Using a water-confined carbon nanotube to probe the electricity of sequential charged segments of macromolecules*

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The detection of macromolecular conformation is particularly important in many physical and biological applications. Here we theoretically explore a method for achieving this detection by probing the electricity of sequential charged segments of macromolecules. Our analysis is based on molecular dynamics simulations, and we investigate a single file of water molecules confined in a half-capped single-walled carbon nanotube (SWCNT) with an external electric charge of $+e$ or $-e$ (e is the elementary charge). The charge is located in the vicinity of the cap of the SWCNT and along the centerline of the SWCNT. We reveal the picosecond timescale for the re-orientation (namely, from one unidirectional direction to the other) of the water molecules in response to a switch in the charge signal, $-e \to +e$ or $+e \to -e$. Our results are well understood by taking into account the electrical interactions between the water molecules and between the water molecules and the external charge. Because such signals of re-orientation can be magnified and transported according to Tu *et al.* [2009 *Proc. Natl. Acad. Sci. USA* **106** 18120], it becomes possible to record fingerprints of electric signals arising from sequential charged segments of a macromolecule, which are expected to be useful for recognizing the conformations of some particular macromolecules.

Keywords: molecular dynamics simulation, macromolecular conformation, single-walled carbon nanotube, water molecule

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1. Introduction

Because the functions (mechanical, dielectric, thermal, and so on) of macromolecular materials are closely related to the conformation of the macromolecules, knowing the macromolecular conformation is of particular importance in the application of macromolecular materials.[1−4] Thus, many experimental apparatuses have been used to detect the macromolecular conformation, such as X-ray crystallography,[5−7] electron microscopy,[8,9] and nuclear magnetic resonance.[10,11] However, up to now, it is still a big challenge to detect the conformation of an individual macromolecule. If successful, many more applications can be expected. For example, if a specific macromolecule with a certain conformation is fabricated for medical purposes in pharmacy, the quality of the product involving such macromolecules can be efficiently controlled on a single macromolecular scale by comparing the conformation of the macromolecules in the product with that of the specific macromolecule.

Here we theoretically propose a method for detecting the conformation of an individual macromolecule by probing the electricity of sequential charged segments of the macromolecule. The method is illustrated in Fig. 1. Figure 1 displays a schematic graph showing our proposal for extracting the fingerprint (Fig. 1(c)) of charge signals of sequential charged segments (Fig. 1(b)) of a model macromolecule, aquaporin (Fig. 1(a)).[12] Because the macromolecule of the aquaporin protein (Fig. 1(a)) is just a linear chain of amino acids, figure 1(b) only displays a certain series of charged segments, ASP–ARG–ARG–ARG–ARG–ASP. At a physiological pH=7.4,[13] the amino acid arginine (ARG), has a net charge $+e$ (e is the elementary charge), and the amino acid aspartic acid (ASP), has a net charge $-e$.[14] Figure 1(b) also shows a membrane with a nanopore, through which the linear chain of the aquaporin protein can be expanded and transported under an external pulling force,[15−17] say, a

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force exerted by an optical tweezer. In Fig. 1(b), a single-walled carbon nanotube (SWCNT) containing a single file of water molecules is located parallel to the membrane, and the series of amino acids pass through the nanopore, and approach to touch the cap of the SWCNT one by one. According to the research presented in the rest of this work, the water molecules in the SWCNT can be re-oriented on the picosecond timescale once the amino acid touching the cap is changed from ASP→ARG (namely, $-e \to +e$), or from ARG→ASP (i.e., $+e \to -e$). Also, for the case of ASP→ASP or ARG→ARG, the orientation of the water molecules will remain unchanged. As a result, we get a fingerprint (namely, a pattern of bars in blue and orange) of the charge signals of the consequential charged segments, as shown in Fig. 1(c). In Fig. 1(c), the bar in blue (orange) denotes the case of ASP (ARG) touching the cap, which just corresponds to -dipole ($-e$) (+dipole ($+e$)) (-dipole and +dipole will be defined in Section 3). By using this method, each macromolecule, being beyond the aquaporin macromolecule model, should have a specific fingerprint of charge signals of its charged segments, which is closely related to its conformation. Nevertheless, to show the reasonability of our proposal, we have to solve the following two fundamental problems.

