Lattice thermal conductivity for strongly anharmonic materials

SSCHA School 2026.

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Stochastic Self-Consistent Harmonic Approximation

Outline

- Introduction
- Boltzmann transport equation
- Green – Kubo formalism
- SSCHA implementation
- Application – CsPbBr3

Introduction

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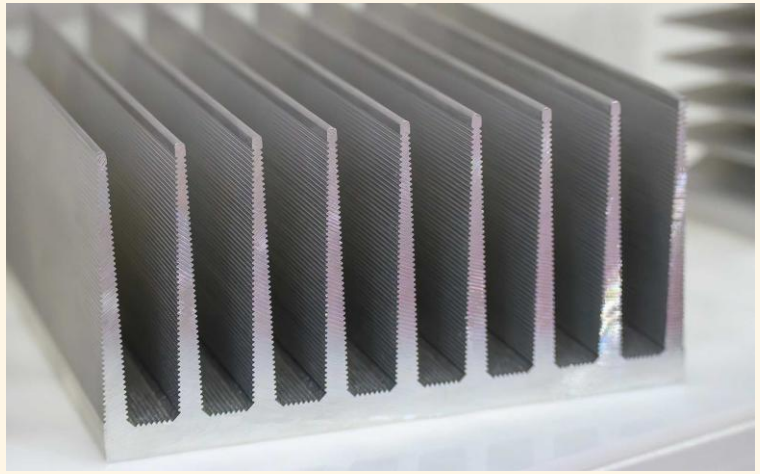
- What is thermal conductivity?

$$q = -\kappa \nabla T$$

- Why do we care about it?



Heat sink

Insulation

Introduction

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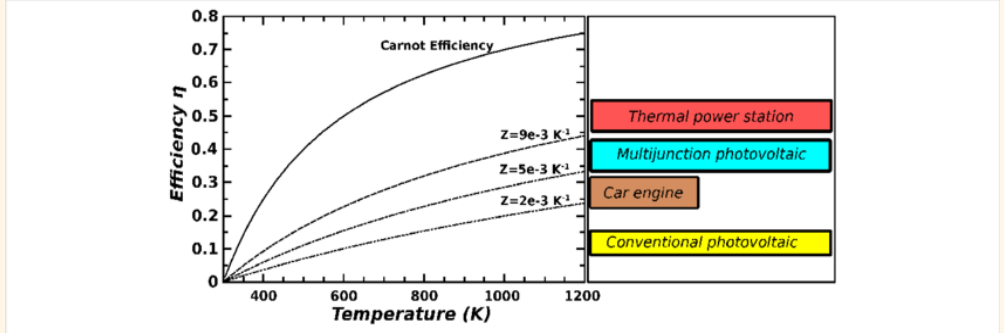
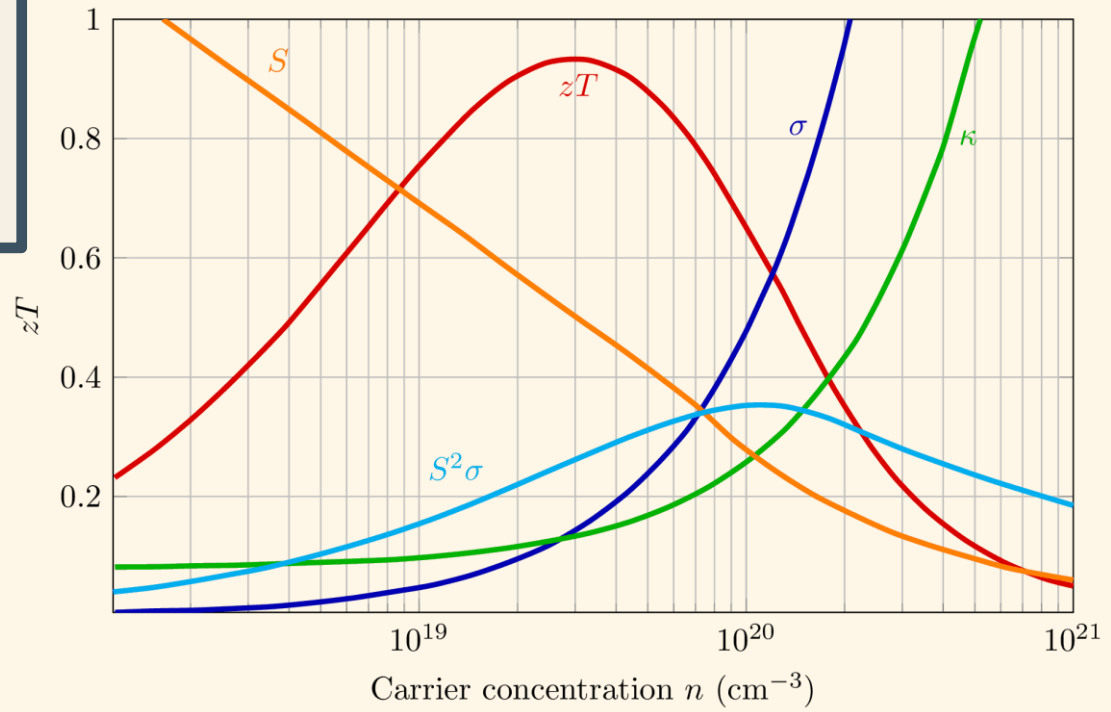
- Especially important for thermoelectric materials
- Converting heat to electricity and vice versa
- Efficiency is quantified through thermoelectric figure of merit *zT*

