

# Molecular Dynamics Simulation of Water in Single Wall Carbon Nanotube

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## **Abstract:**

*The overall aim of this study is to calculate some water properties in the single wall carbon nanotubes (SWCNT) and compare them to the bulk water properties to investigate the deviation of water properties inside the SWCNT from those in the bulk. Here some physical and transport properties of water molecules in the single wall carbon nanotube were reported by performing molecular dynamics (MD) simulation. Radial and axial density; hydrogen bond numbering; hydrogen bond distribution and diffusivity of water molecules inside the SWCNT were calculated. Results have good agreements with other researcher results. These calculations show that molecular dynamics simulation would be a reasonable method to analyze the properties of the new nanoscale systems.*

**Keywords:** *molecular dynamics simulation, Gromacs software, Einstein equation, diffusion coefficient.*

## **1. INTRODUCTION**

Carbon nanotubes (CNTs) are one of the most active areas in new technologies. The extraordinary physical, chemical, and mechanical properties [1,2] of carbon nanotubes have made them attractive materials for numerous applications [3,4].

The unique mechanical and electrical properties of carbon nanotubes [5] have prompted an interest for technical application in a number of fields including biosensors [6], atomic force microscopy [7-13]. A key aspect of these applications is the interaction of the surrounding fluid with the carbon nanotube.

The study of water confinement in CNTs would still maintain a high theoretical importance to chemistry, biology, and materials science. [14,

15] In fact, water-filled and water-permeable pores are present in biological cells, membranes, and surface of proteins [16] and in other relevant biological and geological [17] systems that may present a strict analogy with water confined in carbon nanotubes [18].

The Navier-Stokes equation can provide a reasonable description of fluids hydrodynamics only at very small Knudsen numbers. [19] When the system length scale reduces to the nanometer, however, the behavior of the flow is mainly affected by the movements of the discrete particles that compose the system at atomic level [20].

At this scale, Molecular dynamics becomes the most effective way to describe the details of the flow and to study many fundamental nanofluid problems, which can be extremely difficult to

investigate by other means. Molecular dynamics (MD), which can be as accurate as experiments and much easier to perform at the nanoscale, has proven to be the most flexible tool for this kind of analysis. Molecular dynamics simulation is a form of investigation where the motion and the interaction of a certain number of “virtual” atoms or molecules are studied. Molecular simulation is a very powerful toolbox in modern molecular modeling, and enables us to follow and understand structure and dynamics with extreme detail-literally on scales where motion of individual atoms can be tracked.

In the specific field of fluids confined in nanotubes, early works were focused on the behavior of simpler fluids like methane [21,22] ethane [21] ethylene [21] argon [23, 24] helium, [24] neon, [23] and hydrogen [25,14] or water confined in simpler nanopores [15,26-29]. The first article, to our knowledge, dedicated to MD of water in CNTs was written by Gordillo and Martı [30] and followed by many others.

In the present study we examine the structural properties of water surrounding a carbon nanotube by performing detailed, fully atomistic molecular dynamics simulations of a carbon nanotube in water at room temperature.

## 2. CALCULATION METHOD

The carbon nanotub-ewater system is modeled using classical molecular dynamics simulations in the isothermal-isobaric ensemble (NPT). In classical MD simulations atoms move according to the Newtonian equations of motion:

$$m_i \frac{\partial^2 \vec{r}_i}{\partial t^2} = - \frac{\partial}{\partial \vec{r}_i} U_{tot}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N), \quad i=1,2,\dots,N \quad (1)$$

Where  $m_i$  is the mass of atom  $i$ ,  $r_i$  is its position, and  $U_{tot}$  is the total potential energy that depends on all atomic positions. The potential energy is the most crucial part of the simulation because it must faithfully represent the interaction between atoms in the form of a simple mathematical function that can be calculated quickly by a computer [20]. The potential functions that are used in this study are as below:

