

Water Permeation through a Subnanometer Boron Nitride Nanotube

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Water-filled nanometer-scale porous structures have gained considerable attention over the past decade due to their enormous promise in substantially improving the performance and efficiency of many applications such as biological/chemical systems,^{1–3} water purification systems,⁴ fuel cell devices,⁵ etc. Single-walled carbon nanotubes (SWCNTs), due to their extraordinary physical and chemical properties, are currently being investigated for a number of the above-mentioned applications. Molecular dynamics (MD) simulations by Hummer and his co-workers⁶ have indicated that a (6,6) CNT with a diameter of approximately 8 Å can conduct water at 300 K. The wetting behavior of the carbon nanotube was confirmed by experimental study.⁷ Boron nitride nanotubes (BNNTs) possess many of the superior properties of CNTs such as a high Young's modulus⁸ and thermal conductivity,⁹ but unlike CNTs, BNNTs exhibit high resistance to oxidation¹⁰ and a wide band gap regardless of its chirality.¹¹ These exciting properties allow BNNTs to act as complementary materials to CNTs or even replace the CNTs for applications requiring chemical stability, high-temperature resistance, or electrical insulation. There have been, however, no studies on the water conduction properties of BNNTs. In this work, we report that a (5,5) BNNT with a diameter of 6.9 Å and a finite length of 14.2 Å can conduct water, while a CNT with a similar diameter and length has only intermittent filling of water.

To gain fundamental insights into the water permeability of BNNTs and to compare the results with those in CNTs, we performed molecular dynamics simulations on a finite length (5,5) BNNT and (5,5) CNT, with a diameter of 6.9 Å and length of 14.2 Å (for longer nanotubes, the filling kinetics could be different as discussed in the case of CNTs¹²). Both tubes are saturated at the ends with hydrogen atoms. The MD simulation domain consists of the nanotube, water, and a slab. The nanotube is fixed in a slab, as shown in Figure 1. The boron and nitride atoms in the BNNT and carbon atoms in the CNT are modeled as uncharged Lennard-Jones particles. The extended simple point charge (SPC/E) model¹³ was used in the simulations. The simulations were performed for 40 ns with a 1.0 fs time step using modified GROMACS 3.2.1¹⁴ with a constant pressure¹⁵ of 1 bar and a constant temperature¹⁶ of 300 K.

The MD simulation was started with an empty (5,5) BNNT. The water from the water reservoir filled the empty (5,5) BNNT within 50 ps of simulation time (Figure 2a). There was a small fluctuation in the number of water molecules occupying the BNNT, but during the simulation time of 40 ns, the BNNT is occupied by approximately five water molecules forming a single-file chain. In addition, water molecules traversed the tube at a rate of about 5.1 molecules/ns. Despite the same size as the BNNT, the initially empty (5,5) CNT was barely filled by water. A few water molecules enter the CNT during the simulation time. The water molecules inside the CNT formed a single-file chain only a few times, but it did not last longer than 1 ns (Figure 3a). Water structure inside the nanotube can be best understood by examining the water density

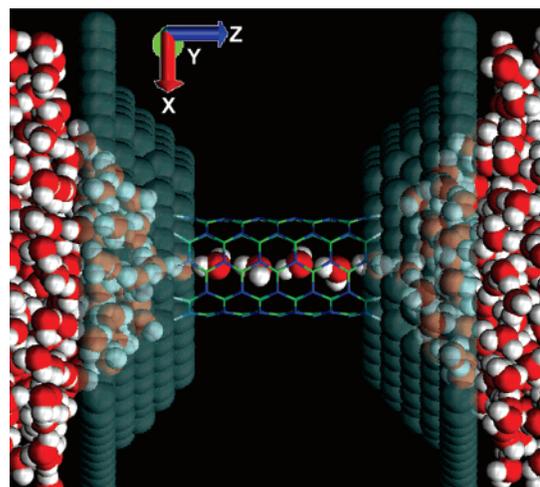


Figure 1. Visualization of a boron nitride nanotube in a water bath.

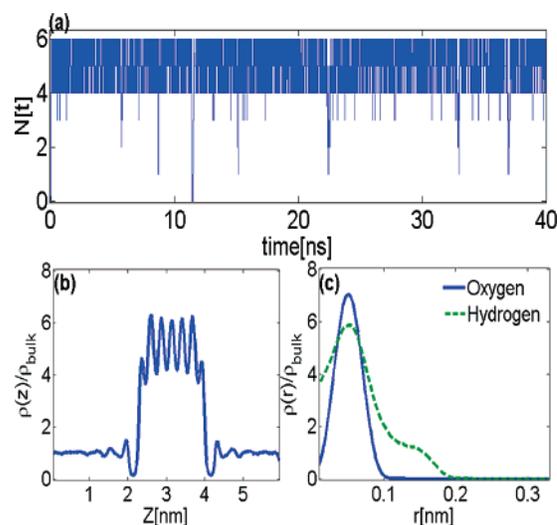


Figure 2. Number, $N(t)$, of water molecules inside the (5,5) boron nitride nanotube (a); density of water along the tube axial direction, $\rho(z)$, within 0.8 Å from the tube axis, $r = 0$ (the BNNT is located from 2.43 to 3.85 nm) (b); radial density profiles, $\rho(r)$, of water inside the tube (c).

