カーボンナノチューブ伝熱への周囲材料の影響

INFLUENCE OF SURROUNDING MATERIALS ON CARBON NANOTUBE HEAT TRANSFER

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The current study intends to characterize the heat transfer of single-walled carbon nanotubes (SWNTs) under the influence of the surrounding materials using molecular dynamics (MD) simulations. Investigations of such systems are of great importance for the prospective device applications. In this report, firstly, the radial thermal boundary conductance (K) at interface between an SWNT and surrounding materials was examined. As a general case, we take an SWNT surrounded with argon (Ar) molecules. By varying the density and temperature of Ar, we investigate the influence of the Ar phase on K. K was computed by recording the temperature history of the non-stationary heat transfer from the SWNT to Ar and applying the lamped heat capacity method. The resulting trend of K suggests that the key physics for heat transfer depends on the phase of the Ar material. Closer observation of the molecular dynamics reveals that, for the gas phase, heat transfer is diffusive where random molecular collisions are in charge. On the other hand, in the solid phase, the dominant part of heat transfer can be attributed to certain modal interactions which can be estimated by the convolution of lattice vibrations of the SWNT and the surrounding matrix. Secondly, the attenuation of SWNT heat conduction due to the interference with the surrounding materials was demonstrated. As a preliminary case, we investigate such an effect in an SNWT confining water inside. On freezing the water with the SWNT as a cast, the water molecules either form an ice nanotube or a tube-like structure with the hollow filled with water molecules lined along the axis, depending on the number of water molecules or the cooling speed. By performing non-equilibrium MD simulations, thermal conductivity was measured by imposing a temperature gradient and applying the Fourier's law. It is demonstrated that the effective thermal conductivity of the SWNT can be attenuated by the interaction with the confined ice. The reduction increases but gradually saturates as the number of water molecules increases.

1. INTRODUCTION

It is theoretically predicted that single-walled carbon nanotubes (SWNTs) may possess extremely high thermal conductivity [1]. Furthermore, some experimental reports are for the prediction, though with certain uncertainty due to technical difficulties in probing the nanoscale material. Nevertheless, with the quasi-one-dimensional structure constructed with the tight bonds, it should be fair to expect an SWNT to be a good heat conductor.

The expected high thermal conductivity of SWNTs has encouraged various applications that accompany heat generation. Having actual applications in scope, it is important to characterize SWNT heat transfer in more practical situations, for instance SWNTs in contact with other surrounding materials. In such situations, the heat transfer from the SWNT to the surrounding material would play an important role on deciding the acceptable heat load to the device. Here the heat transfer would be strongly dependent on the density and phase of the material. These aspects are investigated in the first part of this study, where we simulate an SWNT surrounded by argon (Ar) in various phases.

The interaction of SWNT and surrounding materials could also attenuate the axial heat conduction. Especially, when the material is in solid phase, the lattice vibration of the SWNT may experience a significant restriction. In second part of the current report, we present the simulations of the heat conduction of an SWNT with water inside. We adopt the system as an initial study of this kind since the quasi-dimensional confinement of the water realizes efficient coverage over SWNT with fewer molecules compared with the case of external adsorption. This severely impacts the cost of computation as thermal conductivity measurements usually require considerable number of samples to obtain acceptable statistics.

2. MOLECULAR DYNAMICS SIMULATIONS

The carbon interactions were expressed by the Brenner potential function [2], where the total potential energy of the system is modeled as,

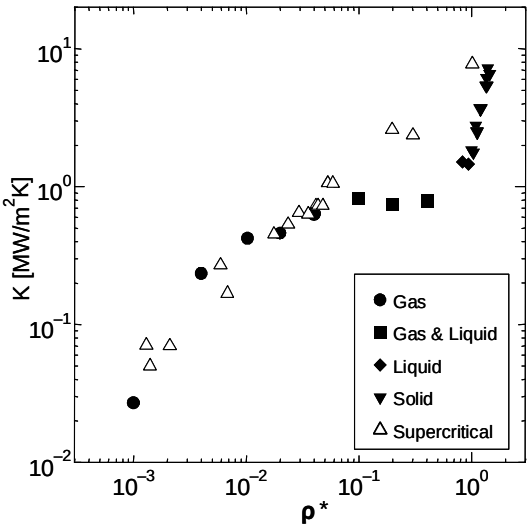

Fig. 1 Thermal boundary conductance at the interface of an SWNT and bulk argon in various phases.

