Supporting Information For

Molecular insights into hybrid CH$_4$ physisorption-hydrate formation in spiral halloysite nanotubes: Implications for energy storage

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Additional Methods

The Halloysite nanotube (HNTs) has a unique structure, featuring the hydrophobic siloxane on its outer surface and the hydrophilic gibbsite on its inner lumen surface.[1, 2] The outer surface of the HNTs can adsorb CH_4 molecules. At the same time, an abundant relatively confined space will be formed between the HNTs. In the confined space, CH_4 molecules adsorbed on the outer surface of the HNTs can be trapped through physisorption. The hydrophilic inner surface of the HNTs can adsorb a large number of water molecules, and the presence of these water molecules provides a sufficient water source for hydrate formation inside of the HNTs.[3] In this study, CH_4 and water molecules can freely exchange between inside and outside of the HNTs. The mole fraction of CH_4 inside and outside of the HNTs was set to the same value, eliminating the impact of the initial configuration on the migration of CH_4 inside and outside the halloysite. The detailed force field parameters for H_2O, CH_4, and HNT in the system are shown in Table S2. To explore the physisorption processes of CH_4 molecules on the surface of the HNTs, a 20-ns adsorption simulation was performed under the isothermal-isobaric (*NPT*) ensemble. The temperature of 300 K is controlled by the velocity-rescaling thermostat,[4] and the pressure of 10 MPa is controlled by the Berendsen barostat.[5]

Table S1. Parameters for the three simulation systems for CH_4 storage.

System	Simulation	N_{CH4}	N_{H2O}	Temperature	Simulation Time
	Pressure in the three simulation systems: 10 MPa				
$R_{0.08}$	Adsorption	2260	25986	300 K	20 ns
	Hydrate-formation	2260	25986	240 K	2.0 µs
$R_{0.12}$	Adsorption	3390	24856	300 K	20 ns
	Hydrate-formation	3390	24856	240 K	2.0 µs
$R_{0.148}$	Adsorption	4184	24062	300 K	20 ns
	Hydrate-formation	4184	24062	240 K	2.0 µs

Table S2. Parameters for the TIP4P/ice water model,[6] OPLS-UA methane,[7] and the CLAYFF force field.[8] σ and ε are the Lennard-Jones parameters, in units of nm and kJ/mol, respectively; q is the partial charge of an atom in units of elementary charge (e); m is the atomic mass in units of g/mol.

atom	ε / [kJ/mol]	σ / [nm]	q / [e]	m / [g/mol]
H_2O				
O (MW)	0	0	-1.1794	0
O	0.8822	0.31668	0	16
H	0	0	0.5897	1.008
CH_4	1.23	0.373	0	16
Halloysite				
Si (st)	7.70065×10^{-6}	0.3302	2.1	28.09
Al (ao)	5.56388×10^{-6}	0.4271	1.575	26.98
O (ob)	0.65017	0.316556	-1.05	16
O (oh)	0.65017	0.316556	-0.95	16
H (ho)	0	0	0.425	1.008

Calculation of the diffusion coefficient (K_{DC})

Mean square displacement (MSD) and diffusion coefficient K_{DC} are calculated by the program *gmx_mpi msd* in GROMACS manual 5.0.7. Normally an index file containing atom numbers is used and the MSD is averaged over these atoms. For water molecules consisting of more than one atom, r_i can be taken as the O atom.

$$K_{DC} = \frac{lim_{t \to \infty} \langle \| r_i(t) - r_i(0) \|^2 \rangle_{i \in A}}{6\Delta t} \qquad (1)$$

In this study, each MSD is calculated within 1 ns for methane molecules and water molecules. Therefore, each diffusion coefficient is the average value within each 1 ns period.

Calculation of the distance between hydrate and HNTs (HHD)

To reveal the positional relationship between hydrate solids and HNTs, we define a parameter HBD, which is the distance between hydrates (comprising CH_4 and H_2O molecules) and HNTs surfaces. CH_4 hydrate is composed of CH_4 and H_2O molecules. We first select each CH_4 molecule or H_2O molecule that forms a hydrate and then calculate the distance between each atom in the HNTs surfaces and the hydrate (the CH_4 molecule or H_2O molecule). The minimum value is the distance between the CH_4 molecules or H_2O molecules in the hydrate and the HNTs surfaces.

$$HBD \in \{D_1, D_2, D_3, D_4 \cdots\}_{min} \qquad (2)$$

Where D_1 is the distance between the CH_4 or H_2O molecule and an atom in the HNTs surfaces. D_2 is the distance between the CH_4 or H_2O molecule and another atom in the HNTs surfaces. We count all distance values and only take the minimum value.

Calculation of the conversion ratio

We define the conversion ratio. CH_4 hydrate is composed of CH_4 and H_2O molecules. Conversion ratio is defined as the number of CH_4/H_2O in hydrate divided by the total number.

$$\text{Conversion ratio} = \frac{N_{Hydrate}}{N_{total}} \qquad (3)$$

Where $N_{Hydrate}$ is the number of the CH_4 or H_2O molecule formed hydrate. N_{total} is the total number of the CH_4 or H_2O in the system. In this study, each conversion ratio is calculated within 1 ns for CH_4 or H_2O molecules. Therefore, each conversion ratio is the average value within each 1 ns period.