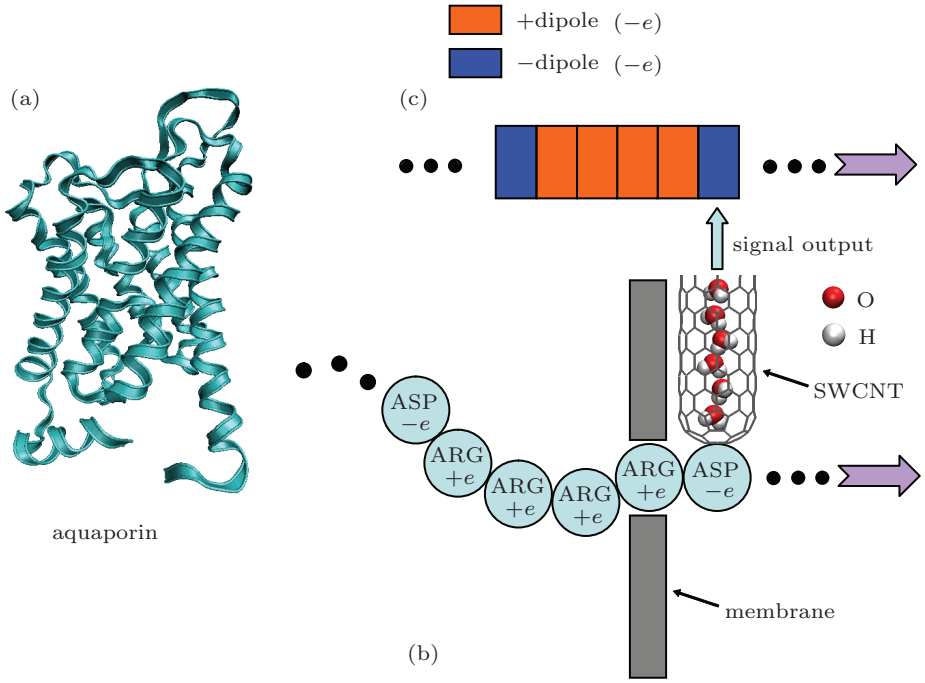


Fig. 1. (colour online) Schematic diagram (b) showing the proposed method for extracting the fingerprint (c) of charge signals of sequential charged segments of a model macromolecule, aquaporin (a).

Problem 1 For either $+e$ or $-e$ touching the cap of the SWCNT, can the water molecules confined in the SWCNT be unidirectionally oriented? Clearly, this is related to a static situation when the external charge, $+e$ or $-e$, is stationary.

Problem 2 If the answer to Problem 1 is yes, we are in a position to consider the second problem related to a dynamic situation. Namely, for either $-e \to +e$ or $+e \to -e$, can the re-orientation (from one unidirectional direction to the other) of the water molecules be completed within a reasonable time period? Apparently, this corresponds to the transporting process when the external charge is changed from $-e \to +e$ or $+e \to -e$.

Obviously, Problem 1 is the basis for Problem 2. Now it becomes clear that the task of this work is to solve Problems 1 and 2.

