Influence of disorder on thermal transport properties of boron nitride nanostructures

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The impact of isotopes on thermal transport in boron nitride nanotubes (BNNTs) and boron nitride white graphene is systematically studied via molecular dynamic simulations. By varying the concentration of the ^{10}B isotope in these materials, we find that thermal conductivity ranges from 340 to 500 W/m^{-1} K^{-1}, closely agreeing with experimental observations for isotopically pure and natural (19.9% ^{10}B) BNNTs. Further, we investigate the interplay between dimension and isotope disorder in several C-based materials. Our results show a general trend of decreasing influence of isotope disorder with dimension of these materials.

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I. INTRODUCTION

Recent technological advances in the synthesis of boron nitride isomorphs of carbon nanostructures[1,2] have led to special interest in these materials for applications such as high-temperature catalysts and photovoltaic devices.[3] Several experiments have been carried out concerning the mechanical, structural, and thermal properties of these nanomaterials,[4–17] the results of which are parallel to that of their carbon counterparts.[18–26] Isotopic disorder, however, has been reported to significantly deteriorate the thermal transport properties in BN-based nanomaterials.[27] Several authors[28,29] have speculated that this effect is the main mechanism responsible for the degradation of lattice thermal conductivity (κ) in boron nitrite nanotubes (BNNTs), especially considering the much higher natural abundance of isotopes in boron compared to carbon. Recent studies performed using an atomistic Green's function transport formalism (AGTF) coupled with first-principles phonon data have predicted that the isotopic purification enhances $[(\kappa^{\text{pure}}/\kappa^{\text{natural}} - 1) \times 100]$ the room-temperature ballistic thermal conductivity more than ∼400% and ∼150% in C-based (with 10.7% of ^{14}C isotope) and BN-based (with 18.8% of ^{10}B isotope) nanotubes, respectively.[30] It is claimed that the ratio $(\kappa^{\text{pure}}/\kappa^{\text{natural}})$ is not a strong function of contact resistance because of the small diameter of single-wall nanotubes. The source of such a significant decrease in thermal conductivity with isotope disorder has been correlated to diffusive scattering rather than an increase in disorder-induced localization effects as reported elsewhere.[29] In a subsequent work, using a similar method, Savić *et al.* discussed isotope, anharmonic, and intershell scattering in isotopically disordered BNNTs. Although the simulations were done for single-wall nanotubes, intershell effects are considered with a scaling factor emanating from the ratio of multiwall and single-wall nanotube diameters. The introduction of this scaling factor produced good agreement with the previous thermal conductivity measurements in multiwall BNNTs.[27] The authors concluded that anharmonic and intershell scattering could not be determinant factors in the reduction of κ without shadowing isotopic effects. In another study, utilizing the exact numerical solution of the phonon Boltzmann transport equation (PBTE), Lindsay and Broido[31] reported an enhancement in room-temperature thermal conductivity ranging from 26% for a system size of 1 μm to 37% for a system size of 10 μm when natural (19.9% ^{10}B, 80.1% ^{11}B) and pure (100% ^{11}B) forms of single-layer hexagonal BN (white graphene) are considered. These results are also close to the magnitude of reduction predicted in experiments carried out with BNNTs.[27] Compared to C-based materials, one can speculate that the difference in mass of boron and nitrogen will cause a major reduction in κ; however, it is not clear that further mass differences due to isotopes of boron should lead to drastic reductions in room-temperature lattice thermal conductivity of these materials.

In order to investigate the effect of boron isotopes on the room-temperature lattice thermal conductivity of BN nanostructures, we have performed equilibrium molecular dynamics simulations utilizing the Einstein relation. We have considered different concentrations and masses for boron isotopes. In addition to BN-based systems, we have also studied their C isomorphs, and have predicted a significant difference between the responses of different dimensional systems, namely, nanotube, graphene, and diamond, to isotopic disorder. The rest of the paper is organized as follows. After describing the models and methods used in this study, we demonstrate the suitability of our optimized potential parameter set (OPS)[32] for studying thermal transport properties of BN nanostructures. This is followed by a detailed description of how the isotopic disorder affects the thermal transport on BN nanostructures and a comparison to their C isomorphs.

