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Dear *Physical Review B* Editor:

We are submitting the manuscript titled “Evaluation of the virtual crystal approximation for predicting alloy vibrational mode 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 low thermal conductivities, where significant underprediction of thermal conductivity is likely.

Referee 1 Comments and Response

1) I cannot recommend publication of this paper as a regular article in

Phys. Rev. B as it is far too long and conveys little new physics.

The topic of thermal conductivity of amorphous materials has a long

history, with different views on the nature and role of vibrational

modes. This paper claims to predict the properties of the propagating

and non-propagating vibrational modes in a-SiO2 and a-Si, based upon

the application of molecular dynamics simulations.

There is too much detail of mathematical stuff already published in

several books and articles.

1) The structural model employed in the lattice dynamical calculations

has not been defended. Why has Eq. (2) been evaluated using Eq. (3)

when lattice dynamical calculations have been performed?

The use of Eq. 3 is explained in Section , P.:

“When using mode properties obtained from calculations on finite-sized systems, it is common to write Eq. (2) as a summation over the available modes.4,6 We choose the integral form because the required use of finite-sized simulation cells limits the lowest frequency modes that can be accessed. An extrapolation must be made to the zero-frequency limit that is more easily handled with the integral.4–8,16,19”

We are using the Debye DOS where the lattice dynamics DOS is Debye-like.

Discuss validity of amorphous structures:

1) a-SiO2:

While there are differences in our model's predicted mode properties compared with experiments, the differences are within reason. Both materials, experimental and our numerical a-SiO2, show no evidence for important contribution to thermal transport from propagating modes. Any difference in our model compared with experiment is likely outside the current resolution of the broadband FDTR experimental technique. Because of this, we are satisfied with our model's accuracy to compare to experiment.

1) Use of Eq. (3) is too simplistic to obtain any firm conclusion

regarding vibrational lifetimes. It does not include any temperature

dependence, and only employs a single adjustable parameter. Either the

authors do not differentiate between 'anharmonic processes' and

'Umklapp processes' or indeed do not appreciate that an Umklapp

process is only valid for a crystalline structure.

Eq. 3 does not predict the vibrational mode lifetimes. The lifetimes are obtained from the MD-based NMD method. We make no assumptions about the lifetimes at this stage of our manuscript.

The temperature-dependent DOS does not show significant deviation from the DOS obtained from lattice dynamics calculations (i.e., the zero temperature limit), see Fig. 11 of Ref. [feldman\_numerical\_1999]. Because of this, we do not think that the temperature-dependent DOS plays an important role in our predicted thermal conductivity accumulation functions.

Eq. 3 only assumes only a single phonon polarization, which is supported by the predicted mode lifetimes and diffusivities in Figs. and , which show no distinct or separate scalings for longitudinal and transverse polarizations. Using multiple polarizations does not change our predicted accumulation functions significantly either qualitatively or quantitatively. We commented on this on Page 4:

“The choice of a single polarization (i.e., an averaging of the transverse and longitudinal branches) does not significantly change the results predicted in this work or that of others.4–8,19”

We do not differentiate between different anharmonic processes. Umklapp processes are anharmonic and, like Normal processes, occur strictly in crystalline materials. Umkalpp scattering processes are usually discussed in the context of disordered materials because it has been shown experimentally and numerically (Ref) that the low-frequency lifetimes scale as \omega^{-2}, a scaling sometimes referred to as “Umklapp”. We avoided the use of this terminology and focused on the scaling itself.

The term 'supercell Gamma modes' has not been explained.

We have changed this terminology on P. to read “disordered modes of the supercell at the Gamma point”

While use of Eq. (25) is technically correct, the authors should

realize that the 'bulk' term should also include 'size or thickness'

term. In the present context, the use of the formula for the

'thickness' contribution seems rather too simple.

Eq. (25) does take into account thickness dependance, albeit in a simple method. Because we use an infinite film thickness for a-SiO2 and 80 \mum film thickness for a-Si, Eq. (25) does not modify the NMD-predicted bulk lifetimes significantly. Eq. (25) is used to ensure that the thermal conductivity predicted using an \omega^{-4} scaling for Eq. Is finite. While it is simple, Eq. (25) has been used in Refs. and to predict the thermal conductivity of a-Si thin films using an \omega^{-4} scaling of the lifetimes. Using a more complicated model does not change the predicted thermal conductivity accumulation function significantly, qualitatively or quantitatively. The main result of our paper is the much steeper accumulation of a-Si from experiments by Regner et al. Compared with our model's predictions. This clear difference does not depend significantly on the detals of the model.

