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Water transport through T-shaped carbon nanotubes

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Abstract The effect of an external charge on water transportation through T-shaped carbon nanotubes is tested by molecular dynamics simulations. The simulation results show that a relatively small charge reduces the water flux through the canbon nanotubes, but a large enough charge prompts the water transportation. This finding may be helpful to biological amplifiers and nanodevices researches.

Key words External charge, T-shaped nanotube, Water transportation

1 Introduction

Water transportations through channels in membrane have been studied experimentally, and theoretically by using molecule dynamics simulation in the past two decades years[1–8]. Understanding the permeation mechanism of water molecules is of great importance for designing molecular devices, machines or sensors[5,9,10]. The single-walled carbon nanotubes (SWNTs) have been used as model systems for the studies [4-6,11-14]. In 2007, Li *et al*.[15] assigned an external charge close to a nanochannel, and found that the nanochannel was an excellent on-off gate. In 2009, Tu *et al*.[14] reported that a single charge could induce remarkable transduction capability of the water-mediated signal through the Y-shaped carbon nanotubes. They found that the electric charge fixed on the main tube could control the water dipole orientations in the main channel, hence a further control of the water dipole orientations in the two branches[14].

However, if an osmotic pressure is given to a complex system of several carbon nanotubes, one can hardly predict the charge effect on flux of the whole system. Shall the charge control the water molecule dipole orientation the same as the Y-shaped carbon tube system without osmotic pressure? This needs to be clarified. In this paper, we use T-shaped carbon nanotubes[14] to study the charge effect on water transport and water molecule dipole orientation.

2 Methods

2.1 The model system

Configuration of the model system is shown in Fig.1.

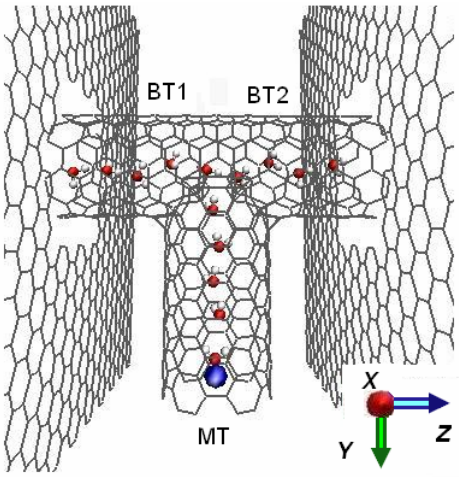

Fig.1 Simulation framework. The T-shaped nanotube, in gray, features a main tube (MT) and 2 branch tubes (BT1, BT2) positioned in the same plane (the yz plane). Two carbon sheets are placed at the ends of two branch tubes and an external charge is fixed on the main tube, in blue.

The (6,6) uncapped armchair SWNTs are used to construct the T-shaped nanotubes by joining three SWNTs symmetrically, each of Φ8.1 Å× 1.21 nm in

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size. The vertical tube (*Y*-axis) is designated as the main tube (MT), while the horizontal tubes (*X*- and *Z*-axis) as the branch tubes (BT1 and BT2). The external charge q is positioned at the center of a second carbon ring of the main tube, and is used to control the dipole orientations of the water molecules inside the tube. Two graphite sheets placed at the ends of the T-shaped tubes divide the simulation box into three parts. All carbon atoms are fixed, and an opposite charge is assigned at edges of the box to keep the whole system electrically neutral.

2.2 The simulation

The simulation consists of two parts: without osmotic pressure difference, and with an artificial osmotic pressure from one branch to the other end[16,17]. The artificial osmotic pressure is obtained by exerting an additional acceleration of 0.1 nm/ps^2 along Z direction on each water molecule. TIP3P water model[7,18] is used in all the simulations.

The molecular dynamics simulations are carried out in NVT ensemble at a constant temperature of 300 K using Berendsen thermostat[14,19], and in constant volumes (L_x×L_y×L_z=5.2 nm×4.5 nm×5.6 nm in the T-shaped carbon nanotubes system) with 3042 water molecules using the molecular modeling package Gromacs 4.0.5. The particle-mesh Ewald method[20] is used to treat the long-range electrostatic interactions. The periodic boundary conditions are applied in all directions[12].

The time for each numerical simulation is 120 ns, and the last 100 ns are collected for analysis. A 2-fs time step is used, and data are collected every 2 ps. To prevent the SWNTs from being swept away, each carbon atom has a constraint to fix the solid part in the simulations. The carbon atoms are modeled as uncharged Lennard-Jones particles with a cross-section of σ_{cc}=0.34 nm and σ_{co}=0.3275 nm and a potential well depth of ε_{cc}=0.3612 kJ·mol^{-1} and ε_{co}=0.4802 kJ·mol^{-1}[4,12].

3 Results and discussion

The average flow and net flux of the system with artificial osmotic pressure differences are shown in Fig.2. If A is the average number of water molecules entering the system from the left side of BT 1 and leaving the system from the right side of BT 2, and B is the average number of water molecules entering the system from the right side of BT 2 and leaving the system from the left side of BT 1, the net flux can be defined by the difference of A and B, per nanosecond, and the average flow is defined by the sum of them, per nanosecond[15]. The average number of water molecules that move across the main tube is too small to affect the calculation result, therefore, this part is not considered in the simulation.

From Fig.2, one finds that the net flux is minimized at q=−0.4 e and q=+0.5 e, and especially, the net flux increases with q for $|q|$>0.4 e. The flow has a similar behavior.

