THESIS

STRUCTURE AND DYNAMICS OF WATER CONFINED IN SINGLE-WALLED NANOTUBES: A MOLECULAR DYNAMICS STUDY

NONGNUCH ARTRITH

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Structures and dynamics of water molecules in nanoporous media exhibit interesting characteristics different from their ordinary bulk properties and may lead to potential applications in sophisticated nanofludic devices. In this study, molecular dynamics simulations were performed to investigate water molecules confined in single-walled carbon nanotubes (SWCNTs) and boron nitride nanotubes (SWBNNTs). Water density of 1.00 g cm^{-3} was placed inside the models of (n,n)-armchair nanotubes with different diameterrs (n = 9, 10, 12, 14, 16 and 20) and the simulations were performed in the canonical *NVT* ensemble at 298 K by using the Nosé-Hoover thermostat in DL_POLY program package. The wall-water interactions were varied within reasonable limits by changing the strength of the Lennard-Jones (LJ) parameters. Distribution functions were reported for the water in the tubes in spherical and cylindrical coordinates and the single-molecule dynamics, in particular self-diffusion, were monitored. While this motion was very much slowed down in narrow tubes, in keeping with previous findings (Mashl, R.J. *et al*. 2003 Nano Lett. 3(5):589-592.), bulk-water like self-diffusion coefficients were found in wider tubes. Axial diffusion coefficient increased with increasing tube diameter and reached its bulk value in the widest tubes with diameters of about 24 Å. The convergence was faster for smaller wall-water interactions. An anomaly is, however, found for the SWBNNTs where the convergence was not monotonous.

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Student's signature Thesis Advisor's signature

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Nongnuch Artrith
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LIST OF ABBREVIATIONS

Dz = Self-diffusion coefficient (z axis)
BLYP = Beck-Lee-Yang-Parr functional
BN = Boron nitride
BNNTs = Boron nitride nanotubes
CNTs = Carbon nanotubes
GlpF = Glycerol the crystal structure (F is symbol of native glycerol)
HF = Hartree-Fock
Ix = Angular momentum x component
Iy = Angular momentum y component
Iz = Angular momentum z component
LJ = Lennard-Jones
MC = Monte Carlo
MD = Molecular dynamics
MSD = Mean square displacement
MWCNT = Multi walled carbon nanotube
n(r) = Coordination number
NPT = Isothermal-Isobaric (NPT) ensemble
NT = Nanotubes
NVE = Microcanonical ensemble (NVE)
NVT = Canonical ensemble (NVT)
PW = Plane-Wave
RDF = Radial distribution function
SPC = Simple point charge
SPC/E = Extended simple point charge
STM = Temperature scanning tunneling microscope
SWBNNT = Single walled boron nitride nanotube
SWCNT = Single walled carbon nanotube
TEM = Transmission electron microscopy

STRUCTURE AND DYNAMICS OF WATER CONFINED IN SINGLE-WALLED NANOTUBES: A MOLECULAR DYNAMICS STUDY

INTRODUCTION

Carbon nanotubes (CNTs) (Iijima, 1991) have gained recognition as prominent building blocks of nano-materials. Due to their exceptional mechanical and electrical properties, several potential applications have been proposed such as nanoelectronic devices, composite materials, molecular sieves/membrane separation, nanofluidic devices, etc. (Meyyappan, 2005). The transport of molecules in these nanoporous media exhibits interesting characteristics, different from those of transport in ordinary bulk media (Behler *et al.*, 2001; Hummer *et al.*, 2001), since the interactions between the pore wall and molecules become rather strong when the dimensions of the pore approach the size of the transported molecule (Hummer *et al.*, 2001). Although the mechanical and electrical properties of CNTs can be measured explicitly by experiments (Wang *et al.*, 2000), the understanding on transport and conduction mechanisms through their pores is still uncertain. This is partly due to the difficulty of preparing CNTs with uniform pore sizes and distributions and of tracing diffusive behaviors of molecules inside nanopores. Computational studies, thus, play an important role in the interpretation of experimental data and provide predictive information on molecular transport through nanopores.

Because of the simplicity and hydrophobicity of their interior, CNTs are recognized as promising prototype models. They are frequently used as models for systems such as water transport in aquaporin water channels (Sui *et al.*, 2001), water migration in xylem vessels of plants (Kolesnikov *et al.*, 2004) and the delivery of beneficial molecules to the target cells (Bianco *et al.*, 2005; Chou *et al.*, 2008; Tajkhorshid *et al.*, 2002) and other biological nano-fluidic systems.

A previous molecular dynamics (MD) simulation study (Hummer *et al.*, 2001) on water conduction through the channel of single-walled carbon nanotubes (SWCNTs) showed that under normal conditions of pressure and temperature the filling of an empty (6,6)-CNT channel (8.1 Å in diameter and 13.4 Å in length) with water takes place within a few ten picoseconds. The channel then remained filled during the entire simulation time of 66 ns. The water molecules constrained in such a narrow space form a one-dimensionally ordered hydrogen-bond network that is not observed in bulk water. It was shown that the channel occupancy and conductivity are dramatically decreased by a reduction of the attractive nanotube–water interactions. A 25% reduction (Waghe *et al.*, 2002) leads to fluctuations between filled and empty sections in the tube and a 40% reduction to an emptying of the CNT channel (Hummer *et al.*, 2001). The filling and conducting behavior has also been observed in an isoelectronic nanotube (a subnanometer boron nitride nanotube (BNNT) (Won and Aluru, 2007)) and other hydrophobic nanopores (Joseph and Aluru, 2008; Noy *et al.*, 2007; Won and Aluru, 2008).

Recently, several MD simulation studies have been performed on the diameter dependence of the CNT hydration. It was found that water confined in a critical-size armchair-(9,9) CNT can undergo a transition into a state having ice-like mobility with a average number of hydrogen bonds close to that in bulk water under ambient temperature and pressure (Mashl *et al.*, 2003). Unusual features, not seen in bulk ice, can also be observed with other CNT diameters under conditions of high water densities (Liu *et al.*, 2005a; Mashl *et al.*, 2003) and extremely high axial pressures (50 Mpa to 500 Mpa) (Koga *et al.*, 2000). The radial distribution functions reveal highly ordered layer water structures of water in this case. For the dynamic properties, the radial and axial diffusivity of water encapsulated in SWCNTs are smaller than that the bulk water diffusivity; both decrease as the diameter of SWCNTs decreases (Koga *et al.*, 2000; Liu and Wang, 2007; Liu and Consta, 2005; Liu and Wang, 2005; Liu *et al.*, 2005a; Liu *et al.*, 2005b). In other tubes with similar diameters, the flow of water was found to be strongly influenced by the hydrophilicity of the wall. The strong interfacial water-nanotube attraction causes a significant reduction of the water flow rate.

