



China Geology

Journal homepage: <http://chinageology.cgs.cn>
<https://www.sciencedirect.com/journal/china-geology>



Influence of salinity and electrostatic fields on CO₂ hydrate formation and the interfacial quasi-liquid layer in clay nanoconfinement: A molecular dynamics study

Jie Chen^{a, g}, Jia-fang Xu^{a, b, *}, Zheng-cai Zhang^d, Ling-feng Kong^{a, e}, Cheng-dong Yuan^f, Anastasia Ivanova^f, Abdolreza Farhadian^h, Ya-hua Wang^{a, g}, Yuan-hang Zhang^{a, g}, Li-yuan Zhang^{f, g}, Gao-wei Hu^{c, *}

^a School of Petroleum Engineering, China University of Petroleum (East China), Qingdao 266580, China

^b State Key Laboratory of Deep Oil and Gas, Qingdao 266580, China

^c The Key Laboratory of Gas Hydrate, Ministry of Natural Resources, Qingdao Institute of Marine Geology, China Geological Survey, Qingdao 266237, China

^d Laboratory for Marine Mineral Resources, Laoshan Laboratory, Qingdao 266237, China

^e China National Oil and Gas Exploration and Development Corporation, Beijing 100034, China

^f Center for Petroleum Science and Engineering, Skolkovo Institute of Science and Technology, Moscow 121205, Russia

^g Department of Geology, M. V. Lomonosov Moscow State University, Moscow 119991, Russia

^h Department of Petroleum Engineering, Kazan Federal University, Kazan 420008, Russia

ARTICLE INFO

Article history:

Received 11 July 2025

Received in revised form 24 December 2025

Accepted 21 January 2026

Available online 25 February 2026

Keywords:

CO₂ hydrate

Combustible ice

Clay nanoconfinement

Quasi-liquid layer

Salinity

Electrostatic fields

Molecular dynamics simulation

Carbon sequestration

Carbon neutrality

Carbon capture, utilization, and storage (CCUS)

ABSTRACT

Marine clay reservoirs are considered ideal substrates for hydrate-based CO₂ capture and storage owing to their large specific surface area, high porosity and favorable adsorption capacity. Understanding the evolution mechanism of quasi-liquid layers (QLLs) and hydrate formation at clay interfaces under nanoconfinement is crucial for evaluating the spatial potential of storage matrices and enhancing CO₂ sequestration efficiency. In this study, molecular dynamics (MD) simulations were conducted at 250 K and 300 bar with a time step of 2 fs to investigate the effects of salinity and electrostatic fields on CO₂ hydrate formation and QLL thickness within montmorillonite (MMT) slit pores. Simulation results indicate that CO₂ hydrate nucleation and growth predominantly occur away from MMT interfaces, with elevated salinity significantly delaying nucleation onset. Dynamic salt exclusion during hydrate formation inhibits interfacial hydrate growth toward clay surfaces. Elevated salinity increases QLL thickness from 1.2 nm to 1.6 nm near isomorphic substitution surfaces and from 1.1 nm to 1.4 nm near non-substituted MMT surfaces. Notably, under seawater salinity conditions, QLL thickening demonstrates dynamic coupling with salt exclusion effects. Electrostatic fields substantially influence nucleation stochasticity and spatial distribution through electric double-layer restructuring and ion migration. QLL thickness near isomorphic substitution surfaces shows limited sensitivity to electrostatic fields, stabilizing at about 1.15 nm. Conversely, QLLs adjacent to non-substituted surfaces exhibit significant field dependence due to surface ion redistribution, with thickness increasing to 1.55 nm at an applied field of 0.3 V/nm before reaching a plateau. These molecular-scale insights into salinity and electrostatic effects on hydrate formation and interfacial QLL evolution provide critical references for optimizing clay-based carbon storage matrices and advancing CO₂ sequestration technologies.

©2026 China Geology Editorial Office.

1. Introduction

Carbon dioxide (CO₂), a primary greenhouse gas, has

First author: E-mail address: chenjie3545@163.com (Jie Chen).

* Corresponding author: E-mail address: xjiafang@upc.edu.cn (Jia-fang Xu); hgw-623@163.com (Gao-wei Hu).

Literary editor: Jie Meng

doi:10.31035/cg2025183

2096-5192/© 2026 China Geology Editorial Office.

experienced a rapid increase in atmospheric concentration to $>400 \times 10^{-6}$, posing significant challenges to global carbon cycle equilibrium (Yang S et al., 2022; Kabir M et al., 2023; Wang T et al., 2024). In this context, carbon capture and storage (CCS) technologies are widely regarded as critical pathways toward achieving carbon neutrality (Ali M et al., 2022; Davoodi S et al., 2023). Among these approaches, hydrate-based CO₂ sequestration has attracted considerable attention owing to its unique physicochemical properties (Nguyen NN et al., 2022a; Pandey G et al., 2022; Aminnaji M

et al., 2024; Wang P et al., 2024). This technology exploits the cage-like structure of gas hydrate crystals to encapsulate CO₂ molecules through hydrogen-bond networks, enabling millennial-scale stability under phase equilibrium pressure conditions and positioning it as a promising strategy for deep-sea carbon storage (Rehman AN et al., 2021; Cao X et al., 2022; Gurjar P et al., 2023; Liu X et al., 2025).

Marine clay sediments, are key components of natural gas hydrate (NGH) reservoirs and serve as primary hosts for NGH deposits. Among these, clay minerals such as montmorillonite (MMT), illite, and kaolinite represent some of the most abundant components in NGH-bearing marine sediments (Clennell MB et al., 2006; Seo Y et al., 2009; Lamorena RB et al., 2011; Kim D et al., 2015). Consequently, these minerals are recognized as promising candidates for CO₂ storage owing to their substantial storage capacity and compatibility with existing oil and gas extraction infrastructure. Previous studies demonstrate that MMT, through lattice substitutions, develops negative charges and forms expandable interlayer structures, providing confined spaces for hydrate nucleation (Guggenheim S and Koster van Groos AF, 2003; Li Y et al., 2022a). The MMT slit pores are considered primary potential carbon storage spaces (Koster van Groos AF and Guggenheim S, 2009; Li Y et al., 2022a). In addition, the influence of clay minerals on the formation kinetics (nucleation and growth) and phase equilibrium conditions of natural gas hydrates has been investigated (Yan KF et al., 2016; Jin D and Coasne B, 2021; Sun Y et al., 2021; He ZJ et al., 2022; Mi F et al., 2022a, 2022b; Zhang ZC et al., 2022a, 2022b; Zhang Z et al., 2022; Li Y et al., 2020, 2023). For instance, Li Y et al. (2022a) employed molecular dynamics (MD) simulations to investigate the effects of external surfaces of various clay minerals on CO₂ hydrate nucleation. Results revealed that surface functional groups on clay minerals significantly govern the distribution of CO₂ and water molecules. Mi F et al. (2024) examined CO₂ hydrate growth and dissociation in brine-urea-illite systems, as well as mechanical instabilities at CO₂ hydrate-illite interfaces. Simulation results indicated that hydrate growth is cooperatively influenced by confinement effects, illite surface properties and urea presence. Fan S et al. (2024) explored the formation mechanisms of CO₂ hydrates on hydrophilic and hydrophobic kaolinite surfaces in brine solutions and demonstrated that both kaolinite surface chemistry and salt ions regulate hydrate formation. Tang R et al. (2025) revealed through MD simulations that isomorphous substitutions in clays alter CO₂ hydrate formation kinetics, with CO₂ preferentially adsorbing onto hydrophobic clay surfaces. These studies confirm that clay minerals are potential CO₂ hosts and their interfacial properties are central to sequestration efficiency. Despite existing insights into clay mineral-mediated hydrate dynamics, long-term storage stability critically depends on the quasi-liquid layer (QLL) at clay-CO₂ hydrate interfaces within nanopores, which governs both thermodynamic stability and storage capacity.

The evolution of the QLL at clay mineral-CO₂ hydrate interfaces is essential in determining effective storage space.

The QLL constitutes a nanoscale transitional zone (1–3 nm thick) located between mineral surfaces and bulk phases. It exhibits dynamic properties, such as hydrogen-bond ordering and molecular mobility, which directly regulate CO₂ adsorption and hydrate cage growth pathways (Zhang X et al., 2022; Li Y et al., 2022b; Rao S et al., 2023; Chen J et al., 2024). A fundamental characteristic of the QLL is its thickness, a parameter central to numerous processes (Nguyen NN et al., 2022b). For instance, understanding this parameter clarifies the structural evolution of confined hydrates. Fundamentally, the hydrate lattice terminates at the hydrate-solid interface (Nguyen NN et al., 2022b). Recent simulations support this observation, revealing a mismatched water layer between methane hydrates and hydrophilic clay surfaces in which no persistent hydrate structure exists (Li Y et al., 2020; He Z et al., 2022; Wang R et al., 2023; Chen J et al., 2024). How interfacial QLLs influence confined hydrates remains an underexplored question, yet this knowledge is crucial for leveraging natural hydrates in CO₂ storage applications. Furthermore, hydrate formation in deep-sea reservoirs drives ion enrichment at interfaces through “salt exclusion effects”, providing evidence regarding the impact of salinity on QLL thickness, though quantitative validation of this relationship remains lacking. Concurrently, electrostatic fields (e.g., inherent geological fields or engineered fields) have been shown to restructure electrical double layers by driving counterion migration, thereby disrupting QLL ordering (Mackenzie RC, 1951; Park T and Kwon TH, 2018). With the recognition of electrostatic fields as critical physical tools to promote or inhibit hydrate nucleation and growth, their effects on CO₂ hydrate formation and QLL behavior in clay reservoirs warrant investigation for CCS (English NJ and MacElroy JMD, 2004; Luis DP et al., 2015; Carpenter K and Bahadur V, 2016; Park T and Kwon TH, 2018; Xu T et al., 2019; Pahlavanzadeh H et al., 2020; Hao Y et al., 2022; Chen J et al., 2023). However, within nanoconfined clay pores, the influences of salinity (through ion hydration and electrostatic screening) and electrostatic fields (through driving ion migration and restructuring of the electric double layer) on interfacial QLL evolution and hydrate nucleation/growth are not merely independent but instead exhibit profound synergistic and antagonistic coupling. The molecular-scale mechanisms through which this coupling governs the stability of the storage interface and the CO₂ storage capacity remain unclear, representing a critical knowledge gap in the field. Understanding the impacts of salinity and electrostatic fields on QLL thickness can provide critical benchmarks for carbon sequestration assessment by defining the effective spatial range for hydrate-mediated CO₂ storage in nanopores. While experimental methods can characterize static QLL thickness, their spatiotemporal resolution remains insufficient to resolve dynamic QLL fluctuations and transient correlations with ion concentration gradients at the nanoscale.

Herein, MD simulations were employed to investigate CO₂ hydrate formation in MMT slits under varying salinity (0–3.5%) and electrostatic field (0–0.9 V/nm) conditions. The

core innovation of this study lies in its systematic revelation of the coupling mechanism between salinity and electrostatic fields within MMT slit pores. It aims to elucidate how these factors synergistically regulate the nucleation kinetics, spatial distribution of CO₂ hydrates, and the evolutionary behavior of the interfacial QLL. The authors monitored parameters such as $F_{4\phi}$ order parameters, root mean square displacement (RMSD), density profiles, and hydrate cage counts to explore the molecular-scale regulation of hydrate nucleation and growth, as well as interfacial QLL behavior by salinity and electric fields. In particular, this study elucidate how salinity modulates QLL thickness through charge-specific ion adsorption and dynamic salt exclusion, and how electrostatic fields restructure interfacial ion distributions to induce asymmetric QLL evolution. These molecular-scale insights into the drivers of QLL stability directly inform the optimization of clay-based storage matrices; for instance, enhancing practical CO₂ sequestration capacity in deep-sea clay reservoirs by balancing salinity to mitigate nucleation barriers while preserving QLL-mediated interfacial integrity. These findings provide theoretical references for assessing CO₂ storage capacity in deep-sea clay reservoirs.

