Detailed study on self- and multicomponent diffusion of CO₂-CH₄ gas mixture in coal by molecular simulation

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Abstract:

Gas diffusion plays a key role in CO₂-enhanced recovery of coal bed methane (ECBM), where more than one types of gases coexist and multicomponent gas diffusion occurs. Such process is now usually described by non-coupled two-component gas diffusion equations which exclude the interactions between gases. Self-diffusion and mutual diffusion of CO₂-CH₄ mixture are investigated through molecular simulation for the first time. The self-diffusion coefficients of CO₂ and CH₄ decrease with gas concentration but increase with temperature. The mutual diffusion coefficients of binary gas mixture of CO₂-CH₄ in coal are computed through Maxwell-Stefan diffusion theory. A 2D diffusivity matrix $|D|$ (with diagonal element D_i and non-diagonal element D_{ij}) is obtained to depict the mutual diffusion of the gas mixture. It is found that CO₂ (CH₄) diffusion is coupled with CH₄ (CO₂). The diffusion coupling strength of CO₂ and CH₄ decreases with increasing gas

concentration. Temperature positively affects D_{ij} but minimally influences D_i , resulting in large ratios of D_{ij}/D_i at high temperatures. It means that CO₂–CH₄ diffusion correlation interactions, which are not present in non-coupled pure gas diffusion equations, are necessary to analyze gas mixture diffusion in coal. In this case, non-coupled pure gas diffusion equations are inadequate for description of CO₂–CH₄ mixture diffusion. The coupling between the gases can be ignored only at very high temperatures ($T > 400$ K), which means a large depth of coal bed in ECBM engineering.

Keywords: multicomponent diffusion; mutual diffusion coefficients; self-diffusion; coal bed methane; molecular simulation

1. Introduction

Large amounts of methane (CH_4) are adsorbed in coal bed and can be extracted as high-efficiency energy. Injection of CO_2 enhances the production of coal bed methane because coal tends to adsorb higher amounts of CO_2 than CH_4 . In enhanced coal bed methane recovery (ECBM), methane adsorbed in micro-pores is desorbed first, then diffuses into fractures of coal bed, and finally is extracted through permeation flow [1]. Diffusion is an important means to transport methane from micro-pores to fractures. This process is relatively slower than permeation flow, which occurs in fractures of coal bed, and regarded as a rate-limiting step during gas production. Therefore, the diffusion mechanisms of the CH_4 and CO_2 in coal must be elucidated to increase coal bed methane yield and quality [2].

Many experiments were conducted to study gas diffusion in coal. Thimons [3] considered methane flow through coal as Knudsen diffusion and determined methane diffusion coefficients at relatively high pressures. Olague et al. [4] analyzed diffusivities for methane and nitrogen through gas–solid chromatography coupled with moment analysis. “Solid coal discs” method [5] and volumetric methods [6, 7] are also used to obtain gas diffusivities in coal block. Gas diffusion is influenced by the pore structure of coal [4], methane concentration [8], gas pressure upon CO_2 and CH_4 [9, 10], and adsorbate molecule size [11]. Yao et al. [12] proposed that low-field nuclear magnetic resonance (NMR) method is a potential noninvasive analytical technique

used to characterize the methane adsorption capacity of coals.

Molecular dynamics (MD) is an effective tool used in numerical simulation to explore the underlying mechanism of macroscopic processes at the atomic level [13]. Some scholars employed MD simulation to investigate coal–gas interactions. Niekerk [14] applied MD simulations to examine the initial stages of solvent–coal interactions during solvent swelling. Tambach et al. [15] explained the preferential CO₂ adsorption over CH₄ in the pores of specific coal types at the atomic scale. MD simulations are also used to investigate gas diffusion [16]. In our previous work [17], the gas sorption isotherms and self-diffusivities of CO₂ and CH₄ were calculated. Zhang et al. [18] reported that the moisture content of brown coal considerably affects O₂ diffusion during coal oxidation. Xiang et al. [19] determined the adsorption isotherm and self-diffusion coefficients (SDC) of pure components of coal (CH₄, CO₂, and H₂O).

