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Helical ice-sheets inside carbon nanotubes in the physiological condition

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Abstract

Molecular dynamics simulations were performed, in the physiological condition (300 K and 1 atm), on nanotube segments of various diameters submerged in water. The results show that water molecules can exist inside the nanotube segments, and, most importantly, the water molecules inside the tubes tend to organize themselves into a highly hydrogen-bonded network, i.e., solid-like wrapped-around ice sheets. The disorder-to-order transition of these ice-sheets can be achieved purely by tuning the size of the tubes. The results also suggest that the nanotubes have the potential to be used as proton-conducting pores for a variety of biological applications.

Single-walled carbon nanotubes (SWNT) have elicited great research interest in recent years due to their unique anisotropic mechanical and electrical properties [1]. A promising area of study involves introducing nanotubes, with unusual new properties of both organic and inorganic materials, into biological systems. However, in order to successfully incorporate foreign materials into living cells, issues such as water solubility, biocompatibility, and biodegradability must be addressed. This can only be possible with a comprehensive understanding of the interactions of nanoparticles with basic biological molecules such as proteins, nucleic acids, and membrane lipids in the aqueous environment [2]. Therefore, the first fundamental step is to understand the interactions of nanoparticles with water molecules.

Carbon nanotubes are generally hydrophobic, therefore, the dynamical and structural properties of surrounding water molecules are expected to differ greatly from those of bulk water. In this work, we have carried out molecular dynamics (MD) simulations [3] of segments of pristine SWNT of different sizes submerged in a periodic hexagonal prism of water in the physiological condition (300 K and 1 atm). Segments of SWNT with a length of 20 Å and indices of (n, n) were studied ($n = 5$, 6, 7, 8, 9, 10, 15). We are particularly interested in the behavior of water molecules inside the nanotube segments.

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We found the size of the $(5,5)$ tube (6.75 Å in diameter) is too small to accommodate any water molecules inside, and the behavior of the water molecules inside the $(15,15)$ tube (20.26 Å in diameter) is the same as that of bulk water. However, the behavior of the water molecules inside tubes of intermediate sizes is significantly different. The oxygen–oxygen radial distribution functions of water molecules, $g_{OO}(r)$, inside the $(7,7)$, $(8,8)$, and $(9,9)$ tubes are shown in Fig. 1. The origin is set at the center of the tube. From the positions of the peaks, it is evident that water molecules tend to stay about 3 Å away from the wall, consistent with the results of a recent high-level quantum mechanical calculation of smaller model systems [4]. Strikingly, along the central axis, there is a much lower water density. In addition, we also observed unconventional behavior of the water trajectory along the inner wall of the tube. The water molecules inside the tube appear to be arranged in a very ordered fashion. For example, there are a total of six columns of water molecules inside the $(9,9)$ tube (12.16 Å in diameter) forming a perfectly hydrogen-bonded network (water cylinder), reminiscent of the wrapped-around graphene sheet

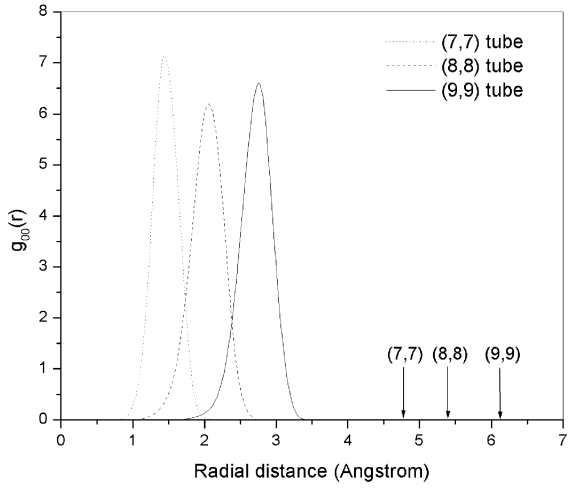

Fig. 1. Oxygen–oxygen radial distribution functions, $g_{OO}(r)$, of water molecules inside the tubes. The x-axis is the radial distance from the center of the tube. The results of the $(7,7)$ tube (9.46 Å in diameter), the $(8,8)$ tube (10.81 Å in diameter), and the $(9,9)$ tube (12.16 Å in diameter) are shown. The positions of the walls for the tubes are indicated by the arrows.

of a nanotube (Fig. 2). Due to the obtuse triangular shape of a water molecule, the cylinder formed by the six water columns present some degree of spiral nature in the axial direction of the tube. Each water molecule in the water sheet is hydrogen-bonded with four nearest neighbors in a nearly two-dimensional net. This is clearly different from the conventional tetrahedral arrangement of water molecules in ice. The formation of such a water sheet is due to the unique shape and size of the tube and also due to the iceberg effect [5,6], which states that, on a hydrophobic surface, the water molecules in the first shell tend to have their O–H bonds tangential to the surface. The water sheet appears to be very stable in the simulations. Only occasionally, individual water molecules fall off from the sheet and result in a 'defect', but it is quickly re-sealed. Similarly, the simulations of tubes of various sizes show that the $(6,6)$ tube (8.11 Å in diameter) can accommodate a hydrogen-bonded single-file water network [7], the $(7,7)$ tube (9.46 Å in diameter) with a three-column water network, the $(8,8)$ tube (10.81 Å in diameter) with a four-column water network, and the $(10,10)$ tube (13.51 Å in diameter) with a seven-column water network.

