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Water permeation across nanochannels with defects

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Abstract
Defects are common in fabricated nanochannels. In this paper, water permeation across a single-walled carbon nanotube with defects was studied using molecular dynamics simulations. It is found that the impact on water permeation is negligible when the density of the defects is small, while a significant reduction in water permeation is observed when the density of the defects is high. These findings should be helpful in both understanding water permeation across nanochannels and designing efficient artificial nanochannel.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the synthesis of carbon nanotubes in 1991 by Iijima [1], it has been recognized via both computer simulations and experiments that carbon nanotubes have great potential for designing novel molecular devices/machines/sensors [2–5]. In 2006, Holt *et al* reported their important observation that the water flow rate through a carbon nanotube with a radius of 1–2 nm is more than three orders of magnitude higher than nonslip, hydrodynamic flow, as calculated from the Hagen–Poiseuille equation [6]. If this tube can be used in the desalination of seawater, it is expected that the energy required will be greatly reduced [7]. In the meantime, there have been many theoretical investigations and numerical simulations on water permeation across nanochannels [8–19]. About three years before the experiment by Holt *et al* [6], Hummer *et al* [8] used molecular dynamics simulations to predict water flow through a carbon nanotube membrane, which was consistent with the experimental results of Holt *et al*. Very recently, Gong *et al* presented a molecular water pump that used a combination of charges positioned adjacent to a nanopore, mimicked from the charges in biological water channels, Aquaporins (AQPs), using molecular dynamics simulations [20]. We note that most theoretical and numerical simulations have focused on perfect single-walled carbon nanotubes (SWNTs). However, defects are common in practical fabricated nanochannels [21–23]. It has been reported that about 10% of samples with SWNT structure exhibited stable defect features according to a scanning tunneling microscope observation [23]. Moreover, by using state-of-the-art classical and quantum simulations, Nardelli *et al* showed that fabricated SWNTs usually have a high density of defects [22]; Hashimoto *et al* found experimentally that defects in the graphene layers of the SWNTs, such as topological defects, vacancies and adatoms, were numerous [21]. In recent years, it has been found that defects have a significant influence on the formation as well as on the electronic and mechanical properties of carbon nanotubes [24–28], but rarely has attention been paid to the effect of the defects on water permeation across an SWNT.

In this study we studied the impact of defects on water permeation across a channel by molecular dynamics simulation. We take an SWNT with 5/7 pair topological defect(s) (Stone–Wales defects) [29] as an example. This kind

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Table 1. Positions of C–C bond rotation and number of defects in the seven types of systems studied in this article.

System	Bond rotation (Cn–Cn′)	Number of defects
I	0	0
II	C2–C2′	1
III	C1–C1′, C3–C3′	2
IV	C1–C1′, C2–C2′, C3–C3′	3
V	C1–C1′, C3–C3′, C4–C4′, C6–C6′	4
VI	C1–C1′, C2–C2′, C3–C3′, C4–C4′, C6–C6′	5
VII	C1–C1′, C2–C2′, C3–C3′, C4–C4′, C5–C5′, C6–C6′	6

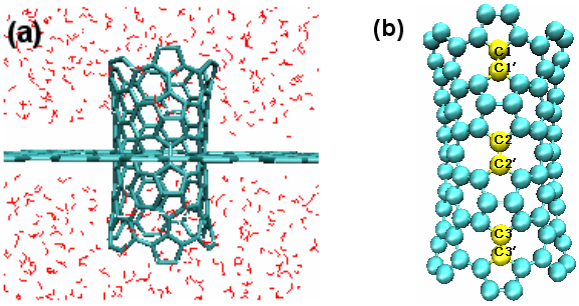

Figure 1. (a) Snapshot of the simulation systems. A (6, 6) single-walled carbon nanotube with triple 5/7 pair defects together with the graphite sheet are dissolved in water. (b) C1–C1′, C2–C2′ and C3–C3′ are rotated by 90°, forming triple 5/7 pair defects in the nanotube.

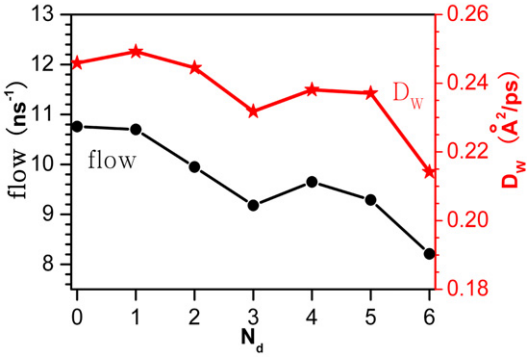

Figure 2. Water flow and one-dimensional diffusion coefficient D_{W} of water molecules inside the channel with respect to the number of 5/7 pair defects N_{d}.

of defect is one of the most important topological defects in carbon nanotubes. We find that the impact on water permeation is negligible when the density of defects is small, while a significant reduction in water permeation is observed when the density of defects is high. Our model systems also have implications for the impact of the internal rough surfaces on water permeation across various channels, including biological channels.

