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RESEARCH ARTICLE

Molecular dynamics studies on the thermal conductivity of single-walled carbon nanotubes

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We have studied the thermal conductivity of single-walled carbon nanotubes (SWCNTs) using the NEMD method. The results indicate that the thermal conductivity values are not profoundly influenced by the specific simulation-technique used in the MD simulations. Some possible reasons, which could be responsible for the discrepancy on thermal conductivity values of SWCNTs in the literatures, are discussed.

Keywords thermal conductivity, molecular dynamics, carbon nanotube

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1 Introduction

With the dimensions of electronic and mechanical devices approaching the nanometer scale, efficient heat removal is of crucial importance to both performance and function. New thermal management strategies are thus critically important to continued high performance, reliability, and lifetime. Since carbon nanotubes are one of the most exciting nanoscale materials, which reveal many excellent mechanical, thermal, and electronic properties, one such strategy is to develop novel high thermal conductivity materials based on carbon nanotubes [1].

Although experiments [2–6] were made to measure the thermal conductivity of individual multi-walled carbon nanotubes (MWCNTs) and SWCNTs, it is still difficult to obtain satisfactory result because of difficulties in directly measuring the thermal conductivity in nanosized system. There is also significant discrepancy in thermal conductivity of SWCNTs with different diameters and lengths [5–7].

On the theoretical aspects, there are mainly two approaches to theoretically study the thermal conduction phenomena of nanoscale materials: the first is a macroscopic method using continuum models and kinetic theories, such as Boltzmann transport equation, and the second is a fundamental microscopic method based on first-principles atomistic simulations or quantum mechanical models. In the second approach, various microscopic methods are proposed to model the physical system and calculate the thermal conductivity. Among them, molecular dynamics (MD) simulation is a very powerful and prevalent option being capable of investigating the thermal properties of SWCNTs, which can be roughly classified into two types: equilibrium molecular dynamics (EMD) method based on Green–Kubo relations and nonequilibrium molecular dynamics (NEMD) method from Fourier's law [8].

There were many investigations on the thermal conductivity of SWCNTs based on the EMD and NEMD methods, though it is still not clear which is better for simulating SWCNTs [9]. In addition, very different thermal conductivity values, varying from several hundreds to even several thousands of W/mK, had been reported in the literatures [9–18]. Although some investigations have been made, the reasons for the discrepancies in the literatures are still confused [17].

In the MD simulation, many simulation-technique factors, such as boundary conditions, integral algorithms, thermostats, C–C potentials etc. may influence the calculated thermal conductivity. Whether the discrepancies of the thermal conductivity are resulted from the different simulation-technique factors used in different literatures is not clear so far. In this paper, using the NEMD method, we study the influence of various simulation-technique details on the thermal conductivity of SWCNTs. Some possible reasons for the discrepancies in the literatures are also discussed.

2 Influence of simulation-technique factors

What shown in Table 1 is the thermal conductivity of (10, 0) SWCNT with a length of 10 nm at 300 K [19]. In the simulation, the two end unit cells of the nanotube are to put into contact with thermostats with temperature fixed to at 310 and 290 K, respectively. We chose $d = 3.4$ Å as the tube thickness; thus, the cross section is $2\pi rd$, where r is radius of the tube. Heat flux is calculated by computing the power of thermostats (thermostat-form) [20].

Table 1 Thermal conductivity of (10, 0) SWCNT with a length of 10 nm at 300 K.

K/ ($\mathrm{W{\cdot}mK^{-1}}$)	Boundary condition	Integral algorithm	Thermostat	Heat flux calculation
107.5	Free	Verlet	Nosé–Hoover	Thermostat form
110.5	Free	4th Runge–Kutta	Nosé–Hoover	Thermostat form
99.1	Fixed	Verlet	Nosé–Hoover	Thermostat form
111.4	Fixed	4th Predictor Corrector	Nosé–Hoover	Thermostat form
116.5	Fixed	Verlet	Berendsen	Thermostat form
78	Free	Verlet	Nosé–Hoover	Green–Kubo form

Boundary condition effect is first considered. The Velocity Verlet algorithm is employed to integrate the equations of motion. As shown in Table 1, thermal conductivity of (10, 0) SWCNT in the free boundary condition is 107.5 W/mK, which is larger than that calculated in the fixed boundary condition (99 W/mK). This can be attributed to the boundary scattering at each end of the tube, which is more intensive in the fixed boundary condition than that in the free boundary condition. In addition, if periodic boundary condition is applied in the simulation, the boundary scattering would be eliminated; thus the largest thermal conductivity could be obtained [17].

