Supplementary Information

Competition between CH_4 hydrate formation and phase separation in a wetted metal-organic framework MIL-101 at moderate subcooling: molecular insights into CH_4 storage

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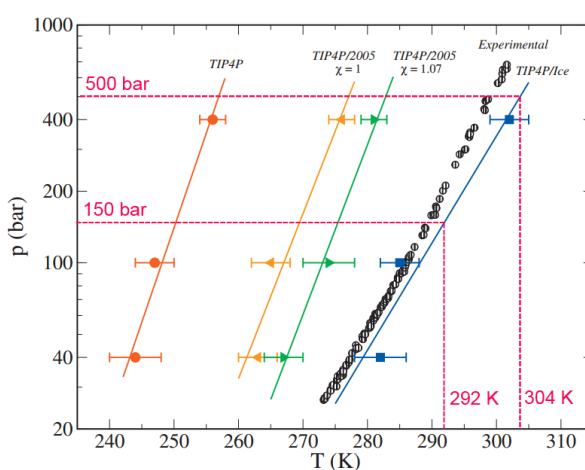
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Fig. S1 Three-phase (water-hydrate-methane) coexistence curve of CH_4 hydrate, from which subcooling temperature was estimated. The red dash lines indicate the pressure of 150 and 500 bar and their corresponding temperatures of 292 and 304 K. The temperature used in this work was 285 K, and thus the subcooling temperatures were 7 and 19 K at 150 and 500 bar, respectively. This figure was modified from Fig.11 in *Determining the three-phase coexistence line in methane hydrates using computer simulations, J. Chem. Phys. 133 (2010), 064507.*
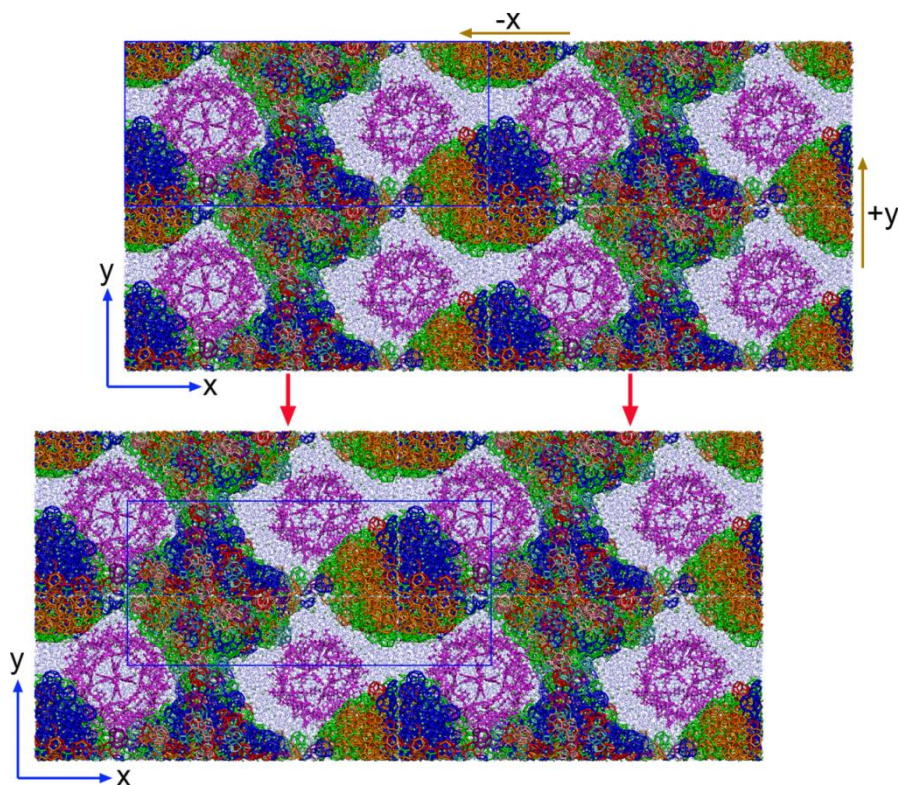
Fig. S2 Modification of the periodic boundary to assure the nucleation and growth of CH_4 hydrate within the simulation box (the blue rectangle with fixed position), *i.e.*, not crossing the box boundary.
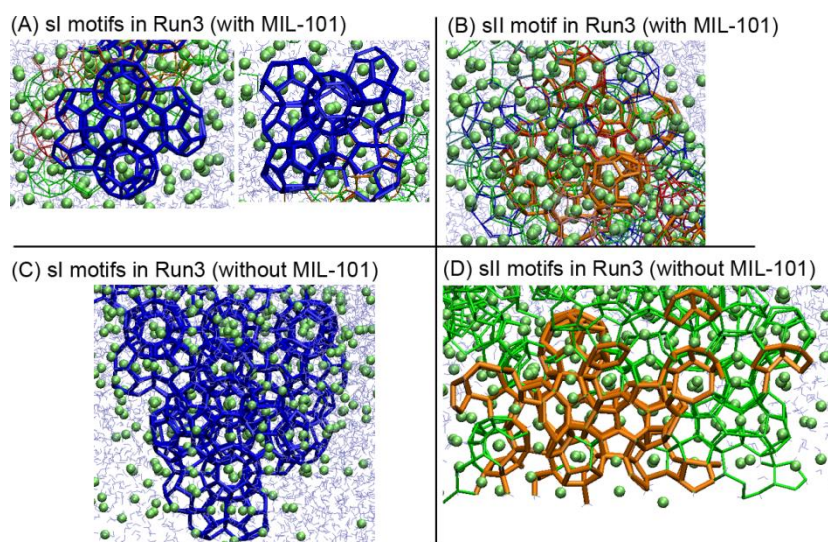

