

## Predicting the thermal conductivity of inorganic and polymeric glasses: The role of anharmonicity

Sergei Shenogin,<sup>1,a)</sup> Arun Bodapati,<sup>1</sup> Pawel Keblinski,<sup>1</sup> and Alan J. H. McGaughey<sup>2</sup>

<sup>1</sup>*Department of Materials Science and Engineering and Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York 12180, USA*

<sup>2</sup>*Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, USA*

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The thermal conductivity of several amorphous solids is numerically evaluated within the harmonic approximation from Kubo linear-response theory following the formalism developed by Allen and Feldman [Phys. Rev. B **48**, 12581 (1993)]. The predictions are compared to the results of molecular dynamics (MD) simulations with realistic anharmonic potentials and to experimental measurements. The harmonic theory accurately predicts the thermal conductivity of amorphous silicon, a model Lennard-Jones glass, and a bead-spring Lennard-Jones glass. For polystyrene and amorphous silica at room temperature, however, the harmonic theory underestimates the thermal conductivity by a factor of about 2. This result can be explained by the existence of additional thermal transport via anharmonic energy transfer. More surprisingly, the thermal conductivity of polystyrene and amorphous silica at low temperature (MD and experimental) are significantly below the predictions of the harmonic theory. Potential reasons for the failure of the harmonic theory of disordered solids to predict the thermal conductivity of glassy polymers are discussed. © 2009 American Institute of Physics. [DOI: 10.1063/1.3073954]

### I. INTRODUCTION

The temperature  $T$  dependence of the thermal conductivity  $k$  of a broad range of inorganic and polymeric glasses is very similar, showing a monotonic increase with increasing temperature.<sup>1</sup> Despite a highly disordered structure, at temperatures below 10 K, the thermal energy is carried by polarized and delocalized vibrations, i.e., propagating phonons. Consequently, below 10 K,  $k \sim T^2$  is observed, a trend usually attributed to the phonon scattering in a two-level system.<sup>2</sup> In the temperature range of 10–20 K, a plateau is observed, followed by further increase in the thermal conductivity at higher temperature, which has been attributed to excitations of higher frequency vibrations and/or anharmonic effects.<sup>3</sup> Contrary to the behavior of dielectric crystals, there is no decrease in the thermal conductivity at higher temperatures caused by a reduction of phonon mean free path by phonon-phonon scattering.

The thermal conductivity of a glass can be interpreted in terms of the Boltzmann transport theory for a phonon gas in a dielectric,<sup>4</sup>

$$k = \frac{1}{3V} \sum_i C_i v_i l_i, \quad (1)$$

where the summation is performed over all vibrational modes,  $C_i$  is the spectral heat capacity,  $v_i$  is the group velocity, and  $l_i$  is the phonon mean free path. A temperature-dependent average phonon mean free path may be introduced to fit experimental data in the plateau region, following the idea that phonons with energy below the mobility edge can propagate through the structure.<sup>5</sup> In glasses,

with the exception of very-long-wavelength modes, the vibrational modes are not polarized and do not propagate like phonons in a crystal. Therefore, Eq. (1) can only describe the few low-frequency acoustic modes for which a nonzero group velocity can be assigned. However, when Eq. (1) is used to estimate thermal conductivity in a glass, one typically assumes that the group velocity for all the modes is equal to the speed of sound and the mean free path is given by the average interatomic distance. This approach can give qualitatively correct results above the plateau region with the temperature dependence of the thermal conductivity entirely explained by the increase of the heat capacity at higher temperatures.<sup>6</sup> However, because lattice dynamics calculations clearly show that the majority of the vibrational modes in a glass are nonpropagating,<sup>7</sup> Eq. (1) will be used here only for qualitative comparison between glasses and crystals.

The thermal conductivity of a crystal decreases at higher temperature due to the reduction of phonon mean free path, which is caused by increased phonon-phonon scattering. The underlying mechanism is the strain dependence of the elastic constants of the crystal, which results from the anharmonicity of the atomic interactions.<sup>1</sup> Unlike in a crystal, the thermal conductivity of a glass increases monotonically with increasing temperature, suggesting that the role of anharmonicity is different. Heat transfer in a glass can be analyzed in terms of energy hopping between *localized* nonpropagating vibrational modes,<sup>3,8–11</sup> with anharmonicity contributing positively to the thermal conductivity, and its contribution increasing with increasing temperature. Therefore, the increase of thermal conductivity with increasing temperature above the plateau region results not only from the increased heat capacity of the vibrational modes but also from stronger anharmonic coupling between the modes.<sup>10</sup>

<sup>a)</sup>Electronic mail: shenos3@rpi.edu.

