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Significant decrease in thermal conductivity of multi-walled carbon nanotube induced by inter-wall van der Waals interactions

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ABSTRACT

The thermal transport properties of multi-walled carbon nanotubes (MWCNTs) were investigated by using non-equilibrium molecular dynamics simulation. The results show that the thermal conductivity of MWCNTs decreases significantly comparing to that of single-walled carbon nanotubes (SWCNTs) due to the inter-wall van der Waals interactions. The more interesting is a fact that the thermal conductance of MWCNTs is significantly greater than the thermal conductance summation of each SWCNTs. This is because the thermal conductance of a carbon nanotube protected by an outer tube is much larger than that of one that is not protected. Moreover, we also studied the thermal flux distribution of MWCNTs, and found that the outer tube plays a dominant role in heat energy transfer.

1. Introduction

Low dimensional nanostructures have received considerable attention in recent years due to their great potential in both fundamental research and novel device applications [1–9]. One-dimensional (1D) tubular nanostructures – carbon nanotubes (CNTs), as the typical kind of low dimensional materials, have many unique mechanical and high directivity properties. And single-walled carbon nanotubes (SWCNTs) are one of potential materials for nano-mechanical resonators [10], nanotransistors [11], photosensors [12], and nanoscale thermal rectifiers [13–16], because of their physical properties, such as high electronic and thermal conductivity, stability, and flexibility [17,18]. However, these physical properties of SWCNTs are very sensitive and can be easily destroyed by heating [19], chemical modification [20] and inducing defects [21].

Fortunately, double-walled carbon nanotubes (DWCNTs) can overcome these difficulties [22–24] because of their unique double-wall structure, which allows the outer wall to be selectively functionalized while maintaining an intact inner-tube. Similarly, multi-walled carbon nanotubes (MWCNTs) can gain more thermal and chemical stability [20] from the inter-wall interactions, and their electronic and thermal properties can be further modified [25,26] because of more layers of the wall. Recently, the properties of MWCNTs have been widely studied. In 2006, Sun et al. [27] estimated the van der Waals (vdW) interactions between CNTs. Their results show that all the vdW potentials between two arbitrary CNTs fall on the same curve when plotted in terms of certain reduced parameters, the well depth, and the equilibrium vdW gap. Hu et al. [28] reported that the heat transport channels are different with different temperature control methods. Zhou et al. [24] found that the thermal conductivities of composites reached maxima by adding 6 wt% MWCNTs to epoxy composites. Gordiz et al. [15] reported a molecular dynamics (MD) simulations for thermal rectification in MWCNTs and showed that the thermal rectification in this carbon nanotube based thermal rectifier does not diminish by increasing the system size, and exists in a wide range of temperatures. These results suggest that nanoscale engineering of thermal transport devices can be achieved by MWCNTs.

However, the systematic study of the thermal transport properties of MWCNTs is still in its infancy. In particular the contribution of each single tube to the thermal conductance of the whole MWCNT has not yet been reported. Therefore, in the present work, we investigate the thermal transport properties and internal competition mechanisms in MWCNTs using molecular dynamics simulation. The calculation results show that the thermal conductivity of MWCNTs is lower than the thermal conductivity of SWCNTs corresponding to the outer wall in MWCNTs. This is because of the competition between thermal conductance and cross-sectional area. It is very interesting to find that the thermal conductance of MWCNTs is significantly greater than the thermal conductance summation of each SWCNT, which arises from the competition between inter-wall van der Waals interactions and the protection afforded by the outer tube. Moreover, we also studied the ther-

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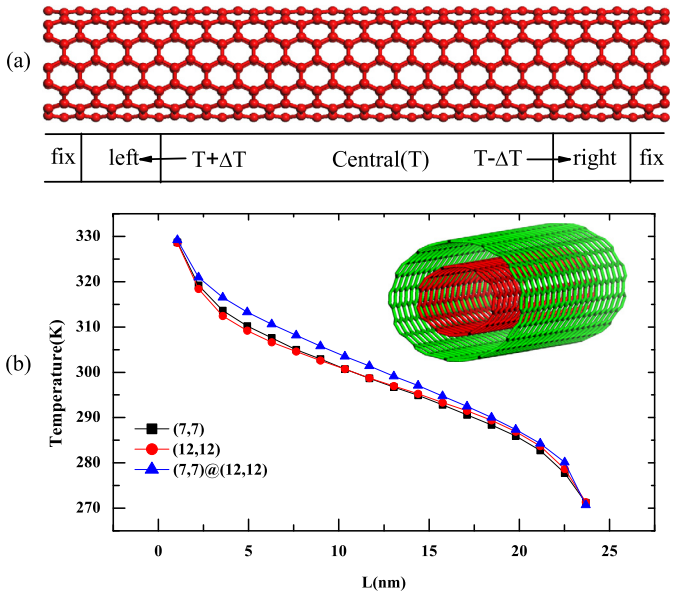

Fig. 1. (a) Schematic representation of the SWCNT (7, 7) studied in this work. (b) The temperature profiles and linear fitting curves of SWCNT (7, 7), SWCNT (12, 12) and DWCNT (7, 7) @ (12, 12) at 300 K. The inset is the configuration of DWCNT (7, 7) @ (12, 12).

mal flux distribution of MWCNTs, and found that the outer tube plays a dominant role in heat energy transfer.

