Phonon Transport Simulator (PhonTS)

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Abstract

Thermal conductivity prediction remains an important subject in many scientific and engineering areas. Only recently has such prediction become possible on the basis of the first principles calculations, thus ensuring high quality results. Implementation of the methodology, however, is technically challenging and requires a lengthy development process. We thus introduce the Phonon Transport Simulator (PhonTS), a Fortran90, fully parallel code to perform such calculations. PhonTS possesses a large array of options and returns the thermal conductivity tensor together with related quantities, such as spectral thermal conductivity, phonon lifetimes, mean free paths and Grüneisen parameters. First principles calculations are implemented via convenient interfaces to widely-used third-party codes, while many classical potentials are included in PhonTS itself. The code is carefully validated against data published in the literature from various thermal conductivity computational techniques and against experimental data.

Keywords

Thermal conductivity, Boltzmann transport equation

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Program title: PhonTS

Licensing provisions: GNU

Programming language: Fortran90

Computer(s) for which the program has been designed: Linux cluster

Operating system(s) for which the program has been designed: Linux

RAM required to execute with typical data: 200 MB

Has the code been vectorised or parallelized?: Yes, via the MPI-libraries

Number of processors used: Any

Keywords: Thermal conductivity, Boltzmann transport equation, phonon transport

CPC Library Classification:

External routines/libraries used: LAPACK, MPI-libraries

Nature of problem: Computes thermal conductivity in crystal solids from the level of the interatomic interactions.

Solution method: Iterative or variational solution of the Boltzmann Transport Equation for phonons, by treating anharmonicity as a perturbation to the harmonic problem.

Running time: Problem dependent. For solid argon (4 atoms in the conventional cell, k-space mesh of 9x9x9, classical potential, fully convergent results) simulations take $\sim 10^4$ seconds on a single processor.

References:

A. Chernatynskiy and S. R. Phillpot, "Evaluation of computational techniques for solving the Boltzmann transport equation for lattice thermal conductivity calculations" Phys. Rev. B 82, 134301 (2010)

A. Chernatynskiy, J. E. Turney, A. J. H. McGaughey, C. H. Amon and S. R. Phillpot, "Phonon-Mediated Thermal Conductivity in Ionic Solids by Lattice Dynamics-Based Methods", J. Amer. Ceram. Soc. 94, 3523 (2011)

A. Chernatynskiy and S.R. Phillpot, "Thermal conductivity of argon at high pressure from first principles calculations", J. Appl. Phys., 114, 064902 (2013)

1. Introduction

Thermal transport properties of materials are attracting significant interest from many fundamental and technological perspectives. Of particular importance are applications in energy sciences, where the development of novel thermoelectric materials¹ and improvements in performance of nuclear fuels² offer to be important parts of the solution to the energy puzzle. Other areas include on-chip thermal management³, thermal barrier coatings^{4,5} and geophysics applications⁶. Many relevant materials in these applications are electrical insulators; thus the dominant thermal transport mechanism is phonon-mediated conduction. In all of the examples above, the challenge is to optimize the thermal conductivity of the active material, subject to a number of other constraints. For example, thermoelectric applications require low thermal conductivity, but efficient electrical conductivity and large thermopower. On the other hand, the thermal conductivity of potential next generation nuclear fuels need to be maximized; moreover the fuel has to be mechanically and chemically stable under conditions of intense irradiation and strong thermomechanical forces. Geophysical applications require knowledge of the thermal transport properties at the extreme conditions of very high pressure and temperature. These challenges clearly indicate the need for an efficient and accurate predictive tool for thermal transport properties.

Molecular dynamics (MD) with classical potentials, a very popular approach for the investigations of the lattice thermal transport from the atomic level simulations, was developed in 70's and 80's^{7,8}. A number of variants have been developed over the years, and currently two methods have emerged as the most successful⁹ and both are considered to be standard tools: Green-Kubo MD and non-equilibrium, or direct MD. For practical applications of both of these methods one requires only a molecular dynamics code, possibly slightly modified to accumulate required statistics in each case. Some popular MD codes, such as LAMMPS¹⁰, have all of the necessary capabilities and provide a turn-key system for performing such thermal transport simulations. One advantage of MD approaches is that due to simplicity of the classical potentials it is possible to study rather large model systems that can include microstructural features, such as grain boundaries¹¹⁻¹⁶, dislocations¹⁷ and other microstructural defects, or study low symmetry systems, such as nanowires^{18,19}. The disadvantage of MD approaches is that they are time consuming due to the system size effects that must be analyzed and that they need to accumulate statistics over long MD trajectories. Most importantly, however, these simulations rely on classical potentials to describe the interatomic interactions. The key issue here is that classical potentials are rarely fitted to reproduce anharmonic properties of the material which are responsible for the thermal transport. While *ab-initio* MD has been demonstrated as a possibility for the thermal transport studies as well^{20,21}, limited system size and simulation times result in rather large uncertainties, while the computational load is even more daunting.

A direct calculational approach to the thermal conductivity in the form of solution of the Boltzmann Transport Equation (BTE) for phonons was worked on as far back as 50's and 60's. This early work was analytic, see^{22,23} and references therein. Since accurate descriptions of interatomic interaction were not available at that time, nor would they have been conducive to analytic analysis of the BTE even if they had existed, the analytical calculations inevitably had to make a number of approximations. In this approach, the BTE is typically solved in the Relaxation Time Approximation (RTA) with the phonon structure of the solid considered within the Debye approximation, and phonon-phonons interaction usually considered in the limit of long-waves, but applied to the entire spectrum. The RTA treats the relaxation of each phonon mode to equilibrium as if all other modes were in equilibrium; it is typically very successful if the overall thermal conductivity is small, or relaxation times are short. These conditions

are usually realized at relatively high temperature (comparable with Debye temperature²⁴) or in materials with relatively strong anharmonicity²⁵. The Debye approximation is most suited for monoatomic solids; it is thus not surprising that results of this approach differ significantly from experimental data for two-atom solids with large mass difference between constituents²². Finally expanding the long-wave-limit of phonon-phonon interactions to the entire spectrum is an uncontrolled approximation, as was noted by Klemens, which however might work reasonably well if long-wavelength phonons are the dominant heat carriers. Despite the large number of approximations this theory results in very good qualitative agreement with experiment for the thermal conductivity as a function of other materials specific parameters. Specifically, it predicts the thermal conductivity to be proportional to the cube of the Debye temperature θ_D and inversely proportional to temperature for $T > \theta_D$. Quantitatively, however, the predictions can be off by as much as an order of magnitude.^{22, 26} With the advent of powerful computers and the development of appropriate algorithms, there is no longer a need to make some of these approximations. As a result thermal transport properties can now be successfully determined from numerical analysis of the BTE starting directly from the level of the interatomic interactions²⁷⁻²⁹, with the quality of these interactions being the key approximate quantity. The BTE approach gained a new level of sophistication through the pioneering works of Broido and coworkers³⁰, where highly accurate Density Functional Theory (DFT) calculations were used to describe the interatomic interactions. An iterative solution of the BTE was used, thus allowing for the determination of the thermal conductivity from first principles. These recent developments are surveyed in recent reviews^{26, 31, 32}. It is also noteworthy that very similar calculations were performed earlier for the simulations of the phonon line shape in the context of inelastic neutron scattering³³ and Raman linewidths in solids³⁴.