2. Molecular dynamics simulations

To solve Problems 1 and 2, we resort to molecular dynamics simulations, which have been widely used for the study of water dynamics in SWCNTs.[18–32] Our simulation framework is shown in Fig. 2(a). Figure 2(a) shows an x-directed, half-capped, semiconducting (10, 0) SWCNT with diameter $d = 0.772$ nm and length L, which is fixed at the center of the simulation box with dimensions $l_x \times l_y \times l_z =$

50.00 nm×6.00 nm×6.00 nm. A vertex of the simulation box is set as the origin of the coordinates. In the current work, the water molecules inside the SWCNT are located in a single file and have a constant linear density, 3.7 molecules/nm (the x-direction average distance of two adjacent water molecules is 0.27 nm). To avoid the leakage of water molecules from the SWCNT, a carbon atom is fixed at the right-hand exit of the SWCNT, as shown in Fig. 2(a). An external signal charge, $+e$ or $-e$, is set at $S = 0.05$ nm (at coordinates (15.00 nm, 3.00 nm, 3.00 nm)) away from the apex of the carbon cap, and is along the centerline of the SWCNT. Its opposite charge for neutralization is fixed near the edge of each simulation box at coordinates (50.00 nm, 0.00 nm, 0.00 nm), which is far enough to have no meaningful influence on the water molecules inside the SWCNT. All simulations are carried out in the NVT ensemble at the constant temperature of 300 K by using the velocity rescaling thermostat[33] on the basis of the molecular dynamics package Gromacs 4.0.5. Periodic boundary conditions are applied in the simulations by taking the simulation box as a unit cell. In doing so, due to the length scale of the unit cell and the SWCNT, the interaction between two SWCNTs located in the nearby unit cells is small enough to be neglected. The force field parameters of the SWCNT come from Hummer *et al.*,[26] and the TIP3P water model (namely, the charge on the oxygen atom is $-0.834e$, and that on the hydrogen atom is $+0.417e$) is applied.[34] The van der Waals interactions are calculated with a cutoff of 1.4 nm. The particle-mesh Ewald method[35] is used to treat the long-range electrostatic interactions. At the beginning of each simulation, a Maxwellian velocity distribution of 300 K is generated from random numbers. As shown in Fig. 2(b), the simulations are first run under an external charge of $+e$ or $-e$ for 10.0 ns (-10.0 ns $< t < 0$ ns). Then the charge is switched, either from $+e \to -e$ or from $-e \to +e$, and the simulation is subsequently carried out for 10.0 ns (0 ns$< t <$10.0 ns). A time step of 2.0 fs is used, and data are collected every 40.0 fs.

Here we should claim that the framework displayed in Fig. 2(a) differs from that considered by Tu *et al.*,[22] they investigated a framework by putting an external charge outside of an uncapped, conducting (6, 6) SWCNT with diameter 0.81 nm and length 5.13 nm. To deal with Problems 1 and 2 mentioned above, we design our system as displayed in Fig. 2(a) by taking into account two features. One is the unidirectional ability of the orientation/re-orientation of the water molecules in the SWCNT, which is in contrast to the bi-directional ability considered in the paper of Tu *et al.*[22] The other is the shorter time scale for re-orientating water molecules confined in the SWCNT, which is about 3 orders of magnitude shorter than the nanosecond timescale reported by Tu *et al.*,[22] as to be shown in the following figure.

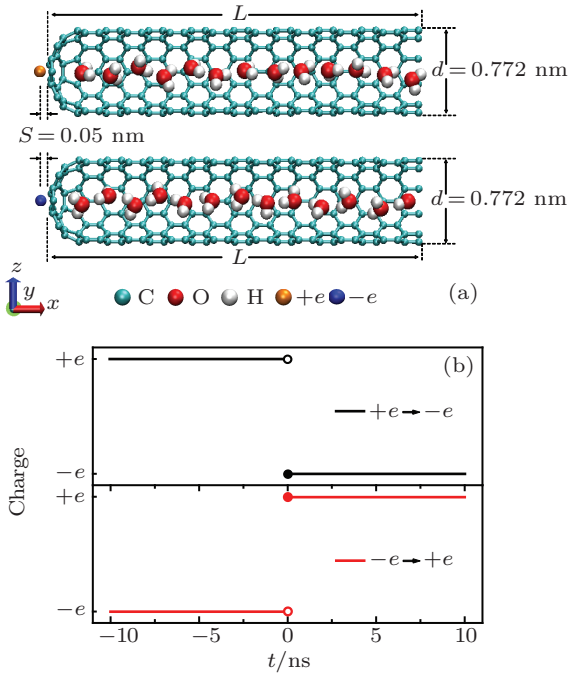


Fig. 2. (colour online) (a) Simulation frameworks with length scales indicated. (b) Charge switches of $+e \to -e$ (upper panel) and $-e \to +e$ (lower panel) in the simulations as a function of time t.

