

## Separation of gases from gas–water mixtures using carbon nanotubes

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We investigate equilibrium transport of gas–water mixtures, such as CO<sub>2</sub>–water, O<sub>2</sub>–water and H<sub>2</sub>–water mixtures, in carbon nanotubes using molecular dynamics simulations. Our results indicate that gases are selectively physisorbed in carbon nanotubes forming single-file gas chains. Once the single-file gas chains are formed, they prevent entry of water into the nanotube, suggesting that the presence of gas molecules can significantly affect the equilibrium transport of water in carbon nanotubes. The diffusion of single-file gas chains in nanotubes for gas–water mixtures is found to be lower compared to the single-file diffusion of gases in gas–only cases. © 2010 American Institute of Physics. [doi:10.1063/1.3374363]

The transport of water and gases through carbon nanotubes (CNTs) has been investigated extensively.<sup>1–4</sup> The remarkably smooth structure of CNT makes it a promising material for various applications relying on fast transport of water and gases.<sup>3,5</sup> Furthermore, CNTs, similar to activated carbons,<sup>6</sup> can be adsorbents of gases as gas can condense to high density in nanometer scale pores.<sup>7–10</sup> Even though the transport of various liquids and gases through CNTs has been investigated, the transport of gas–water mixtures has not received significant attention. Kotsalis *et al.*<sup>11</sup> considered nitrogen molecules dissolved in water to study the nanobubble effect on transport through (20,20) CNTs. It was shown that nitrogen forms droplets on the carbon surface and this reduces the slip length. Kalra *et al.*<sup>12</sup> studied transport of methane–water mixture in CNTs. They have shown that methane molecules are selectively transported through the CNT. Given the technological importance of gas–water mixtures, in this paper, we investigate the equilibrium transport of various gas–water mixtures, such as CO<sub>2</sub>–water, O<sub>2</sub>–water and H<sub>2</sub>–water mixtures, through CNTs. Our results indicate that the presence of gas molecules in water can significantly affect the occupancy of water molecules in small diameter CNTs. In the presence of water molecules, gas molecules are selectively adsorbed into the interior of CNTs and the motion of single-file gas chains in the CNT is different from the motion of gas molecules in the CNT when only gas molecules are present.

To understand the spontaneous transport of gas–water mixtures in CNT systems, we performed equilibrium molecular dynamics (MD) simulations with gas–water mixture reservoirs attached to the CNT. The forces arising from van der Waals and electrostatic interactions were considered in the simulations. For the van der Waals interactions between molecules, the 6–12 Lennard–Jones potential was used with a cut-off distance of 1.2 nm and the electrostatic interactions were computed using the Particle Mesh Ewald method with a grid spacing of 0.15 nm. Lennard–Jones parameters and point charges for the gas molecules (CO<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>), CNT and graphene slab were taken from Refs. 13–16. Water is modeled by using the SPC/E model.<sup>17</sup> Water–gas Lennard–

Jones parameters were obtained by applying the Lorentz–Berthelot mixing rules,  $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$  and  $\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}$ . Time integration is performed by using the leap-frog algorithm with a time step of 1.0 fs. The temperature of the system is maintained at 300 K by using the Nosé–Hoover thermostat<sup>18</sup> with a time constant of 0.1 ps. The Parrinello–Rahman scheme<sup>19</sup> with a time constant of 0.1 ps and compressibility of  $4.5 \times 10^{-5}$  bar<sup>-1</sup> was employed to regulate the pressure of the system at 0.1 MPa. Simulations were performed using GROMACS 3.3.1.<sup>20</sup>

A (10,0) single-walled CNT fixed in a graphene slab was considered [see Fig. 1(a)]. The diameter of the CNT is 0.78 nm and the length is 2.06 nm. The ends of the CNT have

