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The structure and dynamics of water inside armchair carbon nanotube

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In this paper we present some simulation results about the behaviour of water molecules inside a single wall carbon nanotube (SWNT). We find that the confinement of water in an SWNT can induce a wave-like pattern distribution along the channel axis, similar phenomena are also observed in biological water channels. Carbon nanotubes(CNTs) can serve as simple nonpolar water channels. Molecular transport through narrow CNTs is highly collective because of tight hydrogen bonds in the protective environment of the pore. The hydrogen bond net is important for proton and other signal transports. The average dipoles of water molecules inside CNTs (7,7), (8,8) and (9,9) are discussed in detail. Simulation results indicate that the states of dipole are affected by the diameter of SWNT. The number of hydrogen bonds, the water–water interaction and water–CNT interaction are also studied in this paper.

Keywords: carbon nanotube, molecular dynamics simulation, water channel
PACC: 0520D, 0540

1. Introduction

Transport of water through narrow pores is important in chemistry, biological and technical processes.[1−3] The behaviour of water confined in narrow pores differs considerably from bulk behaviour, as the characteristic dimensions of the confining volume reduce to the nanometre scale.[4] Microscopic fluctuations play a key role, and it no longer makes sense to describe the permeant fluid as a continuum. This is a grey area where our understanding of physicochemical processes is perhaps the fuzziest and is clouded by controversy.[1,5−7]

Carbon nanotubes are molecular-scale tubes of graphitic carbon with outstanding properties.[8−12] Many potential applications have been proposed, including hydrogen storage media, molecule separation devices, probes and sensors *et al.*[13−17] Carbon nanotubes form structurally simple channels—similar in both size and hydrophobic character to protein channels, and can be filled with water in ambient conditions. It is a properly simple model of channels to exploit primary characteristics of those biological channels, considering the complex structure of membranes and membrane-water interactions. A key step of developing novel nanomedicine technologies consists in delivering a small amount of aqueous solution through the hollow interior of carbon nanotubes. Research like Striolo's[18] is crucial for achieving a complete understanding of the properties of confined water that is undoubtedly necessary for the design of novel nano-machinery such as nano-syringes or CNT-embedded membranes for the controlled delivery of nanometre quantity of aqueous solutions. They have aroused huge scientific and industrial interest. In 2001, Hummer *et al*[19] have shown SWNT can be designed to be molecular channels for water. Kalra *et al*[20] have investigated osmotically driven transport of water molecules through hexagonally packed carbon nanotube membranes. In channels with radii between 2.5 and 5.5Å the water molecules form a cylindrical solvation shell inside the channel walls, and some evidence shows a second shell additionally existing in the centre of the largest channel.[21] The density distribution patterns of water inside and outside neutral and charged SWNTs soaked in water have been studied using molecular dynamics simulations.[22] This indicates that by adjusting the electric charge quantity on the SWNTs one can control the adsorption and transport behaviours of polar molecules.

In our previous studies, we have studied the behaviour of water molecules in a SWNT with 8.1 Å in

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diameter and 13.1 Å in a length under deformation.[23] It has been found that the system is effectively resistant to deformation noises and sensitive to available signals. The average number of water molecules inside the channel is about 5. There exists a clear wave-like pattern of the water molecules, and we have found that it plays an important role in the high signal-to-noise ratio in the deformation field. The similar phenomena have also been observed in biological water channels.[24]

In the present work, we focus on the collective dipolar orientations of water chains or nets by considering water–water interaction, water–CNT interaction and water distribution. We find that the water molecular transport through quasi-one-dimensional pores is highly collective when the radius of SWNT is small enough. Such a collective transport is studied on atomic scale in a molecular dynamics simulation. When the radius of SWNT increases, the single file changes into a quasi-one-dimensional file or hydrogen-bonded water molecule net. But the chain rarely ruptures because of the tight hydrogen bonds in the protective environment of the pore. Simulation results indicate that CNT(n,n) has three states of dipole when n is less than 9. It has only one intermediate state when n is larger than 9.

The rest of this paper is organized as follows. The simulation model and parameters are introduced in Section 2. Section 3 is devoted to the simulation results and discussion. Finally, the conclusions are presented in Section 4.

