

Fast phase transition of water molecules in a defective carbon nanotube under an electric field

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We utilize molecular dynamics simulations to study the effect of an electric field on the permeation of water molecules through a defective single-walled carbon nanotube (DSWCNT). Compared with a perfect single-walled carbon nanotube (PSWCNT), the behaviors of water molecules respond more quickly under the same electric field in a DSWCNT. Wet–dry phase transition of water molecules occurs when the electric field reaches 0.32 V/nm, which is much lower than the case of the PSWCNT. Besides, the critical electric field is affected by the number of defects. These results pave a way for designing fast wet–dry transition devices and provide a new insight into water permeation through a defective nanochannel.

Keywords: Carbon nanotube; water molecules; molecular dynamics simulations.

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1. Introduction

The study on the flow of water molecules through nanochannels or microchannels has many applications, e.g., for understanding biological activities,^{1–7} for designing nano-devices or nano-machines.^{8–10} According to the World Health Organization, 1.2 billion people worldwide do not have access to clean drinking water, and a further 2.6 billion lack adequate sanitation services. Every year, millions of people die of basic hygiene-related diseases. The great majority are children in developing countries.¹¹ Nowadays, it is widely accepted that the ability to produce clean water

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is one of the key technological, social and economical challenges. As a consequence, there is a large interest in seeking for the low-cost methods of obtaining clean water. Luckily, a previous research has shown that the measured water flow rate through nanotubes is higher than predicted.¹² Therefore, these nanodevices are especially efficient in seawater desalination or water purification.¹³ Meanwhile, how to control water molecules through nanochannel has been investigated widely.¹⁴⁻¹⁶

Wan *et al.* have studied that the water transfer behavior can be controlled by an external force on the carbon nanotube.¹⁴ In their consideration, the origin of the force can be seen to originate from effective techniques and/or other molecules. Further, the water transfer behavior through water nanochannels was also revealed by using a single external charge of value $+1.0e$,¹⁵ in order to study the response to the indispensable charges as well as the possible charge noise near water nanochannels. Their study utilizes the interaction between a point charge outside the single-walled carbon nanotube (SWCNT) and charge-neutral water molecules inside. Furthermore, the transfer behavior of water molecules in the nanochannel can be controlled by dipolar molecules.¹⁶

In our opinion, controlling water molecules through a nanochannel by an electric field is more convenient. Thus, many methods are proposed to control water molecules through the nanochannel by the electric field.^{17,18} In practice, SWCNT defects are usually indispensable. Such defects were shown to greatly affect transport individual nanotubes¹⁹ as well as the electronic and mechanical properties of carbon nanotubes.²⁰⁻²² The defects can also greatly influence the localization of magnetic and electronic excitation in graphene nanotubes²³ and water molecules through a nanochannel.²⁴ Besides, the electric field greatly influences the surface properties of graphene-like materials.²⁵ However, how the SWCNTs with defects affect water permeation under an electric field has rarely been discussed. It is widely accepted that the external conditions of the nanochannel system greatly affects the permeation of water molecules. Many external conditions (say, adding external mechanical forces, pressure gradient, or electric fields/charges) are applied in these fields for studying the transport of water molecules through nanochannels, while taking the nanochannel without defects.²⁶⁻³³ With the purpose of seeking for an energy-saving devices, here we design a defective single-walled carbon nanotube (DSWCNT) as a model of a defective nanochannel; see Fig. 1.

2. Methodology

To achieve our purpose, we use molecular dynamics simulations, which have been widely used for studying water dynamics in SWCNTs, in proteins, in-between proteins and water dynamics with a dissolved gas.³⁴⁻³⁸ Our simulation framework is shown in Fig. 1: two parallel graphite sheets with a separation of 3.120 nm dividing the full space into three parts. There is a DSWCNT with six defects between the two graphite sheets. Every defect is designed by removing six carbon atoms (a circle of carbon atoms). The DSWCNT is a *Z*-directed, uncapped, (20, 0) DSWCNT

