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# Effect of Charge on Water Filling/Emptying Transitions of Nanochannel

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The effect of external charge on distribution properties of water molecules confined inside the single-walled carbon nanotube (SWNT) with modified carbon–water interactions is investigated by the molecular dynamics simulations. It is found that when a single external charge (of value  $+1.0e$ ) is in the middle region of the SWNT, the nanotube is filled by the single-file water chain. Sharp transitions between empty (closed) and filled (open) states occur once the charge moves out the middle region. Simulation results indicate that filling and emptying kinetics depend sensitively on the position of external charge. These findings are helpful to understand the mechanism of charge-dependent gating of hydrophobic nanotubes.

## I. Introduction

Water-filled channels of nanometer dimensions has attracted increasing attention due to their importance in biological activities and potential application in nanotechnology.<sup>1–5</sup> It is well known that the ability of living cells to transport water, ions, and water-solute molecules across their cell membrane is mediated by proteins which function as transporters and channels (these channels are usually “gated”).<sup>6</sup> They contain a region that can interrupt the flow of molecules (water, ions) and thus can switch between open and closed states.<sup>7–10</sup> However it is not easy to gain a clear insight into the mechanism of gating by direct investigation, since the structure and the interactions among proteins of biological channels are so complex.

In recent years, numerous simulations of water confined in or transporting through single-walled carbon nanotubes (SWNTs) have shown many interesting dynamical properties of water which are shared by most biological channels.<sup>11,12</sup> Therefore, SWNTs with proper diameter are often used as prototype to study two-state transitions between empty and filled states which is possibly relevant to the gating of the channels.<sup>12–16</sup> In 2001, Hummer et al. found that water molecules not only form a single-file ordered chain inside the hydrophobic carbon nanotube but also transport through it fastly. They also found that a small reduction in the nanotube–water interaction leads to sharp transitions between empty and filled states on a nanosecond time scale.<sup>12</sup>

Subsequently, several groups had introduced charges, electronic field, and dipoles to design more realistic models to mimic biological channels considering that they are indispensable in both membrane proteins and circumference of the living cells.<sup>11,13,17–20</sup> With these model systems, the Coulombic effect on the water permeation through the channel were studied. In our previous work, water permeation across a SWNT under the influence of a mobile external charge has been studied with molecular dynamics simulations, and electrostatic gating was discussed.<sup>17</sup> On the basis of that work, we went one step further and proposed a design for a molecular water pump using a combination of charges positioned adjacent to a nanopore.<sup>18</sup> In 2001, Sansom et al.<sup>13</sup> revealed that there is an abrupt transition between a closed (empty) state and an open (filled) state for water passing through atomistic models of nanopores once the

radii of the pores reach a critical value. They further studied the electrostatic effect on the water confinement in the nanopores by adding dipoles to its lining. Allen et al.<sup>15</sup> found that the permeation of water across cylindrical nanopores is intermittent on a nanosecond time scale when the radius or the electric polarization is at threshold value. Dzubiella and Hansen<sup>19</sup> also found that there will be intermittent filling of the pore by water as the radius reaches a critical value and that a strong electric field generated by an ion concentration imbalance can decrease the critical radius of hydrophobic nanopore for water permeation.

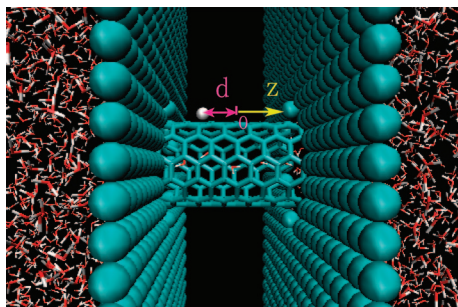
In this study, we choose the modified SWNT proposed by Hummer et al.<sup>12</sup> with an external positive charge to investigate the influence of indispensable charges as well as the possible charge noise near water channels on the two-state transitions between empty and filled states. Unlike the previous studies, the charge we introduced here can move along the wall of the SWNT (its track parallel to the axis of the nanotube). Considering the symmetric structure of the system, we only move the external charge to one side from the middle point of the nanotube. Two-state transitions between empty and filled states have been found by Hummer et al. in this modified SWNT without external charge. Remarkably, this hydrophobic SWNT exhibits filled state when an external charge is assigned in the middle region of the nanotube. The transitions between empty (closed) and filled (open) states occur once the charge moves out the middle region of the nanotube.

