Molecular dynamics simulations of CH$_4$ diffusion in kaolinite: influence of water content

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Abstract Understanding the interaction of CH$_4$ with kaolinite is significant for researchers in the fields of coalbed CH$_4$ and shale gas. The diffusion behaviors of CH$_4$ in kaolinite with water contents ranging from 0 to 5 wt% have been analyzed by molecular dynamics simulations. The results of the simulations indicate that CH$_4$ molecules can jump between adjacent holes in the kaolinite matrix. CH$_4$ diffusion coefficient was very low (3.28×10^{-9} m^2/s) and increased linearly with the increasing of water content. As the water content decreased, the value of radial distribution function first peak between CH$_4$ and oxygen was larger, meaning that with lower water content, the interaction energy between CH$_4$ and oxygen in kaolinite is stronger. The interaction between CH$_4$ and water is linearly positively correlated with water content, in contrast, the interaction energy between kaolinite and water as well as between kaolinite and CH$_4$ decreased linearly with increasing water content. On the other hand, the diffusion of CH$_4$ molecules adsorbed on the surfaces also can be accelerated by the fast diffusion of water molecules in the middle micropore of the kaolinite.

Keywords Molecular dynamics · Kaolinite · Water content · Diffusion · Interaction energy

1 Introduction

As the important cements and inorganic components of shale and coal seams, clay minerals interacting with CH$_4$ have been one of the research hotspots in the energy field (Zhang et al. 2014; Zhao et al. 2016). Kaolinite is the most common clay mineral with large specific surface area and complex pore structure (from micropore to mesopore), which makes kaolinite have strong adsorption capacity

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(Murray 1999) and. The composition of kaolinite is Si$_4$Al$_4$O$_{10}$(OH)$_8$ and it consists of 1:1 dioctahedral layers which is composed of a sheet of corner-sharing SiO$_4$ tetrahedra and a sheet of edge-sharing AlO$_6$ octahedra linked by common oxygen atoms parallel to the (001) sheet (Warne et al. 2000). Hence, it is necessary and important to be able to understand the interaction mechanism between CH$_4$ and kaolinite for the researchers in the fields of shale gas and coal bed methane.

Shale and coal seams are generally rich in water, making the surface of clay minerals easily occupied by water molecules (Zhang 2005; Jenkins and Charles Boyer 2008). Some molecular simulations have been implemented to study the effect of water content on CH$_4$ adsorption on kaolinite in the past few years. Zhang et al. utilized the molecule simulations to research the effect of water content on CH$_4$ adsorption on kaolinite. It is illustrated that the water has a side effect on the CH$_4$ adsorption capacity and the adsorption rate of kaolinite. The oxygen atom in kaolinite is the preferential adsorption site for water molecules and CH$_4$ molecules, while the hydrogen atom is

only the preferential adsorption site for water molecules. Xiong et al. utilized GCMC simulations to research the influence of water on CH4 sorption in kaolinite. The results reflected the CH$_4$ and water molecules competed in the kaolinite pores, and the water molecules preferentially occupied the low-energy adsorption sites, which reduced the adsorption space and adsorption sites of the CH$_4$ molecules. However, these research outcome focusing on the effect of water content on adsorption behavior of CH$_4$ in kaolinite paid little attention to the transport aspect of the effect of water content, for example, the influence of water content on diffusion of CH$_4$ in kaolinite.

Diffusion is a very important phase in unconventional natural gas extraction, reflecting the speed of CH$_4$ migration from micropores to fractures (Hu et al. 2017). This process is much slower than permeation flow, occurring in natural and artificial cracks in coal seams and shale, and is regarded as an intermediate process for CH$_4$ production. So the molecular dynamics (MD) method was utilized to study the CH$_4$ diffusion in kaolinite with pre-absorbed water contents of 0–5 wt% simulated at 293.15 K and 5 MPa in our paper. However, this paper mainly focuses on the water content on methane diffusion in kaolinite. Therefore, there are still many other basic parameters including pore size, pressure, temperature, etc., which also can influences the methane diffusion in kaolinite and need further research. We hope that this study can quantitatively analyze the diffusion properties of kaolinite and lay the foundation for further research on the storage and exploration of CH$_4$ and shale gas reservoirs.

