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# Phase transition study of confined water molecules inside carbon nanotubes: Hierarchical multiscale method from molecular dynamics simulation to ab initio calculation

Soheila Javadian[a,*], Fariba Taghavi[a], Faramarz Yari[b], Seyed Majid Hashemianzadeh[c,**]

[a] Department of Physical Chemistry, Tarbiat Modares University, P.O. Box 14115-117, Tehran, Iran
[b] Department of Biology, Science and Research Branch, Islamic Azad University, Tehran, Iran
[c] Molecular Simulation Research Laboratory, Department of Chemistry, Iran University of Science and Technology, Tehran, Iran

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ABSTRACT

In this study, the mechanism of the temperature-dependent phase transition of confined water inside a (9,9) single-walled carbon nanotube (SWCNT) was studied using the hierarchical multi-scale modeling techniques of molecular dynamics (MD) and density functional theory (DFT).

The MD calculations verify the formation of hexagonal ice nanotubes at the phase transition temperature $T_c = 275\,\text{K}$ by a sharp change in the location of the oxygen atoms inside the SWCNT. Natural bond orbital (NBO) analysis provides evidence of considerable intermolecular charge transfer during the phase transition and verifies that the ice nanotube contains two different forms of hydrogen bonding due to confinement. Nuclear quadrupole resonance (NQR) and nuclear magnetic resonance (NMR) analyses were used to demonstrate the fundamental influence of intermolecular hydrogen bonding interactions on the formation and electronic structure of ice nanotubes. In addition, the NQR analysis revealed that the rearrangement of nano-confined water molecules during the phase transition could be detected directly by the orientation of $^{17}$O atom EFG tensor components related to the molecular frame axes. The effects of nanoscale confinements in ice nanotubes and water clusters were analyzed by experimentally observable NMR and NQR parameters. These findings showed a close relationship between the phase behavior and orientation of the electronic structure in nanoscale structures and demonstrate the usefulness of NBO and NQR parameters for detecting phase transition phenomena in nanoscale confining environments.

## 1. Introduction

From an application standpoint, increasing our understanding of the behaviors of nanoscopic confinement systems is important for designing new molecular devices in physics, chemistry, biology and material science [1]. The essential roles of water in nature and the unique properties of water have motivated numerous investigations to find the anomalous properties of water that is confined in nanometer porous environments [2,3].

Single-wall carbon nanotubes (SWCNTs) are the most favored material in nanotechnology because of their structural stability, low reactivity and unique electric and mechanical properties. These structures have motivated the use of water-filled SWCNTs as an ideal model for studying confined nano-fluid systems [4,5]. The behaviors of water inside and outside a nanoscopic pore are completely different from those of bulk liquid water [6–11]. To determine how the properties of water depend on nanoscale confinement, the structural and thermodynamic properties of water in the nanoscale hollow interior of SWCNTs have been investigated in many recent theoretical [4,5,12–14] and experimental studies, including those that used natural scattering [15], IR spectroscopy [16], Raman spectroscopy [17] and X-ray diffraction (XRD) [18]. These studies have shown that the effects of confining surfaces are strongly related to the diameter of a carbon nanotube. The properties of water in tubes with diameters larger than 25 Å are very similar to those of bulk water. However, when the CNTs are narrower, certain properties, including the hydrogen bond network and self-diffusion coefficient, differ significantly from those of bulk water [5].

An understanding of the unexpected phase behaviors of systems under confinement facilitates the development of innovative applications such as nanopower harvesting devices [19] and ferroelectric nano devices [14]. Confined water in a carbon nanotube could be an ideal model for studying the anomalous phase behaviors of confined systems. In 2001, Koga et al. used a computation method to determine that water can exhibit a first-order phase transition to

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* Corresponding author. Fax: +98 21 82883455.
** Corresponding author.
*E-mail addresses:* javadian_s@modares.ac.ir, javadians@yahoo.com (S. Javadian), hashemianzadeh@yahoo.com (S.M. Hashemianzadeh).

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n-gonal ice nanotubes (ice NTs) [20]. Following that study, there has been a great deal of interest in simulating the properties of freezing water inside carbon nanotubes [12,21–25]. Although there have been widespread reports on this subject, the simulation results were not all in agreement, particularly with respect to the choice of Lennard–Jones parameters, the method of calculating long-range forces and the water molecular models such as SPC/E or TIP3P [26]. However, all of the simulation studies revealed the possible existence of a new water phase inside SCNTs at temperatures below room temperature.

Experimental investigations have shown that there is an ordered structure of water in carbon nanotubes at low temperatures [15,27,28], and it was recently confirmed that water shows a transition from a liquid-like structure to novel ice structures known as ice NTs [14,29]. However, a fundamental understanding of the electronic features of freezing water inside carbon nanotubes remains unclear. In addition, there is no evidence of how the phase transition of water inside SWCNTs as thermodynamic bulk phenomena could be detected through the electronic properties of a water molecule in this system.