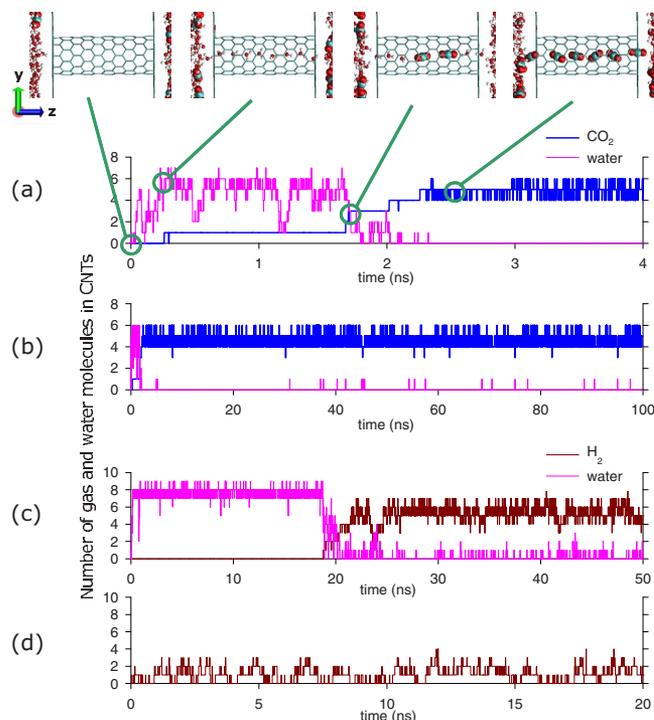


FIG. 1. (Color online) (a) Snapshot of the system and the number of gas and water molecules in the CNT for CO<sub>2</sub>–water mixture as a function of time. (b) Number of gas and water molecules in the CNT for CO<sub>2</sub>–water mixture. (c) Number of gas and water molecules in the CNT for H<sub>2</sub>–water mixture. (d) Number of gas molecules in the CNT for H<sub>2</sub>–only simulation (no water molecules).

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TABLE I. Occupancy and diffusion of gases,  $\langle \Delta x^2 \rangle = 2Ft^\alpha$ , for various gas-water mixtures and gas-only cases.

	$\alpha$	F(using $\alpha=0.5$ ) ( $\times 10^{-12} \text{ m}^2 \text{ s}^{-0.5}$ )	Number of gas molecules in the CNT
CO <sub>2</sub> -water	0.51	0.0021	4.8
CO <sub>2</sub> only	0.51	0.0073	4.9
O <sub>2</sub> -water	0.50	0.0026	5.7
O <sub>2</sub> only	0.52	0.0119	4.4
H <sub>2</sub> -water	0.51	0.0034	5.5
H <sub>2</sub> only	...	...	1.0

zigzag structure and the ends are not functionalized. The simulation box size was  $3.834 \times 3.935 \times 9.1 \text{ nm}^3$ . Periodic boundary conditions were used in all the three directions. The reservoirs were initially filled with well-mixed and supersaturated gas-water mixture using a ratio of 1:100 ( $N_{\text{wt}}=3200$  and  $N_{\text{gas}}=32$ ). The concentration of water in the reservoir is 55 M at 0.1 MPa. For the CO<sub>2</sub>-water mixture case, water molecules from the reservoir filled the empty (10,0) single-walled CNT within 100 ps. The first CO<sub>2</sub> molecule entered the tube around 250 ps, and after that the passage of water molecules into the tube was blocked and more CO<sub>2</sub> molecules entered the tube [see Fig. 1(a)]. Once the CO<sub>2</sub> molecules completely filled the CNT (it took about 2.5 ns from the beginning of the simulation), the interior of the CNT is occupied by approximately 4.8 CO<sub>2</sub> molecules forming a single-file chain and water molecules were blocked from entering the tube during the simulation time of 100 ns [see Fig. 1(b) and Table I]. In all the three gas-water mixture cases, adsorption of gas molecules to the interior of the CNT was observed, even though the time it took for the gas molecules to completely fill the CNT varied according to the type of the gas and the initial configuration of the gas-water system. High gas concentration was also observed near the graphene slab. The number of gas molecules in the (10,0) CNT after equilibration were found to be 4.8 for CO<sub>2</sub>, 5.7 for O<sub>2</sub>, and 5.5 for H<sub>2</sub> and they formed single-file configurations in the nanotube (see Table I). For comparison purpose, we also simulated the gas-only cases without water, and we found that the average number of gas molecules in the CNT was 4.9 for CO<sub>2</sub>, 4.4 for O<sub>2</sub>, and 1.0 for H<sub>2</sub>. CO<sub>2</sub> and O<sub>2</sub> formed single-files in the nanotube, but, H<sub>2</sub> rarely filled the CNT and did not form a single-file configuration inside the nanotube.

