INTEGRATION OF MOLECULAR DYNAMICS SIMULATIONS AND BOLTZMANN TRANSPORT EQUATION IN PHONON THERMAL CONDUCTIVITY ANALYSIS

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ABSTRACT

The thermal conductivity of the Lennard-Jones argon crystal is predicted using the Boltzmann transport equation under the single mode relaxation time approximation. The temperature and frequency dependence of the phonon dispersion and phonon relaxation times are obtained from lattice dynamics calculations based on the results of molecular dynamics simulations. No fitting parameters are required. The thermal conductivity results are in agreement with predictions from the simulations using the Green-Kubo method. Assuming that the dispersion is linear or temperature independent, as is often done in analytical calculations, leads to large errors in the predictions. This result suggests that the fitting parameters required in such calculations offset significant errors introduced by these simplifying assumptions.

Keywords: thermal conductivity, molecular dynamics simulations, phonon, single mode relaxation time

NOMENCLATURE

A constant
E energy (potential and kinetic)
F force vector
L length of simulation cell
N number of atoms
P projection of atomic coordinates onto normal mode
S normal mode coordinate

T temperature
U potential energy
V volume
a conventional unit cell parameter
cv specific heat
e polarization vector
g weighting function
h Planck constant divided by 2π
k thermal conductivity
kB Boltzmann constant
m mass
n phonon occupation number
n′ h(n)
qu heat flux vector
r position vector, particle separation vector
t time
u relative displacement vector
v velocity vector
x hω/kBT

Greek
Γ line width
εLJ Lennard-Jones energy scale
kk’ wave vector, wave number
σ standard deviation
σLJ Lennard-Jones length scale
τ relaxation time

*Address all correspondence to this author.
\[ \omega \] angular frequency

**Subscripts**
- \( L \): longitudinal
- \( N \): normal
- \( T \): transverse
- \( U \): Umklapp
- \( c \): effective relaxation time
- \( g \): group
- \( i \): label
- \( j \): label
- \( o \): equilibrium
- \( p \): phase
- \( r \): relaxation
- \( \lambda \): distribution towards which normal processes tend
- 1: short range acoustic phonons
- 2: long range acoustic phonons

**Superscripts**
- \( m \): constant
- \( n \): constant
- \( * \): dimensionless, complex conjugate
- \( \text{average} \): average value

**INTRODUCTION**

While the lattice dynamics of a harmonic solid can be readily analyzed \([1, 2]\), such a model predicts an infinite phonon thermal conductivity for a perfect crystal. To obtain a finite thermal conductivity, anharmonicities in the interatomic potential, which lead to three-phonon (and higher) processes, must be considered. The inclusion of even three-phonon interactions in the lattice dynamics is a formidable task. A number of solution techniques based on the Boltzmann transport equation (BTE) have been developed \([1]\). Notable are those involving the single mode relaxation time (SMRT) approximation, where every phonon mode is assigned a relaxation time corresponding to the net effect of different scattering mechanisms. A lack of understanding of multi-phonon interactions requires that the predictions be fit to the experimental data. Therefore, while such approaches are useful for qualitatively validating the models developed, the quantitative validity of the models cannot be assessed. As they are currently used, SMRT techniques are thus not suitable for the analysis of materials whose thermal properties are not already known.

The phonon thermal conductivity can also be predicted using the Green-Kubo (GK) method \([3]\) and molecular dynamics (MD) simulations. In this case, the analysis is based on a statistical mechanics approach, and is performed in real space. No assumptions about the nature of the thermal transport are required before determining the thermal conductivity. The only required inputs are the atomic positions and an appropriate interatomic potential.

This approach has generated reasonable agreement with experimental data for a number of dielectric materials \([4-9]\). Molecular dynamics is limited in applications to real devices by the small system sizes (\(\sim \)nm) required for reasonable computational times.

The finite size of an MD simulation cell leads to a discrete number of allowed phonon modes, for which relaxation times can be predicted using lattice dynamic techniques \([10, 11]\). The purpose of this investigation is to use the predicted phonon relaxation times from a Lennard-Jones (LJ) crystal to develop a continuous relaxation time model that can be used in the BTE-SMRT technique to predict the thermal conductivity. Such an approach will allow results from MD simulations to be applied to larger systems. A summary of this approach, and those described in the preceding two paragraphs, is shown in Fig. 1.

