Molecular Dynamics Mechanism of CH₄ Diffusion Inhibition by Low Temperature in Anthracite Microcrystallites

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ABSTRACT: Understanding the adsorption/diffusion characteristics of CH₄ at low temperatures (<273.15 K) is of great significance not only for coal bed methane estimation but also for gas disaster prevention and methane storage in deep coal beds. In this work, the adsorption configurations of anthracite macromolecules were constructed with Materials Studio, and then, the adsorption and diffusion behaviors of CH₄ at 233.15−363.15 K were simulated, respectively, using grand canonical Monte Carlo (GCMC) and molecular dynamics (MD) algorithms. The results show that the absolute adsorption capacities of CH₄ at low temperatures are substantially larger than those at high temperatures, and the adsorption amount further increases with the continued cooling at a given sorption pressure. The isosteric heat of CH₄ adsorption ranges from 8.715 to 11.746 kJ/mol, belonging to a spontaneous physical adsorption. The self-diffusivity $D_s$ of CH₄ at low temperatures is substantially smaller than that at high temperatures and further decreases with cooling. The most probable velocity of CH₄ molecules ($v_m$) greatly decreases, and the number of gas molecules with a higher energy is significantly reduced by a low temperature, resulting in the diffusion inhibition of CH₄.

1. INTRODUCTION

As an associated mineral resource of coal, coal bed methane (CBM), also known as coal seam gas, is a kind of unconventional hydrocarbon gas, which is mainly composed of methane (CH₄).¹ CBM is a clean, high-quality energy and raw material, whose use has grown in the world in the past few decades, and its calorific value is 2−5 times that of general coal.²,³ The estimated CBM resources buried at depths above 2000 m underground are around 256 Tm³ worldwide, and most of these are distributed in the former Soviet Union, North America, and the Asia-Pacific region.⁴,⁵ If these resources cannot be effectively extracted and utilized from coal beds, it will augment the hidden dangers threatening miner safety, such as the triggering of coal and gas bursts, gas explosions, and underground fires.⁶,⁷ Therefore, the Chinese State Administration of Coal Mine Safety stipulates that the premining coal beds must be predrained to reduce the gas content below the safe critical value of 8 m³/t.⁸ CBM is mainly adsorbed on the surface of coal pores, partially free in fissures or dissolved in coal bed water.⁹ It is vital to explore the sorption/diffusion characteristics of methane in the coal matrix not only for the CBM resource estimation and exploitation but also for methane storage in the reduction of greenhouse gas emissions.¹⁰ Numerous adsorption isotherm experiments targeted at the organic-rich coal above 293.15 K have demonstrated that the process of gas absorbed into coal pores belongs to physical adsorption, and temperature and sorption pressure are the two major external factors affecting the adsorption capacity of coal.¹¹−¹³ Generally, the adsorption capacity of CH₄ decreases with the increase of ambient temperature, and this negative correlation is more significant under high pressures.¹⁴,¹⁵ The sampling results from Huntly coalfield showed that the gas adsorption capacity decreases by 1 cm³/g for the each 10 K temperature rise.¹⁶ Oppositely, the adsorption capacity on homogeneous/heterogeneous surfaces increases with the decrease in temperature under high pressures.¹⁷ The Langmuir equation (single site) was widely used to describe the adsorption isotherms of methane on coal by the virtues of simplicity and a good fitting effect under low-pressure conditions.¹⁸ Subsequently, the improved Dubinin−Astakhov model has been proven to be more accurate in predicting the effect of temperature on the adsorption affinity of supercritical methane at high pressures.¹⁹−²¹

The processes of methane adsorption and desorption on adsorbent pores were considered to be basically reversible, but the desorption hysteresis also appeared in different degrees.²²,²³ From the perspective of activation energy, Nandi...
and Walker discussed the influences of temperature, pressure, and coal metamorphism on the diffusion capacity of methane, and concluded that the diffusion coefficient, which also refers to the particle size of samples, increases with the temperature increase.\textsuperscript{24,25} It was found that the organic matters around the original pores can be thermally expanded by heating up, resulting in enhanced gas diffusion capacity, and the diffusion amount has a positive exponential relation with the temperature.\textsuperscript{26} Subsequently, Nie, et al. carried out the CH\textsubscript{4} desorption experiments on the granular coal at 20−60 °C, and found that both the total desorption amount and the initial effective diffusion coefficient increase with the increase in ambient temperature.\textsuperscript{27} Besides, the diffusion rate (\(Q_t/Q_\infty\)) is linearly related to the square root of time (\(\sqrt{t}\)) within a short desorption time.\textsuperscript{28}

Limited by the experimental conditions, previous literature on the characteristics of gas adsorption and diffusion under the low temperature (<273.15 K) are few. To reduce the gas loss during the coal coring process in the gas content determination, a freezing coring method was proposed.\textsuperscript{29} A series of isothermal adsorption/desorption tests at 243.15−303.15 K demonstrated that the methane diffusion through coal pores is greatly inhibited, while the adsorption capacity is enhanced below 273.15 K.\textsuperscript{29−31} Moreover, the mean isosteric heat of adsorption can be used to estimate the gas adsorption affinity of coal with different metamorphic ranks.\textsuperscript{30} Successively, a refrigeration mode using dry ice as the refrigerant and alcohol as the catalyst was selected for the freezing coring, in which the cooling rate of the coal sample gradually accelerates with the rising sorption pressure of methane.\textsuperscript{32} In addition, the artificial freezing technology was also utilized to achieve the fast and safe rock cross-cut coal uncovering, and to store more adsorbed natural gas (ANG) with a comparable methane density based on the effects of gas absorption promotion and diffusion inhibition at low temperatures.\textsuperscript{33,34} Although several isothermal tests focus on CH\textsubscript{4} adsorption/desorption at low temperatures, there is limited information related to the molecular dynamics (MD) mechanism of this phenomenon.