This paper is organized as follows. The simulation model and parameters are introduced in Section II. Section III is devoted to the simulation results and discussion. Finally, conclusions are presented in Section IV.

## II. Model and Key Parameters

The simulation framework is shown in Figure 1. An uncapped, SWNT<sup>21</sup> with modified carbon–water interaction, 13.4 Å in length and 8.1 Å in diameter, was embedded along  $z$  direction in two carbon sheets. The distance in  $z$ -direction between the left end of the SWNT and the carbon sheet is 0 Å. The 144-carbon (6, 6) nanotube is formed by folding a carbon sheet of  $5 \times 12$  carbon rings to a cylinder. Periodic boundary conditions are applied in all directions. To study the influence of external charge on the structure and dynamical properties of water confined in the SWNT, a positive charge with a quantity of 1.0  $e$  is placed outside the carbon nanotube with a fixed

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**Figure 1.** Snapshot of the simulation system (side view). The SWNT and the graphite sheet are solvated in a box ( $5 \times 5 \times 6$  nm) with 3441 water molecules. The white point is the imposed charge and  $d$  is the displacement of the charge from its initial origin position.

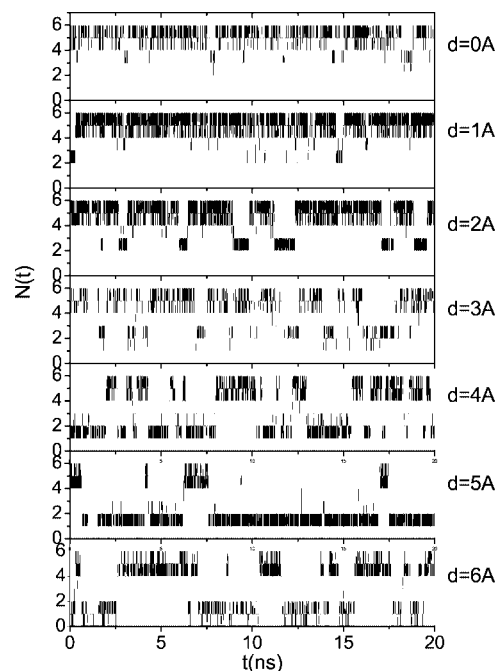
distance of 1 Å from the wall of the nanotube. To keep the simulation system electronically neutral, a contrary charge is assigned close to the boundary. Different from our previous simulation system,<sup>17</sup> there is no water near the external charge for the middle part isolated by two carbon sheets. Without the screening effect of the water surrounding the external charge, the critical distance increase from 0.85 to about 1 Å. The external charge can move freely along the nanotube axis,  $z$ , ranging from 0 to 6 Å. For the convenience of analysis, this distance between charge and origin point is denoted by  $d$ . In our simulations,  $d$  ranges from 0 to 6 Å. The induced polarization and deformation due to the external charge have not been accounted for in our present simulations.

Molecular dynamics simulations were carried out at a constant particle number, temperature (300 K) and pressure (1 bar) with Gromacs 3.2.1. Here, Berendsen algorithms were used to simulate at constant temperature (time constant 0.5 ps) and constant pressure (compressibility  $4.5 \times 10^{-5}$  bar<sup>-1</sup>, time constant 0.5 ps) with the  $x$  and  $y$  dimensions of the simulation box held fixed.<sup>22</sup> The TIP3P water model<sup>24</sup> was applied. A time step of 2 fs was used and data were collected every 0.5 ps. In the simulations, carbon–water attractive interactions are reduced by tubing Lennard-Jones parameters.<sup>12,25</sup> The modified carbon–water interactions<sup>12</sup> are  $\sigma_{\text{CO}} = 0.34138$  nm and  $\epsilon_{\text{CO}} = 0.27136$  kJ mol<sup>-1</sup>. Carbon–carbon bond lengths of 0.14 nm and bond angles of 120° are maintained by harmonic potentials with spring constants of 393 960 kJ mol<sup>-1</sup> nm<sup>-2</sup> and 527 kJ mol<sup>-1</sup> rad<sup>-2</sup> before relaxation. In addition, a weak dihedral angle potential is applied to bonded carbon atoms. The long-range electrostatic interactions were computed by using a particle-mesh Ewald method<sup>26</sup> (real space cutoff, 1.0 nm; FFT grid spacing, 0.12 nm, fourth-order interpolation). The short-range interactions were computed using a cutoff scheme (cutoff distance, 1.0 nm).

