

Vibrational Mean Free Paths and Thermal Conductivity Accumulation Functions for Amorphous Materials

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Understanding thermal transport in crystalline systems requires detailed knowledge of phonons, which are the quanta of energy associated with atomic vibrations. By definition, phonons are non-localized vibrations that transport energy over distances much larger than the atomic spacing. For disordered materials (e.g., alloys, amorphous phases), with the exception of very long wavelength modes, the vibrational modes are localized and do not propagate like phonons. The Einstein model assumes that the mean free path of these localized vibrations is the average interatomic distance and that their group velocity is equal to the speed of sound. The Cahill-Pohl model assumes that the mean free path of the localized modes is equal to half of their wavelength. While these approach can be used to estimate the thermal conductivity of disordered systems, they only provide a qualitative description of the vibrations that contribute to the lattice thermal conductivity. Using lattice dynamics calculations and molecular dynamics simulations on model amorphous silicon and silica, we predict and characterize the contributions from phonons and localized vibrations to lattice thermal conductivity. The vibrational mean free paths are predicted for these two amorphous materials and the thermal conductivity accumulation function is compared with recent experimental results.

I. INTRODUCTION

Amorphous silicon (a-Si) and nanocrystalline silicon have applications in high-efficiency solar cells.^(cite) Films and substrates made of a-SiO₂ and a-Si have wide application in. ^(cite)

Thermal transport at scales comparable to phonon wave-lengths and mean free paths (MFPs) is presently a topic of considerable interest [14].¹⁻⁴

Recently, nanostructured materials such as nanowires, superlattices, and nanocomposites with strongly reduced thermal conductivities due to phonon scattering at interfaces and boundaries have been reported and are being considered for use in thermoelectrics applications.³⁻⁶ Recent empirical and first-principles calculations show that MFPs of phonons relevant to thermal conductivity vary by more than 5 orders of magnitude in crystalline materials.⁷ Traditionally, empirical expressions and simple relaxation time models have been the only means to estimate MFPs [11].⁸

The thermal conductivity of amorphous solids⁹ Cahill argued that the lattice vibrations in a disordered crystal are essentially the same as those of an amorphous solid.¹⁰

Experimental

Broadband Techniques

Experimentally, inelastic neutron scattering has been used to measure phonon lifetimes in certain materials, but this technique is more suited for single crystal samples [13].¹⁴ Koh et al. proposed a technique which uses a variation of modulation frequency to measure MFPs, but this technique is limited by the modulation frequency [15].¹⁵ An x-ray diffraction and thermorefectance technique can measure ballistic transport in some structures [14].¹⁶

The understanding of the accumulation function for bulk crystalline has made significant advancement experimentally¹⁷ and theoretically.¹⁸ However, understanding of accumulation in amorphous systems is still not well understood.¹⁹⁻²¹ recent measurements of the accumulation function by Regner.²²

Film Thickness Dependence

Measurements of the thermal conductivity of a-SiO₂ thin films show no significant dependence on the film thickness.^{23,24} Measurements by all the refs from Galli paper, showing strong dependence on film thickness.²⁵⁻³¹

a-Si

²⁵ find 1.8 W/m-K, similar to the SW results presented here. Yang et al find as high as 6 W/m-K.²⁷ Liu et al. find a film dependence between 60 and 80 microns.³¹ Claim the HWCVD method and hydrogenation creates the most ordered a-Si. zink shows no plateau at low T for a-Si thin film, indicating the scattering of long-wavelength phonon-like modes by the boundaries.²⁶ Show film thickness dependence up to 10 microns.²⁹ 4.8 W/m-K.³²

The predictions of these theories have been difficult to test because a-Si is available only in thin-film form, making thermal conductivity and specific heat measurements difficult.

A. Low-frequency Scalings: w_4 vs w_2

The Lorentzian breadths below and above xT ; max are roughly of the forms Q_2 and Q_4 , respectively.³³

In conclusion, we have reported on a new experimental determination of the elastic properties of the silica glass by means of high resolution IXS. The data give clear evi-

dence of a Rayleigh scattering regime.³⁴ The acousticlike modes that persist at terahertz frequencies represent a heat conduction channel which accounts for only a fraction, although relevant, of the thermal conductivity. The failure of this approach to fully describe the conductivity data is attributed to the nondiagonal elements of the heat current operator that are not experimentally accessible.³⁴

In conclusion, we have reported on a new experimental determination of the elastic properties of the silica glass by means of high resolution IXS. The data give clear evidence of a Rayleigh scattering regime. This observation represents the first direct measurement of the Rayleigh law up to the BP frequency in vitreous silica, confirming the theoretical prediction of the existence in glasses of this peculiar attenuation mechanism.³⁵

B. w4

w4: as predicted for phonons scattering off point defects under the Debye approximation.

Thermal diffusivity was predicted for a percolation network which showed Rayleigh type scattering dependance in the low-frequency limit.¹¹⁰

Initial work by Zeller and Pohl³⁶ and later by Grabner et al.³⁷ demonstrated that the low-frequency, long-wavelength vibrations in glasses that dominate at low temperature can be characterized using Rayleigh type scattering, $\Lambda \propto \omega^{-4}$.

Experimental measurements of linewidths in a-SiO₂ seemed to be explained by Rayleigh scattering.³⁸ However, in a separate experiment on a-SiO₂, a cross-over from w2, to w4, and back to w2 was observed.³⁹ This was confirmed by⁴⁰ and also in⁴¹.

Theory from Schirmacher et al. predicted an w4 scaling below a system dependent onset frequency.^{42,43}

A field-theoretically motivated mean-field theory self-consistent Born approximation applied to this model^{42,44,45} showed that the frequently observed enhancement of the vibrational DOS over the Debye one boson peak marks the crossover between wavelike and random-matrixlike states, which occurs with increasing frequency. In the harmonic sound attenuation this crossover results in a change from a Rayleigh 4 law to a much weaker law with $s = 2$. This approach involves as input the statistics of the elastic constants, e.g., their variance and correlation length. Compared to the microscopical treatment this approach is much more modest, as it only qualitatively explains the salient features of the vibrational spectrum of disordered solids.

We show rigorously that a topologically disordered system interacting harmonically via force constants, which have a sufficiently short-ranged site-distance dependence, exhibits Rayleigh scattering in the low-frequency limit, i.e., a sound attenuation constant, which is proportional to $d+1$, where ω is the frequency and d the dimensionality.⁴⁶

Another experiment reported Rayleigh-like scattering

(and even stronger) while demonstrating that w2-like scaling can be mistaken by considering large intervals of frequency and wavelength.⁴⁷

sound-wave scattering in a-SiO₂ shows Rayleigh type³⁸ numerical study of disordered lattices with varying coordination show Rayleigh type scattering.⁴⁸

C. w2

model of a-SiO₂ shows $\omega^{-2.49}$

the Brillouin linewidth scales like p^2 in the stable phase.⁵⁰

w2: as predicted for phonons scattering off other phonon, where the Debye approximation is often used.

but it should be noted that published low-temperature thermal conductivity data for a-Si and a-Si:H vary with fabrication methods.^{26,28,51,52}

Low temperature conductivity and specific heat measurements demonstrate that the propagating modes in a-Si and doped a-Si follow $\Lambda \propto \omega^{-2}$.^{26,53} Comparison of experimental measurements by Pompe⁵¹ and Cahill^{28,52} show a plateau of thermal conductivity with temperature, which can be predicted by the theory from FKA⁵⁴ which assumes a ω^{-4} scaling.¹⁹ Zink et al. measured the thermal conductivity of e-beam evaporated amorphous silicon thin films over a wide temperature range and found no plateau, which is predicted from the FAB theory and an ω^{-2} scaling.²⁰

Thermal conductivity of 2.0 W/m-K for $t_f = 130$ nm and 1.8 W/m-K for $t_f = 277$ nm.²⁶

Fabian and Allen predict w2 dependance for model of a-Si.⁵⁴

shows $\tau \propto \omega^{-2}$ for a hard-sphere model.⁵⁵ shows w2 scaling of the inverse linewidths from structure factor of model glasses.⁵⁶ shows w2 for long, w2.5 for tran for a model of a-SiO₂.⁵⁷

review paper on a-SiO₂: models and experimental data for a-SiO₂ shows w2 for short wavelength, high frequency modes and scaling near w2.5 at low frequency.⁵⁸

Using theory based on the random spatial variation of the shear modulus, a transition from w4 to w2 scaling is observed at frequencies much lower than the so-called "Boson peak" frequency.⁴³

experiment from Benassi et al. show a k^2 dependance.⁵⁹

Experimentally, for Q larger than 1 nm⁻¹, all glasses studied so far show $\tau \propto k^x$, with x very close to 2, see Ref. 39 for a review.

a-Si Christie et al. find a best fit of w2.5 for a model of a-Si, although adequate fits to w2 and w4 were shown.⁶⁰

The nature of vibrations in amorphous systems in this frequency region is not yet fully understood. It is known that a force-constant-disordered crystalline lattice gives w4,^{61,62} while many positionally disordered materials, including a-Si, give w2, as does a positionally disordered analytical model.^{50,63}

It may therefore be positional disorder which is responsible for the reduction in the exponent from 4 to 2, although the mechanism of this reduction remains unclear. Of particular interest is the recent experimental work of Masciovecchio et al.,³⁹ which suggests that there may be three regimes in vitreous silica, with respectively w_2 to w_4 and back to w_2 . If this behavior is generally true, then these regions could occur at different ranges of wavevector for different materials, and this could account for different dependences being observed between different materials; the w_4 dependence in lithium diborate,⁴⁷ and for the intermediate value of exponent 2.54 found for the transverse polarization by Christie et al.⁶⁰ and others.

In conclusion we have shown that in a system without any periodic order such as a monatomic liquid, one observes in-elastic excitations that can be interpreted as the noncrystal- line counterpart of Umklapp peaks.⁶⁴

The goal of this work...

In this work, we consider two “stiff glass” amorphous systems: Structural relaxation phenomena do not dominate the dynamics of the.⁵⁵

For modeling the low frequency vibrational modes, two types of scattering mechanisms are considered: (a) phonon-phonon scattering (b) Rayleigh scattering.