3. Results

Now we present our simulation results. To study Problem 1, we first analyze the response of the water molecules confined in the SWCNT before the switch of the external charge. Figure 3(a) shows the probability distribution of the averaged angle $\langle\theta\rangle$ of the water molecules during -8.0 ns$< t <$0 ns in the presence of an external charge of $+e$ or $-e$, where θ denotes the angle of the dipole moment $\boldsymbol{p}$ of the water molecule with respect to the x axis, as shown in the inset of Fig. 3(a). We find that in the case of $+e$ or $-e$, two symmetric peaks with respect to $\langle\theta\rangle = 90^\circ$ appear clearly (Fig. 3(a)). To account for this finding, we resort to a simplified model by assuming the water molecule as a linear dipole,[34] as shown in Figs. 3(b)–(e). According to Figs. 3(c) and 3(d), we find that the dipole–dipole interaction ($E_{\rm pp}$) is stronger than the charge–dipole interaction ($E_{\rm cp}$) for $N_{\rm sn} \geq 2$, where $N_{\rm sn}$ is the serial number of the water

molecule along the x axis. Thus, the dipole–dipole interaction plays a more important role in re-orientating the water molecules (with $N_{\rm sn} \geq 2$) in the SWCNT, which causes the water molecules to flip one by one (starting from small $N_{\rm sn}$ to large $N_{\rm sn}$; further analysis is shown in Fig. 4).[22] Because the dipole–dipole interaction energy decreases rapidly with the increasing distance according to electrodynamics,[36,37] here we have only considered the effect of the closest water molecules (dipoles). Thus, only the dipole–dipole interaction energy is calculated as a function of θ and shown in Fig. 3(e). Figure 3(e) shows that in the case of the external charge $+e$ ($-e$), $\theta = 0°$ ($\theta = 180°$) is the most stable state for the water molecule. This explains the appearance of the two symmetric peaks in Fig. 3(a). It is worth noting that more factors like thermal fluctuation and detailed microstructure of the water molecule (beyond the linear dipoles without thermal fluctuation assumed for Figs. 3(b)–(e)) have been included for plotting Fig. 3(a), thus causing the two peaks to occur at $\langle\theta\rangle = 30°$ and $\langle\theta\rangle = 150°$ (rather than $\langle\theta\rangle = 0°$ and $\langle\theta\rangle = 180°$), respectively. So we have answered Problem 1 satisfactorily, that is, an external single charge, either $+e$ or $-e$, can orient the water molecules uni-directionally.

