\ldots;\ell_n\kappa_n) = \left. \frac{\partial^n U}{\partial u_{\mu_1}(\ell_1\kappa_1)\cdots\partial u_{\mu_n}(\ell_n\kappa_n)} \right|_{\{u\}=0}
$$

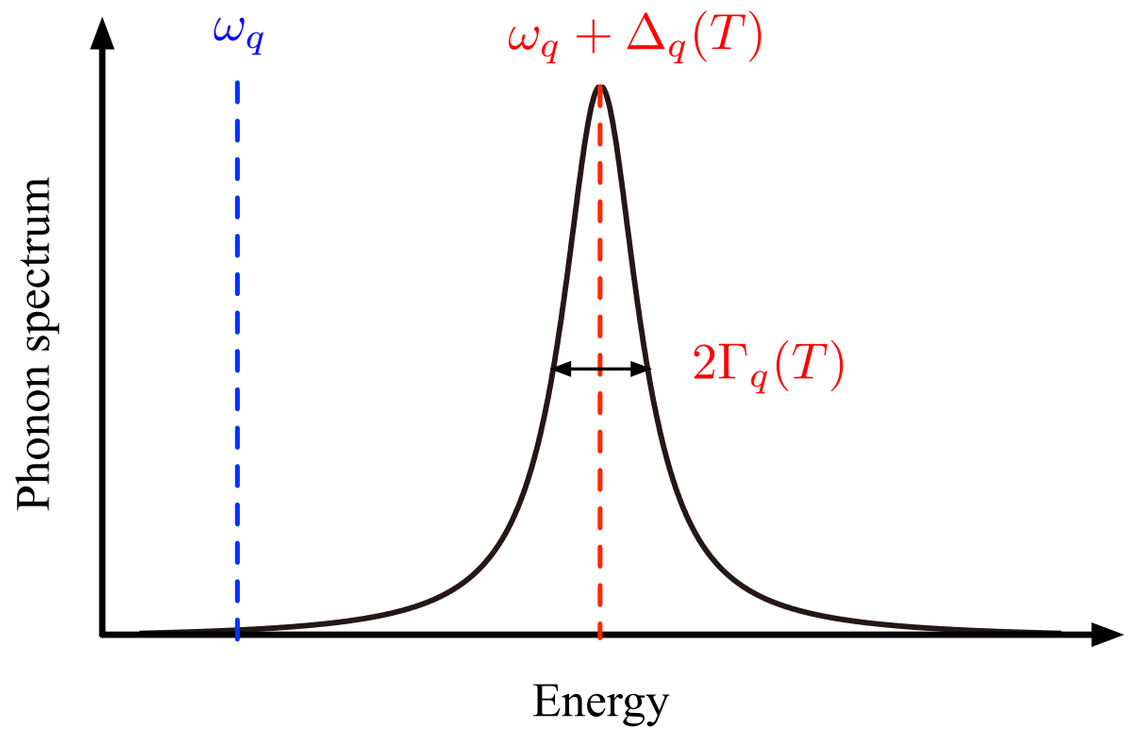
Limitation of the harmonic approx.

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

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

✗ Phonon is volume-independent
→ no thermal expansion

✗ Phonon is temperature-independent
→ no structural phase transition



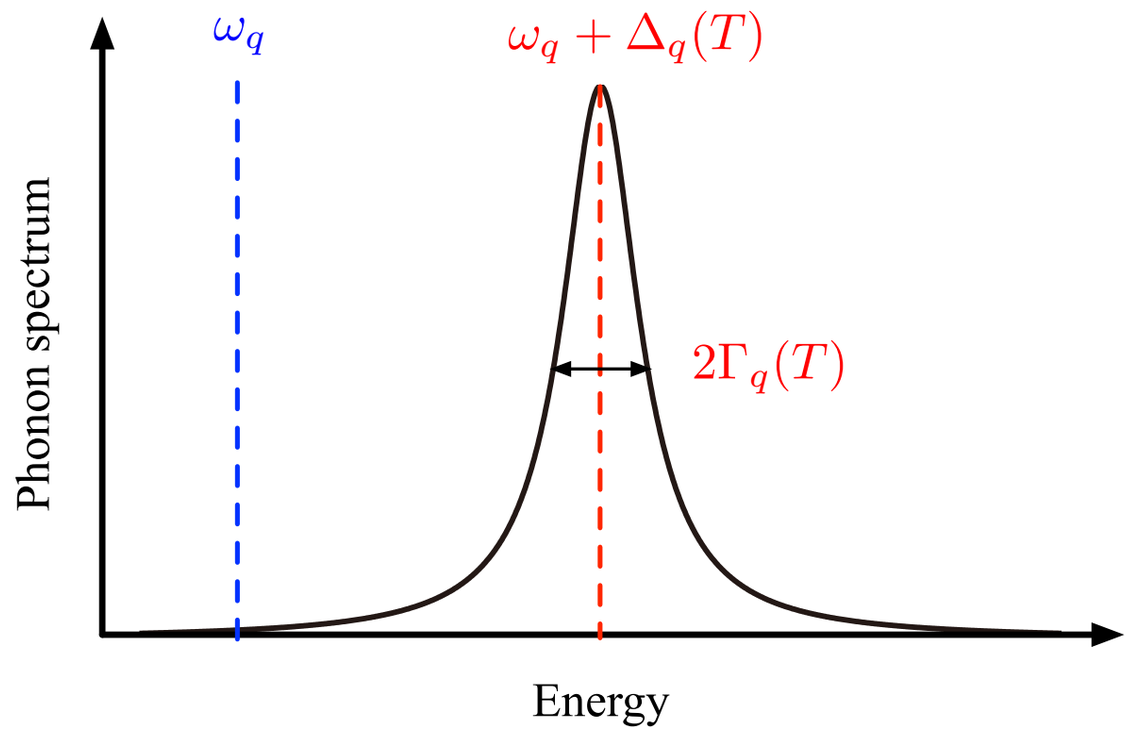
Anharmonicity (phonon-phonon interaction)

$$\hat{H}_0 = \sum_q \hbar\omega_q \left(\hat{b}_q^\dagger \hat{b}_q + \frac{1}{2}\right) + \hat{U}_3 + \hat{U}_4 + \cdots$$

✓ 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



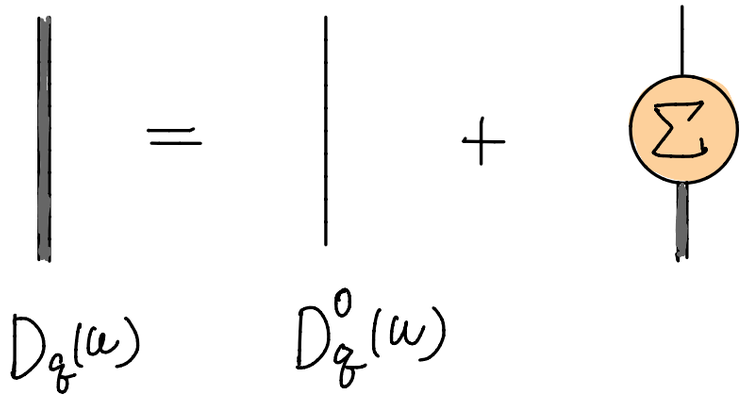
Vibrational many-body theory

$$\hat{H}_0 = \sum_q \hbar\omega_q \left(\hat{b}_q^\dagger \hat{b}_q + \frac{1}{2}\right) + \hat{U}_3 + \hat{U}_4 + \cdots$$

$\hat{H}_0$ $\qquad$ $\hat{H}'$

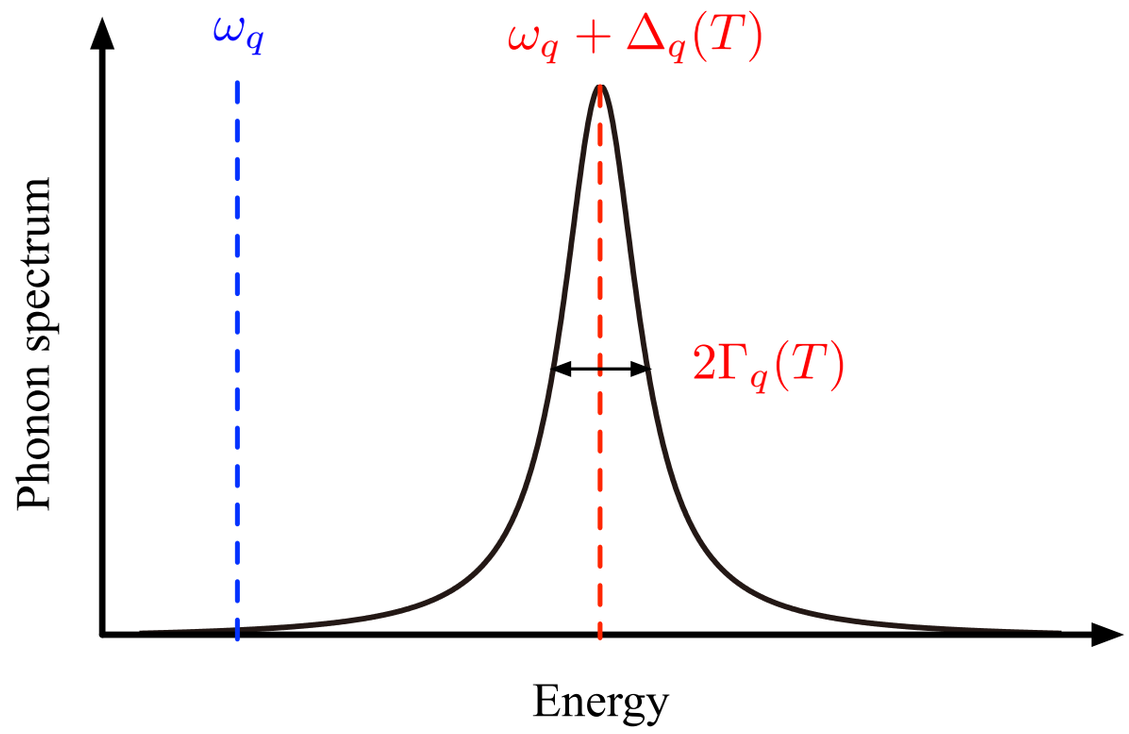
Dyson equation

$$[\boldsymbol{D_q}(\omega)]^{-1} = [\boldsymbol{D_q^0}(\omega)]^{-1} - \boldsymbol{\Sigma_q}(\omega)$$



Spectral function

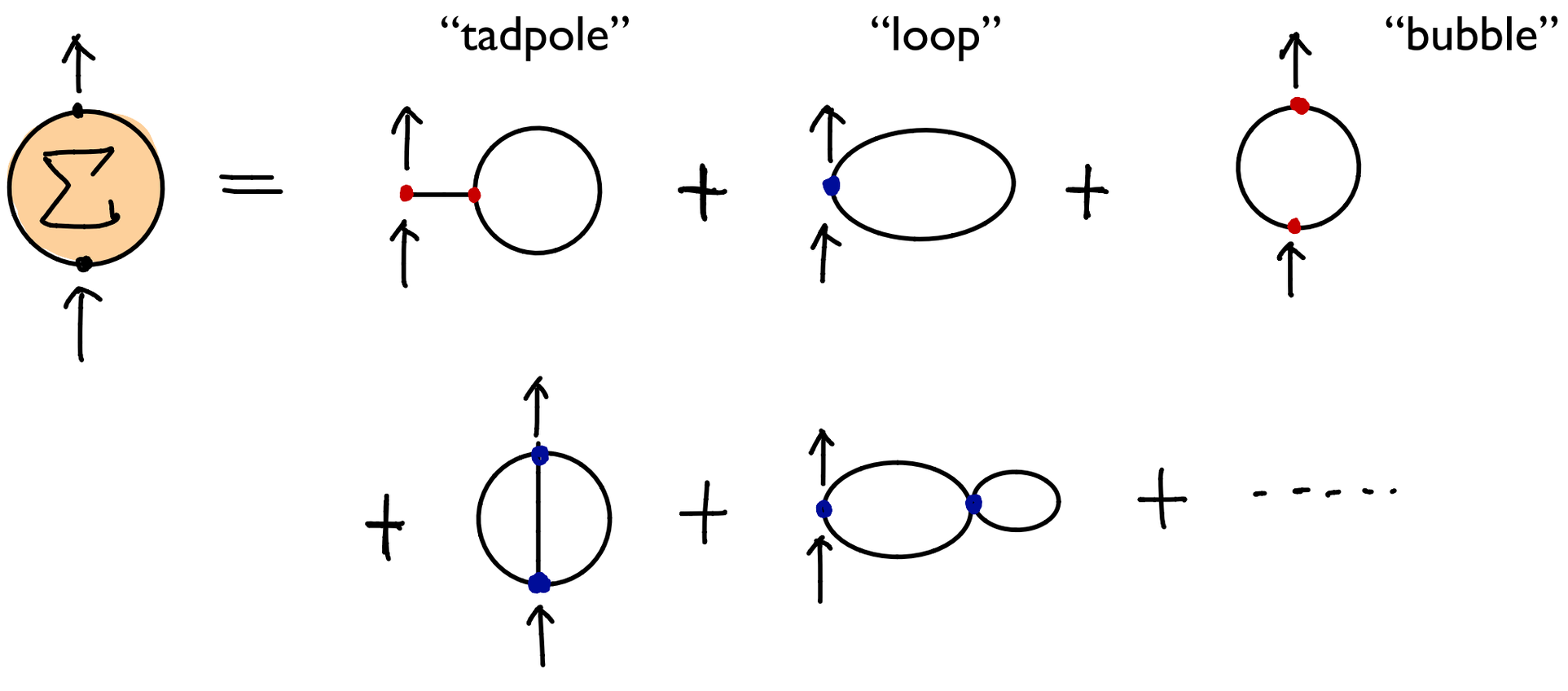
$$A_q(\omega) = \frac{1}{\pi}\mathrm{Im}D_q(\omega)$$

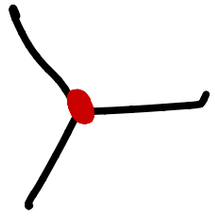


$$\Delta_q(\omega) = -\mathrm{Re}\Sigma_q(\omega)$$

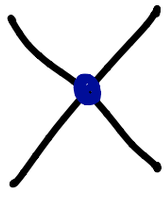
$$\Gamma_q(\omega) = \mathrm{Im}\Sigma_q(\omega)$$

Anharmonic self-energy





3-phonon
interaction
(cubic anharmonicity)



4-phonon
interaction
(quartic anharmonicity)

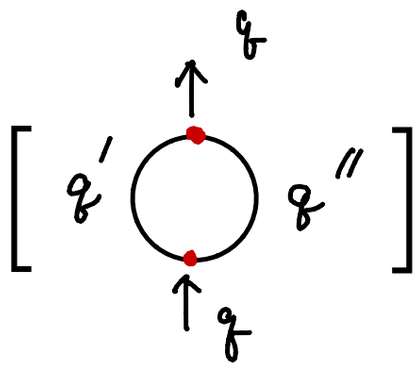
Bubble self-energy

Phonon scattering by the three-phonon process

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

Linewidth

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

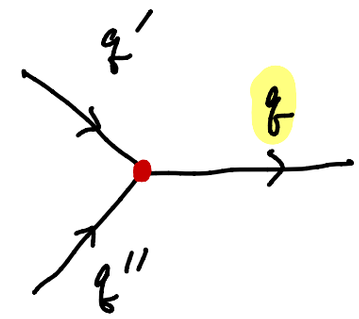


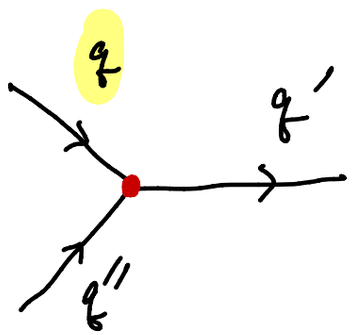
$$= \frac{\pi}{2N}\sum_{q',q''}\frac{\hbar|\Phi_3(-q,q',q'')|^2}{8\omega_q\omega_{q'}\omega_{q''}}\Delta(-\boldsymbol{q}+\boldsymbol{q}'+\boldsymbol{q}'')$$

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

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

$\propto T$ (in high-T region $kT \gg \hbar\omega$)

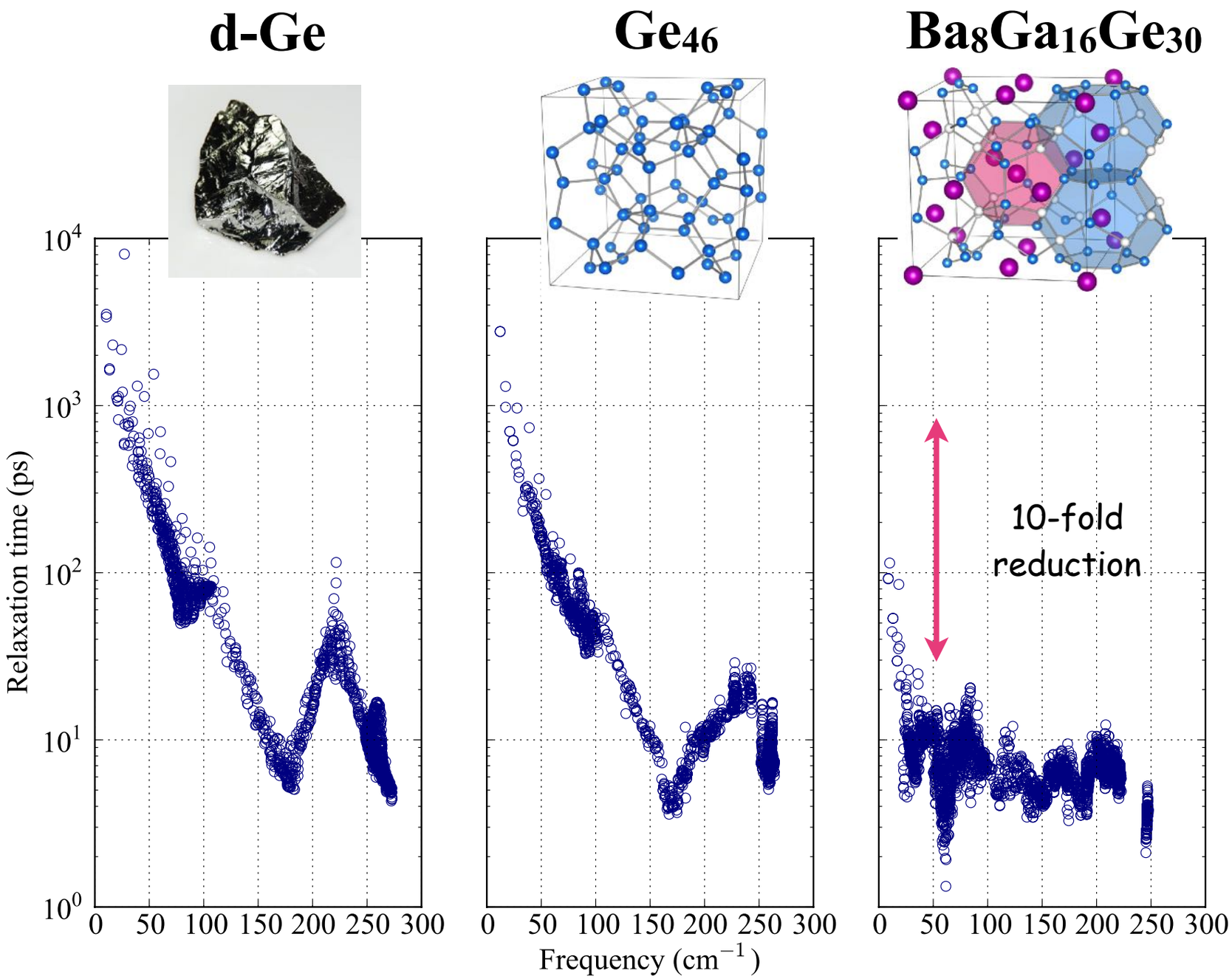




Lifetime

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

Phonon lifetimes in Ge-based materials



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).

Lattice thermal conductivity

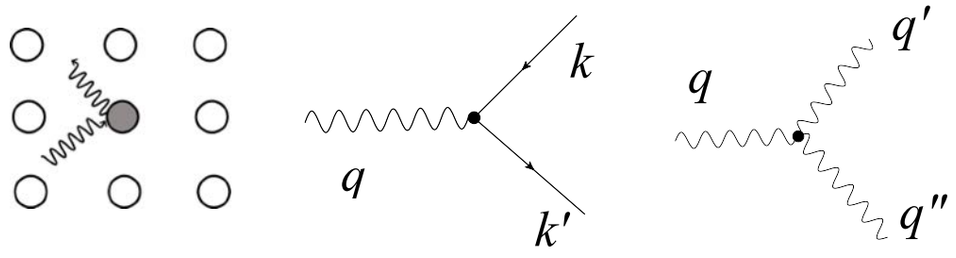
Fourier's law $\boldsymbol{j} = -\kappa \nabla T$

Heat flux in "phonon gas" model $\boldsymbol{j} \approx \boldsymbol{j}_{\mathrm{ph}} = \sum_q \hbar \omega_q \boldsymbol{v}_q n_q$

Boltzmann transport equation (BTE)

$$-\boldsymbol{v}_q \cdot \nabla T \left(\frac{\partial n_q}{\partial T} \right) = -\left(\frac{\partial n_q}{\partial t} \right)_{\mathrm{scatt}}$$

$$= \sum_{q'} \tilde{P}_{qq'} + \sum_{kk'} \tilde{P}_{qkk'} + \sum_{q'q''} \tilde{P}_{qq'q''} + \cdots$$



linearization

$$n_q \approx n_q^0 + \Delta n_q$$

$$n_q^0 = \frac{1}{e^{\beta \hbar \omega_q} - 1}$$

Relaxation-time approx.

$$-\left(\frac{\partial n_q}{\partial t} \right)_{\mathrm{scatt}} = \frac{\Delta n_q}{\tau_q}$$

