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Molecular dynamics insights into gas-water interfacial tension: Optimizing hydrogen storage in subsurface conditions

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Abstract

This study presents a comprehensive analysis of interfacial tension (IFT) between pore water and hydrogen-cushion gas mixtures in subsurface porous media, a key variable in the distribution of gas mixtures for hydrogen storage. Employing molecular dynamics simulations, we developed two IFT models at 20 MPa and 373 K: one for an H₂-CO₂-H₂O system and another for an H₂-CH₄-H₂O system. The models reveal that increasing cushion gas concentration reduces gas-water IFT. Notably, for H₂-CO₂-H₂O mixtures, the IFT substantially decreases with CO₂ concentration up to 40%, after which the reduction rate diminishes. In H₂-CH₄-H₂O mixtures, the IFT decreases linearly with CH₄ concentration. The study attributes these variations to local density distributions and molecular orientation effects. Specifically, CO₂ adsorption at the interface up to 40% concentration significantly lowers IFT, while CH₄ adsorption proportionally decreases IFT. The influence of CO₂ on water molecule orientation at the interface, in contrast to the non-effect of CH₄, is also critical in enhancing IFT reduction. Our results also highlight the reduction of H₂ self-diffusion at the interface caused by CO₂ and CH₄, an essential factor in optimizing subsurface hydrogen storage operations.

1 Introduction

Hydrogen has long been recognized as a cornerstone for the transition to a sustainable energy landscape. From its nascent inclusion in the energy dialogue to its pivotal role in achieving global net-zero emission targets, hydrogen’s versatility is undisputed in its application across transportation, industrial processes, and electricity generation sectors [1–3]. Its versatility is evident in applications from transportation fuel to electricity generation, with its production exceeding 90 million metric tons in 2020 and projected to increase annually [4,5]. The Hydrogen Council estimates that achieving net-zero will require around 660 million tons of hydrogen by 2050, equating to 22% of forecasted global energy demand [6]. The surface storage technologies such as physical storage through compression, liquefaction, and adsorption or chemical storage through metal hydrides and fuel cells may eventually be unable to meet such large hydrogen demand [7–10]. On the other side, given the experimental nature of conventional storage methods, the vast capacity of underground porous media like aquifers and depleted hydrocarbon reservoirs has proven essential for large-scale hydrogen storage, as demonstrated by successful global implementations [11–14]. The operational cornerstone of subsurface hydrogen storage lies in the injection of a cushion gas—commonly CO_2 or CH_4 —to form a compressible gas plume, enabling cyclical storage modulation through pressure dynamics [11,15–20]. A critical determinant in this process is the interfacial tension (IFT) between the hydrogen-cushion gas mixture and in-situ water. IFT dictates the displacement efficiency of water and the distribution of the gas within the porous media, influencing the overall storage efficacy [21–26].

While historical research on IFT has been primarily centered on hydrogen-water interactions, recent investigations have illuminated the intricate effects of temperature, pressure, and salinity on these interactions. For instance, studies by Slowinski et al., and Massoudi and King reported minimal pressure effects on the IFT at standard temperatures [27,28], while Chow et al., observed a pronounced temperature dependency within an extensive pressure range [29]. Similarly, Al-Mukainah et al., and Hosseini et al., correlated IFT increases directly with salinity across diverse temperature and pressure conditions [30,31]. The recent body of work delves into the IFT dynamics of hydrogen when combined with cushion gases. It has been established that CO_2 integration reduces the IFT, with the most notable effects under increased temperatures and pressures, though

diminishing above 20 MPa [29,32]. Investigations by Zoha et al., Doan et al., and Mirchi et al., extended these findings, linking CO₂ concentration and CH₄ presence with reduced IFT, particularly under varying temperature conditions [21,33–35].

Yet, the current scientific understanding remains limited, especially concerning the effects of fluctuating gas concentrations over time—a critical aspect affecting the relative permeability in multi-component flow and, hence, the spatial distribution of gas and water in underground storage porous media [36–41]. Traditional laboratory approaches have been unable to decipher the nanoscale mechanisms that drive IFT changes. This study, therefore, focuses on an analysis of the IFTs between water and H₂–CO₂, and H₂–CH₄ mixtures across the full concentration range, and under typical subsurface storage conditions (20 MPa, 373 K) [42,43]. Using molecular dynamics (MD) simulations, we explore the molecular behaviors at the gas-water interface, focusing on adsorption, orientation, and diffusion. Our insights contribute to a refined understanding of IFT evolution, which will contribute to more efficient and secure hydrogen storage. The manuscript is structured sequentially: Section 2 defines the gas-water models and simulation details; Section 3 describes the findings on gas-water IFT and molecular interactions; Section 4 proposes avenues for future research; and Section 5 presents our conclusions.

2 Models and simulation details

We used the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) for MD simulations to quantify the interfacial properties of two distinct systems at 20 MPa and 373 K: (a) binary gas-water systems, specifically H₂/H₂O, CO₂/H₂O, and CH₄/H₂O; and (b) ternary systems comprising H₂/CO₂ and H₂/CH₄ gas mixtures with water. This methodology builds upon our previously established approach for investigating interfacial phenomena between immiscible phases [44].

For the binary systems, we initiated the simulations by positioning 3000 water molecules centrally, flanked by 1000 gas molecules of either H₂, CO₂, or CH₄ on each side, creating a system of 5000 molecules within a simulation box measuring 5 nm by 5 nm by 30 nm. For each system, the 1-ns equilibration in the canonical ensemble (NVT) was firstly performed to mitigate molecular overlap, followed by another 15-ns calculation in the isothermal–isobaric ensemble (NPT) to further

equilibrate the system. Then, a production run of 10 ns was performed, with the last 2-ns trajectory collected for the property analysis. Each simulation model was repeated four times for each concentration case to ensure the robustness and reproducibility of our results. The ternary systems followed a similar setup, with 3000 water molecules at the core and varying ratios of cushion gas to H₂ on either side. We explored six different molar ratios for CO₂ and CH₄ with H₂, ranging from 10% to 80% cushion gas concentration. A table of the number of gas molecules in each system was listed in the supporting materials (Table S1). The simulation protocols for the ternary systems mirrored those of the binary systems, including ensemble application and data collection phases. We note that for reporting bulk vapor pressure in our simulations, we reported the pressure as the average of $(P_{xx} + P_{yy} + P_{zz})/3$. The use of the NPT ensemble is supported by its successful application in similar interfacial studies [45–48]. These studies demonstrated the NPT ensemble’s ability to equilibrate vapor-liquid and liquid-liquid systems, justifying its selection for our work on gas-water interfaces. However, if the system involves a solid substrate, for example, the liquid/solid system, reporting the P_{zz} value and utilizing the NP_{zz}T ensemble would be better, as the P_{zz} component accurately represents the tension along the interface normal [49–51].

