

The Effects of Ice on Methane Hydrate Nucleation: A Microcanonical Molecular Dynamics Study

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Fig. S1-S2 and S4-S5 show that methane hydrate nucleates on the ice surface.

Fig. S3 and S6 show that methane hydrate nucleates in the bulk solution phase.

Fig. S7-S8 show the methane bubbles in the simulation system.

Fig. S9-S10 are similar to Fig. 8.

Fig. S11-S12 are similar to Fig. 9.

Fig. S13-S14 are similar to Fig. 10.

Fig. S15-S16 are similar to Fig. 11.

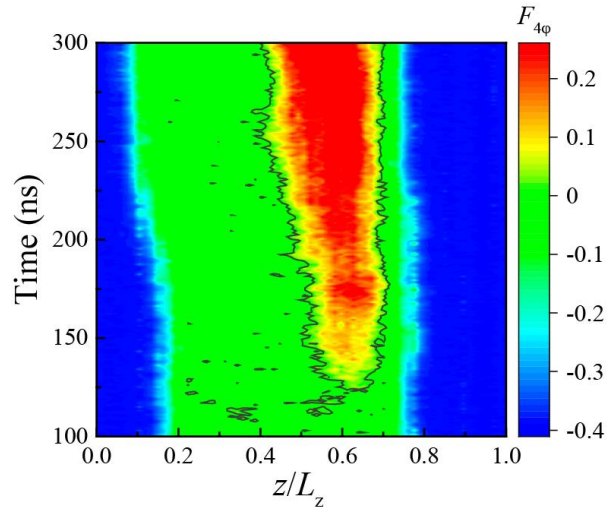


Fig. S1 Temporal and spatial evolution of $F_{4\phi}$ order parameter for the trajectory PP-1 from 100 ns to 300 ns. The horizontal and vertical axes are the time and the position, z/L_z , in the simulation box, respectively. The black contour lines of $F_{4\phi}=0.0$ are shown to aid eyes. The average values of $F_{4\phi}$ for cubic ice, hexagonal ice, liquid water, and hydrate are -0.8, -0.4, -0.04, and 0.7, respectively.

