Transport of a Liquid Water-Methanol Mixture in a Single Wall Carbon Nanotube

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Abstract:
In this work, a molecular dynamics simulation of the transport of water - methanol mixture through the single wall carbon nanotube (SWCNT) is reported. Methanol and water are selected as fluid molecules since water represents a strongly polar molecule while methanol is as an intermediate between polar and strongly polar molecules. Some physical properties of the methanol-water mixture such as radial and axial density, hydrogen bonding, number of contacts and minimum distance between mixture and SWCNT molecules and also diffusivity of the mixture as a transport property were calculated during the simulation. Results showed that mixture of the selected molecules inside SWCNT have different properties during transport along the SWCNT in comparison with pure fluids inside SWCNT. Also methanol molecules diffuse faster than water molecules inside nanotube due to a weaker hydrogen bonding network. These differences among physical properties of the fluids inside SWCNT can be a key parameter for designing the new separation equipments and sensors using SWCNT.
Keywords: Molecular Dynamics Simulation, Diffusion, Hydrogen bond, minimum distance.

1. INTRODUCTION

Carbon nanotubes (CNTs) are one of the most active areas in new technologies. The extraordinary physical, chemical, and mechanical properties of carbon nanotubes have made them attractive materials for numerous applications [1,2].The unique mechanical and electrical properties of carbon nanotubes [3] have prompted an interest for technical application in a number of fields including membranes, biosensors [4], atomic force microscopy [5]. A key aspect of these applications is the interaction of the surrounding fluid with the carbon nanotube. In macroscopic scale the Navier-Stokes equation can provide a reasonable description of fluids hydrodynamics only at very small Knudsen

numbers [6]. 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 the atomic level [7]. At this scale, molecular modeling becomes the effective methods. Among them molecular dynamics (MD) simulation is 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 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 a pure and simple fluids like methane [8, 9] ethane[8] ethylene[8] argon[10, 11] helium, [11] neon,[10] and hydrogen [12,13] or water confined in simpler nanopores [14,15-16]. The first article, to our knowledge, dedicated to MD of water in CNTs was written by Gordillo and Martı [17] and followed by many others [18-23]. In all previous studies, the movement of a pure component was investigated in the SWCNT while in many industrial applications it is necessary to know the properties of a mixture in the CNT's. In the present study, we examine the properties of both pure and mixture liquids in the SWCNT. Our study can be divided to these sections:

- Molecular Dynamics Simulation Methodology
- Calculation the properties of water in the SWCNT
- Calculation the properties of methanol in the SWCN
- Calculation the properties of a mixture of water-methanol (50 %mol) in the SWCNT

2. MODELS AND SIMULATION METHODOLOGY

2.1. Simulation Methodology

Molecular dynamics simulation method was used to investigate the physical properties of components in the SWCNT. Molecular dynamics simulation involves integration of Newton's equation of motion for each atom in an ensemble in order to generate information on the variation in the position, velocity, and acceleration of each particle as a function of time. The equations solved are [24]:

$$f_i = m_i a_i \tag{1}$$

$$f_i = -\frac{\partial U}{\partial r_i} \tag{2}$$

Where f_i is the force exerted on the ith atom, m_i is its mass, and a_i is its acceleration. The force acting on each atom is obtained from a potential function U, such as that depicted below [24]:

$$U = \sum_{bond} \frac{k_{ij}^b}{2}(r_{ij} - r_{ij}^{eq})^2 + \sum_{angle} \frac{k_{ijk}^\theta}{2}(\theta_{ijk} - \theta_{ijk}^{eq})^2 + \tag{3}$$

$$\sum k^\phi \left[1 + \cos(n(\phi - \phi^{eq}))\right] + \sum_{i<j} \left[\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6} + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}\right]$$

where the first three terms reflect intramolecular interactions between covalently bonded atoms and the last term describes the non-bonded interactions (van der Waals and electrostatic). The constants k^b, k^θ, and k^ϕ are force constants for the covalent bonds, bond angles, and dihedrals, respectively, r_{ij} are the distances between atoms i and j, A_{ij} and B_{ij} are the Lenard Jones parameters, and q is a partial charge
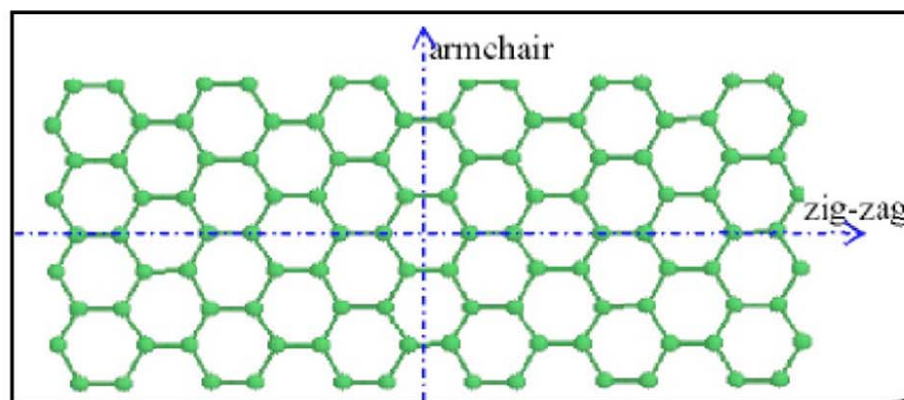

Figure 1: A hexagonal graphite sheet to create a zig-zag or armchair nanotube by rolling up along x or y axis

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[24]. Simulations were performed using Gromacs software [25] and visualization was done by VMD V.3.1 package [26].

