Molecular dynamic simulations of selective self-diffusion of CH₄/CO₂/H₂O/N₂ in coal

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Abstract. The self-diffusion coefficients ($D$) of CH₄/CO₂/H₂O/N₂ at a relatively broad range of temperatures (298.15–458.15 K) and pressures (1–6 MPa) under the NPT, NPH, NVE, and NVT ensembles were obtained after the calculations of molecular mechanics (MM), annealing kinetics (AK), giant canonical Monte Carlo (GCMC), and molecular dynamics (MD) based on Wiser bituminous coal model (WM). The $D$s of the adsorbates at the saturated adsorption configurations are $D_{\text{CH}_4}<D_{\text{CO}_2}<D_{\text{H}_2\text{O}}<D_{\text{N}_2}$ (NPT, 298.15 K, 0.1 MPa). The diffusion activation energy ($E$) is $E_{\text{H}_2\text{O}}$ (1.07 kJ/mol) $<E_{\text{N}_2}$ (1.82 kJ/mol) $<E_{\text{CO}_2}$ (2.94 kJ/mol) $<E_{\text{CH}_4}$ (10.88 kJ/mol), indicating that CH₄ diffusion requires to overcome the highest adsorption energy barrier and N₂ and H₂O to the lowest. The order of different ensembles is $D_{\text{N}_2}$ (NVE) $<D_{\text{N}_2}$ (NVT) $\approx D_{\text{N}_2}$ (NPH) $\approx D_{\text{N}_2}$ (NPT) ($T<418 K$) and $D_{\text{N}_2}$ (NVE) is remarkably higher than other ensembles when $T>418 K$. The average swelling ratios manifest as H₂O (14.7–35.18%) $>\text{CO}_2$ (13.38–32.25%) $>\text{CH}_4$ (15.35–23.71%) $>\text{N}_2$ (11.47–22.14%) (NPH, 1–6 MPa). There exits differences in $D$, swelling ratios and $E$ among various ensembles, indicating that the selection of ensembles has an important influence on the MD calculations for self-diffusion coefficients.

Keywords: Molecular dynamic; Selective self-Diffusion; CH₄/CO₂/H₂O/N₂; Wiser model

1. Introduction
Mainly existing as adsorption state, coalbed methane (CBM) is first desorbed from the micro-pores surface [1-2] then diffuses to the macro-pore and fracture systems. Finally, CBM enter the gas phases. The yields of the CBM well are determined by the micro-pore diffusion ability of the main components [3]. The investigations on the self-diffusion characteristics of CBM main components (CH₄/H₂O) and driving gases (CO₂/N₂) are the basis to reveal mass transport diffusion coefficients and Fick diffusion coefficients, which is of significant practical and theoretical importance in CBM development and CO₂ storage.

The investigations on organic–inorganic nanocomposites and the microscopic interactions are of great importance for advanced materials exploration [4]. Due to the remarkable electrical and magnetic properties, organic nanoparticles have received an increasing interest in the literature, which open a great potential for both fundamental and application device [5-6]. As a porous composite, coal has nano-pores in are multiscale ranging from millimeter to angstrom. In nano-pores of >15 nm and
2~15nm, the diffusion types are dominant by Fick diffusion and transitional diffusion respectively. Knudsen diffusion is significant in micro-pores of 1.2~2.0nm [7]. Suffered from strong adsorption affinity in molecule scale micro-pores, gas mainly exists as adsorbed phase and only surface diffusions of adsorption phase and solid solution diffusions occur [8-9], which obeys the molecular sieve principles and controlled by geometric shapes of adsorbates, as well as the micro-pore structures of adsorbents. The self-diffusion coefficients of gases in coal macro-molecule can be obtained through molecule simulation. Hu et al. [10] simulated the adsorption and diffusion of CH$_4$ and CO$_2$ in coal by GCMD and molecule dynamic (MD) and the results show that CH$_4$ has higher diffusion velocities and lower saturated adsorption capacities than CO$_2$ at the same temperature. Based on Wiser model and Einstein equation, Zhao et al. [11] investigated the self- and transport-diffusion characteristics of CO$_2$/CH$_4$ in coal under NPT ensemble and demonstrated that the simulated self- and transport-diffusion coefficients are both consistent with the experimental results based on GCMD and MD, indicating that the self-diffusion coefficients can effectively characterize the diffusion characteristics of CO$_2$/CH$_4$ in micro-pores of coal. Xiang et al. [8] calculated the self-diffusion coefficients of CO$_2$/CH$_4$/H$_2$O in Yanzhou coal based on the isothermal absorption curves of ternary mixtures (CO$_2$:CH$_4$:H$_2$O=1:1:1) coupled with Einstein equation under NVT ensemble and revealed that the self-diffusion coefficients of CO$_2$, CH$_4$, and H$_2$O are 3.35×10$^{-12}$, 1.42×10$^{-11}$ and 1.86×10$^{-11}$m$^2$s$^{-1}$ respectively at 298.15K. Nierkerk et al. [12] studied the non-bonding’s key roles in the swelling mechanisms between coal and pyridine, methyl pyrrole and CS$_2$/NMP solvents through MD. Hu et al. [13] analyzed diffusion coefficients of one-component in CO$_2$-CH$_4$ mixture based on MD calculations and pointed that the self-diffusion coefficients of CO$_2$ and CH$_4$ decrease with gas concentration but increase with temperature (268~428K).

The apparent diffusion coefficients of gases in coal can also be obtained through experiments. Cai et al. [14] analyzed the effects of nano-pore structures on adsorptions and diffusions of adsorbates based on high-pressure mercury intrusion and low-pressure liquid nitrogen adsorption. Dutka et al. [15] investigated the replacement processes of CO$_2$ for CH$_4$ at the CH$_4$’s saturated adsorption states based on the experiment methods and acquired the replacement rates at the various pressures. Coupled with low-pressure liquid nitrogen adsorption and isothermal adsorption experiments, Ji et al. [16] extracted the small organic molecule from coal by microwave-assisted method and studied the effects of small organic molecules on gas diffusions in coal. Saghafi et al. [9] applied the newly self-developed instruments to explore the self-diffusion coefficients of CO$_2$ (1.18×10$^{-10}$~10.2×10$^{-10}$m$^2$s$^{-1}$) and CH$_4$ (1.23~4.88×10$^{-10}$m$^2$s$^{-1}$) in Sydney basin coal ($R_{o_{max}}$=0.66~1.45%). Staib et al. [17] analyzed the effects of pressures and concentrations on CO$_2$’s diffusions in Australia bituminous coal through the experimental kinetic adsorption data based on unipore, bidisperse, and Fickian diffusion-relaxation model (FDR). By gravimetric experimental, Delphine et al. [18] reported the adsorption kinetics of CO$_2$ and CH$_4$(0.1~5MPa, 283.15~333.15K)and demonstrated that the diffusion coefficient was estimated at about 10$^{-12}$ m$^2$s$^{-1}$ and the activation energy of CO$_2$ adsorption was about 18 kJ mol$^{-1}$ compared with CH$_4$ (34 kJ mol$^{-1}$).