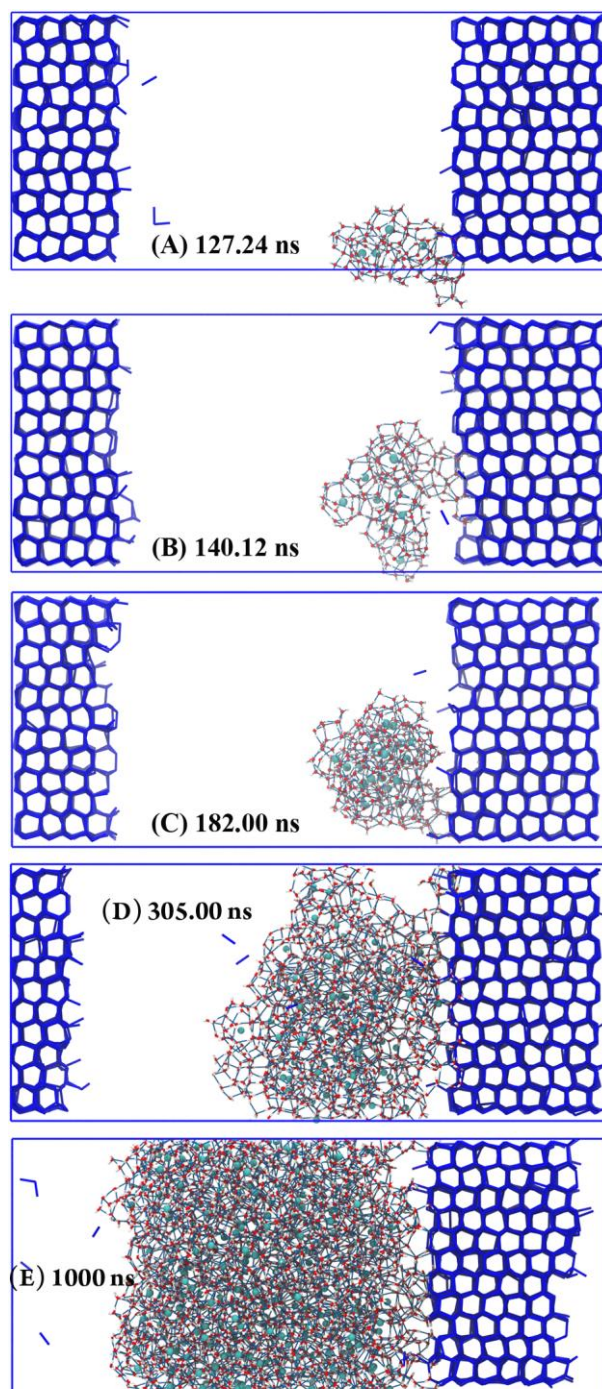


Fig. S2 Snapshots during methane hydrate nucleation for the trajectory PP-1. Only ice water and cage cluster are shown. Water molecules in ice are represented by blue tubes. Oxygen and hydrogen atoms in cage cluster are in red and white, respectively. Hydrogen bonds are in light blue. Methane molecules are shown as the cyan spheres.

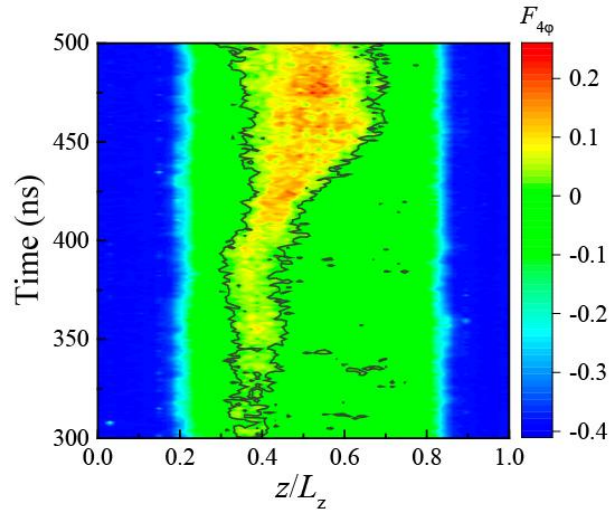


Fig. S3 The same as Fig. S1 but for the trajectory PP-2.

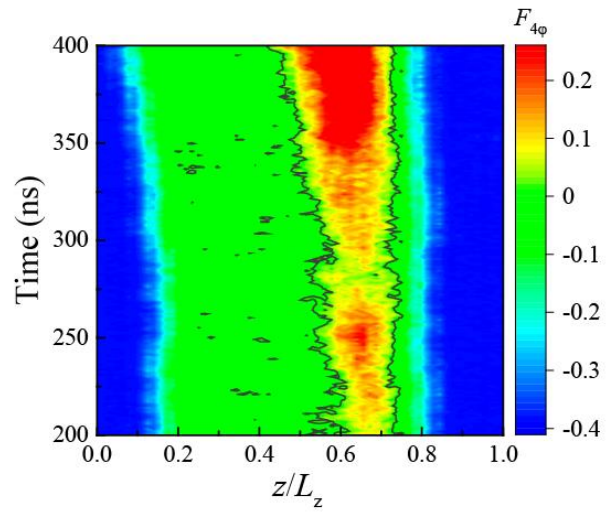


Fig. S4 The same as Fig. S1 but for the trajectory SPP-1.

