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Thermal conductivity in strongly anharmonic crystals

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Introduction

Introduction

- Lattice thermal conductivity κ
- $\mathbf{Q} = -\kappa \nabla T$
- Impacts technological application of materials
- High thermal conductivity - thermal management
- Metals: Al alloys or Cu (electrons carry heat)
- Insulators: diamond or boron arsenide (phonons carry heat)

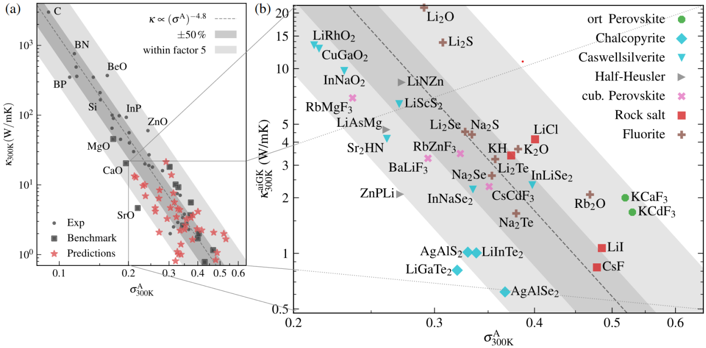
Low thermal conductivity

- Thermal insulation
- Thermoelectric materials - efficiency is inversely proportional to thermal conductivity:

$$zT = \frac{\sigma S^2 T}{\kappa}$$

- Insulators to minimize the electronic contribution
- Highly anharmonic

Low thermal conductivity



Florian Knoop, et al. Phys. Rev. Lett. **130**, 236301

How to calculate κ?

- Two most common ways to calculate κ:
  - Lattice dynamics: Boltzmann transport equations (BTE)
  - Molecular dynamics MD: direct method (non-equilibrium MD) or Green-Kubo (equilibrium MD)
- We are going to focus on lattice dynamics LD methods
- LD uses a phonon or phonon-like picture (perturbative method)

Boltzmann transport equation.

Boltzmann transport

- Weakly interacting phonon gas conducts heat
- Phonons are well-defined quasiparticles

$$\frac{\partial n_{\mathbf{q},s}}{\partial t} = \frac{\partial n_{\mathbf{q},s}}{\partial t}\Big|_{diff} + \cancelto{0}{\frac{\partial n_{\mathbf{q},s}}{\partial t}\Big|_{field}} + \frac{\partial n_{\mathbf{q},s}}{\partial t}\Big|_{scatt}$$

$$\mathbf{v}_{\mathbf{q},s} \cdot \frac{\partial n_{\mathbf{q},s}}{\partial \mathbf{r}} = \mathbf{v}_{\mathbf{q},s} \cdot \frac{\partial n^0_{\mathbf{q},s}}{\partial \mathbf{T}} \nabla T$$

$$\frac{n_{\mathbf{q},s} - n^0_{\mathbf{q},s}}{\tau_{\mathbf{q},s}}$$

Boltzmann transport

$$n_{\mathbf{q},s} = n^0_{\mathbf{q},s} - \mathbf{v}_{\mathbf{q},s} \cdot \frac{\partial n^0_{\mathbf{q},s}}{\partial T} \nabla T \tau_{\mathbf{q},s}$$

- Inserting this equation in the expression for heat current $\mathbf{Q} = \frac{1}{NV} \sum_{\mathbf{q},s} \hbar\omega_{\mathbf{q},s} \mathbf{v}_{\mathbf{q},s} n_{\mathbf{q},s}$ and matching terms with Fourier law ($\mathbf{Q} = -\kappa \nabla T$):

$$\kappa^{i,j} = \frac{1}{NV} \sum_{\mathbf{q},s} \hbar\omega_{\mathbf{q},s} \frac{\partial n^0_{\mathbf{q},s}}{\partial T} v^i_{\mathbf{q},s} v^j_{\mathbf{q},s} \tau_{\mathbf{q},s}$$

Boltzmann transport

- From the above derivation we see that phonons need to have well-defined energies, lifetimes and population numbers
- Since they have a single relaxation time displacement-displacement correlation function takes the form:

$$\langle u_{\mathbf{q},s}(t)u_{\mathbf{q},s}(0)\rangle = A_{\mathbf{q},s}e^{-\frac{t}{2\tau_{\mathbf{q},s}}}e^{i\omega_{qs}t}$$