Most of previous experimental and MD works focused on diffusion of pure components (CO₂ or CH₄). However, more than two gases exist as mixture in ECBM. Thus far, coupled diffusion of gas mixture (CO₂–CH₄ mixture) in coal has not been investigated yet. Diffusion of gas mixture follows multicomponent diffusion theory [Eq. (2)], in which diffusion of one species is related not only to its own chemical gradient but also to the chemical gradient of another species [20]. Therefore, gas diffusion in a gas mixture differs from pure-component diffusion. Multicomponent gas diffusion is common in industries [21]. Researchers investigated the mutual diffusion of fluid mixtures in porous media, including metal–organic frameworks,

silica, and carbon materials [22-28]; in several situations, mutual diffusion of gas mixtures is not equivalent to that of pure gases. As such, the cross term in Eq. (2), namely, D_{ij} , is not negligible. In the present work, coal is treated by a special porous material. Mutual and self-diffusion of CO₂–CH₄ mixture are investigated by MD simulations for the first time. The effects of gas concentration, component mole fraction, and temperature on mutual and self-diffusivity are discussed. This study aims to determine the mutual diffusion coefficient of CO₂–CH₄ mixture in coal first, then evaluate whether or not gas mixture diffusion in ECBM follows the multicomponent gas diffusion equation, and assess whether or not non-coupled pure gas diffusion equations are adequate for analysis of gas mixture diffusion.

2. Simulation method

2.1 Theory of diffusion

Diffusion coefficients are categorized as SDC and transport diffusivity, which are used to characterize molecular transport and mobility within porous materials. Self-diffusion indicates random motions or mixing of particles in the thermodynamic equilibrium. In MD simulation, SDC $D_{i\text{self}}$ of component i is computed by Einstein equation [29]

$$D_{i\text{self}} = \frac{1}{2dN_i} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{l=1}^N \left(r_{l,i}(t) - r_{l,i}(0) \right)^2, \quad (1)$$

where N_i is the number of molecules of the component i , d is the dimension of the

system, and $r_{l,i}(t)$ is the position vector of molecule l at time t .

Transport diffusion represents particle motions driven by chemical or concentration gradient, which results in net mass transport. Maxwell and Stefan [20] proposed a general theory, namely Maxwell–Stefan (M-S) theory, for multicomponent diffusion in porous materials. Gases are mainly adsorbed in the micro-pores (less than 2 nm diameter) of coal, and diffusion in small pores are dominated by surface diffusion [30]. Diffusing molecules never escape from the force field of pore walls. With coal as (n+1)th component in the coal–gas diffusion system with n types of gas and based on dusty gas model, the M-S diffusion equations for the mutual diffusion in the coal are [30-33]:

$$-\rho \frac{\theta_i}{k_B T} \nabla \mu_i = \sum_{j=1; j \neq i}^{j=n} \frac{\Theta_j N_i - \Theta_i N_j}{\Theta_{i,sat} \Theta_{j,sat} D_{ij}} + \frac{N_i}{\Theta_{i,sat} D_i}; \quad i = 1, \dots, n \quad (2)$$

where ρ is the coal density expressed as the number of unit cells per cubic meter, k_B is the Boltzmann constant, T is the temperature, Θ_i is the loading of the component i , $\Theta_{i,sat}$ is the saturation loading of the component i , μ_i is the chemical potential expressed in Joules per molecule, N_i is the molar flux of component i expressed in molecules per square meter per second, and n is the total number of diffusing species. The fractional occupancy θ_i is defined as

$$\theta_i = \frac{\Theta_i}{\Theta_{i,sat}} \quad (3)$$

D_i is mutual diffusion coefficient (MDC) that reflects the interactions between species i and the coal. The binary exchange coefficient D_{ij} reflects the correlation effect among

different components in mixture diffusion. Eq. (2) can be rewritten into n-dimensional matrix notation as [31, 32]

$$\mathbf{N} = -\rho [\mathbf{B}]^{-1} [\mathbf{\Gamma}] (\nabla \Theta) \quad (4)$$

where n-dimensional square matrix $[\mathbf{B}]$ is defined as:

$$B_{ii} = \frac{1}{D_i} + \sum_{j=1; j \neq i}^n \frac{\theta_j}{D_{ij}}, B_{ij} = -\frac{\theta_i}{D_{ij}} \quad i, j = 1, 2 \dots n \quad (5)$$

Thermodynamic factor $[\mathbf{\Gamma}]$ is defined by

$$\frac{\theta_i}{k_B T} \nabla \mu_j = \sum_{j=1}^n \Gamma_{ij} \nabla \theta_j, \Gamma_{ij} = \left(\frac{\Theta_{j,sat}}{\Theta_{i,sat}} \right) \frac{\Theta_i}{\Theta_j} \frac{\partial f_i}{\partial \Theta_j} = \frac{\theta_i}{\theta_j} \frac{\partial \ln f_i}{\partial \ln \theta_j} \quad i, j = 1, 2 \dots n \quad (6)$$

Eq. (4) is similar to (n+1)-component Fick diffusion equation, where fluid flux ($\mathbf{N}$) is proportional to the concentration gradient [34].

