ABSTRACT: Understanding the role of fillers in the thermal transport of composite materials is of great importance to engineering better materials. The filler induces material interfaces within the composite, which influence the thermal transport between the matrix and themselves. The filler can also alter the molecular arrangement of the matrix in its vicinity, which may also impact the thermal transport ability. In this paper, molecular dynamics simulations are performed to study the thermal transport across the matrix–filler interfaces in hexagonal boron nitride (h-BN)–organic molecule composites. Four different organic molecules are studied as the matrixes. They include hexane (C₆H₁₄), hexanamine (C₆H₁₃NH₂), hexanol (C₆H₁₃OH), and hexanoic acid (C₆H₁₁COOH), which feature the same molecular backbone but increasingly different polar functional groups. The nominal local thermal conductivities of the hexane matrix with varying distances to the interface are calculated to demonstrate the influence of the filler on the thermal transport properties of the matrix. It is found that a more polar matrix exhibits a higher density in the near-interface region and a higher nominal local thermal conductivity, suggesting that the interfacial interaction can impact the local heat transfer ability of the matrix. In addition, the more polar matrix also leads to a larger interfacial thermal conductance with h-BN (hexane: 90.47 ± 14.49 MW/m²K, hexanamine: 113.38 ± 17.72 MW/m²K, hexanol: 136.16 ± 25.12 MW/m²K, and hexanoic acid: 155.17 ± 24.89 MW/m²K) because of the higher matrix density near the interface and thus more atoms exchanging energy with the filler. The results of this study may provide useful information for designing composite materials for heat transfer applications.

INTRODUCTION

Thermal transport is critical to a wide range of applications such as advanced electronics, optoelectronics, photovoltaic solar cells, and Li-ion batteries. It is also the key to determining the lifetime and performance of these devices. There has been an increasing demand for polymeric materials with high thermal conductivity that can dissipate heat generated by electronic devices in operation. To create efficient heat transfer pathways, various attempts have been exploited to increase the thermal conductivity of these materials by compositing high thermal conductivity fillers, such as carbonaceous materials, boron nitride, and silicon nitride. Thus, to facilitate the design of nanocomposites with high thermal conductivity, a fundamental and comprehensive understanding of the thermal transport in polymeric nanocomposites is essential.

Though it is universally known that adding high thermal conductivity materials into a low thermal conductivity matrix can improve the thermal transport, the fundamental mechanism that links the role of fillers to the overall thermal transport in nanocomposites is still lacking. A typical problem being addressed in nanocomposites is the thermal transport across the interface between the matrix and the fillers. Extensive studies have demonstrated that the interface plays a critical role in determining the thermal energy transport in nanocomposites, as the interface can influence and even dominate the thermal transport in nanocomposites. Recent studies show that the interfacial thermal resistance could be decreased by tuning the alignment or surface functionalization of graphene in composites. Most of these studies only address the heat flux exchange across the interface. Beyond the direct impact on interfacial thermal conductance, the fillers also affect the nominal local thermal conductivity of the matrix, which has been studied much less intensively. It has been

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demonstrated that the arrangement of matrix molecules close to the interface is influenced by their dipoles, resulting in a different density near the interface. This may imply that the nominal local thermal properties of the matrix can also be changed by the fillers, as the thermal conductivity of polymers is a strong function of their molecular-level conformations.

In this work, we perform molecular dynamics (MD) simulations and analyses to explore the impact of the h-BN fillers on the thermal transport. As an insulator, h-BN fillers are preferred over graphene, a semimetal, in many applications (e.g., electronics packaging). The size dependence of interfacial thermal conductance is first examined on a single-layer hexagonal boron nitride (h-BN)/hexane (C6H14) system. Then, a series of h-BN interfaces with organic molecules of different polarization groups as the matrixes are investigated. These include hexanamine (C6H13NH2), hexanol (C6H13OH), and hexanoic acid (C6H11COOH). We note that our focus of interest divided by the region length in each region; the temperature difference between the two ends of the chosen region and ΔT/L is the temperature difference divided by the region length in each region; the smaller the absolute value of ΔT/L, the larger the nominal local thermal conductivity.