distribution in the tube axial and radial directions (Figures 2b,c and 3b,c). Figure 2b shows the water density averaged within 0.8 Å from the tube axis along the z -axis. The five peaks indicate that there are five favorable locations of water inside the tube. Unlike in (5,5) BNNT, the axial density distribution of water inside the (5,5) CNT (Figure 3b) indicates that the water molecules like to reside at the ends of the nanotube. Following Beckstein et al.,¹⁷ we define the openness ω of the nanotube for water conduction based on water density; we assign $\omega(t) = 1$ (open) when water density in the tube at any instant is greater than 50% of the density

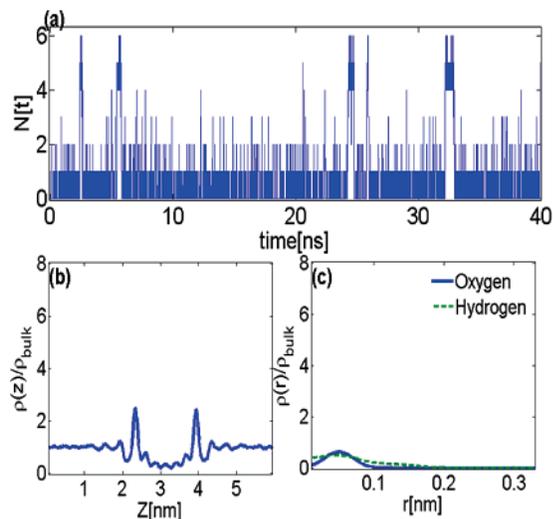


Figure 3. Number, $N(t)$, of water molecules inside the (5,5) single-walled carbon nanotube (a); density of water along the tube axial direction, $\rho(z)$, within 0.8 Å from the tube axis ($r = 0$); the CNT is located from 2.43 to 3.85 nm (b); radial density profiles, $\rho(r)$, of water inside the tube (c).

of a completely filled tube. The tube is closed ($\omega(t) = 0$), otherwise. The average openness, $\langle \omega \rangle = T_{\text{open}}/T_{\text{simulation}}$, of the BNNT and the CNT is 0.986 and 0.058, respectively.

The different wetting behavior of the (5,5) BNNT and CNT can be explained by the potential of mean force¹⁸ (PMF) analysis. The mean force distribution was obtained by sampling the force experienced by the water molecules in each bin. The energy barrier (E_b) was found to be $5.29 K_B T$ for the (5,5) BNNT and $9.83 K_B T$ for the (5,5) CNT. An energy barrier of around $5 K_B T$ is considered small for water permeation.^{19,20} The probability for the water to overcome the energy barrier, $K_r \propto \exp(-E_b/K_B T)$, indicates that the water molecules in the (5,5) CNT case have approximately 90 times lower chance to overcome the barrier compared to the (5,5) BNNT case.

To further understand the wetting behavior of BNNT, we performed an MD simulation where the nitride atoms in the BNNT were assigned the same Lennard-Jones (LJ) parameters as the boron atom and another MD simulation where the boron atoms in the BNNT were assigned the same LJ parameters as the nitride atom. We found that in the first case (when all the atoms in the BNNT had boron LJ parameters) the BNNT was almost empty of water and in the second case (when all the atoms in the BNNT had nitride LJ parameters) the BNNT was completely filled with water. From these results, we can conclude that, even though the water molecule–boron atom van der Waals attractions ($\epsilon_{B-O} = 0.5082$ kJ/mol) are stronger than the water molecule–carbon atom van der Waals attractions ($\epsilon_{C-O} = 0.4340$ kJ/mol), they are not strong enough for water molecules to enter the BNNT, and water conduction in BNNT is primarily due to the water molecule–nitride atom van der Waals interactions ($\epsilon_{N-O} = 0.6277$ kJ/mol).