2. Computational details

2.1. Models

MD simulation models were constructed (Fig. 1) to investigate the effects of electrostatic field intensity on CO₂ hydrate formation processes and QLL thickness in MMT nanoconfinement. The system comprises an MMT layer and a solution layer containing a CO₂ nanobubble (diameter = 3 nm) (Figs. 1a, b). The size of the CO₂ nanobubble was selected based on the following rationale: (1) It approximates a thermodynamically relevant critical nucleus size for hydrate formation under nanoscale confinement. A diameter of 3 nm is within the range of metastable nuclei that can be observed

to form or dissolve within feasible simulation timescales in similar slit-pore environments (Jin D and Coasne B, 2021). (2) This size enables clear observation of the nucleation and growth processes and does not impose artificial spatial constraints on hydrate development within the 5.8 nm slit pore. The bubble was positioned centrally within the aqueous phase to minimize initial boundary effects and simulate a representative CO₂-enriched environment. Lattice substitutions were implemented in the MMT structure to approximate natural clay mineral compositions. In particular, it involves partial replacement of aluminum atoms with magnesium in aluminum-oxygen octahedra, and partial substitution of silicon atoms with aluminum in silicon-oxygen tetrahedra (Fig. 1c). Post-equilibration at target conditions (250 K and 300 bar), the system dimensions stabilized at $5.16 \times 5.38 \times 5.8 \text{ nm}^3$.

2.2. Simulation settings

All MD simulations were performed using the GROMACS package (version 2021.4) (Van Der Spoel D et al., 2005). MMT unit cells were constructed based on the clay mineral model developed by Skipper's group (Skipper NT, 1995). Lattice substitutions ($\text{Al}^{3+} \rightarrow \text{Mg}^{2+}$ in Al–O octahedra; $\text{Si}^{4+} \rightarrow \text{Al}^{3+}$ in Si–O tetrahedra) endowed the MMT layer with a net negative charge density. Water molecules were modeled using the TIP4P/Ice force field (Abascal JLF et al., 2005), while CO₂ molecules were described by the TraPPE force field (Potoff JJ and Siepmann JI, 2001; Zhang Z et al., 2021) (Table 1). Interatomic interactions were calculated through Lorentz-Berthelot combination rules. Equations of motion were integrated using the leap-frog algorithm (1 fs timestep). Long-range electrostatic interactions were treated using Particle Mesh Ewald (PME, 1.0 nm cutoff), with van der Waals interactions governed by a Lennard-Jones potential (1.0 nm cutoff). System pressure (300 bar) and temperature (250 K) were maintained using a Parrinello-Rahman barostat

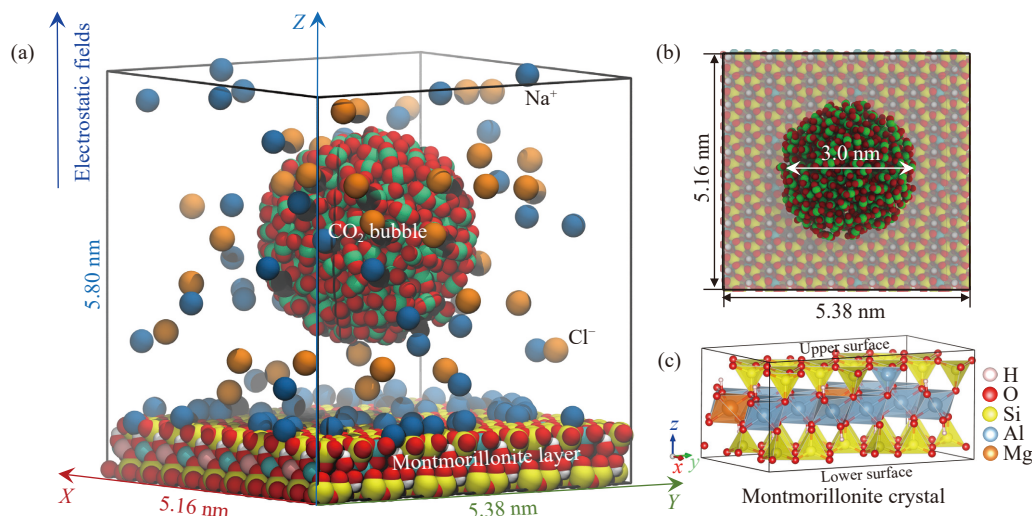


Fig. 1. a–Initial configuration of the simulation system; b–top view of the model used to display the size of droplets; c–crystal cell structure of montmorillonite. In the bulk phase, the blue, orange, red and green balls represent Na⁺ ions, Cl[−] ions, oxygen atoms and carbon atoms, respectively.

(2.0 ps time constant, anisotropic Z-axis coupling) and Nosé-Hoover thermostat (1.0 ps time constant), respectively. Periodic boundary conditions were applied in *X/Y* dimensions, with free surfaces maintained along the Z-axis.

The simulation protocol initiated with energy minimization through the steepest descent algorithm, was followed by a 200 ps NVT equilibration phase with constrained MMT layers. Subsequently, a 2 ns NPT pre-equilibration was performed to stabilize the system density. Production simulations were executed under varying salinity conditions (0–3.5%) (5 independent runs, 2 μ s each) and electric field intensities (0–0.9 V/nm) (30 independent runs, 2 μ s each), accumulating a total simulation time of 70 μ s. The selection of the electric field intensity range is grounded in MD studies indicating its critical relevance to hydrate dynamics. This range of electric field intensities can modulate hydrate stability and formation (Hao Y et al., 2022; Chen J et al., 2023). Investigating this spectrum enables a systematic assessment of the dual role electric fields may play in either promoting or inhibiting CO₂ hydrate formation within MMT slit pores.

2.3. Analysis methods

Hydrate formation and QLL thickness were monitored through the system potential energy, hydrate cage number, and $F_{4\phi}$ order parameter. Increasing potential energy indicates hydrate dissociation, whereas the cage number and $F_{4\phi}$ values exhibit inverse correlations with decomposition. Hydrate cages were quantified using the iterative cup overlapping (ICO) algorithm (Hao Y et al., 2021). The $F_{4\phi}$ order parameter, calculated through the torsion angles (ϕ) between hydrogen-bonded water molecules, evaluates system crystallinity with reference values of 0.7 (hydrate phase),

−0.04 (liquid water), and −0.4 (ice) (Rodger PM et al., 1996; Chen J et al., 2024). The parameter is defined as (Eq. 1):

$$F_{4\phi} = \langle \cos(3\phi) \rangle \quad (1)$$

where ϕ denotes the dihedral angle between adjacent hydrogen-bonded water molecules. RMSD was used to analyze water molecular mobility and dynamic evolution (Eq. 2):

$$\text{RMSD} = \sqrt{\frac{1}{N_t} \sum_{i=1}^{N_t} (r_i - \bar{r})^2} \quad (2)$$

where N_t indicates the number of time steps in the analysis window, r_i represents the atomic coordinates at step i , and $\bar{r}$ represents the time-averaged coordinates.

3. Results

3.1. CO₂ hydrate formation under different salinity

The temporal evolution of system potential energy (Fig. 2a), $F_{4\phi}$ order parameter (Fig. 2b) and hydrate cage count (Fig. 2c) in 0–3.5% salinity systems were calculated to investigate the effects of salinity on the hydrate growth processes. Simulation results revealed significant reductions in the system potential energy with simulation time across all systems, accompanied by synchronous increases in $F_{4\phi}$ values and cage numbers, confirming CO₂ hydrate nucleation and growth behaviors in MMT slits under various salinities. In particular, low-salinity systems (0–2.5%) exhibited hydrate nucleation within the initial 200 ns, followed by rapid growth during 200–500 ns. Growth rates subsequently decreased after 500 ns due to spatial constraints. By contrast, the high-salinity system (3.5%) showed delayed nucleation until 750 ns (550 ns later than low-salinity systems). Although initial growth rates were comparable, hydrate formation primarily occurred in the central slit region away from clay surfaces due to interfacial ion enrichment. Conformational analysis of CO₂ hydrate formation during 2000 ns simulation (Fig. 3) revealed substantial hydrate accumulation in bulk regions distant from clay surfaces in 0–2.5% systems by 400 ns. The 3.5% system only developed limited hydrates by 800 ns. Prolonged simulation demonstrated stable hydrate growth, with saline systems maintaining mid-slit hydrate distribution until 2000

Table 1. Atomic van der Waals potential parameters used in simulation calculations.

Molecule	Model	Atom	$\varepsilon/(\text{kJ/mol})$	$\sigma/\text{\AA}$
H ₂ O	TIP4P/Ice	O	0.88217	0.31668
		H	0	0
		M	0	0
CO ₂	TraPPE	C	0.224478	0.28
		O	0.656806	0.305
		MO	0	0

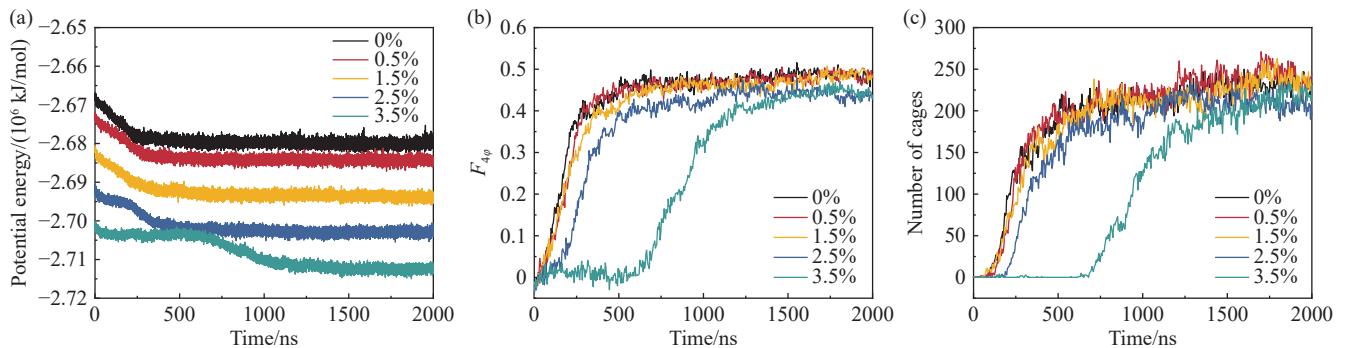


Fig. 2. Temporal evolution of potential energy (a), $F_{4\phi}$ order parameter (b), and number of hydrate cages (c) in MMT systems with varying salinities (0–3.5%).