Additional Results and Discussions

In adsorption simulations, the inner and outer surfaces of the HNTs exhibit different affinities for CH_4/H_2O molecules. Outside of the HNTs, CH_4 molecules will quickly form an obvious wave peak on the outer surface of the HNTs, while H_2O molecules will form a relatively flat wave peak on the outer surface of the HNTs (Figure S3). This indicates that the outer surface of the HNTs has a strong affinity for CH_4 molecules and a weak affinity for H_2O molecules. Inside of the HNTs, CH_4 molecules form small wave peaks farther away from the inner surface, while H_2O molecules can form obvious peaks near the inner surface (Figure S3). This shows that the inner surface of the HNTs can strongly adsorb H_2O molecules and repel CH_4 molecules. The adsorption process occurs in a short time. During the period of 1 - 20 ns, the number of adsorbed CH_4 and H_2O molecules on the inner and outer surfaces of the HNTs changes little.

We pre-filled the inner and outer regions of the HNTs with a homogeneous CH_4 solution, which skips the initial diffusion process that would typically occur in a real system. This setup leads to a different mass transfer pattern (Figure S5(a-b)). Moreover, the CH_4 solution in the simulation is supersaturated, resulting in the rapid formation of CH_4 nanobubbles. This rapid nanobubble formation significantly affects the mass transfer of CH_4 and H_2O molecules. In a real system, the hydrophilic inner surface would indeed attract more H_2O molecules, and the hydrophobic outer surface would promote CH_4 adsorption. The dynamics observed in the simulation are strongly influenced by the pre-filled setup and supersaturated CH_4 solution, which temporarily alters the expected diffusion

behavior.

In the $R_{0.08}$ simulation system, due to the low gas-water ratio, a large number of CH_4 molecules can be converted into hydrates. Conversion ratio is defined as the number of CH_4/H_2O in hydrate divided by the total number. The conversion ratio of CH_4 molecules inside and outside of the HNTs is high (Figure S11). Likewise, CH_4 hydrate formation also means that a large number of H_2O molecules participate in hydrate formation. Hence, the conversion ratio of H_2O molecules inside and outside of the HNTs also maintains a high value. In contrast, in the $R_{0.148}$ system, a large number of CH_4 molecules cannot be converted into hydrates immediately due to the high gas-water ratio, resulting in a low conversion ratio of CH_4 molecules, especially inside of the HNTs (Figure S12).

Figure S17(a-c) shows the evolution of the number of CH_4/H_2O molecules migrating from the inside to the outside of the HNTs. It is found that the migration number of CH_4 and H_2O molecules inside and outside of the HNTs is small, indicating that the mass transfer of CH_4/H_2O molecules inside and outside of the HNTs exhibits no significant variation. In the $R_{0.08}$ and $R_{0.12}$ simulation systems, the migration direction of CH_4 molecules is from the outside to the inside of the HNTs, while the migration direction of H_2O molecules is from the inside to the outside of the HNTs (Figure S17(a-b)). In the R0.148 simulation system, the migration direction of CH_4 molecules is from the inside to the outside of the HNTs, while the migration direction of H_2O molecules is from the outside to the inside of the HNTs (Figure S17(c)). There are different initial trends between Figure S17(a), (b), and (c). The initial difference observed in Figure S17(c) can be attributed to the higher CH_4 concentration (0.148) in the $R_{0.148}$ system. At high CH_4 concentrations, CH_4 nanobubbles form more rapidly inside the HNTs, which significantly influences the initial mass transfer process. The quick aggregation of CH_4 molecules into nanobubbles alters the diffusion dynamics of CH_4/H_2O molecules, causing the migration pattern of CH_4/H_2O molecules to differ from the patterns seen at lower concentrations, as shown in Figure S17(a-b). However, once the nanobubbles stabilize, the overall trend becomes consistent with the other systems. *i.e.*, a few H_2O molecules migrate from inside to outside of the HNTs, while a small number of CH_4 molecules diffuse in the opposite direction.

Figure S1. The schematic diagram of the final simulation model for the (a) $R_{0.08}$, (b) $R_{0.12}$, and (c) $R_{0.148}$ simulation systems.
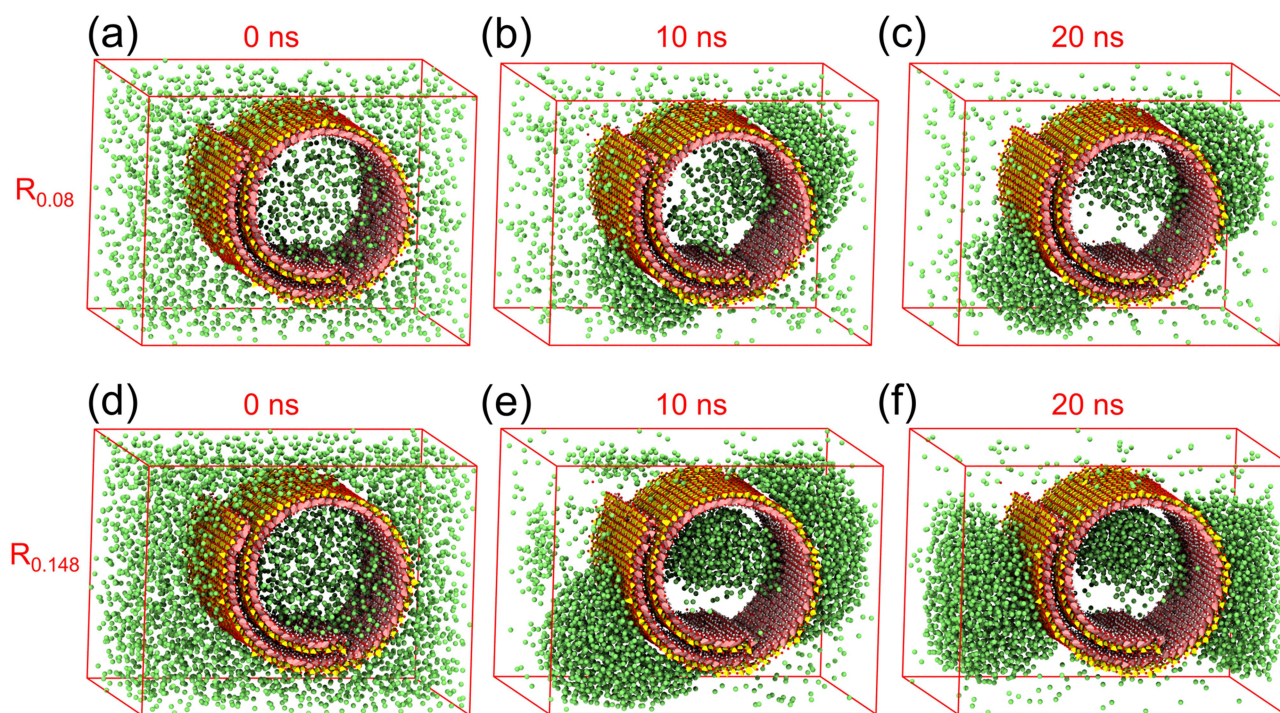