2.2. Model Systems

A single-walled carbon nanotube can be viewed as a graphite sheet that is rolled up into a cylinder. As shown in Figure 1, either the zig-zag (n,0) nanotube along x axis or the armchair (n,n) nanotube along y axis can be formed, where the index (n,m) indicates the helical structure of a nanotube. In this study, we construct the armchair (n,n) nanotube.

The applied carbon nanotube is modeled by terms describing morse bond, harmonic cosine of the bending angle, and a 2-fold torsion potential as equation 4:

$$U(r_{ij}, \theta_{ijk}, \phi_{ijkl}) = K_{Cr}(\xi_{ij} - 1)^2 +$$
$$\frac{1}{2}K_{C\theta}(\cos\theta_{ijk} - \cos\theta_C)^2 +$$
$$\frac{1}{2}K_{C\phi}(1 - \cos 2\phi_{ijkl})$$

(4)

where

$$\xi_{ij} = e^{-\gamma(r_{ij} - r_C)}$$

(5)

and θ_{ijk} and ϕ_{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, θ_C, and ϕ_C the corresponding reference geometry parameters for graphite. The Morse stretch and angle bending parameters were first given by Guo et al.[27] and subsequently used by Tuzun et al [11]. These parameters, listed in Table 1, were originally derived to describe the geometry and phonon structure of graphite and fullerene crystals.

A binary mixture of water and methanol is examined in this study. The simple point charge (SPC) model of Berendsen et. al [28] was used to describe water-water interactions. The SPC model gives reasonable structural and thermodynamics properties, such as

liquid density, heat of vaporization and diffusion constant as compared with experimental data [28]. This model is described by intra-molecular harmonic stretching and bending between the hydrogen and oxygen atoms as equation 6:

$$U(r_{ij}, \theta_{ijk}) = \frac{1}{2}K_{Wr}(r_{ij} - r_W)^2 + \frac{1}{2}K_{W\theta}(\theta_{ijk} - \theta_W)^2$$

(6)

Where K_{wr} and $K_{W\theta}$ are the parameters of the potential; r_W and θ_W are the reference bond length and angle, respectively.

Non-bonded interactions of water molecules are comprised of a Lennard-Jones (LJ) term between the oxygen atoms, and a Coulomb potential:

$$U(r_{ij}) = \frac{1}{4\pi\varepsilon_0}\frac{q_i q_j}{r_{ij}}$$

(7)

where ε_0 is the permittivity in a vacuum, and q_i, q_j are the partial charges[29]. Table 2 shows some parameters of the SPC water model.

Table 1: *Parameters for the carbon interaction potentials [27]*

$K_{Cr} = 478.9 kJmol^{-1}A^{-2}$	$r_C = 1.418A$
$K_{C\phi} = 562.2 kJmol^{-1}$	$\theta_C = 120.00^0$
$K_{C\phi}{}^b = 25.12 kJmol^{-1}$	$\gamma = 2.1867 A^{-1}$

Table 2: *Parameters for the SPC water model and the carbon-water potentials [30]*

$K_{Wr} = 4637 kJmol^{-1}A^{-2}$	$r_W = 1.0A$
$K_{W\theta} = 383 kJmol^{-1}rad^2$	$\theta_W = 109.47^0$
q_O= - 0.82	q_H= 0.41

For methanol molecules, a number of simple models have been previously proposed. The models proposed by Jorgensen et al.[30] and by Haughneyet al.[27] have been widely used for liquid simulations. Both models give results for a range of properties that are in good agreement

Table 3: *Lenard-Jonzes parameters and partial charges for water, Methanol and nanotube.*

	Site	σ (nm)	ε (kJ/mol)	q (e)
H$_2$O				
	O	0.31656	0.1554	-0.82
	H	0.0	0.0	0.41
CH$_3$OH				
	CH$_3$	0.3775	0.8661	0.265
	O	0.3070	0.7113	-0.7
	H	0.0	0.0	0.435
Nanotube				
	C	0.34	0.2328	0.0

with the available experimental values. In our simulations, each methanol molecule is described with the model for optimized potentials for liquid simulations (OPLS) proposed by Jorgensen et al. [30], because Jorgensen's model can reproduce both gas-phase dimmer properties and liquid density at ambient temperature and pressure. In the OPLS model, three interaction sites are positioned on the oxygen (O) nuclei, hydroxyl proton (H), and united methyl (CH$_3$) group centered on the carbon (C), respectively. Table 3 shows LJ parameters and partial charges for methanol, water and nanotube.