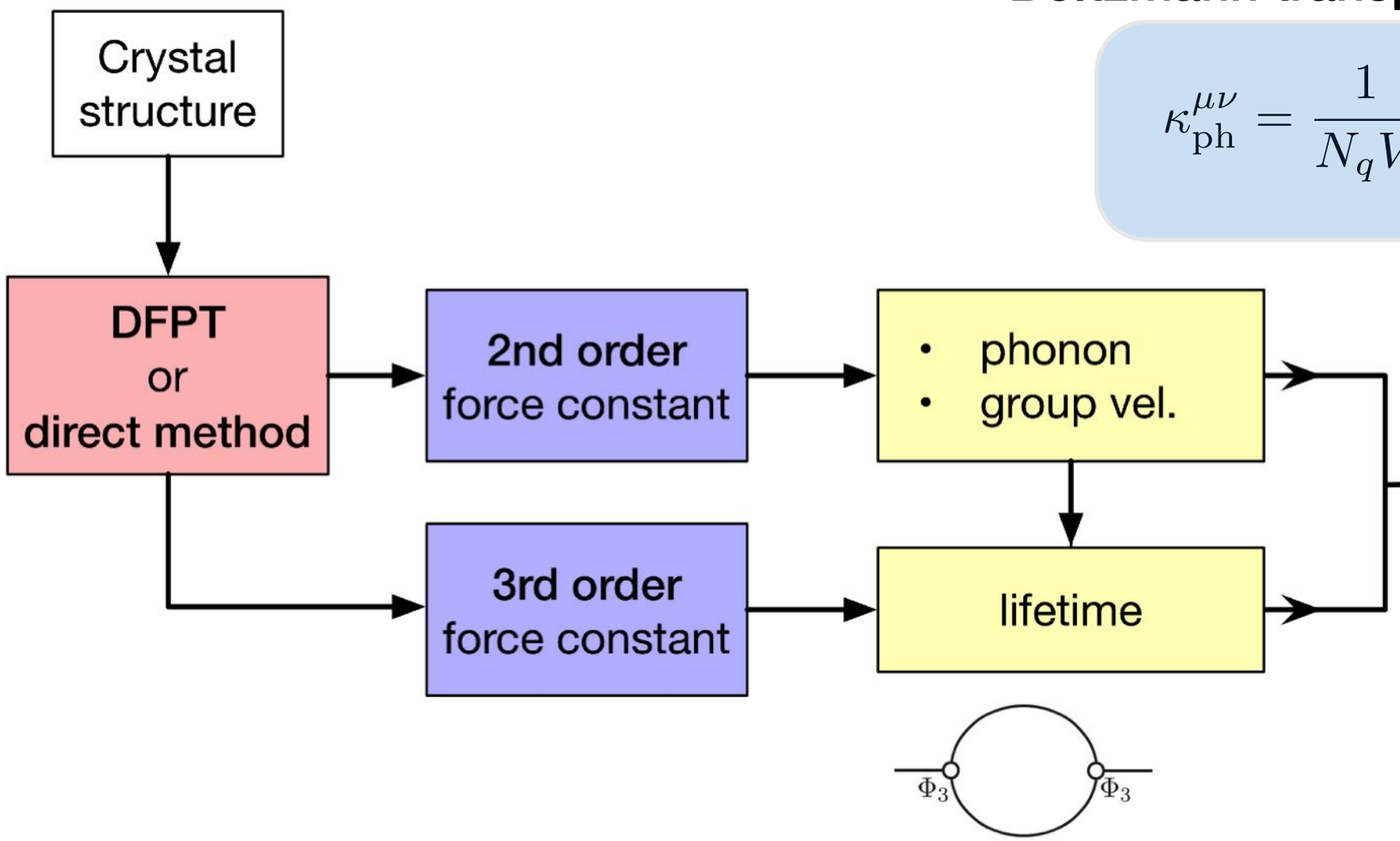
BTE-RTA

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

Lattice thermal conductivity from Peierls-Boltzmann theory

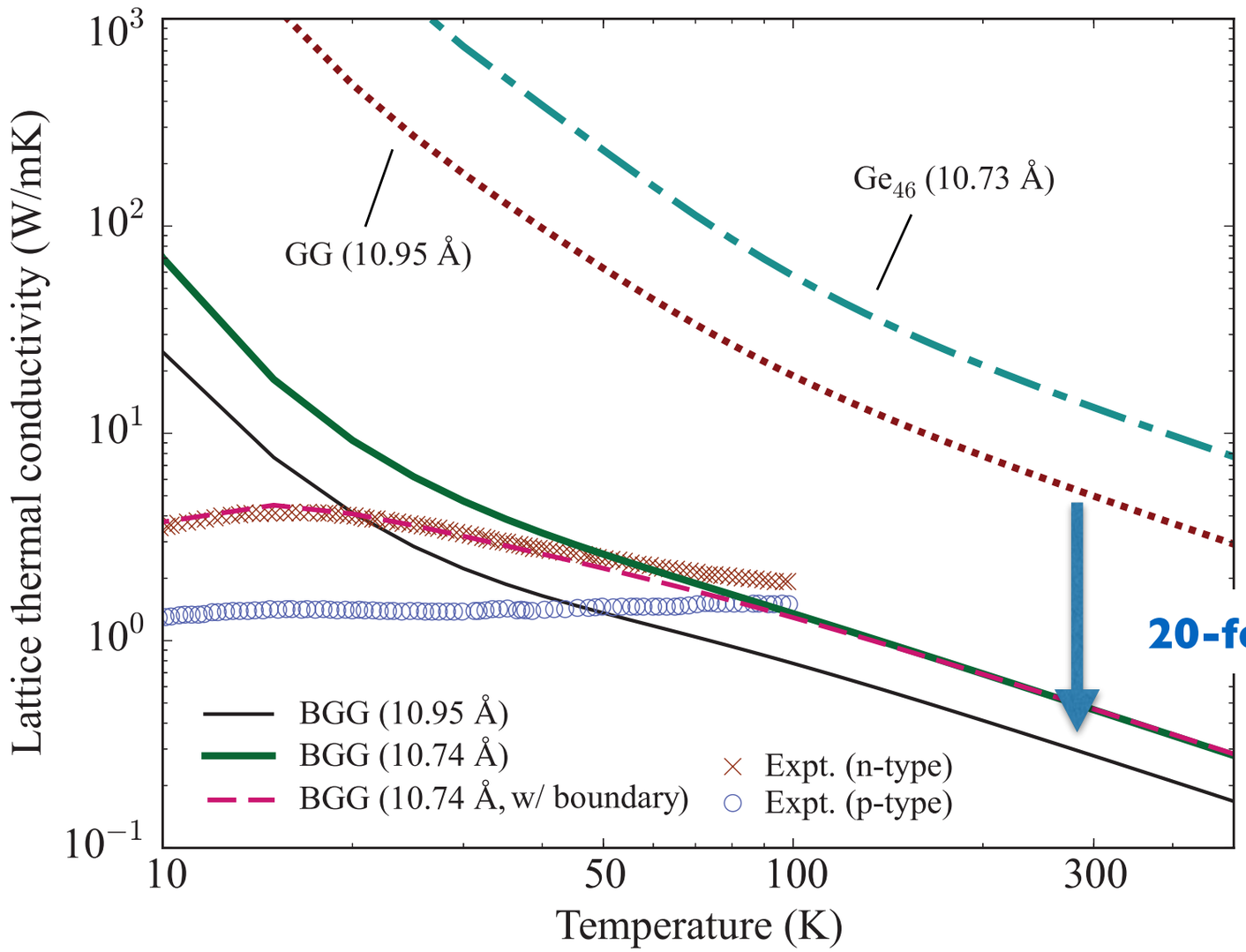
Boltzmann transport eq. (BTE)

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

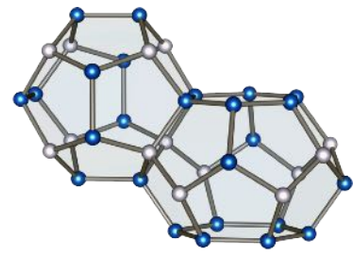


- ✓ Correct treatment of zero-point vibration
- ✓ Reasonably accurate & efficient
- ✗ **Neglect 4th-order anharmonicity**
- ✗ **Breakdown when an imaginary mode exists**

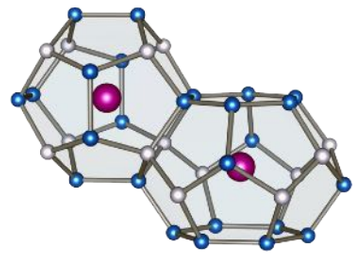
LTC reduction by rattler



empty clathrate



20-fold reduction



filled clathrate

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

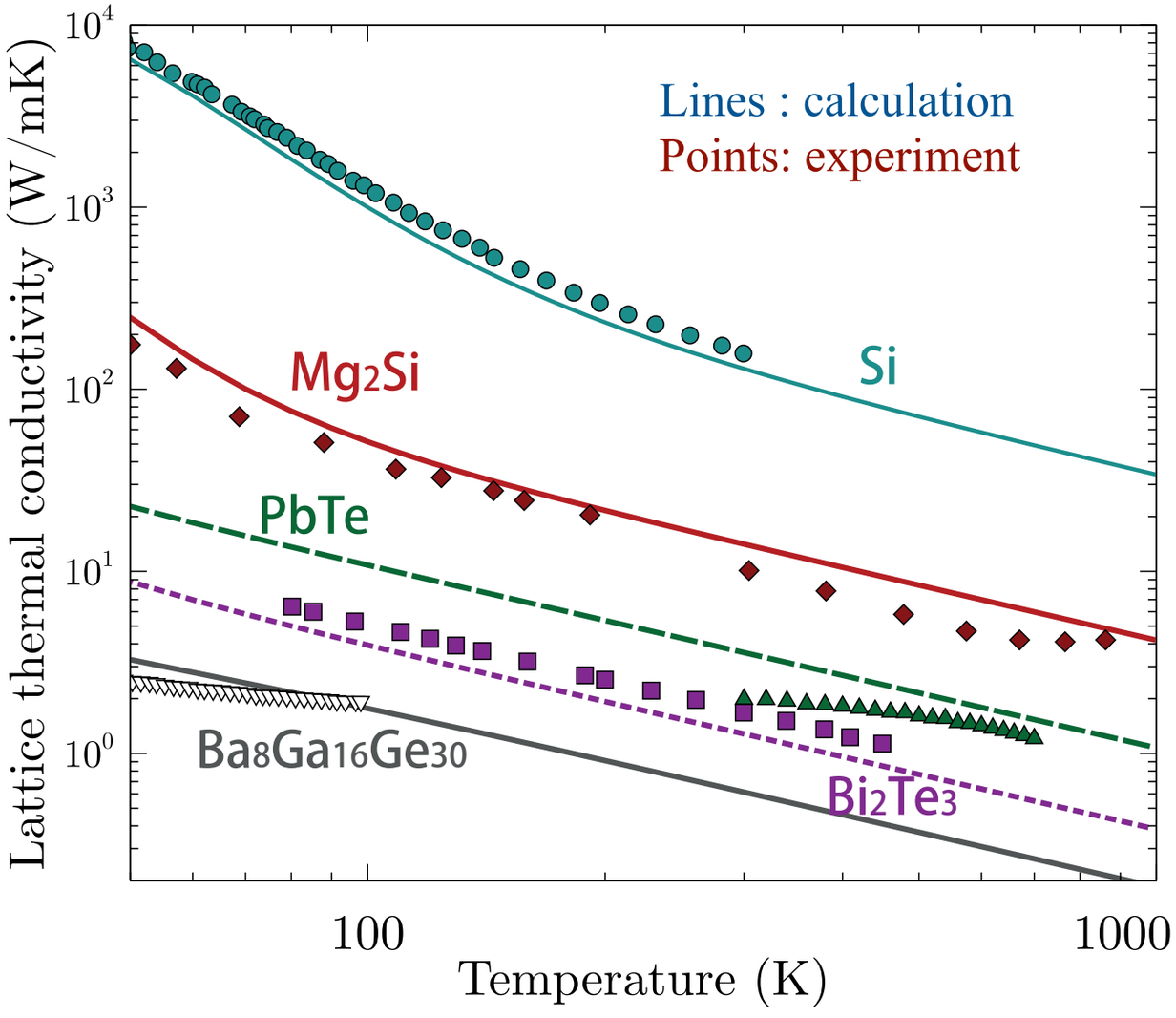
TT, Y. Gohda, and S. Tsuneyuki, PRL **114**, 095501 (2015).

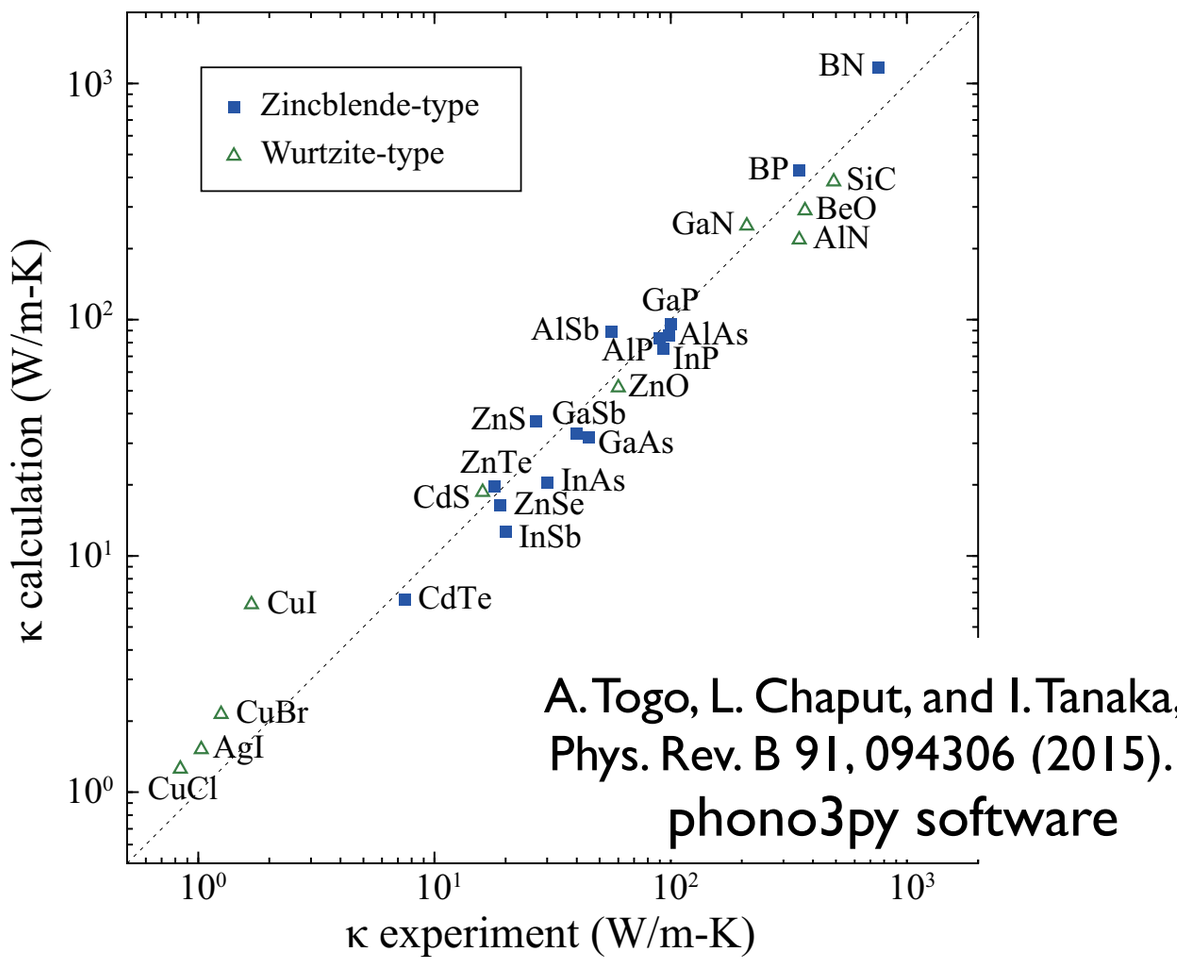
First-principles calculation of κ_{ph}

BTE-RTA

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

- VASP code
- PBEsol xc-functional
- ALAMODE package





A. Togo, L. Chaput, and I. Tanaka,
Phys. Rev. B 91, 094306 (2015).

phono3py software

Code	Developer	Language, License	Features	Interfaces
ShengBTE (almaBTE)	N. Mingo (CEA, France)	Fortran (C++), GPL	• **Iterative** solution to BTE • Thermal transport in **nanostructure** • **MPI** parallelization	VASP, QE, GULP
phonopy, phono3py	A. Togo (Kyoto)	Python & C, BSD 3-clause	• **Direct** solution to BTE • QHA • API for python and C • Easy to use	VASP, ABINIT, QE, SIESTA, Elk, FHI-aims, WIEN2k, CRYSTAL
PhonTS	A. Chernatynskiy (U. Florida)	Fortran, GPL	• **Iterative and variational** solution to BTE • QHA • Includes empirical force fields • **MPI** parallelization	VASP, QE, LAMMPS
ALAMODE	T. Tadano (NIMS)	C++, MIT	• RTA • **Self-consistent phonon calculation** • **MPI + OpenMP** parallelization	VASP, QE, xTAPP, OpenMX, LAMMPS, GULP

Outline

1. Introduction to phonon anharmonicity
2. Perturbative treatment of anharmonicity
3. Non-perturbative treatment of anharmonicity
4. Efficient calculation of anharmonic force constants
5. Applications
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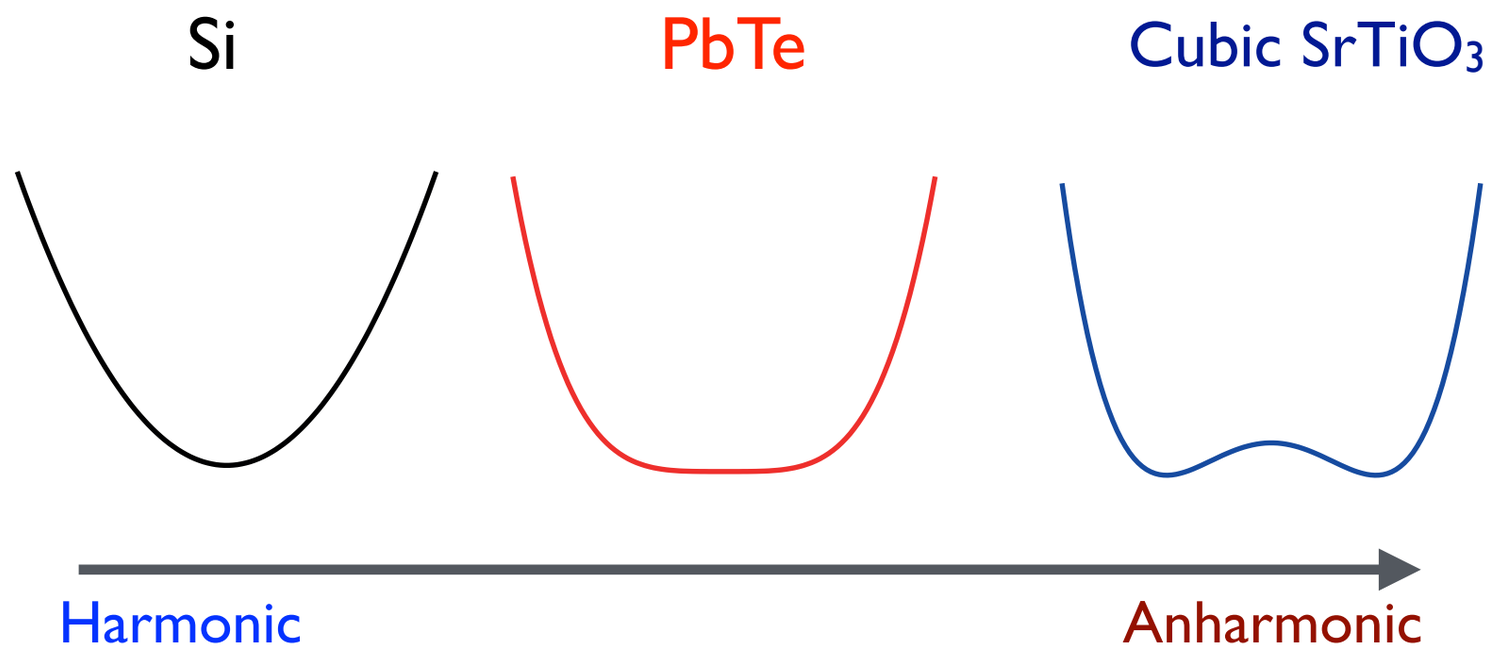
Limitation of the perturbative approach

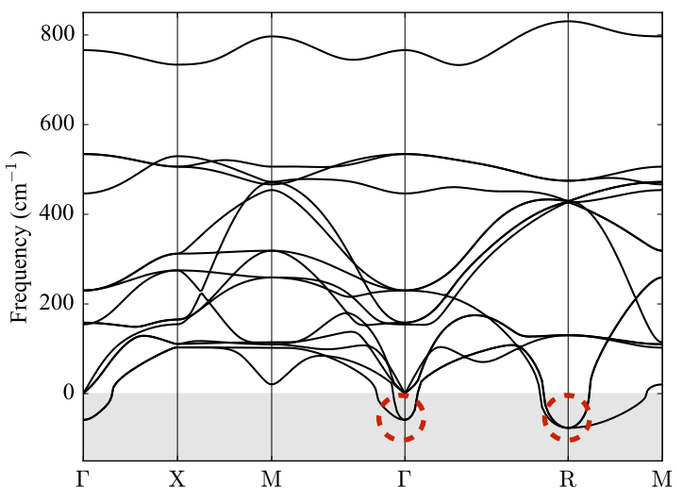
The perturbation approach

- tends to become inaccurate when the anharmonicity is strong
- breaks down when the harmonic phonon is unstable ($\omega_q^2 < 0$)



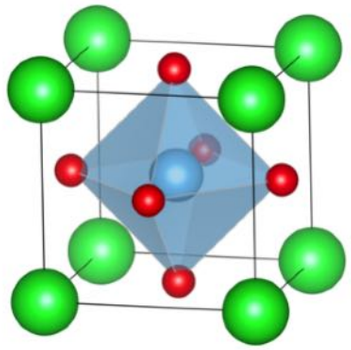
$$\hat{H}_0 = \sum_q \hbar\omega_q \left(\hat{b}_q^\dagger \hat{b}_q + \frac{1}{2}\right)$$

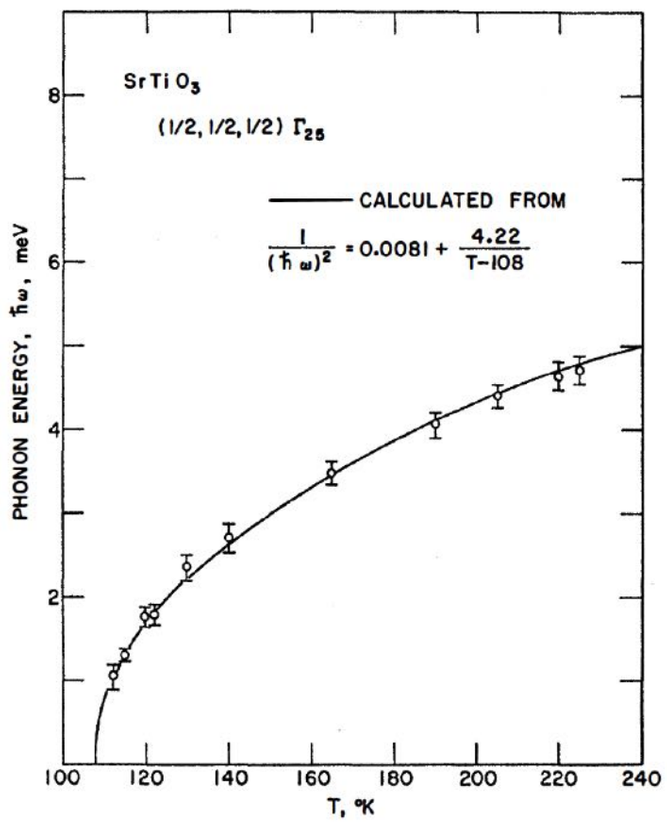
"imaginary phonon"



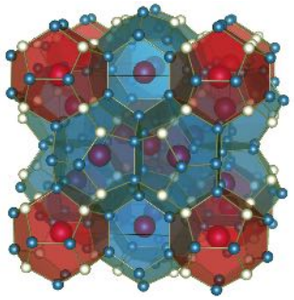
Temperature dependence of phonon frequency

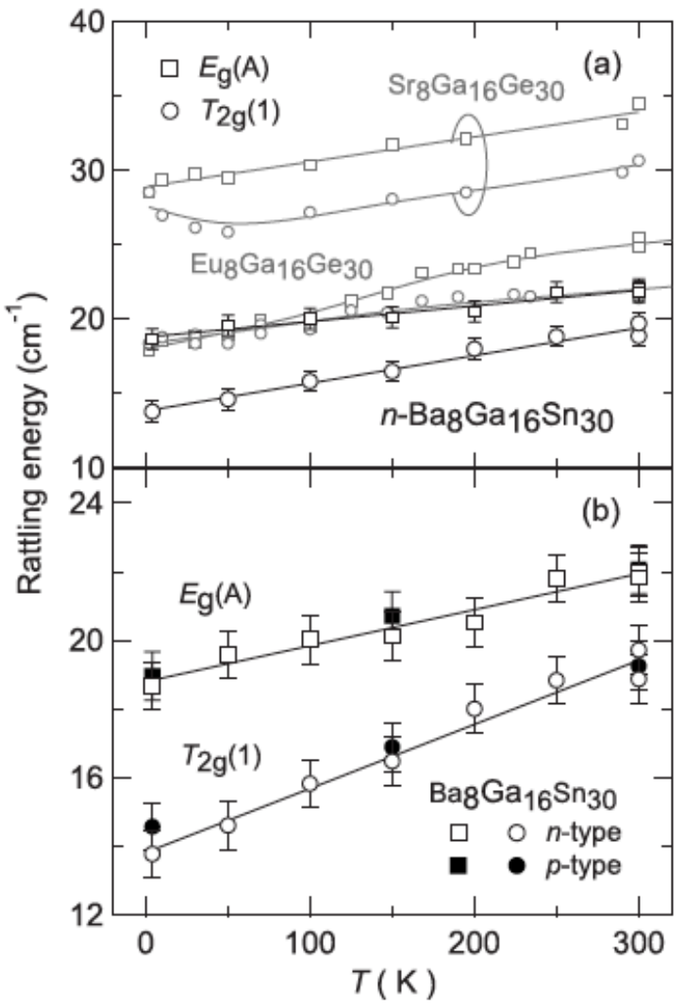
Temperature dependence of phonon frequency ω_q and eigenvector $\boldsymbol{e}_q$ is significant in energy harvesting materials!