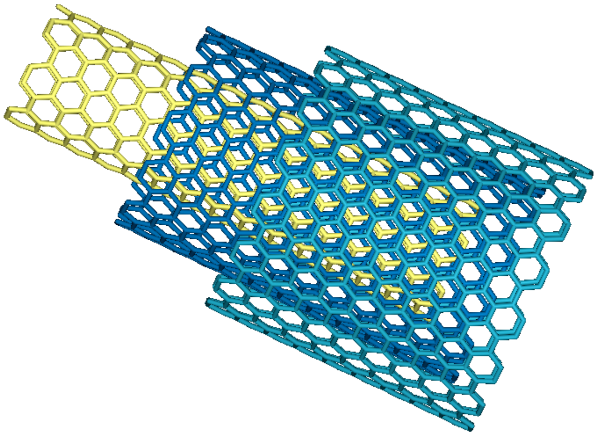
Even though the structure and dynamics of water confined in SWCNTs have been extensively studied by MD simulations, most efforts have been directed toward small diameter tubes, in which the characteristics of bulk water at the tube center will never be attained. Thus, a more comprehensive understanding of the structural and dynamic properties of confined water in larger diameter SWCNTs remains to be unraveled. Here, this research studies tubes with effective diameters between 8.86 to 23.74 Å and report on the influences of the attractive interactions between the water and the wall on structural and dynamic properties of confined water at average density of 1.00 g cm^{-3} under ambient conditions.

In the next section, the models and simulation details will be presented. Then, this work will investigate the structure of the water in the tubes in terms of radial and spherical distribution functions. A detailed study of the self-diffusion will then be presented.

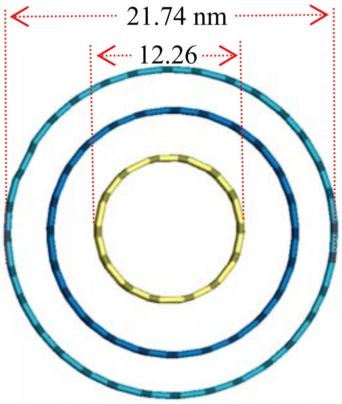
LITERATURE REVIEW

Sumio Iijima discovered a novel carbon allotrope carbon tubule, formed by a high current arc discharge process to evaporate graphite (Iijima, 1991; Iijima *et al*., 1993). The small tubes consisted of layer tube-like graphene structures, each succeeding outer shell having a larger diameter. These tubules were called multi-walled carbon nanotubes (MWCNTs). Carbon nanotubes consist of a shell of sp^2-hybridized carbon atoms forming a hexagonal network similar to a graphene sheet, which has been rolled up into a cylindrical shape.

The single-shelled nanotube, made up of a single layer of carbon atoms was called single-walled carbon nanotube (SWCNT) (Iijima *et al*., 1993). A typical SWCNT will have a cylindrical structure with diameter in the order of nanometers and can be a few micrometers long. SWCNT should be at least 0.4 nm large to afford strain energy and at most about 3.0 nm large to maintain tubular structure and prevent collapsing. Typical experimentally observed SWCNT is between 0.6 to 2.0 while smaller (0.4 nm) and large (3.0 nm) SWCNTs have been reported (Wang *et. al*., 2000). A larger SWCNT tends to collapse unless it is supported by force or surrounded by neighboring tubes, such as in a MWCNT. Typically MWCNT diameter is larger than 2.0 nm inside and smaller than 100 nm outside see the example of MWCNT in Figure 1. A SWCNT rope is formed usually through a self-organization process in which van der Waals force holds individual SWCNT together to form a triangle lattice with lattice constant of 0.34 nm (Meyyappan, 2005).



(a)



(b)

Figure 1 Multi-walled carbon nanotubes (MWCNTs) structures: 3 layers model of side view MWCNTs **(a)** and 3 layers model of top view MWCNTs **(b)**; diameter of (9,9)-CNT (smallest tube), (12,12)-CNT (middle tube) and (16,16)-CNT (biggest tube).

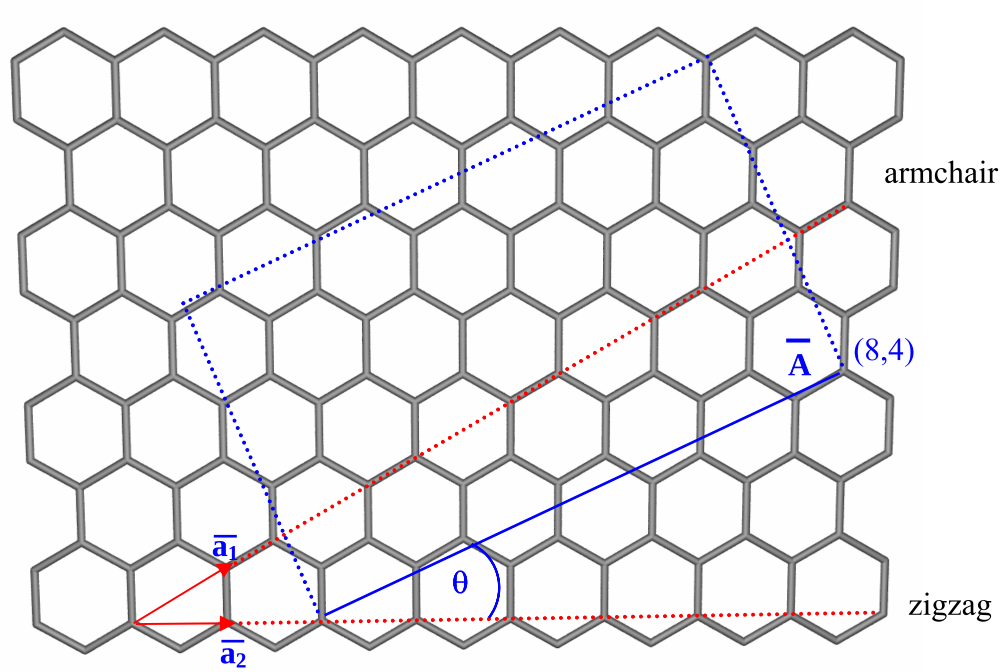
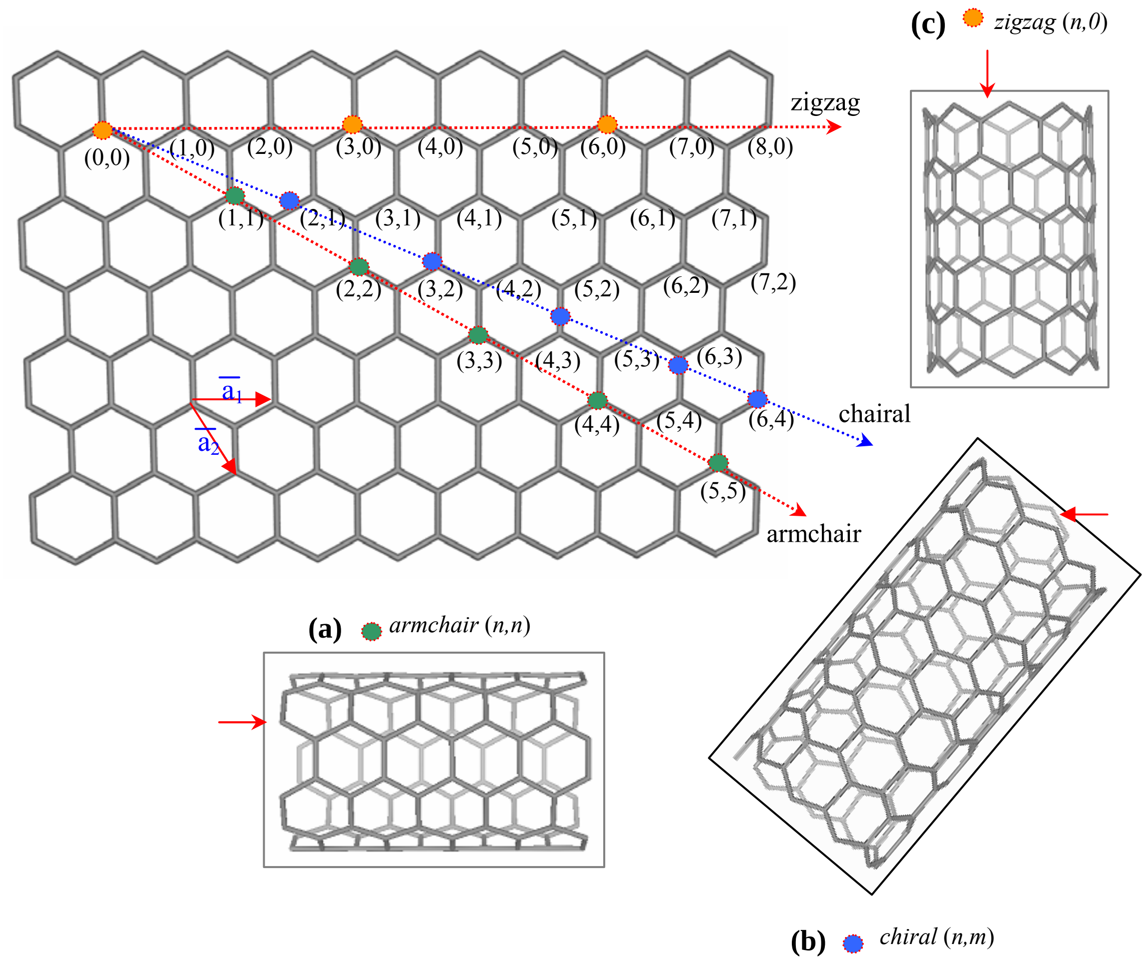