### 2.1. Carbon-Carbon Interactions

The carbon nanotube is modeled by terms describing Morse bond, harmonic cosine of the bending angle, and a 2-fold torsion potential as:

$$U(r_j, \theta_{ijk}, \phi_{ijkl}) = K_e (\xi_j - 1)^2 + \frac{1}{2} K_{C\theta} (\cos \theta_{ijk} - \cos \theta_C)^2 + \frac{1}{2} K_{C\phi} (1 - \cos 2\phi_{ijkl}) \quad (2)$$

Where

$$\xi_j = e^{-\gamma(r_j - r_C)} \quad (3)$$

and  $\theta_{ijk}$  and  $\phi_{ijkl}$  represent all the possible bending and torsion angles, and  $r_{ij}$  represents all the distances between bonded atoms.  $K_C$ ,  $K_{C\theta}$  and  $K_{C\phi}$  are the force constants of the stretch, bend, and torsion potentials, respectively, and  $r_C$ ,  $\theta_C$ , and  $\phi_C$  the corresponding reference geometry parameters for graphite. The Morse stretch and angle bending parameters were first given by Guo et al. [31] and subsequently used by Tuzun et al. [32]. These parameters, listed in Table 1, were originally derived to describe the geometry and phonon structure of graphite and fullerene crystals.

A Lennard-Jones term is added to the nanotube potential to account for the steric and van der

**Table 1:** Parameters for the carbon interaction potentials [31]

$K_{C_r} = 478.9kJmol^{-1}A^{-2}$	$r_c = 1.418A$
$K_{C_\phi} = 562.2kJmol^{-1}$	$\theta_c = 120.00^\circ$
$K_{C_\phi}^b = 25.12kJmol^{-1}$	$\gamma = 2.1867A^{-1}$
$\epsilon_{CC}^c = 0.4396kJmol^{-1}$	$\sigma_{CC}^c = 3.851A$

**Table 2:** Parameters for the flexible (SPC) water model and the carbon-water potentials [34]

$K_{w_r} = 4637kJmol^{-1}A^{-2}$	$r_w = 1.0A$
$K_{w_\theta} = 383kJmol^{-1}rad^2$	$\theta_w = 109.47^\circ$
$\epsilon_{OO} = 0.6502kJmol^{-1}$	$\sigma_{OO} = 3.166A$

Waals carbon-carbon interaction:

$$U(r_j) = 4\epsilon_c \left[ \left( \frac{\sigma_c}{r_j} \right)^{12} - \left( \frac{\sigma_c}{r_j} \right)^6 \right] \quad (4)$$

## 2.2. Potential Model for Water

The flexible SPC water model by Teleman et al. [33] is described by intramolecular harmonic stretching and bending between the hydrogen and oxygen atoms as

$$U(r_j, \theta_{ijk}) = \frac{1}{2} K_w (r_j - r_w)^2 + \frac{1}{2} K_{w\theta} (\theta_{ijk} - \theta_w)^2 \quad (5)$$

Where  $K_w$  and  $K_{w\theta}$  are the parameters of the potential, and  $r_w$  and  $\theta_w$  the reference bond length and angle, respectively.

Nonbonded interactions between the water

molecules are comprised of a Lennard-Jones term between the oxygen atoms, equation 4, and a Coulomb potential:

$$U(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \quad (6)$$

Where  $\epsilon_0$  is the permittivity in a vacuum, and  $q_i$ ,  $q_j$  are the partial charges,  $q_o = -0.82$  and  $q_H = 0.41$ , respectively. [34] Table 2 shows some parameters of the (SPC) water model and carbon – water potentials:

## 2.3. Carbon-Water Interaction

The carbon-water interaction consists of a Lennard-Jones term between the carbon and oxygen atoms where the parameters of the potential,  $\epsilon_{CO}$  and  $\sigma_{CO}$  are obtained from Bojan and Steele [35] and a quadruple interaction between the carbon atoms and the partial charges on the water hydrogen and oxygen

atoms is as below.

