

Article

Investigation of CO₂-CH₄-H₂O Diffusion in Gas Reservoirs: Combining Experimental Measurement and Molecular Dynamics Simulation

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Abstract

Accurate prediction of CO₂ diffusion in multicomponent fluids is crucial for efficient enhanced oil and gas recovery (EGR) and carbon capture, utilization and storage (CCUS) operations. Conventional experimental methods struggle to accurately reproduce diffusion processes under reservoir conditions and provide limited insight into molecular-scale mechanisms. Therefore, a detailed microscopic understanding of CO₂ diffusion in complex fluids is urgently needed. In this study, the diffusion behavior and underlying mechanism of the CO₂-CH₄-H₂O system under reservoir temperature and pressure conditions were explored using both experimental techniques and molecular dynamics (MD) simulations. The results indicate that at 354.15 K, the diffusion coefficients follow the order $D_{CH_4} > D_{CO_2} > D_{Fick}$ and decrease with increasing pressure. Higher CO₂ concentrations and water content lead to a reduction in D_{CO_2} . Gravity exhibits a relatively minor influence, slightly enhancing D_{CO_2} while marginally reducing D_{CH_4} . Near the critical point, a significant decrease in the thermodynamic factor indicates drastic changes in thermodynamic properties. Furthermore, the presence of water promotes CO₂ enrichment at the gas-water interface, consequently reducing both D_{CO_2} and D_{CH_4} . This work provides valuable insights into bulk-phase transport in multicomponent aquifer systems under reservoir conditions and offers theoretical support for optimizing gas injection strategies and improving the efficiency of EGR and CCUS processes.



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Keywords: CO₂ diffusion; molecular dynamics simulation; multicomponent fluids; gas-water interface

1. Introduction

CCUS technology has attracted widespread global attention as a key strategy for mitigating CO₂ emissions in the pursuit of carbon neutrality [1,2]. In geological CO₂ storage, the primary objective is to inject captured CO₂ into deep underground porous media (e.g., depleted oil and gas reservoirs or saline aquifers) for long-term and secure storage.

When CCUS is coupled with enhanced oil and gas recovery, the injected supercritical CO₂ interacts with in-situ fluids and formation water, forming a complex CO₂-CH₄-H₂O multi-component system within the reservoir [3–5]. In such systems, CO₂ plays a critical role in governing the overall phase behavior and mass transport properties. It alters the solubility and distribution of CH₄ and H₂O, shifts phase boundaries, and modifies the stability of gas–liquid equilibria [6–10]. These changes directly affect diffusion coefficients and mixing dynamics, thereby governing the migration and interaction of components over time. At a macroscopic scale, these microscale processes impact fluid displacement efficiency, CO₂ trapping mechanisms, and potential leakage risks. Therefore, understanding the role of CO₂ in controlling the thermophysical behavior of these systems is not only critical for improving EGR and CCUS performance but also forms the basis for accurately predicting their transport behavior in the bulk phase [11]. Such understanding is essential for assessing CO₂ storage capacity, ensuring long-term security, and optimizing injection strategies.

However, accurately obtaining the bulk diffusion parameters and elucidating the microscopic transport mechanisms of these complex multi-component systems under reservoir temperature and pressure conditions presents considerable challenges. Li et al. [12] determined the single molecular diffusion coefficient of each component in the solvent/CO₂ mixture in heavy oil under reservoir conditions using the pressure decay theory, and found that the molecular diffusion coefficient of the solvent in heavy oil was significantly greater than that of CO₂ in heavy oil. Wang et al. [13] calculated the diffusion coefficient of CO₂ in liquid and porous media at 50 MPa and 393 K by using pressure decay method and numerical simulation method. It was found that the diffusion coefficient increased with the increase of permeability and decreased with the increase of water saturation. Although traditional experimental methods provide essential macroscopic data under reservoir conditions, they often fail to capture molecular-scale mechanisms such as interfacial interactions and hydrogen bonding [14]. Advanced techniques like Quasi-Elastic Neutron Scattering (QENS) and Pulsed Field Gradient Nuclear Magnetic Resonance (PFG-NMR) can partially overcome these limitations [15–17], yet their application is frequently constrained by high experimental costs. MD simulations complement these approaches by offering atomic-level insights into diffusion behavior and intermolecular forces.

Specifically, MD simulation has been widely employed as a powerful tool for studying fluid behavior at atomic and molecular scales in various geological media. Numerous studies have successfully employed MD simulations to investigate gas diffusion behavior in complex geological media. For example, for the coal system, Liu et al. [18] studied the diffusion behavior of CH₄, CO₂ and N₂ in the vitrinite of medium-rank coal by MD simulation, and obtained the diffusion coefficient in the saturated adsorption state. The order is $D(N_2) > D(CO_2) > D(CH_4)$, and is affected by gas concentration, temperature and pressure. Long [19] studied the gas loading, diffusion and adsorption characteristics of CH₄, CO₂ and N₂ in coal pore models with different pore sizes by MD, revealing that the adsorption capacity and adsorption heat ranked as $CO_2 > CH_4 > N_2$, and the diffusion follows $CH_4 > N_2 > CO_2$, and the larger pore size is more conducive to gas diffusion. Gao [20] also used molecular simulation to study the adsorption characteristics and diffusion rules of CH₄, N₂, CO₂ and H₂O in coal. The results show that the adsorption capacity and diffusion coefficient of CO₂ are the largest under the same conditions, and the adsorption of CO₂ is the least affected by the component content. Hu et al. [21] systematically studied the self-diffusion and multi-component diffusion characteristics of CO₂-CH₄ mixture in a coal matrix, and found that the component diffusion was coupled with each other. For kerogen, Vasileiadis [22] studied the effects of porosity and shale gas composition on the adsorption and transport properties of kerogen structure. It was found that the gas adsorption amount was linearly related to the porosity of kerogen, the diffusion

was anisotropic, and the diffusion coefficient was linearly related to the limited pore size. Yuan [23] used Grand canonical Monte Carlo (GCMC) and MD methods to study the adsorption and diffusion behavior of gas and water on different types of kerogen models. The results showed that the adsorption and diffusion capacity of CO₂ decreased with the increase of water content, but the adsorption selectivity of CO₂/CH₄ increased with the increase of water content. Bonnaud et al. [24] also studied the competitive adsorption and diffusion of CH₄/CO₂ mixture in kerogen by MD. In addition, in the silica nanopore model, Mohammed [25] studied the organization and transport behavior of CO₂ and CH₄ molecules through MD simulation. It was found that the diffusion behavior was regulated by wall hydrophobicity, and the diffusion coefficient of CH₄ on some modified pores was higher than that of CO₂ molecules. Zhao et al. [26] simulated the self-diffusion coefficient of various gases (including CO₂) in supercritical water, and concluded that temperature, density and viscosity were the main influencing factors and deduced the correlation. In general, these simulation studies accurately reveal the microscopic influence mechanism of gas type, pore structure, component content and medium type on adsorption and diffusion behavior.

