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Manipulating the Flipping of Water Dipoles in Carbon Nanotubes *

Dang-Xin Mao(毛党新)[1], Xiao-Gang Wang(汪小刚)[1], Guo-Quan Zhou(周国泉)[1], Song-Wei Zeng(曾松伟)[2], Liang Chen(陈亮)[1], Jun-Lang Chen(陈均朗)[1**], Chao-Qing Dai(戴朝卿)[1]

[1]*Department of Optical Engineering, Zhejiang A&F University, Hangzhou 311300*
[2]*School of Information and Industry, Zhejiang A&F University, Hangzhou 311300*

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Flipping of water dipoles in carbon nanotubes is of great importance in many physical and biological applications, such as signal amplification, molecular switches and nano-gates. Ahead of these applications, understanding and inhibiting the non-negligible thermal noise is essential. Here, we use molecular dynamics simulations to show that the flipping frequency of water dipoles increases with the rising temperature, and the thermal noise can be suppressed by imposed charges and external uniform electric fields. Furthermore, the water dipoles flip periodically between two equiprobable and stable states under alternating electric fields. These two stable states may be adopted to store 0 and 1 bits for memory storage or molecular computing.

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In recent years, the conversion, transmission and amplification of signals at the molecular scale have been proposed in many fields, such as nano-gates, biosensors and artificial nervous systems.[1−5] Carbon nanotubes (CNTs), as nanochannels for signal transduction and amplification, have become ideal candidates thanks to their unique and superior properties. Researchers have shown that water molecules confined in the single-walled CNTs with suitable diameters can form a single-file water chain, with ordered orientations and rhythmically flipping.[6−10] For example, Tu *et al.* explored signal conversion and amplification by an external charge through a water-mediated Y-shaped nanotube using molecular dynamics (MD) simulations.[11−13] The results showed that the concerted water dipoles in the two branches of the Y-shaped nanotubes can be modulated by the water chain in the main channel. Using the same method, Lv *et al.* replaced the water molecules in the Y-shaped CNTs with other polar molecules (urea), and achieved the similar results.[14]

These previous studies demonstrate that water and small polar molecules confined in the CNTs can form a concerted single-file chain, and they then collectively flip. Furthermore, the flipping of these dipoles can be manipulated by external charges. However, the other factors that can affect the flipping of water dipoles to facilitate better manipulation remains unclear. In this work, we systematically investigate some of the potential factors that can modulate the flipping behavior of water chain confined in the CNTs, using MD simulations. Three factors are taken into consideration, namely: temperature, electric fields and external charges. The simulation results show that we can manipulate the flipping frequency and orientation of water dipoles by controlling these factors, which may provide a theoretical basis for the design and manufacture of such electronic devices for the water-mediated signal transduction based on nanochannels.

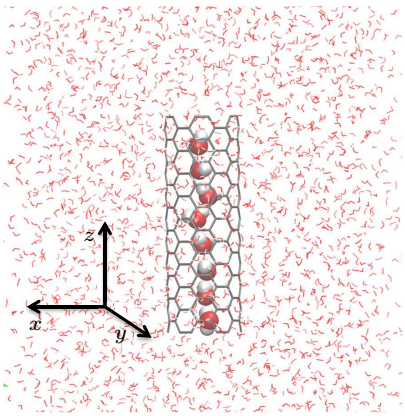

Fig. 1. A schematic illustration of the simulation system. The CNT is shown as bonds in gray. The water molecules inside the CNT are highlighted as van der Waals (vdW) balls. The central axis of CNT is defined as z-direction.

The simulation system was composed of a single-walled carbon nanotube (SWCNT) and 2577 water molecules (Fig. 1), whereas there were 2576 water molecules when two external charges were imposed. An uncapped armchair (6,6) SWCNT was used, with a length of 2.4 nm and a diameter of 0.81 nm. The SWCNT was fixed at the center of the simulation box ($4.0 \times 4.0 \times 5.0\,\mathrm{nm}^3$). When exploring the effects of external charges on the flipping of water dipoles in the CNT, we introduce two external charges to the system.