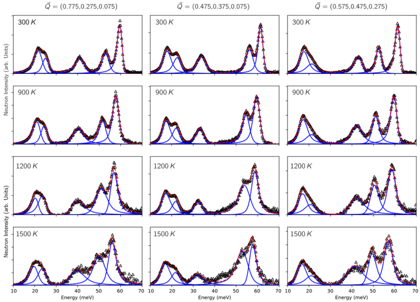
Boltzmann transport

- Fourier transform of this quantity is closely related to scattering cross-section:

$$\langle u_{\mathbf{q},s} u_{\mathbf{q},s} \rangle(\omega) \sim \frac{A_{\mathbf{q},s} \frac{1}{2\tau_{\mathbf{q},s}}}{(\omega - \omega_{\mathbf{q},s})^2 + \left(\frac{1}{2\tau_{\mathbf{q},s}}\right)^2}$$

- Scattering cross section should be Lorentzian

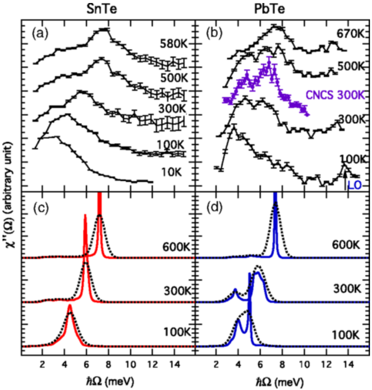
- This is experimentally confirmed for low-anharmonicity materials



D.S. Kim, et. al., Phys. Rev. B **102**, 174311, 2020

Boltzmann transport

- What happens for highly anharmonic materials which are very interesting from the technological perspective



C. W. Li, et al. Phys. Rev. Lett. **112**, 175501

Boltzmann transport

- Non-Lorentzian lineshapes are a common feature of all highly anharmonic materials
- Especially pronounced close to the structural phase transition
- Phonons can not be regarded as good quasiparticles: is BTE applicable
- Green-Kubo MD simulations can capture this regime, but very cumbersome to converge
- Lattice dynamics implementation of Green-Kubo approach

Green-Kubo method.

Green-Kubo in MD

- Lattice thermal conductivity in classical MD:

$$\kappa^{i,j} = \frac{1}{NVk_{\mathrm{B}}T}\int_0^{\infty}\langle J^i(t)J^j(0)\rangle \mathrm{d}t$$

- Heat current definition:

$$J^i(t) = \sum_a e_a v_a^i + [\hat{S}_a \cdot \mathbf{v}_a]^i$$

- One needs to converge wrt length of the simulation, maximum correlation time, size of the supercell

Green-Kubo in LD

- Start from the Green-Kubo expression in the quantum limit:

$$\kappa^{i,j} = \frac{NV}{k_{\mathrm{B}}T}\int_0^{\infty}\mathrm{d}t\frac{1}{\beta}\int_0^{\beta}\mathrm{d}s\langle J^i(0)J^j(t+is)\rangle$$

- We take the definition of heat current from Hardy (Phys. Rev. 132, 168 (1963)):

$$J^i(t) = \frac{1}{2NV}\sum_{\mathbf{q},s,s'}\omega_{\mathbf{q},s'}v^i_{\mathbf{q},s,s'}A_{\mathbf{q},s}(t)B_{-\mathbf{q},s'}(t)$$

- $A_{\mathbf{q},s}(t)$ and $B_{-\mathbf{q},s'}(t)$ are scaled displacement and momentum operators

Green-Kubo in LD

$$A_{\mathbf{q},s}(t) = a_{\mathbf{q},s} + a^{\dagger}_{-\mathbf{q},s} \qquad B_{\mathbf{q},s}(t) = a_{\mathbf{q},s} - a^{\dagger}_{-\mathbf{q},s}$$

- $a_{\mathbf{q},s}$ & $a^{\dagger}_{-\mathbf{q},s}$ phonon annihilation and creation operators
- Inserting these definitions in the previous heat current we obtain the Peierls's heat current:

$$J^{i}(t) = \frac{1}{NV}\sum_{\mathbf{q},s}\omega_{\mathbf{q},s}v^{i}_{\mathbf{q},s}n_{\mathbf{q},s}$$