2.3. System Preparation

Here, a detailed comparison among physical properties of the molecules in the pure and mixture fluids along SWCNT has been performed by using three simulation systems defined as below:

2.3.1. Water Transport through SWCNT
The system consists of 216 molecules of water and a single wall carbon nanotube with the diameter of 2 nm and the length of 4 nm. CNT type is armchair. The box size is 4nm × 4nm × 4nm. Simulation was performed for 2 ns at the NVT ensemble. The Berendsen algorithm was used to control the temperature of the system. The boundary condition was selected as periodic type.

2.3.2. Methanol Transport through SWCNT

The system consists of 216 molecules of methanol and a single wall carbon nanotube with the diameter of 2 nm and the 4 nm length. CNT type is armchair. The box size is 4nm × 4nm × 4nm. Simulation was performed for 2 ns at the NVT ensemble. The Berendsen algorithm was used to control the temperature of the system. The boundary condition was selected as periodic type.

2.3.3. Methanol-Water Mixture Transport through SWCNT
216 molecules of water and 216 molecules of methanol were selected to examine transport properties of the mixture (50 % mol) in the CNT according above specification at 300 K for 2 ns. The selected CNT and simulated systems are shown in Figure 2.

3. RESULTS AND DISCUSSION

For the different systems as defined in the previous sections, MD calculations were performed. Results are shown in the following sections:

3.1. Density

At the first step, the radial and axial densities of the molecules were calculated inside SWCNT. As Figures 3 and 4 show for both systems (Water-CNT, Methanol-CNT), radial densities have the
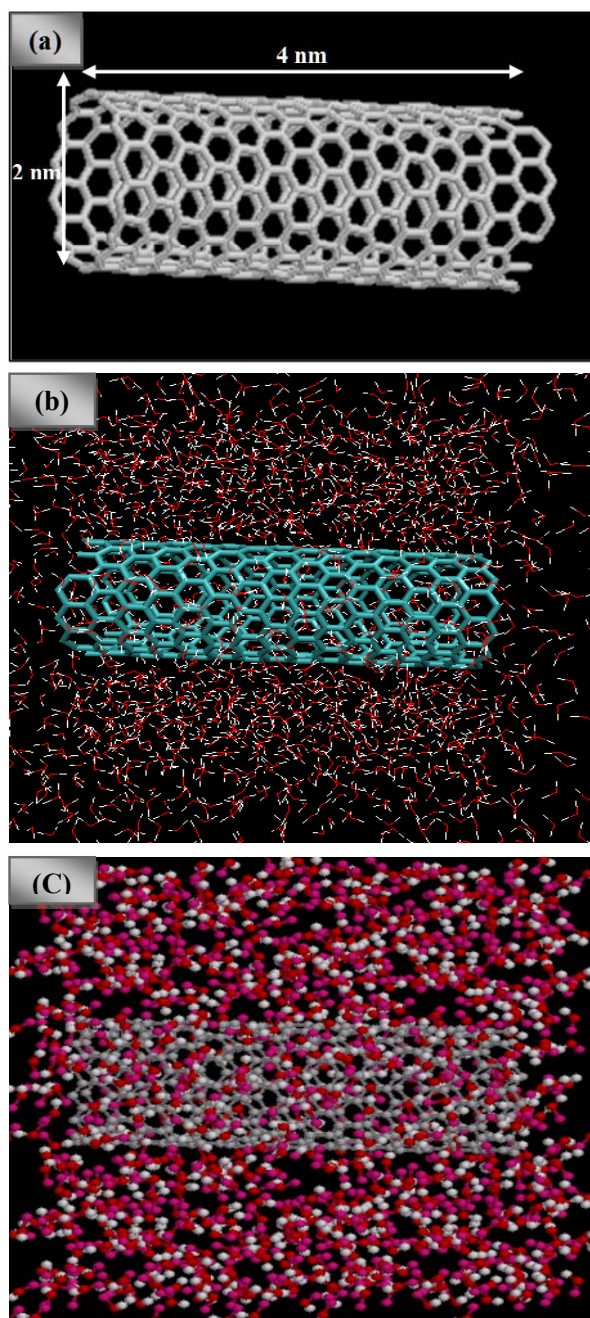
Figure 2: (a) CNT configuration and size, (b) Water-CNT simulated system, (c) methanol-CNT simulated system.

