Tuning interfacial thermal conductance of graphene embedded in soft materials by vacancy defects

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Nanocomposites based on graphene dispersed in matrices of soft materials are promising thermal management materials. Their effective thermal conductivity depends on both the thermal conductivity of graphene and the conductance of the thermal transport across graphene-matrix interfaces. Here, we report on molecular dynamics simulations of the thermal transport across the interfaces between defected graphene and soft materials in two different modes: in the “across” mode, heat enters graphene from one side of its basal plane and leaves through the other side; in the “non-across” mode, heat enters or leaves graphene simultaneously from both sides of its basal plane. We show that as the density of vacancy defects in graphene increases from 0% to 8%, the conductance of the interfacial thermal transport in the “across” mode increases from $160.4 \pm 16$ to $207.8 \pm 11$ MW/m$^2$ K, while that in the “non-across” mode increases from $7.2 \pm 0.1$ to $17.8 \pm 0.6$ MW/m$^2$ K. The molecular mechanisms for these variations of thermal conductance are clarified using the phonon density of states and structural characteristics of defected graphene. On the basis of these results and effective medium theory, we show that it is possible to enhance the effective thermal conductivity of thermal nanocomposites by tuning the density of vacancy defects in graphene despite the fact that graphene’s thermal conductivity always decreases as vacancy defects are introduced. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4922775]

I. INTRODUCTION

Graphene-based nanocomposites with graphene fillers dispersed in host matrices have attracted significant attention in the last few years and very impressive effective thermal conductivities have been demonstrated by several groups.1–5 The existing development of such materials was mainly based on empirical approaches, while effective design rules are not yet available. To enable rational design and optimization of these nanocomposites, a fundamental understanding of the thermal transport in these materials is essential. In this regard, effective medium theories for nanocomposites have established that the effective conductivity of a nanocomposite is governed primarily by the thermal conductivity of the fillers and the matrix materials, the volume fraction, morphology, and distribution of the fillers, and the thermal conductance for the heat transport across filler-matrix interfaces.6–12 Recent studies have shown that graphene’s thermal conductivity is greatly reduced compared to that in vacuum once it is supported on solid substrates or embedded into another material.13–16 However, the impressive effective thermal properties reported for graphene-based nanocomposites17 suggest that the reduced thermal conductivity of embedded graphene may not be the most limiting factor in determining the overall thermal performance of these nanocomposites. Given that interfacial thermal transport can strongly affect the effective thermal conductivity of nanocomposites, thermal transport across graphene-matrix interfaces has also been investigated. Depending on the choice of matrix materials and the methods used to quantify the thermal transport, interfacial thermal conductance at room temperature in a broad range from 5 to 200 MW/m$^2$ K has been reported.7,9,18–20 These studies also showed that interfacial thermal conductance depends on the matrix-graphene interactions and pressure, and can be tuned by functionalizing the graphene fillers.18,21,22

Prior research has significantly advanced our understanding of thermal transport in graphene-based nanocomposites. However, many issues remain open. For example, many methods for making graphene often end up with defected graphene.23–26 It is already known that the thermal conductivity of graphene can be suppressed by defects.27–29 e.g., the thermal conductivity of a suspended graphene is reduced by nearly 300 times by introducing 7.5% of vacancy defects.25 However, how such defects would affect the performance of graphene-based nanocomposites is still not well understood. In particular, it is not clear how the defects in graphene affect the interfacial thermal transport between graphene and the surrounding soft materials. Even less is known about how defects may affect the effective thermal conductivity of graphene-based nanocomposites. For example, will defects in graphene always reduce the thermal conductivity of graphene-based nanocomposites?

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In this work, we study the thermal conductance across the interfaces between defected graphene and soft materials as a function of vacancy defects in graphene. Using molecular dynamics (MD) simulations, we show that the thermal conductance of these interfaces increases as the density of vacancy defects in graphene increases but the magnitude of increase depends strongly on how the interfacial thermal transport is probed. We clarify the molecular mechanisms of these observations by analyzing how the phonon density of states (DOS) and molecular structure of graphene evolve as vacancy defects are introduced. Using the interfacial thermal conductance obtained from the MD simulations and on the basis of effective medium theory, we show that under certain conditions, the effective thermal conductivity of graphene-based nanocomposites can be enhanced by adjusting the density of vacancy defects in graphene.