As mentioned above, domestic and overseas studies on gases diffusion in coal are mainly concentrated on certain single ensemble during molecule simulations. The effects of various ensembles on the self-diffusion coefficients of CH$_4$/H$_2$O/CO$_2$/N$_2$ in coal at a relatively broad temperatures and pressures have minimally been reported. Actually, self-diffusions are originated from the atoms’ incessant generation and recombination caused by the vacancies and clearances among atoms in the crystal. Hence, self-diffusions are born in the randomized Brownian motions from one location/site to another, which is independent of the concentration gradient and promoted by the thermal vibration generated from the migration of atoms. Therefore, the self-diffusion coefficients are the basis to investigate the mass transport/Fick diffusion coefficients [11], [13]. As the thermal motions are significantly affected by the temperature, pressure and enthalpy and each system in the ensemble have the identical structures and macro-restrictions, thus the self-diffusion coefficients of CH$_4$/H$_2$O/CO$_2$/N$_2$ in coal should be influenced by the identical structures and macro-restrictions in different ensembles. Micro-canonical ensemble (NVE) ensemble is an isolated conservative statistical ensemble, in which the atom number
(N), pore volume (V) and energy (E) all stay constant during molecule simulation. Canonical ensemble (NVT) ensemble is in thermal equilibrium condition with the virtual caldarium and has the constant N, V and temperature (T). Isothermal-isobaric ensemble (NPT) is similar to NVT ensemble in the constant temperature method and implemented by regulating the velocity or constrained force of the systems. Because of \( H = E + PV \), the pressure and enthalpy in constant pressure and enthalpy (NPH) ensemble maintain constant during the molecule simulation. Hence, the self-diffusion coefficients of CH\textsubscript{4}/H\textsubscript{2}O/CO\textsubscript{2}/N\textsubscript{2} in various ensembles should exit differences and the analysis on these differences is the basis to further understand the diffusion mechanisms and tp accurately conduct the molecular simulation.

Therefore, the energy-optimized configuration were obtained through molecule mechanics (MM), MD to optimize the geometric configuration and annealing kinetics (AK) to overcome the molecular structure energy barrier based on WM model in periodic boundary conditions (PBC). Then the saturated adsorption configurations of WM for CH\textsubscript{4}/H\textsubscript{2}O/CO\textsubscript{2}/N\textsubscript{2} were calculated through GCMC. Finally the self-diffusion coefficients of CH\textsubscript{4}/CO\textsubscript{2}/H\textsubscript{2}O/N\textsubscript{2} in WM were computed through MM and MD under NPT, NPH, NVE and NVT ensembles respectively. Coupled with slit-shape pore models, Steele potential function, and cavity theory, the diffusion mechanisms of CH\textsubscript{4}/CO\textsubscript{2}/H\textsubscript{2}O/N\textsubscript{2} in WM and the effects of temperature (298–458K) and pressures (1–6MPa) were revealed in NPT and NPH ensembles, as well as the corresponding diffusion activation energy (E). The study is of significant practical and theoretical importance for comprehensive and profound recognitions on efficiently promoting the CBM recovery, as well as perfecting CO\textsubscript{2}-ECBM theory, and developing the geological disposal technologies of CO\textsubscript{2} in deep un-minable coalbeds [19-20].

2. Model and calculation methods

2.1. Calculation methods and parameter settings

2.1.1. MM and MDs. The charge distributions of the molecular force field were obtained through the charge equilibrium method in MM and MD calculation in Materials studio8.0 [11], [21]. The \( E_{\text{van der Waals}} \) and \( E_{\text{electrostatic}} \) were calculated based on the atom base method with a cut off distance of 12.5 Å and an initial charge of 0 (Convergence:5.0e-4) in the dreiding force field. The parameters of MM were set as follows: smart minimizer method iterative steps, 50000; RMS force standard, 0.1 kcal/mol·Å; and energy difference, 0.001 kcal/mol. MD were run in a NPT ensemble with the following parameters: initial velocities, random; temperature, 298K; pressure, 0.1 MPa; time; 0.1fs; total simulation time, 2000 ps; number of steps, 50000; thermostat, nose; barostat, Berendsen; and energy deviation, 50000.0 kcal/mol.

Three-dimensional PBCs and relaxations were applied to ensure the energy minimization and geometry optimization of the WM and CH\textsubscript{4}/H\textsubscript{2}O/CO\textsubscript{2}/N\textsubscript{2}. Then, MD calculations of 1500 ps were conducted under NPT, NPH, NVE, and NVT ensembles to reach the thermodynamic equilibrium states. The atoms’ initial velocities were randomly given according to the Boltzmann distribution. The temperatures and pressures were controlled through the Nose [22] and Berendsen methods in a dreiding force field [23]. The effects of various ensembles, gas species, temperatures and pressures on gas diffusion activities are discussed based on the simulated results.

2.1.2 Self-diffusions. The mean square displacement (MSD) is the deviation degree of the spatial position at \( t \) from the initial position at \( t=0 \). As a result of the special chemistry environment created by the abundance of aliphatic side chains and surface oxygen-containing functional groups in WM, the porosity zigzag factors of diffusion particles would be changed, resulting in the delayed diffusion of the particles due to their adaptation to pore morphology [21], [24]. Hence, the abnormal diffusion existed before the self-diffusion of CH\textsubscript{4}/CO\textsubscript{2}/H\textsubscript{2}O/N\textsubscript{2} on the surface of WM. When the anomalous diffusion occurs [7-8], [25]:
where $t$ is the time from 0 to the anomalous diffusion, ps; $r(t)$ is Cartesian coordinate tensor of gas molecules at $t$ moment, Å; and $m$ is the fitting constants, $m=1,2$ (Einstein diffusion).

When Einstein diffusion occurs, it follows Einstein’s diffusion law [26]. The diffusion coefficient of the adsorbate is proportional to the MSD of the mass centre of the diffusion particles. The equation is:

$$D=\frac{m}{6k_\text{B}}\sum_{i=1}^{10}\left[(z+\delta)_{i}\right]^{1}$$

where $N$ is the number of diffusion particles.

The adsorbates diffusing are an activation process. According to the Arrhenius equation, the reaction rate constants have an exponential relationship with the activation energy ($E$):

$$k=Ae^{-\frac{E}{RT}}$$

where $A$ is the pre-exponential factor, $s^{-1}$; $E$ is the apparent activation energy of the reactants, kJ/mol; $R$ is the universal gas constant, 8.314 J/(mol·K); and $T$ is the reaction temperature, K.

The adsorption pores are constituted by micro-pores (<2 nm) and ultra-micro-pores (<1 nm). The mass transfer of CH$_4$/CO$_2$/H$_2$O/N$_2$ in nanopores contains two stages: (1) continuous diffusion or viscous flow, caused by the collision among the adsorbates; (2) the migration in micro-pores [7], dominated by the adsorption forces (dispersion force and induced force) and Knudsen diffusion, resulting from the collision and surface diffusion between adsorption layers, and configurational diffusion in the ultra-micro-pores. For the slit-shape pores (Figure 1), when the pore width is $L$, the distance between the adsorbate molecule and pore well is $z$. Then, the potential can be calculated through the Steele 10-4-3 potential function [27]:

$$\phi(z)=\psi(z)+\psi(L-z)\quad (0<z<L)$$

$$\psi(z)=4\phi_{\text{atom}}\epsilon_{\text{eff}}\sigma_{\text{eff}}^{3}\left[\frac{\sigma_{\text{eff}}^{6}}{8z^{6}}+\frac{1}{2}\sum_{i}^{10}\frac{\sigma_{\text{eff}}^{6}}{[z+(i-1)\sigma_{\text{eff}}]^{6}}\right]$$

where $\epsilon_{\text{eff}}=\epsilon_{\text{gg}}\epsilon_{\text{ss}}^{0.5}$, $\sigma_{\text{eff}}=(\sigma_{\text{gg}}+\sigma_{\text{ss}})/2$, and $\rho_{\text{atom}}$ is the number of molecules per unit lattice, 114 nm$^{-3}$; $\sigma_{\text{gg}}$ and $\sigma_{\text{ss}}$ are the effective distances of adsorbate and adsorbent, respectively, 0.375, 0.335 nm for CH$_4$, 0.330, 0.400 nm for CO$_2$, and 0.364, 0.368 nm for N$_2$; $\epsilon_{\text{gg}}$ is the well depth of cross potential and $k$ is the Boltzmann constant, 1.381×10-23 J/K; $\epsilon_{\text{gg}}/k$ and $\epsilon_{\text{ss}}/k$ are 148.1 and 24.0 K, respectively, for CH$_4$; and $(\epsilon_{\text{gg}},\epsilon_{\text{ss}})$ and $(\sigma_{\text{gg}},\sigma_{\text{ss}})$ are the characteristic parameters of the Lorentz-Jones potential between C and CH4/N2/CO2 on the coal matrix surface.