BEGIN

In this work, we perform Molecular Dynamics (MD) simulations and Lattice Dynamics calculations on large models of a-SiO₂ and a-Si. The results are used to understand recent experimental measurements using a broadband frequency domain thermal reflectance (FDTR) technique with varying penetration depths L_p .²² Large MD simulations of models for a-SiO₂ show (within the errors) no dependence on the system size, indicating that propagating modes do not make a significant contribution to thermal conductivity. This is confirmed by modal analysis, which demonstrates that propagating modes contribute a negligible amount to thermal conductivity. At low frequency, a quadratic scaling of the vibrational mode lifetimes is a reasonable fit to the predictions, in agreement with previous models of a-SiO₂.(cite)

We predict the thermal conductivity of bulk a-Si using (to our knowledge) the largest MD simulation for a model of a-Si.(cite) Scaling of thermal conductivity with system size indicates that the low-frequency propagating modes in bulk a-Si follow a Debye-like model with a quadratic scaling of the mode lifetime with frequency. (cite) A modal analysis of a large a-Si model supports the evidence for quadratic scaling of lifetimes at low frequency, which is not definitive using the AF diffuson theory.^{19,20} The propagating modes are found to contribute significantly to the thermal conductivity of a-Si an amount similar to that predicted by other models of a-Si.(cite)

The spectrum of vibrational MFPs and the accumulated thermal conductivity (cite) are predicted for a-SiO₂ and a-Si. The thermal conductivity for our model of a-SiO₂ accumulates within 95% of its bulk value for vibrational mean free paths (MFPs) < 10 nm. This result

explains the experimental measurements of Regner et al, which show no measured dependance of the thermal conductivity on L_p ,²² and experimental measurements of the thermal conductivity of thin films which show no dependance on film thickness.(cite)

Using a simple boundary scattering model, the accumulated thermal conductivity of a-Si thin films are predicted from our model of bulk a-Si. The predicted accumulated thermal conductivity reproduces the experimentally measured penetration depth-dependent thermal conductivity qualitatively.(cite) We consider both quadratic and quartic scalings of the low-frequency vibrational lifetimes. By considering both scalings, our model of thin-film a-Si thermal conductivity accumulation can span the range of the lower(cite) and higher^{27,31} experimentally measured thermal conductivity of varying thickness a-Si thin films.

The predicted contribution to thermal conductivity of non-propagating modes from our model of a-Si is in good agreement with the plateau of accumulated thermal conductivity from broadband FTDR. The quadratic scaling of low-frequency mode lifetimes does not predict the steep dependance of thermal conductivity on L_p , while the quartic scaling can qualitatively. Given the lack of experimental measurements of the low-frequency scaling of vibrational mode lifetimes,(cite) low-temperature broadband FDTR measurements can help to show which scaling, quadratic or quartic, is present in a-Si thin films with varying deposition technique. The results could answer the question of whether quartic versus quadratic scaling is responsible for the large thickness variation of the thermal conductivity of a-Si thin films.

END

II. THEORETICAL FORMULATION

A. Vibrational Thermal Conductivity

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To calculate the total vibrational thermal conductivity k_{vib} of amorphous solids, we predict the contributions from k_{ph} and k_{AF} ,

$$k_{vib} = k_{ph} + k_{AF}, \quad (1)$$

where k_{ph} ^{65–67} is the contribution from phonons or phonon-like modes and k_{AF} is the contribution from the Allen-Feldman (AF) theory of diffusons.¹⁹ The form of Eq. has been used in several previous studies with varying assumptions. The various assumptions all lead to predictions that k_{ph} is a significant fraction(> 20%) of k_{vib} .(cite)

We predict the contribution k_{ph} using a Debye-like model,

$$k_{ph} = \frac{1}{V} \int_0^{\omega_{cut}} d\omega DOS(\omega) C(\omega) D(\omega), \quad (2)$$

and the diffuson contribution k_{AF} using^{19,20}

$$k_{AF} = \frac{1}{V} \sum_{\omega_i > \omega_{cut}} C_i(\omega) D_{AF,i}(\omega) \quad (3)$$

The phonon contribution k_{ph} is written as an integral because the finite simulation sizes studied in this work (and others)^{19,20} limit the lowest frequency vibrational modes which can be studied. The diffuson contribution k_{AF} is written as a sum because there are enough high-frequency diffuson modes in the finite-size systems studied.^{19,20} The cut-off frequency ω_{cut} identifies the transition from phonon-like to diffuson modes.^{19,20,27,28,31}

Phonon-like behavior can be identified for a-Si in this work and others, both experimentally^{17,22,27,31} and numerically.^{19,20,68,71} Including the phonon-like contribution k_{ph} for a-Si is not qualitatively sensitive to the choice of model^{19,20,31} or ω_{cut} .^{19,20,27,31,70}

In this work, we identify the phonon limit by ω_{cut} in Eq. , in Section . By identifying ω_{cut} the contribution of phonon-like modes in a-Si and a-SiO₂ is quantified in Section and the thermal conductivity accumulation is predicted in Section .

B. Phonons

Eq. can be derived starting with the Kubo theory^{27,34,75?} and taking the limit of zero phonon self-energy.³⁴ Eq. can also be obtained using the single-mode relaxation time approximation to solve the Boltzmann transport equation.⁶⁷ Assumed in Eq. are isotropy (valid for an amorphous material) and a single phonon polarization,(cite) making the properties a function of the mode frequency ω only. The choice of a single phonon polarization (i.e., an averaging of the transverse and longitudinal branches)(cite) does not significantly change the results predicted in this work or others.^{19,20,27,28,31,34}

For a phonon gas, Eq. has mode diffusivity

$$D(\omega) = \frac{1}{3} v_g^2(\omega) \tau(\omega). \quad (4)$$

The physical picture is of propagating plane waves which travel with velocity v_g for a time τ before scattering. An equivalent physical picture in terms of a scattering length is

$$D(\omega) = \frac{1}{3} v_g(\omega) \Lambda(\omega), \quad (5)$$

where Λ is the phonon mean free path (MFP), defined as

$$\Lambda(\omega) = v_g(\omega) \tau(\omega). \quad (6)$$

Both Eq. and are valid in the propagating limit, i.e. the Ioffe-Regel limit.(cite)

In disordered system, Eqs. and are only valid in the low-frequency, long-wavelength limit.(cite) Because of

this, we focus on the mode diffusivity D as the fundamental quantity. The phonon thermal diffusivity, $D_{ph}(\omega)$, is modeled using

$$D_{ph}(\omega) = B\omega^{-2} \quad (7)$$

which is a scaling predicted for Umklapp phonon-phonon scattering, (cite callaway) and

$$D_{ph}(\omega) = B\omega^{-4} \quad (8)$$

which is the scaling predicted by Rayleigh scattering.¹²⁰ Both scalings Eqs. and also assume

Since we use MD simulations, which are classical and obey Maxwell-Boltzmann statistics,⁷² we take the phonon and diffuson specific heat to be $C(\omega) = C(\omega_i) = \frac{k_B}{V}$ in the harmonic limit, where V is the system volume. This harmonic approximation has been shown to be valid for a-Si modeled using the Stillinger-Weber potential at the temperatures of interest here.(cite) Taking the classical limit for the specific heat allows for a direct comparison between the MD- and lattice dynamics-based methods.

While the classic limit for the mode specific heat is an over-prediction for the high frequency modes in a-Si, the non-propagating contribution predicted by broadband FTDR matches the prediction from the AF diffuson theory. Adjusting the specific heats to include quantum statistical effects...

We can thus focus on the less understood low-frequency propagating contribution.

Because we use molecular dynamics (MD) simulations, we

In general, the thermal conductivity k_{ph} and group velocity v_g depend on the spatial direction \mathbf{n} . Since the amorphous materials studied in this work are isotropic, k_{ph} and v_g are scalar quantities independent of the direction \mathbf{n} .

Under the Debye approximation, which assumes isotropic and linear dispersion (i.e., $v_g = v_s$), the density of states, $DOS(\omega)$, is

$$DOS(\omega) = \frac{3\pi\omega^2}{2v_{s,DOS}^3}, \quad (9)$$

where v_s is an appropriate sound speed (see Section).(cite)

The form for $D(\omega)$ (Eq.) and the $DOS(\omega)$ (Eq.) cause a cancellation of ω dependence in Eq. and ensures the thermal conductivity (Eq.) is finite. The form for $D(\omega)$ (Eq.) causes the thermal conductivity (Eq.) to diverge in the low-frequency limit as the system size is increased as $L^{1/4}$.(cite)

C. Diffusons

For disordered systems, the vibrational modes are no longer pure plane-waves (i.e., phonon modes), except in the low-frequency (long-wavelength) limit.(cite)

When applied in the classical limit, the Allen-Feldman (AF) theory computes the contribution of diffusive, non-propagating modes (i.e., diffusons) to thermal conductivity⁷⁵

$$D_{AF,i} = \frac{\pi V^2}{\hbar^2 \omega_i^2} \sum_{j \neq i} |\langle i | J_{x,y,z} | j \rangle|^2 \delta(\omega_i - \omega_j) \quad (10)$$

where $D_{AF,i}$ is the mode diffusivity and ω_i is the frequency of the i th diffuson. The diffusivity of diffusons can be calculated from harmonic lattice dynamics theory.^{19,20,75}

D. Thermal Diffusivity and Conductivity Limits

The relative contribution of k_{ph} and k_{AF} to k_{vib} has been estimated to be approximately equal for a model of a-Si at 300 K,⁶⁸ while earlier studies find that k_{ph} is less than half.^{19,20} Assuming a constant contribution k_{AF} 1 W/m-K, experimental measurements and estimates show that the contribution from k_{ph} is low as 20%,^{20,28} 40%,³¹ and as high as,²⁷ all depending on the assumed scaling of the low-frequency vibrational scattering. The thermal conductivity k_{vib} has also been estimated for a-GeTe⁶⁹, where $k_{ph} \approx 0$ and $k_{vib} \approx k_{AF}$, and silicon nanowires,⁷⁰ where $k_{ph} \approx k_{AF}$.