Table 1. L-J Potential Parameters between the h-BN Atoms and the Rest of the Atoms

<table>
<thead>
<tr>
<th>pair type</th>
<th>ε (kcal/mol)</th>
<th>σ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–B</td>
<td>0.1374772708486750</td>
<td>3.53419521486273</td>
</tr>
<tr>
<td>O–B</td>
<td>0.103923048000000000</td>
<td>3.37784249000000</td>
</tr>
<tr>
<td>N–B</td>
<td>0.111445053000000000</td>
<td>3.44911438700000</td>
</tr>
<tr>
<td>H–B</td>
<td>0.088994381451480</td>
<td>3.10433658336001</td>
</tr>
<tr>
<td>C–N</td>
<td>0.0851175657546667</td>
<td>3.34577013597604</td>
</tr>
<tr>
<td>O–B</td>
<td>0.063428310000000000</td>
<td>3.18941741000000</td>
</tr>
<tr>
<td>N–N</td>
<td>0.059000000000000000</td>
<td>3.66000000000000</td>
</tr>
<tr>
<td>H–N</td>
<td>0.0550999992588236</td>
<td>2.91591504733</td>
</tr>
</tbody>
</table>

Figure 1. (a) Simulation setup for ITC calculations in the NEMD method: heat flows across the interface from the heat source (red region) to the heat sink (blue region), with the fixed regions (black region) set at the end of the system; the arrows in the graph represent the direction of heat flow; the length of both the heat source and heat sink is 10 Å, and the length of each fixed region is 5 Å. (b) The chemical structures of hexane (C6H14), hexanamine (C6H13NH2), hexanol (C6H13OH), and hexanoic acid (C6H11COOH); the order of polarity is C6H11COOH > C6H13OH > C6H13NH2 > C6H14. (c) Steady-state temperature profile of the simulation system (shown in a) and the temperature difference (ΔT) across the interface. (d) Temperature points leveraged to calculate ΔT for regions A, B, and C (highlighted in different colors), where ΔT is the temperature difference between the two ends of the chosen region and ΔT/L is the temperature difference divided by the region length in each region; the smaller the absolute value of ΔT/L, the larger the nominal local thermal conductivity.
BN are respectively 1.0 and −1.0, and the Hockney particle–
particle particle–mesh31 method is used here for the
evaluation of coulomb energies and forces. The organic
molecules are simulated using the polymer consistent force
field.32 All simulations are carried out using the large-scale
atomic/molecular massively parallel simulator.33 A timestep
size of 0.25 fs is used for all simulations.

A typical structure is shown in Figure 1a. A single layer of h-
BN is centered in the simulation domain with periodic
boundary conditions (PBCs) in all three directions. The PBCs
in the lateral directions model h-BN effectively infinite in size
without edges. This is reasonable as the focus here is the
interfaces between the basal plane of h-BN and the organic
matrixes, and in reality, such interfaces are dominant in the
composite. Each organic molecular system contains 200
molecules. The whole system is heated up to 600 K under
an NPT (constant number of atoms, pressure, and temper-
ature) ensemble to achieve a disordered amorphous phase and
then cooled down to 300 K with an annealing speed of 12 K/
ps. We note that the PBC in the direction perpendicular to the
h-BN surface is necessary to ensure that the NPT optimization
leads to the correct density of the organic liquid, which is
important to the interfacial thermal transport.34,35

Nonequilibrium MD (NEMD) is used to calculate the
interfacial thermal conductance. After the NPT relaxation at
300 K and 1 atm for 1.5−2 ns, the system is then simulated
using an NVE (constant number of atoms, volume, and
energy) ensemble with a heat source (320 K) and sink (280 K)
imposed at the two ends of the system using Langevin
thermostats (Figure 1a). A layer of atoms at each end of the
simulation domain is fixed to prevent the heat transfer across
the periodic boundaries, forcing all heat flux to cross the h-
BN−organic molecule interface. The fixed atoms also prevent
the translational drift of the whole system and thus help “lock”
the position of the interface and extract the temperature
profile. The relatively large temperature difference (40 K) is
used to establish a measurable temperature gap across the
interface. Except the fixed atoms, the rest of the system,
including the thermostated regions, is simulated in the NVE
ensemble for 10 ns for nominal local thermal conductivity and
interfacial thermal conductance calculations at steady state. A
typical temperature profile at the steady state is shown in
Figure 1c. The heat flux (q) is calculated by averaging the
energy input and output rates from the heat source and sink.

The temperature jump (ΔT) across the interface is defined by
the temperature difference between the organic molecules at
the two sides of the h-BN layer. The interfacial thermal
conductance (G) is then calculated as G = q/ΔT. The nominal
local thermal conductivity (κ) of the matrix is calculated as κ =
q/(ΔT/L), where ΔT is the temperature difference between
the two ends of the chosen region and L is the length of the
chosen region. Figure 1d shows the temperature points used to
calculate ΔT in regions A, B, and C; h-BN/hexane system is
used here as an example. The whole system is divided into
several equal-length bins, and the corresponding temperature is
 calculated for each bin. Then, the temperature points selected
for each region are strictly based on the length of each region.