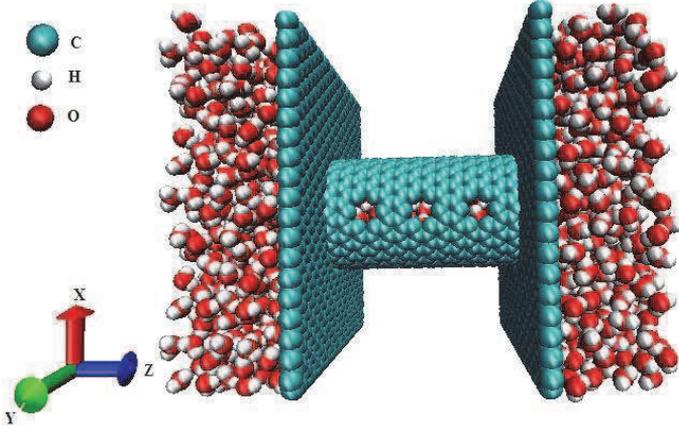


Fig. 1. (Color online) Snapshot of the simulation system with a Z -directed DSWCNT perpendicularly joining the centers of two graphite sheets. The system is filled by water molecules (H_2O). An uniform electric field is applied along Y -direction, which is perpendicular to the DSWCNT. There are six defects on the DSWCNT. The defects distribute symmetrically.

with a diameter of 1.544 nm. It is worth mentioning that the diameter of DSWCNT is large enough to contain many water chains in the nanochannel, which will accelerate the transfer rate of water molecules through the DSWCNT. An uniform electric field is applied along Y -direction, which is perpendicular to the DSWCNT. Models of water molecules and carbon atoms come from the Refs. 34 and 35. The system is solvated in a water box ($4.652 \text{ nm} \times 4.646 \text{ nm} \times 6.220 \text{ nm}$) with 1896 water molecules; Initially, the DSWCNT is full of water molecules. There are no water molecules outside the DSWCNT between the two graphite sheets. All the carbon atoms are frozen at their original lattices in the simulations to prevent the DSWCNT and graphite from being swept away.

We perform molecular dynamics simulations with Gromacs 4.0.5.³⁹ All simulations are carried out under the NVT ensemble (constant number of molecules, constant volume, and constant temperature). We adopt the thermostat of Nosé and Hoover^{40,41} with a time constant of 0.5 ps to maintain the system's temperature at 300 K. Periodic boundary conditions are applied to all three directions of the simulations box. The initial atomic velocities are generated by a Maxwellian distribution at the temperature of 300 K. The timestep is set to be 2 fs and the total simulation time is 40 ns (the first 10 ns is used for equilibration and the remaining 30 ns are used for statistics). Here, the transfer rate of water molecules through the DSWCNT, N_f , is calculated according to the following equation: $N_f = N(t)/t$. $N(t) = (1/3) \sum_{k=1}^3 N_k(t)$. Here, $N_k(t)$ is the number of water molecules transported through the DSWCNT from one end to the other end within the statistic time $t = 10 \text{ ns}$. Clearly, for the total statistic simulation time of 30 ns, $N_k(t)$ have three values. The particle-mesh Ewald⁴² method is used for the long-range electrostatic interaction and the cut-off distance for LJ forces is set to be 1.4 nm.

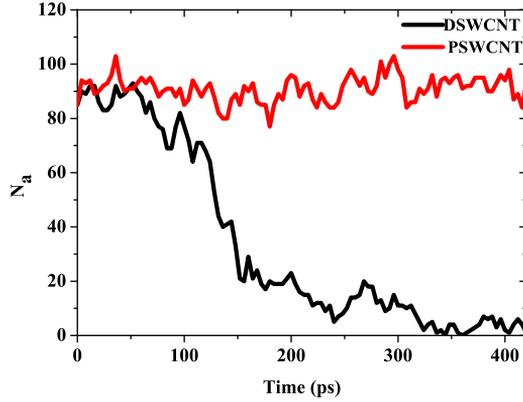


Fig. 2. (Color online) The number of water molecules, N_a , in a DSWCNT shown in black (or a PSWCNT shown in red) as a function of time (with step size 2 fs) under the electric field strength 1 V/nm.

3. Results

Figure 2 shows the number of water molecules, N_a , in the DSWCNT or perfect single-walled carbon nanotube (PSWCNT) as a function of time under the same electric field, 1.0 V/nm. Initially, the DSWCNT (or the PSWCNT) is full of water molecules. we find that the responses of water molecules in the DSWCNT are more quickly than the responses of water molecules in the PSWCNT. The number of water molecules in the PSWCNT fluctuates around 90 water molecules with small fluctuations. However, the number of water molecules in the DSWCNT decreases rapidly under 1.0 V/nm. It just takes no more than 0.2 ns to achieve a fast wet-dry transition. Thus, it will save much energy if we use DSWCNT to replace PSWCNT to control water wet-dry transition.

