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Nanoscale Heat Transfer in Carbon Nanotubes - Sugar Alcohol Composite as Heat Storage Materials

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S Supporting Information

ABSTRACT: Nanoscale carbon structures such as graphene and carbon nanotubes (CNTs) can greatly improve the effective thermal conductivity of thermally sluggish heat storage materials, such as sugar alcohols (SAs). The specific improvement depends on the heat transfer rate across the carbon structure. Besides, the heat transfer rate is further dependent on the material and the CNT diameter. In this paper, molecular dynamics simulations are applied to graphene/CNT-SA interfacial systems. Using erythritol and xylitol as model materials, we find the cross-plane thermal contact conductance to decrease as the CNT diameter decreases, with an exception for CNT(7,7). A phonon mode analysis is carried out to explain the general decreasing trend. The larger phonon mode mismatch observed between the molecules on both sides of smaller diameter CNTs is found to be a finite size effect of the confinement, instead of an interfacial effect. From the molecular collision point of view, a higher molecular density promotes heat transfer. In the case of CNT(7,7), the effective density of molecules enclosed in the CNT is found to be much higher than that of CNT(8,8). This may be the cause of the higher heat transfer rate across CNT(7,7). Molecular orientations and hydrogen bond structures of the molecules inside the CNTs are investigated to demonstrate the finite size effect of the confinement. For graphene-SA composites, five model materials are considered and their cross-plane thermal contact conductance values fall into a narrow range.

INTRODUCTION

Compact heat storage using phase change materials (PCMs) is a promising way to reduce the heating or cooling demand in the built environment. By recovering the solar heat stored in summer, the energy consumption during winter time can be greatly reduced.^{1,2} In such seasonal heat storage systems, a chemically stable and nontoxic material with high heat storage capacity is required. In recent studies, sugar alcohols (SAs), in particular C4–C6 acyclic polyalcohols, have attracted much attention to function as the heat storage medium.^{3–6} The large amount of latent heat absorbed upon melting satisfies the aforementioned capacity requirement. The high supercooling effect of sugar alcohols enables the storage in liquid phase at atmospheric temperature, cutting down the insulation cost for long-term storage. Additionally, as byproducts of the food industry, the huge bulk production has made sugar alcohols very economically competitive. In particular, erythritol and xylitol have suitable melting points for domestic and industrial heating applications and have, therefore, attracted much research.^{6–13} Despite the advantages, a major challenge is the relatively low heat conductivity of SAs and their sluggish crystallization kinetics.⁵ One way to solve the problem is by mixing in carbon nanostructures, in particular, graphene nanoplatelets and carbon nanotubes (CNTs). Because a single layered graphene can be viewed as an unfolded CNT, we briefly use the term “CNT” for both allotropes for the rest of this paper, if not otherwise specified. For some organic PCMs, a few

weight percentage of CNT can bring in a manifold increase in the effective thermal conductivity.^{14–17} The specific improvement is dependent on the PCM compound and the type, the size, and the surface condition of the carbon nanostructures.^{18,19} Therefore, we need some fundamental understandings of the nanoscale heat transfer across single layered carbon structures solvated in various SA compounds.

In a simplified multiscale approach, the effective heat conductivity of carbon-SA composite material can be calculated using effective medium approximations.²⁰ The key parameter used in this theory is the interfacial contact resistance, also named Kapitza resistance, R_K .²¹ One purpose of this research is to characterize R_K between single layered carbon structures and various SA liquids. In the literature referring to carbon nanostructures embedded in various materials, this value ranges from 0.76 to 40×10^{-8} $\text{K m}^2/\text{W}$ depending on the matrix material and the experimental or simulation setup.^{22–25} Temperature, size, and shape are also factors that play a role in R_K . It is therefore very difficult to predict R_K between a given carbon structure and a specific SA material. To solve this problem, we select two model materials, erythritol ($\text{C}_4\text{H}_{10}\text{O}_4$) and xylitol ($\text{C}_5\text{H}_{12}\text{O}_5$), to represent the much broader SA

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family and study the factors that influence the nanoscale heat transfer when carbon nano structures are added.

The heat transfer in the liquid phase is usually treated as diffusive, however near a smooth solid–liquid interface, the structural ordering of liquid alters its phonon structures and results in a non-Fourier behavior.²⁶ Also, the heat transfer across a single-layered carbon structure is found to be ballistic dominated by the low frequency phonons.^{25,27,28} In the acoustic mismatch model, the difference in phonon mode strength is used to explain the origin of the interfacial resistance.²⁹ The above facts emphasized the importance of phonon transport in nanoscale systems. We hence apply phonon mode analysis to improve our understandings in the origin of R_K and its correlation with the CNT diameter.

