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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. (ii) **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.*

*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.*

We believe our manuscript presents important new physics concerning the behavior of propagating modes in a-Si. 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.

The manuscript is long because we present, for the first time, a detailed comparison of the mode properties, thermal conductivity, and thermal conductivity accumulation functions for a-SiO2 and a-Si using realistic atomistic models. We use three different predictive methods (NMD, AF, and GK) and compare their predictions simultaneously to predict the thermal conductivity accumulation functions. Using our predicted thermal conductivity accumulation functions, we compare with the experiments by Regner et al. and demonstrate that further experimental measurements are necessary to resolve the low-frequency scaling of the mode thermal diffusivities.

In addition to the timely comparison with the recent experimental measurement of Regner et al., we believe we have presented a thorough and self-consistent method for predicting the mode properties, thermal conductivity, and accumulation functions for amorphous materials. From a methodology perspective, we can predict the mode properties self-consistently using three predictive methods and avoid using predictive methods for the mode group velocities which are not well-defined theoretically.[9,77,85–88] With a trend in research towards utilizing more disordered materials for diverse applications, our study is also a timely one for thermal transport research in general.

*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 validate 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 μm 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 ω-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 ω-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 constructive 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 in the Introduction:

“Overall, experimental measurements of the temperature-varying and film thickness-varying thermal conductivity of a-Si show a large variation that depends on the deposition method and impurity concentration (e.g. H, C, and O).7,8,94,110 In our present study, these effects are not included because the necessary empirical potentials do not exist and computationally-expensive density functional theory calculations limit the model sizes accessible,4,6–8,72,74 which prevents the study of low-frequency propagating modes.”

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]”

*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 applicability 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.

*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 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 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 Γ << ω0.

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 by up to one order of magnitude. 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 1012 < ω < 2 1013 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 1012 < ω < 1.5 1013 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 ω > ωcut 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 IV.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 ωcut. To avoid potential confusion, in the revised manuscript we omitted NMD-predicted diffusivities for ω > ωcut from Figs. 5 (a) and (b). There is a related comment in Section IV.E. P. 19.