Fig. S3 (A,C) sI motifs and (B,D) sII motif in the amorphous hydrates formed during Run3 in the presence and in the absence of MIL-101 under 285 K and 50 MPa with subcooling of 19 K. Color code: green for 5^{12}, blue for $5^{12}6^2$, red for $5^{12}6^3$, orange for $5^{12}6^4$, cyan for $4^15^{10}6^2$, purple for $4^15^{10}6^3$, and pink for $4^15^{10}6^4$.
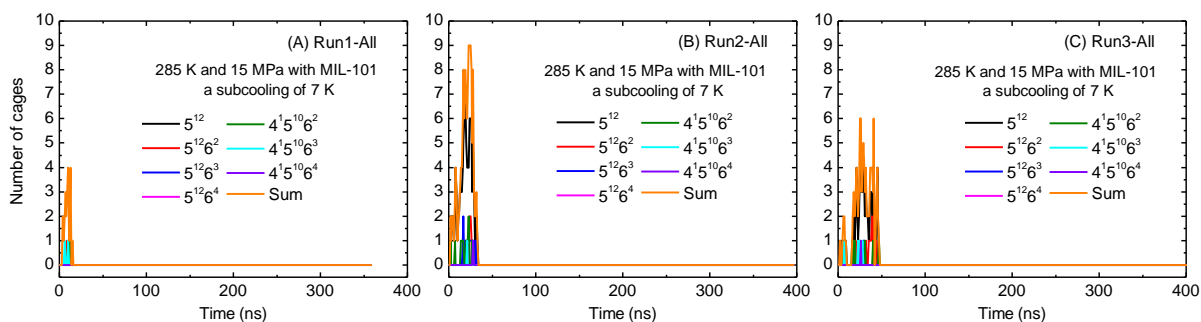
Fig. S4 Number of seven types of cages formed in (A) Run1, (B) Run2 and (C) Run3 in the presence of MIL-101 under 285 K and 15 MPa with subcooling of 7 K.
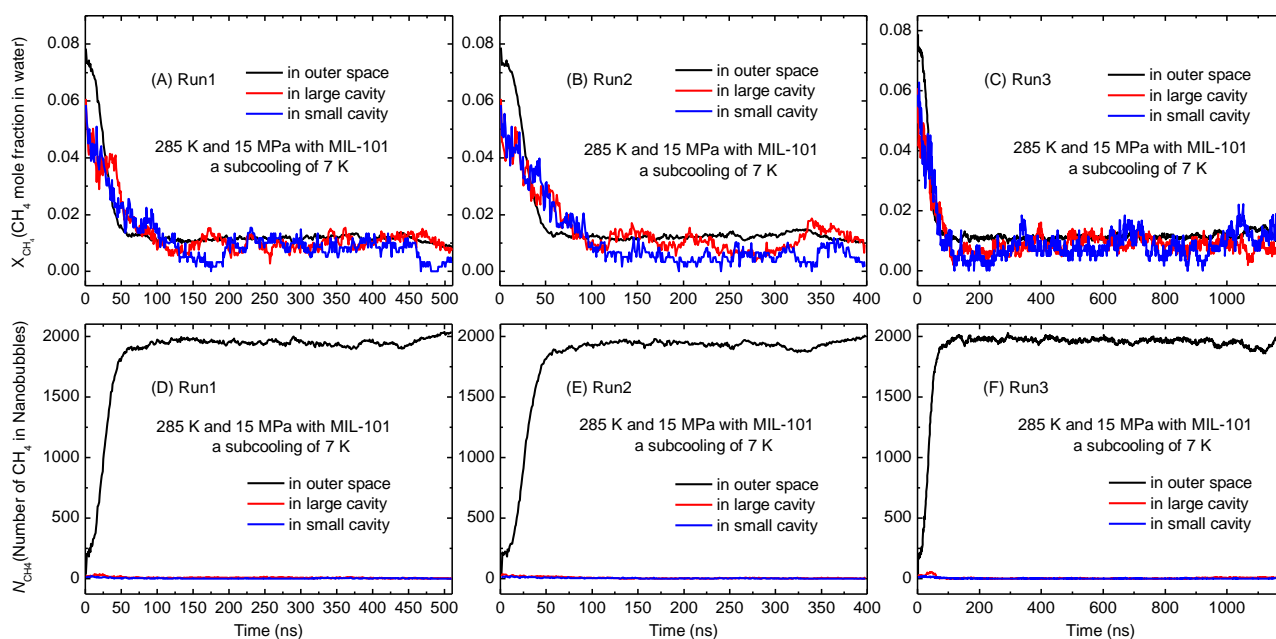

