Thermal contact resistance in carbon nanotube enhanced heat storage materials

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Thermal Contact Resistance in Carbon Nanotube Enhanced Heat Storage Materials

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Nano-scale heat transfer, thermal contact resistance, molecular dynamics, heat storage materials, sugar alcohol

ABSTRACT
Solid-liquid phase change is one of the most favorable means of compact and economical heat storage in the built environment. In such storage systems, the vast available solar heat is stored as latent heat in the storage materials. Recent studies suggest using sugar alcohols as seasonal heat storage materials for their large storage capacity, moderate melting point, and evident supercooling effects. However, the heat transfer in such materials is sluggish and hence carbon structures are proposed to enhance their overall heat conductivity. In this work, we focus on sugar alcohol - carbon nanotube system, analyze the heat transfer in the radial direction of the nanotube using molecular dynamics simulations. The thermal contact resistance is calculated using Nosé-Hoover dynamics and is found dependent on the diameter of the tubes. We validate our results using water - nanotube simulations. Then the simulation method is extended to sugar alcohol - nanotube systems.

1. INTRODUCTION
Solid-liquid phase change is one of the most favorable means of compact and economical heat storage in the built environment. Recently, sugar alcohols are proposed to function as heat storage medium in long term seasonal storage systems. Sugar alcohols have high latent heat of fusion and evident supercooling effect which prevents loss upon spontaneous phase transition. Additionally, as byproducts of the food industry, sugar alcohols are non-toxic, non-corrosive, and the huge bulk production has made them very economically competitive. Despite of the advantages, a major challenge that hampers large scale implementation is their relatively low heat conductivity and sluggish crystallization kinetics. Previous research have suggested using carbon structures to enhance the material [1] or making eutectic mixtures [2, 3]. Other research has been done to fully characterize the materials [4, 5, 6]. However, little is known on the heat transfer mechanisms in the carbon-sugar alcohol composite materials. In this study, we choose carbon nanotubes (CNT), a widely researched material and xylitol, one of the most promising sugar alcohol species, to characterize the thermal contact resistance in carbon-xylitol composites. Graphene layers is also included in this research. We focus on the geometry and size effect of CNTs to the radial heat transfer through the tubes.

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Lots of research has been done in CNT-water systems. Water, as a natural phase change material, has played an important role in shaping the earth climate and is already widely used in domestic heating and cooling applications. In this work, CNT-water system is studied as a validation for our further works. Though carbon structures are considered as good thermal conductors, the heat is generally hard to flow from the molecular fluids to the carbon due to the high thermal contact resistance. Huxtable stated the thermal resistance does not depend critically on the surfactant[7]. Thus we choose single walled nanotubes (SWNT) for this research. Regarding organic phase change materials, Singh and Banerjee studied the contact resistance between SWNT and paraffin wax [8], which provided valuable reference to our work.

To fully understand the heat transfer on the nano-scale level, we choose molecular scale methods for the study. Using non-equilibrium molecular dynamics simulations, an artificial heat flux can be applied to the systems and the contact resistance can be calculated. In the following sections, we briefly introduce the molecular models and the Nosé-Hoover dynamics used. Then the results will be discussed to guide the designs of composite heat storage materials.

2. Methodology

2.1 Molecular models

The sugar alcohol molecules are modeled using a generalized AMBER force field [9]. The force field is tailored to match electronic density function theory calculations and is proven to be successful in reproducing sugar alcohol material properties [10, 4]. The carbon nanotubes (CNT) and graphene layers are modeled using a quantum mechanics based force field recommended by Pascal et al. [11]. This force field can well reproduce mechanical and phonon properties of graphene layers and therefore believed to be suitable for heat conduction studies in this work. The water molecules are modeled using a four point model TIP4P/2005 [12] which is advantageous in predicting the phase diagram and mass diffusion of water [?]. The water-CNT interactions are modeled following Wu and Aluru’s work [13]. The sugar alcohol-CNT interactions are solely the non-bonded interactions in Lennard-Jones (LJ) 12-6 form, with parameters generated according to Lorentz-Bethel mixing rule. The total potential energy $E_p$ is expressed as

$$E_p(r_1, r_2, \ldots, r_N) = E_{el} + E_{vdW} + E_{bond}$$

where $r_i$ is the Cartesian coordinate of the $i$-th atom, and on the right hand of the equation are the non-bonded electrostatic interaction energy, non-bonded van der Waals interactions in LJ 12-6 form, and the bonded energies with details described in the referred force fields, respectively.