Figure S2. The adsorption processes of CH_4 molecules inside and outside of the HNTs in the (a-c) $R_{0.08}$ and (d-f) $R_{0.148}$ simulation systems. Green balls represent CH_4 molecules. The HNTs are displayed as polyhedral, *i.e.* yellow (Si atom) and pink (Al atom).
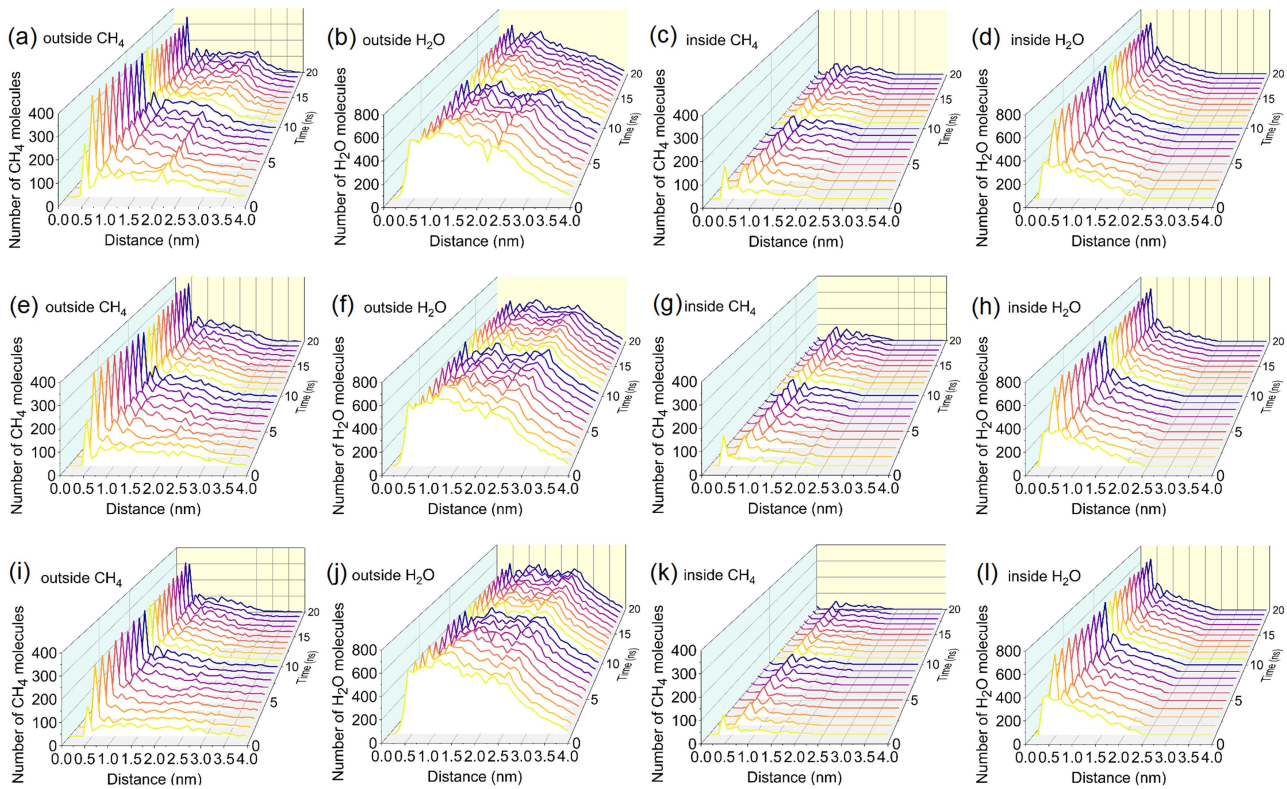
Figure S3. The evolution of the number of CH_4/H_2O molecules for different distances from the inner and outer surfaces of the HNTs for the (a-d) $R_{0.148}$, (e-h) $R_{0.12}$, and (i-l) $R_{0.08}$ simulation systems.

Figure S4. The number of CH_4/H_2O molecules at various radial distances from the inner and outer surfaces of the HNTs at the end of 20-ns adsorption simulation for the (a-b) $R_{0.148}$ and (c-d) $R_{0.08}$ simulation systems.

Figure S5. The evolution of the number of CH_4 adsorbed on the outer surface and the percentage of CH_4/H_2O molecules inside of the HNTs relative to the total number of CH_4/H_2O molecules during 20-ns adsorption simulation for the (a) $R_{0.148}$ and (b) $R_{0.08}$ simulation systems.

Figure S6. The evolution of the number of CH_4/H_2O molecules inside and outside of the HNTs for the (a) $R_{0.148}$, (b) $R_{0.12}$, and (c) $R_{0.08}$ systems for adsorption simulation.