Allen and Feldman put forward an alternative mechanism based on the “diffusion” of energy between the *extended* nonpropagating vibrational modes (AF theory).<sup>7,12</sup> They applied the energy flux operator method<sup>13</sup> to an amorphous structure and calculated the thermal conductivity within the harmonic approximation. The AF theory successfully predicts the temperature dependence of thermal conductivity in amorphous silicon<sup>14,15</sup> and Lennard-Jones (LJ) glasses,<sup>16</sup> but the applicability of AF theory for other amorphous materials such as polymers has not been studied. Because the majority of vibrational modes in amorphous-Si and LJ glasses are spatially extended and nonpolarized, it is perhaps not surprising that the harmonic theory works well. For amorphous solids with a large fraction of localized modes, energy hopping may be applicable.

To investigate the roles of harmonic and anharmonic transport channels, and the related localization of vibrations on the thermal conductivity of glasses, we here use molecular dynamics (MD) simulation and several model amorphous systems including amorphous Si, amorphous silica, and an amorphous polymer. We note that in MD simulations realistic interaction potentials that include anharmonic effects are used, while the AF theory considers only harmonic energy transfer. The results of the MD simulations are compared with the predictions of the AF theory.

## II. SIMULATION SETUP AND THERMAL CONDUCTIVITY PREDICTION

Five model amorphous structures were generated for our study and these are as follows: (i) 600 identical beads interacting by a 12-6 LJ potential, (ii) the 600 beads combined into 15 linear chains with 40 beads in each, and the finitely extendable nonlinear elastic interaction potential within the chain,<sup>17</sup> (iii) amorphous silicon, with 512 atoms interacting by the Stillinger–Weber potential,<sup>18</sup> (iv) amorphous silica, with 288, 576, or 972 atoms interacting by the van Beest–Kramer–van Santen (BKS) potential (Ref. 19), and (v) an atactic polystyrene model consisting of one, two, or three chains (338, 676, or 1014 explicit carbon and hydrogen atoms), prepared according to conformational statistics at room temperature<sup>20</sup> and further equilibrated at standard temperature and pressure using the polymer consistent force field.<sup>21</sup> The choice of the structures includes the most popular simplified glass models [(i) and (ii)], and realistic models of inorganic [(iii) and (iv)] and organic (v) glasses with well established force fields for each structure. All simulations have periodic boundary conditions applied in all three dimensions. Snapshot images of the five studied models are shown in Fig. 1.

The theoretical calculation of the thermal conductivity is done according to the following AF theory:<sup>7</sup>

$$k = \frac{1}{V} \sum_i C_i(T) D_i, \quad (2)$$

where  $V$  is the volume and the sum is over all vibrational modes. The thermal diffusivity of each mode  $D_i$  is calculated with the heat current operator  $S_{ij}$  with summation over all other vibrational modes,<sup>12</sup>

