Gases of driving methane out of a carbon nanotube

Xianwen Meng and Ling Shen

School of Materials and Physics, China University of Mining and Technology, Xuzhou 221116, People’s Republic of China

E-mail: xwmeng@cumt.edu.com

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Abstract

Methane is a kind of clean energy resource. Driving methane molecules out of a nanochannel efficiently is helpful to increase mining efficiency. Injecting other gas molecules is an ideal method to increase methane production. By molecular dynamics simulation, we take the adsorption behaviors of methane (CH₄) and nitrogen (N₂) mixture in a carbon nanotube for example. Compared with nitrogen (N₂), methane (CH₄) obtains an advantage on adsorption in a carbon nanotube when methane concentration changes from 0.1 to 0.9. By changing the parameters of ε and σ, we find two parameters can regulate the adsorption behaviors of methane in a carbon nanotube. The probability of driving CH₄ molecules out of a carbon nanotube increases with increasing the parameter of ε at the same σ, while the probability of driving CH₄ out of a carbon nanotube increases at first and then decreases with increasing σ at the same ε. We expect the results could guide the process of methane production efficiently in a physical view.

1. Introduction

Along with the increasing demand of the energy all over the world, there is a large gap between the supply of conventional natural gas resources and the increasing energy demand. Exploring the unconventional gas is a promising method to alleviate the serious energy crisis [1]. With the properties of wide distribution, large quantity and low pollution, shale gas as one kind of unconventional energy resource attracts more and more attention in recent years [2–8]. Most of shale gas adsorbs on the wall of pores in shale [9], especially pores at nanoscale [10–12]. Shale gas exists in three forms: as free gas in cracks, as free gas in matric pores, and as adsorption gas. A large proportion of shale gas is in adsorption form. However, shale gas is difficult to desorb from the shale, which hinders the production of shale gas efficiently. The main component of shale gas is methane (CH₄). As a result, it is essential to investigate the adsorption behaviors of methane molecules in a nanoconfined system.

A carbon nanotube offers an ideal nanoconfined environment. The dynamic properties of gas mixtures in a carbon nanotube may give some clues on methane production [13–15]. For example, Joonho Lee and N. R. Aluru investigated equilibrium transport of gas-water mixtures in carbon nanotubes, such as CO₂-water, O₂-water and H₂-water mixtures. They found 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 [13]. Due to excellent mechanical, electrical and chemical properties, carbon nanotubes have attracted much attention. It is also connected with gas separation, purification, the development of storage media for natural gas and the behavior of methane in underground reservoirs [16–19].

In recent years, adsorption of CH₄ in porous materials have been studied experimentally and theoretically [20–27]. Yi obtained the adsorption equilibrium isotherms of CO₂, CH₄ on microwave activated carbon [28]. Their results indicate that CO₂ dominates the adsorption system in the mixtures. Malek and Sahimi examined the adsorption and diffusion of different gas types in Si-carbon nanotubes as a function of the pressure and the type of the carbon nanotubes [29]. Their results demonstrated that at ambient temperature (300K) and high pressure (10–1000 bar), the gas adsorption is obviously in the order of CO₂ > CH₄ [29]. Among these investigations, much more attention than ever before have been paid to gas competitive adsorption. It is
reported that coal seams can adsorb more CO$_2$ than CH$_4$ and, under competitive sorption scenario, CO$_2$ is preferentially adsorbed in the coal structure over CH$_4$ \[30\]. Although there are a lot of research on this subject, it is still a challenge to find a correct candidate, which can drive CH$_4$ efficiently out of a nanochannel. Due to N$_2$ accounts for the largest volume proportion (about 78\%) in the air, we take N$_2$ and CH$_4$ mixture for example to simplify the processes of finding the proper candidate, and then change the type of gas molecule mixtures.

2. Methodology and and simulation details

We display the partial framework in figure 1, which contains two parallel graphite sheets with a carbon nanotube. The diameter and the length of the (10, 0) carbon nanotube is 0.772 nm and 2.380 nm. It should be noted that the diameter of the carbon nanotube is small enough that it only allows gas molecules form a single file in the interior. The Lennard-Jones (LJ) potential parameters of carbon atoms come from \[31\]. The system is solvated with 200 gas molecules. The framework is kept at its original place in the simulations.

