Materials Physics Center
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Thermal conductivity in strongly anharmonic crystals

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Content

Introduction

Introduction

Lattice thermal conductivity

Q = r *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

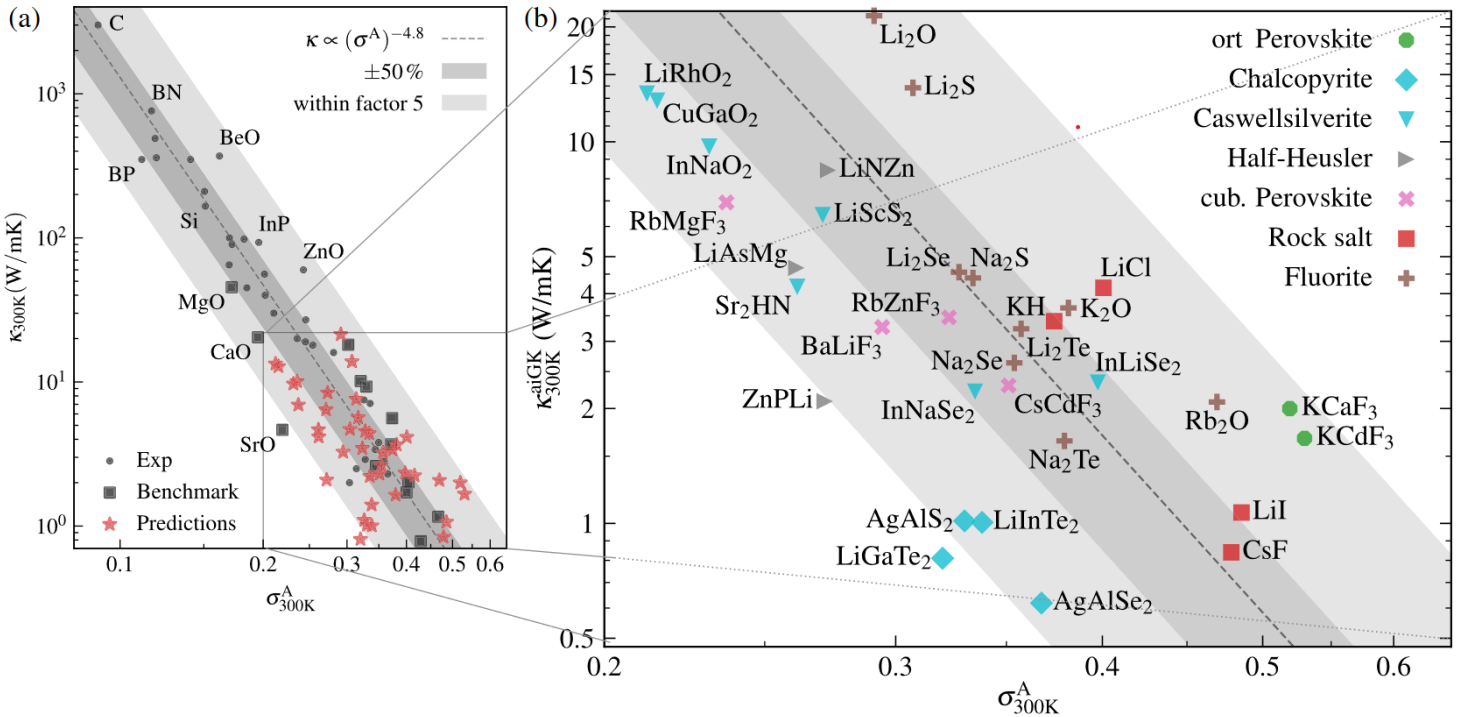
Thermoelectric materials - efficiency is inversely proportional to thermal conductivity:

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

Insulators to minimize the electronic contribution

Highly anharmonic

Low thermal conductivity



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

How to calculate ?