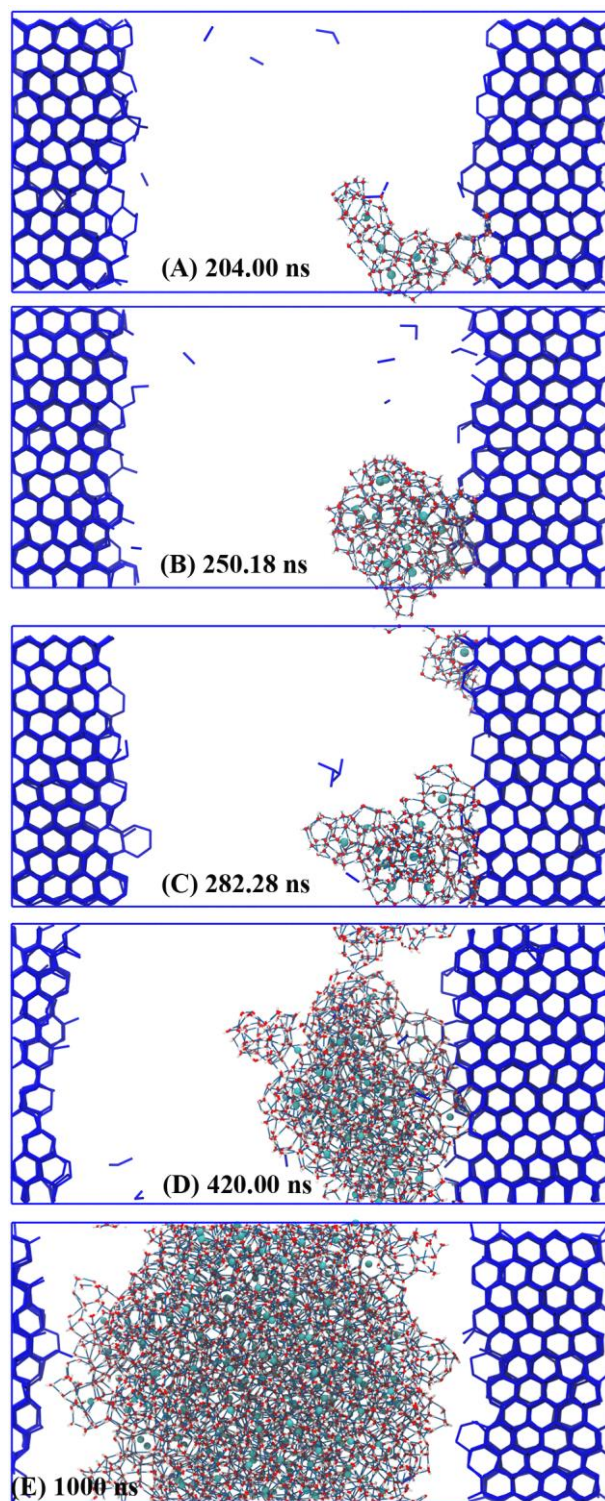


Fig. S5 The same as Fig. S2 but for the trajectory SPP-1.

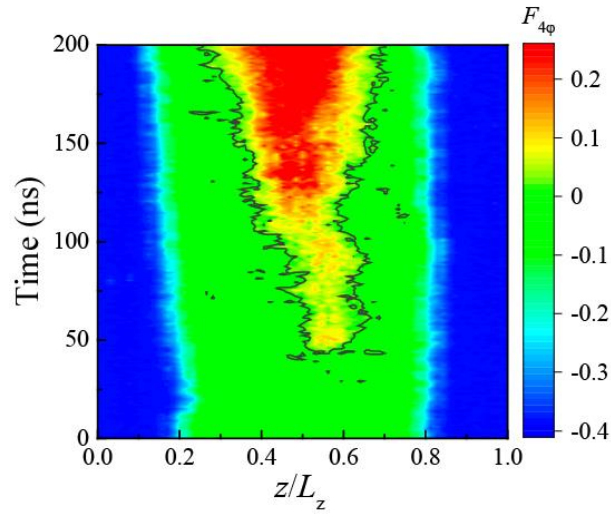


Fig. S6 The same as Fig. S1 but for the trajectory SPP-3.

