

Alan McGaughey  
Associate Professor  
Department of Mechanical Engineering  
Carnegie Mellon University  
Pittsburgh, PA 15213-3890  
Tel: (412) 268-9605  
Fax: (412) 268-3348  
Email: mcgaughey@cmu.edu

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Dear *Physical Review B* Editor:

We are submitting the manuscript titled “Evaluation of the virtual crystal approximation for predicting alloy phonon properties and thermal conductivity” by Jason M. Larkin and Alan J. H. McGaughey for consideration for publication in *Physical Review B*.

Due to their low thermal conductivities, alloys are currently an active area of research, notably in the thermoelectric energy conversion field. The ability to predict alloy thermal conductivity is critical in narrowing down a large materials design space. Recent papers [e.g., *PRL* **106**, 045901 (2011), *PRL* **109**, 095901 (2012), *PRB* **85**, 184303 (2012)] have used anharmonic lattice dynamics and the virtual crystal approximation (an approach we call VC-ALD) to make such predictions.

In VC-ALD, the disorder in the alloy is treated as a perturbation. The limits of this approach have yet to be determined. In our work, we use computationally-inexpensive empirical potentials to assess the virtual crystal approximation by self-consistently treating the disorder explicitly and as a perturbation. We are not aware of any such previous study. Our results indicate that while VC-ALD is generally an accurate method, care must be taken when modeling alloys with very low thermal conductivities, where significant underprediction of thermal conductivity is likely.

We suggest the following reviewers:

Junichiro Shiomi  
Xiulin Ruan

We look forward to your response.

Sincerely,



Alan McGaughey

**Response to the First Referee**

*In Section IV.4, the comparison between the accumulation curve of bulk and thin films is interesting. This reviewer, however, has a couple of questions.*

*1. “The accumulation function for the 500 nm film closely follows the bulk curve up to a mean free path of about 500 nm. This result indicates that phonons with mean free paths smaller than the film*

*thickness remain bulk-like.” For 500 nm film, it is easy to understand that phonons with mean free path larger than 500 nm would be influenced by the phonon-boundary scattering. But this should lead to*

*more phonons with mean free path smaller than 500 nm. Why does the accumulation curve of 500 nm film fall on top of the bulk curve, below 500 nm?*

*2. “The 50 nm and 100 nm accumulation functions then cross the bulk curve at 70 nm and 95 nm, values close to their thicknesses.” What is the physical meaning of the crossing points? Could the authors give a*

*clear derivation of why these crossing points should be close to the film thicknesses?*

The referee raises some very interesting questions, which caused us to reinterpret the accumulation function data. Please see the revised Fig. 4, where an additional sub-figure has been added. In Fig. 4(a), which is new, the film accumulation functions are plotted vs. bulk mean free path. In Fig. 4(b), the former Fig. 4(a), we plot the film accumulation functions vs. the film mean free path. Fig. 4(c) is the former Fig. 4(b), showing results for the porous films. In Figs. 4(a) and 4(b), we added data for a 1000 nm thick film.

By plotting against the bulk mean free path in Fig. 4(a), we see where phonons start to be affected by boundary scattering. For all films, deviations in the accumulation functions from bulk occur at bulk mean free paths smaller than the film thickness (e.g., around 100 nm for the 500 nm thick film). This result makes sense because phonons can start anywhere in the film. It is also important to note that most phonons do not travel purely in the cross-plane direction. As such, depending on how its group velocity vector is oriented compared to the film, each phonon mode will start to be affected at a different film thickness.

When plotted vs. the film mean free path in Fig. 4(b), the accumulation functions shift to the left as there are more phonon modes with smaller mean free paths. For the 50 and 100 nm films, the accumulation functions rise more quickly than the bulk curve starting at a mean free path of 20 nm. The film accumulation functions must then cross the bulk curve (at 70 and 95 nm) as their total thermal conductivities are smaller. For the 500 nm film, the mean free path reductions cause the film accumulation function to follow the bulk curve up to a mean free path of 400 nm. It then rises above the bulk value (difficult to see in the figure), crossing back over at 500 nm. For the 1000 nm film, the film accumulation function rises above the bulk curve at 600 nm, then cross it at 1300 nm.

Based on these results, we believe that our initial statement about the 50, 100 and 500 nm films were too strong. The analysis of accumulation functions for nanostructures is clearly subtle and requires careful examination. Because the accumulation functions are not the main focus of this work, we plan to explore this area in future studies. Based on the above discussion, the text in Section IV has been revised to reflect our current understanding.

*3. The reviewer suggests removing Equation (2), or adding the equation for min(Lamda\_pp, Lamda\_pb). Otherwise, those who quickly go over the article might think that the authors just use Matthiessen’s rule.*

To clarify the calculations, we added the equation suggested by the referee to the revised manuscript [Eq. (3) on page 6].

