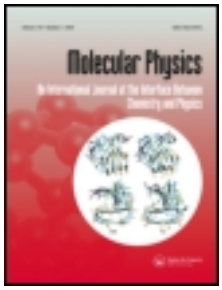

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Distinct transport properties of O_2 and CH_4 across a carbon nanotube

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It is of fundamental importance to investigate either O_2 or CH_4 molecules across nanochannels in many areas such as breathing or separation. Thus, many researches have focused on such a single type of molecules across nanochannels. However, O_2 and CH_4 can often appear together and crucially affect human life, say, in a mine. On the basis of molecular dynamics simulations, here we attempt to investigate the mixture of O_2 and CH_4, in order to identify their different transport properties in a nanochannel. We take a single-walled carbon nanotube (SWCNT) as a model nanochannel, and find that their transport properties are distinctly different. As the concentration of O_2 increases up to a high value of 0.8, it is always faster for CH_4 molecules to transport across the SWCNT, and the total number of gas molecules transporting across the SWCNT is decreased. Meanwhile, CH_4 molecules are always dominant in the SWCNT, and the total number of O_2 or CH_4 inside the SWCNT is a constant. By calculating the van der Waals interaction between the SWCNT and O_2 or CH_4, we find that the net interaction between CH_4 and the SWCNT is much stronger. Our findings may offer some hints on how to separate CH_4 from O_2, and/or store CH_4 efficiently.

Keywords: carbon nanotube; methane; oxygen; diffusion; MD simulations

1. Introduction

It is of fundamental importance to investigate either oxygen (O_2) or methane (CH_4) molecules across nanochannels. For instance, in the study of breathing, the investigation of the transportation of O_2 in or out of lung is important for understanding the human metabolic system [1, 2]. And the investigation of the transportation of CH_4 molecules out of porus media is important for extracting CH_4 from natural gas hydrate [3–5]. Therefore, many researches have focused on such a single type of molecules across nanochannels [6–8]. However, O_2 and CH_4 can often appear together and crucially affect human life or plants [9–12]. For example, O_2 and CH_4 in a mine can threaten miners' lives [11, 12]. In such a case, it is of particular importance to separate CH_4 from O_2, and/or store CH_4 efficiently. For the purpose of separation, a membrane with nanochannels is a candidate, which only allows CH_4 to transport. Accordingly, one must investigate the transport properties of CH_4/O_2 mixtures across nanochannels. In the literature, researchers often take a single-walled carbon nanotube (SWCNT) as a model nanochannel [6, 13, 14] after the pioneering work by Hummer *et al.* [32] where they first investigated the transportation of water molecules across a SWCNT. In this direction, Lee and Sinnot [6] used classical molecular dynamics simulations to investigate equilibrium and non-equilibrium transportation of O_2 molecules in a SWCNT and found that O_2 molecules formed well-defined layers around the nanotube interior and/or exterior. Karla *et al.* [13] also adopted molecular dynamics simulations to investigate the behaviour of CH_4 molecules across a SWCNT in the presence of water (H_2O), and they found that CH_4 molecules entered the SWCNT prior to H_2O molecules and formed a single file inside the SWCNT. Recently, Yu *et al.* [14] also utilised molecular dynamics simulations to study the transport behaviour of water molecules along an end-opened SWCNT. They found that CH_4 molecules pulled the water molecules from the inner of the SWCNT along the axial direction of the SWCNT, and that the transport velocity of H_2O molecules could be affected by the number of CH_4 molecules. Katarzyna and Aleksander [15] studied properties of methane in CNT and showed the decrease of the diffusion coefficient of methane molecules with density used molecular dynamics. Similarly, for our purpose, we also adopt molecular dynamics simulations.

2. Computational details

Molecular dynamics, which has been used widely for the studies of dynamics in the SWCNTs, in proteins, and in-between proteins [16–35], is adopted in this work.

