

Orientations of special water dipoles that accelerate water molecules exiting from carbon nanotube*

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Abstract One-dimensional ordered water molecules entering and exiting from a carbon nanotube with an appropriate radius are studied with molecular dynamics simulations. It can be found that a water molecule near the nanotube end is more likely to be expelled from the nanotube if its dipole is almost perpendicular to the nanotube axis. The key to this observation is that those water molecules are closer to the wall of the nanotube away from the equilibrium position of the Lennard-Jones (LJ) potential. Thus, the interaction energy for those water molecules is relatively high. There are two particular structures of the perpendicular water molecule depending on the dipole direction of the adjacent water molecule in the nanotube. Although the probabilities of these structures are quite small, their contributions to the net flux across the nanotube end are approximately equal to the predominant structures. The present findings further show the possibility of controlling the water flow by regulating the dipole directions of the water molecules inside the nanochannels.

Key words water, carbon nanotube, single-file water chain, Lennard-Jones (LJ) interaction

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1 Introduction

The presence of water inside carbon nanotubes^[1–5], together with the existence of biological water channels^[6–7], has greatly promoted the study of the water permeation through nanochannels^[8–19] and, in particular, the mass transportation induced by the thermo-migration in carbon nanotubes^[20]. The mechanisms for the flux generation in water-filled nanochannels

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can be employed to study the coupling between the translational momentum and the rotational momentum using a generalized Navier-Stokes equation^[21]. Specifically, in the narrow channels of appropriate radii, the water molecules form a single-file chain^[12,22], and the electric dipole orientations are nearly aligned with the channel axis. Taking advantage of this single-file structure, Wan et al.^[23] found that the water molecules flowed through the nanochannel spontaneously in the dipole directions of the quasi one-dimensional (single-file) chain. Inspired by biological channels, Gong et al.^[24] found that a charge distribution resulted in a unidirectional transportation of water molecules. In that system, the dipole orientations of the water molecules inside the carbon nanotube were influenced by the charge distribution. However, the mechanism behind the fluxes of the water molecules across the nanochannels associated with the particular dipole orientations has not been studied in detail.

In this article, we study the events of water molecules entering and exiting from the narrow nanotube by molecular dynamics simulations. It is found that a water molecule near the nanotube end tends to be expelled from the nanotube if its dipole moment is almost perpendicular to the nanotube axis. There are two structures of the perpendicular water molecule depending on the dipole direction of the adjacent water molecule in the nanochannel. Although the probabilities of these structures are quite small, their contributions to the net flux are approximately equal to the contributions from the predominant structures. These particular structures result in the decrement in the Lennard-Jones (LJ) attraction between the water molecule and the nanotube. The LJ attraction compensates the energy lost caused by the water molecules entering the nanotube. If the electric dipole of the adjacent water molecule points outward from the nanochannel, the decrement in the LJ attraction is 10.0 kJ/mol. If the dipole of the adjacent water points inward, the decrement is only 4.0 kJ/mol. These decrements in the LJ attraction result in the easy expulsion of the water molecules near the nanotube end. We find that the hydrogen bond extension between the two water molecules in the first structure is responsible for the large potential decrement. The present findings give a fundamental description of the water molecules exiting from the carbon nanotube and show the possibility of controlling the water flow by regulating the dipole direction of the water molecules in the single-file chain that is very important in applications, such as the desalination of seawater and the design of novel nano devices.

2 System and simulation methods

An uncapped armchair (6, 6) single-walled carbon nanotube (SWNT) with the length of 1.34 nm and the diameter of 0.81 nm is embedded in a water container of the volume of 4.50 nm×4.50 nm×4.50 nm. The simulation settings include maintaining the container at the constant pressure (100 kPa) and temperature (300 K) using the Parrinello-Rahman method^[25] for the pressure coupling and the Nose-Hoover^[26-27] method for the temperature coupling with Gromacs 4.0^[28] and the TIP3P^[29] model for water. A time step of 1 fs is used, and the data are collected every 0.25 ps. In the simulations, the carbon atoms are modeled as the uncharged LJ particles with a cross-section of

$$\delta_{CC} = 0.340 \text{ nm}, \quad \delta_{CO} = 0.333 \text{ nm}$$

and a potential well depth^[2] of

$$\varepsilon_{CC} = 0.36 \text{ kJ/mol}, \quad \varepsilon_{CO} = 0.48 \text{ kJ/mol}.$$

The carbon-carbon bond length of 0.140 nm and the bond angle of 120° are maintained by the harmonic potentials with the linear and angular spring constant set at 3.940×10⁹ kJ·mol⁻¹·nm⁻²

and $5.270 \times 10^2 \text{ kJ} \cdot \text{mol}^{-1} \cdot (\text{^\circ})^{-2}$, respectively. In addition, a weak dihedral angle potential is applied to the bonded carbon atoms^[2]. The simulations are performed for 300 ns with the last 295 ns sampled for the analysis.