II. METHOD

Lattice thermal conductivity $\boldsymbol{\kappa}$ of a system can be calculated by using the Green-Kubo theorem[33–35] or the Einstein relation[36] in equilibrium molecular dynamics (MD). In this study, the Einstein relation [see Eq. (1)] has been employed with a modified energy moment $\boldsymbol{R}$ that is applicable to periodic boundary conditions. The details for the calculation of $\boldsymbol{R}$ were given elsewhere.[37,38] The volume and average temperature of the system and Boltzmann constant are represented by V, T, and k_B, respectively, in Eq. (1). The volumes of the nanotubes and graphene are defined as $2\pi rl\Delta$ and $(lw \times \Delta)$, where r is the nanotube radius, w is the graphene width, l is the structure length, and Δ (0.335 nm) is the mean Van der Waals diameter for B, N, and C atoms of boron nitride white graphene (BNWG)

and graphene,

$$\kappa = \frac{1}{Vk_BT^2}\lim_{t\to\infty}\frac{1}{2t}\langle[\boldsymbol{R}(t)-\boldsymbol{R}(0)]\otimes[\boldsymbol{R}(t)-\boldsymbol{R}(0)]\rangle. \quad (1)$$

Molecular dynamics simulations are performed in the microcanonical ensemble for 5 ns with a time step of 0.5 fs. Each data point for κ is obtained by averaging the results of six distinct simulations, which have different initial particle velocities. In isotopically disordered systems, the isotope distribution considered is random. The standard deviation of these six calculations is shown as the error on data points.

Empirical potentials are generated to mimic particle interactions. These potentials have been shown to produce very accurate ground-state forces and equation of states. This in turn gives reliable phonon dispersion and anharmonic behavior. Thus, empirical potentials can be used in several methods, such as molecular dynamics for the correct definition of particle motion and Boltzmann transport,[31] and Green's function[39] for dependable phonon band structure. These potentials inherently contain anharmonicity, which can be extracted via higher-order (third, fourth, fifth, etc.) derivatives of potential energy.[40] The derivatives can also be related to phonon-phonon interactions[31,41] and be used in the BTE. As the order of energy derivatives considered in the BTE calculation increases, more phonon-phonon processes (three-, four-,. . ., n-phonon) can be included and thus a better accuracy is obtained in the calculations.

In molecular dynamics, all phonon-phonon processes, defect scattering, boundary scattering, etc. are innate to the calculation. It can be assumed that the natural evolution of the dynamics through thermal excitations possesses the anharmonic behavior of the potential. So, molecular dynamics is very flexible in the simulation of complex systems and the calculation of total lattice thermal conductivity. But it is inflexible in modularity in examining the effect of structural features from a single simulation. As a result, complexities should be investigated separately if one needs individual contributions. The classical nature of MD inhibits the phonon population from strictly obeying Bose-Einstein statistics. Classical distribution lets all phonons be excited equally. This generally results in a reduction of group velocities below the Debye temperature (T_D) because relatively flat optical modes are equally emphasized as relatively steep acoustic modes in phonon dispersion. However, this reduction is balanced by an increase in heat capacity such that the results are comparable to experiments shown in many previous studies.[38,42,43] Briefly, it has been claimed that the MD predictions for lattice conductivity can be credible above $T_D/10$.[41,44] This conclusion is parallel to a previous discussion of the relationship between the quantum canonical correlation function and the classical heat current autocorrelation function.[18,45]

As described above, the accurate description of phonon dispersion, corresponding group velocities, and equations of state are critically important in thermal transport calculations.[46,47] In this study, a recently optimized Tersoff-type potential (OPS), which yields very accurate results for dynamical, mechanical, and thermal transport properties of BN nanostructures, is used.[32] For instance, the calculated phonon transmission data for BNNT(8,0), shown in Fig. 1, is in good agreement with the first-principles results reported by Savić *et al.*.[28]

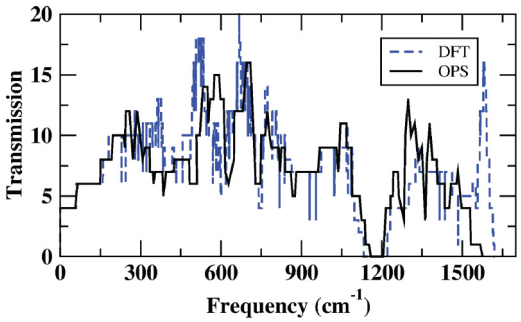

FIG. 1. (Color online) A comparison of the phonon transmission function of BNNT(8,0) calculated from density functional theory (DFT) (Ref. 28) and the optimized Tersoff potential used in this work.