2 Molecular dynamics simulation details

2.1 Models

To study the kaolinite–water–CH$_4$ systems, the initial state of all models used here are the final output of Monte-Carlo simulations computed in our preceding work (Zhang et al. 2018a) in which the temperature was fixed at 293.15 K and pore size was 0.72 nm. The number of water molecules was 0, 9, 18, 27, 36, and 45, corresponding to the water contents of 0, 1, 2, 3, 4, and 5 wt%, respectively. Then, in order to reach the equilibrium state, these configurations were implemented geometry optimization by 1 ns NVT and 1 ns NPT run (Hu et al. 2017). For the purpose of clarity, only the structure of kaolinite–H$_2$O–CH$_4$ system with different water content was shown in Fig. 1.

2.2 Implementation of simulation

The Dreiding force field (Mayo et al. 1990; Fafard et al. 2017; Zhou et al. 2017) was selected in all simulations and

can be utilized to study the physical and diffusion properties of kaolinite structures which has been confirmed in our previous works (Zhang et al. 2018a, b). The electrostatic and van der Waals interactions between CH$_4$ and kaolinite were simulated by Ewald method with a cut-off value of 0.8 nm (Rutkai and Kristóf 2008). CH$_4$ diffusions were computed as follows: the initial state of all models used here are the final output of Monte-Carlo simulations to obtain new kaolinite–H$_2$O–CH$_4$ systems. Then, these systems were run in 1 ns NPT and 1 ns NVT ensemble for minimized to relaxation. At last, 5 ns NVT MD simulations were implemented to obtain the displacement, CH$_4$ self-diffusivity, interaction energy, and radial distribution functions (RDF). Water contents were varied to investigate its effects on CH$_4$ diffusion. The Andersen barostat (Fernández-Pendás et al. 2014) and Berendsen thermostat (Evans and Holian 1985) were utilized to control the pressures and temperatures. And we used the Accelrys Material Studio software (X. Accelrys & Software Inc) to implement all the MD simulations.

3 Results and discussion

3.1 Diffusion trajectories

Molecular simulations can direct obtain the trajectories of gas molecules through the porous matrix with different water contents (Hu et al. 2010; Zhang and Yan 2011). These trajectories should be able to provide a mechanistic picture of the diffusive process which cannot be directly obtained through experimentation (Hu et al. 2017). The displacements of CH$_4$ and H$_2$O molecule according to the motion behaviour, $|r(t) - r(0)|$ was illustrated in Fig. 2. For the sake of clarity, only the system for the CH$_4$-saturated kaolinite with 4% water is displayed. Figure 3 displayed the simulated motion of a CH$_4$ molecule and a water molecule in kaolinite. From Figs. 2 and 3, it was seen that CH$_4$ and H$_2$O molecule have highly irregular movements. Small displacement oscillations occurring between 200 ps and 500 ps represent that the CH$_4$ and H$_2$O molecule motions were limited in a single hole which represents a single silicone tetrahedral ring or aluminum oxide octahedral ring. On the other hand, large displacement oscillation illustrated that gas jump from one hole to another. In all water contents systems, the hopping mechanism is the underlying process of the diffusion, which is to some extent similar to the diffusion mechanism in other porous media systems (Schaefer et al. 1997).