In the following discussion, the water molecules closest to the ends are numbered as 1, and the adjacent molecules inside the nanotube are numbered as 2 (see Fig. 1(a)). To quantitatively describe the water dipole orientation in the SWNT, an angle ϕ_i between the i th water molecule and a unit vector along the central axis of the SWNT is calculated as

$$\phi_i = \cos^{-1} \left(p_i \frac{\hat{\mu}}{|p_i|} \right),$$

where $\hat{\mu}$ is a unit vector aligned along the SWNT central axis and pointing outward the SWNT^[17]. p_i is the dipole of the i th water molecule (see Fig. 1(b)). The state of the dipole direction of a water molecule, D_i , is defined as

$$D_i = \begin{cases} 1, & 0^\circ \leq \phi_i < 65^\circ, \\ -1, & 115^\circ < \phi_i \leq 180^\circ, \\ 0, & 65^\circ \leq \phi_i \leq 115^\circ. \end{cases}$$

In Fig. 1(a), the sticks (green) represent the SWNT. Some carbon atoms of the SWNT are not shown or are drawn to be transparent for ease of demonstration. The water molecules are shown with oxygen in red (dark balls) and hydrogen in light gray (light balls). The water molecules outside the nanotubes are omitted in the figure. In Fig. 1(b), the dashed vertical line marks the end of the SWNT, the two solid horizontal lines represent the wall of the SWNT, and the horizontal dot dashed line indicates the SWNT central axis. In total, we have four states shown in Fig. 2.

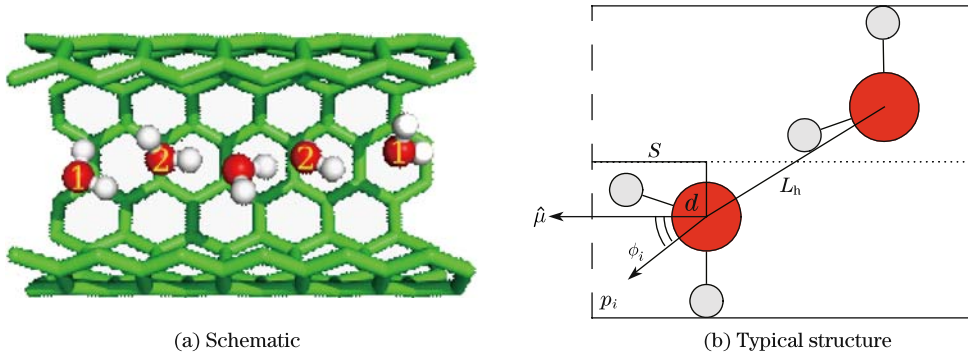


Fig. 1 Schematic of SWNT and serial numbers of water molecules and typical structure of two water molecules near end of SWNT

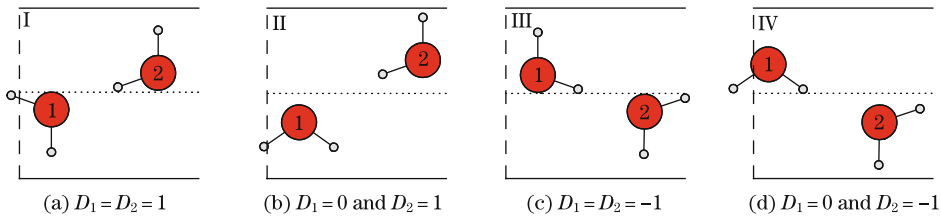


Fig. 2 Schematic diagram of water molecule structures in four states of different D_1 and D_2

The dipole directions of the inside water molecules near the SWNT ends are recorded in every frame. The numbers of the water molecules entering and exiting from the SWNT are determined by comparing the indices of the water molecules in the SWNT from two successive frames.

3 Results and discussion

Table 1 shows the probability densities (ρ) of different water dipole orientation states, the average numbers of the water molecules entering (N_{in}) and exiting (N_{out}) from the nanotube every nanosecond in each dipole orientation state, the flux (F), and the net number of the water molecules flowing through the nanotube end contributed by each state ($F\rho$). The flux is defined by the difference of the the numbers of the water molecules entering and exiting from the SWNT ends per nanosecond ($F = N_{\text{out}} - N_{\text{in}}$).