II. INTERFACIAL THERMAL TRANSPORT IN NANOCOMPOSITES

An interesting observation emerging from prior studies of interfacial thermal transport across graphene-soft material interfaces is that for the same interface, its thermal conductance can depend very strongly on how the interfacial thermal transport is probed. One can differentiate two different modes of thermal transport, which lead to an apparent duality of interfacial thermal conductance.\(^\text{30}\) In the first “across” mode of thermal transport (Fig. 1(a)), heat enters graphene from one side of its basal plane and leaves through the other side. The corresponding interfacial thermal conductance \(G_a\) is high (~100-200 MW/m² K).\(^\text{9,18,19,30,31}\) The efficient interfacial thermal transport in this mode is due to the facile coupling of the out-of-plane, the low-frequency flexural acoustic (low-\(f\) ZA) modes of the graphene with the vibrational modes of the soft materials surrounding the graphene. In the second “non-across” mode of thermal transport (Fig. 1(b)), heat enters or leaves graphene simultaneously from both sides of its basal plane. The corresponding interfacial thermal conductance \(G_{na}\) is low (~5-30 MW/m² K).\(^\text{7,9,19,30,31}\) The inefficient interfacial thermal transport in this mode has been attributed to the poor coupling between the in-plane high-frequency longitudinal acoustic (LA) and transverse acoustic (TA) modes (high-\(f\) LA/TA phonons) and the low-\(f\) ZA phonons.\(^\text{18,19}\) Specifically, as show in Fig. 1(b), for the interfacial thermal transport in this mode, heat passes from the matrix to the graphene, transfers along graphene’s basal plane, and finally enters the matrix again. Since the heat transfer between graphene and its surrounding matrix relies on the coupling between graphene’s low-\(f\) ZA phonons and the matrix’s low-\(f\) vibrational modes, the dominant energy carriers in the first and the last steps are the low-\(f\) ZA phonons. However, the heat transfer in the second step must rely on, to a large extent, the high-\(f\) LA/TA phonons rather than the low-\(f\) ZA phonons as energy carriers.\(^\text{32}\) Therefore, in order for the second step of heat transfer to occur, energy exchange between low-\(f\) ZA and high-\(f\) LA/TA phonons is needed. Since the coupling between these phonons is poor, this exchange incurs a large resistance. This large resistance is encapsulated in the interfacial thermal conductance\(^\text{6,19,30}\) and consequently it leads to a small effective interfacial thermal conductance. In addition, the strong positive correlations between the heat transfer at the two sides of a single/few-layer graphene contribute to the small thermal conductance for interfacial thermal transport in the “non-across” mode.\(^\text{30}\) The apparent duality of the interfacial thermal conductance makes the description of interfacial thermal transport complicated. However, we recently showed that\(^\text{31}\) by replacing the classical Kapitza model for interfacial thermal transport with a nonlocal formulation, the interfacial thermal transport in different modes can be described quite well using a single equation featuring a pair of nonlocal conductance that is closely related to the \(G_a\) and \(G_{na}\) mentioned above.

For thermal transport in graphene-based nanocomposites, both the “across” and “non-across” modes of interfacial thermal transport are relevant. Consider, for example, the limiting case in which graphene layers are fully aligned. When the externally imposed temperature gradient is parallel to graphene’s surface, the prevailing mode of interfacial thermal transport is the “across” mode (see Fig. 1(a)). However, the “non-across” mode of interfacial thermal transport prevails when the externally imposed temperature gradient is parallel to graphene’s surface (see Fig. 1(b)). For general cases in which graphene layers are not fully aligned, both modes of interfacial thermal transport contribute to the overall heat conduction in the nanocomposite. For simplicity, only the ideal situations of “across” and “non-across” modes are examined in the present work.