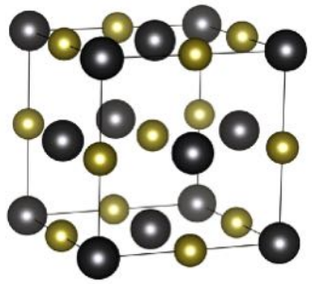


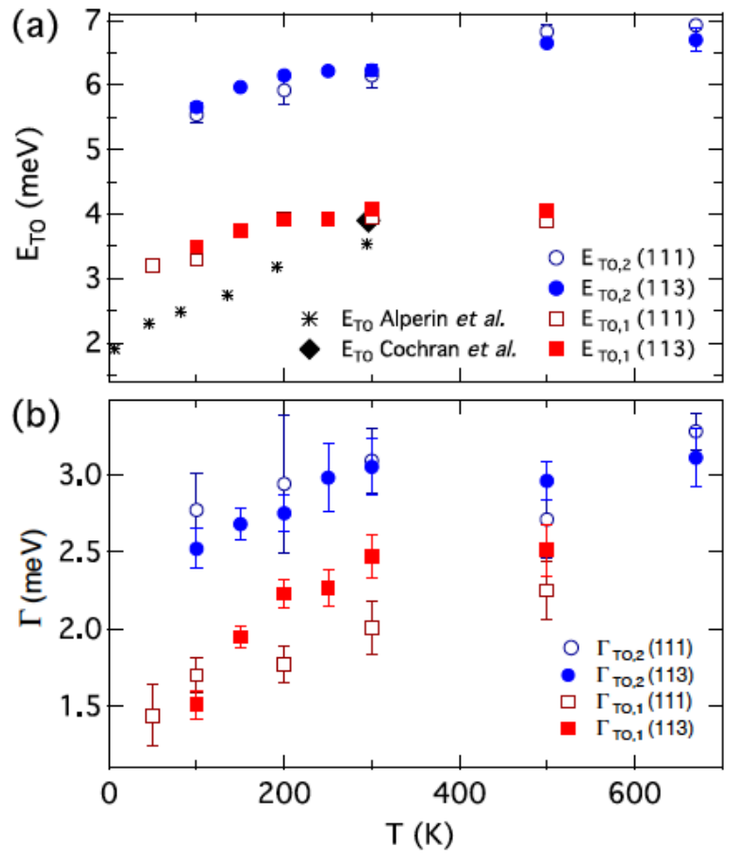
G. Shirane and Y. Yamada, Phys. Rev. **177**, 858 (1969).





K. Suekuni et al., PRB **81**, 205207 (2010)



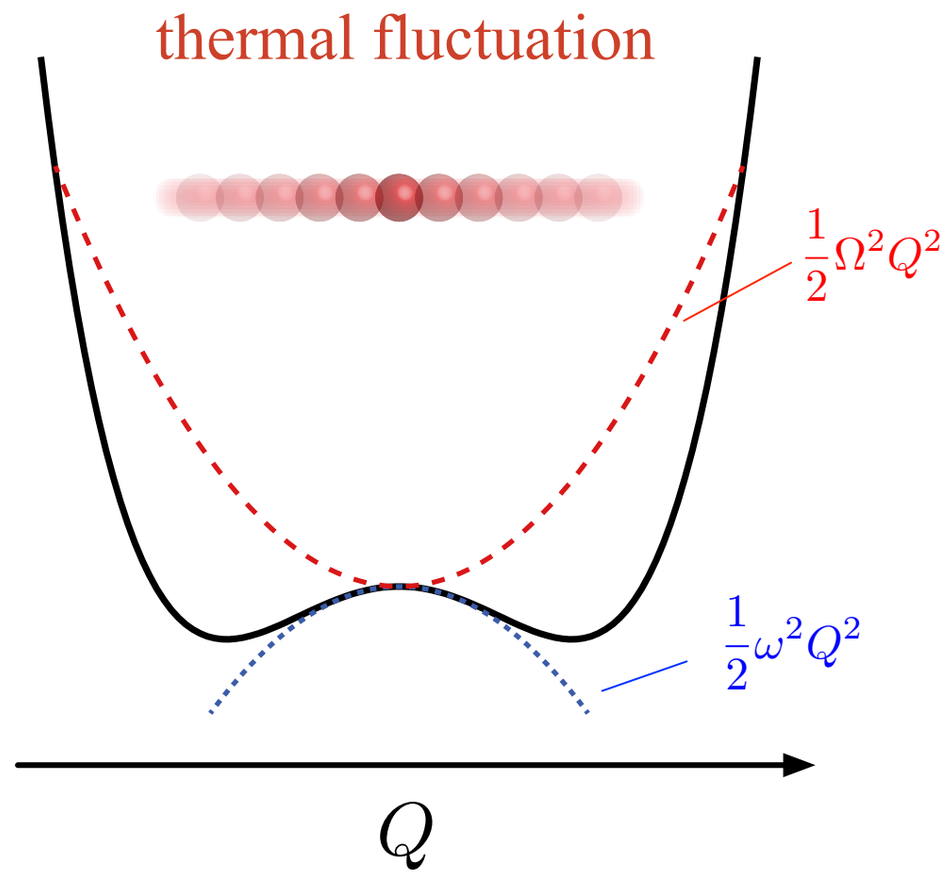


O. Delaire et al, Nature Mater. **10**, 614 (2011)

Frequency renormalization

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

$$\Omega^2 \propto T - T_c$$



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 2013

Self-consistent phonon theory

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

Effective one-body Hamiltonian : $\tilde{H}_0 = \sum_q \hbar\Omega_q (a_q^\dagger a_q + \frac{1}{2})$

Let us introduce an operator ρ defined as $\rho = \frac{e^{-\beta\tilde{H}_0}}{\mathrm{Tr} e^{-\beta\tilde{H}_0}}$

Then, the following Gibbs inequality holds:

$$F[\rho] = F_0 + \langle H - H_0 \rangle_0 \geq F$$

The self-consistent phonon (SCP) frequency is obtained via $\frac{\delta F[\rho]}{\delta \rho} = 0$

"Hatree-Fock" theory for phonons. (mean-field approximation)

Self-consistent phonon theory

How to update ρ (effective Hamiltonian)?

- **Stochastic self-consistent harmonic approximation (SSCHA)**

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

  - Use conjugate gradient method to update ρ and F[ρ] by repeatedly calculating atomic forces in supercells.
  - The gradient of F[ρ] is calculated stochastically.
  - Full anharmonicity included

- **Self-consistent phonon approach based on force constants (SCP)**

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

  - Compute $\delta F[\rho]/\delta\rho = 0$ analytically and derive the self-consistent equation by truncating the higher-order anharmonic terms.

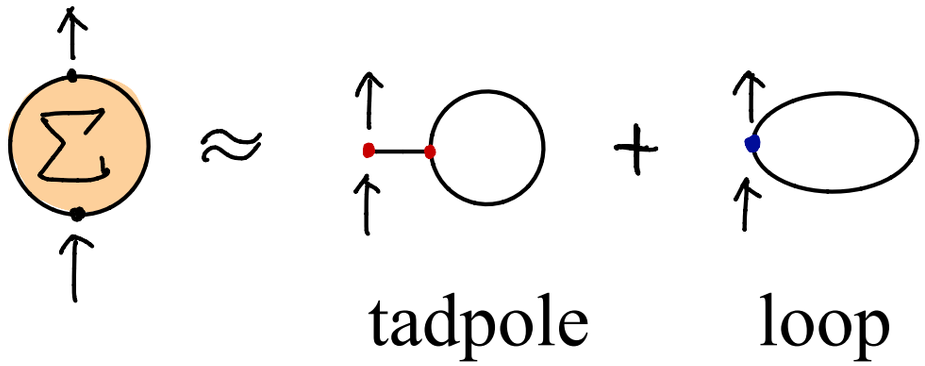
$$\langle H - \tilde{H}_0 \rangle_0 = \langle H_0 - \tilde{H}_0 + U_3 + U_4 + \ldots \rangle_0 \approx \langle H_0 - \tilde{H}_0 + U_4 \rangle_0$$

  - Efficient calculation of ρ and F[ρ] **at various temperature**
  - Higher-order terms (sixth, eight, …) are neglected.

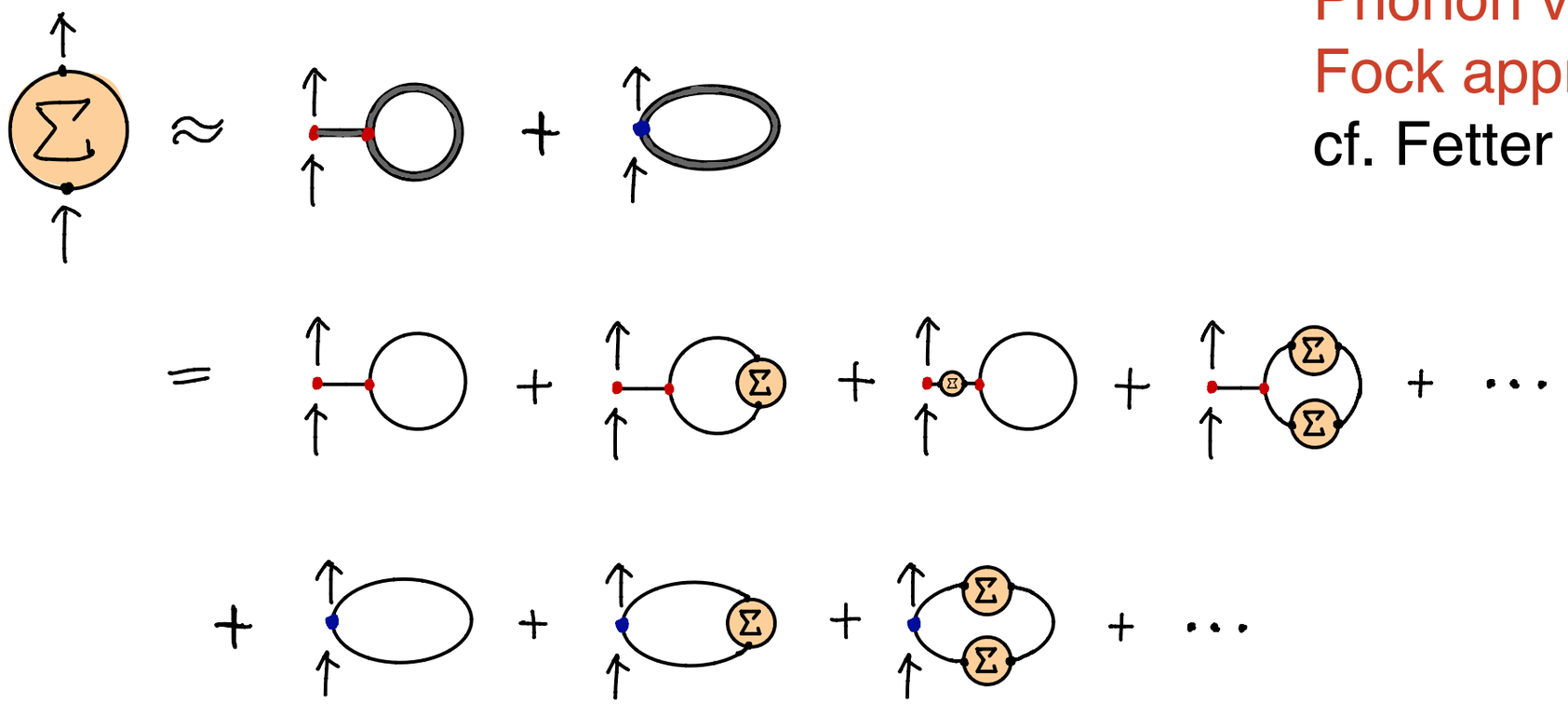
Self-energy in SCP theory

We only consider the frequency-independent first-order self-energies (loop and tadpole):

Self-energy in perturbation theory



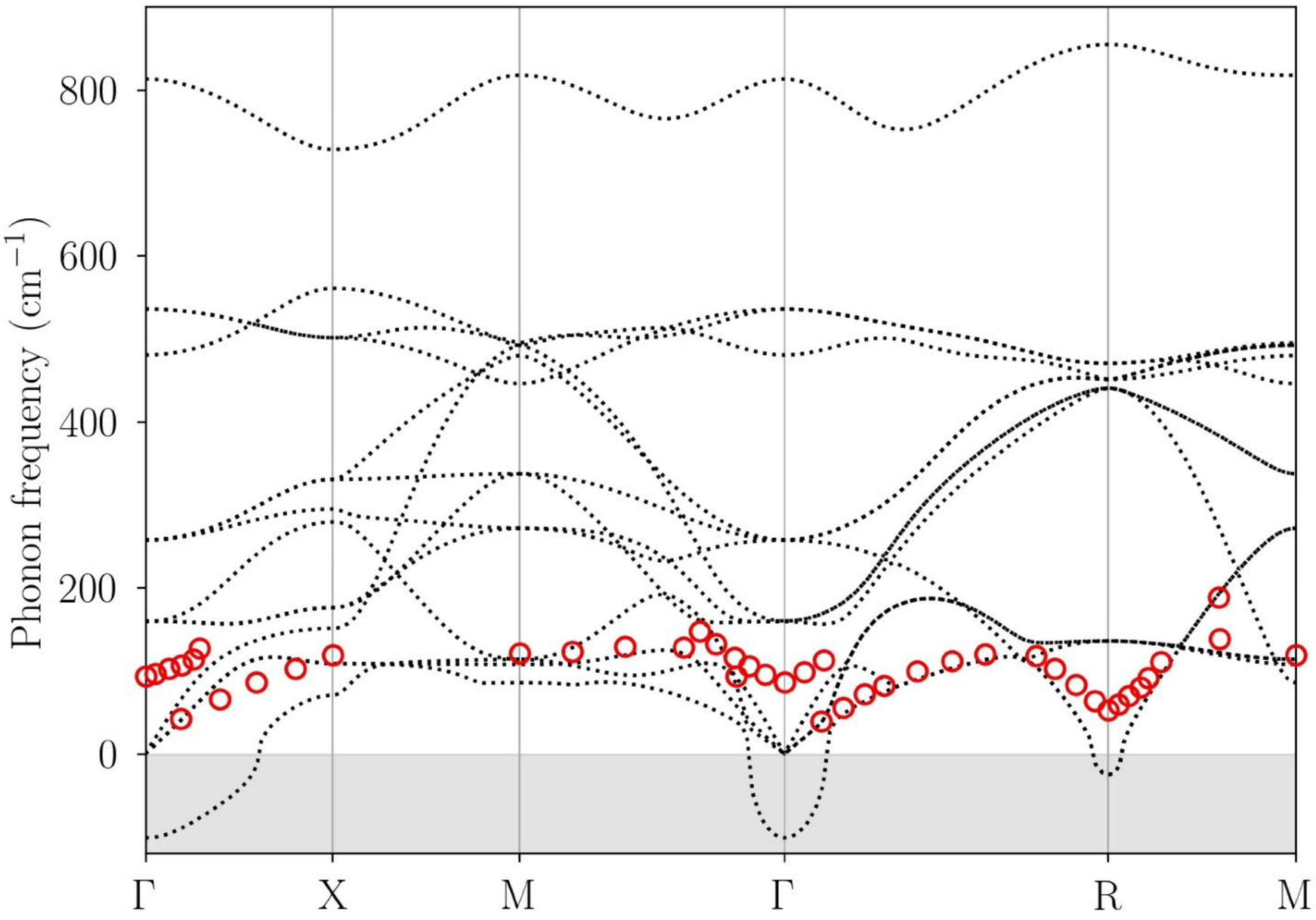
Self-energy in self-consistent phonon theory

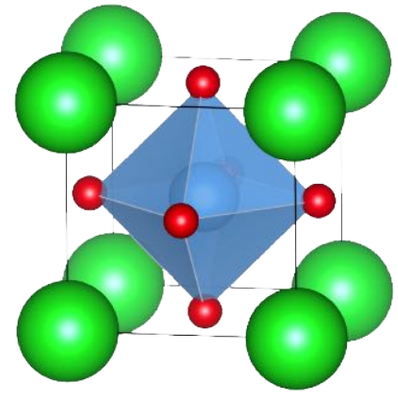


Phonon version of Hartree-Fock approximation.

cf. Fetter & Walecka chap. 4

Temperature dependent phonon in cubic $SrTiO_3$





Green line:
SCP result@300K

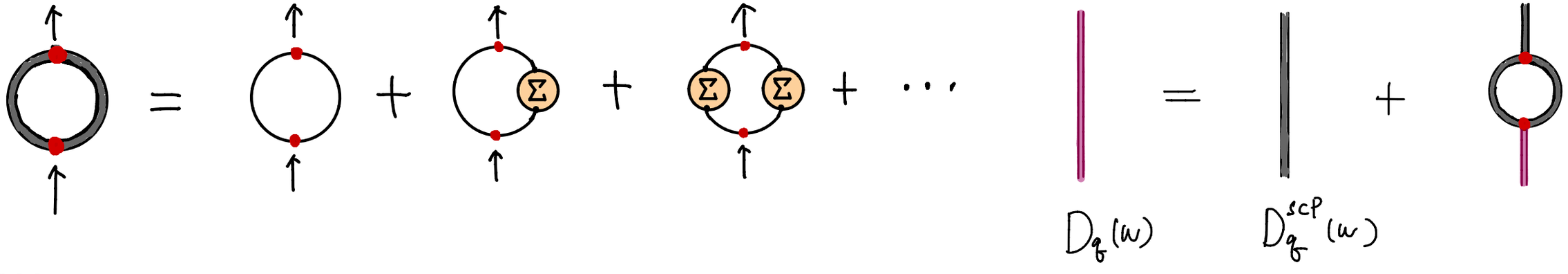
Red circle:
INS result@300 K

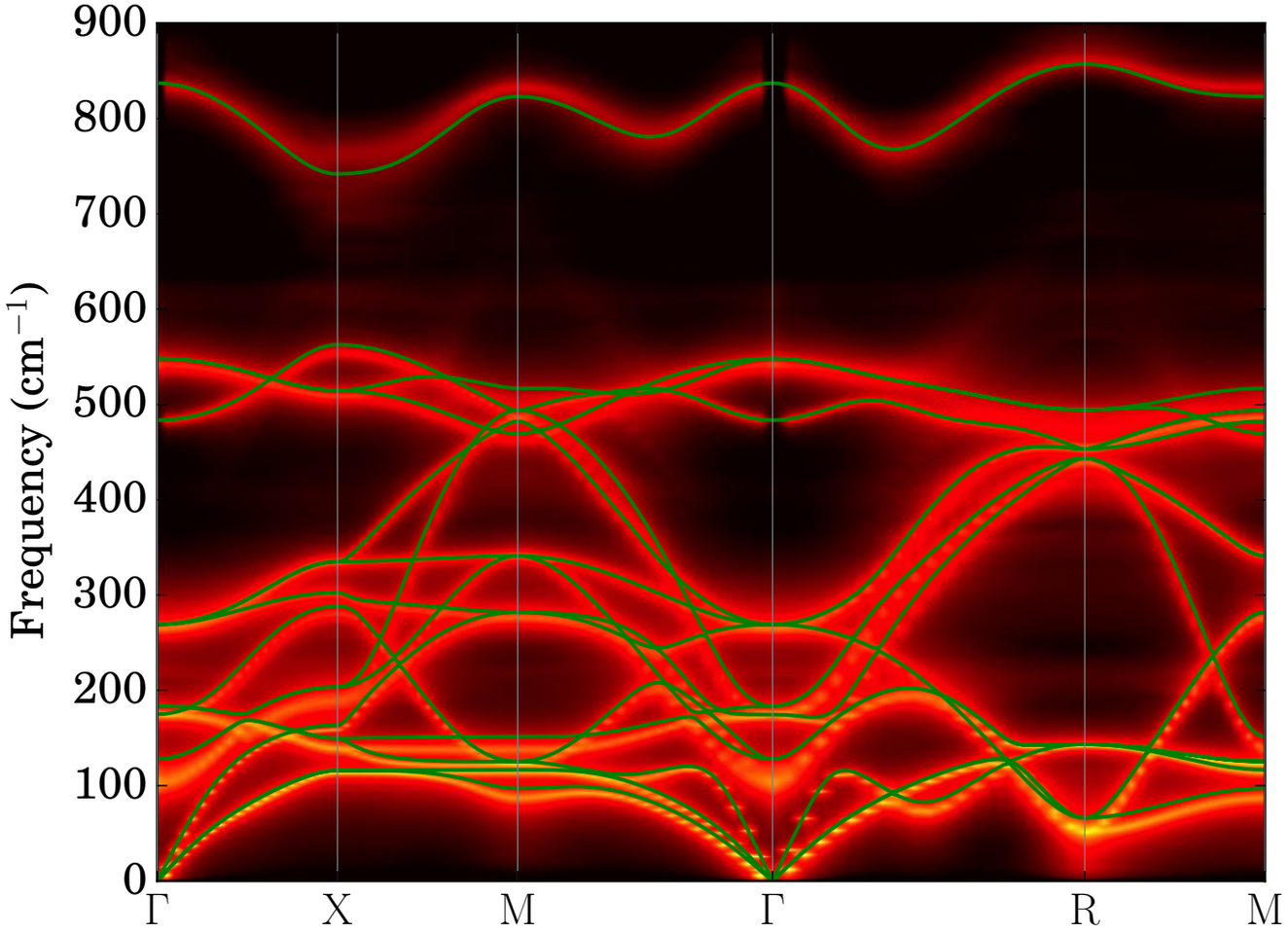
- ☑ HSE hybrid functional
- ☑ Anharmonic stabilization of soft modes

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

What about the bubble self-energy?

The SCP propagator does not include the bubble self-energy, which gives the lowest-order contribution to the phonon line width. How can we include it?





