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Dear Victor Vakaryuk:

Thank your for organizing the review of our manuscript BH12397, “Thermal Conductivity Accumulation in Amorphous Materials.” We thank the referees for their helpful comments and were please that the Second Referee found the work to be “timely and extremely thorough.” We have responded to all referee comments in the attached rebuttal and in revisions to the manuscript that strengthen but do not change our conclusions.

In response to the First Referee’s main criticism, we believe that our manuscript is suitable for publication in *Physical Review B* for the following two key reasons: (i) It is a timely comparison with the work of Regner et al. [*Nat. Commun*. **4**, 1640 (2013)], who present the first-ever experimental measurements of thermal conductivity accumulation in amorphous silica and amorphous silicon. Specifically, our findings question their interpretation of the experimental data. (ii) It provides detailed insight into why amorphous silica and amorphous silicon, two materials that may seem similar at first glance, show very different thermal transport behavior. Specifically, we find that the absence of a propagating mode contribution to the thermal conductivity of amorphous silica (which is strong in amorphous silicon) is directly related to an earlier transition away from Debye-like behavior in the low-frequency mode properties.

We look forward to your response.

Sincerely,

Alan McGaughey

Response to First Referee

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.

We believe that our manuscript presents important new physics concerning the behavior of diffusive and propagating modes in a-SiO_2 and a-Si. Notably, our comparison with the recent work of Regner et al., who reported the first-ever experimental measurements of thermal conductivity accumulation in a-SiO_2 and a-Si, raises important questions about their interpretation of the experimental data. Furthermore, the parallel study of a-SiO_2 and a-SI allows for a comparison and explanation of their very different thermal transport behaviors. Our work indicates that the differences emerge from the extent over which the density of states remains Debye-like, allowing more phonon-like modes to exist in a-Si compared to a-SiO_2. This difference is in turn related to differences in the bonding structure in these two amorphous materials.

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-SiO_2 and a-Si at the same time using realistic atomistic models. Previous studies focused on just one of these two materials. The manuscript is also long because we present a thorough and self-consistent method for making these calculations using three different predictive methods (NMD, AF, and GK), all of which require explanation. Such detail is important so that future researchers can apply the techniques to other materials. With a trend in research towards using disordered materials for diverse applications, our study is timely for the thermal transport community in general.

2. 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. [4–8,15,18]”

We use the Debye DOS, Eq. (3), where the lattice dynamics-predicted DOS is Debye-like [see Section IV.A (page 9) and Fig. 2].

To validate our structural models of a-SiO_2 and a-Si, we computed the radial distribution functions and compared them with experimental measurements in the new Figs. 1 (a) and 1(b). Our models compare well with the experimental measurements. Further comparison of our models with experiment is the subject of the rest of the manuscript.

3. 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), which is the density of states, 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]. As such, we do not think that the temperature-dependent DOS plays an important role in our predicted thermal conductivities or accumulation functions.

Eq. (3) only assumes a single phonon polarization, which is supported by the predicted mode lifetimes and diffusivities in Figs. 4 and 5, which do not show 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 point in Section II (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 in that of others.[4–8,18]”

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. 6,9,25,36) that the low-frequency lifetimes scale as ω^{-2}, a scaling sometimes referred to as “Umklapp”. Other than when it is introduced on page 5, we avoided the use of this terminology throughout the manuscript and focused on the scaling itself.

4. 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”

5. 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 manner. Because we use an infinite film thickness for a-SiO_2 and an 80 μm film thickness for a-Si, Eq. (25) modifies the NMD-predicted bulk lifetimes by less than one percent. 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, and 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.

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

This comment is fair and was also noted by the Second Referee. We note that the unusual number of references is due to several factors:

(a) We study two materials, a-SiO_2 and a-Si, each of which has a large body of literature that is nearly exclusive (only Ref. [107] studied both a-SiO_2 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, 79, 87-90), which predict the mode group velocities using questionable theoretical techniques, and work reporting very large mode lifetimes and mean free paths for a-Si (Ref. 9) We feel that it is important to highlight well-accepted works that disagree with these recently published results.

Based on the referees' comments, we removed references regarding point (c) that are not concerned with a-Si or a-SiO_2. The total number of references is now 112, which includes some new references based on the referees' comments.

Response to Second Referee

We thank the referee for their positive and constructive comments about our manuscript.

1) The title should be more specific. "…accumulation in a-SiO2 and a-Si". Only two materials have been studied.

We changed the title 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 and was also noted by the First Referee. We note that the unusual number of references is due to several factors:

(a) We study two materials, a-SiO_2 and a-Si, each of which has a large body of literature that is nearly exclusive (only Ref. 106 studied both a-SiO_2 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, 79, 87-90), which predict the mode group velocities using questionable theoretical techniques, and work reporting very large mode lifetimes and mean free paths for a-Si (Ref. 9) We feel that it is important to highlight well-accepted works that disagree with these recently published results.

Based on the referees' comments, we removed references regarding point (c) that are not concerned with a-Si or a-SiO_2. The total number of references is now 112, which includes some new references based on the referees' comments.

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 (page 3):

“Overall, experimental measurements of the temperature- and film thickness-varying thermal conductivity of a-Si show a large range that depends on the deposition method and impurity concentration (e.g. H, C, and O).[7,8,37,38] In this study, in-line with previous modeling efforts, these effects are not included because (i) the necessary empirical potentials do not exist and (II) computationally-expensive density functional theory calculations limit the model sizes accessible,[4,6–8,39-42] preventing the study of the important low-frequency propagating modes.”

Related comments are also included on pages 15 and 26.

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

“We note that a-Si can be only prepared experimentally as a thin film, where voids and other inhomogeneities are unavoidable[4,7,8,37,38] and can influence the vibrational structure at low frequencies.[7,41]”

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.

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 the sum of Eqs. (2) and (9), there are many inputs that we must predict from atomistic models and methods. An additional focus of this work is the comparison of the predicted mode properties and thermal conductivities of a-SiO_2 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 on different materials.

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 predicted and compared the RDF for our models of a-SiO_2 and a-Si with previous experimental work. The results are now plotted in Figs. 1 (a) and 1(b). Our models compare well with the experimental measurements.

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-SiO_2 samples are the same as those used in Ref. 64 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 Å.”

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).[46]”

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 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 [Eq. (12)] predicts the timescale for dispersion 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-SiO_2 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-SiO_2 in Section IV.D (page 17):

“The timescales 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-SiO_2 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-SiO_2, modes with $4 \times 10^{12} < \omega < 2 \times 10^{13}$ rads/s are affected by the linewidth constraint. Because of the good agreement between the NMD-predicted and AF-predicted diffusivities at low frequencies, we believe 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 $\Gamma(\nu) << \omega 0\ (\nu)$, only a limited number of these lifetimes are used to determine the coefficient of the low-frequency scaling [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 using 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. The comparison between NMD and AF-predicted diffusivities was helpful in determining ω_{cut}. To avoid potential confusion, in the revised manuscript we omitted the NMD-predicted diffusivities for $\omega > \omega_{cut}$ from Figs. 5 (a) and 5(b). This point is addressed in Section IV.E. (page 19):

"Using the sound speeds predicted from the DOS (Table I), the NMD-predicted lifetimes for a-SiO_2 and a-Si are used to predict the mode diffusivities with Eq. (5). The results are plotted in Figs. 5(a) and 5(b) for the low-frequency modes where the DOS scales as ω^{-2} (Fig. 2)."