The BTE-SMRT and GK thermal conductivity prediction methods are introduced. The GK results are presented, and the decomposition of the thermal conductivity into components associated with short and long length scale interactions is de-
scribed. Two methods for predicting the phonon relaxation times using MD are presented and shown to be consistent. A continuous model for the relaxation times is developed, and together with temperature dependent dispersion data, is used to predict the thermal conductivity with the BTE-SMRT method. To our knowledge, this is the first such calculation performed with no fitting parameters. The GK and BTE-SMRT results agree to within their respective uncertainties. Common simplifications used in the BTE-SMRT method are investigated, and found to strongly affect the results.

**Thermal Conductivity Prediction**

**Boltzmann Transport Equation**

**Preliminaries** The BTE for a phonon mode \( i \) under a temperature gradient \( \nabla T \) is given by [1]

\[
-v_g,i \cdot \nabla T \frac{\partial n_i}{\partial T} + \left( \frac{\partial n_i}{\partial T} \right)_{\text{coll}} = 0, \tag{1}
\]

where \( n \) is the phonon mode occupation number, \( t \) is time and \( v_g \) is the phonon group velocity, defined as \( \partial \omega / \partial \mathbf{k} \), where \( \omega \) is the angular frequency and \( \mathbf{k} \) is the wave vector. Equation (1) predicts the steady state distribution of phonons in a system, and how that distribution comes about through the effects of diffusion (first term) and scattering (second term, also known as the collision term).

The main challenge in the solution of Eq. (1) is the modeling of the collision term. Under the SMRT approximation, a relaxation time, \( \tau_r \), is assigned to each phonon mode such that [1]

\[
\left( \frac{\partial n_i}{\partial t} \right)_{\text{coll}} = \frac{n_i - n_{i,o}}{\tau_r}, \tag{2}
\]

where \( n_o \) corresponds to the equilibrium phonon occupation number, given by the Bose-Einstein distribution. This relaxation time describes how the system will respond when that mode is activated and all others are at equilibrium. By using Eq. (2) to solve Eq. (1) for \( n \), neglecting the contribution of optical phonons, and assuming an isotropic phonon dispersion with degenerate transverse branches, the phonon thermal conductivity, \( k \), can be expressed as [12]

\[
k = \frac{1}{6\pi^2} \left( \int_0^{\omega_{L,max}} \omega L c_v \frac{v_g L}{v_p L} \tau_{r,L} \omega^2 d\omega + 2 \int_0^{\omega_{T,max}} \omega T c_v \frac{v_g T}{v_p T} \tau_{r,T} \omega^2 d\omega \right). \tag{3}
\]

Here, \( L \) and \( T \) correspond to longitudinal and transverse phonon modes, respectively, \( \omega_{L,max} \) is the frequency of branch \( i \) \((i = L, T)\) at the edge of the first Brillouin zone, \( c_v \) is the specific heat per mode at constant volume (and thus has units of \( J/K \)) and \( v_p \) is the phonon phase velocity, defined as \( \omega / \kappa \). All of the quantities inside the integral are functions of frequency.

**Callaway-Holland Approach** The challenge in the evaluation of the integrals in Eq. (3) is the specification of the phonon relaxation times and how the phonon dispersion (which affects the velocity terms and the upper limit of the integration) is modeled. In the current investigation, an MD simulation cell with periodic boundary conditions and no defects is used, so that the only source of phonon scattering is through anharmonic interactions between the normal modes. There are two types of interactions: normal \((N)\) processes, which conserve crystal momentum, and Umklapp \((U)\) processes, which do not. An effective relaxation time for each mode, \( \tau_i \), is then defined as [13]

\[
\frac{1}{\tau_i} = \frac{1}{\tau_{i,c}} + \frac{1}{\tau_{i,N}} + \frac{1}{\tau_{i,U}}. \tag{4}
\]

Note that \( \tau_c \) is not the same as the relaxation time \( \tau_r \) that appears in Eq. (3). This is because the \( N \) and \( U \) processes have different effects on the phonon distribution, such that in this formulation, the collision term must be modeled as [13]

\[
\left( \frac{\partial n_i}{\partial t} \right)_{\text{coll}} = \frac{n_{i,\lambda} - n_i}{\tau_{i,N}} + \frac{n_{i,o} - n_i}{\tau_{i,U}}, \tag{5}
\]

where \( n_{i,\lambda} \) is the distribution that normal processes tend towards. The relationship between \( \tau \), \( \tau_c \), \( \tau_N \) and \( \tau_U \) was first established by Callaway [13].