Currently, molecular simulation has become an effective measure to explore the thermodynamic properties and the dynamic behaviors of gas in porous medium. By employing the grand canonical Monte Carlo (GCMC) method to simulate the CO\textsubscript{2}/CH\textsubscript{4} adsorption in shale kerogen, it was found that the interactions between CH\textsubscript{4} molecules and kerogens mainly rely on van der Waals forces rather than the Coulomb interactions, which differs from the interactions of CO\textsubscript{2} adsorption.\textsuperscript{35,36} The effects of electrostatic interactions and oxygen functionalities on the CO\textsubscript{2}/CH\textsubscript{4}/N\textsubscript{2} competitive adsorption were further discussed using the MD simulation.\textsuperscript{37,38} Moreover, the effects of moisture and temperature on the maximum adsorption capacity, coal swelling, and the adsorbed phase density were investigated. The results showed that the existence of water in the coal matrix weakens the interaction between CH\textsubscript{4} and the vitrinite macromolecule.\textsuperscript{39} The benzene adsorption on activated carbon with various microporous structures were also simulated under different temperatures (>273.15 K), which suggested that benzene prefers to adsorb on the surface of activated carbon with the

### Table 1. Adsorption Isotherm Data of CH\textsubscript{4} under Different Temperatures

| pressure (kPa) | 233.15 K | 238.15 K | 243.15 K | 248.15 K | 303.15 K | 333.15 K | 343.15 K | 353.15 K | 363.15 K |
|---------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 100           | 1.713    | 1.482    | 1.367    | 1.103    | 0.522    | 0.376    | 0.340    | 0.312    | 0.263    |
| 1590          | 14.628   | 13.881   | 12.993   | 11.637   | 6.745    | 5.166    | 4.759    | 4.364    | 3.817    |
| 3080          | 21.156   | 20.134   | 19.272   | 17.709   | 11.388   | 8.900    | 8.232    | 7.744    | 6.878    |
| 4570          | 26.582   | 25.020   | 24.046   | 22.196   | 15.004   | 12.087   | 11.220   | 10.732   | 9.527    |
| 6060          | 31.454   | 29.803   | 28.180   | 26.293   | 17.947   | 14.711   | 13.957   | 13.061   | 11.595   |
| 7550          | 36.096   | 33.705   | 32.894   | 29.711   | 20.658   | 17.216   | 16.184   | 15.327   | 13.784   |
| 9040          | 39.646   | 37.945   | 35.798   | 33.358   | 23.221   | 19.238   | 18.280   | 17.388   | 15.622   |
| 10530         | 42.386   | 40.952   | 38.867   | 36.389   | 25.402   | 21.304   | 20.363   | 19.257   | 17.407   |
| 12020         | 44.818   | 43.287   | 41.140   | 38.183   | 27.377   | 23.218   | 21.945   | 20.839   | 19.151   |
| 13510         | 47.235   | 45.261   | 43.848   | 40.930   | 28.943   | 25.054   | 23.846   | 22.193   | 20.346   |
| 15000         | 48.746   | 47.321   | 45.545   | 43.032   | 30.724   | 26.446   | 24.929   | 23.958   | 21.696   |

### Figure 1. Adsorption isotherms of CH\textsubscript{4} in anthracite at different temperatures: (a) high-temperature environment and (b) low-temperature environment.
larger micropores and mesopores at low temperatures, while the smaller micropore structure is favorable for the adsorption at high temperatures. This work aims to investigate the differences of CH4 diffusion on coal at low and high temperatures. The adsorption configurations of the anthracite microcrystallite were constructed with the GCMC algorithm. The adsorption isotherms and the isosteric heats of CH4 were obtained at 233.15−363.15 K, respectively, and the saturated adsorption configuration of anthracite was selected. Then, the self-diffusivities Di were calculated according to the mean square displacement (MSD) of methane molecules in MD simulations. It reveals the essence of the CH4 diffusion inhibition by low temperature from the perspective of MDs.

2. RESULTS AND DISCUSSION

2.1. Differences of Adsorption Isotherms at Low/High Temperatures. To investigate the effects of low and high temperature on the CH4 adsorption capacity of the anthracite crystallite, the GCMC algorithm was adopted, and the simulation results of CH4 adsorption at 233.15−363.15 K are listed in Table 1.

The CH4 adsorption capacity on a monolayer of anthracite can be then obtained by substituting the adsorption data into the following equation:

$$M = \frac{1000 \times N_{\text{am}}}{N_A \times M_s}$$

where M is the CH4 adsorption capacity on a monolayer, mmol/g; Nam is the number of adsorbed CH4 molecules in molecular simulation; N_A is the Avogadro constant, 6.02 × 10^{23}; M_s is the molecular weight of a monolayer anthracite, M_s = 1.2 g/cm^3 × 7.904 × 10^3 Å³.

As shown in Figure 1, the adsorption capacities of CH4 on the anthracite macromolecule are well-fitted by the Langmuir isotherm model. Because the spacing between CH4 molecules decreases with the increase of sorption equilibrium pressure in the low-pressure stage, the intermolecular attraction gradually increases and dominates, resulting in a significant growth in the CH4 adsorption capacity.  While the equilibrium pressure rises to 10 MPa, the intermolecular repulsion also increases, and the growth rate of adsorption capacity slows down with pressure, indicating that the number of CH4 molecules adsorbed in the anthracite microcrystallite gradually tends to be saturated.

