

# Structures of filled ice nanotubes inside carbon nanotubes

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We report ordered structures of water in carbon nanotubes that are different from previously found  $n$ -gonal ice nanotubes and may be called filled ice nanotubes. Spontaneous formation of the filled ice nanotubes is observed in molecular dynamics (MD) simulations of water at fixed densities and a fixed temperature. Outer layers of filled ice nanotubes are characterized by a roll-up vector  $(n, m)$  while inner files of molecules do not have definite ordered structures. With this notation the filled ice nanotubes are of the  $(6, 0)$ ,  $(7, 0)$ ,  $(8, 0)$  and  $(8, 1)$  types, the last of which has a helical structure in its outer layer whereas the outer layers of the first three have the same achiral structures as the  $n$ -gonal ice nanotubes. Structure analysis is done for their hydrogen-bond networks and average dipole moments.

*Keywords:* Water; Nanotube; Ice; Simulation

## 1. Introduction

When a substance is confined in a space as narrow as a few diameters of molecules, it may exhibit properties that are not shared with the bulk substance. Atoms and spherical molecules such as  $C_{60}$  in cylindrical pores may have chiral close-packed structures [1–3], which would be impossible for bulk systems, while water confined in carbon nanotube freezes into one-dimensional ordered ices, called ice nanotubes [4].

Water in and around carbon nanotubes have been holding much attention, topics of which include effects of pressure and diameter on the adsorption of water [5], structure of water and ice in carbon nanotubes [4–10], phase transitions of water in nanotube bundles [11], and dynamical properties of water in one-dimensional pores as a model of water channels [12,13].

However, structure of water in carbon nanotubes has not been as fully explored as that of bulk water. There are at least 13 ice polymorphs for bulk water whereas what we now know for “one-dimensional” water may well be just a minor portion of many structures. Structures of ice nanotubes reported by experimental studies are those in carbon nanotubes with particular diameters at ambient pressure [14,15]. In earlier simulation studies, a pressure range is limited below 500 MPa and a range of the carbon nanotube diameter is between 11 and 14 Å.

A main purpose of this paper is to report and analyze possible one-dimensional ice polymorphs in carbon nanotubes. We perform canonical-ensemble molecular dynamics (MD) simulations of the confined water at various densities  $\rho$  and find that water freezes into what may be called filled ice nanotubes. Unlike the  $n$ -gonal ice nanotubes found earlier, these structures consist of an outer layer of water molecules and an inner file of molecules. When an outer layer is unrolled and mapped on a two-dimensional plane, there appears a square-net structure. It is then noticed that a roll-up vector, which instructs how to fold the square net to the original cylindrical layer, characterizes each structure of the ice nanotubes. Structure of the outer layer and the relation between outer layer and inner file of molecules are analyzed in terms of hydrogen-bond networks and average dipole moment components along the tube axis.

## 2. Systems and simulation methods

A model system is the same as that in earlier studies [4] and so is described briefly. The system is composed of  $N$  molecules in a portion of a cylindrical pore with diameter  $D$ . The portion is of length  $L$  and is subject to a periodic boundary condition in the direction parallel to the cylinder axis. The potential energy  $U$  of the system is defined as a sum of the potential energy among water molecules and

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Table 1. Properties of filled ice nanotubes in carbon nanotubes.

SWCN index, diameter (nm)	Number density ( $1/\text{nm}^3$ )	Molar volume ( $\text{cm}^3$ )	Roll-up vector	$\omega$
(15, 0), 1.185	44.90	13.41	(6, 0)	$0.163 \approx 1/6$
	51.33	11.73	(7, 0)	$0.143 \approx 1/7$
(16, 0), 1.263	43.18	13.94	(7, 0)	$0.143 \approx 1/7$
	48.59	12.39	(8, 0)	$0.160 \approx 1.28/8$
	53.97	11.15	(8, 1)	$0.234 \approx 1.87/8$

that of the water-pore interaction, both being pair-wise additive. A pair of water molecules a distance  $r$  apart interact with each other via the TIP4P potential [16] multiplied by a switching function that smoothly goes from 1 at  $r = 6.75 \text{ \AA}$  to 0 at  $8.655 \text{ \AA}$ . Contribution to  $U$  from a molecule interacting with the pore of diameter  $D$  is modeled by an integrated Lennard–Jones (LJ) function, which is given by integrating an LJ 12–6 function for the water–carbon interaction ( $\epsilon = \sqrt{\epsilon_w \epsilon_c} = 0.3886 \text{ kJ/mol}$  and  $\sigma = (\sigma_w + \sigma_c)/2 = 3.277 \text{ \AA}$ , where  $\epsilon_w, \epsilon_c, \sigma_w, \sigma_c$  are LJ energy and size parameters for water–water and carbon–carbon [17] interactions) with respect to the position of a carbon atom over the cylindrical surface of infinite length.

