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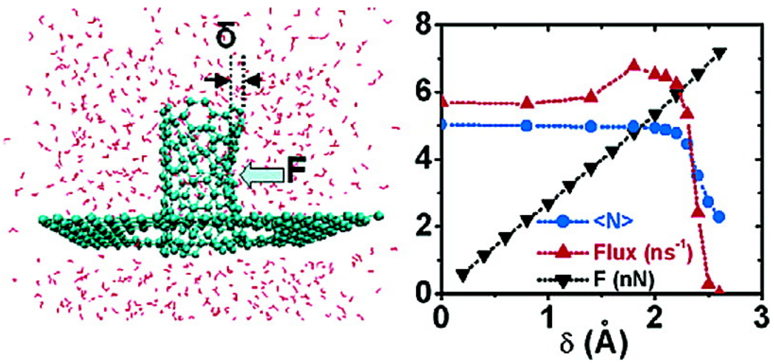

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Controllable Water Channel Gating of Nanometer Dimensions

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Abstract: The dynamics of water molecules in a single-walled carbon nanotube (SWNT) under continuous deformations was studied with molecular dynamics simulations. The flux and occupancy remain almost fixed within a deformation of 2.0 Å but decrease sharply for a further deformation of 0.6 Å. The nanopore is an excellent on−off gate that is both effectively resistant to deformation noises and sensitive to available signals. Biological water channels are expected to share this advantage due to similar wavelike water distributions. The minimal external force required for triggering an open−close transition falls within the working range of many available experimental facilities, which provides the possibility of developing SWNT-based nanoscale devices.

Introduction

Water channels of nanometer dimensions play a key role in biological membrane transport.[1−5] How the behavior of water molecules depends on the shape and dimension of biological pores is far from being understood.[6] Recently, water permeations across the biological membranes such as Aquaporin, Glpf, and MscS have been studied by molecular dynamics simulations.[5,7−10] Unfortunately, the complicated structure of membranes and membrane−water interactions often make it highly complex for direct investigations. On the other hand, primary characteristics can usually be exploited by studying a similar but structurally less complicated problem. In 2001, Hummer et al. showed that single-walled carbon nanotubes (SWNT) can be designed as molecular channels for water.[11] They observed that a minute reduction in the attraction between the tube wall and water dramatically affected pore hydration, leading to sharp, two-state transitions between empty and filled states on a nanosecond time scale.[11] Beckstein et al. have investigated the passage of water through atomistic models of hydrophobic nanopores embedded with a membrane minetic by molecular dynamics simulations.[12] An abrupt transition from a closed state (no water in the pore cavity) to an open state (cavity water at approximately bulk density) has been found once a critical pore radius is exceeded.[12] The vapor−liquid transition has also been observed in mechanosensitive channels[10,13,14] and other hydrophobic nanopores.[15−18]

Biological channels are usually gated. They contain a region that can interrupt the flow of molecules (water, ions) and thus can switch between open and closed states.[5,7−9,19−21] This region plays a central role in water permeation across a biological membrane. In this study, a simple hydrophobic nanopore is used as a prototype to study the response of such a region under continuous deformations by mechanical stress. Explicitly, an atom of a SWNT is affected by an external force (hereafter we refer to this atom as the *forced-atom*), which pushes this atom, together with neighbor atoms, to leave their initial equilibrium locations. The origin of the force can come from effective techniques and/or other molecules. Hydrostatic pressure is applied between two ends of the SWNT to exploit the flux change due to deformations. We found that the nanopore was an excellent on−off gate that is both effectively resistant to noises and sensitive to available signals. Within a displacement of about 2.0 Å of the forced-atom, the average number N of water molecules inside the nanotube, denoted by $\langle N \rangle$, remains almost unchanged and the water flux even increases a little. This critical value of the displacement depends on the peak-to-peak value of the wavelike pattern of the water distribution