We perform molecular dynamics simulations with Gromacs 4.0.5 \[32\], and adopt the thermostat of Nosé and Hoover \[33, 34\] with a time constant of 0.5 ps. All simulations are carried out under the NVT ensemble (constant number of molecules, constant volume, and constant temperature). Periodic boundary conditions are applied to all three directions of the simulation box. The initial atomic velocities are generated by a Maxwellian distribution at the temperature of 300 K. The timestep is set to 2 fs, and the total simulation time is 90 ns (the first 20 ns is used for equilibration and the remaining 70 ns are used for statistics). In order to save simulation time, the cut-off distance for LJ forces is set to 1.4 nm.

3. Results and discussion

First, we test the adsorption behaviors of N$_2$ and CH$_4$ mixtures in the carbon nanotube. When the concentration of N$_2$ and CH$_4$ is 1:1, we adopt a coarse-grained model and an all-atom model respectively \[35–37\]. Figure 1(a) shows the adsorption behaviors of N$_2$ and CH$_4$ mixtures when the concentration of N$_2$ and CH$_4$ is 1:1 by an all-atom model. CH$_4$ molecules form a single file in the interior of the carbon nanotube while we do not find a chain of N$_2$ molecules. It is clearly that CH$_4$ molecules are prior to entering into the carbon nanotube compared with N$_2$ molecules. If we change the gas model from an all-atom model to a coarse-grained model, it is unclear whether the adsorption behaviors of N$_2$ and CH$_4$ changes. As a contrast, figure 1(b) shows the adsorption behaviors of N$_2$ and CH$_4$ mixtures when the concentration of N$_2$ and CH$_4$ is 1:1 by a coarse-grained model. Similarly, we observe a CH$_4$ chain in the same carbon nanotube. It also indicates that CH$_4$ molecules enters into the carbon nanotube selectively and preferably compared with N$_2$ molecules. From this view, the adsorption behaviors of CH$_4$ and N$_2$ mixtures display similar results by using an all-atom model and a coarse-grained model.

Now that, CH$_4$ molecules are the dominant gas molecules in the carbon nanotube compared with N$_2$ molecules in the CH$_4$ and N$_2$ mixtures when the concentration of N$_2$ and CH$_4$ is 1:1. With the purpose of

\[Image 216x578 to 456x770\]
investigating CH₄ concentration on gas adsorption in the interior of the carbon nanotube. CH₄ concentration is defined as C and changed from 0.1 to 0.9. Figure 2 shows the average number of CH₄ and N₂ in the interior of the carbon nanotube. The average number of CH₄ gas molecules increases with increasing C. As a contrast, the average number of N₂ gas molecules decreases gradually with increasing C. It is worth mentioning that CH₄ molecules play the dominant role in the interior of the carbon nanotube. The average number of CH₄ molecules is larger than the average number of N₂ molecules in the interior of the carbon nanotube even at C = 0.1. For example, the average number of CH₄ in the interior of the carbon nanotube is 3.311, while the average number of N₂ in the same interior of the carbon nanotube is 2.743 when CH₄ concentration is 0.1. The average number of CH₄ molecules in the interior of the carbon nanotube increases to 5.356 molecules, while the average number of N₂ in the interior of the carbon nanotube decreases to 0.605 3 molecules when CH₄ concentration is changed to 0.5. It should be noted that the average number of CH₄ molecules in the interior of the carbon nanotube increases to 5.927 5 molecules while the average number of N₂ molecules in the interior of the carbon nanotube decreases to 0.056 3 molecules when CH₄ concentration is 0.9. CH₄ molecules form a single-file in the interior of the carbon nanotube under this condition.

Next, we need to understand the above results. Let us start by considering the Van der Waals interactions between the gas molecules and the carbon nanotube. We calculate the interaction potential, $V_{LJ}$, between gas molecules and all the carbon atoms along the axis of the carbon nanotube 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 [37] for the interaction between atom i and atom j with separation $r_{ij}$. The calculation results are shown in Figure 3. We find that the Van der Waals interaction between CH₄ molecules and the carbon nanotube are always stronger than that between N₂ molecules and the carbon nanotube. This explains the reason why CH₄ molecules can be adsorbed in the carbon nanotube more easily. Due to thermal fluctuations, collisions between particles and the different Van der Walls interactions between different gas molecules and the carbon nanotube, the density fluctuations of N₂ or CH₄ molecules can appear on the two sides of the carbon nanotube. Owing to these density fluctuations, CH₄ and N₂ 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 carbon nanotube, in the duration, CH₄ molecules can dominate in the carbon nanotube due to its stronger van der Waals interactions with the carbon nanotube. Thus, CH₄ molecules have more opportunities to be adsorbed in the carbon nanotube.

