

Article

Adsorption and Diffusion Characteristics of CO₂ and CH₄ in Anthracite Pores: Molecular Dynamics Simulation

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Abstract: CO₂-enhanced coalbed methane recovery (CO₂-ECBM) has been demonstrated as an effective enhanced oil recovery (EOR) technique that enhances the production of coalbed methane (CBM) while achieving the goal of CO₂ sequestration. In this paper, the grand canonical Monte Carlo simulation is used to investigate the dynamic mechanism of CO₂-ECBM in anthracite pores. First, an anthracite pore containing both organic and inorganic matter was constructed, and the adsorption and diffusion characteristics of CO₂ and CH₄ in the coal pores under different temperature and pressure conditions were studied by molecular dynamics (MD) simulations. The results indicate that the interaction energy of coal molecules with CO₂ and CH₄ is positively associated with pressure but negatively associated with temperature. At 307.15 K and 101.35 kPa, the interaction energies of coal adsorption of single-component CO₂ and CH₄ are $-1273.92 \text{ kJ}\cdot\text{mol}^{-1}$ and $-761.53 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. The interaction energy between anthracite molecules and CO₂ is significantly higher compared to CH₄, indicating that coal has a greater adsorption capacity for CO₂ than for CH₄. Furthermore, the distribution characteristics of gas in the pores before and after injection indicate that CO₂ mainly adsorbs and displaces CH₄ by occupying adsorption sites. Under identical conditions, the diffusion coefficient of CH₄ surpasses that of CO₂. Additionally, the growth rate of the CH₄ diffusion coefficient as the temperature increases is higher than that of CO₂, which indicates that CO₂-ECBM is applicable to high-temperature coal seams. The presence of oxygen functional groups in anthracite molecules greatly influences the distribution of gas molecules within the pores of coal. The hydroxyl group significantly influences the adsorption of both CH₄ and CO₂, while the ether group has a propensity to impact CH₄ adsorption, and the carbonyl group is inclined to influence CO₂ adsorption. The research findings are expected to provide technical support for the effective promotion of CO₂-ECBM technology.

Keywords: anthracite; coalbed methane; molecular dynamics simulation; diffusion coefficient; radial distribution function



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1. Introduction

Coalbed methane (CBM) represents a significant non-traditional source of natural gas and contains predominantly CH₄ with small quantities of CO₂, N₂, and other gases [1–3]. China has rich CBM resources in high-rank coal, with a total resource base of 30.05 trillion cubic meters, but most gas wells have low production, generally at medium and low levels [4]. CO₂-enhanced coalbed methane recovery (CO₂-ECBM) has been proven to be an efficient technique for enhancing CBM recovery by taking advantage of the high adsorption capacity of CO₂ to desorb CH₄ without significantly reducing the seam pressure [5–9]. CO₂-ECBM technology can not only greatly improve the recovery of CBM but also effectively replace CH₄ with CO₂ in the coal seam so as to achieve the effect of geological sequestration of CO₂. This is an important direction for CO₂ capture, utilization, and storage (CCUS) technology and has essential practical significance for promoting the realization of “carbon peak and carbon neutrality” [10,11].

The interaction mechanism and transport mechanism between fluids are the core issues of CO₂-ECBM [12]. To date, conventional experimental methods combined with nuclear magnetic resonance (NMR) testing and computerized tomography (CT) analysis have been used to study the adsorption and transport characteristics of gas in the CO₂-ECBM process. In addition, a theoretical model has been developed through traditional fluid dynamics analysis to study the dynamic process of gas adsorption, diffusion, and gas transport. Zheng et al. studied the dynamic characteristics of multiphase CH₄ in the CO₂-ECBM process by using the NMR method and confirmed that the desorption efficiency of CH₄ was significantly improved after injecting CO₂ [13]. Dutka et al. conducted a CO₂-ECBM physical simulation experiment, which showed that injecting CO₂ has the potential to enhance the recovery of CBM [14]. Majewska et al. experimentally observed that bituminous coal had a higher affinity for CH₄ than for CO₂ at 2.6 MPa and a similar affinity at 4 MPa, indicating that CO₂ was not always preferentially adsorbed by coal [15]. Topolnicki et al. developed a mathematical framework to characterize CO₂-ECBM, and the model's computed outcomes closely aligned with empirical findings [16]. Due to the intricate nature of CO₂-ECBM, encompassing processes such as gas adsorption, desorption, diffusion, and seepage, there are interdependencies between different stages that pose challenges in comprehensively elucidating the flow characteristics and transport mechanisms of gas molecules using conventional methodologies [17,18].

Molecular dynamics (MD) simulation represents a novel computational experimental methodology distinguished by its cost-effectiveness, minimal risk, and capacity for microscopic analysis [19–23]. MD simulations have widespread applications in the fields of materials and thermal analysis. Mahjoory et al. conducted research on enhancing the mechanical properties of calcium phosphate cement (CPC) for bone regeneration by incorporating Mg nanoparticles (NPs). Their findings indicated that the initial temperature and percentage of NPs have an impact on the mechanical performance of CPC [24]. Shahgholi et al. utilized MD simulations to examine the thermal and mechanical characteristics of Mg NPs in enhancing CPC, revealing a significant enhancement in the mechanical performance of the final cement due to the quantity and size of magnesium NPs [25]. In addition to the above fields, MD simulations are also well suited for investigating the flow behavior of gas molecules. To date, many scholars have carried out related research on the CO₂-ECBM process by using MD simulations. Brochard et al. conducted MD simulations of CO₂ and CH₄ adsorption processes at different reservoir depths using a coal molecular model and found that CH₄ adsorption increased with depth, while CO₂ adsorption decreased slightly [26]. Gao et al. conducted molecular simulations on gas adsorption and diffusion in the micropores of coal and found that for multi-component adsorption, CO₂ had a significant advantage but was significantly affected by H₂O [27]. Long et al. conducted further research on the CO₂-ECBM process in different pore diameters and found that as the pore diameter increased, the gas adsorption capacity also increased. They also noted that CO₂ had a higher adsorption capacity than CH₄, while CH₄ exhibited better diffusion ability compared to CO₂ [28]. In the current CO₂-ECBM molecular simulation, the pore models constructed are mainly single organic pores or single inorganic mineral pores, which are used to study the adsorption and transport characteristics of gas. However, in real CBM pores, most of the gas is adsorbed on organic and inorganic minerals, except for some free gases. The analysis of a certain type of pore alone cannot fully reveal the transport mechanism of CO₂-ECBM fluid at the microscale. In other fields, researchers have initiated the development of composite pore structures that integrate organic compounds and inorganic minerals to more accurately replicate reservoir properties. This facilitates a visual comparison of how organic and inorganic compositions influence gas storage, distribution, and flow characteristics under identical conditions. Tao et al. utilized methyl naphthalene as a representation of the organic component and formed the composite pore structure of illite–methyl naphthalene [29]. Kim et al. referenced kerogen macromolecules in their description of asphaltene and resin components and developed a shale model consisting of a combination of kerogen and illite. The established composite system has