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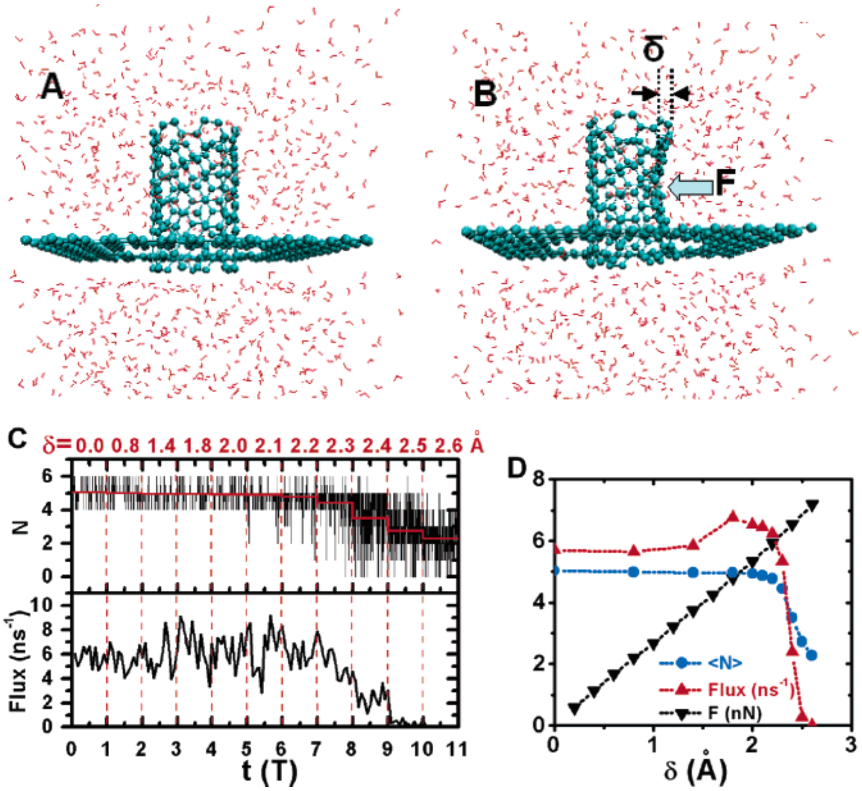

Figure 1. (A, B) Snapshot of the simulation system. The carbon nanotube in (A) is unperturbed. An external force, marked by F, acts on an atom of the carbon nanotube in (B), and a deformation can be clearly seen. δ is the displacement of the forced-atom from its initial equilibrium position in (A). The green spheres are the carbon atoms of the nanotube. (C) Number N of water molecules inside the tube and the water flux as a function of time for each conformation. The time period for each conformation is T, where $T = 12$ ns for the occupancy and 216 ns for the flux. The flux is defined by the difference of the numbers of water molecules entering the SWNT from the bottom and upper ends, left on the other sides, per nanosecond. The flux shown is averaged at each 18 ns. The red numbers at the top of the figure show the value of δ for each conformation. (D) Average number of N and the water flux for the whole period of T, together with the force F acting on the atom, for different δ. $\langle N \rangle$ converges very quickly so that 12 ns is enough to achieve an acceptable accuracy.

inside the unperturbed nanotube. An abrupt transition from the open state to the closed state occurs by an additional displacement of about 0.6 Å. Interestingly, the wavelike patterns have also been observed in biological water channels so that a similar critical displacement is expected.[7] This open−close transition can be triggered by an external force of only ∼1.8 nN, which falls within the force range of many available experimental facilities. This provides the possibility of controlling the water flow across the nanotube and developing SWNT-based nanoscale devices.

