Asymmetry of the water flux induced by the deformation of a nanotube*

He Jun-Xia(何俊霞)[a], Lu Hang-Jun(陆杭军)[a]†, Liu Yang(刘 扬)[b], Wu Feng-Min(吴锋民)[a], Nie Xue-Chuan(聂雪川)[a], Zhou Xiao-Yan(周晓艳)[a], and Chen Yan-Yan(陈艳燕)[a]

[a] *Department of Physics, Zhejiang Normal University, Jinhua* 321004, *China*

[b] *Department of Mechanical Engineering, the Hong Kong Polytechnic University, Hong Kong, China*

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The behavior of nano-confined water is expected to be fundamentally different from the behavior of bulk water. At the nanoscale, it is still unclear whether water flows more easily along the convergent direction or the divergent one, and whether a hourglass shape is more convenient than a funnel shape for water molecules to pass through a nanotube. Here, we present an approach to explore these questions by changing the deformation position of a carbon nanotube. The results of our molecular dynamics simulation indicate that the water flux through the nanotube changes significantly when the deformation position moves away from the middle region of the tube. Different from the macroscopic level, we find water flux asymmetry (water flows more easily along the convergent direction than along the divergent one), which plays a key role in a nano water pump driven by a ratchet-like mechanism. We explore the mechanism and calculate the water flux by means of the Fokker–Planck equation and find that our theoretical results are well consistent with the simulation results. Furthermore, the simulation results demonstrate that the effect of deformation location on the water flux will be reduced when the diameter of the nanochannel increases. These findings are helpful for devising water transporters or filters based on carbon nanotubes and understanding the molecular mechanism of biological channels.

Keywords: single-walled carbon nanotube, deformation position, molecular dynamics simulation, water flux

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1. Introduction

Carbon nanotubes have attracted growing attention due to their outstanding properties and their wide potential applications in nanotechnology.[1−9] By using appropriate diameters, they offer a unique system for fabricating novel nanostructures by virtue of molecules trapped in mid-nanotubes, exploiting new behaviors induced by confinement, and studying molecular transport.

In 2001, Hummer *et al.* showed, by using molecular dynamics (MD) simulation, that water can occupy a single-walled carbon nanotube (SWNT), and that speedy molecular transport occurs.[10] Later, numerous experimental results confirmed this idea. Recently, both experimental and theoretical studies have indicated that the confinement of water molecules inside a carbon nanotube can lead to interesting structures and behaviors not seen in the bulk, such as the ordered water structure,[11,12] non-Fickian-type diffusion,[13] and extra fast motion of water molecules.[14] Aluru *et al.* have demonstrated that there are depletion layers at the liquid interface near the wall of a carbon nanotube where the velocity "jump" occurs. They attributed this to the fact that water can transport through the carbon nanotubes very quickly due to the velocity jump in a depletion region, water orientation, and hydrogen bonding at the interface.[15]

Understanding and controlling the transport of water through carbon nanotubes are crucial for the applications of nanochannels and biological activities. Mechanical and electrical methods are the main methods used to control the opening and closing of the channels.[16−21] Several groups showed that the effect of the charge, electronic field, and dipoles on the behavior of water molecules inside the nanochannel is important.[22−24] Recently, the influence of a

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†Corresponding author. E-mail: zjlhjun@zjnu.cn

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mobile charge on the transport of water through a carbon nanotube has been studied in terms of molecular dynamics simulation.[17] Simulation results demonstrated that the single-file structures of water molecules inside nanochannels have excellent charge gating properties. On the basis of Ref. [17], we choose a modified SWNT with an external positive charge, which can move along the wall of the SWNT and allow us to investigate the influence of indispensable charges. Simulation results indicate that charge-dependent gating depends sensitively on the position of the external charge.[22] Fang's group have studied the behavior of water molecules in a (6, 6) SWNT with deformation. Interestingly, excellent deformation gating properties have been found. In addition, the gating of the water permeation across a carbon nanotube was considered to be correlated with the wavelike pattern of water density distribution.[25]

It is known that both the geometrical deformation and the charge position in the middle region of nanotubes can effectively regulate water transport. Nevertheless, it is not clear what will happen if the gating region moves toward the end of the nanotube.[26] Previous studies concentrated mainly on understanding the water transport through perfect carbon nanotubes. However, radial deformation often occurs in carbon nanotubes.[27,28] We know that the deformation plays a key role in the water transport through carbon nanotubes. However, the effect of the deformation position on water transport still remains an open question. When the symmetry of geometrical confinement is broken by the deformation of carbon nanotubes, the symmetry of water flux is also broken. It is still not completely understood whether water flows more easily along the convergent direction or along the divergent one.

