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Dear *Physical Review B* Editor:

Thank your for organizing the review of our manuscript BH12397 titled “Thermal Conductivity Accumulation in Amorphous Materials.” We thank the referees for their helpful comments and were please that the Second Referee found the topic to be “timely and extremely thorough.” We have responded to each comment below and in an updated version of the manuscript.

We have addressed all referee comments. We believe that our manuscript is suitable for publication in Physical Review B for the following key reasons: (i) It is a timely comparison with the recent experimental measurement of Regner et al., who present the first-ever experimental measurements of thermal conductivity accumulation in amorphous silica and amorphous silicon. **Our manuscript highlights 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.**

We look forward to your response.

Sincerely,



Alan McGaughey

**Response to First Referee**

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.

A-Si vs a-SiO2

too long...

comparisons which are made

providing this level of detail allows reproduction

no one has produced accumulation functions

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 II (page 4):

“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.[4–8,16,18]”

We use the Debye DOS, Eq. (3), where the lattice dynamics-predicted DOS is Debye-like [see Section IV.A (page 9)].

To validite our structural models of a-SiO2 and a-Si, we computed the radial distribution functions and compared them with experimental measurements in Figs. 1 (a) and (b) (see reply to Referee 2 comment # 6). Further comparison of our models with experiment is the subject of the rest of the manuscript.

2. 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, for example, Fig. 11 of Ref. [6]. 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. 4 and 5, 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 in Section II. P. 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 (Refs. [4–9,26,27,33–37]) that the low-frequency lifetimes scale as omega^{-2}, a scaling sometimes referred to as “Umklapp”. We avoided the use of this terminology throughout the manuscript and focused on the scaling itself.

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

We changed this terminology in Section IV. B (page 10) to read:

“disordered modes of the supercell at the Gamma point”

4. 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 the thickness dependence, albeit in a simple method. Because we use an infinite film thickness for a-SiO2 and 80 micron 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. (8) Is finite. While it is simple, Eq. (25) has been used in Refs. [4,5,7] 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 on the details of the model.

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

We reduced the number of references to 113 based on Referee 2 comment # 2.

**Response to Second Referee**

We thank the referee for their positive comments on our manuscript.

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

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

We have changed the title accordingly to:

“Thermal Conductivity Accumulation in amorphous silica and amorphous silicon”

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 comment is fair but we note that the unusual number of references is due to several factors:

(a) We study two materials, a-SiO2 and a-Si, each of which has an immense body of literature that is nearly exclusively (only Ref. [106] studied both a-SiO2 and a-Si).

(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 recently published works (Refs. [9,77,85-88]), which predict the mode group velocities using questionable theoretical techniques, and work reporting very large mode lifetimes and mean free paths for a-Si [9] We feel it is important to highlight well-accepted work on a-SiO2 and a-Si which disagree with these recently published results.

Based on the referee's comments, we removed Refs. regarding point (c) that are not concerned with a-Si or a-SiO2. The total number of references is now 113.

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 addressed this important comment in the revised manuscript. A comment regarding the impurity content is in Section IV. C (page 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).[7,8,94] These effects are not included in our model.”

A comment on the difficulty of producing bulk a-Si is in Section V.A (page 22):

“Amorphous silicon, however, can be prepared only in thin films, where voids and other inhomogeneities are unavoidable [4,7,8,94,110] and can influence the vibrational structure at low frequencies.[7,111]”

and a comment on page 25:

“The propagating contribution to the accumulation is predicted using omega−2 and omega−4 lifetime scalings, which have both been inferred from thin film experiments.[4–8,26,37] Predictions for both the omega−2 and omega−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 that depends on the deposition method and impurity concentration (e.g. H, C, and O).[7,8,94,110] These effects are not included in our model.”

Move this to introduction

We did not include hydrogen in our model of a-Si because no classical potential exists to model the H-Si interaction and density functional theory calculations are too expensive for our large model sizes.

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.

We removed the comment regarding the limited applicabilty of INS to the study of amorphous materials.

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 atomistic models and methods. An additional focus of the paper is the comparison of the predicted mode properties and thermal conductivity of a-SiO2 and a-Si, which requires a careful comparison with the large body of literature that exists for these two materials. As such, we do not feel that any of the content is superfluous. Furthermore, we believe that the level of detail provided will be of benefit to future researchers trying to perform similar calculations.

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 assume that by “PDF” the referee is referring to the radial distribution function (“RDF”). We have predicted and compared the radial distribution function for our models of a-SiO2 and a-Si with previous experimental work in Figs. 1 (a) and (b). Our models compare well with the experimental measurements, and further comparison is made at the mode property and thermal conductivity level throughout the rest of the manuscript.

**Double column figures**

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 (page 6):

“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 on page 7:

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

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

We changed the wording to read:

“The Green-Kubo (GK) method is used to predict a thermal conductivity k\_{GK} 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 clarified that the dashed lines are extrapolations and changed the wording to:

“...with a high-frequency gap in the DOS that separates the modes involving Si-O interactions.”

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.

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.” Our objective was to compare these two quantities as a means to further understand how thermal transport is different in a-SiO2 and a-Si. We note that only the NMD method is constrained by \Gamma << \omega\_0.

In Fig. 4 we plot the timescales predicted by the static structure factor and the lifetimes predicted by the NMD method. We commented on the large difference for a-SiO2 in Section IV.D (page 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 on page 17:

“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”

For a-SiO2, modes with 4 \times 10^{12} < \omega < 2 \times 10^{13} rads/s are affected by the linewidth constraint. They don't satisfy the criterion, but because they agree with AF we trust the values...

Because of the good agreement between the NMD-predicted and AF-predicted diffusivities at low frequencies, we determine that the NMD-predicted lifetimes are not significantly affected by the linewidth constraint. For a-Si, only modes with 7 \times 10^{12} < \omega < 1.5 \times 10^{13} rads/s are affected by the constraint. We added a comment on page 17:

“While lifetimes predicted near the IR limit do not satisfy the constraint Γ(ν) << ω0 (ν), only a limited number of these lifetimes are used to perform the necessary extrapolation procedure [see Figs. 5 (a) and (b)].”

We did not use the NMD-predicted lifetimes of modes with \omega > \omega\_{cut} to predict thermal conductivity because there is no accepted theoretical method to predict the group velocities of these modes, which are diffusons. The mode diffusivity is the fundamental quantity for diffusons, which is accurately predicted by the AF diffuson theory. We do use the NMD-predicted lifetimes of the diffusons to estimate the order of magnitude of the effective diffuson mean free paths, Eq. (24).

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. This point was addressed in Section E (page 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).”

The comparison between NMD and AF-predicted diffusivities was helpful to determine \omega\_{cut}. To avoid potential confusion, in the revised manuscript we omitted NMD-predicted diffusivities for \omega > \omega\_{cut} from Figs. 5 (a) and (b). There is a related comment on P. 19...