$$U(r) = \frac{1}{3} \frac{q}{4\pi\epsilon_0} \sum_{\alpha,\beta} \Theta_{\alpha,\beta} \frac{3r_\alpha r_\beta - r^2 \delta_{\alpha\beta}}{r^5} \quad (7)$$

Where  $\alpha, \beta$  run over all Cartesian coordinates  $x, y, z$ , and  $r$  is the distance between an O or H charge site and the quadrupole carbon site.  $\delta_{\alpha\beta}$  is the delta function, and  $\Theta_{\alpha,\beta}$  is the quadrupole moment tensor [36].

#### 2.4. Preparing the system for simulation

GROMACS software [37] was selected as the

useful tool to study the properties of water inside the single wall carbon nanotube. Gromacs is a versatile package to perform molecular dynamics, i.e. simulate the Newtonian equations of motion for systems with hundreds to millions of particles.

Our system consists of 216 molecules of water and a single wall carbon nano tube. Simulation was carried out using a fully atomistic system with the maximum size 4\*4\*4 nm. The diameter of SWCNT is 2 nm and its length is 4 nm. Simulation was performed using GROMOS 96 [10,11] force field for 2 ns at the room temperature of 300 K and atmospheric pressure

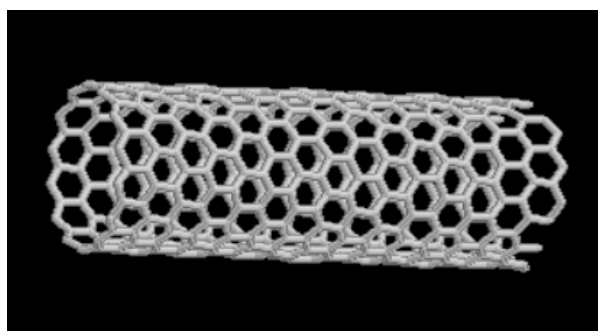


Figure 1: Simulation snapshot of the SWCNT

