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2010 Nanotechnology 21 285706

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The intriguing thermal conductivity of ice nanotubes

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Received 16 February 2010, in final form 18 May 2010

Published 28 June 2010

Online at stacks.iop.org/Nano/21/285706

Abstract

We have investigated the thermal conductivity of various ice nanotubes (Ice-NTs) using the nonequilibrium molecular dynamics method. The results indicate that Ice-NTs have an unusually high thermal conductivity compared to that of the bulk ices. The thermal conductivity is sensitive to temperature, tube length and diameter, while being insensitive to polarization. We have also studied the confinement effect from single-walled carbon nanotubes (SWCNs). A very remarkable increase in the thermal conductivity is further observed after the Ice-NTs are confined in SWCNs.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Water confined in nanoscale one-dimensional (1D) channels is of great interest to biology, geology, and materials science. Recently, theoretical studies on water confined in single-walled carbon nanotubes (SWCNs) and the experimental studies that followed have demonstrated that water freezes into tubular structures (so-called ice nanotubes (Ice-NTs)) rather than freezing into the bulk ices [1–3]. Many intriguing physical properties of Ice-NTs, such as anomalous phase transitions, extremely soft dynamics, and very large electronic energy bandgaps, have been extensively studied since their discovery [1, 2, 4, 5]. Owing to the unique 1D proton-ordered structure, Ice-NTs are also expected to exhibit some unusual thermal conduction properties different from the bulk ices; these, to our knowledge, have hardly been investigated.

It is known that the structures of Ice-NTs are very varied [6]. Different Ice-NTs may have very different polarizations along their axes. For example, it was reported that the odd number-gonal [(5, 0), (7, 0)] Ice-NTs have notable net polarizations along their axes, while the even number-gonal [(4, 0), (6, 0)] ones are antiferroelectric [7]. Whether the polarizations affect the thermal conductivity (K) of Ice-NTs is an interesting issue, and its clarification is very desirable.

On the other hand, although there were studies on the thermal conductivity of SWCNs filled with nanomaterials, the main objectives of these studies are only focused on the SWCNs [8]. Recently, the thermal conductivity of water

confined in SWCNs has been investigated, enriching our understanding of the influence of confinement on the thermal conduction of fluids [9]. However, how the confinement affects the thermal conductivity of a solid nanomaterial is still poorly understood. Therefore, to investigate thermal conductivity of Ice-NTs, both with and without SWCN confinement, is very significant for both the fundamental science and future application technologies.

In this paper, using the nonequilibrium molecular dynamics (NEMD) method, we first investigate the thermal conductivity of isolated (4, 0), (5, 0), and (6, 0) Ice-NTs. The results indicate that the thermal conductivity of Ice-NTs is distinctly larger than that of the bulk ices, and the polarizations have only a minor effect on it. The thermal conductivity of (4, 0) Ice-NT confined in (14, 0) SWCN is further calculated to explore the confinement effect on the thermal conductivity.

2. Simulation techniques

In the simulation, water–water inter-molecular interaction is described by the TIP4P potential [10] and carbon–carbon interaction is described by the Tersoff potential [11]. As for the coupling term, the carbon–water interaction is described by a LJ potential [12]. All the pair interactions are truncated at 10 Å by a switching-function [12–14]. Moreover, the adopted potentials here have been widely used in the water(ice)–SWCN system, which has proven their effectiveness [1, 6, 7, 9, 13].

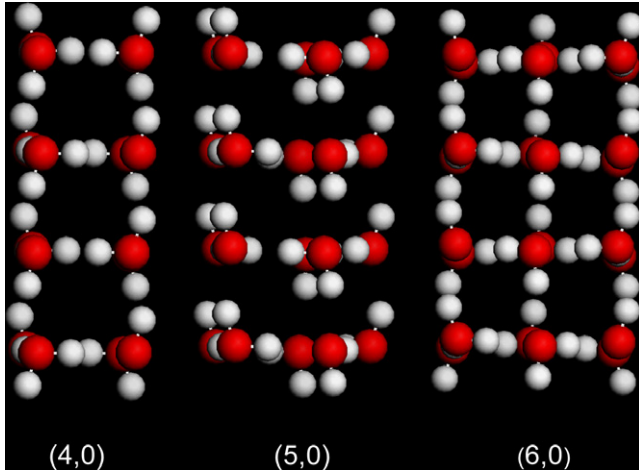


Figure 1. Optimized structures of isolated (4, 0), (5, 0), and (6, 0) Ice-NTs. These structures are consistent with those in previous reports [1, 3, 7, 13].