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**Corresponding author. Email: chenjunlang7955@sina.com

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One is positioned at the center of the last ring of the CNT. Its opposite charge (for electroneutrality) is far away from the CNT to avoid any meaningful influence. Both of them are fixed during the simulations. Water is realized by the SPC model.[15] The carbon atoms in the CNT are treated as uncharged Lennard–Jones (LJ) spheres with a cross section of $\sigma_{cc} = 0.34$ nm and a depth of the potential well of $\varepsilon_{cc} = 0.36$ kJ/mol.[6]

All of the MD simulations were performed using the GROMACS 5.1.2 software package in an NVT ensemble.[16,17] Periodic boundary conditions were employed in all directions. The vdW interactions were determined by the LJ potential, with a cutoff radius of 1.0 nm. Particle mesh Ewald was used to deal with the long-range electrostatic interactions.[18,19] The v-rescale thermostat was adopted to keep the temperature constant.[20] Bond lengths within the CNT and water molecules were constrained by the LINCS and the SETTLE algorithms, respectively.[21,22] Each system was simulated for 100 ns. A time step of 2 fs was used and data were collected every 10 ps.

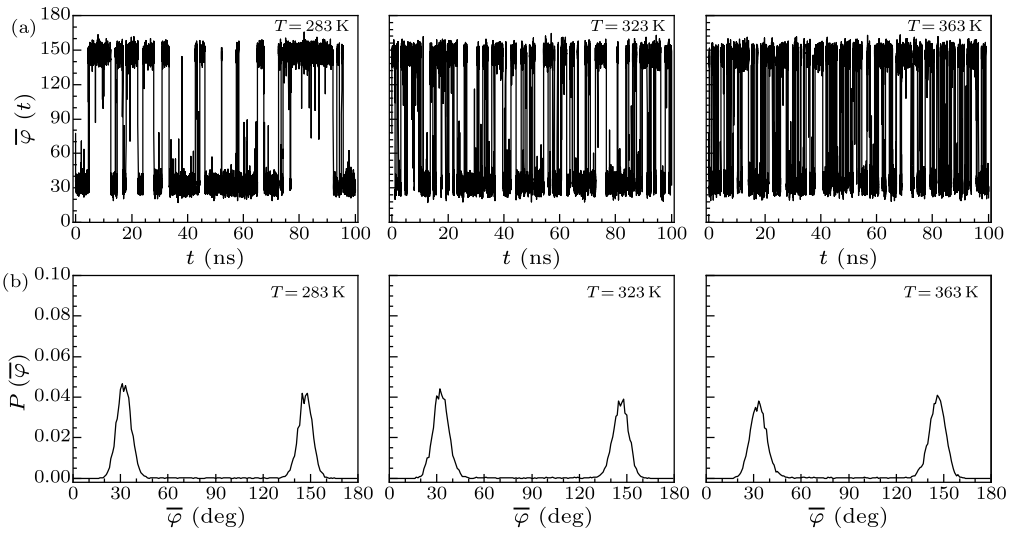

Fig. 2. (a) The average dipole angle $\bar{\varphi}$ against the simulation time t at 283 K, 323 K and 363 K, respectively. (b) The corresponding probability distribution $P(\bar{\varphi})$.