There are four dipole orientation states in our simulation, which are numbered as I, II, III, and IV corresponding to the states

$$D_1 = D_2 = 1; \quad D_1 = 0, \quad D_2 = 1; \quad D_1 = D_2 = -1; \quad D_1 = 0, \quad D_2 = -1,$$

respectively (see Fig. 2). The probability of the state I, ρ_{I} , is 0.490. For the other states, ρ_{II} is 0.009, ρ_{III} is 0.497, and ρ_{IV} is 0.004. The probabilities of the states II and IV are quite small compared with the predominant states I and III. However, the fluxes of the states II and IV, denoted by F_{II} and F_{IV} , have much larger values of 1001.4 ns^{-1} and 1395.7 ns^{-1} , respectively (here, the positive value of the flux indicates the water molecules exiting from the nanotube). Their values are much larger than those of the fluxes of the states I and III ($F_{\text{I}} = -12.6 \text{ ns}^{-1}$ and $F_{\text{III}} = -19 \text{ ns}^{-1}$). Consequently, the net numbers of the water molecules flowing through the nanotube end contributed by the states II and IV ($F_{\text{II}}\rho_{\text{II}} = 9.0 \text{ ns}^{-1}$ and $F_{\text{IV}}\rho_{\text{IV}} = 5.6 \text{ ns}^{-1}$) per nanosecond are comparable to the numbers contributed by the states I and III ($F_{\text{I}}\rho_{\text{I}} = -6.2 \text{ ns}^{-1}$ and $F_{\text{III}}\rho_{\text{III}} = -9.4 \text{ ns}^{-1}$). There are some other possible water dipole orientation states. However, they rarely occur for the water in nanotubes, and they have very small contributions to the net flux across the nanotube end (see Table A1 in Appendix A).

We also compute the energy values and the relative positions of the water molecules in the SWNT to understand the physics meaning behind the different ratios between N_{out} and N_{in} in these four states. The results are shown in Table 2. Here, P_{LJ} is the average LJ potential between the 1st water molecule and the SWNT, E_{ww} is the average electric potential energy between the 1st water molecule and the 2nd water molecule, d is the average distance of the water molecule to the main SWNT axis (see Fig. 1(b)), L_{h} is the average hydrogen bond length between the 1st and the 2nd water molecules (see Fig. 1(b)), and S is the average distance between the 1st water molecule and the nearest end of the SWNT (see Fig. 1(b)).

Table 1 Probability densities (ρ) of different water dipole orientation states, average numbers of water molecules entering (N_{in}) and exiting (N_{out}) from nanotube every nanosecond in each dipole orientation state, fluxes (F , $F = N_{\text{out}} - N_{\text{in}}$) of different states, and net number of water molecules flowing through the nanotube end ($F\rho$) contributed by each state

D_1	D_2	ρ	$N_{\text{out}}/(\text{n}\cdot\text{s}^{-1})$	$N_{\text{in}}/(\text{n}\cdot\text{s}^{-1})$	F	$F\rho$
1	1	0.488	487.8	500.6	-12.8	-6.2
0	1	0.009	1178.4	172.0	1006.4	9.0
-1	-1	0.495	503.1	522.1	-19.0	-9.4
0	-1	0.004	1550.8	169.5	1381.3	5.6

In the predominant states I and III, there are negligible differences in P_{LJ} , E_{ww} , d , and L_h . Compared with the state I, E_{ww} increases by about 4.0 kJ/mol, and L_h is extended by about 0.007 nm in the state II. These variations stem from the hydrogen atoms of the 1st water molecule approaching the hydrogen atoms of the 2nd water molecule shown in Figs. 2(a) and 2(b). As a result of the extended L_h , the two water molecules move away from the SWNT axis. Compared with the state I, the distance between the 1st water molecule to the SWNT axis increases by about 0.002 nm, and the approach of the water molecules to the SWNT induces the increment of P_{LJ} by about 10.0 kJ/mol in the state II.

Table 2 LJ potential between 1st water molecule and SWNT (P_{LJ}), electric potential energy between 1st water molecule and 2nd water molecule (E_{ww}), distance between 1st water molecule to SWNT axis (d), length of hydrogen bond between 1st and 2nd water molecules (L_h), and distance from 1st water molecule to nearest ends of SWNT (S) for different water dipole states

D_1	D_2	$E_{ww}/(\text{kJ}\cdot\text{mol}^{-1})$	L_h/nm	d/nm	$P_{LJ}/(\text{kJ}\cdot\text{mol}^{-1})$	S/nm
1	1	-27.4	0.282	0.062	-36.7	0.139
0	1	-23.6	0.289	0.065	-26.3	0.103
-1	-1	-27.6	0.281	0.062	-34.6	0.133
0	-1	-27.9	0.282	0.063	-30.5	0.089

The same comparison between the state III and the state IV shows that there is no difference in E_{ww} and L_h in the two states except for a small increment in d of about 0.001 nm in the state IV. The small increment comes from the different orientations of the hydrogen bond in the two states shown in Figs. 2(c) and 2(d). As a result, P_{LJ} increases by about 4.0 kJ/mol in the state IV compared with the state III.