2. Model and key parameters

Our simulations were performed with the Gromacs 3.2.1 molecular dynamics program.[25−27] The solvent used here was TIP3P water molecules. We studied three different systems: (7,7), (8,8) and (9,9) uncapped, single-walled carbon nanotubes solvated in water, each is composed of six repeated unit cells. Each unit cell consists of a ring of carbon atoms in the armchair configuration. All carbon nanotubes used in our simulations were relaxed due to the interaction between carbon atoms. This interaction had been described with the parameterized potential by Brenner[28] according to the Tersoff formulism. Initially water molecules were filled in the other space of the system but not in the channel of the SWNT. Periodic boundary conditions were applied in all directions. One of simulation frameworks is shown in Fig.1.

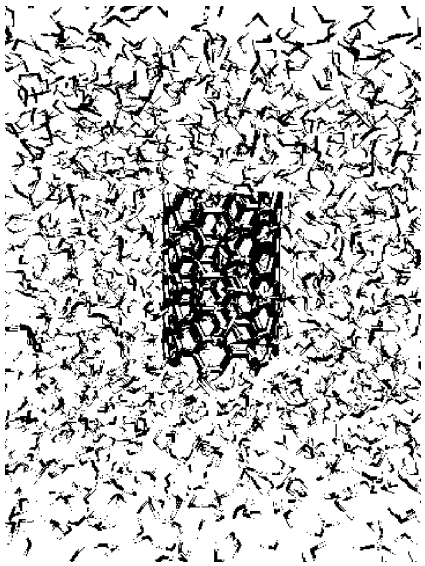


Fig.1. Snapshot of the simulation system.

The molecular dynamics simulations were carried out at a constant pressure of 1×10^5 Pa and a temperature of 300 K with initial box size being $L_x = 4.0$ nm, $L_y = 4.0$ nm, and $L_z = 4.0$ nm. A time step of 2 fs was used and data were collected every 0.5 ps. In the simulation, the carbon atoms were modelled as uncharged Lennard–Jones particles with a cross-section of $\sigma_{CC} = 0.34$ nm, $\sigma_{CO} = 0.3275$ nm and a depth of the potential well of $\varepsilon_{CC} = 0.3612$ kJ mol^{-1}, $\varepsilon_{CO} = 0.4802$ kJ mol^{-1}. Carbon-carbon bond length of 0.14 nm and bond angle of 120° were maintained by harmonic potentials with spring constants of 393960 kJmol^{-1}nm^{-2} and 527 kJmol^{-1}rad^{-2} before relaxation. In addition, a weak dihedral angle potential was applied to bonded carbon atoms.

3. Results and discussion

For each system corresponding to a radius R, the time for the numerical simulation is 120 ns. The last 110 ns of simulation were collected for analysis. For each simulation, the nanotube was rapidly filled up with water from the surrounding reservoir.

Figure 2 shows the distribution of water molecules inside the nanotube along the z-direction. As the radius of SWNT increases, the number of water molecules confined in nanotube increases. The average number of water molecules inside SWNT(6,6) is

about 5.0 where the water molecules line up to a single file. The average number of water molecules inside SWNT(7,7) is about 7.7. The average numbers of water molecules inside SWNT(8,8) and SWNT(9,9) are about 17.0 and 23.1 respectively. They form a water molecule net, not a single file. The water distribution has a wave-like structure with minimal values at the openings. As the radius of SWNT increases, the wave-like structure remains unchanged and it plays an important role in the high deformation signal-to-noise ratio. Wave-like patterns of the distributions of atoms O and H of water have also been observed in GlpF channels.[24]

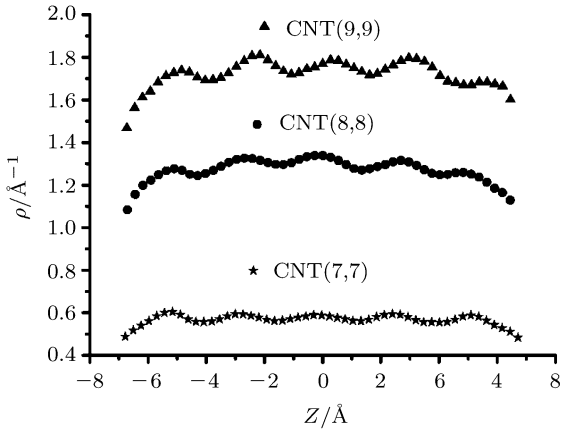


Fig.2. Water distribution along the nanotube axis for different radii.