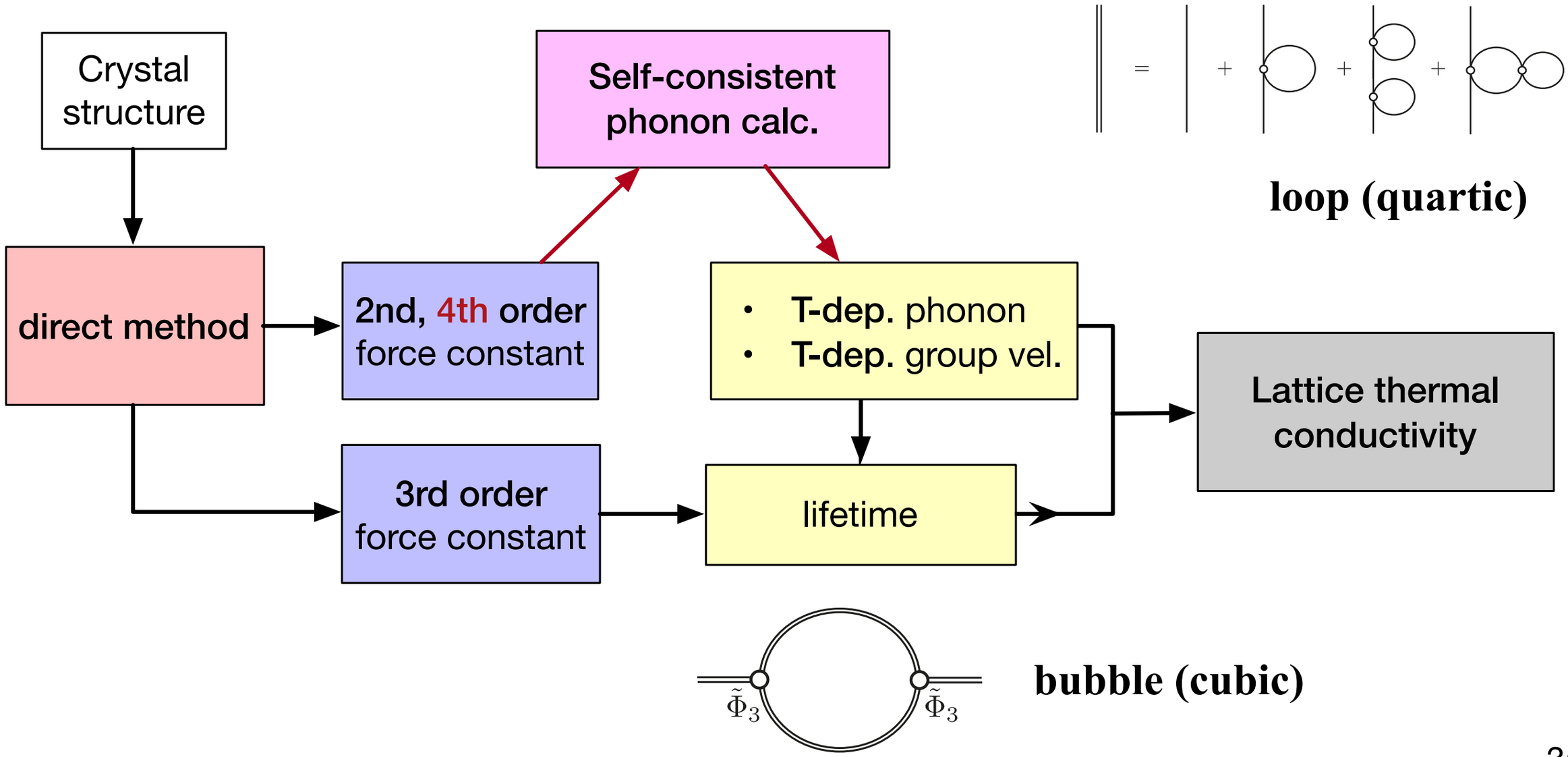
$$A_q(\omega) = \frac{1}{\pi}\mathrm{Im}D_q(\omega)$$

Green line:
SCP result@300K

Improved theory for lattice thermal conductivity

SCP + BTE

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



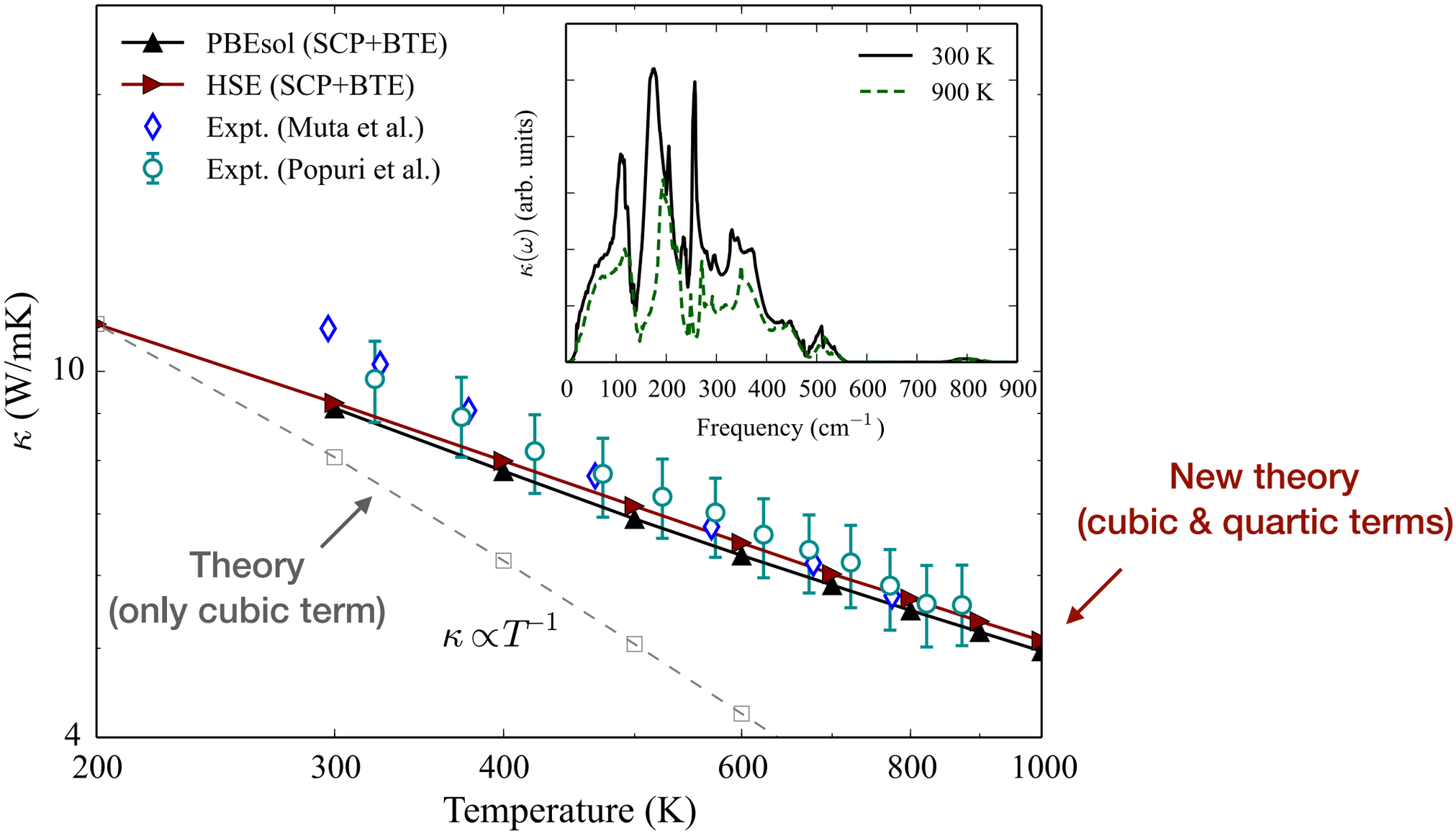
loop (quartic)

bubble (cubic)

Phonon transport in cubic $SrTiO_3$

SCP + BTE

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



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

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Anharmonic lattice model (ALM)

Taylor expansion of potential energy:

Parameters:
maximum order, cutoff radii

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

parameters

basis

$$\boldsymbol{\Phi} = \left[\Phi_1, \Phi_2, \ldots, \Phi_M\right]^T$$

M: The number of independent parameters

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

$$
A = \begin{bmatrix}
-u_i^{(1)} & -\frac{1}{2}u_i^{(1)}u_j^{(1)} & -\frac{1}{3!}u_i^{(1)}u_j^{(1)}u_k^{(1)} & \cdots \\
-u_i^{(2)} & -\frac{1}{2}u_i^{(2)}u_j^{(2)} & -\frac{1}{3!}u_i^{(2)}u_j^{(2)}u_k^{(2)} & \cdots \\
 & \cdots & & \\
-u_i^{(L)} & -\frac{1}{2}u_i^{(L)}u_j^{(L)} & -\frac{1}{3!}u_i^{(L)}u_j^{(L)}u_k^{(L)} & \cdots
\end{bmatrix}
$$

Parameter estimation by least squares

The parameter vector is determined so that the ALM force best reproduces the DFT force (a.k.a. force matching method).

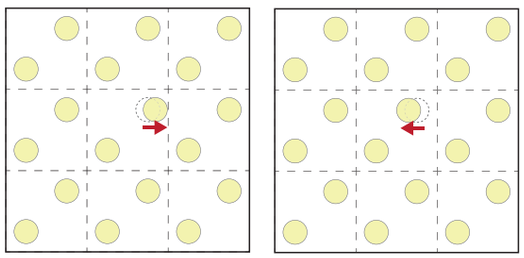
$$\tilde{\boldsymbol{\Phi}} = \arg\min_{\boldsymbol{\Phi}} \| A\boldsymbol{\Phi} - \boldsymbol{F}^{\mathrm{DFT}} \|_2^2$$

All parameters can be determined uniquely if matrix A is overdetermined.

Necessary displacement patterns can be generated systematically.

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

2 patterns

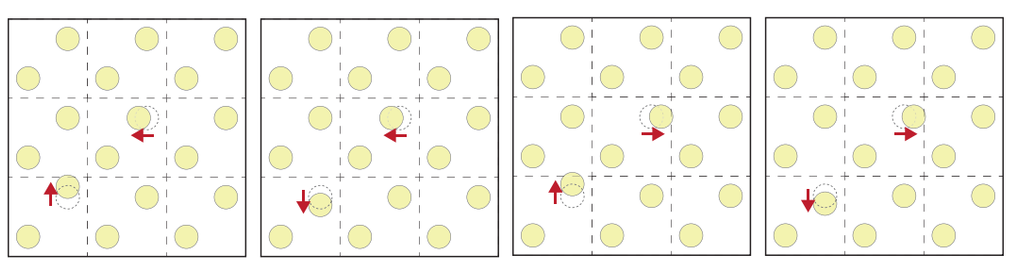


$$\Phi_{ijk} = \frac{\partial^3 V}{\partial u_i \partial u_j \partial u_k} = -\frac{\partial F_k}{\partial u_i \partial u_j}$$

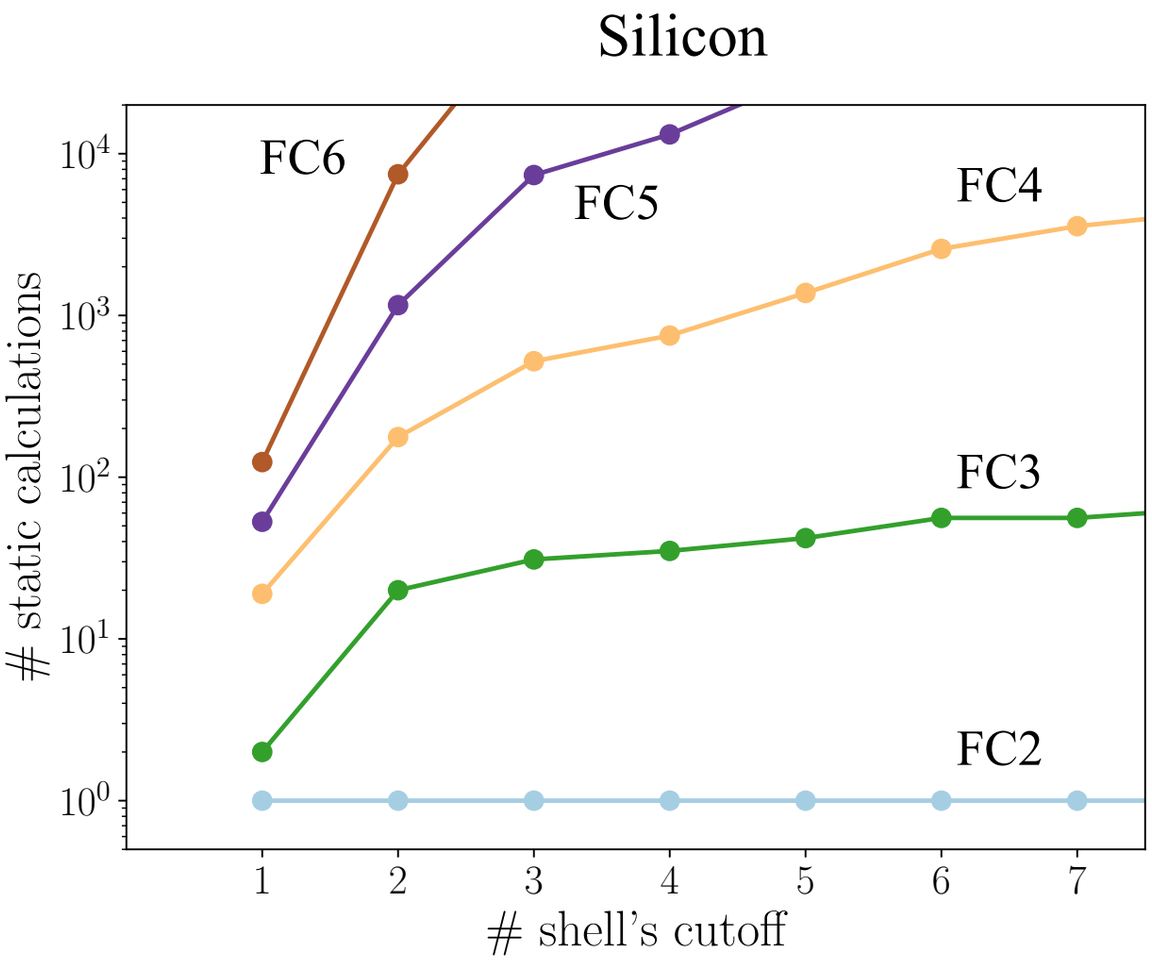
$$\approx -\frac{1}{4h^2}\,[F_k(u_i = h, u_j = h) - F_k(u_i = h, u_j = -h)$$

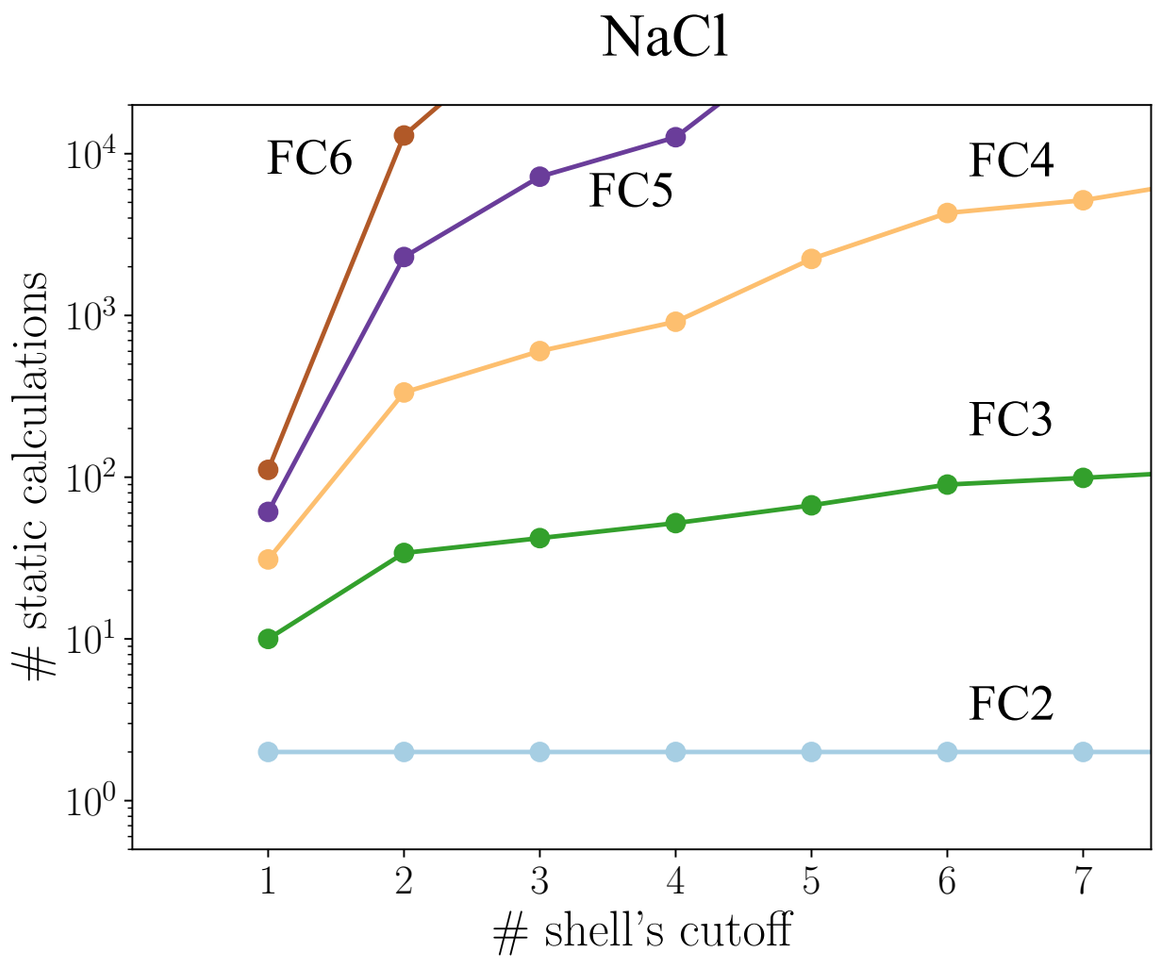
$$-F_k(u_i = -h, u_j = h) + F_k(u_i = -h, u_j = -h)]$$

4 patterns



Rapid increase of displacement patterns



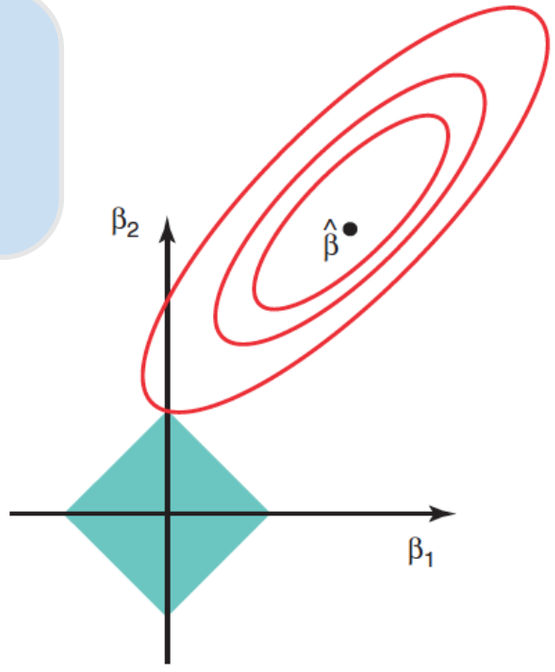


More than 1,000 DFT calculations will be necessary to compute higher-order anharmonic terms (>3) if the finite-displacement approach is employed.

Compressive sensing

LASSO

$$\tilde{\boldsymbol{\Phi}} = \arg\min_{\boldsymbol{\Phi}} \|A\boldsymbol{\Phi} - \boldsymbol{F}^{\mathrm{DFT}}\|_2^2 + \lambda\|\boldsymbol{\Phi}\|_1$$



PRL **113,** 185501 (2014) PHYSICAL REVIEW LETTERS week ending 31 OCTOBER 2014

Lattice Anharmonicity and Thermal Conductivity from Compressive Sensing of First-Principles Calculations

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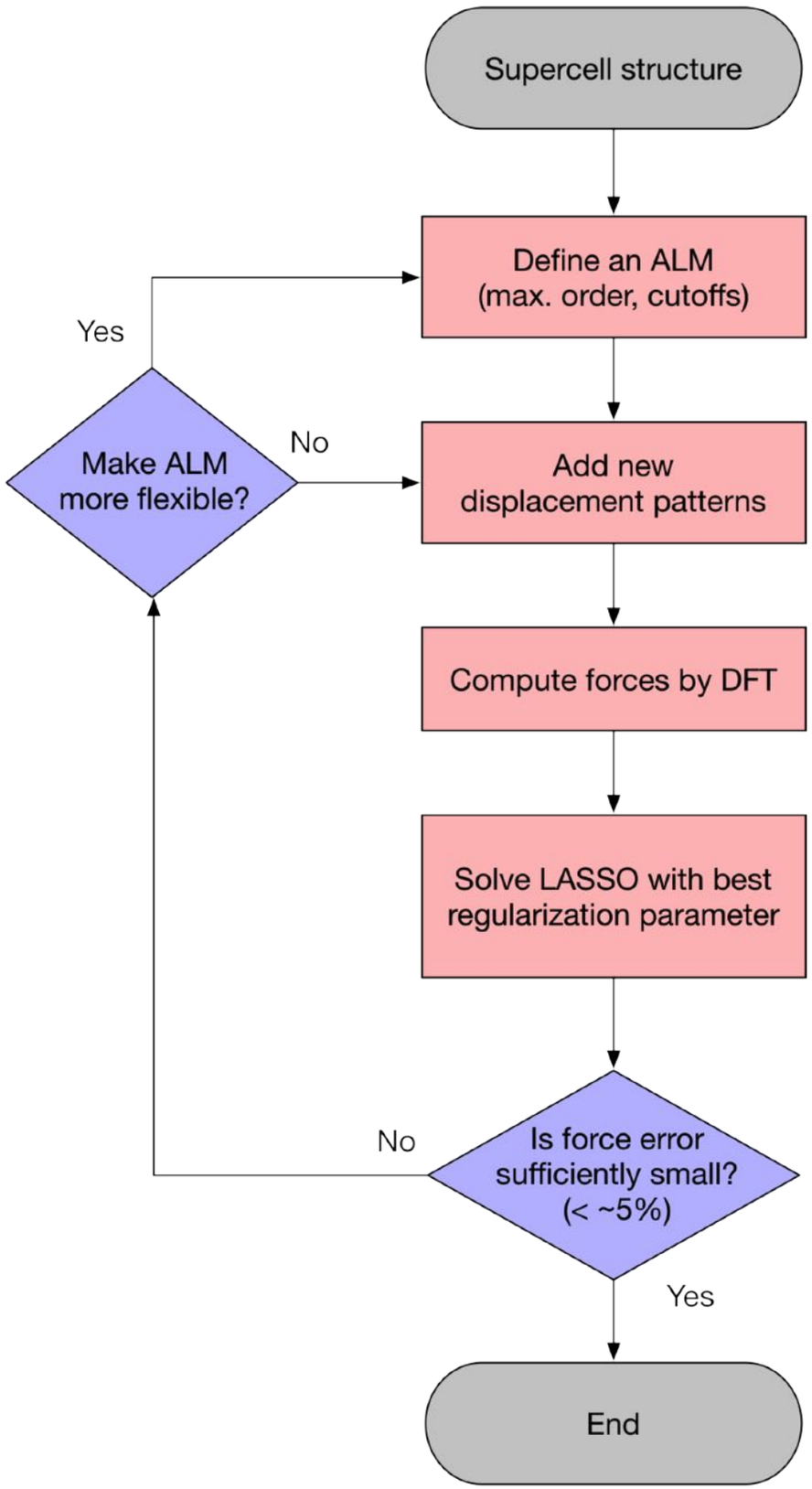
(Received 22 April 2014; published 27 October 2014)

G. James, D. Witten, T. Hastie, and R. Tibshirani, "*An Introduction to Statistical Learning with Applications in R*"

- Avoid over-fitting
- Improve the generalization ability
- Improve the computational efficiency

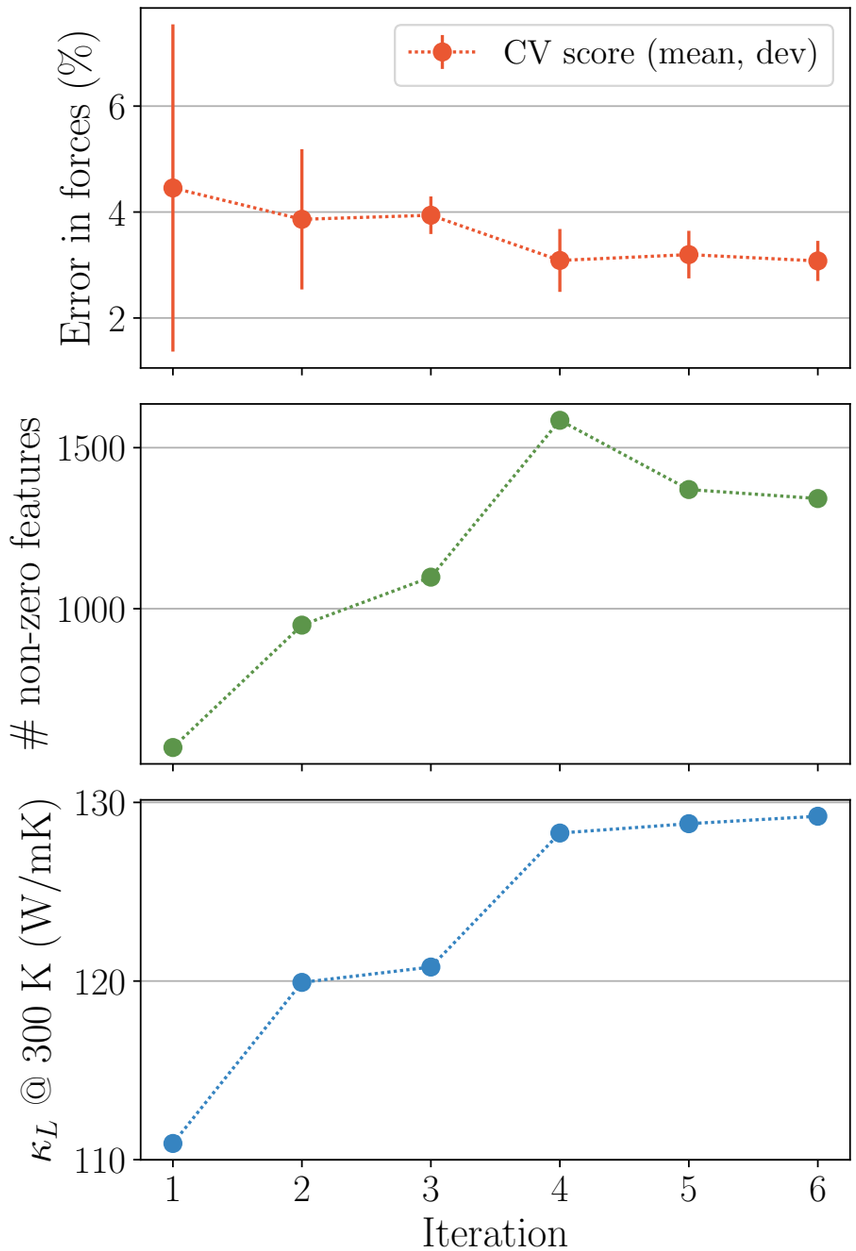
Each row of the sensing matrix A should be uncorrelated.
Use DFT-MD + random displacement.