The modified Onsager coefficient matrix $[\mathbf{\Lambda}]$ is given by

$$[\mathbf{\Lambda}] = [\mathbf{\Theta}_{sat}]^{-1} [\mathbf{L}] \frac{k_B T}{\rho} \quad (7)$$

$$\mathbf{N} = -\rho [\mathbf{\Theta}_{sat}] [\mathbf{\Lambda}] \frac{1}{k_B T} (\nabla \mu) \quad (8)$$

$$(\mathbf{N}) = -\rho \begin{bmatrix} \Theta_{1,sat} & 0 & 0 & 0 \\ 0 & \Theta_{2,sat} & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & \Theta_{n,sat} \end{bmatrix} \frac{[\mathbf{\Lambda}]}{k_B T} (\nabla \mu) \quad (9)$$

The elements of $[\mathbf{L}]$, namely, phenomenological coefficients, can be obtained through MD simulations using [16]

$$L_{ij} = \frac{1}{6V k_B T} \lim_{\Delta t \rightarrow \infty} \frac{1}{\Delta t} \left\langle \left(\sum_{l=1}^{N_i} (r_{l,i}(t + \Delta t) - r_{l,i}(t)) \right) \cdot \left(\sum_{k=1}^{N_j} (r_{k,j}(t + \Delta t) - r_{k,j}(t)) \right) \right\rangle \quad (10)$$

where $\langle \dots \rangle$ indicates the average of the cross-displacement correlation function

(CDCF) of a number of independent MD runs.

After combining Eqs. (6) and (8), the flux N is related to the concentration gradient for binary diffusion.

$$N = -\rho[\Lambda] \begin{bmatrix} 1/\theta_1 & 0 \\ 0 & 1/\theta_2 \end{bmatrix} [\Gamma](\nabla\Theta) \quad (11)$$

By comparing Eq. (11) with Eq. (4), the following interrelationship is obtained:

$$[\Lambda] \begin{bmatrix} 1/\theta_1 & 0 \\ 0 & 1/\theta_2 \end{bmatrix} = [B]^{-1} \quad (12)$$

$$\begin{bmatrix} \Lambda_{11} & \Lambda_{12} \\ \Lambda_{21} & \Lambda_{22} \end{bmatrix} = \begin{bmatrix} \frac{1}{D_1} + \frac{\theta_2}{D_{12}} & -\frac{\theta_1}{D_{12}} \\ -\frac{\theta_2}{D_{21}} & \frac{1}{D_2} + \frac{\theta_2}{D_{21}} \end{bmatrix}^{-1} \begin{bmatrix} \theta_1 & 0 \\ 0 & \theta_2 \end{bmatrix} \quad (13)$$

$[L]$ is first calculated with Eq. (10) using trajectories of gas molecules obtained through MD simulation. $[\Lambda]$ is then computed using Eq. (7), and the mutual diffusion coefficient matrix for binary gases $[D]$ in coal is obtained by solving Eq. (13).

2.2 Molecular dynamics simulation details

In this study, simulations are performed with Accelrys Materials Studio software (<http://accelrys.com>). Coal is a porous material composed of various cross-linked molecules with high molecular weight. For simplicity, a modified version of Wiser model is chosen as the average molecular model of coal [35]. An amorphous cell containing 10 coal molecules is first built and used as the initial configuration for subsequent simulations. This configuration is then subjected to geometry optimization, followed by 1 nanosecond (ns) NVT and 1 ns NPT run, to reach the equilibrium state

(Fig. 1). As a natural porous material, free volumes (FV) of coal provide the space and channels for gas diffusion. Gas diffusion strongly depends on the size and distribution of FV. In molecular simulation, fractional free volumes (FFV, the ratio of FV versus volume of coal cell) can be analyzed quantitatively using a molecular probe. The FFV of coal is determined to be 3.1%. The gases are then inserted into the coal through Monte Carlo (MC) simulation to simulate a gas–coal system. For simplicity, coal–gas system with different gas molecules is referred to as n-m system, where n represents the molecular number of CO₂ and m indicates the molecular number of CH₄.

The Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) is used as force field in all simulations [36, 37]; our previous work confirmed that this force field can reproduce physical properties of coal structures [17]. Ewald method is used to simulate electrostatic and van der Waals interactions with a cut-off value of 12.5 Å. Gas diffusions are simulated as follows: a number of gases are inserted into the equilibrium configuration by grand canonical Monte Carlo (GCMC) method to obtain a new coal–gas cell. The cell is then minimized and run in NPT (1 ns) and NVT ensemble (0.5 ns) for relaxation. Subsequently, the cell is subjected to long-time (3 ns) NVE production run. The trajectories in the last 2 ns are saved for computation of diffusion coefficient. The integration time step is 1 femtosecond. Gas concentration (loading) and temperature are varied to investigate their effects on gas diffusion.

3. Results and discussion

Fig. 1 shows the snapshots of the CO₂–CH₄–coal system. The saturation loadings $\Theta_{i,sat}$ of CO₂ and CH₄ in coal are simulated by GCMC (Table 1). Self- and mutual diffusion of gases in coal is discussed in detail in the following sections.

3.1 Computation of SDC

MD can provide the microscopic details of gas diffusion to reveal the underlying mechanism of diffusion; such details cannot be directly obtained through experimentation. The diffusion path of gases is important in diffusivity calculation and elucidation of diffusion mechanism. The obtained gas diffusion paths and displacement are shown in Fig. 2, where a coal-gas system containing 25 CO₂ and 25 CH₄ molecules (25-25 in abbreviation) is used as an example. Displacement of a single molecule of CO₂ and CH₄, $|r(t)-r(0)|$, is displayed as a function of time in Fig. 2(a); highly irregular movements of gases are noted. Small displacement fluctuations (e.g., between 250 and 410 ps) indicate the gas motions confined in a single micro-pore, and large displacement represent gas jump from one pore to another (e.g., displacement at about 150 and 1300 ps). Diffusion is anomalous if only confined fluctuations in a single pore occurs, that is, $MSD \sim t^n$ ($0 < n < 1$). Einstein diffusion requires frequent jumps among different pores. In this case, Eq. (1) is valid. As shown in Fig. 2(a), several jumps are found during the simulation, implying the occurrence of Einstein diffusion. The diffusion paths of CO₂ and CH₄ are illustrated in

Figs. 2(b) and (c), respectively; the jumps between two adjacent pores are also clearly observed.

The slope of the MSD-t curve is necessary for diffusion coefficient calculation, assuming that MSD changes linearly with time. MSD in Eq. (1) is a statistic quantity on trajectories of a number of molecules. The presence of numerous statistic samples indicates high linearity of the MSD-t curve, resulting in accurate calculation of the diffusion coefficient. Abnormal diffusion, which usually occurs at the beginning of simulation, is nonlinearly related to time in short simulation duration ($t < t_{\min}$) and progresses into normal diffusion after long time ($t > t_{\min}$). Then MSD varies with time linearly, as indicated in Eq. (1). At the end of simulation ($t > t_{\max}$), MSD becomes irregular because few statistic samples are available. These irregular data should not be used to calculate the diffusion coefficient. Therefore, determining $t_{\min}$ and $t_{\max}$ is important to calculate reliable diffusivity. An example for selection of $t_{\min}$ and $t_{\max}$ is shown in Fig. 4. Each diffusion simulation is repeated more than 10 times to obtain good statistic on MSD. Fig. 3 depicts the MSD of CO₂ and CH₄. MSD is proportional to $t^{1/2}$ for small duration, then becomes linear within large duration and slightly deviates from linearity at the end of the simulation. This linear relation can be observed in Fig. 4(a), which shows the plot of slope variation through linear fitting of the MSD-time curve. The slope of MSD initially decreases drastically but becomes relatively stable for a long time. The stable stage should be used to calculate the diffusion coefficient by using Eq. (1). The derivate of the MSD slope is displayed in

Fig. 4(b) to quantitatively demonstrate slope variations. MSD is taken as constant if derivative fluctuation is less than 0.005, based on which $t_{\min}$ and $t_{\max}$ are determined. Finally, the D_{iself} values of CO₂ and CH₄ are 2.51×10^{-10} and $2.41 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, respectively.