2. System and methods

An uncapped, single-walled carbon nanotube [30] with triple 5/7 pair defects, 16.6 Å in length and 8.1 Å in diameter, was embedded along the z direction in a graphite sheet which subdivided the SWNT into two equal parts, as shown in figure 1(a). The 156-carbon (6, 6) nanotube was formed by folding a graphite sheet of 5.5 × 6 carbon rings with triple 5/7 pair defects into a cylinder and then it was relaxed with interactions between the carbon atoms. The carbon–carbon interaction parameters were adopted from the previous work by Brenner [31] according to the Tersoff formalism [32]. The 5/7 pair defects can be formed in a normal nanotube by 90° rotation of the C–C bond between two hexagons, which changes four neighboring hexagons into two pentagons and two heptagons (5/7 pairs) [33], as shown in figure 1(b). C1–C1′, C2–C2′ and C3–C3′ are the positions of C–C bond rotation in a nanotube. This kind of defect causes little change in the diameter, while considerably elongating the tube in the axial direction [25, 34]. Seven types of model system were prepared, which we refer to as I, II, III, IV, V, VI, VII. Table 1 summarizes the number and positions of C–C bond rotation in these systems. For example, in system VII, there are six 5/7 pair defects in the nanotube, comprising C1–C1′, C2–C2′, C3–C3′ shown in figure 1(b) and C4–C4′, C5–C5′, C6–C6′, which are positioned symmetrically in the other half of the nanotube with respect to the corresponding C1–C1′, C2–C2′, C3–C3′.

The molecular dynamics (MD) simulations were carried out at a constant pressure of 1 bar with an initial box size of $L_x = 3.0$ nm, $L_y = 3.0$ nm, $L_z = 4.0$ nm and a constant temperature (300 K) using Gromacs 3.3.1 [35]. The electrostatic interactions were handled using the particle-mesh Ewald summation method [36]. Periodic boundary conditions were applied in all directions. Here the TIP3P [37] water model was used. A time step of 2 fs was used and data were collected every 0.5 ps. In the simulations, the carbon atoms were modeled as uncharged Lennard-Jones particles with a cross section of $\sigma_{\mathrm{CC}} = 0.34$ nm, $\sigma_{\mathrm{CO}} = 0.3275$ nm and a depth of potential well of $\varepsilon_{\mathrm{CC}} = 0.3612$ kJ mol^{-1}, $\varepsilon_{\mathrm{CO}} = 0.4802$ kJ mol^{-1} [8]. In order to prevent the SWNT from being swept away, the carbon atoms at the inlet and outlet were fixed in the simulations.

3. Results and discussion

For each system, a 120 ns MD simulation was performed. The last 110 ns of the simulation were collected for analysis. Initially, there were no water molecules in the nanotube. The nanotube was rapidly filled by water molecules from the surrounding reservoir in each simulation.

Figure 2 displays the water flow through the channel with respect to the number of 5/7 pair defects, denoted by N_{d}. The

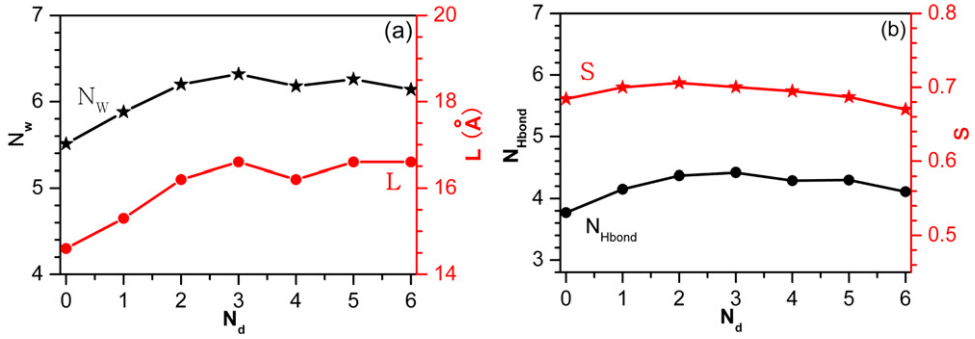

Figure 3. (a) Average number of water molecules N_w inside the nanotube together with the length of nanotube L with respect to the number of 5/7 pair defects N_d. (b) Average number of hydrogen bonds N_{Hbond} inside the nanotube and $S = N_{Hbond}/N_w$ in different model systems.