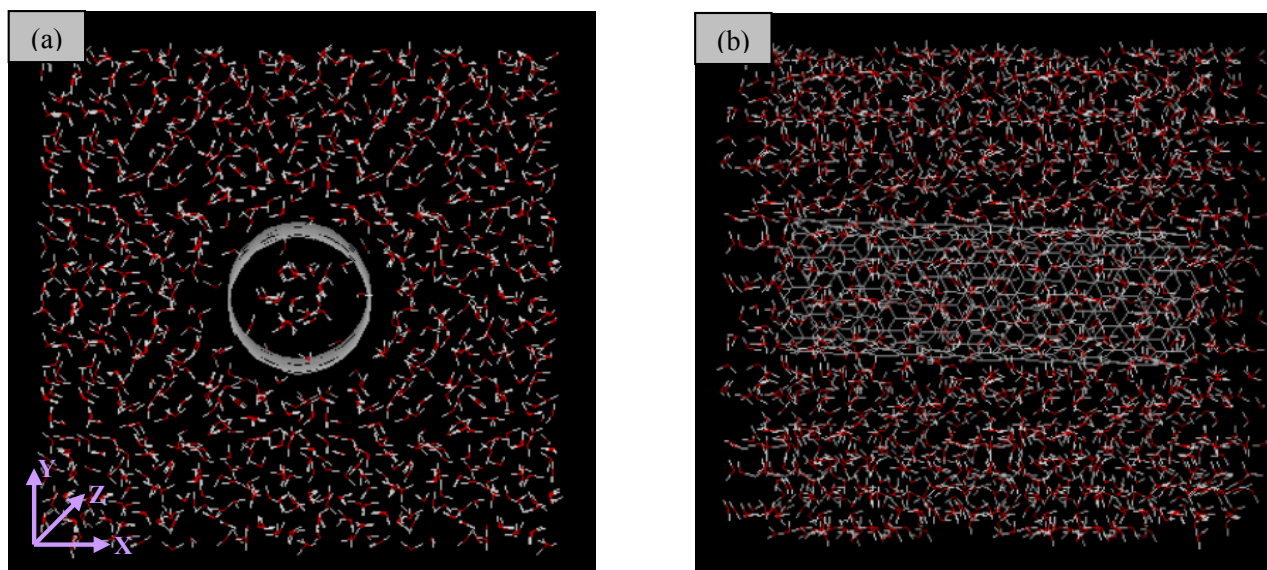


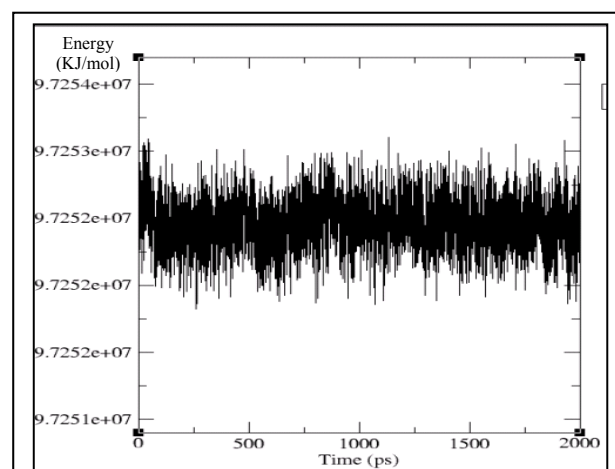
Figure 2: Simulation snapshots of the system (water and SWCNT). Figures are plotted with rasmol software.

(NPT ensemble). The Berendsen algorithm was used to control the temperature and pressure of the system. The boundary condition was selected as periodic type.

The CNT was described by a Morse bond, a harmonic cosine bending angle, a twofold torsion, and a Lennard-Jones (LJ) 12-6 term and water molecules were modeled with the SPC water model. Simulation was performed where the nanotube was in contact with an external water bath and molecules were free to enter and exit the nanotubes from the time zero. The snapshots of SWCNT and system are shown in figures 1 and 2.

### 3. RESULTS AND DISCUSSIONS

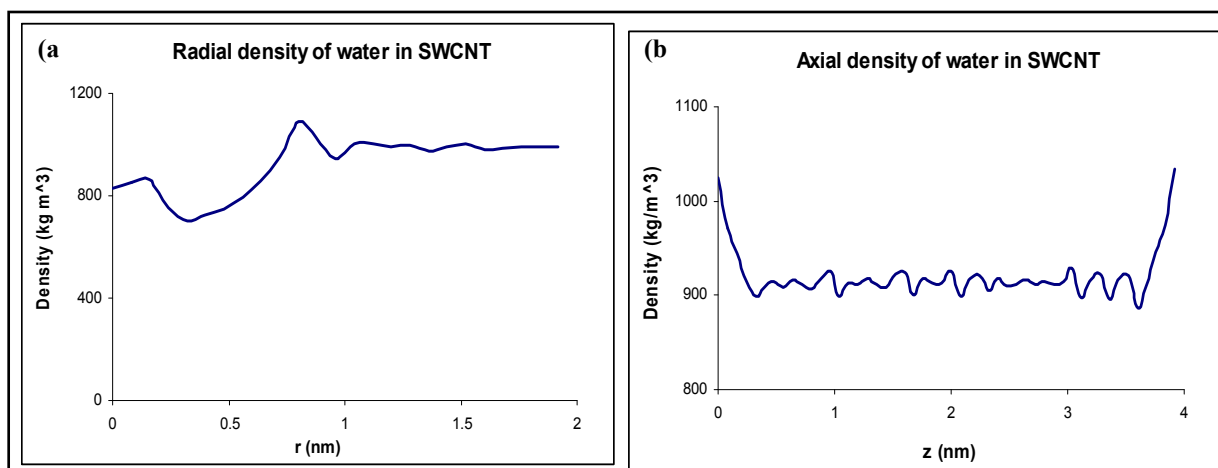
At first the energy minimization of the system was performed for 200 ps. After that MD simulation has been done for 2 ns. The equilibrium state of the system was monitored using the total energy curve versus time. As figure 3 shows the system has no considerable energy fluctuation after 100 ps so the properties of the system can be calculated after this time.