$$zT = \frac{S\sigma}{\kappa_e + \kappa_p} T$$





Introduction

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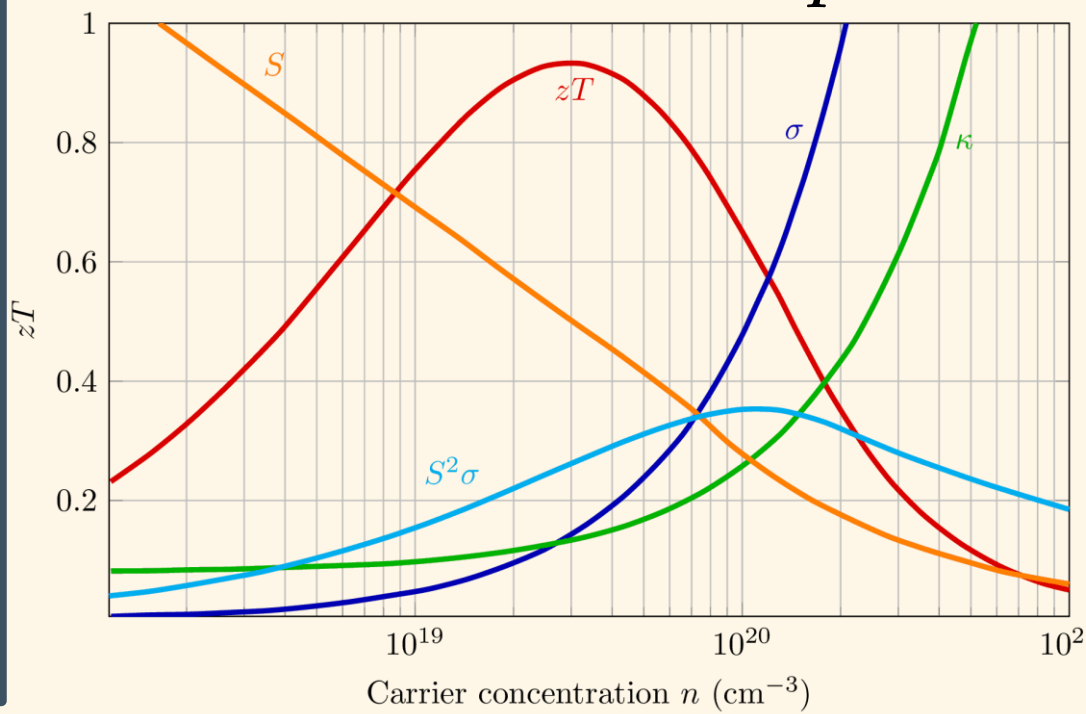
- What is happening microscopically?
- Mostly electrons κ_e and phonons κ_p carry heat
- In insulating materials – only phonons available
- Basic design principle – reduce κ_p

$$zT = \frac{S\sigma}{\kappa_e + \kappa_p} T$$



Introduction

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- Harmonic phonons do not interact with anything → infinite lifetimes and thermal conductivity
- Realistically, they scatter from other phonons, electrons and crystal impurities
- We are mostly interested in insulators/semiconductors so interactions with electrons are neglected
- The most important scattering mechanism is phonon-phonon through anharmonic force constants

Boltzmann transport equation

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- Basic approach is through Boltzmann transport equation (BTE)

$$\frac{\partial n_{\mathbf{q},j}}{\partial t} = \left.\frac{\partial n_{\mathbf{q},j}}{\partial t}\right|_{diff} + \left.\frac{\partial n_{\mathbf{q},j}}{\partial t}\right|_{scatt} = 0$$

- Linearize the deviation: $\left.\frac{\partial n_{\mathbf{q},j}}{\partial t}\right|_{scatt} = \frac{n_{\mathbf{q},j} - n^0_{\mathbf{q},j}}{\tau_{\mathbf{q},j}}$ & $\left.\frac{\partial n_{\mathbf{q},j}}{\partial t}\right|_{diff} = v_{\mathbf{q},j}\frac{\partial n^0_{\mathbf{q},j}}{\partial T}\nabla T$

$$n_{\mathbf{q},j} = n^0_{\mathbf{q},j} - v_{\mathbf{q},j}\frac{\partial n^0_{\mathbf{q},j}}{\partial T}\nabla T \tau_{\mathbf{q},j}$$

$$S^x = \frac{1}{V N_{\mathbf{q}}} \sum_{\mathbf{q},j} \omega_{\mathbf{q},j} v^x_{\mathbf{q},j} n_{\mathbf{q},j}$$

Boltzmann transport equation

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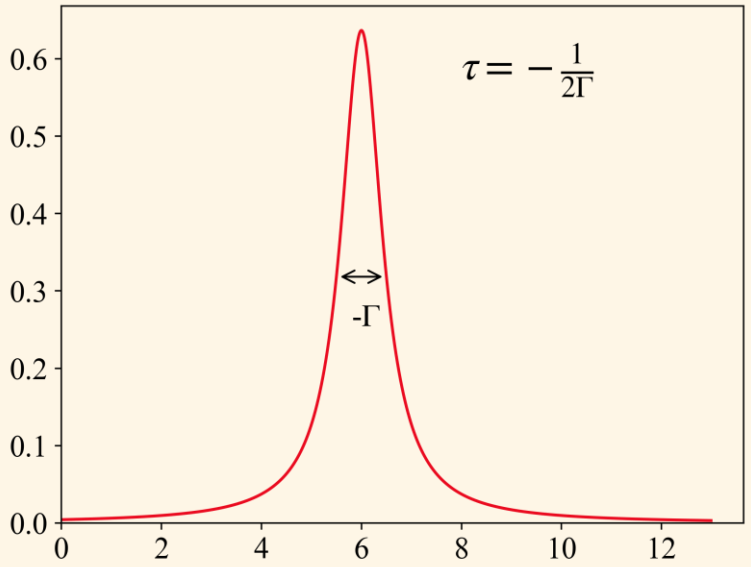
$$\kappa_p^{\alpha,\beta} = \sum_{\mathbf{q},n} c_{\mathbf{q},n} v^{\alpha}_{\mathbf{q},n} v^{\beta}_{\mathbf{q},n} \tau_{\mathbf{q},n}$$

- Phonons are quasiparticles with well-defined lifetimes ie. their spectral functions are Lorentzians rather than Dirac deltas like in harmonic approximation
- Lifetimes can be calculated from the Fermi golden rule using anharmonic force constants
- Works very well for low-anharmonicity materials (silicon, diamond etc.)



Anharmonic materials

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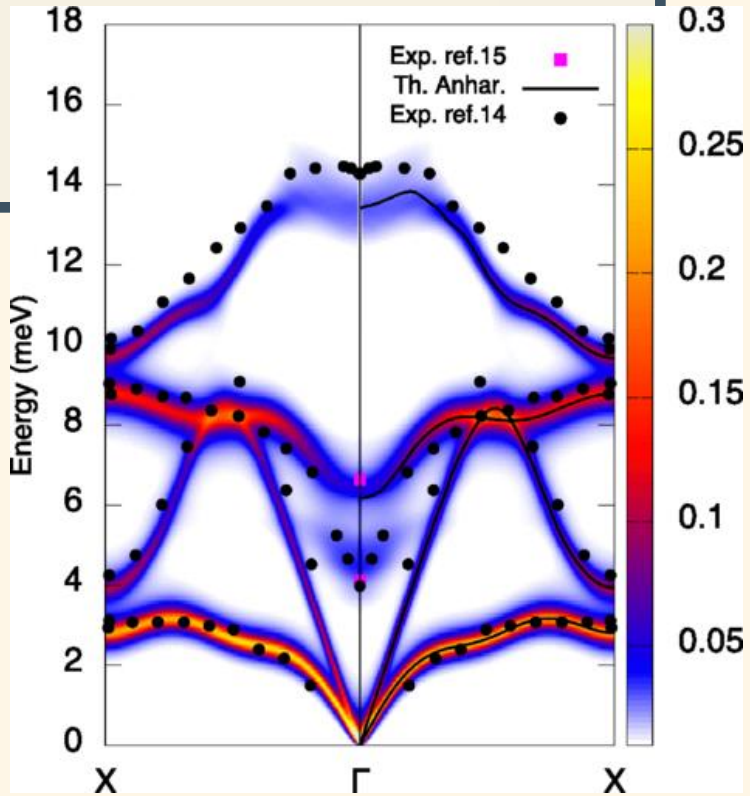
- Materials interesting for thermoelectric applications have low thermal conductivity implying short phonon lifetimes and strong anharmonicity
- In these cases, the assumptions made in BTE fail