Two most common ways to calculate :

- 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

$$\frac{@n_{\mathbf{q};s}}{@t} = \left(\frac{@n_{\mathbf{q};s}}{@t}\right)_{diff} + \left(\frac{@n_{\mathbf{q};s}}{@t}\right)_{field}^{*0} + \left(\frac{@n_{\mathbf{q};s}}{@t}\right)_{scatt}$$

$$\mathbf{v}_{\mathbf{q};s}\,\frac{@n_{\mathbf{q};s}}{@\mathbf{r}} = \mathbf{v}_{\mathbf{q};s}\,\frac{@n^{0}_{\mathbf{q};s}}{@\mathbf{T}}\,\nabla T \qquad \frac{n_{\mathbf{q};s} - n^{0}_{\mathbf{q};s}}{\tau_{\mathbf{q};s}}$$

Boltzmann transport

$$n_{\mathbf{q};s} = n^0_{\mathbf{q};s} \quad \mathbf{v}_{\mathbf{q};s} \quad \frac{@n^0_{\mathbf{q};s}}{@T} \, \mathrm{r}\, T \quad {}_{\mathbf{q};s}$$

Inserting this equation in the expression for heat current $\mathbf{Q} = \frac{1}{NV} \sum_{\mathbf{q};s} \sim ! {}_{\mathbf{q};s} \mathbf{v}_{\mathbf{q};s} n_{\mathbf{q};s}$ and matching terms with Fourier law ($\mathbf{Q} = \quad \mathrm{r}\, T$):

$$^{i;j} = \frac{1}{NV} \sum_{\mathbf{q};s} \sim ! {}_{\mathbf{q};s} \frac{@n^0_{\mathbf{q};s}}{@T} v^i_{\mathbf{q};s} v^j_{\mathbf{q};s} \quad {}_{\mathbf{q};s}$$

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:

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

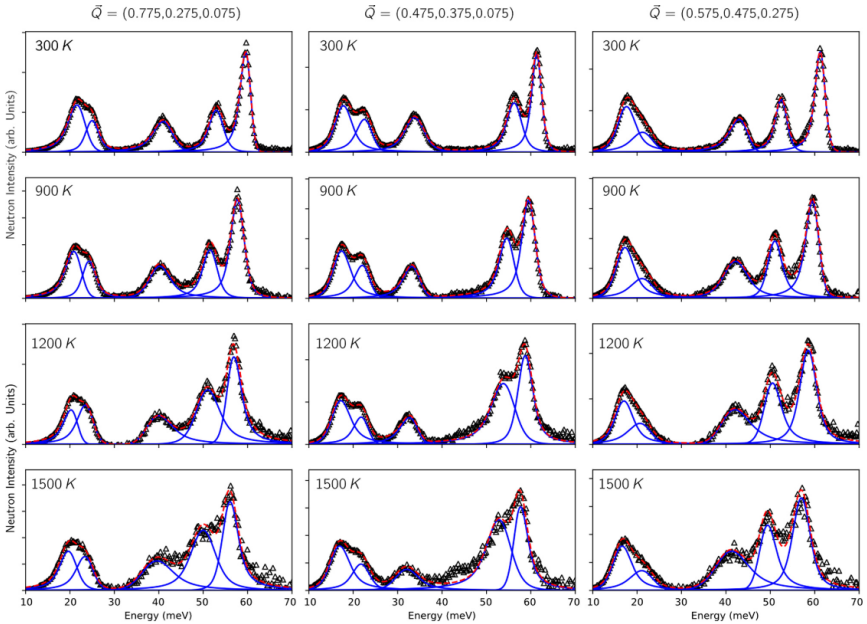
Boltzmann transport

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

$$\langle u_{\mathbf{q};s} u_{\mathbf{q};s} \rangle(\omega) \quad \frac{A_{\mathbf{q};s} \frac{1}{2\ _{\mathbf{q};s}}}{(\omega \quad \omega_{\mathbf{q};s})^2 + \left(\frac{1}{2\ _{\mathbf{q};s}}\right)^2}$$