Our simulation framework is shown in Figure 1: two parallel graphite sheets with a separation of 2.380 nm dividing the full space into three parts. A *Z*-directed, uncapped, (10, 0) SWCNT with diameter 0.772 nm is used to perpendicularly join the two graphite sheets. The

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parameters of carbon nanotube come from Hummer *et al.* [32]. The SWCNT and graphite sheets are in a box (4.652 nm $\times$ 4.646 nm$\times$ 6.480 nm) with the total 200 molecules of both O_2 and CH_4 molecules. For the O_2/CH_4 mixture, the concentration of O_2 molecules, C_n (which equals to the ratio between the number of O_2 molecules and the total number of both O_2 and CH_4 molecules), are equal in both sides. In the simulations, C_n ranges from 0.07 to 0.9. The parameters of O_2 and CH_4 molecules come from Gaurav and Stanley [36] and Borja and Romáan [37], respectively. In order to prevent the SWCNT and graphite sheets from being swept away, partial carbon atoms are restrained at their initial positions.

We perform molecular dynamics simulations with Gromacs 3.3.1, and adopt the thermostat of Nosé–Hoover *et al.* [38, 39]. All simulations are carried out under the *NVT* (constant number of molecules, constant volume and constant temperature) ensemble. Periodic boundary conditions are applied to all three directions of the simulations box. The initial atomic velocities are generated by a Maxwellian distribution at a given temperature, 300 K. A time step is set to 2 fs and the total simulation time is 90 ns. Electrostatic interactions belong to long range interactions, and the model of a CH_4 molecule we have chosen contains both negative and positive charges (namely, one C atom contains $-0.024\,e$, and one H atom contains $+0.006\,e$. Here e means the elementary charge). Thus, the particle-mesh Ewald [40] method has been used to treat electrostatic interactions in the simulations. The cut-off distance for Lennard–Jones interaction is set at $r = 1.0$ nm.

3. Results and discussion

The SWCNT is empty at the beginning of the simulations, and the interior pore of the SWCNT is large enough to hold a single file of CH_4 or O_2 molecules. The initially empty SWCNT is rapidly full of CH_4 or O_2 molecules during the simulations, which can be seen from Figure 2. Figure 2 shows a filling process as time τ elapses. In Figure 2, the arrow-marked O_2 molecule moves near the pore opening of the SWCNT from bulk at $\tau = 9.6$ ps, which is driven by a thermodynamic driving force. Then, the marked O_2 molecule, two other O_2 molecules and one CH_4 molecule enter into the interior of the SWCNT by overcoming barriers at $\tau = 49.6$ ps. Meanwhile, the SWCNT is half-filled with gas molecules. Finally, the SWCNT is filled with gas molecules and the marked O_2 molecule is transported across the SWCNT at $\tau = 275.2$ ps.

To proceed, the number of gas molecules transported per unit time across the SWCNT, N_f, is computed by

$$N_f = N'(t)/t, \tag{1}$$

where $N'(t)$ is the total number of gas molecules transported across the SWCNT, and t is the total effective simulation