The \( \tau_N \) and \( \tau_U \) terms are generally modeled with expressions of the form [13-20]

\[
\frac{1}{\tau_i} = A \omega m T^n, \quad i = N, U, \tag{6}
\]

where \( m \) and \( n \) are integers and \( A \) is a constant. The choice of \( m \) and \( n \) is often based on predictions limited to low frequencies (where an elastic medium can be assumed), or for convenience in the subsequent calculations. At low temperatures, it has been predicted that the sum of \( m \) and \( n \) should be five, and at high temperatures, that \( n \) should be unity [1, 15]. There is no available method for predicting the \( A \) coefficients, and closure of SMRT techniques is dependent on the fitting of these parameters with the experimental data. There is no comprehensive closed form expression available for the relaxation times that covers the entire frequency and temperature range for a given material. As will be shown, an expression of the form of Eq. (6) is not adequate for this purpose.

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Using a formulation based on Eq. (5) in modeling germanium, Callaway [13] used a Debye model for the phonon density of states (i.e., linear dispersion), did not distinguish between longitudinal and transverse polarizations, and accounted for the three phonon interactions using terms with \( m \) and \( n \) equal to two and three, respectively. The resulting expression for the thermal conductivity contained two terms. The first was in the form of Eq. (3) with \( \tau_r \) equal to \( \tau_c \). The second term, often referred to as the Callaway correction term, results from the different effects of \( N \) and \( U \) processes described by Eq. (5). Scattering from imperfections and at boundaries was included. The fitted function gives reasonable values below and around the maximum in the thermal conductivity \((\approx 12 \, \text{K})\), but not at higher temperatures [16].

Holland [16] extended the work of Callaway by separating the contributions of longitudinal and transverse phonons, slightly improving the phonon dispersion model, and using different forms of the relaxation times. Better high temperature agreement than the Callaway model was found for germanium. The Callaway correction term was ignored. The Holland model has since been used to investigate many other materials, and refined to account for more realistic phonon dispersion [18], the effect of the Callaway correction term [19], and additional scattering mechanisms [20] (e.g., four phonon processes and dislocations). The added complexity leads to more fitted parameters. One could argue that better fits with the experimental data are a result of the additional fitting parameters, and not an improvement of the actual physical model.

More refined BTE-SMRT models have been developed [1], and solutions based on variational methods exist [21]. However, due to the complexity of the required calculations, investigators continue to use the models of Callaway and Holland with only slight modifications, due to the ease with which they can be implemented and their general success.

**Green-Kubo Method: Statistical Mechanics Approach**

In an MD simulation, the position and momentum space trajectories of a system of particles are determined using interatomic forces calculated from an appropriate potential energy function, Newton’s second law, and the kinematic equations of motion. The net flow of heat, given by the heat current vector \( \mathbf{q} \), fluctuates about zero at equilibrium. In the Green-Kubo method, the thermal conductivity is related to how long it takes these fluctuations to dissipate, and is given by [3]

\[
k = \frac{1}{k_B V T^2} \int_0^\infty \langle \mathbf{q}(t) \cdot \mathbf{q}(0) \rangle \, dt,
\]

where \( k_B \) is the Boltzmann constant, \( V \) is the volume of the simulation cell, and \( \langle \mathbf{q}(t) \cdot \mathbf{q}(0) \rangle \) is the heat current autocorrelation function (HCACF). The heat current vector for a pair potential is given by [3]

\[
\mathbf{q} = \frac{d}{dt} \sum_i E_i \mathbf{r}_i = \sum_i E_i \mathbf{v}_i + \frac{1}{2} \sum_{ij} (\mathbf{F}_{ij} \cdot \mathbf{v}_i) \mathbf{r}_{ij},
\]

where \( E_i, \mathbf{r}_i, \mathbf{v}_i \) are the energy, position vector, and velocity vector of a particle, respectively, and \( \mathbf{r}_{ij} \) and \( \mathbf{F}_{ij} \) are the inter-particle separation vector and force vector between particles \( i \) and \( j \), respectively. The Green-Kubo method has been used in simulations of materials such as LJ argon [5, 8], \( \beta \)-silicon carbide [6], silicon [7], amorphous silicon [4], and silica based crystals [9].