In light of the discussion above, a computational tool for the study of the thermal transport within the BTE is highly desirable. In this work we present PhonTS (Phonon Transport Simulator), a simulation package that employs analysis of the BTE for thermal transport and related properties of single crystals. PhonTS is written in Fortran90, is fully parallelized via MPI and driven by a single, freestyle input file. It includes the ability to use interatomic interactions from first-principles codes. Interfaces to the popular VASP³⁵⁻³⁸ and QuantumEspresso³⁹ DFT codes are built into the distributed version. Interatomic forces can also be taken from classical empirical potential: an interface to LAMMPS is also part of the distributed version. Development of interfaces to other programs is relatively straightforward. Depending on the availability of the Density Functional Perturbation Theory (DFPT) calculations, PhonTS will use either first derivatives of the energy (i.e., forces) only, or second derivatives as input for the BTE calculations. Solution of the BTE can be performed using either the variational or iterative techniques; the first step in the iterative solution also gives the RTA result. In addition to three-phonon scattering processes, isotope and system size scattering mechanisms are included. Together with the overall thermal conductivity, PhonTS produces other related properties, such as the spectral thermal conductivity, phonon lifetimes, mean free paths and Grüneisen parameters. Recently Li et al. have released a software package with some similar capabilities.⁴⁰ In contrast to that work, PhonTS provides the capability to use wide array of classical potentials and flexibility to compute 3rd derivatives by using forces only, thus not requiring Density Functional Perturbation Theory implementation for the first principles calculations.

The rest of the paper is organized as follows. Section 2 briefly outlines the theoretical background and provides an overview of the algorithms employed. Section 3 discusses the most important technical details of the implementation, while Section 4 gives a short overview of the input and output from the code. Section 5 provides validations for the PhonTS implementation and presents illustrative results for

various systems, using energetics from first-principle calculations and from empirical potentials. This section also provides a brief description of the inherent limitations of the BTE approach, and the implementation within PhonTS in particular. Section 6 contains our conclusions.

2. Theory background

We start with a brief outline of the theory of the thermal conductivity in the framework of the Boltzmann transport equation. Extensive details of the transport theory can be found, for example, in the classic text by Ziman²³. Standard equilibrium thermodynamics is not sufficient to describe thermal conductivity, which is an inherently non-equilibrium property. Consider a gas of particles (gas atoms or phonons) that may interact with each other, and describe such a gas by a probability distribution function $f_\lambda(r, t)$, where λ indicates possible quantum numbers for the particles states. This function specifies the probability of finding a particle in the given state in the volume element position r at time t . This function can change during the evolution in the system due to flow of particles in and out of the volume element (diffusion term), due to the external forces, or due to the interaction between particles (scattering term). The Boltzmann Transport Equation (BTE) describes the evolution of such a system. In its linearized canonical form with the assumption of weak non-equilibrium, local equilibrium, and in the absence of the external forces, the BTE reads

$$-\vec{v}_\lambda \cdot \frac{\partial f_\lambda^0}{\partial T} \nabla T = \frac{1}{k_B T} \left\{ \sum_{\lambda'} (\Phi_\lambda - \Phi_{\lambda'}) \Lambda_{\lambda\lambda'}^{\lambda'} + \sum_{\lambda'\lambda''} \left[(\Phi_\lambda + \Phi_{\lambda'} - \Phi_{\lambda''}) \Lambda_{\lambda\lambda'}^{\lambda''} + \frac{1}{2} (\Phi_\lambda - \Phi_{\lambda'} - \Phi_{\lambda''}) \Lambda_{\lambda\lambda'}^{\lambda'\lambda''} \right] + \dots \right\} \quad (1)$$

where Φ_λ characterizes deviation from equilibrium function f_λ^0 and is given by

$$f_\lambda = f_\lambda^0 - \Phi_\lambda \frac{\partial f_\lambda^0}{\partial E_\lambda} \quad (2)$$

while $\vec{v}_\lambda$ is the particle velocity. The left-hand side of the Eq. 1 describes the diffusion term, while the right hand side is a collision integral (the scattering term). The latter term is generically expanded to include 2-body, 3-body and so on interactions, with Λ describing the probabilities of transitions between the states of different sets of quantum numbers. Scattering off imperfections in the crystal lattice formally has the same form, but the scattering amplitudes Λ produced by the details of the phonon defect interactions are different²². Thus Eq. 1 is also applicable for the description of phonon-defect interactions. From this equation, one can immediately observe that a gas of non-interacting particles (i.e., the right hand side is zero) cannot support a thermal gradient or, in other words, it has an infinite thermal conductivity. Thus, the proper description of the thermal conductivity requires an account of particle-particle interactions, or other scattering mechanisms. The thermal conductivity tensor κ itself can be found by using the distribution function to obtain the heat current $\vec{q}$ and applying Fourier's law²³:

$$\vec{q} = \sum_\lambda \hbar \omega_\lambda \vec{v}_\lambda f_\lambda = \sum_\lambda \hbar \omega_\lambda \vec{v}_\lambda \frac{\partial f_\lambda^0}{\partial E_\lambda} \Phi_\lambda = \kappa \nabla T. \quad (3)$$

Consider a crystal lattice containing N atoms in the primitive cell, such that the position of each atom is given by $\vec{R}_{I,l}$ with $I=1\dots N$ and l being the lattice index, which runs over all periodic images of the primitive cell. In the harmonic approximation (small deviations of atom positions from the equilibrium positions), the dynamics of this lattice can be represented by a collection of lattice waves, or phonons. Phonons are indexed by the vector of the reciprocal space $\vec{k}$ belonging to the first Brillouin zone and “branch” index n , which runs from 1 to $3N$. Each phonon is further characterized by the frequency $\omega_{\vec{k};n}$ and the eigenvector $\vec{e}_{J;\vec{k};n}$ which describes the displacement of the atom J in the cell if the phonon mode $\vec{k};n$ is excited. Both frequencies and eigenvectors are obtained by solving the eigenvalue equation:

$$\sum_J (M_I^{-1/2} M_J^{-1/2} \bar{A}_{IJ;\vec{k}} - \omega_{\vec{k};n}^2 \delta_{IJ}) \vec{e}_{J;\vec{k};n} = 0 \quad (4)$$