2.2. Coal molecule model

Mathews et al. [24], [28] conducted comprehensive reviews on domestic and overseas coal molecule models and revealed that at least 134 molecular level coal models, ranging from low to high rank coals, have been put forward between 1942 and 2012, such as the Wender lignite and brown coals models [29], the Given bituminous model [30], the Shinn subbituminous model [31], the Wiser bituminous model [32] and Vishnyakov anthracite model [33]. Wiser bituminous model can reflect the modern concepts of coal model [21], [28]; thus, this article adopts the Wiser model (Figure 2a). Figure 2b
shows the final stable Wiser bituminous model after MM, MD and AK calculations, whose corresponding lattice parameters are $a=b=c=15.4$ Å and $\alpha=\beta=\gamma=90^\circ$. As the optimization process goes on, the energy change and energy gradient both decrease with the increasing optimization steps (Figure 3a), indicating that the energy compositions of WM gradually tended to be stable. $E_{\text{total energy}}$ (720.898 kcal/mol) was dominated by $E_{\text{non-bond}}$ (393.609 kcal/mol, $E_{\text{van der Waals}}=393.752$ kcal/mol). $E_{\text{Valence}}$ (327.290 kcal/mol) mainly consisted of $E_{\text{angle}}$ (132.089 kcal/mol) and $E_{\text{inversion}}$ (111.133 kcal/mol). The energy composition indicates that $E_{\text{van der Waals}}$ has an important role on structural stability under PBCs. The increase of $E_{\text{angle}}$ and $E_{\text{inversion}}$ reveal the increases of the crooked degrees in the final structure (Figure 3b, Table 1). Belonging to ultra-micropores, the average pore diameter of WM is 0.5 nm. The microporous porosity is 9.7%, which is within the scope of 6%~14% reported by Brochard et al [34]. The flow chart illustrating the molecule model and diffusion coefficient calculation method is shown in Figure 3c.

**Figure 2.** WM plane structure (a) and the optimal configuration (b).

**Figure 3.** Energy change during the optimization process (a), energy composition of the optimal configuration (b), and flow chart illustrating the molecule model and diffusion coefficient calculation method (c).
Table 1. Energy composition after optimization.

| Total energy (kcal/mol) | 720.898 |
|-------------------------|---------|
| $E_{\text{valence}}$  | 327.29  |
| $E_{\text{Bond}}$     | 81.904  |
| $E_{\text{Angle}}$    | 132.089 |
| $E_{\text{Torsion}}$  | 111.133 |
| $E_{\text{Inversion}}$| 2.164   |
| $E_{\text{Non-bond}}$ | 393.609 |
| $E_{\text{Hydrogen bond}}$ | -0.144 |
| $E_{\text{van der Waals}}$ | 393.752 |
| $E_{\text{Electrostatic}}$ | 0       |

GCMC is applicable to the microscopic particle adsorption simulations of fixed chemical potential and variable particle number. Hence, it is a powerful tool for analysing the adsorption characteristics and mechanisms of porous materials [8], [11]. GCMC simulation was conducted using 5 optimal configurations as adsorbents under PBCs (Figure 3b). The calculation of saturated adsorption capacity was calculated using an isotherm adsorption task in a dreiding force field. The potential constitution of a dreiding force field is as follows [35]:

$$E_{\text{total}} = E_{\text{valence energy}} + E_{\text{non-bond energy}}$$  \hspace{1cm} (6)

$$E_{\text{valence energy}} = E_{\text{Bond}} + E_{\text{Angle}} + E_{\text{Torsion}} + E_{\text{Inversion}}$$ \hspace{1cm} (7)

$$E_{\text{non-bond energy}} = E_{\text{van der Waals}} + E_{\text{Electrostatic}} + E_{\text{Hydrogen bond}}$$ \hspace{1cm} (8)

The simulated temperature and pressure were set at 298~458K (temperature interval: 10K) and 1~6 MPa, respectively. The initial configuration was the lowest energy of the WM stereoscopic model after MM, MD and AK optimizations. Then, and thereafter, each configuration was determined by the energy change, based on the Metropolis rules [36], to accept or reject the generation, disappearance, translation and rotation of an adsorbate, which ensured the adsorption compound in the lowest energy state and the then output of the new configuration. The convergence criterion was $5 \times 10^{-4}$. The Ewald sum method was used for electrostatic action, with a precision of $4.186 \times 10^{-3}$kJ/mol. To ensure the balance of the system, $2 \times 10^7$ GCMC steps were adopted. The former $10^7$ steps were used to reach the balance state and the latter $10^7$ steps were to calculate the statistical averages. The final result was the average of three parallel run processes, with a variation coefficient of less than 0.01.

In the process of gradually increasing the adsorbate, the $E_{\text{Bond}}, E_{\text{Angle}}, E_{\text{Torsion}}$ and $E_{\text{Inversion}}$ of the adsorption complex was 0 and released heat, resulting in the gradual decreasing of $E_{\text{non-bond}}$. $E_{\text{non-bond}}$ decreased to a minimum and then gradually increased with the increasing of the adsorbates, indicating the adsorbate was no longer absorbed and begun to repel. The adsorption numbers of the adsorbates at the lowest $E_{\text{total}}$ was the saturation adsorption capacity per WM. Finally, they reached saturated states after absorbing 30 CH$_4$s, 42 CO$_2$s, 56 H$_2$Os, and 17 N$_2$s per 5 WMs. The saturated adsorption configurations are shown in Figure 4a–d. The difference in the adsorbate molecules numbers indicates that the adsorption capacity of coal for different gases is: H$_2$O> CO$_2$> CH$_4$> N$_2$. Taking the saturated adsorption configurations as the initial structures, the MD for 1500ps was computed.
3. Results and discussions

3.1. Simulation reliability demonstration
To approach the Einstein diffusions, the MD conclusions were conducted for quite a long time (1500 ps), until reaching the linear region of MSD vs $t$ curves to ensure the kinetic equilibrium of the WM-adsorbate systems, based on the saturated adsorption configurations. The abnormal diffusion and Einstein diffusion are characterized by slopes of 0.5 and 1, respectively, in the final\[\text{log}(\text{MSD})\sim\text{log}(t)\] curves [10-11].