Force field models—EPM2 for CO₂ [52,53], TIP3P for water [54,55], TraPPE-UA for CH₄ [56], and the Vrabec single-site model for H₂ [57]—were selected based on their demonstrated reliability in simulating interfacial interactions involving these species [44,58–61]. The suitability of TIP3P for these systems is well-established in literature, including the works of Vega and de Miguel [62], and Chen and Smith [63], who have previously reported the surface tensions using the TIP3P model. Our choice of the TIP3P water model is further supported by its adequacy in describing vapor-liquid equilibria (VLE) of H₂O–H₂ mixtures as demonstrated by Rahbari et al. [64], and its accuracy for predicting IFT in CH₄-water and CO₂-water systems at high pressures, as shown by Chen et al. [55]. However, interfacial property studies with other water models, such as TIP4P/2005(59), have been reported.

Throughout the MD simulations, we applied periodic boundary conditions across all three dimensions for binary and ternary systems. The leapfrog integrator was utilized with a time step of 1 fs. Electrostatic interactions were computed using the particle-particle-particle mesh (PPPM) method, and the non-bonded van der Waals forces were described by the 12-6 Lennard-Jones potential. A cutoff radius of 15 Å was applied for LJ interactions. A cutoff of 15 Å was applied for

Coulombic interactions, beyond which the PPPM method, with the accuracy of 1.0e-5, was used to handle long-range electrostatic interactions. The LJ interatomic potential parameters between species were calculated using the Lorentz-Berthelot mixing rules. Temperature and pressure were controlled using the Nose-Hoover thermostat and barostat during the simulations within the NVT and NPT ensembles, respectively. Fig. 1(a), 1(b), and 1(c) depict the equilibrium states of the binary and ternary systems, respectively, as obtained from the MD simulations.

3 Results and discussions

3.1 Interfacial tension

The interfacial tension between the gas and water was determined through the Gibbs IFT formulation [65]:

$$r = -\frac{1}{2} \left(\frac{P_{xx} + P_{yy}}{2} - P_{zz} \right) L_z$$

where L_z is the length of the simulation box along the z-direction. P_{xx} , P_{yy} , and P_{zz} are three diagonal elements of the pressure tensor. The coefficient $\frac{1}{2}$ represents the two interfaces existing. Fig. 1 shows the existence of two interfaces, perpendicular to the z-direction.

The calculated interfacial tensions (IFTs) for binary H₂-H₂O, CH₄-H₂O, and CO₂-H₂O systems at 20 MPa and 373 K were 55 mN/m, 42 mN/m, and 31 mN/m, respectively. These values exhibit strong concordance with reference data reporting IFTs of 58 mN/m for H₂-water [29], 44 mN/m for CH₄-water [66], and 29 mN/m for CO₂-water [67], as detailed in Table 1. Despite the underestimate for the CH₄/H₂O system, those general agreements corroborate the reliability of our MD simulations. In addition, the densities of CH₄, CO₂, H₂, and H₂O were calculated separately and compared with the NIST database at 373 K and 20 MPa in the supporting material (Table S2) for the validation of the force fields.

In Fig. 2(a), we present the quantified interfacial tension (IFT) at the gas-water interface as a function of CO₂ and CH₄ concentrations in their respective ternary systems with H₂ under 20 MPa and 373 K conditions. The data illustrate a trend where an increase in the proportion of cushion gas in the mixture with H₂ corresponds to a decrease in the IFT. This finding generally aligns with the observations of Chow et al. [29] for the CO₂-H₂-H₂O system and with the results

140 obtained by Zoha et al. [21] and Doan et al. [33] for their respective $\text{CO}_2\text{-H}_2\text{-H}_2\text{O}$ and $\text{CH}_4\text{-H}_2\text{-H}_2\text{O}$
 141 H_2O systems. However, direct quantitative comparisons with existing literature are challenging due
 142 to the scarcity of data under identical conditions. For instance, Chow et al.'s study was limited to
 143 a 0.3 CO_2 concentration, whereas Zoha et al. conducted their research at different temperatures.
 144 Nevertheless, the $\text{CO}_2\text{-H}_2$ gas mixture exhibits a lower IFT than the $\text{CH}_4\text{-H}_2$ mixture at equivalent
 145 concentrations of cushion gas. Furthermore, as depicted in Fig. 2(b), a significant observation within
 146 the $\text{CO}_2\text{-H}_2\text{-H}_2\text{O}$ system is that the IFT decreases substantially as the CO_2 concentration increases
 147 from 0% to 40%, after which the rate of decrease moderates from 40% to 100% CO_2 . In contrast,
 148 the IFT in the $\text{CH}_4\text{-H}_2\text{-H}_2\text{O}$ system diminishes linearly with increasing CH_4 concentration.

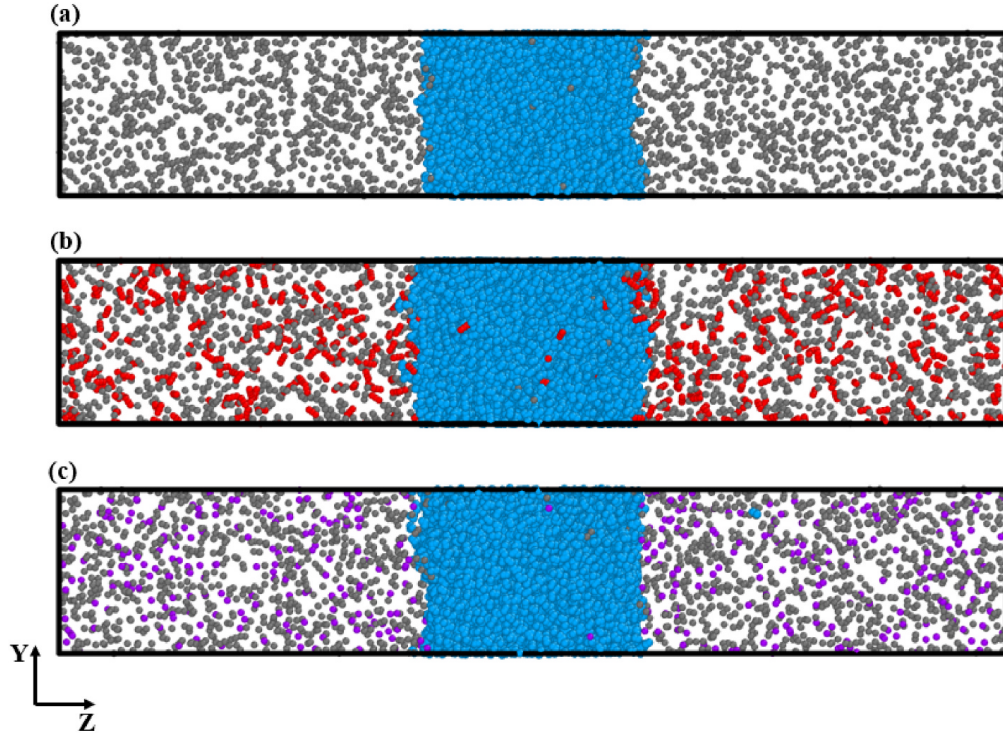


Fig. 1. The equilibrium state of binary and ternary systems at 20 MPa and 373 K. (a). Binary system of hydrogen and water, grey: H_2 , blue: H_2O . (b). Ternary system of $(\text{CO}_2+\text{H}_2)/\text{H}_2\text{O}$, red: CO_2 . (c). Ternary system of $(\text{CH}_4+\text{H}_2)/\text{H}_2\text{O}$, purple: CH_4 . (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1

The IFT of three binary systems from this work and previous publications.