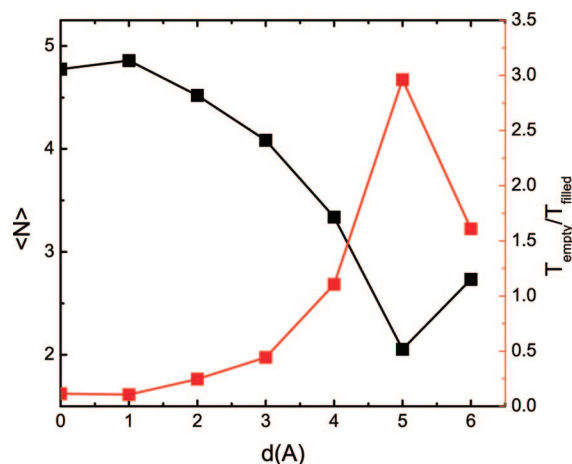
### III. Results and Discussion

As shown in Figure 1, we set the imposed charge at different positions along the nanotube axis to study the influence of external charge on two-state transitions between empty and filled states. For each case with different distances, a 100 ns molecular dynamics simulation is performed. The last 90 ns of the simulation were collected for analysis.

The number  $N(t)$  of water molecules inside the nanotube for different  $d$  are shown in Figure 2. In this paper, a nanotube is said to be in the empty state if the number of water molecules inside the nanotube,  $N(t)$ , is less than 4, otherwise it is in filled state. Interestingly, we find the water occupancy of the channel with the two-state transitions between empty and filled states



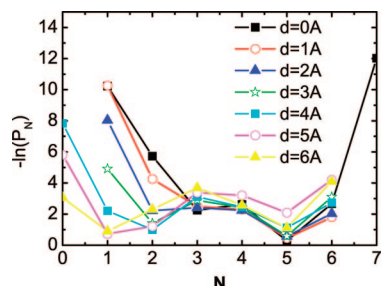
**Figure 2.** The number  $N(t)$  of water molecules inside the tube for different  $d$ .



**Figure 3.** Average value of number  $N$  of water molecules inside the tube and the ratio of the average time for empty and filled state under different  $d$ .

is very sensitive to the position of the external charge. The nanotube is almost in filled state when the charge is in the middle region ( $d \leq 2$  Å) of the tube. And the average number of water molecules inside the nanotube,  $\langle N \rangle$  is larger than 4 (see Figure 3). When the external charge moves out this region, the probability of empty state increases sharply. For  $d = 5$  Å, the nanotube favors to be in the empty state and  $\langle N \rangle$  is about 2.05. Remarkably, when the charge is at  $d = 6$  Å, the channel is more easier to be filled by water molecules than the channel with charge at  $d = 5$  Å. For  $d = 6$  Å,  $\langle N \rangle$  increases to 2.75.

To characterize this filling/emptying transition more clearly, we have calculated the ratio between the average time of empty state  $T_{\text{empty}}$  and the average time of filled state  $T_{\text{filled}}$  in the whole simulation time, denoted by  $T_{\text{filled}}/T_{\text{empty}}$ . Simulation results show that  $T_{\text{empty}}/T_{\text{filled}}$  increases for  $d \leq 5$  Å as the charge moves away from the middle region of the channel (see Figure 3). In the case of  $d = 4$  Å, the probability of empty state is just close to that of filled state.  $T_{\text{empty}}/T_{\text{filled}}$  increases to about 3.0 when distance of the charge site away from the inlet of the channel

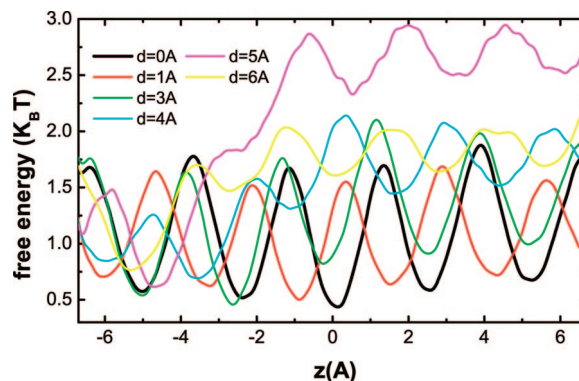


**Figure 4.** Free energy of occupancy fluctuation under different distances of the imposed charge away from the middle point of the tube.

is about 1.7 Å (correspondingly,  $d = 5$  Å). However, if the charge moves closer to the inlet of the channel, for example,  $d = 6$  Å, the average filled time is larger than that for  $d = 5$  Å.