**Figure 3:** Calculated the total energy of the system

#### 3.1. Radial and Axial water density

In the first step the radial and axial density of water molecules in the box were calculated. Figures (4-a) and (4-b) show the results. From figures (4-a) and (4-b), radial density has the maximum peak near the CNT's radius and after that becomes constant equal to the bulk water density while axial density at the enter point and exit point of the carbon nanotube is higher than bulk density but after entrance of water molecules in the nanotube it is coming up and down around the constant value. Carbon



**Figure 4:** (a) Radial and (b) axial density of water in the SWCNT

nanotube has the hydrophobic property so the density of water molecules inside the carbon nanotube is less than of that in the bulk. It can be seen in both radial and axial curves.

### 3.2. Hydrogen Bonds

The H-bond is a special type of attractive interaction that exists between an electronegative atom and a hydrogen atom bonded to another electronegative atom. Each water molecule can form up to four hydrogen bonds at the same time. The average number of H-bonds per molecule calculated in bulk water varies approximately from 2.3 to 3.8 according to the water model and the way used to define the H-bond [38,39]. In MD simulations of water inside the SWCNT, the geometrical definition [40] of H-bond is the most used. A common result of all the articles taken into account is that the average H-bond of water molecules decreases in confined space. This value reaches approximately 1-1.5 bonds for small CNTs, where only a monomolecular layer of water is allowed. The number of layers  $n$  that can be accommodated in a tube with radius  $R_n$  depends on both  $\sigma_{O-O}$  and  $\sigma_{C-O}$  and can be calculated by the following equation [41]:

$$n = 1 + \frac{R_n - \delta_{C-O}}{\delta_{O-O}} \quad (8)$$

Which:

$$\delta_{C-O} = 0.319 \text{ \AA} [30]$$

$$\delta_{O-O} = 3.166 \text{ \AA} [31]$$

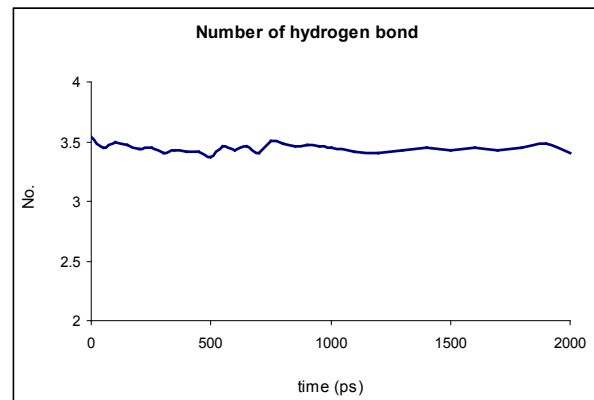
In this study,  $R_n$  is 10 \text{ \AA}. So the number of water layer in this CNT is:

$$n = 1 + \frac{10 - 0.319}{3.166} = 4.06 \cong 4$$

Besides this, the number of hydrogen bond

was calculated. As figure 4 shows the average calculated number of H-bond is around 3.5. Results were compared with previous studies [25] that have good agreements to each other.

In the next step, hydrogen bond distribution was calculated. Figure (6-a) shows the maximum probability of hydrogen bond take place in the center of carbon nanotube. Also Lenard Jones (LJ) potential energy, potential and total energy was calculated (figure 6). These figures have some peaks because of the CNT existing and potential energy has the maximum proportion of the total energy.