Figure 4a–f revealed that the pathway of a CH$_4$ molecule through the kaolinite matrix with different water contents. Diffusion is not just a limited fluctuation in a single pore, which is unreasonable, and Einstein diffusion
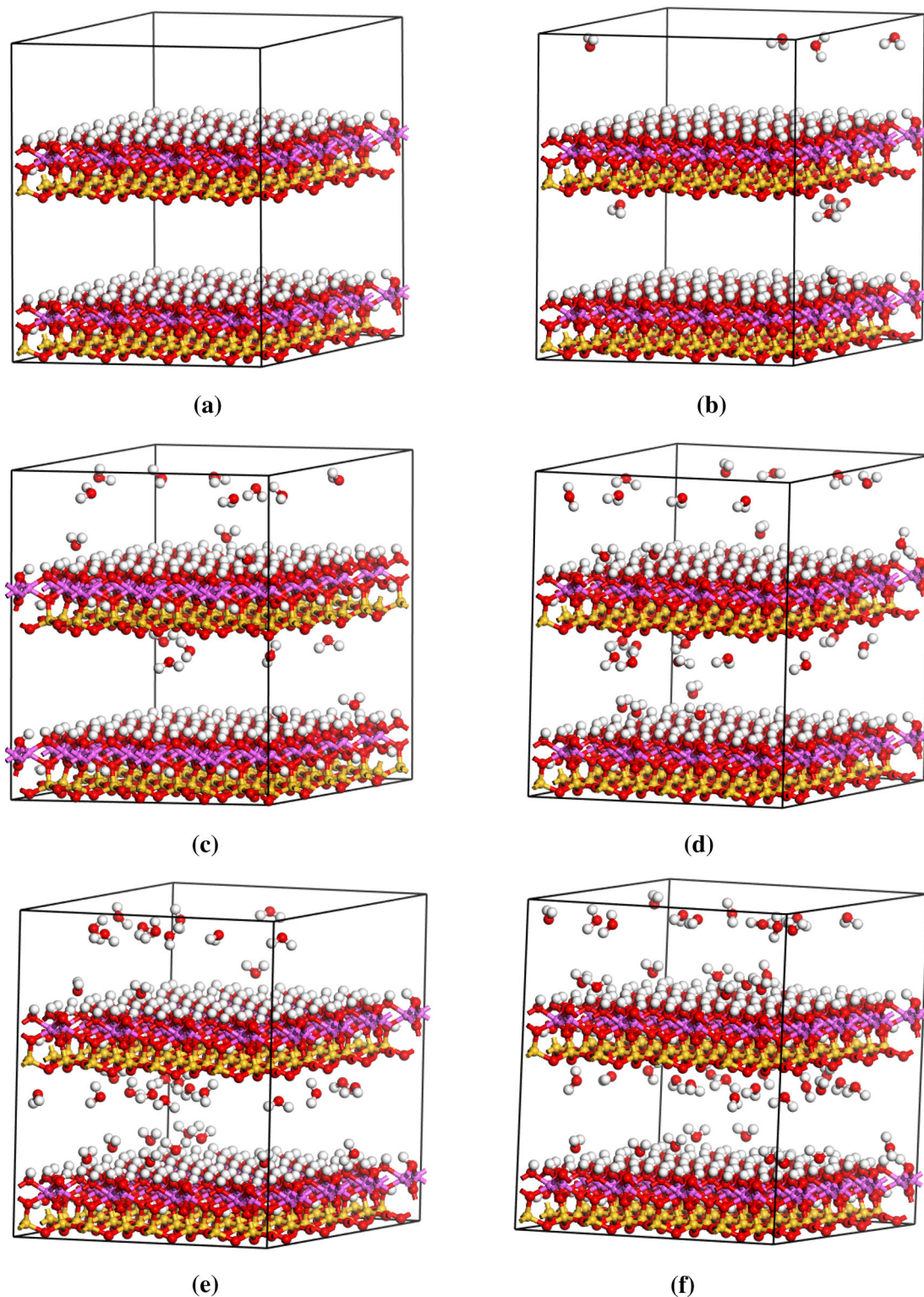
Fig. 1 Equilibrium configuration snapshot of kaolinite–H_2O–CH_4 system with **a** 0%, **b** 1%, **c** 2%, **d** 3%, **e** 4%, and **f** 5% water contents

can reflect the frequent jumps of gas between different pores (Hu et al. 2017). In this case, many phenomena of jumps between different pores were found, indicating that CH_4 mainly act as the Einstein diffusion in kaolinite during the simulation. From Fig. 4c–e, the jumps of CH_4 between two adjacent holes are also clearly obtained. The simulation results reflected that the jumps of CH_4 between two
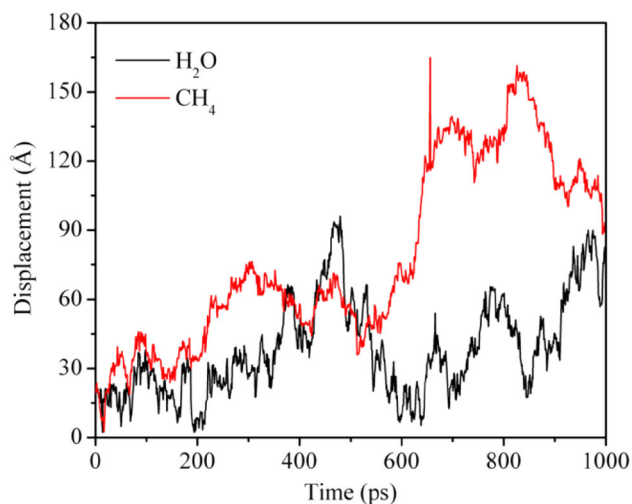
Fig. 2 Displacement of the CH$_4$ and H$_2$O molecule for moist kaolinite with 4 wt% water at 293.15 K
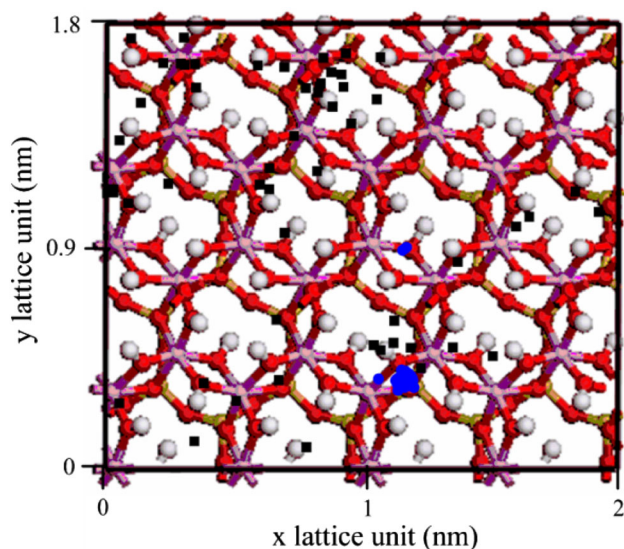