At the same time, molecular simulation is also used to analyze the influence of specific external conditions on gas behavior. For example, Bai et al. [27] studied the desorption behavior of CH₄ after injecting N₂ and CO₂ into a coal model containing adsorbed methane at different temperatures, indicating that the effect of CO₂ on promoting CH₄ desorption is better than that of N₂, and high temperature is conducive to CH₄ movement, which is closely related to the application of injected gas. Yang [28] studied the microscopic mechanism of adsorption and diffusion of CH₄ and CO₂ in coal under ultrasonic excitation through experiments and MD methods, and found that ultrasonic excitation can promote the diffusion behavior, which provides a new idea for strengthening desorption. Zhang [29] studied the effect of uniaxial strain on the adsorption-migration of CH₄/CO₂/N₂ in bituminous coal micropores by MD simulation, and revealed the influence of in-situ stress changes on gas occurrence and migration. The conclusion is that the adsorption concentration is positively correlated with the strain, the strain affects the thermodynamic factor and Henry's constant, and the CH₄ self-diffusion coefficient is greater than CO₂/N₂. In summary, molecular simulation can not only accurately simulate the diffusion behavior of fluid under formation conditions, but also conduct in-depth exploration of specific external conditions, thus revealing its microscopic influence on fluid diffusion. Although a larger number of studies have focused on the influence of porous media on CO₂ transport, an accurate understanding of its basic diffusion behavior in an unconstrained bulk phase is still a key prerequisite for constructing more complex porous media models and optimizing the design of fluid components.

In addition, both numerical simulation and laboratory experiments show that ignoring the nano-scale diffusion effect in porous media will overestimate the recovery of CH₄ and other gases [30–33]. The water phase in the reservoir environment greatly increases the complexity of molecular transport. For example, the formation of water film will affect the interaction between gas and mineral surface, and then change the diffusion behavior of gas [34–36]. At the same time, the weak acid formed by CO₂ dissolved in water will react with carbonate minerals in the reservoir, induce mineral dissolution, and dynamically change the pore structure, forming a complex reactive transport process [37]. These complex microscopic mechanisms and coupling effects make it difficult to accurately describe the traditional macroscopic models based on the continuum hypothesis, which limits the accurate prediction of reservoir fluid behavior and ultimate recovery/storage. To better understand these mechanisms, simplified systems under controlled conditions are often employed.

In this study, the diffusion kinetics and intermolecular interaction mechanisms of a representative $\text{CO}_2\text{-CH}_4\text{-H}_2\text{O}$ ternary system were systematically investigated using a combination of experimental measurements and molecular dynamics simulations. The $\text{CH}_4\text{-CO}_2$ binary system was initially investigated via experimental and molecular simulation approaches, followed by extension to the $\text{CH}_4\text{-CO}_2\text{-H}_2\text{O}$ ternary system using molecular dynamics simulations. This system is critically important as it reflects the actual fluid composition encountered in $\text{CO}_2\text{-EGR}$ and CCUS projects, where injected CO_2 interacts with residual methane and formation water. By integrating high-pressure gas chromatography experiments with molecular dynamics simulations, this study bridges macroscopic observations and molecular-scale insights. The insights gained from analyzing the thermodynamic factor, radial distribution functions, van der Waals interactions, and density distributions contribute to the understanding of multicomponent fluid transport under the conditions investigated and provide theoretical support for optimizing gas injection strategies and improving the predictive accuracy of models for CCUS and EGR applications.

2. Experiment and Simulation Preparation

2.1. Experiment Methods

In this study, high-pressure gas chromatography (HPGC) was used to measure the bulk molecular diffusion coefficients of the target gas components under different temperature and pressure conditions. The method is based on the Taylor dispersion principle and calculates the diffusion coefficient by analyzing the broadening of chromatographic peaks due to axial diffusion and radial convection as the sample is transported in a diffuser.

The experimental setup, designed to measure gas concentrations during diffusion, is schematically shown in Figure 1. The core components include a temperature-controlled chamber equipped with two gas sample cylinders and a PVT cell (DBR Group of Companies, Edmonton, AB, Canada) serving as the diffusion chamber. The diffusion chamber has an inner diameter of 3.15 cm and a depth of 23.0 cm, and is designed to withstand a maximum pressure of 70 MPa and a temperature of up to 473 K. The control of the gas flow path is achieved through two valves. The use of two syringe pumps (Nanchong Southwest Petroleum New Technology Co., Ltd., Nanchong, China) allows for precise control of the transfer and volume operation of the gas. Pump 1 is connected to the inlet of the gas sample cylinder via valve 1. Valve 2 connects the outlet of the gas sample cylinder to the diffusion cylinder. The outlet of the diffusion cartridge is connected to pump 2, which in turn is connected to the gas chromatograph's inlet (Agilent Technologies, Santa Clara, CA, USA) for analysis. The chamber maintains a stable, controlled temperature for the gas sample and the diffusion cartridge during the experiment.

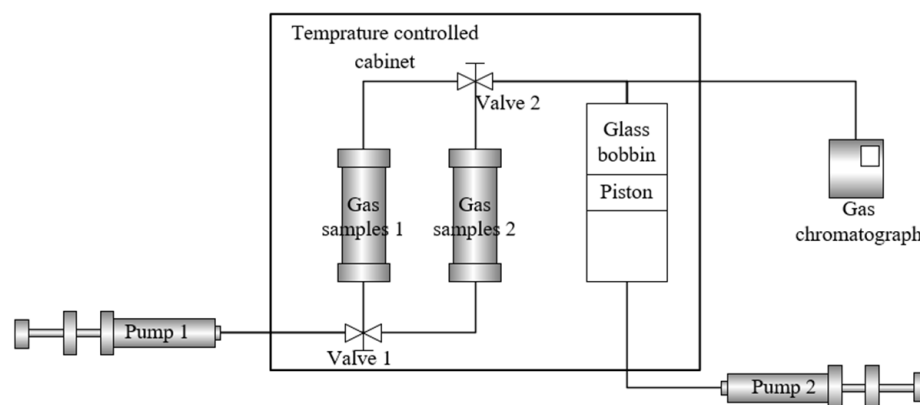


Figure 1. Diagram of experimental device.

The detailed specifications and uncertainties of the key experimental equipment are summarized in Table 1.

Table 1. Specifications and uncertainties of key experimental equipment.

Equipment	Parameter	Specification/Value	Uncertainty
PVT cell	inner diameter	3.15 cm	± 0.01 cm
	Depth	23 cm	± 0.05 cm
	Maximum pressure	70 MPa	
	Maximum temperature	473 K	
pump	Pressure range	0–70 MPa	± 0.02 MPa
	Temperature range	273–473 K	± 0.1 K
Gas chromatograph	Detector	TCD	
	Carrier gas	Helium	
Gas mixing system	CO ₂ mole fraction	0.9	$\pm 0.5\%$

CO₂ (99.99% purity) and CH₄ (99.95% purity) were supplied by Chengdu Keyuan Gas Co., Ltd., Chengdu, Sichuan, China. The binary gas mixture was prepared with carbon dioxide and methane at a ratio of 9:1, and the total uncertainty of composition was $\pm 0.5\%$. The content of natural gas components is shown in Table 2. Gas chromatography was performed using an Agilent 7890B gas chromatography system equipped with a thermal conductivity detector (TCD) and a HP-PLOT column. High purity helium (99.99%) was used as the carrier gas, and the flow rate was 2.0 mL/min. All measurements were performed in a three-fold manner, and the results were reported as mean $\pm$ standard deviation. The expanded uncertainty $k = 2$ of the measured diffusion coefficient is estimated to be within $\pm 5\%$, taking into account the uncertainties of temperature (± 0.1 K), pressure (± 0.02 MPa) and chromatographic peak area integral ($\pm 2.0\%$).

Table 2. Natural gas component content.