*4. Section V., “…an absence of scattering requires either very low temperatures or very high thermal conductivity,…”: The reviewer could not fully agree on the second part. From the reviewer’s point of view, very high thermal conductivity could be the \*result\* of coherence, but not the condition for it.*

We revised this statement to be:

“For thermal phonons, which have THz frequencies, very low scattering rates require a lack of scattering channels. Such a condition may be found at low temperatures and/or in materials with a large phonon band gap or reduced dimensionality. A secondary periodicity is not required.”

**Response to the Second Referee**

*1. I find quite misleading the way in which the authors describe their computational approach.*

*They never provide the details of the approach; they just make reference to other papers, and then they use the following words.*

*In the abstract: "phonon properties from first principles calculations"*

*At the end of Sec. III: "The second and third order force constants are obtained from the ab initio calculations of Refs. 14-15"*

*In the summary: "We used phonon properties from first-principles calculations"*

*The words "first-principles" and "ab initio" usually refere to quantum mechanical calculations (density functional theory, configurational Hartree-Fock, etc.). Those sentences in the key points of the paper*

*give the wrong impression that the authors performed DFT calculations. On the contrary, the reference cited by the authors discuss an oversimplified model which is \*fitting\* density functional theory*

*calculations.*

*The authors should state explicitly the model that they are using. The words "first-principles" and "ab initio" are meaningless when taken by themselves, as in the present case, and they are confusing. The words "first-principles" and "ab initio" should be simply deleted from the paper.*

We thank the referee for this comment but respectfully disagree that the approach described by Esfarjani and co-workers is “oversimplified.” It is true that the force constants in this approach are obtained by performing numerical analysis on forces obtained from DFT calculations (as opposed to obtaining the force constants directly from density functional perturbation theory). The resulting thermal conductivities, however, are in very good agreement with experimental measurements for a range of materials [*PRB* **84**, 085204 (2011); *PRB* **84**, 104302 (2011); *PRB* **85**, 155203 (2012); *PRB* **85**, 184303 (2012); *EPL* **101**, 16001 (2013)]. These results point to the rigor of the numerical approach.

We agree that the language used in the manuscript is potentially misleading. As such, we modified the description of the methodology to reflect that forces from DFT calculations are used to obtain the force constants needed to predict phonon properties. The terms “first-principles” and “ab initio” have been removed. Because this work is focused on the use of the resulting mean free paths, we do not believe that a full description is necessary due to the completeness of Esfarjani’s work. Relevant changes to the abstract and Sections I, III, and VI are colored red in the revised manuscript.

*2. Section II, "Molecular dynamic simulations have the advantage of naturally including coherent phonon effects...": I do not understand this sentence. If the term "coherence" implies the interference of waves (as the authors state in Sec. V), how can molecular dynamics--in which the atomic motion is treated classically--include coherence effects?*

The referee raises a good point related to the meaning of the term coherence. We use the term coherence to indicate the interference of vibrational waves, a phenomena that can exist in either a classical or quantum framework. Molecular dynamics simulations have the potential to capture phonon particle and wave effects.

Others have previously used coherence to describe phonon modes that emerge due to a secondary periodicity in a nanostructure, which we do not believe to be the correct usage. While we attempted to make this distinction in Section V, we now realize that there was ambiguity present in the earlier parts of the manuscript. To address this point, we made changes to the abstract, and Sections I, II, IV.3.1, V, and VI that are colored red in the revised manuscript.

*3. Sec. III, last paragraph: The authors talk about "34,9923 evenly spaced phonon modes". If I understand correctly, the sentence should be more comprehensible if they say that they are using a uniformly spaced grid of wavevectors of NxNxN points in the Brillouin zone, centered (or not) on the origin. Do they consider all the phonon modes, or just the three acoustic branches?*

We agree with the reviewer than more detail is needed. We modified this sentence to be:

“Based on the two-atom (i.e., primitive) unit-cell description, harmonic and anharmonic lattice dynamics calculations are performed to calculate the bulk silicon phonon frequencies and mean free paths for an 18x18x18 grid of uniformly-spaced wave vectors centered at the origin of the Brillouin zone. 34,992 total phonon modes are considered, which includes acoustic and optical branches.

*4. Sec. IV.1: They say, "A further 10% increase in the thermal conductivity is found if one solves BTE iteratively without making the relaxation time approximation." This sentence is misleading. Did the*

*authors solve the BTE iteratively, or did they assume that the increase is 10% on the basis of other works? The authors should be more explicit on this point.*

We did not solve the BTE iteratively. This comment is based on the work of Broido et al. (Ref. 38, cited in the manuscript at this location). To make this comment clearer, we modified this sentence to be:

“Based on the work of Broido et al., a further 10% increase in the thermal conductivity of silicon is expected if one solves the BTE iteratively without making the relaxation time approximation,..."

*5. Sec. IV.3.1: What is "COMSOL"?*

COMSOL Multiphysics is simulation package that solves a variety of coupled PDEs. We modified this sentence to be:

“For the in-plane direction, the correction factor is calculated using the COMSOL Multiphysics simulation package ® to solve the heat conduction equation using the finite element method (FEM).”