Molecular dynamics investigation of the thermal properties in single-walled boron nitride nanotube

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Abstract

The thermal properties of single-walled boron nitride nanotubes (BNNTs) are studied in this paper based on molecular dynamics (MD) simulations. The influence and mechanism of tubular configuration, temperature, length, diameter and chirality on the thermal conductivity of BNNTs are systematically analyzed. The results show that the thermal conductivity decreased with increasing temperatures. The values of thermal conductivity of BNNTs and boron nitride nanoribbons (BNNRs) confirm that the tubular configuration is more conducive to phonon propagation. The thermal conductivity is raised by increasing the length of BNNTs. Moreover, the thermal conductivity changes slightly with further increase of diameter and various chirality. The results share guiding significance for thermal transport characterization of nanoscale thermal conductive component based on boron nitride nanotubes.

1. Introduction

As the microelectronic devices develop toward extremely miniaturization and high integration, the size of the component reduced to the nanometer scale, which has spawned the nanoelectromechanical system [1, 2]. Due to the reduction of feature size, the heat dissipation problem has become more prominent as well as an important affecting factor to the normal operation of nanodevices, while the thermal properties of the material has greatly changed at the same time [3, 4]. Recently, hexagonal boron nitride (h-BN) has attracted widely attentions of nanoscale material research owing to its unique physical and chemical properties [5–7]. The h-BN, called ‘White graphene’, due to its similar structure with graphene, as well as BNNTs has similar structure with carbon nanotubes (CNTs) [1, 8–10]. Boron nitride single layer possesses superior thermal conductivity (400 Wm⁻¹k⁻¹) [11] which is higher than general non-metallic materials. Moreover, BNNTs have the advantages of high thermal conductivity and controllable thermal conductivity as a quasi-one-dimensional nanomaterial. Thus, BNNTs are regarded as a novel type of semiconductor as well as a terrific thermal conductive material [12, 13]. In addition, boron nitride nanomaterial has become one of the ideal materials for building nanoelectromechanical systems owing to its excellent thermal stability and oxidation resistance at high temperatures [14, 15], both of which are higher than graphene and its derivatives material [16, 17].

Until now there are several methods for calculating thermal conductivity including Boltzmann transport equation, molecular dynamics simulations and non-equilibrium Green’s function. The Boltzmann transport equation needs to solve the phonon’s state density, group velocity and relaxation time, involved many theories and the process is more complicated. While the method of non-equilibrium Green’s function is limited by the small size of the model, and can only accurately calculate the low-temperature thermal conductivity of nanomaterials. Molecular dynamics does not require a detailed understanding of the phonon scattering mechanism, and can directly simulate the heat transfer properties of the material. Molecular dynamics is an efficient numerical method for studying nanomaterials at the atomic scale.

Ting Li et al [18] used molecular dynamics (MD) found that the thermal conductivity of CNTs is higher than BNNTs. They also calculated the thermal conductivity of (10,10) CNT and BNNT under various axial
compressive stress respectively, indicating the low-frequency phonons which are mainly from flexure modes make dominant contribution to the thermal conductivity. It is supported by the study of Sevik et al [19] employing the equilibrium molecular dynamics simulation (EMDS) that the h-BN nanostructures have high thermal conductivity which are still quite lower than carbon based counterparts, due to the mass difference between B and N and the softer phonon modes for h-BN nanostructures. Additionally, they also found that the thermal conductivity of CNTs and BNNTs are independent on their chirality. This conclusion is also supported by the simulation results later in this paper. Khan et al [20] have investigated the influence of environmental temperature as well as the size effects on thermal conductivity of h-BNNRs, and concluded that thermal conductivity is sensitive to temperature, length and width. Thermal conductivity is improved with the increase of factors mentioned above, and the mechanism is elucidated by the calculated phonon density of states. Rabczuk et al [21] computed the thermal conductivity of graphene and h-BN sheets with different grain boundary configurations, length and temperature by carrying out molecular dynamics simulations. Their results showed that for each grain boundary configurations the thermal conductivity remains constant with different length and temperature. Yin-Chung Chen et al [22] calculated the thermal conductivity along different chiral direction in BNNRs by means of the non-equilibrium molecular dynamics simulation (NEMDS). It is found that different chiral angles lead to various extent anisotropic effects of boundary scattering. The thermal conductivity has a local maximum at the chiral angle of 19.17°. The thermal conductivity also increases with increasing the ribbon length. Mashreghi et al [23] calculated the apparent coefficient of thermal expansion (CTE) to describe the variety of thermal property and found that apparent CTE is nearly small diameter independent. Tabarrai et al [24] investigated the effects of width and two kinds of defects on the thermal conductivity of BNNRs using the reverse NEMDS. The results showed that thermal conductivity of BNNRs slightly changed by increasing the width of nanoribbons, indicating the weak dependence of thermal conductivity on the width. The defects reduce the thermal conductivity of BNNRs, owing to the reduction of phonon mean free path induced by phonon-defects scattering.