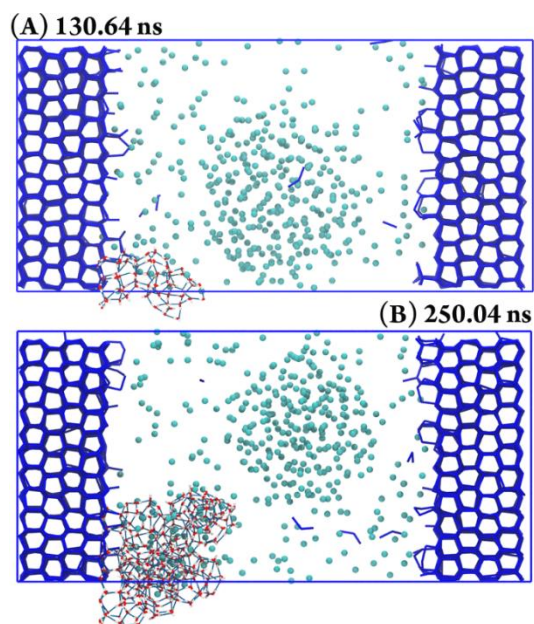


Fig. S7 The same as Fig. 5 but only for 130.64 ns and 250.04 ns. Methane molecules are shown in cyan.

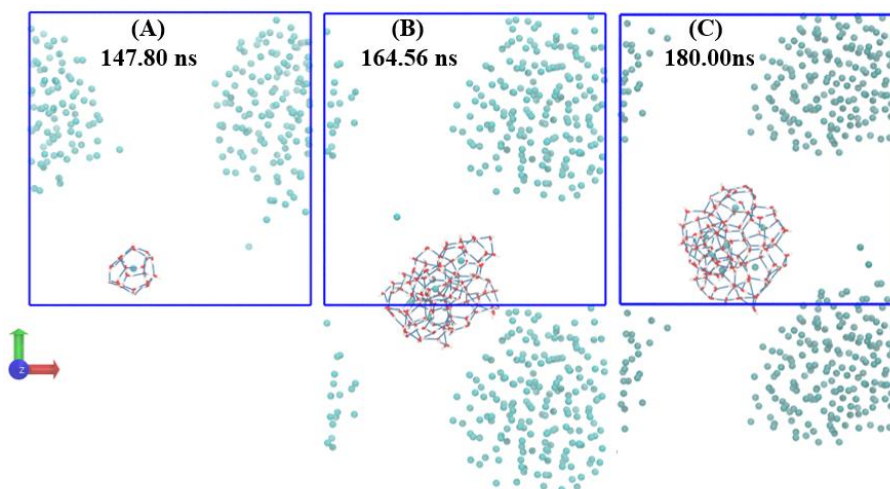


Fig. S8 Snapshots for the trajectory BP-2 to show the spatial relationship between methane nano-bubble and cage cluster. Only methane molecules in gas phase and hydrate phase are shown (in cyan). Those methane molecules outside the box consist the nano-bubble's periodic image.