Ref Ankit paper on free path sampling

There are too many references for the amount of contribution made.

It is not clear what the referee is trying to say.

In conclusion, this manuscript does not significantly advance the

physics of the topic under study. Once the authors have clarified the

points raised above, the manuscript may become suitable for

publication in a more relevant journal.

We believe we have addressed the points raised by Referee 1 inside this letter of response and through minor modifications to our manuscript. We feel that our manuscript is still suitable for publication in Physical Review B since it is a timely comparison with the recent experimental measurement of Regner et al. . Our predcitions highlight important unknown behavior of propagating modes in a-Si and/or an incorrect interpretation of the results of the broadband FDTR measurements of Regner et al...or our model is not right.

**Referee 2 Comments and Response**

1) The title should be more specific. “…accumulation in a-SiO2 and

a-Si”. Only two materials have been studied.

The referee raises a good point, we have changed the title accordingly to:

Thermal Conductivity Accumulation in a-SiO2 and a-Si

2) 121 papers are cited. I’m sure the authors believe they are being

thorough but I am left with the impression that they have failed to

critically consider which work in the literature has been most

valuable for advancing the field. It is simple task to cite everything

that has ever been published on a subject but a more difficult and

valuable task to be selective.

This is a fair comment. The amount of referencing is due to several factors:

(a) We study two materials, a-SiO2 and a-Si, with an immense body of literature... and separate.

(b) We use several predictive techniques (lattice dynamics, MD-based NMD, MD-based GK, AF theory), all of which have a large body of literature.

(c) We attempt to clarify recent published work (Refs. ) which predicts the mode group velocities using questionable theoretical techniques, and recent published work reporting very large mode lifetimes and mean free paths for a-Si. We feel it is important to highlight well-accepted work on a-SiO2 and a-Si which disagree with these recenty published results.\cite{}

Based on the referee's comments, we have removed Refs. regarding point (c) which are not concerned with a-Si or a-SiO2.

3) The authors should keep in mind that while a-SiO2 is a well-defined

material that can be accurately reproduced in every lab, a-Si is not.

The atomic-scale, nanometer-scale, and micrometer-scale structure of

a-Si varies with deposition method, deposition temperature, and

impurity content such as C, O, and, of course, hydrogen. Hydrogen

content is sometimes intentional and sometimes not. All a-Si has some

hydrogen content. The author’s model has none.

We have addressed this comment in the resubmitted manuscript. New comments regarding the impurtiy content can be found on P. 15:

“It is clear that the experimentally-measured sound speeds for a-Si show a wide range which depends on the deposition method and impurity concentration (e.g. H, C, and O)\cite{}. These effects are not included in our model.”

a comment on the difficulty of producing bulk a-Si:

“”

and a comment on P. 25:

The propagating contribution to the accumulation is predicted using ω −2 and ω −4 lifetime scalings, which have both been inferred from thin film experiments.4–8,27,38 Predictions for both the ω −2 and ω −4 scalings pass reasonably through the thin film thermal conductivity measurements, particularly for thicknesses in the 50-2000 nm range. Overall, the film-thickness dependent measurements show a large variation which depends on the deposition method and impurity concentration (e.g. H, C, and O)\cite{}. These effects are not included in our model.”

Acknowledgement for why we didnt include H in our model. Answer: no classical potential for H-Si, stuck with DFT. DFT is too expensive.

4) The authors state at the bottom of page 2 that INS can only be

applied to bulk single crystals but I don’t think that is true. I’m

sure that INS has been applied to a-SiO2, by Buchenau and by others if

I recall correctly. The volume of a-Si is typically too small to study

by INS but I think a-Si (or maybe a-Ge) was studied by INS about 30

years ago by Lannin and maybe also by Buchenau.

Comment...

5) Evaluating Eq. 1 is a clear and focused goal for the paper but the

work reported in the paper seems to include many aspects of the

problem that are not related to Eq. 1.

Because Eq. (1) is a sum of Eqs. (2) and (9), there are many inputs that we must predict from our atomic models and methods. We had to compare a-SiO2 and a-Si.

6) Figure 1 is not useful. There is nothing quantitative presented in

this figure. If the authors could comment on how the PDF of their

model compares with the experimental PDF, that would be helpful.

We have predicted the radial distribution function for our model of a-SiO2 and compared with previous experimental and numerical work. This is now Fig. and is located in the Appendix. For a-Si, the structural characteristics are presented in Ref. which is where our a-Si structures are obtained from.

7) It seems that the authors are forcing the density of a-Si to be the

same as crystalline Si. That should be stated more clearly. The

density of the a-SiO2 model should also be stated.

