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Journal of Physics: Condensed Matter

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Dear Rosalind Barrett and Kayleigh Parsons:

Thank you for organizing the review of our manuscript CM/436836/PAP/289167: “Comparison and evaluation of spectral energy methods for predicting phonon properties.” Based on the referees’ reports, we believe that the objective, contribution, and importance of our manuscript were not clear to Referees 1 and 2. We are convinced that our manuscript is suitable for Journal of Physics: Condensed Matter and argue so in our response to the referee comments below.

Before addressing the referee comments, however, we first want to emphasize the significant contributions of this manuscript:

1. The demonstration that the Phi’ method for predicting phonon properties (which was previously proposed but never comprehensively validated) is incorrect, while it has been (and continues to be) used in research articles.
2. The formal derivation of the Phi method for predicting phonon properties (which is rigorous and correct) in the frequency domain. This new formulation has not been published before and has particular advantages over a similar time-domain approach described previously.

**Response to Referee 3** (referee’s text in *“italics”*)

We thank Referee 3 for the positive comments.

*1. “Can the authors comment on the applicability of these methods for oxideslike UO2 which are nuclear fuel materials and for which studies of thermal conductivity is*

*very important? In addition to changes in the nature of interaction (interatomic potentials), would additional changes be required? Interatomic potentials for UO2 have been reported in the literature (Goel et al., Journal of Nuclear materials, 377, 438(2008))”*

The Φ method can be used to predict the phonon properties and thermal conductivity for any material system where there are available interatomic potentials. The form of the interatomic potential does not affect the methodology beyond any standard changes in the harmonic lattice dynamics calculations and/or molecular dynamics simulations. For example, oxide potentials will contain long-range electrostatic terms that require special treatment (e.g., an Ewald sum). Such approaches are well established and available in the GULP and LAMMPS packages. To make this point clear, we added the following text to … (JASON: ADD ONE OR TWO SENTANCES IN A GOOD PLACE.)

*2. “In the conclusions the authors comment on the surprisingly good agreement for thermal conductivity while the lifetimes show scatter- is it also due of the nature of systems studied (LJ and CNT ) ?”*

Our results show that the thermal conductivities predicted by Φ and Φ' differ outside of their uncertainties for LJ at T = 5 and 20 K and for Si at T = 300 K. For LJ at T=40 K and the CNT, the two methods agree within their uncertainty.We do not believe that the nature of the systems studied has any effect. For example, the Si and CNT systems are both much stiffer than the LJ system, but show different behaviors with Φ and Φ'.

*3. “How can this method incorporate also phonon eigenvectors?”*

The correct SED expression, Φ, uses the phonon eigenvectors. One of our major conclusions (stated WHERE) is that one of the reasons that the Φ' form of the SED expression does not work is because it does not require the phonon eigenvector*.* REFERENCE WHERE YOU SAID THIS.

*4. “What are the limiting conditions for the use of this approach ?”*

This approach performs best when the eigenvectors predicted from harmonic lattice dynamics calculations are a good approximation to the normal modes of the system. This is true typically at low temperatures (e.g., up to half the melting temperature, as found by ???) and is better for stiff systems like silicon and CNTs. This point is addressed in the manuscript …

**Response to Referee 2** (referee’s text in italics)

*1. “Whereas such a study may have a limited interest, I think that the paper in its present form*

*is not appropriate for publication. First, the manuscript is far too long; it contains repetitions, for example, Eqs. (4-6) appear also in Appendix A)*

Based on the referee’s comment, we removed Eqs. (1-6) from the main text. To ensure that Appendix A is complete, Eqs. (1)-(3) now appear there. We believe that the flow of the manuscript is improved. We also note that while the total length of the manuscript is somewhat long, this is in large part due to the appendices, which we believe to be important and essential components of this work.

*2. “Second, one wonders why the two formal expressions, denoted as Φ*

*and Φ' , are not compared theoretically* *by introducing into the second the normal-mode expansions, for example;”*

This step was not performed because introducing the normal-mode expansions does not allow for any further progress in the derivation of Φ' [Eq. (9) of the manuscript, proposed in [37]]. Φ' is not an expression that has a theoretical basis. It was incorrectly derived (without a formal derivation) and proposed in [37]. Thus, our goal was to examine Φ' and its ability to predict phonon properties. In terms of theoretical work, we show in Appendix B why it is that Φ' is able to predict the phonon frequencies.,

*5. “Third, the comparison is between two different sets (for each system)*

*of numerical results obtained for small systems, and one wonders what are the computational*

*errors in each of them, and how does the numerical protocol affect the comparison;*

We commented about the errors and uncertainties in the numerical results in the following locations:

3.2. Phonon Lifetimes and Frequencies

The uncertainty in the predicted phonon frequencies is on the order of the frequency resolution used to perform the fast Fourier transform required to evaluate Φ and Φ , which is 102 − 104 less than the phonon frequencies studied in this work (see Sections 4.1, 4.2, and 4.3). At the temperatures studied in this work, we find that fitting single or simultaneous peaks in either Φ or Φ results in less than five percent difference in the predicted lifetimes. The uncertainty from fitting the Lorentzian functions is between five and ten percent of the predicted lifetimes, with the error increasing with increasing temperature.†

† The range of data must be selected when fitting the Lorentzian functions to Φ or Φ . This range

should be large enough for the Lorentzian functions to decrease significantly from their value at half-width at half-maximum, where the linewidth is specified, but not too large as to pick up noise. The error in predicting the lifetime is obtained by varying the range of data used to fit the Lorentzian function.