It is noted that the adsorption capacity obtained by molecular simulation refers to the total amount of CH4 molecules on the porous adsorbent, including the molecules adsorbed on the pore wall and the free molecules in the microcrystalline structure, which is called absolute adsorption capacity. Whereas, the amount of CH4 molecules adsorbed on pore wall is called the excess adsorption capacity, usually measured from the isothermal adsorption experiment.

Figure 1a shows that the absolute adsorption capacities of anthracite at the high temperatures of 333.15−363.15 K are substantially less than that at the normal temperature (303.15 K), and the CH4 absolute adsorption capacity subsequently decreases with the increase of temperature at the same sorption pressure. Compared with the absolute adsorption capacity of 5.339 mmol/g at 303.15 K, those at 333.15−363.15 K are 4.596, 4.332, 4.163, and 3.77 mmol/g, respectively, at a sorption pressure of 15 MPa, and the decrements are 13.92, 18.86, 22.03, and 29.39%, respectively. It indicates that the average kinetic energy of CH4 molecules increases in the high-temperature environment, so that the probability to escape the van der Waals force of anthracite is greatly promoted. On the contrary, the low temperature is beneficial to the CH4 adsorption onto the anthracite microcrystallite. At the sorption pressure of 15 MPa, the absolute adsorption capacity at 233.15−248.15 K are 8.471, 8.223, 7.915, and 7.478 mmol/g, respectively (Figure 1b), significantly higher than that at 303.15 K. It is clearly seen that the kinetic energy of free CH4 molecules can be reduced by cooling, so that more gas molecules are easily captured by the van der Waals force of anthracite. Furthermore, the number of the colliding gas molecules per unit area increases, leading to the gradual increase of adsorption capacity with cooling under the same pressure.

2.2. Isosteric Heat of CH4 Adsorption. The isosteric heat of adsorption is a crucial thermodynamic indicator to distinguish chemical adsorption (84−417 kJ/mol) and physical adsorption (<42 kJ/mol), which presents the interaction between gas molecules and the solid absorbent. It can be derived based on the Clausius−Clapeyron equation written at a constant adsorbed-phase concentration as follows:

$$Q_{st} = -\Delta H = RT \left( \frac{\partial \ln P}{\partial T} \right)$$

where Q_{st} is the isosteric heat of CH4 adsorption, kJ/mol; R is the ideal gas constant, 8.314 J/mol K; T is the ambient temperature, K; P is the adsorption pressure, MPa.
Regardless of the ambient temperature varying from 233.15–363.15 K, the isosteric heats of CH₄ adsorption are in the range of 2.082–2.806 kcal/mol, that is, 8.715–11.746 kJ/mol, belonging to the physical adsorption. Figure 2a shows that the adsorption heat decreases with the temperature increase at a given pressure. It is mainly because the occupying probability of CH₄ molecules on a strong adsorption site is weakened at high temperatures. Meanwhile, a higher temperature is not conducive to the CH₄ adsorption owing to the exothermic effect, which leads to the decrease in the isosteric heat of adsorption. Moreover, the isosteric heat of adsorption generally increases with the increasing sorption pressure at a fixed high temperature, which indicates that pressurization can promote CH₄ adsorption. With the increase of sorption pressure, CH₄ molecules transfer from the monolayer to the multilayer adsorption on the anthracite surface, and the interactions of multilayer adsorption become greater than the monolayer adsorption force, which results in a gradual rise in the isosteric heat of adsorption at higher pressures.

Figure 2b shows that the isosteric heat of CH₄ adsorption increases with cooling under the low-temperature environment (233.15–248.15 K). The isosteric heat does not continuously increase with gas pressure as that in the high temperature environment at a given low temperature, but presents a trend of first increasing, then decreasing, and eventually increasing again with the sorption pressure increase. The initial isosteric heat is 2.449 kcal/mol at 248.15 K, and then, it increases to 2.594 kcal/mol at 3.08 MPa; however, when the pressure increases to 7.55 MPa, the isosteric heat decreases to 2.53 kcal/mol; as the pressure continues to increase, the final isosteric heat increases again and reaches 2.683 kcal/mol at 15 MPa. This is probably due to the heterogeneous adsorption on the microcrystalline skeleton surface of anthracite. Generally, CH₄ molecules are preferentially adsorbed on active sites with higher energy. In the low-temperature environment, CH₄ molecules adsorbed in the early stage gradually occupy most of the active adsorption sites. Then, CH₄ molecules adsorbed in the later stage can only be transferred to the relatively inactive adsorption sites. The repulsion between the adsorbed gas molecules gradually increases with further reduction of molecular spacing, which results in a phase decline in the isosteric heat. As the pressure increases further, the multilayer adsorption of CH₄ molecules happens, and the isosteric heat increases again.

2.3. Selection of CH₄ Adsorption Configuration. In order to simulate the diffusion behavior of CH₄ molecules in the anthracite microcrystallite, a stable adsorption configuration should be established to provide sufficient adsorbates and time for the statistical calculation. Therefore, the lowest energy configuration of adsorption was selected by gradually loading CH₄ molecules onto the microcrystalline surface using locate task item in sorption module at 303.15 K as the normal temperature of the coal bed. The change of van der Waals energy during the adsorption process by gradual CH₄ pressurization is plotted in Figure 3. Figure 3 shows that the change of van der Waals forces between CH₄ molecules and the anthracite in the sorption process at 303.15 K also conform to the Langmuir isothermal model. The bonding energies ($E_{\text{Bond}}, E_{\text{Torsion}}, E_{\text{Angle}},$ and $E_{\text{Inversion}}$) of the sorption system are 0 kcal/mol. The van der Waals force always keeps negative, indicating that the CH₄ adsorption process is exothermic. The van der Waals force

Figure 3. Adsorption configurations of anthracite under different CH₄ sorption pressures at 303.15 K.