For disordered materials In the low-frequency, long-wavelength limit, the mode thermal diffusivity has the form of Eq. or .(cite) The mode diffusivities generally decrease with increasing frequency,(cite) often reaching a plateau,(cite) and then decrease exponentially to zero as the modes become localized.(cite) Diffuson thermal diffusivities, Eq. , can not, in general, be expressed as either Eq. or , as the mode group velocities, lifetimes, and/or MFPs can not be estimated independently.^{19,20,75,76}

It is useful to consider a high-scatter limit for the mode diffusivity,

$$D_{HS} = \frac{1}{3} v_s a, \quad (11)$$

where it is assumed that all vibrational modes travel with the sound speed, v_s , and scatter over a distance of the lattice constant, a . This diffusivity assumption leads to a high-scatter (HS) limit of thermal conductivity in the classical limit⁷⁷

$$k_{HS} = \frac{k_B}{V_b} b v_s a, \quad (12)$$

where V_b is the volume of the unit cell and b is the number of atoms in the unit cell.

For amorphous systems, the spatial disorder creates strong scattering, and k_{vib} tends to be near the high-scatter limit k_{HS} .(cite) It was demonstrated by Kittel that the thermal conductivity of glasses above 20 K could be interpreted using a temperature-independent high-scatter diffusivity on the order of Eq. . Since this corresponds to a phonon model with MFP $\Lambda = a$, too small to

justify use of the model, implies that the dominant modes in most glasses are diffusons and not phonons.(cite)

One way to interpret this result is to use assume $k_{vib} = k_{AF} = k_{HS}$. Amorphous Lennard-Jones argon is dominated by high-scatter modes,⁷⁸ as is a model of a-GeTe, and both their $k_{vib} \approx k_{HS}$.⁶⁹ For a-SiO₂, $k_{vib} \approx 2k_{HS}$, while it is unclear what the appropriate lattice constant a should be.(cite) For a-Si, the experimentally measured thermal conductivity at 300 K $k_{vib} \approx (1-6)k_{HS}$,¹⁰ indicating that there may be a large contribution from k_{ph} .

While Eqs. and are commonly used to establish a high-scatter limit for diffusivity and thermal conductivity, predictions for a-SiGe alloys demonstrated that these are not true high-scatter limits.¹⁹ Recently, the thermal conductivity of several materials has been measured to be significantly below k_{HS} .(cite)

By using lattice dynamics calculations and molecular dynamics simulations, we predict the inputs to Eq. in Section and the thermal conductivity k_{vib} in Section . The MFPs of phonons and diffusons is predicted from Eqs. and , and the thermal conductivity accumulation is predicted in Section

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III. CALCULATION DETAILS

A. Sample Preparation

1. Amorphous Si

For a-Si, we use models created by the Wooten-Winer-Weaire (WWW) algorithm in Ref. 79. Sample sizes with $N_a = 216, 1000, 4096$, and 100,000 were provided, where N_a are the number of atoms in the disordered supercell.(cite) A large sample was created from the $N_a = 100,000$ sample by treating it as a unit cell and tiling twice in all directions to create an $N_a = 800,000$ sample with box size L nm. All a-Si structures used have a density ρ equivalent to the perfect crystal with a lattice constant of $a = 5.43$ Å.(cite)

The Stillinger-Weber potential is used with these samples. The samples were annealed at a temperature of 1100 K for 5 ns to remove meta-stability. Amorphous materials have many different atomic (potential energy) configurations with nearly equivalent energies.^{80,81} The removal of meta-stability is demonstrated by an increase in the predicted sound speeds, $v_{s,T}$ and $v_{s,L}$, after annealing (see Table).⁸¹ This meta-stability can cause errors when predicting vibrational lifetimes using Normal Mode Decomposition (NMD, see Section).(cite)

Similar structures and results can be obtained with a-Si samples created using a melt-quench-anneal procedure,(cite) similar to that used to create a-SiO₂ samples in Section .

(footnote)In an amorphous material, there are many potential energy configurations (atomic positions) which

are nearly equivalent in energy. At a sufficient temperature, the meta-stable configurations cause the equilibrium atomic positions to vary in time. This can effect on the prediction of the vibrational mode lifetimes when using the normal mode decomposition method. In the time domain, the average normal mode potential and kinetic energy must be calculated and subtracted from the normal mode energy autocorrelation function.(cite) If the average energy is not specified correctly, unphysically large or small mode lifetimes can be predicted.(cite)

(footnote) The entire procedure is performed at constant volume. Crystalline silicon (c-Si) is first melted at a temperature of 10,000 K. The liquid is then quenched instantaneously to 300 K, and then annealed at 1100 K for 10 ns to remove meta-stability.

2. Amorphous SiO₂

The a-SiO₂ samples are used from Ref. 71 and have size $N_a = 288$, 576, and 972. The atomic potentials used for a-SiO₂ are the same as in Ref. 71 except the 24-6 Lennard-Jones potential is changed to a 12-6, which has a negligible effect on the predictions presented in this paper. Larger systems of $N_a = 2880$, 4608, and 34562 are created by a similar melt-quench technique as that used in Ref. 71

(footnote) The entire procedure is performed at constant volume. Crystalline silicon (c-Si) is first melted at a temperature of 10,000 K. The liquid is then quenched instantaneously to 300 K, and then annealed at 1100 K for 10 ns to remove meta-stability.

B. Simulation Details

Molecular dynamics simulations are performed using the disordered a-SiO₂ and a-Si supercells described in Sections and . The MD simulations were performed using LAMMPS⁸² with time steps of $dt = 0.00905$, 0.0005 for a-SiO₂ and a-Si. Ten MD simulations with different initial conditions were run for 2^{21} time steps and the atomic trajectories sampled every 2^8 time steps. For the GK method, the thermal conductivity k_{GK} is predicted by window averaging the integral of the heat current autocorrelation function (HCACF).(cite) For a-SiO₂ and a-Si, a interval of the the HCACF integral can be found which is constant within the statistical noise.(cite) Large system sizes up to $N_a = 34,000$ and 800,000 can be used to predict k_{GK} for a-SiO₂ and a-Si (see Section). For smaller systems, the trajectories from the MD simulations used for the GK method are also used in the NMD method to predict the vibrational mode lifetimes (Section).

For the amorphous supercells studied, the only allowed wave vector is the gamma-point (i.e., $\kappa = 0$), where κ is the wavevector and there are $3N_a$ polarization branches labeled by ν . Calculation of the vibrational modes at the

Gamma point require the eigenvalue solution of a dynamical matrix of size $(3N_a)^2$ that scales as $[(3N_a)^2]^3$, limiting the system sizes that can be considered to $N_a = 4608$ and 4096 for a-SiO₂ and a-Si. This eigenvalue solution is also required to perform the NMD (see Section ??) and AF calculations (see Section IV E). The frequencies and eigenvectors were computed using harmonic lattice dynamics calculations and GULP.⁸³ The calculation of the AF diffuson thermal diffusivities (Eq.) is performed using GULP and a Lorentzian broadening of $5\delta\omega_{avg}$ and $14\delta\omega_{avg}$ for a-Si and a-SiO₂, where $\delta\omega_{avg}$ is the average mode frequency spacing.(cite) Varying the broadening around these values does not change the resulting thermal conductivity k_{AF} significantly (see Section).

IV. VIBRATIONAL PROPERTIES

A. Density of States

In this section, we examine the frequencies and density of states (DOS) for the vibrational modes of a-SiO₂ and a-Si described in Section and . The vibrational DOS is computed by

$$DOS(\omega) = \sum_i \delta(\omega_i - \omega), \quad (13)$$

where a unit step function is used to broaden $\delta(\omega_i - \omega)$.(cite) The DOS for a-SiO₂ and a-Si are plotted in Fig. using two values of broadening, $10\delta\omega_{avg}$ and $100\delta\omega_{avg}$. Because of the finite model size, the low-frequency modes are sparse and the DOS has a large variability dependent on the broadening.²⁰ As the system size L is increased, the lowest frequency mode will continue to decrease and the gaps in frequency will fill in.(cite) The DOS for a-Si is similar to the DOS of crystalline silicon,^{70,84} particularly at low-frequency, and with pronounced features as in disordered lattices.^{78,85} The DOS for a-SiO₂ is essentially constant over most of the frequency-range, except at the lowest frequencies.

While the DOS has a large amount of variability at low frequency, there is a clear scaling of $DOS \propto \omega^{-2}$ for both a-Si and a-SiO₂. The range of this scaling is larger for a-Si than a-SiO₂. By fitting the DOS from Fig. to Eq. , a sound speed is predicted at reported in Table . For both a-Si and a-SiO₂, the sound speeds predicted from the DOS are close to the transverse sound speeds predicted from the elastic constants and the structure factor. The Debye model (Eq.) predicts that the contribution from the larger longitudinal sound speed compared to the smaller transverse sound speed will scale as the difference cubed. For a-Si, the contribution from longitudinal modes to the Debye DOS is nearly an order of magnitude less than the transverse modes for a given frequency interval. For a-SiO₂, the longitudinal and transverse sound speeds are closer.(cite experimental a-DOS)

The intensity for the dynamic structure factor of the TA branch was found to be 6-8 times larger than the LA

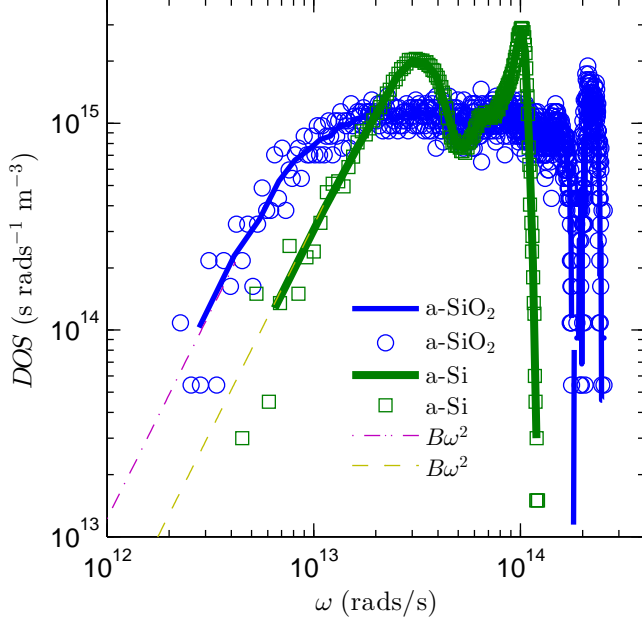


FIG. 1: Vibrational DOS predicted for our models of a-SiO₂ and a-Si using Eq. (14). Both models show a scaling at low frequency $DOS(\omega) \propto \omega^{-2}$, which is predicted by the Debye approximation (Eq. (10)) using the transverse sound speeds predicted using various methods (Table I). At high frequency, the DOS of a-SiO₂ shows a plateau and then a sharp feature corresponding to a gap in the vibrational spectrum due to the Si and O bonds.(cite) For a-Si, there are two sharp peaks, which show as small peaks in the predictions of the vibrational mode lifetimes (Fig. 3) and mode diffusivities (Fig. 4).

branch for a model of a-SiO₂.⁵⁷ A similar factor of 4-5 difference was found in the static structure factors for a mode of a-SiO₂.⁸⁶ We find that the DOS for our model of a-SiO₂ is also dominated by transverse modes (see Table).