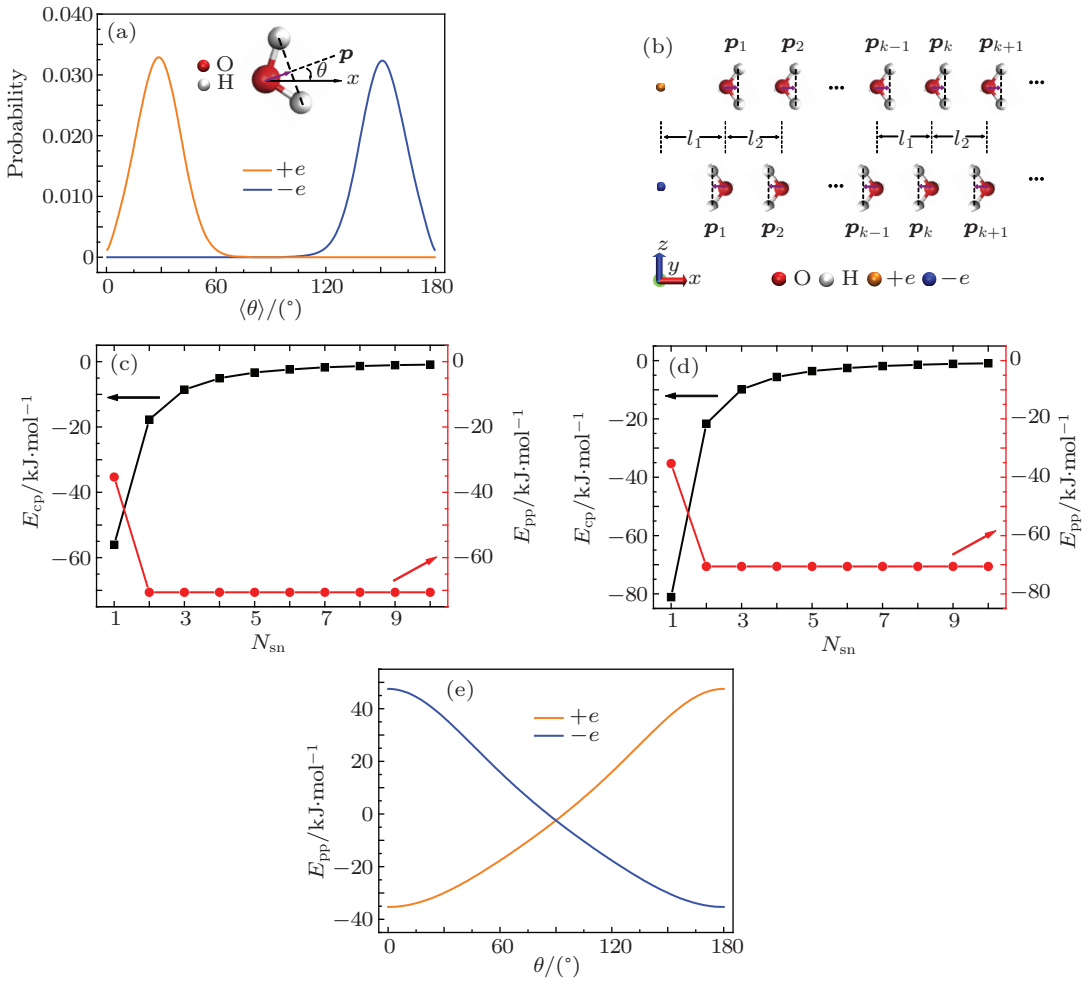


Fig. 3. (colour online) (a) Probability distribution of the angle averaged over all the 30 water molecules inside the SWCNT (with length $L = 8.1$ nm) during -8.0 ns$< t <0$ ns for an external charge of $+e$ or $-e$. θ denotes the angle of the dipole moment $\boldsymbol{p}$ of the water molecule with respect to the x axis, as shown in the inset. (b) Schematic diagram of a simplified model showing a linear chain of water molecules. An external signal charge, either $+e$ or $-e$, is set at $l_1 = 0.32$ nm away from the first water molecule. For clarity, the SWCNT has been omitted. All the oxygen and hydrogen atoms are fixed on a beeline as shown herein, with a separation of $l_2 = 0.27$ nm (corresponding to the linear water density of 3.7 molecules/nm) between two adjacent oxygen atoms. (c) For $+e$ and (d) for $-e$, $E_{\rm cp}$ and $E_{\rm pp}$ each as a function of $N_{\rm sn}$, where $E_{\rm cp}$ is the electrostatic interaction energy of $+e$ with each water molecule, and $E_{\rm pp}$ is the electrostatic interaction energy of a water molecule with its closest one or two water molecules. For the 1st water molecule, $N_{\rm sn} = 1$, $E_{\rm pp}$ is the interaction energy of $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$; for the k-th ($k \geq 2$) water molecule, $N_{\rm sn} = k$, $E_{\rm pp}$ is the sum of the interaction energies of $\boldsymbol{p}_{k-1}$, $\boldsymbol{p}_k$ and $\boldsymbol{p}_{k+1}$, $\boldsymbol{p}_k$. The solid lines are a guide for the eye. (e) For the k-th ($k \geq 2$) water molecule with dipole moment $\boldsymbol{p}_k$, $E_{\rm pp}$ is plotted as a function of θ.