The unit simulation cell has a length of 30.25 Å and the total number of water molecules inside is $11 \times n$ for the $(n, 0)$ Ice-NT, where $n = 4, 5$, and 6. The simulation supercells are constructed by replicating the unit simulation cell along the axial direction. Figure 1 shows the optimized structures of isolated (4, 0), (5, 0), and (6, 0) Ice-NTs. These structures are consistent with those in previous reports [1, 3, 7, 13].

The thermal conductivity of Ice-NTs is calculated using a straightforward method introduced by Müller-Plathe in which a heat source and sink of the system are created by switching the velocity of the hottest atom in the heat sink with the velocity of the coldest atom in the heat source [15]. Then the thermal conductivity can be expressed as

$$K = -\frac{\sum_{\text{transfers}} \frac{1}{2} m (v_h^2 - v_c^2)}{2tS\nabla T}. \quad (1)$$

The sum is taken over all transfer events during the simulation time t . The subscripts h and c refer to the hot and the cold particle whose velocities are interchanged. Moreover, S is the cross-sectional area of the Ice-NTs. Here we define it similar to that in the SWCNs [16–18]: the cross-sectional area (S) equals the nanotube circumference (C) times the nanotube-wall thickness (d). For the Ice-NTs, C is the circumference of the O–O rings in the cross section, and we choose $d = 2.75$ Å (the O–O bond length between the nearest two water molecules) as the nanotube-wall thickness. $\nabla T = dT/dz$ is the temperature gradient in the length direction of the Ice-NTs and is obtained by an ensemble average.

To integrate the equations of motion, the velocity Verlet method is employed with a fixed time step of 1 fs. To simulate heat flow from the heat source to heat sink, the Ice-NT is divided into N equal slabs. The thermal conductivity is then calculated using the method described above, with the velocity being exchanged between the heat source and sink, each of which is 5.5 Å in length (one slab), every 400 fs. All results are obtained by averaging about 1 ns after a sufficient long transient time (2 ns) to set up a nonequilibrium stationary state.