- PbTe is one of highest *zT* materials
- Spectral function has two peaks for zone center optical mode
- Clearly, we cannot determine linewidth of such phonon mode



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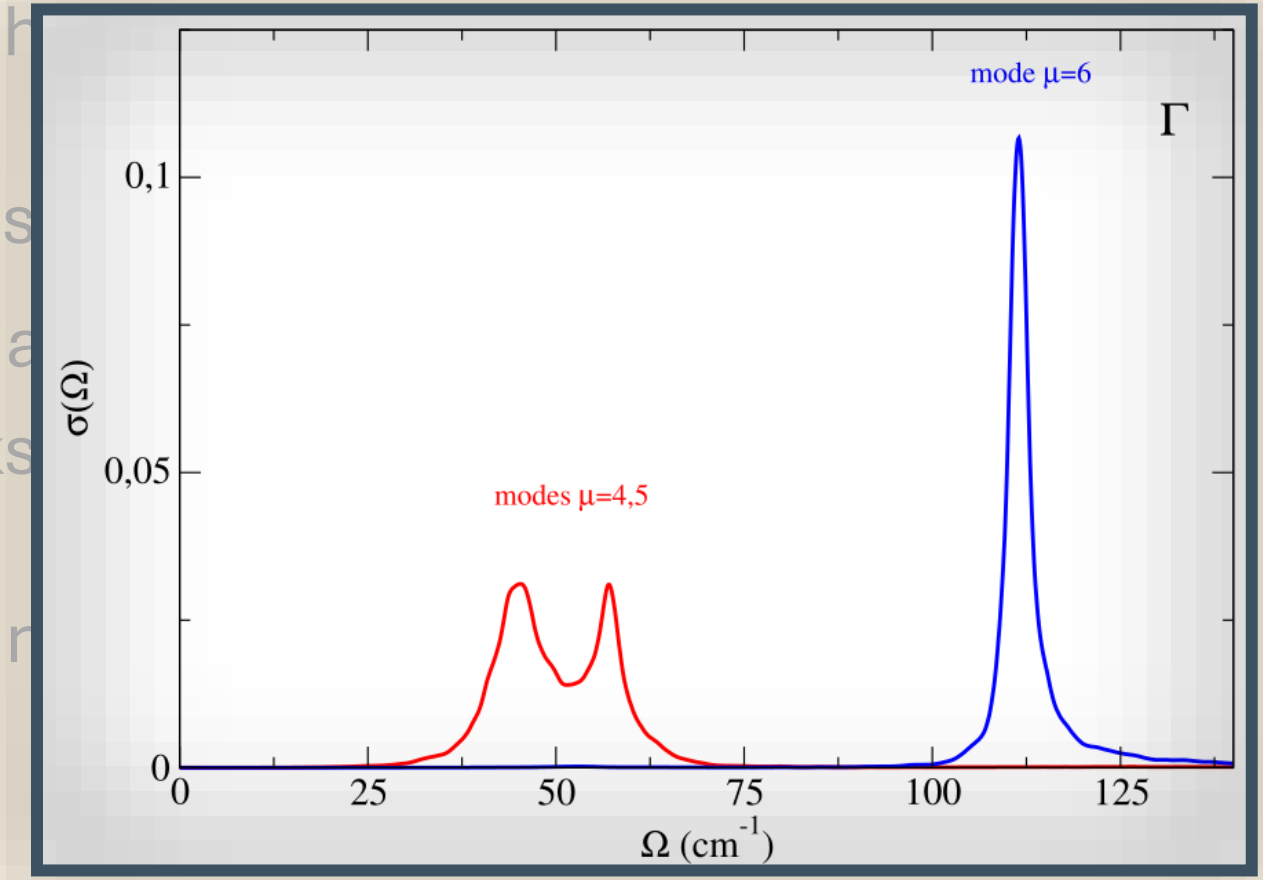

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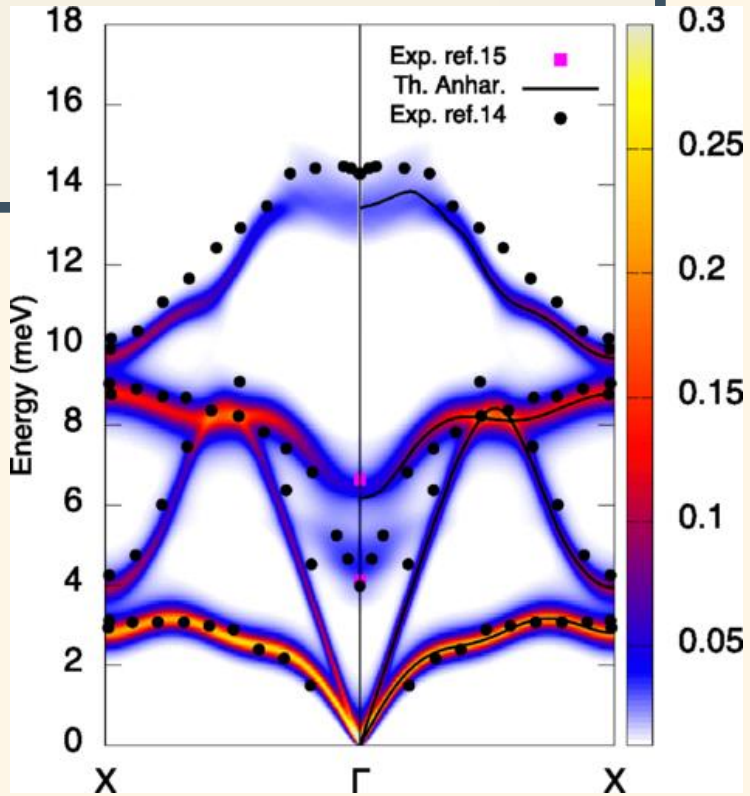