Figure 2 Carbon nanotube (*n,m*) is formed by rolling a graphite sheet along the chiral vector **A =** $n\mathbf{a}_1 + m\mathbf{a}_2$ on the graphite where $\mathbf{a}_1$ and $\mathbf{a}_2$ are graphite lattice vector; *m* and *n* are integers.



(c) ● *zigzag* (*n,0*)

(a) ● *armchair* (*n,n*)

(b) ● *chiral* (*n,m*)

Figure 3 Single-walled carbon nanotubes (SWCNTs) by rolling a graphene sheet in different chirality: armchair (*n,n*)**(a)**; chiral (*n,m*)**(b)**; zigzag (*n,0*)**(c)**. In the example, they are (5,5), (6,4) and (8,0) nanotubes.

Single wall carbon nanotube (SWCNT) can be viewed as a single sheet of graphite that has been rolled up along the chiral vector **A**, which can be characterized by the diameter and the chiral angle θ (see Figure 2).

$$\mathbf{A} = n\mathbf{a}_1 + m\mathbf{a}_2 \qquad (1)$$

where $\mathbf{a}_1$ and $\mathbf{a}_2$ are unit vectors of the hexagonal honeycomb lattice and n and m are integers. This chiral vector **A** also defines a chiral angle, θ which is the angle between **A** and the zigzag direction of the graphene sheet. All nanotube's type is usually characterized by these two integer numbers (n,m), such as *armchair* (n,n) and *zigzag* (n,0) or *chiral* (n,m) classes (see Figure 3). The electronic properties of nanotubes can be metallic and semiconductor and follow a general rule: all armchair SWCNTs are metals; those with $n – m = 3i$, where i is a nonzero integer, are semiconductors with a small band gap; and all others are semiconductors with a band gap that inversely depends on the nanotubes diameter (Saito *et al.,* 1992).

Despite their simple chemical composition and atomic bonding configuration, carbon nanotubes (CNTs) exhibit a great variety in structures and structure–property relations. CNTs exhibit rather outstanding and unique mechanical and physical properties, and immediately after their discovery were regarded as new materials for future technologies. In the present they are widely known as the necessary contributors to nano-technology, a technology concerned with the control and practice of matter on the nanometer to molecular scale and with the creation of nanoscale building blocks with fundamentally new physical, chemical, biological properties and functions. Their great progress has been made toward many applications for example; chemical and biological separation, energy storage, composite materials, probes, sensors and actuators for molecular imaging, sensing and manipulation, transistors, memories, logic devices, field emission devices, flat panel display and other nanoelectronic devices (Meyyappan, 2005). The advantages of these applications have been demonstrated, including their small size, low power, and low weight. These applications and advantages can be understood by the unique structure and properties of nanotubes.

Diffusion and molecular distribution of simple and complex fluid in carbon nanotubes are important as of both fundamental science and applications (Kalra *et al.*, 2003; Kalra *et al.*, 2004; Supple and Quirke, 2003; , 2004; , 2005). The motivation to study of water confined in CNTs, because of they have gained much attention as prototypes for biological water channels due to their simplicity, stability, and nanoporosity. This basic knowledge has led to development of theoretical predictions of the availability of carbon-nanotube-based membranes will permit the experimental verification. Understanding the mechanism of water diffusion under this condition, the goal of this contribution, is crucial for designing novel nanomachine such as water channel in biosystem, nanosyringes and synthetic nanomembranes for the controlled delivery of nanometer quantities of aqueous solutions.

CNTs are recognized as promising prototype models. They are frequently used as models for systems; water transport in aquaporin water channels (Sui *et al.*, 2001), water channels facilitate the rapid transport of water across cell membranes in response to osmotic gradients. These channels were believed to be involved in many physiological processes that included renal water conservation, neuro-homeostasis, digestion, regulation of body temperature and reproduction. Additionally, water migration in xylem vessels of plants, the delivery of beneficial molecules to the target cells (Tajkhorshid *et al.*, 2002) and other biological nano-fluidic systems are also interesting for modeled.