III. RESULTS AND DISCUSSIONS

A. BN nanostructures

In studying the isotope effect, we have built BNNT and BNWG structures with varying concentrations of randomly distributed ^{11}B or ^{10}B isotopes, as see in Fig. 2(a). First, it is important to note that pure BNNTs and BNWG (formed with 100% ^{11}B or ^{10}B) have the largest values of κ, while the maximum reduction from isotope scattering is found in the materials with an equal ratio of ^{11}B and ^{10}B. The enhancement of κ for a pure sample (100% ^{11}B) over an isotopically disordered system as a function of isotope concentration n_i can be given as $[\kappa^{\text{pure}}/\kappa^{\text{natural}}(n_i) - 1] \times 100$. Based on this formula, our calculations show 27% and 33% enhancement in BNNTs and BNWG, respectively, noting that the results

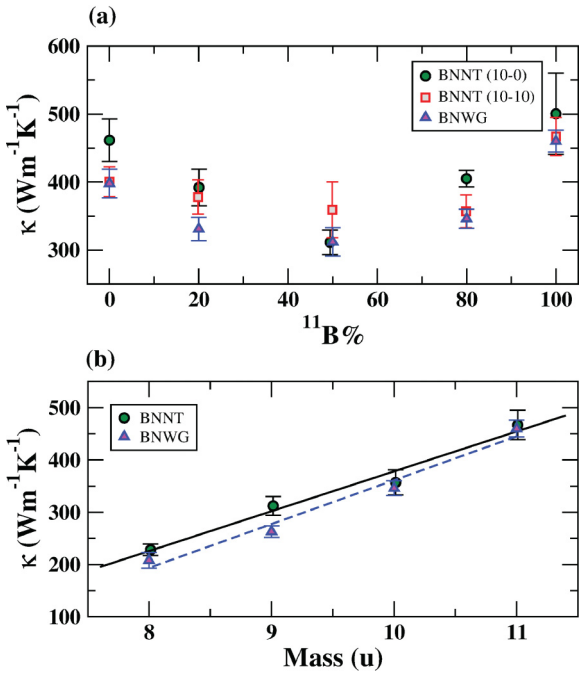

FIG. 2. (Color online) (a) Room-temperature lattice thermal conductivity of isotopically disordered zigzag and armchair BNNTs and BNWG for various ^{10}B and ^{11}B ratios. (b) Evaluation of lattice thermal conductivity of natural (formed with 19.9% ^{x}B and 80.1% ^{11}B) BNNT and BNWG with different isotope masses, x.

for nanotubes are given as an average of (10,0) and (10,10) types. These results are fairly close to recently reported PBTE calculations[31] on a single-layer hexagonal BN structure (∼26–37% increase).

As a test case, we calculated the effect of isotope disorder considering the unstable isotopes ^{8}B and ^{9}B as well. Our results show that when the mass of the scarce isotope decreases further in the natural composition, linear decreases are observed in thermal conductivities of both BNNT and BNWG, as seen in Fig. 2(b). The slopes of these lines are only 9% different from each other, but still for almost all isotopes, BNWG has smaller thermal conductivity. Even when ^{8}B is used, the reduction in room-temperature lattice thermal conductivity of isotopically disordered BNNTs and BNWG is still smaller than the amount of reduction predicted in the ballistic thermal conductivity of BNNTs (AGTF-based calculations).[30]