Fig. S5 Evolution of (A-C) CH_4 mole fraction in water (x_{CH4}) and (D-F) number of CH_4 molecules in nanobubbles (N_{CH4}) in the small and large cavities of MIL-101 and their outer space during three repeated runs in the presence of MIL-101 under 285 K and 15 MPa with subcooling of 7 K.
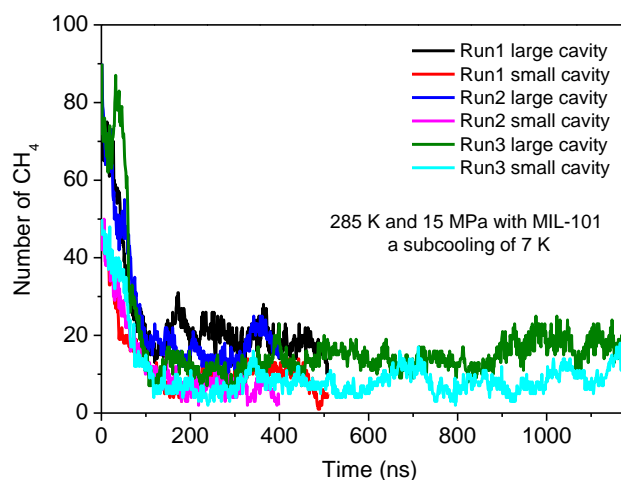