Component	Content (%)	Component	Content (%)
N ₂	25.04	C ₂ -NC ₄	3.44
CO ₂	5.05	IC ₅ -C ₆	0.81
CH ₄	65.67	C ₇₊	0

The procedure for measuring the diffusion coefficient is as follows:

1. Sample preparation: injection gas and formation gas samples were prepared. The purity of all gas samples was ensured to meet experimental requirements.
2. System purging: the air inside the diffusion cylinder was removed by flushing the system via Pump 2, and the piston was pushed to its uppermost position to eliminate residual gases.
3. Sample injection: the gas sample was connected to the top of the diffusion cylinder. CO₂ was slowly injected using the high-pressure displacement Pump 1, followed by the injection of the prepared formation gas after system stabilization. To minimize nonlinear effects, the injection rate was controlled at 0.05 mL/min.
4. Component transfer and detection: the gas sample entered the diffusion column, where axial diffusion and radial dispersion occurred simultaneously during flow. Gas samples were collected from the diffusion cylinder at 2, 4, 8, and 16 h for gas chromatographic analysis. The concentration changes of the upper gas phase were monitored, and chromatographic peaks were recorded.
5. Data recording and reproducibility: the retention time, peak shape, and peak width of chromatographic signals were accurately recorded. All experiments were performed in triplicate to ensure data reliability and reproducibility.

6. Diffusion coefficient calculation: the molecular diffusion coefficient D of each component was calculated based on known parameters, including carrier gas velocity, diffusion column length, and inner diameter.

All experiments were conducted at 354.15 K and pressures of 5, 10, and 14 MPa. Each measurement was repeated three times. The overall uncertainty of diffusion coefficients was estimated to be within $\pm 5\%$.

2.2. Modelling

Based on the experimental conditions described above, a molecular simulation system was constructed. In this model, CH_4 represents natural gas, H_2O represents formation water, and the CH_4 - CO_2 mixture represents the injected gas.

The simulation pressures were set at 2, 5, 8, 10, and 14 MPa to systematically investigate the diffusion behavior of CO_2 and CH_4 near the critical point and under supercritical conditions. CO_2 injection mole fractions of 0.5, 0.7, 0.9, and 1.0 were selected to represent typical gas injection scenarios. The temperature was fixed at 354.15 K to simulate reservoir conditions, while pressure was controlled by adjusting the system density [38]. The corresponding density values were obtained from the NIST database and are summarized in Table 3.

To maintain consistency with the experimental setup, a binary simulation model was first established, as shown in Figure 2a. For the ternary system, a simulation box was constructed with dimensions of $5 \times 5 \times 10 \text{ nm}^3$ for the formation water phase and $5 \times 5 \times 20 \text{ nm}^3$ for the gas phase, as illustrated in Figure 2b. Periodic boundary conditions were applied in all directions. Carbon walls were placed at both ends of the z-axis to confine the system.

Along the z-direction, the injected gas, natural gas, and formation water were arranged sequentially. The molecular structures of H_2O , CH_4 , and CO_2 used in the simulations are shown in Figure 2c.

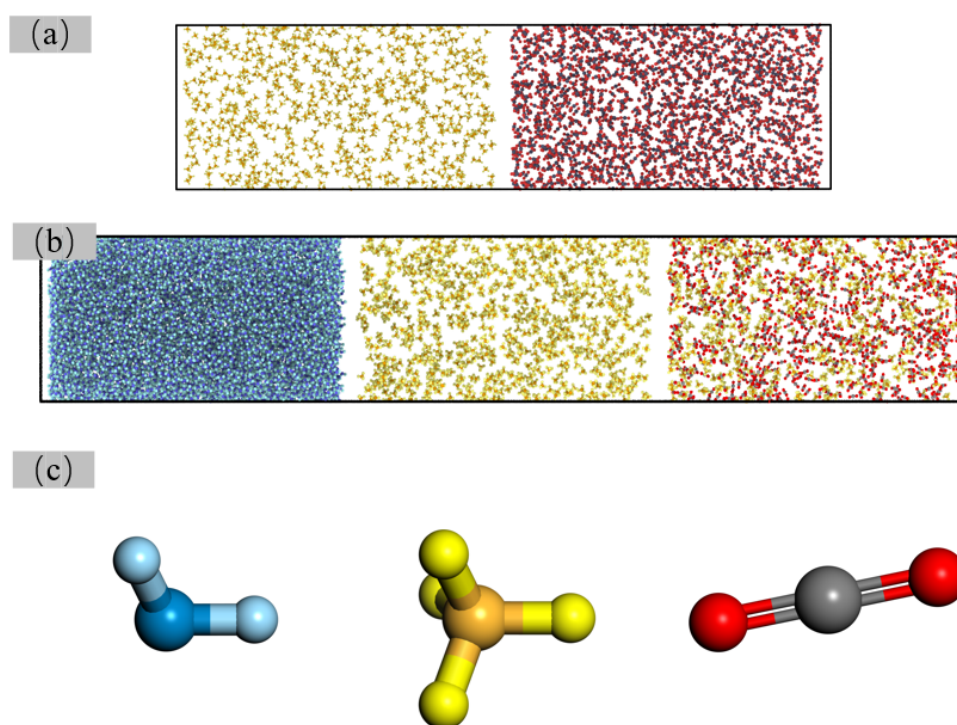


Figure 2. (a) Initial configuration of binary diffusion model; (b) initial configuration of ternary diffusion model; (c) molecular model H_2O , CH_4 , CO_2 (blue: H_2O ; yellow: CH_4 ; red-gray: CO_2).

Table 3. Fluid density in 90% CO₂ injection gas simulation system.

Pressure (MPa)	Natural Gas (g/cm ³)	Injected Gas (g/cm ³)	Stratum Water (g/cm ³)
2	0.0111	0.0296	0.8633
5	0.0283	0.0818	0.8645
8	0.0461	0.1478	0.8656
10	0.0581	0.2033	0.8664
14	0.0823	0.3480	0.8680

2.3. Simulation Details

MD simulations were employed to investigate the diffusion behavior of CO₂ and natural gas under reservoir conditions, with particular emphasis on the effects of temperature, pressure, fluid composition, water content, and gravity on CO₂-CH₄ diffusion.

A two-stage simulation protocol was adopted. First, the mixed system containing injected gas and natural gas was fully equilibrated to obtain a uniform composition and thermodynamic equilibrium state. Subsequently, a production run was performed based on the equilibrated configuration to calculate diffusion coefficients at specified temperature and pressure conditions. All simulations were carried out using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator, <https://www.lammps.org>).

In the simulation system, the OPLS-AA force field was used for alkanes [39], the Trappe force field for CO₂ [40], and the SPC force field for H₂O [41]. The Lennard-Jones parameters and charge parameters are shown in Table 4.

Table 4. Non-bonded interaction parameters.

Molecule	Type	Molar Mass	Electric Charge (e)	σ (nm)	ϵ (KJ/mol)
CH ₄	H	1.00797	0.060	0.250	0.012552
	C	12.0107	−0.240	0.350	0.276144
CO ₂	C	12.0107	0.700	0.280	0.224475
	O	15.9994	−0.350	0.305	0.656799
H ₂ O	H	1.00797	0.41	0	0
	O	15.9994	−0.82	0.3166	0.649984

The Lennard–Jones (LJ) interactions were truncated at a cutoff radius of 1.5 nm. Long-range electrostatic interactions were calculated using the particle–particle particle–mesh (PPPM) method. Gravity was introduced by applying a constant acceleration of 9.8 m/s² to all fluid molecules.

Energy minimization was first performed for 1×10^6 steps to eliminate unfavorable contacts. This was followed by 1×10^6 steps of equilibration under the NVT ensemble to ensure thermodynamic stability. After equilibration, a production run of 2×10^6 steps was conducted for data collection. The simulation time step was set to 1 fs, resulting in a total simulation time of 4 ns. System configurations were recorded every 1000 steps.