Figure S7. Diffusion coefficients (K_{DC}) of CH_4/H_2O molecules at various radial distances from the inner and outer surfaces of the HNTs at the end of 20-ns adsorption simulation for the (a, b) $R_{0.148}$ and (c, d) $R_{0.08}$ simulation systems.

Figure S8. Formation processes of CH$_4$ hydrate inside and outside of the HNTs for the (a-i) R$_{0.08}$ simulation system. The HNT is displayed as polyhedral, *i.e.* yellow (Si atom) and pink (Al atom). Orange and green balls represent CH$_4$ molecules in nanobubble and solution, respectively. Hydrate cages are shown as sticks in various colors (green for 5^{12}, blue for $5^{12}6^2$, red for $5^{12}6^3$, orange for $5^{12}6^4$, cyan for $4^15^{10}6^2$, purple for $4^15^{10}6^3$ and pink for $4^15^{10}6^4$).

Figure S9. Formation processes of CH$_4$ hydrate inside and outside of the HNTs for the (a-i) R$_{0.148}$ simulation system. The HNT is displayed as polyhedral, *i.e.* yellow (Si atom) and pink (Al atom). Orange and green balls represent CH$_4$ molecules in nanobubble and solution, respectively. Hydrate cages are shown as sticks in various colors (green for 5^{12}, blue for $5^{12}6^2$, red for $5^{12}6^3$, orange for $5^{12}6^4$, cyan for $4^15^{10}6^2$, purple for $4^15^{10}6^3$ and pink for $4^15^{10}6^4$).

Figure S10. Number density distribution of CH_4 molecules for the last 0.001 μs in the three simulation systems *i.e.* (a-c) $R_{0.08}$, (d-f) $R_{0.12}$, (g-i) $R_{0.148}$ simulation systems.

Figure S11. The evolution of the (a-b) conversion ratio of CH_4/H_2O molecules and (c-d) number of CH_4/H_2O molecules in solution and hydrate inside and outside of the HNTs for the $R_{0.08}$ simulation system. Conversion ratio is defined as the number of CH_4/H_2O in hydrate divided by the total number.

Figure S12. The evolution of the (a-b) conversion ratio of CH_4/H_2O molecules and (c-d) number of CH_4/H_2O molecules in solution and hydrate inside and outside of the HNTs for the $R_{0.148}$ simulation system. Conversion ratio is defined as the number of CH_4/H_2O in hydrate divided by the total number.

Figure S13. The evolution of the number of (a) H_2O and (b) CH_4 molecules in solution and hydrate for the $R_{0.12}$ simulation system.

Figure S14. The evolution of the number of hydrogen bonds between water molecules and both the inner and outer surfaces of the HNTs for the (a) $R_{0.148}$, (b) $R_{0.12}$, and (c) $R_{0.08}$ simulation systems.

Figure S15. The evolution of the CH_4 mole fraction in water x_{CH4} inside and outside of the HNTs and total for the (a) $R_{0.148}$, (b) $R_{0.12}$, and (c) $R_{0.08}$ simulation systems.
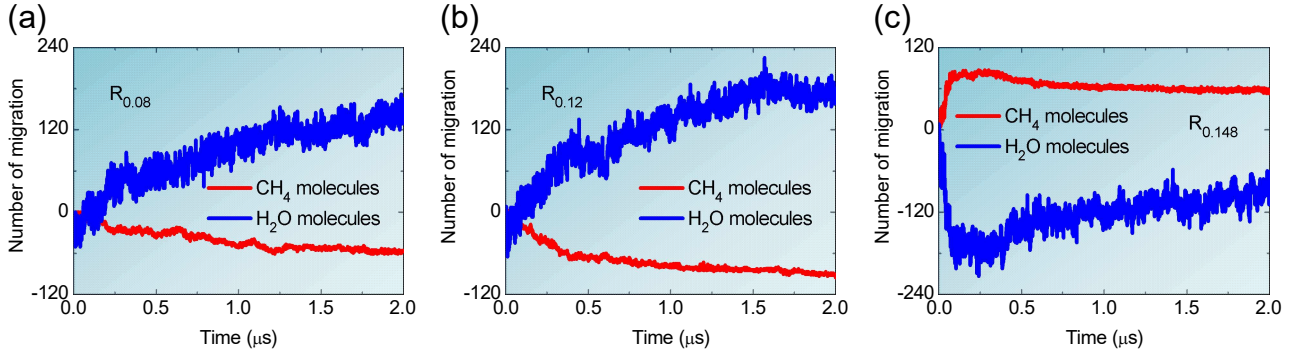

Figure S16. The evolution of the CH_4 in the nanobubbles N_{CH4} inside and outside of the HNTs and total for the (a) $R_{0.148}$, (b) $R_{0.12}$, and (c) $R_{0.08}$ simulation systems.