In the current work, we choose molecular dynamics simulations to study the cross-plane heat transfer in carbon-SA systems. In the **Methodology** section, the physical model and simulation setup are explained. In the result sections, the thermal contact conductance values $U = 1/R_K$ of xylitol and erythritol are given first. Then the phonon mode analysis is applied to explain the decreasing trend of U as the CNT diameter decreases. As a confinement effect, the density, orientation, and hydrogen bond properties are different from those in bulk liquid state and is linked to the anomaly observed in CNT(7,7). At last, the cross-plane heat transfer for graphene solvated in D-arabinitol, D-mannitol, and D-glucitol is studied to conclude the topic on the heat transfer enhancement in general CNT-SA composites.

METHODOLOGY

Nonequilibrium Molecular Dynamics. In the heat transfer rate calculations, a nonequilibrium source-sink algorithm is used in the molecular dynamics (MD) simulations, as used in our previous study.²⁵ In a periodic simulation box, part of the system is maintained at a higher temperature, i.e., the heat source, while another part at a lower temperature, i.e., the heat sink. Both temperatures are controlled using Nosé–Hoover (NH) dynamics.³⁰ According to Esposito and Monnai, systems driven by NH dynamics allow for a consistent nonequilibrium thermodynamics description.³⁰ This enables us to calculate the energy flow into a partial system from the NH reservoir as

$$Q = \frac{p_\xi^2}{2m_\xi} + 3Nk_B T_0 \xi \quad (1)$$

where ξ is a fully dynamic quantity with its own mass m_ξ and momentum defined as $p_\xi = m_\xi d\xi/dt$, $3N$ is the degrees of freedom of the partial system, and T_0 is the target temperature. m_ξ is set based on³¹

$$m_\xi = 3Nk_B \frac{\tau_T^2 T_0}{4\pi^2} \quad (2)$$

where τ_T represents the oscillation period of the kinetic energy between the partial system and the reservoir. Using ξ and p_ξ outputted from the simulation trajectory as extended coordinates, the heat Q that flowed into the thermostated region over time can be obtained and the heat flow rate q is calculated as the fitted slope of the Q - t curves.

Molecular Models. The carbon–carbon interactions are modeled using a recently developed force field by Pascal et al.³² for its good prediction on mechanical and thermal properties of

graphene. This model includes cross terms between angle bending and bond stretching. The sugar alcohols are modeled using the generalized AMBER force field³³ for its successful applications in previous works.^{5,12,34} The Lorentz–Berthelot mixing rule is applied to intermolecular Lennard-Jones interactions.

Setups and Simulation Details. Two simulation setups are constructed as illustrated in Figure 1. In graphene-SA

Figure 1. Top view of the nonequilibrium simulation setups used in this work. The snapshots are taken from (a) graphene-xylitol simulation and (b) CNT(30,30)-xylitol simulation.

simulations, the SA liquids are separated by two single-layered graphene of $8 \times 8 \text{ nm}^2$ in size. The two separated compartments of SA liquids then act as the heat source and sink, respectively. In the CNT-SA simulations, the enclosed SA liquids act as the heat source while the rest act as the heat sink. The working conditions of the SAs as PCMs are around their melting points. Therefore, the target temperatures for the heat sources and sinks are set to $T_1 = T_m + 20 \text{ K}$ and $T_2 = T_m - 20 \text{ K}$, respectively, where T_m is the melting points of each SA compound. During the nonequilibrium simulations, T_1 and T_2 are controlled using the NH thermostat, while the carbon structures are free from thermostats. In this way the temperature jump across the carbon structure can be better controlled.²⁵

To generate the initial configurations for the above nonequilibrium simulations, we adopted procedures similar to those used in previous works.^{25,35}