Fig. S6 Evolution of number of CH_4 molecules in the large and small cavities of MIL-101 during three repeated runs in the presence of MIL-101 under 285 K and 15 MPa with subcooling of 7 K.
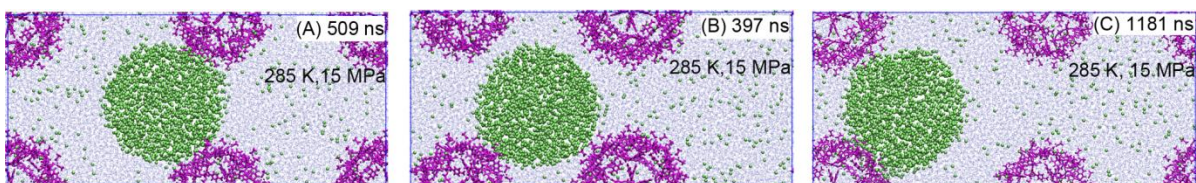
Fig. S7 Top views on the cylindrical CH_4 nanobubbles formed during Run1, Run2 and Run3 under 285 K and 15 MPa with subcooling of 7 K. MIL-101, CH_4 and water molecules are shown as magenta sticks, green balls and light blue lines, respectively.
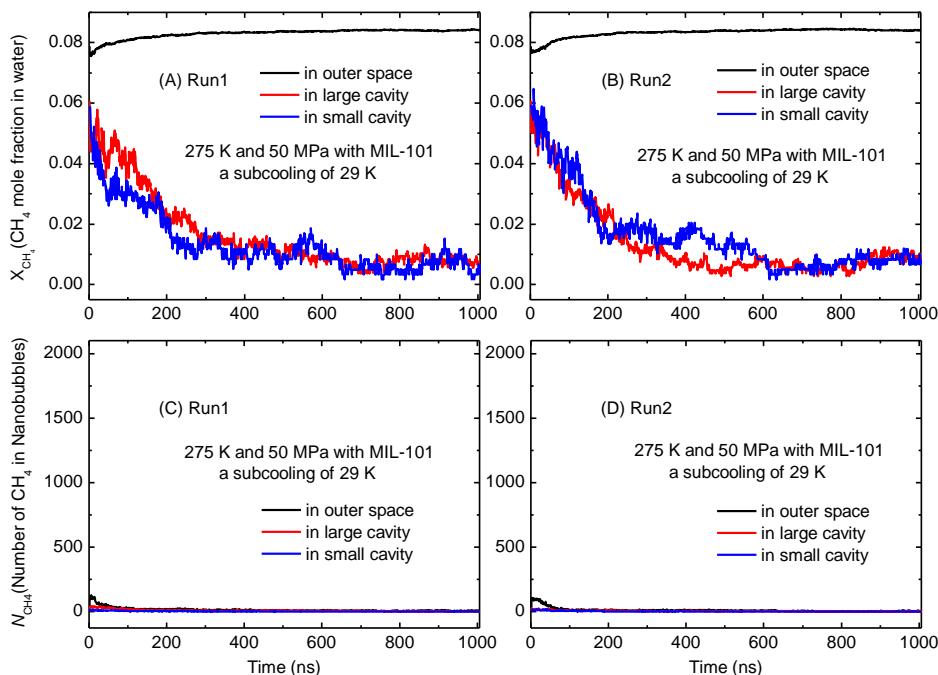

Fig. S8 Evolution of (A,B) CH_4 mole fraction in water (x_{CH4}) and (C,D) number of CH_4 molecules in nanobubbles (N_{CH4}) in the small and large cavities of MIL-101 and their outer space during two repeated runs in the presence of MIL-101 under 275 K and 50 MPa with subcooling of 29 K. The results were calculated using the simulation trajectories in our previous work: *Formation of CH_4 Hydrate in a Mesoporous Metal-Organic Framework MIL-101: Mechanistic Insights from Microsecond Molecular Dynamics Simulations, J. Phys. Chem. Lett. 10 (2019) 7002-7008,* where the simulation set-up and other parameters were the same as in the present study except for different temperature and pressure.

Videos S1, S2 and S3: hydrate formation and phase separation of CH_4 in a homogeneous CH_4 solution with initial x_{CH4} = 0.08 in the presence of MIL-101 at 285 K and 50 MPa with moderate subcooling of 19 K during Run1, Run2 and Run3, respectively.

Videos S4 and S5: the formation process of large ordered hydrate at 285 K and 50 MPa with moderate subcooling of 19 K during Run1 and Run2, respectively.

Videos S6, S7 and S8: the phase separation of CH_4 in a homogeneous CH_4 solution with initial x_{CH4} = 0.08 in the presence of MIL-101 at 285 K and 15 MPa with subcooling of 7 K during Run1, Run2 and Run3, respectively.

Videos S9, S10 and S11: the phase separation of CH_4 in a homogeneous CH_4 solution with initial x_{CH4} = 0.08 in the absence of MIL-101 at 285 K and 50 MPa with subcooling of 19 K during Run1, Run2 and Run3, respectively.