Figure S17. The evolution of the number of CH_4/H_2O molecules migration from inside to outside of the HNTs for the (a) $R_{0.08}$, (b) $R_{0.12}$, and (c) $R_{0.148}$ simulation systems.
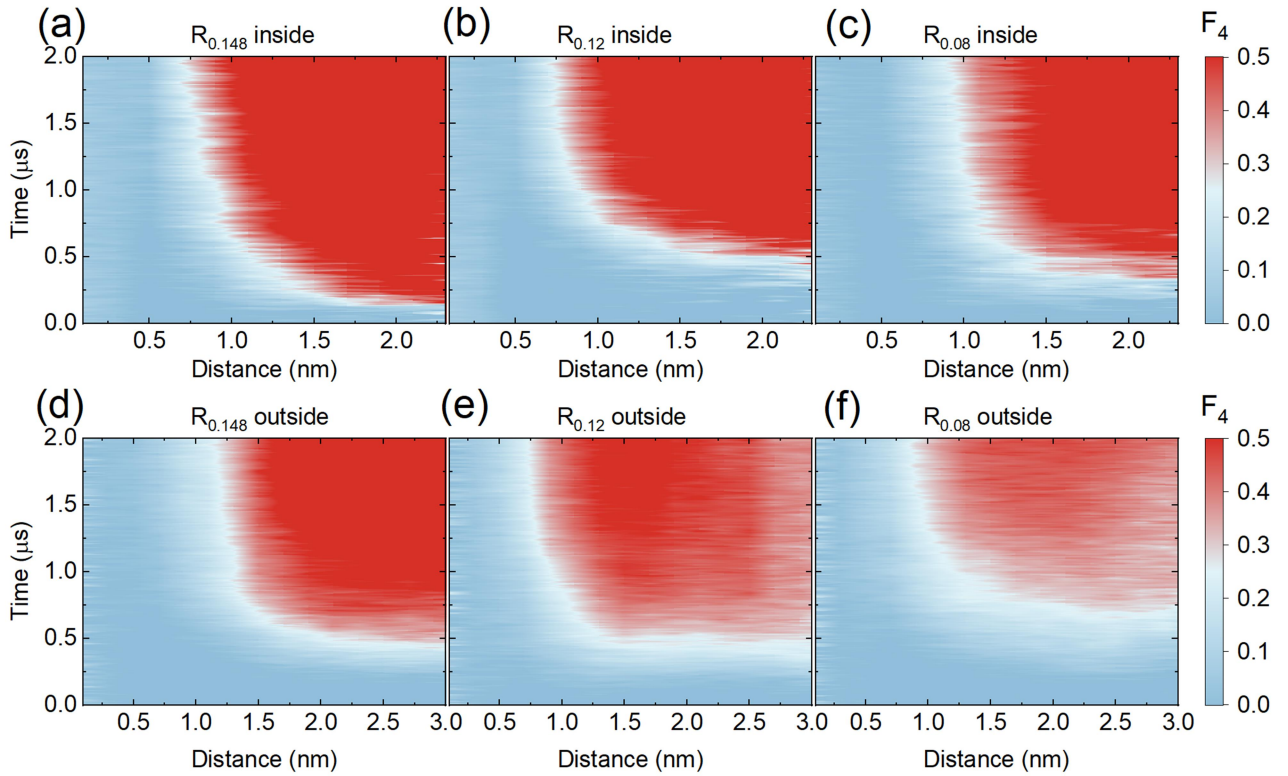