How strong electric field must be added to control water transfer through the DSWCNT worth being investigated systematically. Figure 3 shows the transfer rate, N_f , the number of water molecules in the DSWCNT, N_a as a function of the electric field and a dynamic process of wet-dry transition under the critical electric field. As Fig. 3(a) shows, the electric field has a great effect on the transfer rate of water molecules through the DSWCNT. It is worth noting that there is a critical point of the electric field, $E_C = 0.32$ V/nm. Below the critical electric field, the transfer rate of water molecules through the DSWCNT has not been affected dramatically by the electric field, and N_f maintains a fast and stable transfer rate. However, N_f decreases to nearly zero if the electric field above the critical electric field. Similarly, the average number of water molecules in the DSWCNT, N_a has a similar phenomena [shown in Fig. 3(b)]. There is a critical point of the electric field, $E_C = 0.32$ V/nm. Below the critical electric field, the number of water molecules in the DSWCNT has not been affected dramatically by the electric field, and N_a maintains a stable number. However, N_a decreases to nearly zero if the electric

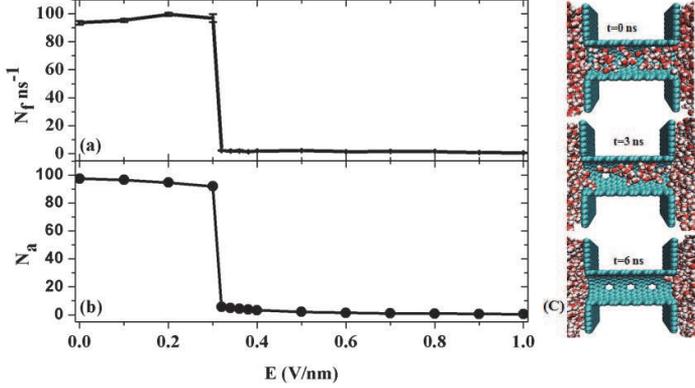


Fig. 3. (Color online) (a) The number of water molecules flowing across the DSWCNT, N_f , as a function of the electric field. (b) The number of water molecules in the DSWCNT, N_a , as a function of the electric field. (c) A dynamic wet-dry phase transition under the critical electric field 0.32 V/nm.

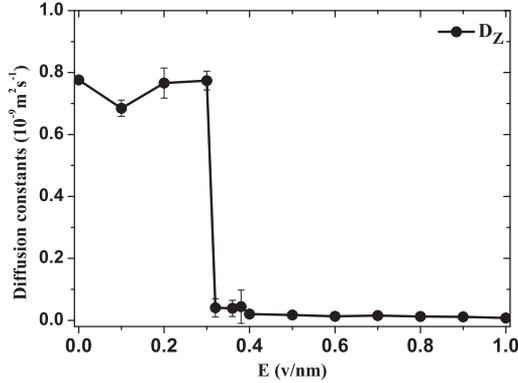


Fig. 4. D_Z , the average diffusivity of water molecules within the nanochannel as a function of the electric field.

field above the critical electric field. Figure 3(c) shows a dynamic process of wet-dry transition under the critical electric field, $E_C = 0.32$ V/nm. Initially, the DSWCNT is full of water molecules. The number of water molecules in the DSWCNT reduces a lot and the DSWCNT is partially dry when time is 3 ns. When time is 6 ns, the DSWCNT is almost completely dry and almost no water molecules exist in the DSWCNT.

In order to understand Fig. 3, we calculate D_Z in Fig. 4 according to both the Einstein expression for diffusivity and the Green-Kubo formula,⁴³

$$D_Z = \frac{1}{300} \sum_{i=1}^{300} \left(\frac{1}{6N_i(t_i - t_{i-1})} \sum_{j=1}^{N_i} |r_j(t_i) - r_j(t_{i-1})|^2 \right),$$

where $t_i - t_{i-1} = 0.1$ ns denotes the time step within the whole statistical time 30 ns, thus yielding $t_1 = 0.1$ ns and $t_{300} = 30$ ns. Here, $r_j(t_i)$ is the position of the j th water molecule at t_i along Z -direction and N_i is the number of water molecules within the DSWCNT at t_i . By calculation, we find a critical electric field, $E_C = 0.32$ V/nm. D_Z has not been affected by the electric field, keeping almost as a constant if the electric field below the critical electric field. Thus, the transfer rate of water molecules through the DSWCNT almost has not been affected when the electric field below the critical electric field. However, D_Z decreases almost to zero immediately when the electric field reaches the critical electric field, 0.32 V/nm. So, the transfer rate of water molecules across the DSWCNT decreases to almost zero when the electric field reaches the critical electric field.