been verified to be highly rational [30]. At present, the use of MD simulations of composite pores in CBM reservoirs is still at an early stage, and there is a shortage of MD simulation research in this area.

In this study, the grand canonical Monte Carlo simulation was used to study the dynamic mechanism of the CO₂ displacement of CBM in anthracite pores. A kind of anthracite pore containing organic and inorganic materials was constructed, and the adsorption and diffusion characteristics of CO₂ and CH₄ in the anthracite pore under different temperature and pressure conditions were studied by MD simulation, which provides theoretical support for the efficient development of CO₂-ECBM.

2. Simulation Method

2.1. Molecular Model

Since CH₄ is the main component of CBM, we use it to represent CBM. In this paper, the molecular model of anthracite established by Xiang is selected to study the adsorption and diffusion characteristics of CO₂ and CH₄ in coal pores [31]. The molecular formula of the model is C₁₉₉H₁₄₈N₂O₉. A series of energy minimization simulations were conducted on the planar configuration of coal macromolecules, and a stable three-dimensional configuration was obtained. The simulation processes included geometric optimization, annealing treatment, and dynamic relaxation. Figure 1 is the molecular model of anthracite.

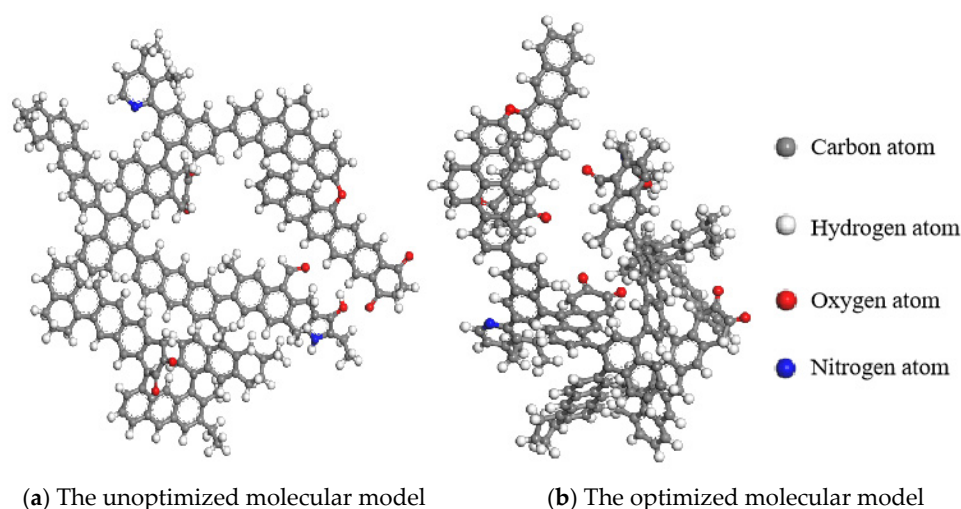


Figure 1. The molecular model of anthracite.

2.2. Model Basis and Conditional Configuration

We assembled a simulation box comprising two inorganic layers and one organic layer (refer to Figure 2). Montmorillonite slices are used to represent the inorganic layer, while the anthracite molecules are used to represent the organic layer. The structural information of the montmorillonite slices was retrieved from the Cambridge Crystallography Data Centre (CCDC) database. First, two montmorillonite slices are arranged as depicted in Figure 2, followed by the absorption of a set of coal molecules into the interlayer space. In three-dimensional space, periodic boundary conditions are employed with a unit size of 41.4 Å × 35.8 Å × 30.5 Å, and each unit contains 4280 atoms. In our simulation, the coal pore model, which consists of both organic and inorganic matter, is considered a rigid atomic material. The simulation calculation was conducted using Material Studio visual software (latest v. 2023), with the adoption of the COMPASS II force field and medium geometric optimization method. The charge calculation process utilized the force field distribution algorithm, while the atom-based method was employed for the summation of electrostatic forces and van der Waals forces. Following molecular mechanics optimization, the model was subjected to local energy minimization and subsequently globally optimized through a dynamic annealing simulation to achieve global energy minimization.