It has been shown [8] that the thermal conductivity of a crystal with a monatomic unit cell can be decomposed into contributions from short and long length scale interactions by fitting the HCACF to a function of the form

\[
\frac{\langle \mathbf{q}(t) \cdot \mathbf{q}(0) \rangle}{3} \equiv A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2).
\]

Here, the subscripts 1 and 2 refer to short range and long range acoustic phonon components, respectively, the \( A \) terms are constants, and the \( \tau \) terms are time constants. Using Eqs. (7) and (9),

\[
k = \frac{1}{k_B V T^2} (A_1 \tau_1 + A_2 \tau_2) \equiv k_1 + k_2.
\]

The short range component is associated with phonons with a mean free path equal to one half of their wavelength (the limiting physical value), while the long range component describes phonons with longer mean free paths. The short range component and its associated time constant are independent of temperature. The long range component is temperature dependent. It accounts for the majority of the thermal conductivity except at high temperatures, where it is diminished due to the increased anharmonicity in the atomic interactions brought about by larger atomic displacements.

The MD approach cannot explicitly take into account quantum effects, although temperature and thermal conductivity scaling factors have been suggested [4, 6, 7]. This technique is thus not suitable near and below the maximum in the thermal conductivity. In this region, the temperature and frequency dependence of the specific heat are important, which is only properly modeled in a full quantum mechanical treatment. The thermal conductivity in this region is also strongly affected by impurities and boundary effects, which are not considered in the current investigation. Thus, a classical MD simulation of a perfect crystal with periodic boundary conditions will lead to an infinite thermal conductivity at zero temperature.
MOLECULAR DYNAMICS SIMULATIONS

A face-centered cubic LJ crystal is studied. The plane formed by the [100] and [010] axes is shown in Fig. 2. In the figure, $a$ is the side length of the conventional unit cell and $L_i$ ($i = x, y, z$) is the length of side $i$ of the simulation cell. This leads to $L_i/a$ unit cells in the $i$ direction.

The potential energy, $U_{ij}$, between atoms $i$ and $j$ ($i \neq j$) is given by [22]

$$U_{ij}(r_{ij}) = 4\varepsilon_{\text{LJ}} \left[ \left( \frac{\sigma_{\text{LJ}}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{\text{LJ}}}{r_{ij}} \right)^{6} \right]. \quad (11)$$

The depth of the potential energy well is $\varepsilon_{\text{LJ}}$, and corresponds to an equilibrium particle separation of $2^{1/6}\sigma_{\text{LJ}}$. The LJ potential describes the Noble elements well. Argon, for which $\sigma_{\text{LJ}}$ and $\varepsilon_{\text{LJ}}$ have values of $3.40 \times 10^{-10}$ m and $1.67 \times 10^{-21}$ J, respectively [22], is chosen for the current investigation. The use of a simple system allows for fast simulation runs and the elucidation of results that may be difficult to resolve in more complex materials.

The simulations are run in the NVE (constant mass, volume and energy) ensemble at zero pressure, and periodic boundary conditions are imposed in all directions. Here, results at a temperatures 50 K are presented. The details of the procedures have been described elsewhere [8]. The only significant changes are that the potential cutoff is fixed at 2.5$\sigma_{\text{LJ}}$ and no correction is made to the pressure calculation. These changes ensure that the atomic spacing is the same in different sized simulation cells.

GREEN-KUBO THERMAL CONDUCTIVITY PREDICTION

The simulation cells considered and the predicted thermal conductivities using the GK method are given in Table 1. Each set of data corresponds to the average of five independent simulations. For the $4 \times 4 \times 4$ and $5 \times 5 \times 5$ configurations, two sets of five simulations were performed. In subsequent discussions, the data presented corresponds to the second of each of these, unless noted. Also included is the decomposition of the thermal conductivity into the short range and long range components and the associated time constants.

The thermal conductivity predictions fall within ±4% of the mean value, which is consistent with previous results [8]. The results are lower than our previously reported data [8], due to the smaller lattice spacing that results from the smaller potential cutoff and removal of the pressure correction. There is no size effect, consistent with the result of Kaburaki et al. for $N > 256$ [5]. Compared with the total thermal conductivity, there is more variation in the components of the thermal conductivity decomposition and associated time constants, which is due to the nature of the fit of Eq. (9). While the total value of the resulting integral is consistent, there is some ‘exchange’ between the two terms around the transition point where the dominant behavior changes from $\tau_1$ to $\tau_2$.