Fig. 3 Simulated motion of a CH$_4$ molecule and a water molecule in kaolinite. Color scheme: CH$_4$, black; water, blue

adjacent pores became more frequent with the increase of water content.

3.2 Self-diffusion coefficient

At present, the self-diffusion coefficient D_s (m^2/s) is mainly determined by microscopic techniques, which can describe the motion of a single labeled particle. (Jobic and Theodorou 2007). The self-diffusion coefficient is usually obtained by calculating the mean squared displacement (MSD) of each molecule over time. The MSD of a single molecule is calculated by Einstein's law of diffusion (Einstein 1905)

$$D_S = \frac{1}{6N} \lim_{t \to \infty} \frac{d}{d_t} \left\langle \sum_{t=1}^{N} [r_i(t) - r_i(0)]^2 \right\rangle \quad (1)$$

The influence of water on CH$_4$ diffusion coefficients at 293.15 K and 5 MPa are displayed in Fig. 5. It was shown that the CH$_4$ diffusion coefficient was very low (3.28×10^{-9} m^2/s) and increased linearly at $D_{CH4} = 1.6395$ wt $+ 3.5362$ with the increasing of water content, reflecting that water can increase the diffusion capacity of CH$_4$ in kaolinite. The reason is that when the water molecules move, the CH$_4$ molecules will be carried along with them and this is conducive to the CH$_4$ diffusion in kaolinite. The similar phenomenon was also found in the micro-pores of other porous media (Zhang and Yan 2011).

3.3 Transport diffusion coefficient

In addition, the transport or Fickian diffusion coefficient D_t (m^2/s) is more important in practical applications. Thus, the CH$_4$ transport diffusion coefficient D_t (m^2/s) in kaolinite was also calculated by the Maxwell–Stefan diffusion model (Kärger et al. 2014)

$$D_t = D_s \left(\frac{\partial \ln f}{\partial \ln c} \right) \quad (2)$$

where f is the bulk gas fugacity, C is the sorption concentration, and $\frac{\partial \ln f}{\partial \ln c}$ is the thermodynamic factor.

Figure 6a showed the curve of lnf (logarithm of the fugacity), which was obtained based on the Peng–Robinson equation of state (Zhang et al. 2018a) versus lnC (logarithm of the sorption concentration) calculated according to the study of Zhang et al. (Zhang et al. 2018a, b). In Eq. (2), the thermodynamic factors were defined as the slope of Fig. 6a. The results reflected that the thermodynamic factors with different water content and pressure are positively correlated. Additionally, the thermodynamic factors increase with an increase in the water content. Thus, this provides a foundation to study the conversion between transport diffusivities and self-diffusivities.