First, we investigate the effects of temperature on the flipping of water dipoles confined in the CNT. An angle φ_i is adopted to quantitatively describe the water dipole orientations in the CNT, which is defined as

$$\varphi_i = \arccos(\boldsymbol{p}_i \cdot \boldsymbol{j}/|\boldsymbol{p}_i|),$$

where $\boldsymbol{p}_i$ is the dipole moment of ith water molecule inside the tube, $\boldsymbol{j}$ is the unit vector of the CNT axis, $\varphi < 90°$ and $\varphi > 90°$ mean the dipole orientation upward and downward, respectively. The average angle $\bar{\varphi}(t)$ is obtained by

$$\bar{\varphi}(t) = \frac{1}{N(t)} \sum_{1}^{N} \varphi_i(t),$$

where the average value of all water molecules in the CNT at a certain time t, and $N(t)$ is the total number of water molecules in the nanotube. The results are presented in Fig. 2. In general, the flipping of water dipoles becomes more frequent with the increasing temperature. That is, the driving force behind the flipping is the random thermal motion of water molecules because the thermal motion enhances with the increasing temperature. Probability density calculations show that $\bar{\varphi}$ mainly falls into two ranges, $15° < \bar{\varphi} < 50°$ and $130° < \bar{\varphi} < 165°$, indicating that water molecules confined in the CNT are well ordered,[23] and the water dipole moments oscillate between these two complementary ranges randomly. Meanwhile, because of the randomness of thermal motion, the two states are almost equiprobable (see Fig. 2(b)).

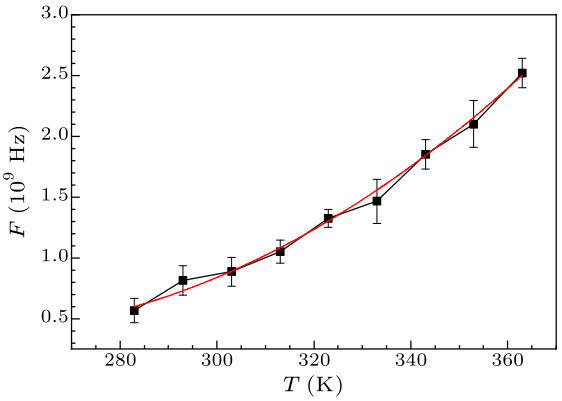

Fig. 3. The relationship between the frequency of the flipping of water dipoles and the temperature. The red line is the parabolic fit between the frequency of flipping and the corresponding temperature.

To quantitatively describe the relationship be-

tween the flipping frequency and the temperature, we perform nine independent simulations with different initial velocities at each temperature to obtain the average flipping frequency of water dipoles. As shown in Fig. 3, the frequency increases with the increasing temperature. Based on this tendency, we perform the linear and parabolic fit, and find that the parabolic fit is more accurate. The quadratic function is

$$F(10^9\,\mathrm{Hz}) = 1.543\times10^{-4}T^2\,(\mathrm{K}) - 0.076T\,(\mathrm{K}) + 9.717,$$

where the correlation coefficient is 0.993, indicating that they are highly relevant. As an application, we can predict the flipping frequency of water dipoles in the CNT at a certain temperature.