BOLTZMANN TRANSPORT EQUATION FORMULATION

To use Eq. (3) to predict the thermal conductivity, $c_v$, $\tau_r$, $v_g$, and $v_p$ must be specified.

Specific Heat

The specific heat is defined as the rate of change of the total system energy (kinetic and potential) as a function of temperature at constant volume [22]. At a temperature of 50 K, the MD simulations give a value for $c_v$ of 0.940$k_B$. This value is used in the subsequent calculations. No frequency dependence is taken into account. The classical value of the specific heat, $k_B$, which is often used in MD calculations, is based on an assumption of equipartition of kinetic and potential energy between modes. The
equipartition assumption is always valid for the kinetic energy. However, for the potential energy, it is only true under the harmonic approximation, which itself is only valid at zero temperature.

**Phonon Relaxation Time**

In a simulation cell with \( N \) atoms, there are \( N \) points in the first Brillouin zone, each of which has one longitudinal and two transverse modes associated with it. This leads to the \( 3N \) normal modes. By assuming an isotropic phonon dispersion, a smaller subset can be considered in the thermal conductivity calculation. Here, the [100] direction is chosen. There will be \( 6 \) points within the first Brillouin zone to form a continuous \( \tau \) function, different sized simulation cells must be considered. These are listed in Table 1. Two methods by which the relaxation time may be calculated are examined.

**Phonon Occupation Number Method** Ladd et al. [10] present a method by which the relaxation time is found using a calculation of the phonon occupation number (referred to here as the \( n \)-method).

The normal modes of a system, \( S(\mathbf{q}, \mathbf{v}) \), where \( \mathbf{q} \) is the wave vector, and \( \mathbf{v} \) corresponds to the mode polarization described by a vector \( \mathbf{e}(\mathbf{q}, \mathbf{v}) \), can be expressed as a sum over the positions of the atoms in the system as

\[
S(\mathbf{q}, \mathbf{v}) = N^{-1/2} \sum_{i} m_i^{1/2} \exp(-i\mathbf{q} \cdot \mathbf{r}_{i,o}) \mathbf{e}^\ast(\mathbf{q}, \mathbf{v}) \cdot \mathbf{u}_i. \tag{12}
\]

Here, \( m \) is the mass of an atom, \( ^\ast \) denotes the complex conjugate, \( \mathbf{r}_{i,o} \) is the equilibrium position of atom \( i \), and \( \mathbf{u}_i \) is the relative displacement of atom \( i \) from its equilibrium position (i.e., \( \mathbf{r}_i - \mathbf{r}_{i,o} \)).

Under the harmonic approximation, the expectation value of the energy of each mode of a classical system is given by

\[
\langle E_{i,c} \rangle = \omega_i^2 \langle S_i^\ast S_i \rangle, \tag{13}
\]

where the \( \langle \rangle \) brackets indicate an ensemble average. For the associated quantum system, the expectation value of the energy is

\[
\langle E_{i,q} \rangle = \hbar \omega_i \langle n_i \rangle, \tag{14}
\]

where \( \hbar \) is the Planck constant divided by \( 2\pi \). As the MD simulations are classical, they do not have the zero-point energy, and the factor of \( 1/2 \) normally appearing in Eq. (14) is not included. The energy of the classical and quantum systems must be the same, and by using Eq. (12), and defining \( n_i' \) as \( \bar{h}(n_i) \),

\[
n_i' = \omega_i\langle S_i^\ast S_i \rangle = \frac{m_0\omega_i}{N} \langle |\mathbf{e}^\ast(\mathbf{q}, \mathbf{v}) \cdot \sum_{i} \exp(-i\mathbf{q} \cdot \mathbf{r}_{i,o}) \mathbf{u}_i|^2 \rangle. \tag{15}
\]

The temporal decay of the autocorrelation of \( n_i' \) (based on deviations from its mean value) is related to the relaxation time of that mode. The resulting curve for the transverse polarization at \( \kappa^* = 0.5 \) for the \( 4 \times 4 \times 4 \) simulation cell is shown in Fig. 3(a). The ensemble averaging is realized by averaging the autocorrelation functions over the [100], [010] and [001] directions over five independent simulations. This leads to fifteen data sets for the longitudinal polarization and thirty data sets for the transverse polarization. It has been found that the best way to obtain the relaxation time is to fit the envelope formed by the maxima with an exponential decay, starting at the second maximum after the zero time intercept. This fit is shown in the plot. Based on this formulation, the calculated time constant must be multiplied by two to get the value to be used in the BTE. The frequency of the oscillations within the decay envelope is double that of the phonon mode in question because of the squaring operation in Eq. (15).