Since the long time simulation is necessary for the system to get stationary nonequilibrium state in the NEMD simulation, accurate integral algorithm is required. Velocity Verlet algorithm is usually used in the simulations. Some groups also used more precise integral algorithms such as the Runge–Kutta and the Predictor–Corrector algorithms. We further calculated the thermal conductivity of (10, 0) SWCNT using such integral algorithms. Very slightly different results are obtained (see Table 1). This indicates that the integral algorithm effect does not play an important role in the NEMD simulation.

Different thermostats used in the simulation may also induce different thermal conductivity values. To investigate such influence, both Nosé–Hoover and Berendsen thermostats are used in our calculation [21–23]. As shown in Table 1, the thermal conductivity calculated using Berendsen thermostat is only about 17 W/mK higher than that using Nosé–Hoover thermostat, indicating that such discrepancy is not significant. Similar conclusion has also been reported in previous studies [24].

It should be mentioned that the way of computing heat flux in the NEMD simulation could influence the thermal conductivity value. Except the thermostat form mentioned above, the heat flux can also be directly calculated using the Green–Kubo form [8]. The thermal conductivity of the (10, 0) SWCNT, calculated using the Green–Kubo form, is 78 W/mK (see Table 1), which is smaller than that calculated using the thermostat form (107 W/mK). This discrepancy may come from the uncertainty of defining how many atoms are in the across-section due to the unique geometry structure of the SWCNTs. This is because there are two different carbon layers in one unit cell of the (10, 0) SWCNT, with 20 atoms in each layer. So, the number of atoms in an across section should be 20 to 40, and the thermal conductivity should be from 78 to 156 W/mK. In the simulation, we just consider 20 atoms being in an across-section. Thus, the calculated thermal conductivity is smaller than that calculated using the thermostat form.

In addition, different C–C potential adopted in the simulation can also result in different thermal conductivity values, which has not been payed much attention in previous studies. Using both Tersoff and Brenner potentials, we further calculate the thermal conductivity of (10, 10) SWCNT with a length of 10 nm at 300 K [19, 25]. Velocity Verlet algorithm and free boundary condition are employed. The two end unit cells of the nanotube are put into contact with Nosé–Hoover thermostat, and the heat flux is calculated in use of the thermostat form. It is found that the thermal conductivity calculated using Tersoff potential is about 130 W/mK, which is 30% larger than that calculated using Brenner potential (100 W/mK).

In the NEMD simulations discussed above, the temperature gradients are all created via controlling a fixed temperature difference at each end of the nanotube by the thermostats. Another NEMD method, which creates the temperature gradient by switching the velocity of the hottest atom in the cold region with the velocity of the coldest atom in the hot region, is also widely used [26]. Using this method, the thermal conductivity of (10, 10) SWCNT of 10 nm at 300 K is calculated to be about 71 W/mK when Brenner potential is adopted, which is 30 W/mK smaller than that obtained by the former NEMD method.

From the above investigations, there are many simulation-technique factors influencing the thermal conductivity in the NEMD simulation. However, these factors are not crucial and can not induce very large thermal conductivity discrepancy. In our calculations, the thermal conductivity discrepancy with different detailed techniques should be within 50 W/mK for both (10, 0) and (10, 10) SWCNTs with a length of 10 nm at 300 K. Shown in Table 2 is the thermal conductivity of (10, 10) SWCNT of 10 nm reported by different groups, most of which are in the region from about 50 to 250 W/mK. This indicates that our simulation results (around 100 W/mK) are very reasonable.

Table 2 Thermal conductivity of (10, 10) SWCNT with a length of 10 nm at 300 K reported by different groups.