Computational Methods

The simulation framework is shown in Figure 1(A, B). A single graphite sheet divided the full space into two parts. An uncapped, single-walled carbon nanotube[22] 13.4 Å in length and 8.1 Å in diameter was embedded in the graphite sheet along the z direction. The distance between the bottom end of the SWNT and the graphite sheet is 2 Å. The 144-carbon (6,6) nanotube was formed by folding a graphite sheet of 5×12 carbon rings to a cylinder and then relaxed with the interaction between carbon atoms. This interaction was described with the parametrized potential by Brenner[23] according to the Tersoff formulism.[24] Initially water molecules were filled in the other space of the system except for the channel of the SWNT. Periodic boundary conditions were applied in all directions. A force $F(t)$ was applied to one carbon atom (the forced-atom) in the right side of the carbon nanotube. Consequently some of the neighboring carbon atoms were pushed away from their initial positions. The carbon atoms in the left half of the carbon nanotube were fixed. For each external force F, an equilibrium state $\mathscr{R}$ of a SWNT could be obtained by relaxation, corresponding to a displacement of the forced-atom, denoted by δ.

When two sides of a membrane have the same hydrostatic pressure but different concentrations of an impermeable solute, an osmotic pressure difference is established and water flows from the side with lower solute concentration to the other side. In this paper, we applied a force to each water molecule along the $+z$ direction to obtain a pressure difference between two ends of the SWNT. This pressure difference is something like the osmotic pressure difference.[9,25] It was found that the pressure difference between two ends of the SWNT is 133 MPa for an additional acceleration of 0.1 nm ps^{-2} at each atom, smaller than that used in ref 25. To prevent the SWNT from being swept away, the carbon atoms at the inlet, outlet, and where the external force was exerted were fixed in the simulations.

The molecule dynamics simulations were carried out at a constant pressure (1 bar with initial box size $L_x = 3.0$ nm, $L_y = 3.0$ nm, $L_z = 4.0$ nm) and temperature (300 K) with Gromacs 3.2.1.[26] Molecular dynamics has been recognized as one of the most effective tools in the study of water in SWNT, in proteins, and between proteins.[5,7−11,13,17,27−29,32] Here the TIP3P [30] water model was applied. A time step of 2 fs was

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used, and data were collected every 0.5 ps. In the simulations, the carbon atoms were modeled 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 $\epsilon_{CC} = 0.3612$ kJ mol^{-1}, $\epsilon_{CO} = 0.4802$ kJ mol^{-1}.[11] Carbon−carbon bond lengths of 0.14 nm and bond angles of 120° were maintained by harmonic potentials with spring constants of 393 960 kJ mol^{-1} nm^{-2} and 527 kJ mol^{-1} deg^{-2} before relaxation.[31] In addition, a weak dihedral angle potential was applied to bonded carbon atoms.[11]

Results and Discussion

For each state $\mathscr{R}$, corresponding to an external force F and displacement δ, the time for the numerical simulation is 232 ns. The last 216 ns of the simulation were collected for analysis. For each simulation, the nanotube is rapidly filled by water from the surrounding reservoir.[11] Figure 1C displays the average number of water molecules inside the tube $\langle N \rangle$, together with the water flux averaged by each 18 ns, as a function of time for each conformation. The average values for all the 216 ns simulations, together with the external force F acting on the force-atom, for different δ are shown in Figure 1D.

For the unperturbed nanotube, the nanotube is occupied by about five water molecules.[11] During the entire 216 ns simulation, 726 and 1955 water molecules entered the SWNT from the upper and bottom ends and left on the other sides, respectively, resulting in a water flux of 5.69 water molecules per nanosecond from bottom to upper through the SWNT. This value is comparable to the measured 3.9 ± 0.6 ns^{-1} for aquaporin-1.[4] Comparable flow rates have also been observed in recent simulations on a biological channel[25] and a carbon nanotube membrane.[32]