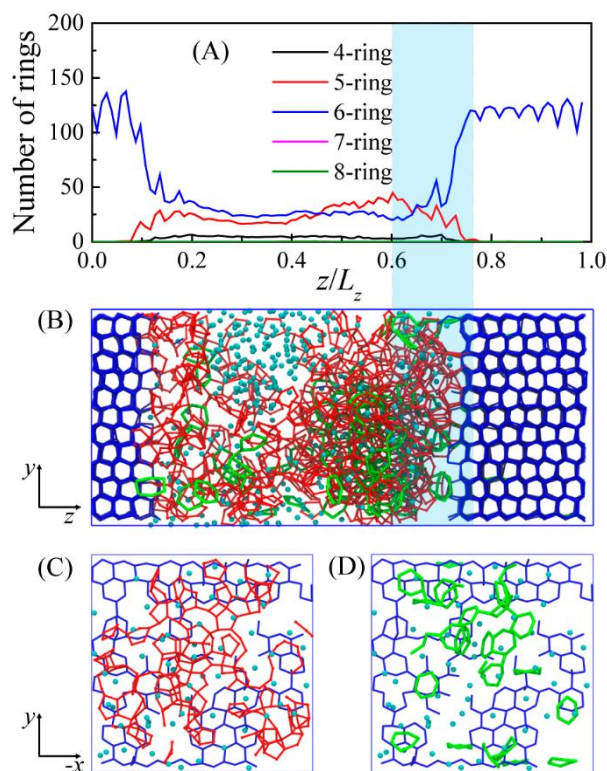


Fig. S9 Water ring profiles along the z direction at 250 ns for the trajectory PP-1. (A) Distribution of 4-8 membered primitive water rings along the z direction. (B) The system configuration with only ice and the planar primitive 5- and 6-membered water rings shown. Water molecules in ice are represented by blue tubes. Methane molecules are shown in cyan. To clearly show the system structure, only planar 5- and 6-membered rings are shown with the red and green tubes, respectively (we define a ring as a planar primitive ring if the minimum dihedral angle of the ring is larger than 135°). (C) and (D) are the cross section of the light blue shadow area of (B). Only 5- or 6-membered rings are shown in (C) and (D) for clarity, respectively.

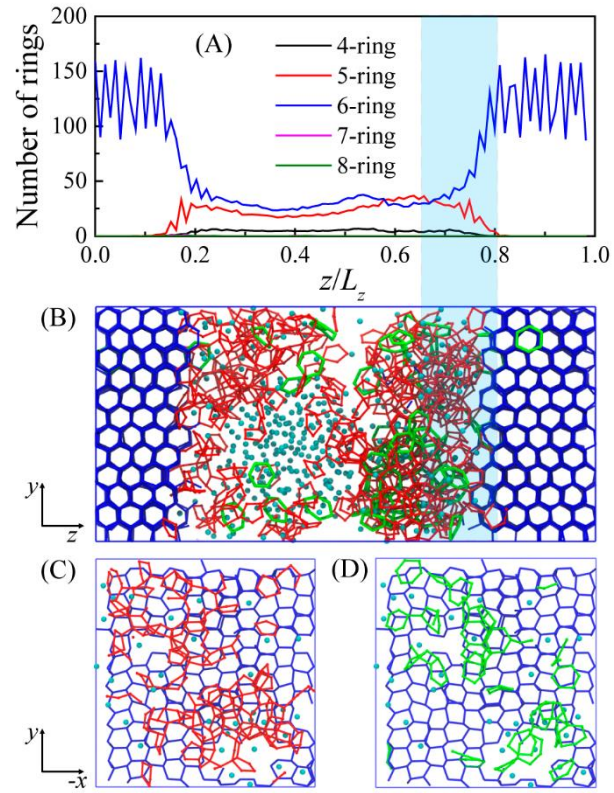


Fig. S10 The same as Fig. S9 but for the trajectory SPP-1

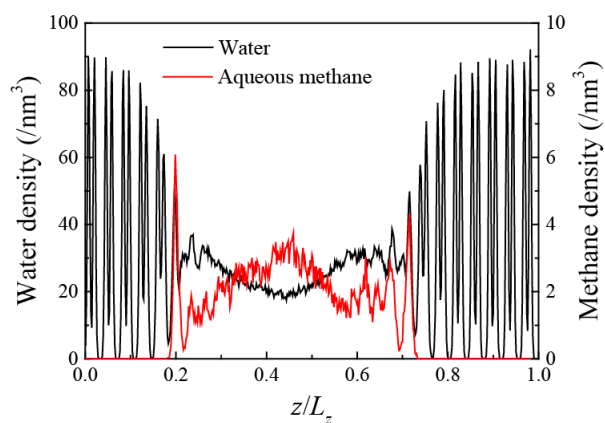


Fig. S11 The density profiles for water and methane in solution along the z direction at 100ns for the trajectory PP-1. The methane peaks lying in the middle are due to the adsorption between gas and solution. A methane molecule is classified as aqueous methane if the number of hydration water within 5.4 \AA of this methane is larger than 15.