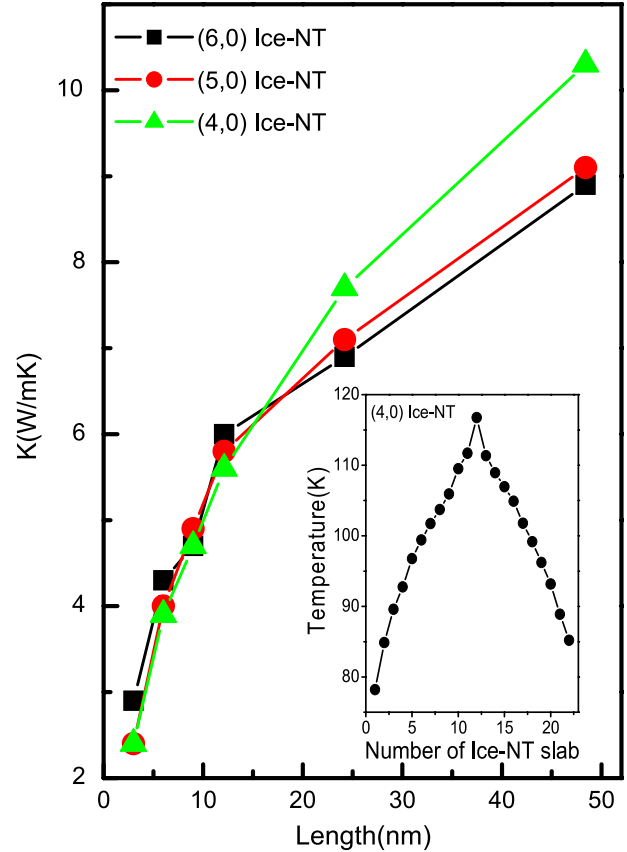


Figure 2. Length dependence of thermal conductivity of isolated (4, 0), (5, 0), and (6, 0) Ice-NTs at 100 K. The thermal conductivity obviously increases with the tube length increasing, implying large PMFPs of Ice-NTs. The inset shows the temperature profile of isolated (4, 0) Ice-NT with a length of 22 slabs.

In addition, all the simulation parameters used in this paper, such as the switching-function cutoff distance, time step, transient time, and velocity exchange interval had been tested by simulating the thermal conductivity of (4, 0) Ice-NT with a length of 6 nm at 100 K.

- (i) *Switching-function cutoff distance.* We had calculated the thermal conductivity of isolated (4, 0) Ice-NT by considering all the inter-molecular interactions in the system using the fixed boundary condition NEMD method (the latter NEMD method described in the paper). The obtained thermal conductivity is $3.3 \text{ W m}^{-1} \text{ K}^{-1}$. Compared with the result obtained by the switching-function treatment with 10 Å as the cutoff distance ($3.1 \text{ W m}^{-1} \text{ K}^{-1}$, see figure 4), there is no significant difference between them. This means that choosing 10 Å as the cutoff distance is sufficient to treat the long-range inter-molecular interactions in the 1D ice system.
- (ii) *Time step.* Test calculation was carried out with a time step of 0.5 fs. The thermal conductivity of isolated (4, 0) Ice-NT was calculated to be $3.82 \text{ W m}^{-1} \text{ K}^{-1}$ using the Müller-Plathe NEMD method, which is very close to that obtained by the 1 fs time step ($3.76 \text{ W m}^{-1} \text{ K}^{-1}$, see figure 2). This justifies the use of a 1 fs time step.

- (iii) *Transient time.* A 5 ns transient time simulation was applied to calculate the thermal conductivity of isolated (4, 0) Ice-NT using the Müller-Plathe NEMD method. The obtained heat flux and temperature gradient have little difference from those obtained from the 2 ns transient time. Also, the thermal conductivity ($3.9 \text{ W m}^{-1} \text{ K}^{-1}$) is very close to that obtained with a 2 ns transient time ($3.76 \text{ W m}^{-1} \text{ K}^{-1}$).
- (iv) *Velocity exchange interval.* Adopting 100 fs as the exchange interval in the Müller-Plathe NEMD method, the thermal conductivity of isolated (4, 0) Ice-NT was found to be $4.25 \text{ W m}^{-1} \text{ K}^{-1}$. Although it is a little larger than that obtained with the 400 fs exchange interval ($3.76 \text{ W m}^{-1} \text{ K}^{-1}$), the difference is not too large. We believe that a longer interval would have an even smaller difference.

As one can see from above discussion, the results obtained with more accurate simulation parameters show only small differences from the ones obtained with the parameters in this paper (within 10%). Also, a different choice of velocity exchange intervals in the Müller-Plathe NEMD method does not have a significant effect on the obtained results. So we believe that the results obtained by them are reliable.

The periodic boundary condition (PBC) is applied along the tube axis, since it can more quickly approach the steady nonequilibrium states. It should be mentioned that although the PBC is applied, the calculated thermal conductivity still represents the characteristic of a system with finite length in the NEMD simulation, owing to the phonon scattering that occurs at the interfaces with the heat source and sink [19–21], which is different from that in the EMD simulation [19, 22, 23]. Thus finite-size effects on the thermal conductivity arise when the length of the simulation supercell is not significantly longer than the phonon mean-free path (PMFP) of an infinite system [19, 20, 24]. To explore such finite-size effects on the thermal conductivity, the tube length L (half length of the supercell) was varied from several nanometers to 50 nm in the present work. The thermal conductivity of infinitely long Ice-NTs (K_∞) can be further predicted by the extrapolation procedure, which assumes $1/K_L = 1/K_\infty + A\rho/L$, where A and ρ are parameters that do not vary with L [19–21, 24, 25].