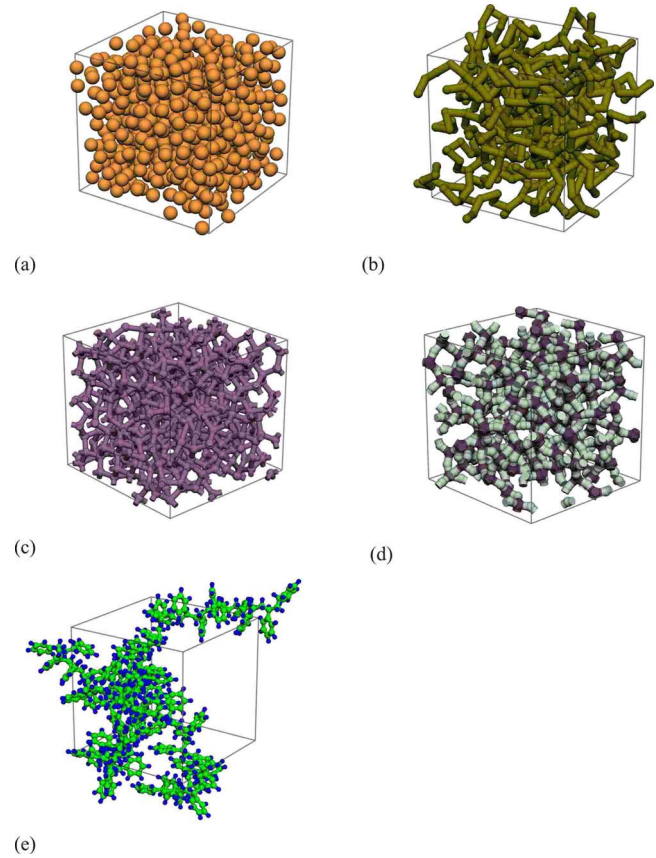


FIG. 1. (Color online) Snapshot images of five amorphous molecular models: (a) LJ beads, (b) bead-spring model, (c) amorphous silicon, (d) amorphous silica, and (e) atactic polystyrene.

$$D_i = \frac{\pi V^2}{3\hbar^2 \omega_i} \sum_{j \neq i} |S_{ij}|^2 \delta(\omega_i - \omega_j), \quad (3)$$

where  $\hbar$  is the Planck constant divided by  $2\pi$  and  $\omega_i$  is the angular frequency of mode  $i$ . For our finite-size systems with periodic boundaries, the  $\delta$ -function in Eq. (3) is broadened to a Lorentzian-shaped peak with a width exceeding the mean energy-level spacing.<sup>12</sup> The elements  $S_{ij}$  are calculated from the mass-scaled force constant matrix, as shown in Appendix A of the Allen and Feldman paper.<sup>12</sup> For all structures, a careful energy minimization was done prior to the calculation of the force constant matrix and the vibrational mode analysis. Because the force constant matrix depends only on a quadratic expansion of the potential energy around its minimum, we will refer to the results of these calculations as the thermal conductivity under the harmonic approximation. Within this approximation, the temperature dependence of the thermal conductivity will only be a result of the temperature dependence of the heat capacity. If the predictions of the harmonic approximation are to be compared with results of classical MD simulations, one should use the classical limit for the heat capacity  $C_i = k_B$ , where  $k_B$  is the Boltzmann constant, in Eq. (2).

Since the nonzero heat current operator in Eq. (3) requires that two modes overlap in space, the thermal diffusivity of a mode strongly depends on its degree of localization. In fact, the diffusivity of a localized mode calculated by Eq.

(3) is strictly equal to zero. In order to characterize the degree of mode localization we calculated the inverse of the participation ratio  $p_i$ ,

$$\frac{1}{p_i} = \sum_a^{\text{All atoms}} [\varepsilon_{ai}^2]^2 \quad (4)$$

where  $\varepsilon_{ai}$  are the components of the normalized polarization vectors for each mode, which satisfy

$$\sum_a^{\text{All atoms}} \varepsilon_{ai}^2 = 1. \quad (5)$$

By comparing  $p_i$  and  $D_i$  for different modes, we conclude that modes with participation ratio greater than 0.3–0.4 are not localized.

To predict the thermal conductivity from nonequilibrium MD (NEMD), the length of the simulation cell in one direction for each structure was multiplied by 6. The structure was then equilibrated at a specified temperature, and a constant heating power  $W$  was applied to the center of the structure, and the same constant cooling power  $-W$  was applied to the periphery. Once a constant temperature gradient  $\nabla T$  is reached, the thermal conductivity is calculated according to the following Fourier law:<sup>22</sup>

$$k = \frac{W}{\nabla TA}, \quad (6)$$

where  $A$  is the effective heat flux area (double the area of the cell face normal to the flux direction). Additional simulations were performed on longer simulation cells to make sure that no size effects exist at these lengths for NEMD simulations. For the amorphous silica structure, the thermal conductivity is predicted from equilibrium MD and the Green–Kubo method.<sup>23</sup>

### III. RESULTS

A comparison of the results for the LJ glass and the LJ glass with particles grouped in linear chains is presented in Fig. 2. The normalized vibrational density of states, plotted versus reduced frequency in Fig. 2 (top plot), shows that polymerization shifts approximately 1/3 of the vibrational modes to higher frequency. This result simply reflects the fact that for the linear chain, two of the three degrees of freedom associated with each bead are unaffected by bonding, while the frequencies of the modes associated with intrachain motion increase. As seen in Fig. 2 (middle plot), the participation ratio of the high frequency modes is less than 0.15, indicating that these modes are localized in contrast to the rest of the spectrum, which has participation ratio  $\sim 0.5$ . The analysis of the associated eigenvectors shows that each of the high-frequency modes is associated with the oscillation of several chain segments along the local chain direction (i.e., longitudinal modes). The thermal diffusivity of the high frequency modes, evaluated from AF theory, is negligible compared to the diffusivity of lower-frequency modes (Fig. 2, bottom plot). As a result, the thermal conductivity calculated from AF theory for the bead-spring model is almost exactly 2/3 of that of the original LJ glass