The constant-temperature and -volume MD simulations are implemented by the Nosé thermostat [18]. The diameter of the model carbon nanotube is set to 11.85 and 12.63  $\text{ \AA}$ , which corresponds to those of the (15, 0) and (16, 0) single-walled carbon nanotubes (SWCNs). The number density  $\rho = N/V$  is chosen to be those which enable a defect-free structure of a  $N$ -gonal ice nanotube, where  $V = (\pi/4)(D - \sigma_c)^2 L$ , an effective volume for water. But we start all the simulations from random arrangements of water molecules. The number  $N$  of molecules is chosen such that the cell length becomes larger than 60  $\text{ \AA}$  with a given number density. Temperature is fixed to 300 K. The simulation time at each thermodynamic state ranges from 4 to 40 ns.

The potential-energy local minimum structure is obtained by a steepest-descent method [19]. In this method, positions and orientations of molecules are changed successively in a direction to which the force acts on each molecule in an instantaneous configuration until no force acts on each molecule, that is, the arrangement of molecules becomes a structure at a potential-energy local minimum.

### 3. Structure of filled ice nanotubes

#### 3.1 Structure of the outer layer

It is known [4–6] that water in the SWCNs under pressures below 1 GPa freezes into  $n$ -gonal ice nanotubes composed of  $n$ -membered rings of water molecules. To find other possible ordered structures, we examine a range of preset  $\rho$  larger than those of the  $n$ -gonal ice nanotubes. From the  $NVT$ -constant MD simulations of water in (15, 0) and (16, 0) SWCNs at densities  $\rho$  in that range, we find

that several ordered ice-like structures do form spontaneously at particular densities. Table 1 shows properties of the ordered ices obtained from the MD calculations.

The ordered structures are characterized as filled ice nanotubes composed of an outer layer of molecules and an inner single file of molecules. In any case there is a clear separation between the outer layer and the inner single file; radial density profiles perpendicular to the tube axis have two peaks that are completely separated from each other: one at a distance where water molecules feel strong repulsion due to the cylindrical wall and another at a short distance from the axis.

The outer layer is either an  $n$ -gonal ice nanotube or a helical ice nanotube while the single file is along the axis of the carbon nanotube. They are a new class of ice nanotubes to be added to a family of ordered ice nanotubes. An earlier computational study showed that a mixture of water and hydrophobic molecules can be stable as an octagonal ice nanotube filled with hydrophobic molecules such as argon [10]. But the present results indicate that water alone may form a variety of filled ice nanotubes if the pressure is high enough.

When the outer layer of a filled ice nanotube is helical, it is no longer characterized by an  $n$ -membered ring because water molecules do not form a ring but an infinitely long helix. But there is a way to characterize both helical and  $n$ -gonal ice nanotubes. When an outer layer is opened, whether it is helical or  $n$ -gonal, one finds a two-dimensional square net of water molecules located at its nodes. This is shown in figure 1. If the square net is folded such that each node matches another node represented by a vector  $(n, 0)$  measured from it, one finds an  $n$ -gonal ice nanotube. If it is folded in a way represented by another vector  $(n, m)$  with  $n \neq m$ , then the

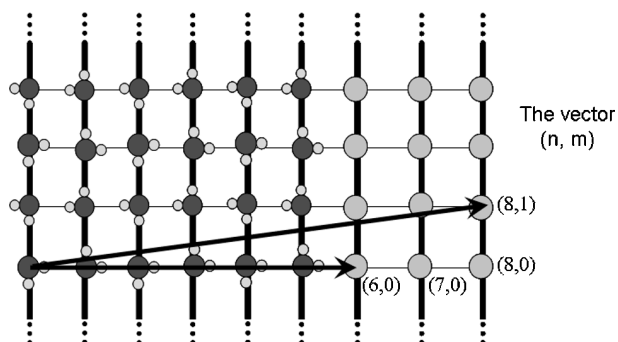


Figure 1. A schematic square net of the two-dimensional water and roll-up vectors.

resulting structure is a helical one. Thus structures of an empty ice nanotube and the outer layer of a filled ice nanotube are characterized in a systematic way by the roll-up vector  $(n, m)$ . The vector is an analog of that of the carbon nanotube [20] and that of cylindrically confined close-packed spherical molecules [3].