Following their discovery, carbon nanotubes have attracted interest because of their unusual electrical and mechanical properties, and their hollow interior that can serve as a nanometre-sized conduit, or template in material fabrication. The ability to encapsulate a material in a nanotube also offers new possibilities for investigating dimensionally confined phase transitions. Matter within the narrow confines of a carbon nanotube might exhibit a solid-liquid critical point beyond which the distinction between solid and liquid phases disappears (Koga and Tanaka, 2005; Koga *et al.*, 2000). This unusual feature, which cannot occur in bulk material, would allow for the direct and continuous transformation of liquid matter into a solid. CNTs have emerged as a new alternative and efficient tool for transporting and translocating therapeutic molecules. CNTs can be functionalized with bioactive peptides, proteins, nucleic acids and drug, and used to deliver their cargos to cells and organs, because functionalized CNTs display low toxicity and they are not immunogenic, such systems hold great potential in the field of nanobiotechnology and nanomedicine (Bianco *et al.*, 2005).

In 2001, Hummer and *et al*. studied the system of (6,6)-armchair SWCNT put in water bath and reported that confinement of matter on the nanometer scale could induce phase transitions not seen in bulk systems (Hummer *et al*, 2001). In case of water, so-called drying transitions occur on this scale as a result of strong hydrogen bonding between water molecules. The molecular dynamics simulations showed spontaneous and continuous filling of a nonpolar carbon nanotube with a one-dimensionally ordered chain of water molecules. The observations revealed pulse-like transmission of water through the nanotube. These transmission bursts resulted from the tight hydrogen-bonding network inside the tube. The attraction between the tube wall and water dramatically affects pore hydration, leading to sharp, two-state transitions between empty and filled states on a nanosecond timescale. That work suggested that carbon nanotubes, with their rigid nonpolar structures, might be exploited as unique molecular channels for water and protons. The channel occupancy and conductivity may be tunable by changes in the local channel polarity and solvent conditions.

Recently, many MD simulation studies have performed on the diameter dependence of the CNT hydration. By varying CNT diameter, it is found that water confined in a critical-size armchair-(9,9) CNT can undergo transition into a state having ice-like mobility with a number of hydrogen bonds close to that in bulk water under ambient temperature and pressure (Mashl *et al.*, 2003). The unusual features unseen in bulk ice can also be observed in other diameters of CNT under conditions of high water densities (Liu *et al.*, 2005a) and of extremely high axial pressures (50 Mpa to 500 Mpa) (Bai *et al.*, 2006; Koga *et al.*, 2000). The radial distribution functions reveal highly ordered layer structures of water confined in CNTs. For the dynamic properties, the radial and axial diffusivity of water encapsulated in SWCNTs are smaller than that in bulk water and decrease as the diameter of SWCNTs decreases (Liu and Wang, 2005; Liu *et al.*, 2005a; Liu *et al.*, 2005b; Mashl *et al.*, 2003; Striolo, 2006; Striolo *et al.*, 2003; , 2006). With a similar size in diameter, the flow of water in nanotubes is strongly influenced by the hydrophilicity of the nanotube wall. The strong interfacial water-nanotube attraction causes the reduction of the water flow rate significantly (Joseph and Aluru, 2008). Although the structure and dynamics of water confined in SWCNTs have been extensively studied using MD simulations, much effort has been mainly paid on small diameter nanotubes in which the characteristic of bulk water at the tube center will never been attained.

A new anomalously immobilized water phase induced by confinedment in nanotubes was reported by Mashl *et al*, 2003. The MD simulations showed that water confined in CNTs of a critical size (8.6 Å Van der Waals diameter nanotube) under ambient conditions (1 bar, 300 K) had anomalouse icelike behaviors. Moreover, because of a variety of evidence suggesting that water ordering may modulate proton conductance via a proton wire; hydrogen bonding network, the ability to modulate water ordering with geometry suggested a possible mechanism for a switchable nanoscale semiconductor. Also, to study the water alignment and proton conduction inside CNTs, first-principles molecular dynamics simulations have been carried out to investigate the structure, electronic properties, and proton conductivity of water confined inside single-walled carbon nanotubes (Mann and Halls, 2003). The simulations predict the formation of a strongly connected one-dimensional hydrogen-bonded water wire resulting in a net electric dipole moment directed along the nanotube axis. An excess proton injected into the water wire has found to be significantly stabilized, relative to the gas phase, due to the high polarizability of the carbon nanotube.

Molecular distribution and dynamic properties of confined water were most studied. Temperature effects on the static and dynamic properties of liquid water inside carbon nanotubes were studied by Marti and Gordillo (Marti and Gordillo, 2001a; 2001b; , 2002; , 2003). They reported a series of MD simulation of the behavior of SPC liquid water adsorbed in carbon nanotubes under different thermodynamics. A flexible simple point charged potential was employed to model internal and intermolecular water interactions. System was radii ranging from 4.1 Å to 6.8 Å and three temperatures from 298 K to 500 K for density of 1.00 g cm^{-3}. Results showed the gradual destruction of the hydrogen-bond network together with faster diffusive regimes as temperature increases. The vibrational mode absent in bulk-unconstrained water appeared in the power spectra obtained from hydrogen velocity autocorrelation functions for all thermodynamic states. That frequency mode attributed to confinement effects. Diffusive behavior and the vibrational, rotational, intra- and intermolecular motions of the constrained molecules were investigated by means of the spectral densities computed from atomic velocity autocorrelation functions. The results showed new vibrational bands and frequency shifts that were not observed in bulk water. Other system studied, Marti and Gordillo chose to model water-water and water-carbon forces, respectively. It showed that system underwent a first-order phase transition between low- and high-density phases.

A similar research of the role of transport phenomena of confined water has explored the osmotically driven transport of water molecules through hexagonally packed CNT membranes. Simulation set up two types such semipermeable membranes separate compartments of pure water and salt solution (Kalra *et al.*, 2003). The resulted flow rates were high (average 5.8 water molecules per ns and nanotube, comparable to those through the trans-membrane protein aquaporin-one), and were practically independent of the length of the nanotube, in contrast to predictions of macroscopic hydrodynamics. All of these distinct characteristics of nanoscopic water flow modeled by one-dimensional continuous-time random walk. At long times, they reported that the pure water compartment drained, and the net flow of water interrupted by the formation of structured solvation layers of water sandwiched between two nanotube membranes.