$$E = \sum_i \sum_{j(i<j)} \left[V_R(r_{ij}) - B^*_{ij} V_A(r_{ij}) \right] \quad (1)$$

Here, $V_R(r)$ and $V_A(r)$ are repulsive and attractive force terms which take the Morse type form with a certain cut-off function. B^*_{ij} represents the effect of the bonding condition of the atoms. As for the potential parameters, we employ the set that was shown to reproduce the force constant better (table 2 in [2]). The velocity Verlet method was adopted to integrate the equation of motion with the time step of 0.5 fs.

Water molecules were expressed by SPC/E potential [3]. SPC/E potential is expressed as the superposition of Lennard-Jones function of oxygen-oxygen interaction and the electrostatic potential by charges on oxygen and hydrogen. The Coulombic interaction is the sum of 16 pairs of point charges. The potential function between water molecules and carbon atoms are represented by Lennard-Jones function. Here, we have ignored the quadropole interactions as they were found to have minute influence [4].

3. THERMAL BOUNDARY RESISTANCE

The heat transfer from SWNTs to the surrounding material can be characterized by thermal boundary conductance (K) at the material interface. Here, we examine a general case of such by performing non-stationary MD simulations of a (5,5)-SWNT surrounded by Ar molecules in a periodic cell. Ar-Ar and Ar-C interactions were expressed by the standard Lennard-Jones potential functions. After equilibrating the entire system at the room temperature, the SWNT was heated (T=400 K) for a certain time duration (~100 ps), and the relaxation time of the heat transfer from the SWNT to Ar was measured. Consequently, the temperature difference of the SWNT and Ar exhibits a single timescale exponential decay. This is attributed to the small Biot number, the ratio of K to the internal thermal conductance. Hence, with the computed relaxation time, K can be computed by adopting the convectional lamped capacity method.

Performing such analyses for different trajectories (T*=1.0 and T*=2.5) in the phase diagram of bulk Ar [5], we obtain the phase dependence of K as shown in Fig 1. On increasing the density of Ar, for T*=1.2 (filled marks), Ar experiences phase transition as gas, gas-liquid, liquid and solid, whereas for T*=2.5 (empty marks), the matrix is always in supercritical phase. In the fluid phase regime, the heat transfer is diffusive where random molecular collisions are in charge. In this phase, K shows a good correlation with the Ar coverage rate over the SWNT which saturates in the gas-liquid phase regime. In this regime, the state of Ar around the boundary remains similar independently of the Ar density.

On the other hand, in the solid phase regime, the dominant part of the heat transfer can be attributed to interaction of vibration modes of SWNTs and Ar lattices. On performing similar MD simulations by initially freezing the surrounding Ar, one can visualize the leading contribution of the transverse acoustic modes of the SWNT with long wavelength. Therefore, K can be estimated by the convolution of lattice vibrations of the Ar matrix and SWNT.

4. RESTRICTED HEAT CONDUCTION

As a representative case of reduction of axial heat conduction due to surrounding materials, we take an SWNT with a water cluster inside Water confined in such a low dimensional geometry can exhibit anomalous phases, such as the formation of ice nanotubes whose polygonal dimensions are determined by the diameter of the surrounding nanotubes [6]. The existence of ice nanotube has been also demonstrated in experiments by means of X-ray diffraction analyses [7].

On freezing the water using an SWNT as a cast, in

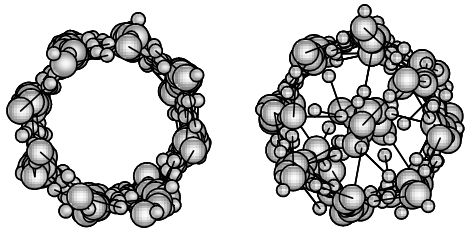

Fig. 2 Axial view of two different structures of solid water cluster confined in an SWNT at 130 K (a) N_w=192, (b) N_w=96.