Figure 4 displays the free energy of occupancy fluctuations,  $F(N) = -k_B T \ln p(N)$ , where  $k_B$  is the Boltzmann constant,  $T$  is the temperature and  $p(N)$  is the probability of finding exactly  $N$  water molecules inside the nanotube. For  $d \leq 2$  Å, the situation of  $N = 5$  holds the lowest free energy; however, there is no minimum in the range of  $N \leq 3$ . These results are consistent with previous work.<sup>12,27</sup> So the probability of filled state is larger than that of empty state.  $T_{\text{empty}}/T_{\text{filled}}$  is less than 1. The free energy of  $N = 5$  increases as the charge moves further toward inlet of the SWNT and reaches the maximal value at  $d = 5$  Å (see the pink line in Figure 4). On the contrary, the free energy of  $N = 0, 1, 2$  decreases correspondingly. As  $d$  is larger than 3 Å, there are two minimums in the free energy profile. It indicates that there are two metastable states (filled/empty state) for the nanotube. For  $d = 4$  Å, the probability of  $N \geq 4$  almost equals to that of  $N \leq 3$ . The free energy of  $N \leq 3$  decreases during the process of the charge moves from middle to the left inlet of the SWNT while that of  $N \geq 4$  increases. We also find that the two situations of  $d = 5$  Å and  $d = 6$  Å have the same free energy of  $N = 1$ , but the free energy of filled state ( $N \geq 4$ ) for the latter situation of  $d = 6$  Å is evidently lower than that for  $d = 5$  Å. So the average number of water molecule for  $d = 6$  Å is greater than that for  $d = 5$  Å. And the  $T_{\text{empty}}/T_{\text{filled}}$  is consistent with the above fact also.

The potential of mean force (PMF) is often used as input in a stochastic model, based on the Fokker–Planck equation, to characterize the behavior of water molecules inside the nanotube.<sup>28–30</sup> We obtained PMF,  $F(z)$ , from the equilibrium water probability density  $\rho(z)$  by  $F(z) = -k_B T \ln \rho(z)$ .<sup>29,31</sup> The PMFs of water molecules along the axis of the tube for each situation are shown in Figure 5. We find out that the wavelike patterns are retained after the introduction of the external charge, but with the charge moving the curves have a corresponding transfer in horizontal direction. Remarkably, the PMF curves can be divided into two parts by the site of the imposed charge. The right parts are lifted greatly while the left parts retain almost on the same level as the charge moves out the middle region. As  $d \geq 3$  Å, the right part of the PMF curves are not only lifted greatly but also the peak-to-peak value (min to max) decreased observably. To our surprise, when the charge is placed at  $d = 5$  Å, the right part of PMF is far greater than others. It means the water molecules are unwilling to stay in the right part of the tube, leaving it empty most of the time. On the contrary, the left part is almost filled by one or two water molecules due to the attraction from the charge. This is consistent with that the average number of water molecules inside the tube becomes smaller when the charge moves apart from the middle region ( $d > 3$  Å).

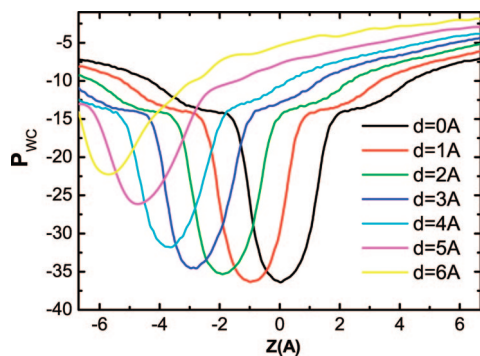


**Figure 5.** The profile of potential of mean force (PMF) corresponding to different distances of the imposed charge outside the channel.