Figure 4. Changes of CH₄ MSD with time in anthracite at different temperatures: (a) high temperature and (b) low temperature.

Figure 4.
gradually decreases to the minimum value with the increase in the number of CH$_4$ molecules absorbed; meanwhile the adsorption configuration with the lowest interaction is generally stable. Consequently, the adsorption configuration at the pressure of 15 MPa is adopted to conduct the CH$_4$ diffusion simulation, and the number of CH$_4$ molecules adsorbed is 31.

### 2.4. CH$_4$ Diffusion at Low/High Temperatures

The MSD of adsorbate molecules is defined as the average distance a molecule travels over an interval. The self-diffusivity $D_s$ that relates the MSD to the observation time, is generally used to reflect the diffusion capacity of gas molecules in the MDs (MD) simulation. The MSD of CH$_4$ is expressed as follows:

$$\text{MSD} = \frac{1}{N} \langle (r(t) - r(0))^2 \rangle$$

where $N$ is the number of CH$_4$ molecules; $r(t)$ is the Cartesian position vector of the CH$_4$ molecule in the microcrystallite at the time $t$; and $r(0)$ is the initial position vector of the CH$_4$ molecule. Thus, the self-diffusivity $D_s$ can be derived based on the Einstein diffusion equation:

$$D_s = \frac{1}{6Nt} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{N} \langle r_i(t) - r_i(0) \rangle^2 = \frac{k_{\text{MSD}}}{6}$$

where $k_{\text{MSD}}$ is the slope of the fitting curve of MSD. The selected adsorption configuration of anthracite was studied using MD simulation to explore the differences of the CH$_4$ diffusion behavior at low/high temperatures. The MSD changes of CH$_4$ molecules with the observation time are shown in Figure 4, and the self-diffusivity $D_s$ calculated is listed in Table 2.

It can be seen that the MSD of CH$_4$ molecules maintains a good linear relationship with time, both at high and low temperatures within 1000 Ps, which indicates the self-diffusivities $D_s$ obtained by fitting are reliable. The self-diffusivities $D_s$ of CH$_4$ at low temperatures (0.11–0.24 $\times$ 10$^{-10}$ m$^2$/s) are substantially smaller than those at high temperatures (0.93–1.17 $\times$ 10$^{-10}$ m$^2$/s), and it gradually decreases with the ambient temperature drop and vice versa. The CH$_4$ molecules continually vibrate with a small amplitude in the free space of the anthracite microporecrystallite. Once the kinetic energy is weakened by cooling, so that the frequency of CH$_4$ transitions between capillary pores is reduced. Thus, the self-diffusivity $D_s$ of CH$_4$ sharply decreases at low temperatures, which is in agreement with the experimental conclusion of CH$_4$ diffusivity inhibition by low temperatures.

### 2.5. Discussion

The bulk diffusion of CH$_4$ molecules through the capillary pores of anthracite is often sorted into Fick diffusion, Knudsen diffusion, and transitional diffusion, according to the different resistances (the Knudsen number $K_n$). The Knudsen number is defined as the ratio of the diameter of the capillary pore $d$ to the mean free path of a CH$_4$ molecule $\lambda$.

#### 2.5.1. Fick Diffusion

Fick diffusion, $D_F$, is defined as follows:

$$D_F = \frac{\bar{u}_s}{3} \lambda$$

where $\bar{u}_s$ is the mean square velocity of the CH$_4$ molecule, m/s, which can be described as:

$$\bar{u}_s = \sqrt{\frac{8RT}{\pi M}}$$

From which, $M$ is the mean square velocity of the CH$_4$ molecule, 16.043 kg/mol. $\bar{u}_s$ demonstrate that the Fick self-diffusivity $D_F$ of CH$_4$ is mainly affected by the ambient temperature and the pressure of adsorption. When $K_n > 0.1$, the mean free path $\lambda$ of the CH$_4$ molecule is much larger than the pore diameter $d$. In this case, there is no mirror-reflecting collision between CH$_4$ molecules in the free space, but the diffusion caused by scattering from the pore wall happens, which is Knudsen diffusion. The self-diffusivity $D_K$ is expressed as follows. Therefore, $D_k$ is mainly related to the adsorber structures and temperature, but not to the gas pressure:

$$D_K = \frac{2}{3} \sqrt{\frac{8RT}{\pi M}}$$

When $0.1 \leq K_n \leq 10$, the mean free path $\lambda$ is comparable to the pore diameter $d$, and the collision probability between CH$_4$ molecules is almost equivalent to that with the pore wall. Consequently, the transitional diffusion is characterized by Fick and Knudsen diffusion at the same time. The self-diffusivity $D_T$ is expressed as:

$$\frac{1}{D_T} = \frac{1}{D_F} + \frac{1}{D_K}$$

| Temperature (K) | $D_s$ ($10^{-10}$ m$^2$/s) | $D_F$ ($10^{-10}$ m$^2$/s) | $D_K$ ($10^{-10}$ m$^2$/s) | $D_T$ ($10^{-10}$ m$^2$/s) |
|-----------------|----------------|----------------|----------------|----------------|
| 233.15          | 0.109          |               |               |               |
| 238.15          | 0.154          |               |               |               |
| 243.15          | 0.194          |               |               |               |
| 248.15          | 0.241          |               |               |               |
| 303.15          | 0.668          |               |               |               |
| 333.15          | 0.927          |               |               |               |
| 343.15          | 0.966          |               |               |               |
| 353.15          | 1.074          |               |               |               |
| 363.15          | 1.167          |               |               |               |
From this, we can conclude that the self-diffusivity of CH₄ is directly proportional to the square root of the ambient temperature (√T). Additionally, the diffusion velocities of all CH₄ molecules (v) follow the Maxwell distribution law, expressed in eq 11.  