4.1. Lennard-Jones Argon

There, ω0 , ω0 , τ , and τ refer to the mode properties predicted using Φ and Φ . The phonon frequencies agree well at all three temperatures, with increasing scatter at high temperatures and high frequencies. This scatter is due to the high-frequency peak broadening seen in Fig. 2 at T = 40 K, which can force peaks close in frequency for Φ to be fit as a single Lorentzian function.

The lifetimes show large scatter between Φ and Φ on a mode-by-mode basis, with increasing scatter at high temperature that shows no systematic difference. The scatter at high frequencies is in part due to the peak broadening seen in Fig. 2, which can force peaks close in frequency for Φ to be fit as a single Lorentzian function with a single lifetime. The broadening does not affect fitting at low frequencies, where the linewidths are much smaller than the peak spacings. There, any scatter comes solely from the difference between Φ and Φ'.

While the bulk thermal conductivities at a temperature of 40 K agree within their uncertainties, the predicted mode-by-mode lifetimes show large scatter [Fig. 3(c)] and the agreement should be regarded as coincidental.

The disagreement between Φ and Φ' in thermal conductivity comes directly from the differences in the phonon lifetimes. All other properties (frequencies, group velocities, specific heats) are nearly or exactly the same for the two calculations.

Appendix C. Finite Simulation-Size Scaling for Thermal Conductivity

For the LJ argon system studied in Section 4.1, a finite simulation-size scaling procedure[28, 30] is used to compare the thermal conductivity predictions from Φ and Φ' to those from the Green-Kubo method. The scaling procedure is demonstrated in Fig. C1. The uncertainties in the predicted thermal conductivities for Φ and Φ' come predominantly from the finite simulation-size scaling procedure.

As with the extrapolated bulk thermal conductivities at temperatures of 5 and 20 K (see Table 1), the predicted thermal conductivities at each system size (N0 = 4, 6, 8, and 10) are systematically smaller and outside the prediction uncertainties for Φ compared to Φ'.

The predictions for Φ and Green-Kubo for the LJ system are in good agreement with those from other atomistic simulation methods[28] while those from Φ differ and show no systematic behavior.

*6. “and last but not least, the vast use of the term ’predict’ leads the reader to believe that the predictive power of Φ and Φ' will be examined by comparing the results with those measured on real systems; however, it seems that the term predict serves as a synonym to values extracted by fitting.”*

We realize that our understanding of the word predict is different from that of the referee, but believe that it is appropriate. It was not our objective here to compare against experimental measurements. The predictions of the potential functions used to model the three systems (argon, silicon and a carbon nanotube) have been compared to experimental results in other works (see for example 34,45). For the CNT, we use the Brenner potential simply for convenience. It is known that improved potentials can better capture experimental data, see Phys. Rev. B 81, 205441 (2010). As stated, our primary goal was to compare the two SED method, Φ and Φ'. Fitting procedures are necessary to make predictions of the phonon properties.

*7. “In summary, it is not at all clear why do the authors prefer one definition over the other,.and what is the actual difference of the two–from the theoretical point of view.*

*”*

We regret that our conclusion was not clear to the reviewer. The conclusion is that the Φ method is correct and that the Φ' method is not correct. This conclusion is made by comparing the predictions of each to predictions from the Green-Kubo method on the same system. The difference between the two methods from a theoretical point of view is that the Φ method uses the phonon mode eigenvector while the Φ' method does not. These points are all made in the Summary section, which we have revised for clarity,

**Response to Referee 1** (referee’s text in italics)

*1. “The paper Comparison and evaluation of spectra energy methods for predicting*

*phonon properties is devoted to comparison of two methods of prediction the phonon properties and the related thermal conductivities. The authors show that, although an alternative method formulated by Thomas et al. is two orders of magnitude less expensive than the method based on the spectral energy density, it predicts correctly only the phonon frequencies. The phonon life-times cannot be correctly predicted. Therefore the method proposed by Thomas et al. cannot properly predict various properties of lattices, in particular, thermal conductivities. Since comparison is performed on the known examples, the paper by Larkin et al. has rather methodological character.*

*I agree with the second referee. This paper does not provide enough new*

*physics to be suitable for Journal of Physics: Condensed Matter. It should*

*be rejected.”*

Our manuscript is concerned with the comparison of two methods and inherently has a methodological character. The incorrect Φ' method has been used to study important aspects of phonon physics in a wide-range of systems (37,39-41). Thus we believe that it is an important contribution to the field of condensed matter physics to clearly demonstrate that it does not work and why.

We would like to highlight Journal of Physics: Condensed Matter articles which examine the same phonon physics that can studied using the Φ method:

P. Pavone J. Phys.: Condens. Matter 13 7593 2001

J. Wang and J.-S. Wang, J. Phys.: Condens. Matter 19 236211 2007

K. Imamur et. al, J. Phys.: Condens. Matter 15 8679-8690 2003

In summary, we have made several modifications to the original manuscript, which are listed below:

1. Eqs (1-6) have been moved to Appendix A.
2. We modified the text in section (2.1) and Appendix A to reflect the moved Eqs.

Sincerely,

Jason M. Larkin, Joseph E. Turney, Alexandre D. Massicotte, Cristina H. Amon, and Alan J. H. McGaughey