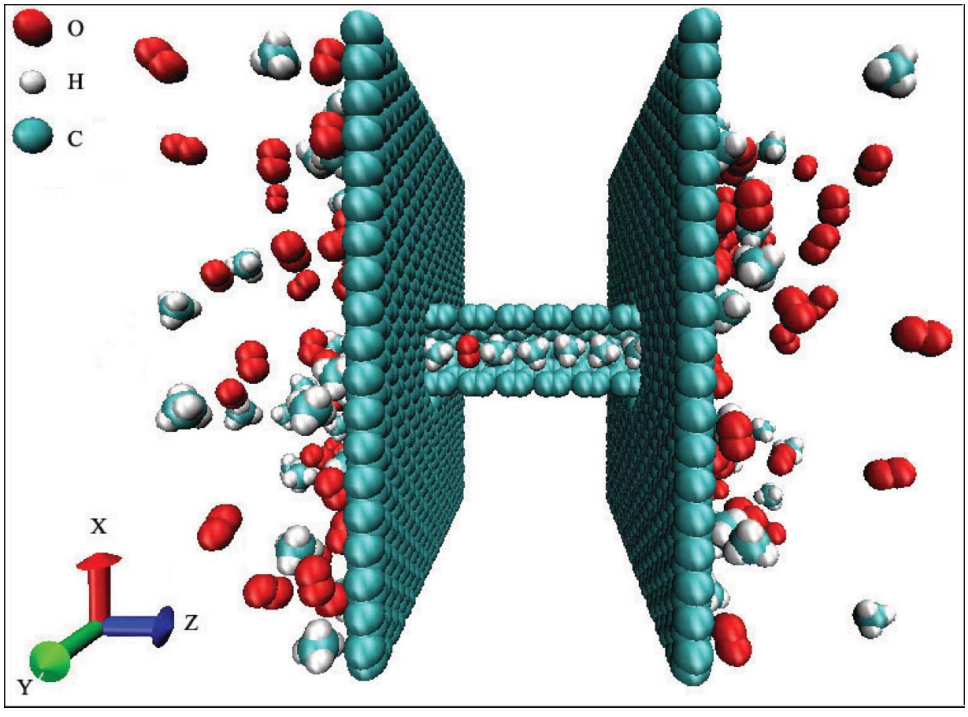

Figure 1. Snapshot schematically showing the simulation system with a Z-directed SWCNT perpendicularly joining the centres of two graphite sheets. Both O_2 and CH_4 molecules are filled in the space as shown.

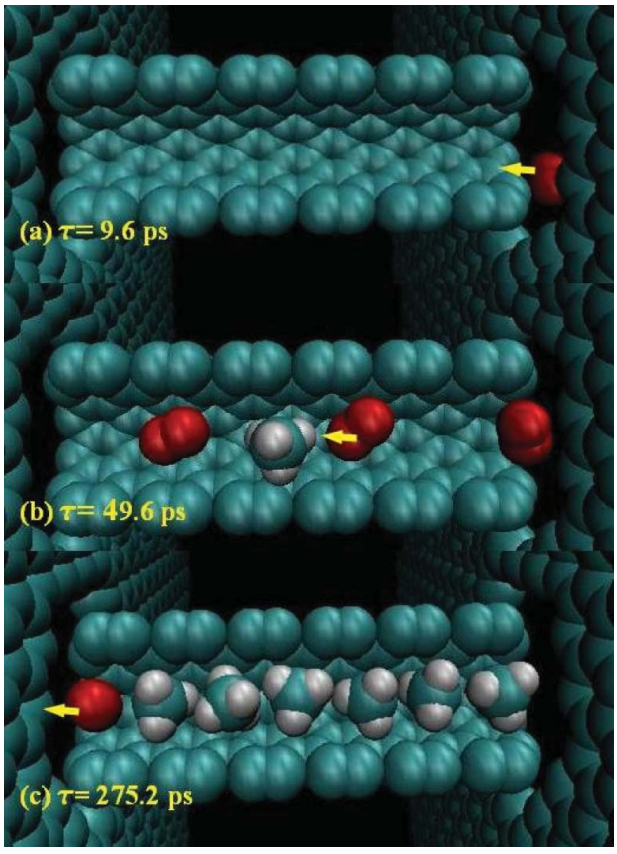

Figure 2. Snapshots showing a filling process in the SWCNT as time τ evolves from (a) $\tau = 9.6$ ps, to (b) $\tau = 49.6$ ps and to (c) $\tau = 275.2$ ps. The arrow is used to indicate the transportation of a specific O_2 molecule during the filling process. Parameter: $C_n = 0.5$

time, $0 \leq t \leq 80$ ns. Note $t = 80$ ns actually means the end of the total simulation time of 90 ns. Namely, the range of $0 \leq t \leq 80$ ns originates from the total simulation time of 90 ns by subtracting the initial 10 ns for equilibration. Owing to the results obtained from Figure 2, it is clear that the SWCNT is already filled with O_2 and CH_4 molecules for the whole range of $0 \leq t \leq 80$ ns. As Figure 3(a) shows, with increasing C_n, N_f of O_2 molecules is increased gradually, and N_f of CH_4 molecules is decreased gradually. In the mean time, N_f of O_2 and CH_4 is also decreased with increasing C_n, see Figure 3(b). As C_n increases up to a high value of 0.8, it is always faster for CH_4 molecules to transport across the SWCNT than O_2 molecules (Figure 3(a)). So, the transport of CH_4 molecules across the SWCNT is easier than O_2 molecules. If we calculate the total transportation ability, as shown in Figure 3(b), the total number of gas molecules transported per unit time across the SWCNT is decreased with increasing C_n, that is to say, if C_n increases, it is not helpful for increasing the total transport ability of nanochannel in the presence of O_2/CH_4 mixture.