An earlier model study on simulation of water molecules in confined spatial regions [8] suggested qualitatively similar features of the radial distribution function to what is shown in Fig. 1. However, it did not demonstrate the ordered spiral network that we have observed. More recently, Koga et al. [9] presented the possibility of forming n-gonal ring structures of water within carbon nanotubes. However, it was reported that such ring structures could *only* be formed at much higher pressures (500–5000 atm) that are far away from physiological conditions. This clearly contradicts what we have shown in this report that the ordered water network can be formed inside the nanotubes in the much milder physiological condition. It is also clear from our study that the disorder-to-order transition of the water network can be achieved by varying the tube size, rather than the pressure [9]. The discrepancy may also come from the fact that the tube indices discussed in the article [9] do not seem to be in accord with the stated diameter values of the (n,n) armchair

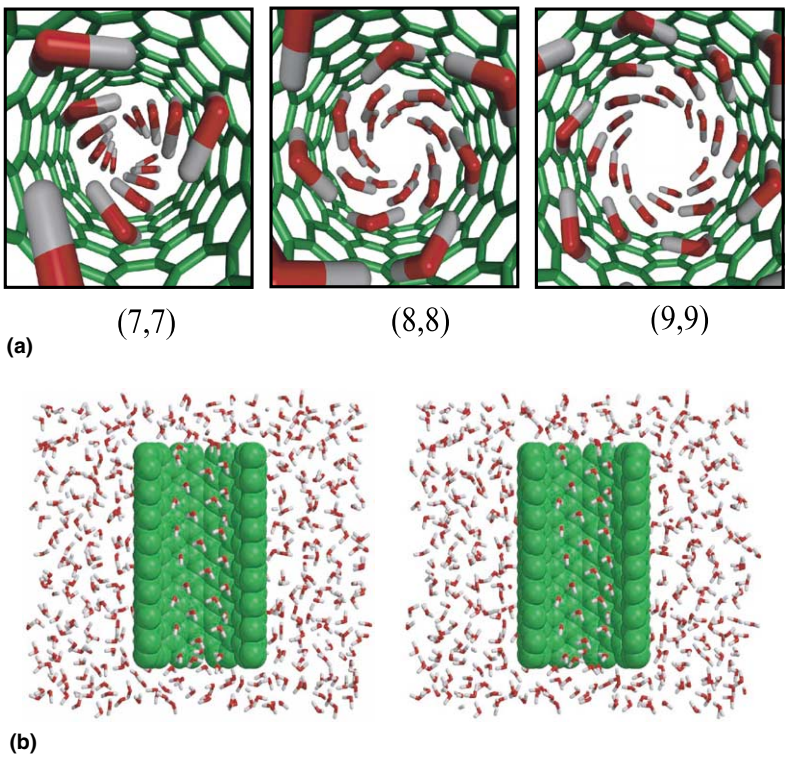

Fig. 2. Cross-sections of the water configurations inside various tube segments. (a) A top view. The ordered water columns are clearly visible. There are three water columns in the $(7,7)$ tube, four water columns in the (8,8) tube, six water columns in the $(9,9)$ tube. The water structures were energy-minimized with 50 steps of steepest descent method [21]. The highly spiral nature of the water columns inside the (8,8) tube makes the network not so visually obvious. (b) Stereo diagram of a cut-through side view of the $(9,9)$ tube. For clarity, inside the tube, only the water columns in the front are shown. The disorder-to-order transition is evident.

tubes, nor are those diameter values in accord with the diameter values of the standard armchair tubes [10].

It is important to point out that the behavior of water molecules inside the hydrophobic nanotubes is of great interest for biological applications. There are growing lines of evidence suggesting that, in the biological world, the transmembrane channels, such as K^+-channels [11] and water channels [12–14], all have a pore lined with hydrophobic residues. Such a 'greasy' pore is believed to be important for facilitating efficient axial passage of small ions or water molecules without getting 'stuck' to the wall. The lengths of the nanotube segments simulated here are in general comparable with those of the hydrophobic pores in transmembrane channels. This creates a possibility of using segments of nanotubes as cell transmembrane channels or pores. Moreover, the extremely ordered hydrogen-bonded water network inside the tubes is intriguing given that many proton conducting membrane channels use a continuously hydrogen-bonded water column (or so-called water bridge) acting concertedly for proton translocation [15]. It is worth pointing out that, in another recent paper by Hummer et al. [7], the authors used similar simulation protocol and confirmed that the $(6,6)$ tube can accommodate a single file of water network that can be established very quickly in the simulation. However, no results were presented on the formation of water network inside tubes of different sizes. We believe that the phenomenon of formation of different sizes of ordered water network inside different tubes is extremely important. Although it is known that some channel proteins employed singe-file water

network to conduct protons, it is also known that the continuous single-file of water in these channel proteins are stabilized by polar interactions provided by surrounding protein residues [14–18], which is a feature that $(6,6)$ nanotube does not have. Therefore, it remains to be an open question on the efficiency of proton conduction by the single-file water inside a $(6,6)$ nanotube [19]. We are actively pursuing the research in this direction.

Methods

The simulations were carried out in an isothermal–isobaric ensemble [20] by CHARMM program [21]. The length of simulation for each tube size was 2 ns. The atoms on the tubes were fixed in the simulations and the van der Waals parameters of the carbon atoms were chosen from those for benzene molecules in CHARMM force field. The atomic charges of atoms on the tubes were set to neutral. No polarizibility effect was included in the simulations. A modified TIP3P water model [22] was used for the water molecules. All bonds involving hydrogen atoms are fixed by the SHAKE algorithm [23]. The length of the edge of the hexagonal water prism used for periodic boundary condition varied from 18 to 30 Å depending on the size of the tube and the number of water molecules inside the simulation boxes was in the order of 1000.

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