Outer layers of the ice nanotubes in the  $(15, 0)$  SWCN are characterized by roll-up vectors  $(6, 0)$  and  $(7, 0)$ : they are hexagonal and heptagonal ice nanotubes. Those in the  $(16, 0)$  SWCN have  $(7, 0)$ ,  $(8, 0)$  and  $(8, 1)$  structures, corresponding to heptagonal, octagonal and helical ice nanotubes.

Structure analysis of the outer layer of the filled ice nanotubes will be easier if the cylindrical outer layer is unrolled such that coordinates of molecules are mapped onto a two-dimensional plane. Specifically, we calculate an average radial distance  $r_{\text{outer}}$  of molecules in the outer layer from the tube axis and project coordinates of oxygen and hydrogen atoms on the cylindrical surface of radius  $r_{\text{outer}}$ . Figure 2 shows two-dimensional structures of molecules in the outer layers of the  $(8, 0)$  and  $(8, 1)$  ice nanotubes. A roll-up vector of each structure is also given in the figure. The original coordinates of molecules are those of structures at potential energy local minima, often called inherent structures, which are obtained from instantaneous configurations in MD simulation via the steepest descent calculation. Hydrogen bonds in the inherent structures are defined by an energy criterion: pair potential energy less than  $-12$  kJ/mol. For the  $(8, 0)$  ice nanotube, as shown in figure 2a, each group of molecules forming an 8-membered ring forms zigzag lines, indicating that the 8-membered rings are not flat but puckered; but each of the eight rows that are parallel to the

tube axis forms a near straight line. In the case of  $(8, 1)$  ice nanotube (figure 2b), the eight rows again form near straight lines but they make an angle with the tube axis; groups of molecules arranged perpendicular to the eight rows do not form 8-membered rings but forms a single helix: so the ice nanotube is helical. Unlike the empty  $(n, 0)$  ice nanotubes, the hydrogen bond network of the outer layer is not perfectly connected. Let  $OO'$  be a line segment from  $O$  to  $O'$ , where  $O$  and  $O'$  are positions of oxygen atoms of a hydrogen bonded pair of molecules in the two-dimensional plane. Let  $\phi$  be an angle that  $OO'$  makes with the tube axis in the unwrapped two-dimensional structure. and let its range be  $[-\pi/4 : (3/4)\pi]$ , noting that  $\phi$  and  $\phi + \pi$  are equivalent. Distributions of  $\phi$  for the  $(8, 0)$  and  $(8, 1)$  ice nanotubes are shown in figure 3. In the case of the  $(8, 0)$  ice nanotube, there is a single peak centered at  $\phi = 0$  and there are two peaks centered at  $\phi = 70$  and  $110^\circ$  and symmetrical with respect to  $\phi = 90^\circ$ . This is consistent with what is shown in figure 2a: series of the hydrogen bonds crossing 8-membered rings are straight and are parallel to the tube axis whereas series of the bonds making 8-membered rings form zigzag lines. In the case of the  $(8, 1)$  ice nanotube, there is a single peak centered at around  $-5^\circ$ , corresponding to series of the bonds that are nearly but not exactly parallel to the tube axis, and there are two peaks at around  $60^\circ$  and  $100^\circ$ , corresponding to a zigzag line winding around the tube axis.

### 3.2 Relation between the outer layer and the inner file

Let  $\omega$  be a ratio of the mole fraction of inner molecules to that of outer molecules. Then in the  $(15, 0)$  SWCN,  $\omega \approx 1/6$  for the  $(6, 0)$  ice nanotube and  $\omega \approx 1/7$  for the  $(7, 0)$  ice nanotube; in the  $(16, 0)$  SWCN,  $\omega \approx 1/7$  for