**Normal Mode Projection Method** The relaxation time can also be calculated using a modification of the technique of Oligschleger and Schon (referred to here as the \( P \)-method) [11]. They suggest applying a perturbation to a system corresponding to a particular eigenvector, and then observing how the projection of the system coordinates onto that mode, \( P(\mathbf{q}, \mathbf{v}) \), decays with time. That is, observing

\[
P(\mathbf{q}, \mathbf{v}) = \sum_i \mathbf{u}_i \cdot \mathbf{e}(\mathbf{q}, \mathbf{v}) \sin \left( \frac{2\pi \mathbf{q} \cdot \mathbf{r}_{i,o}}{d} \right). \tag{16}
\]

A drawback to this approach is that the simulation cell is not at equilibrium during the relaxation. If the simulation is done in the \( NVE \) ensemble (as all runs here are), the temperature will not be constant during the decay of the mode due to the extra potential energy introduced by the perturbation. This makes it difficult to associate a specific temperature with the calculated relaxation time. As an alternative to this approach, we instead observe \( P(\mathbf{q}, \mathbf{v}) \) in the equilibrium system, and then form its autocorrelation. The result for the transverse polarization at \( \kappa^* = 0.5 \) for the \( 4 \times 4 \times 4 \) simulation cell is shown in Fig. 3(b). As with Fig. 3(a), the result shown is based on averaging over three directions and five independent simulation runs. Here, the oscillation frequency within the envelope matches the phonon frequency, and the decay envelope corresponds to the relaxation time. The most
consistent way to obtain the relaxation time from this approach is to fit the envelope formed by the absolute value of the extrema with an exponential decay starting at the second extremum after the zero time intercept.

Analysis and Comparison of the $n$- and $P$-Methods

An indication of the error in the relaxation time prediction can be obtained by finding $\tau_r$ for each of the samples in the ensemble average before averaging the autocorrelation functions, and looking at the resulting spread. The mean values and standard deviations for all $n$-method cases corresponding to the $4 \times 4 \times 4$ simulation cell are given in Table 2. The standard deviation is on average 12% of the mean value for the longitudinal direction and 21% for the transverse direction.

A comparison of the $n$- and $P$-methods for the $4 \times 4 \times 4$ simulation cell is given in Table 3. The numerical results are slightly different than those in Table 2 as here the autocorrelation functions have been averaged before the relaxation time is obtained. The two methods agree to within at most 12% of their average value (for the longitudinal polarization and $\kappa^* = 0.5$), within one standard deviation of the predicted spread for that case (16%). In subsequent calculations, the $n$-method is used. Its associated autocorrelation function is found to have less noise than that from the $P$-method, which results in a smoother envelope for fitting the exponential decay.

Continuous Relaxation Time Functions

Having obtained a series of discrete $\tau_r$ values for a given temperature and polarization, a continuous function must now be constructed. The results at a temperature of 50 K are plotted as $1/\tau_r$ vs. $\omega$ [after Eq. (6)], in Fig. 4.

To be physically meaningful, the mean free path of a phonon should be longer than one half of its wavelength [23]. This limit can alternatively be stated as

$$\frac{1}{\tau_r} \leq \frac{\omega v_p}{\pi v_p},$$

(17)
and is also shown in Fig. 4. Relaxation times that satisfy Eq. (17) fall below these curves. The phonons at the edge of the Brillouin zone (κ* = 1) are outside of the allowed range at this temperature for both polarizations, and are not considered in the subsequent fits.

The data for each polarization can be broken into two distinct regions, which are fit with low-order polynomials. For the longitudinal polarization, the first region is fit with a linear function through the origin, and the second region is fit with a third order polynomial. For the transverse polarization, the first region is fit with a second order polynomial through the origin, and the second region is fit with a linear function. In both cases, the switch in the functional form takes place at a κ* value of 0.4.

The resulting functions are also shown in Fig. 4 and are considered satisfactory fits to the MD data. The continuous relaxation time functions are taken up to the maximum frequency using Eq. (17). Theoretical calculations predict that in the κ* range of 0 to 0.2, the longitudinal and transverse curves should follow ω2 and ω dependencies, respectively [15, 17]. This is not seen in the relaxation times predicted by the MD simulations. The average value of τ2 obtained in the GK thermal conductivity decomposition is also shown in Fig. 4.