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:

$$\kappa^{i;j} = \frac{1}{NVk_BT} \int_0^{\infty} \langle J^i(t) J^j(0) \rangle \, dt$$

Heat current de nition:

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

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:

$$\kappa^{i;j} = \frac{NV}{k_B T} \int_0^{\infty} dt \frac{1}{\hbar} \int_0^{\infty} ds \langle J^i(0) J^j(t + is) \rangle$$

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

$$J^i(t) = \frac{1}{2NV} \sum_{q;s;s^0}^{X} ! _{q;s^0} v^i_{q;s;s^0} A_{q;s}(t) B_{q;s^0}(t)$$

$A_{q;s}(t)$ and $B_{q;s^0}(t)$ are scaled displacement and momentum operators

Green-Kubo in LD

$$A_{q;s}(t) = a_{q;s} + a^{y}_{q;s} \qquad B_{q;s}(t) = a_{q;s} \quad a^{y}_{q;s}$$

$a_{q;s}$ & $a^{y}_{q;s}$ phonon annihilation and creation operators

Inserting these de nitions in the previous heat current we obtain the Peierls's heat current:

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

Green-Kubo in LD

Inserting the Hardy's de nition 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:

$$\langle A_{q;j}(0)B_{q;j'}(0)A_{q';l}(t)B_{q';l'}(t)\rangle \approx \langle A_{q;j}(0)B_{q;j'}(0)\rangle\langle A_{q';l}(t)B_{q';l'}(t)\rangle +$$
$$\langle A_{q;j}(0)B_{q';l'}(t)\rangle\langle B_{q;j'}(0)A_{q';l}(t)\rangle + \langle A_{q;j}(0)A_{q';l}(t)\rangle\langle B_{q;j'}(0)B_{q';l'}(t)\rangle$$

We use shorthand notation:

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

Green-Kubo in LD

After the Fourier transform of the correlation functions we obtain:

$$ {}^{i;j} = \frac{{}^{2}k_B}{4NV} \sum_{q;s;s^0} \sum_{q^0;l;l^0} ! {}_{q;s^0} v^{i}_{q;s;s^0} ! {}_{q^0;l^0} v^{j}_{q^0;l;l^0} $$

$$ \int_{1}^{1} d \; (C_{AA}( ) \; C_{BB}( ) + \; C_{AB}( ) \; C_{BA}( )) $$

Since $i\dot{A}_{q;s}(t) = [A_{q;s}; H] = ! {}_{q;s} B_{q;s}(t)$ we can represent $C_{AB}; C_{BA}$ and C_{BB} through C_{AA}

$$ C_{AA}( ) = - \frac{1}{e \quad 1} \; {}_{qs}( ) $$

Green-Kubo in LD

Final expression:

$$ {}^{i;j} = \frac{2\ \ {}^{2}k_B}{NV} \sum_{q;s;s^0} ! \ {}_{q;s} v^{i}_{q;s;s^0} ! \ {}_{q;s^0} v^{j}_{q;s^0;s} \int_{1}^{1} d \ \frac{e}{(e\ \ 1)^2} \ {}_{q;s} \ \ {}_{q;s^0} $$

Phonon spectral function:

$$ {}_{q;s} = \frac{1}{2} \left[\frac{\mathrm{Im} Z_{q;s}}{\mathrm{Re} Z_{q;s}^{\ 2} + \mathrm{Im} Z_{q;s}^{2}} + \frac{\mathrm{Im} Z_{q;s}}{+ \ \ \mathrm{Re} Z_{q;s}^{\ 2} + \mathrm{Im} Z_{q;s}^{2}} \right] $$