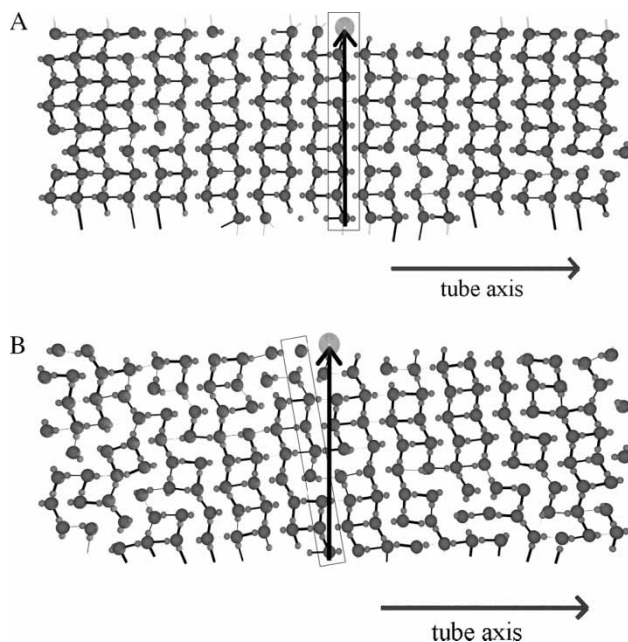


Figure 2. Structure of the outer layer of the filled ice nanotubes: (a) the  $(8, 0)$  “octagonal” ice nanotube, and (b)  $(8, 1)$  “helical” ice nanotube. These are projections of the three-dimensional structures on the cylindrical surface of a radius  $r_{\text{outer}}$ .

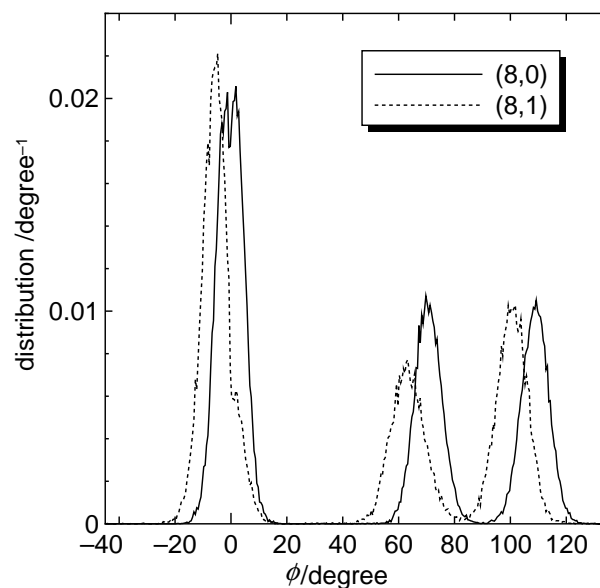


Figure 3. Distributions of  $\phi$  an angle that the oxygen-to-oxygen line segment of a hydrogen bonded pair makes with the tube axis in the unwrapped structure of the outer layer.

the (7, 0) ice nanotube,  $\omega \approx 1.28/8$  for the (8, 0) ice nanotube, and  $\omega \approx 1.87/8$  for the (8, 1) ice nanotube. These results indicate that there is one inner molecule per  $n$ -gonal ring for the (6, 0) and (7, 0) ice nanotubes. Figure 4 shows the equilibrium density profiles  $\rho(z)$  along the cylinder axis. It is clearly shown in figure 4a,b that for the (6, 0) and (7, 0) ice nanotubes each molecule of an inner single file is located at the midpoint between two neighboring  $n$ -membered rings in the outer layer. For (8, 0) ice nanotube (figure 4c), the distribution of inner water molecules is uniform along the tube axis and so uncorrelated with the periodic structure of the outer layer. In case of the (8, 1) helical ice nanotube (figure 4d), some periodicity is found for the inner water molecules along the axis but apparently they are not correlated with the outer molecules that form a helical network structure. Each peak that corresponds to each  $n$ -membered ring is splitting for the (7, 0) and (8, 0) ice nanotubes, reflecting that their  $n$ -membered rings are not flat as shown in figures 2a and 3.