In fact, small number of researches on the thermal properties of boron nitride nanostructures (BNNSs) compared to the amounts of reports of the carbon nanostructures, especially the studies related to the thermal conductivity. Hence, for the significance of BNNS in nanoscale thermal device, much more attentions need to be paid to thermal properties of BNNSs, particularly on thermal conductivity. With development of electronic device component toward miniaturization and high integration, heat dissipation is becoming crucial in microelectronic device. The investigation of thermal conductivity is particularly important since nanostructures are generally in a dynamic state in practice applications. Besides, it is still controversial about the convergence of thermal conductivity with length for the sample with feature size higher than the mean free path of the phonon [25]. The impact of structural parameters and various ambient temperatures on thermal conductivity need to be investigated systematically.

In this study, the non-equilibrium molecular dynamics is adopted to investigate thermal properties of BNNTs. The influence and mechanism of tubular configuration, temperature, length, diameter and chirality on the thermal conductivity of BNNTs are analyzed. Due to the difference in the chirality with different arrangement of atoms in BNNTs, discrepancy of thermal properties is induced. Besides, a large number of molecular dynamics simulations are carried out to reveal the effects of chirality on thermal conductivity. The work in this paper may be beneficial to understanding and manipulating the heat dissipation of nanodevices based on boron nitride nanotubes and have guiding instruction for the construction and application of them.

2. Simulations and method

The NEMD simulations are performed to calculate thermal conductivity of BNNTs using LAMMPS package. The Tersoff [26] potential is employed to model the interaction of B-N as the length of B-N bond and the wall thickness are set to be 1.446 Å and 15.54 Å respectively. The physical models of BNNTs are shown as figure 1. The length of BNNT models with two kinds of chirality ((10,10) and (17,0)) are 20 nm. The two ends of BNNT model along the heat flow are fixed, as shown in figure 2. During all the simulations, an integration time step of 1 fs is used. First, the system is relaxed at 300 K within the NVT ensemble for 100 ps. The hot reservoir and cold reservoir are applied to the region nearby the two ends of BNNT respectively to generate the heat flow. In the temperature gradient simulation process, the central region between the ‘hot’ and ‘cold’ tips is switched to the micro-canonical (NVE) ensemble without thermostat to simulate temperature gradient. In the simulation, the ambient temperature is simulated as the average temperature. The definition of high and low temperature is compared with the simulated ambient temperature. The influence of temperature on the result is mainly simulated by different simulated ambient temperatures to analyze the influence on the thermal conductivity. In the simulations, the model is divided into the 80 parts along the x-axis and each interval includes about 40–45 atoms to calculate the temperature profile. The amount of calculated interval is adequate to ensure the accuracy
of simulated temperature profile. Similar simulation method can be found in other published researches [27]. The temperature gradient is established across the BNNTs in the x-direction, which determines the direction of heat flux. In thermal conduction, the energy is conducted along the boron nitride nanotube as the heat flux. The rate of heat flux through the boron nitride nanotube is proportional to the product of thermal conductivity and thermal gradient as stated according to Fourier’s law [28]:

$$\lambda = \frac{J}{\nabla T}$$  \hspace{1cm} (1)

where $J$ is the heat flux density in the cross-sectional area along heat flow direction, and $\nabla T$ is the temperature gradient. After the temperature gradient is steady, the heat current can be calculated using:
where $\Delta E$ is the energy at every swap, $\Delta t$ is the timestep, $A$ is the cross-sectional area which heat flux flows through. When the system reaches stability, we obtain the figure of temperature distribution of the system by calculating the temperature of divided partition, as shown in the figure below. The temperature distribution diagram is inserted in the paper, as shown in Figure 3. It can be seen from the figure that the temperature gradient is well established in the $x$ axis direction, and the temperature gradient can be obtained by linearly fitting the temperature curve. Since the model size is much smaller than the mean free path of the phonon, the thermal conductivity has a size effect, so the thermal conductivity calculated by the model is still far from the experimental value. While this method has been used successfully for investigating the thermal properties of nanomaterials [1, 23, 27], thus the MD method was chosen for the research in this work.

3. Results and discussions

3.1. Effects of temperature and tubular configuration

In practical applications, environmental temperature is an important affecting factor to the thermal conductivity of nanomaterials [29]. The effect of temperature is studied in this work. The thermal conductivity of single-walled (10,10) and (17,0) BNNTs with the length of 20 nm and BNNRs with the size of $20 \text{ nm} \times 5 \text{ nm}$ under 200–1000 K temperature are calculated respectively. Figure 3 shows the thermal conductivity of BNNRs and BNNTs at different temperatures.

Figure 4 indicates that with the increase of temperature, the thermal conductivity of BNNRs and BNNTs show an obvious decreasing trend. For each result, five simulations are performed. Then the average and standard deviation of data are obtained. The standard deviation of data is drawn as error bars in the figures 4–7. The thermal conductivity of BNNTs decreases with temperature and the trend becomes more stable. The
Figure 5. (10,10), (17,0) BNNTs at 300 K with different length.

Figure 6. BNNTs with length of 20 nm at 300 K with different pipe diameter. (5,5), (8,8), (15,15), (20,20), (25,25), (30,30), (9,0), (14,0), (26,0), (34,0), (43,0), (52,0) chiral index of BNNTs are chosen to investigate the diameter effect.

Figure 7. BNNTS with length of 20 nm at 300 K with different chirality.
thermal conductivity of BNNRs decreases with temperature smoothly. With the increase of temperature, the velocity of phonon group decreases. Meanwhile the interaction between phonons and the scattering of phonons become severer and the free path of phonons decreases, leading to the gradual decrease of thermal conductivity. The thermal conductivity of BNNTs with armchair chirality (BNNTs-armchair) is higher than which of BNNTs with zigzag chirality (BNNTs-zigzag). It can be considered that the different phonon propagation speed along the chirality directions in the BNNTs causes the anisotropy of thermal conductivity. And the propagation speed of the phonon along the axial direction in BNNTs-armchair is greater than the one in BNNTs-zigzag. In addition, the difference in the boundary structure of BNNT will also induce the difference in the degree of phonon scattering. The phonon scattering of the zigzag boundary is greater than that of the armchair, and the thermal conductivity of the BNNTs-armchair is higher than that of the BNNTs-zigzag as result. At the same temperature, the BNNTs have a higher thermal conductivity than the BNNRs, it showed that the tubular configuration is more conducive to phonon propagation, while the flaky configuration enhanced the degree of phonon scattering at the same time.