Gas-Water	IFT-MD (mN/m)	IFT-Ref (mN/m)	Error%
H ₂ -Water	57	53-58([29,58,68])	1.7–7.5
CH ₄ -Water	42	44-49([66,69,70])	4.5–14.3
CO ₂ -Water	31	29-32([67,71,72])	3.1–6.9

3.2 Local density profile

In analyzing phase separation within the simulated H₂-H₂O system, local density profiles serve as a critical metric for delineating the bulk and interfacial regions. Fig. 3 illustrates the calculated local densities of H₂ and H₂O molecules along the z-axis. Given the negligible solubility of H₂ in water, a distinct separation between the gas and liquid phases is observed. In the H₂-dominated phase (region I), the water density profile is near zero, signifying a gas-rich environment. Conversely, in the water-dominated phase (region III), the H₂ density profile tends toward zero, indicating a liquid-rich region. The interface between these phases (region II) is identified by the points where the density profiles of water and hydrogen fall to zero, marking the boundaries of the interfacial region. The local density profiles of CO₂-Water and CH₄-Water systems were determined and plotted in Fig. S1 of the supporting materials. In addition, the solubilities of gases in the water were determined based on their densities in the water and compared with reference values in Table S3 of the supporting materials for further validation.

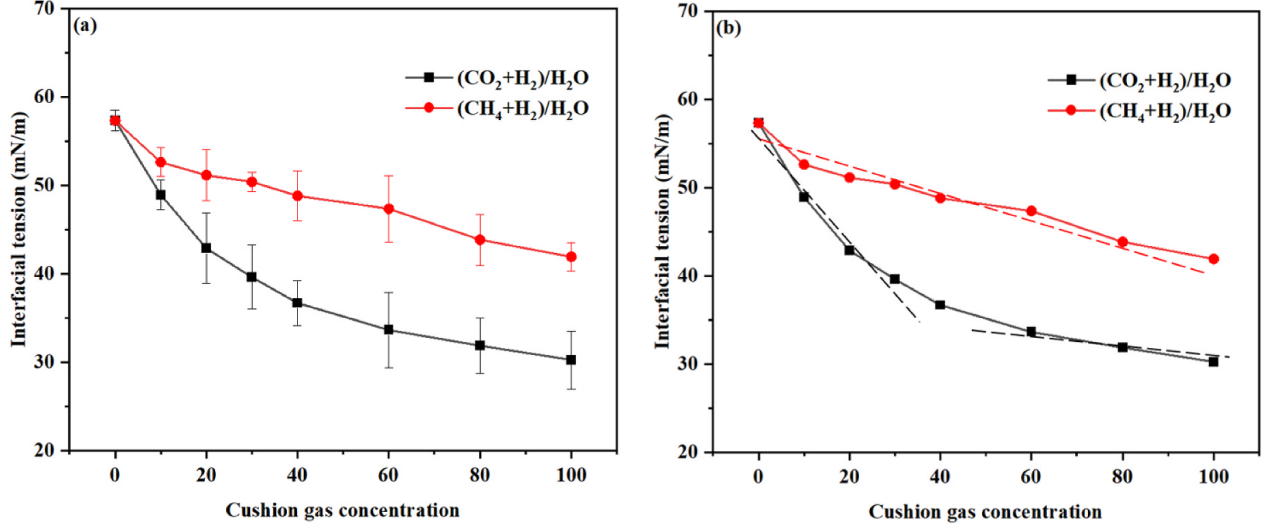


Fig. 2. (a) IFTs of $(\text{CO}_2 + \text{H}_2)/\text{H}_2\text{O}$ and $(\text{CH}_4 + \text{H}_2)/\text{H}_2\text{O}$ systems at 20 MPa and 373 K with different cushion gas concentrations. (b) The IFT curves fittings.

In the studied ternary systems, such as the (30% CO_2 + 70% H_2)/ H_2O and (30% CH_4 + 70% H_2)/ H_2O configurations depicted in Fig. 4, the local density profiles for CO_2 and CH_4 , alongside H_2O and H_2 , were analyzed. The profiles reveal a significant decline in the local densities of CO_2 and CH_4 within the water-rich phase, corroborating their limited solubility in water. Distinct from H_2 , the local densities of CO_2 and CH_4 are elevated in the interfacial region compared to the gas-rich phase. This indicates their preferential adsorption and accumulation at the gas-water interface—a phenomenon previously documented in the literature [73–75].

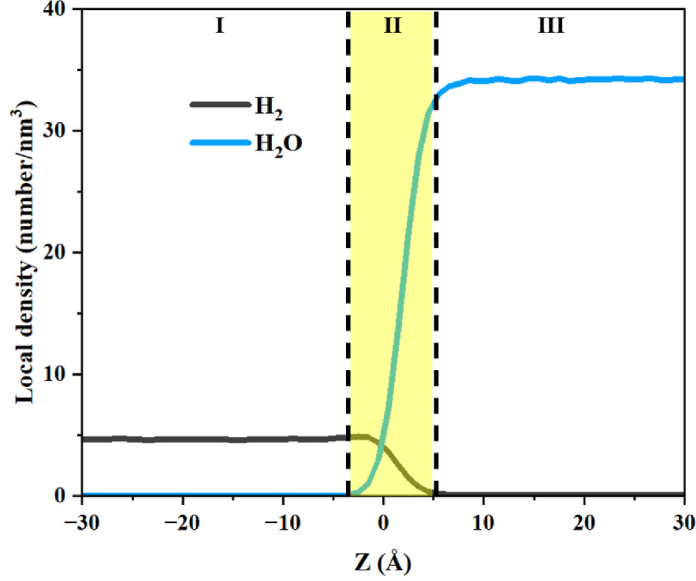


Fig. 3. The local density profiles of the H₂-water system at 373K and 20 MPa.

Notably, the interface region's local density of CO₂ exceeds that of CH₄ at an equivalent 30% concentration, suggesting a superior adsorption propensity of CO₂ molecules. This differential adsorption is attributed to the molecular interactions between the gas molecules and water at the interface. Quantitative analysis of the interaction energies reveals that CO₂-H₂O interactions (-537 kcal/mol) are substantially stronger than CH₄-H₂O interactions (-122 kcal/mol). Consequently, CO₂ exhibits a more pronounced adsorption at the gas-water interface than CH₄, as reflected by the higher interaction energy values.

In Fig. 5, we present the local density profiles of CO₂ and CH₄ across different concentrations, while Fig. 6 outlines the corresponding profiles for H₂. The local densities of the cushion gases in both the gas-rich phase and the interface region exhibit an increase correlating with rising cushion gas concentrations. At the studied conditions of 20 MPa and 373 K, CO₂ exists in a supercritical state, unlike CH₄, which remains gaseous [76]. This distinction results in a higher local density for supercritical CO₂ than for gaseous CH₄ within the gas-rich phase at equivalent concentrations. Additionally, CO₂'s more robust adsorption capacity than CH₄ leads to its greater local density at the gas-water interface for each concentration.

Furthermore, Fig. 6 indicates a decrease in H₂ local densities within the gas-rich and interface regions with increasing cushion gas concentration. This trend suggests that increased cushion gas adsorption at the interface diminishes the direct interaction between H₂ and H₂O molecules—

consequently, the gas-water IFT transition from being predominantly influenced by H₂ to being governed by cushion gases.