Green-Kubo approach

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- Since BTE fails fundamentally, we need a different approach
- The approach was summarized in Phys. Rev. B 111, 104314 (2025)
- Green-Kubo formula for lattice thermal conductivity:

$$\kappa^{xy}(\nu) = \frac{NV}{k_B T^2} \int_0^\infty \mathrm{d}t \frac{e^{i\nu t}}{\beta} \int_0^\beta \mathrm{d}s \langle S^x(0) S^y(t + is) \rangle$$

Green-Kubo approach

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- Heat flux: $$S^x(t) = \frac{1}{2NV} \sum_{\mathbf{q},j,j'} \omega_{\mathbf{q},j'} v^x_{\mathbf{q},j,j'} A_{\mathbf{q},j}(t) B_{\mathbf{q},j'}(t)$$
- ***A*** and ***B*** operators are related to ion displacement/velocity
- Generalized group velocity: $\mathbf{v}_{\mathbf{q},j,j'} = \frac{1}{2\sqrt{\omega_{\mathbf{q},j}\omega_{\mathbf{q},j'}}} \sum_{a,b} e^{a*}_{\mathbf{q},j} e^{b}_{\mathbf{q},j'} (\nabla_{\mathbf{q}} \overset{(2)}{\mathcal{D}}_{\mathcal{R}} (\mathbf{q}))_{ab}$
- SSCHA auxiliary phonon frequency $\omega_{\mathbf{q},j}$

Green-Kubo approach

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- We get four-point spectral function which we decouple:

$$\langle A_{\mathbf{q},j}(0)B_{\mathbf{q},j'}(0)A_{\mathbf{q}',l}(t)B_{\mathbf{q}',l'}(t)\rangle \approx$$
$$\langle A_{\mathbf{q},j}(0)B_{\mathbf{q}',l'}(t)\rangle\langle B_{\mathbf{q},j'}(0)A_{\mathbf{q}',l}(t)\rangle + \langle A_{\mathbf{q},j}(0)A_{\mathbf{q}',l}(t)\rangle\langle B_{\mathbf{q},j'}(0)B_{\mathbf{q}',l'}(t)\rangle =$$
$$J^{AB}_{\mathbf{q},j,\mathbf{q}',l'}(t)J^{BA}_{\mathbf{q},j',\mathbf{q}',l}(t) + J^{AA}_{\mathbf{q},j,\mathbf{q}',l}(t)J^{BB}_{\mathbf{q},j',\mathbf{q}',l'}(t)$$

- These two-point spectral function are just a differently scaled displacement-displacement spectral function

Green-Kubo approach

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- Phonon spectral function in SSCHA:

$$J^{AA}_{\mathbf{q},j}(\Omega) = -\frac{2}{\exp(\beta\Omega) - 1}\mathrm{Im}G^{AA}_{\mathbf{q},j}(\Omega)$$

$$\sigma_{\mathbf{q},j} = -\frac{1}{2\omega_{\mathbf{q},j}}\frac{\Omega}{\pi}\mathrm{Im}G^{AA}_{\mathbf{q},j}(\Omega)$$

- Lorentzian structure

$$\sigma_{\mathbf{q},j}(\Omega) = \frac{1}{2\pi}\left[\frac{-\mathrm{Im}\mathcal{Z}_{\mathbf{q},j}(\Omega)}{\left(\Omega - \mathrm{Re}\mathcal{Z}_{\mathbf{q},j}(\Omega)\right)^2 + \mathrm{Im}\mathcal{Z}^2_{\mathbf{q},j}(\Omega)} + \frac{\mathrm{Im}\mathcal{Z}_{\mathbf{q},j}(\Omega)}{\left(\Omega + \mathrm{Re}\mathcal{Z}_{\mathbf{q},j}(\Omega)\right)^2 + \mathrm{Im}\mathcal{Z}^2_{\mathbf{q},j}(\Omega)}\right]$$

Green-Kubo approach

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- We started from:

$$\kappa^{xy}(\nu) = \frac{NV}{k_B T^2} \int_0^\infty \mathrm{d}t \frac{e^{i\nu t}}{\beta} \int_0^\beta \mathrm{d}s \langle S^x(0) S^y(t + is) \rangle$$

- Taking static limit and expressing all spectral function through displacement – displacement one we get:

$$\kappa^{xy} = \frac{2\pi\beta^2 k_B}{NV} \sum_{\mathbf{q},j,j'} v^x_{\mathbf{q},j,j'} v^{y*}_{\mathbf{q},j,j'} \omega_{\mathbf{q},j} \omega_{\mathbf{q},j'} \int_{-\infty}^{\infty} \mathrm{d}\Omega \frac{\exp(\beta\Omega)}{(\exp(\beta\Omega) - 1)^2} \sigma_{\mathbf{q},j}(\Omega) \sigma_{\mathbf{q},j'}(\Omega)$$

Green-Kubo approach

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- The integral is overlap of two spectral functions weighted by exponent terms that resemble heat capacity structure
- We have *j* and *j'* terms including coherent contribution which should be large in strongly anharmonic materials
- Most importantly we keep entire structure of phonon lineshape

$$\kappa^{xy} = \frac{2\pi\beta^2 k_B}{NV} \sum_{\mathbf{q},j,j'} v^{x}_{\mathbf{q},j,j'} v^{y*}_{\mathbf{q},j,j'} \omega_{\mathbf{q},j} \omega_{\mathbf{q},j'} \int_{-\infty}^{\infty} \mathrm{d}\Omega \frac{\exp(\beta\Omega)}{(\exp(\beta\Omega)-1)^2} \sigma_{\mathbf{q},j}(\Omega) \sigma_{\mathbf{q},j'}(\Omega)$$

Green-Kubo approach

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- In the limit of low anharmonicity, we can approximate the spectral functions as Lorentzians and evaluate integral directly
- We obtain basically BTE solution in single relaxation time approximation:

$$\kappa^{xy} = \frac{1}{NV} \sum_{\mathbf{q},j} v^x_{\mathbf{q},j} v^y_{\mathbf{q},j} c_{\mathbf{q},j} \frac{-1}{2\mathrm{Im}\mathcal{Z}_{\mathbf{q},j}(\omega_{\mathbf{q},j})}$$

- Lorentzian approximation for phonon lifetime: $\tau_{\mathbf{q},j} = \frac{-1}{2\mathrm{Im}\mathcal{Z}_{\mathbf{q},j}(\omega_{\mathbf{q},j})}$