Green-Kubo in LD

- Inserting the Hardy's definition of $J(t)$ in Green-Kubo expression gives us two phonon correlation function
- These are quite hard to calculate so we will decouple it into products of one phonon correlation function:

$$\langle A_{\mathbf{q},j}(0)B_{-\mathbf{q},j'}(0)A_{\mathbf{q}',l}(t)B_{-\mathbf{q}',l'}(t)\rangle \approx \cancel{\langle A_{\mathbf{q},j}(0)B_{-\mathbf{q},j'}(0)\rangle\langle A_{\mathbf{q}',l}(t)B_{-\mathbf{q}',l'}(t)\rangle} + \langle A_{\mathbf{q},j}(0)B_{-\mathbf{q}',l'}(t)\rangle\langle B_{-\mathbf{q},j'}(0)A_{\mathbf{q}',l}(t)\rangle + \langle A_{\mathbf{q},j}(0)A_{\mathbf{q}',l}(t)\rangle\langle B_{-\mathbf{q},j'}(0)B_{-\mathbf{q}',l'}(t)\rangle$$

- We use shorthand notation:

$$C_{AB}(t) = \langle A_{\mathbf{q},j}(0)B_{-\mathbf{q}',l'}(t)\rangle$$

Green-Kubo in LD

- After the Fourier transform of the correlation functions we obtain:

$$\kappa^{i,j} = \frac{\pi\beta^2 k_\mathrm{B}}{4NV}\sum_{\mathbf{q},s,s'}\sum_{\mathbf{q}',l,l'}\omega_{\mathbf{q},s'}v^{i}_{\mathbf{q},s,s'}\omega_{\mathbf{q}',l'}v^{j}_{\mathbf{q}',l,l'}\times$$
$$\times\int_{-\infty}^{\infty}\mathrm{d}\Omega\,(C_{AA}(\Omega)C_{BB}(\Omega)+C_{AB}(\Omega)C_{BA}(\Omega))$$

- Since $i\dot{A}_{\mathbf{q},s}(t)=[A_{\mathbf{q},s},H]=\omega_{\mathbf{q},s}B_{\mathbf{q},s}(t)$ we can represent C_{AB}, C_{BA} and C_{BB} through C_{AA}
- $C_{AA}(\Omega)=\frac{\pi}{\Omega}\frac{1}{e^{\beta\Omega}-1}\sigma_{\mathbf{q}s}(\Omega)$

Green-Kubo in LD

- Final expression:

$$\kappa^{i,j} = \frac{2\pi\beta^2 k_{\mathrm{B}}}{NV} \sum_{\mathbf{q},s,s'} \omega_{\mathbf{q},s} v^{i}_{\mathbf{q},s,s'} \omega_{\mathbf{q},s'} v^{j}_{\mathbf{q},s',s} \int_{-\infty}^{\infty} \mathrm{d}\Omega \frac{e^{\beta\Omega}}{(e^{\beta\Omega}-1)^2} \sigma_{\mathbf{q},s}\sigma_{\mathbf{q},s'}$$

- Phonon spectral function:

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

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

Green-Kubo in LD

$$\Pi_s(\mathbf{q},\omega) = \frac{1}{N_\mathbf{k}} \sum_{\mathbf{k}_1,l} \sum_{\mathbf{k}_2,m} \sum_{\mathbf{G}} \delta_{\mathbf{G},\mathbf{q}+\mathbf{k}_1+\mathbf{k}_2} |D^{slm}_{\mathbf{q}\mathbf{k}_1\mathbf{k}_2}|^2 \frac{\hbar}{4\omega_l(\mathbf{k}_1)\omega_m(\mathbf{k}_2)} \times$$
$$\times \left(\frac{(\omega_l(\mathbf{k}_1) - \omega_m(\mathbf{k}_2))(n_l(\mathbf{k}_1) - n_m(\mathbf{k}_2))}{(\omega_l(\mathbf{k}_1) - \omega_m(\mathbf{k}_2))^2 - \omega^2} - \frac{(\omega_l(\mathbf{k}_1) + \omega_m(\mathbf{k}_2))(n_l(\mathbf{k}_1) + n_m(\mathbf{k}_2) + 1)}{(\omega_l(\mathbf{k}_1) + \omega_m(\mathbf{k}_2))^2 - \omega^2} \right)$$

