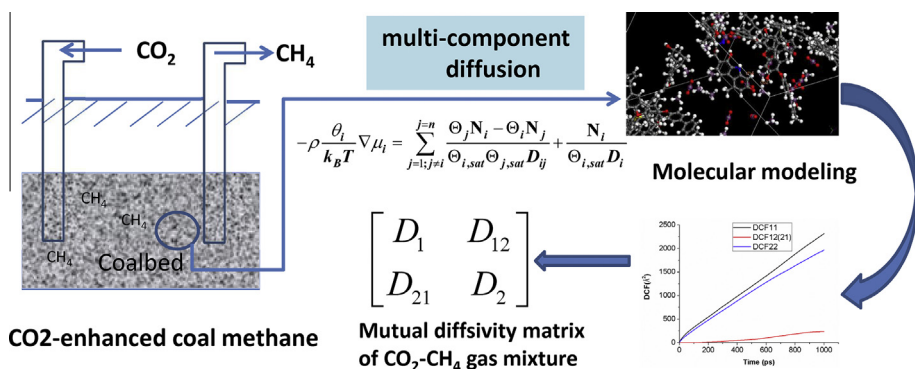




Full Length Article

Detailed study on self- and multicomponent diffusion of CO₂-CH₄ gas mixture in coal by molecular simulationHaixiang Hu ^{a,*}, Lei Du ^{b,c}, Yanfei Xing ^a, Xiaochun Li ^{a,*}^aState Key Laboratory of Geomechanics and Geotechnical Engineering, Institute of Rock and Soil Mechanics, Chinese Academy of Sciences, Wuhan, Hubei 430071, China^bOil & Gas Fire Protection Key Laboratory of Sichuan Province, Chengdu, Sichuan 610041, China^cChina Petroleum Engineering Co. Ltd. Southwest Company, Chengdu, Sichuan 610041, China

GRAPHICAL ABSTRACT



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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.

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1. Introduction

Large amounts of methane (CH₄) are adsorbed in coal bed and can be extracted as high-efficiency energy. Injection of CO₂ enhances the production of coal bed methane because coal tends to adsorb higher amounts of CO₂ than CH₄. 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 CH₄ and CO₂ 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 CO₂ and CH₄ [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 $D_{i, self}$ of component i is computed by Einstein equation [29]

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

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_j is the chemical potential expressed in Joules per molecule, N_j is the molar flux of component j 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]

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

where n-dimensional square matrix $[B]$ is defined as:

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

Thermodynamic factor $[\Gamma]$ is defined by

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

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

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