1. Prepare the bulk crystalline structure of xylitol and erythritol;^{36,37}
2. Gradually increase temperature until it fully melts (typically until $T_m + 100 \text{ K}$); then equilibrate the liquid SAs for a few nanoseconds;
3. Prepare the coordinates of graphene or the open-ended CNT of choice (from ten sizes: (6,6), (7,7) (8,8), (9,9), (10,10), (12,12), (14,14), (17,17), (20,20), and (30,30)) and insert it into the equilibrated liquid;
4. Gradually cool the system to the SA's melting point while the SA molecules fill in the CNT (no spontaneous filling observed in the case of CNT(6,6));
5. Pick out the CNT and SA molecules geometrically "enclosed";
6. Construct a new simulation box with height equal to the CNT's length and put the picked-out molecules in the center of the simulation box with the CNT's axis aligning to the z -direction;
7. Enable the "periodic molecule" boundary condition to allow cross-boundary bonded interactions; now we have an infinitely long tube with SA enclosed;
8. Insert the CNT along with the SA molecules impregnated into another box of equilibrated SA liquid;

- Run an equilibration simulation starting at $T_m + 100$ K and gradually cool to T_m ; this allows the liquid molecules to be well adsorbed onto the CNT outer surface;
- Run another equilibration simulation at $T_1 = T_m + 20$ K and $T_2 = T_m - 20$ K; now the end configuration is ready to be used for the nonequilibrium simulation with a well established temperature profile.

In all simulations, periodic boundary conditions are applied. The time step is set to 1 fs. The O–H and C–H bond stretching is constrained using LINCS algorithm with fourth-order matrix inversion and four iterations for bond length correction.³¹ Particle meshed Ewald summation is applied to long-range electrostatics with Fourier spacing of 0.12 nm. The long-range LJ interaction is gradually switched off from 1.2 to 1.4 nm. In all equilibration simulations explained in the last paragraph, Berendsen thermostat and barostat (1.0 bar) are applied with time constants $\tau_{T,B} = 0.1$ ps and $\tau_{p,B} = 0.5$ ps, respectively.³⁸ In the nonequilibrium simulations for heat transfer calculation, Nosé–Hoover thermostat is used with $\tau_{T,NH}$ set to 0.5 ps and no pressure coupling. The trajectories and velocities are outputted every 5 ps and the energies are outputted every 0.1 ps for data analysis.

Vibrational Density of States. The phonon modes and strengths are characterized using the vibrational density of states (VDOS), denoted as S , as a function of the vibrational frequency ν . $S(\nu)$ is defined as the mass weighted sum of atomic spectral densities³⁹

$$S(\nu) = \frac{2}{k_B T N_m} \sum_{k=x,y,z} \sum_{j=1}^{N_m} \sum_{l=1}^{N_a} \lim_{\tau \rightarrow \infty} \frac{M_l}{2\tau} \left| \int_{-\tau}^{\tau} v_{j,l}^k(t) e^{-i2\pi\nu t} dt \right|^2 \quad (3)$$

where N_m is the number of molecules in the system, N_a is the number of atoms in a molecule, $v_{j,l}^k$ is the velocity of the l th atom in the j th molecule in the k direction, M_l is the mass of the l th atom. Note that $\int S(\nu) d\nu$ represents the total degrees of freedom of a molecule.

The VDOS is used to calculate the phonon mode mismatch of the liquid molecules on both sides of the carbon structures. In the VDOS calculations, the times span τ is set to 20 ps with coordinates and velocities sampled in every 4 fs.

■ THERMAL CONTACT CONDUCTANCE AND PHONON MODES

Cross-Plane Thermal Contact Conductance versus CNT Diameter. The cross-plane thermal contact conductance U is a key parameter used in the mean field theories to predict the effective conductivity of the composite material. U is defined as

$$U = \frac{1}{A \Delta T} \frac{dQ}{dt} \quad (4)$$

where ΔT is the temperature difference of the liquid on each side of the graphene layer, A is the heat transfer area of the CNT, and Q is the heat calculated using eq 1. In this study, ΔT is counted as the difference in the averaged temperatures of the first boundary layers (also named the first absorption layers) on the two sides of the CNT. The first boundary layer is defined as the region holding the first density peak of the liquid adjacent to the CNT wall, as illustrated in Figure 6. ΔT is calculated as such instead of using extrapolations (in refs 25, 27, and 40) for the following considerations. First, the extrapolation method implies the diffusive heat transfer can be applied until the

interfacial region, which is in contradiction to the non-Fourier transfer observed within a few phonon mean free paths ($\sim \text{\AA}$) to the interface.^{26,27} Second, as indicated by Chilukoti et al., the first boundary layer of liquid plays an important role in the interfacial thermal transport.⁴¹ Third, the extrapolation yields to large uncertainties in small diameter CNTs. To be noted, despite of the above considerations, ΔT defined using the mean first boundary layer temperature is only 0–1.5 K higher than ΔT defined using extrapolations, which yields a less than 5% difference between the two methods.