Why is the right part of PMF lifted as  $d$  increases? For  $d = 0$ , the middle water molecule is easy to be pinned due to attraction from the external charge. When the charge moves to the left inlet of the SWNT (i.e.,  $d = 2, 3$  Å) instead of the middle water molecule, the one on the left side of it will be attracted strongly so that it destroys the symmetry of the single-file water chain inside the SWNT. The part of the water chain right to the charge is longer than the part of the water chain left to the charge. So the right part of the water chain is easier to be interrupted than the left part. Once the water chain is interrupted at the right side of the water nearest to the charge, only two water molecules locate in the left part of the tube. The water molecules outside the SWNT are difficult to enter from the right entrance for the weak attractive potential induced by the charge, leaving the right part of the tube empty. In the same way, as the charge moves further to the left entrance, such as  $d = 5, 6$  Å, the water molecule can enter the left entrance by the attractive potential of the imposed charge. Interestingly, when the charge is at  $d = 5$  Å, responding to  $z = -5$  Å, once a water molecule is attracted into the left entrance, it would like to stay at around  $z = -5$  Å, because the distance to the left entrance at this point is just a little larger than the radius of a water molecule (about 1.4 Å). So the whole water molecule is inside the tube. However, when the charge is at  $d = 6$  Å, the distance apart from the left entrance is less than half the water molecule size. If the water molecule is unwilling to stay at the site  $z = -6$  Å, it enters furthermore and is willing to stay near the site  $z = -5$  Å. The strength of attracting the water molecules near the left inlet from the charge at  $d = 6$  Å is greater than that from the charge is at  $d = 5$  Å. Therefore, water molecules are easier to enter the tube for  $d = 6$  Å than for  $d = 5$  Å.

To understand the properties of the water occupancy and distribution inside the SWNT under the influence of the imposed charge, we calculated the electrostatic potential between the imposed charge and the water molecule at position  $z$  inside the SWNT by the direct Coulomb sum, denoted by  $P_{\text{WC}}$ . The results are shown in Figure 6. We can see that each water-charge interaction profile along the  $z$  axis forms a valley in the region where the imposed charge locates. Though the widths of those valleys are all approximately equal to one-fifth the length of the channel, the absolute value of  $P_{\text{WC}}$  decreases monotonously as the imposed charge moves from the middle to the left side of the SWNT. For easy discussion, we denote the water molecule in the region where the valley is formed in  $P_{\text{WC}}$  by FCW (facing-charge water molecule) hereafter. The valleys indicate that the FCW is attracted much more stronger than its neighboring water molecules. For  $d \leq 2$  Å, the electrostatic energy is about 36 kJ/mol, while the electrostatic interaction

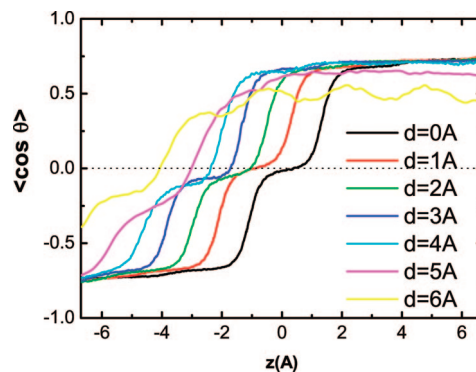




**Figure 6.** The water-charge interactions between the water molecule facing the charge and the imposed charge outside the channel.

energies between charge and the two nearest water molecules (left and right) are both about 13 kJ/mol. The attractive energy becomes weaker for the next neighboring water molecules. We know that this modified SWNT is more hydrophobic without the imposed charge than that with the external charge. The ratio of  $T_{\text{empty}}$  and  $T_{\text{filled}}$  is about 8.3 without the external charge,<sup>12</sup> so we can conclude that the water molecules inside the tube favor to come out to the bulk. For the water molecules, next neighboring to the FCW are very easy to be pulled out from the channel by the bulk water molecules since the attraction from the charge is so weak. The single water chain inside the channel will be interrupted at the position where the next neighboring water molecule locates. As  $d = 0$  Å, the FCW together with its two nearest water molecules are attracted by the imposed charge and can stay inside the channel stably, while the next neighboring water molecules near the outlet/inlet frequently move out to the bulk due to the thermal fluctuations of the bulk. Water molecules in the bulk are easily attracted back to the channel due to the strong hydrogen bond with the water molecules inside the channel. Therefore, the channel is usually in filled state. When  $d = 5$  Å, the FCW is the first one in the whole water chain, and the charge can only dictate the FCW and its nearest neighbor, thus causing the other part of the water chain to move out the channel. Furthermore, the remainder two water molecules are unstable for the strong fluctuation of the bulk, the FCW is easily pulled out to the bulk, and the next neighboring water molecule replaced its place. It is the reason why the number of water molecule inside the channel is one most of the time when the charge is at  $d = 5$  Å.