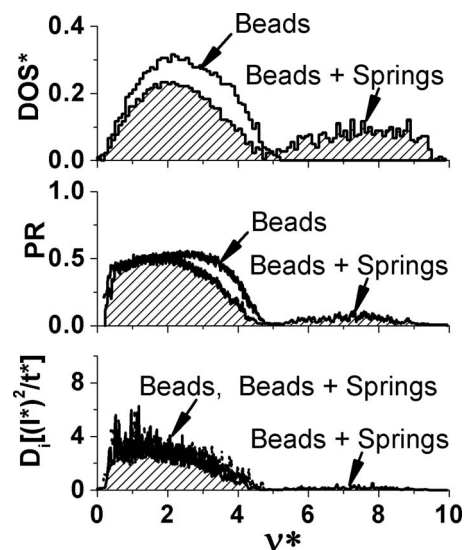


FIG. 2. Vibrational density of states, participation ratio, and mode diffusivity plotted as a function of reduced frequency for LJ bead and bead-spring models.

(0.102 W/m K compared to 0.150 W/m K). These predictions agree with the results of the NEMD simulations (0.097 and 0.142 W/m K). The major conclusion from these results is that the harmonic approximation for thermal conductivity works very well for these model LJ systems. The other important observation is that contrary to intuition, the introduction of strong covalent bonds reduces the thermal conductivity of the structure. This latter observation is perhaps associated with the fact that the chains are fully flexible and thus do not allow for the possibility of rapid energy transport along the straight chain segments. This observation, however, is valid only for chemically uniform glasses in which the fraction of localized vibrations is negligible and the mechanism of thermal transport is primarily diffusive as suggested by AF theory. As we will show, for glasses with complex chemical structure, such as silicates and aluminosilicates, the diffusive mechanism does not work and the experiments show the opposite tendency (i.e., glasses with stronger covalent bonding exhibit higher thermal conductivity).<sup>24</sup>

The results of the vibrational mode analysis for amorphous silicon are plotted in Fig. 3. The density of states for amorphous silicon consists of two characteristic peaks and compares favorably with previously reported results.<sup>7,25</sup> The spectrum consists mostly of delocalized vibrational modes (participation ratio  $p \sim 0.5$ ), which will contribute to the thermal conductivity. Only a small fraction of the highest frequency modes are localized and have essentially zero diffusivity. A comparison of the thermal conductivity calculated from AF theory with the predictions of the NEMD simulations is shown in Fig. 4. Two important observations can be made and these are as follows: (i) the classical MD simulations show no temperature dependence for the thermal conductivity and (ii) the constant value of the thermal conductivity obtained by NEMD is very close to the classical limit for harmonic theory (0.91 and 0.85 W/m K). As previously reported by Allen and Feldman,<sup>7,12</sup> the harmonic theory cal-

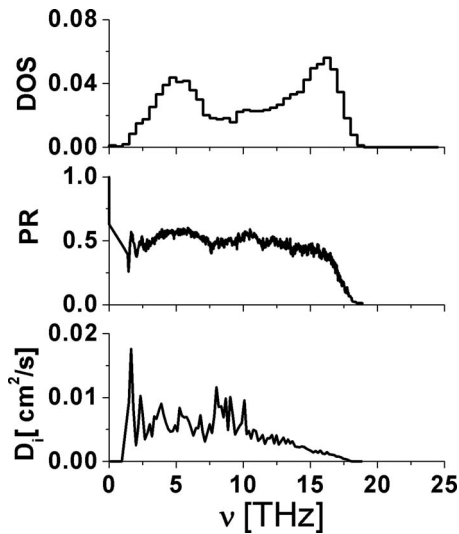


FIG. 3. Vibrational density of states, participation ratio, and mode diffusivity plotted as a function of frequency for amorphous silicon.

culations are close to the experimental results. The temperature independent value obtained by NEMD is close to the experimental values at temperatures above 100 K. These results simply restate the Allen and Feldman conclusion that the anharmonicity-related hopping mechanism between localized modes does not play an important role in the thermal conductivity of amorphous silicon.