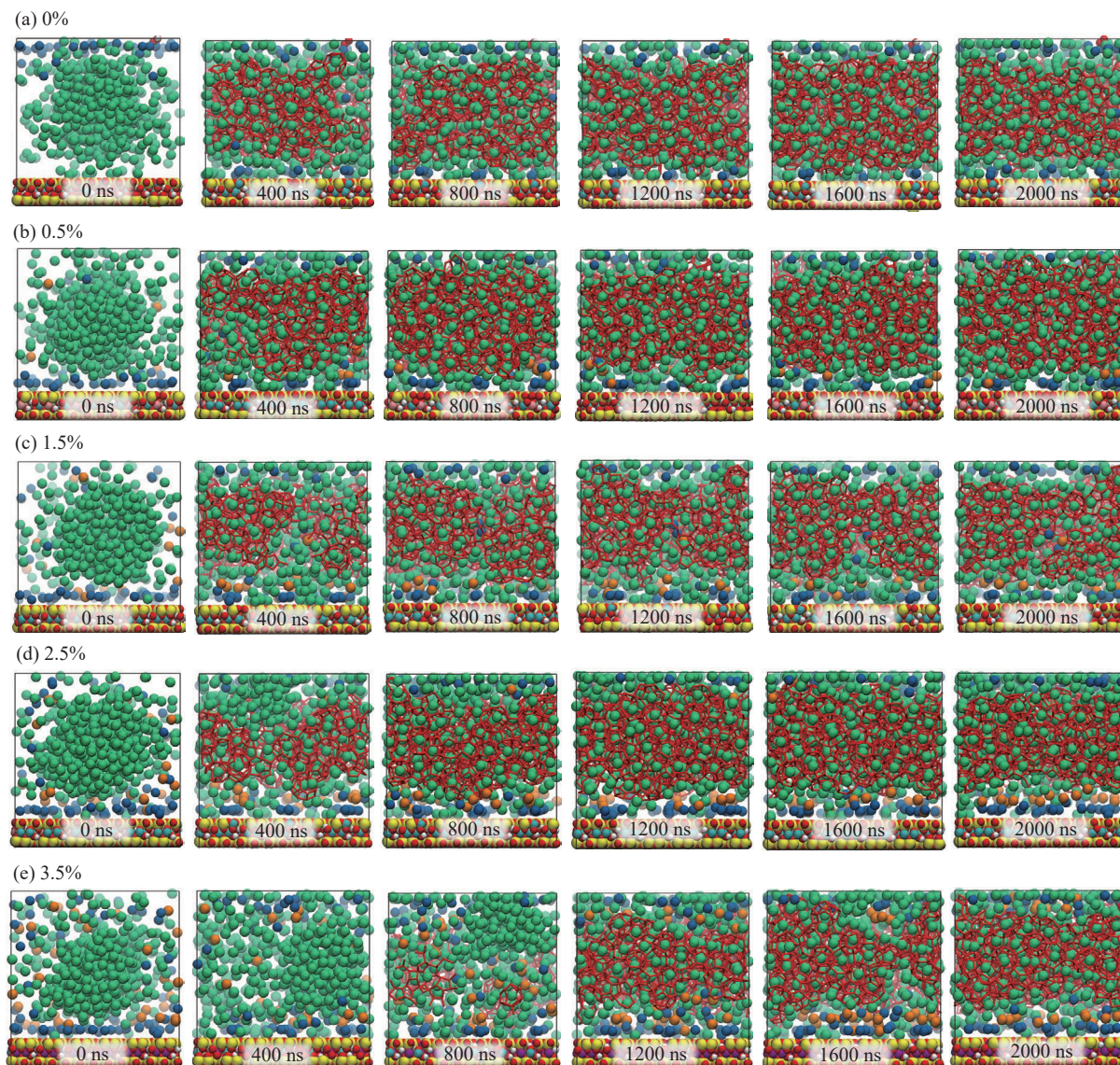


Fig. 3. CO₂ hydrate formation processes during 2000 ns simulations across salinity-modified MMT systems. In the bulk phase, red polyhedra, green, blue, and orange spheres represent hydrate cages, CO₂ molecules, Na⁺ ions, and Cl⁻ ions, respectively.

ns. This phenomenon originated from dynamic salt-exclusion effects during hydrate growth, where expelled Na⁺/Cl⁻ ions accumulated at interfaces, forming an ionic shielding layer. The resulting continuous modification of local thermodynamic conditions maintained elevated interfacial salinity, persistently restricting hydrate formation to central regions away from clay surfaces throughout the simulation period.

The time evolution of the number of hydrate cages (Fig. 2c) reveals that CO₂ hydrate nucleation progresses faster in 0–1.5% systems compared to 2.5% and 3.5% systems. Notably, compared with pure water systems, the 0.5% and 1.5% systems exhibit similar or even faster nucleation times, potentially linked to ionic perturbations at moderate salinities enhancing local water molecule reorganization; though further validation is required. Despite delayed nucleation in high-salinity systems, their initial growth rates approximate those of low-salinity systems, indicating that salinity primarily influences nucleation energy barriers rather than growth

kinetics. The simulation snapshots within 600 ns for each system (Fig. 4) were extracted to investigate salinity-dependent nucleation localization in slit systems. Results show hydrate cages are preferentially formed away from MMT surfaces. Sparse hydrate cages emerged in 0–1.5% systems by 120 ns, while the 2.5% system exhibited initial cage formation at 240 ns. By contrast, no hydrate cages were observed within 600 ns in the 3.5% system, attributed to high salinity-induced suppression.

3.2. Characteristics of QLL under different salinities

The Z-axis profiles of $F_{4\phi}$ order parameters and RMSD at simulation endpoints were calculated to investigate salinity-dependent effects on QLL thickness at MMT-CO₂ hydrate interfaces (Figs. 5, 6). The QLL thickness exhibited pronounced salinity dependence and interfacial asymmetry, with formation mechanisms closely correlated to interfacial ion enrichment and reorganization of the water molecule

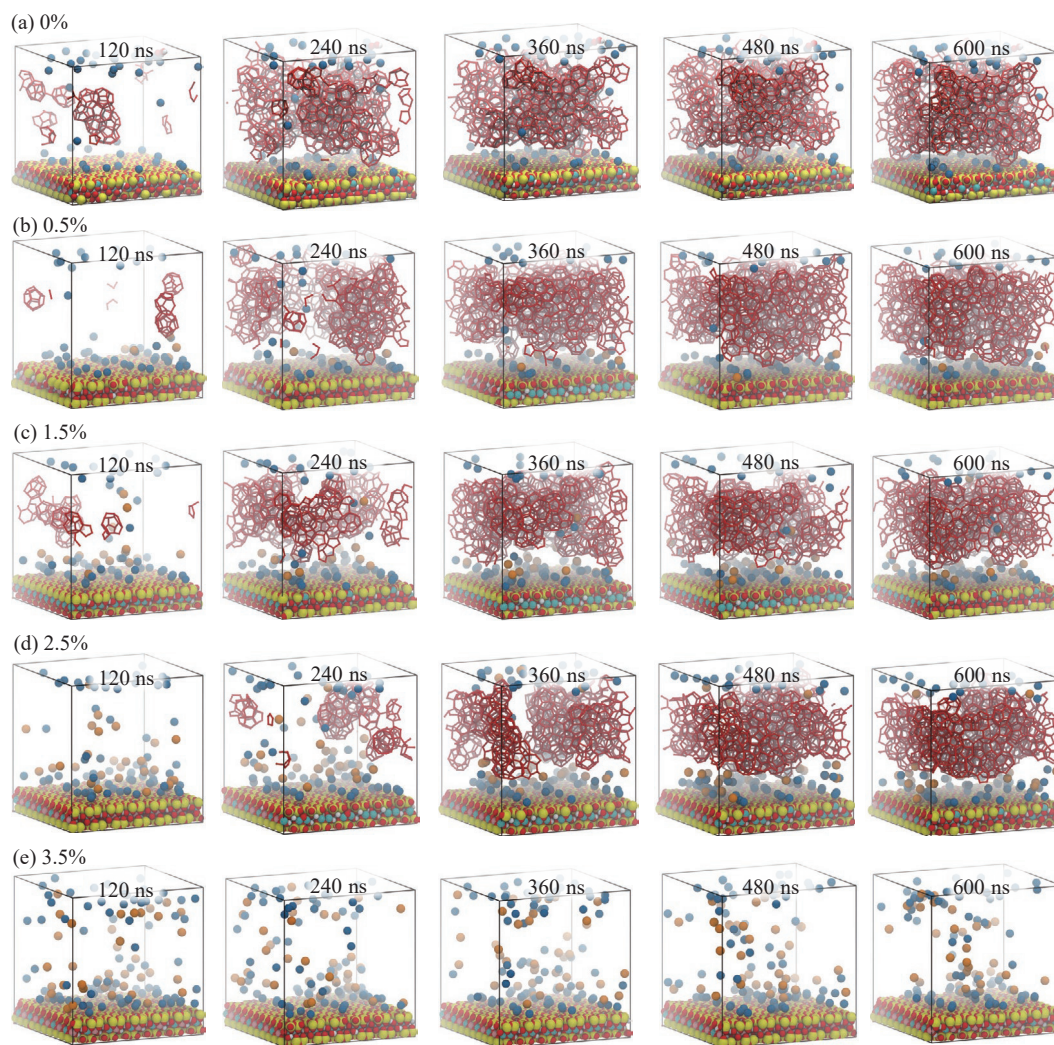


Fig. 4. Snapshots of CO₂ hydrate formation progress within 600 ns simulations for MMT systems with different salinities. In the bulk phase, the blue, orange, and red polyhedra represent Na⁺ ions, Cl⁻ ions, and hydrate cages, respectively.

hydrogen bond network. Notably, water molecules proximal to MMT surfaces demonstrated enhanced liquid-like characteristics and higher mobility compared to those in bulk regions. In high-salinity systems (2.5% and 3.5%), water molecules adjacent to the lower MMT surface demonstrated greater mobility than those near the upper surface. Comparative analysis revealed a positive correlation between increase in salinity and QLL thickness enhancement, particularly at the lower MMT interface.

Figs. 7a–d display the Z-axis profiles of the $F_{4\phi}$ order parameters, RMSD, and water density distributions across systems with varying salinities. The mid-slit region exhibits elevated $F_{4\phi}$ values, reduced RMSD, and lower density, whereas the interfacial regions show inverse trends. QLL thickness was determined using inflection points in the RMSD and $F_{4\phi}$ rate of change curves. At 0.5% and 1.5% salinity, the QLL thickness near both upper and lower MMT surfaces was 1.2 nm. Under 2.5% salinity, the thickness of the lower interfacial QLL increased to 1.5 nm, while that of the upper surface remained unchanged. For 3.5% salinity, the lower and upper QLL thicknesses increased to 1.6 nm and 1.4 nm, respectively. Statistical analysis of salinity-dependent

QLL thickness variations (Fig. 7e) revealed a marked jump in the lower-surface QLL thickness (1.2 nm to 1.6 nm) at salinities of >1.5%, which contrasts with the modest increase in the upper-surface (1.2 nm to 1.4 nm). This asymmetry originates from charge heterogeneity in MMT interlayers: The lower surface, bearing inherent negative charges from silica tetrahedral sheets, exhibits stronger Na⁺ adsorption, generating steeper local ion concentration gradients. This enhances electrical double layer compression, thereby weakening hydrogen bonding interactions between water molecules and the surface. While analogous to permeability variations induced by ion-specific adsorption in porous media, this study identifies asymmetric effects in nanoconfined spaces. In addition, the QLL thickening is related to the salt-removing effect during the hydrate growth progress. Concomitant to the hydrate formation in the bulk region, ions are pushed to the interface, forming localized high-concentration zones that disrupt interfacial water ordering.