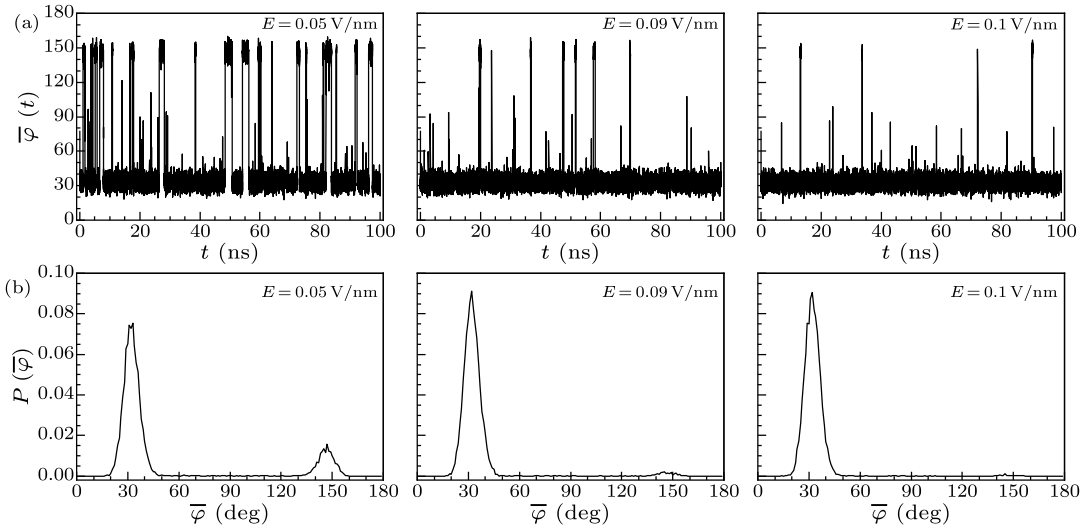

Fig. 4. (a) The average dipole angle $\bar{\varphi}$ as a function of time t under the uniform electric fields of 0.05 V/nm, 0.09 V/nm and 0.1 V/nm, respectively. (b) The corresponding probability distribution $P(\bar{\varphi})$ of the average dipole angle $\bar{\varphi}$.

The thermal motion of water molecules brings the noise to the signal modulated by water dipoles. To inhibit this thermal noise, we attempt to impose uniform electric fields on the simulation system along the CNT axis. The temperature in these and following simulations is kept to be constant at 300 K. We observe that electric fields can directly affect the orientations of water dipoles in the CNT (see Fig. 4). The probability of $\bar{\varphi} = 30°$ (approximately 0.08) is obviously larger than that of $\bar{\varphi} = 150°$, when the electric field intensity is 0.05 V/nm. As the electric field strength increases, the flipping of water dipoles becomes more difficult and the orientations of water dipoles are in line with the direction of electric field. Furthermore, we find that the probability $P(\bar{\varphi} = 150°)$ is close to zero, when the electric field intensity reaches 0.1 V/nm. That is, the flipping of water dipoles in the CNT is almost suppressed. We therefore conclude that 0.1 V/nm is the critical value to control the flipping of water dipoles. In other words, the thermal disturbance can be well suppressed by extra electric fields, when the intensity is larger than 0.1 V/nm.

To ensure that the thermal noise is thoroughly inhibited, we enhance the electric field intensity to 0.2 V/nm. As a comparison, we also impose an opposite electric field with the same intensity. As shown in Fig. 5, the results are much reasonable, namely, (1) the thermal noise is completely inhibited, (2) the average dipole angle $\bar{\varphi}$ fluctuates at 150° under the opposite electric field. The two insets in Fig. 5(b) clearly demonstrate that the orientations of water dipoles in the CNT are well ordered and opposite, in line with the directions of two opposite electric fields.

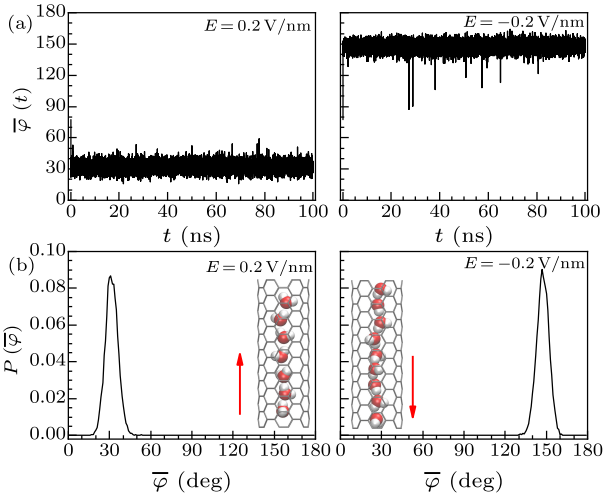

Fig. 5. (a) The average dipole angle $\bar{\varphi}$ under two opposite uniform electric fields of ±0.2 V/nm. (b) The corresponding probability distribution $p(\bar{\varphi})$. The insets specify the illustration of water molecules in the CNT. The rest of the system is not shown for clarity. Two arrows demonstrate the opposite directions of electric fields.