The observation that the acoustic modes are located on top of a flat background for intermediate values of q has recently been found by Götze and Mayr as an essential result in their analytic calculation of the spectra within mode-coupling theory.⁵⁵

The DOS predicted for jammed systems are similarly dominated by the transverse sound speed,⁸⁷ while results for disordered lattices demonstrate^{78,85}

B. Group Velocity

For a disordered solid, the three acoustic group velocities (two transverse and one longitudinal) can be predicted using the elastic constants⁸³ or by finite differencing of the three lowest frequency branches of the dispersion relation of the supercell.^{19–21,68,70,78,88} Except for this low-frequency behavior, there is not an accepted

method to predict the group velocity of a vibrational mode in a disordered system, although there have been attempts.^{21,68,70,77,89} In the Cahill-Pohl (CP) model, for example, the group velocity of all disordered modes is the sound speed, v_s , which is also assumed for the HS model, Eq. (??).⁷⁷ This assumption is not generally valid for any material.^{20,21,68,70,78,89}

Experimentally determined values Freeman gives 4100 m/s for a-SiO₂⁹ 3,700 5,100 from⁹⁰ for a-Si 3,800-4,800⁹⁰ Experimentally measured values of sound speed for a-Si are 4,160⁹¹ and 4,290 m/s^{92,93} For chemical vapor deposited a-Si thin films, the transverse sound speed is markedly increased $v_{s,T} = 4,740$ m/s.³¹

1. From Elastic Constants and DOS

The transverse and longitudinal sound speeds of a material can be related to the material's elastic constants, which determine the bulk (G) and shear (K) moduli.(cite) The transverse sound speed is given by(cite)

$$v_{s,T} = \frac{G^{1/2}}{\rho}, \quad (14)$$

and the longitudinal by

$$v_{s,L} = \frac{4G + 3K^{1/2}}{3\rho}. \quad (15)$$

We use the bulk and shear moduli defined in terms of the elastic constants according to the Voight convention.(cite) The sound speeds calculated from the elastic constants are reported in Table . It is clear that the DOS of our models for a-Si and a-SiO₂ are characterized by using the transverse sound speeds, rather than an averaging of the transverse and longitudinal,

$$v_s = \frac{2}{3}v_{s,L} + \frac{1}{3}v_{s,T}. \quad (16)$$

This is backed up by theoretical(cite) and experimental(cite) results.

2. From Structure Factor

Calculating the structure factors of the supercell Gamma modes is a method to test for their plane-wave character at a particular wave vector and polarization corresponding to the VC.^{20,94} Feldman et al. used the structure factor to predict an effective dispersion for a model of amorphous silicon, but did not predict group velocities.²⁰ Volz and Chen used the dynamic structure factor to predict the dispersion of crystalline SW silicon using MD simulation.⁹⁵ Has also been used to determine the dispersion relation from experimentally derived predictions.⁹⁶

The structure factor at a VC wave vector κ_{VC} is defined as⁹⁴

$$S^{L,T}(\omega) = \sum_{\nu} E^{L,T}(\kappa_{\nu}) \delta(\omega - \omega(\kappa_{\nu}=\mathbf{0})), \quad (17)$$

where the summation is over the Gamma modes, E^T refers to the transverse polarization and is defined as

$$E^L(\kappa_{\nu}) = \left| \sum_b \hat{\kappa} \cdot e(\kappa_{\nu}=\mathbf{0} \atop \alpha) \exp[i\kappa \cdot \mathbf{r}_0^{(l=\mathbf{0}) \atop b}] \right|^2 \quad (18)$$

and E^L refers to the longitudinal polarization and is defined as

$$E^T(\kappa_{\nu}) = \left| \sum_b \hat{\kappa} \times e(\kappa_{\nu}=\mathbf{0} \atop \alpha) \exp[i\kappa \cdot \mathbf{r}_0^{(l=\mathbf{0}) \atop b}] \right|^2. \quad (19)$$

In Eqs. (19) and (20), the b summations are over the atoms in the disordered supercell, $\mathbf{r}_0^{(l=\mathbf{0}) \atop b}$ refers to the equilibrium atomic position of atom b in the supercell, l labels the unit cells ($l = 0$ for the supercell), α labels the Cartesian coordinates, and $\hat{\kappa}_{VC}$ is a unit vector. Explicit disorder is included in the Gamma frequencies $\omega(\kappa_{\nu}=\mathbf{0})$ and the $3N_a$ components of the eigenvectors, $e(\kappa_{\nu}=\mathbf{0} \atop \alpha)$.

The structure factors $S^{L,T}(\kappa, \omega)$ are plotted in Fig. for a-SiO₂ and a-Si (left and right panels) for wavevectors along the [100] direction of the supercells. The length scale used for the wavevectors, $\kappa = 2\pi/a[100]$, are $a = 4.8$ and 5.43 Å for a-SiO₂ and a-Si, which are based on the atomic number densities.^(cite) Frequencies $\omega_0(\kappa)$ and lifetimes $\Gamma(\kappa)$ are predicted by fitting each structure factor peak $S^{L,T}(\omega)$ to a Lorentzian function

$$S^{L,T}(\omega) = \frac{C_0(\kappa)}{[\omega_0(\kappa) - \omega]^2 + \Gamma^2(\kappa)}, \quad (20)$$

where $C_0(\nu)$ is a constant related to the DOS.⁸⁵ A dispersion relation is identified by plotting $\omega_0(\kappa)$ in the middle panel of Fig. , where the bars indicate the peak widths $\Gamma(\kappa)$.

For a-Si, the peaks are reasonably Lorentzian for all wavenumbers considered.³³ For a-SiO₂, the peaks are Lorentzian only at the smallest wavenumbers. For large wavenumber, the structure factors peaks are much less than an order of magnitude larger than the background, and the widths are on the order of the frequency range considered in Fig. .^(cite)

Sound speeds are estimated by finite differencing,

$$v_s = \frac{\delta\omega_0(\kappa)}{\delta\kappa}. \quad (21)$$

Estimates of the sound speeds are found from using finite difference of the peaks in $S_{T,L}$ are shown in Table. The values are close to those obtained from the elastic constants (see Section).

The dispersion for a-SiO₂ For intermediate κ , the longitudinal dispersion for a-SiO₂ more closely resembles the so-called "dispersion law for diffusons", where $\omega \propto q^2$.⁸⁵

TABLE I: Estimated from the elastic constants, the pre-annealed group velocities are $v_{s,T} = 3,670$, $v_{s,L,elas} = 7,840$, $v_{s,T,elas} = 2,541$, $v_{s,L,elas} = 4,761$ (see Section).

method	Eqs. (15), (16)	Eqs. (18), (22)	DOS Eq. (10)
a-SiO ₂			
transverse	3,161	2,732	2,339
longitudinal	5,100	4,779	
a-Si			
transverse	3,886	3,699	3,615
longitudinal	8,271	8,047	

The structure factor gives the frequency spectrum needed to construct a (nonstationary) propagating state with a pure wave vector \mathbf{Q} and pure longitudinal or transverse polarization¹⁹. Only low-frequency vibrations have an (approximate) wavevector in disordered systems, and there is no theorem guaranteeing this.²⁰ you cannot assign a unique wavevector to individual modes, even for low frequency modes.^{19,97,98}

Fig 4 of this work shows a dispersion extracted by locating the peaks in the structure factor. The dispersion at low frequency is also dominated by transverse sound speed.⁸⁷

The transverse sound speed predicted by the DOS is used for both a-SiO₂ and a-Si throughout the rest of this work.

As in other studies we find that there is a positive dispersion of the longitudinal branch initially and then there is the usual negative dispersion at higher frequencies. The onset of this positive dispersion seems to be approximately associated with the IoffeRegel crossover for transverse polarization.³³

showed that when the $\tau \approx 2\pi/\omega$, the dynamical structure factor starts its collapse onto the density of states.⁶³ It was also demonstrated using a generic model of topologically disordered systems that both a frequency crossover of linewidth scalings, $\Gamma \propto \omega^{-2}$ and $\Gamma \propto \omega^{-2}$. Experimental measurements of a-SiO₂ demonstrate such a cross-over.³⁹

As the wave vector is increased, the coherence content in the dynamic structure factor tends to fade out. The spectra then merge in an effective density of vibrational states.³⁴

The same positive dispersion was observe in experimental measurements of the structure factor for a-SiO₂,⁹⁹ which was termed the dispersion law for diffusons.⁸⁵

A second new observation is the presence of a softening of the acoustic modes in the frequency range where they experience strong scattering.³⁵

C. Mode Lifetimes

In conclusion, we have found that the high-frequency VS in a realistic model of amorphous Si decay on picosec-