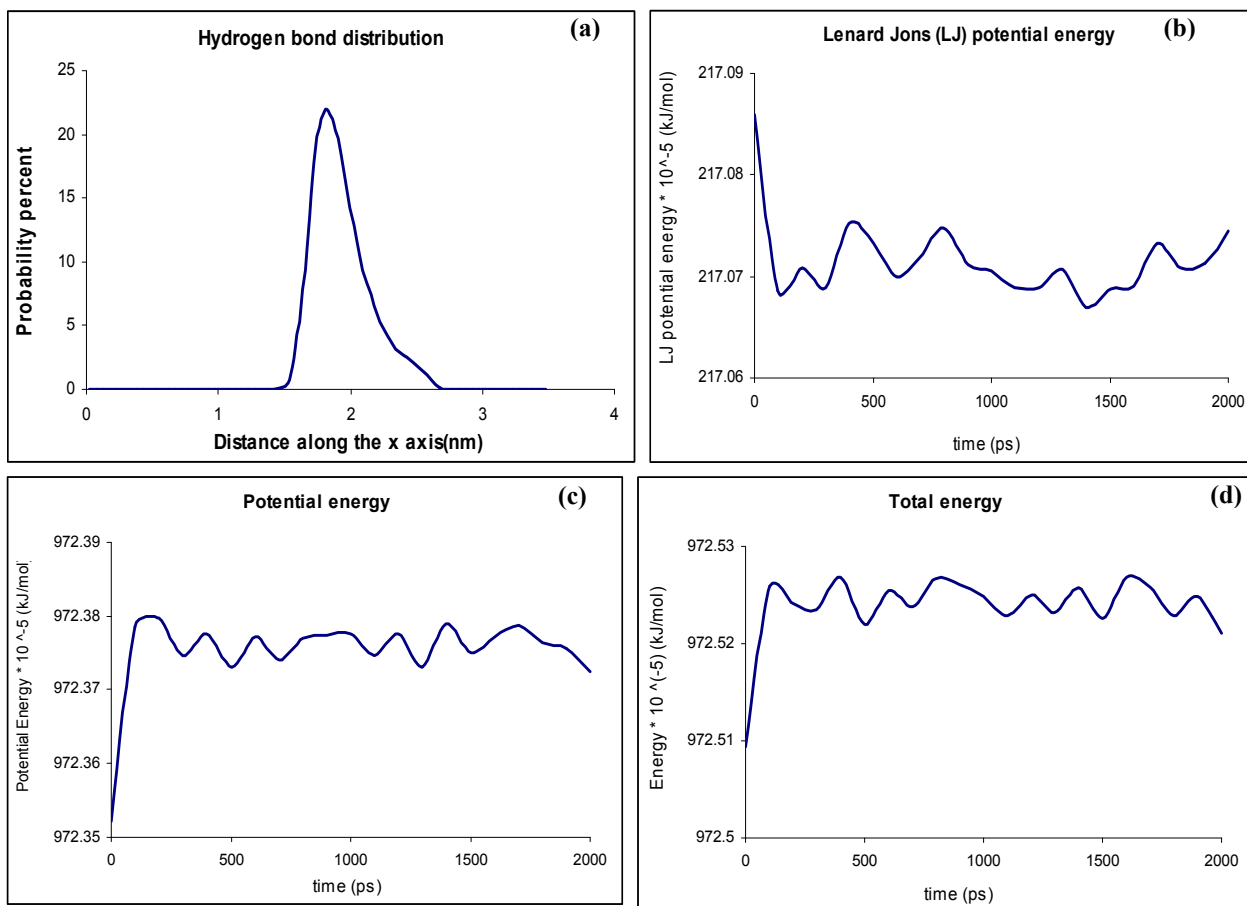
**Figure 5:** Number of calculated hydrogen bond among water molecules in the SWCNT