maximum peak near the CNT's wall and after that density reaches to the constant value equal to the bulk density while axial density at the entrance and exit point of the carbon nanotube is higher than that of bulk density. Howevr, upon molecules entrance
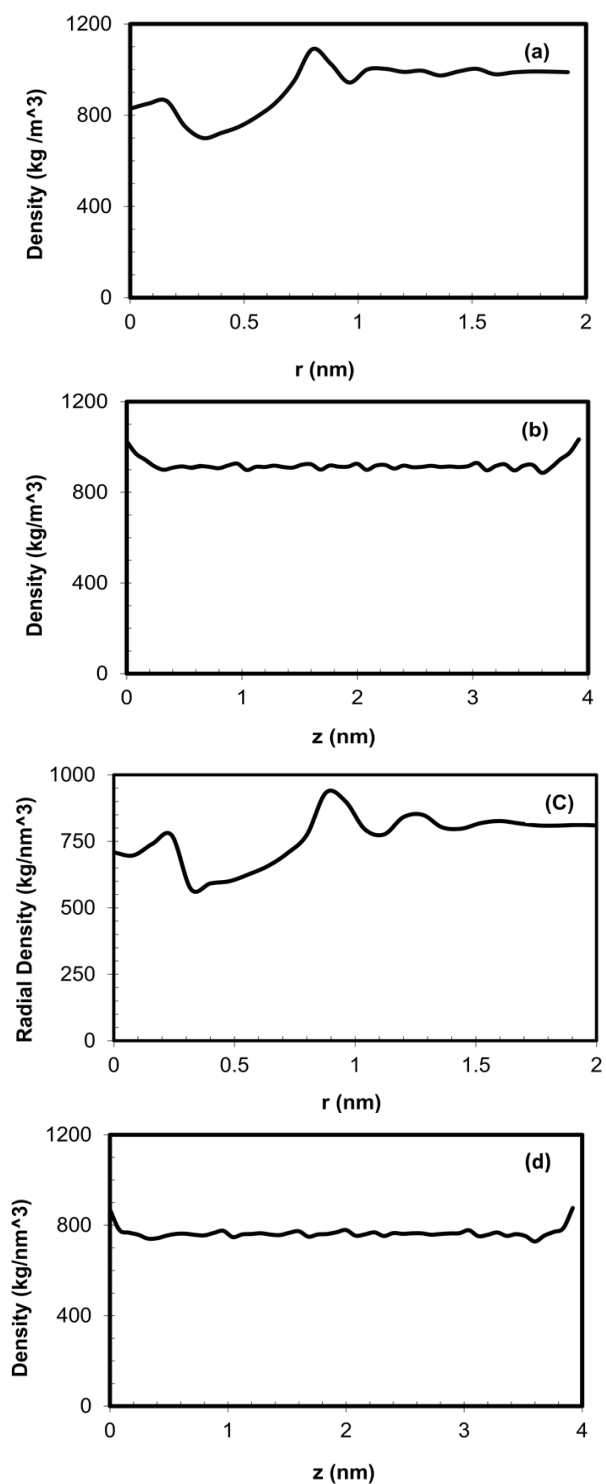
Figure 3: (a) Radial density of water in water-CNT system, (b) Axial density of water in water-CNT system, (c) Radial density of methanol in methanol-CNT system, (d) Axial density of methanol in methanol-CNT system.
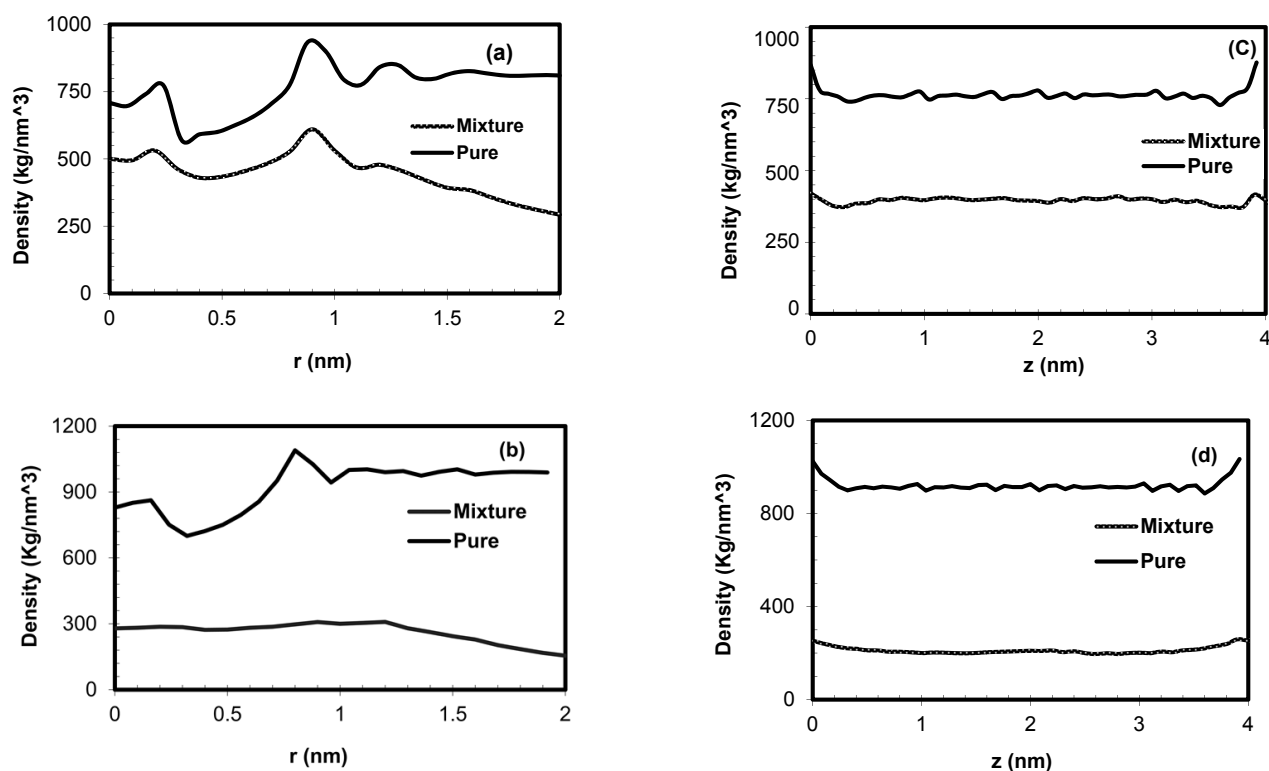
Figure 4: (a) Radial density of methanol in water-methanol-CNT system, (b) Radial density of water in water-methanol-CNT system, (c) Axial density of methanol in water-methanol-CNT system, (d) Axial density of water in water-methanol-CNT system.

