Heat Transport in Anharmonic Solids

Understanding Thermal Conductivity Beyond the Phonon Picture

***F. Knoop, M. Scheffler, C. Carbogno**, Fritz Haber Institute of the Max Planck Society*

In Short

- Improved thermal insulators are urgently needed for advancing and establishing a sustainable "green energy" economy. However, data in this regard is scarce and often unreliable.
- We aim at computing thermal conductivities with an unprecedented accuracy for more than 50 materials that have already been identified as promising thermal insulators in our previous work [1].
- For this purpose, we will perform non-pertubative *ab initio* Green Kubo simulations, which are ideally suited to reliably describe thermal insulators, since strong anharmonic effects that are not accurately captured by perturbative approaches dominate the nuclear dynamics in these materials.

The thermal conductivity plays a pivotal role for a multitude of material-science applications. Most importantly, the optimization and improvement of thermal insulators is a key technology for facilitating and establishing a sustainable "green energy" economy [2]. Yet the number of materials for which the thermal conductivity is well characterized is limited both experimentally and computationally. Experimental thermal conductivities have only been reported for about 200 inorganic solids according to Springer Materials [3] and only a small fraction of these data points have been verified by independent measurements. Computationally, even less systems have been studied so far and most of the studies rely on a multitude of questionable approximations, for instance the use of the harmonic approximation plus low-order perturbative corrections. This approximation is particularly problematic for thermal insulators, which feature strong anharmonic effects not assessable in a pertubative approach. This lack of reliable and comparable data across material space severely hinders progress in this field.

To overcome this hurdle in this work, we aim at simulating thermal transport for more than 50 thermal insulators with an unprecedented accuracy. For this purpose, we plan to perform non-perturbative *ab initio* Green Kubo (aiGK) calculations [4], which capture all orders of anharmonic effects and are thus ideally suited to accurately assess and predict heat transport in strongly anharmonic thermal insulators, see Fig. 2. The obtained results will provide a reliable and systematic data set on heat transport in strongly anharmonic thermal insulators and will dwarf all existing thermal conductivity data, thus propelling the field on a new level.

In a preliminary screening, we have already identified more than 100 strongly anharmonic materials using our recently developed anharmonicity measure σ^{A} [1]. As shown in Fig. 1, good thermal conductors like silicon typically exhibit $\sigma^{\mathrm{A}} \ll 0.2$, while efficient thermal insulators exhibit values of $\sigma^{\mathrm{A}} > 0.2$, thus signaling the occurrence of strong anharmonic effects and hence a (partial) breakdown of the harmonic approximation. Accordingly, the already identified strongly anharmonic materials are very promising thermal insulators. In this work, we aim at simulate thermal conductivities for more than 50 of these materials with the most accurate and advanced first-principles formalism available to date, thus shedding light on the actuating microscopic mechanisms and on trends in chemical space.

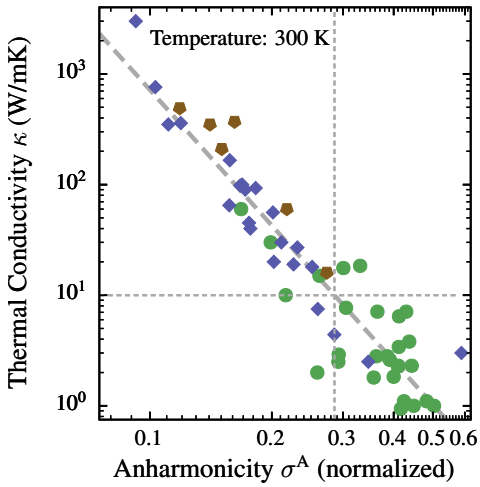

Figure 1: *Our presentation of the experimental lattice thermal conductivities for selected materials at 300 K as function of the anharmonicity metric σ^{A} computed at 300 K from first principles. A vanishing value of σ^{A} designates a perfectly harmonic material, whereas values of $\sigma^{\mathrm{A}} \gg 0.2$ are typical for strong anharmonic solids. Details and references in [1].*