The results for amorphous silica are quite different (see Figs. 5 and 6). The high-frequency part of the vibrational spectrum ( $\nu > 30$  THz) consists mostly of localized modes ( $p < 0.2$ ). These localized modes have thermal diffusivities close to zero. Contrary to amorphous silicon, the thermal conductivity obtained from classical MD simulations is temperature-dependent and at room temperature is about 30% larger than that predicted by AF theory (solid line in Fig. 6). This result indicates that anharmonic transport mechanisms are more important in amorphous silica than in amorphous silicon. These mechanisms are likely associated with anharmonic energy transfer between localized vibrational modes or between localized and delocalized modes. The contribution from energy hopping increases with temperature, and after the addition of a temperature-independent

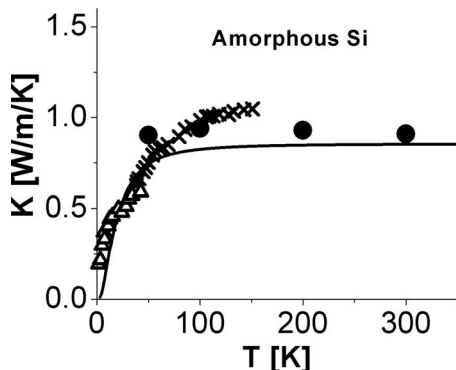


FIG. 4. Temperature dependence of thermal conductivity for amorphous silicon predicted by AF theory (solid line), calculated from NEMD (solid circles) and obtained in experiments [triangles (Ref. 27) and crosses (Ref. 28)].

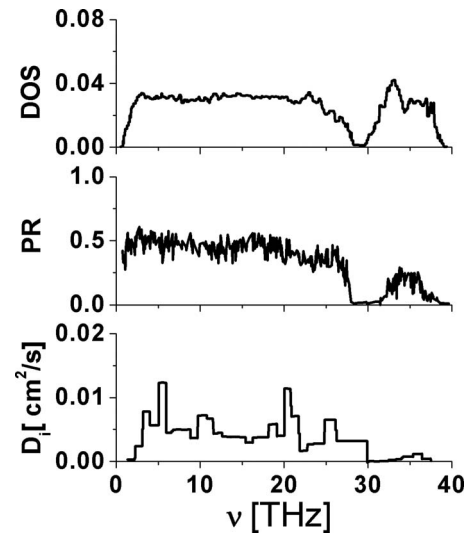


FIG. 5. Vibrational density of states, participation ratio, and mode diffusivity plotted as a function of frequency for amorphous silica.

harmonic thermal conductivity, can qualitatively explain the results of the classical MD simulations. In particular, the MD-measured thermal conductivity of amorphous silica shows the linear temperature dependence often found in polymers and other glasses with complex composition.<sup>3,10</sup>

What is quite surprising, however, is that the predictions of the AF theory in the classical limit [ $C_i = k_B$  in Eq. (2)] show strong disagreement with the results of MD at low temperatures, where the harmonic theory should describe the behavior of the system reasonably well. In particular, the thermal conductivities obtained from MD fall below the AF predictions at sufficiently low temperatures. This result is contrary to the expectation that the harmonic contribution to the thermal conductivity should be temperature independent for a classical system and converge to a constant value at low temperature. In addition, we observed that the AF prediction is dependent on the sample size, with larger values predicted for larger samples. In particular, the classical limit yields thermal conductivities of 0.94, 1.33, and 1.64 W/m K for 288, 576, and 972 atom samples. By contrast, the results of the AF theory for amorphous silicon are essentially size independent.<sup>7,14</sup> A similar size dependence was previously

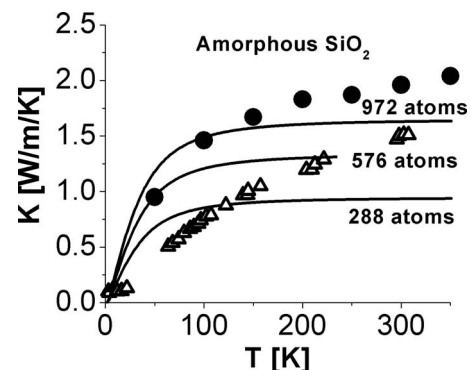


FIG. 6. Temperature dependence of thermal conductivity for amorphous silica predicted by AF theory with different number of atoms in the model (solid lines), calculated from NEMD (circles) and obtained in experiments [triangles (Ref. 29)].