to the nanotube, it is coming up and down around the constant value. The fluctuation of this property in the Water-CNT system is more than that of the Methanol-CNT system. In the mixture, above observation can be seen for methanol molecules but there is no peak for radial density of water molecules and the absolute value of the curves for both components is less than that of the pure state.

3.2. Hydrogen Bonding

The averaged number of H-bonds per molecules for different systems is shown in Figure 5 and table 4. The hydrogen bond numbering between water molecules at Water-CNT system is about 3.5, while this value is about 1.2 for methanol molecules at Methanol-CNT system. The hydrogen bond numbering for mixture inside the CNT decreases for both components ranges from 0.5-1.2. In the mixture, new hydrogen bonding between methanol and water molecules was created which decreases

the hydrogen bonding between pure molecules. Totally, the summation of the hydrogen bonding at any time is less than those of pure fluids inside SWCNT.

3.3. Diffusion

To calculate the diffusion coefficient of the molecules inside SWCNT by MD calculation, it is necessary to calculate the mean square displacement (MSD) of the molecules, at first. Figure 6 shows the MSD of water and methanol molecules inside SWCNT and Figure 7 shows the MSD of the mixture inside SWCNT. All systems the MSD curves have the linear trend versus time which shows the diffusive behavior of the fluids inside SWCNT. To calculate the self diffusion coefficient (D_α^s) of the molecules inside nanotube Einstein equation can be used as follows:
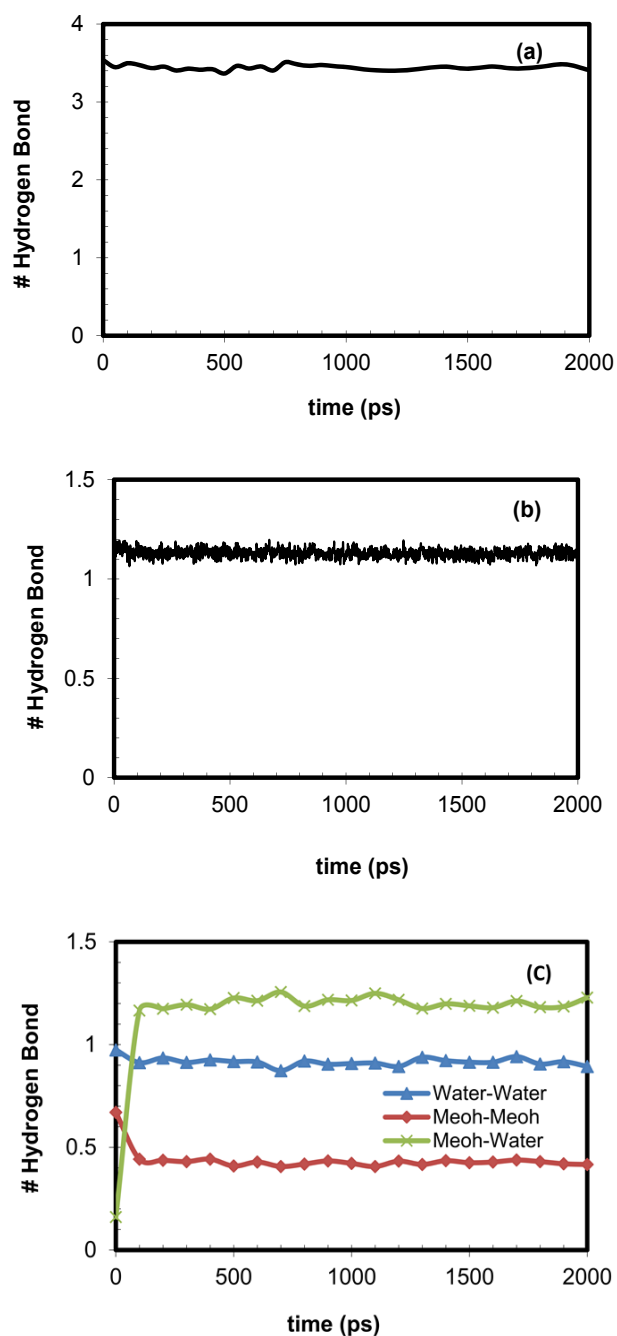
(6)

$$D_\alpha^s = \frac{1}{2dN_\alpha} \lim_{t\to\infty} \left\langle \sum_{i=1}^{N_\alpha} (r_i^\alpha(t) - r_i^\alpha(0))^2 \right\rangle$$