3.2 Effect of concentration and temperature on SDC

Diffusion coefficient is influenced by many factors, including gas type, absorbent property, temperature, pressure and humidity. In this study, only total gas concentration and temperature are considered. Total gas concentration or loading is defined as the total number of all molecules in a unit coal cell. Fig. 5 shows the SDCs of gases at different gas concentrations with a fixed gas composition (CO₂:CH₄ = 1:1, T = 313.15 K). SDC slightly decreases with increasing gas concentration. High gas concentrations correspond to high pressure and gas density, resulting in strong interactions among gas molecules. Such interactions hinder the random movement of gases, thereby slowing down the gas diffusion. Similar decreasing trends are reported for SDCs of various gases in metal–organic frameworks [24]. Hence, CO₂ and CH₄ diffuse slowly without concentration gradient in deep coal bed, where pressure is high.

The radial distribution function [RDF, $g(r)$] measures the density variation of an atom (centroid) located at a certain distance from another reference atom (centroid). This function provides the relative position information of different molecules. RDF

of $\text{CO}_2\text{-CO}_2$ ($g(r)_{11}$), $\text{CH}_4\text{-CH}_4$ ($g(r)_{22}$) and $\text{CO}_2\text{-CH}_4$ ($g(r)_{12}$) in systems with different concentrations are calculated. Fig. 6(a) shows that all $g(r)$ s values in 75-75 systems exhibit the same peak, implying that the two gases appear to be equally mixed, without clustering of same types of gas molecules. $g(r)$ s is almost undistinguishable in all systems, as shown in Figs. 6(b–d).

Temperature also affects gas diffusion. In this study, the temperature is varied from 273.15 K to 353.15 K (Fig. 7). The effect of temperature on SDC is quantitatively investigated using a fixed total gas loading of 100 and a mole fraction of 1:1. D_{iself} increases with increasing temperature in both pure gas and mixture systems because the motion of gas can be enhanced significantly by temperature. In many systems, the dependence of diffusivity on temperature follows the Arrhenius law

$$D = D_0 e^{-\frac{E_a}{RT}} \quad (14)$$

or equally

$$\ln(D) = \ln(D_0) - \frac{E_a}{RT} \quad (15)$$

where D is the diffusion coefficient, D_0 is the pre-exponential factor, T is the absolute temperature, E_a is the activation energy, and R is the molar gas constant. E_a can be calculated from the slope of linear fitting of $\ln(D)$ plot versus $1/T$. The E_a value of CO_2 and CH_4 in the binary mixture systems is 1.18 and 1.25 kJ/mol, respectively.

3.3 Computation of MDC

Compared with the self-diffusion coefficient, the mutual-diffusion coefficient in

binary system requires the calculation of CDCF, which is more irregular than MSD. Therefore, the average on a large number of CDCFs obtained from independent MD runs must be determined to obtain statistical results, namely, good linearity between CDCF and time [38]. The average of 40 independent MD runs is sufficient to achieve satisfactory CDCF–time linear relation. The procedure to obtain the mutual-diffusion coefficient is described by using the 50-50 system (313.15 K) as an example (Fig. 8). Forty independent MD simulations are performed, and gas trajectories are determined. Once the diffusion trajectories are achieved, the phenomenological coefficient L is first calculated based on Eq. (10). Using the procedure described in self-diffusivity, we determine $t_{\min}$ and $t_{\max}$ in the CDCF curve. The coefficient L is then calculated from the slope of the curve between $t_{\min}$ and $t_{\max}$. As an example, the elements of $[L]$ in the 50-50 system are listed in Table 2. $[L]$ is a diagonal matrix, as predicted from Eq. (10). The cross coefficients L_{12} and L_{21} are lower than L_{11} and L_{22} . Once $[L]$ is available, Onsager matrix $[\Lambda]$ can be calculated using Eq. (7). Finally, the mutual diffusion coefficient $[D]$ is solved with Eq. (13) by feeding gas saturation loadings. The saturation loadings of gases simulated by GCMC are listed in Table 1. CO_2 saturation loading is higher than CH_4 , and all saturation loadings decrease with increasing temperature. The results for $[D]$ in the 50-50 system are shown in Table 2. The mutual diffusion coefficient matrix $[D]$ in Eq. (2) is characterized by two different interactions in binary gas diffusion; these interactions include diagonal elements D_1 and D_2 , which reflect the strength of gas–coal interaction, as well as cross

