Abstract. The thermal conductivity at 300K of (6,6) carbon nanotubes functionalized by methyl groups at random positions through covalent bonding (chemisorption) has been calculated as a function of adsorption density using molecular dynamics. The results exhibit a rapid drop in thermal conductivity with chemisorptions, even chemisorption as little as 1.0% of the nanotube carbon atoms reduces the thermal conductivity very much. Investigate its reason, defects caused by chemisorption blocking the transmission of phonons which plays a leading role in the heat conduction of nanotubes, affecting the temperature distribution and energy transmission, leading to the thermal conductivity decline.

Introduction

Thermal conductivities of 400-6000W/(mK) in the axial direction of isolated carbon nanotubes (CNTs) calculated from molecular simulations suggest that CNTs may have applications for thermal management in polymer composites\cite{1,2}. However, experimental measurements of the thermal properties of CNT-polymer composites showed mixed results; some report that the addition of a little of carbon nanotubes to a polymer matrix greatly improves the system’s thermal conductivity\cite{3,4}, while others report that the effect is less than predicted and is due to the interface thermal conductance\cite{5}. One possible method to improve the thermal conductance between CNTs and matrix is by chemically functionalizing the CNTs into the matrix. Modeling studies have suggested that such functionalization can improve load transfer in CNT-polymer composites without significantly sacrificing the high axial Young’s modulus of CNTs\cite{6,7}. Xie\cite{8} et al and Daniel have introduced some chemisorption methods to improve the thermal conductance. The most commonly chemisorption is attaching atom or atom group to the surface of CNTs through covalent bonding, such as hydrogen atom and methyl.

So far, for the pristine CNTs have been done a series of extensive work, while for the studies of defective CNTs have Cummings\cite{9}, Meng\cite{10} and Fan\cite{11} using the method of molecular dynamics simulation to calculate the thermal conductivity, but studies involving the influence of chemical functionalization on thermal properties of CNTs still very rare.

In the following, molecular dynamics was performed to calculate thermal conductivities of (6,6) CNTs on which methyl groups have been attached. Then these results are compared with the thermal conductivities of pristine CNTs. Results show that chemisorbing methyl groups to as little as 1.0% of the carbon atoms in a CNTs reduces the thermal conductivity by 90%.

Theoretical Model and Calculation of Thermal Conductivity

The structure model of pristine (6,6) single-walled carbon nanotube (SWNT) is shown in Figure 1, the radius $R = 4.07\, \text{Å}$, the length $L = 12.298\, \text{nm}$, C-C bond length $b_{c-c} = 1.42\, \text{Å}$, carbon atom number $N = 1200$. Simulations were performed on pristine CNTs and CNTs on which 0.5%, 1.0%, 2.5%, 5.0% of the carbon atoms had a bonded methyl group (adsorption density = chemisorption carbon atom number ÷ CNTs’ atom number × 100%).

![Figure 1. The pristine (6,6) CNTs](image-url)
The thermal conductivities of the chemisorptions and pristine CNTs are calculated using equilibrium molecular dynamics (EMD). Carbon nanotubes are considered as a thick cylinder of 1Å. Adaptive intermolecular reactive empirical bond order (AIREBO) are used to describe the interaction,

\[ E = \frac{1}{2} \sum_{ij} \left[ E_{ij}^{\text{REBO}} + E_{ij}^{J} + \sum_{k \neq i \neq j} E_{ijkl}^{\text{torsion}} \right] \]  

(1)

Nose-Hoover thermostat mechanism and three-dimensional periodic boundary condition (due to the larger SWNT aspect ratio, non-SWNT-axis direction is much larger than the size of the SWNT diameter, which make it beyond the scope of the long-range force) are used. The time step was set to 0.1fs to cover the high-frequency C-H vibration.

Zone temperature \( T \) is given by the Boltzmann energy equipartition and it is the temperature of statistical significance, i.e. the average kinetic energy of all atoms.

\[ T = \frac{1}{3nk_B} \sum_{i=1}^{n} m_i v_i^2 \]  

(2)

The EMD method is based on the linear response theory, using the Einstein or Green-Kubo (GK) formula to calculate thermal conductivity of CNTs. In this article, GK formula is used

\[ k = \frac{V}{k_B T^2} \int_0^\infty \left\langle J_z(0) J_z(t) \right\rangle dt \]  

(3)

In the above formula, \( k \) is the thermal conductivity, \( V \) is the volume of simulation system, Boltzmann constant \( k_B = 1.3806505 \times 10^{-23} \) J/K, \( T \) is the temperature of simulation system, \( t \) is the time, \( \left\langle J_z(0) J_z(t) \right\rangle \) is the heat current autocorrelation function (HCACF) of nanotubes axial direction.

**Results and Analysis**

As is well know, length, radius, temperature and functionalization all have effect on the thermal conductivity of CNTs. This paper discussed the influence of adsorption density on the thermal conductivity.

HCACF and thermal conductivity with the change of adsorption density are shown in figure 3 to 5.
In this simulation HCACFs converged well to obtain stable thermal conductivity values. The thermal conductivities of different adsorption density are shown in the following table.
Tab.1 Thermal conductivity of different adsorption density

<table>
<thead>
<tr>
<th>Adsorption density</th>
<th>0%</th>
<th>0.5%</th>
<th>1.0%</th>
<th>2.5%</th>
<th>5.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity: W/m K</td>
<td>1361.1</td>
<td>49.53</td>
<td>31.10</td>
<td>22.53</td>
<td>12.42</td>
</tr>
</tbody>
</table>

The results showed that,

(1) The pristine CNTs due to good structure exhibits excellent thermal conductivity.

(2) Thermal conductivity dropped rapidly with chemisorption, where chemisorption as little as 1.0% of the nanotube carbon atoms drastically reduces the thermal conductivity.

(3) The larger the adsorption density, the lower the thermal conductivity. This indicates that increasing the heat transfer between CNTs and a polymer matrix in a composite via chemisorption is not a good way.

(4) The atoms on which the methyl groups are bonded have hybridizations that change from sp$^2$ to sp$^3$. The associated change in geometry of these atoms is illustrated in the Figure 2, where the bonded nanotube atoms are "raised" away from the nanotube axes. The introduction of sp$^3$ carbon into the nanotube structure creates defects for the phonons to interact with and scatter off of, thus reducing the thermal conductivity.

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Reference:

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