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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 referee's report, we believe that the objective, contribution, and importance of our manuscript were not clear to the referees. We are convinced that our manuscript is suitable for Journal of Physics: Condensed Matter and argue so in our response to the referee's comments below.

Before addressing the referee's 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"*)

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 requires the quasi-harmonic eigenvectors using Lattice Dynamics and atomic velocities using Molecular Dynamics. Both Lattice and Molecular Dynamics are performed in Goel et al., Journal Of Nuclear Materials 377 438 (2008). If interatomic

potentials are available, the Φ method can be used to study UO2. *Ab initio* methods (Density Functional Theory) are typically too expensive to perform Molecular Dynamics for the amount of time-steps required for the Φ method.

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) ?"

As for predicted thermal conductivity, our results show that Φ and Φ' differ significantly for LJ at T = 5 K and for Si at T = 300 K. For the CNT, the two methods agree within the uncertainty. There doesn't seem to be any trend due to the nature of the system studied.

3. "How can this method incorporate also phonon eigenvectors?"

The correct SED expression Φ must use the phonon eigenvectors.
While we do not recommend Φ', it does not require the phonon eigenvector.

4. "What are the limiting conditions for the use of this approach ?"

Limitations of the Φ method has been investigated using a time-domain approach in (28). Basically, the approach performs best at low temperatures where the harmonic approximation is good.

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)..."

We have moved these Eqs. to Appendix A.

2. "...and it repeats basic textbooks
expressions [Eqs. (1-3)]."

We feel it is fine to repeat these equations which may be basic textbook expressions, but are essential to the method(s) presented in this paper. We have also moved these Eqs. to Appendix A.

3. "Second, one wonders why the two formal expressions, denoted as Φ
and Φ' , are not compared theoretically..."

They are compared theoretically, here is the summary:

1) 2.1. As Derived from Normal Mode Coordinates, Φ

"The correct expression for the phonon SED, Φ, can be derived from the formulation of anharmonic lattice dynamics theory [3–6]. The derivation of Φ is presented in detail in Appendix A."

2) 2.2. Alternative Formulation, Φ'

"Now that the phonon SED, Φ, has been properly derived, we seek to motivate the expression Φ' that was proposed in previous studies but has not been validated [35–37]."

3) Appendix B. Interpretation of Φ'

"As demonstrated in Section 4.1, Φ' is not the phonon spectral energy density, Φ, defined by Eq. (5)."

4) 5. Summary

"The phonon SED Φ is well-defined theoretically, while Φ' does not properly map to the phonon energies since it is missing the phonon mode eigenvector. We deduce that this is the reason Φ' does not accurately predict the phonon lifetimes."

As summarized above, the formal derivation of Φ in the frequency domain is presented, which has not been published before. Φ' is shown to be an incorrect expression for the phonon spectral energy density.

4. "...are not compared theoretically by introducing into the second the normal-mode expansions, for example;"

This was not done 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 which has any theoretical basis. It was incorrectly derived (without a formal derivation) and proposed in [37]. Thus, our goal was to examine Phi', which is shown to be related to the phonon frequencies as discussed in Appendix B. Interpretation of Φ'.

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;

Since the focus of this manuscript was the comparison of two SED methods for predicting phonon properties (Φ and Φ'), we commented several times about the errors and uncertainties in the numerical results:

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 transforms 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, $\omega 0$, $\omega 0$, 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."

The potential functions used to model the 3 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 conveinience. 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'. This does not require comparison with experimental data. Fitting procedures are certainly 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,..."

5. Summary

Still, the most important predictions are the mode-by-mode phonon properties. Of particular importance are the lifetimes, which are the key input for Boltzmann transport equation-based models [18]. Thus, we do not recommend Φ' for predicting phonon lifetimes or thermal conductivity.

8. "...and what is the actual difference of the two–from the theoretical point of view. "

5. Summary

We derived the correct phonon SED, Φ, and its relation to the phonon frequencies and lifetimes by starting from the normal mode coordinates. We then presented an alternative formulation to the phonon spectral energy density, Φ , which does not require the phonon mode eigenvectors. Because Φ does not contain the eigenvectors, this alternative formulation does not represent the phonon spectral energy density, but does

contain information about the phonon dispersion as the temperature approaches 0 K (see Appendix B).

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."

Since our manuscript is concerned with the comparison of two methods, it does have a methodological character. However, the incorrect Φ' method has been used to study important aspects of phonon physics in a wide-range of systems (37,39-41). Thus it is very important for the understanding of theoretical phonon physics that the Φ' method has proven incorrect.

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)

Sincerely,

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