To ensure the reliability of the calculated diffusion coefficients, the mean square displacement (MSD) of both CO₂ and CH₄ was monitored. A clear linear relationship between MSD and time was observed after approximately 1.5 ns, indicating the onset of the diffusive regime. The remaining simulation time (2.5 ns) provided sufficient sampling for stable averaging. Convergence was further confirmed by comparing diffusion coefficients calculated from the final 2 ns with those obtained from the entire trajectory, with deviations less than 5%.

2.4. Model Verification

Accurate force field selection is essential for ensuring the reliability of simulation results. Therefore, the simulated fluid densities were compared with reference data from the NIST database, as shown in Figure 3. The excellent agreement between simulated and reference densities confirms that the selected force fields can reliably reproduce the thermophysical properties of the system.

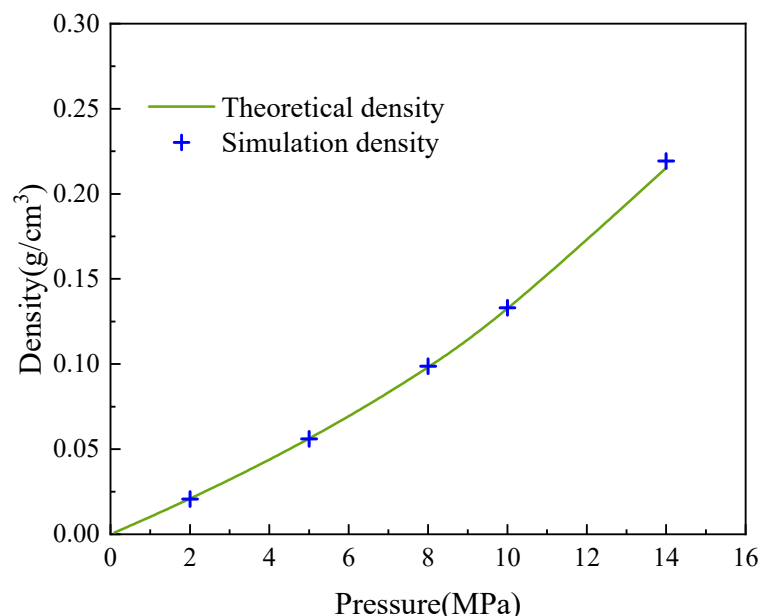


Figure 3. Comparison of theoretical density and simulated densities of mixed fluid.

The finite-size effect must be considered when calculating diffusion coefficients using MD simulations [42]. Previous studies have demonstrated that the simulation box size under periodic boundary conditions can significantly influence the calculated diffusion coefficients, particularly due to hydrodynamic interactions, as reported by Simonnin [43]. Therefore, finite-size correction is required.

In this study, all diffusion coefficients were corrected using the Yeh-Hummer (YH) method [44]:

$$D(\infty) = D(L) + \frac{k_B T \gamma}{6\pi\eta L} \quad (1)$$

where $D(\infty)$ is the diffusion coefficient in the infinite box, the ideal real system, L is the simulation box length, η is the shear viscosity, k_B is the Boltzmann constant, T is the absolute temperature, and γ is a dimensionless constant.

To evaluate the validity of representing natural gas using pure methane, diffusion coefficients obtained from the pure methane system were compared with those from a real gas system containing components such as N_2 , C_2H_6 , and C_5H_{12} (Table 5). At 354.15 K and 14 MPa, the self-diffusion coefficient of methane in the simplified system shows good agreement with that in the real gas system, with deviations within 15%.

Table 5. Diffusion coefficients of methane system and real system.

System Types	Self-Diffusion Coefficient (m ² /s)	
	CH ₄	CO ₂
Methane system	1.0267×10^{-7}	7.5500×10^{-8}
Real system	8.6333×10^{-8}	6.4833×10^{-8}

This result supports the feasibility of using pure methane as a representative component for bulk-phase diffusion studies under the investigated conditions. Therefore, to reduce computational complexity, methane was used to represent hydrocarbon components in subsequent simulations.

However, this simplification may not be universally applicable. At higher pressures or for specific compositions, minor components may significantly influence diffusion behavior by altering fluid viscosity, density, and intermolecular interactions. Therefore, the conclusions of this study are mainly applicable to methane-dominated systems. Future work should consider the effects of additional components for more accurate predictions in complex systems.

3. Result and Discussion

3.1. Experimental Results

The diffusion behavior of the mixed system of injected gas with 90% CO₂ content and formation gas at 5, 10, 14 MPa was studied and tested, as shown in Figure 4. The diffusion coefficients of CH₄ at 5, 10, and 14 MPa are 2.578×10^{-7} , 1.049×10^{-7} , and 6.402×10^{-8} m²/s. For CO₂, the corresponding diffusion coefficients at 5, 10, and 14 MPa are 1.288×10^{-7} , 7.712×10^{-8} , and 6.258×10^{-8} m²/s.

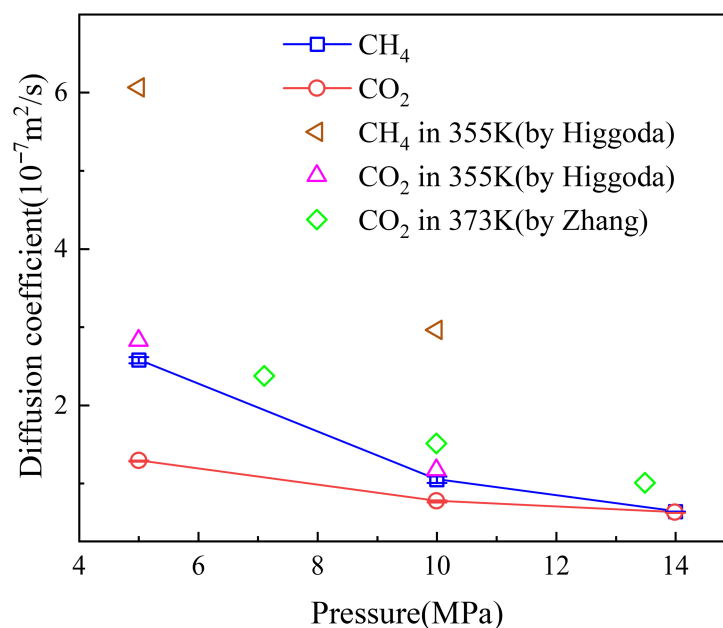


Figure 4. Experimental diffusion coefficients under different pressures.

To validate the reliability of the experimental results, the measured diffusion coefficients were compared with data reported in the literature. At a temperature of 354.15 K, the diffusion coefficients obtained in this study are generally lower than those reported by Higgoda et al. [45] at 355 K for the CO₂-CH₄ binary system. For instance, at 10 MPa, our measured D_{CO_2} is 7.712×10^{-8} m²/s, while Higgoda et al. [45] reported approximately 1.1654×10^{-7} m²/s from molecular simulations under similar conditions. This deviation may be attributed to the use of real gas mixtures in our experiments versus pure components in simulations, as well as the influence of diffusion cell walls. Additionally, Zhang et al. [46] reported CO₂ self-diffusion coefficients of about 1.505×10^{-7} m²/s at 373 K and 10 MPa, which are higher than our values at 354.15 K, consistent with the expected temperature dependence. Overall, all values remain on the order of 10^{-8} m²/s, supporting the reasonableness of our experimental measurements.