In this paper, we investigate the effect of deformation position on water transportation by moving the deformation position from the middle region to the two ends of carbon nanotubes with different diameters. We find that the water flux is sensitive to the position of the deformation. The water flux decreases sharply when the deformed region is close to the ends of the nanotubes. Asymmetry of flux occurs when the water transport through the deformed carbon nanotube from the left end to the right end changes as the water transports reversely. Our theoretical results based on the Forker–Planck equation are in good agreement with simulation results. Further simulation demonstrates that the influence of the deformation position on water flux is gradually weakened with the increase of the diameter of carbon nanotubes.

2. Model and method

We studied six different systems involving carbon nanotubes with different diameters, each of which is composed of 11.5 repeated unit cells (29.52 Å). One of the simulation frameworks involving (6,6) carbon nanotubes is shown in Fig. 1. An uncapped SWNT is embeded in two graphite sheets along the z direction. In order to explore the effect of deformation position on the water permeation through the carbon nanotube, one carbon atom is pushed away from the original position, resulting in a radial displacement of 2.2 Å in each system. The radial displacement is denoted as δ, which pushes a carbon atom named the forced atom. Consequently, the neighboring atoms are pushed away from their initial positions to form a narrow region (or deformation region) in the carbon nanotube due to the bond interaction among carbon atoms. In order to fix the carbon nanotube in the simulation, each carbon atom in the bottom half of the tube is fixed in its initial position by a restrain force. The middle carbon atom is taken as the origin of the z axis, and the coordinate of the forced atoms is denoted by d. For a (6,6) carbon nanotube, there are thirteen possible forced atoms. They are symmetrical and the seventh atom is the center of symmetry. The positions d of thirteen forced atoms are -14.76, -12.3, -9.84, -7.38, -4.92, -2.46, 0, 2.46, 4.92, 7.38, 9.84, 12.3, and 14.76 Å, respectively. The SWNT together with two graphite sheets are solvated in a box ($4 \times 4 \times 10$ nm^3). The TIP3P water model[29] is applied in all directions. Water molecules between the two sheets are removed. According to the method in Ref. [30], we established a pressure difference between the two ends of the nanotube to drive water molecules by adding an additional velocity of 0.01 nm·ps^{-1} to each water molecule along the $+z$ direction.

The MD simulations are performed at a constant particle number, volume (box size: $L_x = 4.0$ nm, $L_y = 4.0$ nm, $L_z = 10.0$ nm), and temperature (300 K) using GROMACS 4.0.7.[30] The Lennard–Jones parameters for the interaction among carbon atoms are $\varepsilon_{\mathrm{C-C}} = 0.3612$ kJ·mol^{-1} and $\sigma_{\mathrm{C-C}} = 0.34$ nm from the GROMACS force field. In addition, the parameters for carbon–water interaction[10] are $\sigma_{\mathrm{CO}} = 0.32753$ nm and $\varepsilon_{\mathrm{CO}} = 0.47945$ kJ·mol^{-1}.

We applied the Berendsen algorithms to simulate at a constant temperature with a constant time of 0.5 ps. The time step is 2 fs and data are collected every 1 ps. The periodic boundary conditions are applied. The long-range electrostatic interactions are handled by using the particle mesh Ewald (PME) summation method.[32] The PME parameters include the real space cutoff of 1.4 nm, the FFT grid spacing of 0.12 nm, the fourth-order interpolation, and the cutoff distance of 1.4 nm. The short-range van der Waals forces are calculated by applying a cutoff scheme with a cutoff distance of 1.4 nm.