In this expression $\bar{A}_{IJ;\vec{k}}$ is the so-called dynamical matrix which is given by

$$\bar{A}_{IJ;\vec{k}} = \sum_l \left. \frac{\partial^2 E}{\partial \vec{R}_{I;0} \partial \vec{R}_{J;l}} \right|_{\vec{R}_{I;0}^0, \vec{R}_{J;l}^0} e^{-i\vec{k}\vec{R}_l} \quad (5)$$

where E is the total energy of the system. Since Eq. 4 also describes an harmonic oscillator, the theory is easily quantized; thus quantum-mechanically, phonons are bosons with momentum $\hbar\vec{k}$ and energy $\hbar\omega$, and the dynamics of the lattice can be represented as a non-interacting gas of bosons. The equilibrium distribution of phonons at any given temperature is then given by Bose-Einstein statistics. It is this gas of phonons to which the BTE formalism is applied in order to describe lattice thermal conductivity.

The last, and most difficult, piece of the puzzle in determining the thermal conductivity is defining the particle-particle interaction. In the harmonic approximation phonons do not interact. Interaction between phonons is provided by the high-order terms in the energy expansion around the equilibrium lattice, known as anharmonic terms. These correspond to interactions among three or more phonons. Since a general solution for the anharmonic oscillator does not exist, progress can be made by considering anharmonicity as a perturbation to the harmonic picture. Physically this means that the dynamics of the system are still described as a phonon gas, but now transitions between phonons states with different wavelengths and branch indexes are allowed. Transition probabilities between initial $|i\rangle$ and final states $|f\rangle$ caused by perturbation $\hat{H}_p$ can be written by following the Fermi Golden Rule

$$P_{if} = \frac{2\pi}{\hbar} \langle f | \hat{H}_p | i \rangle^2 \delta(E_f - E_i) \quad (6)$$

The leading anharmonic term is the cubic term, which involves third derivatives of the total energy and corresponds to three-phonon interactions in Eq. 1. Appropriate matrix elements are obtained by rewriting this term in the harmonic basis which results in the following expressions for the transitions probabilities

$$\begin{aligned}
\Lambda_{\vec{k};n\vec{k}';n'}^{\vec{k}'';n''} &= \frac{2\pi}{\hbar} \Gamma_{nn'n'';\vec{k}\vec{k}'\vec{k}''}^2 f_{\vec{k};n}^0 f_{\vec{k}';n'}^0 (f_{-\vec{k}'';n''}^0 + 1) \delta(\hbar\omega_{\vec{k};n} + \hbar\omega_{\vec{k}';n'} - \hbar\omega_{-\vec{k}'';n''}) \\
\Lambda_{\vec{k};n}^{\vec{k}'';n'';\vec{k}';n'} &= \frac{2\pi}{\hbar} \Gamma_{nn'n'';\vec{k}\vec{k}'\vec{k}''}^2 f_{\vec{k};n}^0 (f_{-\vec{k}';n'}^0 + 1) (f_{-\vec{k}'';n''}^0 + 1) \delta(\hbar\omega_{\vec{k};n} - \hbar\omega_{-\vec{k}';n'} - \hbar\omega_{-\vec{k}'';n''})
\end{aligned} \tag{7}$$

In these expressions,

$$\Gamma_{nn'n'';\vec{k}\vec{k}'\vec{k}''} = i \frac{(\hbar/2)^{3/2}}{V^{1/2}} \omega_{\vec{k};n}^{-1/2} \omega_{\vec{k}';n'}^{-1/2} \omega_{\vec{k}'';n''}^{-1/2} \sum_{IJK} \frac{\bar{B}_{IJK;\vec{k}\vec{k}'\vec{k}''}}{m_I^{1/2} m_J^{1/2} m_K^{1/2}} \vec{e}_{I;\vec{k};n}^* \vec{e}_{J;\vec{k}';n'}^* \vec{e}_{K;\vec{k}'';n''}^* \tag{8}$$

and B is a Fourier transform of the cubic anharmonic term

$$\bar{B}_{IJK;\vec{k}\vec{k}'\vec{k}''} = \delta_{\vec{q}, \vec{k} + \vec{k}' + \vec{k}''} \sum_{ll'} \frac{\partial^3 E}{\partial \vec{R}_{I;0} \partial \vec{R}_{J;l} \partial \vec{R}_{K;l'}} \bigg|_{\vec{R}_{I;0}^0, \vec{R}_{J;l}^0, \vec{R}_{K;l'}^0} e^{-i\vec{k}\vec{R}_I - i\vec{k}'\vec{R}_J - i\vec{k}''\vec{R}_K} \tag{9}$$

Note the $\delta_{\vec{q}, \vec{k} + \vec{k}' + \vec{k}''}$ term in this expression, where $\vec{q}$ is the reciprocal lattice vector. This term arises due to the periodicity of the lattice and signifies the conservation of the pseudomomentum. $\vec{q}$ can be either zero or non-zero; in the first case the actual momentum is conserved in the interaction process. Such processes are called normal, or N processes, and due to their momentum conserving nature they do not directly contribute to the thermal resistance, but do redistribute the heat current between different modes. The second case, $\vec{q} \neq 0$, describes Umklapp, or U processes, which do not conserve the momentum and do contribute to thermal resistance. Separation into such processes has proven to be useful in order to understand certain features of the thermal transport. In particular, it led to the development of the very successful Calloway-Holland-type^{41, 42} models for the thermal conductivity.

Our algorithm to compute thermal conductivity thus follows these steps:

1. Start with material of interest, determine its lattice and obtain real-space first-order, and where possible second-order and third-order derivatives with respect to atomic positions using an appropriate classical potential or first principles calculations.
2. Discretize the first Brillouin zone into a grid of k-points to sample phonons in the system
3. Compute phonon properties at each k-point.
4. Compute the transitions probabilities for all three-phonon combinations. This includes integration over the Brillouin zone of the function that includes k-space and energy δ -functions. This is technically challenging and described in detail in the next section. Once this is done, the BTE is fully defined.
5. Solve the linearized form the BTE as a set of $3NN_k$ linear equations, where N_k is the number of the k-points. A number of methods for doing this have being proposed^{29, 43} and compared to each other⁴⁴. The PhonTS current code implements the relaxation time approximation and variational and iterative solutions.

6. Sum contribution from all phonons to give the heat current and determine the thermal conductivity from Fourier's Law.
7. Extract other related properties as desired, such as phonon lifetime, spectral thermal conductivity, Grüneisen parameters and others.