3.2. Diffusion Coefficient of Binary Fluid

At 354.15 K, the diffusion behavior of the CO₂-CH₄ system was investigated using molecular dynamics simulations under various pressures and CO₂ mole fractions. The calculated diffusion coefficients are presented in Figure 5. Consistent with previous molecular simulation studies, the diffusion coefficient of CH₄ is higher than that of CO₂ over the entire pressure range considered. For instance, Vella [47] reported that CH₄ diffuses faster than CO₂ under ideal gas conditions, which is mainly attributed to the stronger intermolecular interactions of CO₂. This behavior can be interpreted from a molecular perspective. Although the molecular diameter of CH₄ (0.38 nm) is slightly larger than that of CO₂ (0.33 nm), CO₂ exhibits higher polarizability, resulting in stronger van der Waals and electrostatic interactions with surrounding molecules. Moreover, as a linear and more polarizable molecule, CO₂ is more likely to form transient intermolecular associations, which hinder its mobility. In contrast, CH₄ is a nonpolar molecule with weaker intermolecular interactions, allowing it to diffuse more readily under the identical conditions.

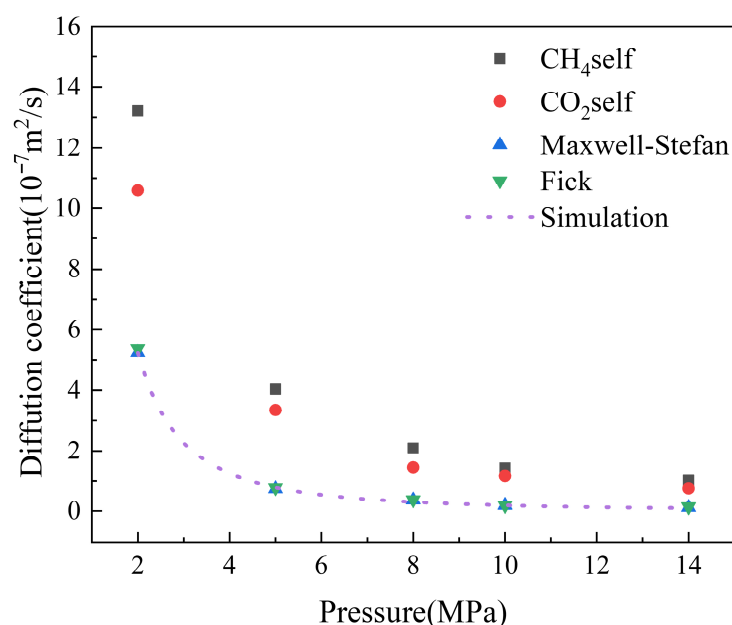


Figure 5. Calculated diffusion coefficients under different pressures.

This bulk-phase result contrasts with the behavior commonly observed in micro-nano systems, where CO₂ often diffuses faster than CH₄ due to confinement effects, as reported by Liu et al. [18]. Nevertheless, bulk-phase diffusion provides a fundamental basis for understanding confined transport. Given that most reservoir pore sizes are significantly larger than molecular dimensions, molecular diffusion remains the dominant mass-transfer mechanism, underscoring the importance of bulk-phase analysis. In addition, the self-diffusion coefficients are slightly higher than the corresponding Maxwell–Stefan and Fick diffusion coefficients, as self-diffusion reflects the mobility of individual molecules, whereas mutual diffusion is influenced by intermolecular interactions between different species.

Furthermore, as shown in Figure 5, the self-diffusion coefficients of CO₂ and CH₄ converge with increasing pressure. At 354.15 K, CH₄ becomes supercritical above 4.6 MPa, and its diffusion coefficient drops sharply; CO₂ enters the supercritical state above 8 MPa, after which the two coefficients approach each other. Near the critical point, long-range density fluctuations dominate diffusion, and as noted by Zhao et al. [26], such fluctuations weaken differences in diffusion behavior between molecular species. As pressure increases further, the intense thermal motion in the supercritical state largely overcomes the elec-

trostatic interactions that distinguish polar CO₂ from nonpolar CH₄, further promoting convergence of the diffusion coefficients.

Figure 6 illustrates the results of the experimental and simulated diffusion coefficients. Although the diffusion laws obtained by experiments and simulations are consistent, the diffusion coefficients obtained by simulations are always greater than those obtained by experiments. This discrepancy can primarily be attributed to the use of real gas mixtures in the experiments, while the simulations were based on simplified pure-component systems. In addition, the physical constraints imposed by the diffusion cell walls in the experiments may hinder molecular diffusion. As shown in Table 5, other components or impurities in the real gas may form agglomerates, which hinder the diffusion of molecules, resulting in low experimental measurements.

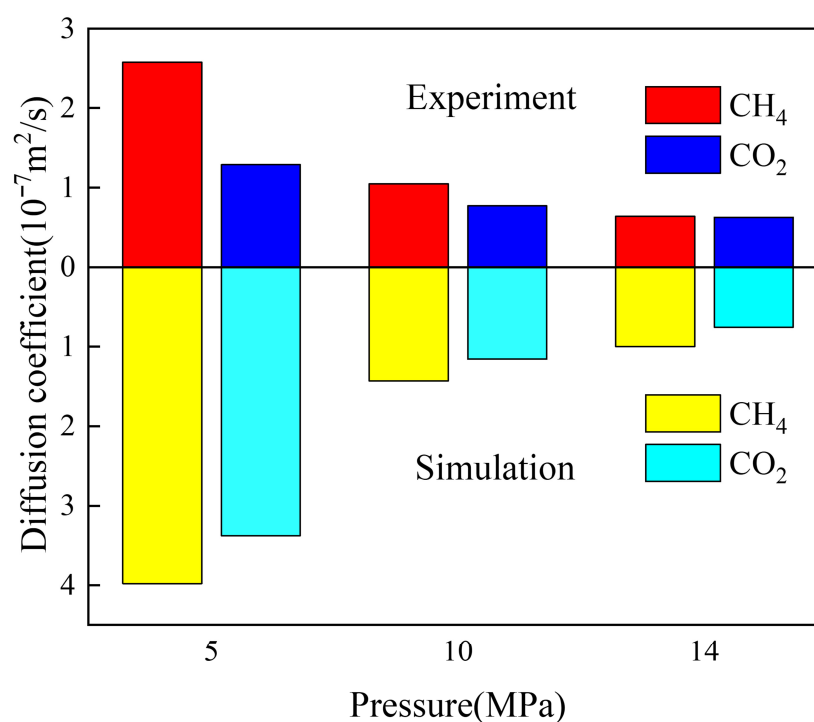


Figure 6. Comparison of experimental and simulated diffusion coefficients.

As shown in Figure 7, the diffusion coefficient of the system decreases with the increase of CO₂ mole fraction. Hu et al. [21] reported this phenomenon. This behavior is primarily attributed to enhanced intermolecular interactions among polar CO₂ molecules in the dense supercritical fluid, which increase resistance to molecular diffusion. Under supercritical conditions, binary mixtures exhibit significant non-ideal behavior. Moreover, the self-diffusion coefficient is no longer only determined by temperature and molecular properties, but is closely related to the mole fraction of the component. Although the concentration gradient is the driving force of macroscopic diffusion, the intermolecular interaction and the resulting molecular migration ability are significantly affected by the composition of the mixture. In contrast, as the pressure decreases, the system behavior is closer to the ideal gas state, and the kinetic factors affecting the diffusion are less dependent on the composition of the mixture. Therefore, in the lower pressure region, the change of the diffusion coefficient by the injected gas composition is relatively small.