It is remarkable to find that even when F is increased to 5.34 nN, which corresponds to δ of 2.0 Å, $\langle N \rangle$ is almost unchanged and the water flux even increases a little, as shown in Figure 1C,D. Note that 2.0 Å is larger than the radius of a water molecule (∼1.4 Å). The water flux and the occupancy $\langle N \rangle$ decrease as F (and thus δ) is further increased. For $F = 7.18$ nN, corresponding to $\delta = 2.6$ Å, the water flux inside the tube becomes a negligible value. In the entire 216 ns simulation, no water molecules entered the SWNT on one end and left on the other end, indicating that the nanotube is functionally closed. At $\delta = 2.6$ Å, the minimal value of the distance between two carbon atoms in the opposite direction is 5.6 Å, comparable to the pore radius R_P that the channel is constitutively closed in the model pore.[16] It is clear that a SWNT can be completely closed ($\delta = 2.6$ Å) from an open ($\delta = 2.0$ Å) state by moving the forced-atom by as little as 0.6 Å, which is much smaller than the radius change of 1 Å to switch a hydrophobic pore from closed to open.[16]

The minimal external force F needed to switch a SWNT from full open ($\delta = 2.0$ Å, $F = 5.34$ nN) to closed ($\delta = 2.6$ Å, $F = 7.18$ nN) is about 1.8 nN, which is in the working range of an atomic force microscopy and optical tweezers. This provides the possibility for the fabrication of nanosyringes to conduct water molecules.[33,34]

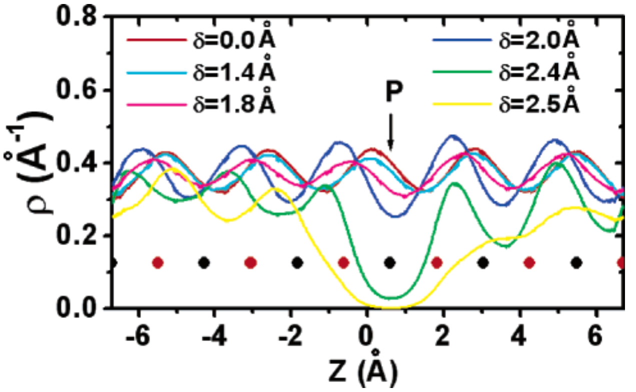

Figure 2. Water distribution along the nanotube axis together with the positions of carbon atoms for $\delta = 0$, 1.4, 1.8, 2.0, 2.4, and 2.5 Å. The red and black filled circles denote the locations of the carbon atoms. The arrow, marked by P, is the position of the atom affected by an external force.

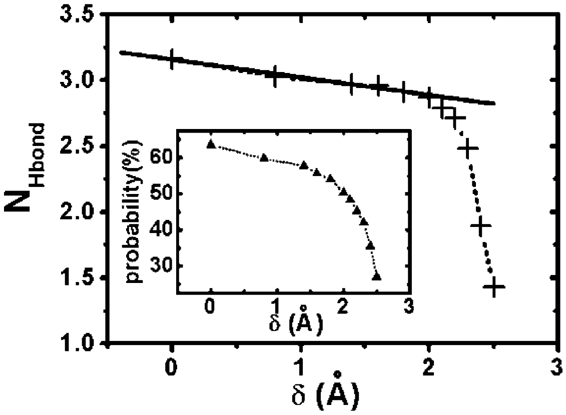

Figure 3. Average number of the hydrogen bonds inside the nanotube and (inset) the probability of the hydrogen bond formed by those two water molecules neighboring the forced-atom for different δ. The solid line is a linear fit for $\delta < 2.0$ Å.

For an unperturbed SWNT, it remains completely open for a maximal external force of 5.34 nN, which may come from thermal fluctuations, while closes at 7.18 nN or more.

Figure 2 shows the distribution of water molecules inside the nanotube along the z direction under different values of δ. The red and black filled circles denote the locations of the carbon atoms. In the case of $\delta = 0$ the distribution has a wavelike structure with minimal values at the openings.[11] Wavelike patterns of the distributions of atoms O and H of water have also been observed in GlpF channels.[7] In contrast to the water occupancy, which remains almost fixed for $0 \leq \delta \leq 2.0$ Å, the distribution changes gradually and the peaks (dips) move leftward as δ increases in this δ range. The water distribution at P, the location facing the forced-atom, decreases, corresponding to the narrowing of the nanotube at P. The inlet and outlet are no longer in the positions for the minimal distributions when $\delta > 0$. From $\delta \approx 2.0$ Å and up the distribution at P is smaller than those of the other dips, and the wavelike pattern is considerably deformed when $\delta \geq 2.4$ Å. The distribution at P is very close to zero for $\delta = 2.5$ Å. However, we can still observe that about one water molecule entered on one side and left on the other side per nanosecond at this δ value. Careful