Green-Kubo approach

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- Phonon self-energy:

$$\mathcal{Z}_{\mathbf{q},j}(\Omega) = \sqrt{\omega^2_{\mathbf{q},j} + \Pi_{\mathbf{q},j}(\Omega)}$$

$$\mathbf{\Pi}(\Omega) = \overset{(3)}{\boldsymbol{\mathcal{D}}}_{\mathcal{R}} : \mathbf{\Lambda}_{\mathcal{R}}(\Omega) : (\hat{\mathbf{1}} - \overset{(4)}{\boldsymbol{\mathcal{D}}}_{\mathcal{R}} : \mathbf{\Lambda}_{\mathcal{R}}(\Omega))^{-1} : \overset{(3)}{\boldsymbol{\mathcal{D}}}_{\mathcal{R}}$$

- Assuming self-energy is small – perturbative approximation:

$$\mathcal{Z}_{\mathbf{q},j} = \omega_{\mathbf{q},j}\sqrt{1 + \frac{\Pi_{\mathbf{q},j}}{\omega^2_{\mathbf{q},j}}} \approx \omega_{\mathbf{q},j} + \frac{\Pi_{\mathbf{q},j}}{2\omega_{\mathbf{q},j}}$$

- Self-consistent lifetime: $\Omega_{\mathbf{q},j} = \mathrm{Re}\mathcal{Z}_{\mathbf{q},j}(\Omega_{\mathbf{q},j}) \Rightarrow \tau_{\mathbf{q},j} = \dfrac{-1}{2\mathcal{Z}_{\mathbf{q},j}(\Omega_{\mathbf{q},j})}$

Green-Kubo approach

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- With the same approach we can derive the low-anharmonicity limit of the coherent transport
- Two contributions, resonant and anti-resonant

$$\kappa_R^{xy} = \frac{1}{2NV} \sum_{\mathbf{q},j,j'} v^x_{\mathbf{q},j,j'} v^{y*}_{\mathbf{q},j,j'} \left(\omega_{\mathbf{q},j'} \frac{c_{\mathbf{q},j}}{\omega_{\mathbf{q},j}} + \omega_{\mathbf{q},j} \frac{c_{\mathbf{q},j'}}{\omega_{\mathbf{q},j'}} \right) \frac{\Gamma_{\mathbf{q},j} + \Gamma_{\mathbf{q},j'}}{(\omega_{\mathbf{q},j} - \omega_{\mathbf{q},j'})^2 + (\Gamma_{\mathbf{q},j} + \Gamma_{\mathbf{q},j'})^2}$$

$$\kappa_A^{xy} = \frac{1}{2NV} \sum_{\mathbf{q},j,j'} v^x_{\mathbf{q},j,j'} v^{y*}_{\mathbf{q},j,j'} \left(\omega_{\mathbf{q},j'} \frac{c_{\mathbf{q},j}}{\omega_{\mathbf{q},j}} + \omega_{\mathbf{q},j} \frac{c_{\mathbf{q},j'}}{\omega_{\mathbf{q},j'}} \right) \frac{\Gamma_{\mathbf{q},j} + \Gamma_{\mathbf{q},j'}}{(\omega_{\mathbf{q},j} + \omega_{\mathbf{q},j'})^2 + (\Gamma_{\mathbf{q},j} + \Gamma_{\mathbf{q},j'})^2}$$

SSCHA implementation

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- Both SRTA and full Green-Kubo formulas are implemented
- In the case of SRTA, three different ways to calculate phonon lifetimes: perturbative, Lorentzian and self-consistent
- For calculation of phonon spectral functions and lifetimes we only consider bubble diagram due to third order anharmonicity

SSCHA implementation

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$$\mathbf{\Pi}(\Omega) = \overset{(3)}{\boldsymbol{\mathcal{D}}}_{\mathcal{R}} : \boldsymbol{\Lambda}_{\mathcal{R}}(\Omega) : (\hat{\mathbf{1}} - \overset{(4)}{\boldsymbol{\mathcal{D}}}_{\mathcal{R}} : \boldsymbol{\Lambda}_{\mathcal{R}}(\Omega))^{-1} : \overset{(3)}{\boldsymbol{\mathcal{D}}}_{\mathcal{R}}$$

- Phonon self-energy is calculated by approximating Dirac delta functions as either Lorentzian or Gaussian functions

$$\Lambda^{abcd}_{\mathcal{R}}(\Omega) = \sum_{jl} \frac{1}{4\omega_j\omega_l} \left[\frac{(\omega_j - \omega_l)(n_j - n_l)}{(\omega_j - \omega_l)^2 - \Omega^2 + i\epsilon} - \frac{(\omega_j + \omega_l)(1 + n_j + n_l)}{(\omega_j + \omega_l)^2 - \Omega^2 + i\epsilon} \right] e^a_j e^b_l e^c_j e^d_l .$$

- The smearing parameter is taken to be constant or adaptive (depending on the phonon density of states)

Example – $CsPbBr_3$

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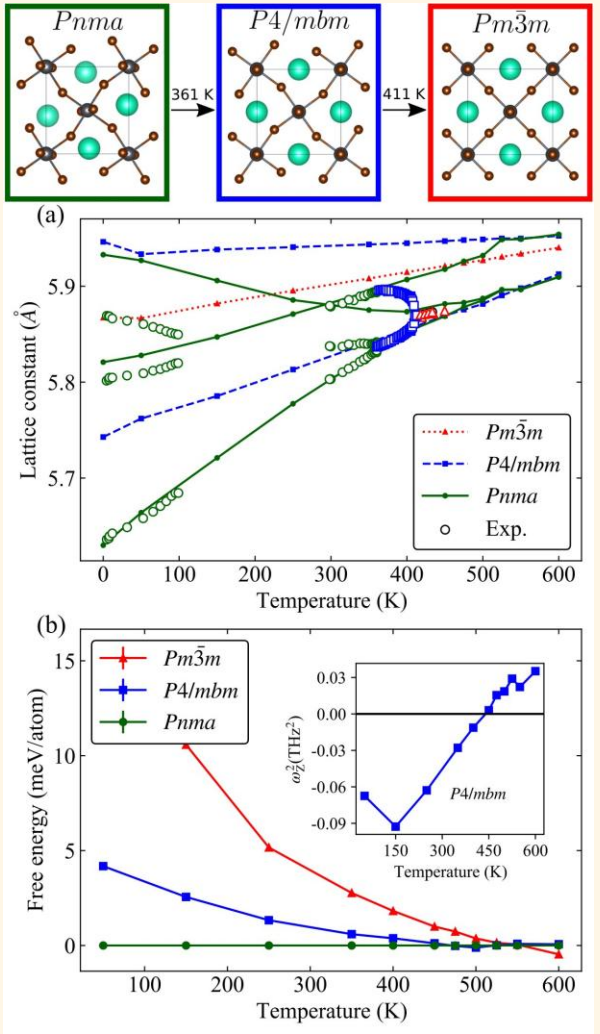
- $CsPbBr_3$ undergoes two phase transitions with temperature
- Second order phase transition from orthorhombic to tetragonal at 450 K
- First order phase transition at 550 K from tetragonal to cubic
- Transition temperature overestimated by 100 K due to DFT