It is of interest to examine a net dipole moment of the filled ice nanotubes and the distribution of each molecule's orientation. It is known from earlier studies [21,4] that an empty  $n$ -gonal or  $(n, 0)$  ice nanotube has a zero net dipole moment if  $n$  is even and a non-zero moment if  $n$  is odd. This is because every molecule in any one of  $n$  rows parallel to the tube axis points its OH arm to one direction ("up" or "down") and that direction alternates from one row to the next (because that makes the potential energy lower than otherwise). Then if  $n$  is even the OH-bond directions of any pair of neighboring rows can be opposite with each other and so the net dipole moment can be zero; but if  $n$  is odd the number of rows with the same OH-bond direction cannot be equal to the number of rows with the opposite OH direction and thus the net dipole moment cannot be zero. In cases of the filled ice nanotubes, not only the overall distribution of the dipole orientation but that for the outer layer and that for the inner region may be calculated separately. Let  $\theta$  be an angle that a dipole moment of a water molecule makes

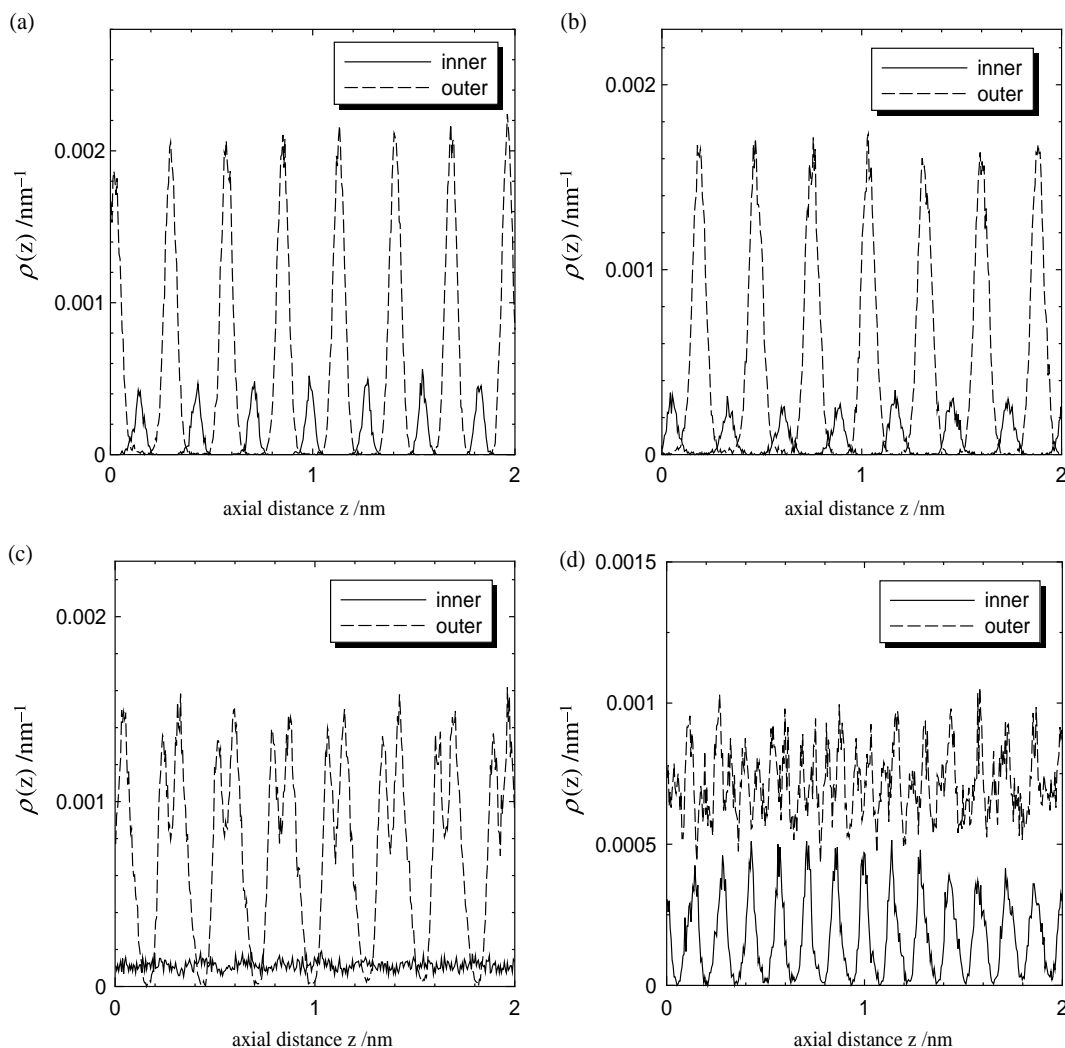


Figure 4. Density profiles  $\rho(z)$  along the tube axis. (a) the (6,0) ice nanotube in the (15,0) SWCN, (b) the (7,0) ice nanotube in the (15,0) SWCN, (c) the (8,0) ice nanotube in the (16,0) SWCN, and (d) the (8,1) ice nanotube in the (16,0) SWCN.