Now we continue to study Problem 2. That is, we need to discuss the response of the water molecules confined in the SWCNT to a switch of the external charge, either $+e \to -e$ (Fig. 4(a)) or $-e \to +e$ (Fig. 4(b)). Figure 4 shows the angle θ as a function of $N_{\rm sn}$ for different time $t \geq 0$. For $+e \to -e$, all the water molecules are in the +dipole state (namely, the state with $0° \leq \theta < 90°$) at t=0 ps. As time elapses, the water molecules are re-oriented one by one from the +dipole state to the -dipole state (i.e., the state with $90° \leq \theta < 180°$). Then, all the water molecules are located in the -dipole state after $t = 11.2$ ps. On the other hand, for $-e \to +e$, an inverse process occurs, namely, the water molecules turn from the -dipole state to the +dipole state one by one.

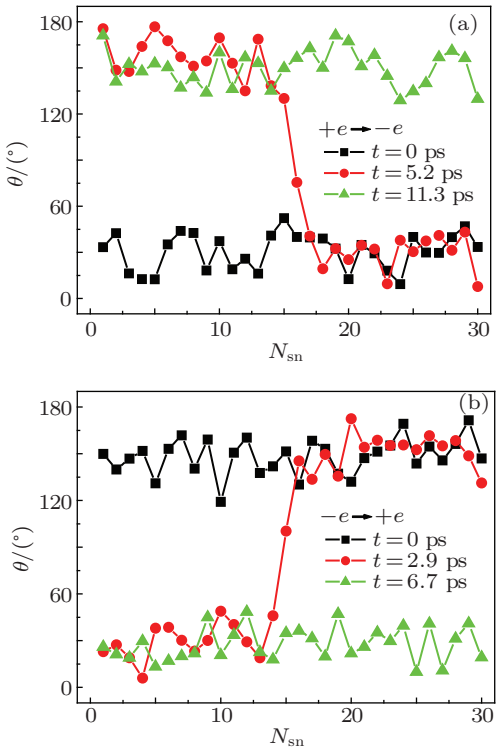


Fig. 4. (colour online) The θ versus $N_{\rm sn}$ at different t≥0 for (a) $+e \to -e$ and (b) $-e \to +e$.

According to Fig. 4, the water molecules confined in the SWCNT are re-oriented one by one. Fig. 5 shows the numbers of the water molecules fliped, $N_{\rm f}$, as a function of time for the two switches $+e \to -e$ and $-e \to +e$. We find that the re-orientating velocity for $-e \to +e$ is faster than that for $+e \to -e$. The same results occur if the length L of the SWCNT varies, see Fig. 6. Besides Figs. 4 and 5, figure 6 also shows that the re-orientation of the water molecules confined in the SWCNT can be completed on the picosecond timescale despite of the various lengthes L. This timescale seems to be reasonable for possible applications.

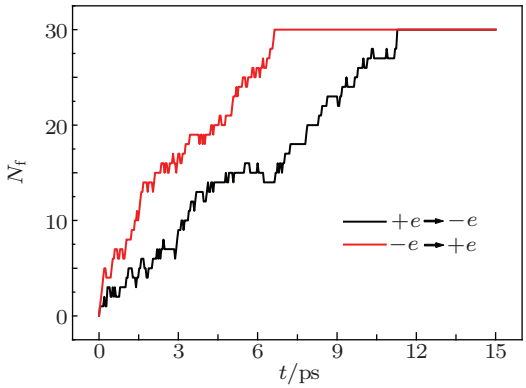


Fig. 5. (colour online) The number of water molecules, $N_{\rm f}$, flipped in the case of $+e \to -e$ and $-e \to +e$, each as a function of time. The total number of water molecules in the SWCNT with $L = 8.1$ nm is 30.