One important issue is the limitations of this approach. The main drawback is the inclusion of the cubic anharmonicity only. Indeed, it has been shown⁴⁵, that finite order perturbation theory of thermodynamics properties will fail as the temperature approaches the melting point. The theory therefore is unreliable above some fraction of the melting temperature; for most solids this is $1/3$ - $1/2$ T_m . Also, the entire theory is constructed under the condition of the constant volume; however thermal expansion increases the volume of real materials with increasing temperature. During validation of PhonTS by comparing with NEMD simulations we found that thermal expansion needs to be taken into account for good agreement with MD data (see below). PhonTS can currently compute thermal expansion via the quasi-harmonic approximation⁴⁶; this approach is also limited to temperatures below roughly the same fraction of the melting temperature as the perturbation theory.

Further, while the theory is quite successful in predicting thermal conductivity in pure, defect-free crystals, it is difficult to apply for real microstructures. The effect of some imperfections, such as isotopic substitution,²² can be treated rigorously at the level of perturbation theory. However, without further approximations this approach has not yet been applied for other microstructural defects. The main reason for this is the computationally prohibitive scaling with the number of atoms in the cell and k-point mesh; namely the algorithm scales as $\sim N^4 N_k^2$. Such a high power in dependence on the number of atoms stems from the summation over the phonons eigenvectors in Eq. 8. It has been suggested by Ipatova et al.⁴⁸ that the sum in the Eq. 8 should be a slowly varying function of the k-vector; thus attempts have been made to approximate it by a constant value⁴⁷ in the context of the phonon lifetime calculations. While good agreement with experiment for phonon lifetimes was demonstrated⁴⁷ and this approach mitigates an unfavorable scaling with the number of atoms, the general applicability of this approximation to thermal transport calculations is unclear.

3. Implementation details

3.1. Derivatives calculations

The most important components of the calculations are the spatial derivatives of the total energy with respect to atomic positions. The PhonTS code includes a number of two-body potentials (Lennard-Jones, Born-Mayer, Morse, Coulomb), three-body potentials (Tersoff, Stillinger-Weber) and the shell model⁴⁹ for ionics. EAM potentials are not included because they are primarily used for describing metals in which heat transport is dominated by electrons. The addition of many other classical potentials is straightforward. PhonTS can also use external codes for first principles calculations (VASP, QuantumEspresso), or MD codes, such as LAMMPS for other classical potentials not implemented in PhonTS itself. Generally, there are two ways to compute the derivatives: via analytical differentiation, or via the finite differences. Analytical differentiation is numerically accurate, but can be very tedious, depending on the potential form. Numerical differentiation requires only the forces to be available; thus it is much simpler in implementation, but does introduce a source of numerical inaccuracy. In the case of numerical differentiation PhonTS uses crystal symmetries to reduce the number of computed derivatives.

In the case of classical potentials, analytical differentiation is straightforward but may be extremely cumbersome, especially for the three-body potentials and third derivatives. PhonTS currently computes both second and third derivatives for all two-body potentials analytically, while three-body potentials includes only second derivatives analytically, and third derivatives via the finite differences from the second derivatives. At the same time, the user can request to compute all derivatives numerically for any potential, which is a useful testing capability, as well as allowing for easy interfacing with other codes. The shell model for ionics is a special case of the classical potentials since the shell degrees of freedom are unphysical, and all derivatives have to be evaluated at the configurations where the shells positions are optimized with respect to total energy. For the shell model, second derivatives might be obtained analytically, but for the third derivatives numerical calculations need to be performed²⁵. The derivatives calculations in the electrostatic interactions are also a special case due to their long-range nature. Second derivatives have to take into account the non-analyticity at the gamma point⁵⁰ in order to correctly treat TO-LO splitting of the phonon modes in ionic materials. Third derivatives, however, seem to be relatively short-ranged²⁵; thus no special care is needed in most cases. For some systems, such as silicon, the short range of the interactions results in significant violation of the translational invariance for third derivatives; hence PhonTS includes a simple acoustic sum rule correction⁵¹.

For first principles calculations, Density Functional Perturbation Theory (DFPT) calculations can be used to compute derivatives analytically; however this approach is limited to the second derivatives and only a limited subset of third derivatives in currently available codes. In addition, second derivatives are only implemented for the standard DFT; thus use of DFT+U or hybrid functionals is not possible via DFPT and numerical differentiation has to be used. In the current implementation, we use numerical differentiation based on forces from VASP or QE calculations. This approach also requires separate calculations to properly include electrostatic interactions; in particular, Born effective charges and the dielectric constant need to be computed. This data is used in the approach proposed by Wang and coworkers⁵² to compute phonons properties in ionic systems.

3.2. Scattering cross-section calculation

Once the derivatives have been computed, phonon properties can be calculated in a straightforward manner, and calculations can proceed to the transitions probabilities. The chief technical difficulty in these calculations is the handling of the δ -functions involved, most notably, the energy δ -function. The δ -function in k-space is relatively easy to handle by the construction of an appropriate the k-point grid: for the cells with orthorhombic symmetry or higher (a limitation of the current implementation) a choice of odd-valued k-meshes (7x7x7, 9x9x9, etc.) ensures that sum of any two k-vectors from the first Brillouin zone considered for the calculations is also a mesh k-vector (but not necessarily from the first BZ). Correspondingly, as long as three vectors $\vec{k}$, $\vec{k}'$ and $\vec{k}''$ sum up to zero or the reciprocal lattice vector $\vec{Q}$, this term can make a contribution.

The energy δ -function is more subtle and at least three different approaches have being used in its calculation. The simplest way⁴⁰ is to use an approximate δ -function representation, such as a Gaussian, for its evaluation. We found that in this approach the results are very sensitive to the width of the Gaussian due to relatively coarse k-meshes typically employed for the thermal conductivity simulations. A more sophisticated approach was developed by Turney and coworkers⁵³, who argued that the natural line width of the phonon state should be considered, and used it in the representation of the δ -function.

Since this natural line width is not known *a priori*, a self-consistency loop is set up, where the output line width is used as an input to next iteration. In addition to the issue of the width described previously, this approach also adds to the computational expense of self-consistent loop for linewidths calculation with unproven convergence properties. Finally, the approach due to Pettersson^{27, 28} attempts to explicitly reduce the three dimensional integration over the Brillouin zone to the two-dimensional one over the “energy conservation surface”. In practice this is achieved by the following procedure, used in PhonTS, with more details given elsewhere⁴⁴.