In this study, we investigated the electric mechanism of the phase transition in water-filled SWCNTs using density functional theory (DFT) and molecular dynamic (MD) simulations. We discussed how confinement within SWCNT pores affects the electronic configuration and hydrogen bond network of the water structure inside SWCNTs by natural bond orbital (NBO) [30,31], nuclear magnetic resonance (NMR) [32] and nuclear quadrupole resonance (NQR) [33] analyses. Accordingly, the molecular aspects underlying the first-order phase transition of water inside SWCNTs were clarified. We also introduced novel experimental techniques for recognizing this phase transition. In this study, we considered useful approximations to carry out first-principle calculations; interestingly, our results of the phase transition temperature range remained in very good agreement with the experimental data [18]. These results are useful because we can relate the molecular electronic configuration of water molecules inside SWCNTs to the phase transition phenomena.

In the next section, we explain the model that was used in this study and the computational details. In the following sections, MD simulations, natural bond orbital (NBO), nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) analyses of our system of interest will be presented.

## 2. Methods

### 2.1. Simulation model and computational details

We first performed MD simulations for water molecules encapsulated in a (9,9) SWCNT to analyze the first-order phase transition of water in a range of temperatures from 300 K to 200 K.

Then, DFT calculations were carried out for output structures from the MD calculations to provide comprehensive insight into the molecular view of the behavior of confined water molecules inside an (9,9) SWCNT during a first-order phase transition (which could not be followed from empirical simulations). Because of the difficulties of performing DFT calculations for a large system that was investigated by MD simulations, some approximations were used to create a simpler model of the large system for the purpose of performing DFT calculations. This simple model was able to predict the phase transition temperature area correctly, as will be discussed in subsequent sections.

#### 2.1.1. Simulation model

First, classical MD simulations were performed with a DL-POLY Classic molecular simulation package [34]. The MD calculations were carried out for water molecules filling the interior part of an isolated armchair SWCNT (9,9) with a fixed length of 43 Å and diameter of 12.2 Å. The carbon nanotube in the MD simulations is considered to be fixed with respect to the center of the simulation box.

The number of encapsulated water molecules in this (9,9) SWCNT is 83 [14]. The water molecules were considered rigid structures and were described by the potential model SPC/E [35] because this model can correctly predict the phase transition temperature [36]. The SPC/E potential is the sum of the short-range interaction potential of Lennard–Jones centers in the positioning of oxygen atoms and the long-range potential electrostatic potential between the point oxygen and hydrogen atoms on different water molecules [37]:

$$V_{WW} = V_{LJ} + V_{Coulombic}$$

$$V_{LJ} = \sum_{i \neq j} 4\varepsilon_{OO} \left[ \left( \frac{\sigma_{OO}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{OO}}{r_{ij}} \right)^{6} \right] \tag{1}$$

$$V_{Coulombic} = \sum_{l \neq m} \frac{1}{4\pi\varepsilon_0} \frac{q_l q_m}{r_{lm}}$$

where the $r_{ij}$ is the oxygen-oxygen distance, $\sigma_{OO}$ and $\varepsilon_{OO}$ are the Lennard–Jones parameters, $r_{lm}$ is the distance between two point charges $q_l$ and $q_m$ in different molecules, and $\varepsilon_0$ is the vacuum permittivity.

The intermolecular interaction potentials between the carbon atoms in the SWCNT and the water molecules inside it were considered a Lennard–Jones (LJ) function and were calculated using the Lorentz–Berthelot combining rule [37]. The LJ parameters were: $\varepsilon_{OO}/k_B = 76.6$ K, $\sigma_{OO} = 3.15061$ Å, $\varepsilon_{OC}/k_B = 46.3$ K, and $\sigma_{OC} = 3.27531$ Å for oxygen–oxygen and oxygen–carbon interactions, respectively, where $k_B$ is the Boltzmann constant [38]. The parameters of the AMBER force field [38] were used for the carbon atoms in a nanotube. The quadrupole interactions were not taken into account in our simulations because they have a minuscule effect on the resultant water structure [39].

Classic molecular simulations were first performed at a high temperature (300 K). The temperature was then decreased stepwise to 200 K with a temperature variation of 5 K at each run. All simulations were performed for a canonical ensemble (NVT) using the velocity Verlet algorithm [37] for the integration of equations of motion. A step time of 0.1 fs was chosen for the simulation because the typical time required for the dipolar reorientation of water molecules inside carbon nanotube has been reported to be in the order of picoseconds [40]. The Brendsen thermostat [41] was coupled to the system to ensure that the average system temperature is maintained close to the requested temperature at each run. Representative structures at 300 K and 200 K are shown in Fig. 1. The cutoff length for van der Waals forces was set to 20 Å, and Coulombic interactions were ignored at 40 Å. To make the simulation results more applicable for finite systems, periodic boundary conditions were not used in the system of confining a constant number of water molecules with a constant volume inside a SWCNT. The heating and cooling processes were performed to evaluate the reliability of equilibration by reproducing the properties of interest. There was no evidence of a sharp deviation in the tendencies of the properties of interest (especially potential energy), with the exception of the phase transition temperature.

#### 2.1.2. Density functional theory computation methods

Despite the outstanding achievements in empirical MD simulation studies [4,5,14], the microscopic mechanism underlying the hydrogen bond network between water molecules encapsulated within SWCNTs during the cooling process remains unclear.