As is shown in Figure 5a~d, the required times to reach the Einstein diffusion of the adsorbates manifests as $t_{\text{CO}_2}(200\text{ ps})<t_{\text{N}_2}(250\text{ ps})<t_{\text{H}_2\text{O}}(600\text{ ps})<t_{\text{CH}_4}(650\text{ ps})$ at 298.15K and 0.1 MPa under the NPT ensemble. The self-diffusion coefficients of CH$_4$, CO$_2$, H$_2$O, and N$_2$ were further obtained through equation (2), and the order is $D_{\text{CH}_4}(4.7*10^{-9}\text{ m}^2/\text{s})<D_{\text{CO}_2}(6.9*10^{-9}\text{ m}^2/\text{s})<D_{\text{H}_2\text{O}}(14*10^{-10}\text{ m}^2/\text{s})<D_{\text{N}_2}(1.8*10^{-10}\text{ m}^2/\text{s})$ at 298.15K. Hu et al. [13] calculated the self-diffusion coefficients of CH$_4$ and CO$_2$ based on the MD methods and $D_{\text{CO}_2}(2.51*10^{-10})$ and $D_{\text{CH}_4}(2.41*10^{-10}\text{ m}^2\text{ s}^{-1})$ are both slightly higher than the values obtained in this paper at the same temperature. The reasons for the lower self-diffusion coefficients are that Hu investigated mixture systems (25 CO$_2$ and 25 CH$_4$ molecules) in unsaturated configurations. Saghafi et al. [9] investigated the diffusion coefficients of CH$_4$ (1.23–4.88×10$^{-10}$ m$^2$s$^{-1}$) and CO$_2$ (1.18×10$^{-10}$–10.2×10$^{-10}$ m$^2$s$^{-1}$) in coal ($R_{\text{min}}=0.66–1.45\%$) from the Sydney basin, New South Wales, Australia, based on a gravimetric method and the results are close to the diffusion coefficients in this paper, indicating the rationality of the model and method in this paper. Xiang et al. [8] analysed the isothermal adsorption curves and self-diffusion coefficients of CO$_2$, CH$_4$, CO$_2$, H$_2$O, and N$_2$.
and H₂O in coal (C₂₂₂H₁₈₈N₂₀₁₇S₅, Rₑₐₓₐₜ=0.60%) at 298.15K under the NVT ensemble. The similar results of $D_{CH₄}(3.35\times10^{-12}$ m²/s)$<D_{CO₂}(1.42\times10^{-11}$ m²/s)$<D_{H₂O}(1.86\times10^{-11}$ m²/s) was obtained.

![Graphs showing Log(MSD) vs log(t) for CH₄, H₂O, CO₂, and N₂](image)

**Figure 5.** Log(MSD)–log(t) curves of CH₄(a), H₂O(b), CO₂(c) and N₂(d).

3.2. Self-diffusion mechanisms

The distributions of the interaction potentials between CH₄/CO₂/N2 and pore wells in micro- and ultra- micro-pores in WM are shown in Figure 6a, b, as well as the lowest potential energy distribution (Figure 6c). Figure 6a and Figure 6b shows a normalized pore wall in WM macromolecule interaction potential along the dimensionless distance from the pore center. When the pore half width is larger than 0.7 nm, enhancement of the negative potential in the center of the pore begins and a double minimum of the potential develops near the two pore walls. This gives the onset of the overlapping of the potential fields of the opposing walls. Strong enhancement of potential minimum begins when the pore half width is lower than 0.7 nm and larger than 0.5 nm. The double minimum is replaced by a single minimum in the pore. The potential reaches its negative minimum at pore center. Further decrease of the pore width causes a significant positive increase of the potential and the potential becomes positive when the pore half width is lower than 0.5 nm and larger than 0.2 nm.

For CH₄, when $L≥1.5$ nm, the maximum $Φ$ at $z=0$ is larger than 0, indicating that CH₄ in the pore centre are not affected by the potential energy field of the pore walls. The diffusions are dominant by the gas phases’ Knudsen diffusions and adsorbed phases’ surface diffusions [37]. When 0.7 nm<$L≤1.5$ nm, the maximum $Φ$ at the $z=0$ is negative, and there exist two lowest points, which are higher than the adsorption surface free energy. The energy required to desorb CH₄ from the adsorption sites to the gas’s phases of the pore centre decreases with decreasing $L$. The corresponding diffusive types are activation desorption and Knudsen diffusion along the pore centre in these pores [38]. When 0.5 nm<$L≤0.7$ nm, there exists only one negative maximum value at $z=0$, and the corresponding adsorption potential is the lowest. In these pores, the adsorption phases do not exist and the configuration
diffusion dominates, which needs to overcome the adsorption energy barrier. In pores of 0.2 nm ≤ L ≤ 0.5 nm, the adsorption potential increases and becomes positive. The adsorption potential minimums locate at z=0 and other locations are repulsive forces, indicating that it is difficult for CH4 to enter pores of 0.2 nm ≤ L ≤ 0.5 nm (Figure 6a, b).

The lowest potentials at different diameters in Figure 6a, b were extracted and the adsorption potential distributions of CH4/CO2/N2 were obtained. As is shown in Figure 5c, CH4, CO2, and N2 have highest adsorption energy at the pore widths of 0.72, 0.67, and 0.65 nm, respectively, half of which are equal to the gases’ diameters, indicating that pores with a half-width (radius) close to the adsorbates’ diameters are the most beneficial to adsorption. The optimum aperture of CH4 in the Steele potential analysis are close to the adsorption equilibrium distances (3.6~4.0 Å) in our previous work of molecular simulation of CH4 absorbing on coal vitrinite [35]. Shieh et al. [39] considered that the aerodynamic diameters of CH4/CO2/N2 are close to their respective molecular sieve dimensions and are critical for gas diffusion in porous media through investigations on the gases’ permeability, diffusivity and solubility in poly (4-vinylpyridine). The adsorption potential order manifests as CO2 (24.28 kJ/mol)>CH4 (22.26kJ/mol)>N2 (17.27kJ/mol), indicating that the adsorption affinity of coal-CO2 is the strongest, and second strongest for CH4. The highest adsorption potentials are about two times larger than those in pores >1.5 nm for CH4, CO2, and H2O (CH4: 11.28kJ/mol; CO2: 12.42kJ/mol; N2: 8.79kJ/mol).

CH4, CO2 and N2 cannot enter pores with widths <0.56 nm, and CO2 and N2 can enter pores <0.62 nm, indicating that the minimum pore widths that can be entered by CO2 and N2 are lower than that of CH4. From the above analysis, the diffusions of gases in micro-pores are controlled by the adsorption energy and the molecular dynamics diameters. CO2 a has larger adsorption energy and lower aerodynamic diameter, therefore it is easier to diffuse in micro-pores, followed by N2, meanwhile indicating that differences exist for various gas types in pore tortuosity factors due to the different diameters. The larger the gas diameter, the higher the pore tortuosity factors, which was also revealed in polymer (4-vinylpyridine) and other porous medias [39]. The adsorption potential of CH4 is higher than CO2 only in pores of 0.72~0.91 nm, which may be attributed to limitations of the 10-4-1 model. In addition, the adsorption force of CO2 is larger than CH4 and N2 in almost all of the microporous segments, and has the lowest aerodynamic diameter. Hence, CO2 can enter smaller micro-pores than CH4, leading to advantages in the competitive adsorption and selective self-diffusion among the main components of CBM.

