

## Fast reverse osmosis using boron nitride and carbon nanotubes

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We investigate reverse osmosis through commonly used polymeric and advanced inorganic nanotube based semipermeable membranes by performing nonequilibrium molecular dynamics simulations. Simulations indicate that there is a significantly higher water flux through boron-nitride nanotube (BNNT) and carbon nanotube (CNT) compared to a polymethyl methacrylate (PMMA) pore, and a slightly higher water flux through BNNT as compared to CNT. The calculated permeation coefficient is in reasonable agreement with the theoretical single-file “hopping” model. Potential of mean force analysis indicates that the irregular nature of PMMA pore surface can cause significant localized energy barriers inside the pore, thereby reducing the water flux. © 2008 American Institute of Physics. [DOI: 10.1063/1.2907333]

Reverse osmosis (RO) is a widely used membrane technology for desalination and industrial water reuse. The fact that water is essential to human life has led to research on energy efficient membranes to provide high water flux and salt rejection rates. Early studies on polymethyl methacrylate (PMMA) membranes revealed higher water fluxes compared to widely used cellulosic-type membranes though solute permeability remained the same.<sup>1</sup> Carbon nanotubes (CNTs) are currently being investigated for water purification studies as they have shown several orders of magnitude higher water flux compared to classical theory predictions.<sup>2</sup> Boron-nitride nanotubes (BNNTs) are structurally similar to carbon nanotubes and exhibit interesting nanofluidic transport properties.<sup>3</sup> In recent work,<sup>4</sup> the effect of pore characteristics on osmosis has been investigated, but the fundamental mechanisms governing RO are still not clear. In this work, RO through three different semipermeable membranes (BNNT, CNT, and PMMA) was characterized by using non-equilibrium molecular dynamics (MD) simulations. We observed that single-file water flux through the BNNT membrane was slightly higher than that in the CNT membrane, and the PMMA membrane showed significantly lower water flux. We explain our observations using a theoretical single-file model and the potential of mean force (PMF) analysis. Translocation time and entrance time are also calculated to further understand the transport behavior.

MD simulations were performed on a semipermeable pore connecting the solution chamber and the pure water chamber (see Fig. 1). Two pressure pistons, as shown in Fig. 1, are used to initiate RO. BNNT and CNT pores were modeled using a (6,6) configuration. The Lennard-Jones (LJ) parameters for BNNT and CNT are taken from Ref. 5. PMMA membrane was simulated using a united atom model with GROMOS96 force field.<sup>6</sup> Diameters for the BNNT and CNT are 0.83 and 0.81 nm, respectively, while the PMMA pore has a minimum diameter of 0.82 nm and an average diameter of 1.08 nm. The lengths of BNNT, CNT, and PMMA pores were 2.135, 2.090, and 1.8 nm, respectively. Simple point charge-extended<sup>7</sup> model was used for water and ions were modeled as charged LJ atoms.<sup>8</sup> Pressure pistons were made

of silicon atoms with GROMOS96 force field. To prevent distortion of the pressure pistons,  $x$  and  $y$  positions of piston atoms were fixed. At every time step, average force between the piston atoms and the liquid atoms was added to the external target pressure, and applied to each piston atom.<sup>9</sup> Pressure piston attached to the pure water chamber was maintained at 100 MPa, and different pressures ranging from 200 to 600 MPa were applied to the pressure piston attached to the solution chamber. Water molecules moved from the solution chamber to the pure water chamber against the osmotic pressure gradient while the ions did not go through because of steric hindrance and a large energy barrier at the mouth. Simulation was run until at least 180 water molecules were transported to the pure water chamber. A high pressure gradient was necessary to observe sufficient RO of water molecules and thus to obtain reasonable statistics.

From the MD simulation of RO, we observed a higher water flux for BNNT and CNT membranes compared to the PMMA membrane (see Fig. 2). Also, the water flux for the BNNT membrane was slightly higher compared to the CNT membrane. Figure 2 (inset) shows the number of water molecules accumulated in the pure water chamber for the BNNT case when the applied pressure gradient,  $\Delta P$  is varied from 100 to 500 MPa in increments of 100 MPa. From the observed linear relation between the pressure gradient and the water flux, we calculate the permeation coefficient,  $p_n$ , de-

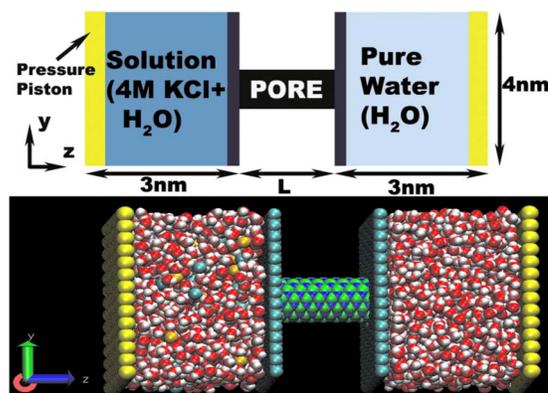


FIG. 1. (Color online) Schematic (top) and snapshot (bottom) of the MD setup for reverse osmosis.