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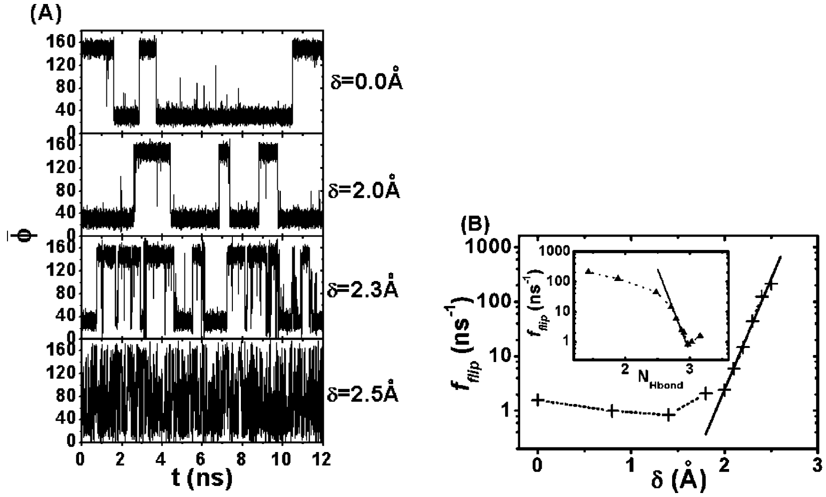

Figure 4. (A) $\bar{\phi}$ for $\delta = 0$, 2.0, 2.4, and 2.5 Å. (B) Dependence of flipping frequency f_{flip} on δ and the number of hydrogen bonds N_{Hbond} inside the nanotube. The solid lines are the fits for the exponential growth vs δ and decay vs N_{Hbond} (inset) for different δ ranges.

inspection of the data shows that water molecules can pass *P* very rapidly without staying.

Figure 2 clearly shows that the water distribution has a similar wavelike pattern in the parameter range $0 \leq \delta \leq 2.0$ Å, except for the shift of peaks and a small change of the peak-to-peak value. The maintenance of the similar wavelike pattern with an almost constant average value leads to the invariability of the total number of water molecules inside the nanotube. The shift of the peaks and slight modification of the peak values are believed to accommodate the deformation of the SWNT due to the external force. It seems that the wavelike pattern at $\delta = 0$ determines a critical value of δ_c. Denoted by W_0, the minimal value of the water distribution at $\delta = 0$, the distribution at *P* is approximately equal to W_0 at $\delta = \delta_c$. $\langle N \rangle$ is almost unchanged in the range of $\delta \leq \delta_c$. $\delta_c \approx 2.0$ Å in the present system.

The water molecules in the SWNT form a single hydrogen-bonded chain. The hydroxyl OH bonds involved in hydrogen bonds (here we adopt a geometric definition of hydrogen bonds, according to which a water pair is hydrogen-bonded if the O−O distance is less than 3.5 Å and simultaneously the bonded O−H···O angle is less than 30°)[35] are nearly aligned along the nanotube axis and collectively flip directions.[36,37] Due to the deformation of the SWNT, the total number of hydrogen bonds in the nanotube decreases as δ increases (Figure 3). The average number of the hydrogen bonds, denoted by N_{Hbond}, decreases very slowly in an linear fashion as $N_{\text{Hbond}} = 3.16 - 0.136$ Å for $\delta < 2.0$ Å. In the δ range with $2.0 \text{ Å} \leq \delta \leq 2.5$ Å, N_{Hbond} decreases sharply from 2.87 to 1.43 Å. The decreasing of N_{Hbond} results from the decreasing of the total water molecules inside the nanotube as well as the increasing of the distance between those two water molecules' neighbor to the position *P*. The increasing of the distance between those two water molecules neighboring *P* leads to a smaller probability of a hydrogen bond between them. The inset in Figure 3 displays the probability, which is only 27% for $\delta = 2.5$ Å.