Workflow of compressive sensing



Silicon (64 atoms), VASP (PBEsol)

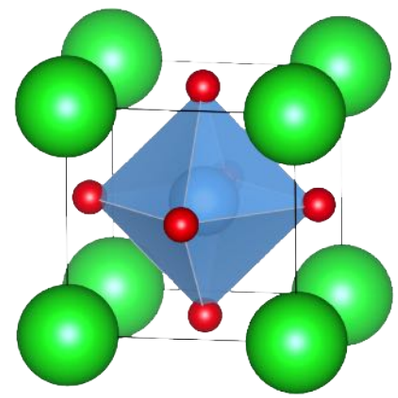
- Add 5 new configurations per each iteration
- 5-fold CV
- 2747 total features



Converge in 4-5th iterations (20-25 DFT calculations).

Cubic $SrTiO_3$

- 2x2x2 supercell (40 atoms)
- **3,018 anharmonic force constants** (3rd, 4th, 5th, 6th)



finite displacement method
with central difference → **more than 5,000 DFT calc.**

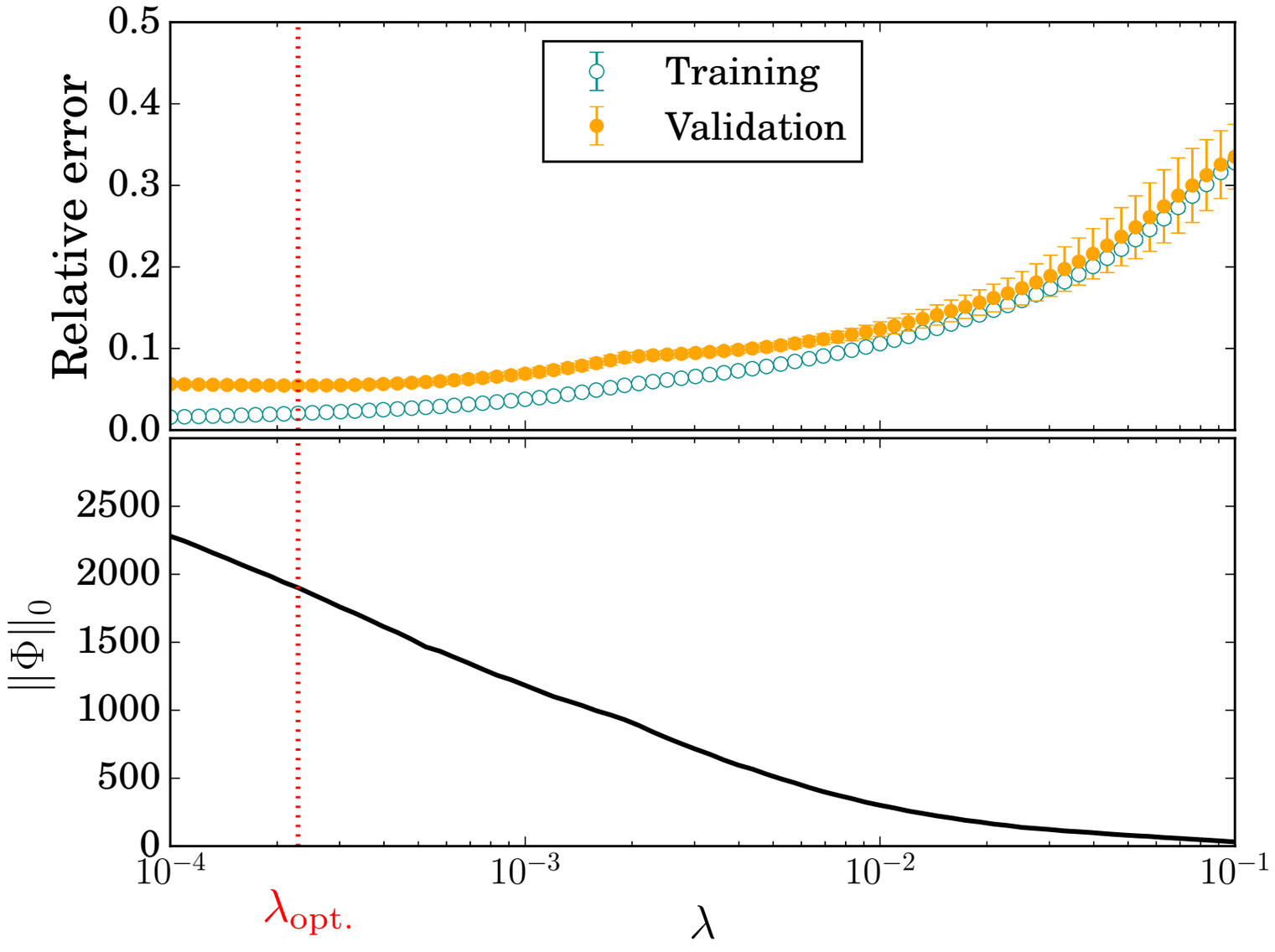
↓ **100x more efficient!**

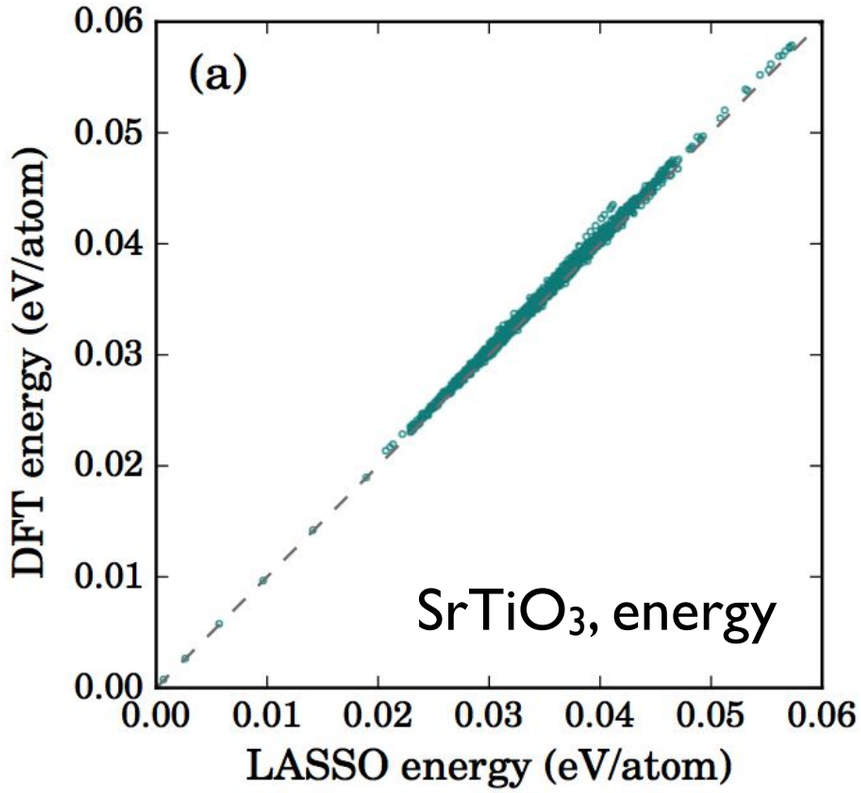
ab initio MD + LASSO → **40 DFT calc.**

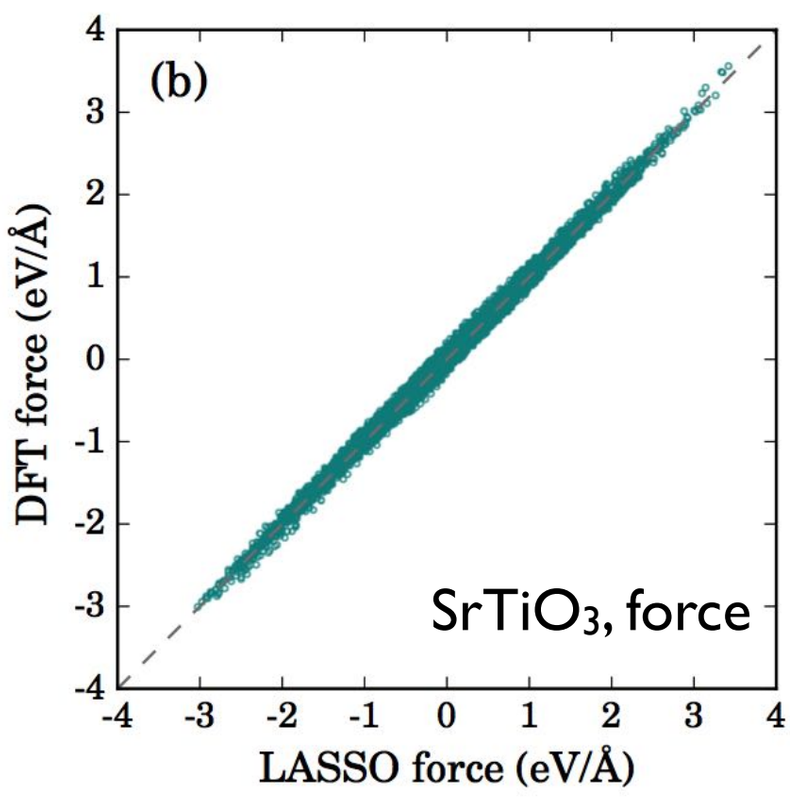
Accurate DFT calculations based on hybrid functions are also possible

Model selection ($SrTiO_3$)

$$\tilde{\boldsymbol{\Phi}} = \arg\min_{\boldsymbol{\Phi}} \|A\boldsymbol{\Phi} - \boldsymbol{F}^{\mathrm{DFT}}\|_2^2 + \lambda\|\boldsymbol{\Phi}\|_1$$



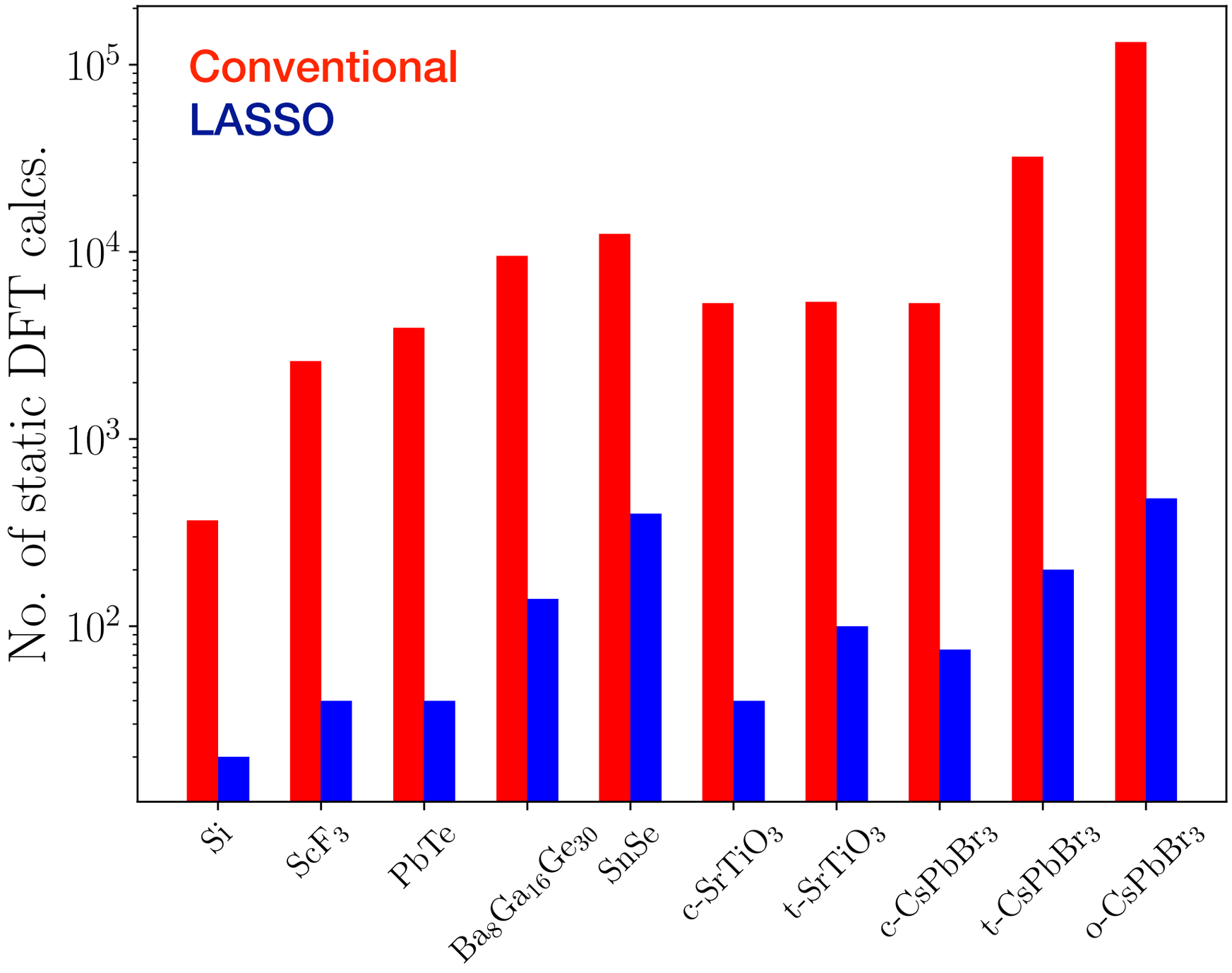




- 40 training structures
- 2024 coefficients out of 3018 are nonzero (~67%)

Efficiency improvement

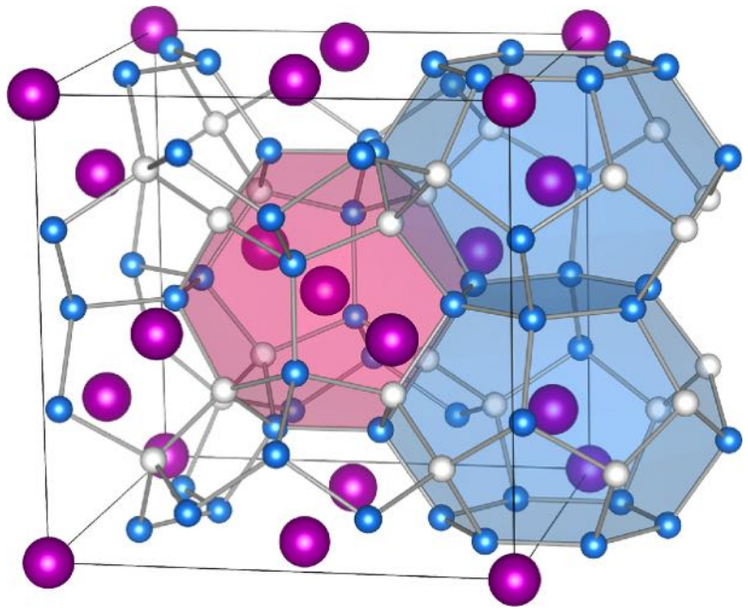
100x speedup is possible



Outline

1. Introduction to phonon anharmonicity
2. Perturbative treatment of anharmonicity
3. Non-perturbative treatment of anharmonicity
4. Efficient calculation of anharmonic force constants
5. Applications
6. Summary

Intermetallic clathrate



Type-I clathrate

- $A_8X_{16}Y_{30}$ (A= Ba, Sr, Eu; X, Y = Si, Ga, Ge, Sn)
- sp3 host framework & guest atom
- "Rattling motion" of guest atoms

  Large amplitude (~0.4 Å) thermal motion

  → **Strong anharmonicity**

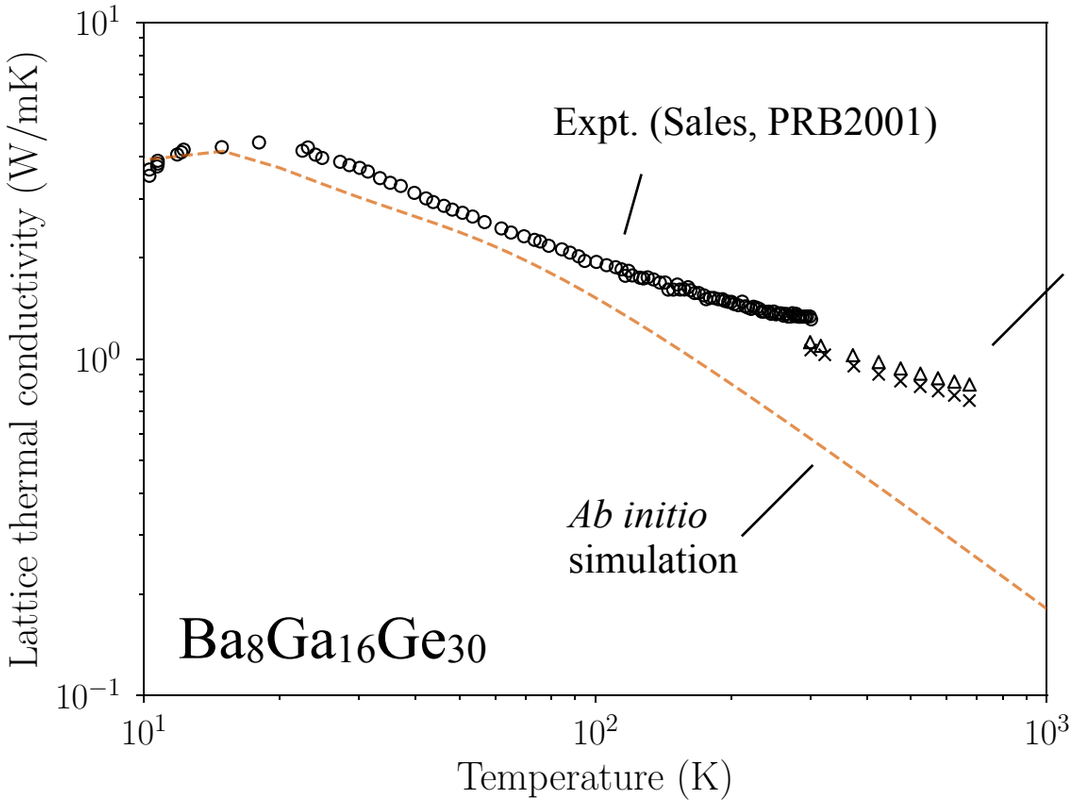
- High thermoelectric figure-of-merit ZT (~1.3)
- Low lattice thermal conductivity (< 1 W/mK)

Failure of conventional theory at high-T

Peierls-Boltzmann theory

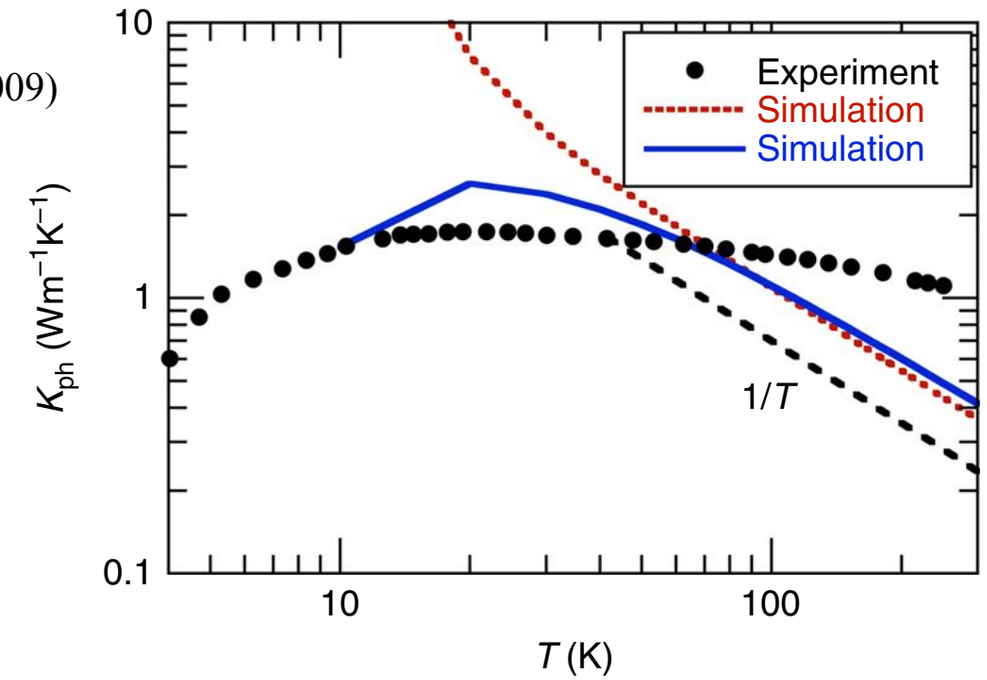
$$\kappa_{\mathrm{ph}}^{\mu\nu} = \frac{1}{N_q V} \sum_q c_q(T) v_q^\mu v_q^\nu \tau_q(T)$$

- Consider cubic anharmonicity for calculating phonon lifetimes
- Neglect higher-order anharmonicity



Ab initio data: TT, Y. Gohda, and S. Tsuneyuki, PRL. **114**, 095501 (2015).