3.3. CO₂ hydrate formation under different electrostatic fields

The effect of electrostatic fields (0–0.9 V/nm) on CO₂

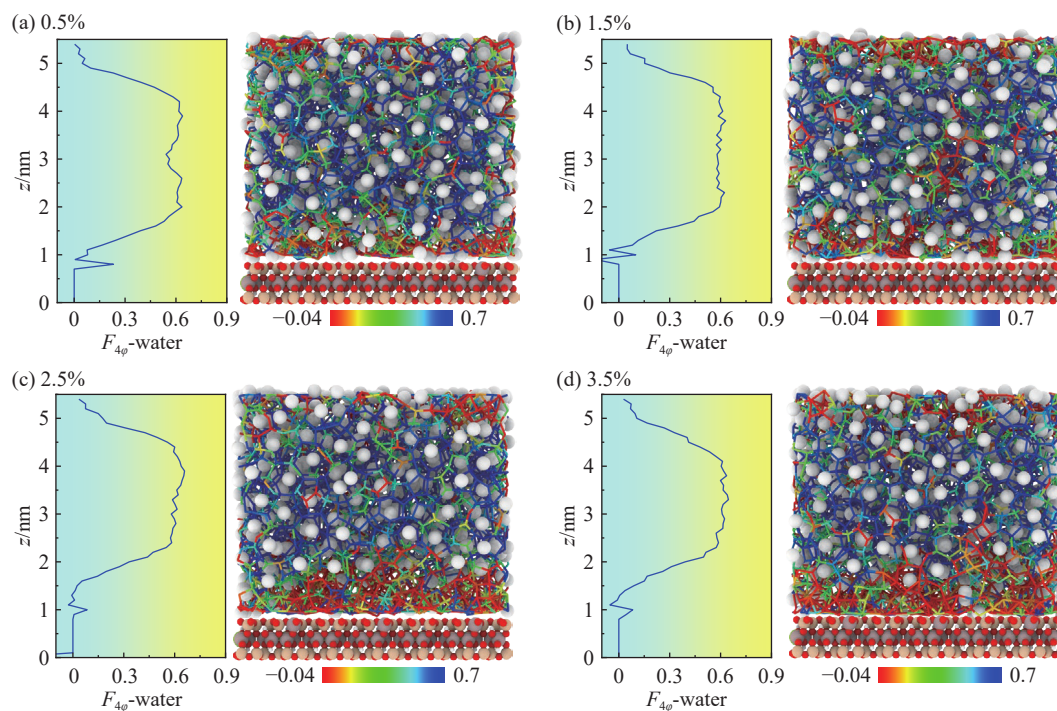


Fig. 5. Z-axis distributions of $F_{4\phi}$ order parameters and system conformations at 2000 ns for systems with varying salinities. In the conformations, water molecules are color-mapped by $F_{4\phi}$ values, with red denoting the most disordered and mobile molecules. White spheres represent CO_2 molecules.

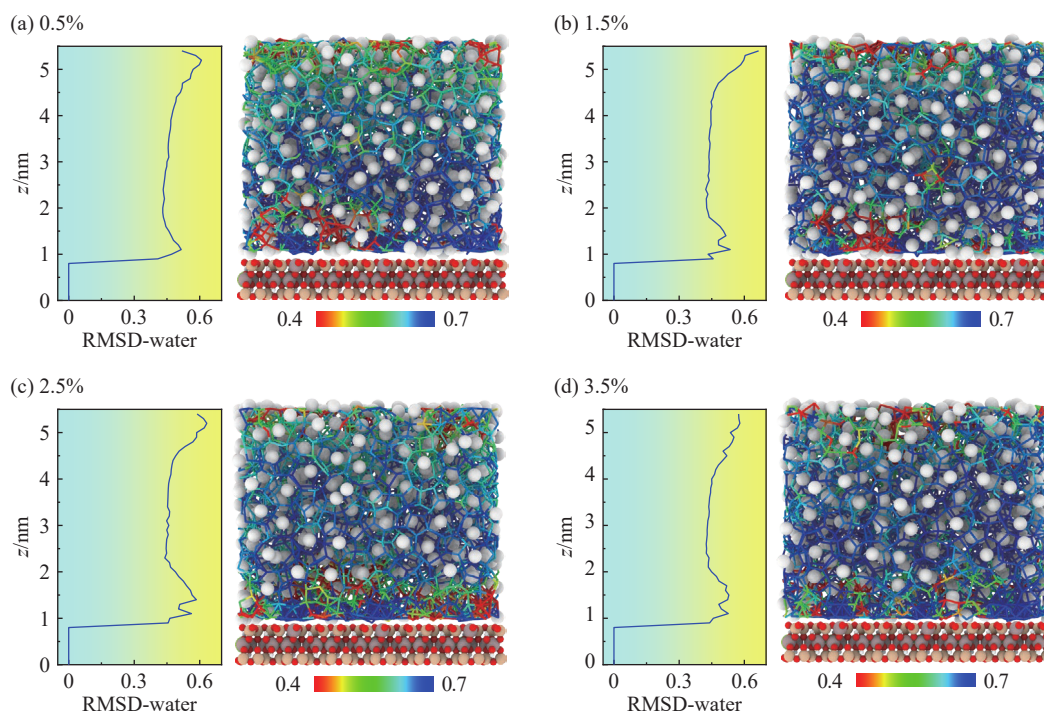


Fig. 6. Z-axis distributions of RMSD and system conformations at 2000 ns for systems with varying salinities. In the conformations, water molecules are color-mapped by RMSD values, with red indicating the most disordered and mobile molecules. White spheres represent CO_2 molecules.

hydrate formation under clay nanoconfinement was studied through MD simulation to investigate the dynamic regulation of electric field intensity on CO_2 hydrate nucleation and growth in MMT slits. Combined analysis of the number of hydrate cages, $F_{4\phi}$ order parameter evolution (Fig. 8), and conformational profiles (Fig. 9) demonstrates that electrostatic

fields critically modulate nucleation stochasticity and spatial distribution through electric double-layer restructuring and ion migration effects. Simulation data indicate synchronized increase in $F_{4\phi}$ values and number of hydrate cages over time, confirming stable hydrate formation across all field intensities. However, post-nucleation growth rates during

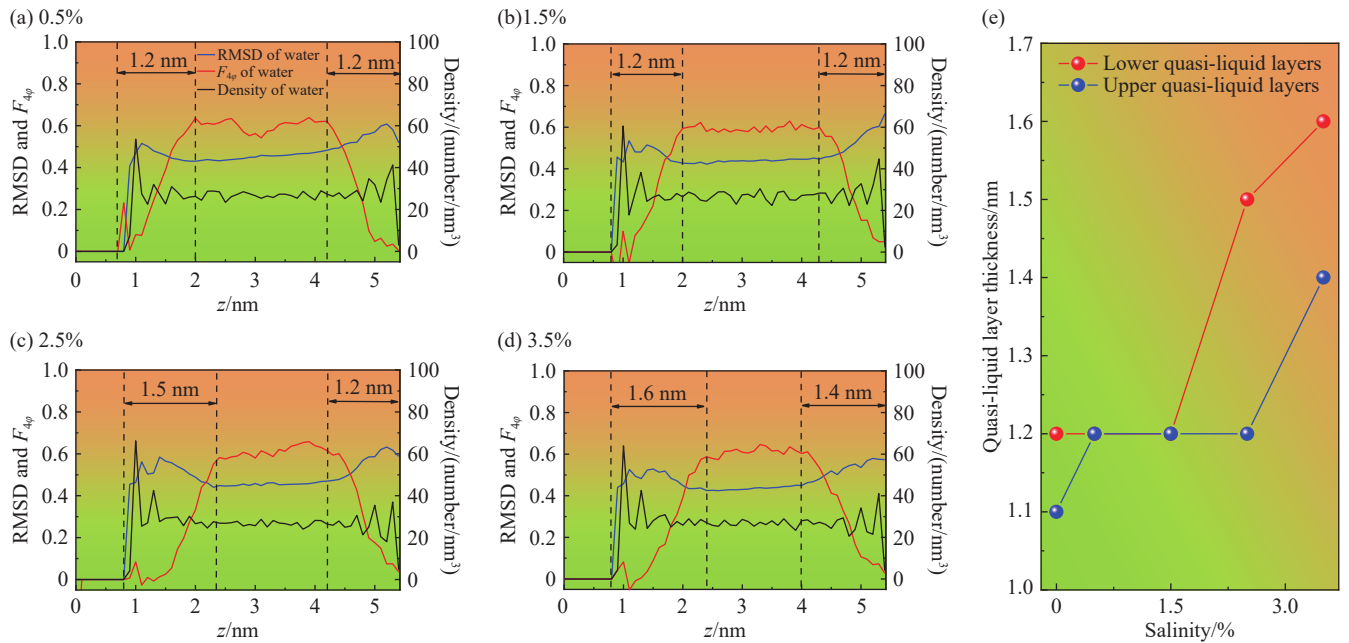


Fig. 7. a–d–Z-axis distributions of RMSD, F_{4p} order parameter, and water density at 2000 ns for systems with varying salinities; e–variations in the QLL thickness at upper and lower MMT interfaces as a function of system salinity.

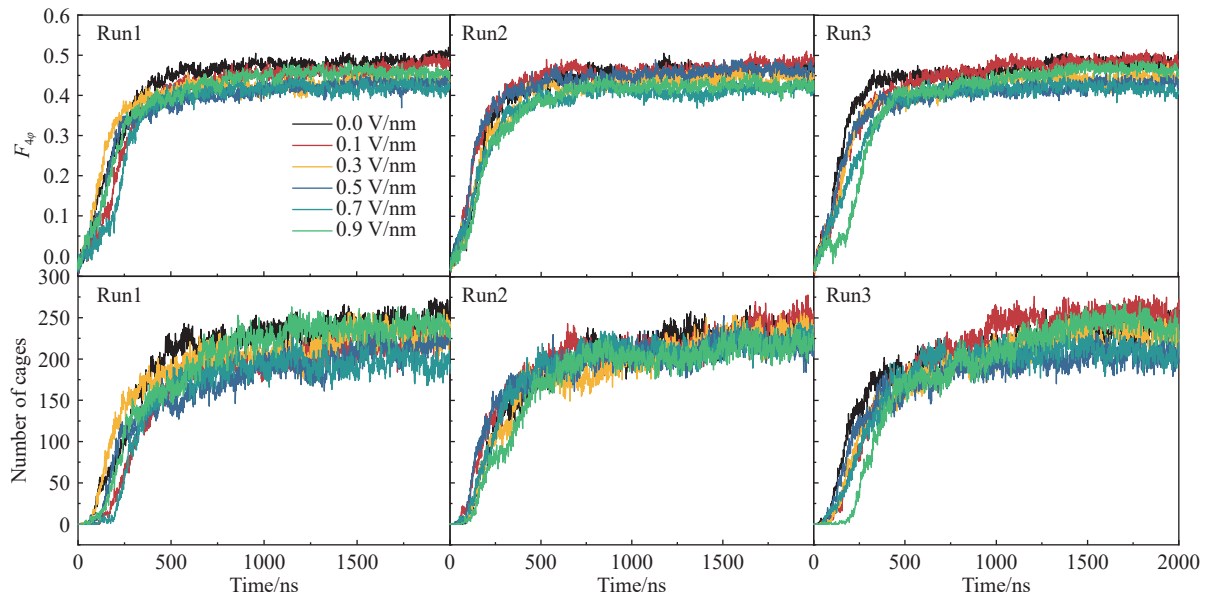


Fig. 8. Temporal evolution of F_{4p} order parameters and number of hydrate cages under different electrostatic fields in three runs of simulation. The simulation results of the first, second, and third runs are shown from left to right.

0–500 ns markedly exceed those in later stages (500–1000 ns), with the disparity arising from molecular diffusion constraints imposed by slit confinement, though gradual hydrate growth persists. Conformational snapshots of nucleation and growth processes during the first 1000 ns of the simulation (Fig. 9) reveal hydrate formation initiated within 200 ns. Notably, nucleation consistently occurs in regions >1.2 nm from clay surfaces. Subsequent stable growth maintains hydrate localization in areas distant from clay mineral surfaces throughout the simulation, even at 1000 ns.