Where Nα is the number of molecules of component α, d is the dimension of the system, t is the time, and r_i^α is the center of mass of molecule i of component α. Results are shown in table 5. The diffusion coefficient of water molecules inside CNT in the mixture decreases rather than pure water inside SWCNT while for methanol molecules this value increases during mixture transport along SWCNT. Also in the mixture, the self diffusion coefficient of methanol is more than water molecules which shows the faster dynamics movement of methanol inside CNT, This maybe because of the weaker hydrogen bond network between methanol molecules rather than water. In table 5, the deviation of diffusion coefficient of water and methanol molecules inside CNT rather than pure components (bulk) was reported.

3.4. Minimum Distance

Finally, the minimum distance and the number of contacts of water and methanol molecules in the mixture with the SWCNT wall were calculated. Figure 8a shows that the number of contacts for methanol molecules is more than two-fold in comparison with the water molecules. This curve has the local maximum and minimum points at some special times. Figure 8b shows that water molecules have the nearly constant distance with the SWCNT wall during the simulation time while for methanol molecules this distance has some more vibration because of the more and unconstant number of contacts of the methanol molecules.

4. CONCLUSIONS

In this work, MD simulations were performed to study the physical properties of the pure components and the mixture of water-methanol (50 mol %) through a single wall carbon nanotube. Density analysis showed that radial densities of the molecules inside the SWCNT have a maximum peak near the CNT's wall and after that become constant equal to the bulk

Figure 5: (a) Number of hydrogen bonding among water molecules in the water-CNT system, (b) Number of hydrogen bonding among methanol molecules in the methanol-CNT system, (c) Number of hydrogen bonding among water, methanol and water-methanol molecules in the water-methanol-CNT system.

Table 4. *Averaged number of hydrogen bonds per molecule.*

H-bond Numbering / System	H-bond Water - Water	H-bond Methanol - Methanol	H-bond Water-Methanol
Experiment			
Pure Methanol	-	1-3 [30]	-
Pure Water	3-4 [30]	-	-
Methanol - Water	-	-	1 [31]
Modeling			
Water-CNT	3.50	-	-
Methanol-CNT	-	1.20	-
Water-Methanol-CNT	0.93	0.46	1.20

Table 5. *Calculated diffusion coefficients inside SWCNT at the different systems*

System	Diffusion Coef. (cm²/s)		Percent Deviation from pure component	
	D_water	D_methanol	Water	Methanol
Pure water	5.100×10^{-5} [30]	-	-	-
Pure methanol	-	2.2×10^{-5} [30]	-	-
Water inside CNT	3.100×10^{-5}	-	-39.22	-
Methanol inside CNT	-	3.310×10^{-5}	-	+50.45
Methanol-Water inside CNT	2.802×10^{-5}	3.930×10^{-5}	-45.05	+78.63

density, but axial density in the box is fluctuating around a constant value. These calculations provide a picture of how water and methanol molecules arrange themselves inside a SWCNT and produce a certain value of density across the diameter and axial axes. Total calculated number of hydrogen bond for the mixture inside SWCNT was between those values for two pure systems. This shows the new hydrogen bond formation between water and methanol molecules in the mixture. The diffusion coefficient of water molecules in the mixture was decreased along the SWCNT but this value was increased for methanol molecules. Totally methanol molecules can move faster than water molecules because of their weaker hydrogen bond network. This observation has been seen by the analysis of the minimum distance and number of contacts of the molecules inside SWCNT. All results showed that methanol molecules have faster dynamics behavior rather than water molecules in the mixture of water-methanol-CNT system. Understanding the different physical and transport properties of the mixture along SWCNT can be useful for designing the new nano-scale systems.

REFERENCES

1. Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. Science 2002, 297, 787.

