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Athanasios Chantis
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Dear Athanasios Chantis:

Thank you for organizing the review of our manuscript BP11533: “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 referee. We are convinced that our manuscript is suitable for *Physical Review B* 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, including ones published in *Physical Review B*.
- 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 (referee’s text in italics)

1. *“The authors present a theoretical article where they propose an alternative expression to calculate the phonon properties (phonon frequencies and life-times) in a molecular dynamics simulation (MD). The quantity proposed (called Phi’) in the article has the advantage that it does not require a priori the knowledge of the phonon eigenmodes.*

I would have recommended the authors to publish the article in its current form in a more specialized journal, the predictions of phonon properties using MD has been reported a

number of times and is now even discussed in text books. The use of Phi' does not improve the traditional methods.

We can not see the point of using Phi' instead of the frequency-energy spectral density (called Phi in the text)."

Response: We did not propose the Phi' method in our manuscript. In fact, Phi' was proposed in a previous work [PRB 81, 081411(R) (2010)] and has since been used, without full validation, by others [e.g., PRB 84, 165418 (2011), PRB 84, 104302 (2011), Comp. Mat. Sci. 53, 278285 (2011)]. The objective of our work was to perform a detailed study of the Phi' technique to assess whether or not it can accurately predict phonon properties.

We highlight the sections of the manuscript where we believe this point is clear:

Page 2, last paragraph: "An alternative expression for the phonon SED (referred to herein as Φ'), was recently proposed but has not been rigorously tested.³⁵⁻³⁷"

Page 3, first full paragraph: "The objective of this work is to assess the validity of Φ' as a phonon SED by comparing the phonon properties it predicts to those predicted by Φ ."

We conclude that the Phi' method is incorrect and recommend that it not be used. This point is made in the following places in the manuscript:

Page 3, first full paragraph: "While Φ' is found to accurately predict the phonon frequencies, we find that it does not correctly predict the phonon lifetimes."

Page 18: "Thus, we do not recommend Φ' for predicting phonon lifetimes or thermal conductivity."

2. On the contrary, Phi' doesn't predict correctly the phonon lifetimes even at moderate temperature (Si SW and CNT) and even at low temperatures it poorly predict the thermal conductivity of the LJ crystal at low temperature;

The reviewer is correct. We tried to emphasize the disagreement in phonon lifetimes throughout the manuscript. We summarized this finding on pages 17-18: "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. Thus, we do not recommend Φ' for predicting phonon lifetimes or thermal conductivity."

3. Finally, the phonon properties may be determined using real time domain analysis with the same accuracy than Phi see refs 25 and 33 quoted in the manuscript.

The reviewer is correct, others have used a time-domain analysis similar to the Phi method. Our derivation of Phi, which is a frequency-domain approach, has not been

previously presented and is itself a new contribution to the literature. As stated at the end of Section II A (page 5):

“Previous work using normal mode analysis has represented the phonon energy in the time domain,^{24,25,28,30,33,34} while Φ is a representation of the phonon energy in the frequency domain. The time- and frequency-domain approaches are mathematically equivalent by use of the Wiener-Khinchin theorem.^{38,45} The frequency-domain approach has the advantage of predicting both the phonon lifetime and frequency by fitting a simpler function than required in the time-domain approach.”

4. As a result, there is nothing particularly new in this article. So the manuscript does not fit the physical review B style.

We disagree with the reviewer. Our manuscript presents new information: (i) the rigorous theoretical derivation of the frequency-domain representation of the Φ technique and (ii) the comprehensive testing of the proposed Φ' technique. Both of these contributions fit into a long history of articles in the Physical Review on the topic of predicting phonon properties [e.g., PRB 34, 5058 (1986), PRB 61, 2651 (2000), PRB 69, 094303 (2004), PRL 99, 255502 (2007), PRL 103, 125902 (2009), PRB 79, 064301 (2009), PRB 79, 144305 (2009), PRB 81, 081411(R) (2010), PRB 84, 165418 (2011), PRB 84, 104302 (2011)].

5. "While substantial effort..., the current understanding is lacking, even in bulk materials" Not really in bulk, see the book of Srivastava "the physics of phonons"

We agree with the referee that the language used here was potentially misleading and have changed the text to read:

“While substantial effort has been devoted to developing theories of phonon transport, the current understanding is incomplete, even in bulk materials.”

6. Table I. Why does Φ' predict such a low value of LJ thermal conductivity at the lowest temperature? What is the longest relaxation time at this temperature?

The reason that Φ' predicts a lower value of thermal conductivity than Φ is due to the differences in phonon lifetimes predicted by the two methods. We did not seek to understand this disagreement any further after discovering that Φ' was incorrectly derived. The longest relaxation time is on the order of 80 ps for both methods, which is much less than the MD simulation time of 4.5 ns.

7. SW Si: The authors may have compared the conductivity obtained with Φ and Φ' to Green-Kubo simulations at room temperature

Once we demonstrated with the LJ system that Φ and Φ' disagree in both predicted lifetimes and thermal conductivity, we did not see the benefit of comparing the results for SW silicon to Green-Kubo or any other method.

8. *CNT: similarly, some Green-Kubo thermal conductivity of CNT are available in the literature, see e.g. Donadio and Galli, PRL 2009*

Donadio and Galli (PRL 2007) used the Tersoff potential to model the CNT. Here, we are using the REBO potential. These two potentials are known to predict very different thermal conductivities, and so a comparison between the two would not be appropriate. Furthermore, the heat current (needed in the Green-Kubo method) for the four-body REBO potential has not been formulated.

9. *Appendix A: eq. A7: what does the index j exactly represent? what are exactly the t_j 's? How are they estimated in a MD simulation?*

The indices j label the “events” related to changes in the phonon mode population. For a harmonic system, the phonons are non-interacting and their populations do not change with time. For an anharmonic system, the phonon populations fluctuate. To predict a phonon lifetime, we wish to average over many of these phonon population fluctuations (referred to as “events”). This is done by running the MD simulation longer (by at least a factor of 10) than the longest phonon lifetime in the system. Thus, the predicted phonon lifetimes are in this sense “time-averaged” or “event-averaged”.

10. *Conclusion: "Any agreement in thermal conductivity predictions between atomic studies and experiment must be regarded as coincidental " Why ?*

Because Φ' is derived incorrectly. We did not seek to identify why for some systems/temperatures (LJ $T=40K$, CNT) the thermal conductivity predictions for Φ and Φ' are so close. We feel that such an investigation would confuse readers and actually encourage people to continue using Φ' , which we have shown to be incorrect.

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

- 1) We revised the abstract to make the point of the article clearer.
- 2) A number of small grammatical changes to make the article clearer.
- 3) The SW silicon data (predicted lifetimes from Φ and Φ' as well as thermal conductivity) have been updated. We found our original data was calculated using a lattice constant which did not result in a zero pressure simulation. We have also added a citation to a recently published article where Φ and Φ' are compared using SW silicon:

⁵⁴ S. M. Takuma Hori, Takuma Shiga and J. Shiomi, Transactions of the Japan Society of Mechanical Engineers **78**, 328 (2012).

Sincerely,

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