exchange (correlation) coefficients D_{12} and D_{21} ($D_{12} \neq D_{21}$ in general), which are related to gas–gas ($\text{CO}_2\text{--CH}_4$) interactions. The high value of D_{ij} calculated using Eq. (2) indicates weak gas–gas interactions. These cross exchange coefficients describe how the mobility of species 1 is correlated with that of another species [39]. In limited cases ($D_{ij} \gg D_i$), the first term of Eq. (2) vanishes, and the diffusion of one species is not coupled with another species. Therefore, Eq. (2) can be simplified into the form of pure gas diffusion:

$$-\rho \frac{\theta_i}{k_B T} \nabla \mu_i = \frac{N_i}{\Theta_{i,sat} D_i}; \quad , \quad i = 1, 2 \quad (16)$$

where the diffusion of the gas component in the $\text{CH}_4\text{--CO}_2$ binary mixture is only dominated by gas–coal interaction and is independent of another gas component. Therefore, the pure gas diffusion equation can estimate gas mixture diffusion. Moreover, whether or not the $\text{CO}_2\text{--CH}_4$ gas mixture diffusion equation for coal can be simplified into the pure gas diffusion must be determined if matrix $|D|$ is available. Table 2 shows that all elements of $|D|$ for the 50-50 system are comparable values, but cross-exchange coefficients are higher than those of the diagonal elements. First, gas–coal interactions provide higher contributions to diffusion of gas mixture than gas–gas interactions ($\text{CO}_2\text{--CH}_4$ interaction) because D_{ij} is about two to three times higher than D_i . Second, the influence of CH_4 (CO_2) on CO_2 (CH_4) diffusion is not negligible because D_{ij} is only a few times of D_i and the condition $D_{ij} \gg D_i$ is not fulfilled. As such, gas–gas interactions play a significant role in gas mixture diffusion

in coal. Consequently, diffusion of CO₂–CH₄ gas mixture in coal should follow the mutual diffusion form [Eq. (2)], rather than the pure gas diffusion [Eq. (16)].

3.4 Effect of concentration and temperature on the MDC

The effect of gas concentration (loading) on mutual diffusivity is investigated using a mole ratio of 1:1 (CO₂:CH₄) and a fixed temperature of 313.15 K. The results are displayed in Fig. 9. All elements of $|D|$ are comparable valued, revealing that not only gas–coal interactions but also gas–gas interactions are important in gas mixture diffusion. For any gas concentrations, diffusion of CO₂–CH₄ gas mixture in coal should be represented by the mutual diffusion form and the corresponding pure-component diffusion form is insufficient. Interestingly, the elements of $|D|$ behave differently. The off-diagonal mutual diffusivities increase with concentration [Fig. 9(a)] and reach a saturated value at high gas loadings, whereas diagonal diffusivities decrease with concentration [Fig. 9(b)]. Low values of D_{ij} correspond to strong interactions among gas species in diffusion of gas mixture. The increasing values of D_{12} and D_{21} reveal that the coupling strength between CH₄ and CO₂ is reduced with increasing gas concentration. Furthermore, D_{12} is always higher than D_{21} , indicating that interaction exerted by CO₂ on CH₄ diffusion is stronger than that exerted by CH₄ on CO₂ diffusion. Hence, CH₄ diffusion is significantly influenced to a higher extent by CO₂ than CO₂ diffusion. D_i is related to interactions between coal and gases (gas jumping among adsorption sites). The decreasing values of D_1 and D_2

imply that gas–coal interactions are strengthened by high gas concentrations because numerous adsorption sites are occupied by gases under high gas concentrations. Similar results of decreasing M-S diffusivity with gas concentration were obtained through molecular dynamics in previous studies [25, 27]. To the best of our knowledge, no experiment results of CO₂-CH₄ MDC in coal is reported. Diffusion flow of gas mixture, rather than multicomponent diffusivity, was studied by a few authors [33, 40]. In Ref. [40], an empirical formulation for correlation diffusivity, which relates diffusivity with total surface occupancy (loading), was introduced and it was found that diagonal elements of $|D|$, D_i , decreased with total occupancy while correlation diffusivities, D_{ij} , increase with occupancy, which was qualitatively in accordance with our results.