Liu and coworkers published 4 papers in 2005 reported behaviors of water confined in SWCNTs based on MD simulation (Liu and Consta, 2005; Liu and Wang, 2005; Liu *et al.*, 2005a; Liu *et al.*, 2005b). They summarized the investigation of the molecular distribution and transport properties (self-diffusion coefficient, thermal conductivity, and viscosity) of water confined in SWCNT with diameter from 11 Å to 21 Å. Many conditions have been taken in their work such as difference pore sizes, nanotube helicity, and variance density of water and thermal conductivity. For molecular distributions, the water molecules ordered in helix inside the (10, 10) SWCNT. It was also found that the axial thermal conductivity and shear viscosity in SWCNTs were greater than those of the bulk and self-diffusion coefficients of water in the order of armchair CNTs have higher than in zigzag CNTs (Liu and Wang, 2005). Moreover, they pointed that the axial diffusion coefficient was lower than that characteristic of bulk water and that it had decreased as the pore diameter narrows. For the largest nanotube considered (21 Å in diameter), the calculated diffusion coefficient equaled 0.9423×10^{-5} cm^2 s^{-1}. It should however be pointed out that Fickian motion only occurs when the molecules pass each other uncontrollably in the direction of flow. For diffusivity, results showed in model nanotube (fitting curve of NT) > in armchair CNT > in zigzag CNT at similar conditions. However in contrast to the diffusivity, the thermal conductivity and the shear viscosity have increased as the pore size decreases, in zigzag CNT > in armchair CNT > in model NT. The ordered layer distribution of water molecules in nanotubes was clear. It suggested the structure of fluid in the zigzag CNTs was more ordered, and more solidlike. In the nanotubes, where the molecule and the pore dimensions were of similar order of magnitude, the nature of water-water and water-wall interactions, the confinement effect of space, and the helicity of CNT become more significant.

However, Striolo (Striolo, 2006) mentioned a work of Liu and Wang (Liu and Wang, 2005) that may not be true when fluid molecules were confined in long and narrow nanotubes. Striolo reported the confined water diffuse thought in narrow SWCNT, which occurred via a coordinated motion, and the mean square displacement (MSD) followed as a ballistic-type dependence on time for up to hundreds of picoseconds. As same as previous work, they observed the layered ice-like structures of water confined in SWCNT (Striolo, 2006; Striolo *et al.*, 2003; , 2006; Striolo *et al.*, 2004a; Striolo *et al.*, 2004b). Basic study of those researches would like to use theoretical predictions of the availability of carbon-nanotube-based membranes will permit the experimental verification. Understanding the mechanism of water diffusion under this condition, the goal of this contribution, is crucial for designing nano-machine, nano-injector and synthetic membranes as well as for the development of novel drug-delivery devices.

The filling and ordering properties of water restrained in MWCNTs are also interesting. SWCNTs with different diameters, lengths, and chiralities, could coaxially self-assemble into MWCNTs in water via spontaneous insertion of smaller tubes into larger ones (Zou *et al.*, 2006a; 2006b). The assembly process was tube-size-dependent, and the driving force was primarily the intertube van der Waals interactions. The simulations also suggested that a MWCNT might be separated into SWCNTs under appropriate solvent conditions. Their study proposed possible bottom-up self-assembly routes for the fabrication of novel nanodevices and systems.

The structures of water confined in carbon nanotubes were found to be *n*-gonal ice nanotubes and may be called filled ice nanotubes. In very small tubes (effective diameter of 6-8 Å), water formed a single file ice nanotube (Hummer *et al*, 2001; Marshl *et al.*, 2003; Gordillo *et al.*, 2000; Gordillo *et al.*, 2001). In the critical size tubes (effective diameter of 8-12 Å), one-gonal ice nanotube and in the large tubes (effective diameter up to 12 Å), multi-gonal ice nanotubes were formed (Bai *et al.*, 2006; Li *et al.*, 2007; Li *et al.*, 2006; Takaiwa *et al.*, 2007; Yang and Garde, 2007). Spontaneous formation of the filled ice nanotubes was observed in MD simulations of water at fixed densities and a fixed temperature. Outer-layered filled ice nanotubes characterized by a roll-up vector (*n, m*), while inner files of molecules did not have definite ordered structures. With this notation the filled ice nanotubes are of (*n, n*), (*n, 0*) and (*n, m*) types, the last of which has a helical structure in its outer layer whereas the outer layers of first of two structures as the *n*-gonal ice nanotubes. Structure analysis was done for their hydrogen-bond networks and advanced dipole moments.

Behavior of water encapsulated in carbon nanotubes recommended the existence of a variety of new ice phases not seen in bulk ice, and of a solid-liquid critical point (Koga *et al.*, 2001). Using carbon nanotubes with diameters ranging from 11 Å to 14 Å and applied axial pressures of 50 MPa to 500 MPa, they found that water can exhibit a first-order freezing transition to hexagonal and heptagonal ice nanotubes, and a continuous phase transformation into solid-like square or pentagonal ice nanotubes. Concerning to answer the question what the unit cell of ice nanotube looks like for an *n*-gonal ice nanotube built from stacking a single type of *n*-gonal rings of water, the unit cell consists of two stacked *n*-gonal rings (Koga *et al.*, 2000a; Koga *et al.*, 2000b). The ring of O-H bonds of water molecules line up clockwise whereas in the other ring the O-H bonds line up as counterclockwise. Among the *n*-gonal ice nanotubes examined, the pentagonal or hexagonal ice nanotube appears to be the most stable. The phase diagram of water between hydrophobic surfaces (CNTs) was also studied by using *MD* simulations (Koga and Tanaka, 2005). There were two classes of quasi-two-dimensional solid water into which liquid water confined between hydrophobic surfaces freezes spontaneously and whose hydrogen-bond networks were as fully connected as those of bulk ice. It was found that the phase transformations among liquid, bilayer amorphous (or crystalline) ice, and monolayer ice phases at various thermodynamic conditions, then determined curves of melting, freezing, and solid-solid structural change on the isostress planes where temperature and intersurface distance were variable.

MD simulations have investigated the fundamental of diffusion mechanisms of water driving in nanoporous (Wang *et al.*, 2003). One talented area of studying nanotubes involved modeling them to mimic real ion channels in biological systems, which reduced the complexity of modeling ion channels. The properties of a nanotube strongly depend on its helicity; therefore the effect of helicity on behaviors of water molecules confined in nanotubes deserved further investigation. Behaviors of water molecules confined in (6,6) armchair and (10,0) zigzag types were analyzed by MD simulation at 300 K and 1.01×10^5 Pa. It was indicated that water molecules could flow into hydrophobic carbon tubes to form a stable hydrogen-bonded chain called single file, and spontaneously conduct through tubes as the single file form and the ability of water conduction through (10,0) zigzag tube was stronger than that through (6,6) armchair tube.