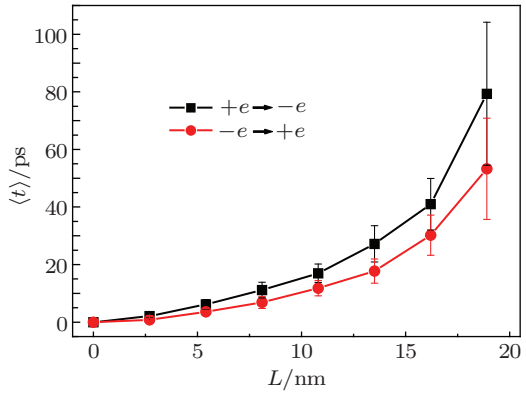


Fig. 6. (colour online) The $\langle t \rangle$ versus L. The linear density of water molecules is always fixed at 3.7 molecules/nm for various L. The $\langle t \rangle$ is the average time when all the water molecules inside the SWCNT are re-orientated. For each L, the transfer procedure has been repeated 500 times to obtain the data with error bars as indicated.

So far, we have solved the above-mentioned two problems, Problems 1 and 2. However, a question arises from Figs. 4–6. That is, how to understand the time inequality of re-orientating the water molecules for the two switches? Here we try to answer this question. In Fig. 7, we still adopt the simplified model by assuming a water molecule as a linear dipole. Because the mass of the oxygen atom is 16 times larger than that of the hydrogen atom, we assume that all the oxygen atoms are fixed on a beeline, while the hydrogen atoms may flip (Fig. 7(a)). Namely, in the present model, each linear dipole is allowed to flip as shown by the two curved headed arrows, while the oxygen atom is fixed at the original place. According to Figs. 3(c) and 3(d), the external charge of $+e$ or $-e$ only has a more evident effect on triggering the flipping of its closest water molecule with $N_{\rm sn} = 1$,

so we conclude that the time inequality under consideration mainly originates from the electrostatic interaction between the water molecules (dipoles). Thus, here we only calculate $E_{\rm pp}$ for the water molecules except for the one with $N_{\rm sn} = 1$, the results are shown in Fig. 7(b). For $-e \to +e$ (corresponding to -dipole→+dipole in Fig. 7(a)), the flipping of the water molecule ($\boldsymbol{p}_k$) passes through a potential trap of $\Delta E_1 = 28.673$ kJ/mol according to Fig. 7(b), and thus this flipping can easily happen even if the initial angular momentum of the water molecule is zero. On the other hand, for $+e \to -e$ (corresponding to +dipole→-dipole in Fig. 7(a)), the flipping of the water molecule ($\boldsymbol{p}_k$) must overcome a potential barrier of $\Delta E_2 = 11.568$ kJ/mol according to Fig. 7(b), and thus this flipping can only occur after the water molecule has enough initial angular momentum to overcome the potential barrier. Therefore, the flipping in $-e \to +e$ occurs more easily than that in $+e \to -e$, yielding the time inequality under discussion.