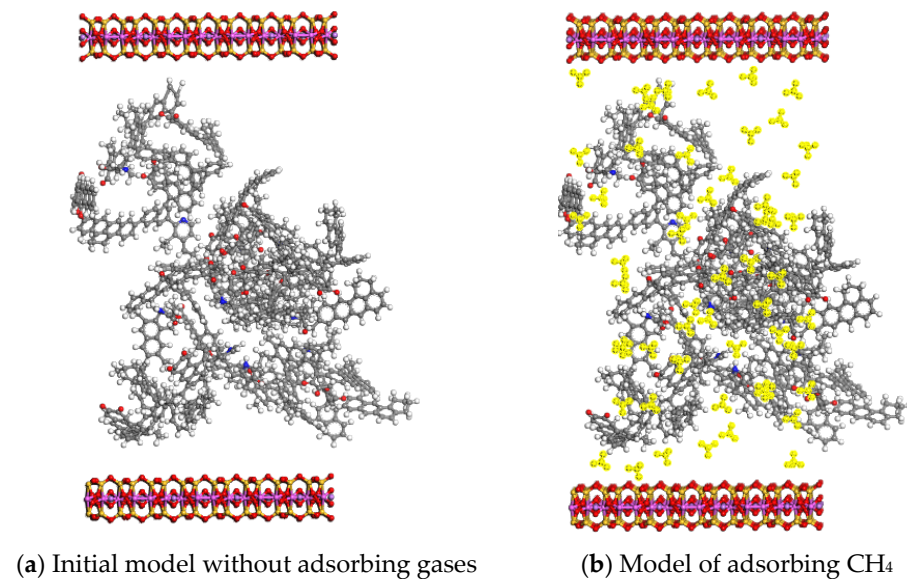


Figure 2. Molecular pore model of anthracite.

The initial model had a density of 1.23 g/cm^3 , which is consistent with the density range of anthracite reported in the literature, which ranges from approximately 1.2 to 1.3 g/cm^3 . Using the Atom Volumes & Surfaces tool in MS, the pore volume of the model was calculated to be $0.00118 \text{ cm}^3/\text{g}$. The calculated pore volume of the model also agrees with the experimental results obtained on the anthracite sample. The physical parameters of our established coalbed methane composite porosity model closely approximate those of the actual model. The primary advantage of this model lies in its comprehensive consideration of the chemical composition of real anthracite, enabling a thorough reflection of the physical and chemical properties of anthracite pores, a characteristic lacking in previous studies related to coalbed methane MD simulations.

The specific simulation process is as follows: First, CH_4 molecules are adsorbed to the established pore model, then a small number of CO_2 molecules are injected into the model, and once the process reaches equilibrium, the adsorption and diffusion characteristics of CO_2 and CH_4 in the coal pore model are calculated by analyzing the composition and energy changes in the gas mixture. In the actual CO_2 -ECBM process, the adsorption of CH_4 is physical adsorption, while the adsorption of CO_2 is mainly physical adsorption with weak chemical adsorption. Unless explicitly stated otherwise, the adsorption referred to in this article during the MD simulation process is exclusively physical adsorption. Dynamic calculations were performed on the model using the Focite and Sorption module, and the optimization process involved the use of the NVT system. The Focite module parameters were set with dynamics as the task item, temperature ranging from 297.15 K to 327.15 K , and Nose for temperature control and Berendsen for pressure control methods. The total step number is 10,000, the time step is 1 fs , and the simulation time is 50 ps . Table 1 provides specific information about the simulation.

Table 1. MD simulation setting information.

Setting	Parameter	Setting	Parameter
Forcefield	COMPASSII	Cutoff distance	$12.5 \text{ \AA}$
Charges	Forcefield assigned	Ensemble	NVT
Quality	Medium	Temperature control method	Nose
Electrostatic	Ewald	Pressure control method	Berendsen
Van der Waals	Atom-based	Simulation time	50 ps
Ewald accuracy	0.001 kcal/mol	Time step	1 fs

3. Results and Discussion

3.1. Interaction Energy and Adsorption Capacity

The adsorption of gases by solid surfaces is due to the tendency of any surface to spontaneously decrease its energy. The interaction energy between the adsorbent and adsorbate is defined as the sum of van der Waals interactions and Coulomb interactions, and its expression is shown in Equation (1) [32].

$$E = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \frac{Cq_iq_j}{\epsilon r} \quad (1)$$

where q_i and q_j are the charges of the atoms; r is the distance between the interacting particles; C is the energy conversion constant; ϵ is the depth of the potential energy well; and σ is the distance between two molecules at which the interaction potential energy is zero.

To analyze molecular interactions, we calculated the van der Waals and Coulomb interactions of coal with CO₂ and CH₄. Figure 3 shows the van der Waals interactions, Coulomb interactions, and interaction energies of CO₂ and CH₄ adsorbed to coal at different temperatures. With the increase in temperature, the values of van der Waals and Coulomb actions decrease, and both van der Waals and Coulomb interactions are negative, indicating that this physical adsorption process mainly relies on van der Waals forces and electrostatic forces, and the greater the absolute value is, the stronger the force is. With the increase in temperature in the simulation range, the absolute value of interaction energy decreases, and the adsorption effect weakens. High temperatures will inhibit physical adsorption. The interaction energy increases with the increase in pressure, and the adsorption effect is enhanced. With the increase in temperature (297.15 K to 307.15 K), the change in van der Waals interactions after CO₂ adsorption is 143.29 kJ·mol^{−1}, and the change in Coulomb interactions is 52.62 kJ·mol^{−1}; the change in van der Waals interactions after CH₄ adsorption is 109.96 kJ·mol^{−1}, and the change in Coulomb interactions is 26.09 kJ·mol^{−1}, which indicates that the adsorption of CO₂ and CH₄ is still dominated by van der Waals forces, and the Coulomb force is weak. At 307.15 K and 101.35 kPa, the interaction energies of coal adsorption of single-component CO₂ and CH₄ are −1273.92 kJ·mol^{−1} and −761.53 kJ·mol^{−1}, respectively. The interaction energy between CO₂ and coal is absolutely dominant, indicating that the adsorption capacity of coal to CO₂ is greater than that to CH₄. CH₄ molecules, being nonpolar in nature, exhibited variation in van der Waals energy of 384.3 kJ·mol^{−1} post-adsorption, alongside minimal alteration in electrostatic Coulombic energy, signifying the predominant involvement of van der Waals forces in the adsorption process. The CO₂ molecule possesses a significant electric quadrupole moment, resulting in an adsorption-induced alteration of 143.6 kJ·mol^{−1} in electrostatic Coulomb energy and a van der Waals interaction energy changing from −769.5 kJ·mol^{−1} to −1137.2 kJ·mol^{−1} (101.35 kPa, 297.15 K). Consequently, the adsorption of CO₂ continues to be primarily governed by van der Waals forces, with a subtle electrostatic interaction. Therefore, unless the research aim is to scrutinize the chemical adsorption process, the impact of chemical adsorption can typically be disregarded in MD simulations of CO₂-ECBM.