3. Results and discussions

The inset of figure 2 shows the temperature profile of isolated (4, 0) Ice-NT with a length of 22 slabs at 100 K. Within 2 slabs of the heat source (sink), a very predominant nonlinear character of the temperature profile is observed, which can be attributed to the strong phonon scattering caused by the source (sink) [19]. In the intermediate region, the temperature profile is fitted to a linear function, and the temperature gradient therefore can be obtained for the calculation of equation (1). It should be mentioned that a different choice of intermediate region has only a minor effect on the obtained temperature gradient [19]. In our simulation, the intermediate region is chosen about 1 nm away (2 slabs) from the heat source (sink). Shown in figure 2 is the length dependence

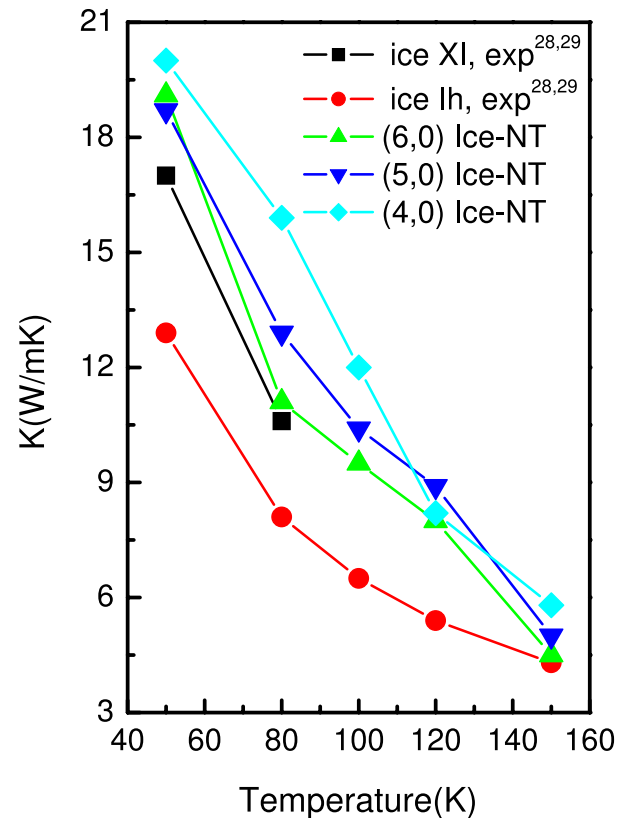


Figure 3. Temperature dependence of thermal conductivity of isolated (4, 0), (5, 0), and (6, 0) Ice-NTs in comparison to experimental results of ices Ih and XI. The thermal conductivity of the Ice-NTs is sensitive to the temperature and tube diameter, but insensitive to the polarization. The Ice-NTs have distinctly higher thermal conductivity than that of the bulk ices.

of thermal conductivity of isolated (4, 0), (5, 0) and (6, 0) Ice-NTs at 100 K. As one can see, the thermal conductivity obviously increases with the tube length increasing, and does not converge to a finite value with a tube length up to 50 nm, implying a very large PMFP for Ice-NTs, larger than that of bulk ices [26].

In order to make a comparison, we have also calculated the thermal conductivity of ice Ih at 100 K (the simulation supercell was constructed by replicating the $(6 \times 3 \times 3)$ orthorhombic simulation cell of Hayward and Reimers [27] twice along the X direction). It is found the thermal conductivity is only about $1 \text{ W m}^{-1} \text{ K}^{-1}$,¹ much smaller than the experimental value ($6.5 \text{ W m}^{-1} \text{ K}^{-1}$) [26, 28, 29], indicating that the MD simulation underestimates the thermal conductivity values as usual, which is consistent with previous results [25, 30]. From the extrapolation procedure [19, 20, 24, 25], the thermal conductivity of Ice-NTs with infinite length is further predicted. Figure 3 shows the temperature dependence of thermal conductivity

¹ The calculated thermal conductivity value of ice Ih is consistent with the EMD results in [30], while smaller than the NEMD results in [25]. The difference may be due to the smaller simulation cell and a simple cutoff method for treating the long-range electrostatics in our method. Nevertheless, a qualitative agreement of these results is sufficient for the purpose of our investigation.