In Fig. 5, we display the average orientation of water molecules inside the DSWCNT, in the presence of the electric field. Here, the orientation is defined as the average angle, $\langle\phi(t)\rangle$, at time t : $\langle\phi(t)\rangle = \sum_{i=1}^N \phi_i(t)/N(t)$ where $N(t)$ is the number of water molecules and $\phi_i(t)$ denotes the angle between μ_i (dipole moment of the i th water molecule) and $\hat{\mathbf{u}}$ (axis unit vector of the electric field) according to $\phi_i(t) = \arccos(\mu_i \cdot \hat{\mathbf{u}}/|\mu_i|)$. Compared with Figs. 3 and 4, the average angle of water molecules in the DSWCNT has not a sharp transition with increasing the electric field. This is because the DSWCNT is not completely dry when the electric field reaches the critical electric field. Although the transfer rate of water molecules through the DSWCNT is almost zero if electric field reaches E_C , water molecules can spontaneously move in and out of the entrance of the DSWCNT frequently. Thus, the average angle of water molecules in the DSWCNT does not have a sharp transition with increasing the electric field. According to electrodynamics, if one puts the i th water molecule with dipole moment μ_i , the water molecule will tend to move to the direction of the field. Thus, water dipole will repel each other. This can explain the results obtained in Figs. 3 and 4.

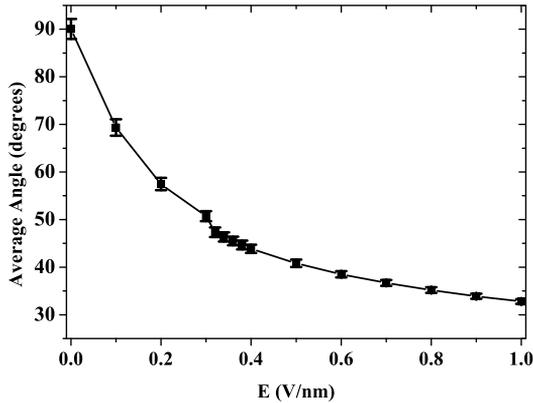


Fig. 5. The average angle of water molecules between water dipole and the direction of the electric field, $\langle\phi(t)\rangle$, as function of the electric field.

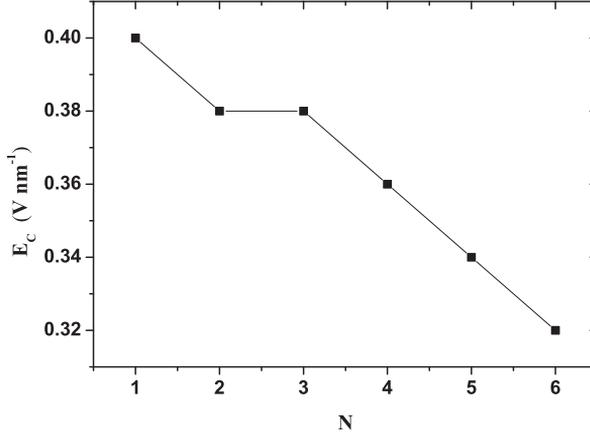


Fig. 6. The critical electric field, E_c , as function of the number of defects, N .

Owing to the above analysis, one may infer that more defects in a DSWCNT might help to enhance the wet–dry phase transition. Is this true? To answer this question, we attempt to change the number of defects from six to one. Figure 6 shows our simulated results. As shown in this figure, the critical electric field is affected by the number of defects. The tendency of critical electric field shows that E_C is reduced if the number of the defects increases. It means it is easier to achieve a wet–dry phase transition if the DSWCNT with more defects.

4. Discussion and Conclusion

In summary, compared with the PSWCNT (that has been extensively used in the literature), the DSWCNT has an evident effect on the transfer rate of water permeation under the electric field. Remarkably, the transfer rate of water molecules across the DSWCNT has not been effected by the electric field if the electric field is below the critical electric field. The transfer rate of water molecules across the DSWCNT decreases to zero immediately if the electric field reaches the critical electric field. We attribute these results to the independent of D_Z . D_Z almost keeps as a constant if the electric field below the critical electric field. Besides, the tendency of critical electric field is reduced if the number of the defects increases. Our findings may be helpful for designing fast wet–dry transition devices and for providing new insights into the role of controlling water permeation.

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