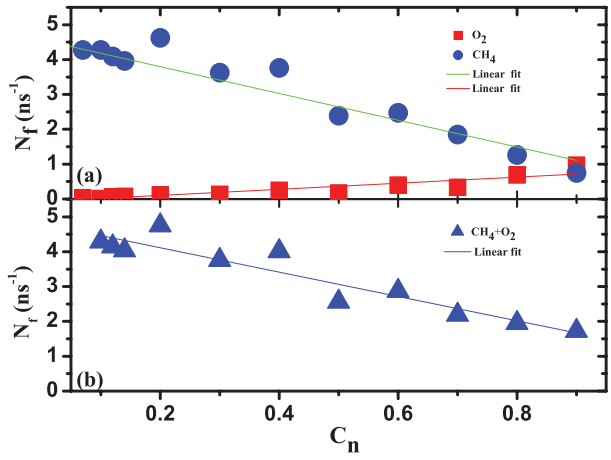

Figure 3. (a) The number of O_2 or CH_4 molecules, N_f, transporting across the SWCNT as a function of O_2 concentrations, C_n. (b) The total number of O_2 and CH_4 molecules, N_f, as a function of C_n. The three straight lines are a guide for the eye.

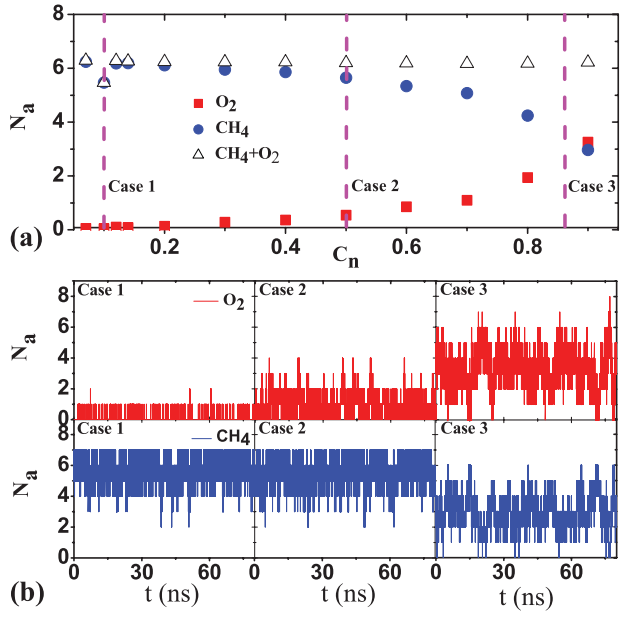

Figure 4. (a) The number of O_2 or CH_4 molecules, N_a, confined in the SWCNT as a function of C_n. The total number of O_2 and CH_4 is also shown. 'Case 1', 'Case 2' and 'Case 3' are indicative of three vertical lines corresponding to $C_n = 0.1$, $C_n = 0.5$ and $C_n = 0.9$, respectively. (b) N_a confined in the SWCNT as a function of simulation time for Case 1 ($C_n = 0.1$), Case 2 ($C_n = 0.5$) and Case 3 ($C_n = 0.9$), respectively.

Gas molecules can form a single file if the radius of the SWCNT is small enough.

In Figure 4(a), we display the average number of gas molecules confined in the SWCNT, N_a, according to

$$N_a = \sum_{i=1}^{n} N'_a(i)/n \qquad (2)$$

where $N'_a(i)$ is the gas number in the ith frame, and n is the total frames. The average total number of O_2 and CH_4 molecules in the SWCNT are independent of C_n, which is due to the fact that the size of an O_2 molecule is comparable to the size of a CH_4 molecule, and the molecules of the mixture form a single file in the SWCNT. However, the change of C_n can affect the proportion of O_2 and CH_4, see Figure 4(a). When C_n is less than 0.4, N_a of O_2 or CH_4 molecules does not obviously change. For $C_n > 0.4$, with increasing C_n, N_a of O_2 molecules is increased gradually, and N_a of CH_4 is decreased gradually. As C_n increases up to a high value of 0.8, comparing with O_2 molecules, CH_4 molecules are always dominant in the SWCNT. In Figure 4(b), we show the dynamics process of O_2 and CH_4 mixtures at three cases corresponding to $C_n = 0.1$, 0.5 and 0.9, respectively. When C_n equals 0.1, the number of O_2 molecules is very small, which approximately ranges from 0 to 1 in the simulation time. Meanwhile the number of CH_4 approximately ranges from 4 to 7. At $C_n = 0.5$, the number of O_2 approximately ranges from 0 to 2, the number of CH_4 molecules approximately ranges from 4 to 7. For $C_n = 0.9$, the number of O_2 molecules approximately ranges from 1 to 5, and the number of CH_4 molecules approximately ranges from 1 to 5 as well. Figure 4 indicates that CH_4 molecules generally dominate the interior of the SWCNT more easily than the O_2 molecules when $C_n \leq 0.8$.