\[ f_m(v) = \frac{m}{2\pi kT}^{3/2} v^2 e^{-mv^2/2kT} \]  

where \( m \) is the mass of a CH₄ molecule, g. While, the distribution range of all molecular velocities is divided into several equal intervals. The velocity corresponding to the maximum ratio of the number of molecules to the total is called the most probable velocity of molecules. The velocity distribution of single-component gas molecules at different temperatures is shown in Figure 6.

![Figure 6. Velocity distribution of gas molecules under different temperatures.](image)

The most probable velocity of CH₄ molecules (\( v_p \)) can be expressed as follows

\[ v_p = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}} \]  

Equation 12 indicates that the \( v_p \) of CH₄ molecules also decreases with the decrease in temperature, and the number of molecules in the velocity range of \( v_p \) is the most. While the number of molecules with a higher energy is significantly reduced. Obviously, the probability that the CH₄ molecules get high enough to get rid of the adsorption potential well is weakened with cooling. Therefore, the diffusion capacity of CH₄ in the anthracite microcrystallite is greatly reduced, and the total diffusion time is also shortened at low temperatures, compared with the high temperatures.

3. CONCLUSIONS

To reveal the MDs mechanism of the CH₄ adsorption promotion and the diffusion inhibition under low temperatures (<273.15 K), the adsorption configurations of the anthracite microcrystallite were constructed with the GCMC algorithm. The adsorption isotherms and the isosteric heats of CH₄ were obtained at 233.15–363.15 K, respectively, and then the self-diffusivities \( D_i \) were calculated according to the MSD of methane molecules in MD simulations. The following conclusions can be drawn:

1) The absolute adsorption capacities of CH₄ at the high temperatures are substantially less than those at the low temperatures (<273.15 K), and the adsorption capacity further increases with the continuous cooling at a given sorption pressure.

2) The isosteric heat of CH₄ adsorption ranges from 8.715–11.746 kJ/mol at 233.15–363.15 K, respectively, and it presents a trend of first increasing, then decreasing, and eventually increasing again with the sorption pressure increase at low temperatures.

3) The MSD of CH₄ keeps a linear relationship with the observation time. The self-diffusivities \( D_i \) of CH₄ at low temperatures are substantially smaller than those at high temperatures, and further decrease with cooling.

4) The most probable velocity of CH₄ molecules (\( v_p \)) greatly decreases, and the number of molecules with a higher energy is significantly reduced by the low temperature, resulting in the diffusion inhibition of CH₄.

4. SIMULATION METHODOLOGY

4.1. Establishment of Anthracite Microcrystallite. The macromolecular model of anthracite proposed by Wender was adopted here as the porous adsorbent. As drawn in Figure 7 using Materials Studio, the anthracite structure with a chemical formula of C₄₂H₂₀O₂ mainly consists of benzene rings, aliphatic branch chains, and oxygenated functional groups. The macromolecular structure of coal is widely regarded as a kind of microcrystalline structure from amorphous to crystalline by means of X-ray diffraction (XRD). Thus, the molecular model of anthracite supercells was first put into a crystal box with a periodic boundary. The space group 1p1 was set in the box, and the lattice parameters were set as a = 16, b = 13, and c = 38 Å and the angles were α = 90°, β = 90°, and γ = 60°. In order to reserve sufficient free space for CH₄ adsorption/diffusion, the crystal lattice was cut along the plane (0, 0, −1) using the command of Cleave Surface, and then a vacuum layer was left as capillary pores in the anthracite structure. Finally, the porosity and the density of macromolecular model in simulation were essentially in agreement with those of the anthracite samples collected from Jiuilishan coal mine, Jiaozuo, China.

Under the actions of geostresses and the swelling effect in a real-occurring environment, coal molecules present a three-dimensional structure rather than a plane structure. Therefore, it is necessary to perform the molecular mechanics optimization and the annealing treatment on the plane structure of the anthracite macromolecule before the CH₄ adsorption/diffusion simulation. The molecular energy minimization was conducted by Geometry Optimization in Forcite modules of Materials Studio. Choosing the COMPASSII force field and the NVE ensemble with Smart algorithm, the
calculation accuracy was set as Fine; both Coulomb and van der Waals force were atom-Based. The allowable energy deviation and the force field interval were set at $2 \times 10^{-5}$ kcal/mol and 0.001 kcal/mol/Å, respectively, and the displacement step was $5.0 \times 10^{-5}$ Å. After the geometric optimization, the energy minimization model finally converged, and the total energy change is shown in Figure 8.

While, geometric optimization only focuses on the localized energy of the anthracite molecule, not the global energy. Consequently, annealing treatment was performed to get the lowest energy configuration on the whole potential surface by periodically increasing and decreasing the configuration temperature. The temperature ranged from 300 to 600 K using the thermostat of Nose. After five annealing optimizations, the bridge bond and functional groups in the anthracite macromolecule were twisted, causing the bonding energy reduction. Eventually, the structure with the least energy was obtained.