The transport diffusivity D_t can be calculated according to Eq. (2) and the self-diffusivity D_S. Figure 7 showed that the CH$_4$ transport diffusion coefficient on kaolinite as a function of the water content at 293.15 K and 5 MPa. It can be seen that the water content can significantly influence the CH$_4$ transport diffusion coefficient. The CH$_4$ transport diffusion coefficient also increased lineally with the water content. The CH$_4$ transport diffusion coefficient increased by approximately 1.67×10^{-9} m^2/s (30%), 8.20×10^{-9} m^2/s (150%), 10.39×10^{-9} m^2/s (190%), 11.21×10^{-9} m^2/s (204%) and 14.34×10^{-9} m^2/s (262%) for water content of 1, 2, 3, 4, and 5 wt%, respectively, when compared to the dry kaolinite.
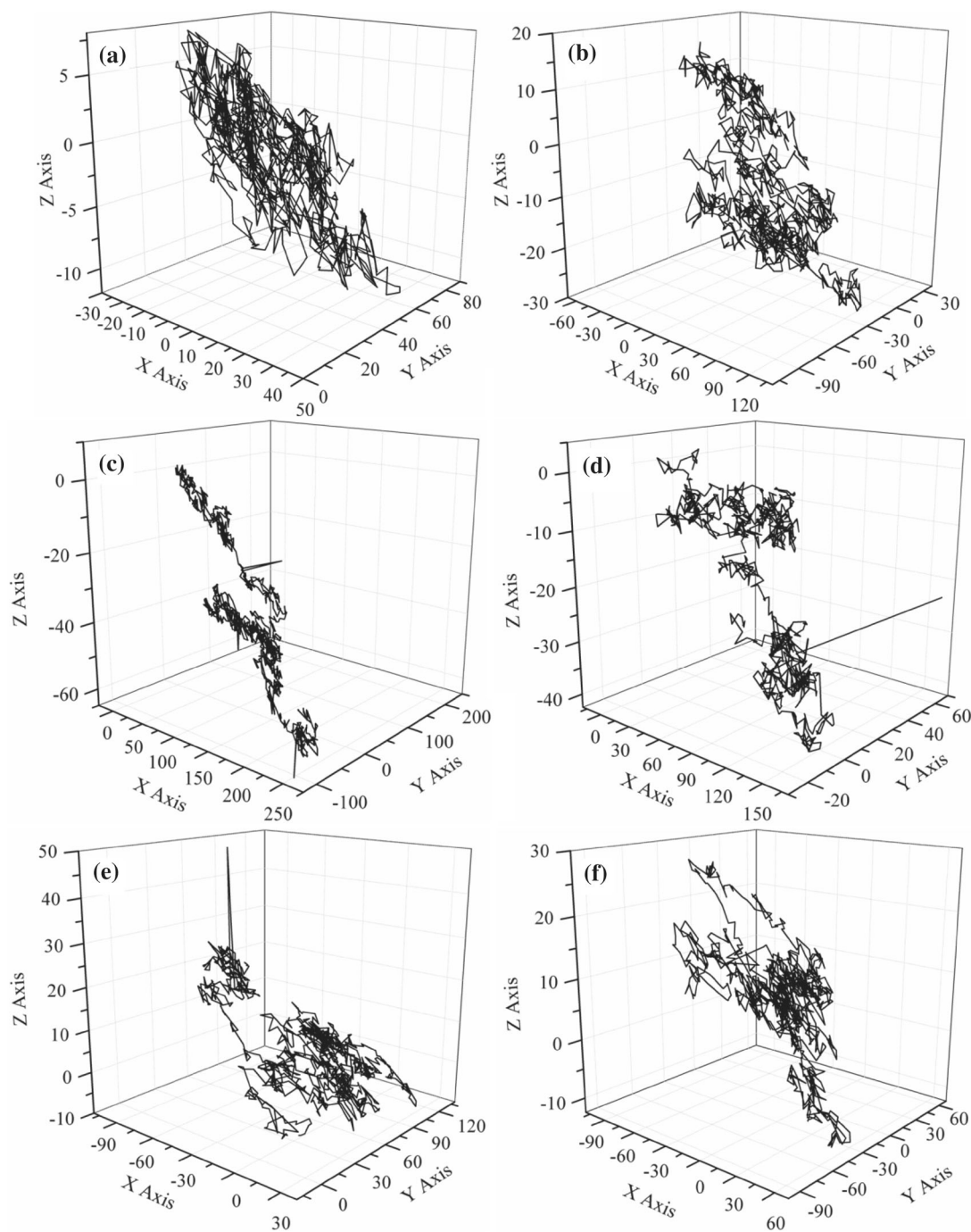
Fig. 4 Diffusion pathway of a CH_4 molecule in kaolinite matrix with **a** 0%, **b** 1%, **c** 2%, **d** 3%, **e** 4%, and **f** 5% water contents during a time period of 1000 ps

3.4 Radial distribution function

To reflect the influence of water on strength of the intermolecular interaction force between the CH_4 molecules and kaolinite, the radial distribution function, $g(r)$, was implemented that can measure the law of the change of atomic density and the distance of a specific atom (Kong and Wang 2016).