The aiGK method used for this purpose relies on the fluctuation-dissipation theorem, which relates the Cartesian components of the thermal conductivity tensor κ to the time-autocorrelation function of the heat flux. The dynamics of the system is explored via *ab initio* Molecular Dynamics (aiMD) simulations, thereby accounting for all orders of anharmonicity. Details on the required evaluation of the heat flux from first principles can be found in Ref. [4]. We note in passing that it is necessary to run multiple,

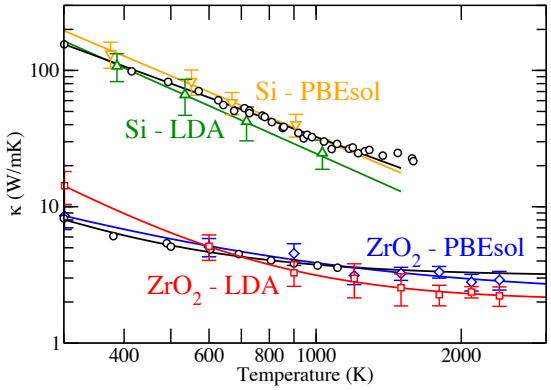

Figure 2: *Thermal conductivity κ computed using the aiGK method for Si (LDA green and PBEsol orange triangles) and tetragonal ZrO_2 (LDA: red squares; PBEsol: blue diamonds). Black circles denote experimental results. Details and references in Ref. [4].*

loosely-coupled aiMD simulations for each material in parallel to achieve maximal computational efficiency and accuracy. The respective routines to manage, run, and submit such calculations are alreay implemented in our in-house Python framework *FHI-vibes*. As an example, Fig. 3 shows the evaluation of the heat flux autocorrelation function (HFACF) and the integrated thermal conductivity κ for the representative simple yet anharmonic material γ-CuI.

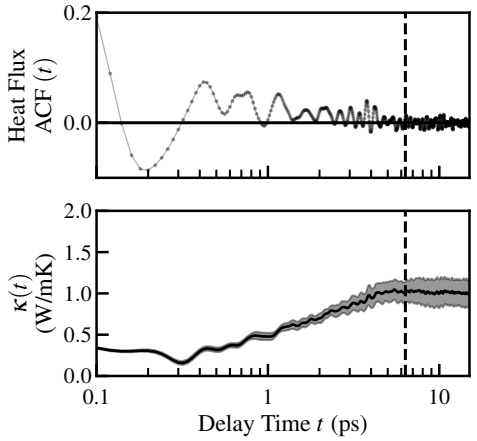

Figure 3: *ab initio Green Kubo simulation for γ-CuI at 300 K. The upper panel shows the heat flux autocorrelation function (HFACF) as a function of the delay time t obtained from the mean of three independent simulations up to a delay of 15 ps. The lower panel shows the thermal conductivity integrated up to a given delay with a standard error estimated from the standard deviation of the three independent trajectories (gray area). The cutoff time of 6.3 ps (dashed vertical line) is chosen based on the noise-over-signal ratio of the HFACF and can be further improved by running more trajectories in parallel.*

The obtained data on thermal conductivity is useful in multiple ways: First and foremost, the data possibly reveals novel thermal insulators beyond the experimentally charted chemical space. Second, qualitative trends with respect to thermal transport across material classes can be assessed by using artificial-intelligence approaches such as SISSO [6]. Third, the obtained aiMD data is shared via the NOMAD Repository [7] and made available as a valuable ressource to the community of first-principles methods developers, for instance to benchmark and improve existing approximative descriptions of thermal transport, but also for the development of aiMD techniques beyond the realm of thermal transport.

The work is performed using our newly developed python framework *FHI-vibes* for *ab initio* vibrational simulations which facilitates to bridge seamlessly from the harmonic approximation to fully anharmonic aiMD simulations. *FHI-vibes* provides all the necessary tools and formalisms from anharmonicity screening to performing aiMD and aiGK simulations [3] by using the Atomic Simulation Environment (ASE) [10] to integrate third-party packages such as *phonopy* [11]. The calculation of *ab initio* energy, forces, stress, and heat flux is performed by the all-electron, numeric atomic orbitals code FHI-aims [4,8,9].

WWW

https://vibes.fhi-berlin.mpg.de/

More Information

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