Example - $CsPbBr_3$

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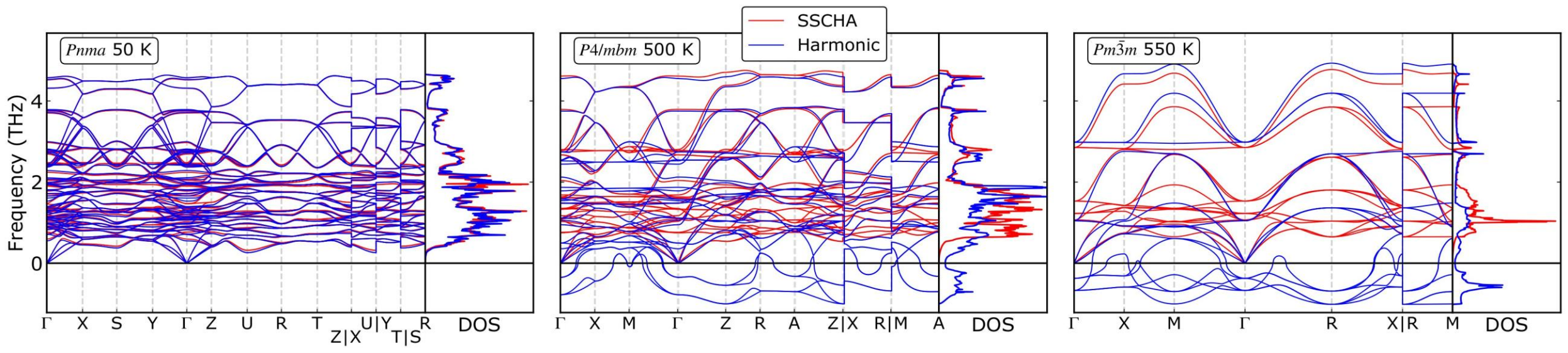
- SSCHA phonons show strong renormalization at elevated temperatures compared to finite difference (harmonic) results



Example - $CsPbBr_3$

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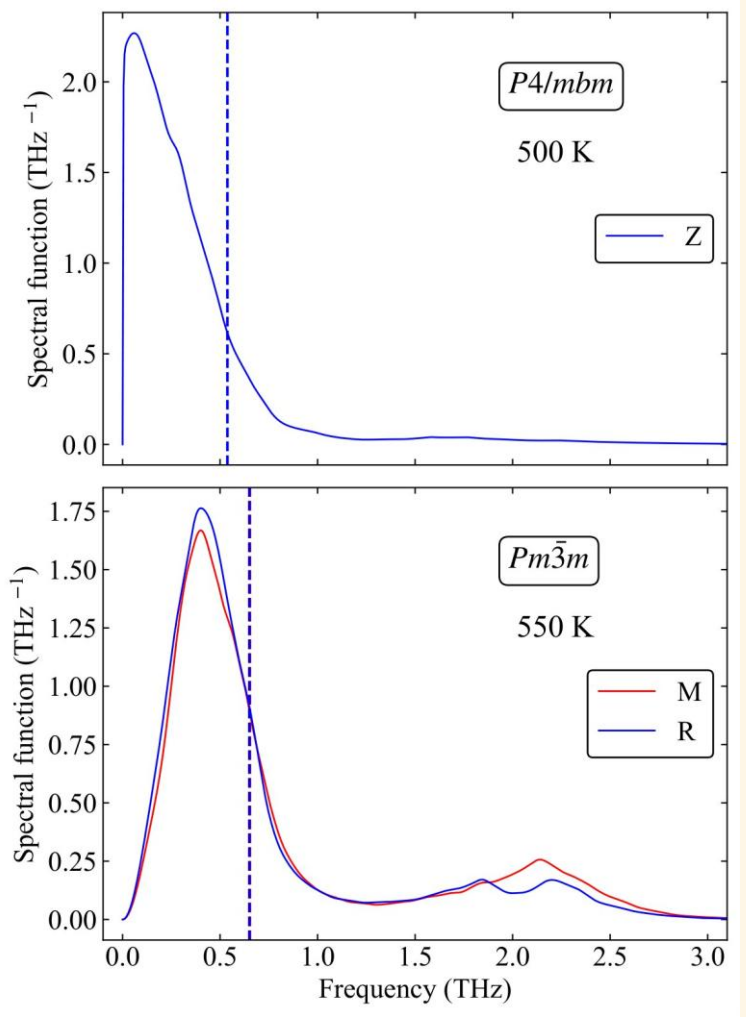
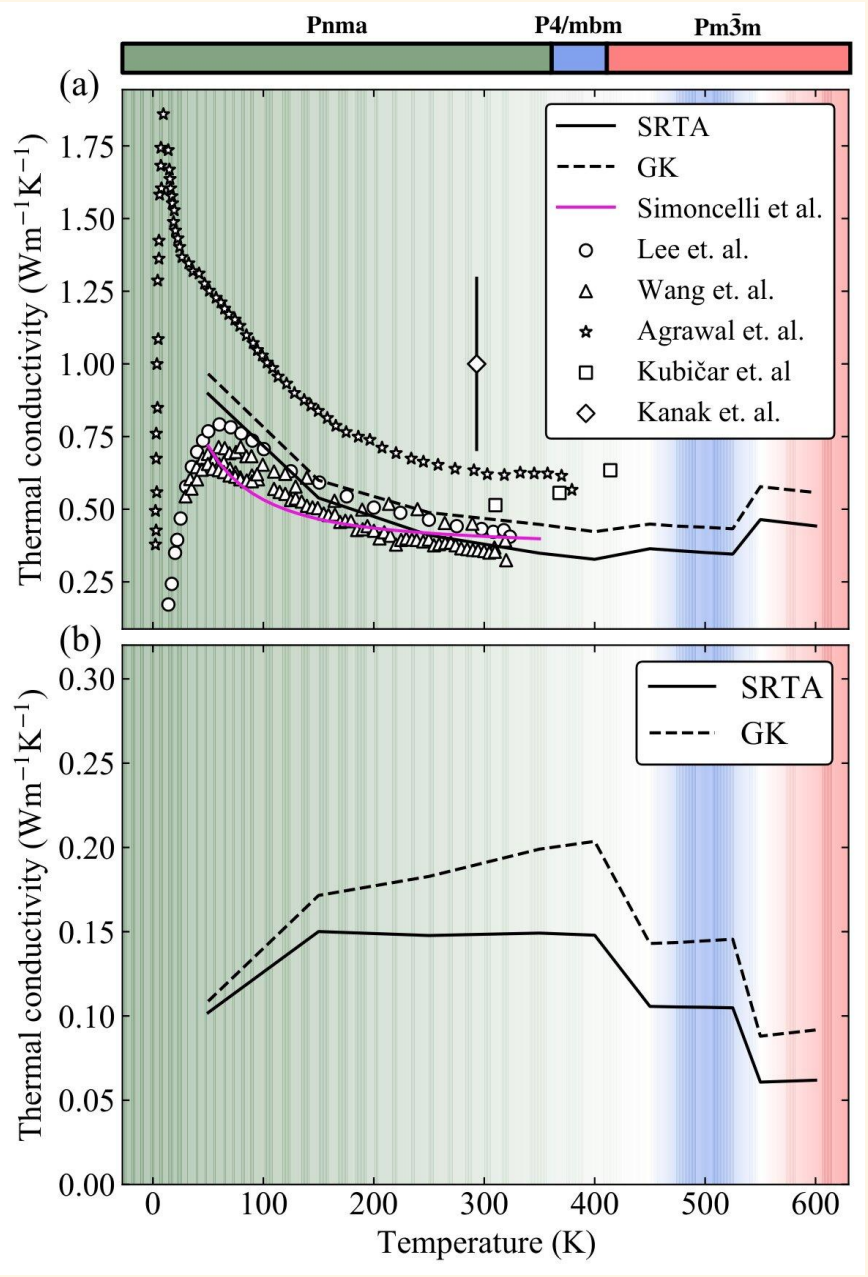
- Spectral function of soft modes show extreme non – Lorentzian behavior
- Large shift of the peak from SSCHA auxiliary frequency
- Large broadening accompanied with satellite peaks : good test example for Green – Kubo method