As shown in Fig. 7, the right-side interface region of the (CO₂+H₂)/H₂O system is depicted for various CO₂ concentrations, illustrating the adsorption behavior at the molecular level as obtained from the MD simulation. The visualization reveals a higher accumulation of CO₂ molecules within the interface region compared to the gas-rich phase, particularly pronounced at 20% and 40% CO₂ concentrations. This observation aligns with the local density profiles presented in Fig. 4(a). Furthermore, a positive correlation is noted between the CO₂ concentration and its accumulation at the interface region, corroborating the data in Fig. 5(a). This trend underscores the concentration-dependent nature of CO₂ interfacial adsorption behavior in the studied system.

3.3 Incremental adsorption mechanism

As discussed in Section 3.2, we observed an increase in cushion gas densities within the gas-rich phase and at the interface as the gas concentration in the system was raised. To elucidate the adsorption mechanisms at the gas-water interface, we evaluated the relative density profiles of the cushion gases at varying concentrations. Here, the relative density (ρ_r) of a cushion gas is defined as the ratio of its local density at the interface (ρ_{local}) to its bulk density in the gas-rich phase (ρ_{bulk}):

$$\rho_r = \frac{\rho_{local}}{\rho_{bulk}}$$

Fig. 8(a) and 8(b) display the relative density profiles for CO₂ and CH₄, respectively. In the (CO₂+H₂)/H₂O system, relative densities of CO₂ remain approximately constant at 2 for concentrations ranging from 10% to 40%. This constancy suggests a proportional relationship between the adsorbed CO₂ at the interface and the CO₂ in the gas-rich phase at concentrations below 40%. However, beyond a 40% CO₂ concentration, relative densities at the interface decrease with increasing concentration, indicating a saturation effect where further adsorption of CO₂ becomes increasingly difficult.

Conversely, in the (CH₄+H₂)/H₂O system, the relative densities of CH₄ at the interface maintain a steady proportionality to the densities in the gas-rich phase, irrespective of concentration. This behavior aligns with the IFT findings: in the (CO₂+H₂)/H₂O system, CO₂ molecules are readily

213 adsorbed at the interface at lower concentrations (0–40%), leading to substantial reductions in IFT.
 214 Once the interface region becomes saturated with CO_2 at around 40% concentration, additional
 215 CO_2 adsorption becomes more challenging, resulting in minor IFT variations. Meanwhile, in the
 216 $(\text{CH}_4+\text{H}_2)/\text{H}_2\text{O}$ system, a consistent decrease in IFT is observed as the CH_4 concentration increases,
 217 attributed to the continuous adsorption of CH_4 at the interface.

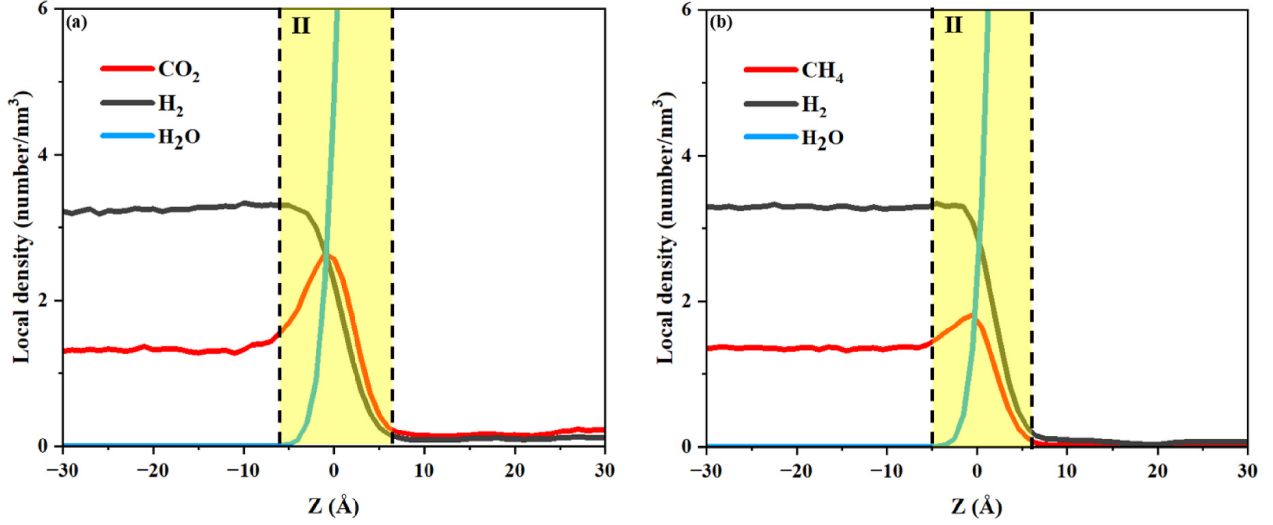


Fig. 4. The local density profiles: (a) $(\text{CO}_2+\text{H}_2)/\text{H}_2\text{O}$ system with 30% CO_2 concentration. (b) $(\text{CH}_4+\text{H}_2)/\text{H}_2\text{O}$ system with 30% CH_4 concentration.

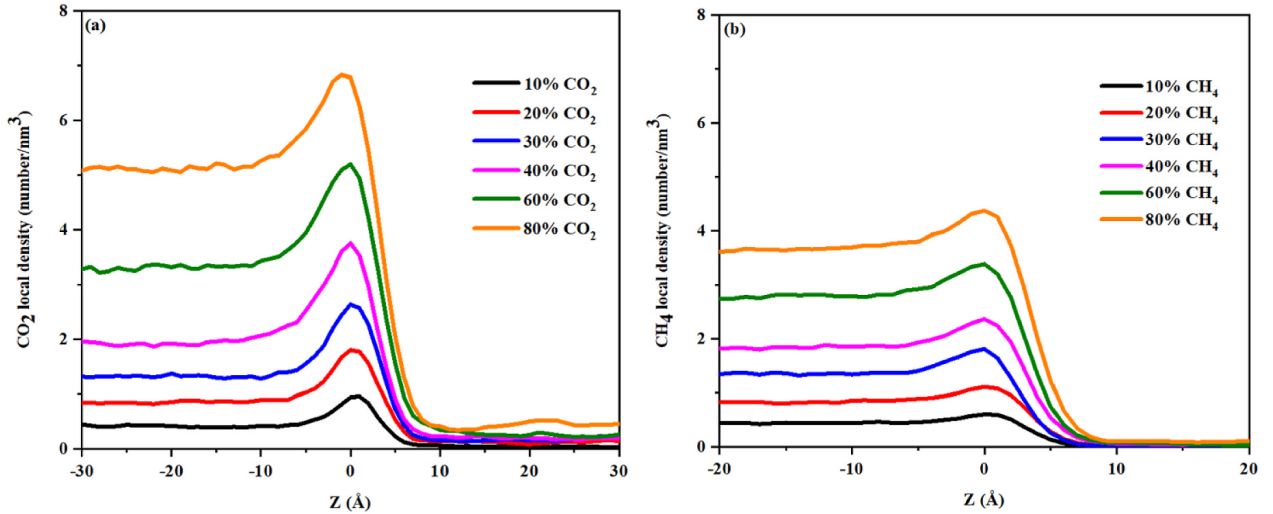


Fig. 5. The local density profiles: (a) CO_2 in $(\text{CO}_2+\text{H}_2)/\text{H}_2\text{O}$ system with different CO_2 concentrations. (b) CH_4 in $(\text{CH}_4+\text{H}_2)/\text{H}_2\text{O}$ system with different CH_4 concentrations.