III. SIMULATION SYSTEMS AND METHODS

In the following, we study the thermal transport across graphene-soft material interfaces in both the “across” and “non-across” modes (see Fig. 1) using non-equilibrium MD simulations. Liquid n-octane was used as the matrix material.

![FIG. 1. Two different modes of interfacial thermal transport in graphene-based nanocomposites: the “across” mode (a) and “non-across” mode (b). Arrows indicate the direction of heat conduction.](image-url)
because the heat conduction in this media is representative of that in a broad class of soft materials such as oil, grease, and polymer melts. For the interfacial thermal transport in the “across” mode, the simulation system featured a single-layer graphene embedded in n-octane liquids. To drive interfacial thermal transport, a heat source (sink) is positioned in the octane fluid above (below) the graphene as shown in Fig. 2(a). For the interfacial thermal transport in the “non-across” mode, two simulation methods can be used. In the first method, a graphene layer is embedded horizontally in matrix material, and a temperature difference along the graphene surface is imposed by placing a pair of heat source/sinks in the matrix material near the two ends of the graphene. This method requires a large size graphene and long simulation time to reach steady state, both of which demand significant computational resources. Given the large number of systems to be studied here, we resorted to a different method. In this method, the MD system is the same as that for studying interfacial thermal transport in the “across” mode except that heat is directly added into the graphene and removed from a pair of heat sinks symmetrically positioned with respect to the graphene in the octane fluid (see Fig. 2(b)). While the situation shown in Fig. 2(b) appears to be very different from that shown in Fig. 1(b), it can be used to approximate the interfacial thermal transport in the “non-across” mode for two reasons. First, similar to that shown in Fig. 1(b), heat leaves graphene from its two surfaces simultaneously. Second, in both Figs. 1(b) and 2(b), the interfacial thermal transport is throttled by the poor coupling between graphene’s high- and low- LA, TA, and ZA phonons. Since heat passes between graphene and the matrix via facile coupling between graphene’s low- f ZA phonons and the matrix’s low- f vibrational modes, the energy exchange between the high- f LA/TA modes and the low- f ZA modes is a bottleneck for the heat transfer, which is also encountered in the setup shown in Fig. 1(b). Indeed, the interfacial thermal conductances \( G_{na} \) computed using these methods are qualitatively similar and both are much smaller than \( G_d \); for single-layer graphene (modeled using the PPBE-G force field) immersed in octane, \( G_d \) was predicted to be 150 ± 15.3 MW/m² K, while \( G_{na} \) was predicted to be only 4.33 ± 0.44 MW/m² K using the first and the second methods described above, respectively. As a further precaution, we also compared \( G_{na} \) computed using the setups in Figs. 1(b) and 2(b) for a few selected graphenes and the results indicated that the \( G_{na} \) obtained using these two different setups are similar.

![Fig. 2. Simulation of thermal transport at graphene-octane interfaces. (a) and (b) are snapshots of the MD system for studying thermal transport in the “across” and “non-across” modes, respectively. Heat transfer across the graphene-octane interface is achieved by imposing heat source and sinks explained in the main text. (c) and (d) are the temperature profiles of the graphene and octane fluid near the graphene in (a) and (b), respectively (the graphene is defect-free). Note that the octane fluid at the two ends of the simulation box, shown as shaded region in panels (a) and (b), were frozen to prevent thermal short circuiting.](image-url)
These runs were followed by a 9 ns long NVE run during which heat was added to (removed from) the heat source (sink) by velocity rescaling.7,9,19,30,38 Note that the total energy of the system is conserved because the heat added to the atoms in the heat source zone is identical to that removed from the atoms in the heat sink zone. Indeed, examination of the trajectories indicated that the total energy of the system drifted by less than 0.002% during a typical production run. The temperature of the octane fluid and graphene in the z-direction was computed during the last 5 ns of NVE run, after the system had reached steady state. Figures 2(c) and 2(d) show temperature profiles of the octane fluid and graphene when the interfacial thermal transport was probed in the “across” and “non-across” modes, respectively. To compute \( G_a \), we extrapolated the octane temperature profile at two sides of the graphene to its nominal surfaces (i.e., \( z = \pm t/2 \), where \( t = 0.34 \) nm is the nominal thickness of graphene) and measured the temperature difference between these two surfaces \( \Delta T_z \) as shown in Fig. 2(c). \( G_a \) was then computed using \( G_a = 2q'/(A\Delta T_z) \), where \( q' \) is the total heat flux imposed in the heat source and \( A \) is the cross-section area of the graphene. The factor of two accounts for the fact that there are two graphene-octane interfaces along the heat transfer path from the heat source to the heat sink. To compute \( G_{na} \), we again extrapolated the octane temperature profiles at the two sides of the graphene to the graphene’s nominal surfaces. The extrapolated temperature was taken as the temperature of the octane fluid at the graphene-octane interface, and its difference from the graphene’s temperature was determined as \( \Delta T_{na} \) (Fig. 2(d)). \( G_{na} \) was then computed using \( G_{na} = q'/(2A\Delta T_{na}) \), where \( q' \) is the total heat flux imposed on the graphene and the factor of two accounts for the fact that only half of the imposed heat flux passes through each graphene-octane interface.