The equal-mass case (i.e., atomic weight of B = atomic weight of N) is another interesting point in understanding the effect of mass difference on the lattice thermal conductivity of BN structures. In a previous study, a hypothetical case was investigated where a single mass ($x = 12$ u) is used for all B and N atoms.[32] Such an equality increased the thermal conductivity more than 20% compared to the heteromass system composed of ^{11}B and ^{14}N only. Here, two additional systems are considered. First, all atom masses are equated to 14 u. The resulting thermal conductivity of this system is 549 ± 61 W/m^{-1} K^{-1}, which represents a similar increase when all masses are 12 u. Second, only 19.9% of the ^{11}B is replaced with ^{14}B. In this case, the calculated thermal conductivity is 264 ± 36 W/m^{-1} K^{-1}. At first, it may be expected that this value should be larger than the κ for the system without isotopic disorder since it is also a two-mass system and there is less mass difference between B and N atoms in total. However, the broken order due to randomly distributed ^{14}B at the boron site results in stronger phonon scattering. Still, B(19.9% ^{14}B + 80.1% ^{11}B)N has larger thermal conductivity than the system containing ^{8}B with the same concentration, although both structures have |3 u| difference from ^{11}B. It could be concluded that lowering the mass difference between boron and nitrite may improve the thermal conduction, as predicted by the Rayleigh model, but the random distribution of isotopes limits the improvement over the isotopically pure structures.

The reported experimental values for isotopically pure and natural BNNTs at 300 K are ∼300 and ∼200 W/m^{-1} K^{-1}, respectively.[27] This range has been supported by AGTF results;[28] however, these computations have considered a scaling factor in order to represent the multiwall nanotubes that are used in the experiment. Our simulations predict the κ of BNNTs between 350–400 W/m^{-1} K^{-1}, which is directly comparable with both the experimentally reported value (i.e., if only the outer shell in a multiwall nanotube is active in heat conduction) and those calculated by an exact numerical solution of the PBTE.[31] The similarity in percent changes in thermal conductivity due to isotope disorder with the PBTE is not surprising because, in principle, both methods obtain anharmonic behavior from the same source, namely, interatomic potential. Moreover, it should be noted that both our and Lindsay-Borido's potentials have similar forms. The differences in absolute values of thermal conductivity in these two studies should be caused by the difference in phonon populations and the order of included phonon-phonon interactions. As mentioned before, the classical approach used here equipartitions energy into the phonon modes, whereas in PBTE, Bose-Einstein statistics was used. Also, only three-phonon processes are considered in Ref. 31. On the other hand, the effect of anharmonic scattering seems to be the main cause of the lower impact of isotopic scattering in our calculations, that is, 33% enhancement, in comparison to 50% in AGTF calculations.[28] In Ref. 28, anharmonic relaxation is considered through an empirical relation[48] and it is claimed to be less pronounced than isotope disorder.

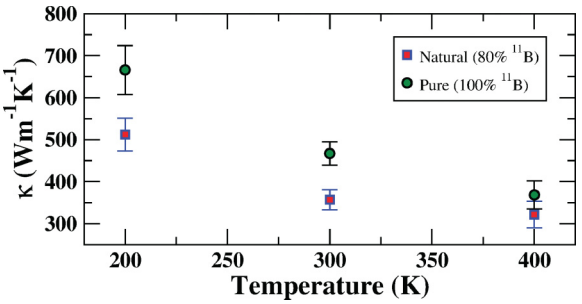

FIG. 3. (Color online) Evaluation of lattice thermal conductivity of natural (formed with 19.9% ^{10}B and 80.1% ^{11}B) and pure (formed with 100% ^{11}B) BNNTs with temperature.

The effect of isotopic disorder for different temperatures is also investigated, as depicted in Fig. 3. Here, the convergence of the lattice thermal conductivity of pure and natural BNNTs with temperature reveals the dominant effect of scattering due to anharmonic interactions over isotopic scattering at temperatures above 350 K. Inversely, the larger difference in thermal conductivities of pure and natural systems at lower temperatures suggests that isotopic disorder has more influence in ballistic thermal transport.