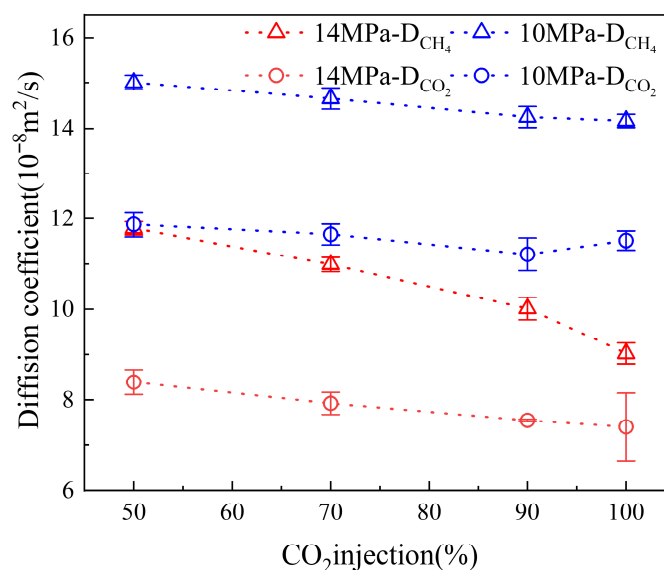


Figure 7. Self-diffusion coefficient under different injection gas concentration conditions.

In this study, MD simulation was used to investigate the effects of gravity and different gas injection positions on the diffusion behavior of the system. The calculation results are shown in Figure 8. Under formation conditions, gravity has a weak promoting effect on the migration process of fluid molecules. Although the diffusion coefficient increases slightly, its influence is not enough to change the order of magnitude of diffusion, and has limited influence on the actual macroscopic mixing of injected gas and formation gas. Under the influence of gravity, the effect of gas injection position (upper or lower) on the overall diffusion behavior of the system was further examined. The results indicate that the injection position has a negligible impact on the average diffusion coefficient of the mixture. However, the gas injection position has a significant effect on the diffusion behavior of the component itself: the upper gas injection significantly weakens the diffusion of methane and enhances the diffusion of carbon dioxide, while the lower gas injection is opposite. This arises from two mechanisms: gravity stratification, driven by the molecular mass difference, which causes CH₄ to accumulate in the upper region and CO₂ in the lower region, and density-driven convection, triggered when heavier CO₂ is injected below lighter CH₄ (unstable configuration), which promotes vertical mixing and enhances CH₄ diffusion.

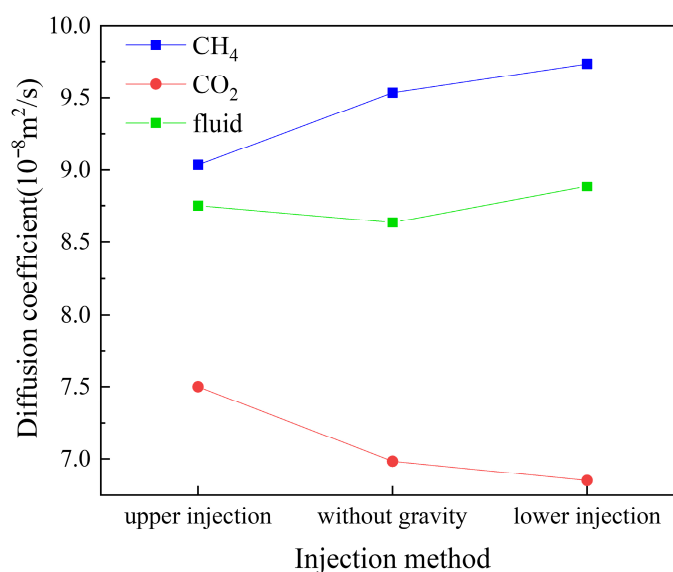


Figure 8. Effect of gas injection mode on diffusion coefficient.

3.3. Thermodynamic Factor Γ

The thermodynamic factor Γ quantifies the non-ideality of a mixture [48], where $\Gamma = 1$ indicates ideal behavior, and $\Gamma \neq 1$ reflects deviation from ideality. The $\text{CO}_2\text{-CH}_4$ system was simulated by MD, and the thermodynamic factor Γ data after equilibrium are shown in Figure 9. Except for a significant minimum value region, Γ is generally greater than 1, indicating positive deviation from ideality, which becomes more pronounced as pressure increases.

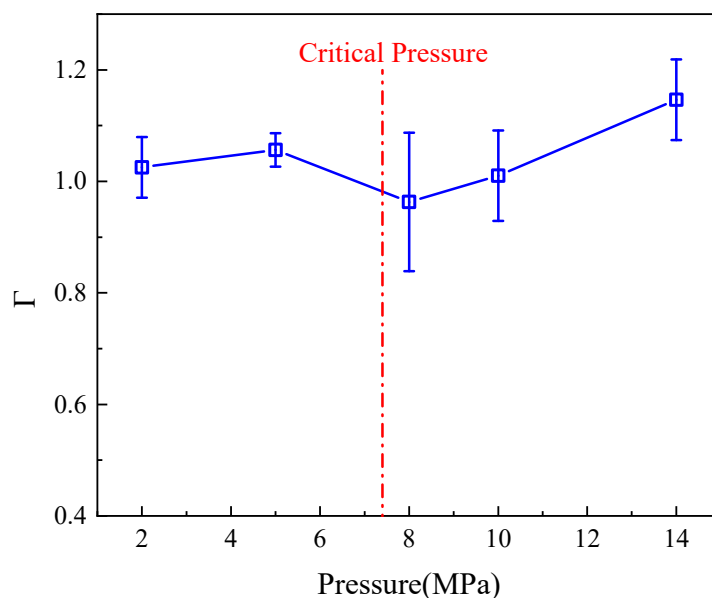


Figure 9. Variation of thermodynamic factors with pressure. (The red dotted line represents the critical pressure of carbon dioxide).

According to its definition, the thermodynamic factor approaches zero near the phase transition point. At this condition, the system exhibits minimal resistance to compositional fluctuations, resulting in a pronounced minimum in the thermodynamic factor, often manifested as a “well” in the profile.

As shown in Figure 9, the thermodynamic factor of the CO_2 system reaches a very low value in the pressure range of 8–10 MPa, indicating that the system is close to its critical point (the critical pressure of CO_2 is approximately 7.38 MPa). In this near-critical region, although the system exists in a supercritical state above the critical pressure and no macroscopic phase transition occurs, the thermodynamic factor is still strongly influenced by critical fluctuations and decreases significantly.

Furthermore, a Widom line extends into the supercritical region from the critical point. Along this line, the properties of the supercritical fluid undergo a continuous but rapid transition from gas-like to liquid-like behavior. Correspondingly, thermodynamic response functions, including the thermodynamic factor, typically exhibit extrema or peak variations in this region.

3.4. Characterization of $\text{CO}_2\text{-CH}_4$ Interaction

The MD simulation of $\text{CO}_2\text{-CH}_4$ system was carried out, and the van der Waals interaction of the system under different pressures was analyzed. The calculation results are shown in Figure 10a. It can be seen from the figure that the van der Waals interaction energy of the system after equilibrium significantly increases with the rising pressure. This directly reflects that the increased pressure leads to the increase of the density of the system and the decrease of the average distance between molecules, which enhances the attraction between molecular pairs. In the high-pressure supercritical state, the molecules are in a

state of high density and frequent contact. This allows a single molecule to interact with more adjacent molecules, and the superposition of all interactions leads to a significant decrease in the total attractive potential of the system. This enhanced van der Waals interaction at high density plays an important role in understanding fluid structure and diffusion behavior.