The isothermal adsorption characteristics of CO₂ and CH₄ at different temperatures were analyzed. Figure 4 shows the isothermal adsorption curves of CO₂ and CH₄. The results show that at the same temperature, with the increase in pressure at the early stage, the gas molecules in the vacuum state can be quickly adsorbed by coal molecules, showing a faster adsorption rate. When the high-affinity adsorption sites become occupied, the gas molecules shift to adsorption at low-affinity sites, exhibiting a reduced rate of adsorption. With the ongoing injection of gas, the process eventually reaches a point of saturation, demonstrating a gradual rate of adsorption. When the temperature rises at a constant pressure, the energy of CH₄ increases, leading to sharper molecular motion and a decrease in potential energy on the surface of coal pores. As a result, it becomes more difficult for CH₄ molecules to be adsorbed by the coal surface, resulting in a decrease in the adsorption

quantity [33]. In the same coal pore model, the adsorption levels of CO₂ and CH₄ are significantly different, with CO₂ showing better adsorption characteristics, followed by CH₄. Under the conditions of 307.15 K and 101.35 kPa, the adsorption capacity of CO₂ reaches 0.577 mmol/g, while that of CH₄ is only 0.186 mmol/g under the same conditions. Therefore, in coal pores, CO₂ has a stronger adsorption capacity than CH₄, which means that it can displace CH₄ from coal and accelerate CH₄ desorption. The gas adsorption capacity obtained in this study exceeds that reported in the previous literature [34], primarily due to the incorporation of inorganic constituents within the established porous model of anthracite. The presence of inorganic matter can enhance coal's capacity for CH₄ adsorption without fundamentally altering its adsorption characteristics. Further investigation is required to determine whether a synergistic adsorption effect exists between the organic and inorganic components within this composite structure.

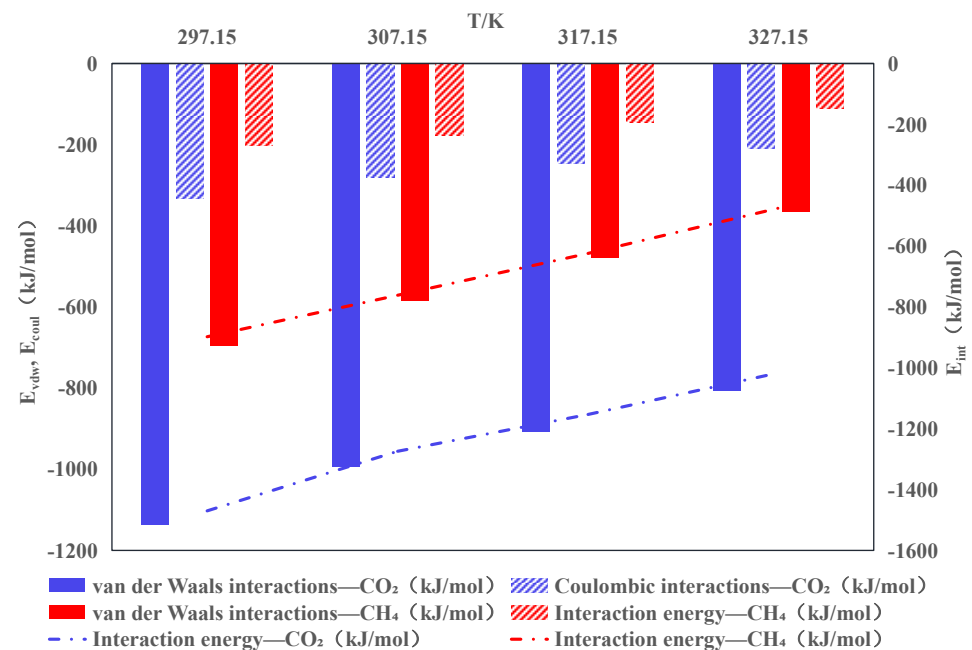


Figure 3. The interaction energy of coal with CO₂ and CH₄.

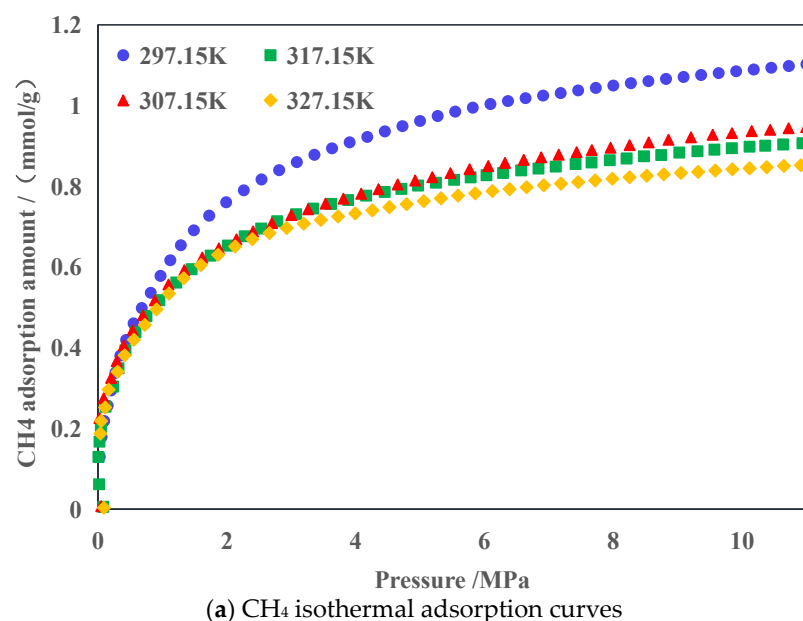


Figure 4. Cont.