In Figure 2, the U values are plotted over the reciprocal diameter of the CNTs impregnated with erythritol or xylitol.

Figure 2. Cross-plane thermal contact conductance U versus reciprocal diameter of CNTs impregnated with erythritol or xylitol. The result of graphene is labeled at $1/d = 0$. The error bars are based on the standard deviations of the heat transfer rates. The three insets are snapshots taken from the CNT-xylitol simulations.

Graphene can be viewed as a CNT with infinite diameter. For both erythritol and xylitol, there is a decreasing trend over decreasing CNT diameter. However, detailed fluctuations are observed, especially when going toward lower CNT diameters. In both materials, the thermal contact conductance across CNT(7,7) is larger than those across CNT(8,8).

Phonon Mode Mismatch and the Decreasing Trend of U . To understand the above diameter dependence of the contact conductance, the phonon modes of each system is calculated by component using the VDOS. In Figure 3, the VDOS of the CNT components in the CNT-xylitol composites

Figure 3. VDOS of the CNTs (S_c) in CNT-xylitol composites. For each curve $\int S d\nu = 3$. The shaded region is zoomed in and plotted in the inset.

Figure 4. VDOS of (a) xylitol and (c) erythritol on either side of the CNT/graphene. Note that $\int S_{\text{vyl}} d\nu = 54$ and $\int S_{\text{ery}} d\nu = 44$. S_{cold} in (a) and (c) labels three VDOS curves on the cold side (outside) taken from (7,7), (10,10), and (30,30). Subfigures (b) and (d) are the VDOS differences calculated using $\Delta S = |S_{\text{hot}} - S_{\text{cold}}|$.

are plotted. Some blue shifts of high frequency phonons are observed as the CNT diameter decreases as seen in the inset of Figure 3. However, in the majority of the frequency range, especially in the low frequency range where most of the phonon transport takes place, there are no evident discrepancies of phonon strengths among the curves. Therefore, the CNT's phonon modes are not the major cause of the decreasing thermal contact conductance.

In the cross-plane heat transfer process, the phonons are transferred between the molecules on each side of the carbon plane. Therefore, the VDOS of xylitol and erythritol on both sides are compared for more clues. In Figure 4a,c, the VDOS of xylitol and erythritol molecules on the hot side (inside) are plotted using colored lines while the VDOS on the cold side are plotted in black. The black lines are beneath the colored lines and are almost identical and independent of the CNT diameter. As the diameter increases, the VDOS of the hot side converges to the smoother VDOS curves of the cold side. To highlight this convergence, the differences in VDOS ΔS between the hot and the cold sides, defined as $|S_{\text{hot}} - S_{\text{cold}}|$, are plotted in Figure 4b,d. The blueish colored ΔS curves have higher magnitudes than the reddish colored ΔS curves. This means the difference is reduced as the CNT diameter increases. In the phonon mode mismatch model, the difference in the phonon mode strengths on the two sides of an interface is the origin of the interfacial resistance.⁴² In our CNT-SA systems, the change in the magnitude of ΔS is believed to be the cause of the reduced thermal contact conductance across smaller sized CNTs' surfaces. Additionally, the VDOS on the hot side has higher peaks, especially in the case of CNT(7,7), CNT(8,8), and CNT(9,9). This means less phonon scattering and results in less thermal dissipation.

Having understood the decreasing trend of U , the next question is where this ΔS originates from. In Figure 5, the

Figure 5. VDOS of xylitol in CNT(7,7) simulation. The molecules outside the CNT are categorized into either the first boundary layer group (Figure 6) or the bulk liquid group.

VDOS of xylitol in CNT(7,7) are calculated based on where the molecules reside. On the cold side, the molecules are categorized into either the first boundary layer group or the bulk liquid group. On the hot side, only one layer of molecules is present (Figure 9) and can be regarded as in the first boundary layer as well. From a comparison between the two first boundary layers near the interface on each side, we notice S_{hot} and $S_{\text{cold,BL}}$ are highly different. On the other hand, the two groups on the cold side, $S_{\text{cold,BL}}$ and $S_{\text{cold,bulk}}$ have almost identical VDOS. This means the distance from the interface is not the cause of the difference in the VDOS, while on which side the molecules are is. Considering that in the composites

with larger sized CNTs, ΔS is greatly reduced, a logical explanation of the large ΔS observed in composites with smaller sized CNTs would be a finite size effect of the confinement. The altered VDOS on the hot side is possibly a result of the molecular configurational rearrangement in the finite space enclosed by the CNT.