Molecular transport through these quasi-one-dimensional pores is highly collective, since motion of a molecule requires concomitant motion of all molecules in the file. Such a collective transport has been studied on atomic scale in a recent molecular dynamics simulation. As the radius of SWNT increases, the single file changes into quasi-one-dimensional chain. But the chain rarely ruptures because of the tight hydrogen bonds in the protective environment of the pore. An important feature of the hydrogen bond is that it possesses directionality. Hydrogen bonds in the SWNT are highly oriented and nearly aligned along the nanochannel axis and collectively flip in their orientations. We quantify the orientation of water chain by defining a characteristic angle denoted by $\bar{\phi}$. ϕ is the angle between a water molecule dipole and the z-axis (nanochannel axis), and taken an average over all the water molecules inside the nanochannel. Inside the CNT(6,6), it is found that $\bar{\phi}$ usually falls to in two ranges, $15^\circ < \bar{\phi} < 50^\circ$ and $130^\circ < \bar{\phi} < 165^\circ$, which were called +dipole and −dipole states, respectively. To describe this property, we refer to $[\phi]$, 1 as +dipole state, $[\phi]$, −1 as -dipole and $[\phi]$, 0 as intermediate state where $50^\circ \leq \bar{\phi} \leq 130^\circ$. Some examples are shown in Fig.3, we can see that the CNT(7,7) mainly has two states. But as the number of water molecules inside the SWNT increases, the CNT(8,8) has three states clearly and the CNT(9,9) has only one intermediate state. What causes this transformation? As the radius of SWNT increases, more water molecules enter into the carbon nanotube. They are connected with hydrogen bond tightly. As the number of water molecules inside the SWNT increases, the thermal noise weakens the cooperative nature of the water dimer hydrogen bond correspondingly.

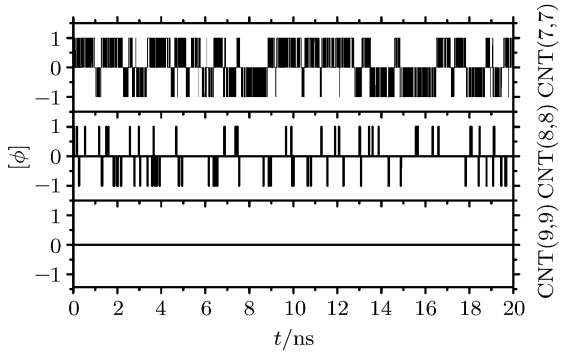


Fig.3. $[\phi]$ for CNT(7,7),(8,8),(9,9). $[\phi]$, 1 is referred to as +dipole state,$[\phi]$, −1 as −dipole and$[\phi]$, 0 as intermediate state where $50^\circ \leq \bar{\phi} \leq 130^\circ$.

It is well known that solvation layers are found in water and other liquids, and near flat walls the solvation shells are seen around spherical and non-spherical solutes.[29,30] We examine the effects of confinement on the water structure and the hydrogen-bond network. The hydrogen bond is really a special case of dipole forces. Some examples are shown in Fig.4. Here, we focus on the water molecules inside the SWNT, so the numbers of hydrogen bonds between water molecules at opening and those outside SWNT are beyond our consideration. The result shows that the number of hydrogen bonds fluctuates over time. The average numbers of hydrogen bonds inside CNTs(7,7),(8,8),(9,9) are 6.34, 19.42 and 27.99 respectively, and each water molecule inside SWNT has about 0.8, 1.1, and 1.2 hydrogen bonds correspondingly. These results are in good agreement with the conclusions in Ref.[4] where the different lengths of SWNT were used in simulation and different methods of counting hydrogen bonds were applied. The number of hydrogen bonds increases with

the increase of radius of CNT. With spectroscopically determined electronic structure criterion in bulk water at 25 °C, each water molecule gives 3.3 (3.6) H-bonds on average.[31]