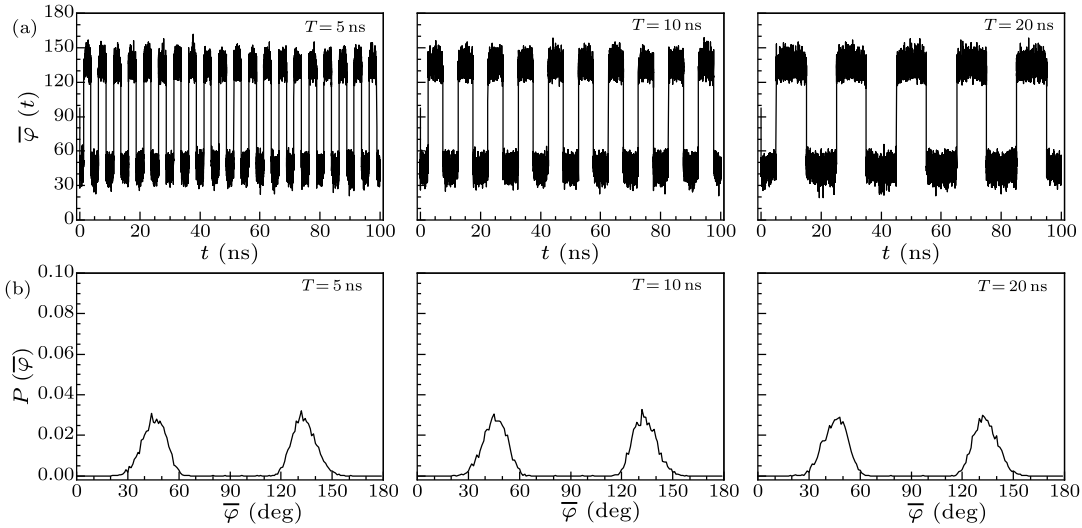

Fig. 6. (a) The average dipole angle $\bar{\varphi}$ under alternating electric fields with different periods ($T = 5$ ns, 10 ns and 20 ns) and the same amplitude of 0.3 V/nm. (b) Probability distribution $P(\bar{\varphi})$ of the average dipole angle $\bar{\varphi}$.