The selective adsorption of gases from gas-water mixtures by CNTs can be understood by calculating the potential of mean force<sup>21</sup> (PMF) along the z-axis. After averaging the force on the molecules at various z positions along the tube axis, the PMF was computed by integrating the mean force along the z-axis. The ends of the reservoirs were taken as the reference position where the PMF is zero. In order to compute the PMF of water, a water molecule, which rarely enters the CNT under equilibrium condition for gas-water mixture cases, was positioned at various locations inside the CNT along the tube axis and umbrella sampling was used.<sup>22</sup> Figures 2(a) and 2(b) show a comparison of the PMF of gas molecules and water. The energy barrier (defined as the difference in the PMF between the reservoir and inside the CNT) for CO<sub>2</sub> is  $-5.4 \text{ k}_B\text{T}$ ,  $-3.7 \text{ k}_B\text{T}$  for O<sub>2</sub> and  $-3.1 \text{ k}_B\text{T}$  for H<sub>2</sub>. The energy barrier for water is  $7.1 \text{ k}_B\text{T}$  in

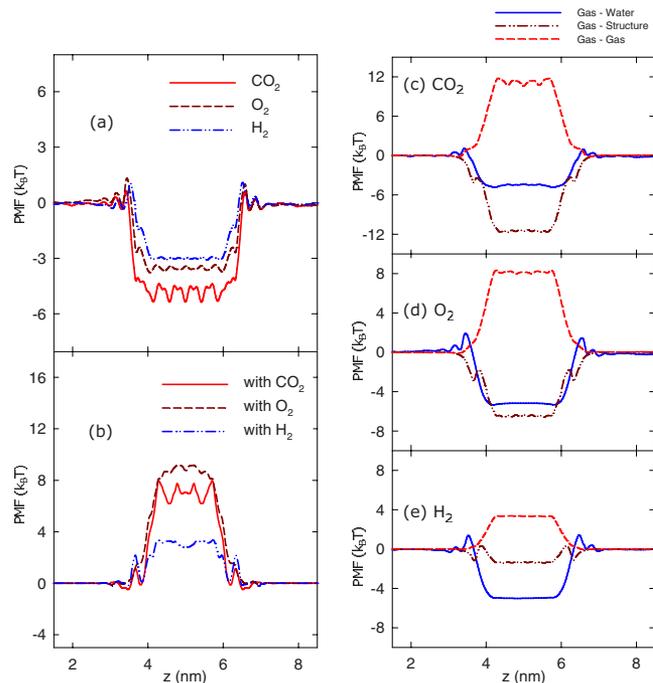


FIG. 2. (Color online) PMF profile along the tube axis (a) PMF of CO<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub> in gas-water mixtures and (b) PMF of water in various gas-water mixtures. [(c)–(e)] Decomposition of PMF of gases CO<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub> to gas-water, gas-structure, and gas-gas interactions in gas-water mixture cases.

CO<sub>2</sub>-water case,  $8.8 \text{ k}_B\text{T}$  in O<sub>2</sub>-water case and  $3.0 \text{ k}_B\text{T}$  in H<sub>2</sub>-water case. The negative values of PMF for gases indicate that all the gases have a strong preference to exist inside the CNT, while the water molecules prefer to stay in the reservoir compared to inside the CNT because of the positive energy barrier.

The PMF of the gas molecules can be decomposed into gas-gas interactions (both van der Waals and electrostatic interactions), gas-water interactions (both van der Waals and electrostatic interactions) and gas-nanotube/graphene interactions also defined as gas-structure interactions (van der Waals interactions only as the CNT and graphene slab does not have any charge). These decompositions are shown in Figs. 2(c)–2(e). The gas-structure interaction gives rise to an energy barrier of  $-11.5 \text{ k}_B\text{T}$  for CO<sub>2</sub>,  $-6.6 \text{ k}_B\text{T}$  for O<sub>2</sub>, and  $-1.4 \text{ k}_B\text{T}$  for H<sub>2</sub>, while the gas-water energy barriers are  $-4.5 \text{ k}_B\text{T}$  for CO<sub>2</sub>,  $-5.2 \text{ k}_B\text{T}$  for O<sub>2</sub>, and  $-5.0 \text{ k}_B\text{T}$  for H<sub>2</sub>. The gas-gas interactions give rise to an energy barrier of  $10.6 \text{ k}_B\text{T}$  for CO<sub>2</sub>,  $8.1 \text{ k}_B\text{T}$  for O<sub>2</sub>, and  $3.3 \text{ k}_B\text{T}$  for H<sub>2</sub>. These results indicate that the gas-structure and the gas-water interactions lead to physisorption of gases inside CNT. In the case of H<sub>2</sub>-water mixture, the magnitude of the gas-water interaction is dominant on the PMF of H<sub>2</sub> compared to the gas-structure interaction. This can explain the observation that H<sub>2</sub> forms a single-file inside the CNT for H<sub>2</sub>-water mixture and not for H<sub>2</sub>-only case.