Figure S18. The evolution of the F_4 order parameter under the different radial distances from the inner and outer surfaces of the HNTs for the (a, d) $R_{0.148}$, (b, e) $R_{0.12}$, and (c, f) $R_{0.08}$ simulation systems.
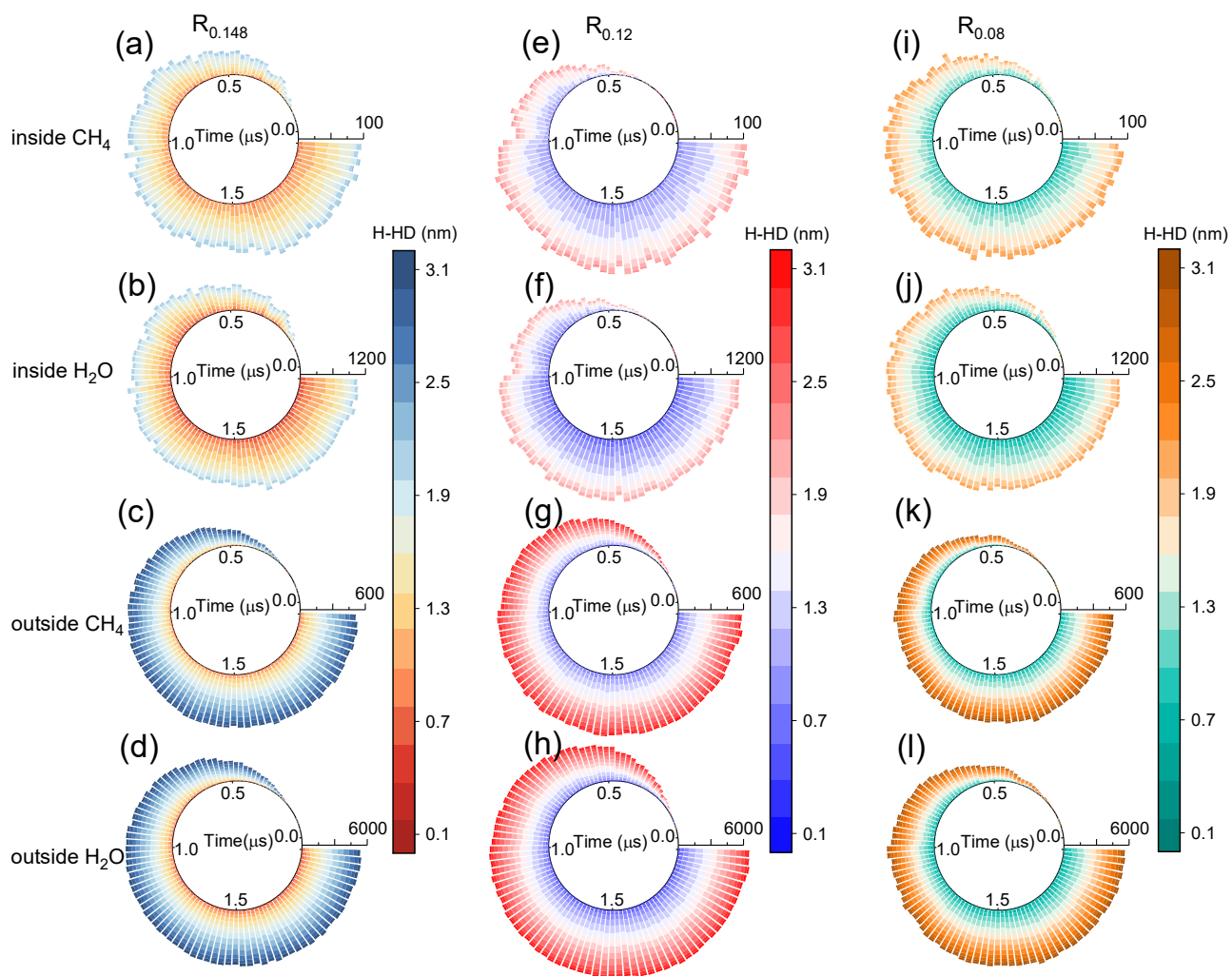
Figure S19. The evolution of the number of CH_4/H_2O molecules in hydrate as a function of the radial distances from the inner and outer surfaces of the HNTs for the (a-d) $R_{0.148}$, (e-h) $R_{0.12}$, and (i-l) $R_{0.08}$ simulation systems. These values were calculated for each 20ns.
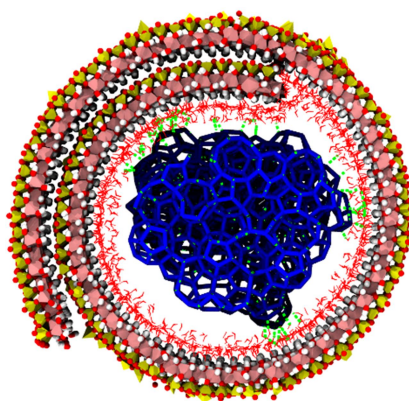
Figure S20. The snapshot of the hydrogen bonds (green lines) between the bound water on the inner surface and the hydrate solids inside of the HNTs at 2.0-μs for the (a-i) $R_{0.08}$ simulation system. The HNT is displayed as polyhedral, *i.e.* yellow (Si atom) and pink (Al atom). Blue bonds represent hydrate solids inside of the HNTs.
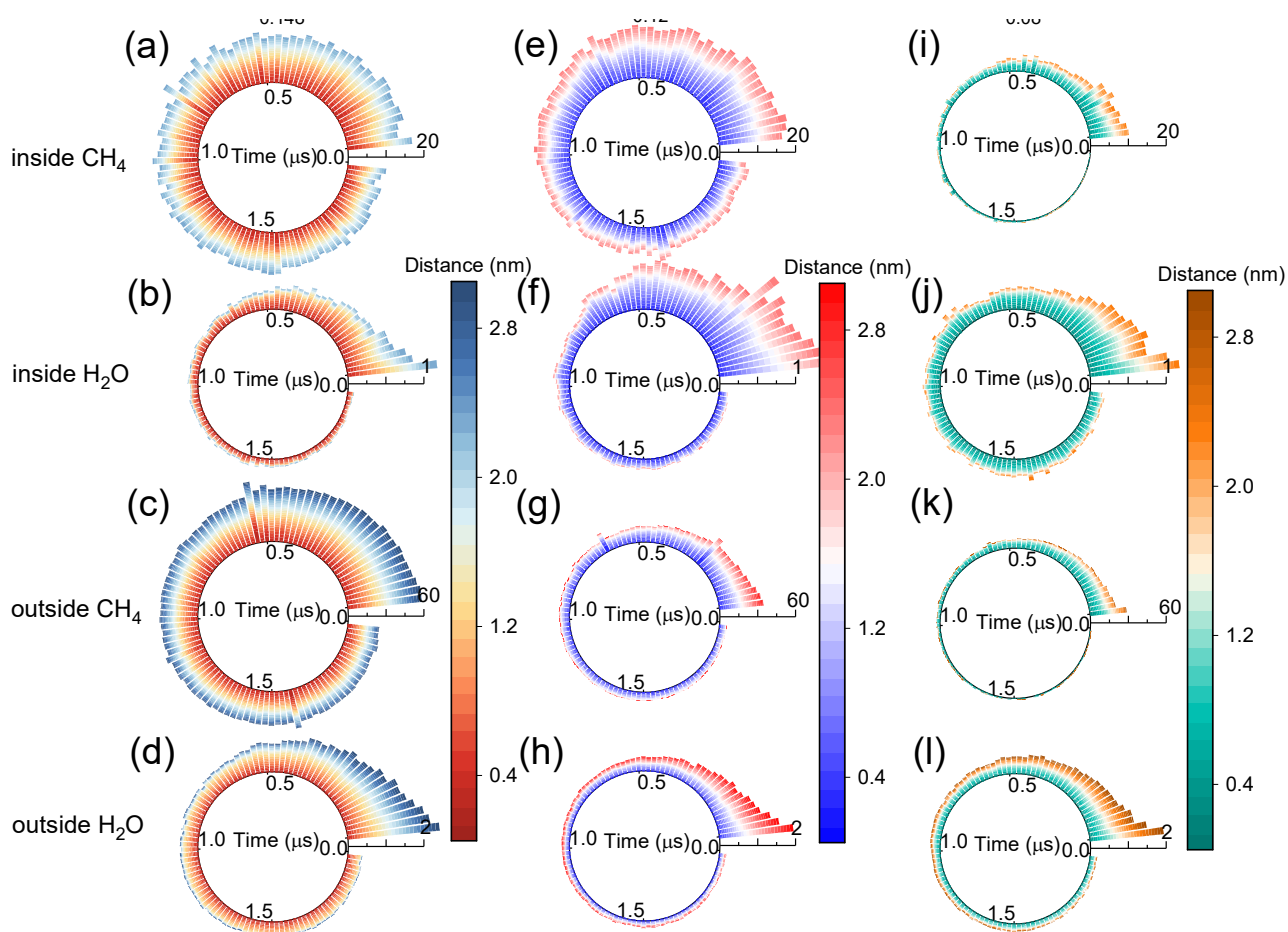