The RDFs of CH_4–oxygen at different water contents for kaolinite were shown in Fig. 8. The results showed that the intermolecular $g(r)$ had a peak around 4.5 Å indicating van der waals interaction (Donley et al. 1998) between the CH_4 molecule and the oxygen atom in the surface of the silicon tetrahedron of the kaolinite molecule. As the water content decreases, the value of RDF first peak between CH_4 and oxygen is larger, indicating that with lower water content,
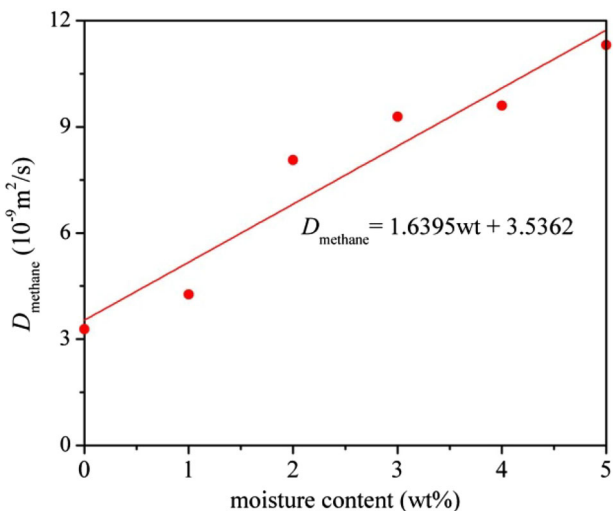
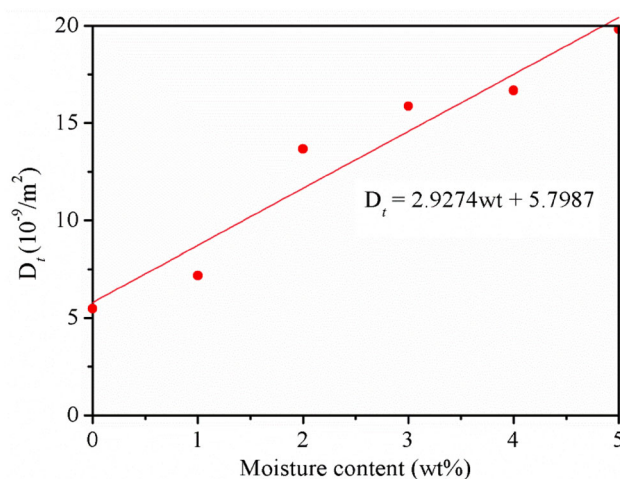**Fig. 5** The CH$_4$ self-diffusion coefficients as a function of water content

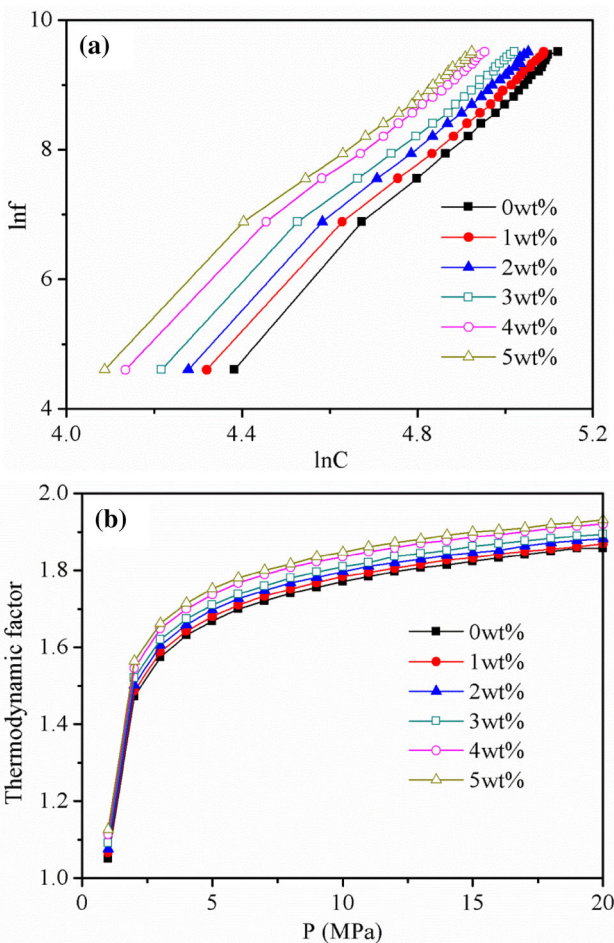**Fig. 7** The CH$_4$ transport diffusion coefficients as a function of water content