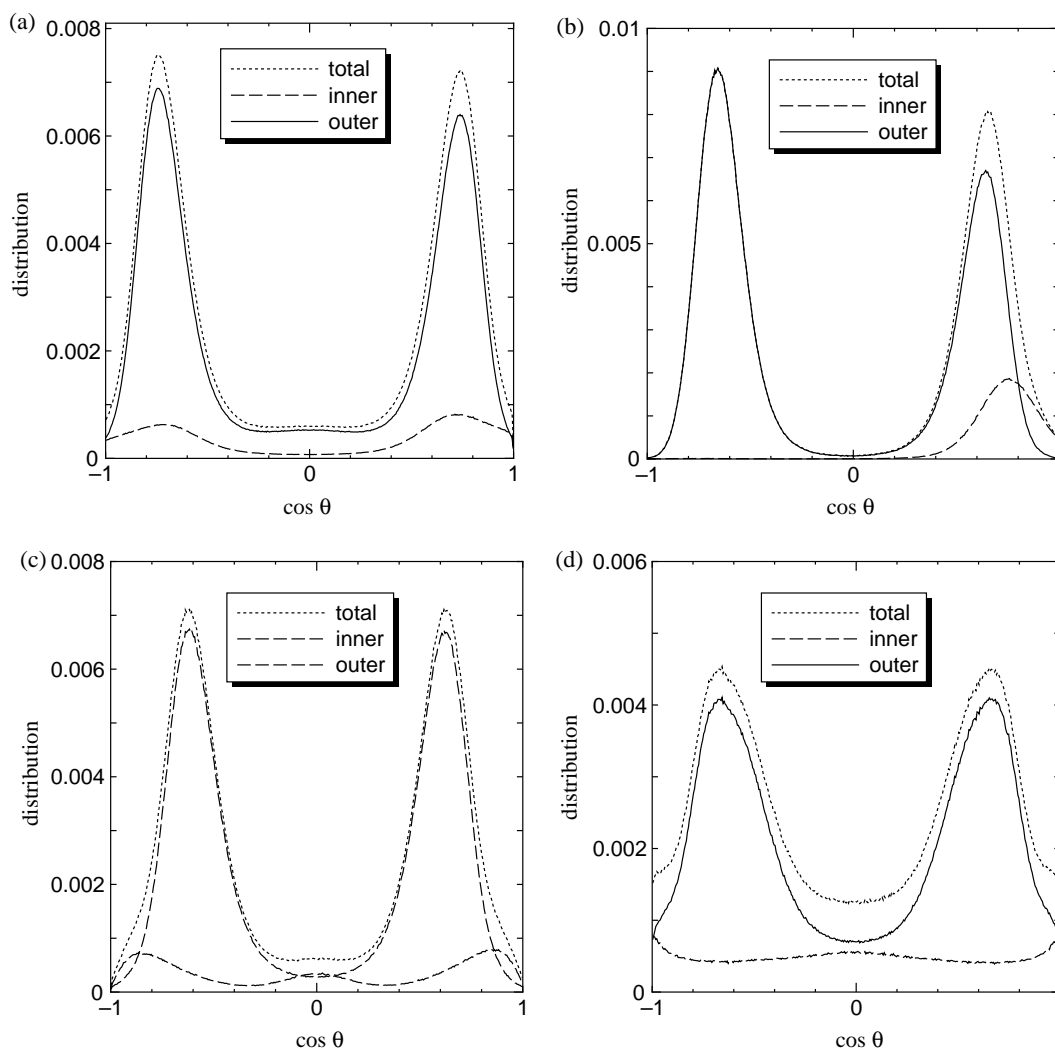


Figure 5. Distributions of  $\cos \theta$ , where  $\theta$  is an angle that a dipole moment vector makes with the tube axis.

with the tube axis. Figure 5 shows distributions of  $\cos \theta$  for outer, inner, and all molecules, obtained from the MD trajectories longer than 16 ns. The distributions are nearly symmetrical for the filled (6, 0) ice nanotube (figure 5a) and almost exactly symmetrical for the filled (8, 0) ice nanotube (figure 5c);  $\langle \cos \theta \rangle = -1.4 \times 10^{-2}$  and  $2.9 \times 10^{-3}$ , respectively.