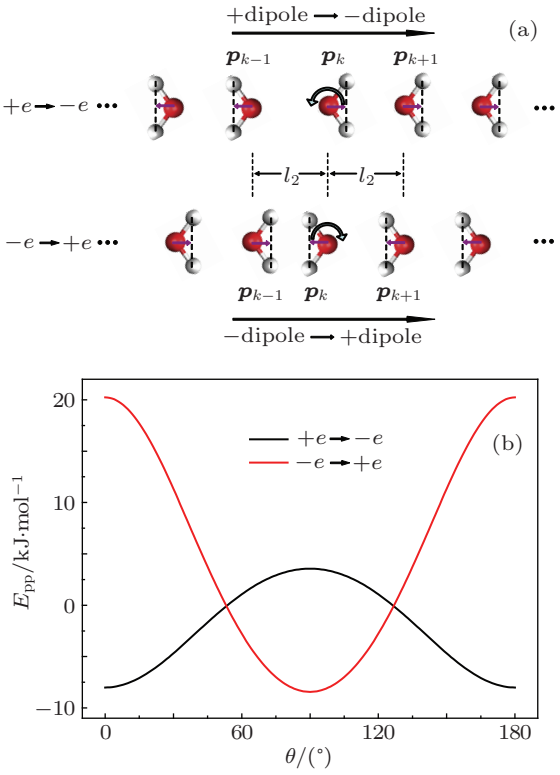


Fig. 7. (colour online) A model for understanding the mechanism underlying the fact that the time for re-orientating all water molecules in the SWCNT for $-e \to +e$ is shorter than that for $+e \to -e$. (a) For $+e \to -e$ (or $-e \to +e$), the +dipole (-dipole) will be turned to -dipole (+dipole) one by one along the x axis due to the domination of electrostatic interaction energy of the dipoles. The curved left-headed (right-headed) arrow denotes the transition point at which +dipole (-dipole) starts to flip into -dipole (+dipole). (b) Electrostatic interaction energy $E_{\rm pp}$ between $\boldsymbol{p}_k$ and its adjacent two dipole moments ($\boldsymbol{p}_{k-1}$ and $\boldsymbol{p}_{k+1}$) in the flipping process of either $+e \to -e$ or $-e \to +e$ indicated in panel (a) as a function of θ.

4. Discussion and conclusion

We have presented a method for detecting the conformation of an individual macromolecule by extracting the fingerprint of charge signals of the series of charged segments of the macromolecule. We, by no means, mean that our method can be applied immediately. For instance, before application, one has to consider how to efficiently extract the signals of orientation or re-orientation of the water molecules confined in the SWCNT to obtain the fingerprint, say, the pattern of bars shown in Fig. 1(c) for an individual macromolecule. This is indeed a difficult task due to the nanometer lengthscale of the system. Fortunately, it might be solved in view of the work of Tu *et al.*,[18] where they have shown that such signals can be converted and multiplied into 2 or more signals by water chains confined in a narrow Y-shaped SWCNT. That is, one may extract the signals for constructing the fingerprint by means of water-mediated signal multiplication with Y-shaped SWCNTs. In fact, the existence of such a possible signal multiplication encouraged us to use the SWCNT with a single file of water molecules to detect the charge signals of charged segments of macromolecules. Here we should also mention that in our simulation box, the water is only within the SWCNT, and no water molecules are present outside the SWCNT and in the gap between the SWCNT and the membrane. Thus, no other water molecules can affect the detection. Another reason for us to use such a SWCNT to detect the charge signals lies in the fact that the SWCNT can also be integrated into many potential applications, such as nanoscale sensors, nanodevices, logic circuits, and nanomachines.[18,19,20,30,32,38–46] We also expect that our method can be integrated into those applications.

On the other hand, our method can only be used to treat those macromolecules whose segments have net charge. Furthermore, we should claim that our proposal is to detect a macromolecular conformation by obtaining the electric fingerprint of the macromolecule. This does not mean that the exact details of the conformation are fully detected. In fact, if one can only detect the net-charge distribution of a certain macromolecule, this partial information of the macro-

molecular conformation can already play the role we expected.

To sum up, on the basis of molecular dynamics simulations, we have investigated a single file of water molecules confined in a SWCNT with an external electric charge of $+e$ or $-e$. The external charge is located at the vicinity of the cap of the SWCNT and along the centerline of the SWCNT. We reveal the picosecond timescale for uni-directionally re-orientating the water molecules in response to a switch of the charge signal, $-e \rightarrow +e$ or $+e \rightarrow -e$. Our results are well understood by taking into account the electrical interactions between the water molecules and between the water molecules and the external charge. Thus, it becomes possible to record fingerprints of electric signals arising from sequential charged segments of a macromolecule, which can be used to recognize the conformation of the macromolecule.

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