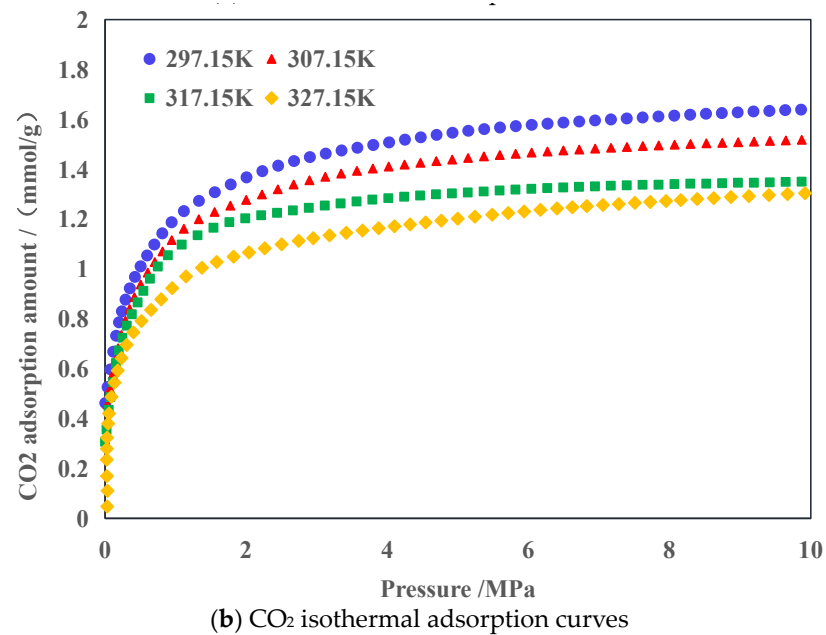


Figure 4. Isothermal adsorption curves of CO₂ and CH₄.

The distribution characteristics of CH₄ and CO₂ in the pore model were further studied, and the results are shown in Figure 5. The data in the figure are the density distributions of CH₄ and CO₂ along the z-axis at the equilibrium of the system measured after CO₂ was injected into the pore model. The density distributions shown are the average density calculated within 1000 time steps after equilibrium. Before CO₂ is injected, most CH₄ is mainly adsorbed on coal molecules, and some of it is adsorbed on the surface of the clay mineral layer. After CO₂ is injected, the density of CH₄ on the coal molecular layer decreases, and the density of CO₂ increases, indicating that CO₂ achieves the displacement effect mainly by occupying the adsorption sites of CH₄, which is consistent with the analysis results of interaction energy and isothermal adsorption curves. Figure 6 is a schematic diagram of this process.

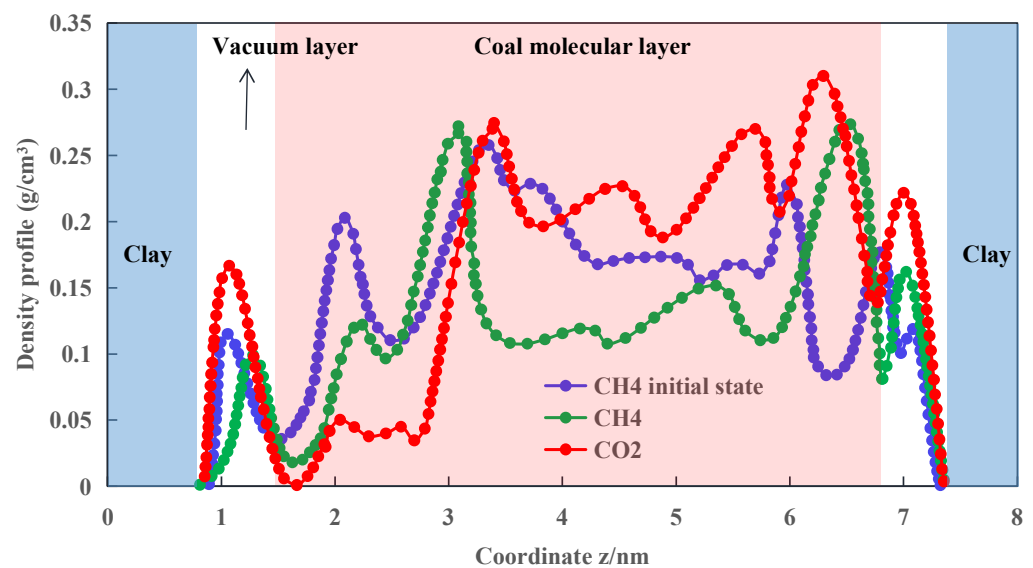


Figure 5. Density distribution of CH₄ and CO₂ in pore model.

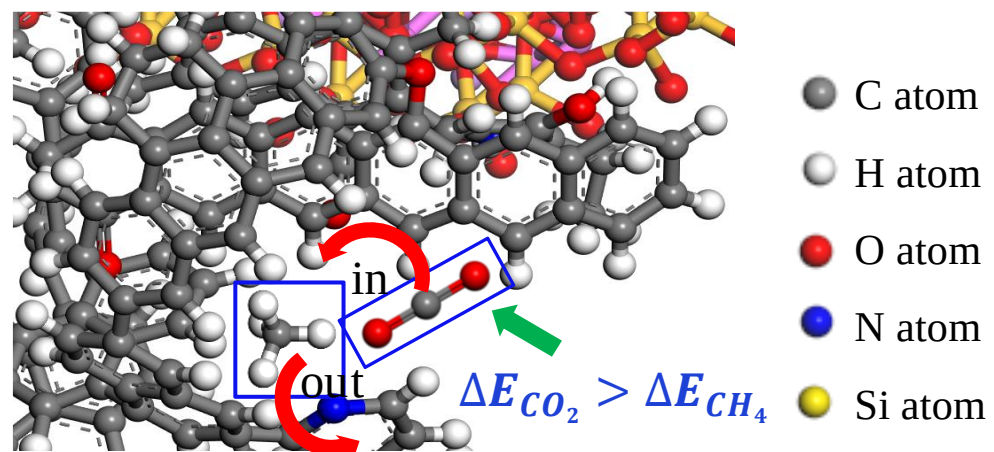


Figure 6. Schematic diagram of process of CO₂ adsorption displacement of CH₄.