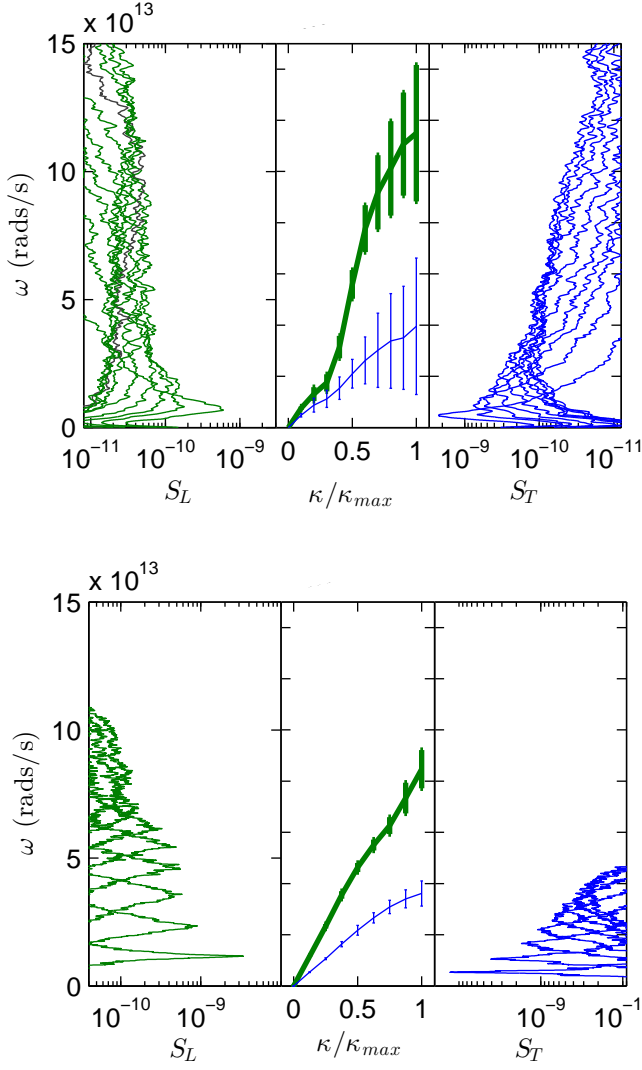


FIG. 2: Longitudinal (left panel) and transverse (right panel) structure factors (Eq. (18)) for a-SiO₂ (top plot) and a-Si (bottom plot). Sound speeds are estimated by finite differencing (Eq. (22)) of the lowest frequency peaks and are reported in Table I. The dispersion for a-SiO₂ is only linear for the lowest frequency, smallest wavenumbers. The dispersion for a-Si is linear over a wider range of wavenumber. Lifetimes are predicted from the widths of the structure factor peaks (Eq. (21)) and are plotted in Fig. 3.

and time scales, and at low temperatures their lifetimes decrease as frequency increases. This is in contrast to recent experimental claims that the modes decay on nanosecond scales and their lifetimes increase as frequency increases.¹⁰⁰

The lifetimes found by this method are in good agreement with the perturbative calculations of Fabian and Allen and are on the order of 10 ps at low temperatures in both 216 and 4096 atom supercells.¹⁰¹

Our results indicate that all of these processes occur on a much faster time scale than the 1 ns temporal resolution of the Raman experiments, so it is not obvious that the measured relaxation rates should be identified with vibrational lifetimes.¹⁰²

1. From Structure Factor

The lifetimes predicted from Eq. are plotted in Fig. for a-SiO₂ and a-Si. There is a clear separation for transverse and longitudinal scalings for a-Si with $\tau \propto \omega^{-2}$, and the lifetimes are above the IR limit (Eq.) for the lowest frequencies.

For a-SiO₂, the separation between transverse and longitudinal is not as clear as in a-Si, and the lifetimes are significantly less than the IR limit, Eq. .

Ioffe-Regel limit¹⁰³.

2. From Normal Mode Decomposition

We use the MD simulation-based normal mode decomposition (NMD) method to predict the lifetimes of each vibrational mode in the disordered supercells (see Section).^{73,104–106} The NMD method can predict vibrational lifetimes which are affected by the disorder in the supercell.(cite)

(footnote) In NMD, the atomic trajectories from MD simulations are first mapped onto the vibrational mode coordinate time derivative,⁶⁶

$$\dot{q}(\kappa=\mathbf{0}; t) = \sum_{\alpha, b, l}^{3, n, N} \sqrt{\frac{m_b}{N}} \dot{u}_{\alpha}(l; t) e^{*}(\kappa=\mathbf{0} \quad b)_{\alpha} \exp[i(\mathbf{0} \cdot \mathbf{r}_0(l))]. \quad (22)$$

Here, m_b is the mass of the b_{th} atom in the unit cell, u_{α} is the α -component of the atomic displacement from equilibrium, \dot{u}_{α} is the α -component of the atomic velocity, and t is time. The spectral energy of each vibrational mode, $\Phi(\kappa; t)$, is calculated from

$$\Phi(\nu, \omega) = \lim_{\tau_0 \rightarrow \infty} \frac{1}{2\tau_0} \left| \frac{1}{\sqrt{2\pi}} \int_0^{\tau_0} \dot{q}(\kappa=\mathbf{0}; t) \exp(-i\omega t) dt \right|^2, \quad (23)$$

The vibrational mode frequency and lifetime is predicted by fitting each mode's spectral energy $\Phi(\nu, \omega)$ (see Appendix) to a Lorentzian function

$$\Phi(\nu, \omega) = \frac{C_0(\nu)}{[\omega_0(\nu) - \omega]^2 + \Gamma^2(\nu)}, \quad (24)$$

where the constant $C_0(\nu)$ is related to the average energy of each mode and the linewidth $\Gamma(\nu)$.¹⁰⁶ The mode lifetime is given by

$$\tau(\nu) = \frac{1}{2\Gamma(\nu)} \quad (25)$$

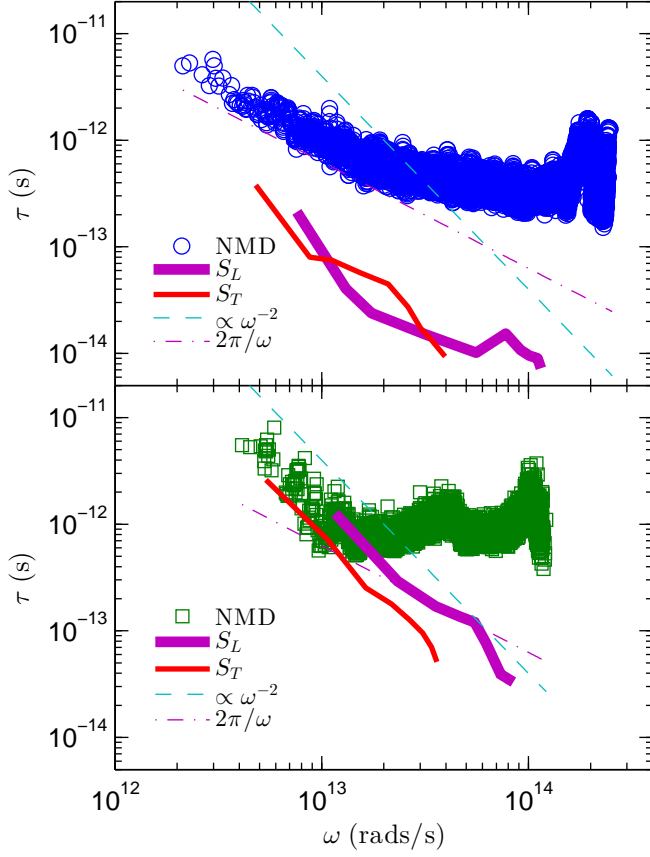


FIG. 3: vibrational mode lifetimes predicted by NMD (Eq.) and the structure factors (Eq.) for a-SiO₂ (top plot) and a-Si (bottom plot). The IR limit (Eq.) is a lower limit for the mode lifetimes, while the lifetimes from the structure factors fall below this limit, particularly for a-SiO₂. The structure factor lifetimes generally follow a scaling $\tau \propto \omega^{-2}$ for both systems, while the mode lifetimes show a plateau before crossing the IR limit.

For a-SiO₂, the mode lifetimes are generally larger than the IR limit Eq. , and follow this limit at low frequency. At high frequency the mode lifetimes are roughly constant without definite scaling. There is a peak near 2×10^{14} rads/s which corresponds to a peak in the DOS (see Fig.).

The mode lifetimes show a similar plateau at higher frequencies, particularly for a-Si, which has been reported for disordered lattices.⁷⁸

For a-Si, a transition to a constant lifetime plateau occurs near 1×10^{14} rads/s, which corresponds to where the DOS peaks in Fig. . Similar behavior was observed for model disordered lattices.^{68,78}

3. Discussion

It has been shown previously using MD simulation that the effect of anharmonicity on thermal conductivity is small.¹⁰⁷ It is not surprising that the lifetimes predicted by the structure factor (which is based on harmonic vibrational modes) agree well with lifetimes predicted by NMD, which include the effects of anharmonicity from the MD simulation.(cite)

While there is some debate as to the frequency of the cross-over from ω^{-4} to ω^{-2} from experiment.^{26,35,39}

For model a-LJ, the lifetimes predicted by the static and dynamic structure factors and the NMD method are in close agreement at low temperature.¹⁰⁸ At low frequency for our model of a-Si, good agreement is found between the structure factor and NMD predicted lifetimes.

The lifetimes predicted by NMD and scaled by the sound speed diverge from the AF predicted mode diffusivities when the mode lifetimes approach the IR limit, shown in Fig. . This is an indication that the modes have transitioned from propagating (where the diffusivity D and lifetime are related by $D = (1/3)v_s^2\tau$) to non-propagating where D and τ need not be related.^{19,20,75,76}

For a model of a-SiO₂, the lowest frequency structure factor lifetimes (inverse linewidths) are already below the IR limit.⁸⁶

These time scales are close to those reported in Ref for similar a-Si structures. The lifetimes are also on the order of those reported for similar models of a-Si using MD-based and anharmonic lattice dynamics methods.(cite)

Fabian finds lifetimes on the order of picoseconds for a-Si and para-crystalline silicon.^{100,109}

A previous study of a-Si predicted vibrational lifetimes on the order of 100 ps, about ten times the values reported here and in other studies.(cite) While the samples

For a-Si, the scaling at low frequency shows $\tau \propto \omega^{-2}$. The same scaling was found in previous studies using similar models for a-Si.(cite)

Also shown as a solid curve is the phonon gas model, where the fitted formula $1/Q^2 + Q^2$ is used for transverse i propagons, and it is assumed that transverse and longitudinal propagons have the same diffusivity. Notice that the gas-model result fits perfectly onto the higher frequency diffuson result, indicating mutual consistency of the two different transport theories in the region of overlap 10 meV 20 meV.