MD simulations, depending of the simulation conditions such as cooling speed and number of water molecules N_w, we obtained different water structures. Here, we demonstrate results of MD simulations where an SWNT confining N_w water molecules was isothermally cooled from T=300 K to T=130 K at a gradient dT/dt=5 K/ns. The water cluster is localized in a (10,10)-SWNT which is sufficiently longer than the characteristic length of the water cluster. Consequently, as shown in Fig. 2, when N_w=96 an ice nanotube was obtained (Fig. 2(a)), but when N_w =192, the hollow was filled with water molecules lined along the axis (Fig. 2(b)). Computing the potential energies of water-water and water-carbon interactions, ice nanotube was found to be more stable than the other for the current SWNT size. As shown in Fig. 3, the potential energy of the two structures, for both water-water and water-carbon interactions, deviates from each other at the solidification temperature, 222 K.

We performed non-equilibrium MD simulations to measure thermal conductivity of the SWNT with ice inside. By using the phantom control technique [8] the two ends of a 25 nm long (10,10)-SWNT were maintained at different temperatures, 190 K and 210 K. Once, the quasi-linear temperature profile was achieved, by measuring the temperature gradient and heat flux, the effective thermal conductivity κ can be computed through the Fourier's law. The data were typically sampled for about 3 ns.

In Fig. 4, we show the preliminary results on varying N_w up to 288. Here, the initial conditions were

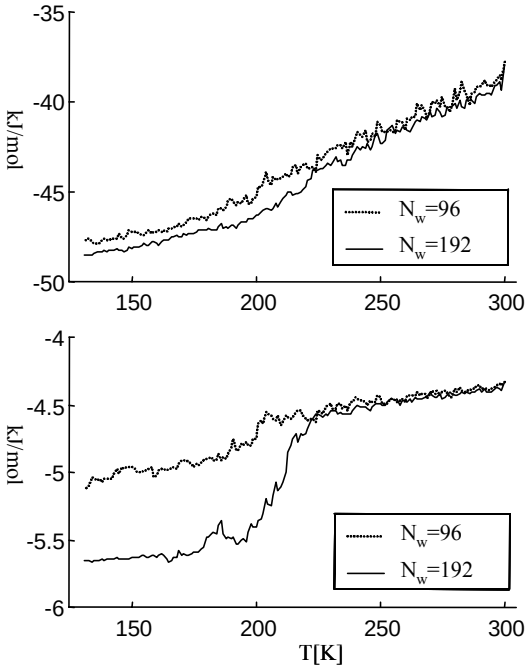

Fig. 3 Temperature dependence of averaged potential energy of water-water (top) and water-carbon (bottom) interactions.

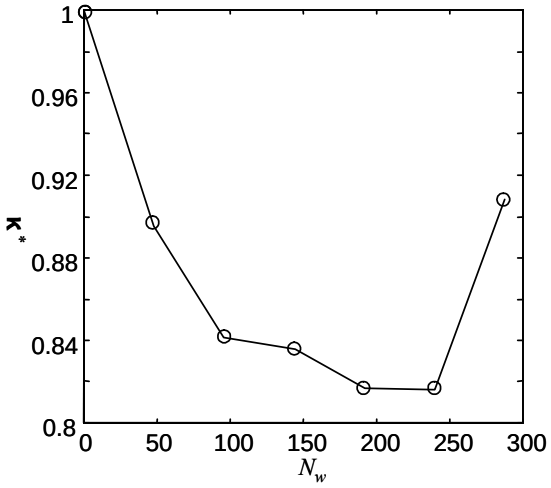

Fig. 4 Dimensionless thermal conductivity κ* of an SWNT confining a cluster of N_w water molecules. κ=814[W/mk] at N_w=0.

set so that the water takes structure (b) in Fig. 3. Fig. 4 exhibits that the interaction with ice attenuates κ which decreases with N_w. The effect of the reduction gradually saturates towards N_w=240. The mark at N_w=288 may suggest that κ has a minimum value, however we would need more data points to draw any conclusions.

5. SUMMARY

We have investigated the influence of surrounding materials on SWNT heat transfer by MD simulations. The radial thermal boundary conductance between SWNT and surrounding Ar shows strong dependence on the phase of Ar, where the key physics changes from diffusive heat transfer (gas) to modal interactions (solid). On the other hand, by adopting the case of SWNT with locally confined water cluster, it was shown that interactions with ice reduce the effective thermal conductivity of the SWNT, which depends on the number of water molecules. Further analysis would be necessary to understand the detail physics.

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