The dependence of MDC in the 50-50 system on temperature (from 273.15 K to 433.15 K) is shown in Fig. 10. All of the off-diagonal elements (D_{ij}) and diagonal diffusivity (D_i) increase with temperature. Furthermore, Fig. 10(a) shows that D_{12} and D_{21} increase with temperature slowly at $T < 353$ K and increase rapidly at $T > 353$ K. The value of D_{12} at 433.15 K is about ten times higher than 273.15 K. The nonlinear fitting reveals a good cubic relation between D_{ij} and temperature. Hence, the interaction between CO₂ and CH₄ is decoupled by temperature. D_{12} is higher than D_{21} . Compared with D_{ij} , the diagonal diffusivity D_i only increase slightly with temperature, indicating that interactions between gases and coal are not significantly influenced by temperature. Increasing $|D|$ can decrease the value of $|B|$, as shown in Eq. (4), thereby

increasing all the fluxes of gas components at high temperatures. Gas molecules become active at high temperatures and then diffuse with high speed. A quantity, coupling intensity, $R_D = D_i/D_{ij}$ is defined to quantify the contributions of gas–gas and gas–coal interactions to gas mixture diffusion. High values of R_D result in weak interaction between CO_2 and CH_4 . As shown in Fig. 10(c), R_D increases rapidly with temperature. At $T = 433 \text{ K}$, R_D approaches to about 30. Hence, the first term of the right hand of Eq. (2) is negligible at high temperatures. Gas mixture diffusion can be approximated using the pure component form. For ECBM, the interactions of CO_2 and CH_4 become weak in the extra deep coal bed (depth $> 3200 \text{ m}$, $R_D > 20$); as a result, pure gas diffusion is sufficient to induce gas transportation because gas interactions can be apparently decoupled by deep underground high temperatures.

4. Conclusions

In ECBM, multicomponent diffusion should be considered to formulate gas diffusion in coal because of the presence of gas mixtures, rather than pure gases, in coal bed. Diffusion of CO_2 – CH_4 gas mixture in coal is investigated using molecular dynamics simulation. The mutual diffusion coefficients of gas mixture in coal are calculated by MD for the first time. The effects of gas concentration and temperature on diffusivity are also discussed. All the SDC values of CO_2 and CH_4 decrease with increasing total concentration, whereas temperature positively affects SDC. RDF analysis reveals that CO_2 and CH_4 are well-mixed, and gas separations are not found.

Diffusion of the CO₂–CH₄ binary gas mixture in coal follows a coupled M-S diffusion equation, where a non-diagonal 2D diffusivity matrix (MDC) is necessary to induce diffusion process. The two types of interactions in gas diffusion are gas–solid interaction, which is related to the diagonal elements of MDC, and gas–gas interaction, which is represented by non-diagonal items (correlation elements). The method for calculating the binary MDC of CO₂ and CH₄ in coal is presented in detail. Moreover, the effects of concentration and temperature on MDC are further discussed. All of the elements of MDC exhibit comparable values for different concentrations; hence, interactions between CO₂ and CH₄ play an important role in diffusion of gas mixture in coals. Diffusion of CO₂–CH₄ gas mixture in coal should follow the mutual diffusion formula Eq. (2), rather than the non-coupled pure diffusion form Eq. (16). Meanwhile, it is revealed that the diagonal and correlation elements of diffusivity matrix $|D|$ show different behavior. The diagonal element D_i decreases, whereas the correlation diffusivity (D_{ij}) increases with increasing gas concentration. This finding indicates that high gas concentrations lead to weak CO₂–CH₄ correlations but strong gas–coal interactions. Furthermore, D_{ij} rapidly increases and D_i slightly increases with temperature. A coupling intensity R_D is introduced to quantitatively depict the contribution ratio of gas–coal and gas–gas interactions to multicomponent diffusion. R_D rapidly increases with temperature and reaches about 30 at $T = 433$ K. It means that at high temperatures (or in the very deep coalbed), correlations between CO₂ and CH₄ may be neglected and gas mixture diffusion can be simplified into pure gas

diffusion.

In a word, this work provides preliminary results on MDC of $\text{CO}_2\text{--CH}_4$ gas mixture in coal by using MD simulations. It is demonstrated that except for very large underground depth (e.g. depth > 3200 m), the diffusion coupling between gases play a key role in multicomponent gas diffusion and therefore the widely-investigated non-coupled pure gas diffusion formula (e.g. Eq. (16)) is not suitable for gas mixture diffusion in coal. The presented method could be extended to investigate diffusion of more complex multicomponent fluids, including $\text{CO}_2\text{--H}_2\text{O}$, $\text{CH}_4\text{--H}_2\text{O}$, $\text{CO}_2\text{--CH}_4\text{--H}_2\text{O}$, and $\text{CO}_2\text{--CH}_4\text{--N}_2$ fluid pairs, in coal, feeding necessary parameters for prediction of gas flow in ECBM engineering.