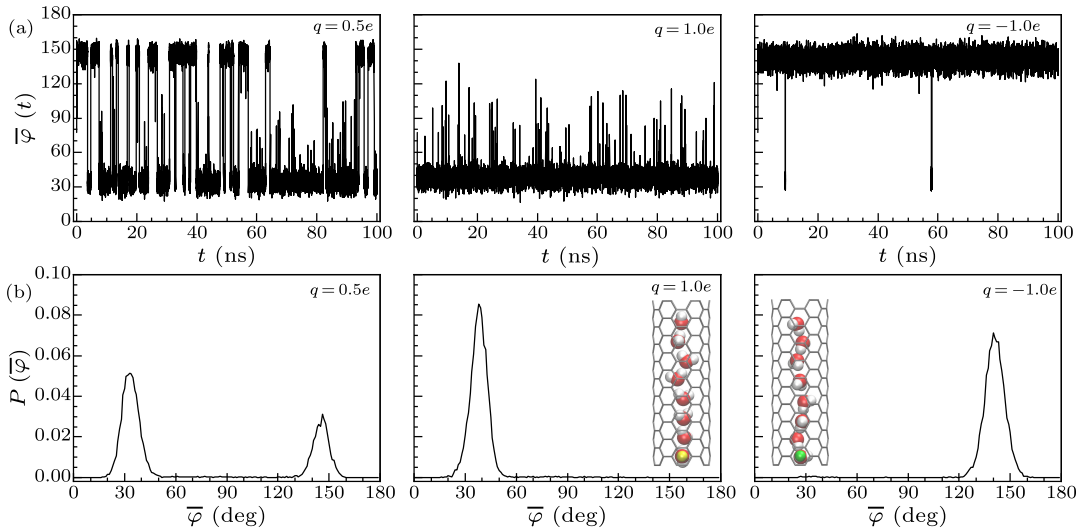

Fig. 7. (a) The average dipole angle $\bar{\varphi}$ against simulation time t under the imposed charges of $0.5e$, $1.0e$ and $-1.0e$, respectively. (b) The corresponding probability distribution $P(\bar{\varphi})$ of the average dipole angle $\bar{\varphi}$. The two insets specify the atomic structure of water chain in the CNT and the imposed charges. The yellow and green spheres represent the positive and negative charges.

Next, we explore the effects of alternating electric fields on the flipping of water dipoles. We select cosinoidal electric fields as model alternating electric fields with the same amplitude of 0.3 V/nm and various periods of 5 ns, 10 ns and 20 ns. The amplitude of alternating electric fields is slightly larger than that of uniform fields because the maximum of ac signals is $\sqrt{2}$ times as the effective value of dc ones. The simulation results are shown in Fig. 6. Interestingly, it is found that the average dipole angle $\bar{\varphi}$ flips periodically, and the periods are consistent with those of electric fields. Probability distribution $P(\bar{\varphi})$ shows that water dipoles have two equiprobable states at approximately $\bar{\varphi} = 45°$ and $\bar{\varphi} = 135°$. As a result, the alternating electric fields can well control the flipping of water dipoles in the CNT. Therefore, CNT-based devices have potential for memory storage applications. In this regard, the two equiprobable and stable states can be adopted to store 0 and 1 bits with different pulse widths.

It has been reported that external charges can manipulate the flipping of electric dipoles and further signal transduction modulated by water molecules in CNTs. Similar to Ref. [13], two external charges are imposed to the simulation system (see Methods). The results are shown in Fig. 7. It is found that the two equiprobable states have been destroyed. Here $P(\bar{\varphi} = 35°)$ reaches 0.05, larger than $P(\bar{\varphi} = 145°)$ (0.03), when $q = +0.5e$. With increasing charges, the flipping of water dipoles in the CNT becomes more difficult, similar with the effects of uniform electric fields. For $q = +1.0e$, the probability peak at $\bar{\varphi} = 145°$ is

completely disappeared, indicating that the flipping of water dipoles is thoroughly inhibited. The manipulation of water dipole by external charges originates from the electrostatic attraction between water molecules and external charges, as shown in Fig. 7(b). When the imposed charge is positive, the oxygen atom of the nearest water molecule in the CNT is attracted by the imposed positive charge. As a result, the orientation of water chain confined in the channel is upward. In contrast, when the imposed charge is negative, one of the hydrogen atoms of the nearest water molecule is attracted by the negative charge, causing the orientations of water dipoles in the CNT downward (see Fig. 7(b), the two insets).

In summary, we have investigated the effects of temperature, electric fields and external charges on the flipping of water dipoles confined in a CNT by MD simulations. It is found that the orientations of water dipoles in the CNT are well ordered. As the temperature rises, the frequency of flipping increases because of the irregular thermal motion. When the uniform electric field strength is larger than 0.1 V/nm, the flipping of water dipoles originated from thermal motion is well inhibited. Similar to the uniform electric fields, the flipping of water dipoles can also be suppressed by external charges. The critical value of external charge imposed to the simulation system is approximately 1.0e. It should be noted that the critical value is related to certain conditions, such as the specific temperature. Under the alternating electric fields, the water dipoles in the CNT will flip periodically between the two equiprobable and stable states, which may be applied to store 0 and 1 bits. Taking the three factors into consideration, we can manipulate the flipping of water dipoles in the CNT, which shows great potential for signal conversion and memory storage.

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