The cell volume of coal molecule is constituted by the occupied volumes and free volumes. The size and shape of the free volumes have a significant effect on the adsorbates’ diffusion activities in coal macro-molecules, which provide both the necessary activity spaces of coal macro-molecules and the diffusion spaces of the adsorbates. Gas molecules are constantly moving in the coal molecules. The magnitude of the displacement is small and can be regarded as vibration in most cases. Occasionally, a big jump to another area such as a cavity, to continue small amplitude vibrations occurs. When small gas molecules vibrate to a certain site where the coal macromolecular structure is or has been twisting or rotating, then small gas molecules may jump to the neighboring cavities and continue vibrating in the cavities. Figure 7a–d show the diffusion trajectories and displacement -t curves of CH4/CO2/H2O/N2 in coal from the initial position(x0, y0, z0)=(0, 0, 0)at 298.15K and 0.1 MPa under an NPT ensemble.
The aerodynamic equivalent diameters ($\sigma$) of CH$_4$, CO$_2$, H$_2$O, and N$_2$ manifest as $\sigma_{CO_2}$ (0.33)$<\sigma_{H_2O}$ (0.35)$<\sigma_{N_2}$ (0.37)$<\sigma_{CH_4}$ (0.38 nm). As is shown in Figure 7a–d, the distance of a single jump of N$_2$ and H$_2$O are significantly higher than those of CH$_4$ and CO$_2$ in the 1500 ps period. The calculated result shows that each transition distance of N$_2$ and H$_2$O are $>0.5$ nm. Because of the weak adsorption capacity of N$_2$ on WM, the jumps among cavities are dominated by configurational diffusion, while activation desorption almost did not exist and was relatively stationary for the rest of the time. Two jumps among cavities occurred within a relatively long time (848 and 1350 ps) and the jump distances of the 848 and 1350ps were 3.36 and 9.88 Å, respectively (Figure 7d), which is related to the smaller lowest accessible pore width and the weak adsorption affinity on coal. The displacement-$t$ curve of N$_2$ indicates the rapid diffusion behavior inside the coal macromolecule.

The displacements of each H$_2$O jump are larger than 1.3 nm, and the diffusion proceeds in a stepwise manner. The displacements generally do not increase within 252–550, 850–1005, and 1300–1400ps, during which the diffusion manner manifests as internal vibration within a certain cavity (Figure 7c). When $t=550$, 1005, and 1400ps, the displacements rapidly increase as the diffusion processes continue, indicating the jumps among the adjacent cavities. The stepwise characteristics resulted from the strong adsorption forces and significant heterogeneities of the coal surface for H$_2$O; especially the interactions between H$_2$O and oxygen-containing functional groups, which are stronger than those of CO$_2$ and CH$_4$.[8] The internal vibration within a certain cavity is caused by the Debye forces and London dispersion forces from the preferential adsorption locations/sites, such as aromatic structures and heteroatom rings. Whereas the jump of large displacements (>10 nm) among the adjacent cavities in activation desorption and surface diffusion manner originated from the strong affinity of neighboring locations/sites where the coal molecule structure is or has been twisting or rotating, leading to surface diffusion from relatively weak adsorption sites to strong adsorption sites. The diffu-
sorption speeds and jump distances of N₂ are lower than those of H₂O, which is related to the strong hydrogen bonding between H₂O and coal. At certain adsorption sites, H₂O will jump for a large displacement when affected by the hydrogen bonding of the adjacent adsorption sites.

![Displacement-t curves and diffusion trajectories of different gases.](image)

The displacement-t curve of CH₄ manifests as a long time period, staying in a single cavity in the abnormal diffusion stages, and the small jumps of 1.2 and 4.5 Å only occur at 502 and 905ps, respectively (Figure 7a). Combined with the Steele potential function results, CH₄ has the lowest adsorption energy and highest molecule diameter among CH₄/CO₂/H₂O/N₂; hence, the required pore width to generate jumps among the adjacent cavities is the largest. The time to reach Einstein diffusion is also the longest (650ps) and the magnitude of the movement is small in most cases. Caused by the highest kinematic viscosity (17.0710) in contrast to CO₂ (8.369) and N₂ (15.753 mm²/s), the diffusion type of CH₄ is dominated by Knudsen diffusion and surface diffusion, and the displacement increases slowly at Einstein diffusion stages. The motion amplitude of CO₂ is even in a smaller variation range than CH₄, and a jump with a displacement of >1 nm only occurs at t=905ps (Figure 7a). The small displacement variation range is created by the high molecule weight and large dynamic viscosity (14.932μPa·s) compared with CH₄ (11.067), N₂ (13.805) and H₂O, leading to a smaller mean free walk. In addition, CO₂ has a strong affinity with coal. Affected by the smaller mean free walk and strong affinity, the diffusion velocity is slow at the anomalous diffusion stage. However, the rapid increase of displacement at Einstein diffusion stage is controlled by its lowest kinematic viscosity. Similar to CH₄ in diffusion behaviour, the vibration displacements of CO₂ are <0.5 nm. The vibration of CO₂ also belongs to motion in a single cavity. The molecule weight of CO₂ is far higher than CO₂ and the occasional jumps among neighbouring cavities will not occur for CO₂. As analysed above, the self-diffusion mechanisms of CH₄, CO₂, H₂O, and N₂ in coal are profoundly influenced by molecular diameter, molecule weight, viscosity and adsorption affinity with coal. At anomalous diffusion stages, the diffusions are mainly dominated by the molecular diameter and adsorption affinity. While at the Einstein diffusion stages, the diffusions are dominated by the molecule weight and kinematic viscosity.
3.3. Effects of temperature

The relationships between the self-diffusion coefficients and temperatures under NPT, NPH, NVE, and NVT ensembles are shown in Figure 8a, c, d and e. The pressure of NPH and NPT ensemble are both 1 MPa. The self-diffusion coefficients of CH₄, CO₂, and N₂ gradually increase with increasing temperature. When the temperature is < 368K, 368–428K, and 438–458K, the self-diffusion coefficients manifest as $D_{CH4}(0.1–2.24\times10^{-9}$ m²/s)$<D_{CO2}(0.69–1.3\times10^{-9}$ m²/s)$<D_{N2}(1.8–4.8\times10^{-9}$ m²/s), $D_{CO2}(1.4–1.6\times10^{-9}$ m²/s)$<D_{CH4}(1.9–4.0\times10^{-9}$ m²/s) $<D_{N2}(4.8–6.8\times10^{-9}$ m²/s) and $D_{CO2}(1.6–2.0\times10^{-9}$ m²/s)$<D_{CH4}(9.6–9.6\times10^{-9}$ m²/s)$<D_{N2}(10.4–29.6\times10^{-9}$ m²/s), respectively. $D_{H2O}(0.1–58.08\times10^{-9}$ m²/s) is higher than $D_{CH4}$, $D_{CO2}$, and $D_{N2}$ at each temperature during 298~458K, and fluctuation increases with increasing temperature. The higher $D_{H2O}$ is related to light molecule weight and small molecular diameter.

![Figure 8](image_url)

**Figure 8.** Relationship between self-diffusion coefficients and temperature under different ensembles (a, c, d, e) and the activation energy calculation method (b).

The self-diffusion of adsorbates in adsorbents is a process of activation. The diffusion reactivity is in accordance with Arrhenius law. As is shown in Figure 8b, log(D) has a good linear relationship with $1/T (R^2=0.7523–0.9157)$ (Figure 8b), which is also consistent with equation (3). Activation energy ($E$) can be obtained through the slopes and manifests as $E_{H2O}(1.07)<E_{N2}(1.82)<E_{CO2}(2.94)<E_{CH4}(10.88kJ/mol)$; the corresponding pre-exponential factors are 24.20, 19.08, 0.83, and 18.75s⁻¹, respectively, indicating that the Einstein diffusion of CH₄ is the most difficult to occur, as CH₄ has a higher adsorption energy barrier to overcome than CO₂, H₂O and N₂. The Einstein diffusion of CO₂ is easier to occur than CH₄, which is related to its lowest kinematic viscosity combined with the Steele 10-4-1 potential function results. The results also revealed that CO₂ should be injected effectively into
the coal bed with high speed to form competitive adsorption and selective self-diffusion with CH₄ in order to replace the CH₄ during E-CBM engineering. The adsorption capacity of N₂ is lower than CO₂ and CH₄ [40]; when the temperature is higher than 208K, D_{N₂} is higher than D_{CH₄}, indicating that the displacement mechanism of N₂ is different from CO₂. The rapid diffusion of N₂ in a coal reservoir can effectively decrease the partial pressure of CH₄, which could further influence the isothermal absorption curve and reduce the methane adsorption capacity. E_{H₂O} and E_{N₂} are both the lowest, and the Einstein diffusions of H₂O and N₂ are the easiest to occur, which is also consistent their highest self-diffusion coefficients.