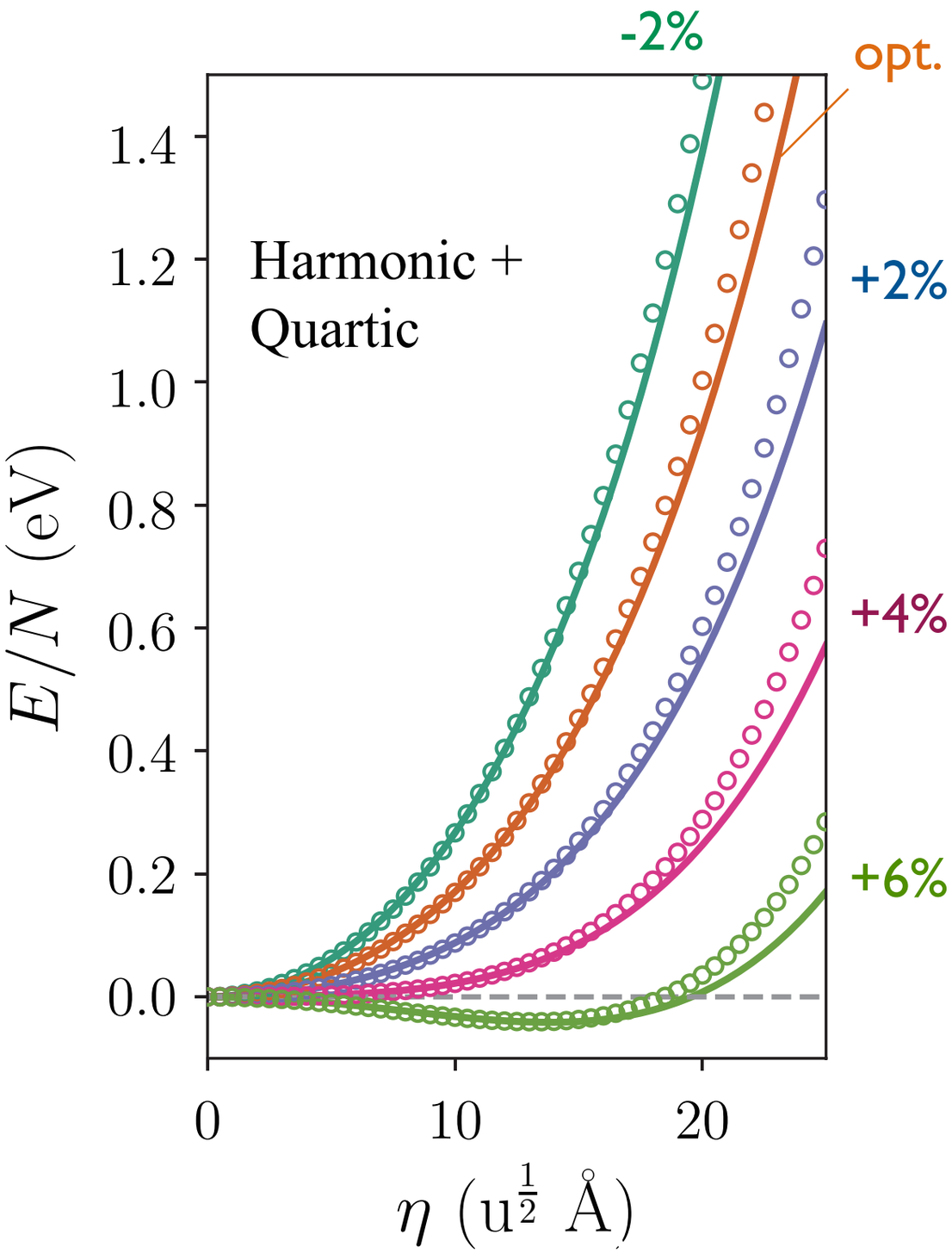
$Ba_{7.81}Ge_{40.67}Au_{5.33}$



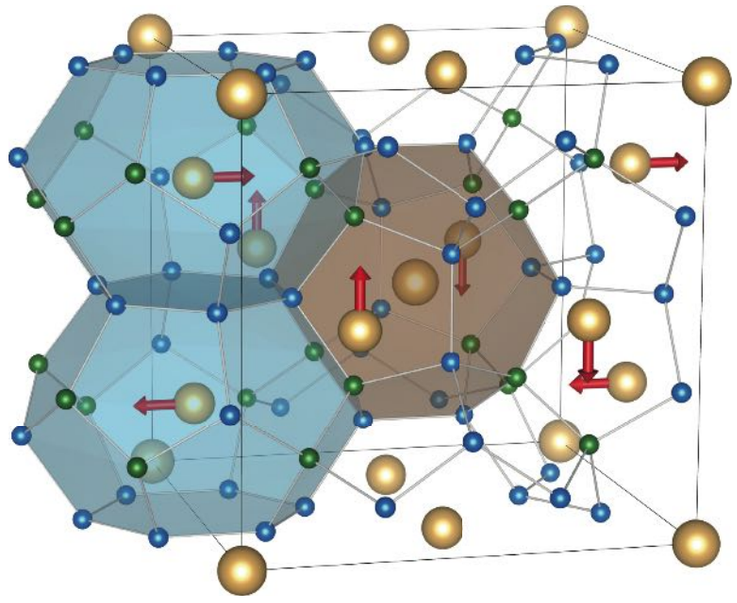
P. F. Lory et al., Nat commun. **8**, 491 (2017)

Quartic anharmonicity in clathrates

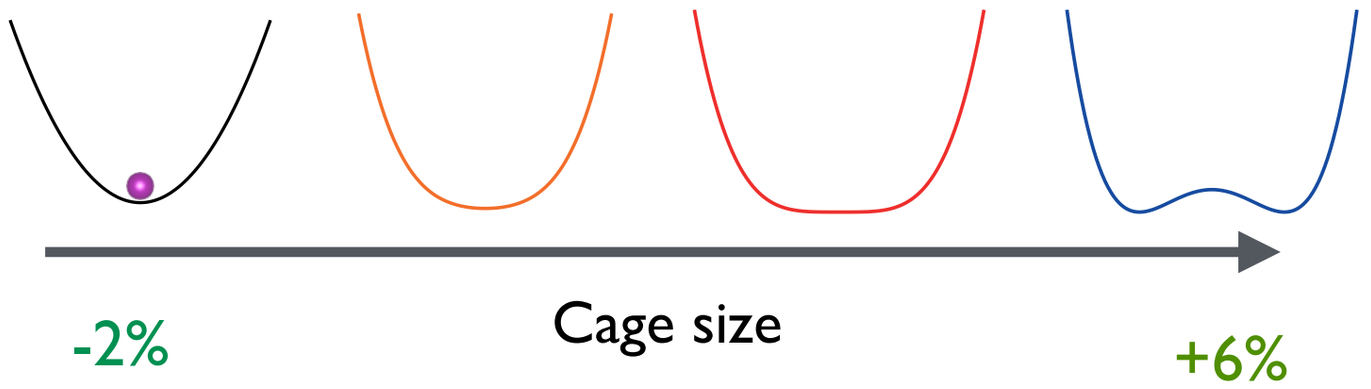
Potential energy surface



$Ba_8Ga_{16}Ge_{30}$ (BGG)

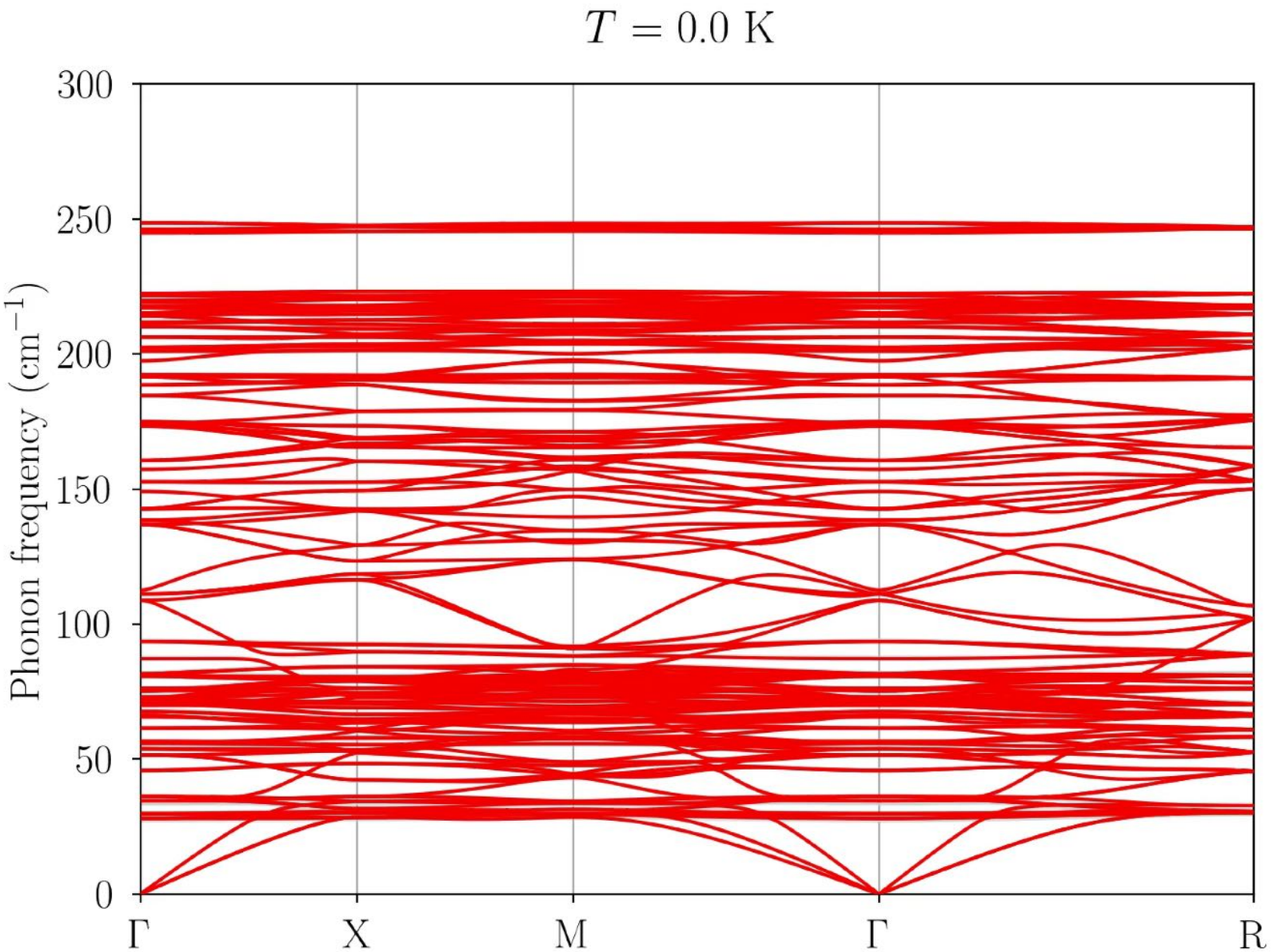


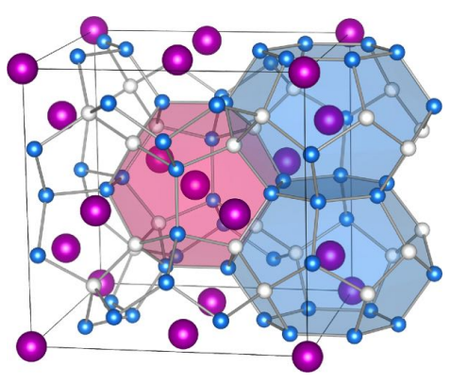
T_{2g} mode



Finite-temperature phonon dispersion

Calculated with the optimized lattice constant (VASP, PBE)

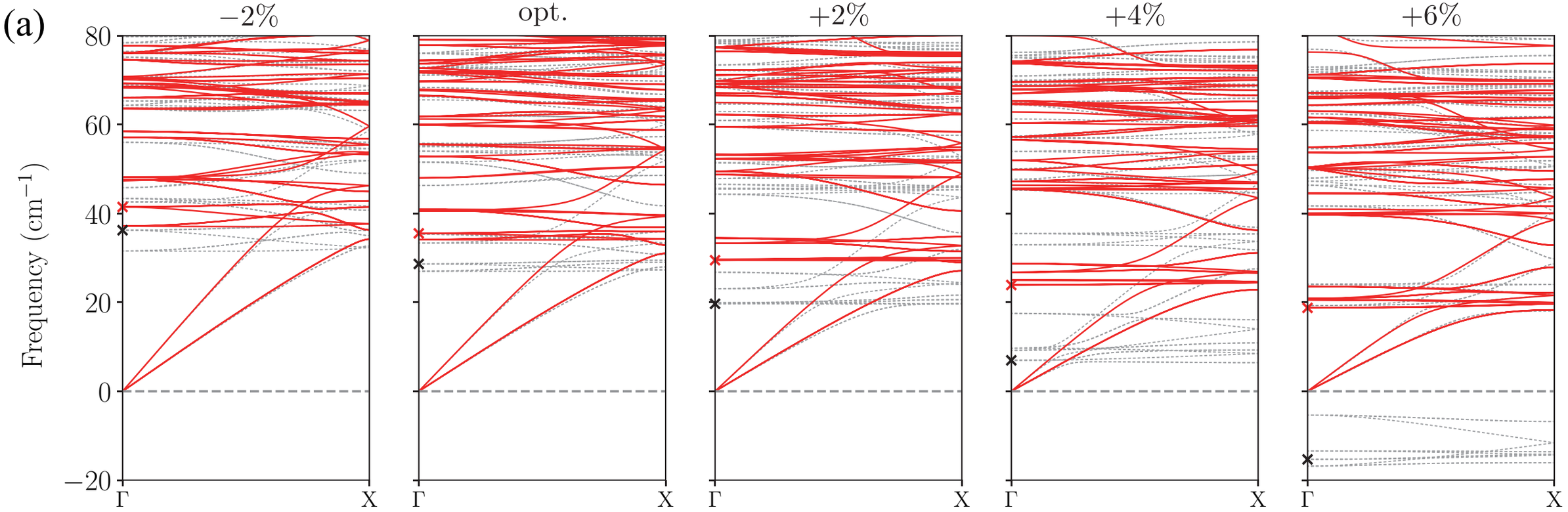


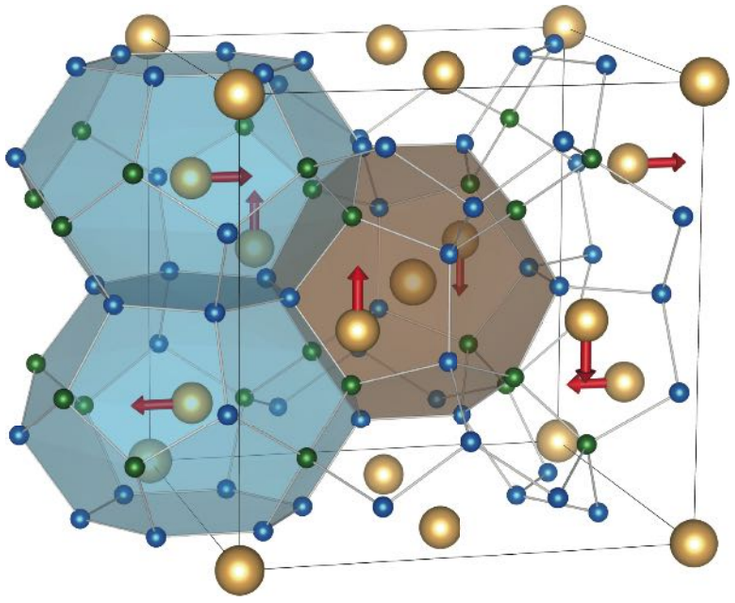


Gray lines: Harmonic phonon dispersion

Red lines : Anharmonic phonon dispersion

Phonon frequency shift in $Ba_8Ga_{16}Ge_{30}$





T_{2g} mode

Phonon frequency (cm^{-1})

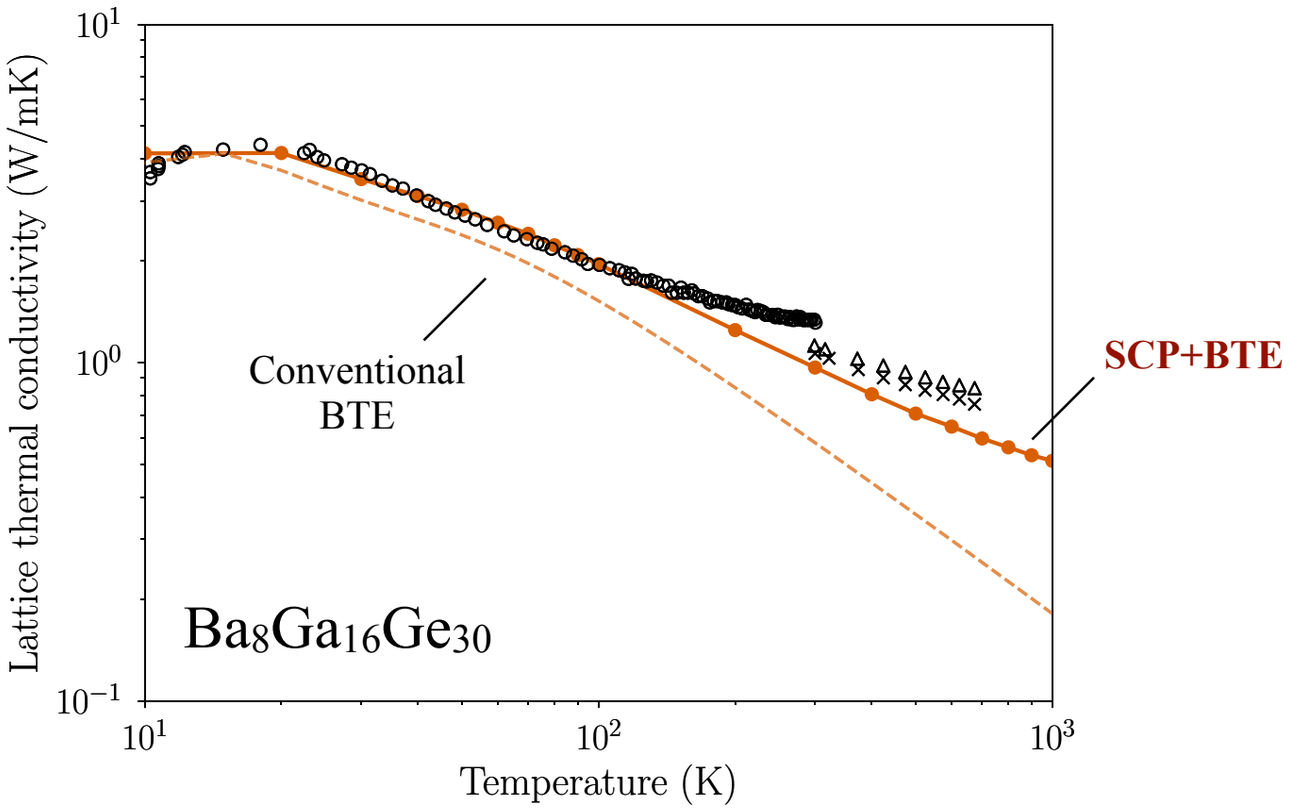
Lattice constants	Harmonic	SCP (300K)
-2%	36.2	41.5
opt.	28.6	35.5
+2%	19.7	29.5
+4%	7.0	23.9
+6%	15.3*i*	18.8

Change of high-temperature behavior of κ_L

SCP + BTE

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

- Consider cubic anharmonicity for calculating phonon lifetimes
- Additionally consider quartic anharmonicity for frequency renormalization



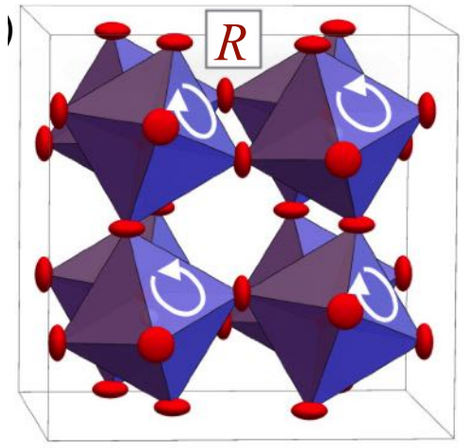
Thermal conductivity (300 K)

Conventional BTE	SCP+BTE	Expt.
0.58	?	1.06

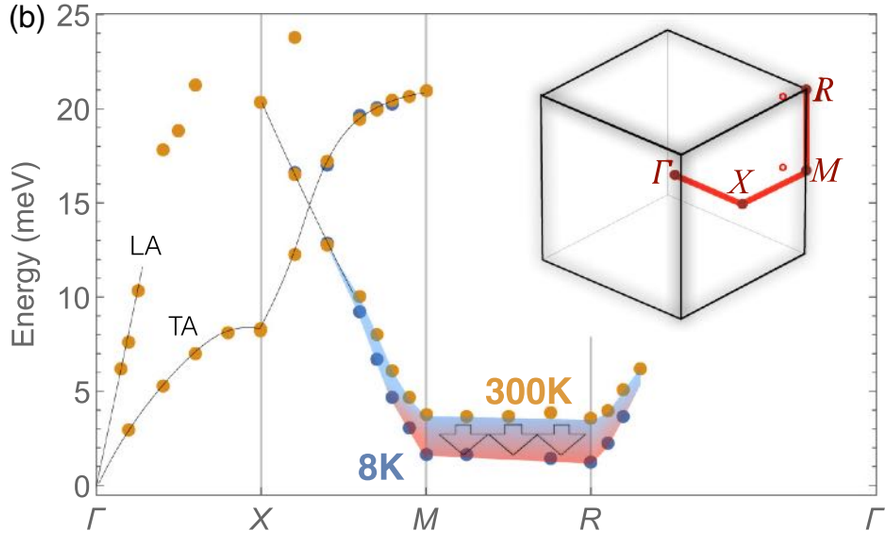
TT and S. Tsuneyuki, PRL **120**, 105901 (2018)

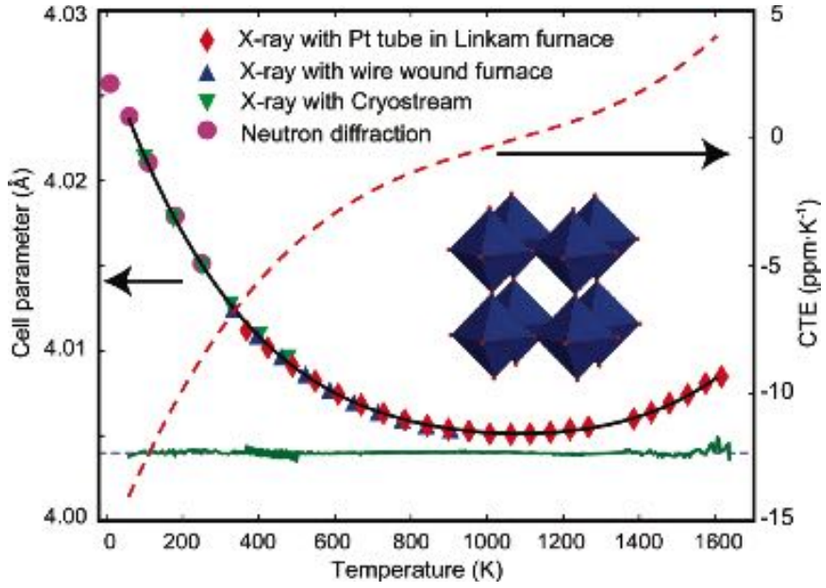
Description of negative thermal expansion

ScF_3 shows large negative thermal expansion, which can be attributed to the rigid unit modes (RUMs) of fluorine octahedra.

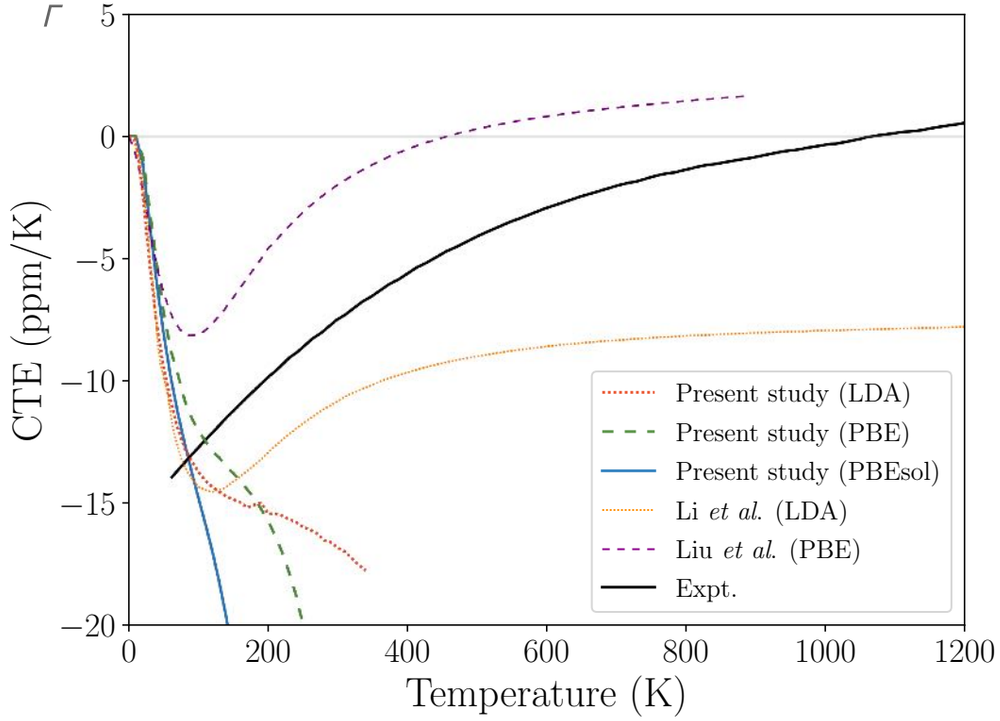


PRB **92**, 134101 (2015)





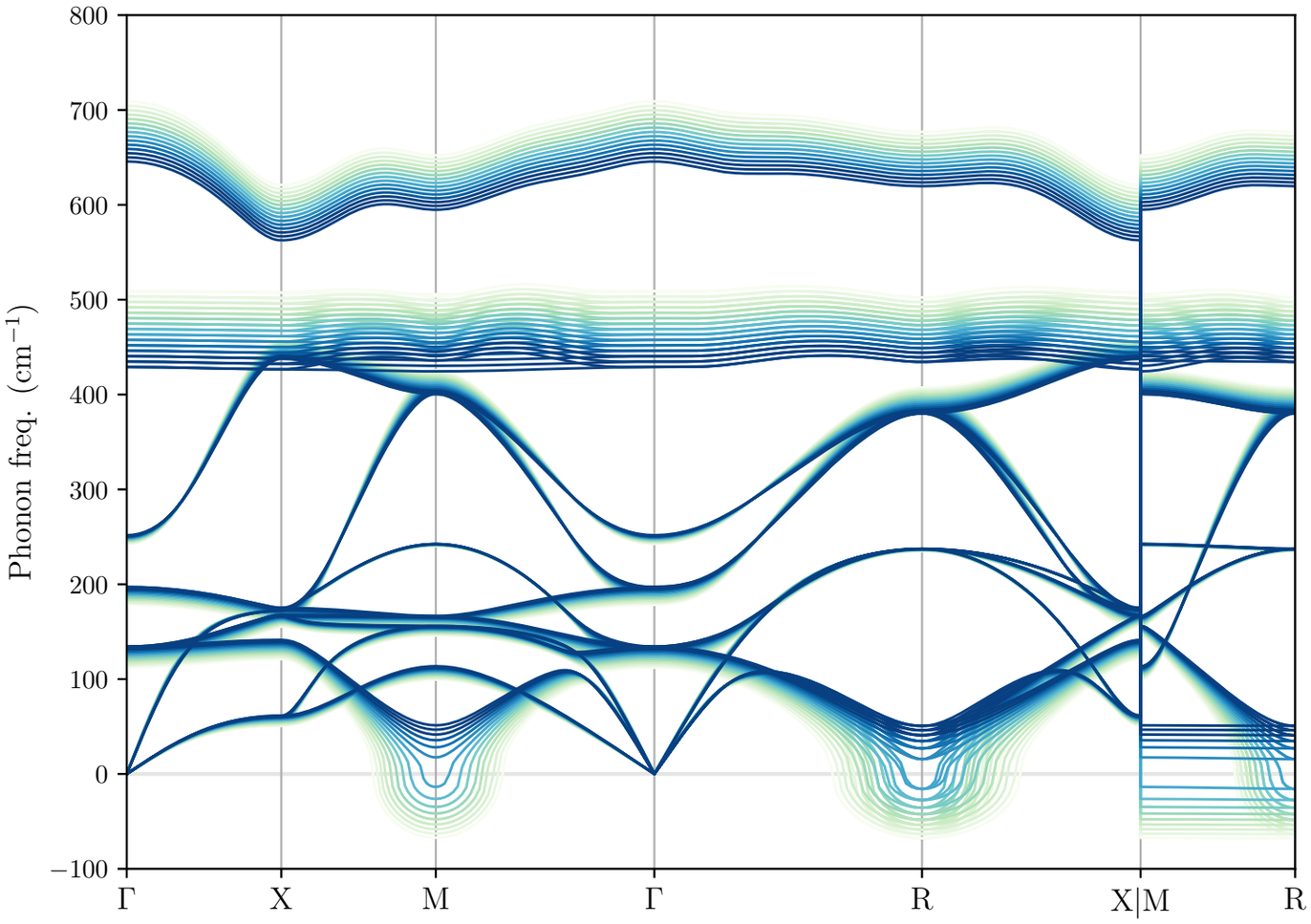
The quasi-harmonic approx. (QHA) breaks down due to strong anharmonic effects of the RUMs.