Phonon Dispersion

Deviation of the phonon dispersion from the zero temperature, harmonic calculation (which is made based on equilibrium atomic positions) is a result of two effects [2]. Based on the higher order terms in the expansion of the potential energy about its minimum, the solid will either expand (as seen here), or contract (e.g., some zeolites), as the temperature increases. An expansion will cause the phonon frequencies to decrease. Recalculating the dispersion harmonically with the new lattice constant is known as the quasi-harmonic approximation [2]. The second effect is a result of anharmonicities in the atomic interactions, which become increasingly important as the temperature is increased, due to larger phonon populations. The exact modeling of this effect is difficult. To account for anharmonic effects, the phonon occupation number autocorrelation data can be used to calculate the frequencies of the allowed modes in the MD simulations. This is shown in Fig. 3(a). An estimate of the anharmonic frequency is obtained by averaging over all non-negligible oscillations in the autocorrelation. This generates a set of discrete frequency data. The percentage deviation of each anharmonic frequency from the associated quasi-harmonic frequency is then calculated, and used to generate a continuous scaling function based on a low order polynomial. This function is then applied
Table 4. BTE-SMRT THERMAL CONDUCTIVITY VALUES. \( k_{\text{BTE}} = k_L + 2k_T \). THE SPECIAL CASES CORRESPOND TO (a) LINEAR DISPERSION, (b) \( T = 0 \) K DISPERSION, (c) QUANTUM SPECIFIC HEAT, (d) SINGLE RELAXATION TIME (\( \tau_2 \)).

<table>
<thead>
<tr>
<th></th>
<th>( k_L ), W/m-K</th>
<th>( k_T ), W/m-K</th>
<th>( k_{\text{BTE}} ), W/m-K</th>
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<tr>
<td>Correct Model</td>
<td>0.187</td>
<td>0.085</td>
<td>0.357</td>
</tr>
<tr>
<td>(a)</td>
<td>0.228</td>
<td>0.118</td>
<td>0.464</td>
</tr>
<tr>
<td>(b)</td>
<td>0.237</td>
<td>0.111</td>
<td>0.459</td>
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<tr>
<td>(c)</td>
<td>0.182</td>
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<tr>
<td>(d)</td>
<td>0.155</td>
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BOLTZMANN TRANSPORT EQUATION THERMAL CONDUCTIVITY PREDICTION

Having specified the heat capacity, phonon velocities, and phonon relaxation times, the thermal conductivity can be calculated from Eq. (3). As the LJ face centered cubic crystal has a monatomic unit cell, there are only acoustic phonon modes present, and the assumption of neglecting optical phonon modes is not relevant. The results at a temperature of 50 K are given in Table 4, and are identified as ‘Correct Model’. Included are the total value of the thermal conductivity and its decomposition into longitudinal and transverse components. In Fig. 6, the cumulative frequency dependence of the thermal conductivity is shown. The total predicted value is 0.357 W/m-K. Considering the many steps and fits needed to get to this final result, the agreement with the mean GK value of 0.339 W/m-K is very good (within ~5%).

To assess the importance of the detail used in the modeling of the terms in Eq. (3), a number of simplifications can be investigated. The results are summarized in Table 4 and shown in Fig. 7 for the following cases: (a) assuming linear dispersion [i.e. \( v_g = v_p \)], so that \( v_g/v_p^2 = 1/v_g \), with the value taken as the mean GK value of 0.339 W/m-K is very good (within ~5%).

\( k^* = 0 \) intercept of Fig. 5(b), (b) using the zero temperature dispersion relation, (c) using the frequency dependent quantum specific heat, \( k_B x^2 e^x/(e^x - 1)^2 \), where \( x = \hbar \omega/k_B T \) (the classical specific heat is found by taking the limit of the quantum expression as \( x \rightarrow 0 \)), and (d) using a single time constant, taken as \( \tau_2 \) from the thermal conductivity decomposition of Eq. (10).