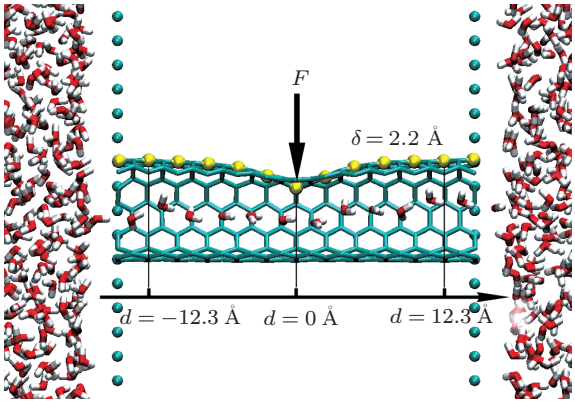


Fig. 1. (colour online) Snapshot of the deformed region located in the middle of the SWNT ($d = 0$ Å). The yellow spheres denote the possible forced atoms. In order to show the position of possible forced atoms clearly, we remove some of the water molecules.

For carbon nanotubes with a larger diameter of 7, 8, 9, 10, and 11 nm, we only investigate the effect of three key positions (left, right, and middle rims) of deformation on the water transportation. The three positions are $d = -12.3$ Å, $d = 0$ Å and $d = 12.3$ Å, respectively. The parameter values are shown in Table 1. We keep the ratio between the radial displacement (δ) and the diameter constant in our simulations.

Table 1. Parameter values of the carbon nanotubes with different diameters.

(n, m)	Diameter/Å	δ/Å	ratio
(6,6)	8.14	2.2	0.27
(7,7)	9.50	2.6	0.27
(8,8)	10.84	3.0	0.27
(9,9)	12.20	3.3	0.27
(10,10)	13.56	3.7	0.27
(11,11)	14.92	4.0	0.27

3. Fokker–Planck theory

The transport of water molecules through the SWNT can be described by the Langevin equation

$$\gamma \frac{\mathrm{d}z}{\mathrm{d}t} = f(z) + \xi(t) + F(t), \tag{1}$$

where γ is the friction coefficient, $f(z) = -U'(z)$ is the deterministic force derived from the potential of mean force, $\xi(t)$ is the Langevin force due to the equilibrium thermal fluctuation, and $F(t)$ is the external force exerted on the water molecules inside the SWNT. The corresponding Fokker–Planck equation is

$$\partial_t p(z,t) = \partial_z \{D(z)[\partial_z - f(z) - F(t)]p(z,t)\}, \tag{2}$$

where z is the SWNT coordinate, $p(z,t)\,\mathrm{d}z$ is the probability of finding a water molecule in $(z,\ z + \mathrm{d}z)$, and $D(z)$ is the possible position-dependent diffusion coefficient. However, we take $D(z)$ as a constant ($D(z) = D$) in the remainder of this work. We mainly focus on the steady state of the system. Setting the time derivative to be zero in Eq. (2), the flux j is

$$j = -D(z)[\partial_z - f(z) - F(t)]p(z,t). \tag{3}$$

We introduce dimensionless units as Kosztin did.[32] All the other units can be expressed in terms of the following units: the length of SWNT $L = 2.95$ nm, the diffusion time $T = \tau_{\mathrm{D}} = L^2/D \approx 2.956$ ns,[33] the thermal energy $E = k_{\mathrm{B}}T$ (k_{B} is the Bolzmann constant, $T = 300$ K), and D is the effective diffusion coefficient of water molecules inside the SWNT ($D \approx 2.94 \times 10^{-9}$ m^2/s). Thus, the force unit is $F = \gamma D/L = k_{\mathrm{B}}T/L = 1.298$ pN.

The constant external force ($F(t) = F_0$) leads to an effective tilted potential of mean force (PMF), $U_{\mathrm{eff}}(z) = U(z) - F_0 z$. The stationary flux j reads

$$j = (1 - \mathrm{e}^{-F_0})\langle e^{U_{\mathrm{eff}}(z)}\rangle^{-1}, \tag{4}$$

and $\langle \int_0^1 \mathrm{d}z\rangle$ is the channel average.

4. Results

Thirteen simulation systems are conducted and the simulation time for each of them is 150 ns. For each simulation system, we collect the last 145 ns for analysis. Our previous work indicated that the water flow changed slightly when δ is less than 2 Å. In order to explore the effect of the position of the narrow region on water permeation, we push forced atoms far

away from the initial position 2.2 Å. The ratio between δ and the diameter is equal to 0.27.