Example - $CsPbBr_3$

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- Experimental results only available for orthorhombic phase and show large variance
- Our results agree well with experimental results and earlier calculations
- There is always an increase in thermal conductivity at the phase transition to a higher symmetry
- Large impact of the coherent contribution

Example - $CsPbBr_3$

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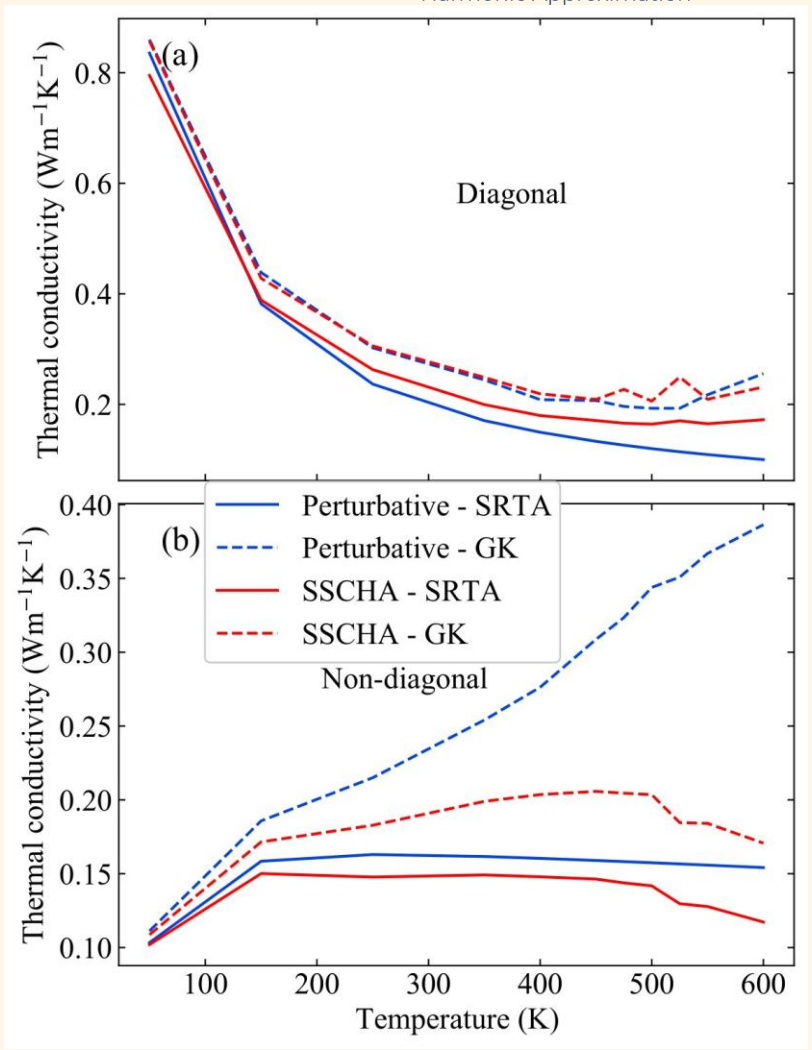
- Green – Kubo method consistently gives larger values of lattice thermal conductivity
- Agreement between SSCHA and finite difference force constants much better in Green – Kubo approach
- Agreement worsens as we increase temperature
- Lattice thermal conductivity is higher with SSCHA force constants