2.2 Nosé-Hoover dynamics

The non-equilibrium simulations in this work with temperature coupling is achieved using Nosé-Hoover dynamics [14]. The equations of motion in Nosé Hoover dynamics are

$$\frac{d^2 r_i}{dt^2} = \frac{m_i}{m_{\xi}} \frac{d}{dt} \left( Fr_i - \frac{p_\xi}{m_{\xi}} \right.$$}

where $m$ is atom mass, $F_i$ is the resultant force obtained using $r_i = -\partial E_p/\partial r_i$, $\xi$ is a fully dynamics quantity with its own mass $m_{\xi}$ and momentum defined as $p_\xi = m_{\xi} d\xi/dt$. The equation of motion for $\xi$ is

$$\frac{d^2 \xi}{dt^2} = \frac{T - T_0}{m_{\xi}}$$

(3)
where $T = 2E_k/(3Nk_B)$ is the systems’ instantaneous temperature, $E_k = \sum p_i^2/m_i$ is the systems’ total kinetic energy, $T_0$ is the target temperature, $N$ represents the total number of atoms in the heat bath. The mass parameter $m_\xi$ describes the coupling strength between the system and the heat bath. However, it is more intuitive to use the period $\tau_T$ of the oscillations of kinetic energy between the system and the reservoir instead. $\tau_T$ is related to $m_\xi$ via

$$3Nk_Bm_\xi = \frac{\tau_T^2 T_0}{4\pi^2}$$  \hspace{1cm} (4)

Esposito and Monnai has shown that systems driven by Nosé-Hoover dynamics allow for a consistent nonequilibrium thermodynamics description [14]. The conserved energy is no longer the system Hamiltonian

$$H_{\text{sys}} = E_k + E_p = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + E_p(r_1, r_2, ..., r_N)$$  \hspace{1cm} (5)

but instead

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + E_p(r_1, r_2, ..., r_N) + \frac{p_\xi^2}{2m_\xi} + 3Nk_BT_\xi$$  \hspace{1cm} (6)

Obviously, this gives the energy flow into the system from the reservoir as

$$Q = H - H_{\text{sys}} = \frac{p_\xi^2}{2m_\xi} + 3Nk_BT_\xi$$  \hspace{1cm} (7)

### 2.3 Simulation details

The CNT-solvent simulations are done in multiple steps. The 4.9-nm long open-ended CNTs are first solvated into 7500 water or 1024 xylitol molecules and equilibrated for 2 ns. Then the equilibrium structures along with the solvent molecules inside are extracted from the equilibrium configurations and rotated to align the z-axis of the simulation boxes. Theses structures are then applied with periodic boundary conditions to form periodic tubes. The top view of these tubes along with the solvent molecules enclosed are illustrated in figure 1. The equilibrium number of solvent water molecules inside the tubes are $115 \pm 2$, $284.6 \pm 4.7$, and $684.5 \pm 6.5$, for CNT(10,10), CNT(14,14), and CNT(20,20), respectively. For CNT-xylitol simulations, the numbers are $18 \pm 0.8$, $44 \pm 4.0$, and $93 \pm 0.9$, respectively. These tubes are then solvated into 4000 water or 750 xylitol molecules and equilibrated for another 2 ns. The above steps are similar to those used by Pascal et al. [15]. The temperatures for CNT-water equilibration simulations are set to $T_{\text{eq}} = 300$ K and for CNT-xylitol 380K. The temperature for CNT-xylitol simulations is chosen to be higher than its melting point $T_m = 367.52$K [16] and lower than that any substantial thermal degradation can occur [6]. The equilibrium structures are then simulated using non-equilibrium Nosé-Hoover dynamics for 500 ps. This ensures a good statistics over the heat transferred through the carbon structure. The solvent inside and outside the CNTs are coupled to separate heat baths of $T_{\text{eq}} + 20$ K and $T_{\text{eq}} - 20$ K, respectively. A larger temperature difference would push the liquid materials to the solid phase while a smaller temperature difference reduces the heat transfer rates and thus adds statistical uncertainties. The temperatures of CNTs are coupled to $T_{\text{eq}}$. The box sizes are fixed in the non-equilibrium simulations.

To study the size effect of the CNTs, graphenes are also modeled to represent CNTs in the limit of infinitely large diameter. The graphene-solvent simulations are done by first equilibrating one graphene layer with solvent molecules (1000 water or 512 xylitol molecules) at $T_{\text{eq}}$ and 1 bar. Then the equilibrium structures are duplicated in the direction perpendicular to the graphene layer. This generates a configuration of 1 layer graphene + solvent molecules + another layer graphene + solvent molecules. This sandwich structure has two groups of solvent molecules separated by the graphene layers. One of
the groups can be considered as the molecules ‘inside’ the tube while the other can be considered as the molecules ‘outside’ the tube. To minimize finite size effects, the two layers of graphene are separated to about 5 nm. Finally the non-equilibrium simulations are done the same way as CNT-solvent simulations.