	$K/(\mathrm{W{\cdot}mK}^{-1})$	Simulation method	Potential
Donadio [18]	5800	EMD	Tersoff
Lukes [17]	75	EMD	REBO [29]
Lukes [17]	240	HNEMD	REBO
Maruyama [15]	260	NEMD	Brenner
Zhang [24]	550	NEMD	Tersoff
Padgett [14]	40	NEMD	REBO
Bi [28]	66	NEMD	Tersoff

As discussed above, different simulation-technique used in the simulation is not the significant reason for the thermal conductivity discrepancy in the literatures. In our opinion, three factors must be considered, which may be the real reasons for the discrepancy.

Nanotube length is a significant reason. It is well known that the SWCNTs have very long phonon mean-free path (PMF), which is about several micrometers. In NEMD calculations, the simulated nanotube is usually much shorter than its PMF. Several simulations at different tube lengths are required to obtain a necessary linear fit of thermal conductivity to the tube length ($K \sim L^{\alpha}$, where K and L are the thermal conductivity and the length of nanotube, respectively). Thus, thermal conductivity of SWCNTs with experimental length can be extrapolated by the K–L relationship [8]. If one performs calculation at different sampling lengths, which are at different locations in the ballistic-diffusive continuum, different α would be obtained in light of these observations. So, various thermal conductivity of SWCNTs at experimental length could be predicted by various groups. Shown in Fig. 1 is the length dependence of thermal conductivity of (5, 5) SWCNT at 300 K, in which the exponent α is fitted to be 0.46. Different exponents, such as 0.32, 0.34 and 0.4, are also obtained by other groups [15, 27, 30].

Temperature effects are also important. As shown in Fig. 2, the thermal conductivity of (5, 5) SWCNT increases first and then decreases with temperature increasing from 100 K to much higher temperatures. There exists a maximum value around 250 K, which is similar with previous results [27]. If different temperatures are used in the MD simulation, different thermal conductivities can be obtained.

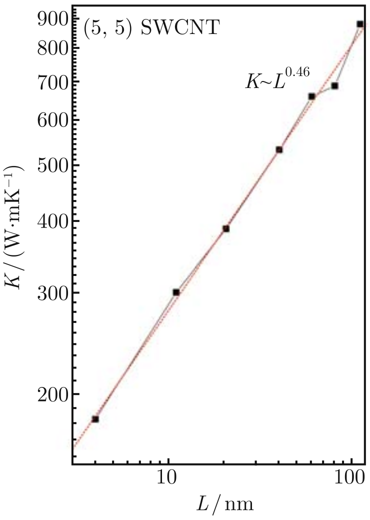

Fig. 1 Length dependence of thermal conductivity of (5, 5) SWCNT at 300 K. The fitted exponent is 0.46.

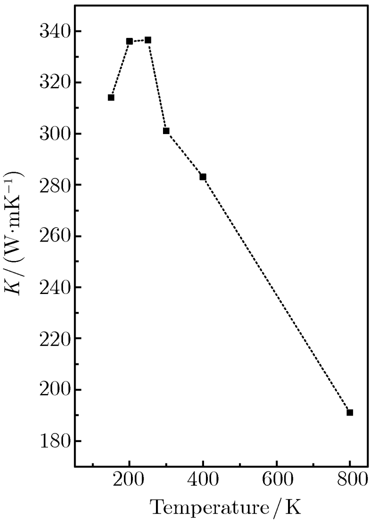

Fig. 2 Temperature dependence of thermal conductivity of (5, 5) SWCNT. The tube length is 10 nm. There exists a maximum value around 250 K.

In addition, the choice for the nanotube cross-sectional area in the calculation is also responsible for the discrepancy in the literatures [17]. It is evident that thermal conductivity is inversely proportional to nanotube volume, which is equal to cross-sectional area multiplied by the nanotube length. The choice of nanotube area thus influences the calculated thermal conductivity. To compare obtained thermal conductivities from different groups, it is imperative to scale all values by the same area.

3 Summary

In summary, we have investigated the influence of various simulation-technique factors on the thermal conductivity of SWCNTs using the NEMD method. We demonstrate that the thermal conductivity values are not profoundly influenced by the specific simulation-technique used in the MD simulations. Some possible reasons such as the tube-length effect, temperature effect, and choice of cross-sectional area are further proposed to be responsible for the discrepancies in the literatures.

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