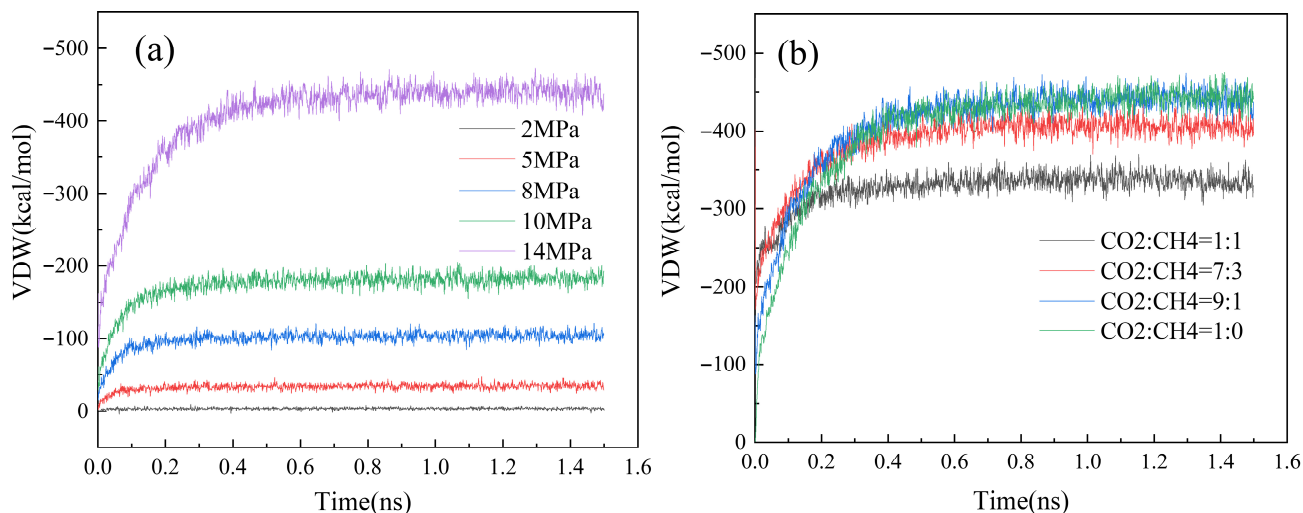


Figure 10. Van der Waals interaction energy: (a) under different pressures; (b) under different injection gas ratios.

The van der Waals interaction of the system under different injection gas concentrations was analyzed. The calculation results are shown in Figure 10b. It can be seen from the figure that the van der Waals interaction energy of the system after equilibrium increases with the increase of CO₂ component concentration. This is mainly due to the change of system composition: with the increase of CO₂ molar fraction, the number of CO₂ molecules per unit volume increases relatively, and CO₂ molecules have higher polarizability and quadrupole moment than CH₄, and their intermolecular and cross-interaction potential energy is lower. At high concentrations, the proportion of interactions involving CO₂ molecules increases. These stronger interactions lead to an increase in the overall van der Waals attraction of the system. The van der Waals interaction increases with the concentration, which is expected to affect the diffusion behavior of the components and the phase equilibrium of the system.

3.5. Ternary Fluid Diffusion Coefficient

In this study, the effect of water content on the diffusion behavior of CO₂-CH₄ system was investigated by MD simulation. The calculation results are shown in Figure 11. In the range of temperature and pressure studied, water always exists in the form of liquid dense fluid, which does not reach the supercritical state, so it does not involve the special effect of supercritical water. Under the condition of water, the diffusion coefficients of CH₄ and CO₂ decreased, which is consistent with the simulation work of Mohammadi et al. [49]. They found that the diffusion coefficient decreased significantly with the increase of water content, which was attributed to the higher solubility and stronger hydrogen bond interaction between CO₂ and water.

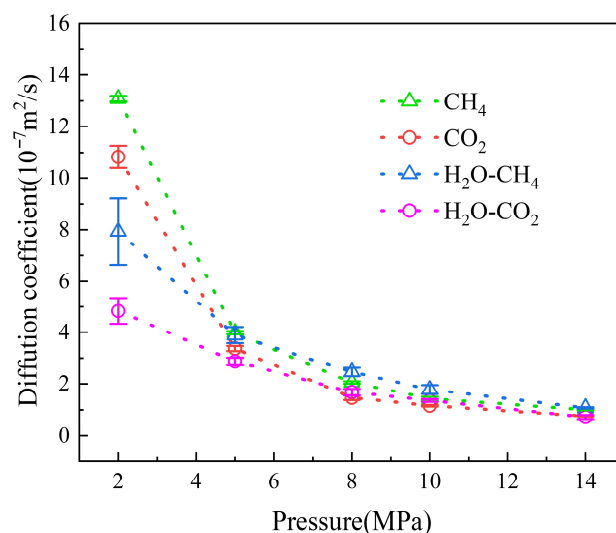


Figure 11. Effect of water content on diffusion coefficient.

It is worth noting that the decrease of CO_2 diffusion coefficient is more significant than that of CH_4 . This is mainly due to the higher solubility of CO_2 in water and the stronger interaction between CO_2 and water molecules, which have a more obvious hindrance to the migration of CO_2 . In contrast, the diffusion coefficient of methane is less affected due to its low solubility and weak interaction with water. The effect of water on diffusion is obviously pressure dependent: the effect is particularly significant at low pressure, while the effect of water molecules on diffusion coefficient is relatively limited at a high-pressure and supercritical state.

3.6. Molecular Spatial Distribution Characteristics

The CO_2 - CH_4 system was simulated by MD, and the radial distribution function (RDF) data of the system after equilibrium were analyzed. As shown in Figure 12, the RDF between gases has a peak at 4.5 Å, indicating that there is a short-range interaction between gas molecules. The RDF of H_2O - H_2O shows a peak at 2.8 Å, which is a typical hydrogen bond structure of liquid water. The RDF of H_2O - CO_2 has a peak at 4 Å, but H_2O - CH_4 does not. This is attributed to the weak electrostatic interaction between the quadrupole moment of CO_2 and the dipole moment of water, while the H_2O - CH_4 is mainly a weak van der Waals force.

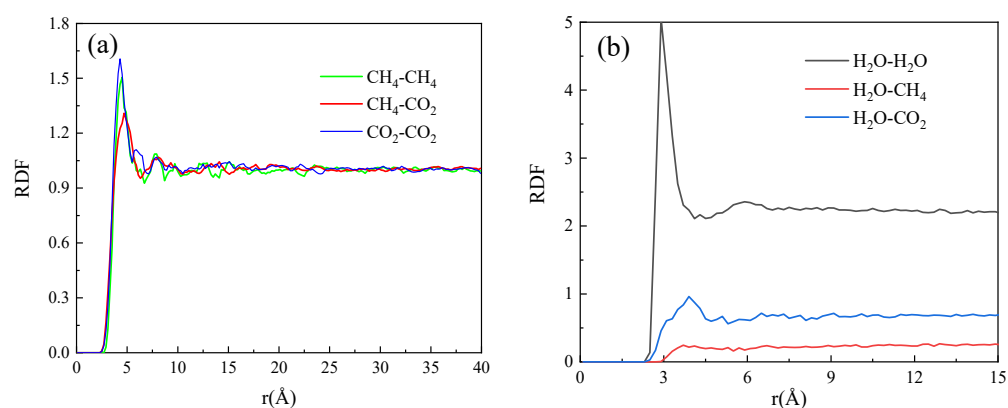


Figure 12. Intermolecular radial distribution functions: (a) Gas-gas radial distribution; (b) Water-gas radial distribution.