B. C nanostructures

It has been shown that the natural abundance of ^{13}C isotopes (∼1.1%) in diamond results in a $\kappa^{\text{pure}}/\kappa^{\text{isotopic}}$ ratio of 1.3–1.4.[45,49] This prepotent change compared to a 27–33% enhancement in κ of isotope-enriched BN nanostructures has encouraged us to further investigate the phenomenon in carbon nanotubes (10,0), graphene, and diamond. Different concentrations from 1 to 20% ^{13}C isotope are randomly distributed in C-based structures, and the corresponding lattice thermal conductivities are evaluated. Both Tersoff's original potential[50] and Lindsay-Broido's optimized Tersoff potential[40] for planar systems are considered in these calculations. In Fig. 4 we present the percent increase in lattice thermal conductivity of the given structures. Just like the BN case, the reduction in κ due to the presence of isotopes is not as strong as suggested in previous literature for one-dimensional (1D) and 2D nanomaterials. On the other hand, the thermal conductivity of diamond is severely reduced even at 1% ^{13}C isotope, in accordance with the computational findings of Che *et al.*[45] and experimental results of Morelli *et al.*.[49] Moreover, there seems to be an order in the way isotopic disorder decreases κ in different dimensional structures, i.e., the diamond (3D) is affected the most and the nanotube (1D)

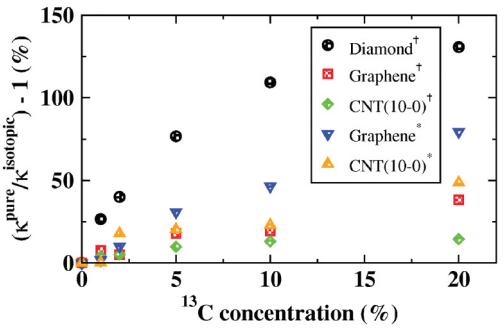

FIG. 4. (Color online) Percent enhancement in the lattice thermal conductivities of isotopically enriched carbon-based materials [diamond, graphene, and (10,0) carbon nanotube (CNT)] with respect to isotopically disordered systems at various isotope concentrations. Here, the symbols † and ∗ denote that the particle interactions are defined via original and optimized Tersoff potentials, respectively.

is affected the least from the presence of isotopes. Classical simulations represent a relationship between average isotope-isotope distance and thermal conductivity. As the average separation between isotopes is shortened, the mean relaxation time for isotope scattering will be lowered. This will give a lower thermal conductivity according to fundamental kinetic theory. For instance, if one assumes an isotope concentration of 0.001, then the average linear spacing (l) between the isotopes in nanotube, graphene, and diamond becomes approximately 108, 54, and 17.8 Å. The variation of l among systems can be given as $l_{\text{tube}} > l_{\text{graphene}} > l_{\text{diamond}}$. Thus, current results about the dimensionality influence on κ of isotopically disordered systems can be explained by the difference in mean isotope-isotope separation. If Fig. 2(a) is reexamined on the basis of this information, one can see a similar case where BNNT(10,0) has almost always higher thermal conductivity than BNNT(10,10) and BNWG. Only at 50% ^{11}B does BNNT(10,10) have higher thermal conductivity, which may be due to an averaging problem, and more simulations may be needed at this point. Furthermore, the κ's obtained for BNNT(10,10) and BNWG are close to each other, which is again expected since the l_{tube} is ∼62.3 Å for BNNT(10,10).

IV. SUMMARY AND CONCLUDING REMARKS

In this work we present molecular dynamics thermal conductivity calculations on BN- and C-based materials with disorder arising from isotopes. We predict a room-temperature κ on the order of 450–500 W/m^{-1} K^{-1}and 340–400 W/m^{-1} K^{-1}for isotopically pure (100% ^{11}B) and natural (80% ^{11}B) BNNTs and BNWG, respectively. This agrees well with the experiments on BNNT that yield values[27] on the order of 200–300 W/m^{-1} K^{-1}. By observing the temperature dependence of BNNTs, we have shown that the influence of isotopes on κ increases at lower temperatures, suggesting the ballistic regime is more susceptible to isotopic scattering. The isotope effect clearly contributes to the reduction of κ, and may have a larger effect on transport in the low-temperature regime. As a result of computations on various dimensional boron nitride- and carbon-based materials, we predict an ascending trend in the effect of isotopic disorder from 1D to 3D structures in the classical regime. This tendency can be explained due to the average isotope-isotope separation, where smaller distances reduce the relaxation length, ultimately decreasing lattice thermal conductivity.

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