**IV. RESULTS AND DISCUSSION**

**A. Effects of vacancy defects on interfacial thermal transport**

Using the methods described above, for a single-layer pristine graphene immersed in the octane fluid, \( G_a \) was determined to be 160.4 ± 16 MW/m² K, close to those reported for pristine, single/few-layer graphene embedded in oil and polymeric melts (142-170 MW/m² K).7,9,19,30,31,38 Meanwhile, \( G_{na} \) was determined to be 7.2 ± 0.1 MW/m² K, similar to the value of 10 MW/m² K reported for a single-layer defect-free graphene embedded in a phenolic resin.30 These results confirm the validity of the methods used in the present study for evaluating interfacial thermal conductance. Figure 3 shows that as the density of vacancy defects (\( \phi_d \)) in graphene increases from 0% to 8%, \( G_a \) increases marginally (by ~30%) and reaches 207.8 ± 11 MW/m² K at \( \phi_d = 8\% \). In comparison, \( G_{na} \) increases with \( \phi_d \) more distinctly and rather linearly: as \( \phi_d \) increases from 0% to 8%, \( G_{na} \) increases by ~150% and reaches 17.8 ± 0.6 MW/m² K. The increase of \( G_a \) and \( G_{na} \) with \( \phi_d \) would have different impact on the performance of nanocomposites. The large \( G_a \) (>150 MW/m² K) indicates that the interfacial thermal transport in the “across” mode barely hinders the thermal transport in nanocomposites depicted in Fig. 1(a). Hence, the increase of \( G_a \) with \( \phi_d \) has little effect on the effective thermal conductivity of the nanocomposites. On the contrary, the low value of \( G_{na} \) (<20 MW/m² K) indicates that the interfacial thermal transport in the “non-across” model can greatly hinder the thermal transport in nanocomposites depicted in Fig. 1(b), and thus its increase with \( \phi_d \) can greatly affect the performance of these nanocomposites.

To understand the evolution of \( G_a \) as the density of defects in graphene increases, we note that the interfacial thermal transport in the “across” mode is governed by the coupling between the low-frequency, out-of-plane vibrational modes of the graphene and the surrounding octane fluid.18,19,21,38 Hence, we computed the vibrational density of states (VDOS) of the graphene and the octane fluid. The VDOS was calculated by taking a Fourier transformation of the velocity auto-correlation function of the graphene and octane atoms. A Gaussian smearing width of 1.5 THz was applied to smooth the spikes in the VDOS. Figure 4 shows the VDOS for the octane atoms and the graphene atoms. In agreement with prior studies,18,19 the overlapping of pristine graphene’s VDOS with that of the octane fluid is mostly contributed by the out-of-plane VDOS at frequency less than 10 THz (hereafter, vibrational
modes with frequency less than 10 THz are referred as low-frequency modes). As shown in earlier studies, the coupling between these modes is the major channel for interfacial thermal transport in the “across” mode.18,19 Figure 4(a) shows that as defects are introduced to the graphene, the out-of-plane VDOS of graphene is shifted toward lower frequency (especially <5 THz), thus enhancing the coupling between the out-of-plane vibration of graphene with that of the octane fluid. Consequently, \( G_a \) increases as the density of defects \( \phi_d \) in graphene increases.