Now that, N₂ can not drive CH₄ molecules out of a carbon nanotube efficiently. Other types of gas molecules should be investigated systematically. In order to find a kind of gas molecule, which can drive CH₄ out of a carbon nanotube efficiently, one should investigate Lennard-Jones empirical parameters of gas molecules on the adsorption behavior of CH₄. We change the parameters $\varepsilon_{ij}$ and $\sigma_{ij}$ in the simulations. $\varepsilon_{ij}$ is changed from 0.760 7 KJ mol⁻¹ to 2.760 7 KJ mol⁻¹, while $\sigma_{ij}$ is changed from 0.245 4nm to 0.445 4nm. By simulations, we find that the parameters of $\varepsilon_{ij}$ and $\sigma_{ij}$ could regulate CH₄ occupation behaviors in the carbon nanotube. By calculating CH₄ occupation ratio in the carbon nanotube, we calculate the probability of driving CH₄ out of the carbon nanotube.
carbon nanotube. We find that there is a special area, which could drive CH$_4$ molecules out of the carbon nanotube efficiently. In other words, CH$_4$ molecules are not easily attracted in the carbon nanotube in the special area, other type of gas molecules form a single chain in the carbon nanotube. Generally, the probability of driving CH$_4$ molecules out of a carbon nanotube increases with increasing the parameter of $\varepsilon_{ij}$ at the same $\sigma_{ij}$. However, the parameter of $\sigma_{ij}$ has a different effect on the probability of driving CH$_4$ out of a carbon nanotube. As figure 4 shows, the probability of driving CH$_4$ out of a carbon nanotube increases at first and then decreases with increasing $\sigma_{ij}$ at the same $\varepsilon_{ij}$. At low $\varepsilon_{ij}$, gas molecules can not be used as a good candidate for driving CH$_4$ molecules. Because, the probability of driving CH$_4$ molecules out of a carbon nanotube below 0.5. With increasing $\varepsilon_{ij}$, the range of good candidates for driving CH$_4$ becomes wider. With increasing $\varepsilon_{ij}$, the probability of driving CH$_4$ molecules out of a carbon nanotube begin to reach and exceed 0.5. So, the candidate drives CH$_4$ molecules out of a carbon nanotube efficiently. From figure 4, we can judge gas molecules whether drive CH$_4$ molecules out of a nanochannel or not. We take CO$_2$ for example, the parameters of CO$_2$ are $\sigma = 0.375$ nm and $\varepsilon = 1.962$ KJ mol$^{-1}$ [38]. The probability of driving CH$_4$ out of a nanochannel by CO$_2$ gas molecules is in the red area of figure 4. The result is compatible with the adsorption order CO$_2$ > CH$_4$ in a carbon nanotube. Another example is the case of N$_2$ and CH$_4$ gas mixture in a carbon nanotube. The parameters of N$_2$ are $\sigma = 0.356$ 2nm and $\varepsilon = 0.833$ 2 KJ mol$^{-1}$ [37]. The probability of driving CH$_4$ out of a nanochannel by N$_2$ gas molecules is in the blue area of figure 4. The result is in accordance with the result obtained in figure 2.
4. Conclusion

Summarizing, by molecular dynamics, we take N₂ and CH₄ mixtures in a carbon nanotube for example, we find the adsorption order in the carbon nanotube is CO₂ > CH₄ > N₂. The Van der Waals interaction between gas molecules and the carbon nanotube play important roles in regulating gas adsorption behaviors in the carbon nanotube. By changing ε and σ, we find the probability of driving CH₄ molecules out of the carbon nanotube increases with increasing the parameter of ε at the same σ, while the probability of driving CH₄ out of the carbon nanotube increases at first and then decreases with increasing σ at the same ε.

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ORCID iDs

Xianwen Meng https://orcid.org/0000-0001-9503-071X

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