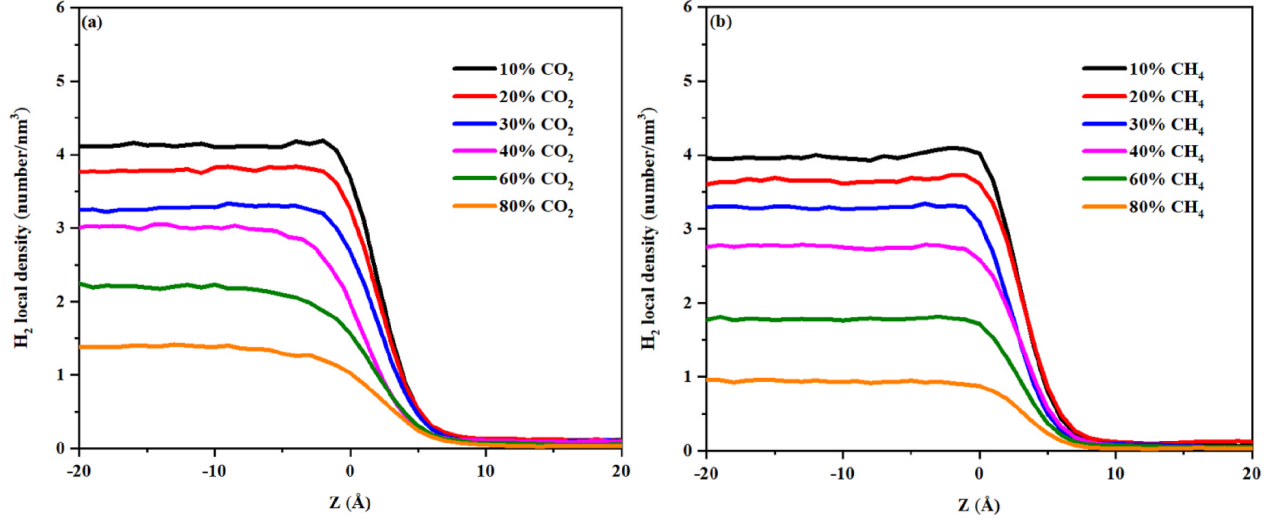


Fig. 6. The local density profiles: (a) H_2 in $(CO_2+H_2)/H_2O$ system with different CO_2 concentrations.
(b) H_2 in $(CH_4+H_2)/H_2O$ system with different CH_4 concentrations.

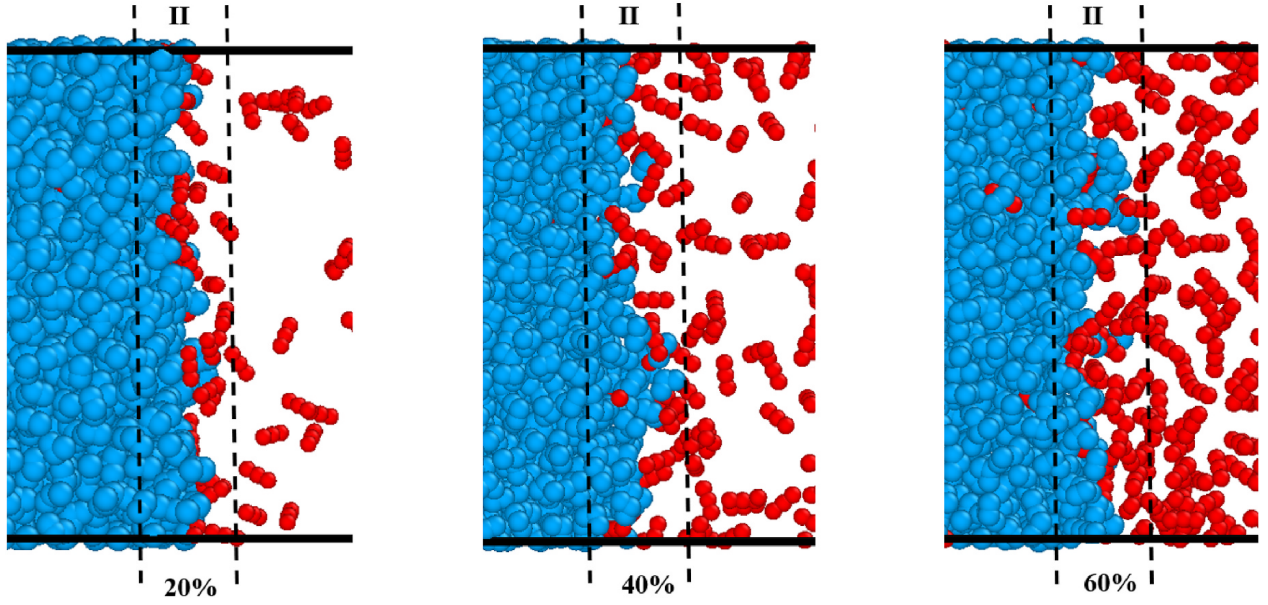


Fig. 7. Visualization of CO_2 molecules near the gas-water interface region with different concentrations.
 H_2 molecules on the right are not shown for clarity.

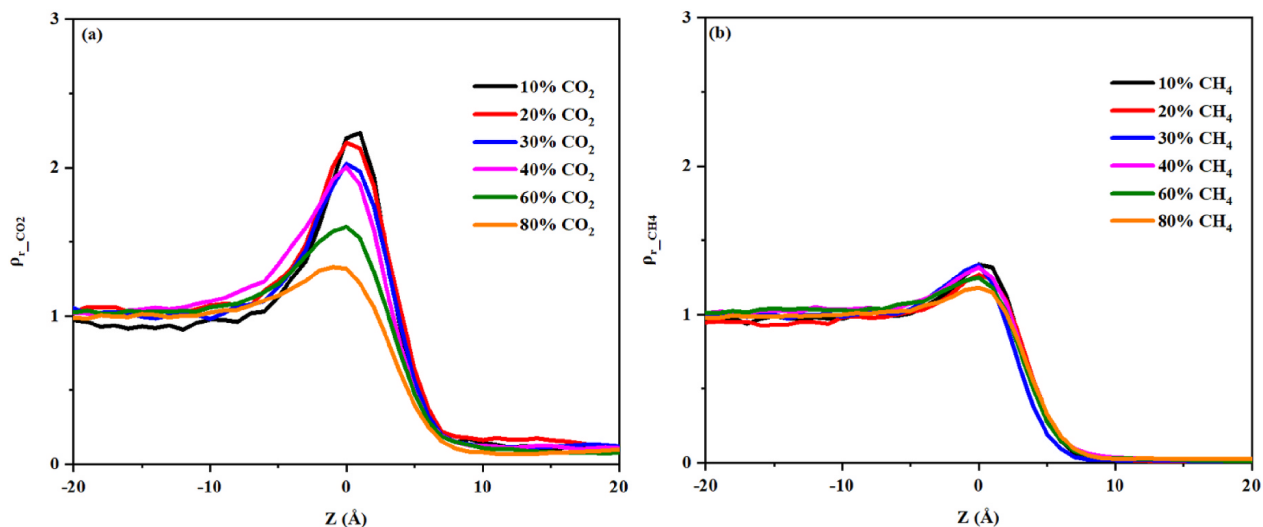


Fig. 8. Relative density profiles at different concentrations: (a) CO₂; (b) CH₄.