Fig. 6 a lnf versus lnC; **b** thermodynamic factor with different water content against pressure
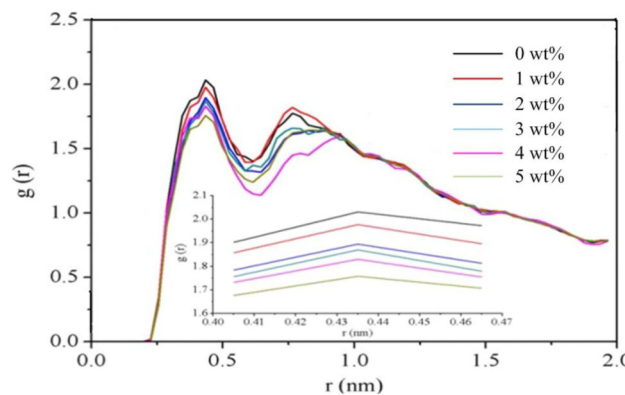

Fig. 8 Radial distribution functions (RDFs) between CH$_4$ and oxygen atoms in kaolinite in dry and moist kaolinite at 293.15 K and 5 MPa

the study of Kong et al., the first peak radial of distribution function (RDF) the larger, the stronger the interaction. In addition, the CH$_4$ can be adsorbed onto the sites of the oxygen atoms of kaolinite. However, the interaction between CH$_4$ and hydroxyl hydrogen atoms of kaolinite is barely detected, showing an extremely weak interaction between CH$_4$ and hydrogen. This should in turn lead to affect the structure and mobility of kaolinite molecules.

3.5 Interaction energy

The effect of pre-adsorbed water on diffusion capacity can be further analyzed by calculating the interaction between kaolinite, H$_2$O and CH$_4$. The calculation of the interaction energy has been shown in detail in our previous work (Zhang et al. 2018a, b).The interaction energy between the CH$_4$ and kaolinite, between the CH$_4$ and water, between the CH$_4$ and CH$_4$, and between the kaolinite and water were analyzed at 293.15 K and 5 MPa, as shown in Fig. 9.

the interaction energy between CH$_4$ and oxygen in kaolinite is stronger. This is due to fact that according to
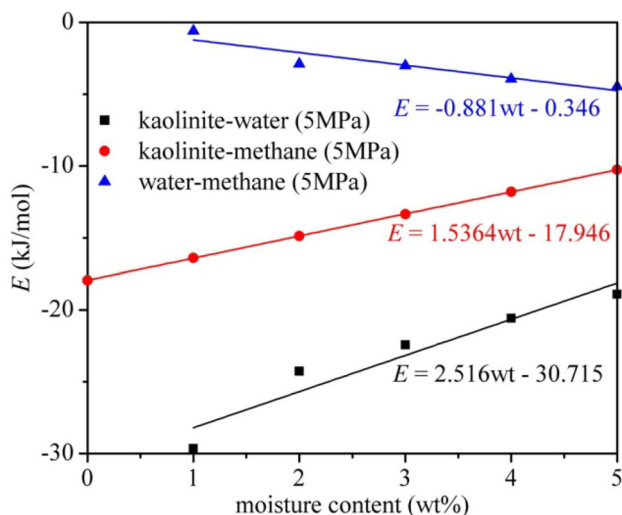
Fig. 9 Interaction energy of CH₄–kaolinite, water–kaolinite, CH₄–water, and CH₄–CH₄ for moist kaolinite with 3 wt% water at 293.15 K and 5 MPa

For the sake of clarity, only the results for the CH₄-saturated kaolinite with 3% water are reflected. The interaction energy between CH₄ and water increased linearly with water content at $E = -0.881\,\text{wt} - 0.346$. On the other hand, the interaction energy between kaolinite and water as well as between kaolinite and CH₄ decreased linearly with the increasing water content. From Fig. 9, it can be seen that $E_{\text{kaolinite–water}}$ is always larger than $E_{\text{kaolinite–CH4}}$ in the range of 0–5 wt% water contents. This means that kaolinite–water interaction is stronger than kaolinite–CH₄ and CH₄–water interactions and the CH₄ molecule is expected to be less tightly bound to the kaolinite structure thermodynamically. In addition, CH₄ molecule is expected to occupy preferentially the water-poor free cavity of kaolinite matrix if these holes are available. If CH₄ molecule jumps into a water-rich cavity, they prefer to stay in the rest space of this cavity where the water cluster does not occupy.