Many types of transportation in small pores, one type is called single-file transport of water molecules through a CNT (Berezhkovskii and Hummer, 2002). MD simulations of water transport through the interior channel of a carbon nanotube in contact with an aqueous reservoir showed that conduction occurred in bursts with collective water motion. A continuous-time random-walk model was used to describe concerted transport through channels densely filled with molecules in a single-file arrangement, found in zeolites, as well as in ion channels and aquaporins in biological membranes. Theoretical predictions for different collective properties of the single-file transport agree with the simulation results. Striolo reported the mechanism of water diffusion in narrow CNT. Results showed exceptional physical properties that render them promising candidates as building blocks for nanostructured materials (Striolo, 2006). Many ambitious applications, ranging from gene therapy to membrane separations, require the delivery of fluids, in particular aqueous solutions, through the interior of carbon nanotubes. To foster these and other applications, it was necessary to understand the thermodynamic and transport properties of water confined within long narrow carbon nanotubes. Previous theoretical study considered only either short carbon nanotubes or short periods of time. By conducting MD simulations in the microcanonical ensemble for water confined in infinitely long carbon nanotubes of diameter 10.8 Å (Striolo, 2006). It was found that confined water molecules diffuse through a fast ballistic motion mechanism for up to 500 ps at room temperature. By comparing the results obtained for the diffusion of water to those obtained for the diffusion of a reference LJ fluid, it proved that long-lasting hydrogen bonds was responsible for the ballistic diffusion of water clusters in narrow carbon nanotubes, as opposed to spatial mismatches between pore-fluid and fluid-fluid attractive interactions which, as shown previously by others (Liu *et al.*, 2005a; Striolo *et al.*, 2003; Striolo *et al.*, 2004a), were responsible for the concerted motion of simple fluids in molecular sieves. Additionally, Striolo proved for the first time that despite the narrow diameter of the CNTs considered which may suggested the existence of single-file diffusion, when the trajectories of confined water were studied at time scales in excess of 500 ps, a Fickian-type diffusion mechanism prevails.

Dynamic Monte Carlo (MC) simulations and analytical calculations investigated the effect of pore surface roughness on Knudsen self- and Fickian diffusion in nanoporous media (Malek and Coppens, 2003). Principle of difference was found between the roughness dependence of the macroscopic, transport diffusivity and the microscopic, self-diffusivity, which was reminiscent of diffusion in zeolites, where a similar difference arises due to adsorption effects and intermolecular interactions. The differences become significant when the pore surface was rough down to molecular scales, as was the case, e.g., for many common sol-gel materials. The results showed that surface roughness could affect self-diffusivity of gas molecules in the Knudsen regime. On the other hand, the molecular trajectories in smooth and rough pores showed the independence of transport diffusivity on surface roughness. The projection of the molecular trajectory pathway in a pore with a rough surface was equivalent to that in a pore with a smooth surface when the molecule performs surface jumps around regions on the order of the diameter of the fjord inlet size. These jumps quickly decorrelate; therefore the transmission was roughness independent. These simulations were in good agreement with analytical calculations for several tested rough, fractal pore structures. The self-diffusivity was more fundamental diffusivity, expressing how the position of a molecule changes with the time as a result of its random motions, influenced by its environment. That environment influenced the total trajectory length. Their results were important for the interpretation of experimental diffusion measurements and for the study of diffusion-reaction processes in nanoporous catalysts with a rough internal surface.

Resemblance the MD simulations showed the Fickian water diffusion in (6,6)-armchair CNTs (Mukherjee *et al.*, 2007a). That size of the nanotube allowed only a single file of water molecules inside the nanotube. Water molecules inside that showed solidlike ordering at room temperature. It was shown that even for the longest observation times, the mode of diffusion of the water molecules inside the nanotube was Fickian and not subdiffusive. It also proposed a one-dimensional random walk model for the diffusion of the water molecules inside the nanotube. That work calculated mean-square displacements (*MDS*) from the random walk model by MD simulations, thereby confirming that the water molecules underwent normal mode diffusion inside the nanotube. It was attributed this behavior to strong positional correlations that caused all the water molecules inside the nanotube to move collectively as a single object. There was good between the results from the model and MD simulation for the time scale (average residence time) of the exponential decay of the survival probability. This time scale was shown to depend on the length of the nanotube, which was another piece of evidence in support of the conclusion that the mode of diffusion was normal. Another case, water molecules inside narrow, open-ended carbon nanotubes placed in a bath of water molecules (Mukherjee *et al.*, 2007b). The radius of the tube was such that only a single file of water molecules was allowed inside the tube. The calculated *MSD* of the confined water molecules reveals that initially the water molecules undergo ballistic motion that crosses over to normal (Fickian) diffusion at longer times.

Properties of boron nitride (BN) nanotubes have investigated (Ishigami *et al.*, 2003a; 2003b). Boron nitride nanotubes were expected to be as desirable for application as carbon nanotubes. Although boron nitride nanotubes were wide band gap semiconductors and electronics nearly insulating, scanning tunneling microscopy can be used to image and characterize them. The studied of electronic properties of BN nanotubes was used a low temperature scanning tunneling microscope (STM) operated at 7 K. STM images of the tubes reveal hexagonal lattices or stripe patterns, which can be caused by interlayer coupling or scattering of electronic states of the nanotubes. Scanning tunneling spectroscopies measurements indicate that the tubes have banded gaps exceeding 4 eV, and reveals van Hove singularities confirming the one-dimensional nature of electronic states of the nanotubes.

There are few theoretical studies of water confined in BNNT. Water permeation through in a subnanometer single-walled boron nitride nanotube (SWBNNT) reported by Won and Aluru (Won and Aluru, 2007). BNNTs possessed many excellent physical properties, including thermal and mechanical properties. They showed the superior water permeation properties of BNNTs by using MD simulation. Specifically, water molecule permeate through the (5,5)-SWBNNT nitride nanotube, while a (5,5)-SWCNT of approximate the same diameter did not conduct water. It suggested that the relatively strong interactions between the nitride atoms of the BNNT and water molecules play a key role in the continuous wetting behavior of the SWBNNT. The properties of water, such as the axial diffusion coefficient and the hydrogen bonding, inside the (5,5) SWBNNT were comparable to those inside the (6,6)-SWCNT, even though the diameter of the (5,5)-BNNT was 1.3 Å smaller than that of the (6,6)-SWCNT.

Other case, Won and Aluru studied water flow in (16,16)-SWCNTs and reported the flow rates from velocity jump in a depletion region at the water-nanotube interface and that the water orientations and hydrogen bonding at the interface significantly affected the water flow rates (Won and Aluru, 2008). It was found that nanotube with the same smooth wall structure but with more hydrophilic Lennard-Jones (LJ) parameters of silicon was deeply reduced because of there was not free OH bonds pointing to the wall as in CNTs that reduce the number of hydrogen bonds in the depletion layer. Another important point to note was that the flow rates were highly sensitive to the interatomic distances. The simulations of (16,16)-SWBNNT presented a B-N bond length of 0.144 nm, which is slightly more than 0.142 nm (the bond length for CNT). It was found that the water structure; OH bond orientations and the hydrogen bonding in the depletion region was less than 5% of the bulk value has a direct effect on the enhancement of flow rates. A unique combination of features such as hexagonal structure, interatomic distances and water orientations with free OH bonds pointing to the wall and the decreased hydrogen bonding in the depletion region contributed the large flow rates in SWCNTs.