- Two ways of dealing with this expression (adding a small imaginary number in the denominator, $i\epsilon$):
  - Lorentzian smearing
  - Gaussian smearing $\frac{1}{x+i\epsilon} = \mathcal{P}\left(\frac{1}{x}\right) - i\pi\delta(x)$
  - ϵ is the smearing parameter (to converge)

Green-Kubo in LD

- Final expression:

$$\kappa^{i,j} = \frac{2\pi\beta^2 k_\mathrm{B}}{NV} \sum_{\mathbf{q},s,s'} \omega_{\mathbf{q},s} v^i_{\mathbf{q},s,s'} \omega_{\mathbf{q},s'} v^j_{\mathbf{q},s',s} \int_{-\infty}^{\infty} \mathrm{d}\Omega \frac{e^{\beta\Omega}}{(e^{\beta\Omega}-1)^2} \sigma_{\mathbf{q},s}\sigma_{\mathbf{q},s'}$$

- Phonon spectral function:

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

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

Green-Kubo in LD

- Diagonal part of the expression $s = s'$
- In the low anharmonicity limit reduces to single relaxation time approximation solution to BTE
- $\mathrm{Re}\Pi_{\mathbf{q},s}(\Omega) = 0$ and $\mathrm{Im}\Pi_{\mathbf{q},s}(\Omega) = \mathrm{const.}$
- One of spectral functions under integral substitute for $\delta(\Omega - \omega_{\mathbf{q},s})$

$$\kappa^{i,j} = \frac{1}{NV}\sum_{\mathbf{q},s} v^{i}_{\mathbf{q},s} v^{j}_{\mathbf{q},s} c_{\mathbf{q},s} \frac{\mathrm{sgn}\left(\mathrm{Im}\mathcal{Z}_{\mathbf{q},s}(\omega_{\mathbf{q},s})\right)}{2\mathrm{Im}\mathcal{Z}_{\mathbf{q},s}(\omega_{\mathbf{q},s})}$$

- Phonon lifetimes: $\tau_{\mathbf{q},s} = -\frac{1}{2\mathrm{Im}\mathcal{Z}_{\mathbf{q},s}}$

Green-Kubo in LD

- Non-diagonal part: $s \neq s'$
- This part describes the wavelike transport significant in amorphous materials and complex crystals
- This term has a non-zero contribution only when there is a significant overlap between two phonon spectral functions inside the integral
- This is the case with large bunching of phonon modes or large non-Lorentzian character of phonon spectral function

Comparing BTE and KG

- For low anharmonicity materials both methods give the same result
- In overdamped regime Green-Kubo is still aplicable
- Green - Kubo is slower compared to BTE
- Implementation of additional scattering mechanisms is more straightforward in BTE
- Hydrodynamics regime is more easily handled in BTE

Implementation in SSCHA code

Implementation in SSCHA code

- SSCHA gives temperature-dependent second and third-order force constants renormalized by anharmonicity
- Thermal conductivity calculations are implemented inside `ThermalConductivity` object
- κ can be calculated using a single relaxation time approximation solution of BTE or the Green-Kubo method
- There are a number of functions available for analyzing the transport properties of modeled system

Boltzmann transport equation solution

- We need phonon group velocities, frequencies and phonon lifetimes
- Phonon lifetimes can be calculated in three different ways:
  - Perturbative: $\tau_{\mathbf{q},s} = -\frac{\omega_{\mathbf{q},s}}{\mathrm{Im}\Pi_{\mathbf{q},s}(\omega_{\mathbf{q},s})}$
  - Lorentzian approximation: $\tau_{\mathbf{q},s} = -\frac{1}{2\mathrm{Im}\mathcal{Z}_{\mathbf{q},s}(\omega_{\mathbf{q},s})}$
  - Self-consistently: $\Omega_{\mathbf{q},s} = \mathrm{Re}\mathcal{Z}_{\mathbf{q},s}(\Omega_{\mathbf{q},s})$
- Calculation of coherent transport is included based on Refs.:
  - M. Simoncelli, et al. Nature Physics volume **15**, pages 809–813 (2019)
  - L. Isaeva, et al. Nature Communications volume **10**, Article number: 3853 (2019)

Green-Kubo method

- Calculation of thermal conductivity in Green-Kubo method is implemented
- Spectral functions are calculated in dressed dynamical bubble approximation
- Spectral functions are sampled on a frequency scale from 0 to $2\omega_{Debye}$ with `ne` frequency steps
- Converge results w.r.t. `ne`

Thank you for your attention!