4.2. Simulation Processes. Isothermal adsorption simulations were performed on the optimized model of the anthracite microcrystallite via the task item of the adsorption isotherm in the Sorption module. The total step size was set to $2 \times 10^7$ steps; the range of sorption pressure was 0.01–15 MPa, and the interval was 1.6 MPa. The ambient temperatures for $CH_4$ adsorption were set at 238.15–363.15 K, respectively, to compare the differences of adsorption properties at low and high temperatures. The electric charge was automatically distributed by COMPASSII force field, the electrostatic force was calculated using the Ewald method, and the van der Waals force was atom-based. The sampling method was based on the Metropolis criterion, and the calculation accuracy was fine. The adsorption configurations were selected using fixed loading task of Locate, and other parameters were the same as those used in isothermal adsorption simulations.

Because the fugacity $f$, representing the effective pressure of $CH_4$ molecules, was the input in sorption simulations, the gas pressure should be converted into fugacity via the Peng–Robinson state equation as follows:

$$P = \frac{RT}{V_m} - \frac{a \cdot \alpha}{V_m^2 + 2bV_m + b^2}$$  \hspace{1cm} (13)

where $a = \frac{0.45724R^2T_c^2}{P}$, $b = \frac{0.07787RT_c}{P}$, $\alpha = [1 + k(1 - T_c^{0.5})]^2$, $k = 0.37464 + 1.5423w_0 - 0.2699w_0^2$, $T_c = T/T_o$, $V_m$ is the molar volume of $CH_4$, L/mol, $T_c$ is the critical temperature of $CH_4$, 190.6 K, $T_o$ is the contrast temperature, K, $P_c$ is the critical pressure of $CH_4$, 4.6 MPa, and $\omega$ is the acentric factor. The fugacity coefficient of $CH_4$ $\phi$ is expressed as

$$RT \ln \phi = \int_0^P \left( \frac{V_m}{RT} - \frac{1}{2\sqrt{\beta}bRT} \right) dP$$  \hspace{1cm} (14)

Substituting eq 14 into the state eq 13, it can be written as

$$\ln \phi = Z - 1 - \ln \frac{P(V - b)}{RT} - \frac{1}{2\sqrt{\beta}bRT} \cdot \ln \frac{V + (\sqrt{\beta} + 1)b}{V - (\sqrt{\beta} - 1)b}$$  \hspace{1cm} (15)

where $Z$ is the gas compression factor, expressed as

$$Z = (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3)$$  \hspace{1cm} (16)

in which $A = \frac{\omega \alpha P}{RT}$ and $B = \frac{\beta P}{RT}$. Therefore, the relation between the fugacity $f$ and the sorption pressure is defined as

$$f = \phi \cdot P$$  \hspace{1cm} (17)

The MD simulations were performed to simulate the diffusion of $CH_4$ molecules on the stable adsorption configuration with the lowest interaction by the Forcite-dynamics module. Because the electrostatic and van der Waals forces can hardly work when the atomic distance exceeds 12.5 Å, the cutoff value of 12.5 Å was set. The ambient temperatures of diffusion were set at 238.15–363.15 K, respectively, by employing the Nose thermostat. The diffusion results were calculated under the NVT ensemble, in which the temperature and the particle number are fixed, but the particle velocity is random. The total production time was 1000 Ps, and COMPASSII force field was also adopted. Other parameter settings were the same as those in adsorption simulations.

# AUTHOR INFORMATION

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**Author Contributions**

All authors have discussed the results and commented on the manuscript; L.W. and Y.Y. conducted the molecular simulations.

