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Gating of Water Flow Induced by Bending of a Carbon Nanotube *

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The ON-OFF state transition of the water transport induced by the structural bending of a carbon nanotube is studied by molecule dynamics simulation. The water permeation through a bent carbon nanotube shows excellent gating property with a threshold bending angle of about 14.6°. We also investigate the water density distribution inside the nanochannel to illustrate the mechanism.

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The water permeation across nanochannels is of great importance for designing molecular devices/machines/sensors.[1−3] In 2001, Hummer *et al.*[1] showed that water can enter the single-walled carbon nanotube (SWNT) although it is believed that SWNTs are hydrophobic. Later, the single-walled carbon nanotube was proposed to be a model to study the mechanism of the biological water channels,[5,6] where the water inside the channels exhibit single file chains as those in the special-sized SWNTs.[3,7−13] In order to control the water permeation across the channel, in 2005, Wan *et al.*[2] demonstrated a gating mechanism of nano water channel by exerting an external pressure vertically to the wall of it. Explicitly, the water net flux remains almost fixed with a deformation of 2.0 Å but decrease sharply with a further deformation of 0.6 Å. Li *et al.*[14−16] used an external charge and found that there is also a gating behavior. In the mean time, the water permeation across a carbon nanotube has been studied experimentally. However, the exerting of external force on the carbon nanotube or precisely positioning a charge near the carbon nanotube is usually difficult. On the other hand, the bending of the carbon nanotube is relatively easy. In this Letter, we use the carbon nanotube[17,18] as an example to show that there is also an excellent gating on the water transportation under the bending of the nanotube.

The simulation framework is displayed in Fig. 1. A single graphite sheet horizontally divided the simulation box into two parts. A (6,6) SWNT 26.8 Å in length and 8.1 Å in diameter was embedded in the graphite sheet perpendicularly along the z direction with the center of the SWNT coinciding with the center of the graphite sheet. Periodic boundary conditions were applied in the x, y and z directions of the simulation box.

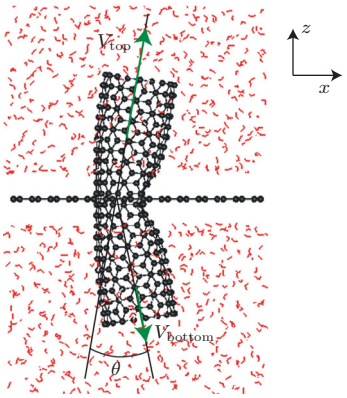

Fig. 1. Snapshot of the simulation system. $V_{\rm top}$ and $V_{\rm bottom}$ are the vectors of the axis of the tube at the top and bottom, the bending angle θ is defined as the angle between the $V_{\rm top}$ and $V_{\rm bottom}$.

The carbon nanotube was bent gradually with two ends of the tube moving simultaneously, forming a bending angle θ. The bending process is supposed to take much longer time than the response of the hydration dynamics; hence we prepared 15 bending angles θ from 0° to 30° with an increase of 2°, and an extra detailed test for θ from 14° to 16° with an increase of 0.2°. These bent carbon nanotubes were then applied to the simulation system individually, each of which was then fixed. During the bending process of the SWNT, the interaction was described with the parameterized potential by Brenner according to the Tersoff formulism.[3,4] The bending process was carried out by Brenner's Code.[3,4] The 96 carbon atoms at the top and the bottom of the tube were bent integrally, namely the conformation of the top and bottom of the tube was fixed, and the middle part of the tube

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was relaxed to form corresponding bending conformation. Since the conformation of the entrance was fixed, the bending angle θ can be defined as the angle between the axis of the top entrance and the bottom entrance. In the simulations, an artificial osmotic pressure difference was established by performing an external acceleration of 0.1 nm/ps^2 on each water molecule. All the carbon atoms in the system, including those of both the carbon nanotube and the graphite sheet, were fixed to prevent the system being swept away.

