From Green-Kubo to the full Boltzmann kinetic approach to heat transport in crystals and glasses

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Introduction - Background

- Thermal conductivity

$$J = -\kappa \nabla T$$

- Linear Response: Quantum Green-Kubo (GK) formalism [1]:

$$\kappa = \frac{1}{VT}\int_0^\infty dt \int_0^{1/k_bT} d\lambda \langle \hat{J}(t - i\hbar\lambda)\hat{J}\rangle$$

$\hat{J}$ is the heat flux operator. In solid insulators it depends on lattice vibrations:

$$\hat{J} = \hbar \sum_{\mathbf{q}\nu\nu'} \frac{\omega_{\mathbf{q}\nu} + \omega_{\mathbf{q}\nu'}}{2} v_{\mathbf{q}\nu\nu'} \hat{a}^\dagger_{\mathbf{q}\nu}\hat{a}_{\mathbf{q}\nu'} + \hbar \sum_{\mathbf{q}\nu\nu'} \frac{\omega_{\mathbf{q}\nu} - \omega_{\mathbf{q}\nu'}}{4} v_{\mathbf{q}\nu\nu'} \left(\hat{a}_{-\mathbf{q}\nu}\hat{a}_{\mathbf{q}\nu'} - \hat{a}^\dagger_{\mathbf{q}\nu}\hat{a}^\dagger_{-\mathbf{q}\nu'}\right)$$

GK formula requires the computation of $\langle \hat{a}^\dagger_{\mathbf{q}\nu}(t)\hat{a}_{\mathbf{q}\nu'}(t)\hat{a}_{\mathbf{k}\mu}\hat{a}^\dagger_{\mathbf{k}\mu'}\rangle$

- κ can also be computed with Boltzmann Transport Equation (BTE):

$J_{\mathbf{q}\nu} = \sum_{\mathbf{q}\nu} \hbar\omega_{\mathbf{q}\nu} v_{\mathbf{q}\nu} \Delta n_{\mathbf{q}\nu}$ where $\Delta n \propto \nabla T$ is obtained through:

$$\frac{\partial n_{\mathbf{q}\nu}(\mathbf{r},t)}{\partial t} + v_{\mathbf{q}\nu}\cdot\nabla n_{\mathbf{q}\nu}(\mathbf{r},t) = \frac{\partial n_{\mathbf{q}\nu}}{\partial t}\Big|_{col}$$

Single-Mode Relaxation-Time Approximation

- dressed-bubble approximation (single-mode)

$$\langle \hat{a}^\dagger_{\mathbf{q}\nu}(t)\hat{a}_{\mathbf{q}\nu'}(t)\hat{a}_{\mathbf{k}\mu}\hat{a}^\dagger_{\mathbf{k}\mu'}\rangle \approx \langle \hat{a}^\dagger_{\mathbf{q}\nu}(t)\hat{a}_{\mathbf{q}\nu}\rangle\langle \hat{a}_{\mathbf{q}\nu'}(t)\hat{a}^\dagger_{\mathbf{q}\nu'}\rangle\delta_{\mathbf{q}\nu\mathbf{k}\mu}\delta_{\mathbf{q}\nu'\mathbf{k}\mu'} + \langle \hat{a}^\dagger_{\mathbf{q}\nu}\hat{a}_{\mathbf{q}\nu}\rangle\langle \hat{a}_{\mathbf{k}\mu}\hat{a}^\dagger_{\mathbf{k}\mu'}\rangle\delta_{\mathbf{q}\nu\mathbf{q}\nu'}\delta_{\mathbf{k}\mu\mathbf{k}\mu'}$$

- Relaxation-Time Approximation (RTA)

$g^>_{\mathbf{q}\nu}(t) \approx -i(n_{\mathbf{q}\nu}+1)e^{i\omega_{\mathbf{q}\nu}t - \gamma_{\mathbf{q}\nu}|t|}$ results in the Quasi-Harmonic Green-Kubo (QHGK) method[2].