There still have been lacks to studies on the water transmission properties of BNNTs. For more extremely study the fundamental insights into the water confined in SWBNNTs and to compare the results with those in CNTs. Therefore, the investigation on structural and dynamical of water confined in SWBNNTs is also of interest. The objectives of this work have focused into study the influence of attractive interactions between water and variance confining walls on structure and dynamics properties of water at density of 1.00 g cm^{-3}. MD simulations studied the effects of confined spaces on molecular distribution and transport behaviors of water confined in SWCNTs and SWBNNTs. Diffusion coefficients and molecular distribution functions of water confined in both nanotubes were discussed.

MATERIALS AND METHODS

Models and Simulation Details

The (*n*,*n*)-armchair type SWCNTs considered in this study were modeled as a rigid networks of uncharged Lennard-Jones (LJ) carbon atoms with C-C bond distances of 1.42 Å and a fixed nanotube length of 36.89 Å. To study the effects of nanotube diameter dependence on structure and dynamics properties of the confined water, the effective diameters of SWCNTs, after excluding the van der Waals radius of C atoms of 1.70 Å, were varied from 8.86 to 23.74 Å, corresponding to the armchair SWCNTs of n = 9, 10, 12, 14, 16 and 20, respectively. These nanotubes were filled with a total number of 77, 102, 162, 237, 327, and 547 water molecules, respectively, which led to an average water density of 1.00 g cm^{-3}. Details of the simulation runs are showed in Table 1.

Table 1 Details for the MD simulation runs of water in carbon- and boron-nitride nanotubes in this work. The length is 36.89Å in all cases.

Nanotubes model	Real / Van der Waals diameter (Å)	Number of water (molecules)	Periodic box size X × Y × Z (Å^3)	Simulation run (ns)
Bulk water	-	1,000	31.03 × 31.03 × 31.03	1
(9,9)-SWCNT, -SWBNNT	12.26 / 8.86	77	24.52 × 24.52 × 36.89	4
(10,10)-SWCNT, -SWBNNT	13.62 / 10.22	102	27.24 × 27.24 × 36.89	4
(12,12)-SWCNT, -SWBNNT	16.32 / 12.92	162	32.64 × 32.64 × 36.89	1
(14,14)-SWCNT, -SWBNNT	19.02 / 15.62	237	38.04 × 38.04 × 36.89	1
(16,16)-SWCNT, -SWBNNT	21.74 / 18.34	327	43.48 × 43.48 × 36.89	1
(20,20)-SWCNT, -SWBNNT	27.14 / 23.74	547	54.28 × 54.28× 36.89	1

Water was described by the extended simple point charge (SPC/E) model ($\varepsilon_{O\text{-}O}$ = 0.1554 kcal mol^{-1} and $\sigma_{O\text{-}O}$ = 3.16 Å) (Berendsen *et al.*, 1987; Guillot, 2002). The geometry of each water molecule was held rigid using the SHAKE algorithm. Two hydrogen atoms were located from the oxygen center by 1.0 Å with an H-O-H angle of 109.5°. Atomic charges of −0.8476*e* and +0.4238*e* were assigned to oxygen and hydrogen sites, respectively (see Figure 4).

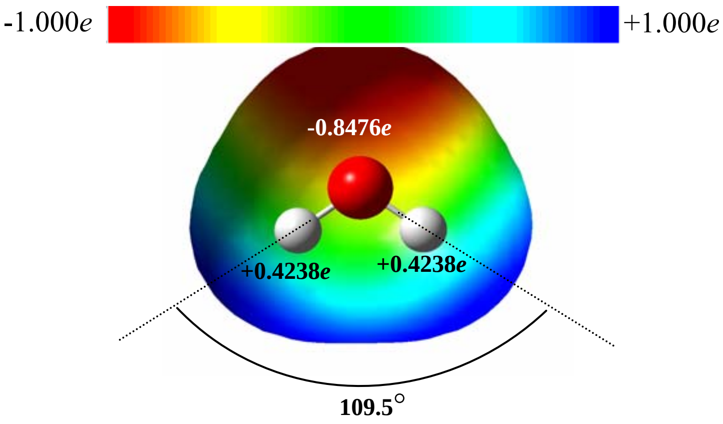


Figure 4 Positive and negative charges surface area described the extended simple point charge (SPC/E) of water model. Isovalue for surface is 0.0004.

Interactions between water and the nanotube wall were described by the 12-6 LJ potential. The LJ parameters for carbon ($\varepsilon_{C\text{-}C}$ = 0.0970 kcal mol^{-1} and $\sigma_{C\text{-}C}$ = 3.36 Å) were taken from Mashl *et al.*, 2003:

$$U(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \qquad (2)$$

where ε_{ij} and σ_{ij} symbolize the size and strength of the LJ potential parameters, and r_{ij} is the distance between the centers of mass of the pair atoms. The water-nanotube interaction parameters were derived by using the Lorentz-Berthelot combining rules i.e. $\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$ and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, where ε_{ij} and σ_{ij} are of the LJ potential parameters between sites *i* and *j*. Lennard-Jones potential parameters are listed in Table 2.

Table 2 The Lennard-Jones (LJ) potential parameters for pair atoms interactions use in this work.

Atom-atom Interactions	σ_{ij} (Å)	ε_{ij} (kcal mol^{-1})
O_{water}-O_{water}	3.166	0.1554
C_{CNT}-O_{water} (a)	3.260	0.1144
C_{CNT}-O_{water} (b)	3.260*	0.1230*
B_{BNNT}-O_{water}	3.260	0.1215
N_{BNNT}-O_{water}	3.260	0.1501

Source: * Mashl *et al.* (2003)

The degree of "nanotube hydrophobicity" was varied for all tubes by changing the strength of LJ potential parameter (ε_{O-C}) between water and the nanotube wall as an independent parameter, keeping the size parameter (σ_{C-C}) unchanged. The hydrophobicity was increased by reducing the ε_{O-C} = 0.1143 kcal mol^{-1} (7% reduction) compared to the full value ε_{O-C} = 0.1230 kcal mol^{-1}. These simulations were labeled a, e.g. (9,9)-SWCNTa; simulations with the full potential were labeled to b. Furthermore, this work studied a case which models boron nitride nanotubes (SWBNNT) isostructural to the carbon nanotubes. Still keeping the σ-value constant, we set ε = 0.1216 kcal mol^{-1} and 0.1502 kcal mol^{-1} for the oxygen-boron and oxygen-nitrogen interactions, respectively, as in the work of Won and Aluru, 2000. Already the 7% decrease in hydrophobicity was found to lead to a loss of water conductivity in the (5,5)-SWCNT (Won and Aluru, 2007). Similarly, it was found that in (5,5)-armchair single-walled boron nitride nanotubes (SWBNNT) attractive interactions between water and nitrogen sites were primarily accountable for the good water conduction ability. Therefore, it seemed interesting to look at the diffusion and structural properties of water confined in large diameter tubes also of this type. A pure water box at 298 K was also run for comparison.