Consider the triplets of k-vectors, $\vec{k}$, $\vec{k}'$ and $\vec{k}''$, for which $\vec{k} + \vec{k}' + \vec{k}'' = \vec{Q}$. If $\vec{k}$ and $\vec{k}'$ are fixed, then $\vec{k}''$ is fixed also, since it is easily verified that for vectors in the first BZ there is only one reciprocal lattice vector that can fulfill this requirement. For a given vector $\vec{k}$, we also fix k'_x and k'_y and scan along the lines of k'_z for the quantity of $\Delta\omega = \omega_{\vec{k};n} + \omega_{\vec{k}';n'} + \omega_{\vec{k}'';n''}$ for all possible combinations of n , n' and n'' . A change of sign in $\Delta\omega$ indicates that the energy conservation surface has been found and that one can proceed to compute its contributions to the transition probability by calculating surface element area. The latter can be determined since the normal to the surface is known and is given by the $\partial\omega_{\vec{k};n}/\partial\vec{k} - \partial\omega_{\vec{k}';n'}/\partial\vec{k}'$. It is important to note that this surface element cannot extend beyond the first BZ and that one has to ensure that phonon states crossings are accounted for correctly. In our experience, accurate determination of the energy conservation surface ensures fast convergence of the result with respect to k-point mesh size. For this reason we introduce an additional fine mesh for phonon calculations along the z-axis only. As a result, our calculations do not require extrapolation to the infinite mesh, as was required in some other studies⁵³.

4. Input and Output

4.1. Input file structure

A single input file named “phonons_input.dat” is required to run PhonTS software. This is a freestyle input file and similar in spirit to the input to the popular GULP⁵⁴ community code. Basic error checking of the input is provided, which attempts to resolve possible inconsistencies or terminate the execution with an error message. There is no specific order in which keywords must appear in the input file, but there is a set of keywords that must be included. These include the specification of the atomic structure: atomic species present, lattice constant, cell dimensions, number of atoms, their positions in the cell and the interaction law between them. All other parameters of the calculations have predetermined default values. For example, by default, the phonon k-mesh of 9x9x9 with the extra refinement of a factor of 10 along the z-axis is used. By default, calculations are performed in the temperature range of 300-1200K at 100K intervals, and RTA solution is performed. The equilibrium distribution is assumed to be the Bose-Einstein distribution, though the user may use the Maxwell-Boltzmann distribution instead. This feature is useful for assessing quantum mechanical effects in thermal transport processes in general, and for comparing with classical MD in particular, since the latter samples Maxwell-Boltzmann statistics. Depending on the interaction law specified, the default is that derivatives are computed analytically, if available, and numerically otherwise. An example of such a minimal input file is given in Figure 1. This input file specifies a cubic cell with lattice constant of 3.962 Å, indicates that only argon atoms will be present, and arranges them in the fcc lattice (4 atoms in the conventional cubic cell). Finally, the

interaction law chosen here is exp-6 potential⁵⁵ developed for high pressure studies of inert gases. This example is worked out in detail in the online manual and is included in PhonTS distribution, as well as considered in the validation section below.

```

cell 1. 1. 1.
species 1
Ar 40.0 0.00
Lattice 3.9620
exp-6 1
Ar Ar 0.01051316 13. 3.85 5.625 9.625
natoms 4
fractional
Ar 0.0000 0.0000 0.0000
Ar 0.5000 0.5000 0.0000
Ar 0.5000 0.0000 0.5000
Ar 0.0000 0.5000 0.5000
end

```

Figure 1. Example of the minimal input file for PhonTS.

4.2. Key Output files

The key quantity of interest, the thermal conductivity tensor, is printed to the screen output at each temperature. The screen output also mirrors the input parameters (and defaults) for verification and archiving. PhonTS produces a number of other output files that contain other information. For example, the phonon density of states (PDOS) is printed to file named “pdos.dat”. Note, that the PDOS produced by the input file in Figure 1 will most likely not be very satisfactory due to the relatively coarse mesh, and more importantly non-uniform sampling of the BZ due to additional k-points along z axis. It is therefore recommended to run a separate calculation if a high quality density of states is desired with a finer mesh and refinement of 1. An example of this is available in the example runs in the PhonTS distribution. Another important output file is “tc_dos.dat” which includes the spectral thermal conductivity as a function of frequency. Finally, “phon_lifetimes.dat” contains the lifetime of each phonon in the system. This information can be used to study the lifetime as the function of phonon energy, a key dependence considered in the approximate theories²² of thermal conductivity. Full details are provided in the complete online manual.

4.3. Interfaces to other codes

PhonTS is designed to directly produce input structure files for specific third-party software and directly read in their output, thus minimizing the number of the intermediate steps needed. The current version supports Density Functional Theory codes VASP³⁵⁻³⁸ and QuantumEspresso (QE)³⁹ and the popular LAMMPS classical molecular dynamics code¹⁰. For all of these codes, files other than the structure files are required to run the simulations: providing these is the user’s responsibility. These files include simulation control files (INCAR and KPOINTS are an examples of such files for VASP) and pseudopotential files for the DFT calculations, the latter are typically included in the distribution of the particular DFT code. Due to the relatively large number of structure files required we use simple shell scripts to move them around and prepare the files for the VASP runs. Such scripts are included in the distribution of PhonTS for the examples of the VASP and LAMMPS calculations. The case of QE is slightly more complicated as the atomic structure is the part of the input file that also contains

calculations controls. Only the structure part is prepared by PhonTS, and needs to be incorporated into the overall input file by scripts.

Calculations of ionic systems again constitute a special case. Supercell calculations of the phonon properties do not include long-range electrostatic interactions, and these need to be calculated separately. Specifically, omission of the long-range part results in incorrect behavior of the optical phonons around the gamma-point,²⁵ which has minor impact on thermal conductivity. Separate calculations are required for the dielectric constant and Born effective charges. These quantities can be obtained from calculations of a primitive cell, rather than supercell, using perturbation theory calculations or via Berry-phase calculations.⁵⁶ Results of these calculations need to be placed in the file “charges.VASP” for PhonTS to use during the calculations. If this file is absent, then PhonTS assumes zero charges and proceeds with thermal conductivity calculations.

5. Representative applications

In this section we present validation of PhonTS software and a few examples of PhonTS capabilities. We begin with the thermal conductivity computed using classical potentials since, in this case, one can conveniently compare with the results of MD simulations. We also present an example of first principles simulations, using MgO as a testing system.