EFFECT OF CNT DIAMETER ON CONFINED MOLECULES

Temperature and Density Profiles. The phonon mode mismatch qualitatively explains the decreasing trend of the thermal contact conductance as the CNT diameter decreases. These phonon structures are determined by the configurations of the SA molecules enclosed in the CNTs. The first feature examined is the density profile. In Figure 6, both the temperature profiles and the density profiles of graphene-xylitol and graphene-erythritol simulations are plotted. The dashed lines are fitted using quadratic curves.²⁵

Figure 6. Temperature (dots and dashed) and density profiles (solid) of graphene-xylitol and graphene-erythritol composites near the graphene interface. Both profiles are calculated based on a bin size of 0.01 nm. The temperature profiles are fitted using quadratic curves. The shaded areas label the region defined as the first boundary layer. Also labeled are the positions, denoted as R_i , of density troughs of xylitol.

The density oscillation in Figure 6 is a typical interfacial effect. From the previous section, we speculated the influence of the CNT diameter on the detailed cross-plane heat transfer rate is more a finite size effect of the confinement. To demonstrate this effect, we show how the density profiles are altered when a finite CNT size is given. The density profiles of SA liquids in both CNT-xylitol/erythritol composites near the carbon interface are given in the Supporting Information. In short, the variant CNT diameter has minor effect on the density profiles on the cold side but does give highly different hot-side density profiles. However, these highly different profiles fail to give an intuitive judgment on how much the hot-side density is altered or how much the mean density of the enclosed molecules is influenced by the CNT diameter. To quantitatively analyze the finite size effect, we define the mean effective density of the enclosed molecules, $\bar{\rho}_e$, averaged over the effective volume. The effective volume, V_e , the volume where SA molecules can effectively occupy, is calculated using $\pi d_e^2 l / 4$ and $d_e = d - \sqrt{2} \sigma_{C-C}$, where $\sigma_{C-C} = 0.3388$ nm is the radius term between the CNT carbon and the SA carbon atoms in the Lennard-Jones potential, and l is the tube length. Using such a definition, the depletion zone occupied by the CNT carbon

atoms is excluded and the mean density would be roughly independent of the CNT diameter (at large diameters) and equal to the bulk density. The $\bar{\rho}_e$ calculated using the above definition is plotted in Figure 7 in solid lines. When the tube

Figure 7. Mean effective density of SA molecules inside the CNTs versus reciprocal CNT diameter. The solid lines are the actual results $\bar{\rho}_e$ obtained from equilibration simulations with error bars denoting standard deviations. The dashed lines are the estimated results $\bar{\rho}'_e$ calculated using eq 5 assuming there is only interfacial effects on the density profile fluctuations. Also labeled are the CNT radii corresponding to the density trough positions R_i of the graphene-xylitol composite in Figure 6.

diameter is only sufficient to enclose a few layers of SA molecules, the mean effective density fluctuates. At first, we expect such a fluctuation to come from the interfacial effect: when the CNT diameter is just sufficient to include an integer number of layers of SA molecules, i.e. $d = R_i$, where R_i , $i = 1, 2, 3, 4$ are the trough positions of the density profile in Figure 6, the mean density should magnify. Indeed, we see in Figure 7 for CNT(10,10) where $d \approx R_1$ and for CNT(17,17), where $d \approx R_2$, the mean densities are higher. However, this is not the complete story. Assuming the SA molecules inside the finite sized CNTs having the same density profiles as the graphene-SA case plotted in Figure 6, then the mean effective density can be estimated based on the profile $\rho_{SA}(x)$ therein using

$$\bar{\rho}'_e(R) = \left[\int_{-R}^0 2\pi(x+R)l\rho_{SA}(x) dx \right] / V_e \quad (5)$$

where the prime mark in $\bar{\rho}'_e$ distinguishes the estimated results from the actual results, $R = d/2$ is the CNT radius. The integral from $-R$ to zero is equivalently an integral from the tube center to the carbon wall's position. The estimated $\bar{\rho}'_e(R)$ is plotted in Figure 7 in dashed lines. As analyzed above, when the CNT radius R is at the trough positions of $\rho_{SA}(x)$, larger mean densities are observed. Comparing $\bar{\rho}_e$ with $\bar{\rho}'_e$, the former is constantly higher than the latter. This is possibly coming from the adjustment of the SA molecular configurations which allows more molecules to fit in the finite space. The discrepancy is much more evident in the case of CNT(7,7). If the SA configurations were still the same as in the graphene-SA case, the 0.941 nm CNT(7,7) diameter would allow only a fraction of a layer of molecules to fit in. The much larger than expected $\bar{\rho}_e$ infers that the molecules may have realigned to the axial direction of the tube. In summary, the finite size effect of confinement altered the mean in-tube density in addition to the interfacial effect.