Figure 2 shows the water flux through the (6,6) carbon nanotube (29.52 Å long) for different deformations. Interestingly, the water flux changes when the deformation location moves from the left end to the right end along the single-walled carbon nanotube. For simplicity, we divide the SWNT into three regions according to the change of the flux: the left region (from −14.76 to −9.84 Å); the middle region (from −7.38 to 7.38 Å); and the right region (9.84 to 14.76 Å). From Fig. 2 we can see that the flux changes slightly in the middle region, and the average value is about 25.7 ns^{-1}. However, when the deformation position moves to the left or the right region, the water flux decreases dramatically to 3 ns^{-1}. It is only about one eighth of the average flux for the deformation located in the middle region. Simulation results indicate that it is easier to regulate the water flux across the channel by narrowing the region near the ends. Here, we call this phenomenon the "end effect".

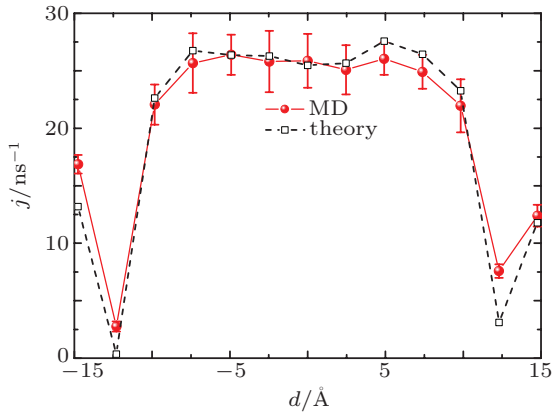


Fig. 2. (colour online) Water flux j through a (6,6) carbon nanotube (29.52 Å long) for different deformations.

From Fig. 2, we note that the flux is asymmetric for the left and right ends. The flux for $d = -12.3$ Å (denoted as $j_{\rm left}$) is about 2.8 ns^{-1}, smaller than the flux of 7.6 ns^{-1} for $d = 12.3$ Å (denoted as $j_{\rm right}$). Water flux asymmetry plays a key role in a water pump driven by ratchet-like mechanism. We check the difference between $j_{\rm left}$ and $j_{\rm right}$ by a series of simulations. It does not result from thermal fluctuation.

The potentials of mean force along the carbon nanotube are shown in Fig. 3. They are calculated from the equilibrium water probability density $\rho(z)$ by virtue of $F(z) = -k_{\rm B}T\ln\rho(z)$. Considering the symmetry of PMF about 0 Å, we only show the PMF curves for $d > 0$ Å. The PMF curves exhibit a wave-like pattern due to the confinement of the carbon nanotube and the hydrogen bonds connecting water molecules. The mechanism has been discussed in our previous work.[25] There are high peaks in the PMF curves, and the highest peak occurs in the narrow region due to the deformation of the SWNT, especially for $d = 12.3$ Å and $d = -12.3$ Å. The peak position translates with the location of the deformed region of the carbon nanotube. Interestingly, the PMF profiles for $d = \pm 12.3$ Å are different from the others. The highest peak is not located at the deformation position, but located at the next position near the end of the SWNT. The distance between the peaks is about 3 Å, almost equal to the length of a hydrogen bond. This abnormal change in PMF induces a sharp decrease of the flux.

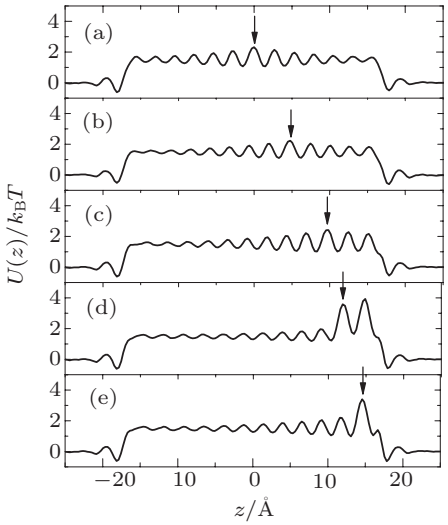


Fig. 3. Potentials of mean force along the carbon nanotube for (a) $d = 0$, (b) 4.92, (c) 9.84, (d) 12.30, and (e) 14.76 Å.

