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Dear Dr. Satish Jumar:

Thanks to the reviewers for the thoughtful comments on our manuscript: MNHMT2012-75071: COMPARISON OF SPECTRAL ENERGY DENSITY METHODS FOR PREDICTING PHONON PROPERTIES, in submission for the ASME 2012 3rd Micro/Nanoscale Heat and Mass Transfer International Conference. We believe we have addressed the issues brought up by the reviewers, which we highlight below.

Reviewer 1:

This paper compares different methods to compute phonon lifetimes. The paper is well written and provides a significant addition to the literature of computation of phonon properties.

The authors should comment on the expected numerical error in computing phonon lifetime by fitting the spectral peaks with Lorentzian functions using a non-linear least squares method.

To address this comment, we add the following to the updated draft:

The phonon frequencies and lifetimes have been extracted for all allowed wavevectors in the first Brioullin zone (BZ) of the cubic conventional cell using both expressions for the spectral energy. This is done by fitting the spectral peaks with Lorentzian functions using a non-linear least squares method. For Φ', the SED for different polarizations at a given wavevector are superimposed by definition of Eq$.$ \ref{Lorentzian_SED}. For Φ or Φ', the different polarizations can each be fit individually using single Lorentzian peaks or simultaneously as a superposition of peaks. At the temperatures studied in this work, we find that the difference between fitting single or simultaneous peaks is less than 5 percent. The error in fitting the Lorentzian functions is between $5-10\%$, with the error increasing with temperature.

Reviewer 2:

This paper compares the computation of phonon properties using spectral energy densities from lattice dynamics and molecular dynamics simulations. Overall the paper makes a good contribution to the existing literature on computation of phonon relaxation times and thermal conductivity. However, the reviewer recommends the authors to address the following issues in the final manuscript

It remains unclear if the spectral energy density {\Phi} (defined by eq. 15) is also computed from molecular dynamics. It appears that the potential energy function and its harmonic/anharmonic derivatives should suffice for the calculation of {\Phi}, since {\Gamma} may be calculated through the procedure detailed in [11]. Please clarify this point since the comment on page 4 suggests that MD is used for computing both the spectral energy densities.

We add this to the updated draft:

To calculate Φ one uses Eq. 12. The allowed wavevectors are determined by the crystal structure and the atomic velocities are supplied by MD simulation. Φ also requires the phonon mode eigenvectors which can be determined {\em a priori} using quasi-harmonic lattice dynamics (QHLD) calculations, which uses the temperature-dependent zero-pressure lattice constant.\cite{mcgaughey2006b}

And this:

Typically, anharmonic LD calculations are limited to 3-phonon scattering events, which is only a good assumption at low temperatures.\cite{turney2009a,esfarjani2011} All order phonon processes are possible in MD simulation as the atoms are evolved dynamically using the full anharmonicity of the interatomic interactions.\cite{mcgaughey2004c,landry2008,schelling2002} Thus, the lifetimes predicted by Eq$.$ \eqref{E:Lorentzian_NMD} include the effect of n-phonon scattering events.

Thus, Eq. 15 is calculated from MD simulation, just as Eq. 22. The procedure outlined in [11] uses anharmonic lattice dynamics, which does not require input from MD. However, the anharmonic lattice dynamics calculations in [11] are limited to 3-phonon scattering events, while the Eq. 15 includes n-phonon scattering events since it is calculated using MD.

The low temperature approximation of the LD methods and how that leads to errors should be discussed in more detail. Is this because four and higher order phonon scattering processes are neglected? Fig 1 seems to suggest otherwise - since the agreement between LD and MD derived SED's looks better at 40 K whereas they are 1-2 orders of magnitude apart at 5 K. What is the origin of "the shifting of peaks in magnitude" - does this have to do with choice of the constant Aj and Bj ?

We add this:

As temperature increases, n-phonon events start to occur naturally in MD because the full anharmonic interatomic interactions are used. The normal mode decomposition method [Eq$.$ \eqref{E:Lorentzian_NMD}] does lose accuracy at higher temperatures because the quasi-harmonic phonon frequencies and eigenvectors are used to perform the energy mapping \cite{turney2009a}. A comparison between LD (anharmonic LD, normal mode decomposition) and MD (non-equilibrium direct-MD, equilibrium Green-Kubo) for LJ argon shows that LD techniques start to diverge from the MD results for the thermal conductivity above half the melting temperature. In this paper, we limit the temperature to below half the melt temperature of both Lennard-Jones argon and Stillinger Weber silicon. In this work, we are not testing the effects of n-phonon scattering events but rather are showing that Φ' is an incorrect phonon SED by comparing it directly to $\Phi.$

The source of discrepancy in the phonon relaxation time between the two methods remains somewhat unaddressed. Is this in part due to a potential that is not strictly third order anharmonic? When

calculating eq. (22), no particular mode excitation is done and the system is thermodynamically simulated through MD which brings up the question of whether the measured linewidth depends on the excitation of other phonon groups (over their equilibrium population at a given temperature) - does this cause any additional scatter in the comparison of phonon lifetime between the two methods?

The source of discrepancy between the two SED methods is because the phonon energy is not mapped properly using Φ'. We add this comment:

The phonon spectral energy density Φ is well-defined theoretically,\cite{dove1993,wallace1972} while Φ' does not properly map the phonon energies since it is missing the phonon eigenvector. We deduce that this is the reason Φ' cannot accurately predict the phonon lifetimes.

Φ' was originally formulated to measure phonon dispersion curves [14], which only requires measuring the phonon frequencies. Since Φ' does not map the crystal energy to the phonon energy correctly, we must deduce that this is the reason it does not accurately predict the lifetimes. We recommend that Φ' be used only for measuring phonon dispersion, as in the original formulation \cite{marayuma2003}.

Please comment on the error associated with a typical relaxation time calculation (such as shown in Fig. 2) - due to MD initial conditions as well as the error in measuring the linewidth from the Lorentzian fitting. Does this alter any conclusions about the disagreement between the two methods?

The error associated with different MD initial conditions is much smaller than the error in fitting the peaks. We added these comments, also in response to Reviewer 1:

This is done by fitting the spectral peaks with Lorentzian functions using a non-linear least squares method. For Φ', the SED for different polarizations at a given wavevector are superimposed by definition of Eq$.$ \ref{Lorentzian_SED}. For Φ or Φ', the different polarizations can each be fit individually using single Lorentzian peaks or simultaneously as a superposition of peaks. At the temperatures studied in this work, we find that the difference between fitting single or simultaneous peaks is less than 5 percent. The error in fitting the Lorentzian functions is between $5-10\%$, with the error increasing with temperature.

We feel that these additions address the reviewers comments,

Sincerely,

Jason Larkin