Comparing $\bar{\rho}_e$ in Figure 7 with the thermal contact conductance in Figure 2, an interesting correlation can be found. Upon the general decreasing trend, the fluctuations seem to be linked with the mean effective density. A similar correlation is also observed in our previous work²⁵ and the work by Pham et al.⁴⁰ As a short explanation, the kinetic energy transfer, as a major component of the overall heat transfer, scales with the number density of the interacting molecules colliding with the interface.

Molecular Orientation. As discussed in the previous subsection, the molecular realignment is possibly the cause to the higher than approximated effective density. To confirm this hypothesis, we computed the orientation angle α of liquid molecules in the CNT-xylitol composites. The angle α is defined as the acute angle formed between the projected vector $\vec{C_1C'_5}$ and the axial vector $\vec{z}$, where C'_1 and C'_5 are the projections of head C_1 and tail C_5 of a xylitol carbon bone (Figure 8). In Figure 9, the orientation angle of each xylitol

Figure 8. Graphical illustration of the definition of the orientation angle α .

Figure 9. Orientation angles α of xylitol molecules calculated using the last frame of the simulations. Each dot (x, α) represents the position and orientation angle of a molecule. The dots that fall in regions shaded with red and blue are used for the angle distribution plot in Figure 10. The thick gray line represents the carbon wall position and the dashed line represents the tube center position. The results of other CNTs and the orientations of erythritol molecules are given in the Supporting Information.

molecule is plotted as a black dot using only the last frame of the simulations (for CNT-xylitol composites with other CNT diameters and CNT-erythritol composites, see the Supporting Information). The thick gray line at $r = 0$ represents the carbon wall position. The shaded regions in red and blue illustrates the first boundary layers. In the case of CNT(7,7)-xyl, the in-tube xylitol molecules all reside in the low- α region while in CNT(30,30)-xyl, the angles are more evenly distributed. This means the molecules inside CNT(7,7) have aligned along the

tubes compared with the more randomly oriented molecules near the CNT(30,30) surface.

The above phenomenon of alignment is quantified using the angle distributions of the first boundary layers. The distribution is averaged from the 101 frames outputted from the simulation, each 5 ps apart, the same as used in the temperature and density profile calculations. These distributions are plotted in Figure 10 with the three most distinguished distributions

Figure 10. Distribution of orientation angles of xylitol molecules in the first boundary layers. Hot: inside tube, cold: outside tube. The three most distinguished distributions are marked with colored squares. The orientation distribution of erythritol is given in the Supporting Information.

marked in colored squares. Indeed most xylitol molecules inside CNT(7,7) have α angles less than 30 degrees. This explains the much higher than estimated effective density. It is interesting to notice the large population of molecules sitting around 45 deg inside CNT(8,8), as a spontaneous packing effect to maximize the in-tube density. For all distributions other than the marked three, the curves are much flatter, although there is a higher chance of finding a low- α molecule. It appears the molecules outside the tube prefer to align with the tube as well. Also there seems to be a slightly higher distribution of α at 50–60 degrees. These interesting phenomena are to be investigated in future work.

Hydrogen Bond Number and Lengths. Apart from the molecular orientations, hydrogen bond (HB) structures are also important in characterizing the equilibrium structure. As hydroxyl-rich compounds, SAs can form complex HB networks. The HB network and energy can determine the latent heat of melting⁸ or structural orderings.⁴³ In this work, the HBs are defined using a 30 degree cutoff in $H-O_D-O_A$ angle and a 0.35 nm cutoff in donor–acceptor length. The HB number per molecule N_{HB}/N_m in the simulations is plotted in Figure 11a,d. The HB number is further decomposed into intramolecular HB number and intermolecular HB number. On the cold side, N_{HB}/N_m is irrelevant to the CNT diameter. However, on the hot side, as a finite size effect of the confinement, the HB number varies. When the CNT diameter is very small, the total HB number on the hot side drops; however, its intramolecular component increases. The HB number is sensitive to the temperature. This can be found by comparing the data points situated at $1/d = 0$. The cold side has more HBs than the hot side in both xylitol and erythritol cases, and the higher total HB number is mostly contributed by the intermolecular HB number. Using exponential Gaussian curves, the donor–acceptor length distributions in Figure 11b,d are fitted for

Figure 11. Hydrogen bond numbers, donor–acceptor length distribution, and mean lengths of (a–c) xylitol and (d–f) erythritol.

mean HB lengths plotted in Figure 11c,f. It appears the HB mean lengths of SAs inside CNT(7,7) and CNT(8,8) are shorter. This indicates stronger HBs.