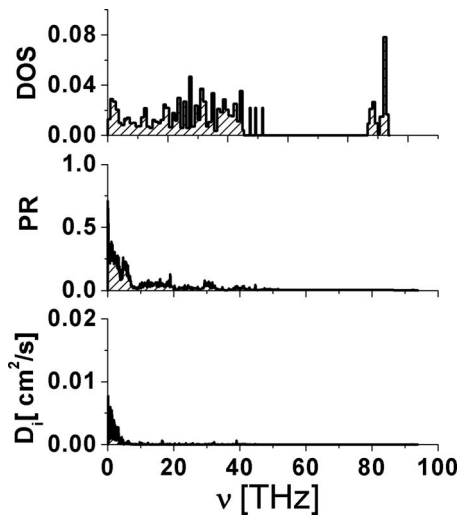


FIG. 7. Vibrational density of states, participation ratio, and mode diffusivity plotted as a function of frequency for atactic polystyrene.

reported from NEMD simulations on a silica glass, while at the same time no strong size dependence was found for amorphous selenium.<sup>26</sup> This finding is quite surprising, considering that the larger number of localized states in the vibrational spectra of chemically nonuniform materials should be less affected by the finite size of a system.

A similarly puzzling behavior is found for amorphous polystyrene. The results of the MD simulations and vibrational mode analysis for the amorphous polystyrene model are presented in Figs. 7 and 8. These results show similar trends as the results for amorphous silica, with an even larger fraction of localized modes (because the ratios of the masses and force constants between the different atom types are larger). In polystyrene, all modes with a frequency above 5 THz are localized and contribute very little to the diffusive thermal conductivity. As a result, almost all of the diffusive thermal conductivity comes from the very small low-frequency part of the vibrational spectrum, which has non-zero thermal diffusivity (see Fig. 7, bottom plot). This finding is in contrast to the behavior of the flexible LJ chain described above, where only 1/3 of the modes were localized and the rest of the modes were delocalized, as in the LJ glass, or in amorphous silicon. It appears that the main difference

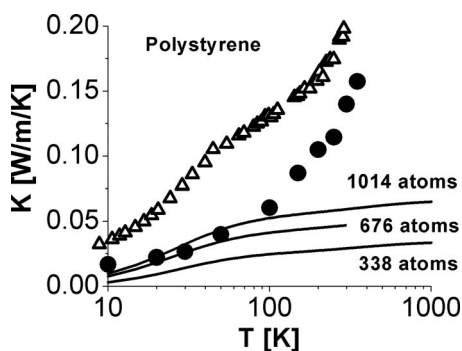


FIG. 8. Temperature dependence of thermal conductivity for atactic PS predicted by AF theory with different number of atoms in the model (solid lines), calculated from NEMD (circles) and obtained in experiment (Ref. 30) (triangles).

between the flexible chains and polystyrene is the chain rigidity, which significantly increases the fraction of localized modes and leads to mode localization on a larger number of atoms along rigid parts of the chain. As can be seen from Fig. 8, as is the case for amorphous silica, at low temperature the classical limit of the thermal conductivity from the AF theory is significantly higher than the results of the MD simulations. This result again shows the puzzling behavior of the harmonic theory overpredicting the thermal conductivity at low temperatures. Also, as for amorphous silica, a size dependence of the AF predictions is found.

#### IV. CONCLUSIONS

From the comparison between the predictions of MD simulations and the AF theory of disordered harmonic solids, several observations can be made. First, the harmonic approximation works well for amorphous materials with one type of atom and identical interaction potentials between all atoms (e.g., a simple LJ glass and amorphous silicon). For these systems, anharmonicity does not play an important role because the number of localized modes is negligible and the major mechanism of energy exchange between extended modes is harmonic in nature and can be well described by AF theory. Second, for systems with forced “anisotropy,” like the linear LJ bead-spring model, the harmonic approximation may still work as long as the energy hopping mechanism is restricted, for example, because of the geometry of localized vibrations. Finally, for systems with complex composition like amorphous silica or an organic polymer glass, anharmonic coupling between localized modes, or between localized and delocalized modes is the major mechanism of heat conduction. More interesting and puzzling is the fact that the harmonic theory overpredicts the MD thermal conductivities at low temperatures for amorphous silica and polystyrene. Therefore, our results indicated that with strong anharmonicity, the harmonic theory of disordered solids is not applicable, even in the low-temperature limit.

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