2. Martin, C. R.; Kohli, P. Nat. ReV. Drug DiscoVery 2003, 2, 29.
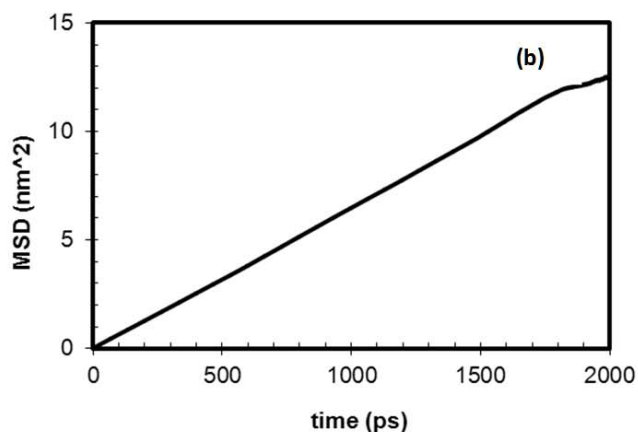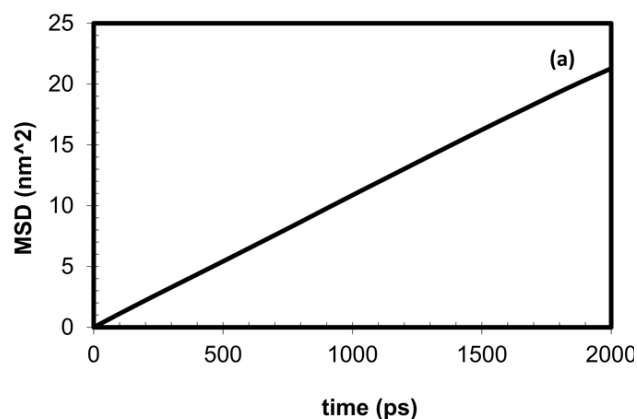
Figure 6: (a) MSD of water molecules along z axis in water-CNT system, (b) MSD of methanol molecules along z axis in methanol-CNT system.
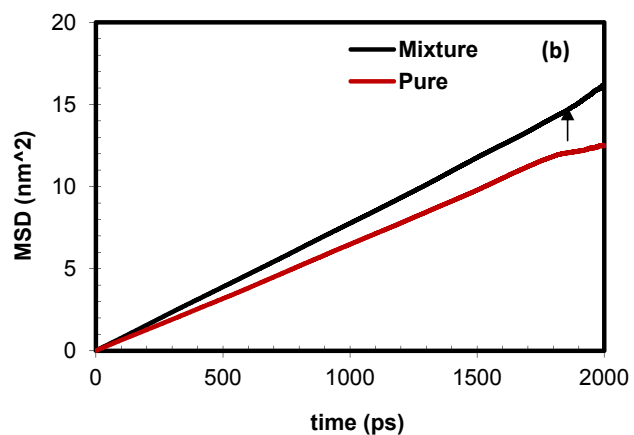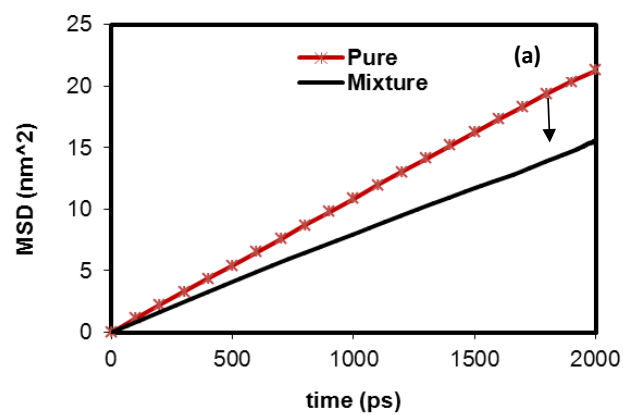
Figure 7: (a) MSD of water molecules along z axis in water- methanol-CNT system, (b) MSD of methanol molecules along z axis in water - methanol-CNT system.
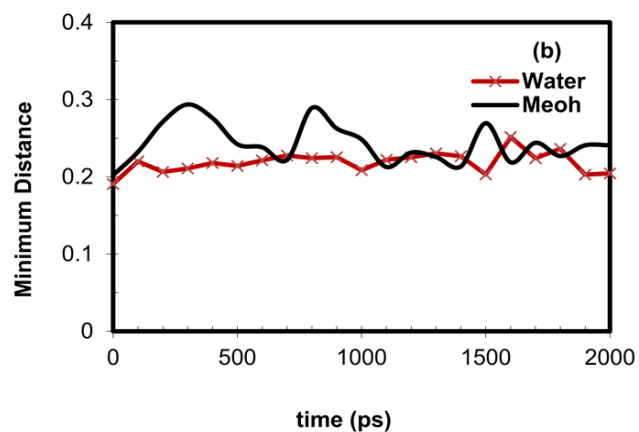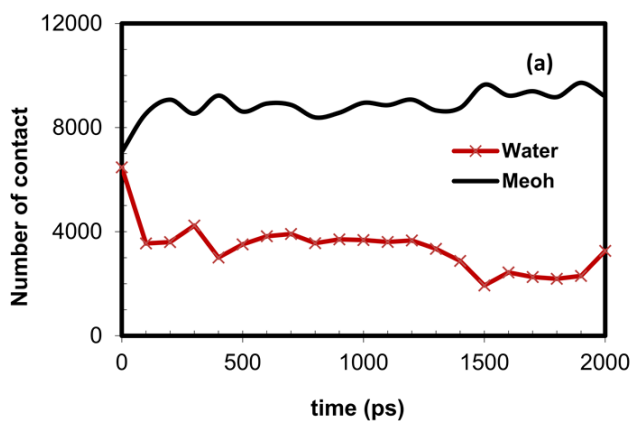
Figure 8: (a) Number of contacts of water and methanol with CNT wall in water-methanol-CNT system, (b) Minimum distance of water and methanol with CNT wall in water-methanol-CNT system.

3. Odom, T. W., Huang, J.-L., Kim, P. &Lieber, C. M. 2000 Structure and electronic properties of carbon nanotubes. J. Phys. Chem. B. 104, 2794-2809.