3.4 Molecular orientation

The influence of molecular orientation on interfacial tension is well-documented at the molecular level [44,77]. We investigated the orientation of cushion gas and water molecules at the gas-water interface by calculating the orientational order parameter (S). This parameter quantifies the preferential alignment of molecules relative to the interface as a function of their z -directional positioning [78]:

$$S = \frac{1}{2} \langle 3 \cos^2(\theta) - 1 \rangle$$

Here, θ represents the angle between the CO₂ molecule's centerline, the water molecule's dipole vector, and the z -axis. For CO₂, the preferential parallel orientation to the interface corresponds to S values nearing -0.5 , whereas S values near unity suggest a perpendicular orientation. Randomly oriented molecules would yield S values around zero.

The tetrahedral structure of CH₄ precludes a similar orientation analysis; hence, it was excluded from this portion of the study. Fig. 9 illustrates the orientational profiles for CO₂ and H₂O from the (CO₂+H₂)/H₂O system with a 20% CO₂ concentration. The CO₂ local density profile aids in delineating the interface region. Within the gas-rich and water-rich phases, the S values for CO₂ and H₂O approximate zero, indicating random molecular orientation. In the interface region, CO₂ molecules exhibit an S value of about -0.05 , indicating a slight preference for a parallel orientation to the interface. Water molecules present S values around -0.18 in the same region, suggesting

235 a more pronounced preference for parallel alignment. These molecular orientations for CO₂ and
 236 water are consistent with previous findings in the literature [44,58,79,80].

237 To delve deeper into the orientation of CO₂ at the gas-water interface, Fig. 10 quantifies the
 238 S values for CO₂ across a range of concentrations. It is consistently observed that CO₂ molecules
 239 prefer alignment parallel to the interface at all studied concentrations. A notable trend is the positive
 240 increase in S values with rising CO₂ concentration, suggesting a diminished parallel orientation as
 241 the interface becomes increasingly populated with adsorbed CO₂ molecules. However, beyond a
 242 40% concentration threshold, the S values plateau; for instance, CO₂ concentrations at 60%, 80%,
 243 and 100% maintain S values of approximately -0.03 within the interfacial region.

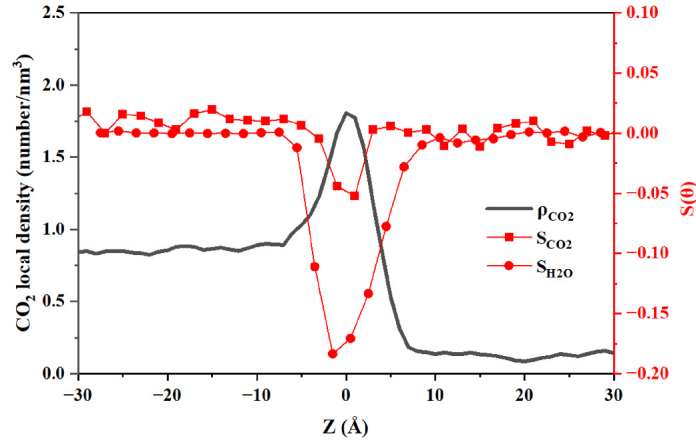


Fig. 9. Orientation profiles of CO₂ and H₂O molecules along the Z direction in the (CO₂+H₂)/H₂O system with the 20% CO₂ concentration. The density profile (black) is used to emphasize the location of the gas-water interface region.

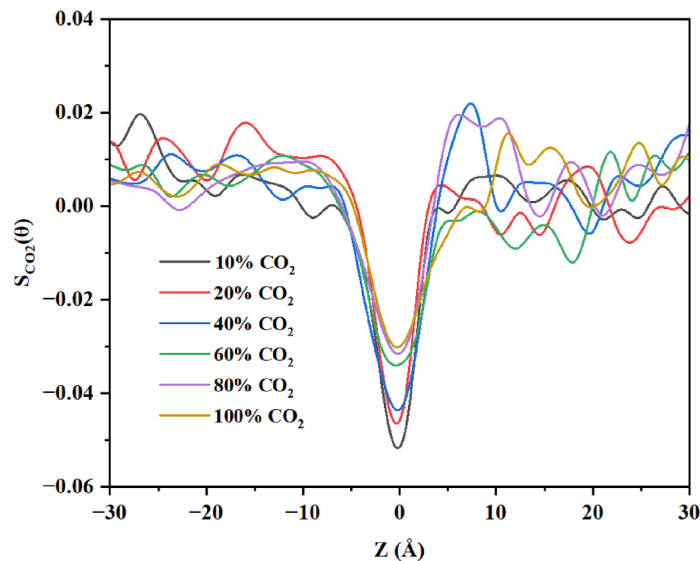


Fig. 10. CO₂ orientation profiles with different CO₂ concentrations.

This behavior aligns with the previously discussed interfacial tension and relative density findings. At CO₂ concentrations exceeding 40%, additional free CO₂ molecules face challenges in adsorbing to the already crowded interface, thus resulting in minor variations in interfacial tension and the orientational behavior of CO₂ molecules.

Fig. 11(a) illustrates the orientational profiles of water molecules within (CO₂+H₂)/H₂O systems across varying CO₂ concentrations, while Fig. 11(b) presents the corresponding data for (CH₄+H₂)/H₂O systems with different CH₄ concentrations. In both ternary systems, water molecules exhibit a preferential orientation at the gas-water interface, aligning their dipole vectors parallel to the interface.

When cushion gas concentration is considered, water's orientational order parameter (*S*) remains consistently unchanged at the interface with increasing CH₄ concentrations. Conversely, the *S* values for water positively increase at the interface with rising CO₂ concentrations. This trend suggests that CO₂ adsorption at the gas-water interface modifies its interfacial orientation and significantly influences that of water molecules. In contrast, the interfacial orientation of water molecules remains unaffected by CH₄ adsorption. This differential impact on water molecule orientation by CO₂ compared to CH₄ could contribute to the observed discrepancy in gas-water IFT reductions between the (CH₄+H₂)/H₂O and (CO₂+H₂)/H₂O systems for the same concentration of cushion gas, as illustrated in Fig. 2.