5.1. Validation: detailed comparison with MD

As a first step in the validation of PhonTS we compare its predictions with those of molecular dynamics simulations. MD simulations rely on a different set of approximations, and its strengths are very much complementary to those of the BTE approach. In contrast to the BTE approach, MD simulations take into account complete anharmonicity and do not rely on perturbation theory. Their predictions therefore are valid even at temperatures around the melting point and higher. On the other hand, MD uses Newton’s equations of motion to govern atomic motion and therefore does not include quantum effects. MD predictions for temperatures below the Debye temperature therefore have to be treated with caution. As discussed above, the BTE based approach can, if desired, use Maxwell-Boltzmann statistics instead of Bose-Einstein as an equilibrium distribution, thus reproducing the conditions of the MD simulations exactly at all temperatures, if the same interatomic potential is employed. This allows a rigorous test of the approximations involved with the BTE framework and, in our case, the verification its implementation in PhonTS, since the only remaining difference is perturbative treatment of the anharmonicity in BTE. We compare our simulations for three different materials of increasing complexity: Ar, Si and UO₂. Argon is described by the simple two-body, exp-6 potential⁵⁵, with the reference simulations being Green-Kubo molecular dynamics simulations⁵⁷. Silicon is described by a three-body Tersoff potential⁵⁸; the reference simulations are non-equilibrium molecular dynamics⁵⁹. UO₂ is an ionic solid which is described by a Buckingham-type potential, with the reference simulations also performed using NEMD¹⁴. Results for these very different solids are presented in Figure 2 (a) and (b). Figure 2(a) shows the thermal conductivity as a function of temperature from these two approaches. Figure 2(b) presents the same data in the form of the MD value vs. the BTE value; thus agreement between the two methods is signified by all the points falling onto y=x line.

For all cases presented here, the results of the PhonTS calculations of thermal conductivity show quantitative agreement with the MD simulations results. We note that this agreement is observed in wide temperature range and for values of thermal conductivity spanning two orders of magnitude. These results

thus validate the PhonTS implementation of the BTE methodology. In the cases of UO_2 and Ar, the BTE data is always within the error bars of the MD simulations, while for Si case BTE results consistently slightly overestimate MD data. Since the temperature for these Si simulations is quite high (up to $\sim 0.6T_m$) it is possible that higher order anharmonic terms are important for this case. Moreover, the reported error bars for the Si MD simulations are unusually small⁵⁹.

We note that this level of agreement is only achievable if the conditions for the BTE simulations are matched carefully to those used in MD.²⁵ The important factors include: i) thermal expansion: Due to strong sensitivity of the phonon modes to the volume and shape of the primitive cell it is important to use the same primitive cell in MD and BTE calculations. Thus one needs to use the MD thermal expansion for the BTE simulations rather than the expansion predicted by the quasiharmonic approximation which becomes less accurate with increasing temperature. ii) The reference MD calculations for UO_2 were performed using the approximate charge-neutralized direct summation method for the coulombic interactions.⁶⁰ As demonstrated by Chernatynskiy et al.²⁵, this approximate treatment of the electrostatics may lead to differences in the calculated thermal conductivity of up to 20%, when compared to calculations via the exact Ewald summation. Both rigorous Ewald summation and approximate direct summation are implemented within PhonTS. For direct comparison with the previous MD data we used direct summation of the electrostatic terms for UO_2 .

Figure 2. Comparison of the thermal conductivity between MD and BTE for Ar, Si and UO_2 systems (a) as a function of temperature, (b) MD vs BTE.

5.2. Example of first principles calculations

Having established that PhonTS correctly reproduces the results from MD simulations, we now turn to the first-principles calculations of thermal conductivity. We choose to calculate the thermal conductivity of MgO , one of the materials for which such results has been reported previously.⁶¹ We employ the VASP computational package³⁵⁻³⁸ to perform the density functional theory (DFT) calculations. Here, we choose to perform the calculations at the experimental lattice constant at 300K of MgO of $a=4.2127\text{\AA}$. In light of our discussion in the previous section, this implies that the thermal conductivity at higher temperatures can be expected to be overestimated due to unaccounted thermal expansion. An important parameter in the BTE calculations is the finite displacement used to determine the derivatives of the energy by finite differences. Here we employ the value of $0.005a = 0.0021\text{\AA}$. Smaller values of the displacement are not

feasible due to numerical errors associated with the DFT calculations. Larger values of displacement, on the other hand, result in large errors in the numerical differentiation. The value of $0.005a$ is a reasonable compromise, and is somewhat smaller than recommended by VASP value for the phonons calculations, reflecting the need accurate determination of the third derivatives in PhonTS. Perhaps the largest source of numerical error is the self-consistency loop, hence we require energy convergence to be below 10^{-9} eV. Calculations performed here employ the local density approximation to DFT within the PAW⁶² framework. The supercell for the DFT calculations is chosen to be $2 \times 2 \times 2$ of the conventional cubic cell of MgO, thus allowing the maximum range of interactions of $4.2 \text{ \AA}$; that is, up to third nearest neighbors. The plane-waves expansion cutoff is 500 eV, and supercell calculations are performed using Γ -point calculations. The parameters of the Coulomb interactions parameters are: dielectric constant $\epsilon=3.09$, the Born effective charges for Mg and O are $z=\pm 1.96$, obtained using perturbation theory calculations on the primitive cell and k-mesh for the DFT calculations of $7 \times 7 \times 7$. Finally, the phonon calculations in the BTE employ a $15 \times 15 \times 15$ k-mesh in the first Brillouin zone, with the additional refinement of a factor of 10 along the z-axis to ensure that the energy δ -function is well obeyed. Bose-Einstein statistics are used to allow direct comparison with the experimental data by Cahill and coworkers⁶³ and previous DFT/LDA data of Tang and Dong⁶¹ in Figure 3. One can see that the DFT results are slightly higher than the experimental data points, but somewhat lower than previously reported DFT results. The former is typically due to the ideal crystal considered in the simulations, while experimental data usually have some imperfections, and/or the possible importance of the high-order anharmonic terms. Differences with the DFT data reported previously⁶¹ are attributable to the fine details of the DFT calculations: we employed a smaller supercell for the derivatives calculations and higher energy cutoff for the wave-function expansion.

Figure 3. Thermal conductivity in MgO based on DFT/LDA calculations in comparison with the experimental results and previously published DFT/LDA results.

Other than the thermal conductivity itself, PhonTS also reports phonon lifetimes and the spectral thermal conductivity, shown in Figure 4 (a) and (b) correspondingly. Figure 4 (c) presents phonon density of states in MgO for reference. Phonon lifetimes, in particular, show much more complex behavior than the $\tau^{-1} \sim \omega^2$ predicted by the simple analytical models²²: an initial increase of the inverse lifetime with frequency followed by a decrease in the mid-frequency range (5-10 THz), and then increase again. In this particular case, this final increase is so dramatic, that phonons with frequencies above 15 THz contribute almost nothing to the thermal conductivity, as one can see from the spectral thermal conductivity in Figure 4 (b). Phonons in the 5-11.5 THz range, which in the case of MgO are mostly acoustic phonons, are the main contributors to the phonon transport.