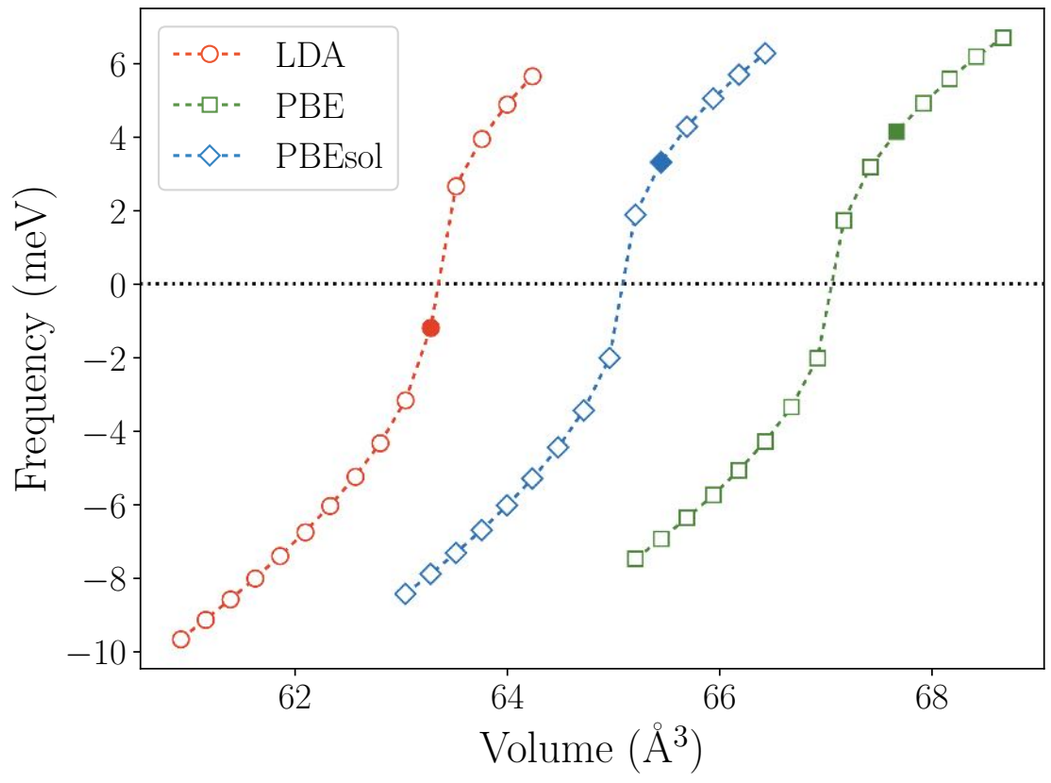
Y. Ooba, TT, R. Akashi and S. Tsuneyuki, Phys. Rev. Materials **3**, 033601 (2019).

Failure of QHA: Pressure induced softening

Pressure induced softening (calculated with PBEsol)



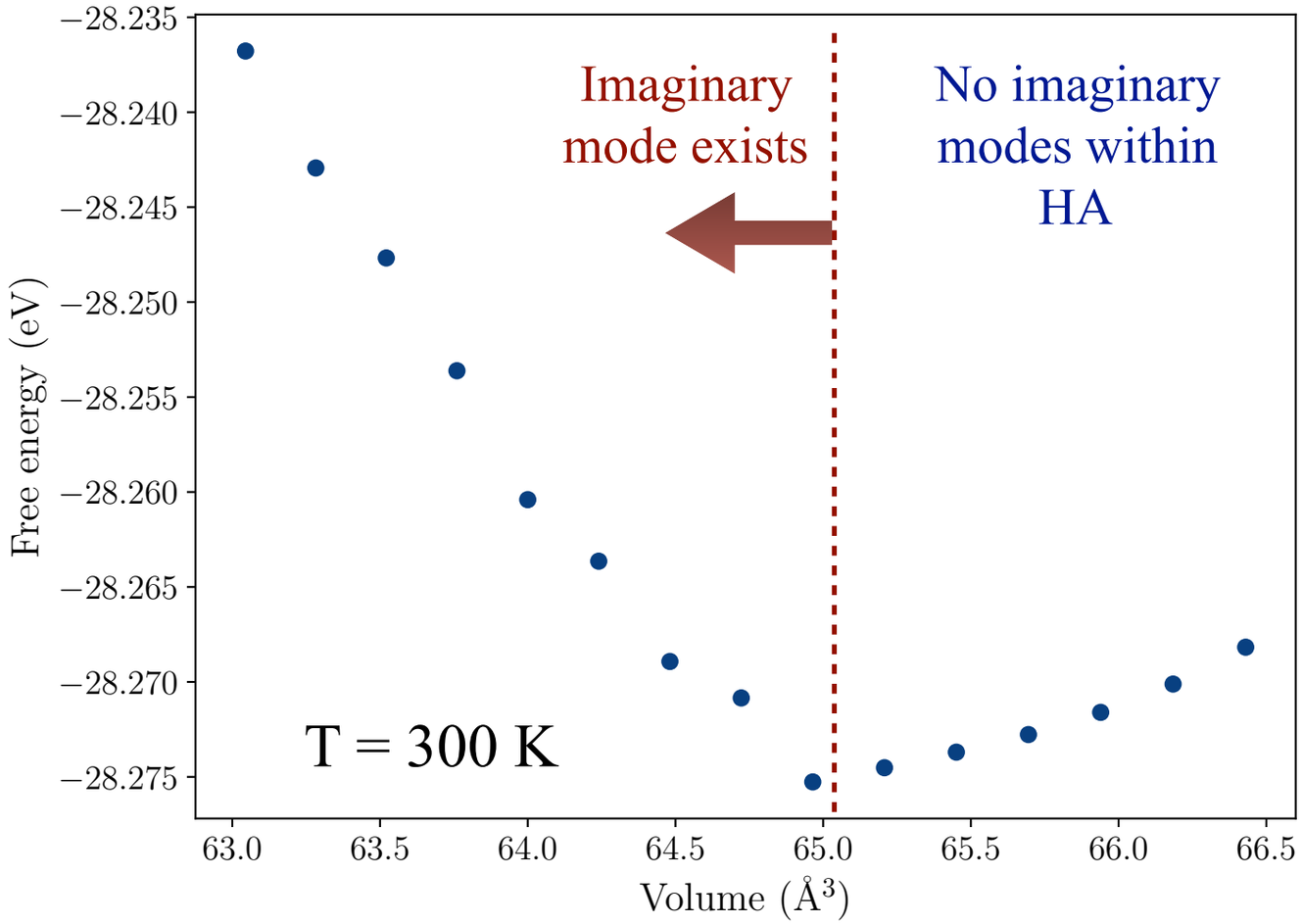
Frequency@ R (1/2,1/2,1/2)



Y. Ooba, TT, R. Akashi and S. Tsuneyuki, Phys. Rev. Materials **3**, 033601 (2019).

Failure of QHA: Equation of states

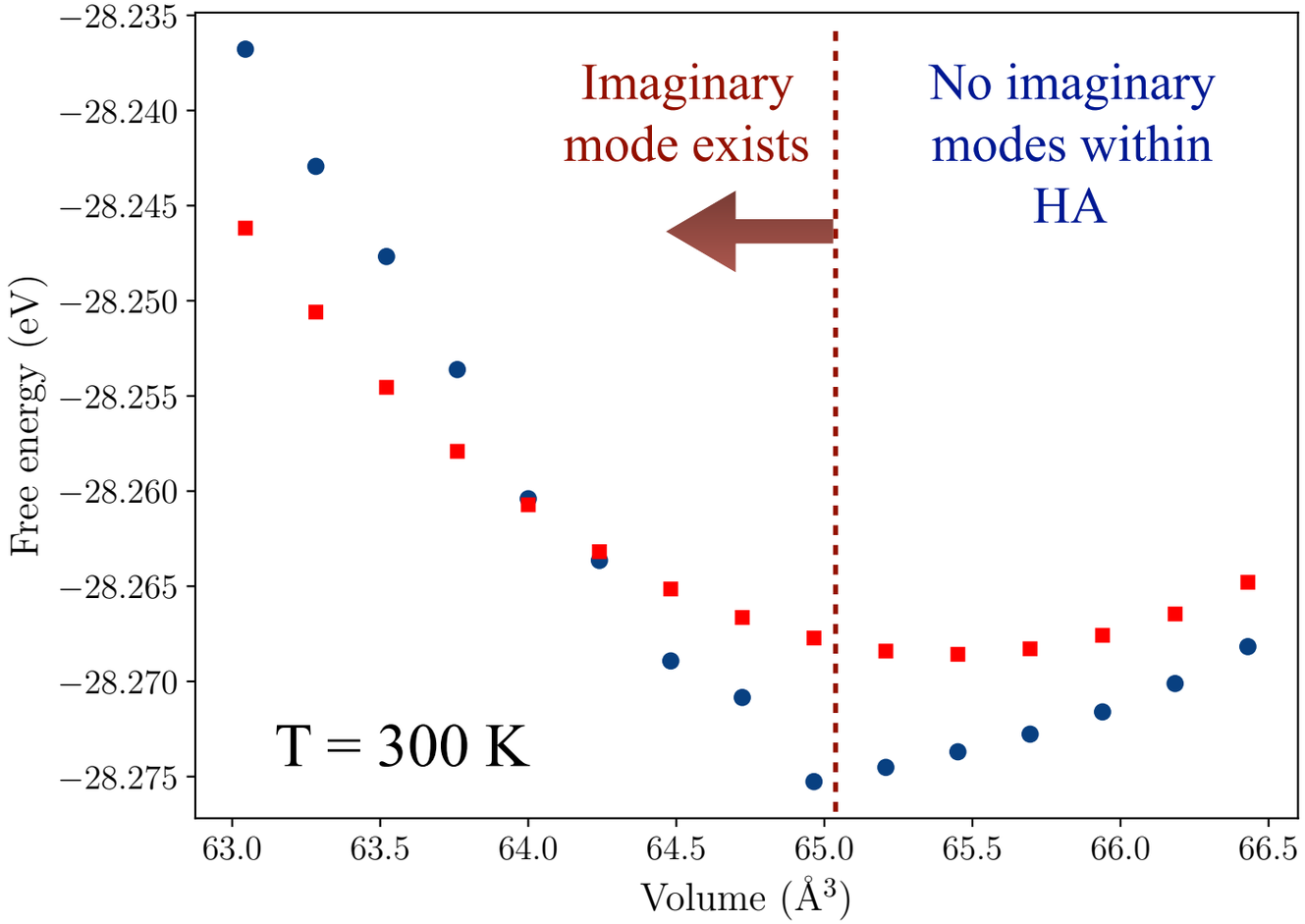
$$F(V,T) = E_0(V) + F_{\mathrm{vib}}(V,T) \qquad F_{\mathrm{vib}}^{(\mathrm{QH})}(V,T) = \frac{1}{\beta}\sum_q \ln\left[2\sinh\left(\frac{1}{2}\beta\hbar\omega_q(V)\right)\right]$$



Y. Ooba, TT, R. Akashi and S. Tsuneyuki, Phys. Rev. Materials **3**, 033601 (2019).

SCP free energy

$$F_{\mathrm{vib}}^{(\mathrm{SCP})}(V,T) = \frac{1}{\beta}\sum_q \ln\left[2\sinh\left(\frac{1}{2}\beta\hbar\Omega_q(V,T)\right)\right]$$
$$-\frac{1}{4}\sum_q\left[\Omega_q^2(V,T) - (C_{\boldsymbol{q}}^{\dagger}\Lambda_{\boldsymbol{q}}^{(\mathrm{HA})}C_{\boldsymbol{q}})_{jj}\right]\alpha_q.$$



Y. Ooba, TT, R. Akashi and S. Tsuneyuki, Phys. Rev. Materials **3**, 033601 (2019).

Anharmonic correction to free energy

Quasiharmonic (QH) theory

$$F_{\mathrm{vib}}^{(\mathrm{QH})}(V,T) = \frac{1}{\beta}\sum_{q} \ln\left[2\sinh\left(\frac{1}{2}\beta\hbar\omega_q(V)\right)\right]$$

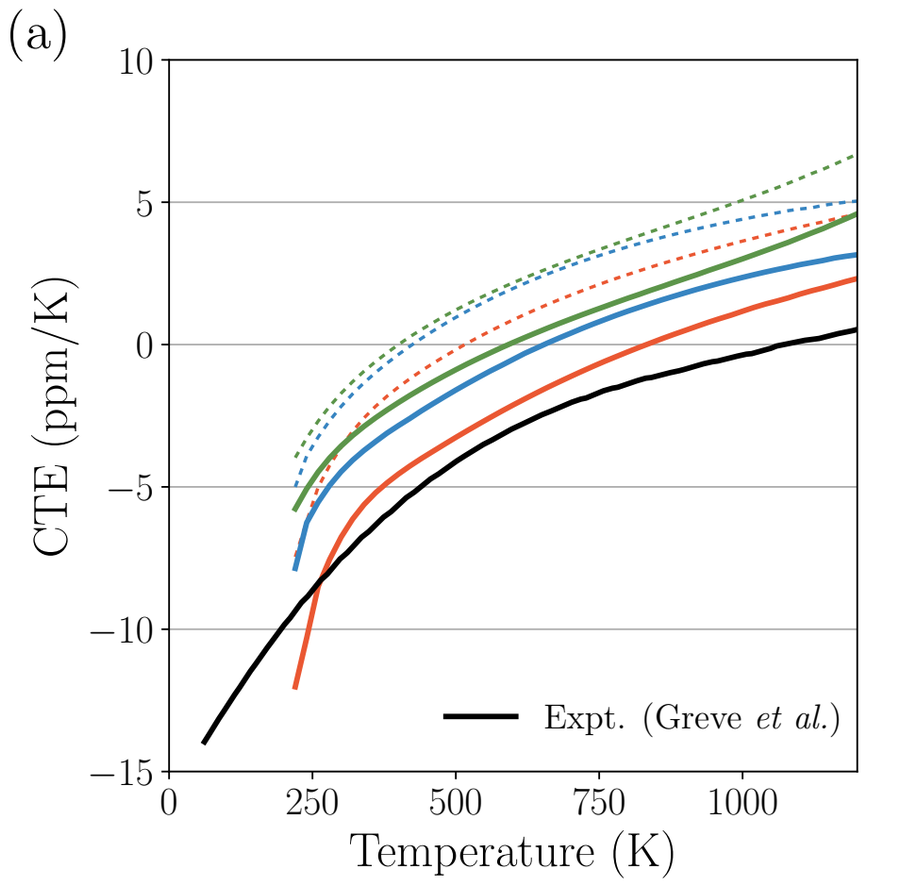
Self-consistent phonon (SCP) theory

$$F_{\mathrm{vib}}^{(\mathrm{SCP})}(V,T) = \frac{1}{\beta}\sum_{q} \ln\left[2\sinh\left(\frac{1}{2}\beta\hbar\Omega_q(V,T)\right)\right]$$
$$- \frac{1}{4}\sum_{q}\left[\Omega_q^2(V,T) - (C_{\boldsymbol{q}}^{\dagger}\Lambda_{\boldsymbol{q}}^{(\mathrm{HA})}C_{\boldsymbol{q}})_{jj}\right]\alpha_q$$

Improved SCP (ISC) theory

$$F_{\mathrm{vib}}^{(\mathrm{ISC})}(V,T) = F_{\mathrm{vib}}^{(\mathrm{SCP})}(V,T) + F_{\mathrm{vib}}^{(\mathrm{B})}(V,T),$$

More accurate

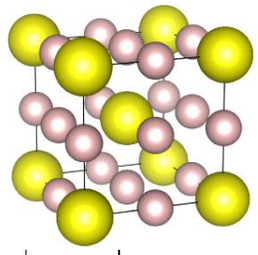


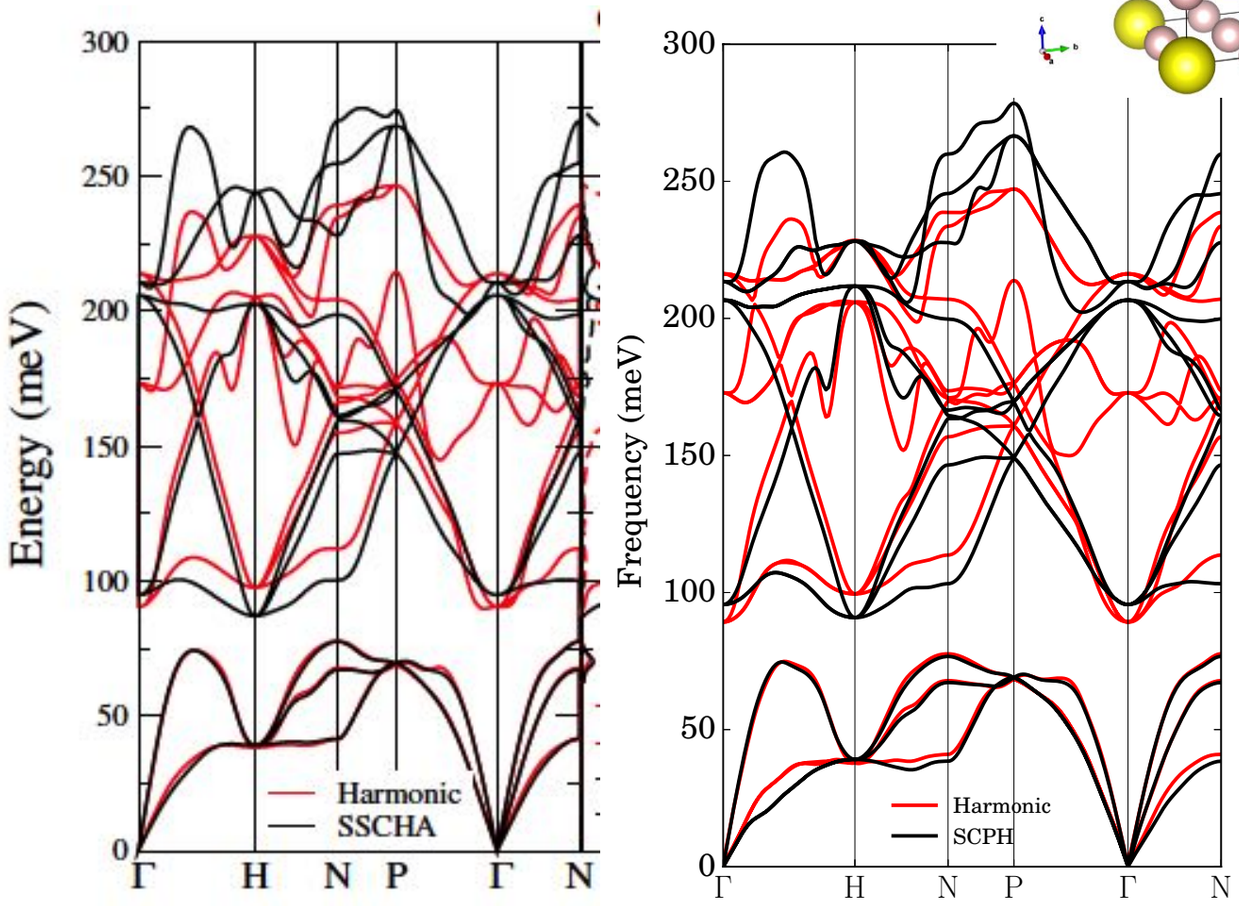
- ☑ Improved prediction of phase boundary
- ☑ Able to compute free-energy of high-T phases

Y. Ooba, TT, R. Akashi and S. Tsuneyuki, Phys. Rev. Materials **3**, 033601 (2019).

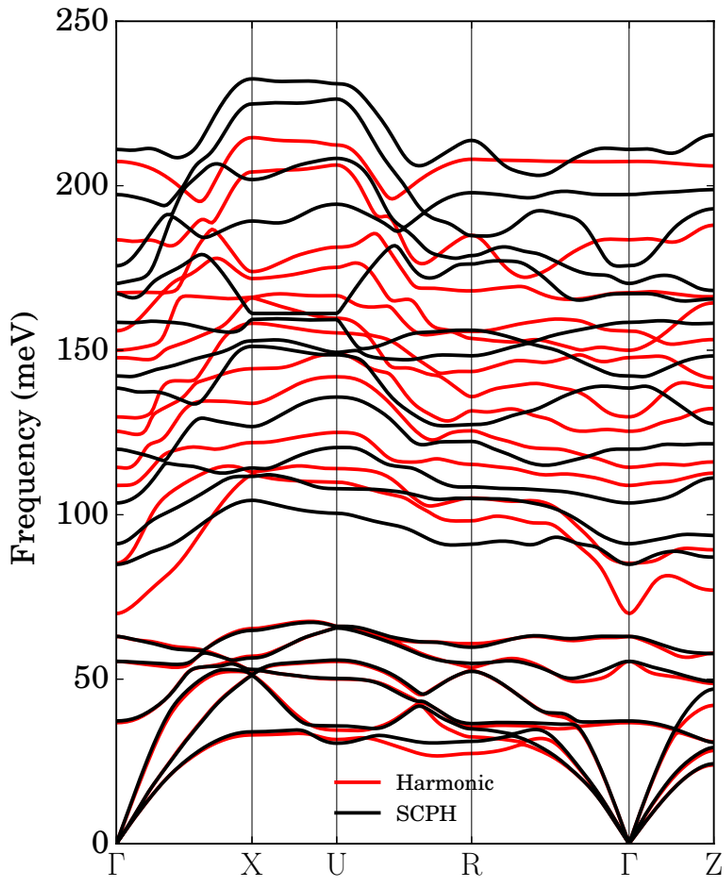
Anharmonic effects in H_xS

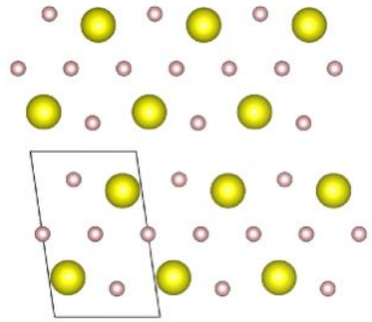
H_3S (Im-3m) @ 250 GPa





H_2S (P-1) @ 140 GPa





SSCHA

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

SCP (our method)

T_c based on the Migdal-Eliashberg theory*

$T_c = 202$ K (Harmonic)

$T_c = 181$ K (Anharmonic)

$T_c = 44$ K (Harmonic)

$T_c = 34$ K (Anharmonic)

Expt. $T_c \sim 160$ K

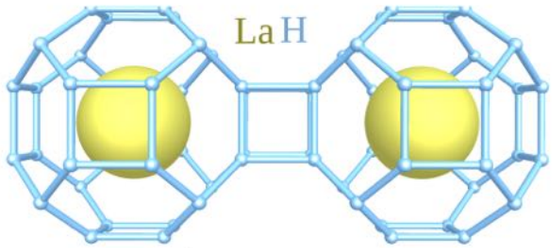
*W. Sano, T. Koretsune, TT, R. Akashi, and R. Arita, PRB **93**, 094525 (2016).