3.2. Effect of Chemical Functional Groups on Gas Adsorption

In order to further elucidate the adsorption mechanism of gas in the pores of anthracite, the influence of different chemical functional groups on gas adsorption in anthracite was studied. The main functional groups of anthracite are ether, hydroxyl, carbonyl, a benzene ring, and other hydrocarbons and oxygen-containing functional groups. In addition, the influence of oxygen atoms in inorganic matter on gas adsorption is also taken into consideration. The radial distribution function (RDF) is used to represent the extent of the functional group's adsorption of gases. The RDF is a physical quantity characterizing the microstructural characteristics of particles. The RDF can not only be used to describe the order of matter but also be used to study the correlation of electrons, which can indicate the features of particle clustering and can be understood as the ratio of the local density to the average volume density in the system. The RDF is an important indicator for measuring the strength of adsorption of specific atoms or functional groups in the large molecules of adsorbents for adsorbate molecules. The size of the peak value of the RDF curve reflects the strength of the interaction between the target particles, and its calculation expression is as follows [35]:

$$g_{ab}(r) = \frac{dN}{4\pi\rho_b r^2 dr} \quad (2)$$

where dN is the number of b particles, and ρ_b is the density of b particles.

Figures 7 and 8 are the RDFs of the main functional groups in coal with CH₄ and CO₂, respectively. CH₄ and an ether group, a hydroxyl group, carbonyl, a benzene ring, and montmorillonite-oxygen (oxygen atom in montmorillonite), respectively, form obvious main peaks at 0.2624 nm, 0.3050 nm, 0.3015 nm, 0.3608 nm, and 0.4276 nm, and the order of the peak values from high to low is as follows: the ether group (2.97), the hydroxyl group (1.99), montmorillonite-oxygen (1.28), carbonyl (1.25), and the benzene ring (1.24). The main peak of CO₂ with the hydroxyl group, carbonyl, the benzene ring, and montmorillonite-oxygen is formed at 0.2925 nm, 0.4292 nm, 0.2785 nm, and 0.3574 nm, respectively, and the corresponding peak values are 2.19, 2.01, 1.36, and 1.31. At the same time, the main RDF peak of CO₂ and the ether group presented a double-peak phenomenon, and the peak values of CO₂ and the ether group are 1.52 and 1.29 at 0.3618 nm and 0.4977 nm, respectively, which promoted the strong interaction between CO₂ and oxygen-containing functional groups. The oxygen atoms on montmorillonite form a weak adsorption layer with CO₂ at a relatively far distance, so the adsorption is the weakest.

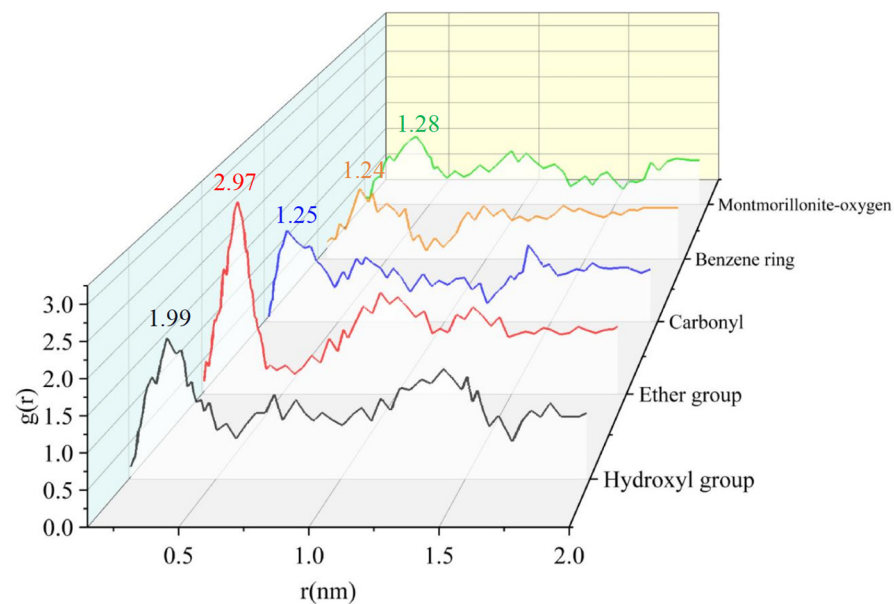


Figure 7. RDF of CH₄ and surface functional groups on coal.

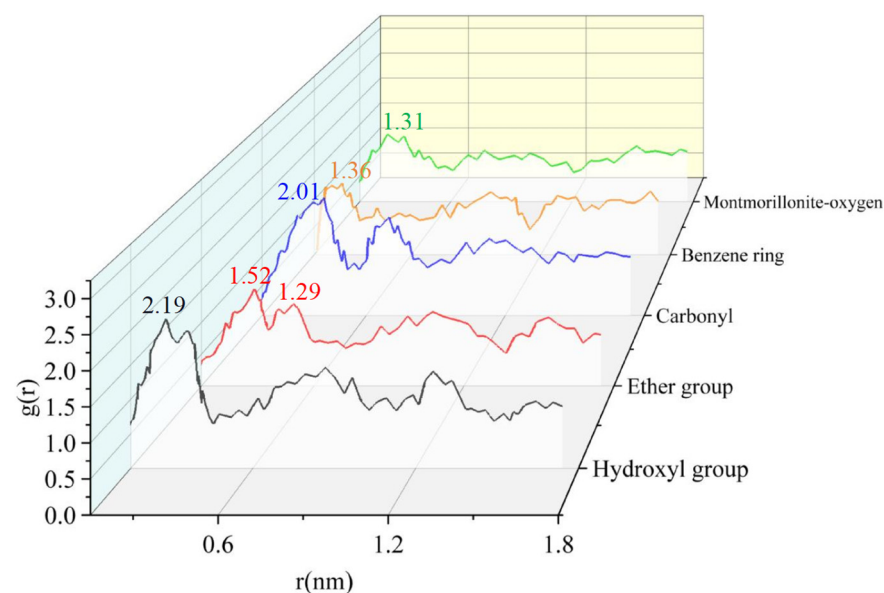


Figure 8. RDF of CO₂ and surface functional groups on coal.