### 3.3. Water diffusion in carbon nanotube

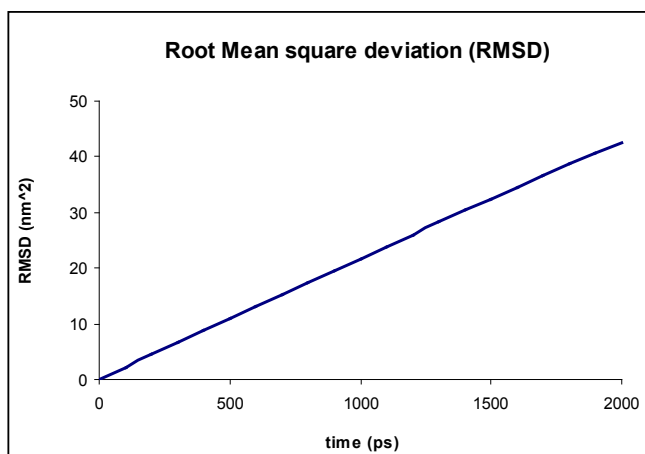
Specific transport properties of water in CNTs such as diffusion coefficient can be calculated from molecular dynamic simulations. Liu and Wang [42] calculate self-diffusivity ( $D$ ) by means of the Einstein [43,44] equations as below.

$$D = \lim_{t \rightarrow \infty} \frac{1}{2k} \langle |r(t) - r(0)|^2 \rangle \quad (9)$$

Where  $r(t)$  is the position of the center of mass of water molecules at time  $t$  and  $k$  is the dimensions



**Figure 6:** (a) Hydrogen bond distribution, (b) Lenard Jones potential energy, (c) potential energy and (d) total energy.



**Figure 7:** Root mean square deviation of water molecules inside CNT.

of the system. To obtain diffusion coefficient of water inside the SWCNT using this equation it is necessary to calculate the root mean square displacement (RMSD). Result is shown in figure 7. The MSD behavior of water molecules inside the SWCNT versus time is linear so Einstein equation can be used to calculate the diffusion coefficient. The calculated value is equal to  $3.29 \times 10^{-5} \text{ cm}^2/\text{s}$  that has a good agreement with previous studies ( $3.1 \times 10^{-5} \text{ cm}^2/\text{s}$  [45]). Because of the hydrophobicity of SWCNT, the water diffusion coefficient inside the SWCNT is less than it from the bulk.

#### 4. CONCLUSIONS

In this study some physical and transport properties of water molecules inside the single wall carbon nano tube were calculated using molecular dynamics simulation. Radial density of water molecules inside the SWCNT has a maximum peak near the CNT's radius and after that becomes constant equal to the water density, but axial density in the box is coming up and down around a constant value. These calculations provide a picture of how water molecules arrange themselves inside a SWCNT and produce a certain value of density across the diameter and axial axes. Water molecules form 4 layers of  $\text{H}_2\text{O}$  inside the SWCNT. The number of calculated hydrogen bond in the SWCNT is about 3.5 and the hydrogen bond distribution has the maximum peak at the center of the box. Hydrogen bond distribution decreases in the points near the box wall because of the decreasing the number of water molecules in all directions. Lenard Jones potential has some peak because of the CNT existing. The mean square displacement of water molecules is linear with time so Einstein equation was used

to calculate the diffusion coefficient of water molecules inside the SWCNT. The calculated diffusion coefficient of water molecules inside the SWCNT is  $3.29 \times 10^{-5} \text{ cm}^2/\text{s}$  which is 67% of the diffusion coefficient of water molecules in the bulk ( $5.1 \times 10^{-5} \text{ cm}^2/\text{s}$ ). These results show that there are some differences between properties of pure water system and water-CNT system. Also molecular dynamics simulation method can be a good method to calculate the properties of the new nanoscale systems instead of experiments studies.

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