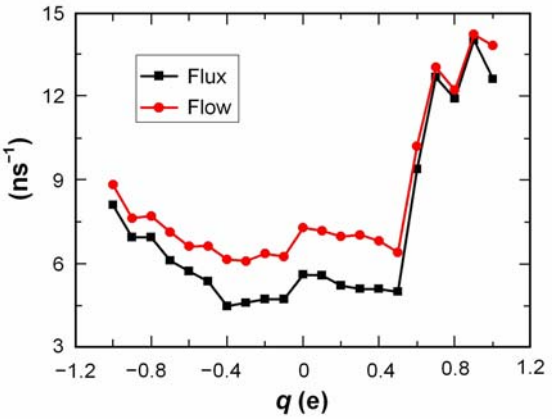

Fig.2 Average flow and net flux *vs.* different charge values q under certain pressure difference. The average flow of the system is red, net flux of the system is black.

Such a phenomenon may be related to the flips of dipole orientations of water molecules inside the tubes with an osmotic pressure, which is different from the corresponding process in a similar system without osmotic pressure. But this is only a hypothesis. In order to understand the physics underlying the simulation results, the average dipole orientation angle $\bar{\phi}$, i.e. the mean angle between water dipole and the nanotube axis, is calculated over all water molecules inside the tubes in the time period of 60–110 ns.

As shown in Fig.3, when q=−0.4e and q=0.5e, $\bar{\phi}$ in all tubes fluctuates between 30° and 150°. Because the hydrogen bonding formation between the water molecules in MT and the water molecules in BT1 and BT2, the flips of the dipoles in MT may

induce the flips of water dipole orientations in BT1 and BT2, so there are more flips in the branches.

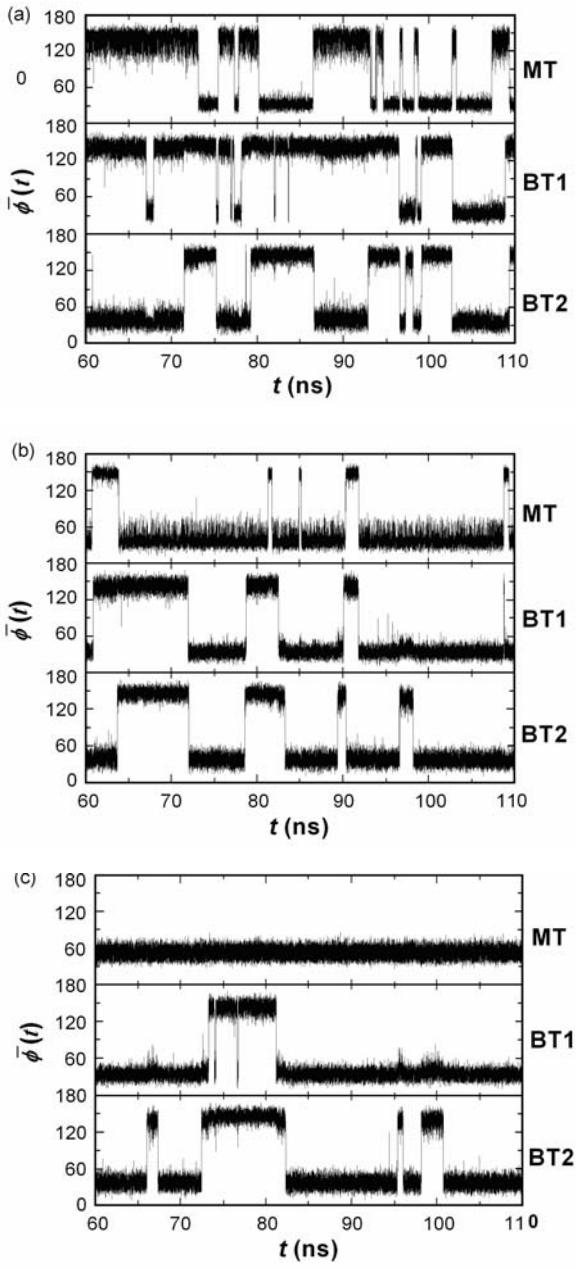

Fig.3 Water dipole orientations ($\bar{\phi}$) inside the T-shaped nanotubes with respect to time t in MT, BT1 and BT2 for (a) q=−0.4 e. (b) q=0.5 e and (c) q=1.0 e.

The water dipole orientation within a simple carbon nanotube is known to have flips, but after the single charge is fixed on the main tube, the balance is broken. We find that the total time of water dipole orientations $\bar{\phi} > 90°$ (the dipole orientations in this range are opposite to the flux direction) increase a little due to the external charge. So the relatively small value of charge may weaken the water transport across the carbon nanotube.

Next, all the water orientations in the main tube show downward behavior for q=1.0 e, and the orientation flipping for the water inside the branch tubes are relatively small, hence a higher ordering of the water molecules inside the nantubes for q=1.0 e. This ordering may make the water permeation across the nanotube easier when there is a pressure gradient in the system. Without osmotic pressure, if a charge, whether negative or positive, is large enough, it can control the water dipole orientations very well. Under osmotic pressure, however, controlling effectiveness of an external charge on the dipole orientations is not as perfect as before. For q=1.0 e, in the same T-shaped carbon nanotube system without osmotic pressure, the water dipole orientations in the two branch tubes are in the same direction, half of time along the Z-axis and the other back to Z-axis[14]. In the present paper, the water orientation in the two branch tubes are in the same direction, however, the time for them to move along Z-axis becomes longer. In this case, the charge prompts the water permeation through the tube.

4 Conclusion

The water permeation across the T-shaped carbon nanotubes by using molecular dynamics simulations was studied. The relatively small value of charge reduced the water flux through the canbon nanotubes, while the large enough value of charge will prompt the water transportation. We contribute the large flux due to the large charge to the concerted orientations of the water molecules inside the nanotubes. It is expected this study have biological significance and shall be of help in design of nanodevices.

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