$$ Z_{q;s}( ) = \frac{q}{! \ {}^{2}_{q;s} + \ \ {}_{q;s}( )} $$

Green-Kubo in LD

$$ {}_{s}(q;!\ ) = \frac{1}{N_k} \sum_{k_1;l\ k_2;m\ \ G} {}_{G;q+k_1+k_2} j D^{slm}_{qk_1k_2} j^2 \frac{\sim}{4!\ {}_{l}(k_1)!\ {}_{m}(k_2)} $$

$$ \frac{(!\ {}_{l}(k_1) \quad !\ {}_{m}(k_2))(n_l(k_1) \quad n_m(k_2))}{(!\ {}_{l}(k_1) \quad !\ {}_{m}(k_2))^2 \quad !^{\ 2}} \quad \frac{(!\ {}_{l}(k_1) + !\ {}_{m}(k_2))(n_l(k_1) + n_m(k_2) + 1)}{(!\ {}_{l}(k_1) + !\ {}_{m}(k_2))^2 \quad !^{\ 2}} \ ! $$

Two ways of dealing with this expression (adding a small imaginary number in the denominator, i):

Lorentzian smearing

Gaussian smearing $\frac{1}{x+i} = P\ \frac{1}{x} \quad i \quad (x)$

is the smearing parameter (to converge)

Green-Kubo in LD

Final expression:

$$ {}^{i;j} = \frac{2\ \ {}^{2}k_B}{NV} \sum_{q;s;s^0} ! \ {}_{q;s} v^{i}_{q;s;s^0} ! \ {}_{q;s^0} v^{j}_{q;s^0;s} \int_{1}^{1} d \ \frac{e}{(e\ \ 1)^2} \ {}_{q;s} \ \ {}_{q;s^0} $$

Phonon spectral function:

$$ {}_{q;s} = \frac{1}{2} \left[\frac{\mathrm{Im} Z_{q;s}}{\mathrm{Re} Z_{q;s}^{\ 2} + \mathrm{Im} Z_{q;s}^{2}} + \frac{\mathrm{Im} Z_{q;s}}{+ \ \ \mathrm{Re} Z_{q;s}^{\ 2} + \mathrm{Im} Z_{q;s}^{2}} \right] $$

$$ Z_{q;s}( ) = \frac{q}{! \ {}^{2}_{q;s} + \ \ {}_{q;s}( )} $$

Green-Kubo in LD

Diagonal part of the expression $s = s^0$

In the low anharmonicity limit reduces to single relaxation time approximation solution to BTE

Re $_{q;s}( ) =$ 0 and Im $_{q;s}( ) =$ const:

One of spectral functions under integral substitute for (! $_{q;s}$)

$$^{i;j} = \frac{1}{NV} \sum_{q;s} v^{i}_{q;s} v^{j}_{q;s} c_{q;s} \frac{\text{sgn } \text{Im} Z_{q;s}(! _{q;s})}{2\text{Im} Z_{q;s}(! _{q;s})}$$

Phonon lifetimes: $_{q;s} = \frac{1}{2\text{Im} Z_{q;s}}$

Green-Kubo in LD

Non-diagonal part: s , s^0

This part describes the wavelike transport signi cant in amorphous materials and complex crystals

This term has a non-zero contribution only when there is a signi cant 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

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: $\tau_{\mathbf{q};s} = \frac{\hbar}{2\,\mathrm{Im}\,\Sigma_{\mathbf{q};s}(\omega_{\mathbf{q};s})}$

Lorentzian approximation: $\tau_{\mathbf{q};s} = \frac{1}{2\,\mathrm{Im}\,Z_{\mathbf{q};s}(\omega_{\mathbf{q};s})}$

Self-consistently: $\tau_{\mathbf{q};s} = \mathrm{Re}\,Z_{\mathbf{q};s}(\tau_{\mathbf{q};s})$

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 $2\,!_{Debye}$ with $\mathtt{ne}$ frequency steps

Converge results w.r.t. $\mathtt{ne}$

Thank you for your attention!