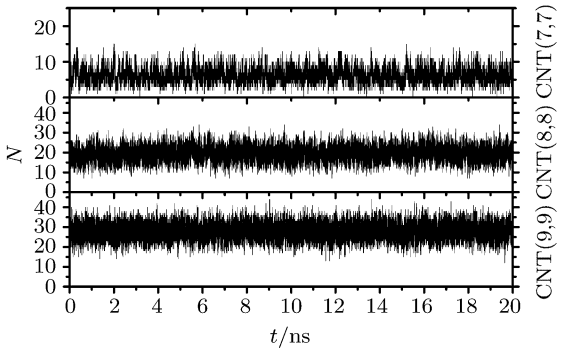


Fig.4. Numbers of the hydrogen bonds inside the nanotube as a function of time for CNTs (7,7),(8,8) and (9,9).

The water–water interaction and water–CNT interaction can make main contributions to the free energy of the system. The interaction between water and water strengthens as the number of water molecules inside SWNT increases, but the interaction between water and carbon nanotube weakens correspondingly. The results are shown in Fig.5 and Fig.6.

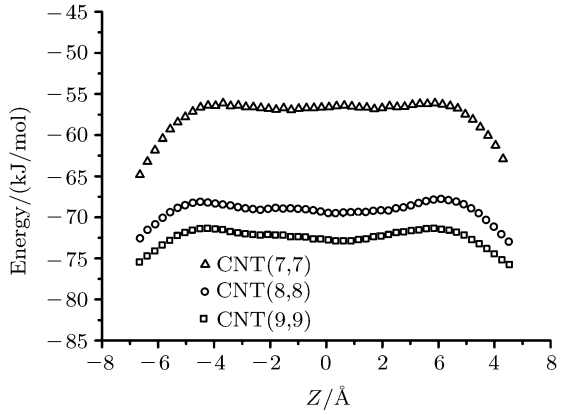


Fig.5. Average water–water interaction along the nanotube axis.

The average number of water molecules inside SWNT increases, and the average number of hydrogen bonds also increases. They construct a water molecule net. So the potential of each water molecule inside SWNT decreases. As the radius of SWNT increases, the average distance between water molecule and carbon atom become larger, therefore the water–carbon nanotube interaction weakens. These characters play a key role in transporting water molecules.

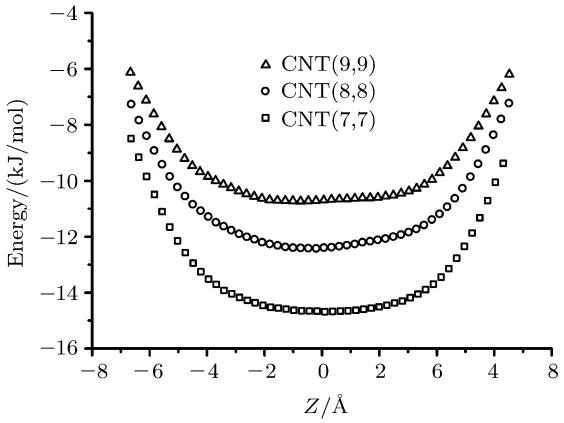


Fig.6. Average water–CNT interaction along the nanotube axis.

4. Conclusions

In this work we have found that water molecules confined in SWNTs(7,7), (8,8) and (9,9) have a marked wave-like pattern though they are not lined up in one file. In a recent paper, it has been found that aqueous solutions in nanopores have a markedly nonuniform density with a layer of water molecules with which the wall of the channel is lined. All these suggest that the treatment of water diffusion by using continuum model is unlikely to be valid for these channels.

In CNT(6,6) water molecules are lined up in one file. There exist two states: +dipole and −dipole clearly and the intermediate state occurs infrequently. Water molecules inside CNT(7,7) are still lined up in quasi-one-file. So the state of system mainly is of +dipole or −dipole. But as the radius of SWNT increases, the single file is destroyed. The probability with which the intermediate state appears increases apparently. In the CNT(9,9), water molecules are arranged into a water net. The system has only one state, i.e. intermediate state. The other two states disappear.