Next, we need to understand the above results. Let us start by considering the van der Waals interactions between the gas molecules and the SWCNT.

We calculate the interaction potential, V_{LJ}, between gas molecules and all the carbon atoms along the axis of the SWCNT according to

$$V_{LJ} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]. \quad (3)$$

Here, ε_{ij} and σ_{ij} are the Lennard–Jones empirical parameters [32, 41] for the interaction between atom i and atom j with separation r_{ij}.

The calculation results are shown in Figure 5. We find that the van der Waals interaction between CH_4 molecules and the SWCNT are always stronger than that between O_2 molecules and the SWCNT. This explains the reason why CH_4 molecules can be transported and/or adsorbed in the SWCNT more easily. Due to thermal fluctuations, collisions between particles and the different van der Walls interactions between different gas molecules and SWCNT, the density fluctuations of O_2 or CH_4 molecules can appear on the two sides of the SWCNT. Owing to these density fluctuations, CH_4 and O_2 molecules can diffuse into the nanotube opening, overcome the barriers of nanotube, and then transport across the nanotube. Because gas molecules form a single file inside the SWCNT, the transportation of the molecules must be one by one. In the duration, CH_4 molecules can dominate in the SWCNT due to its stronger van der Waals interactions with the SWCNT. Thus, CH_4 molecules have more opportunities to be transported across the SWCNT.

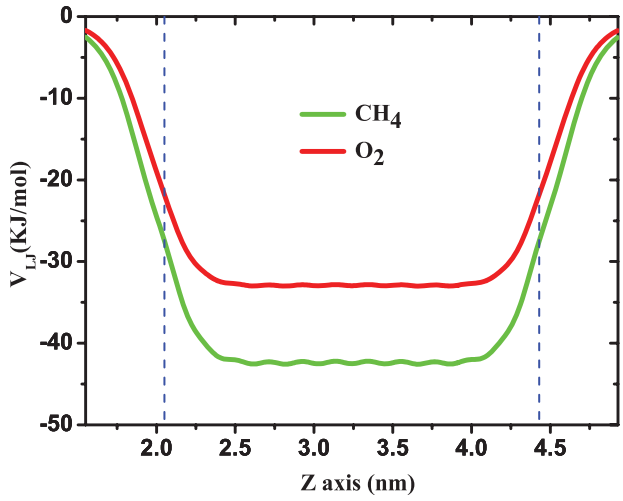

Figure 5. van dar Waals interaction between the SWCNT and O_2 or CH_4 molecules. The two vertical dashed lines indicate the positions of the two boundaries of the SWCNT aligned along Z axis as shown in Figure 1.

4. Conclusion

On the basis of molecular dynamics simulations, we find that the transport properties of O_2 and CH_4 molecules are distinctly different as the concentration of O_2 molecules, C_n, increases. As C_n increases up to a high value of 0.8, it is always faster for CH_4 molecules to be transported across the SWCNT, and the total number of gas molecules transported across the SWCNT is decreased. Meanwhile, CH_4 molecules are always dominant in the SWCNT, and the total number of O_2 or CH_4 inside the SWCNT is a constant. By calculating the van der Waals interaction between the SWCNT and O_2 or CH_4 molecules, we find that the net interaction between CH_4 and the SWCNT is much stronger. Owing to both density fluctuations and stronger van der Waals interactions with the SWCNT, CH_4 molecules have more opportunities to be transported across the SWCNT. Our findings may offer some hints on how to separate CH_4 from O_2, and/or store CH_4 efficiently.

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