To estimate the gas motions in the nanotube, we computed the long-time behavior of the mean-squared displacement, which is given by single-file diffusion  $\langle \Delta x^2 \rangle = 2Ft^{0.5}$ , where  $F$  denotes the mobility factor of the single-file chain and  $t$  is the time.<sup>23,24</sup>  $F$  was calculated using

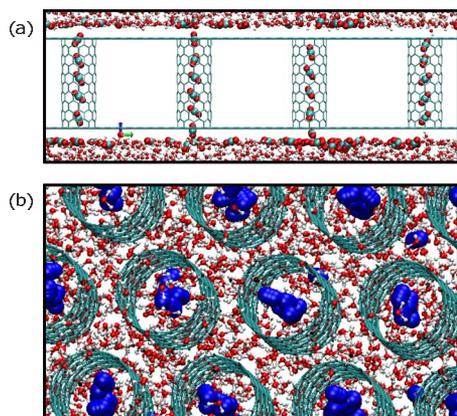


FIG. 3. (Color online) Snapshots of (a) Four (10,0) CNTs aligned in a graphene slab for CO<sub>2</sub>-water mixture simulation at  $t=4.8$  ns and (b) Hexagonal packed bundle of (10,0) CNTs connected to reservoir containing H<sub>2</sub>-water mixture at  $t=9.0$  ns.

$$F = \frac{\langle |\mathbf{R}_{\text{CM}}(t) - \mathbf{R}_{\text{CM}}(0)|^2 \rangle}{2t^{0.5}}$$

As shown in Table I, the values of  $F$  indicate that the diffusion of gases, CO<sub>2</sub> and O<sub>2</sub>, in gas-water mixture cases were decreased compared with the diffusion of gases in gas-only simulations without water. In the case of H<sub>2</sub>, the diffusion changes from single-file diffusion in the case of gas-water mixture to single H<sub>2</sub> molecule diffusion (no single-file chain was observed) in the gas-only case because of the decrease in gas occupancy in the CNT. The reduction in diffusivity in gas-water mixtures compared with the gas-only case indicates that the presence of gas-water interactions near the entrance of the tube restricts the behavior of gas in the tube.

To further understand the adsorption behavior of gas molecules inside CNTs in gas-water mixtures, we performed MD simulations with an array of CNTs as shown in Figs. 3(a) and 3(b). Four (10,0) CNTs are aligned in a graphene slab and the nanotubes are connected to reservoirs as shown in Fig. 3(a). Figure 3(b) shows another simulation of a hexagonal packed bundle of single-walled (10,0) CNTs connected to reservoirs. The reservoirs were filled with CO<sub>2</sub>-water mixture (for CNTs aligned in a graphene slab example) and H<sub>2</sub>-water mixture (for hexagonal packed CNTs) in the ratio of 1:100. All the tubes were initially empty, and within a few hundred picoseconds the tubes are filled with water and after several nanoseconds of simulation time, the water molecules in the tubes are expelled out by CO<sub>2</sub> and H<sub>2</sub> molecules from the gas-water mixtures and all the tubes were completely filled with gas molecules. These simulations suggest potential applications of CNTs as gas storage devices.

To conclude, we investigated the equilibrium transport of gas-water mixtures in CNTs using MD simulations. For the three mixtures investigated (CO<sub>2</sub>-water, O<sub>2</sub>-water and H<sub>2</sub>-water mixtures), we observed adsorption of gases in the CNTs. The gas molecules formed single-file chains and once the nanotube is filled with single-file gas chains they prevented entry of water into the nanotube. The single-file diffusion of gas molecules in the nanotube in the case of gas-water mixtures is lower compared to the single-file diffusion of gases in gas-only simulations, except in the case of H<sub>2</sub>, which does not form a single-file chain in the case of gas-only case. The results presented in this paper suggest that under equilibrium conditions in the presence of gases, water molecules will be blocked from CNTs, and gases from gas-water mixtures will be selectively adsorbed by CNTs.

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