The nominal local thermal conductivity is used to characterize
the heat transfer capability of the region near the interface,
which cannot be interpreted as the thermal conductivity of the
organic liquid. We conduct two independent NEMD
simulations for each system, and in each simulation, data at
eight different time intervals (1 ns each) in the steady state are
used for property calculations. Therefore, there are 16 data
points averaged for each value of the interfacial thermal
conductance. The error bars are the standard deviations of
these data.

## RESULTS AND DISCUSSION

The test on the size dependence of interfacial thermal
conductance is first conducted to choose the appropriate
system size for later simulations. The interfacial thermal
conductance of systems with 200, 400, and 600 hexane
molecules are respectively 88.01 ± 13.77, 104.21 ± 14.49, and
93.62 ± 32.43 MW/m² K. As all results are within their error
bars, no size dependence is observed, and thus the system with
the size of 200 organic molecules is selected, so as to save the
simulation time but still produce justified calculations. We note
that the thermal conductance for the h-BN/hexane interface
 calculated here is larger compared to that of the graphene/
polyethylene interfaces (61 MW/m² K),34 and this may be
attributed to the stronger L-J interactions and additional
electrostatic interactions across the h-BN/hexane interface.

Next, the nominal local thermal conductivities and densities
of the hexane matrix with varying distances to the interface are
 calculated, and the results are shown in Figure 2. Three regions
in the hexane matrix are chosen for exploration. Region A is
the region within a distance of 5 Å next to the interface. Region
B is the region within a distance of 10 Å next to the interface.
Region C is the whole system, except for region B, region A,
fixed region, heat source, and heat sink. Further, all the three
regions contain only organic molecules. In Figure 2, it is found
that when the hexane matrix gets closer to the h-BN interface,
its nominal local thermal conductivity becomes larger. The
higher nominal local thermal conductivity of the matrix near
the interface can be attributed to the higher density of organic
molecules,16 as the corresponding density increases when
approaching the interface.

Figure 3 shows the thermal conductivities and densities of 210
different polar matrixes in region A, which is also called the
near-interface region. According to the results in Figure 2, the
region A shows the highest density and largest nominal local
thermal conductivity. Therefore, the region A is being chosen
for comparison among differently polarized matrixes, so as to
offer the most representative results. It is interesting to find
that when the organic matrix becomes more polarized, the
organic molecules in the near-interface region have larger
nominal local thermal conductivity, which could be explained
by the corresponding higher density, as it is known that a
higher density of a liquid can lead to a higher nominal local thermal conductivity because of the closer intermolecular distance.26

Finally, the thermal transport across the interface is being explored via calculating the interfacial thermal conductance of all the matrixes mentioned above. As Figure 4 shows, when the matrix becomes more polarized, the interfacial thermal conductance becomes larger. Such an observation is well-correlated to the increasing trend of the local density of the matrix near the interface as the molecules become more polar. The more polar organic molecules are attracted by h-BN closer to the interface because of the stronger electrostatic interactions. Such a shorter interatomic distance can significantly enhance the heat flux contributed by the L-J interaction. In addition, the higher local density near the interface also allows more organic molecular atoms to have such close “contact” with the h-BN layer. In other words, it is the collaborative effect of the electrostatic and L-J interactions that leads to the observed increase in interfacial thermal conductance as a function of matrix molecular polarity.

CONCLUSIONS

In summary, we use the steady-state NEMD method to explore both the thermal transport across the interface and heat transfer within the matrix. Four types of organic molecules with different polarities are studied as the matrixes (hexane (C₆H₁₄), hexanamine (C₆H₁₃NH₂), hexanol (C₆H₁₃OH), and hexanoic acid (C₆H₁₁COOH)). The nominal local thermal conductivities of the hexane matrix with varying distances to the interface are calculated to demonstrate the influence of the fillers on the matrix. It is found that the near-interface region will form a denser layer and exhibit a higher nominal local thermal conductivity, and such an effort is more pronounced for a more polar matrix. The higher density of the near-interface region in the more polar matrix also leads to a larger interfacial thermal conductance (hexane: 90.47 ± 14.94 MW/m²K, hexanamine: 113.38 ± 17.72 MW/m²K, hexanol: 136.16 ± 25.12 MW/m²K, and hexanoic acid: 155.17 ± 24.89 MW/m²K). These conclusions may be generalized to other organic molecules and polar filler materials. The results of this study may provide useful information for designing composite materials for heat transfer applications.

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Notes

The authors declare no competing financial interest.

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