**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Moore, T. A. Coalbed methane: a review. *Int. J. Coal Geol.* 2012, 101, 36–81.
(2) Yang, J.; Wu, J.; He, T.; Li, L.; Han, D.; Wang, Z.; Wu, J. Energy gases and related carbon emissions in China. *Resour. Conserv. Recycl.* 2016, 113, 140–148.
(3) Mallick, N.; Prabu, V. Energy analysis on Coalbed Methane (CBM) coupled power systems. *J. CO2 Util.* 2017, 19, 16–27.
(4) Hamawand, I.; Talal, Y.; Sara, G. H. Coal seam gas and associated water: A review paper. *Renewable Sustainable Energy Rev.* 2013, 22, 550–560.
(5) Midgley, D. J.; Hendry, P.; Pinetown, K. L.; Fuentes, D.; Gong, S.; Mitchell, D. L.; Faiz, M. Characterisation of amicrobial community associated with a deep, coal seam methane reservoir in the Giipsbsland Basin, Australia. *Int. J. Coal Geol.* 2010, 82, 232–239.
(6) Kong, S.; Cheng, Y.; Ren, T.; Liu, H. A sequential approach to control gas for the extraction of multi-gassy coal seams from traditional gas well drainage to mining-induced stress relief. *Appl. Energy* 2014, 131, 67–78.
(7) Zhou, F.; Xia, T.; Wang, X.; Zhang, Y.; Sun, Y.; Liu, J. Recent developments in coal mine methane extraction and utilization in China: A review. *J. Nat. Gas Sci. Eng.* 2016, 31, 437–458.
(8) China State Administration of Coal Mine Safety. *Safety Regulations of Coal Mine; China Coal Industry Press:* Beijing, 2016.
(9) Ceglarška-Stefanska, S.; Žaržbska, K. The competitive sorption of CO2 and CH4 with regard to the release of methane from coal. *Fuel Process. Technol.* 2002, 77, 423–429.
(10) Saldarnejad, S. M.; John, H. D.; Kody, P. Performance comparison of low temperature and chemical absorption carbon capture processes in response to dynamic electricity demand and price profiles. *Appl. Energy* 2018, 228, 577–592.
(11) Wei, Q.; Li, X.; Zhang, J.; Hu, B.; Zhu, W.; Liang, W.; Sun, K. Full-size pore structure characterization of deep-buried coals and its impact on methane adsorption capacity: A case study of the Shihezi Formation coals from the Panji Deep Area in Huainan Coalfield, Southern North China. *J. Petrol. Sci. Eng.* 2019, 173, 975–989.
(12) Weishauptová, Z.; Píhýl, O.; Sýkorová, I.; Machovič, V. Effect of bituminous coal properties on carbon dioxide and methane highpressure sorption. *Fuel* 2015, 139, 115–124.
(13) Gensterblum, Y.; Merkel, A.; Busch, A.; Krooss, B. M. High-pressure CH4 and CO2 sorption isotherms as a function of coalmaturity and the influence of moisture. *Int. J. Coal Geol.* 2013, 118, 45–57.
(14) Zhang, X. G.; Ranjith, P. G.; Perera, M. S. A.; Ranathunga, A. S.; Haque, A. Gas transportation and enhanced coalbed methane recovery processes in deep coal seams: a review. *Energy Fuels* 2016, 30, 8832–8849.
(15) Rexer, T. F. T.; Benham, M. J.; Aplin, A. C.; Thomas, K. M. Methane adsorption on shale under simulated geological temperature and pressure conditions. *Energy Fuels* 2013, 27, 3099–3109.
(16) Lama, D.; Bodziojny, J. Outburst of Gas, Coal and Rock in Underground Coal Mines; Pennsylvania State University: Wollongong, 1996; p 499.
(17) Sakurovs, R.; Stuard, D.; Steve, G. D. Temperature dependence of sorption of gases by coals and char coals. *Int. J. Coal Geol.* 2008, 73, 250–258.
(18) Gasparik, M.; Bertier, P.; Gensterblum, Y.; Ghanizadeh, A.; Krooss, B. M.; Littke, R. Geological controls on the methane storage capacity in organic-rich shales. *Int. J. Coal Geol.* 2014, 123, 34–51.
(19) Dubinin, M. Porous structure and adsorption properties of active carbons. *Chem. Phys. Carbon* 1975, 2, 51–120.
(20) Himeno, S.; Komatsu, T.; Fujita, S. High-pressure adsorption equilibria of methane and carbon dioxide on several activated carbons. *J. Chem. Eng. Data* 2005, 50, 369–376.
(21) Giraldo, J.; Nassar, N. N.; Benjumea, P.; Pereira-Almao, P.; Cortés, F. B. Modeling and prediction of asphaltene adsorption isotherms using Polanyi’s modified theory. *Energy Fuels* 2015, 29, 2908–2914.
(22) Wang, K.; Wang, G.; Ren, T.; Cheng, Y. Methane and CO2 sorption hysteresis on coal: A critical review. *Int. J. Coal Geol.* 2014, 132, 60–80.
(23) Nguyen, P. T. M.; Do, D. D.; Nicholson, D. Pore connectivity and hysteresis in gas adsorption: A simple three-pore model. *Colloids Surf., A* 2013, 457, 56–68.
(24) Nandi, S. P.; Walker, P. L. Activated diffusion of methane in coal. *Fuel* 1970, 49, 309–323.
(25) Nandi, S. P.; Walker, P. L. Activated diffusion of methane from coals at elevated pressures. *Fuel* 1975, 54, 81–86.
(26) Liu, Y.; Wei, J.; He, Z.; Liu, M. Influence rules and mechanisms of temperature on dynamic process of gas diffusion from coal particles. *J. China Coal Soc.* 2013, 38, 100–105.
(27) Nie, B.; Guo, Y.; Wu, S.; Zhang, L. Theoretical model of gas diffusion through coal particles and its analytical solution. *J. China Univ. Min. Technol.* 2001, 30, 19–22.
(28) Nie, B.; Yang, T.; Li, X.; Li, L.; Lu, H. Research on diffusion of methane in coal particles. *J. China Univ. Min. Technol.* 2013, 42, 975–981.
(29) Wang, Z.; Tang, X.; Yue, G.; Kang, B.; Xie, C.; Li, X. Physical simulation of temperature influence on methane sorption and kinetics in coal: Benefits of temperature under 273.15 K. *Fuel* 2015, 158, 207–216.
(30) Tang, X.; Wang, Z.; Ripepi, N.; Kang, B.; Yue, G. Adsorption affinity of different types of coal: mean isosteric heat of adsorption. *Energy Fuels* 2015, 29, 3609–3615.