Under the NPH ensemble, the self-diffusion coefficient order is D_{CH₄}(0.01*10⁻⁹) < D_{CO₂}(0.04*10⁻⁹) < D_{H₂O}(0.06*10⁻⁹) < D_{N₂}(0.08*10⁻⁹) m²/s at 298K, which is similar to the NPT ensemble. The self-diffusion coefficients during 298~458K overall manifest as D_{CH₄}(0.01~2.8*10⁻⁹) < D_{CO₂}(0.04~5.5*10⁻⁹) < D_{N₂}(0.06~44.5*10⁻⁹) < D_{H₂O}(0.08~10.6*10⁻⁹) m²/s). The self-diffusion coefficients of CH₄, CO₂, and N₂ gradually increase with increasing temperature, while D_{H₂O} fluctuation increases and is sensitive to temperature (Figure 8c). The self-diffusion coefficients of CH₂/CO₂/H₂O/N₂ under the NVE ensemble are the lowest compared with other ensembles. D_{CH₄} (0.03~0.07*10⁻⁹ m²/s) is even lower than CO₂/H₂O/N₂ during 298~458K, and gradually increases with increasing temperature. During 298~378K, D_{H₂O}(0.14~0.48*10⁻⁹) is slightly higher than D_{CO₂}(0.12~0.42*10⁻⁹) and D_{N₂}(0.04~0.45*10⁻⁹ m²/s). When the temperature is 458K, the self-diffusion coefficients are D_{CO₂}(0.39~0.62*10⁻⁹) < D_{N₂}(0.55~1.18*10⁻⁹) < D_{H₂O}(0.59~2.89*10⁻⁹) m²/s (Figure 8d). While under the NPH ensemble, the self-diffusion coefficients order is D_{CH₄}(0.01~0.06*10⁻⁹) < D_{CO₂}(0.07~0.45*10⁻⁹) < D_{H₂O}(0.54~7.67*10⁻⁹) < D_{N₂}(10~20.4*10⁻⁹) m²/s). The self-diffusion coefficients of N₂ and CH₄ gradually increase and those of CO₂ and H₂O jump increase with increasing temperature (Figure 8e).

![Figure 9](image)

**Figure 9.** Relationships between self-diffusion coefficients and temperatures under the same ensemble.

D_{CH₄} gradually increases with increasing temperature independent of the ensembles. However, the D_{CH₄}, which increases slowly with increasing temperature under NVT and NVE ensembles, increases slowly when the temperature is lower than 418K and rapidly when the temperature higher than 418K...
in NPT and NPH ensembles. At the same temperature, $D_{\text{CH}_4}$ manifests as $D_{\text{CH}_4}$ (NVE)~$D_{\text{CH}_4}$ (NVT)~$D_{\text{CH}_4}$ (NPH)~$D_{\text{CH}_4}$ (NPT) (Figure 9a). $D_{\text{CO}_2}$ leaping increases under NPH and NPT ensembles and gradually increases under NVT and NVE ensembles. $D_{\text{CO}_2}$ manifest as $D_{\text{CO}_2}$ (NVT)~$D_{\text{CO}_2}$ (NPH)~$D_{\text{CO}_2}$ (NPT) (298K~$T$~368K) and $D_{\text{CO}_2}$ (NVT)~$D_{\text{CO}_2}$ (NVE)~$D_{\text{CO}_2}$ (NPH)~$D_{\text{CO}_2}$ (NPT) (378K~$T$~458K) at the same temperature (Figure 9b). The calculated results of Hu et al. (2016) are close to the magnitudes of CO$_2$ and CH$_4$ in this paper, but the values are significantly lower than the values in this paper. The lower values are because the initial configuration (5Wiser model+25CH$_4$, 5Wiser model+25CO$_2$) before MD calculations has not yet reached a saturated adsorption state, still subjected to strong adsorption forces when diffusing in coal. D$_{\text{H}_2\text{O}}$ all show an increase with the temperature independent of the ensembles (Figure 9c). $D_{\text{N}_2}$ gradually increases with temperature in various ensembles, and the amplitude becomes significant with increasing temperature when the temperature higher than 358K. The $D_{\text{N}_2}$ of NVT, NPH, and NPT ensembles are close and obviously higher than those of the NVE ensemble. Unlike other gases, $D_{\text{N}_2}$ of the NVT ensemble is significantly higher than other ensembles when the temperature is higher than 418K (Figure 9d). The diffusion coefficient differences of various ensembles are essentially created by macroscopic conditions, such as temperature, pressure, and enthalpy, as well as the thermodynamic properties of various gases. The NPT ensemble has the highest diffusion coefficients for CH$_4$, CO$_2$, H$_2$O, and N$_2$, which is caused by the violent Monte Carlo movements from one potential energy surface to another. Originating from random impulse force [41]; NPH ensemble has the constant pressure and enthalpy, leading to second highest diffusion coefficients. $D_{\text{CH}_4}$, $D_{\text{H}_2\text{O}}$, and $D_{\text{N}_2}$ are the lowest in the isolated and conservative NVE ensembles, and $D_{\text{CO}_2}$ is the lowest in NVT ensembles of constant kinetic energy, which is controlled by macroscopic conditions and thermodynamic properties.

3.4. Effects of pressure

3.4.1. NPH ensemble. The self-diffusion coefficients of gas molecules at 298K and in the NPH ensemble decrease with increasing pressure (Figure 10a). At higher pressures, the interactions between gas molecules are stronger and the gas density is also higher, leading to a slower diffusion velocity, which is also the reason for CBM’s low diffusion coefficients at a deep buried depth [13]. Skoulidas et al. [42] also found this rule by analysing the self-diffusion and mass-transfer coefficients of small-molecule gases in metal-organic framework materials (MOE) through the MD method. When the pressure is lower than 1.68 MPa and higher than 1.68 MPa, the self-diffusion coefficients manifest as $D_{\text{H}_2\text{O}}$~$D_{\text{CO}_2}$~$D_{\text{N}_2}$~$D_{\text{CH}_4}$ and $D_{\text{H}_2\text{O}}$~$D_{\text{CO}_2}$~$D_{\text{CH}_4}$~$D_{\text{CO}_2}$~$D_{\text{N}_2}$, respectively, showing that higher reservoir pressure is favourable to the replacement of CH$_4$ by CO$_2$ and N$_2$. In contrast to the unipore model of Clarkson et al. [43] and the bidisperse model of Cui et al. [7], the diffusion coefficients in the bidisperse model are obtained through the apparent micro-pore diffusivity (s$^{-1}$) multiplied by the path length (m). The simulation results of CH$_4$ and CO$_2$ in this paper agree with those of the unipore and bidisperse models in the order of magnitude, which further proves the rationality of the MD simulation method. However, the bidisperse model involves pressures below 3 MPa, and $D_{\text{CH}_4}$ and $D_{\text{CO}_2}$ first increased and then decreased with increasing pressure, during which CO$_2$ and CH$_4$ have the largest diffusion coefficients at 0.75 MPa and 1.25 MPa, respectively. The pressure in this paper ranges from 1 MPa to 6 MPa, and the trend in this interval is in consistent with the trends of Cui's bidisperse model and unipore model at 0.5-6.5 MPa. Unlike the diffusion coefficients of temperature-dependence, the diffusion coefficients of various gases are $D_{\text{CH}_4}(0.256*10^{-10}$ m$^2$/s)~$D_{\text{CO}_2}(0.296*10^{-10}$ m$^2$/s)~$D_{\text{N}_2}(0.443*10^{-10}$ m$^2$/s)~$D_{\text{H}_2\text{O}}(2.271*10^{-10}$ m$^2$/s) when the pressure is lower than 1.75 MPa. The diffusion coefficient of H$_2$O is the largest among CH$_4$, CO$_2$, H$_2$O, and N$_2$, which is related to its largest kinetics viscosity and lighter molecule weight. By $^{13}$C NMR and FT IR, Xiang et al. (2014) calculated the self-diffusion coefficients of CH$_4$/CO$_2$/H$_2$O in the self-building Yanzhou coal macro-molecular model at 298K and the results manifested as $D_{\text{CH}_4}(0.335*10^{-12}$ m$^2$/s)~$D_{\text{CO}_2}(0.424*10^{-12}$ m$^2$/s)~$D_{\text{H}_2\text{O}}(0.186*10^{-12}$ m$^2$/s), which are close to the simulated values, in order of magnitude, in this paper. When the pressure is higher than 3 MPa, $D_{\text{CH}_4}$ diffusion coefficients are larger than $D_{\text{CO}_2}$ and $D_{\text{H}_2\text{O}}$.
indicating that higher reservoir pressure is conducive for promoting the diffusion coefficients of CH$_4$. The diffusion coefficient changes of CH$_4$ are caused by the lighter molecule weight and larger molecular free length at higher pressure, when the temperature is constant.