The coordinates for the wall atoms were generated with the "Materials Studio" version 4.1 licensed from NANOTEC Thailand. Short pieces of tube were then surrounded by about 2000 SPC/E water molecules in simulation box and *NPT* simulations were started with *P* = 1 atm and temperature lowered from high values to T = 298 K. In a few 10 picoseconds, depending on tube size, the small sections of the tubes were filled with water. Several of these pieces, details see below, were then put together in periodic box and equilibrated before starting the production runs.

All MD simulations were performed in the canonical (*NVT*) ensemble at a temperature of 298 K by using the Nosé-Hoover thermostat implemented in the DL_POLY program package, version 2.17 (Smith *et al.*, 2006). The dimensions of the periodic simulation box for each system were twice the nanotube diameter in the *x*- and *y*- directions and the length of natube in the *z*-direction. The principle axis of the nanotubes was superimposed onto the *z* axis of the simulation box. Periodic boundary conditions were applied to all three directions. The long-range electrostatic interactions between water molecules confined in SWCNTs were computed by using the Ewald method and the short-range van der Waals interactions are computed using the cutoff radius equal to the nanotube diameter (for $n = 9$, 10, and 12) and 18.44 Å (for $n = 14$, 16, and 20). The equations of motion were integrated with a 0.25-fs time step to ensure that there was no drift of energy and temperature throughout the simulations. Starting geometry of the simulation runs are presented in Figure 5.

The systems were equilibrated to the required temperature for 0.25 ns using the velocity rescaling algorithm. After equilibration period, the velocity rescaling was removed and the production runs were conducted for up to 1 ns. During the production runs, the coordinates and velocities were stored every 50 fs for further analyses.

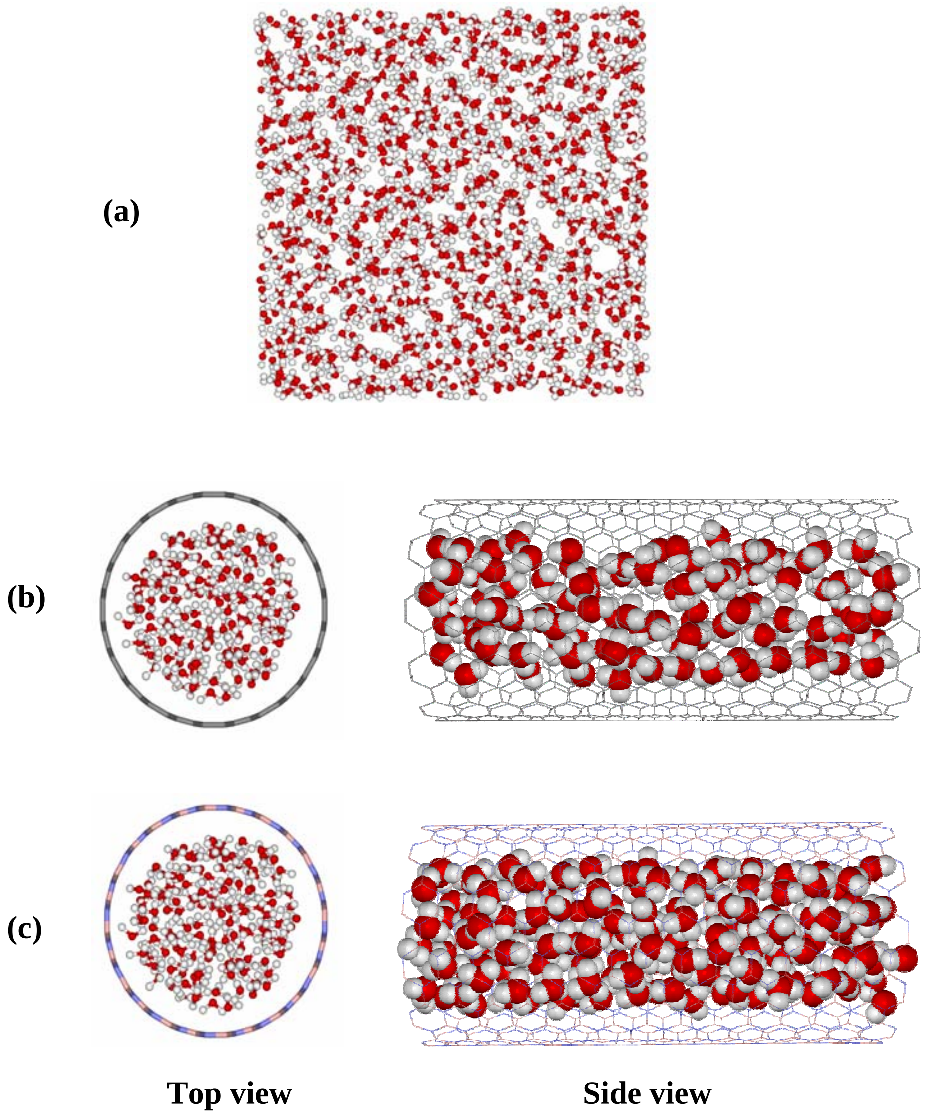


Figure 5 Starting geometry of bulk water**(a)**, water 162 molecules in (12,12)-SWCNT**(b)** and water 162 water molecules in (12,12)-SWBNNT**(c).**

The structure was analyzed by using the pair radial distribution function (*RDF*), $g_{AB}(r)$, specified by the average position r from the center of atom A and B (O_{water} - O_{water}), and r was the radial distance measured in concentric spherical shells from the center of atom A (O_{water}) and cylindrical $g(r)$ distribution functions of water with respect to the center of nanotubes which defined as

$$g_{AB}(r) = \left\langle \frac{dn_{AB}}{dr} \frac{1}{4\pi r^2 \rho_B N_A} \right\rangle \tag{3}$$

where N_A is the number of A centers, ρ_B is the macroscopic density of the B centers and n_{AB} is the number of AB pairs.

The molecular diffusion was analyzed by molecule travels through the time movement of the mean square displacement (*MSD*), which is Einstein expression defined as

$$MSD(t) = \left\langle \left| r_i(t) - r_i(t_0) \right|^2 \right\rangle \tag{4}$$

MSD of confined water molecules was computed in the (*x, y, and z*) directions. The slope of the *MSD* (*t*) was considered for sufficiently long time for it to be in the linear rule, was related to the self-diffusion constant *D*:

$$D = \frac{1}{\delta} \lim_{t \to \infty} \frac{d\left\langle \left| r_i(t) - r_i(t_0) \right|^2 \right\rangle}{dt} \tag{5}$$

where δ depends on the space dimensionality; 6 for three dimensions, 4 for two dimensions and 2 for a dimension.