Beyond the Single-Mode Relaxation-Time Approximation: Mori-Zwanzig Memory-Function formalism

MZ Memory-Function formalism is a technique to compute quantum or classical correlation functions.

- Once defined a scalar product $\left(\widehat{A},\widehat{B}\right) \doteq \int_0^{\frac{1}{k_BT}} \langle \widehat{A}^\dagger(-i\hbar\lambda)\widehat{B}\rangle d\lambda$
- $C_{IJ}(t) = \left(\widehat{A}_I(t),\widehat{A}_J\right)$
- $\int_0^\infty dt\, e^{izt} C_{IJ}(t)$
- $C_{IJ}(z) = i\sum_K \Lambda^{-1}_{IK}(z) C_{KJ}$
- $\Lambda_{IK}(z) = z\delta_{IK} - \Omega_{IK} + i\Gamma_{IK}(z)$

We used this method to compute κ beyond the single-mode RTA approximation (e.g. vertex corrections).

Ladder of lattice thermal conductivity models

Single-Mode RTA approximation

- BTE-RTA $\kappa = \frac{1}{V}\sum_{\mathbf{q}\nu} c_{\mathbf{q}\nu} v_{\mathbf{q}\nu} v_{\mathbf{q}\nu} \tau_{\mathbf{q}\nu}$
- QHGK contains **interband contributions**

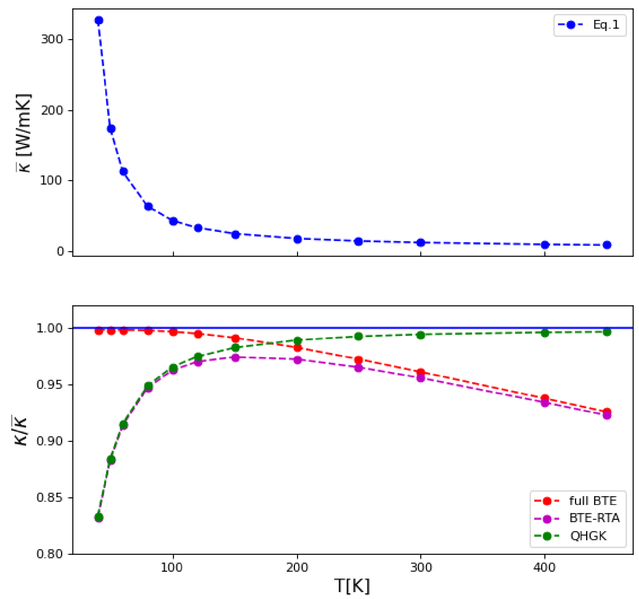
$$\kappa = \kappa^{BTE-RTA} + \frac{1}{V}\sum_{\mathbf{q}\nu\neq\nu'} c_{\mathbf{q}\nu\nu'} v_{\mathbf{q}\nu\nu'} v_{\mathbf{q}\nu\nu'} \frac{\gamma_{\mathbf{q}\nu}+\gamma_{\mathbf{q}\nu'}}{(\omega_{\mathbf{q}\nu}-\omega_{\mathbf{q}\nu'})^2 + (\gamma_{\mathbf{q}\nu}+\gamma_{\mathbf{q}\nu'})^2}$$

Beyond single-mode:

- full BTE $\kappa = \frac{1}{V}\sum_{q\nu k\mu} c_{q\nu} v_{q\nu} v_{k\mu} S^{-1}_{q\nu k\mu}$
- full QHGK $\kappa = \frac{1}{V}\sum_{\mathbf{q}\mathbf{k}\nu\nu'\mu\mu'} c_{\mathbf{k}\mu\mu'} v_{\mathbf{q}\nu\nu'} v_{\mathbf{k}\mu\mu'} \Lambda^{-1}_{\mathbf{q}\nu\nu',\mathbf{k}\mu\mu'}$, approximated with:

$$\kappa = \kappa^{BTE} + \frac{1}{V}\sum_{\mathbf{q}\nu\neq\nu'} c_{\mathbf{q}\nu\nu'} v_{\mathbf{q}\nu\nu'} v_{\mathbf{q}\nu\nu'} \frac{\gamma_{\mathbf{q}\nu}+\gamma_{\mathbf{q}\nu'}}{(\omega_{\mathbf{q}\nu}-\omega_{\mathbf{q}\nu'})^2 + (\gamma_{\mathbf{q}\nu}+\gamma_{\mathbf{q}\nu'})^2} \quad (1)$$

Thermal conductivity of anti-perovskite Li_3ClO



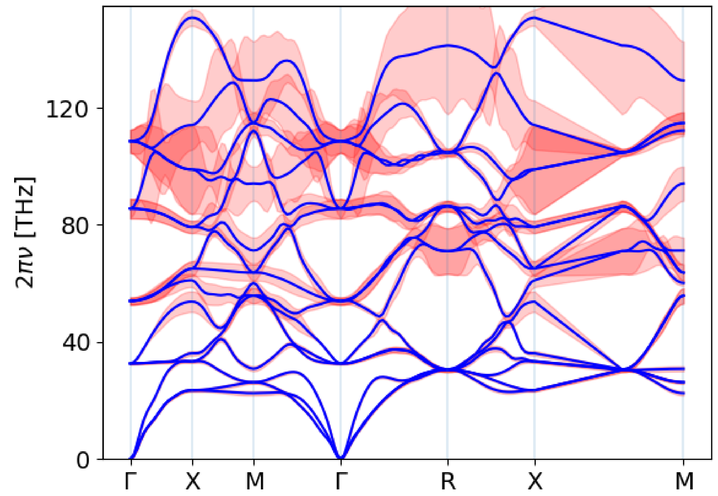
Thermal conductivity from Eq.1 and its comparison with other methods.

Two regimes for interband and beyond single-mode effects

- Room/high temperature: the single-mode RTA approximation works. BTE and QHGK methods differ for interband contributions.
- Low temperature: the single-mode approximation cannot describe the hydrodynamic effects[5], while the interband contributions are negligible.

Interband contributions

Interband contributions cannot be neglected when the distance between bands is in the order of few linewidths. Since anharmonic linewidths increase with temperature, the effect matter most at room/high temperature and for materials with a complex band structure.



Conclusions

- Full QHGK is a unified theory of thermal transport in crystals and glasses, derived from Green-Kubo and MZ Memory-Function Formalism
- It combines interband contributions, which are crucial to extend the work to glasses, with effects that cannot be described by the single-mode approximation.
- Eq. 1 is compatible with the work of Ref.[3]

References

[1] M. S. Green, J. Chem. Phys. **20**(8), 1281-1295 (1952)

[2] L. Isaeva, G. Barbalinardo, D. Donadio, and S. Baroni, Modeling heat transport in crystals and glasses from a unified lattice-dynamical approach, Nat. Commun. 10, 3853 (2019)

[3] M. Simoncelli, N. Marzari, and F. Mauri, Unified theory of thermal transport in crystals and glasses, Nat. Phys. 15, 809 (2019).

[4] P. Pegolo, S. Baroni, and F. Grasselli, Temperature- and441 vacancy-concentration-dependence of heat transport in Li3ClO from multi-method numerical simulations, npj Comput. Mat. 8, 4 (2022).

[5] A. Cepellotti, G. Fugallo, L. Paulatto, M. Lazzeri, F. Mauri, and N. Marzari, Phonon hydrodynamics in two-dimensional materials, Nat. Commun. 6, 6400 (2015).

[6] Fiorentino, A. and Baroni, S., From Green-Kubo to the full Boltzmann kinetic approach to heat transport in crystals and glasses, Arxiv (2022).

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