Distinct transport properties of $\text{O}_2$ and $\text{CH}_4$ across a carbon nanotube

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Distinct transport properties of $\text{O}_2$ and $\text{CH}_4$ across a carbon nanotube

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It is of fundamental importance to investigate either $\text{O}_2$ or $\text{CH}_4$ 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, $\text{O}_2$ and $\text{CH}_4$ 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 $\text{O}_2$ and $\text{CH}_4$, 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 $\text{O}_2$ increases up to a high value of 0.8, it is always faster for $\text{CH}_4$ molecules to transport across the SWCNT, and the total number of gas molecules transporting across the SWCNT is decreased. Meanwhile, $\text{CH}_4$ molecules are always dominant in the SWCNT, and the total number of $\text{O}_2$ or $\text{CH}_4$ inside the SWCNT is a constant. By calculating the van der Waals interaction between the SWCNT and $\text{O}_2$ or $\text{CH}_4$, we find that the net interaction between $\text{CH}_4$ and the SWCNT is much stronger. Our findings may offer some hints on how to separate $\text{CH}_4$ from $\text{O}_2$, and/or store $\text{CH}_4$ efficiently.

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

1. Introduction

It is of fundamental importance to investigate either oxygen ($\text{O}_2$) or methane ($\text{CH}_4$) molecules across nanochannels. For instance, in the study of breathing, the investigation of the transportation of $\text{O}_2$ in or out of lung is important for understanding the human metabolic system [1, 2]. And the investigation of the transportation of $\text{CH}_4$ molecules out of porus media is important for extracting $\text{CH}_4$ from natural gas hydrate [3–5]. Therefore, many researches have focused on such a single type of molecules across nanochannels [6–8]. However, $\text{O}_2$ and $\text{CH}_4$ can often appear together and crucially affect human life or plants [9–12]. For example, $\text{O}_2$ and $\text{CH}_4$ in a mine can threaten miners’ lives [11, 12]. In such a case, it is of particular importance to separate $\text{CH}_4$ from $\text{O}_2$, and/or store $\text{CH}_4$ efficiently. For the purpose of separation, a membrane with nanochannels is a candidate, which only allows $\text{CH}_4$ to transport. Accordingly, one must investigate the transport properties of $\text{CH}_4$/$\text{O}_2$ 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 Sinnott [6] used classical molecular dynamics simulations to investigate equilibrium and non-equilibrium transportation of $\text{O}_2$ molecules in a SWCNT and found that $\text{O}_2$ 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 $\text{CH}_4$ molecules across a SWCNT in the presence of water ($\text{H}_2\text{O}$), and they found that $\text{CH}_4$ molecules entered the SWCNT prior to $\text{H}_2\text{O}$ 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 $\text{CH}_4$ molecules pulled the water molecules from the inner of the SWCNT along the axial direction of the SWCNT, and that the transport velocity of $\text{H}_2\text{O}$ molecules could be affected by the number of $\text{CH}_4$ 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
parameters of carbon nanotube come from Hummer et al. [32]. The SWCNT and graphite sheets are in a box (4.652 nm × 4.646 nm × 6.480 nm) with the total 200 molecules of both O₂ and CH₄ molecules. For the O₂/CH₄ mixture, the concentration of O₂ molecules, Cₙ (which equals to the ratio between the number of O₂ molecules and the total number of both O₂ and CH₄ molecules), are equal in both sides. In the simulations, Cₙ ranges from 0.07 to 0.9. The parameters of O₂ and CH₄ molecules come from Gaurav and Stanley [36] and Borja and Román [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 CH₄ 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 CH₄ or O₂ molecules. The initially empty SWCNT is rapidly full of CH₄ or O₂ molecules during the simulations, which can be seen from Figure 2. Figure 2 shows a filling process as time $\tau$ elapses. In Figure 2, the arrow-marked O₂ 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 O₂ molecule, two other O₂ molecules and one CH₄ 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 O₂ 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

$$N_f = N'(t)/t,$$

where $N'(t)$ is the total number of gas molecules transported across the SWCNT, and $t$ is the total effective simulation.
time, 0 ≤ t ≤ 80 ns. Note t = 80 ns actually means the end of the total simulation time of 90 ns. Namely, the range of 0 ≤ t ≤ 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 O₂ and CH₄ molecules for the whole range of 0 ≤ t ≤ 80 ns. As Figure 3(a) shows, with increasing Cₙ, Nₐ of O₂ molecules is increased gradually, and Nₐ of CH₄ molecules is decreased gradually. In the mean time, Nₐ of O₂ and CH₄ is also decreased with increasing Cₙ, see Figure 3(b). As Cₙ increases up to a high value of 0.8, it is always faster for CH₄ molecules to transport across the SWCNT than O₂ molecules (Figure 3(a)). So, the transport of CH₄ molecules across the SWCNT is easier than O₂ 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 Cₙ, that is to say, if Cₙ increases, it is not helpful for increasing the total transport ability of nanochannel in the presence of O₂/CH₄ mixture.

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, Nₐ, according to

\[ Nₐ = \sum_{i=1}^{n} N′ₐ(i)/n \]  

(2)
where \( N'_n(i) \) is the gas number in the \( i \)th 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, \( N_o \) of \( O_2 \) or \( CH_4 \) molecules does not obviously change. For \( C_n > 0.4 \), with increasing \( C_n \), \( N_o \) of \( O_2 \) molecules is increased gradually, and \( N_o \) 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 \( C_n ≤ 0.8 \).

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

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

Here, \( \varepsilon_{ij} \) and \( \sigma_{ij} \) 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.

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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