Field-induced spatiotemporal heterogeneity was systematically investigated through five independent MD

simulations (including two supplementary runs) to elucidate the electric field intensity-dependent regulation mechanisms of CO₂ hydrate nucleation timing. The hydrate cage count evolution curves from five 300 ns simulations (Fig. 10) demonstrate nucleation occurring within 200 ns across all electric field intensities (0–0.9 V/nm). Under no-field conditions, nucleation consistently occurred within 100 ns, whereas electrostatic fields introduced stochastic nucleation timing without discernible temporal patterns. Nucleation trajectories from the first simulation round (Fig. 11) reveal hydrate cages forming distant from MMT surfaces. Enhanced electric field intensities drive sodium ions at MMT surfaces to

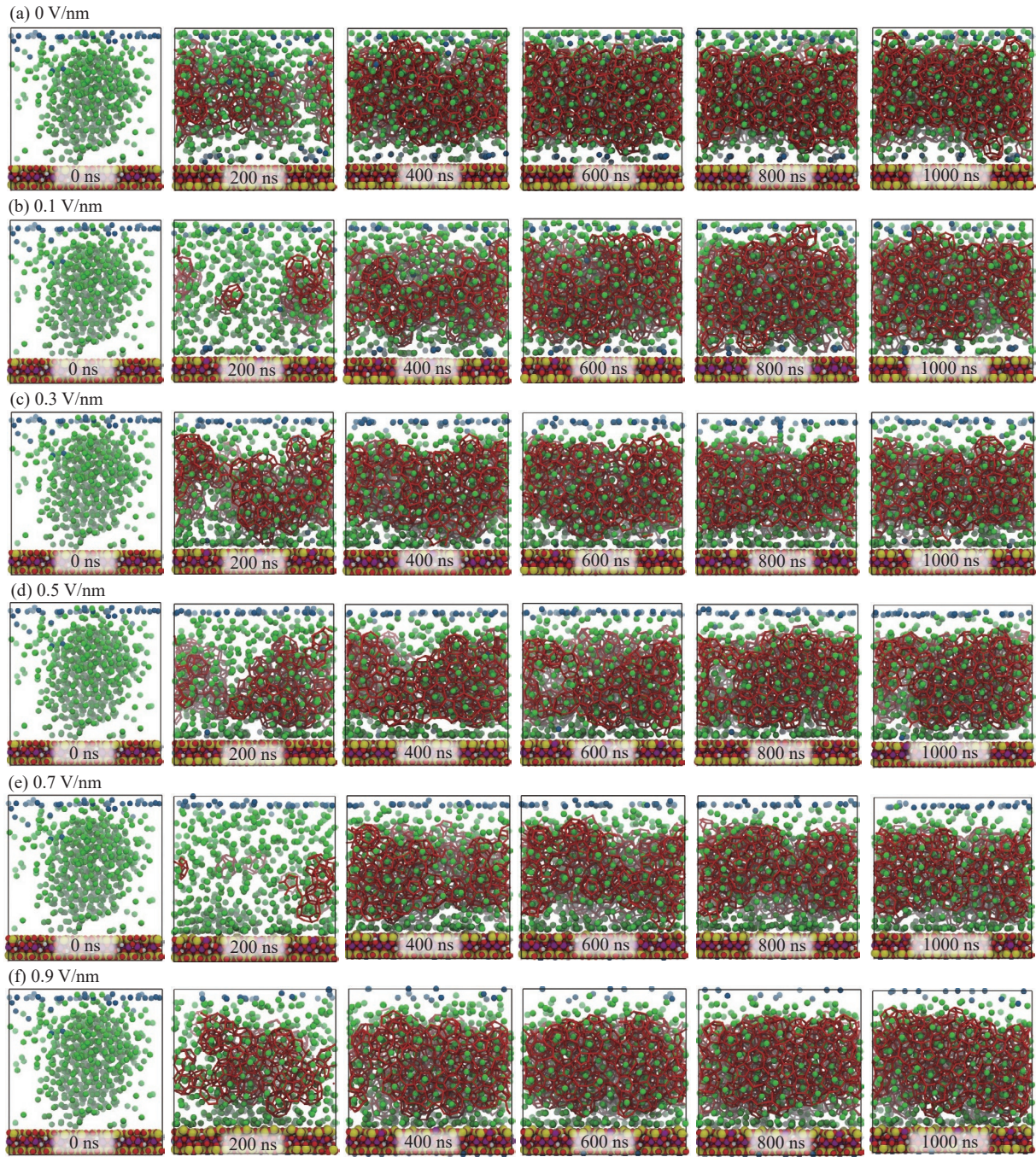


Fig. 9. CO₂ hydrate formation processes in MMT systems under varying electrostatic fields. In the bulk phase, red polyhedra, green spheres, and blue spheres represent hydrate cages, CO₂ molecules, and Na⁺ ions, respectively.

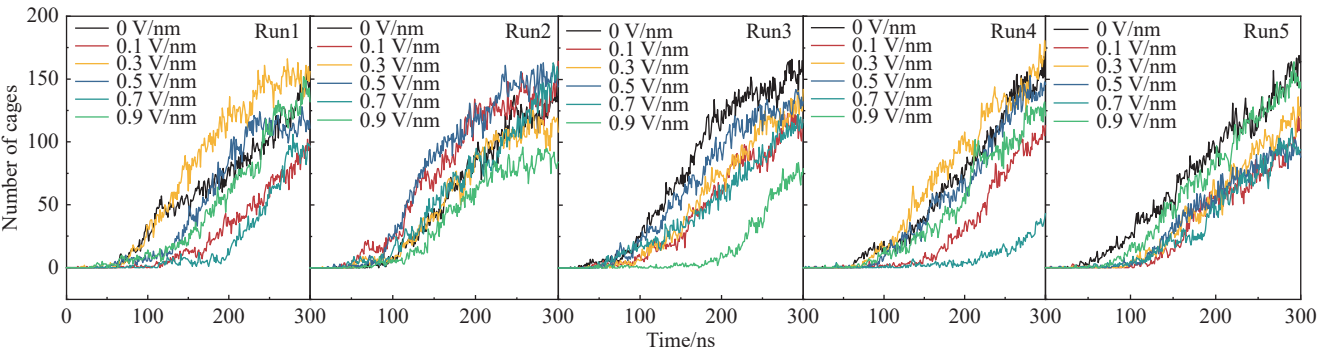


Fig. 10. Evolution in the number of hydrate cages within 300 ns for MMT systems under different electrostatic fields in five runs of simulation. The simulation results of the first to fifth runs are displayed from left to right.

migrate away from the interface. The authors hypothesize that field-driven ionic migration constitutes a primary factor that governs nucleation time stochasticity.

3.4. Characteristics of QLL under different electrostatic fields

The Z-axis profiles of $F_{4\phi}$ order parameters and RMSD were computed at simulation endpoints to investigate electric field intensity effects on QLL thickness in MMT slits (Figs. 12, 13). Water molecules proximal to MMT surfaces exhibited enhanced liquid-like characteristics and higher mobility compared with bulk-phase counterparts. Increasing electric field intensity progressively reduced both mobility and QLL thickness at the lower MMT interface, while simultaneously amplifying these parameters at the upper interface. It is

suggested that under no-field conditions, inherent negative charges in silica tetrahedral sheets and adsorbed interfacial ions elevate mobility at the lower surface. Upon electric field application, field-driven migration redirects lower-surface ions toward the upper interface, forming a concentrated ionic solution near the upper surface. This ion redistribution enhances upper-surface water mobility and expands QLL thickness through electrostatic screening and hydrogen bond network disruption.

Fig. 14 presents the Z-axis profiles of $F_{4\phi}$ order parameters, RMSD, and water density distributions across systems under varying electric field intensities. The mid-slit region exhibits elevated $F_{4\phi}$ values, reduced RMSD, and lower density, while interfacial regions display inverse trends. Under no-field conditions, the QLL thickness near the upper

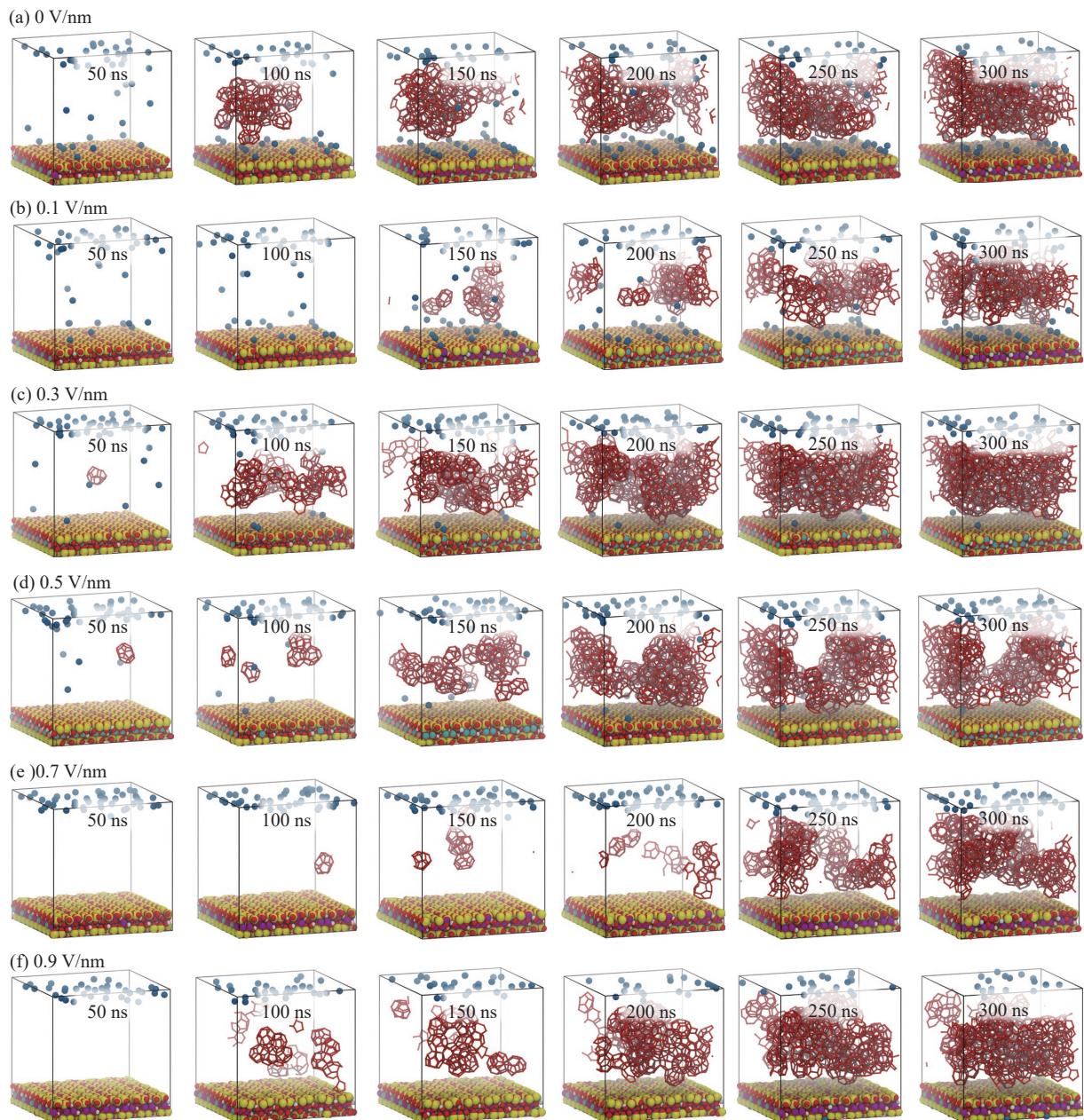


Fig. 11. CO₂ hydrate formation processes within 300 ns of Run 1 simulations for MMT systems under varying electrostatic fields. In the bulk phase, red polyhedra, green spheres, and blue spheres represent hydrate cages, CO₂ molecules, and Na⁺ ions, respectively.