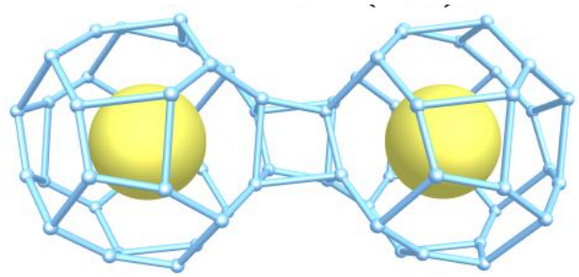
Anharmonic effects in LaH_{10}

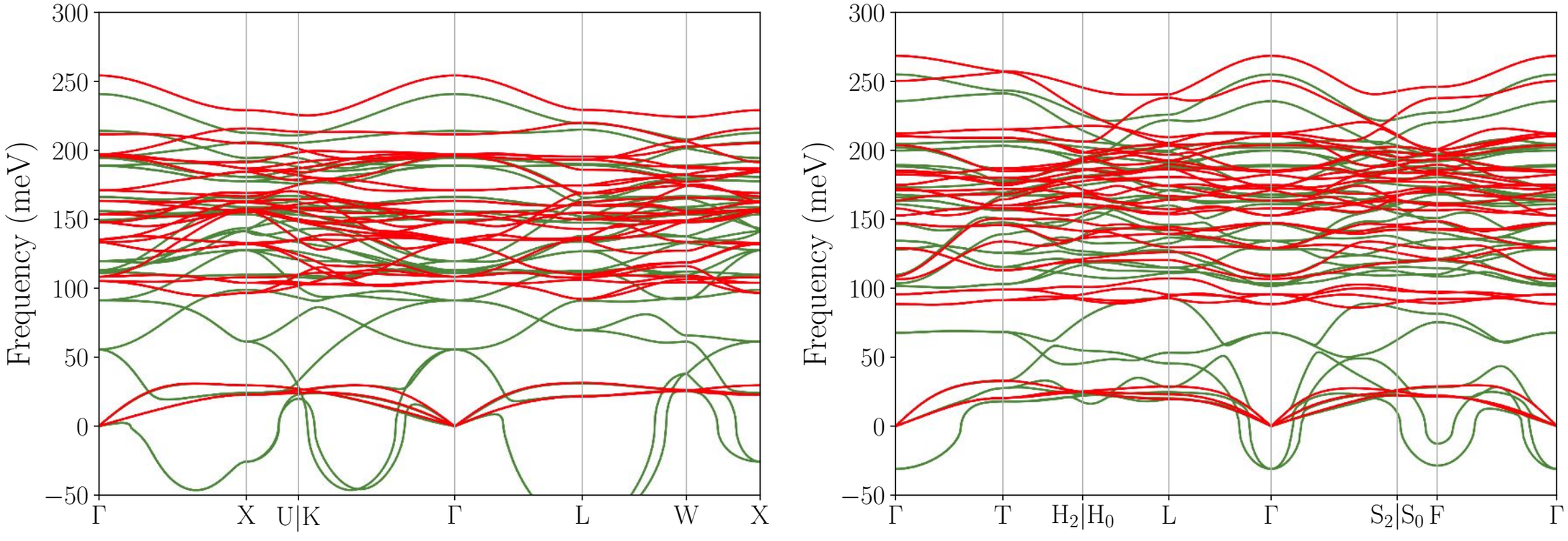
Superconductivity at ~250 K is observed under high pressure (~140—220 GPa)

A.P. Drozdov et al., Nature **569**, 528 (2019).

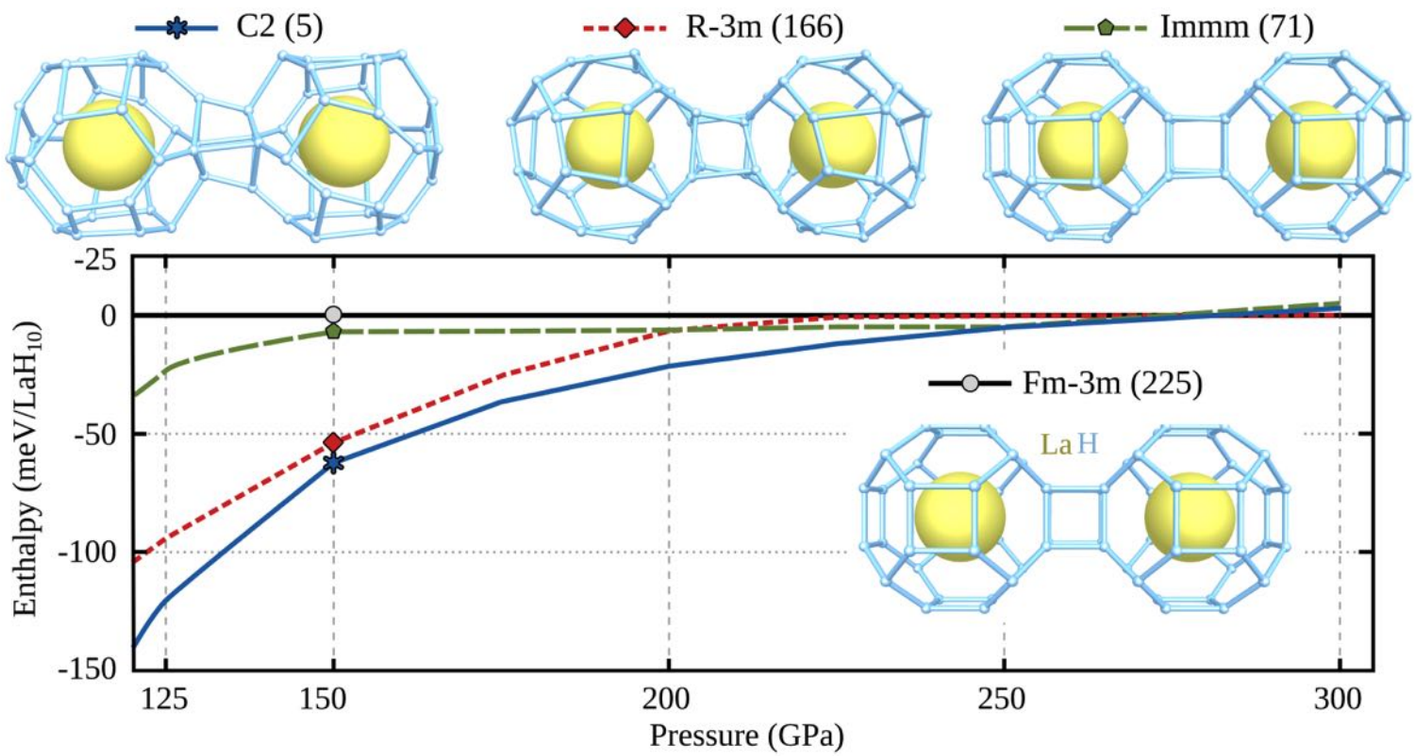
For LaH_{10}, harmonic approximation breaks down.
The SCP theory gives stable phonons at T = 0 K.

Fm-3m 

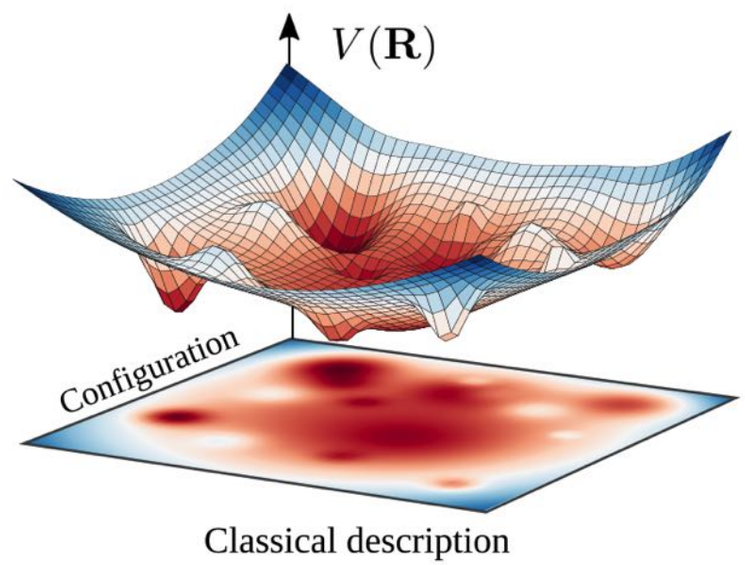
R-3m 



Nuclear quantum effects in LaH_{10}

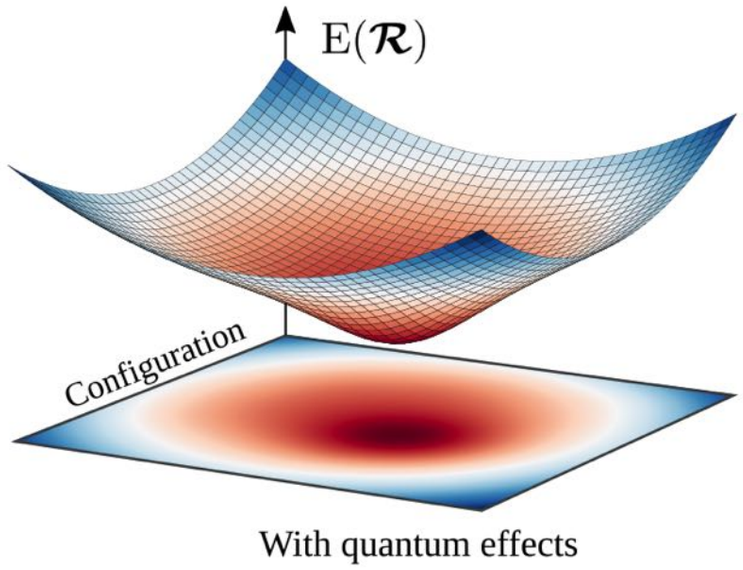


I. Errea, TT et al., arXiv:1907.11916



Comparison of energies (eV / LaH_{10})

Structure	E_0 + PV	$E_{zp\text{-}vib}$	Total
1) Fm-3m	-6350.471	2.266	-6348.205
2) R-3m	-6350.517	2.423	-6348.094
$\Delta=X_2-X_1$	-0.046	0.157	0.111



Fm-3m structure gives the

ALAMODE (Anharmonic Lattice Model)

Software for anharmonicity and thermal transport

- Open source (MIT license)
- Can be combined with any DFT codes and classical MD codes
- Inputs data: crystal structure and training data set (displacement & force)

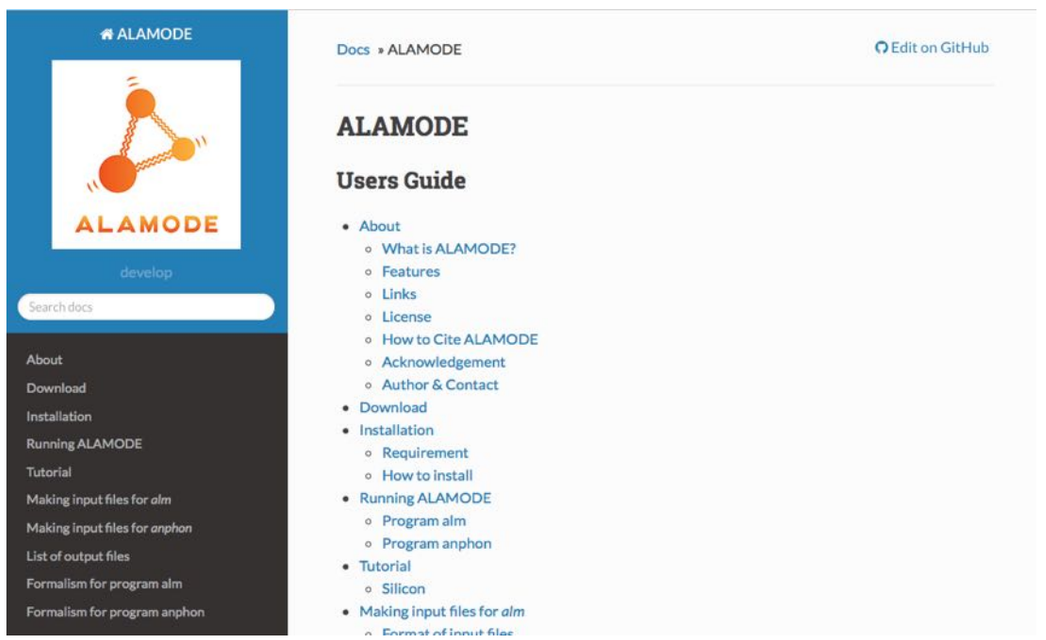
ALAMODE

Main features

(1) Extraction of force constants by linear regression (fourth- and higher-order terms are also supported)

(2) Phonon calculation (harmonic & self-consistent phonon)

(3) Thermal conductivity calculation



http://alamode.readthedocs.io/

Please visit the document page for details

Summary

- ☑ Perturbative treatment of lattice anharmonicity
- ☑ Non-perturbative treatment of fourth-order anharmonicity based on the self-consistent phonon theory

  Able to compute phonon lifetimes and thermodynamic functions of severely anharmonic materials and high-temperature phases.

- ☑ Compressive sensing approach to estimate force constants

  100x speed up is expected!

- ☑ Software development

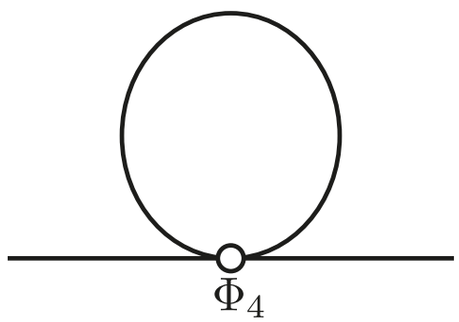
  Features presented today are available in ALAMODE software.

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

ALAMODE hands-on materials:
`https://github.com/ttadano/alamode/tree/gh-pages/files`

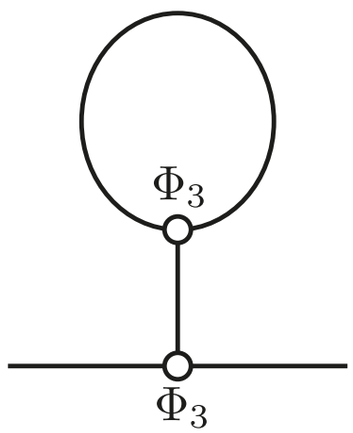
Anharmonic self-energy

First-order diagram



“loop”

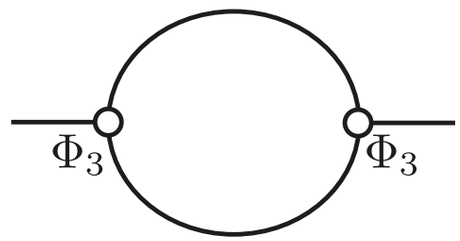
Real



“tadpole”

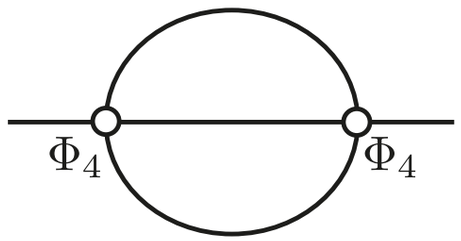
Real

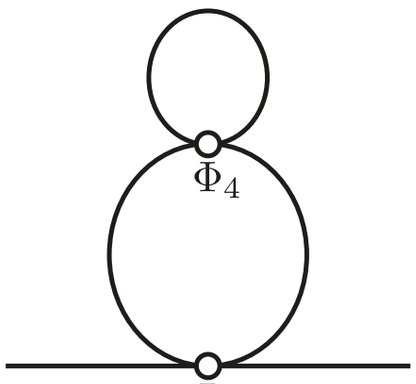
Second-order diagrams



“bubble”

Complex

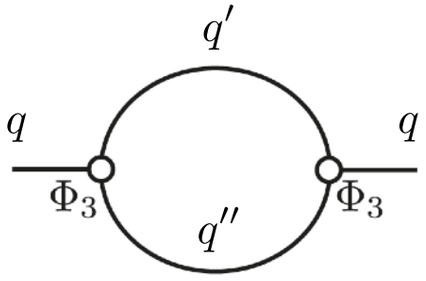




Phonon scattering by the three-phonon process

Linewidth

$$\Gamma_q(\omega) = \mathrm{Im}\left[\quad\right] = \frac{\pi}{2N}\sum_{q',q''}\frac{\hbar|\Phi_3(-q,q',q'')|^2}{8\omega_q\omega_{q'}\omega_{q''}}\Delta(-\boldsymbol{q}+\boldsymbol{q}'+\boldsymbol{q}'')$$
$$\times[(n_{q'}+n_{q''}+1)\delta(\omega_q-\omega_{q'}-\omega_{q''})$$
$$-2(n_{q'}-n_{q''})\delta(\omega_q-\omega_{q'}+\omega_{q''})]$$



Lifetime

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

$\propto T$ (in high-T region $kT \gg \hbar\omega$)

Self-consistent phonon theory from Dyson eq.

The self-consistent phonon (**SCP**) theory is a non-perturbative approach to compute anharmonic phonon frequency $\Omega_q(T)$.

In this study, we estimate $\Omega_q(T)$ from the pole of the Green's function.

$$[\boldsymbol{D_q}(\omega)]^{-1} = [\boldsymbol{D_q^0}(\omega)]^{-1} - \boldsymbol{\Sigma_q}(\omega)$$

$$\det\{[\boldsymbol{D_q^0}(\omega)]^{-1} - \boldsymbol{\Sigma_q}(\omega)\} = 0$$

$$D^0_{\boldsymbol{q}\nu\nu'}(\omega) = \frac{2\omega_{\boldsymbol{q}\nu}}{\omega^2_{\boldsymbol{q}\nu} - \omega^2}\delta_{\nu\nu'}$$

$$\det\{\omega^2 - \boldsymbol{V}_q(\omega)\} = 0,$$

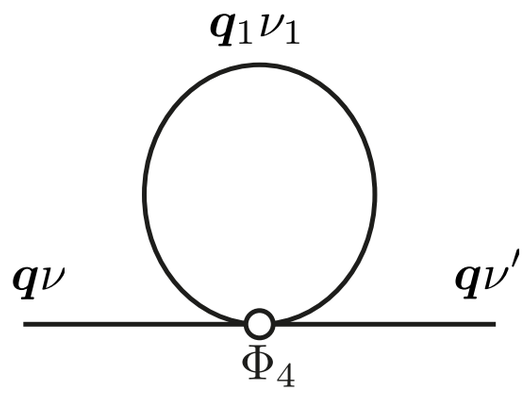
$$V_{\boldsymbol{q}\nu\nu'}(\omega) = \omega^2_{\boldsymbol{q}\nu}\delta_{\nu\nu'} - (2\omega_{\boldsymbol{q}\nu})^{\frac{1}{2}}(2\omega_{\boldsymbol{q}\nu'})^{\frac{1}{2}}\Sigma_{\boldsymbol{q}\nu\nu'}(\omega)$$

Iterative update of phonon frequency

SCP eq.

$$\det\{\omega^2 - \boldsymbol{V}_q(\omega)\} = 0,$$

$$V_{\boldsymbol{q}\nu\nu'}(\omega) = \omega^2_{\boldsymbol{q}\nu}\delta_{\nu\nu'} - (2\omega_{\boldsymbol{q}\nu})^{\frac{1}{2}}(2\omega_{\boldsymbol{q}\nu'})^{\frac{1}{2}}\Sigma_{\boldsymbol{q}\nu\nu'}(\omega)$$



initial value

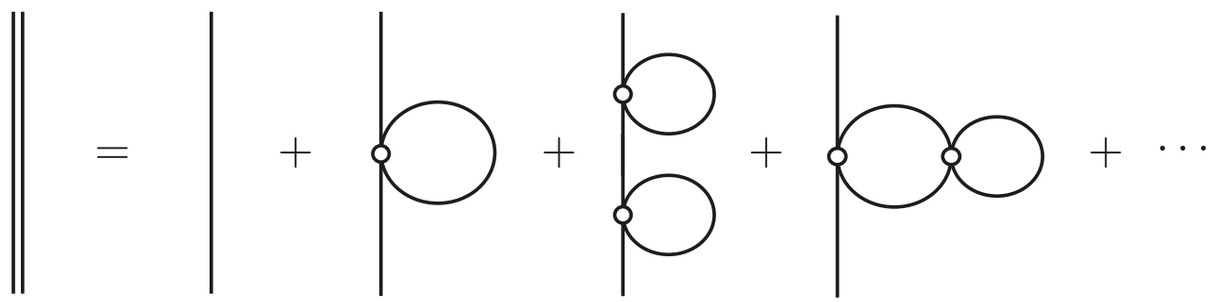
$\{\omega_{\boldsymbol{q}\nu}, \boldsymbol{e}_{\boldsymbol{q}\nu}\}$ → $\boldsymbol{\Sigma}^{(a)}_{\boldsymbol{q}}$ → $\boldsymbol{V}_{\boldsymbol{q}}$

interpolation

diagonalization

$\{\Omega_{\boldsymbol{q}\nu}, \boldsymbol{\epsilon}_{\boldsymbol{q}\nu}\}$ ⋯→ **SCP solution**

converged



Efficient implementation

<u>TT</u> and S. Tsuneyuki,
Phys. Rev. B **92**, 054301 (2015).

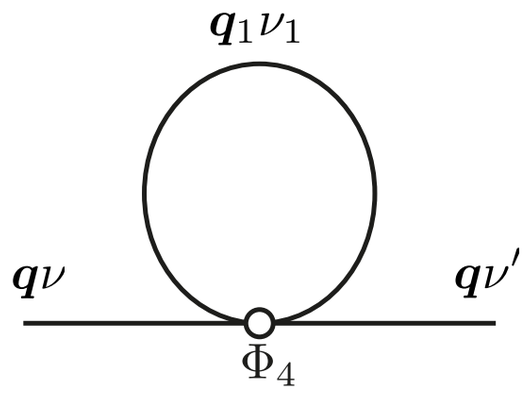
In this work, we only consider the loop diagram, which is ω-independent.

Loop diagram

$$V_{\boldsymbol{q}\nu\nu'} = \omega^2_{\boldsymbol{q}\nu}\delta_{\nu\nu'} - (2\omega_{\boldsymbol{q}\nu})^{\frac{1}{2}}(2\omega_{\boldsymbol{q}\nu'})^{\frac{1}{2}}\Sigma^{\mathrm{loop}}_{\boldsymbol{q}\nu\nu'}$$

$$\Sigma^{\mathrm{loop}}_{\boldsymbol{q}\nu\nu'} = -\sum_{q_1}\frac{\Phi_4(\boldsymbol{q}\nu;-\boldsymbol{q}\nu';q_1;-q_1)}{4\sqrt{\omega_{\boldsymbol{q}\nu}\omega_{\boldsymbol{q}\nu'}}} \times \frac{\hbar[1+2n(\omega_{q_1})]}{2\omega_{q_1}}$$

$$= \langle Q^*_{q_1} Q_{q_1} \rangle$$



✓ Correct treatment of **zero-point vibration**

✓ Easy to check **the finite-size effect** by changing the q_1-grid density

✓ Renormalized frequencies at various T can be calculated efficiently

✓ (Probably) systematically improvable

✗ Need to calculate **fourth-order force constants**

Temperature-dependent effective potential (TDEP)

A MD-based approach to compute effective force constants.

O. Hellman, I. A. Abrikosov, and S. I. Simak, Phys. Rev. B **84**, 180301 (2011).

$$F_i = -\sum_j \Theta_{ij}(T) u_j(T) \qquad \boldsymbol{\Theta} = \arg\min_{\boldsymbol{\Theta}} \| \boldsymbol{F}^{\mathrm{TDEP}} - \boldsymbol{F}^{\mathrm{AIMD}} \|^2$$

- Fit displacement-force data sets sampled by AIMD at finite temperature with *effective harmonic force*
- Full anharmonicity included
- Neglect the effect of zero-point motion

The TDEP method can be extended to include third-order terms:

$$F_i = -\sum_j \tilde{\Theta}_{ij}(T) u_j(T) - \frac{1}{2} \sum_{jak} \tilde{\Theta}_{ijk}(T) u_j(T) u_k(T)$$

$$\Theta_{ij} \neq \tilde{\Theta}_{ij}$$