Example - $CsPbBr_3$

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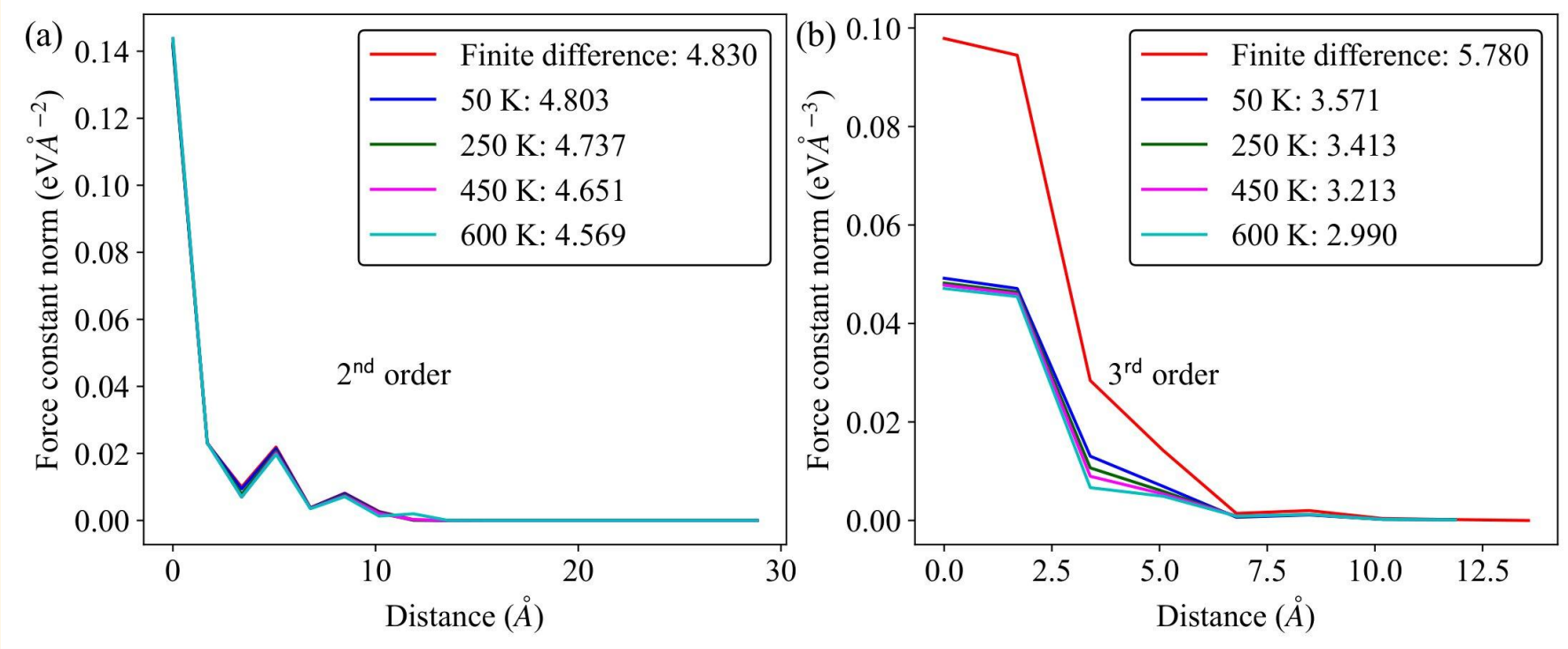
- SSCHA has a major impact on third – order force constants
- Makes them smaller with increasing temperature



Conclusions

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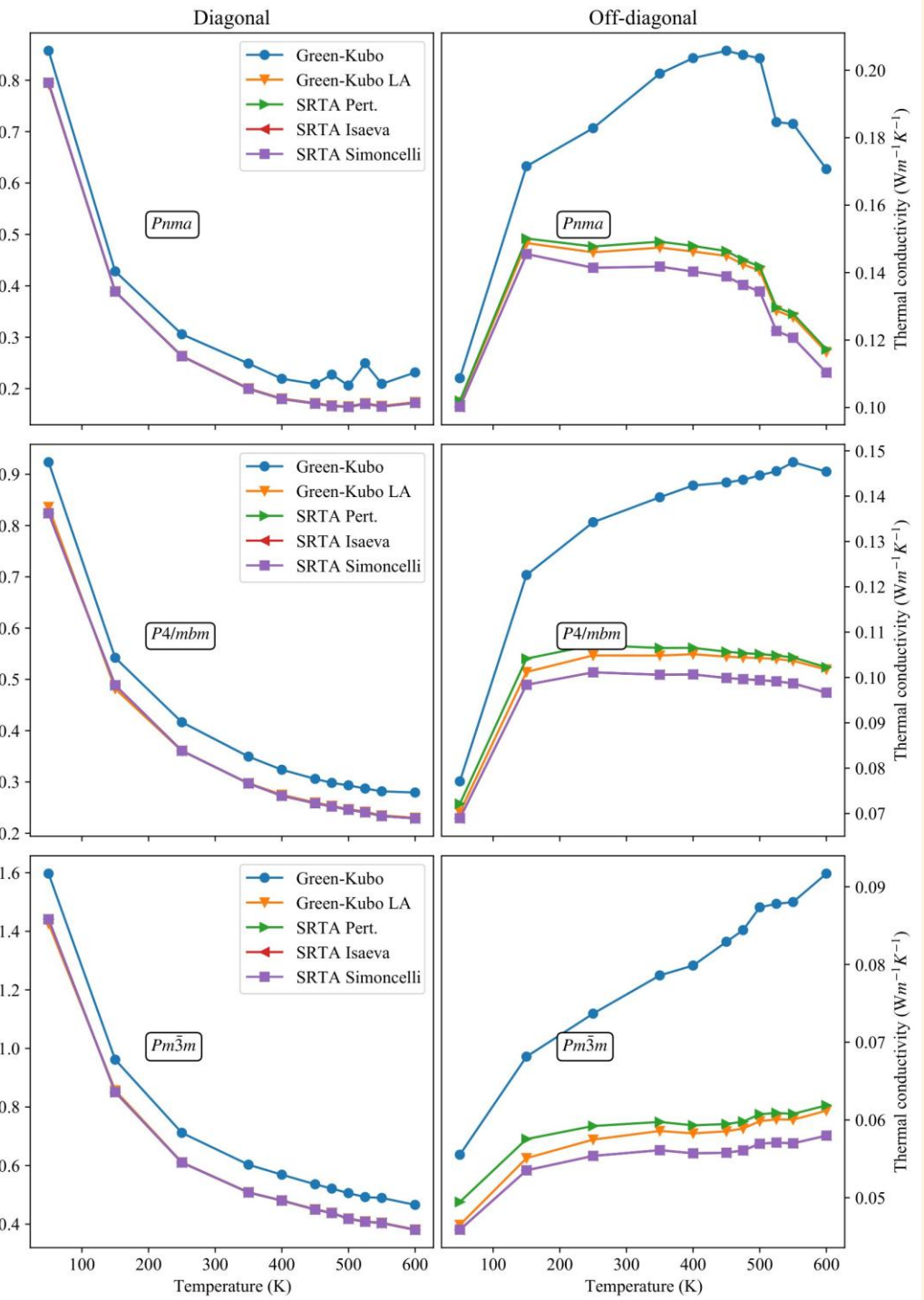
- The Green-Kubo approach accounts for the full lineshape of the phonon spectral function, extending the applicability of first-principles thermal-transport calculations to strongly anharmonic materials.
- In the weak-anharmonicity limit, the Green-Kubo expression reduces to the familiar Boltzmann transport equation in the relaxation time approximation, including both particle-like and coherent contributions.
- The SSCHA code implements both the full Green-Kubo approach and its weak-anharmonicity limit.
- When only third-order force constants are included, the Green-Kubo approach consistently predicts a higher thermal conductivity because phonon softening increases the spectral overlap between modes at lower frequencies.
- SSCHA calculations consistently predict a higher thermal conductivity because the renormalized third-order force constants are reduced.



Example - $CsPbBr_3$

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- We compare different approaches to low anharmonicity limit of the Green – Kubo formula
- In most cases the method presented here agrees better with full calculation, although differences are small, much smaller compared to full Green – Kubo calculation