3.5 Molecular diffusion

Subsurface microorganisms, such as methanogens and acetogens, predominantly thrive at the gas-water interface and their metabolic processes can involve the consumption of H_2 , presenting a significant factor for consideration in UHS [81]. The self-diffusion of H_2 at the gas-water interface is relevant as it can affect microbial activity and, consequently, the consumption rate of H_2 . This section investigates the impact of cushion gases on H_2 self-diffusion at the interface. Utilizing methodologies from Liu et al. [45] and Yuan et al. [82], we divided the binary and ternary systems along the Z-axis into five distinct slabs to calculate H_2 self-diffusion coefficients within each slab: two in the gas-rich phase, two at the interface, and one in the water-rich phase. The mean-squared displacement (MSD) is used to quantify the self-diffusion coefficient of a gas, defined as [83,84]:

$$MSD(t) = \langle |r_i(t) - r_i(0)|^2 \rangle$$

where $r_i(t)$ is the position of particle i at time t , $r_i(0)$ is the particle's initial position, and the brackets denote an ensemble average. The self-diffusion coefficient, D , is subsequently deduced from the MSD as:

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} MSD(t)$$

Self-diffusion coefficients in binary systems are initially evaluated, as indicated by the black line for H_2 in the H_2 - H_2O system and the orange lines for CO_2 and CH_4 in the respective CO_2 - H_2O and CH_4 - H_2O systems depicted in Fig. 12. To validate these results, we referenced self-diffusion data for H_2 within calcite slit pores under comparable conditions of 20 MPa and 340 K [85]. Our simulation findings for the gas-rich phase are consistent with the reference values, exhibiting the same order of magnitude. In addition, Groß et al. [86] reported the experimental self-diffusion of CO_2 at 333 K and 20 MPa which was about $0.27 \times 10^{-7} \text{ m}^2/\text{s}$. With the temperature effect studied in their paper, it is believed that the self-diffusion of CO_2 at 20 MPa and 373 K should be in the range between $0.3 \times 10^{-7} \text{ m}^2/\text{s}$ to $0.4 \times 10^{-7} \text{ m}^2/\text{s}$, which is higher than our simulation result of $0.23 \times 10^{-7} \text{ m}^2/\text{s}$ in the bulk phase but very close to each other. The self-diffusion coefficient of bulk CH_4 reported from the experiment is around $1.4 \times 10^{-7} \text{ m}^2/\text{s}$ at 19 MPa and 353 K [87], compared with our simulation result of $0.6 \times 10^{-7} \text{ m}^2$ at 20 MPa and 373 K, the difference exists but accepted in the

order of magnitude. With the comparison of IFT shown in Table 1, the maximum IFT deviation of the CH₄-Water system could reach around 14.3%. We recommend a further refinement of the force field used for CH₄ in such a vapor-liquid IFT system. Finally, since the solubilities of H₂ and CH₄ in the water are small (as shown in the SI materials), the experimental self-diffusions of H₂ and CH₄ in the water are scarce. However, a comparison was found related to CO₂ diffusion in the water under a similar P/T condition. The self-diffusion of CO₂ in the water from our simulation is around $8.6 \times 10^{-9} \text{ m}^2/\text{s}$, consistent with the experimental result of approximately $7.45 \times 10^{-9} \text{ m}^2/\text{s}$ reported by Shane et al. [88].

Due to molecular weight differences, H₂ exhibits the highest self-diffusion, while CO₂ shows the lowest. In the gas-rich phase (region I), gas molecules demonstrate the highest self-diffusion coefficients, which diminish progressively towards and within the gas-water interface region (region II). Upon dissolution into the water-rich phase (region III), the self-diffusion coefficients of the gas molecules are notably reduced.

In ternary systems, the self-diffusion of H₂ diminishes in the presence of increasing concentrations of cushion gas. In the gas-rich phase, interactions between H₂ and cushion gas molecules lower H₂ self-diffusion due to the inherently lower self-diffusion of the cushion gases. The adsorption of cushion gas at the interface further impedes H₂ penetration, reducing its self-diffusion in this region. As cushion gas concentration escalates, the enhanced molecular interaction in the gas-rich phase and the increasing accumulation of adsorbed cushion gas at the interface concomitantly decrease the self-diffusion of H₂, making it increasingly challenging for H₂ to diffuse through the interface region.

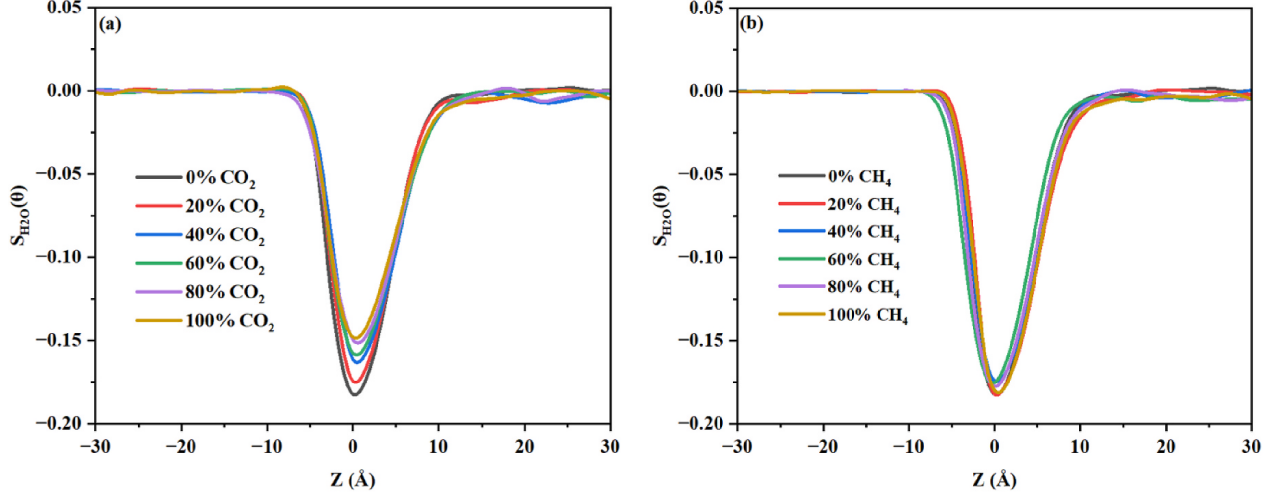


Fig. 11. H_2O orientation profiles from: (a) $(CO_2+H_2)/H_2O$ system with different CO_2 concentrations. (b) $(CH_4+H_2)/H_2O$ system with varying concentrations of CH_4 .