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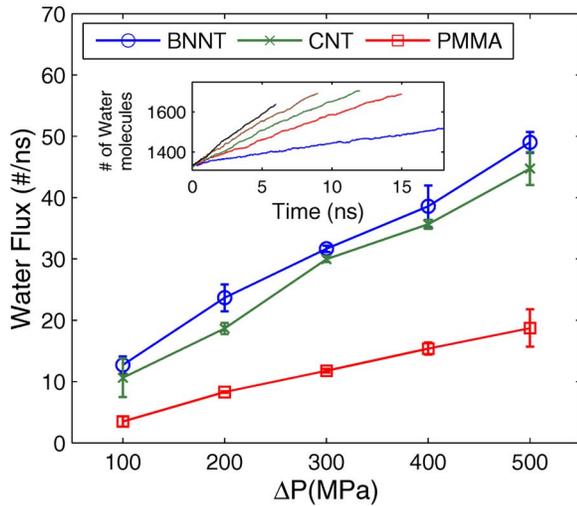


FIG. 2. (Color online) Variation of the RO water flux with applied pressure gradient for BNNT, CNT, and PMMA pores. Inset: variation of water occupancy in the pure water chamber with time for BNNT pore. Each line is for a different  $\Delta P$ , pressure drops of 100, 200, 300, 400, and 500 MPa were considered.

finied by  $J = p_n \Delta \mu / k_B T$ , where  $\mu$  is the chemical potential and  $k_B$  and  $T$  are the Boltzmann constant and temperature, respectively. The chemical potential gradient,  $\Delta \mu / k_B T$ , can be evaluated from the pressure gradient and the concentration gradient of the solute using the expression

$$\frac{\Delta \mu}{k_B T} = -V_w \Delta C_s + \frac{V_w}{N_A k_B T} \Delta P, \quad (1)$$

where  $V_w$  ( $\text{cm}^3/\text{mol}$ ) is the molar volume of water,  $\Delta C_s$  ( $\text{mol}/\text{cm}^3$ ) is the concentration gradient of the solute,  $N_A$  ( $\text{mol}^{-1}$ ) is the Avogadro number, and  $\Delta P$  (MPa) is the hydrostatic pressure difference. The values of  $p_n$  obtained were 14.7 #/ns, 13.4 #/ns, and 5.6 #/ns for BNNT, CNT, and PMMA membranes, respectively. This indicates that BNNT and CNT membranes have an order of magnitude higher permeation coefficient compared to PMMA.

We observed that single-file water molecules transported as collective hopping events.<sup>10</sup> The single-file water molecules hop about a water-water distance,  $d$ , after an average waiting time of  $\tau$ . The hopping rate,  $k$  defined as the number of hopping events during the unit time, is given by  $k = 1/\tau$ . The net water flux is the difference between forward hopping rate and the backward hopping rate. In single-file water transport, the permeation coefficient,  $p_n$  can also be estimated from the equilibrium fluctuation through the relation  $p_n = k_0$  (Ref. 11), where  $k_0$  is the equilibrium hopping rate. In equilibrium, the forward hopping rate and the backward hopping rate are equal, thus  $k_0 = (1/2)k$ . Equilibrium simulations were performed to obtain the hopping rate,  $k_0$ . The hopping rate is determined by counting all the forward and backward hopping events (see Fig. 3) during the simulation time. The movement of water molecule from one minimum of PMF to the next minimum of PMF was counted as one hopping event. It should be noted that in the PMMA pore, there is more than single-file water occupied in parts of the pore mouth region due to the nonuniformity of the pore diameter. In this case, the hopping rate is obtained in the portion of the pore where single-file water is observed. The values of  $k_0$  computed from the equilibrium simulations are

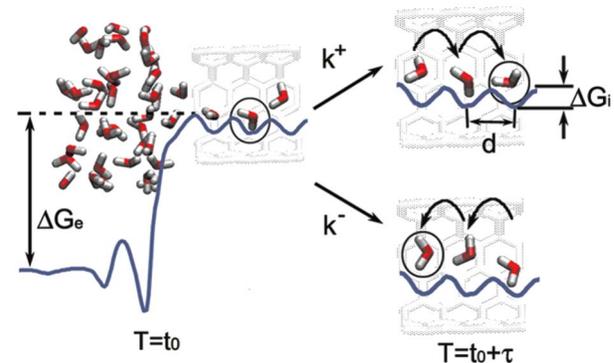


FIG. 3. (Color online) Water configuration snapshot and the underlying PMF profile from equilibrium simulation with CNT pore.  $\Delta G_e$  and  $\Delta G_i$  denote energy barrier at pore entrance and inside, respectively. Water molecules hop to the next PMF minima in a time interval,  $\tau$ . Bidirectional hopping rate,  $k$  (#/ns) is defined by number of hops during unit time.  $k = k^+ + k^-$ , where  $k^+$  is the forward hopping rate (shown in top right) and  $k^-$  is the backward hopping rate (shown in bottom right). At equilibrium,  $k^+ = k^- = k_0$ .