In all simulations, the time step is set to 1 fs. All H-O and H-C bonds are constrained using LINCS algorithm. Particle meshed Ewald summation (PME) are applied to long-range electrostatics with Fourier spacing of 0.12 nm. The long-range LJ interaction is cut-off at 1.4 nm. In the equilibration simulations, Berendsen thermostat and barostat are applied with time constant $\tau_T = 0.1$ ps and $\tau_p = 0.5$ ps, respectively. In the non-equilibrium simulations, $\tau_T$ is set to 0.5 ps.

3. Results and Analysis

3.1 Density profile

We first examine the radial density profiles $\rho(R)$ in the steady-state simulations. $\rho(R)$ is defined as

$$\rho(R) = \lim_{\Delta R \to 0} \sum_{R_1 \in \mathcal{D}} \frac{m_i}{2\pi R_1 \Delta R} \mathcal{D} = [R - \Delta R/2, R + \Delta R/2]$$  (8)

where $l$ is the tube length, $R$ is the distance from the tube center. In the calculations, $\Delta R$ is set to 0.01 nm, and the statistical average is made over 100 configurations, each separated by 5 ps. The results are plotted in figure 2 and figure 3. To make a comparison of all cases, the radial density profiles are shifted by their corresponding CNT radii $R_0$ to align the carbon walls to zero. In the graphene case, $\rho(R)$ is shifted such that the graphene layer is also at position zero. The positions of the tube centers are labeled using black dashed lines. In all cases, there are clear periodic trends. On the inner side with $R - R_0 < 0$, The first
density peak of water smoothen over increasing tube diameter. In CNT(10,10), there is clearly a strong secondary peak. This result is in line with reference [15]. On the outer side with $R - R_0 > 0$, there is no major distinction among the four cases. After a few density peaks, the density of water converge to bulk value. Because of the temperature difference between inner and outer water molecules, the density peak is slightly sharper on the cold side of graphene. The number of layers of solvent molecules enclosed in the tubes are dependent on the tube diameters. In the xylitol case, CNT(10,10) has a radius of roughly one layer of solvent molecules with $-R_0$ sitting at the first periodic density minimum, leaving a hollow region in the center, also as illustrated in figure 1(d).

![Radial density profiles in CNT-water simulations](image)

**Figure 2:** Radial density profiles in CNT-water simulations. The positions of the CNTs are aligned to zero to make a comparison. The center of the tubes are marked with the dark dashed lines.

### 3.2 Temperature profile

The steady state temperature profiles $T(R)$ is calculated using

$$T(R) = \lim_{\Delta R \to 0} \left( \frac{1}{\sum R_i \in D} \sum R_i^{2/m_i} \right) / \left( \sum R_i \in D n_i k_B \right)$$  \hspace{1cm} (9)

where $n_i$ is the number of degrees of freedom in atom $i$. For example, a TIP4P/2005 water molecule has a combined $n_O + 2n_H = 6$ while the carbon atoms in the CNTs have $n_C = 3$. The temperature profiles are plotted in figure 4 and 5 with a statistical average over 100 configurations. The temperatures inside or outside the tubes are not uniform. Therefore linear fits weighted by the number densities are made to demonstrate the trend. The temperature gradient inside the CNT is more evident when it comes to smaller CNTs. The temperature jump at the interface is dramatic. This indicates a large thermal contact resistance. Outside the CNT, the water temperature gradients are less evident.

### 3.3 Thermal contact resistance

Using equation 7, the heat flow over time is calculated for both solvent molecules inside and outside the CNTs. Figure 6 shows the heat flow into the inner solvent molecules $Q_{in}$ and the heat flow into the outer
Figure 3: Radial density profiles in CNT-xylitol simulations. The positions of the CNTs are aligned to zero to make a comparison. The center of the tubes are marked with the dark dashed lines.

Figure 4: Steady-state temperature profiles of CNT-water simulations. The positions of the CNTs are aligned to zero to make a comparison. The dashed colored lines are the linear fits weighted by the number densities.

solvent molecules $Q_{\text{out}}$. The heat flow into the CNTs $Q_{\text{CNT}}$ are also plotted. In the steady state the net heat flow into the CNTs in all cases are nearly zero, and therefore most heat is flowing from the inner
Figure 5: Steady-state temperature profiles of CNT-xylitol simulations. The positions of the CNTs are aligned to zero to make a comparison. The dashed colored lines are the linear fits weighted by the number densities.

water to the outer water. The heat flow rates are calculated by fitting the $Q\cdot t$ curves. The slopes of the linear fits are listed in Table 1.