A numerical investigation of Bickham¹⁰² indeed shows that a strong perturbation of the vibrational spectrum of a-Si can relax on a 100 ps time scale, compared to 10 ps for a weak perturbation. In addition to pure vibrational relaxation, it is also likely, as suggested by Bickham and Feldman,¹⁰¹ that correspondingly large local deviations in the atomic displacements cause local structural rearrangements which may relax to local metastable minima while emitting phonons.

D. Diffusivities

Based on the NMD-predicted diffusivities, the modes at low frequency are dominated by transverse modes. However, given the scatter in the NMD-predicted lifetimes, there is some mixture of transverse and longitudinal modes at low frequency. However, treating these two branches separately is not necessary as similar results are obtained by assuming a single branch scaling $D(\omega) = B\omega^{-2}$ which is fit to coincide with the peak in diffusivity D_{AF} at $\omega_{cut} = 11.6 \text{ E } 12 \text{ rads/s}$. This choice of ω_{cut} is close to that used by FAB ($\omega_{cut} = 9.65 \text{ E } 12 \text{ rads/s}$),¹⁹ and is somewhat smaller than that used by FKA²⁰ and Cahill et al.²⁸ ($\omega_{cut} = 15.2 \text{ E } 12 \text{ rads/s}$).

This choice of ω_{cut} is motivated by the AF predictions, gives a reasonable fit to the NMD predictions, and also an extrapolated total thermal conductivity k_{vib} which is in reasonably good agreement with k_{GK} (Fig.).

For a-SiO₂, we find the same $\omega_{cut} = 4.55 \text{ rad/s}$ as used in Ref 34 gives a reasonably good fit to the low-frequency diffusivities predicted by the AF theory (Fig.). In this work, the predicted contribution $k_{ph} = 0.10 \text{ W/m-K}$ is close to that predicted by Ref. 34. Within the errors of the predictions, the predicted k_{ph} for a-SiO₂ is not significant, contributing about 5% to k_{vib} .

which generally agree with diffusivities computed according to the formula of Edwards and THoules.^{20,85,111}

Thermal diffusivity has been predicted using a wavepacket method

It was shown

Garber shows that these high-frequency modes are localized in the Anderson sense, showing exponential decay of the mode eigenvector.¹¹²

It was shown that the diffusivity $D_{AF}(\omega) \propto DOS(\omega)$ at low frequency when the modes are spatially uncorrelated and the overlap between them is small and independent of the frequency.^{87,113}

At low frequencies, the AF-predicted and NMD-predicted mode diffusivities scale as $D \propto \omega^{-2}$, similar to the scaling due to Umklapp scattering of phonons in a crystalline system. Rayleigh scattering due to point defects predicts $D \propto \omega^{-4}$, but is not observed in the amorphous systems studied in this work. (cite) While Rayleigh-type scaling has been observed in harmonic studies of the diffusivities of modes in disordered lattices and jammed systems,^{87,110,113} it has been demonstrated that the harmonic disorder in a-Si produces a scaling similar to Umklapp scattering.¹⁹

In summary, we obtain a frequency-independent diffusivity when the density of states is frequency-independent and the following conditions are satisfied: A displacements of particles in different modes of similar frequency are uncorrelated; B the directions of changes in the relative displacements of pairs of interacting particles are spatially uncorrelated within a given mode; and C the direction of change in the relative displacement of a pair of interacting particles is uncorrelated from the direction of the displacement.

Both a-SiO₂ and a-Si have a region at higher frequencies where the AF-predicted mode diffusivities are relatively constant. This behavior has been reported for a number of disordered systems such as disordered lattices^{78,85,110} and jammed systems. At the highest frequencies the AF-predicted diffusivities trend exponentially to zero, which is an indication that these modes are "locons", spatially localized modes which do not contribute to thermal conductivity.⁹⁴

This perplexing property of glasses has been explained heuristically by assuming that phonons are scattered so strongly by structural disorder that transport becomes diffusive, with a frequency regime of small, constant thermal diffusivity.^{75,110,114}

E. Discussion

From the NMD and AF-predicted diffusivities we determine the propagating phonon cut-off, ω_{cut} (Eq.). The value we determine ω . The value for the Rayleigh scalings

Based on the lifetimes predicted from NMD, the diffusivities predicted at low frequency for a-Si follow very closely the scaling $\tau \propto \omega^{-2}$ (Fig.). The mode diffusivities show much less scatter than those predicted by the AF theory D_{AF} , which is due to the finite-size system and the broadening which is required to evaluate Eq. (11).¹⁹ By using a much larger broadening ($100\delta\omega_{avg}$) the scatter in the AF-predicted diffusivities at low frequency can be smoothed, but at the cost of decreasing the diffusivities at intermediate and high frequencies. It is possible that a frequency-dependent broadening may be necessary for a-Si, but determining this dependence is not clear nor necessary for interpreting the results in this work.

Because the AF-predicted diffusivities show a large scatter, both ω^{-2} and ω^{-4} scalings can be considered as "fits" to the low-frequency behavior. Both FKA²⁰ and interpretation of experimental results by Cahill et al. have used ω^{-4} scaling at low frequency.

Experimental measurements are also inconclusive with respect to the low-frequency scaling of the vibrational scattering. The experimentally measured frequency dependence of the thermal conductivity of a-Si films was explained by Rayleigh scattering of vibrational modes with frequency less than 5 meV (7.6 E12 rads/s), which is inaccessible using the system sizes that could be studied in this work.²⁷ However, comparing with the predicted k_{GK} demonstrates that ω^{-2} better describes the contribution from low frequency propagating modes k_{ph} .

Yang et al. showed that the variation of thermal conductivity with film thickness was best described by a scattering rate ω^{-2} , while a Rayleigh scattering rate was considered for each film. The low-frequency scaling of the scattering rates in a-Si is clearly still an open question.

That the amorphous phase of Si should have a lower GHz attenuation than many other amorphous materi-

als is not entirely surprising, as the 2002 review of low-temperature thermal conductivity and internal friction by Pohl, Liu, and Thompson certainly indicates that the fourfold coordinated materials tend to demonstrate weaker anharmonicity.⁹⁰

Theoretical predictions of acoustic attenuation in amorphous solids generally agree that at room temperature, a quadratic frequency dependence is expected in the frequency range of 10 GHz–1 THz and its origins are expected to be the anharmonicity of the interatomic bonds.

This supports the idea of Slack for a-SiO₂¹¹⁵ While the thermal conductivity of a-SiO₂, the material is characterized by a constant similar for other amorphous materials such as Lennard-Jones argon⁷⁸ and a model of a-GeTe.⁶⁹

At low frequency, our model supports the scaling $D(\omega) = B\omega^{-2}$ and not $D(\omega) = B\omega^{-4}$ as is predicted by the Rayleigh scattering from density fluctuations acting as scattering centers.^(cite) Rayleigh scattering

Using the NMD-predicted lifetimes and AF-predicted diffusivities, a representative velocity can be computed,

$$v_{AF}(\omega) = \left(3 \frac{D_{AF,i}(\omega)}{\tau(\omega)} \right)^{1/2}, \quad (26)$$

and is shown in the inset of Fig. . For a-Si, v_{AF} follows a decreasing trend with increasing frequency, similar to the trend for group velocities in a simple monatomic crystal.^(cite)

The dependence of v_{AF} in frequency is similar to that found for model LJ glasses where a negative dispersion causes a decrease of group velocity with increasing frequency.¹¹⁶

F. Mean Free Paths

Using the lifetimes predicted from the structure factor peaks and the transverse sound speed, the MFP is about the size of the simulation cell L .

$$\Lambda_{AF}(\omega) = (3D_{AF,i}(\omega)\tau(\omega))^{1/2}, \quad (27)$$

V. THERMAL CONDUCTIVITY

A. Bulk

To predict the bulk thermal conductivity of our models of a-SiO₂ and a-Si, we use Eq. and the GK method.^(cite) The GK method is relatively inexpensive compared to the NMD and AF methods so that large system sizes can be simulated (see Section).

When using the Rayleigh scaling $D(\omega) \propto \omega^{-4}$, the thermal conductivity is divergent as the frequency goes to zero. To cure this divergence, we use a

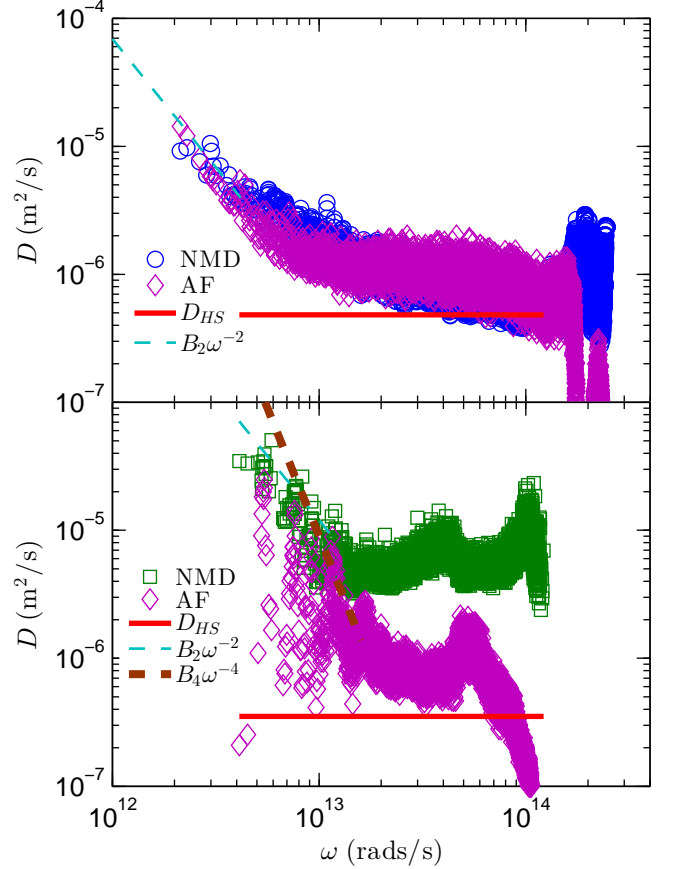


FIG. 4: vibrational mode diffusivities predicted from NMD (using Eqs. (4) and (26) with the sound speed $v_{s,DOS}$ from Table I) and AF theory (Eq. (11)). Also shown are the extrapolations Eqs. (7) and (8), which are used with Eq. (2) to predict the thermal conductivity accumulations in Fig. , and the high-scatter limit Eq. (12).