The molecular dynamics simulations were carried out at a constant pressure 1 bar with an initial box size of $2.98\times2.21\times4.53\,\mathrm{nm}^3$ and temperature (300 K) with Gromacs 3.3.1.[21,22] The interaction between any pair of atoms can be divided into two parts: the van der Waals potential which is in the Lennard-Jones form

$$V_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right],$$

where r is the distance between centers of mass, ε is the dielectric constant. The electrostatic potential can be expressed in the Coulomb form $V_e(r) = \dfrac{q_i q_j}{4\pi\varepsilon r}$ with q_i and q_j being the net charges. We apply a simple point change (SPC) model.[23] The updating time step is 2 fs while the frequency for data collection is 1 ps^{-1}. The carbon atoms are modeled as uncharged Lennard Jones particles with cross sections of $\sigma_{\mathrm{CC}} = 0.34$ nm, $\sigma_{\mathrm{CO}} = 0.33$ nm and the depth of the potential well of $\varepsilon_{\mathrm{CC}} = 0.36\,\mathrm{kJ\cdot mol^{-1}}$, $\varepsilon_{\mathrm{CO}} = 0.36\,\mathrm{kJ\cdot mol^{-1}}$.[1,2] The total simulation time is 120 ns for each bending angle from 0° to 30°, while for the detailed test system with bending angle θ between 14° and 16° the total simulation is just 10 ns, which is long enough for the hydration response of the water.[5]

Figure 2(a) displays the net flux inside the narrow carbon nano-channel. Because of the thermal fluctuation, the water molecules did to-and-fro motion rather than merely permeating in one direction. The flux is defined by the difference of the number of water molecules entering the SWNT from the bottom and upper ends, left on the other sides, per nanosecond. Meanwhile, the flow is the total number of water molecules that leave the nanotube. Interestingly, as displayed in Fig. 2(a) the flow of the permeating water is more stable than the net flux, where the flow is the summary of the number of water molecules entering from the bottom and upper end and leaving on the other side (blue). We find that the flow does not change much with the increasing of the bending angle θ from the original unbent state of the carbon nanotube. However, as θ exceeds 14°, both the net flux and flow of the permeation water become zero, namely the water channel turned off for water permeation.

Figure 2(b) displays the average water number $\langle N\rangle$ inside the narrow carbon nano-channel, the unbent channel is occupied by about 11 water molecules, and $\langle N\rangle$ remains constant till the bending angle reaches 16°. On the contrary, the standard deviation of the $\langle N\rangle$ rises abruptly from less than 0.7 to more than 2 as the bending angle exceeds 16°.

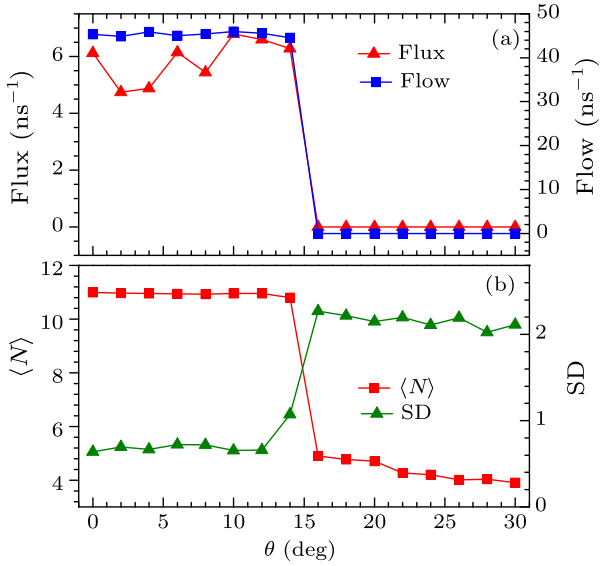

Fig. 2. (a) Net flux (red) and the flow (blue) vs the bending angle θ. (b) Average water number $\langle N\rangle$ (left vertical axis) and the standard deviation SD (right vertical axis) vs the bending angle θ.

To illustrate the detailed water behavior at the sensitive on-off gating region of the net flux in the tube, we calculate the density distribution of the water molecule inside the nanotube along the axis and the result is shown in Fig. 3(a). When $\theta = 0$, it shows a wave-like pattern, with an average value of 0.035 Å^{-1} and the minimum of 0.027 Å^{-1} and the maximum of 0.045 Å^{-1}. As $\theta \le 14.4°$, the probability density does not change much in the entrance region, while it changes slowly in the bending region of the tube. In the case of $\theta > 14.4°$, the density distribution shows a transition from the regular wave-like pattern to partially water exclusion distribution, where the density at the middle part of the channel declines abruptly to 0 as the bending angle θ reaches 14.8°.