Figure 4. (a) Phonon lifetimes as a function of frequency (b) Spectral thermal conductivity in MgO (arbitrary units) and (c) Phonon density of states. All data is at 300K.

Figure 5. Scattering maps of the (a) recombination and (b) dissociation processes in MgO

Finally, PhonTS also computes a scattering map: a 3D representation of the scattering amplitudes for different phonon processes. These are shown in Figure 5(a) for the recombination of two phonons (ω_0 , ω_1) into one (ω_2) and in Figure 5(b) for dissociation of one phonon into two. These two plots are related to each-other, and they essentially illustrate the same scattering amplitudes, so we can analyze either. Looking at Figure 5(b) we observe a strong dissociation process at ~ 12.5 THz: This process corresponds to a dissociation of the flat optical state which stretches across the entire BZ and also to zone edge longitudinal acoustic phonons. These form a strong middle peak in the Figure 4(c). These 12.5 THz phonons most efficiently dissociate into ~ 8 THz and ~ 4.5 THz phonons. The 8 THz phonons most likely corresponds to zone-edge transverse acoustic phonons, represented by the first peak in PDOS. The 4.5THz phonons are acoustic, as there are no optical modes in that energy range. Efficient scattering into 8 THz phonons continues for higher energy phonons also, as shown by flat horizontal band in Figure 5(b) for ω_0 -phonons from ~ 12.5 THz to ~ 20 THz. The second strong scattering spot appear at 17.5 THz – this is the zone edge optical mode (third peak on the PDOS), and these phonons scatter very efficiently into the already mentioned flat 12.5 THz mode and some acoustic modes around 5 THz. It thus appears that the strong scattering processes involve phonons at peak PDOS, and whatever the phonons with the frequency equal to the difference between the peaks. In this case, $12.5-8=4.5$, $17.5-12.5=5$ and $17.5-8=9.95$ are the “hot spots” for three phonon scattering processes. This scattering map, in particular, helps to understand why there is a substantial decrease in phonons lifetimes at around 5 THz in Figure 4 (a).

5.3. Current limitations

From the programming perspective, the algorithm implemented in PhonTS scales unfavorably with regards to computational time ($\sim N^4 N_k^2$) and memory ($\sim N^2 N_k$) requirements. The first of these constraints is effectively mitigated by the parallelization of the code. The thermal conductivity calculations themselves are essentially a three-dimensional integration over first Brillouin Zone, a task that is efficiently parallelizable. Moreover, PhonTS includes the possibility of the parallelization over k-space, or over phonon modes; thus even for a system with a large number of atoms and fewer k-points, a highly parallel environment is usable. Unfortunately however, memory partitioning between processors is not nearly as straightforward, since the phonon-phonon interaction term requires the entire set of phonon eigenvectors to be available on each node. This is somewhat mitigated by the possibility of computing eigenvectors on the fly, though this substantially limits the execution speed. The memory requirements is therefore a real bottleneck that limits the size of the system studied and/or k-space resolution. The largest

system we have attempted consists of 128 atoms on a cluster of 128 nodes with 1 Gb RAM per node. This system probably represents the limit for the current implementation of PhonTS on a typical Linux cluster. Also, the current implementation is limited to simulation cells that have orthorhombic symmetry or higher; this is not a fundamental limitation, but simply reflects the problems that we have been interested in.

6. Conclusions

In this work we have presented PhonTS, an efficient tool for the calculations of the thermal conductivity via the solution of the BTE. The code has been thoroughly validated against other methods for calculations of thermal conductivity and against experimental data for the *ab-initio* calculations. We hope that the large array of capabilities that include both classical potentials and first principles calculations, efficient parallelization, a convenient input file, a host of output quantities and a detailed manual available online at <http://phonts.mse.ufl.edu> will make PhonTS a popular package for solution of the BTE for phonons.

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References

- [1] Z. Tian, S. Lee, and G. Chen, *J. Heat Transf.* 135 (2013) 061605.
- [2] S. Phillpot, A. El-Azab, A. Chernatynskiy, and J. Tulenko, *JOM* 63 (2011) 73–79.
- [3] V. Venkatadri, B. Sammakia, K. Srihari, and D. Santos, *J. Electron. Packaging* 133 (2011) 041011.
- [4] D. Clarke and C. Levi, *Annu. Rev. Mater. Res.* 33 (2003) 383–417.
- [5] W. Pan, S. R. Phillpot, C. Wan, A. Chernatynskiy, and Z. Qu, *MRS Bulletin* 37 (2012) 917–922.
- [6] S. Stackhouse and L. Stixrude, *Rev. Mineral. Geochem.* 71 (2010) 253–269.
- [7] A. J. C. Ladd, B. Moran, and W. G. Hoover, *Phys. Rev. B* 34 (1986) 5058–5064.
- [8] D. J. Evans and O. Morriss, *Comput. Phys. Rep.* 1 (1984) 297–343.
- [9] P. K. Schelling, S. R. Phillpot, and P. Keblinski, *Phys. Rev. B* 65 (2002) 144306.
- [10] S. Plimpton, *J. Comput. Phys.* 117 (1995) 1 – 19.
- [11] A. Maiti, G. Mahan, and S. Pantelides, *Solid State Communications* 102 (1997) 517 – 521.