The presence of chemical functional groups such as carbonyl and benzene rings provides CO₂ with a rich array of adsorption sites, but they have a weaker affinity for CH₄. The hydroxyl group has a strong affinity for both gases. Although the ether group has a strong affinity for CH₄, its quantity is small, so its impact on the final adsorption effect is limited. In general, the presence of oxygen functional groups and aromatic hydrocarbons in anthracite coal facilitates the adsorption of gas molecules on the coal surface. Hydroxyl and ether groups play a crucial role in the adsorption of CH₄, whereas carbonyl and benzene rings are influential in the adsorption of CO₂.

3.3. Gas Diffusivity Capacity

The analysis of Mean Square Displacement (MSD) is a method employed to investigate the temporal movement patterns of particles, offering valuable insights into their modes of diffusion, active transportation, or immobilization. Furthermore, MSD analysis has the capability to offer approximations of motion characteristics, such as the diffusion coefficients of particles undergoing free diffusion. The gas diffusion behavior within

the pore is directly correlated with the root MSD of its molecular centroid. By using Einstein's equation, the MSD curve can be obtained. The formula of Einstein's equation is as follows [36]:

$$MSD = \left\langle [r_i(\bar{t}) - \bar{r}_i(0)]^2 \right\rangle \quad (3)$$

where $r_i(\bar{t})$ and $\bar{r}_i(0)$ refer to the corresponding position vectors of the i -th atom at t and zero, respectively.

The slope k is obtained by the linear regression of the MSD curve. The calculation formula of the diffusion coefficient can be simplified as follows:

$$D = \frac{1}{6N} \lim_{t \rightarrow \infty} \frac{d}{dt} \left\langle \sum_{i=1}^N [r_i(\bar{t}) - \bar{r}_i(0)]^2 \right\rangle \quad (4)$$

where D is the self-diffusion coefficient, m^2/s ; N is the number of diffusing molecules.

The diffusion coefficient is frequently employed as a physical parameter for describing the behavior of gas migration within a medium. Based on Equation (4), it is possible to calculate the gas diffusion coefficient in the pore at various temperatures. Figures 9 and 10 quantitatively characterize the diffusion laws of CH_4 and CO_2 in the coal pore model, and the fitting coefficients of the curves are both high, which ensures the accuracy of the calculated diffusion coefficient. The results show that the MSD of CO_2 and CH_4 in the pore model increases with time, and the MSD of gases increases with temperature. With the increase in temperature, the diffusion coefficient of a gas increases, and the internal molecular energy increases. Based on the law of energy preservation, the internal molecular energy will transform into dynamic energy, leading to an increase in molecular movement [37]. Consequently, with the rise in temperature, there is a corresponding increase in the rate of gas diffusion, facilitating its escape from the coal seam. In this study, with the increase in temperature, the growth rates of the CO_2 and CH_4 diffusion coefficients are different. The growth rates of CO_2 diffusion coefficients at different temperatures are 11.54% (297.15 K–307.15 K), 25.86% (307.15 K–317.15 K), and 12.33% (317.15 K–327.15 K); the growth rates of CH_4 diffusion coefficients are 34.09% (297.15 K–307.15 K), 29.26% (307.15 K–317.15 K), and 24.98% (317.15 K–327.15 K).

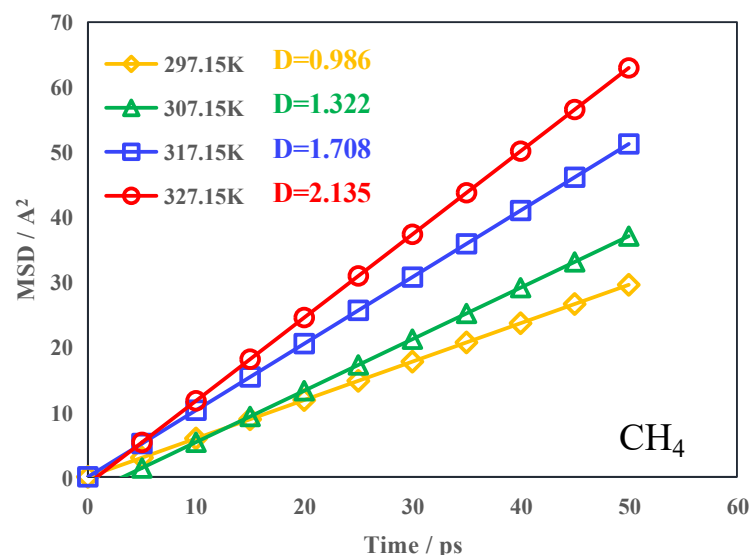


Figure 9. Cont.