We state in Section II.A.:

“The three smallest a-SiO2 samples are the same as those used in Ref. 67 and contain 288, 576, and 972 atoms at a density of 2350 kg/m3 .”

and

“All a-Si structures have a density of 2330 kg/m3 , equivalent to the perfect crystal with a lattice constant of 5.43 A.”

\cite{barkema\_high-quality\_2000} Our results, on the contrary, indicate that there is very little dependence between the density of the amorphous material andits topology, at least within the application of our two empirical potentials. A volume change at the percent level should therefore have very little impact on the topology and will reflect mostly some fine details of the real atomic interactions.

8) On page 8, I do not know what a “top-down” thermal conductivity is.

We have changed the wording to read:

“The Green-Kubo (GK) method is used to predict a thermal conductivity kGK without using Eq. (1)42”

9) The caption to Figure 2 should state that the dashed lines are

extrapolations. In the caption, the sentence that ends with “….with a

gap that separates…the interactions” doesn’t make sense.

We have changed the wording to:

“”

10) The discussion of lifetimes is very confusing. In Figure 4, the

authors plot the lifetimes derived from MD/NMD and from analysis of

dynamic structure factor. The difference is nearly a factor of 30 for

a-SiO2. The authors say almost nothing about this. In fact, they state

earlier that neither approach is valid when the linewidth is broad. I

strongly encourage to the authors to only present results that are

rigorously meaningful and omit the rest. I assume one approach is

better than the other. If so, I encourage the authors to present

results from the best approach and only comment on the results from

other approaches and then state why one is better than the other. The

results in the section are doubly confusing because the authors don't

seem to use the results of NMD at high frequencies to achieve their

stated goal of analyzing the fraction of heat carried by propagating

modes. If the results are never used, I do not see any reason to

present those results.

In Fig. 4 we plot the timescales predicted by the static structure factor and the lifetimes predicted by the NMD method. We commented that the large difference for a-SiO2 on P. 17:

“The lifetimes predicted from the structure factor fall below the NMD-predicted lifetimes and the IR limit. These low values result because the structure factors for a-SiO2 are evaluated for wavevectors where the resulting wavepackets are formed by non-propagating modes.2,4,6”

For a-Si, we commented on the good agreement:

“The agreement between the NMD-predicted lifetimes and the structure factor timescales for a-Si at low frequencies indicates that these modes are plane-wave-like and that the wavepackets formed by these modes are propagating.2,4,6”

Only the NMD method is constrained by \Gamma << \omega\_0. For a-Si, only modes near the IR limit are affected by this constraint, which is a narrow portion of the vibrational spectrum ( < \omega < ). We have added a comment:

“”

For a-SiO2, the modes with \omega < are affected by the linewidth constraint. Because of the good agreement between the NMD-predicted and AF-predicted difusivities at low frequencies, we determine that the NMD-predicted lifetimes are not significantly affected by the linewidth constraint. We have added a comment:

“”

The static structure factor predicts the timescale for diffusion of a wavepacket with well-defined wavevector, while the NMD method predicts the lifetimes of individual modes. Because they predict different quantities, neither method is “better”.

We did not use the NMD-predicted lifetimes of modes with omega > omega\_{cut} directly to predict thermal conductivity because there is no accepted theoretical method to predict the group velocities of these diffuson modes. The mode diffusivity is the fundamental quantity for diffuson modes, which is accurately predicted by the AF diffuson theory (Eq. ). We do use the NMD-predicted lifetimes of the diffusons to predict effective diffuson mean free paths (Eq. ) which is discussed in Section.

11) I am similarly confused about Figure 5. The authors seem to be

taking the NMD lifetimes from Figure 4 and multiplying by a constant

velocity and comparing those mode diffusivities to the predictions of

the AF theory. I do not see how that is valid comparison except at the

very lowest frequencies.

We agree, and this point was addressed in Section E. P. 19:

“Using the sound speeds predicted from the DOS (Table I), the NMD-predicted lifetimes for a-SiO2 and a-Si are used to predict the mode diffusivities with Eq. (5). The results are plotted in Figs. 5(a) and 5(b). We note that the sound speed is most appropriate for the lowest-frequency modes, where the DOS scales as ω 2 (Fig. 2).”

We feel the comparison between NMD and AF-predicted diffusivities is necessary to determine \omega\_{cut}, and is valid since we do not use the NMD predictions for \omega > \omega\_{cut}.

We have omitted NMD-predicted diffusivities for \omega > \omega\_{cut}

We look forward to your response.

Sincerely,



Alan McGaughey