2. Computational method and model

The thermal conductivity can be determined using equilibrium molecular dynamics (EMD) or non-equilibrium molecular dynamics (NEMD) methods. The EMD method is based on the Green–Kubo formula [29] derived from linear response theory, and the NEMD method is based on Fourier's law of heat conduction. In our work, using the LAMMPS package [30] with a time step of 1 fs, we carry out NEMD simulations. We adopt the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential [31] for intra-wall C–C bonding interactions and the Lennard-Jones potential for van der Waals interactions in the inter-wall [32]. The left and right CNTs are put into Nosé–Hoover heat baths [33,34] with temperatures T_L and T_R, respectively. $T_{L,R} = T_0 \pm \delta T$, where T_0 is the mean system temperature of the CNTs and $\delta T = 30$ K. Atoms are fixed at both ends during simulation. The atoms of the central region are free during simulation. The thermal conductivity can be calculated as follows

$$\kappa = -\frac{J}{\nabla T}, \tag{1}$$

where κ is the thermal conductivity, J is the heat flux, and ∇T is the temperature gradient. It can be given by $\nabla T = \frac{T_L - T_R}{L}$, where L is the length of the CNT.

In our simulation, two armchair concentric CNTs are noted as (n, n) @ (m, m), where n stands for the index of the smaller tube, the same as more walled CNTs. The rule $m = n + 5$ leads to an interwall spacing of 0.334 nm [35], close to that of van der Waals-bonded planar graphite sheets, and is followed by any two armchair concentric CNTs. The fixed boundary condition is employed along the Z axis direction. Fig. 1(a) presents the simulation model for computing the thermal conductance of SWCNTs or MWCNTs. The temperature profiles of three types of CNTs with length $L = 21$ nm at $T_0 = 300$ K, are shown in Fig. 1(b). We can see from Fig. 1(b) that the three temperature profiles in the central region all show linear behavior. This means that the simulations are

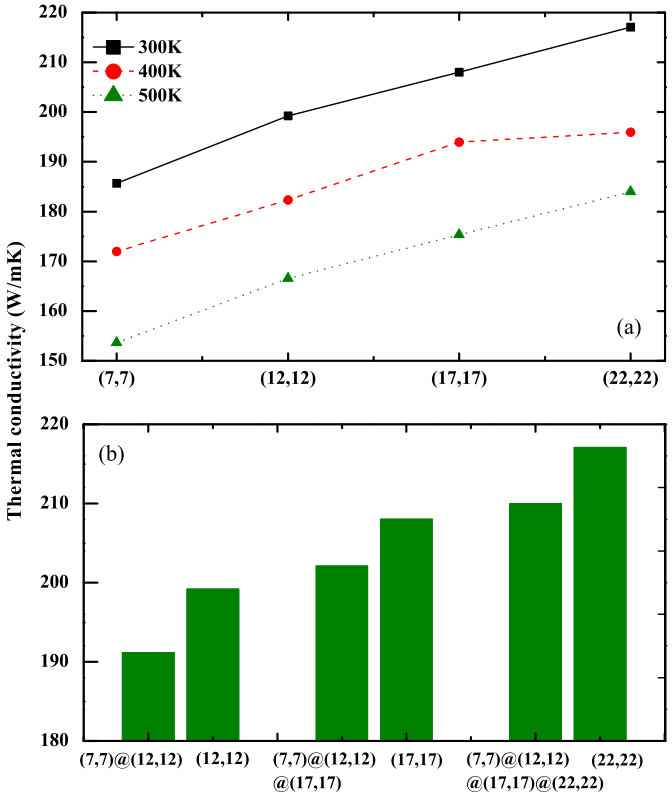

Fig. 2. (a) Thermal conductivity of SWCNT (7, 7), SWCNT (12, 12), SWCNT (17, 17) and SWCNT (22, 22) at different temperature. (b) Thermal conductivity of MWCNTs vs that of SWCNTs corresponding to the outer wall in MWCNTs at 300 K.

performed long enough such that the system reaches a nonequilibrium stationary state [36].

3. Results and discussion

Fig. 2 shows the calculated thermal conductivity of both SWCNTs and MWCNTs. The dependence of the thermal conductivity κ on diameter D and temperature T in armchair SWCNTs with the same length is investigated in our work, as shown in Fig. 2(a). Firstly, it can be found that the thermal conductivity of SWCNT increases with the increasing of D, at the same temperature. This is because larger diameter tubes have relatively more low and mediate frequency range modes in the radial direction of SWCNTs [37]. We know that the high frequency optical modes contribute little to the thermal conductivity because of their near-zero group velocities, but low frequency acoustic modes are more effective in carrying heat. So we can conclude that tubes with larger diameter have higher thermal conductivity because there are more active low frequency optical modes. Secondly, the thermal conductivity of SWCNTs with the change of temperature is also studied, with the same D. It is noted that the thermal conductivity of SWCNTs decrease significantly with the increase of temperature. We know that the phonon–phonon interactions in molecular dynamics simulation is spontaneous. The total momentum is strict conservation during phonon–phonon scattering for low-frequency phonons. This is the normal process, which has no contribution to the decrease of thermal conductivity. However, for the high-frequency phonons, the total momentum transfer occurs in the phonon–phonon scattering process. This is the Umklapp process, which can reduce thermal conductivity [36]. Because a great number of high frequency phonons are activated as the temperature increase, resulting in strengthening of phonon–phonon scattering, significantly reducing