INSIGHT INTO THE BROADER SUGAR ALCOHOL FAMILY

From the above results and analysis, the thermal contact conductance is found to decrease as the CNT diameter decreases. Also, the erythritol and xylitol molecules inside the CNTs are less and less liquid-like and have larger phonon mode mismatch compared with the outer region. We believe this effect can be applied to other SA compounds because smaller sized CNTs result in stronger movement restrictions, less mass diffusion, and less diffusive heat transfer. However, from the results of the two model composites, CNT-xylitol and CNT-erythritol, the decreasing trend is not monotonic. In the case of CNT(7,7), the much larger than expected in-tube effective density results in more collisions and faster heat transfer rate. This phenomenon should also apply to other linear SA compounds. The most promising SAs are C4–C6 acyclic polyalcohols. They all share the linear configuration and have similar molecular widths. These SAs can fit into CNT(7,7) by realigning their orientations along the tube axis and produce a much larger mean effective density.

Knowing the factors that influence the diameter dependence of the thermal contact conductance $U(d)$, we can easily extrapolate the U values using graphene-SA simulation results for which $d = \infty$. Besides erythritol and xylitol, three other commonly used SAs are selected and the results are summarized in Table 1 and plotted in Figure 12. Also given in Table 1 is the thermal conductivity k calculated based on the quadratic curve fittings of the temperature profiles (similar to those plotted in Figure 6) using²⁵

$$q_V = \frac{q}{AL} = k \frac{d^2 T}{dx^2} \quad (6)$$

Table 1. Results of Graphene-SA Simulations^a

	T_m [K]	U [10^6 W/m ² /K]	k [W/m/K]	Λ [nm]
TIP4P/2005 ^b	273	95.0(3)	0.94(6)	9.9(6)
erythritol	393	62.5(7)	0.47(4)	7.6(7)
xylitol ^c	367	66.7(5)	0.49(1)	7.3(2)
D-arabinitol	375	58.8(3)	0.54(1)	9.2(1)
D-mannitol	438	68.2(8)	0.51(11)	7.5(16)
D-glucitol	369	66.6(7)	0.54(6)	8.2(9)

^aData in the parentheses show standard deviations of the last digit(s).

^bSimulated at 300 K. ^cSimulated at 380 K.

Figure 12. Interfacial thermal contact conductance across graphene layers solvated in various SA compounds. The blue bars corresponds to results listed in Table 1. The green side bars are results of additional simulations at 380 K.

where q_V is the volumetric heat generation rate and L is the length of liquid in one compartment. It should be noted that the curve fitting is based on a diffusive heat transfer mechanism and hence the k values are only for validation purposes.

In the last column of Table 1, the Kapitza lengths $\Lambda = k/U$ are given. The Kapitza length describes on what distance the

temperature would drop the same number of Kelvins as dropped at the solid–liquid interface under the same heat flux. As an interesting fact, for all SAs studied along with the referenced material water, the Kapitza lengths are roughly in the same range. To overcome the Kapitza length, which is around 10 nm, CNTs much longer than 10 nm are required to substantially increase the effective conductivity of the complex material. Comparing among the SAs, the thermal contact conductance values are all around $60 \text{ MW m}^{-2} \text{ K}^{-1}$. Because erythritol and D-mannitol have relatively higher melting points, additional simulations are performed for these two materials at 380 K to make better comparisons. The two results are plotted as the side bars in Figure 12. We noticed for both materials, U decreases with temperature. This could be a result of less collisions with the interface and hence less energy transfer.