Molecular swelling of various degrees will occur during the interaction processes of adsorption and diffusion between coal molecules and gases to form a more stable configuration [19],[17], [44]. Xiang et al. holds that the valence electron energy of the coal molecule decreases after absorbing CH$_4$, CO$_2$, and H$_2$O, indicating that the “strain coal” originating from pressure action in the geological conditions may be the results of molecular rearrangement after swelling effects during the interactions between fluids and coal. Gas molecules in the coal diffusion process can also cause swelling phenomenon; the swelling ratio is defined as [11]:

$$\text{swelling ratio} = \frac{(V_f - V_0)}{V_0}$$

where $V_i$ and $V_0$ are the volumes occupied by the molecules before and after diffusion, respectively; A$^3$.

![Figure 10](image-url) Relationships between the $D$ (a), swelling ratio (b) and $E$ (c) with the pressure under the NPH ensemble.

With the increasing pressure, the swelling ratio of gas molecules increases gradually through either the adsorption or diffusion process. During 1–6 MPa, the average swelling ratios of different gases are shown as: H$_2$O(14.7~35.18%)>CO$_2$(13.38~32.25%)>CH$_4$(15.35~23.71%)>N$_2$(11.47~22.14%) (Figure 10b). The increase trend of swelling ratios with pressure becomes significant at high pressures, which are in consistent with Busch’s findings. The swelling action can shrink the micro-pore volume and change the width of the fracture to change the reservoir diffusion coefficient and permeability. For H$_2$O and CH$_4$, when the pressure is less than 5 MPa, the swelling ratio is low, the dominant diffusion type is surface diffusion of the adsorption phase, and the diffusion activation energy increases with the increasing pressure to cause surface diffusion to overcome the higher molecular structural energy barrier (Figure 10c), leading to a gradual decrease in the diffusion coefficients. When the pressure is higher than 5 MPa, the molecular swelling ratio of coal increases sharply, leading to rapidly narrowed micro-pore width, and the dominant diffusion type is configuration diffusion; while the diffusion energy barrier also gradually increased, resulting in a rapid decrease in diffusion coefficients. For CO$_2$, when the pressure is less than 2 MPa, the swelling ratio increases greatly, and the main diffusion type is surface diffusion; when the pressure is higher than 2 MPa, the swelling ratio and diffusion activation energy increases slowly, and the dominant diffusion types are surface diffusion and Knudsen diffusion. The diffusion type of N$_2$ is mainly Knudsen diffusion of gas phases, and surface diffusion
the adsorbed phases rarely exists, which leads to the lowest swelling ratio and the lowest activation energy (Figure 10c). Therefore, the required energy barrier to overcome for Knudsen diffusion is also the lowest among CH4/CO2/H2O/N2.

The WM-N2 diffusion system has the lowest swelling ratios, which indicates that the decrease in the throat radius of the micro porous pores caused by the coal molecular swelling is also the lowest, so that the diffusion of N2 in the coal molecules maintains relatively wide pore throats, which can efficiently reduce the partial pressures of CH4 and the micro-crack reductions caused by CH4-coal’s swelling effects. However, the WM-H2O diffusion system molecular swell has an adverse effect on the pore throat radius, and the swelling ratio of the system is the highest, leading to a significant reduction of the gas inlet radius in coal micro-pores. The average swelling ratio of the WM-CO2 system is higher than that of the WM-CH4 system under different pressures, which indicates that the pore throat radius of the WM-CO2 system is smaller than that of the WM-CH4 system, so that the pressure required for decreasing the diffusion coefficient is lower [11]. Siemons et al. [45] analysed the rate of sorption of CO2 under various pressures and various grain size fractions using volumetric experiments and found that at low pressures (<1 MPa), fast gas diffusion(surface diffusion) is the prevailing mechanism for sorption, whereas at higher pressures, the slow diffusion process controls the gas uptake by the coal.

As analysed above, the WM’s molecular-level micro-pores (<2 nm) contain two transmission mechanisms: (1) diffusion from one end to the other end in ultra-micro-pores: as the pore sizes are close to the diameter of the adsorbates in magnitude, only the gases with diameters smaller than the pore sizes can enter the ultra-micro-pores, while the larger gas molecules could not. (2) surface diffusion: the adsorbates of gas phase jumps from one certain adsorption site to neighbouring sites [7]. Both adsorption mechanisms have to overcome the energy barrier on the surface of the coal matrix. Hereby, the corresponding activation energy of diffusion of CH4/CO2/H2O/N2 in the coal is calculated under the NPH ensemble. Under the pressure of 1-6 MPa, the activation energy of diffusion is shown as follows: $E_{H2O}(0.51~1.48kJ/mol)$$<E_{CO2}(0.63~1.43kJ/mol)<E_{N2}(0.21~2.22kJ/mol)<E_{CH4}(0.78~2.76kJ/mol)$. CH4 has the largest $E$ and needs to overcome the highest energy barrier. $E_{CO2}$ and $E_{H2O}$ are relatively low and they could overcome the energy barriers easily, which is also consistent with the higher self-diffusion coefficients of CO2 and H2O. 