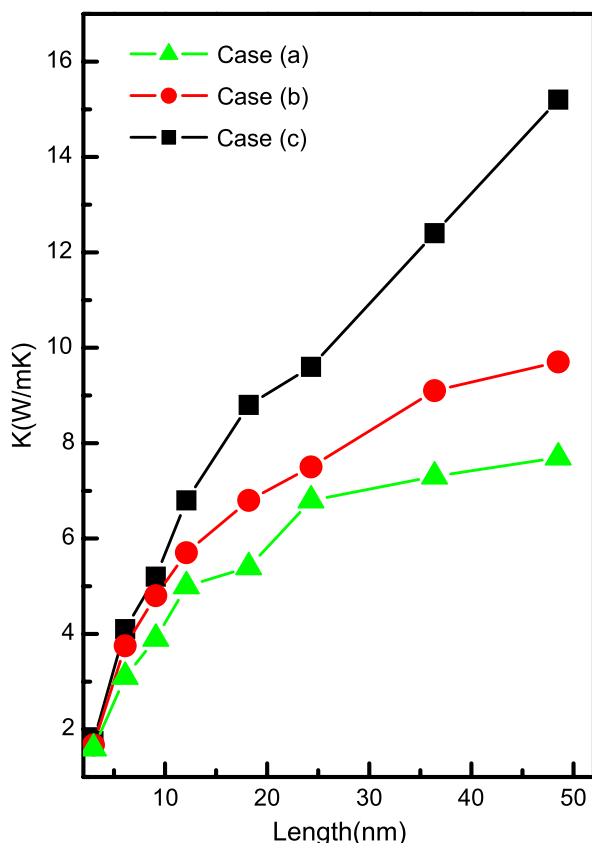


Figure 4. Length dependence of thermal conductivity of (4, 0) Ice-NT for three cases at 100 K: (a) isolated Ice-NT; (b) Ice-NT being confined in a frozen SWCN; (c) Ice-NT being confined in an unfrozen SWCN. The thermal conductivity of Ice-NT has a remarkable increase after being confined in the SWCN which becomes more and more prominent as the tube length increases.

of (4, 0), (5, 0), and (6, 0) Ice-NTs with infinite length (from 50 to 150 K). Here we compare the calculated thermal conductivity values of Ice-NTs with the experimental ones of ices Ih and XI, both of which have the highest thermal conductivity values among the bulk ices in the simulation temperature region [28, 29]. As one can see, a distinctly larger thermal conductivity of Ice-NTs than that of the bulk ices is still observed (figure 3), although the MD simulation underestimates the thermal conductivity values [25, 30]. Consequently, our results show the unusually high thermal conductivity of Ice-NTs, which could be due to their unique 1D proton-ordered structures and thus the phonon dispersions [31].

It is noticed that the (4, 0) Ice-NT usually has the highest thermal conductivity values while the (6, 0) Ice-NT has the lowest ones among the three Ice-NTs tested (figure 3). This suggests that the thermal conductivity of Ice-NTs has an obvious tube-diameter dependence, and the polarizations have only a minor effect on it. The interesting tube-diameter dependence of thermal conductivity can be understood by a phonon scattering mechanism. Similar to that of SWCNs [32, 33], the larger Ice-NTs have more vibration modes. So more phonon modes can be excited for thermal conduction at a given temperature, which greatly increases the probability of the phonon umklapp process, and thus reduces

the thermal conductivity [32, 33]. Moreover, it was reported that the thermal conductivity of bulk ices can be described by an empirical relation, $K \sim T^{-x}$, where the exponent x is a constant specific to different ice phases [28, 29]. Through the fitting procedure, we find that x has a value between 1.1 and 1.3 for the three Ice-NTs, which is larger than that of ices Ih and XI ($x = 1$) [28, 29]. As pointed out by Johari *et al*, the larger exponent for ices ($x > 1$), which has not been fully understood so far, may come from the higher-order phonon processes and/or finite thermal expansion [29]. In our simulation, the thermal expansion of Ice-NTs is very small. Thus we can expect that the larger exponent could be from the higher-order phonon processes of Ice-NTs.