To understand why \( G_{na} \) increases as the density of defects \( \phi_d \) in graphene increases, and more importantly, why \( G_{na} \) increases much more significantly than \( G_a \), we note that the interfacial thermal transport in the “non-across” mode probed in the simulations shown in Fig. 2(b) is more complicated than the interfacial thermal transport in the “across” mode. When heat is injected into the graphene, it is distributed into all vibrational modes in the graphene simultaneously. Because the VDOS in graphene features mostly high-frequency vibrations (cf. Figs. 4(a) and 4(b)), a majority of the heat is distributed into the high-frequency vibrational modes.19 Since heat must leave graphene via the coupling between the low-frequency, out-of-plane vibrational modes of the graphene and the octane fluid, it follows that for heat to enter the octane fluid, the heat existing in graphene’s high-frequency vibrational modes (in-plane and out-of-plane) must first be transferred into graphene’s low-frequency, out-of-plane vibrational modes.19,31 Therefore, qualitatively, interfacial thermal transport in the non-across mode is controlled by two heat transfer processes arranged in serial: (1) the “internal” heat transfer from graphene’s high-frequency vibrational modes to its low-frequency, out-of-plane vibrational modes and (2) an “external” heat transfer from the low-frequency, out-of-plane vibrational modes of graphene to the low-frequency vibrational modes of octane, i.e., the heat transfer process probed in the interfacial thermal transport in “across” mode. Prior research has established that the first heat transfer process, which features a large “internal” resistance due to the poor coupling between the high-frequency and low-frequency vibrational modes in graphene, is the limiting step for the interfacial thermal transport through graphene in the non-across mode.19 Figures 4(a) and 4(b) show that as more defects are introduced to graphene, its high-frequency (<10 THz) vibrational modes are suppressed and meanwhile its low-frequency vibration modes are enhanced. This effect has two consequences: (1) it reduces the need to convert heat from high-frequency vibrational modes to low-frequency out-of-plane vibrational modes, and (2) it tends to reduce the separation between the energy storage phonons and the energy transport phonons. Both of these effects make the overall interfacial thermal transport from graphene to octane less hindered by the first heat transfer process pointed out above. As such, \( G_{na} \) is found to increase with \( \phi_d \). This trend is further compounded by the fact that the second heat transfer process involved in the non-across interfacial thermal transport becomes more effective as \( \phi_d \) increases (cf. Fig. 3(a)). Consequently, \( G_{na} \) increases more significantly with increasing \( \phi_d \) compared to \( G_a \).

The above discussion shows that the increase of \( G_{na} \) and \( G_a \) with \( \phi_d \) can be attributed to the shift of graphene’s VDOS toward lower frequency as defects are introduced. The latter can be understood by examining the evolution of graphene’s structure as \( \phi_d \) increases. To this end, we computed the two-dimensional radial density profile (\( \rho_{C-C}(r) \)) of carbon atoms in graphene, which measures the average area density of carbon atoms around an arbitrary carbon atom in the graphene. Additionally, the coordination number \( n(r) \) of a carbon atom in the graphene was determined by integrating the radial density profile, i.e., \( n(r) = \int_0^r \rho_{C-C}(r) 2 \pi r dr \). Figure 5 shows that as \( \phi_d \) increases, both \( \rho_{C-C}(r) \) and \( n(r) \) decrease, indicating that the average area density decreases due to the presence of vacancies and each carbon atom is bonded to fewer carbon atoms. Therefore, the graphene as a whole becomes structurally less rigid in the in-plane direction and the in-plane vibrational modes shift toward lower frequency. In addition, for atoms losing \( sp^2 \) bonds due to the removal of their neighbor atoms, their out-of-plane vibration is less constrained compared to that in a pristine graphene and thus features more low-frequency modes.