In case of the filled (7, 0) ice nanotube, the distribution of  $\cos \theta$  for the outer layer shows two peaks, a higher one around  $-0.6725$  and a lower one around  $+0.6750$ , and thus it is asymmetrical with respect to 0. But the distribution for the inner molecules has a single peak around  $+0.7575$ : every inner molecule has the dipole moment in the same direction. Although the overall distribution is still asymmetrical, the average net dipole is as small as other filled ice nanotubes:  $\langle \cos \theta \rangle = 5.3 \times 10^{-3}$ . Finally in case of (8, 1) helical ice nanotube, the distribution of  $\cos \theta$  for the outer layer is nearly symmetrical as in the cases of (6, 0) and (8, 0) ice nanotubes and that for the inner molecules is also nearly symmetrical and more or less uniform. The average net dipole is nearly zero:  $\langle \cos \theta \rangle = 4.7 \times 10^{-4}$ .

### 3.3 Hydrogen bond network

Hydrogen bond networks in the filled ice nanotubes are analyzed for inherent structures within a period of 400 ps out of the total MD simulation. The criterion of a hydrogen bond is the same as used in figure 2. But now hydrogen bonds are defined not only for a pair in the outer layer but for a pair in the inner file and for a pair of outer and inner molecules. Figure 6 shows the average numbers of hydrogen bonds per molecule for the total system, the outer layer, and the inner file. None of the filled ice nanotubes has a fully-connected hydrogen bond network, but the networks of the (6, 0) and (7, 0) ice nanotubes in the (15, 0) SWCNs are closer to perfect connectivity than those of the (8, 0) and (8, 1) ice nanotubes in the (16, 0) SWCNs. An average hydrogen-bond number for the outer layers of the filled (6, 0) and (7, 0) ice nanotubes is very close to 4: the hydrogen-bond network has essentially a perfect connectivity just as that of the  $n$ -gonal ice nanotubes without inner molecules. But each molecule of the inner file of the same filled ice nanotubes has hydrogen

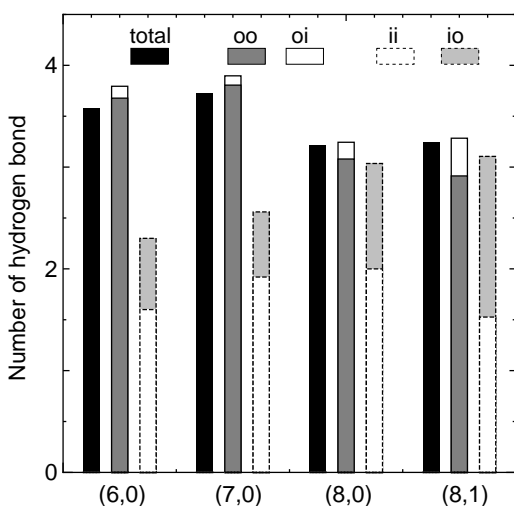


Figure 6. A number of hydrogen bonds per molecule. For each of the ice nanotube, left, middle, right bars indicate the average numbers for all, outer, inner molecules, respectively. The keys “oo”, “ii”, “oi” and “io” in the figure denote contributions from the hydrogen bonds between outer molecules, those between inner molecules, those of outer to inner molecules and those of inner to outer molecules.

bonds less than 3: most defects in the hydrogen bond networks are associated with the inner molecules. In cases of the filled (8, 0) and (8, 1) ice nanotubes, on the other hand, the average number of hydrogen bonds for the outer layer is nearly the same as that for the inner file.

#### 4. Summary

Ordered ices in carbon nanotubes are found in constant-temperature and constant-volume MD simulations. The ordered ices are different from the  $n$ -gonal ice nanotubes in that their inner space is filled with water molecules. The structures of the outer layer characterized by the roll-up vector  $(n, 0)$ , where  $n = 6-8$ , are the same as those of the hexagonal, heptagonal and octagonal ice nanotubes whereas the filled (8, 1) ice nanotube has helicity. The net dipole moments of these ice nanotubes are very close to zero. In case of the filled (7, 0) ice nanotube, the dipole moments of the outer layer and the inner file are not close to zero but they are so in opposite directions and cancel each other out. The hydrogen bond networks of the (6, 0) and (7, 0) ice nanotubes are nearly perfect within their outer layers and most of the defects are found in their inner molecules while those of the (8, 0) and (8, 1) ice nanotubes have defects in the outer layers as much as in the inner files.

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