The heat transfer coefficient $U$ in the carbon-water systems is defined as

$$U = \frac{dQ/dt}{A\Delta T}$$ (10)

where $A$ is the heat transfer area. The contact resistance $R_k$ is defined as the reciprocal of $U$. Both results are listed in Table 1.

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<tr>
<td>*CNT(10,10)</td>
<td>28.82</td>
<td>1.347</td>
<td>4.909</td>
<td>20.77</td>
<td>35.38</td>
<td>62.13</td>
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<td>48.68</td>
<td>1.884</td>
<td>4.912</td>
<td>29.07</td>
<td>36.48</td>
<td>76.23</td>
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<tr>
<td>*CNT(20,20)</td>
<td>83.65</td>
<td>2.693</td>
<td>4.903</td>
<td>41.48</td>
<td>37.44</td>
<td>89.44</td>
<td>1.118×10$^{-8}$</td>
</tr>
<tr>
<td>*graphene</td>
<td>52.16</td>
<td>-</td>
<td>-</td>
<td>23.17</td>
<td>37.89</td>
<td>98.66</td>
<td>1.101×10$^{-8}$</td>
</tr>
<tr>
<td>+CNT(10,10)</td>
<td>19.22</td>
<td>1.345</td>
<td>4.917</td>
<td>20.70</td>
<td>37.65</td>
<td>40.95</td>
<td>2.442×10$^{-8}$</td>
</tr>
<tr>
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<td>30.50</td>
<td>1.884</td>
<td>4.909</td>
<td>28.96</td>
<td>39.65</td>
<td>44.11</td>
<td>2.267×10$^{-8}$</td>
</tr>
<tr>
<td>+CNT(20,20)</td>
<td>39.71</td>
<td>2.693</td>
<td>4.922</td>
<td>41.36</td>
<td>36.27</td>
<td>45.78</td>
<td>2.184×10$^{-8}$</td>
</tr>
<tr>
<td>+graphene</td>
<td>70.95</td>
<td>-</td>
<td>-</td>
<td>52.10</td>
<td>35.49</td>
<td>63.72</td>
<td>1.570×10$^{-8}$</td>
</tr>
</tbody>
</table>

Table 1: Simulated radial heat flow rate and contact resistance of *CNT-water and +CNT-xylitol
Figure 6: Heat flow over time for different groups of molecules. In each figure, the results of all four simulations are plotted. The sum of $Q_{in}$ and $Q_{out}$ is mostly zero. The slopes of the heat flows are the heat flow rates listed in table 1.

4. Discussions

There is a clear size effect on the contact resistance between CNTs and the solvent molecules. The increasing contact resistance with decreasing CNT diameter can be ascribed to the lack of number of contacting molecules on the inner side. The effective contacting area is less than the nominal area of the CNTs. This evident geometry effect can play an important role in composite heat storage material designs.

Comparing with literature values, experimental and numerical works reported 0.77 to $20 \times 10^{-8}$ m$^2$K/W contact resistance values for various carbon nano-structures and are very case dependent [17]. For water, Unnikrishnan et.al. reported 1.7 to $2.6 \times 10^{-8}$ m$^2$K/W at above 500K. For paraffin wax, Singh and Banerjee reported 6.3 to $10.2 \times 10^{-8}$ m$^2$K/W at above 300K. Konatham et.al. [18] reported octane-graphene contact resistance of $5.5 \times 10^{-8}$ m$^2$K/W and graphene-graphene contact resistance of 6.5 to $7.7 \times 10^{-8}$ m$^2$K/W at above 300K. Our calculations provided results in line with the literature results.

The thermal contact resistance values obtained in this study can be used to design composite heat storage materials. According the Maxwell-Garnett-type effective medium theory, the effective thermal conductivity can increase 5% by adding only 1% volume fraction of CNT [8]. In this model, the contact resistance is a key parameter to the effective thermal conductivity of the composite material. Knowing the accurate resistance values can hence help to design the material with the best price-quality ratio. In the work of [19] and [18], detailed CNT-CNT or graphene-graphene contacts are discussed. When using octane as the matrix material, graphene-octane resistance is 15% smaller than the graphene-graphene resistance but in the same order of magnitude. This means the carbon-carbon contact can only have a limited effect on the overall effective conductivity.

5. Conclusions

In this work, we have demonstrated how to characterize the thermal contact resistance between heat storage materials and CNTs. The resistance is found highly dependent on the diameter of the CNTs. We report $1.1\sim1.5 \times 10^{-8}$ m$^2$K/W CNT-water contact resistance and $1.5\sim2.4 \times 10^{-8}$ m$^2$K/W CNT-xylitol contact resistance, depending on the CNT diameters. These values are in line with literature values and expectations. These accurately determined values can be used to design composite material of interest.
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REFERENCES AND CITATIONS