When the water molecules enter the SWNT, nearly two hydrogen bonds are lost. The LJ attraction between the water molecules and the SWNT compensates for a part of the energy loss. Hummer et al.^[2] found that the water molecules were expelled from the SWNT by reducing the LJ potential depth. The increment in the potential P_{LJ} in the states II and IV can result in a preference for the water molecules exiting from the SWNT. The water molecules close to the nanotube ends (i.e., with the small S) are easier to exit from the nanotube. For this reason, we find that the flux of the state IV is larger than the flux of the state II.

The hydrogen bonds existing in the successive water molecules in the single-file chain are almost aligned along the SWNT axis. As a consequence, the molecular dipoles are almost aligned with this axis. It is convenient for the water molecules to rotate around these hydrogen bonds, and it is difficult to rotate their dipoles perpendicular to the SWNT axis. The precondition for D_1 approaching the zero state is that the 1st water molecule needs to form a hydrogen bond as a donor (contributing to its own hydrogen atoms) with a water molecule outside the SWNT. However, the water molecule has a triangle configuration ($\angle\text{HOH} = 109.5^\circ$), and $D_1 = 0$ brings the extension of L_h in the state II ($D_1 = 0$ and $D_2 = 1$) and different orientations of L_h in the state IV ($D_1 = 0$ and $D_2 = -1$), which results in different potential variations in these two states.

We remark that Fig. 2 is only a schematic of physical situations that are very complex in reality. Here, it provides an aid in understanding the critical differences, i.e., the variations of L_h , in the two dipole states.

4 Conclusions

In summary, the water molecule closest to the SWNT end tends to exit from the SWNT when its dipole is almost perpendicular to the SWNT axis. The reduction in the LJ attraction between the water molecules and the nanotube results in a preferential expulsion of these water molecules from the SWNT. Furthermore, there are two structures of the perpendicular water molecule depending on the dipole direction of the adjacent water molecule in the SWNT. In the first structure, the dipole of the adjacent water molecule points outward from the SWNT end, and the consequent extension of the hydrogen bond between the two water molecules forces the water molecules toward the wall of the SWNT away from the equilibrium position of the LJ potential. In the second structure, the dipole points inward, and the reorientation of the hydrogen bond between the pair of water molecules forces the water molecules toward the wall of the SWNT away from the equilibrium position of the LJ potential. As the energy of the LJ interaction increases, the water molecules are easy to be expelled from the nanotube in these two structures. We find that the first structure brings about the larger offset of the water molecule toward the SWNT axis and a bigger decrement in the LJ attraction than the second state. The probabilities of these particular water dipole orientations are very small. However, their contributions to the net flux across the nanotube are approximately equal to those of the predominant states.

These particular water dipole orientations inside the SWNT have been found in the unidirectional transport of the water molecule by Gong et al.^[24]. These dipole orientations can help to control the transport of water molecules. Special water dipole orientations can help to manipulate the biomolecules in nanotubes^[30] and form the hydrophobic water monolayer^[31]. Our findings give a fundamental description of the water molecules exiting from the SWNT and a possible means to control the water flow by regulating the dipole direction of the water molecules that have been formed into a single-file chain.

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Appendix A

Table A1 Probability densities (ρ) of different water dipole orientation states, average numbers of water molecules exiting (N_{out}) from and entering (N_{in}) nanotube every nanosecond in each dipole orientation state, fluxes (F , $F = N_{\text{out}} - N_{\text{in}}$) of different states, and net number of water molecules flowing through the nanotube end ($F\rho$) contributed by each state

D_1	D_2	ρ	N_{out}	N_{in}	F	$F\rho$
1	1	0.4876	487.8	500.6	-12.8	-6.2
1	0	0.0019	604.8	437.1	167.7	0.3
1	-1	0.0000.0	0.0	0.0	0.0	0.0
0	1	0.0093	1178.4	172.8	1006.4	9.4
0	0	0.0003	892.7	192.1	700.6	0.2
0	-1	0.0040	1550.8	169.5	1381.3	5.6
-1	1	0.0002	576.3	457.6	118.7	0.0
-1	0	0.0020	555.9	420.3	135.6	0.3
-1	-1	0.4948	503.1	522.1	-19.0	-9.4