B. Effects of vacancy defects on the performance of nanocomposites

By tuning the thermal conductance at graphene-matrix interfaces, the density of defects in graphene will indirectly influence the effective thermal conductivity of graphene-based nanocomposites. Quantifying such an effect, however, is com-
The radial density profile \( \rho_c(r) \) (a) and the coordination number \( n(r) \) (b) of the carbon atoms in graphene with different defect densities \( \phi_d \).

FIG. 5. The radial density profile \( \rho_c(r) \) (a) and the coordination number \( n(r) \) (b) of the carbon atoms in graphene with different defect densities \( \phi_d \).

Complicated by the fact that the thermal conductivity of graphene also depends on the density of defects. Earlier MD simulations showed that a 7.5% of vacancy defects in suspended graphene can reduce its thermal conductivity by nearly 50 times compared to that of pristine graphene.\(^{25}\) Such a drastic reduction has been attributed to the reduction of the mean free path and relaxation time of phonons within the defected graphene. However, we expect vacancy defects to affect the thermal conductivity of the graphene embedded in soft materials in a less dramatic way. Specifically, once graphene is embedded within a matrix, the mean free path and relaxation time of phonons in graphene are reduced and accordingly the thermal conductivity of graphene is already reduced greatly. Indeed, an earlier experiment suggested that the upper limit of the thermal conductivity of a single-layer graphene encased in SiO\(_2\) slabs is \( \sim 160 \) W/mK,\(^{39}\) which is \( \sim 15 \) times smaller than that of suspended graphene.

To qualitatively assess how vacancy defects may affect the effective thermal conductivity of nanocomposites, we assumed that the thermal conductivity of graphene embedded in soft materials decreases linearly by a factor of ten as the density of vacancy defects increases from 0% to 8%, i.e., \( k_L = k_0^L(1 - 0.9\phi_d/8) \), where \( k_0^L \) is the thermal conductivity of embedded, defect-free graphene. The value of \( k_0^L \) was taken as 200 W/mK, which is within the range of thermal conductivity reported for graphene encased in SiO\(_2\) and supported on solid substrates.\(^{14,39}\) We considered a nanocomposite consisting of a soft material (e.g., polymer melts) and a single-layer, square graphene that is fully aligned with the overall direction of heat flux imposed on the composite (see Fig. 1(b)). The thermal conductivity of the soft material was taken as \( k_m = 0.17 \) W/mK. Since the interfacial thermal transport in this composite is essentially in the “non-across” mode, we obtained \( G = 124\phi_d + 8.017 \) through linear regression of the data shown in Fig. 3(b). According to the effective medium theory by Nan et al.,\(^{40}\) the effective thermal conductivity of such a nanocomposite in the direction parallel to the graphene, \( k_{//} \), is given by

\[
k_{//} = k_m \frac{1 + f \beta_{11}(1 - L_{11})}{1 - f \beta_{11}L_{11}},
\]

where \( k_m \) is the thermal conductivity of the matrix and \( f \) is the volume loading of the graphene. The two other variables \( \beta_{11} \) and \( L_{11} \) are given by

\[
\beta_{11} = \frac{k_{11}^c - k_m}{k_m + L_{11}(k_{11}^c - k_m)},
\]

\[
L_{11} = \frac{p^2}{2(p^2 - 1)} + \frac{p}{2(1 - p^2)^2} \cdot \cos^{-1} p,
\]

\[
k_{11}^c = \frac{k_g}{1 + \gamma L_{11}k_g/k_m},
\]

where \( k_g \) is the thermal conductivity of the graphene, \( p = t/l \) (\( t \) is graphene’s thickness and is taken as 0.34 nm; \( l \) is graphene’s length) is the aspect ratio of graphene, and \( \gamma = (1 + 2p) \cdot \alpha \), where \( \alpha = k_m/G \cdot t \) accounts for the effects of interfacial thermal transport.