(31) Yue, G.; Wang, Z.; Tang, X.; Li, H.; Xie, C. Physical Simulation of Temperature Influence on Methane Sorption and Kinetics in Coal (II): Temperature Evolvement during Methane Adsorption in Coal Measurement and Modeling. *Energy Fuels* 2015, 29, 6555–6562.
(32) Wang, L.; Wang, Z.; Qiu, C.; Ma, S.; Yue, J. Physical simulation of temperature and pressure evolvement in coal by different refrigeration modes for freezing coring. *ACS Omega* 2019, 4, 20178–20187.
(33) Yue, J.; Yue, G.; Wang, Z.; Li, M.; Wang, B.; An, F. Freezing method for rock cross-cut coal uncovering I: Mechanical properties of a frozen coal seam for preventing outburst. *Sci. Rep.* 2019, 9, 16397.
E. M.; Pulin, A. L.; Khozina, E. V. Monolithic microporous carbon interactions and oxygen functionalities. ACS Omega http://pubs.acs.org/journal/acsodf 1997 adsorption isotherms at elevated temperature and pressure. 2012 Coal Geol. Int. J. Energy Fuels Chem. Eng. J. polymers. evidence for anomalous diffusion of small molecules in amorphous CH4 onto coal vitrinite macromolecular: Effects of electrostatic maturity and the influence of moisture. 141 methane in coal. 2939 potential impact of CO2 injection into coal matrix in molecular terms. Potential approximations used in determining the isosteric heat of adsorption CH4 and CO2 sorption isotherms as a function of coal and transport diffusion for CO2/CH4/N2 in low-rank coal vitrinite. 52 Clarkson, C. R.; Bustin, R. M.; Levy, J. H. Application of the Clausius-Clapeyron equation. 501, 126071. 51 Liu, Z.; Feng, Z. C. Theoretical study on adsorption heat of shale organic matter. 235, 23−38. 34 Shkolin, A. V.; Fomkin, A. A.; Men’shchikov, I. E.; Strizhenov, E. M.; Pulin, A. L.; Khozina, E. V. Monolithic microporous carbon adsorbent for low-temperature natural gas storage. Adsorption 2019, 25, 1559−1573. 35 Hu, H.; Li, X.; Fang, Z.; Wei, N.; Li, Q. Small-molecule gas sorption and diffusion in coal: Molecular simulation. Energy 2010, 35, 2939−2944. 36 Sui, H.; Yao, J. Effect of surface chemistry for CH4 /CO2 adsorption in kerogen: A molecular simulation study. J. Nat. Gas Sci. Eng. 2016, 31, 738−746. 37 Yu, S.; Jiang, B.; Qu, M. Molecular dynamic simulation of self- and transport diffusion for CO2/CH4/N2 in low-rank coal vitrinite. Energy Fuels 2018, 32, 3085−3096. 38 Yu, S.; Jiang, B.; Lan, F. Competitive adsorption of CO2/N2/CH4 onto coal vitrinite macromolecular: Effects of electrostatic interactions and oxygen functionalities. Fuel 2019, 235, 23−38. 39 Zhang, J.; Clennell, M. B.; Dewhurst, D. N.; Liu, K. Combined Monte Carlo and molecular dynamics simulation of methane adsorption on dry and moist coal. Fuel 2014, 122, 186−197. 40 Li, S.; Song, K.; Zhao, D.; Rugarabamu, J. R.; Diao, R.; Gu, Y. Molecular simulation of benzene adsorption on different activated carbon under different temperatures. Microporous Mesoporous Mater. 2020, 302, 110220. 41 Turrini, C.; Visintainer, P.; Khomyakova, B.; Petrova, V.; Adam, N. Sorption and desorption of gases (CH4, CO2) on hard coal and active carbon at elevated pressures. Fuel 1998, 77, 1243−1246. 42 Polanyi, M. The potential theory of adsorption. Science 1963, 141, 1010−1013. 43 Liu, Z.; Feng, Z. C. Theoretical study on adsorption heat of methane in coal. J. China Coal Soc. 2012, 37, 647−653. 44 Yang, Y.; Pan, J.; Wang, K.; Hou, Q. Macromolecular structural response of Wender coal under tensile stress via molecular dynamics. Fuel 2020, 265, 116938. 45 Charoeasunpunimit, P.; Mohammad, S. A.; Robinson, R. L.; Gasem, K. A. M. High-pressure adsorption of gases on shales: Measurements and modeling. Int. J. Coal Geol. 2012, 95, 34−46. 46 Pan, J.; Lv, M.; Hou, Q.; Han, Y.; Wang, K. Coal microcrystalline structural changes related to methane adsorption/ desorption. Fuel 2019, 239, 13−23. 47 Chen, L.; Zuo, L.; Jiang, Z.; Jiang, S.; Liu, K.; Tan, J.; Zhang, L. Mechanisms of shale gas adsorption: Evidence from thermodynamics and kinetics study of methane adsorption on shale. Chem. Eng. J. 2019, 361, 559−570. 48 Gensterblum, Y.; Merkel, A.; Busch, A.; Krooss, B. M. High-pressure CH4 and CO2 sorption isotherms as a function of coal maturity and the influence of moisture. Int. J. Coal Geol. 2013, 118, 45−57. 49 Jhon, Y. H.; Cho, M.; Jeon, H. R.; Park, I.; Chang, R.; Rownell, J. L.; Kim, J. Simulations of methane adsorption and diffusion within aky-functionionalized imrof exhibiting severely disordered crystal structures. J. Phys. Chem. C 2007, 111, 16618−16625. 50 Pan, H.; Ritter, J. A.; Balbuena, P. B. Examination of the approximations used in determining the isosteric heat of adsorption from the Clausius-Clapeyron equation. Langmuir 1998, 14, 6323−6327. 51 Liu, Y.; Wilcox, J. Molecular simulation of CO2 adsorption in micro- and mesoporous carbons with surface heterogeneity. Int. J. Coal Geol. 2012, 104, 83−95. 52 Clarkson, C. R.; Bustin, R. M.; Levy, J. H. Application of the mono/multilayer and adsorption potential theories to coal methane adsorption isotherms at elevated temperature and pressure. Carbon 1997, 35, 1689−1705. 53 Wang, K.; Pan, J.; Wang, E.; Hou, Q.; Yang, Y.; Wang, X. Potential impact of CO2 injection into coal matrix in molecular terms. Chem. Eng. J. 2020, 401, 126071. 54 Müller-Plathe, F.; Rogers, S. C.; Gunsteren, V. Computational evidence for anomalous diffusion of small molecules in amorphous polymers. Chem. Phys. Lett. 1992, 199, 237−240.