Using a linear phonon dispersion results in an over prediction of thermal conductivity. As is evident in Fig. 5(b), taking \( v_g/v_p^2 \) to be constant and equal to the \( k^* = 0 \) value will overemphasize the contributions of higher frequencies. Using the zero temperature dispersion also results in an over prediction of the thermal conductivity [due to the extension of the integration limits in Eq. (3)]. Use of the quantum specific heat does not have a significant effect. This is because at a temperature of 50 K, the maximum value of \( x \) is 1.51, and the total specific heat is close to the classical simulation value. Our preliminary results at other temperatures indicate that the effect of using the quantum specific heat becomes more significant at lower temperature, as would be expected. Using \( \tau_2 = 2.612 \) ps as a single relaxation time under predicts the thermal conductivity. This is because there is no significant low frequency contribution. To obtain the same result as the Correct Model using a single relaxation time, a value of 3.32 ps must be chosen. These results indicate that taking into account the temperature and frequency dependence of the relaxation times and phonon dispersion is crucial for obtaining a good prediction of the thermal conductivity.

To compare the GK method to the BTE-SMRT method, the cumulative frequency dependence of the thermal conductivity predicted by Eq. (7) can also be considered [8]. This is shown in Fig. 6. The GK curve corresponds to the first 4 \( \times \) 4 \( \times \) 4 simulation cell from Table 1. The oscillations are a function of the
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normal modes as [10] relaxation must be distinguished. This is seen by expressing the phonon frequency and the frequency associated with the phonon spectrum. To understand this behavior, the difference between the GK method is much smaller than that of the phonon spectrum. The frequency range covered by periodic boundary conditions. The frequency range covered by the GK method is much smaller than that of the phonon spectrum. To understand this behavior, the difference between the phonon frequency and the frequency associated with the phonon relaxation must be distinguished. This is seen by expressing the normal modes as [10]

\[ S_i = S_i,0 \exp[-i(\omega t + i\Gamma_i)] \]  

(18)

where \( \Gamma \) is the line width, equal to \( 1/2\tau_r \) (this is the factor of two that comes into the relaxation time calculation in the \( n \)-method). In the BTE formulation, the integral is over the phonon frequency, \( \omega \). In the GK formulation, the integral is over the frequency corresponding to the phonon lifetime, \( 2\Gamma \), which will be many times the period of oscillation, \( 2\pi/\omega \).

DISCUSSION AND CONCLUSION

The quantitative validity of the BTE-SMRT approach for predicting the phonon thermal conductivity has been validated. The success of the predictions is strongly dependent on the complete modeling of the temperature and frequency dependence of the phonon dispersion and relaxation times. This has been accomplished using lattice dynamics calculations based on the results of MD simulations. Two methods for determining the relaxation times have been presented and found to be equivalent. The \( n \)-method, based on the calculation of the phonon occupation number, was used in the thermal conductivity calculations because of the consistency of the generated data. The assumptions commonly made in the Callaway-Holland approach (linear, temperature independent dispersion) lead to poor predictions, which suggests that the previous success of these models was strongly dependent on fitting the results to existing experimental data (i.e., using empirical constants). The methods described can be extended to other dielectric crystals, including those with multi-atom unit cells (where optical phonons will be important).

Two sets of time constants have been introduced: those associated with the relaxation of particular phonon modes (\( \tau_r \)), and those associated with the thermal conductivity decomposition (\( \tau_1 \) and \( \tau_2 \)). Both sets of relaxation times can be used to predict the thermal conductivity, and good agreement in the results has been found. This agreement suggests that there is some link between these time constants, likely of the form

\[ \tau_i = \sum_j \int_0^{\omega_{\text{max},T}} g_j(\omega) \tau_{ij} d\omega \]  

(19)

where \( i \) is 1 or 2, the sum is over the phonon polarizations, and \( g(\omega) \) is a weighting function. The form of the weighting function may be related to the phonon distribution function and nature of the three-phonon interactions.

The plots of thermal conductivity in Figs. 6 and 7 dispel a common notion that the low frequency/long wavelength modes dominate the thermal conductivity. In fact, long length scale behavior is important [the \( k_2 \) term in Eq. (10)], but it is the phonon mean free path, and not its wavelength, that is relevant. This is the important distinction seen when comparing the GK and BTE results in Fig. 6, as described by Eq. (18).

The development of relaxation time models is useful for thermal conductivity calculations as used, but will also be applicable to other types of calculations using the BTE, including numerical solutions based on the equation of radiative heat transfer [24] and direct simulation Monte Carlo techniques [25].

The described work is ongoing. Efforts are underway to collect data in the temperature range of 20 to 80 K, so that the temperature dependence of the relaxation times can be investigated. This will also allow for verification of the suitability of the techniques developed.

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