Figure 6 shows how the effective thermal conductivity of the nanocomposites varies as a function of the density of vacancy defects in graphene when the volumetric loading of graphene is 10% (results at other loadings are qualitatively similar and therefore not shown). We observe that for graphene with moderate lateral dimension (e.g., 1 \( \mu \)m), the effective thermal conductivity of nanocomposites can increase with \( \phi_d \) at \( \phi_d \) up to \( \sim 6\% \). Such an increase is caused by the fact that the interfacial thermal transport becomes more effective as \( \phi_d \)

FIG. 6. The effective thermal conductivity of a nanocomposite (graphene loading: 10%) as a function of the graphene’s density of defects \( \phi_d \).

The effective thermal conductivity of a nanocomposite featuring defect-free graphene, \( k_{//}^0 \), is used to normalize that of nanocomposites featuring graphene with defects.
increases. For nanocomposites featuring graphene with larger dimensions, however, their effective thermal conductivity always reduces as $\phi_d$ increases. This is because, as graphene’s lateral dimension increases, the thermal transport at graphene-matrix interfaces plays a less and less important role in determining the thermal conductivity of nanocomposites, and may even be safely neglected when graphene’s length far exceeds $L_c = \pi \kappa_{\lambda}/4G$. Consequently, the effective thermal conductivity of nanocomposites is dominated by the thermal transport within the embedded graphene, which becomes less effective as $\phi_d$ increases. These results suggest that the effect of defects on graphene flakes should be taken into account when designing graphene-based nanocomposites.

We caution that the predictions shown in Fig. 6 are based on the assumption that the thermal conductivity of graphene embedded in soft materials decreases linearly with $\phi_d$ due to the lack of systematic experimental data for thermal transport in such defected materials. This assumption is likely reasonable for moderate $\phi_d$ but may not be accurate at very low level of defects ($\phi_d < 0.5\%$) as prior simulations suggested that the thermal conductivity of vacuum-suspended graphene decreases most rapidly at very low defect densities. Therefore, the predictions in Fig. 6 are only qualitative and may apply to only a narrow range of defect densities. Nevertheless, these predictions highlight the fact that as defects are introduced into graphene, the effective thermal conductivity may not decrease monotonically due to the competition between enhanced interfacial thermal transport and reduced thermal transport within graphene.

V. CONCLUSION

Using non-equilibrium MD simulations, we have studied the effects of vacancy defects in graphene on the thermal transport at graphene-octane interfaces. As the density of vacancy defects increases from 0% to 8%, the interfacial thermal conductance in the “across” mode $G_{ia}$ increases marginally, while the interfacial thermal conductance in the “non-across” mode $G_{in}$ increases greatly. The enhancement of $G_{ia}$ and $G_{in}$ as vacancy defects are introduced into graphene is ultimately caused by the fact that as more sp$^2$ bonds between carbon atoms are broken due to vacancy defects, overall graphene becomes structurally less rigid and thus it’s in-plane and out-of-plane vibrational modes shift toward lower frequency. Since the latter helps improve the coupling between the vibrational modes of octane and graphene and reduce the need to convert energy from high-frequency in-plane vibrational modes to low-frequency out-of-plane vibrational modes, both $G_{ia}$ and $G_{in}$ increase with graphene’s density of defects.

The enhancement of interfacial thermal transport by vacancy defects can potentially affect the effective thermal conductivity of graphene-based nanocomposites. Rigorous evaluation of these effects requires detailed knowledge on how vacancy defects affect the thermal conductivity of graphene embedded in matrices, which is not yet available. Nevertheless, using effective medium theory, we have shown that for graphene of sizes less than a few microns, it is possible that the effective thermal conductivity of nanocomposites may increase with graphene’s density of defects under certain conditions. This result strongly suggests that the effect of defects should be considered in the design of graphene-based nanocomposites.

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In suspended graphene, ZA phonons contribute \( \sim 43\% \) to the total in-plane thermal conductivity according to Ref. 25. When graphene is embedded in a soft matrix, low-\( f \) ZA phonons should contribute much less to the in-plane heat conduction as these modes are significantly damped (see Ref. 13).


See supplementary material at http://dx.doi.org/10.1063/1.4922775 for calculation of \( G_{na} \) using setup shown in Fig. 1(b) and effects of interfacial thermal transport on nanocomposite’s thermal conductivity.