Figure S21. The evolution of the diffusion coefficient (K_{DC}) of CH_4/H_2O molecules as a function of the radial distances from the inner and outer surfaces of the HNTs for the (a-d) $R_{0.148}$, (e, h) $R_{0.12}$, and (i-l) $R_{0.08}$ simulation systems. These values were calculated for each 20ns.
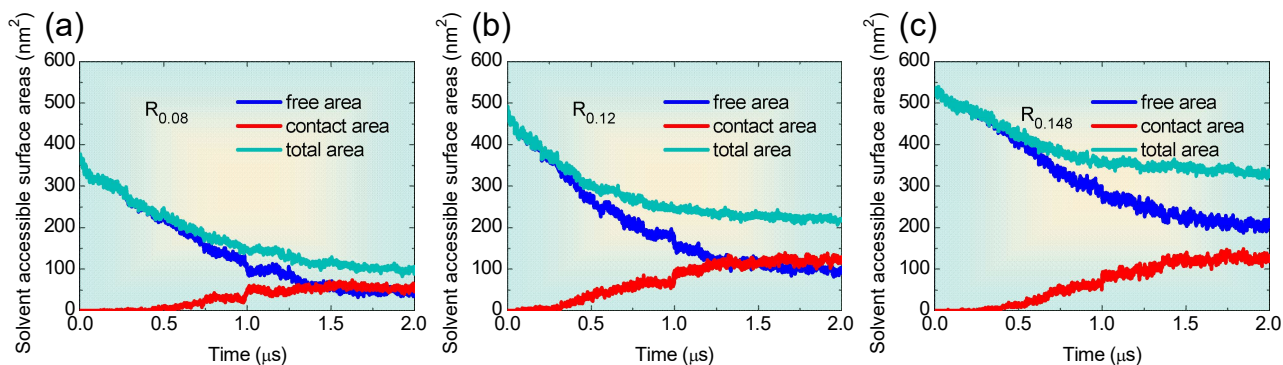
Figure S22. The evolution of the solvent accessible surface area of CH_4 nanobubbles for free, contact and total area in the (a) $R_{0.08}$, (b) $R_{0.12}$, and (c) $R_{0.148}$ simulation systems.
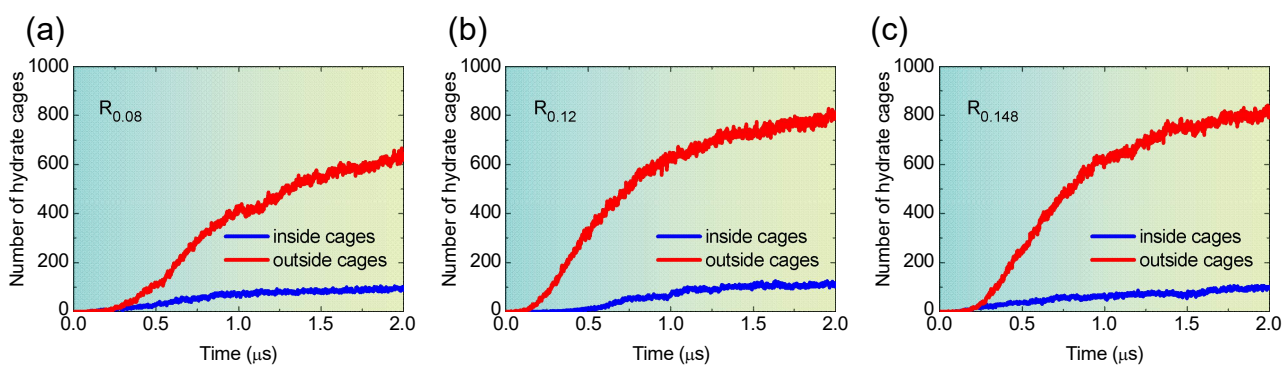

Figure S23. The evolution of the number of hydrate cages inside and outside of the HNTs for the (a) $R_{0.08}$, (b) $R_{0.12}$, and (c) $R_{0.148}$ simulation systems.
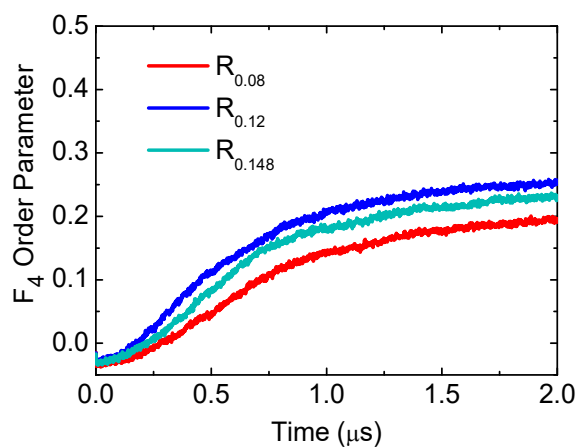