In this study, MD simulation was used to explore the evolution of the system density distribution during the diffusion process, as shown in Figure 13a. Through the statistical

analysis of the displacement of different types of molecules in the diffusion process, the overall diffusion dynamics can be characterized. The results show that the macroscopic displacement of each component tends to be stable at about 1 ns, indicating that the system has basically reached the equilibrium conditions required for diffusion analysis.

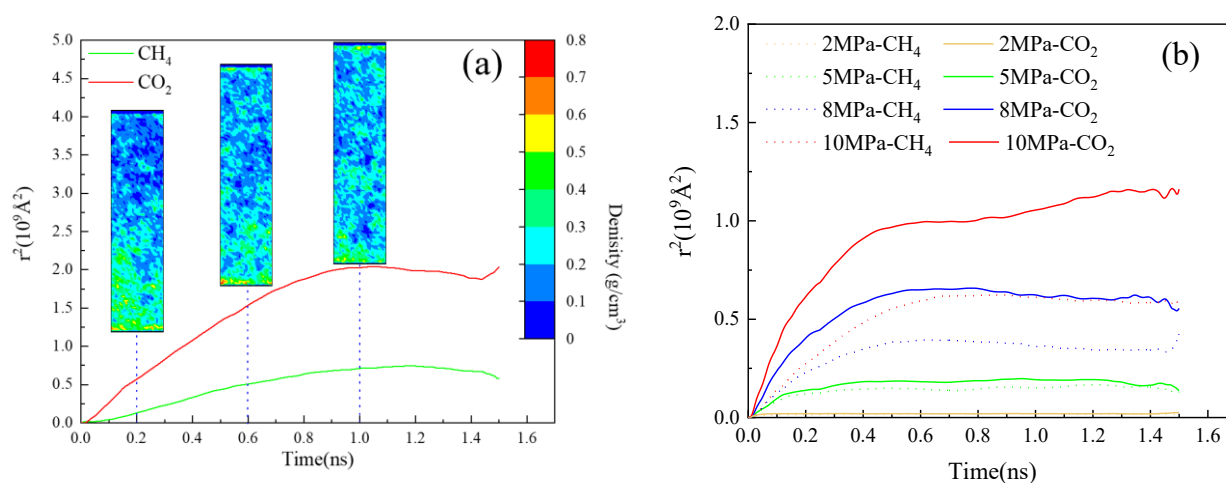


Figure 13. Variation of axial displacement with time: (a) 14 MPa; (b) 2, 5, 8, 10 MPa.

As shown in Figure 13b, it is observed that the total axial diffusion displacement of CO₂ is much larger than that of CH₄ under high pressure, although the self-diffusion coefficient of CH₄ is higher than that of CO₂ in this pressure range. This phenomenon can be explained by the difference in the number density of the two molecules: at high pressure, the molecular number density of CO₂ is significantly higher than that of CH₄, while below 8 MPa, there is no significant difference in the number density between the two molecules. Therefore, when calculating or measuring the displacement parameters involving the total number of molecules, the higher number of molecules of CO₂ compensates for its lower individual mobility, resulting in a total displacement greater than that of CH₄.

Fluid interface primarily forms between immiscible fluids with significant differences in properties, which is usually related to different phase states. In this study, although CO₂ and CH₄ are in a supercritical state, water remains liquid because the critical pressure of water is much higher than the temperature and pressure of the system. This phase difference and the immiscibility between supercritical gas mixtures and liquid water lead to the formation of a stable molecular interface.

This simulation finding is consistent with the field practice of CO₂ geological storage: when supercritical CO₂ is injected into water-bearing porous rocks, a clear interface will be formed with formation water. Due to the immiscibility of the two-phase fluids and the difference in density, CO₂ tends to occupy the upper space of the pores with the continuous phase, while water is distributed in the lower part. The interface is stabilized by capillary force in the pore structure.

Figure 14a illustrates the aggregation of CO₂ molecules at the gas-water interface. This indicates that there is a preferential adsorption behavior of gas molecules at the interface, in which CO₂ molecules with stronger polarity are more easily adsorbed at the interface than methane. Figure 14b depicts a snapshot of the initial contact between CO₂ and CH₄, where no distinct interface is formed between the two gases. Although CH₄ is in a supercritical state and CO₂ is a dense gas, a clear molecular interface cannot be formed between the two components. This is because the transition between gas and supercritical fluid is a continuous physical gradient process rather than a sudden phase transition.

Although this study did not quantitatively analyze the direct effect of dissolution on diffusion and mass transfer, considering the possible reaction between CO₂ and water and

the long-term effect of dissolution, this could have a further impact on the efficiency of CO₂ geological storage. Therefore, in-depth study of the effects of dissolution and related chemical reactions on long-term storage is an important direction that needs attention in the future.

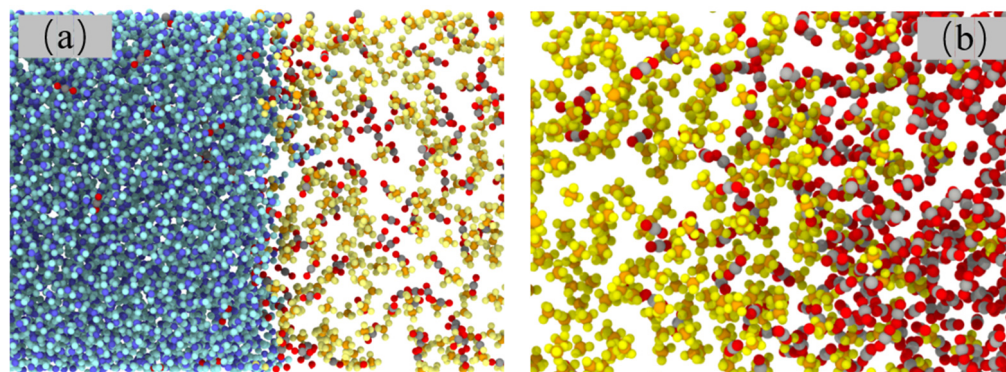


Figure 14. Molecular interfaces: (a) Gas-water interface; (b) Contact of two gases.

4. Conclusions

This study systematically investigates the diffusion behavior of CO₂-CH₄-H₂O systems under reservoir conditions using combined experimental and molecular simulation approaches.

The results demonstrate that diffusion coefficients follow the order $D_{\text{CH}_4} > D_{\text{CO}_2} > D_{\text{Fick}}$ and decrease with increasing pressure. CO₂ concentration and water content significantly reduce diffusion due to enhanced intermolecular interactions and interfacial effects. Gravity has a negligible impact on overall diffusion behavior.

Near the critical region, strong non-ideal behavior is observed, characterized by a pronounced minimum in the thermodynamic factor. Water induces interfacial enrichment of CO₂, further hindering diffusion.

These findings provide fundamental insights into multicomponent transport mechanisms and offer theoretical support for optimizing CO₂ injection strategies in CCUS and EGR applications. Future work should extend this analysis to confined porous systems to better represent realistic reservoir conditions.

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Abbreviations

The following abbreviations are used in this manuscript:

CCUS	Carbon capture, utilization and storage
EGR	Enhanced oil and gas recovery
QENS	Quasi-Elastic Neutron Scattering
PFG-NMR	Pulsed Field Gradient Nuclear Magnetic Resonance
HPGC	High-pressure gas chromatography
MD	Molecular Dynamics
GCMC	Grand canonical Monte Carlo

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