Baldi et al used a $\omega_{cut} = 4.55$ rads/s, which is a reasonable cut-off for our model of a-Si.³⁴ Baldi et al find that the contribution k_{ph} 0.1 W/m-K, which is the same as the contribution k_{ph} predicted in this work for a-SiO₂. This contribution k_{ph} is smaller than the error bars in the predictions of k_{vib} and k_{GK} shown in Figs. and .

the quadratic scaling is responsible for the system size dependent thermal conductivity predicted by the GK method (k_{GK} , see Section) and seems to be the correct scaling to describe the low-frequency modes for our model of bulk a-Si. However,

Comparing with previous MD simulations of a-Si, Lee found a value of around 1 W/m-K but with very small supercell sizes.¹⁰⁷ He et al find for bulk a-Si $k_{vib} = 3$ W/m-K using the Tersoff potential and a linear extrapolation of the form Eq. using non-equilibrium molecular dynamics.

For smaller system sizes, the same trajectories are used for the GK and NMD methods. The MD simulations

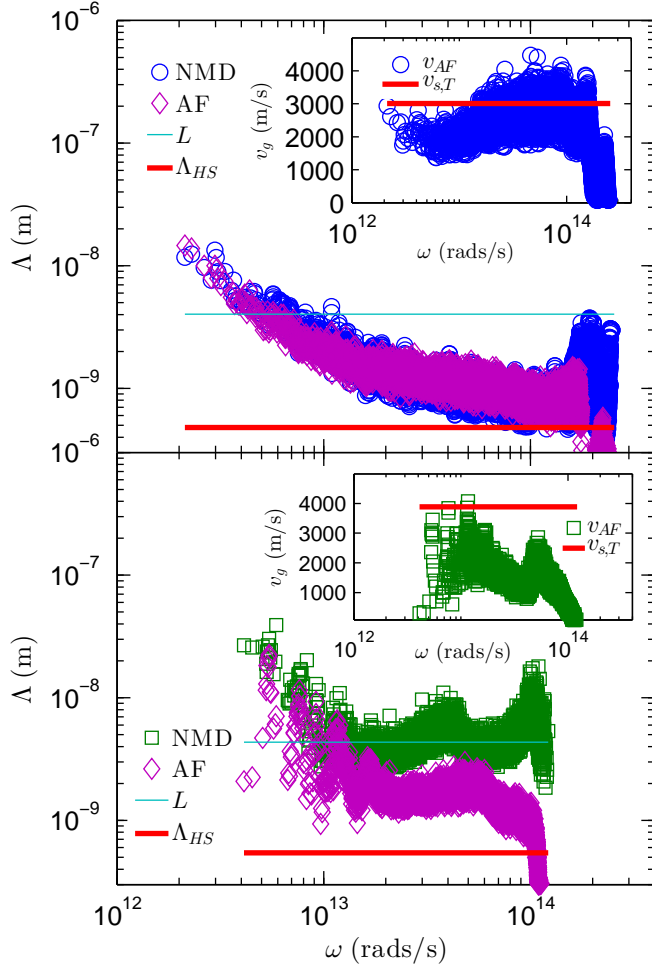


FIG. 5: vibrational MFPs predicted from NMD using Eq. (6) and the sound speed predicted in Table I and from NMD and AF using Eq. (29). Good agreement between the two methods is seen at low frequency, indicating that the modes are propagating and Eqs. (4) and (5) are valid. The majority of MFPs in the intermediate and high-frequency range lie between the simulation box size L and the bond distance a . The inset compares the representative mode velocities Eq. (27) and the sound speeds. For a-Si, v_{AF} decreases with increasing frequency, similar to the behavior of a monatomic crystal.^(cite) The MFPs and mode velocities only approach zero at the highest frequencies, which is an indication that the modes are localized.

were run with the same parameters as the NMD method (see Section).

The predicted thermal conductivities from the GK method are plotted in Fig. . For a-SiO₂, the thermal conductivity is size independent within the errors. For a-Si, there is a clear size-dependence of the thermal conductivity

To compare the results of the mode-based methods (NMD and AF) and the GK method, it is necessary to es-

timate the missing contribution from vibrational modes with frequency less than the minimum frequency of the finite systems.

Assuming the thermal conductivity from Eq. for the lowest frequency modes in the system, the thermal conductivity as a function of the system size takes the form

$$\frac{k(L)}{k_{bulk}} = 1 - \frac{c_0}{L}, \quad (28)$$

“We find that we cannot define a wave vector for the majority of the states, but the intrinsic harmonic diffusivity is still well-defined and has a numerical value similar to what one gets by using the Boltzmann result, replacing v by a sound velocity and replacing l by an interatomic distance a . ”¹⁹

“In order to fit the experimental $\kappa(T)$ it is necessary to add a Debye-like continuation from 10 meV down to 0 meV. The harmonic diffusivity becomes a Rayleigh law and gives a divergent $\kappa(T)$ as $T \rightarrow 0$. To eliminate this we make the standard assumption of resonant-plus-relaxational absorption from two-level systems (this is an anharmonic effect which would lie outside our model even if it did contain two-level systems implicitly). ”¹⁹

The same ω_{cut} was used by Cahill et al. together with a Rayleigh scaling and a boundary scattering model to find $k_{ph} = 0.31$ W/m-K.²⁸

The relative contribution of k_{ph} and k_{AF} is also predicted to be similar for silicon nanowires.⁷⁰

The comparison between theory and experiment supports the description of heat transport in disordered materials developed in Ref. 10, namely, that the dominant heat transport mechanism is coupling between nearly degenerate, extended, but nonpropagating vibrational modes.

B. Accumulation Function

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The thermal conductivity accumulation function,

$$k(\Lambda_{cut}) = \frac{1}{V} \int_0^{\Lambda_{cut}} kbD(\Lambda)DOS(\Lambda) + \frac{1}{V} \sum_{\Lambda < \Lambda_{cut}} kbv_{AF}\Lambda_{AF}, \quad (29)$$

is predicted using our models of bulk a-SiO₂ and a-Si and shown in Fig. . For the phonon contribution k_{ph} , the mode diffusivities ($D(\omega)$) can be transformed $D(\Lambda) = D(\omega)/v_s$. A simple boundary scattering based on the film thickness t_f and the Matthiessen rule is used,

The thermal conductivity accumulation functions for a-SiO₂ and a-Si thin films are shown in Fig. . The thermal conductivity accumulation function for a-SiO₂ saturates at a MFP of 10 nm, which is on the order of the finite size of our model (Section). This sharp accumulation at small MFPs is in good agreement with the prediction that k_{AF} is the dominant contribution to k_{vib} . This result is also in accord with the penetration depth-independent thermal conductivity measurements using

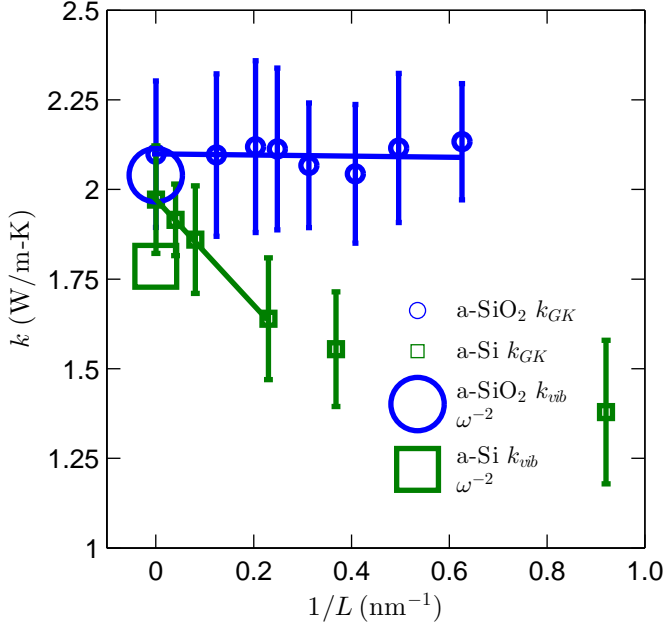


FIG. 6: Thermal conductivities of a-SiO₂ and a-Si predicted using the GK method. For a-SiO₂, the thermal conductivity is size independent, indicating there is no important contribution from phonons (Eq. (2)). While for a-Si, there is a clear size dependence, which is accounted for by using Eq. (3) and extrapolation (Eq. (7), Fig. 4).

broadband FDTR.²² Only the quadratic scaling Eq. is considered for a-SiO₂, which is discussed later in Section .