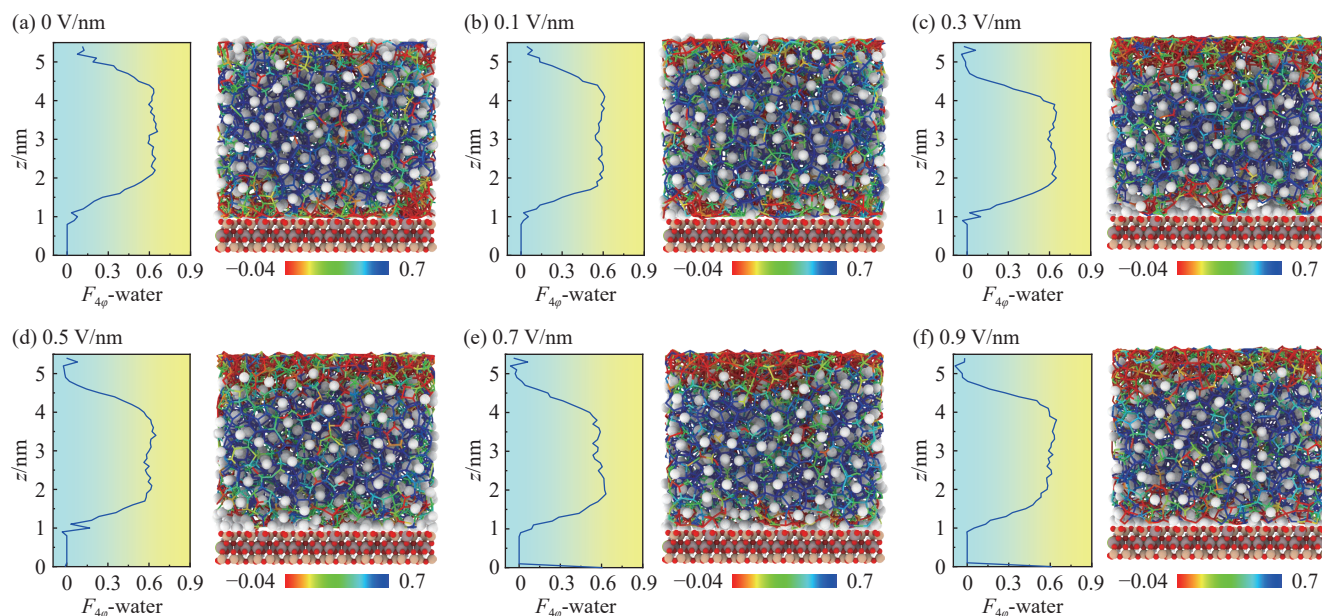


Fig. 12. Z-axis distributions of $F_{4\phi}$ order parameters and system conformations at 2000 ns under varying electrostatic fields. In the conformations, water molecules are color-mapped by $F_{4\phi}$ values, with red indicating the most disordered and mobile molecules. White spheres represent CO_2 molecules.

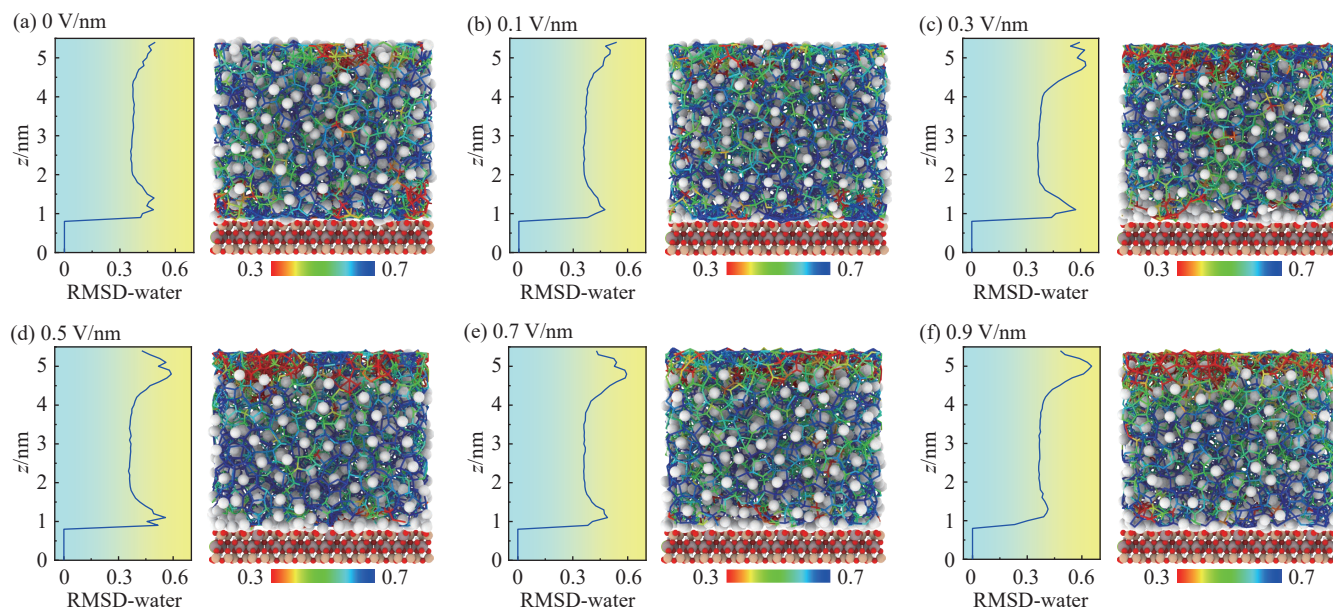


Fig. 13. Z-axis distributions of RMSD order parameters and system conformations at 2000 ns under varying electrostatic fields. In the conformations, water molecules are color-mapped by RMSD values, with red indicating the most disordered and mobile molecules. White spheres represent CO_2 molecules.

MMT surface measures 1.4 nm, which exceeds values observed under applied fields. This discrepancy arises from the electronegative upper surface attracting Na^+ ions in the absence of electric fields, whereas field-driven ionic migration from upper to lower surfaces under applied fields reduces upper-surface QLL thickness. For the lower interface, QLL thickness increases with electric field intensity and reaches a plateau at 0.5 V/nm. The authors statistically analyzed thickness trends using averaged data and error ranges from three independent simulations to quantify field-dependent QLL variations (Fig. 15). Results demonstrate that the lower-surface QLL thickness exhibits limited sensitivity to

electric fields, stabilizing at about 1.15 nm. By contrast, the upper-surface QLL thickness shows pronounced field dependence, increasing progressively until 0.5 V/nm and stabilizing at about 1.55 nm with minor fluctuations beyond this threshold.

4. Discussion

The confinement of CO_2 hydrates within nanoscale clay pores presents a complex interplay of interfacial phenomena, spatial constraints, and thermodynamics. The findings reveal that the behavior of the QLL and the dynamic distribution of

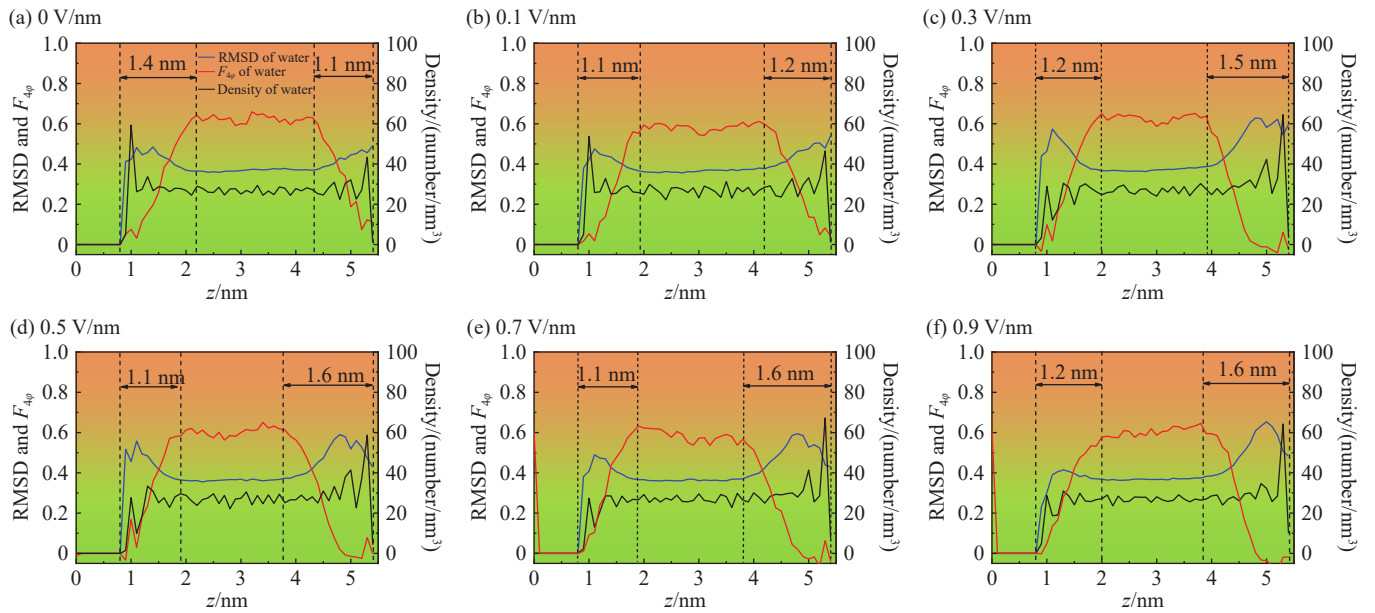


Fig. 14. Z-axis distributions of RMSD, $F_{4\phi}$ order parameter, and water density at 2000 ns under varying electrostatic fields.

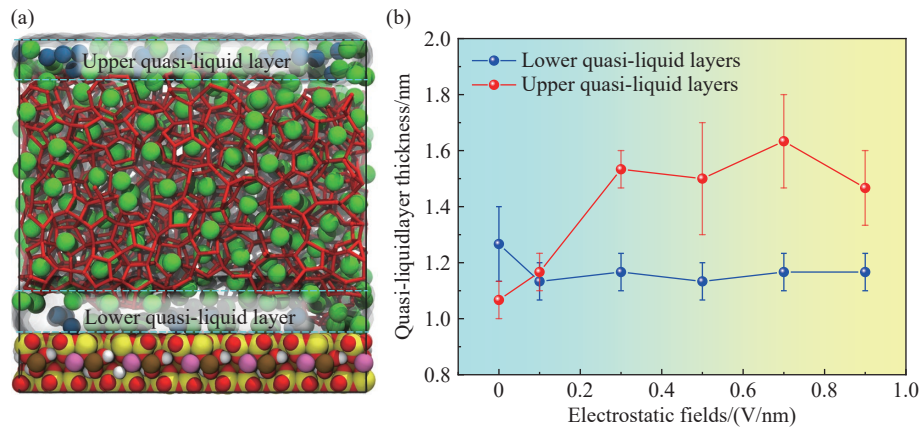


Fig. 15. a–Schematic representation of QLL distributions; b–variations in lower and upper QLL thickness as a function of electrostatic field intensity. In the bulk phase, red polyhedra, green, and blue spheres represent hydrate cages, CO_2 molecules, and Na^+ ions, respectively.

ions fundamentally dictate the feasibility and stability of CO_2 sequestration in deep-sea environments. By bridging these molecular-level insights with macroscale reservoir performance, a foundational framework for advancing hydrate-based carbon capture technologies was established. The critical implications of these interfacial mechanisms, their practical applications, and the necessary pathways for future research are detailed below.

4.1. Dual role of the QLL and interfacial thermodynamics

Under nanoconfinement, the QLL at clay-hydrate interfaces fundamentally governs both the effective CO_2 storage capacity and the interfacial mass transfer kinetics. The QLL acts as a dynamic “soft boundary,” partitioning pores into hydrate-rich and ion-enriched domains. Elevated salinity induces QLL thickening, which spatially restricts hydrate growth due to volumetric constraints while creating kinetic barriers via increased interfacial ion concentrations. However,

this ion enrichment within the QLL simultaneously establishes localized diffusion channels that serve as critical mass transfer zones post-hydrate formation. Ultimately, the intricate dynamic changes among salt exclusion, ion migration, and QLL evolution highlight the critical role of interfacial thermodynamics in dictating overall hydrate stability.