To explore the confinement effect from SWCN, the thermal conductivity of (4, 0) Ice-NT both with and without (14, 0) SWCN confinement at 100 K is further calculated. In order to confirm the simulation results above, another NEMD method is used [17, 34–36]. In the calculation, a fixed boundary condition is applied along the axial direction of the Ice-NTs/SWCNs, where the outermost two layers of each head are fixed [34–36]. Then two layers of each end of the Ice-NTs are put into contact with a Nosé–Hoover thermostat with temperatures 110 and 90 K, respectively, while the SWCN is free of thermostat contact. Using the latter NEMD method, the thermal conductivity of isolated (4, 0) Ice-NT with infinite length is calculated to be about $11.6 \text{ W m}^{-1} \text{ K}^{-1}$, in close agreement with that obtained by the Müller-Plathe NEMD method ($12 \text{ W m}^{-1} \text{ K}^{-1}$). Considering that the calculated thermal conductivity using a fixed boundary condition is usually smaller than that using a periodic boundary condition, due to boundary scattering [16, 37, 38], the results obtained by the two different NEMD methods are actually coincident. Therefore, we believe that the results from the two methods are comparable.

Three cases are considered in investigating the confinement effect on thermal conductivity: (a) isolated Ice-NT; (b) Ice-NT being confined in a frozen SWCN (all the carbon atoms are fixed during the simulation); (c) Ice-NT being confined in an unfrozen SWCN. Figure 4 shows the length dependence of thermal conductivity of (4, 0) Ice-NT for the three cases. It is seen that the thermal conductivity of Ice-NT has a remarkable increase after the confinement in SWCN (for both the frozen and unfrozen SWCN cases), which becomes more and more prominent with as the tube length increases. Moreover, the thermal conductivity increase is more marked in case (c) than that in case (b). This suggests that the vibration of SWCN during the confinement can help to increase the thermal conductivity of Ice-NT. In addition, we have also calculated the thermal conductivity of (5, 0) [(6, 0)] Ice-NT both with and without (15, 0) [(16, 0)] SWCN confinement and obtained very similar results.

Through the extrapolation procedure [19, 20, 24, 25], the thermal conductivity values of (4, 0) infinitely long Ice-NT in the cases (a), (b), and (c) are found to be 11.6 , 17.9 , and $39.1 \text{ W m}^{-1} \text{ K}^{-1}$, respectively, suggesting the ultimate increase of thermal conductivity can be as much as 54% (237%) due to the frozen (unfrozen) SWCN confinement. Accordingly, the present study indicates that a material's

thermal conductivity can be remarkably increased by certain confinements, which provides a new opportunity for the manipulation of thermal conductivity in applications.

4. Conclusions

In summary, we have investigated the thermal conductivity of various Ice-NTs, and the confinement effect of SWCN on the thermal conductivity, using the NEMD method. It is found that Ice-NTs have an unusually high thermal conductivity compared to the bulk ices, which can be attributed to the unique 1D proton-ordered structures and thus the phonon dispersions of Ice-NTs. Moreover, the thermal conductivity is sensitive to temperature, tube length and diameter, while being insensitive to polarization. A very remarkable increase of thermal conductivity is further observed after the confinement in SWCN. These findings can enrich our understanding of the unique thermal conduction properties of 1D nano-ices as well as providing a new insight into thermal conduction manipulation.

Acknowledgments

This work was partially supported by the Special Funds for Major State Basic Research, National Science Foundation of China, Ministry of Education and Shanghai Municipality. The computation was performed at the Supercomputer Center of Shanghai, the Supercomputer Center of Fudan University.

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