For a-Si, the thermal conductivity accumulation function shows that k_{AF} saturates before 10 nm, which is also on the order of our finite model size. The propagating contribution k_{ph} is predicted using both quadratic (Eq.) and quartic (Eq.) scaling for the mode diffusivities. As discussed in Section, the quadratic scaling is responsible for the system size dependent thermal conductivity predicted by the GK method (k_{GK} , see Section) and seems to be the correct scaling to describe the low-frequency modes for our model of bulk a-Si. Using the quadratic scaling, the thermal accumulation functions for our model of a-Si thin films passes reasonably well through many of the experimentally measured values.(cite) The quartic scaling also passes through many of the experimentally measured values reasonably well, particularly for film thicknesses larger than 10 μ m.(cite)

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C. Discussion

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The transverse sound speed predicted for our model

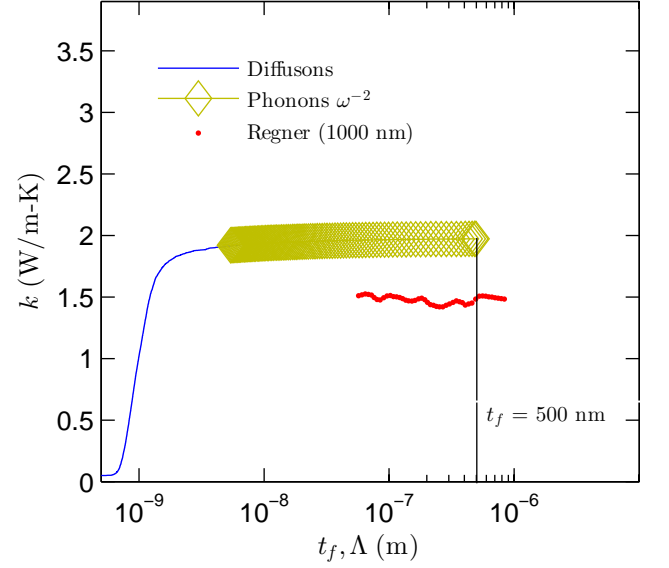


FIG. 7: Thermal conductivity accumulations and thermal conductivities versus film thickness for a-SiO₂ (top plot) and a-Si (bottom plot) from: (i) predictions from this work, (ii) recent broadband measurements of Regner et al, (iii) various experimental measurements for a wide-range of a-Si film thicknesses (see (2)). While the thermal conductivity predictions for a-SiO₂ and a-Si in this work seem to be well-characterized by Umklapp type scaling of the MFPs (Eq. (7)), this scaling is not able to predict the dramatic increase of thermal conductivity with increasing film thickness from experimental measurements of a-Si thin films.

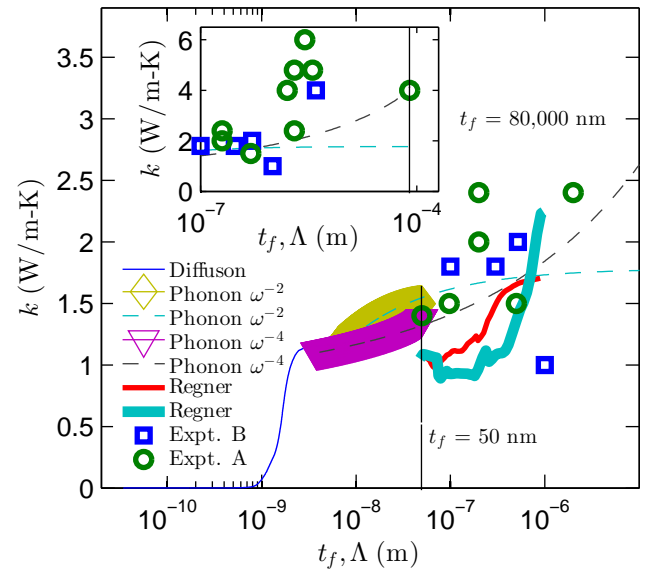


FIG. 8: film thickness dependant thermal conductivity of a-Si from experiment.

of a-Si is about 85% of that measured by experiment.³¹ The same is true for a-SiO₂. While this possibly leads to an underprediction of the mode diffusivity scalings we predict (Eq. , Fig.), it leads to an overprediction of the DOS (Eq.). Overall this leads to an underprediction of the thermal conductivity because the DOS scales as $DOS(\omega) \propto 1/v_s^3$. We can thus regard the predictions from our models, with smaller transverse sound speeds, as an upper bound on k_{ph} for a given diffusivity scaling $D(\omega) = B\omega^{-2}$. The critical parameter is the choice of ω_{cut} . We pick ω_{cut} and the low frequency scaling $D(\omega) = B\omega^{-2}$ based on their ability to describe the low-frequency behavior of the vibrational modes in our finite-size models. The quadratic scaling $D(\omega) = B\omega^{-2}$ has been observed in separate numerical studies for models of a-SiO₂(cite) and a-Si(cite).

Previous experimental studies of a-SiO₂ have estimated negligible the contribution from low frequency ($\omega < \pi 10^{12} \text{rads/s}$)¹¹⁸ vibrational modes to be negligible. Using our model of a-SiO₂, we also find the low-frequency propagating contribution to be negligible (Section). While experiments show there is a cross-over regions from quadratic to quartic scaling of the mode lifetimes in a-SiO₂, the thermal conductivity of thin film a-SiO₂ shows no significant dependence on the thickness.(cite) The cross-over region from quadratic to quartic, then back to quadratic observed in experiments for a-SiO₂ occurs in the frequency range 4.610^9 to 1.5210^{10} rads/s,³⁹ and 3.0410^{11} to 1.5210^{12} rads/s⁴¹. While these frequency ranges are inaccessible by our finite-size models, we estimate that the extrapolated k_{ph} using a quartic scaling in this region to be... The bulk thermal conductivity predicted for our model of a-SiO₂ overestimates that of experimental measurements.²² This can be attributed to either difference between experimental a-SiO₂ and the potential model used in this work,(cite) the lack of anharmonic scattering included in the AF theory,¹⁹ or the assumption of the classical-limit specific heat for all frequencies (Section). Qualitatively, our model confirms that propagating modes do not contribute significantly to the thermal conductivity of a-SiO₂.

The classical-limit mode specific heat is a good approximation for the low-frequency propagating modes in a-SiO₂ and a-Si, which are shown to be fully activated by around 10 K.(cite) The classic limit for the mode specific heat is an over-prediction for the high frequency modes in a-SiO₂ and a-Si at 300 K.(cite) However, the contribution k_{AF} we predict in the classical limit for mode specific heat for a-Si is nearly the same as the non-propagating contribution (plateau) predicted by broadband FTDR.(cite) Adjusting the specific heats to include quantum statistical effects... Taking the diffuson contribution k_{AF} to be a constant, which we predict to be $k_{AF} \approx 1 \text{ W/m-K}$ in agreement with other numerical studies(cite) and experiments(cite), we can thus focus on determining the less understood low-frequency propagating contribution k_{ph} .

There is a question as to the scaling of the low-

frequency vibrational mode lifetimes in a-Si. For a-SiO₂, both quadratic and quartic scalings can be observed experimentally.(cite) For a-Si thin films, varying preparation techniques suggest either quadratic(cite) or quartic(cite) scaling alone. While there is no clear consensus from various experiments, all predictions in this work demonstrate that the low-frequency modes in bulk a-Si follow a quadratic scaling of the mode lifetimes, which has been observed in previous models of a-Si(cite) and a-SiO₂.(cite) Amorphous silicon, however, can be prepared only in thin films,(cite) where voids and other inhomogeneities are unavoidable¹¹⁷ and can influence the vibrational structure at low frequencies.^{31,121} A smooth transition between quadratic and quartic scaling can be achieved using a phenomenological model where a cross-over wavevector (or frequency) must be specified by experiment.⁴⁰ While this cross-over can be identified experimentally for a-SiO₂,³⁹ experiments are limited for a-Si thin films.(cite) Our models are not large enough to investigate the relevant frequency range ($< 110^{12} \text{ rads/s}$),(cite) so we considered both quadratic and quartic lifetime scalings when predicting the thermal conductivity accumulation functions in Fig. . Experimental measurements of the cross-over frequency (wavevector) and steepness parameter are needed from experiment to investigate the applicability of this phenomenological model further.(cite) The dependence of a-Si thin film thermal conductivity on thickness,(cite) preparation method,(cite) and hydrogen content(cite) make this particularly challenging. In fact, different experimental studies can be satisfactorily explained using quadratic(cite) or quartic(cite) scalings found that each was a satisfactory explanation for the results found. (cite)

A number of emerging experimental techniques are capable of studying the low-frequency propagating modes in disordered systems. (cite) For amorphous materials, where the propagating contribution k_{ph} is typically smaller than in the crystalline phase, broadband FDTR has demonstrated it can probe the relatively small effect of propagating modes at 300 K. However, the broadband FDTR studies thus far have been limited to one deposition technique and a relatively small range of film thicknesses ($500 \text{ nm} < t_f < 2000 \text{ nm}$).(cite) The nature of the low frequency scaling can be better elucidated using broadband FDTR on films prepared using varying deposition techniques,(cite) a wider-range of film thicknesses ($1-100 \mu\text{m}$) (cite) and lower-range of temperatures ($10 - 100 \text{ K}$).(cite) For a-Si, propagating low-frequency have been identified qualitatively by both experimental measurements(cite) and numerical modeling.(cite) It is thus interesting to consider thin films of a-SiGe alloys, which have been demonstrated to have reduced thermal conductivities compared to a-Si.¹⁹ It is not clear what vibrational lifetime scaling at low frequency would be observed in a simple topologically disordered alloy given there isn't a consensus for even topologically disordered but chemically ordered systems.(cite) A combi-

nation of frequency-domain, time-domain, and variable-physical-heating size measurements would be helpful in investigating.^{15,17,22,122}

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VI. SUMMARY

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In this work we investigated the contributions of propagating k_{ph} and non-propagating k_{AF} modes to the total vibrational thermal conductivity k_{vib} of two glasses, a-SiO₂ and a-Si. For a-SiO₂, the contribution from propagating modes k_{ph} is shown to be negligible compared to k_{vib} . This is confirmed by various experimental measurements, including a broadband FDTR study which probed the vibrational MFPs of a-SiO₂. The thermal conductivity accumulation function for our model of a-SiO₂ saturates near a MFP of 10 nm, in agreement with the results of Regner et al. who show no systematic variation of the thermal conductivity on L_p .²² and in agreement with experiments on a-SiO₂ thin films which show no systematic variation with film thickness t_f .(cite)

Our model of bulk a-Si has a thermal conductivity k_{vib} with significant contribution from k_{ph} , where the low-frequency propagating modes are best described by a quadratic scaling of the mode lifetimes. The thermal conductivity accumulation predicted for our model of bulk a-Si with a simple boundary scattering model show reasonable agreement with some of the experimentally predicted thermal conductivities using varying film thicknesses and deposition techniques (Fig.).(cite) However, using a quartic scaling with our model also gives a satisfactory agreement with other experimental measurements (Fig.).(cite) These large discrepancies between measured thermal conductivity of various a-Si thin films calls for the need of further experimentation. Broadband techniques,(cite) which have demonstrated the ability to probe a wide-range of vibrational mode frequencies and MFPs, can help elucidate.(cite)

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