To explore the role of the flipping of dipoles of the water molecules inside a SWNT and its sensitivity to the deformation, we have computed the average angle $\bar{\phi}$, where ϕ is the angle between a water dipole and the nanotube axis. The average runs over all the water molecules inside the tube. Some examples are shown in Figure 4A. For the unperturbed SWNT, $\bar{\phi}$ falls in two ranges, $15° < \bar{\phi} < 50°$ and $130° < \bar{\phi} < 165°$, for most of the time, consistent with the observation that the water molecules in SWNT are nearly aligned.[37] If we define a flip as $\bar{\phi}$ passing through 90°, we can compute the number of flips per nanosecond, denoted by the flipping frequency f_{flip}. The results are shown in Figure 4B.

Generally, f_{flip} is governed by the potential barrier against flipping. The increment of δ leads to two aspects of the potential change, decreasing due to the breakage of hydrogen bonds inside the nanotube and increasing due to the narrowing of the nanotube, which confines water molecules to a smaller space. As that shown in Figure 3, N_{Hbond} decreases very slowly with respect to δ for $\delta \leq 1.4$ Å. Consequently, the change of the potential barrier is mainly from the confinement of water molecules, resulting in a slow decreasing of f_{flip}.

As δ further increases, f_{flip} increases. The dependence of f_{flip} on N_{Hbond} is shown in the inset of Figure 4B. In the range of $2.0 \text{ Å} \leq \delta \leq 2.2$ Å, the function

$$f_{\text{flip}} \propto \exp(-\, N_{\text{Hbond}} E_{\text{Hbond}}/kT)$$

can fit the data quite well, where E_{Hbond} is the average energy of a hydrogen bond in the nanotube for $\delta = 2.0$, 2.1, and 2.2 Å. Numerically we find $E_{\text{Hbond}} = 12.96kT$. This exponential decay indicates that the change of the potential barrier mainly results from the decreasing of the hydrogen bonds in the nanotube in this parameter range. For larger δ, say 2.5 Å, the water chain is frequently ruptured. Only for a small time period, $\bar{\phi}$ falls in the two parameter range, i.e., $15° < \bar{\phi} < 50°$ or $130° < \bar{\phi} < 165°$. However, in the interval of $2.0 \text{ Å} \leq \delta \leq 2.5$ Å, we find that the exponential function $f_{\text{flip}} \propto \exp(\{\delta\}/\{\tau\})$ with $\tau = 0.107$ can fit the data very well.

Figure 5 displays the free energy of occupancy fluctuations, $\beta F(N) = -\ln p(N)$, where $p(N)$ is the probability of finding exactly N water molecules inside the nanotube. To obtain good statistics, data were collected every 0.25 ps in the calculation of $p(N)$. An approximate Gaussian occupation fluctuation is found for $\delta = 0$, consistent with the observation by Hummer et al.[11] The free energies for $\delta = 1.4$ and 2.0 Å are similar to

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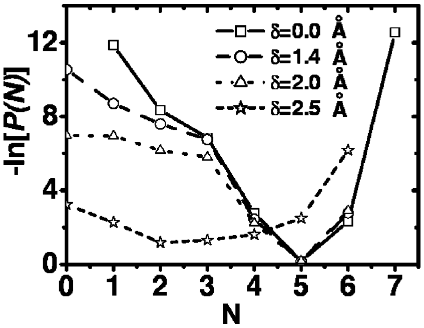

Figure 5. Free energy of occupancy fluctuations, $\beta F(N) = -\ln p(N)$, for $\delta = 0$, 1.4, 2.0, and 2.5 Å.