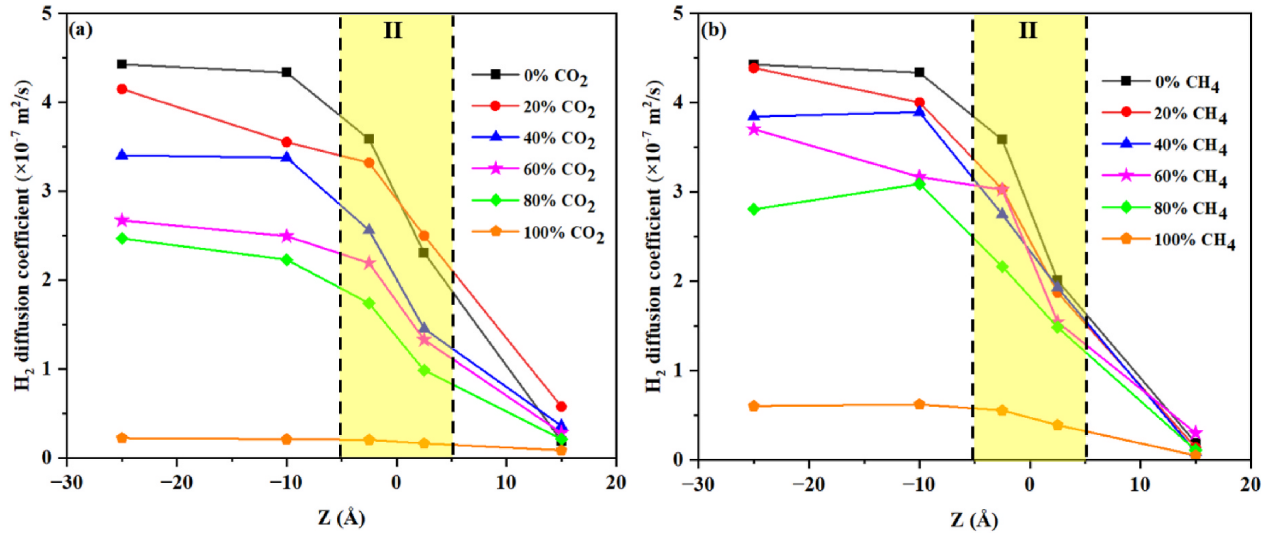


Fig. 12. H_2 self-diffusion coefficients in: (a) $(CO_2+H_2)/H_2O$ system with different CO_2 concentrations. (b) $(CH_4+H_2)/H_2O$ system with varying concentrations of CH_4 .

3.6 Further discussion

In this investigation, we have constructed two models to describe the IFT of gas-water systems at 20 MPa and 373 K, pertinent to UHS: one for $(CO_2+H_2)/H_2O$ mixtures and another for $(CH_4+H_2)/H_2O$ mixtures. It is acknowledged, however, that factors such as pressure and temperature also influence gas-water IFT, beyond gas concentration alone. Chow et al. [29], Pereira

et al. [89], Liu et al. [90], and Kashefi et al. [70] have provided IFT measurements for $\text{H}_2\text{-H}_2\text{O}$, $\text{CO}_2\text{-H}_2\text{O}$, and $\text{CH}_4\text{-H}_2\text{O}$ systems under varying pressures and temperatures, as detailed in Fig. 13. From their findings, we can infer that pressure notably impacts gas-water IFTs primarily at low-pressure regimes. Above the threshold of 20 MPa, IFT exhibits only marginal variations with further pressure increments, which suggests that the models developed herein can be applied across an extensive pressure range above 20 MPa at 373 K. In contrast, temperature has a pronounced effect on IFT; generally, an increase in temperature correlates with a decrease in gas-water IFT. For future work aimed at enhancing the comprehensiveness of IFT models for UHS, it is imperative to integrate the methodology from this study to quantify the (cushion gas + H_2)/ H_2O IFT as a function of gas concentration, particularly at lower pressure ranges or across varying temperatures.

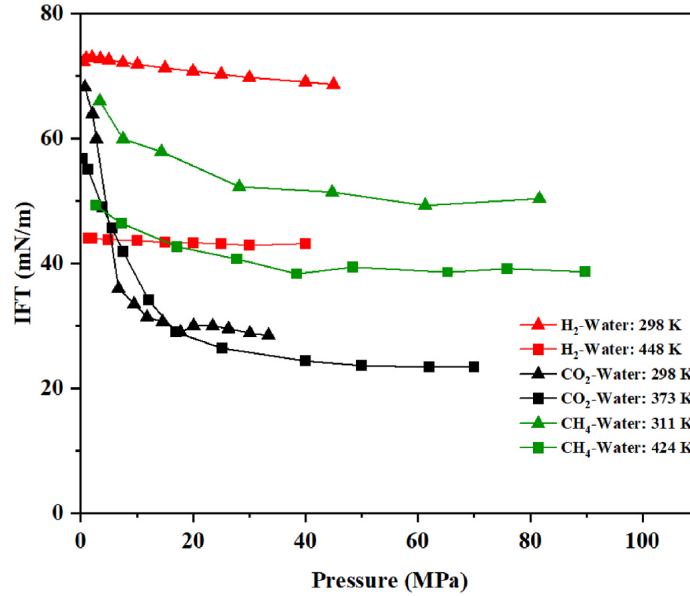


Fig. 13. The IFTs of $\text{H}_2\text{-H}_2\text{O}$, $\text{CO}_2\text{-H}_2\text{O}$, and $\text{CH}_4\text{-H}_2\text{O}$ as a function of pressure and temperature reported from previous publications.

4 Conclusions

When evaluating subsurface porous media for hydrogen storage, the interfacial tension between pore water and a gas mixture of H_2 with a cushion gas is a critical factor influencing the displacement of residual water and the distribution of the gas mixture. Through molecular dynamics simulations, this study has formulated two models for gas-water IFT as a function of cushion gas concentration at

the expected subsurface storage conditions of 20 MPa and 373 K: one for an $\text{H}_2\text{-CO}_2\text{-H}_2\text{O}$ mixture and another for an $\text{H}_2\text{-CH}_4\text{-H}_2\text{O}$ mixture. It has been consistently observed that an increase in the concentration of the cushion gas correlates with a reduction in gas-water IFT. A key finding is that for the $\text{H}_2\text{-CO}_2\text{-H}_2\text{O}$ mixture, the IFT significantly decreases as CO_2 concentration increases up to 40%, beyond which the rate of decrease in IFT tapers off until 100% concentration. In contrast, the IFT declines linearly with increasing CH_4 concentration in the $\text{H}_2\text{-CH}_4$ mixture.

Local density distributions and molecular orientation analyses have elucidated the underlying mechanisms driving these IFT variations. In the $\text{H}_2\text{-CO}_2\text{-H}_2\text{O}$ mixture, up to a 40% CO_2 concentration, there exists a consistent proportional relationship between the increased adsorption of CO_2 at the interface and its concentration in the gas mixture, resulting in a substantial reduction in IFT. Beyond this threshold, the interface becomes predominantly occupied by adsorbed CO_2 , which impedes further adsorption, leading to a marginal IFT reduction with increasing CO_2 concentration. Conversely, the $\text{H}_2\text{-CH}_4\text{-H}_2\text{O}$ mixture exhibits a constant decrease in IFT due to a steady adsorption rate of CH_4 at the interface proportional to its concentration in the gas mixture.

Furthermore, the molecular orientation of CO_2 at the interface aligns with the trends observed in IFT and adsorption behaviors. As CO_2 concentration increases from 0 to 40%, the orientational changes of CO_2 molecules contribute significantly to the reduction in IFT. Above a 40% concentration, there is little change in the molecular orientation of CO_2 , correlating with the smaller IFT reduction observed. Additionally, the orientation of water molecules at the interface is influenced by the presence of adsorbed CO_2 but remains unaffected by CH_4 . This differential impact on water molecule orientation by CO_2 as opposed to CH_4 is postulated as a contributing factor to the higher efficacy of CO_2 in reducing gas-water IFT. Lastly, our study indicates that the presence of both CO_2 and CH_4 at the gas-water interface leads to a decrease in the self-diffusion of H_2 at the interface, which may be relevant for microbial dynamics in subsurface hydrogen storage facilities.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2024.03.341>.

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