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Figure captions

Figure 1. Equilibrium configuration snapshot of 25-25 gas-coal system. Gases are highlighted by VDW representation. All the temperature in the following figures is 313.15 K unless stated otherwise.

Figure 2. (a) Displacement of single CO₂ and CH₄ molecule; (b) The diffusion pathway of CO₂; (c) The diffusion pathway of CH₄. Small-amplitude oscillations in (a) (e.g. within 200-400 ps) indicate the gas movement in a single hole. Large displacement indicates jump from one hole to another (e. g. 100 and 1300 ps). Several jumps are observed in (a), indicating occurrence of Einstein diffusion.

Figure 3. Average MSD in 25-25 system. A good linearity between MSD and time is shown.

Figure 4. (a) The slope of MSD as the function of the $t_{\max}$ in 25-25 systems. (b) The derivation of the slope. $t_{\min}$ and $t_{\max}$ are marked. Black line for CO₂ and red line for CH₄.

Figure 5. The self-diffusion coefficient D_{iself} of equal-mole CO₂-CH₄ mixture at different total loading. SDC of CH₄ is slightly smaller than that of CO₂. Both self-diffusivities of CO₂ and CH₄ decrease with increasing gas loading almost linearly.

Figure 6. (a) Radial distribution functions ($g(r)$) of 75-75 system; (b) CO₂-CO₂ ($g(r)_{II}$), (c) CH₄-CH₄ ($g(r)_{22}$) and (d) CO₂-CH₄ ($g(r)_{I2}$) in 5-5, 25-25 and 75-75 systems respectively.

Figure 7. $D_{i\text{self}}$ of CO₂ and CH₄ at different temperature in 50-50 system.

Figure 8. DCF in 50-50 system at 313.15K. CO₂ and CH₄ is represented by 1 and 2 respectively. DCF increases linearly with time since average on ten times of independent MD run provide good displacement statistics. The phenomenological coefficient L thus can be calculated from slop of DCF-t curve.

Figure 9. (a) M-S correlation coefficient D_{ij} and (b) M-S coefficient D_i in equal-mole fraction gas mixture at different total loading. D_{ij} increases with loading, indicating a weakening interactions between gases, while D_i decreases with loading, implying strengthening interactions between gases and coal. The non-coupled diffusion form Eq. (16) becomes invalid because value of D_{ij} is comparable to D_i and the couplings between gases effect the diffusion of gas mixture.

Figure 10. (a) M-S correlation coefficient D_{ij} ; (b) The M-S coefficient D_i and (c) R_D at different temperature in 50-50 system. D_i increases slightly with temperature whereas D_{ij} increases sharply. The ratio of D_{ij}/D_i , R_D , increases rapidly with temperature, which means that interaction between gases in diffusion is decoupled by high temperature. Only for $T > 400$ K (depth > 3200 m in ECBM), where R_D is up to more than 20, the coupling between gases can be negligible and diffusion of gas mixture therefore can be approximated by it pure component form.

Tables

Table1. The saturation loading ($\Theta_{i,sat}$) of CO₂ and CH₄ in different temperature.

Temperature(K)	273	313	353	393	433
CO ₂	156	152	133	113	94
CH ₄	121	108	97	88	79

Table2. Mutual-diffusivities in 50-50 system at temperature 313.15 K

(10 ⁻⁹ m ² s ⁻¹)	CO ₂ -CO ₂	CO ₂ -CH ₄	CH ₄ -CO ₂	CH ₄ -CH ₄
$\frac{1}{V}k_B T$	10.7921	1.4242	1.4242	9.68439
Λ_{ij}	0.07243	0.00956	0.06602	0.08967
D_{ij}	0.24815	0.6663	0.48296	0.2188

Figure 1

Figure 2a

Figure 2b

Figure 2c

Figure 3

Figure 4a

Figure 4b

Figure 5

Figure 6a

Figure 6b

Figure 6c

Figure 6d

Figure 7

Figure 8

Figure 9a

Figure 9b

Figure 10a

Figure 10b

Figure 10c