Table 1 presents a comparison between the properties of water in the (5,5) BNNT (our simulations indicate that this is the smallest diameter finite length BNNT that will conduct water) and (6,6) CNT (our simulations also indicate that this is the smallest diameter finite length CNT that will conduct water). The dipole orientation of water in the (5,5) BNNT is similar to that in the (6,6) CNT.²¹ All the water molecules in both tubes orient such that the dipole vectors of the water molecules point either toward the top water

Table 1. Comparison of Water Properties in the (5,5) BNNT and (6,6) CNT

tube type	diameter (Å)	$\langle \omega \rangle$	flipping frequency	D_z (10^{-5} cm ² /s)	average # of H-bonds per water
(5,5) BNNT	6.9	0.9858	0.05	1.18×0.06	0.84
(6,6) CNT ²¹	8.2	0.9565	0.375	1.16×0.08	0.86

reservoir or toward the bottom water reservoir at any instant. Once a water molecule flips and reverses its orientation, all other water molecules flip simultaneously. During 40 ns of simulation time, the flipping occurs only twice in the BNNT, while water molecules in the (6,6) CNT flipped six times over a 16 ns sampling time. The axial diffusion coefficient of water in BNNT was found to be 1.18×10^{-5} cm²/s, which is close to the diffusion coefficient in the (6,6) CNT. The average number of hydrogen bonds per water molecule in both tubes is also very similar.

In summary, this work suggests that a (5,5) BNNT with a diameter of 6.9 Å and a length of 14.2 Å can conduct water, while a (5,5) CNT does not conduct water. The van der Waals interactions between water molecules and nitride atoms are primarily responsible for water conduction in a BNNT. The water transport properties in a (5,5) BNNT are found to be very similar to the water properties in a (6,6) CNT. A CNT with a diameter of approximately 8 Å was so far considered to be a promising candidate for a synthetic aquaporin-1 water channel, but the results in this paper suggest that a smaller diameter BNNT could also be a promising candidate.

Acknowledgment. This research was supported by NSF under Grant Nos. 0120978, 0328162, and 0523435, and by NIH under Grant PHS 2 PN2 EY016570B.

Supporting Information Available: Computational details on MD, axial diffusion coefficient, and PMF for water. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Kalra, A.; Garde, S.; Hummer, G. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 10175.
- (2) Weik, M.; Lehnert, U.; Zaccari, G. *Biophys. J.* **2005**, *89*, 3639.
- (3) Murata, K.; Mitsuoka, K.; Hirai, T.; Walz, T.; Agre, P.; Haymann, J. B.; Engel, A.; Fujiyoshi, Y. *Nature* **2000**, *407*, 599.
- (4) Srivastava, A.; Srivastava, O. N.; Talapatra, S.; Vajai, R.; Ajayan, P. M. *Nat. Mater.* **2004**, *3*, 610.
- (5) Wang, Z.; Medforth, C. J.; Shelnett, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 16720.
- (6) Hummer, G.; Rasaiah, J.; Noworya, J. P. *Nature* **2001**, *414*, 188.
- (7) (a) Majumder, M.; Chopra, N.; Andrews, R.; Hinds, B. J. *Nature* **2005**, *438*, 44. (b) Holt, J. K.; Park, H. G.; Wang, Y.; Stadermann, M.; Artyukhin, A. B.; Grigoropoulos, C. P.; Noy, A.; Bakajin, O. *Science* **2006**, *312*, 1034.
- (8) Chopra, N. G.; Zetti, A. *Solid State Commun.* **1998**, *105*, 297.
- (9) Chang, C.; Han, W.-Q.; Zetti, A. *J. Vac. Sci. Technol., B* **2005**, *23*, 1883.
- (10) Chen, Y.; Zou, J.; Campbell, S. J.; Caer, G. L. *Appl. Phys. Lett.* **2004**, *84*, 2430.
- (11) Blasé, X.; Bubbio, A.; Louie, S. G.; Cohen, M. L. *Europhys. Lett.* **1994**, *28*, 335.
- (12) Waghe, A.; Rasaiah, J.; Hummer, G. *J. Chem. Phys.* **2002**, *117*, 10789.
- (13) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. *J. Phys. Chem.* **1987**, *91*, 6269.
- (14) Lindahl, E.; Hess, B.; van der Spoel, D. *J. Mol. Model.* **2001**, *7*, 306.
- (15) Parrinello, M.; Rahman, A. *J. Appl. Phys.* **1981**, *52*, 7182.
- (16) Hoover, W. *Phys. Rev. A* **1985**, *31*, 1695.
- (17) Beckstein, O.; Biggin, P. C.; Sansom, S. P. *J. Phys. Chem. B* **2001**, *105*, 12902.
- (18) Kjenllander, R.; Greberg, H. *J. Electroanal. Chem.* **1998**, *450*, 233.
- (19) de Groot, B. L.; Grubmüller, H. *Curr. Opin. Struct. Biol.* **2005**, *15*, 176.
- (20) Borgnia, M. J.; Agre, P. *J. Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 2888.
- (21) Won, C. Y.; Joseph, S.; Aluru, N. R. *J. Chem. Phys.* **2006**, *125*, 114701.

JA0687318