that for $\delta = 0$. However, three events have been found with $N = 7$ for $\delta = 0$, while none for $\delta = 1.4$ and 2.0 Å. With $N = 0$, it occurs 11 and 388 times for $\delta = 1.4$ and 2.0 Å, respectively, in contrast with none for $\delta = 0$. It seems that the effect of the deformation for $\delta \leq 2.0$ Å is considerable for the possibilities of the rare events, although the change of the average value of the water molecules inside is negligible. For $\delta = 2.5$ Å, the function is somewhat flat between $N = 2$ and 4, with a minimum at $N = 2$, due to the frequent rupture of the water chain. No intermittent filling is found in the range $0 \leq \delta \leq 2.5$ Å, consistent with the fact that there is no minimum at $N = 0$.[11,38] Although there are many cases with $N = 0$ for $\delta = 2.5$ Å, the durations for them are short. We have not found two successive data with $N = 0$, indicating that the duration for each case with $N = 0$ is less than 0.25 ps.

Conclusions

The water molecules inside single-walled carbon nanotubes have distinguished properties as an excellent nano-controllable on−off gate. On one hand, counter to intuition, when the external force exerted on the forced-atom leads to displacements within 2.0 Å, the water occupancy in the nanotube remains almost unchanged and the water flux across the nanotube even increases a little. Note that the critical displacement of 2.0 Å is larger than the radius of a water molecule (∼1.4 Å), indicating that the flux and the water occupancy of an unperturbed SWNT are extremely irrespective of external signals, for example, deformations due to noises. On the other hand, the behavior of water molecules inside the nanotube is sensitive to further deformations. An additional displacement of 0.6 Å of the forced-atom leads to an abrupt transition from an open state (flux at an unperturbed SWNT) to a closed state (no flux). Overall, the nanotube has the advantages of an excellent nanoscale on−off gate that it is both effectively resistant to noises and sensitive to available signals.

The wavelike pattern of the water distribution in the nanotube is the main cause for this interesting anomaly. The initial deformation of the SWNT, before a critical value, is believed to be accommodated by the shift of the peaks and slight modification of the peak values of the wavelike pattern. The critical value of the displacement depends on the peak-to-peak value of the pattern in an unperturbed nanotube. We are reasonably confident that biological water channels share this advantage since wavelike patterns of water distributions have also been observed in Aquaporin water channels.[7]

The wavelike pattern might be particular to a small pore with only a single water chain inside. We have performed numerical simulations by replacing the (6,6) SWNT with a (8,8) SWNT. The water distribution in the nanotube is quite flat for $\delta = 0$, and the average number inside the nanotube is about 15, much larger than that in a (6,6) SWNT, indicating that the single water chain does not exist. Both $\langle N \rangle$ and flux decrease considerably compared to those for a (6,6) SWNT for small δ. Details of SWNTs with larger radii will be presented elsewhere.

The minimal external force required for a deformation of an open−close transition is only ∼1.8 nN, which is in the working range of many available experimental facilities, including atomic force microscopy and optical tweezers. This observation makes it possible to control the water flow across a nanotube.

The deformation has significant impact on the collective flipping of the water dipoles in the nanotube. It is found that the change of the potential barrier against the flipping is dominated by the confinement of water molecules for $\delta \leq 1.4$ Å and the breakage of the hydrogen bonds within the nanotubes for 2.0 Å $\leq \delta \leq$ 2.2 Å. The water chain is frequently ruptured for $\delta \geq 2.5$ Å.

As one can see, it is the simplicity of the carbon nanotube that enables us to carry out numerical simulations over extremely long time periods (216 ns) and with a wide range of parameters of δ. The conclusion obtained may have biological significance, which might be helpful to the understanding of the gating mechanics of biological water channels. It also provides the possibility to develop nanoscale SWNT-based devices, including nanosyringes.

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Supporting Information Available: Complete refs 22, 26, and 31. This material is available free of charge via the Internet at http://pubs.acs.org.

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