In order to explain the mechanism of the asymmetry and the sharp decrease of the water flux for $d = \pm 12.3$ Å, we have studied the water flux across the deformed carbon nanotube based on the Brownian motion theory. In this model, the motion of water molecules inside the deformed channel is modeled as over-damped Brownian motion. From the Fokker–Planck equation (details are described in Section 3), we can calculate the theoretical flux. The results are shown in Fig. 2. We can see that the theoretical prediction is well consistent with the simulation results. The effect of the position of the high free-energy peak is the main reason for the asymmetry and the sharp decrease of flux. When the high peak moves from left to right and keeps the same height and profile, the theoretical flux will increase. It is consistent with the simulation results that the flux for $d = -12.3$ Å is smaller than that for $d = 12.3$ Å. The sharp decrease

of the flux for $d = \pm 12.3$ Å results from the changes of the PMF profile and height. It is noted that two high peaks appear and the height of the free-energy barrier increases obviously. Therefore, it is difficult for single-file water molecules to permeate through the deformed region.

In order to know whether the "end effect" will occur in larger channels, we further investigate the water flux through a carbon nanotube with a larger diameter. Detailed parameters are shown in Table 1. The ratio of pushing the forced atoms far away from the initial position is 0.27, which is in accordance with the (6,6) SWNT. For each SWNT, we simulate three systems. The position d of the three forced atoms is -12.3, 0, and 12.3 Å, respectively. Correspondingly, we can calculate three fluxes: $j_{\rm mid}$ for $d = 0$ Å, $j_{\rm left}$ for $d = -12.3$ Å, and $j_{\rm right}$ for $d = 12.3$ Å. For convenience, we define $R_{\delta f} = (j_{\rm mid} - j_{\rm left})/j_{\rm mid}$ and $R_f = j_{\rm left}/j_{\rm right}$.

Figure 4 shows $R_{\delta f}$ and R_f for SWNTs with different diameters. $R_{\delta f}$ decreases with diameter and approaches zero. For a (6,6) carbon nanotube, $R_{\delta f}$ is about 0.89, which signifies that the water flux decreases sharply to a very small value when the deformation position moves from $d = 0$ Å (mid) to $d = -12.3$ Å (left end). For a (11,11) carbon nanotube, $R_{\delta f}$ is about 0.12. In this case, $j_{\rm left}$ is close to $j_{\rm mid}$. The water flux almost keeps constant when the deformation position moves from the middle to the ends of the carbon nanotube. Therefore, deformation position is especially important for a small nanotube. In contrast, R_f increases with the diameter and approaches 1. For a (6,6) carbon nanotube, $j_{\rm left}$ is only about one third of $j_{\rm right}$, resulting in $R_f = 0.36$. R_f increases with the diameter of the carbon nanotube. Lastly, $j_{\rm left}$ approaches $j_{\rm right}$. The asymmetry of the water flux is weakened with the increase of diameter.

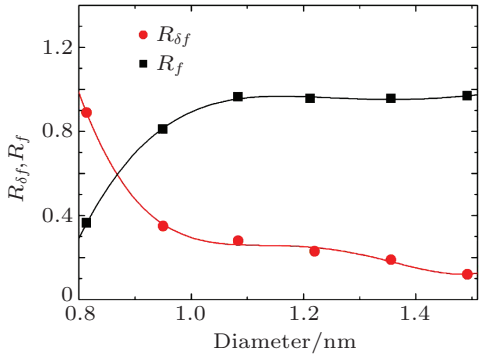


Fig. 4. (colour online) $R_{\delta f}$ and R_f for SWNTs with different diameters.

5. Conclusion

By virtue of molecular dynamics simulation, we explore the effect of deformation position on the water flux through a carbon nanotube. Simulation results indicate that the position of the narrow region plays a key role in controlling the water flux. When the deformation region is located at the rims of the nanotube, the water flux decreases dramatically. In other words, an hourglass shape is more convenient than a funnel one for the water to pass through the nanotube. Note that the deformation depth for all cases is the same ratio of 0.27. It is easily observed from the model that the volume is smallest when the deformation is located in the middle of the tube. Interestingly, the profile of the flux is asymmetrical. The water flux for the deformation located at the right end is larger than that in the left end. We model the motion of water molecules inside the carbon nanotube as over-damped motion. By using the Forkker–Planck equation, we calculate the theoretical flux and find that the theoretical results are well consistent with the simulation results. The asymmetry of the flux profile mainly results from the moving position of the PMF peak, and the sharp decrease of flux for the deformation located at the rims of the carbon nanotube results from the change of the PMF profile.

The diameter effect is also studied. We simulate a series of carbon nanotubes with different diameters. The results show that the effect of the deformation position on the flux weakens with the increase of the nanotube's diameter. The present findings can be helpful for designing nanofluidic devices.

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