4. Balavoine, F., Schultz, P., Richard, C., Mallouh, V., Ebbesen, T. W. &Mioskowski, C. 1999 Helical crystallization of proteins on carbon nanotubes: A first step towards the development of new biosensors. Angew. Chem. 38 (13/14), 1912-1915.

5. Li, J., Cassell, A. M. & Dai, H. 1999 Carbon nanotubes as AFM tips: Measuring DNA molecules at the liquid/solid interface. Surface and Interface Analysis. 28, 8-11.

6. Travis, K. P.; Todd, B. D.; Evans, D. J. Phys. ReV. E 1997, 55, 4288.

7. AlessioAlexiadis and Stavros Kassinos., Molecular simulation of water in carbon naotube., Chem. Rev. 2008, 108, 014-5034.

8. Mao, Z. G.; Sinnott, S. B. J. Phys. Chem. B 2000, 104, 4618.

9. Sokhan, V. P.; Nicholson, D.; Quirke, N. J. Chem. Phys. 2002, 117, 8531.

10. Ackerman, D. M.; Skoulidas, A. I.; Sholl, D. S.; Johnson, J. K. Mol. Simul. 2003, 29, 677.

11. Tuzun, R. E.; Noid, D. W.; Sumpter, B. G.; Merkle, R. C. Nanotechnology 1996, 7, 241.

12. Liu, C.; Fan, Y. Y.; Liu, M.; Cong, H. T.; Cheng, H. M.; Dresselhaus, M. S. Science 1999, 286, 1127.

13. Cheng, H. S.; Cooper, A. C.; Pez, G. P.; Kostov, M. K.; Piotrowski, P.; Stuart, S. J. J. Phys. Chem. B 2005, 109, 3780.

14. Sansom, M. S. P.; Kerr, I.D.; Breed, J.; Sankararamakrishnan, R. Biophys. J. 1996, 70, 693.

15. Allen, T. W.; Kuyucak, S.; Chung, S. H. J. Chem. Phys. 1999, 111, 7985.

16. Travis, K. P.; Gubbins, K. E. J. Chem. Phys. 2000, 112, 1984.

17. Gordillo, M. C.; Martı´, J. Chem. Phys. Lett. 2000, 329, 341.

18. Ziarani, A.S. and Mohamad, A.A., "A molecular dynamics study of perturbed Poiseuille flow in a nanochannel ", Microfluidics and Nanofluidics, Vol. 2, No 1, pp.12-20, 2006.

19. Zhang, W. and Li, D., "Simulation of low speed 3D nanochannel flow", Microfluidics and Nanofluidics,

Vol. 3, No. 4 , pp.417-425, 2007

20. Mansoori, G.A., "Principles of Nanotechnology: Molecular-Based Study of Condensed Matter in Small Systems", world Sci. Pub. Co., Hackensack, NJ, 2005.

21. Keshavarzi, T., Sohrabi, R. and Mansoori, G. A., "An Analytic Model for Nano Confined Fluids Phase-Transition: Applications for Confined Fluids in Nanotube and Nanoslit", J. Comput. Theor.Nanosci, Vol. 3, No. 1, pp.134-141, 2006.

22. Kamalvand, M. and Keshavarzi, E., Mansoori, G. A., "Behavior of the Confined Hard-Sphere Fluid within Nanoslits: A Fundamental-Measure Density-Functional Theory Study", Int'l J. Nanoscience, Vol. 7, Nos. 4&5, pp.245-253, 2008.

23. F. Heidari, T. Keshavarzi and G. A. Mansoori, Attractive energy contribution to nanoconfined fluids behavior: the normal pressure tensor, Microfluidics and Nanofluidics, Volume 10, Number 4, 899-906, 2011.

24. Xiang, T., Anderson, B., "Liposomal drug Transport: A molecular perspective from molecular dynamics simulations in lipid bilayers", Advanced Drug Delivery Reviews, 58, 1357-1378, (2003).

25. Lindahl, E., Hess, B. and Van der Spoel, D. GROMACS 3.0: "a package for molecular simulation and trajectory analysis, J Mol Model, 7:306–317, (2001).

26. Humphrey. W., Dalke. A., Schulten. K., J. Molec. Graphics, 14.1 (1996) 33-38.

27. Guo, Y.; Karasawa, N.; Goddard, W. A. III. Nature 1991, 351, 464-467.

28. Berendsen H. J. C., J. P. M. Postma, W. F. von Gunsteren, and J. Hermans, Intermolecular Forces sReidel, Dordrecht, (1981).

29. Jarvis, S. P., Uchihashi, T., Ishida, T. &Tokumoto, H. 2000 Local solvation shell measurement in water using a carbon nanotube probe. J. Phys. Chem. B. 104 (26), 6091-6094.

30. Perry, R. H., "Perry's chemical engineer's handbook", McGraw-Hill Company, fifth ed., (1984).

31. Farhadian N., Shariaty-niassar M., Calculation of Physical Properties of the Methanol-Water Mixture Using Molecular Dynamics Simulation., Iranian Journal of Chemical Engineering, Vol. 6, No. 4 (Winter), 2009, IAChE.

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