3.2. Effects of length
As the length of BNNT is a significant affecting factor to thermal properties of BNNT, the thermal conductivity of (10,10) and (17,0) BNNTs has been calculated at 300 K temperature with the length from 25 nm to 100 nm and the results are shown in figure 5.

Figure 5 indicates that the thermal conductivity of the boron nitride tube shows a significant upward trend with the increase of the length within the simulation range. The thermal conductivity of BNNTs-armchair is slightly higher than that of BNNTs-zigzag, while there is little difference between them. As the axial length increases, the probability of collision of the phonon to the boundary decreases, which will increase the mean free path of the phonon as well as the thermal transport performance of the BNNT. Since the length simulated in this paper is smaller than the mean free path of boron nitride nanotubes, the phonons are in the ballistic emission region, the calculated thermal conductivity increases with increasing length. Although the calculated thermal conductivity is more dependent on the simulated size, the theoretical studies on thermal transport in BNNT using molecular dynamics simulations reveal the influence rule of temperature on thermal conductivity.

3.3. Effects of diameter
For investigating the effect of diameter, the 20 nm long models with different diameters are established, and the environmental temperature is 300 K. The calculated thermal conductivities are compared and shown in figure 6.

It is found that thermal conductivity is independence on their diameter as shown in figure 6, that is in accordance with the findings of Mashreghi et al [23] using EMD simulation. Since the thermal conductivity follows $L^\alpha$ law where the exponent $\alpha$ is insensitive to the diameter of the BNNTs in the ballistic-diffusive region [30]. The results are in agreement with the similar study of geometry effect on thermal property in CNT material found by Alaghemandi et al [30], the thermal conductivity of the CNTs is also insensitive to the increasing diameter. The value of thermal conductivity has slight change with the diameter, and it is attributed to the perpendicularity between the direction of heat flux and direction of increasing perimeter.

3.4. Effect of chirality
In this paper, the effect of chirality on the thermal conductivity of BNNTs is also investigated. The thermal conductivity of (9,10), (8,11), (7,12), (6,13), (5,14), (3,16), (2,17) BNNTs with the length of 20 nm at 300 K temperature are calculated and shown in figure 7. It is found that the change of thermal conductivity among different chirality is little. All of the results fluctuate within 80 W m$^{-1}$ k$^{-1}$–90 W m$^{-1}$ k$^{-1}$. The results show that chirality has little effect on the thermal conductivity of BNNTs. Different chirality makes little change in the lattice vibration mode of the BNNTs, thus the value of thermal conductivity is not greatly affected. It is also supported by the previously published study for CNTs [25, 30, 31] which showed the CNTs have a chirality insensitive thermal conductivity at room temperature. Zhang et al [25] calculated the thermal conductivity of BNNTs with three kinds of chirality, and the results showed that thermal conductivity did not depend on the chirality sensitively. They found the phonon density of states in different chirality do not show any significant difference. The finding results in our study are consistent with the Landauer transmission theory [32].

4. Conclusions
In summary, the effects of configuration, temperature, length, diameter, and chirality on the thermal conductivity of boron nitride nanotubes were investigated by non-equilibrium molecular dynamics simulation. The results of simulation show that the thermal conductivity of both BNNRs and BNNTs decrease with increasing temperature. The thermal conductivity of BNNTs is slightly higher than that of BNNRs, owing to the
reduction of phonon group velocity and the increase of phonon scattering. The BNNTs have a higher thermal conductivity, indicating that tubular configuration is more conducive to phonon propagation. For the effect of length, the thermal conductivity is proportional to the length, since the simulated length is smaller than the mean free path of boron nitride nanotubes and the phonons are in the ballistic emission region therefore. In regard to the diameter, the diameter has little effect on thermal conductivity as the direction of heat flux is perpendicular to the direction of increasing perimeter. Additionally, the thermal conductivity of BNNTs shows independence to chirality, due to the little change in the lattice vibration mode with chirality.

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Declaration of interest
The authors declare that they have no conflict of interest.

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