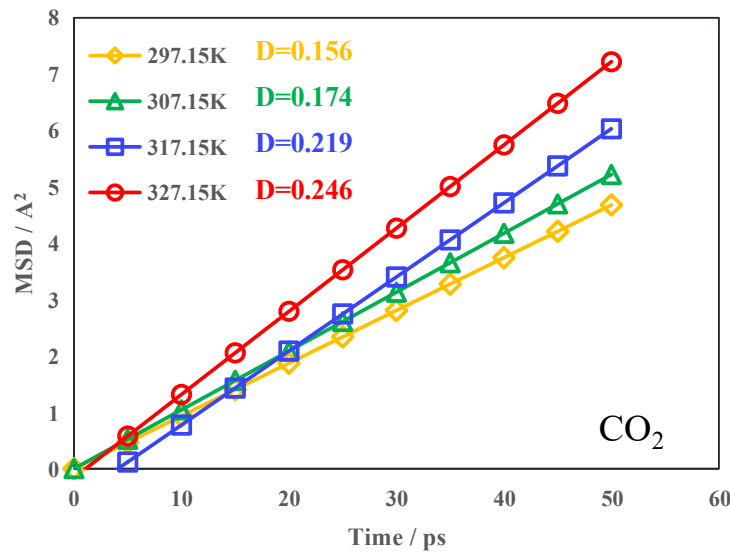


Figure 9. MSD of CH₄ and CO₂ in coal pore model.

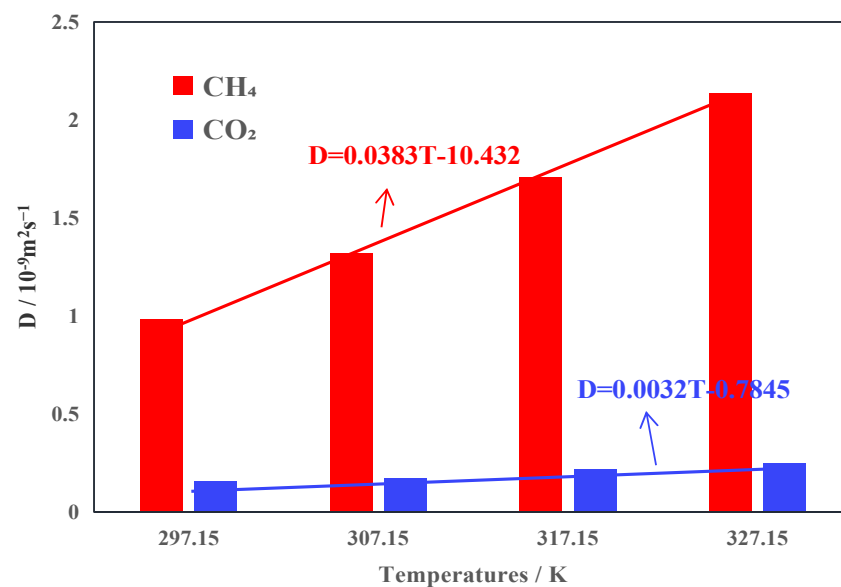


Figure 10. Diffusion coefficients of CH₄ and CO₂ in coal pore model.

The literature reports that the diffusion coefficients for CH₄ and CO₂ are approximately within the ranges of 10^{-11} – 10^{-9} m²/s [38] and 10^{-10} – 10^{-9} m²/s [39], respectively. In this study, the diffusion coefficient range of CO₂ is 0.156×10^{-9} – 0.246×10^{-9} m²/s, and the diffusion coefficient range of CH₄ is 0.769×10^{-9} – 2.135×10^{-9} m²/s, which are consistent with the reference ranges. The diffusion coefficient of CO₂ is smaller than that of CH₄ under the same conditions of the two gases, because CH₄ is a tetrahedral molecule, and the diffusion process in the pore is much less influenced by the coal molecular structure compared to rod-shaped CO₂. Furthermore, the strong adsorption of coal molecules is attributed to the large molecular size of CO₂, leading to an increased likelihood of collision with and adsorption on the pore wall, ultimately resulting in diminished diffusion efficacy within the pore. This characteristic allows CH₄ to diffuse into the fracture more easily than CO₂ after desorption, effectively increasing the recovery of CO₂-ECBM.

4. Conclusions

In previous CO₂-ECBM molecular simulation studies, the pore models constructed were mainly of single organic pores. Therefore, this study is the first to construct a composite

pore model of anthracite that includes both organic and inorganic materials. The adsorption and diffusion characteristics of CH₄ and CO₂ in the composite pore of anthracite were studied using MD simulation. The research results are as follows:

- i. The interaction between coal molecules and CO₂ and CH₄ increases with the increase in pressure, and the adsorption effect is enhanced. Under the same conditions, the adsorption of CO₂ and CH₄ is still dominated by van der Waals forces, and the electrostatic interaction is weak. At 307.15 K and 101.35 kPa, the interaction energies of coal adsorption of single-component CO₂ and CH₄ are -1273.92 and -761.53 kJ·mol⁻¹, respectively.
- ii. The interaction energy between anthracite molecules and CO₂ is significantly higher compared to CH₄, indicating that coal has a greater adsorption capacity for CO₂ than for CH₄. The distribution characteristics of gas in the pores before and after injection indicate that CO₂ mainly adsorbs and displaces CH₄ by occupying adsorption sites.
- iii. Under the same conditions, the diffusivity of CH₄ exceeds that of CO₂; elevated temperatures result in an increase in gas diffusivity, facilitating the diffusion of gas out of the coal pores. With the increase in temperature, the growth rates of CO₂ and CH₄ diffusion coefficients are different, and the growth rate of the CH₄ diffusion coefficient is greater than that of CO₂. This shows that CO₂-ECBM is suitable for coal seams with high temperatures.
- iv. The presence of oxygen functional groups and aromatic hydrocarbons in anthracite coal facilitates the adsorption of gas molecules on the coal surface. The hydroxyl group significantly influences the adsorption of both CH₄ and CO₂, and of the other functional groups, the ethoxy group has the greatest impact on the adsorption of CH₄, while the carbonyl group has a significant impact on the adsorption of CO₂.

Author Contributions: Conceptualization, Y.G.; Methodology, Y.G. and Y.W.; Validation, Y.W.; Investigation, X.C.; Writing—original draft, Y.G., Y.W. and X.C. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to confidentiality issues.

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Conflicts of Interest: Author Yufei Gao, Yaqing Wang and Xiaolong Chen were employed by the company China National Offshore Oil Corporation Research Institute Co., Ltd. The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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