- [12] M. A. Angadi, T. Watanabe, A. Bodapati, X. Xiao, O. Auciello, J. A. Carlisle, J. A. Eastman, P. Keblinski, P. K. Schelling, and S. R. Phillpot, *J. Appl. Phys.* 99 (2006) 114301.
- [13] R. J. Stevens, L. V. Zhigilei, and P. M. Norris, *Int. J. Heat Mass Transfer* 50 (2007) 3977 – 3989.
- [14] T. Watanabe, S. B. Sinnott, J. S. Tulenko, R. W. Grimes, P. K. Schelling, and S. R. Phillpot, *J. Nucl. Mater.* 375 (2008) 388 – 396.
- [15] E. S. Landry and A. J. H. McGaughey, *Phys. Rev. B* 80 (2009) 165304.
- [16] A. Bagri, S.-P. Kim, R. S. Ruoff, and V. B. Shenoy, *Nano Lett.* 11 (2011) 3917–3921.
- [17] B. Deng, A. Chernatynskiy, P. Shukla, S. Sinnott, and S. Phillpot, *J. Nucl. Mater.* 434 (2013) 203 – 209. Special Section on Spent Nuclear Fuel.
- [18] S.-C. Wang, X.-G. Liang, X.-H. Xu, and T. Ohara, *J. Appl. Phys.* 105 (2009) 014316.
- [19] D. Donadio and G. Galli, *Phys. Rev. Lett.* 102 (2009) 195901.
- [20] H. Kim, M. H. Kim, and M. Kaviani, *J. Appl. Phys.* 115 (2014) 123510.
- [21] N. de Koker, *Phys. Rev. Lett.* 103 (2009) 125902.
- [22] P. Klemens, *Solid State Physics*, vol. 7 1. Academic Press, Inc., New-York (1958).
- [23] J. Ziman, *Electrons and Phonons*. Clarendon Press, Oxford (1962).
- [24] A. Ward, D. A. Broido, D. A. Stewart, and G. Deinzer, *Phys. Rev. B* 80 (2009) 125203.
- [25] A. Chernatynskiy, J. E. Turney, A. J. H. McGaughey, C. H. Amon, and S. R. Phillpot, *J. Am. Ceram. Soc.* 94 (2011) 3523–3531.
- [26] A. Chernatynskiy and S. R. Phillpot, *Curr. Opin. Solid State Mater. Sci.* 17 (2013) 1 – 9.
- [27] S. Pettersson, *J. Phys. C Solid State* 20 (1987) 1047.
- [28] S. Pettersson, *Phys. Rev. B* 43 (1991) 9238–9246.
- [29] M. Omini and A. Sparavigna, *Physica B* 212 (1995) 101 – 112.
- [30] D. A. Broido, M. Malorny, G. Birner, N. Mingo, and D. A. Stewart, *Appl. Phys. Lett.* 91 (2007) 231922.
- [31] D. G. Cahill, P. V. Braun, G. Chen, D. R. Clarke, S. Fan, K. E. Goodson, P. Keblinski, W. P. King, G. D. Mahan, A. Majumdar, H. J. Maris, S. R. Phillpot, E. Pop, and L. Shi, *Appl. Phys. Rev.* 1 (2014) 011305.
- [32] N. Mingo, D. Stewart, D. Broido, L. Lindsay, and W. Li, “Ab initio thermal transport,” in *Length-Scale Dependent Phonon Interactions* (S. L. Shinda and G. P. Srivastava, eds.), vol. 128 of *Topics in Applied Physics* 137–173, Springer New York (2014).

- [33] G. Kanellis, W. Kress, and H. Bilz, *Phys. Rev. B* 33 (1986) 8733–8739.
- [34] A. Debernardi, S. Baroni, and E. Molinari, *Phys. Rev. Lett.* 75 (1995) 1819–1822.
- [35] G. Kresse and J. Hafner, *Phys. Rev. B* 47 (1993) 558–561.
- [36] G. Kresse and J. Hafner, *Phys. Rev. B* 49 (1994) 14251–14269.
- [37] G. Kresse and J. Furthmüller, *Phys. Rev. B* 54 (1996) 11169–11186.
- [38] G. Kresse and J. Furthmüller, *Comp. Mater. Sci.* 6 (1996) 15 – 50.
- [39] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *J. Phys.: Condens. Matter* 21 (2009) 395502.
- [40] W. Li, J. Carrete, N. A. Katcho, and N. Mingo, *Comput. Phys. Commun.* (2014) –.
- [41] J. Callaway, *Phys. Rev.* 113 (1959) 1046–1051.
- [42] M. G. Holland, *Phys. Rev.* 132 (1963) 2461–2471.
- [43] L. Chaput, *Phys. Rev. Lett.* 110 (2013) 265506.
- [44] A. Chernatynskiy and S. R. Phillpot, *Phys. Rev. B* 82 (2010) 134301.
- [45] M. L. Klein, G. K. Horton, and J. L. Feldman, *Phys. Rev.* 184 (1969) 968–978.
- [46] B. Fultz, *Prog. Mater. Sci.* 55 (2010) 247–352.
- [47] T. Lan, C. W. Li, J. L. Niedziela, H. Smith, D. L. Abernathy, G. R. Rossman, and B. Fultz, *Phys. Rev. B* 89 (2014) 054306.
- [48] I. P. Ipatova, A. A. Maradudin, and R. F. Wallis, *Phys. Rev.* 155 (1967) 882–895.
- [49] B. G. Dick and A. W. Overhauser, *Phys. Rev.* 112 (1958) 90–103.
- [50] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*. Oxford Univ Press (1954).
- [51] L. Lindsay, D. A. Broido, and T. L. Reinecke, *Phys. Rev. B* 87 (2013) 165201.
- [52] Y. Wang, J. J. Wang, W. Y. Wang, Z. G. Mei, S. L. Shang, L. Q. Chen, and Z. K. Liu, *J. Phys.: Condens. Matter* 22 (2010) 202201.
- [53] J. E. Turney, E. S. Landry, A. J. H. McGaughey, and C. H. Amon, *Phys. Rev. B* 79 (2009) 064301.
- [54] J. Gale, *Journal Of The Chemical Society-Faraday Transactions* 93 (1997) 629–637.

- 1
2
3
4 [55] M. Ross, *J. Chem. Phys.* 73 (1980) 4445–4450.
5
6 [56] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, *Rev. Mod. Phys.* 73 (2001) 515–562.
7
8 [57] K. V. Tretiakov and S. Scandolo, *J. Chem. Phys.* 121 (2004) 11177–11182.
9
10 [58] J. Tersoff, *Phys. Rev. B* 39 (1989) 5566–5568.
11
12 [59] P. C. Howell, *J. Chem. Phys.* 137 (2012) 224111.
13
14 [60] D. Wolf, P. Keblinski, S. Phillpot, and J. Eggebrecht, *J. Chem. Phys.* 110 (1999) 8254–8282.
15
16 [61] X. Tang and J. Dong, *Proc. Natl. Acad. Sci. U. S. A.* 107 (2010) 4539–4543.
17
18 [62] P. E. Blöchl, *Phys. Rev. B* 50 (1994) 17953–17979.
19
20 [63] D. G. Cahill, S.-M. Lee, and T. I. Selinder, *J. Appl. Phys.* 83 (1998) 5783–5786.
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Figure Captions:

Figure 1. Example of the minimal input file for PhonTS

Figure 2. Comparison of the thermal conductivity between MD and BTE for Ar, Si and UO_2 systems (a) as a function of temperature, (b) MD vs BTE

Figure 3. Thermal conductivity in MgO based on DFT/LDA calculations in comparison with the experimental results and previously published DFT/LDA results

Figure 4. (a) Phonon lifetimes as a function of frequency (b) Spectral thermal conductivity in MgO (arbitrary units) and (c) Phonon density of states. All data is at 300K

Figure 5. Scattering maps of the (a) recombination and (b) dissociation processes in MgO