Why does the absolute value of  $P_{\text{WC}}$  decreases monotonously as the imposed charge moves from the middle to the left side of the SWNT? To understand the mechanism behind the phenomenon, the average value of  $\cos(\theta)$  along the SWNT channel was calculated (shown in Figure 7), where  $\theta$  is the angle between a water dipole and the nanotube axis ( $z$  axis), and the average is taken over all of the data from simulations. For  $d = 0$  Å, the curve is symmetric with respect to the center ( $z = 0$ ) of the SWNT, the position in the nanochannel closest to the external charge. Transitions can be found at the boundary of the central-region. The dipole of the middle water molecule and the axis of the tube is about  $90^\circ$ , corresponding the  $\langle \cos(\theta) \rangle = 0$ . It is clear that  $\langle \cos(\theta) \rangle = 0$  everywhere inside the SWNT when there is no external charge, because the probabilities are equal for both directions, either along the  $z$  axis or the opposite, for the dipoles of all water molecules inside the SWNT. As the external charge is introduced, the system shows a bipolar orientation when all of the water dipoles in the outer-region point away from the center of the SWNT. This is consistent with the previous results<sup>11,17</sup> and is linked to the exclusion of



**Figure 7.** Profile of  $\langle \cos(\theta) \rangle$  along the SWNT, where  $\theta$  is the angle between a water dipole and the nanotube axis.

proton conduction in AQP channels.<sup>9</sup> When the charge moves to the left side of the tube for  $d > 1$  Å, the inflection points of the profiles move to the left side and decrease correspondingly.

Why do the inflection points of the curves decrease? Simulation results show that the right part of the SWNT is usually empty as  $d$  increases. In these cases, the dipole of the water nearest to the imposed charge is some different from the case for the SWNT is filled. In the case that a part of the SWNT is empty, the symmetry of the single-file water chain is destroyed. The water molecule nearest to the charge located in the left side. It is connected with the right water molecule by hydrogen bond, but there is usually no water in its right side. It causes the asymmetric hydrogen bonds at two sides of the FCW. This induces that the angle between the FCW dipole and the nanotube axis is larger than  $90^\circ$ , corresponding the  $\cos(\theta) < 0$ . So the electrostatic interaction potential between the charge and the H atom of the FCW increases. The total interaction of the charge and the FCW becomes weaker, as shown in Figure 6.

#### IV. Conclusions

The effect of the imposed charge on transitions between empty and filled state has been studied in detail. Simulation results indicate that the average time of empty/filled state is sensitive to the position of the external charge. When the charge locates in the middle of the SWNT, the channel is the easiest to be filled by water. The average time of filled state and average number of water inside the channel decrease as the charge moves to the left end of SWNT in the range of  $d \leq 5$  Å. Interestingly, we found that they increase reversely for  $d > 5$  Å. The surprising phenomena result from the effect of mouth of the SWNT and interruption of the right part of water chain.

From the free energy of different occupancy of water molecules inside the tube and the PMF along the tube axis of each situation, we can find that the situation of  $N = 5$  holds one and only the lowest free energy for  $d \leq 2$  Å. The free energy of  $N = 5$  increases as the charge moves toward inlet of the SWNT and reaches the maximal value at  $d = 5$ . On the contrary, the free energy of  $N = 0, 1, 2$  decreases correspondingly. For  $d > 3$  Å, there are two minimums in the free energy profile, indicating that there are two metastable states (filled/empty state) for the nano tube.

The strong water-charge interactions play a critical role in the arrangement of water molecules inside the nanotube. The water molecules in the SWNT always show the bipolar orientation as long as the water chain is intact. The right part of single water chain (right side of FCW) is frequently interrupted due to attraction from the bulk water. The great hydrophobic effect of the nanotube leads to the right part of

the nanotube and is empty when the external charge moves out the middle region. For these situations, the water molecule closest to the external charge only has a left neighbor water molecule; this unbalance leads to the dipole of the water molecule nearest to the external charge not to point downward perfectly but point leftwards slightly. In other words, if the nanotube is partly filled by only about two water molecules in the left part of the nanotube, the average dipole of these water molecules always point to left. We know that in biological channels the positive charge is spread over several atoms in lysine or arginine residues. Nevertheless, the dynamics of water molecules confined in the SWNT with slightly weakened water-nanotube interactions is sensitively dependent on the position of the external charge.

Our research indicates that we can impose an external charge to control the transitions between empty and filled states and transport properties. The conclusions obtained may have biological significance which might be helpful to understand the effects of the charge on the gating mechanics.

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