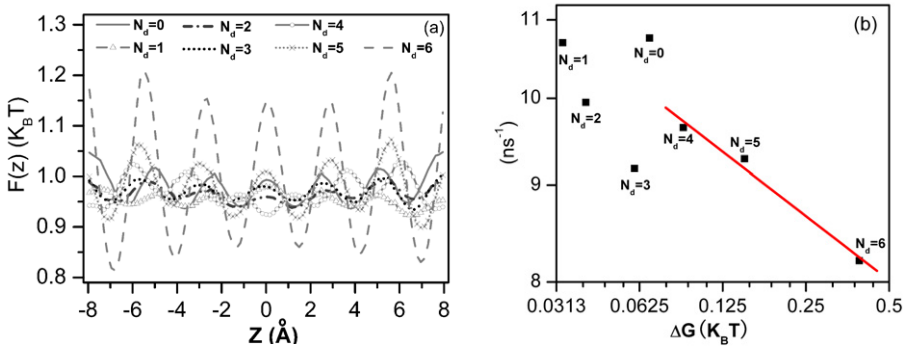

Figure 4. (a) Potential of mean force (PMF) profiles of water molecules inside channel along the z-direction in different systems. (b) The relationship of flow to the height of the barrier, ΔG, in PMF profiles. When $N_d > 3$, the data can be fitted by a power law flow $= 7.4 \times \Delta G^{-0.11}$.

water flow is defined as the total number of water molecules leaving the SWNT, while entering from the opposite side, per nanosecond. In system I without 5/7 pair defects, the flow is 10.8 ns^{-1}. When N_d increases, the flow decreases gradually with respect to N_d down to 8.2 ns^{-1} for $N_d = 6$. We have also computed the one-dimensional diffusion constant D_w, which is calculated from the mean square deviation of water molecules in the SWNT [38], as shown in figure 2. It is clear that D_w has similar behavior to the flow.

Figure 3(a) shows the average number of water molecules N_w inside the nanotube together with the length of the nanotube, L, with respect to N_d. The length of the SWNT gradually increases a little for $N_d \leqslant 3$, but remains almost a fixed value of 16.6 Å for $N_d \geqslant 4$. N_w in the nanotube slowly increases and then remains almost unchanged. It is clear that N_w has a similar trend to the length of the SWNT, suggesting that the change in the number of water molecules is dominated by the change in length due to the defects. Figure 3(b) displays the average number of hydrogen bonds, N_{Hbond}, inside the tube. Here, we adopt a geometric definition of hydrogen bonds, according to which a water pair is hydrogen-bonded if the O–O distance is less than 3.5 Å and simultaneously the bonded O–H$\cdots$O angle is less than 30°. The hydroxyl OH bonds involved in hydrogen bonds are nearly aligned along the nanotube axis and collectively flip directions [39, 40]. N_{Hbond} has a similar trend to the average number of water molecules, N_w, inside the nanotube. In order to show the relationship between N_{Hbond} and N_w, we have plotted the ratio of N_{Hbond} to N_w, denoted by S, in figure 3(b). S first increases and approaches the maximum at $N_d = 2$, and then slightly decreases as N_d becomes larger. Compared with N_{Hbond} and N_w, the change in S is small, suggesting that the number of hydrogen bonds N_{Hbond} inside the channel is dominated by, but not completely determined by, the number of water molecules inside the channel.

The potential of the mean force (PMF) is often used to characterize the behavior of water molecules inside the channel [14, 41]. Figure 4(a) displays the PMF curves of water molecules inside the channel along the z-direction. The PMF is defined as $F(z) = -k_BT \ln \rho(z)$, where $\rho(z)$ is the probability of water molecules appearing at position z, and z is the normalized position in the channel along the z-direction [42]. The wave-like pattern of PMF is retained after the introduction of the 5/7 pair defects. To study further the relationship of flow to the PMF profile quantitatively, the height of the barrier ΔG [15], which is the difference between the maximum and the minimum values in the profile, is calculated. When $N_d \leqslant 3$, ΔG is quite small (less than 0.07 K_BT) and we cannot obtain a clear relationship between N_d and ΔG. When $N_d > 3$, the flow can be fitted to a power law as flow $= 7.4 \times \Delta G^{-0.11}$ as the line in figure 4(b), showing the behavior that, the larger the potential barrier, the smaller the flow. A similar power law has also been observed [15, 19].

4. Conclusions

We have studied the effect of defects on water permeation across a channel by molecular dynamics simulation. We find that the impact on water permeation is negligible when the density of the defects is small, while a significant reduction in water permeation is observed when the density of the defects is high. When the defects in the nanotube are more than three, the flow decreases power exponentially with respect to the height of the PMF barrier. The one-dimensional diffusion constant is also calculated and is found to share a similar behavior to the flow. As the defects increase, the average number of water molecules and hydrogen bonds inside the nanotube slowly increase and then remain almost unchanged. Considering the unavoidable defects in the fabrication of carbon nanotunes, the rough internal surfaces of many of the other kinds of nanochannels [43, 44] and the complex structure of biological channels, these findings should be helpful in understanding water permeation across a nanotube as well as across biological channels, and should be useful in designing an efficient artificial nanochannel.

Acknowledgments

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