DISCUSSION

The goal of this research is to study the nanoscale heat transfer across single layered carbon structures solvated in various SA compounds. As pointed out by previous studies, the cross-plane heat transfer is ballistic and dominated by the low frequency phonons.^{25,27} Therefore, we analyzed the phonon mode mismatch between the in-tube SA and out-of-tube SA. As CNT diameter decreases, more phonon mode mismatch between the SA molecules on the two sides are observed. According to the acoustic mismatch model, a larger mismatch hinders the interfacial heat transfer. On the other hand, the SA molecules in the smaller sized CNTs exhibits sharper VDOS peaks. These molecules are less liquid-like and have less phonon scattering, resulting in a lowered heat transfer rate. It is unclear if the sharper VDOS peaks are a result of the limited molecular mobility. Nevertheless, the sharpness of VDOS peaks and the limitation of the molecular mobility seem correlated and this correlation is consistent with a previous study linking the mass diffusion of enclosed water molecules to the cross-plane thermal contact conductance.²⁵ For all C4–C6 acyclic polyalcohols of our interest, the same decreasing trend should apply.

By comparing the VDOS between the first boundary layer and the bulk region, we are convinced the aforementioned phonon mode mismatch comes from the reaccommodated configurations of the confined molecules, instead of an interfacial effect. By studying the molecular configurations inside the CNTs, the molecules are found to aggregate in specific orientations depending on the CNT diameter. This is a typical finite size effect of confinement. In the case of CNT(7,7), the mean effective density is much larger than expected. From the molecular collision point of view, this larger density is the cause to the larger thermal contact conductance across CNT(7,7). In terms of other C4–C6 acyclic polyalcohols, their similar linear configuration and molecular widths allow them to fit into CNT(7,7) by realigning to the CNT axis. Therefore, we expect a larger thermal contact conductance across CNT(7,7) than the one across CNT(8,8).

In all the simulations, no evident structural orderings are observed. If the SAs crystallize or form a solid-like structure, the phonon modes can be greatly altered and may result in a lower thermal contact conductance. Although such a phenomenon is not observed in this work, this possibility cannot be ruled out considering the length and time scale of our simulations.

The graphene-SA thermal contact conductance is calculated for five SA compounds. It is hard to draw conclusions on how the exact U values are linked to their molecular structures or

their carbon bone lengths, since the results are all within a narrow range. In the direction perpendicular to the graphene plane, the detailed phonon transmission and scattering pattern determine the cross-plane thermal contact conductance of each SA compound.⁴¹ Since all C4–C6 acyclic polyalcohols share similar linear configurations, for a rough estimation, we can assume the U value is around $50\text{--}70 \text{ MW m}^{-2} \text{ K}^{-1}$, based on the results of the five model materials. As another finding, a lower temperature results in a lower thermal contact conductance. However, this effect is not a big concern considering that PCMs usually work at a constant temperature.

CONCLUSIONS

In this research, molecular dynamics simulations and advanced data analyzing techniques are applied to study the nanoscale heat transfer in interfacial systems where graphene and CNTs are submerged into various SA compounds. Using erythritol and xylitol as model materials, we found the cross-plane thermal contact conductance to decrease as the CNT diameter decreases, with an exception of CNT(7,7). The general decreasing trend can be ascribed to the increasing phonon mode mismatch. By comparing the VDOS of molecules in different regions, the mismatch is found to be a finite size effect of the confinement, instead of an interfacial effect. In the analysis of the orientations of the SA molecules enclosed in the CNTs, the mean effective density fluctuation is influenced by both the interfacial effect and the finite size effect of the confinement. The total HB number decreases as CNT diameter decreases. However, the intramolecular HB number increases. In systems with smaller CNTs, the HB donor–acceptor lengths are shorter. From the molecular collision point of view, a higher density promotes heat transfer. In the case of CNT(7,7), the density effect becomes dominant and reverses the general aforementioned decreasing trend. For graphene-SA composites, five SA materials are considered and their cross-plane thermal contact conductance values all fall into a narrow range between 50 to $70 \text{ W/m}^2/\text{K}$. The results obtained in this research deepened the understanding of the nanoscale heat transfer in graphene/CNT-SA composite materials and provided essential data for estimating the effective heat conductivity of any given CNT-SA composite for material design purposes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b05466.

1. Raw data used for calculating the graphene/CNT-SA thermal contact conductance values;
2. VDOS of CNT/graphene in CNT/graphene-erythritol composites;
3. distribution of orientation angles of erythritol molecules in the first boundary layers;
4. density profiles of SA molecules in the composites;
5. orientation angles of xylitol and erythritol calculated using the last frames of each simulation (extension to Figure 9). (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

CNT carbon nanotube
MD molecular dynamics
PCM phase change material
SA sugar alcohol

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