4.2. Strategic optimization for CO_2 storage applications

Maximizing CO_2 sequestration efficiency requires a delicate balance between interfacial stability and storage capacity, which can be achieved through the precise regulation of the storage matrix. Rather than pursuing complete inhibition, the inherent salinity of deep-sea reservoirs can be strategically managed to mitigate nucleation barriers and achieve a controlled, stable hydrate formation regime. Furthermore, the sensitivity of the interfacial QLL and ion distribution to electrostatic fields offers a promising

pathway for the *in-situ* modulation of reservoir properties, potentially through the application of tailored electromagnetic stimuli to enhance long-term hydrate stability in targeted zones. Additionally, a strategic expansion of the QLL thickness in gas hydrate reservoirs may enable the feasible and efficient replacement of CH₄ with CO₂.

4.3. Future research perspectives and multi-scale integration

To bridge the gap between nanoscale mechanisms and the engineering-scale optimization of natural marine reservoirs, future investigations must address complex geological conditions through coupled MD simulations and *in-situ* characterization. Systematic exploration is needed to understand how varying clay mineralogy (e.g., quartz, illite, kaolinite), diverse pore geometries (e.g., tortuosity, slit-width variations), and multi-component ions (e.g., Mg²⁺, Ca²⁺, SO₄²⁻) collectively modulate QLL thickness and hydrate formation. Furthermore, assessing permanent storage security and leakage risks requires an explicit evaluation of long-term geological stability, including slow dynamic processes such as hydrate dissociation/reformation, compositional evolution of the QLL, and mechanical-geochemical coupling under sustained reservoir pressure, temperature, and fluid flow conditions. Finally, integrating these molecular simulation predictions with macroscale reservoir models and experimental validation is crucial for developing robust predictive frameworks for field-scale CO₂ sequestration potential.

5. Conclusions

This study investigated the effects of salinity (0–3.5%) and electrostatic fields (0–0.9 V/nm) on CO₂ hydrate formation kinetics and interfacial QLL evolution within MMT slit pores using MD simulations. The key findings are summarized as follows.

(i) Elevated salinity significantly delays CO₂ hydrate nucleation onset (e.g., 550 ns delay at 3.5% vs. pure water systems) but has a minimal impact on post-nucleation growth rates. Hydrates preferentially form in mid-slit regions, where expelled Na⁺/Cl⁻ ions accumulate at interfaces, creating ionic shielding layers that suppress interfacial hydrate growth.

(ii) The QLL thickness exhibits salinity-dependent asymmetry: Increasing salinity enhances QLL thickness from 1.2 nm to 1.6 nm near isomorphic substitution surfaces and from 1.1 nm to 1.4 nm at non-substituted interfaces. This asymmetry arises from charge heterogeneity-driven ion adsorption gradients, which amplify interfacial water mobility.

(iii) Electric fields modulate nucleation stochasticity and hydrate spatial distribution by restructuring electric double layers and driving ion migration. QLL thickness demonstrates field-dependent interfacial specificity: Upper-surface QLL thickens from 1.1 nm to 1.55 nm with increasing field intensity, while the lower-surface QLL remains stable (about 1.15 nm). This divergence originates from field-induced ion

redistribution.

CRedit authorship contribution statement

Jie Chen, Jia-fang Xu, Zheng-cai Zhang and Ling-feng Kong conceived of the presented idea. Jie Chen, Zheng-cai Zhang, Anastasia Ivanova and Li-yuan Zhang carried out the simulation. Jie Chen, Abdolreza Farhadian, Ya-hua Wang and Yuan-hang Zhang wrote the manuscript with support from Jia-fang Xu, Gao-wei Hu and Zheng-cai Zhang. Jia-fang Xu and Gao-wei Hu helped supervise the project. All authors discussed the results and contributed to the final manuscript.

Declaration of competing interest

The authors declare no conflicts of interest.

Acknowledgment

The authors thank the Center for High Performance Computing and System Simulation, Laoshan Laboratory for the allocation of computing time, as well as the support provided by the Shandong Provincial Key Laboratory of Oilfield Chemistry. This work was financially supported by the Laoshan Laboratory (LSKJ2202203503), National Natural Science Foundation of China (42176212, 51874343 and 42276229), Fundamental Research Funds for the Central Universities (24CX02013A) and Natural Science Foundation of Shandong Province of China (ZR2019BD051).

References

- Abascal JLF, Sanz E, García Fernández R, Vega C. 2005. A potential model for the study of ices and amorphous water: TIP4P/Ice. The Journal of Chemical Physics, 122(23), 234511. doi: [10.1063/1.1931662](https://doi.org/10.1063/1.1931662).
- Ali M, Jha NK, Pal N, Keshavarz A, Hoteit H, Sarmadivaleh M. 2022. Recent advances in carbon dioxide geological storage, experimental procedures, influencing parameters, and future outlook. Earth-Science Review, 225, 103895. doi: [10.1016/j.earscirev.2021.103895](https://doi.org/10.1016/j.earscirev.2021.103895).
- Aminnaji M, Qureshi MF, Dashti H, Hase A, Mosalanejad A, Jahanbakhsh A, Babaei M, Amiri A, Maroto-Valer M. 2024. CO₂ gas hydrate for carbon capture and storage applications – Part 1. Energy, 300, 131579. doi: [10.1016/j.energy.2024.131579](https://doi.org/10.1016/j.energy.2024.131579).
- Cao X, Wang H, Yang K, Wu S, Chen Q, Bian J. 2022. Hydrate-based CO₂ sequestration technology: Feasibilities, mechanisms, influencing factors, and applications. Journal of Petroleum Science and Engineering, 219, 111121. doi: [10.1016/j.petrol.2022.111121](https://doi.org/10.1016/j.petrol.2022.111121).
- Carpenter K, Bahadur V. 2016. Electronucleation for rapid and controlled formation of hydrates. The Journal of Physical Chemistry Letters, 7(13), 2465–2469. doi: [10.1021/acs.jpclett.6b01166](https://doi.org/10.1021/acs.jpclett.6b01166).
- Chen J, Xu J, Zhang Z, Liu C, Hu G, Ding T, Hao Y, Wang X. 2024. Insight on the stability of methane hydrate in montmorillonite slits by molecular dynamics simulations. Applied Surface Science, 654, 159413. doi: [10.1016/j.apsusc.2024.159413](https://doi.org/10.1016/j.apsusc.2024.159413).
- Chen J, Zhang Z, Hao Y, Jiménez DPL, Xu J, Wu N, Ning F, Fang B, Zhang J, Sun J, Hao X, Meng Q, Li Y, Wan Y, Liu C, Hu G. 2023. Molecular insights into ions permeation and destruction behavior in methane hydrate driven by electrostatic fields. Fuel, 346, 128211. doi: [10.1016/j.fuel.2023.128211](https://doi.org/10.1016/j.fuel.2023.128211).
- Clennell MB, Henry P, Hovland M, Booth JS, Winters WJ, Thomas M.