3.4.2. NPT ensemble. The changing laws of the self-diffusion coefficients with the pressure under the NPT ensemble are similar to the NPH ensemble. When the pressure is lower than 2 MPa, the self-diffusion coefficients manifest as $D_{CH4}$ (1.57~1.65*$10^{-10}$)<$D_{N2}$ (2.15~5.12*$10^{-10}$)<$D_{CO2}$ (1.46~1.91*$10^{-10}$)<$D_{H2O}$ (5.49~7.44*$10^{-10}$) m²/s). However, when the pressure is higher than 3 MPa, $D_{CH4}$ is higher than $D_{N2}$ and $D_{CO2}$ and lower than $D_{H2O}$ (Figure 11a). The self-diffusion coefficients of the NPT ensemble are higher than those of the NPH ensemble at each pressure, which is consistent with the temperature effect. Compared with the results of Zhao et al. [8] by WM, this paper’s results and Zhao’s results are both in the $10^{-10}$ magnitude order. Zhao demonstrated that the self-diffusion coefficients of CO2 and CH4 are the highest at 1.5 MPa and 1.2 MPa, respectively, slightly higher than the pressure peak value of 1 MPa in this paper. The simulated diffusion coefficients of pressure-dependence in this paper are of a same trend to the results of the unipore model of Clarkson et al. [43], the bidisperse model of Cui et al. [7] and Zhao at a pressure range of 0~3 MPa. The simulated diffusion coefficients of pressure-dependence in this paper are higher than the bidisperse model by a magnitude order. The deviations are caused by the differences in pore structure and chemical structures of the bidisperse model and WM. Coupled with surface functional groups and heteratomic rings, the WM’s pore structure in this paper is mainly constituted by ultra-micro-pores (<1 nm) and micro-pores (<2 nm). While the bidisperse model is mainly made up of micro-pores (<2 nm) and aromatic nuclei as the basic structure units (BSUs), in which the adsorption capacities for CH4 and CO2 are stronger than WM (adsorption capacities of functional groups are aromatic structure> heteroatom rings> oxygen functional groups; Song et al., [35]. The swelling ratios and E of pressure-dependence under the NPT ensemble gradually increase with increasing pressure (Figure 11b, c). Differences in
the swelling ratios of the NPH and NPT ensembles exist at the same pressure and temperature, indicating that the swelling ratios are also influenced by macro-restrictions. The average swelling ratios of the NPT ensemble for different gases manifest as CH\textsubscript{4} (18.95~24.80%)>H\textsubscript{2}O (16.12~31.73%)>CO\textsubscript{2} (15.21~24.32%)>N\textsubscript{2} (13.17~18.59%) (Figure 11b).

The swelling ratios are of the same trend but significantly higher than Zhao’s results, indicating that the diffusions in saturated adsorption configurations will cause significantly higher swelling ratios than the unsaturated adsorption state. Because of the differences in the thermodynamic properties of the gases and the macro-restrictions of the ensembles, the swelling ratios of various ensembles are close, but differ in the order of various gases. The results in this paper also demonstrate the importance of the ensemble selection during molecule simulation.

![Figure 11. Relationships between the self-diffusion coefficients (a), swelling ratios (b) and pressure in coal under NPT ensemble.](image)

### 4. Conclusions

The self-diffusion coefficients (D) of CH\textsubscript{4}/CO\textsubscript{2}/H\textsubscript{2}O/N\textsubscript{2} at 298.15~458.15K and 1~6MPa under the NPT, NPH, NVE, and NVT ensembles were obtained after the calculations of MM, AK, GCMC, and MD based on WM. The adsorption capacities of 5 WMs for CH\textsubscript{4}/CO\textsubscript{2}/H\textsubscript{2}O/N\textsubscript{2} manifest as H\textsubscript{2}O(56)>CO\textsubscript{2}(42)>CH\textsubscript{4}(30)>N\textsubscript{2}(17) under PBCs at under 298.15K.

The Ds of the adsorbates in saturated adsorption configurations are D\textsubscript{CH\textsubscript{4}}(0.47*10\textsuperscript{-9})<D\textsubscript{CO\textsubscript{2}}(0.69*10\textsuperscript{-9})<D\textsubscript{H\textsubscript{2}O}(1.4*10\textsuperscript{-9})<D\textsubscript{N\textsubscript{2}}(1.8*10\textsuperscript{-9}m\textsuperscript{2}/s) (NPT, 298.15K, 0.1MPa). The diffusion type of N\textsubscript{2} is dominant by configurational diffusion in micro-pores. H\textsubscript{2}O diffuses in micro-pores in a stepwise way(252~550, 850~1005, 1300~1400ps due to the strong heterogeneity of adsorption capacity on coal surface for H\textsubscript{2}O. For CH\textsubscript{4}, Knudsen- and surface diffusions occur in a single cavity occasionally (498, 897ps) associating with a skip between two cavities during the abnormal diffusion stages, resulting a relatively long period of time staying in a single micro-pore cavity. The displacements of CO\textsubscript{2} manifest almost unchanged in the abnormal diffusion stages and rapid increasing in the Einstein diffusion stages respectively.

D\textsubscript{H\textsubscript{2}O} lies between 0.1~58.08*10\textsuperscript{-9} m\textsuperscript{2}/s when 298≤T≤458K and larger than D\textsubscript{CH\textsubscript{4}}, D\textsubscript{CO\textsubscript{2}} and D\textsubscript{N\textsubscript{2}} at each temperature. The diffusion activation energy (E) is E\textsubscript{H\textsubscript{2}O} (1.07)<E\textsubscript{N\textsubscript{2}} (1.82)<E\textsubscript{CO\textsubscript{2}} (2.94kJ/mol)<E\textsubscript{CH\textsubscript{4}} (10.88kJ/mol), indicating that CH\textsubscript{4} diffusion needs to overcome the higher adsorption energy barrier than N\textsubscript{2} and H\textsubscript{2}O. D\textsubscript{CH\textsubscript{4}} increases slowly when T<418K and rapidly when 418~458K. The D\textsubscript{CH\textsubscript{4}} order of different ensembles is D\textsubscript{CH\textsubscript{4}}(NVE)<D\textsubscript{CH\textsubscript{4}}(NVT)<D\textsubscript{CH\textsubscript{4}}(NPH)<D\textsubscript{CH\textsubscript{4}}(NPT) at the same temperatures. D\textsubscript{CO\textsubscript{2}} shows a jump increase in NPH and NPT ensembles and gradual increase in NVE and NVT ensembles. The D\textsubscript{CO\textsubscript{2}} orders of different ensembles are D\textsubscript{CO\textsubscript{2}} (NVT)<D\textsubscript{CO\textsubscript{2}} (NVE)<D\textsubscript{CO\textsubscript{2}} (NPH)<D\textsubscript{CO\textsubscript{2}} (NPT) (298K≤T≤368K) and D\textsubscript{CO\textsubscript{2}} (NVT)<D\textsubscript{CO\textsubscript{2}} (NVE)<D\textsubscript{CO\textsubscript{2}} (NPH)<D\textsubscript{CO\textsubscript{2}} (NPT) (378K≤T≤458K) at the same temperatures. D\textsubscript{N\textsubscript{2}} all displays a jumply increasing under each ensemble with the order of D\textsubscript{N\textsubscript{2}}(NVE)<D\textsubscript{N\textsubscript{2}}(NVT)<D\textsubscript{N\textsubscript{2}}(NPH)<D\textsubscript{N\textsubscript{2}}(NPT) (T≠438K). D\textsubscript{N\textsubscript{2}} increases with the increasing temperatures and the amplifications become significantly when T>358K. The order of different ensembles is D\textsubscript{N\textsubscript{2}}(NVE)<D\textsubscript{N\textsubscript{2}}(NVT)<D\textsubscript{N\textsubscript{2}}(NPH)<D\textsubscript{N\textsubscript{2}}(NPT) (T<418K) and D\textsubscript{N\textsubscript{2}} (NVE) is remarkable higher than other ensembles when T>418K. The self-diffusion
coefficients of CH₄/CO₂/H₂O/N₂ gradually decrease whereas swelling ratios of coal matrix gradually increase with the increasing pressure (NPH, NPT) when T>418K. The average swelling ratios manifest as H₂O (14.7–35.18%) > CO₂ (13.38–32.23%) > CH₄ (15.35–23.71%) > N₂ (11.47–22.14%) (NPH, 1–6MPa). There exits differences in D, swelling ratios and E among various ensembles, indicating that the selection of ensembles has an important influence on the MD calculations for self-diffusion coefficients.

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