Figure S24. The evolution of the F_4 order parameter for the $R_{0.148}$, $R_{0.12}$, and $R_{0.08}$ simulation systems.
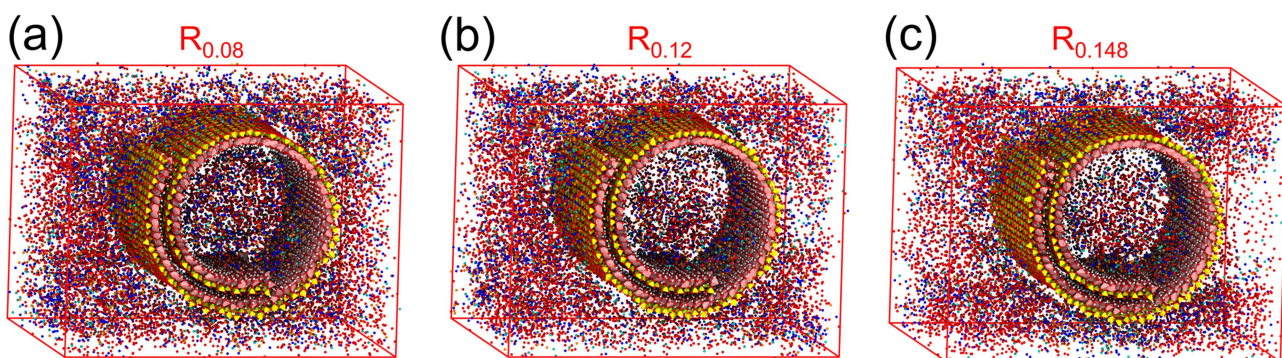
Figure S25. Snapshots of water ring inside and outside of the HNTs at 2 μs (a-c) in the $R_{0.08}$, $R_{0.12}$ and $R_{0.148}$ simulation systems. Cyan, red, blue and orange balls represent ring_4, ring_5, ring_6 and ring_7, respectively.
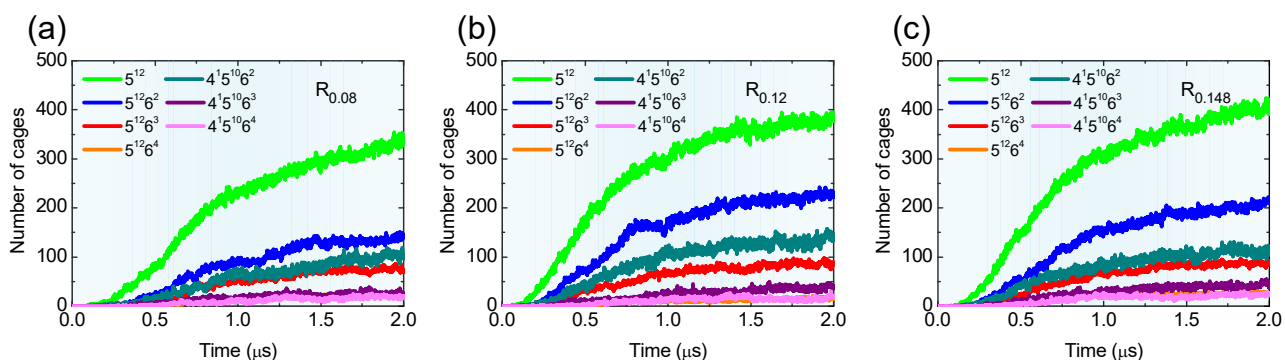

Figure S26. The evolution of the number of hydrate cages for the (a) $R_{0.08}$, (b) $R_{0.12}$, and (c) $R_{0.148}$ simulation systems.

Supporting Videos

Video S1. Adsorption processes of CH_4 molecules inside and outside of the HNTs for the $R_{0.08}$ simulation system. The HNTs are displayed as polyhedral, *i.e.* yellow (Si atom) and pink (Al atom). Green ball represents CH_4 molecules.

Video S2. Adsorption processes of CH_4 molecules inside and outside of the HNTs for the $R_{0.12}$ simulation system. The HNTs are displayed as polyhedral, *i.e.* yellow (Si atom) and pink (Al atom). Green ball represents CH_4 molecules.

Video S3. Adsorption processes of CH_4 molecules inside and outside of the HNTs for the $R_{0.148}$ simulation system. The HNTs are displayed as polyhedral, *i.e.* yellow (Si atom) and pink (Al atom). Green ball represents CH_4 molecules.

Video S4. Formation processes of CH_4 hydrates inside and outside of the HNTs for the $R_{0.08}$ simulation system. The HNTs are displayed as polyhedral, *i.e.* yellow (Si atom) and pink (Al atom). Green ball represents CH_4

molecules. Hydrate cages are shown as sticks in various colors (green for 5^{12}, blue for $5^{12}6^2$, red for $5^{12}6^3$, orange for $5^{12}6^4$, cyan for $4^15^{10}6^2$, purple for $4^15^{10}6^3$ and pink for $4^15^{10}6^4$).

Video S5. Formation processes of CH_4 hydrates inside and outside of the HNTs for the $R_{0.12}$ simulation system. The HNTs are displayed as polyhedral, *i.e.* yellow (Si atom) and pink (Al atom). Green ball represents CH_4 molecules. Hydrate cages are shown as sticks in various colors (green for 5^{12}, blue for $5^{12}6^2$, red for $5^{12}6^3$, orange for $5^{12}6^4$, cyan for $4^15^{10}6^2$, purple for $4^15^{10}6^3$ and pink for $4^15^{10}6^4$).

Video S6. Formation processes of CH_4 hydrates inside and outside of the HNTs for the $R_{0.148}$ simulation system. The HNTs are displayed as polyhedral, *i.e.* yellow (Si atom) and pink (Al atom). Green ball represents CH_4 molecules. Hydrate cages are shown as sticks in various colors (green for 5^{12}, blue for $5^{12}6^2$, red for $5^{12}6^3$, orange for $5^{12}6^4$, cyan for $4^15^{10}6^2$, purple for $4^15^{10}6^3$ and pink for $4^15^{10}6^4$).

Supporting Reference

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