3.6 Weight density distributions

To illustrate the micro-structure of CH₄ in kaolinite, the weight density distributions of CH₄ molecules at bulk pressures of $P = 5$ MPa and $T = 293.15$ K in kaolinite with different water content were analyzed in Fig. 10. For greater clarity, the first peak values and second peak values of the weight density distributions between CH₄ and kaolinite with different water contents are shown in Table 1. It can be seen that the value of $\rho(r)$ were 295, 273, 251, 239, 208, and 186 kg/m³ at a separation of − 0.5 nm in alumina octahedral surface of kaolinite, respectively. Similarly, the values of $\rho(r)$ were 376, 334, 315, 291, 276, and 242 kg/m³ at a separation of 1.6 nm in silicon
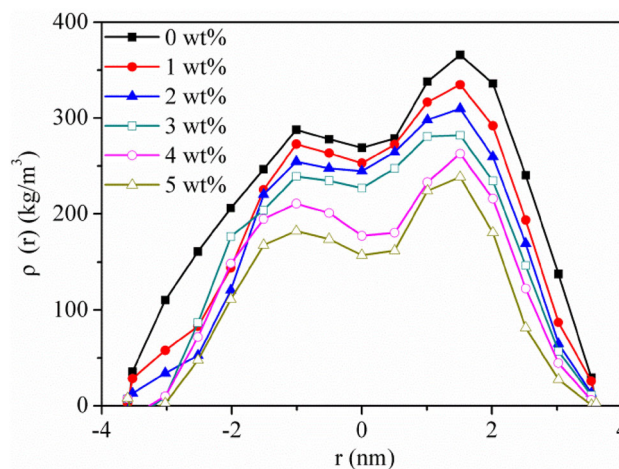

Fig. 10 Density profiles of CH₄ in kaolinite with different water content at 293.15 K and 5 MPa

Table 1 The first peak values and second peak values of weight density distributions between CH₄ and kaolinite with different water contents

Water content (wt%)	First peak values (kg/m³)	Second peak values (kg/m³)
0	295	376
1	273	334
2	251	315
3	239	291
4	208	276
2	186	242

tetrahedral surface of kaolinite, respectively. Moreover, the values of $\rho(r)$ drastically increased with the increasing adsorption distance (r) at − 0.5 nm. Then, the values of $\rho(r)$ slowly decreased to a minimum at 0 nm and slowly increased to a maximum at 1.6 nm. When the adsorption distance (r) was more than 1.6 nm, the values of $\rho(r)$ drastically decrease.

Due to the pore space limitation and the strong interaction between the two walls, the kaolinite surface had a higher adsorption CH₄ concentration in dry condition which determines the CH₄ diffusion coefficient was very small. With the increase of water content, as the interaction of the two walls against CH₄ is weakened, the number of CH₄ molecules in the micro-pores was gradually increased at higher water contents (Fig. 9). In addition, because the affinity of the kaolinite wall to the CH₄ molecule was significantly reduced, the CH₄ molecules in the middle of the kaolinite micro-pores had faster diffusion. In addition, the rapid diffusion of CH₄ molecules and water molecules in the middle of the micro-pores also accelerated the

diffusion of CH$_4$ molecules adsorbed on the surface, which leads to an overall increase in the CH$_4$ diffusion coefficient.

4 Conclusion

Molecular dynamics (MD) simulations were used to study the CH$_4$ diffusion in kaolinite with water contents ranging from 0 to 5 wt%. The results illustrated that CH$_4$ molecules can jump within adjacent holes in the kaolinite matrix. The CH$_4$ diffusion coefficient was about 3.28×10^{-9} m^2/s and water had a positive effect on it. The larger the water content, the larger the value of RDF first peak between CH$_4$ and oxygen, indicating that the interaction energy between CH$_4$ and oxygen in kaolinite is stronger. The interaction energy between CH$_4$ and water increased linearly with water content, in contrast, the interaction energy between kaolinite and water as well as between kaolinite and CH$_4$ decreased linearly with the increasing water content. The rapid diffusion of CH$_4$ molecules and water molecules in the middle of the micro-pores also accelerated the diffusion of CH$_4$ molecules adsorbed on the surface, which leads to an overall increase in the CH$_4$ diffusion coefficient. We hope that our research demonstrates a strategy to facilitate the further exploration of coalbed methane and shale gas.

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