2006. Formation of natural gas hydrates in marine sediments: Gas hydrate growth and stability conditioned by host sediment properties. *Annals of the New York Academy of Sciences*, 912(1), 887–896. doi: [10.1111/j.1749-6632.2000.tb06842.x](https://doi.org/10.1111/j.1749-6632.2000.tb06842.x).
- Davoodi S, Al-Shargabi M, Wood DA, Rukavishnikov VS, Minaev KM. 2023. Review of technological progress in carbon dioxide capture, storage, and utilization. *Gas Science and Engineering*, 117, 205070. doi: [10.1016/j.gjsce.2023.205070](https://doi.org/10.1016/j.gjsce.2023.205070).
- English NJ, MacElroy JMD. 2004. Theoretical studies of the kinetics of methane hydrate crystallization in external electromagnetic fields. *Journal of Chemical Physics*, 120(21), 10247–10256. doi: [10.1063/1.1730092](https://doi.org/10.1063/1.1730092).
- Fan S, Wu S, Lang X, Wang Y, Li G. 2024. Insights of kaolinite surface and salt ions on the formation of carbon dioxide hydrates in confined nanopore: A molecular dynamics simulation study. *Gas Science and Engineering*, 129, 205390. doi: [10.1016/j.gjsce.2024.205390](https://doi.org/10.1016/j.gjsce.2024.205390).
- Guggenheim S, Koster van Groos AF. 2003. New gas-hydrate phase: Synthesis and stability of clay–methane hydrate intercalate. *Geology*, 31(7), 653. doi: [10.1130/0091-7613\(2003\)031<0653:NGPSAS>2.0.CO;2](https://doi.org/10.1130/0091-7613(2003)031<0653:NGPSAS>2.0.CO;2).
- Gurjar P, Dubey S, Kumar S, Palodkar AV, Kumar A. 2023. Carbon dioxide sequestration as hydrates in clayey-sandy sediments: Experiments and modeling approach. *Chemical Engineering Journal*, 475, 146455. doi: [10.1016/j.cej.2023.146455](https://doi.org/10.1016/j.cej.2023.146455).
- Hao Y, Xu J, Yuan S, Meng Z, Wang X, Xue J, Zhang J. 2022. Molecular dynamics study of electric field enhanced hydrate growth for gas storage. *Journal of Natural Gas Science and Engineering*, 103, 104617. doi: [10.1016/j.jngse.2022.104617](https://doi.org/10.1016/j.jngse.2022.104617).
- Hao Y, Xu Z, Du S, Yang X, Ding T, Wang B, Xu J, Zhang J, Yin H. 2021. Iterative cup overlapping: An efficient identification algorithm for cage structures of amorphous phase hydrates. *The Journal of Physical Chemistry B*, 125(4), 1282–1292. doi: [10.1021/acs.jpcc.0c08964](https://doi.org/10.1021/acs.jpcc.0c08964).
- He Z, Mi F, Ning F, Pang J, Jiang G. 2022. Methane hydrate formation in the salty water confined in clay nanopores: A molecular simulation study. *ACS Sustainable Chemistry & Engineering*, 10(18), 6128–6140. doi: [10.1021/acssuschemeng.2c01985](https://doi.org/10.1021/acssuschemeng.2c01985).
- Jin D, Coasne B. 2021. Reduced phase stability and faster formation/dissociation kinetics in confined methane hydrate. *Proceedings of the National Academy of Sciences*, 118(16). doi: [10.1073/pnas.2024025118](https://doi.org/10.1073/pnas.2024025118).
- Kabir M, Habiba UE, Khan W, Shah A, Rahim S, De los Rios-Escalante PR, Farooqi ZUR, Ali L, Shafiq M. 2023. Climate change due to increasing concentration of carbon dioxide and its impacts on environment in 21st century: A mini review. *Journal of King Saud University-Science*, 35(5), 102693. doi: [10.1016/j.jksus.2023.102693](https://doi.org/10.1016/j.jksus.2023.102693).
- Kim D, Ahn YH, Kim SJ, Lee JY, Lee J, Seo Y, Lee H. 2015. Gas hydrate in crystalline-swelled clay: The effect of pore dimension on hydrate formation and phase equilibria. *The Journal of Physical Chemistry C*, 119(38), 22148–22153. doi: [10.1021/acs.jpcc.5b03229](https://doi.org/10.1021/acs.jpcc.5b03229).
- Koster van Groos AF, Guggenheim S. 2009. The stability of methane hydrate intercalates of montmorillonite and nontronite: Implications for carbon storage in ocean-floor environments. *American Mineralogist*, 94(2–3), 372–379. doi: [10.2138/am.2009.3018](https://doi.org/10.2138/am.2009.3018).
- Lamorena RB, Kyung D, Lee W. 2011. Effect of organic matters on CO₂ hydrate formation in Ullung Basin sediment suspensions. *Environmental Science & Technology*, 45(14), 6196–6203. doi: [10.1021/es201261y](https://doi.org/10.1021/es201261y).
- Li Y, Chen M, Song H, Yuan P, Zhang B, Liu D, Zhou H, Bu H. 2020. Effect of cations (Na⁺, K⁺, and Ca²⁺) on methane hydrate formation on the external surface of montmorillonite: Insights from molecular dynamics simulation. *ACS Earth and Space Chemistry*, 4(4), 572–582. doi: [10.1021/acsearthspacechem.9b00323](https://doi.org/10.1021/acsearthspacechem.9b00323).
- Li Y, Chen M, Tang H, Han S, Song H, Wang P, Zhao Y, Zhu J. 2022a. Insights into carbon dioxide hydrate nucleation on the external basal surface of clay minerals from molecular dynamics simulations. *ACS Sustainable Chemistry & Engineering*, 10(19), 6358–6369. doi: [10.1021/acssuschemeng.2c01046](https://doi.org/10.1021/acssuschemeng.2c01046).
- Li Y, Han S, Zhang B, Tang H, Han J, Kang H, Zhao Y, Zhu J. 2022b. Nucleation and dissociation of carbon dioxide hydrate in the inter- and intra-particle pores of dioctahedral smectite: Mechanistic insights from molecular dynamics simulations. *Applied Clay Science*, 216, 106344. doi: [10.1016/j.clay.2021.106344](https://doi.org/10.1016/j.clay.2021.106344).
- Li Y, Zhu J, Han S, Zhang B, Tang H, Yuan B, Wang P, Bao W, Wang X, Zhao Y. 2023. Molecular dynamics simulations of CH₄/CO₂ hydrates nucleation in kaolinite particles. *Applied Surface Science*, 607, 154911. doi: [10.1016/j.apsusc.2022.154911](https://doi.org/10.1016/j.apsusc.2022.154911).
- Liu X, Zhang J, Gu Y, Huang H, Li Y, Sun J, Lu H, Xu C, Ren J, Yin Z. 2025. Investigation on liquid CO₂ forming CO₂ hydrates in sands: A kinetic study with implication on hydrate-based CO₂ sequestration. *Chemical Engineering Journal*, 505, 159179. doi: [10.1016/j.cej.2024.159179](https://doi.org/10.1016/j.cej.2024.159179).
- Luis DP, Herrera-Hernández EC, Saint-Martin H. 2015. A theoretical study of the dissociation of the sl methane hydrate induced by an external electric field. *The Journal of Chemical Physics*, 143(20), 204503. doi: [10.1063/1.4936214](https://doi.org/10.1063/1.4936214).
- Mackenzie RC. 1951. Cation exchange and clay mineral structure. *Nature*, 168(4264), 107–108. doi: [10.1038/168107a0](https://doi.org/10.1038/168107a0).
- Mi F, He Z, Jiang G, Ning F. 2022a. Effects of marine environments on methane hydrate formation in clay nanopores: A molecular dynamics study. *Science of The Total Environment*, 852, 158454. doi: [10.1016/j.scitotenv.2022.158454](https://doi.org/10.1016/j.scitotenv.2022.158454).
- Mi F, He Z, Zhao Y, Jiang G, Ning F. 2022b. Effects of surface property of mixed clays on methane hydrate formation in nanopores: A molecular dynamics study. *Journal of Colloid and Interface Science*, 627, 681–691. doi: [10.1016/j.jcis.2022.07.101](https://doi.org/10.1016/j.jcis.2022.07.101).
- Mi F, Li W, Pang J, Moulton OA, Ning F, Vlught TJH. 2024. Molecular insights into the microscopic behavior of CO₂ hydrates in oceanic sediments: Implications for carbon sequestration. *The Journal of Physical Chemistry C*, 128(43), 18588–18597. doi: [10.1021/acs.jpcc.4c05413](https://doi.org/10.1021/acs.jpcc.4c05413).
- Nguyen NN, La VT, Huynh CD, Nguyen AV. 2022a. Technical and economic perspectives of hydrate-based carbon dioxide capture. *Applied Energy*, 307, 118237. doi: [10.1016/j.apenergy.2021.118237](https://doi.org/10.1016/j.apenergy.2021.118237).
- Nguyen NN, Nguyen CV, Nguyen TAH, Nguyen AV. 2022b. Surface science in the research and development of hydrate-based sustainable technologies. *ACS Sustainable Chemistry & Engineering*, 10(13), 4041–4058. doi: [10.1021/acssuschemeng.2c00028](https://doi.org/10.1021/acssuschemeng.2c00028).
- Pahlavanzadeh H, Hejazi S, Manteghian M. 2020. Hydrate formation under static and pulsed electric fields. *Journal of Natural Gas Science and Engineering*, 77, 103232. doi: [10.1016/j.jngse.2020.103232](https://doi.org/10.1016/j.jngse.2020.103232).
- Pandey G, Poothia T, Kumar A. 2022. Hydrate based carbon capture and sequestration (HBCCS): An innovative approach towards decarbonization. *Applied Energy*, 326, 119900. doi: [10.1016/j.apenergy.2022.119900](https://doi.org/10.1016/j.apenergy.2022.119900).
- Park T, Kwon TH. 2018. Effect of electric field on gas hydrate nucleation kinetics: Evidence for the enhanced kinetics of hydrate nucleation by negatively charged clay surfaces. *Environmental Science and Technology*, 52(5), 3267–3274. doi: [10.1021/acs.est.7b05477](https://doi.org/10.1021/acs.est.7b05477).
- Potoff JJ, Siepmann JI. 2001. Vapor–liquid equilibria of mixtures containing alkanes, carbon dioxide, and nitrogen. *AIChE Journal*, 47(7), 1676–1682. doi: [10.1002/aic.690470719](https://doi.org/10.1002/aic.690470719).
- Rao S, Deng Y, Li Z, Lu H, Zhang Q. 2023. Effect of solid surface properties on spreading of a CO₂ hydrate film in a restricted space between two parallel silicon substrates. *ACS Sustainable Chemistry & Engineering*, 11(39), 14399–14408. doi: [10.1021/acssuschemeng.3c02837](https://doi.org/10.1021/acssuschemeng.3c02837).

- Rehman AN, Bavoh CB, Pendyala R, Lal B. 2021. Research advances, maturation, and challenges of hydrate-based CO₂ sequestration in porous media. *ACS Sustainable Chemistry & Engineering*, 9(45), 15075–15108. doi: [10.1021/acssuschemeng.1c05423](https://doi.org/10.1021/acssuschemeng.1c05423).
- Rodger PM, Forester TR, Smith W. 1996. Simulations of the methane hydrate/methane gas interface near hydrate forming conditions. *Fluid Phase Equilibria*, 116(1–2), 326–332. doi: [10.1016/0378-3812\(95\)02903-6](https://doi.org/10.1016/0378-3812(95)02903-6).
- Seo Y, Seol J, Yeon SH, Koh DY, Cha M, Kang SP, Seo YT, Bahk J, Lee J, Lee H. 2009. Structural, mineralogical, and rheological properties of methane hydrates in smectite clays. *Journal of Chemical & Engineering Data*, 54(4), 1284–1291. doi: [10.1021/jc800833y](https://doi.org/10.1021/jc800833y).
- Skipper NT. 1995. Monte carlo simulation of interlayer molecular structure in swelling clay minerals. 2. monolayer hydrates. *Clays and Clay Minerals*, 43(3), 294–303. doi: [10.1346/CCMN.1995.0430304](https://doi.org/10.1346/CCMN.1995.0430304).
- Sun Y, Jiang S, Li S, Wang X, Peng S. 2021. Hydrate formation from clay bound water for CO₂ storage. *Chemical Engineering Journal*, 406, 126872. doi: [10.1016/j.cej.2020.126872](https://doi.org/10.1016/j.cej.2020.126872).
- Tang R, Ou C, Lyu D, Liu C, Wu H. 2025. Effect of isomorphic substitution of clay mineral layers on CO₂ hydrate formation: Insights from molecular dynamics simulation study. *Geoenergy Science and Engineering*, 250, 213843. doi: [10.1016/j.geoen.2025.213843](https://doi.org/10.1016/j.geoen.2025.213843).
- Van Der Spoel D, Lindahl E, Hess B, Groenhof G, Mark AE, Berendsen HJC. 2005. GROMACS: Fast, flexible, and free. *Journal of Computational Chemistry*, 26(16), 1701–1718. doi: [10.1002/jcc.20291](https://doi.org/10.1002/jcc.20291).
- Wang P, Li Y, Sun N, Han S, Wang X, Su Q, Li Y, He J, Yu X, Du S, Francisco JS, Zhu J, Zhao Y. 2024. Hydrate technologies for CO₂ capture and sequestration: Status and perspectives. *Chemical Reviews*, 124(18), 10363–10385. doi: [10.1021/acs.chemrev.2c00777](https://doi.org/10.1021/acs.chemrev.2c00777).
- Wang R, Liao B, Wang J, Sun J, Wang Y, Wang J, Wang Q, Qu Y, Cheng R. 2023. Microscopic molecular insights into methane hydrate growth on the surfaces of clay minerals: Experiments and molecular dynamics simulations. *Chemical Engineering Journal*, 451, 138757. doi: [10.1016/j.cej.2022.138757](https://doi.org/10.1016/j.cej.2022.138757).
- Wang T, Fan Z, Sun L, Yang L, Zhao J, Zhang L, Song Y. 2024. Evaluation of stratigraphic adaptability for hydrate-based CO₂ sequestration in marine clay-containing reservoirs. *Chemical Engineering Journal*, 501, 157711. doi: [10.1016/j.cej.2024.157711](https://doi.org/10.1016/j.cej.2024.157711).
- Xu T, Lang X, Fan S, Wang Y, Chen J. 2019. The effect of electric fields in methane hydrate growth and dissociation: A molecular dynamics simulation. *Computational and Theoretical Chemistry*, 1149, 57–68. doi: [10.1016/j.comptc.2018.12.018](https://doi.org/10.1016/j.comptc.2018.12.018).
- Yan KF, Li XS, Chen ZY, Xia ZM, Xu CG, Zhang Z. 2016. Molecular dynamics simulation of the crystal nucleation and growth behavior of methane hydrate in the presence of the surface and nanopores of porous sediment. *Langmuir*, 32(31), 7975–7984. doi: [10.1021/acs.langmuir.6b01601](https://doi.org/10.1021/acs.langmuir.6b01601).
- Yang S, Yang D, Shi W, Deng C, Chen C, Feng S. 2022. Global evaluation of carbon neutrality and peak carbon dioxide emissions: Current challenges and future outlook. *Environmental Science and Pollution Research*, 30(34), 81725–81744. doi: [10.1007/s11356-022-19764-0](https://doi.org/10.1007/s11356-022-19764-0).
- Zhang X, Zhang M, Li P, Li J, Wang Y, Wu Q. 2022. Cooperative effect of surfactant and porous media on CO₂ hydrate formation and capacity of gas storage. *Fuel*, 329, 125494. doi: [10.1016/j.fuel.2022.125494](https://doi.org/10.1016/j.fuel.2022.125494).
- Zhang Z, Kusalik PG, Guo GJ, Ning F, Wu N. 2021. Insight on the stability of polycrystalline natural gas hydrates by molecular dynamics simulations. *Fuel*, 289, 119946. doi: [10.1016/j.fuel.2020.119946](https://doi.org/10.1016/j.fuel.2020.119946).
- Zhang Z, Kusalik PG, Wu N, Liu C, Ning F. 2022a. Molecular insights into the impacts of calcite nanoparticles on methane hydrate formation. *ACS Sustainable Chemistry & Engineering*, 10(35), 11597–11605. doi: [10.1021/acssuschemeng.2c03428](https://doi.org/10.1021/acssuschemeng.2c03428).
- Zhang Z, Kusalik PG, Wu N, Liu C, Zhang Y. 2022b. Molecular simulation study on the stability of methane hydrate confined in slit-shaped pores. *Energy*, 257, 124738. doi: [10.1016/j.energy.2022.124738](https://doi.org/10.1016/j.energy.2022.124738).
- Zhang Z, Wu N, Liu C, Hao X, Zhang Y, Gao K, Peng B, Zheng C, Tang W, Guo G. 2022. Molecular simulation studies on natural gas hydrate nucleation and growth: A review. *China Geology*, 5(2), 1–15. doi: [10.31035/cg2022017](https://doi.org/10.31035/cg2022017).