$k_0 = 16.0$  #/ns,  $15.0$  #/ns, and  $3.0$  #/ns for the BNNT, CNT, and PMMA membranes, respectively. These values are close to the permeation coefficient,  $p_n$ , extracted from Fig. 2. For PMMA pore, a smaller value of  $k_0$  compared to the value from Fig. 2 is due to the frequent breaking and reforming of single-file water chain which limits the accuracy of the hopping rate. Solution-diffusion model,<sup>12</sup> widely used in RO, fails to estimate the permeation coefficient in single-file transport as it neglects the collectivity of water molecules.

By evaluating PMF profile<sup>13</sup> along the water passage, larger hopping rate for BNNT can be explained from the lower energy barrier present at the pore entrance and in the pore interior. The energy barrier at the pore entrance for BNNT and CNT membranes is  $5.15k_B T$  and  $5.273k_B T$  (see Fig. 3) and the average energy barrier in the pore interior is  $0.23k_B T$  and  $0.47k_B T$  (see Fig. 3), respectively. Lower energy barrier at the pore entrance for BNNT compared to CNT is primarily due to stronger van der Waals interaction between BNNT and water. The energy barrier inside the pore is primarily due to the collective motion of single-file water molecules, i.e., due to the correlation between water positions inside the pore.<sup>14</sup> Unlike BNNT and CNT pores in which water molecules form a single-file water chain, in the PMMA pore, more than single-file water is present near the pore mouth and water density decreases as we approach the interior of the pore. Even though the energy barrier at pore entrance ( $4.35k_B T$ ) is lower compared to the BNNT and CNT pores, the average energy barrier inside the pore is higher ( $1.76k_B T$ ). Irregular PMMA pore surface contributes to the high energy barrier present in the pore interior leading to the observed low flux.

To further understand the transport behavior of single-file RO, using the MD simulation data, we studied the correlation between the entrance time and the translocation time. Entrance time (denoted by  $T_e$ ) was calculated by averaging successive entrance events of water molecules that have completely translocated, and translocation time (denoted by  $T_t$ ) was measured by averaging the time interval between entrance and exit events of the water molecules that have completely translocated. Variation of the entrance and translocation times with the pressure gradient are plotted in Figs. 4(a) and 4(b), respectively. In single-file water trans-

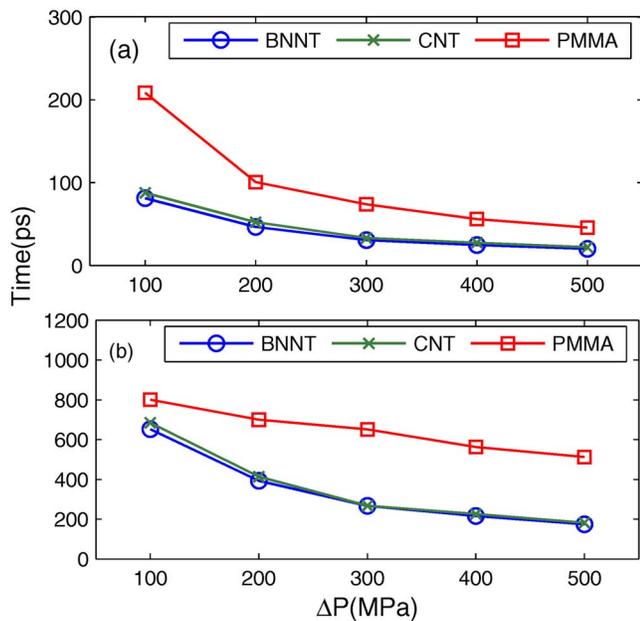


FIG. 4. (Color online) (a) Variation of the entrance time ( $T_e$ ) and (b) translocation time ( $T_t$ ) with the applied pressure gradient.

port, for one water molecule to completely traverse the pore, an average number of water molecules,  $N$ , inside the pore should exit the pore. The calculated translocation time from the MD data is found to be  $T_t \approx NT_e$  with  $N=8$  for BNNT and CNT. The entrance and translocation times in the PMMA case did not strictly obey this condition due to the occupation of more than single-file water at the pore entrance region. Both the translocation time and the entrance time are found to be the shortest in the BNNT pore, and the translocation time of water molecules through the PMMA pore is considerably longer. This is consistent with the results obtained for the water flux.

To conclude, RO through three different membranes made of BNNT, CNT, and PMMA pores was compared using MD simulation. BNNT and CNT had significantly higher water flux compared to that of PMMA pore, and BNNT had slightly higher water flux than CNT pore. This variation in the fluxes was explained using a theoretical model for single-file water transport and the PMF analysis. We observed a reasonable correlation between the entrance and translocation times in single-file “hopping” transport through nanopores. This study suggests that the enhanced water flux in BNNT and CNT in RO can be used in future water purification designs requiring a much lower energy consumption.

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