In Fig. 3(b), we show the free energy of occupancy fluctuation $F(N)$, which is estimated by the formula $\beta F(N) = -\ln[P(N)]$, where $P(N)$ represents the probability of finding N water molecules in the tube and $\beta = 1/k_bT$. $P(N)$ is established by

$$P(N) = \frac{n(N)}{\Sigma_{N=0}^{12} n(N)},$$

where $n_f(N)$ represents the number of frames in the case that N water molecules could be found in the tube, k_b is the Boltzmann constant and T is temperature. The most preferred number of water in the channel is 11 when the bending angle is 14.4°. When the bending angle increases to 14.6°, an additional equally preferred water number of 4 can be observed, as plot-

ted in Fig. 3(b) in green. However, for the bending angle of 14.8° and larger, the confined water number does not show any dominating preference to a certain number and is fluctuating.

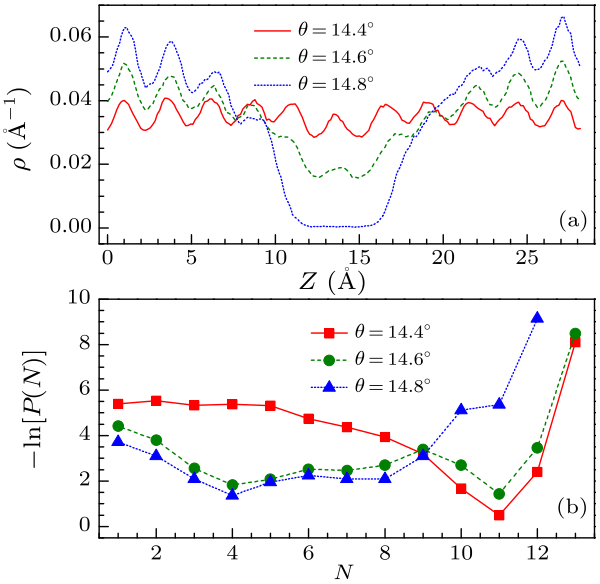

Fig. 3. (a) Water probability density distribution along the nanotube axis for the nanotube bending angle θ = 14.4°, 14.6°, and 14.8°. (b) Free energy of occupancy fluctuation $\beta F(N) = -\ln[P(N)]$.

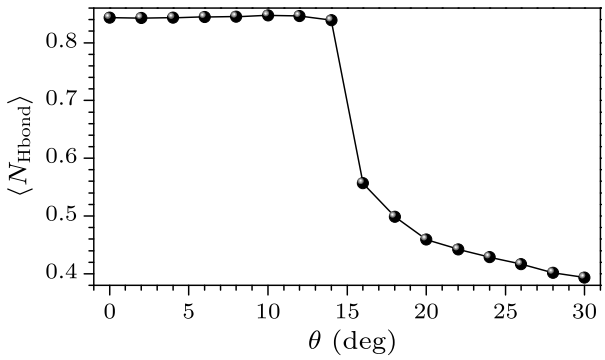

Fig. 4. Average number of hydrogen bond N_{Hbond} vs the bending angle.

The average number of hydrogen bonds to an individual water molecule inside the SWNT is calculated and the result is shown in Fig. 4. Here a hydrogen bond is defined whenever a water molecule has a neighboring water molecule within its vicinity of 0.35 nm and the O–H–O angle smaller than 30°, where the calculated water molecule works as an electron donor in hydrogen bond. It is clear that the number keeps almost as a constant when $\theta < 14.6°$. However, when $\theta > 14.6$, the hydrogen bond decreases. Actually, when $\theta < 14.6°$ the average number of the water molecule occupying the carbon nanotube is 11.0, and the average number of the hydrogen bond of an individual water molecule is 0.85, where the total number of the hydrogen bond in the single file water chain is averagely 9.35. However, when $\theta > 14.6°$ the average number of the water molecule declines to 6.9, while the average hydrogen bond of an individual water molecule is 0.76, where the total number of the hydrogen bond is averagely 5.24. The decrease of the number of the hydrogen bond implies a destruction of the one dimension hydrogen network within the carbon nanotube.

We find that the water permeation across the nanochannels with single file water chains shows excellent ON-OFF state transition when the channel is bent. The probability density of water within the carbon nanotube shows that the water distribution density in the bending part of the carbon nanotube decreases abruptly from a normal wave-like pattern to zero, beginning at the threshold angle. We also find that the number of the hydrogen bonds within the tube decreases rapidly at the threshold angle, which implies the destruction of the hydrogen bond network in the carbon nanotube. Our study is expected to be helpful for understanding biological channels, and suggests a prototype of the nanometer water valve.

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