From our simulation results, we have found that as the radius of SWNT increases, the interaction between water and water becomes stronger, but the interaction between water and carbon nanotube turns weaker.

References

[1] Beckstein O, Biggin P C and Sansom M S P 2001 *J. Phys. Chem.* B **105** 12902

[2] Gallo P, Rovere M and Spohr E 2000 *J. Chem. Phys.* **113** 11324

[3] Gordillo M C and Marti J 2000 *Chem. Phys. Lett.* **329** 341

[4] Mashi R J, Joseph S, Aluru N R and Jakobsson Eric 2003 *Nano Lett.* **3** 589

[5] Truskett T M 2003 *Proc. Natl. Acad. Sci. USA* **100** 10139

[6] Gelb L D, Gubbins K E, Radhakrishnan R and Sliwinska-Barkowiak M 1999 *Rep. Prog. Phys.* **62** 1573

[7] Allen R and Hansen J P 2003 *J. Chem. Phys.* **119** 3905

[8] Iijima S 1991 *Nature* (London) **354** 56

[9] Iijima S and Ichlhashi T 1993 *Nature* (London) **363** 603

[10] Yi S P, Zhang H Y, Ouyang Y, Wang Y H and Pang J S 2006 *Acta Phys. Sin.* **55** 2644

[11] Zhang H Q 2001 *Acta Phys. Sin.* **50** 528

[12] Sun J P, Wang T H 2002 *Acta Phys. Sin.* **51** 2096

[13] Zang J, Triebergs A, Han Y and Liu F 2004 *Phys. Rev. Lett.* **92** 105501

[14] Wu J, Zang J, Larade B, Guo H, Gong X G and Liu F 2004 *Phys. Rev.* B **69** 153406

[15] Xia Y Y, Zhao M W, Ma Y C, Ying M J, Liu X D, Liu P J and Mei1 L M 2002 *Phys. Rev.* B **65** 155415

[16] Xia Y Y, Ma Y C, Xing Y L and Mu Y G 2000 *Phys. Rev.* B **61** 11088

[17] Song L, Liu S, Zhang G M, Liu L F, Ma W J, Liu D F, Zhao X W, Luo S D, Zhang Z X, Xiang Y J, Shen J, Zhou J J, Wang G and Zhou W Y 2006 *Chin. Phys.* **15** 422

[18] Striolo A 2006 *Nano Lett.* **6** 633

[19] Hummer G, Rasalah J and Noworyta J P 2001 *Nature* **414** 188

[20] Kalra A, Garde s and Hummer G 2003 *Proc. Natl. Acad. Sci. USA* **100** 10175

[21] Lynden-Bell R M 1996 *J. Chem. Phys.* **105** 9266

[22] Huang B D, Xia Y Y, Zhao M W, Li F, Liu X D, Ji Y J and Song C 2005 *J. Chem. Phys.* **122** 084708

[23] Wan R Z, Li J Y, Lu H J and Fang H P 2005 *J. Am. Chem. Soc.* **127** 7166

[24] Tajkhorshid E 2002 *Science* **296** 525

[25] Berendsen H J C, van der Spoel D, van Drunen R 1995 *Comp. Phys. Comm.* **91** 43

[26] Lindah1 E, Hess B, van der Spoel D 2001 *J. Mol. Mod.* **7** 306

[27] Beckstein O, Biggin P C, Sansom M S P 2001 *J. Phys. Chem.* B **105** 12902

[28] Brenner D W *Phys. Rev.* B **42** 9458

[29] Lee S H, Rasaiah J C, and Hubbard J 1987 *J. Chem. Phys.* **86** 2383

[30] Gerstein M and Lynden-Bell R M, 1993 *J. Mol. Bio.* **86** 641

[31] Wernet P, Nordlund D, Bergmann U, Cavalleri M, Odelius M, Ogasawara H, Näslund L Å, Hirsch T K, Ojamäe L, Glatzel P, Pettersson L G M and Nilsson A 2004 *Nature* **304** 995