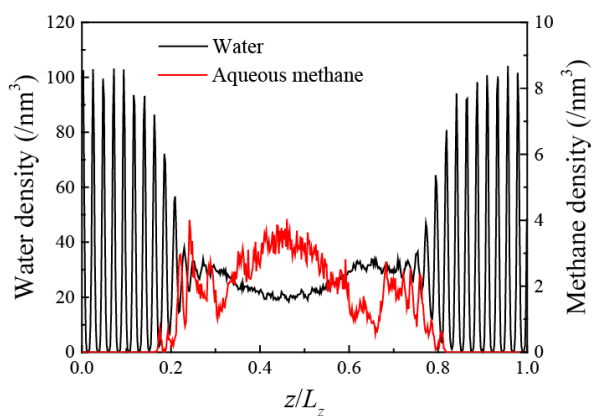


Fig. S12 The same as Fig. S11 but for the trajectory SPP-1.

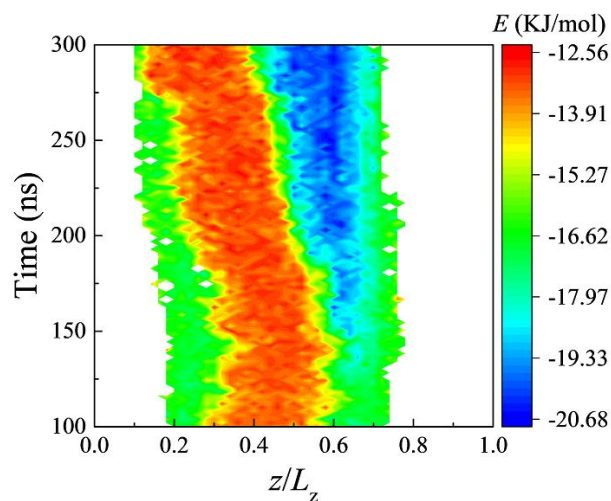


Fig. S13 Temporal and spatial evolution of average potential energy of methane molecules for the trajectory PP-1 from 100 ns to 300 ns. The horizontal and vertical axes are the time and the position, z/L_z , in the simulation box, respectively.

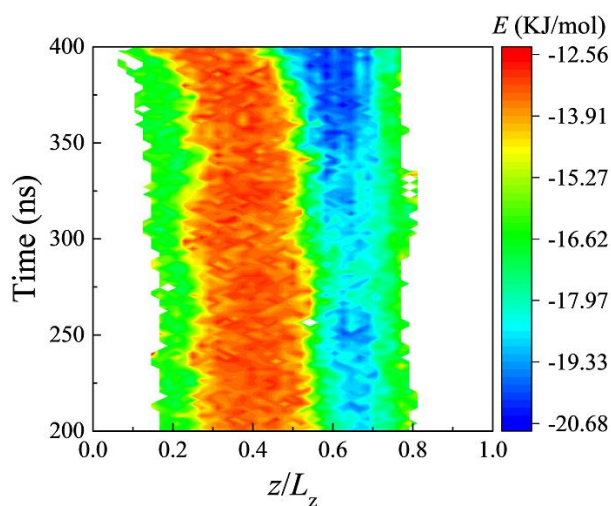


Fig. S14 The same as Fig. S13 but for the trajectory SPP-1 from 200 ns to 400 ns.

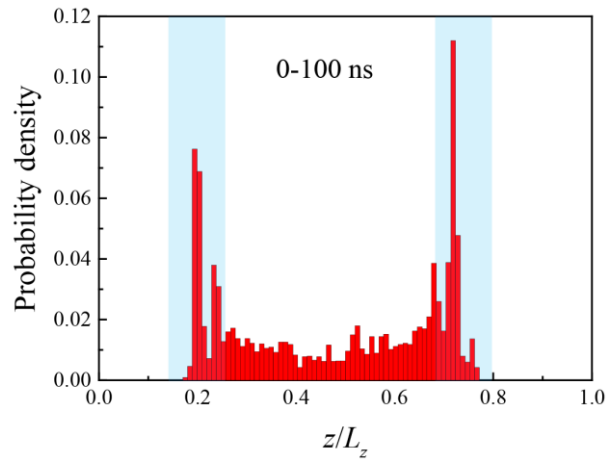


Fig. S15 The probability density of filled face-saturated cages along the z direction during the induction time of the trajectory PP-1. The light blue area is the ice-solution interface.

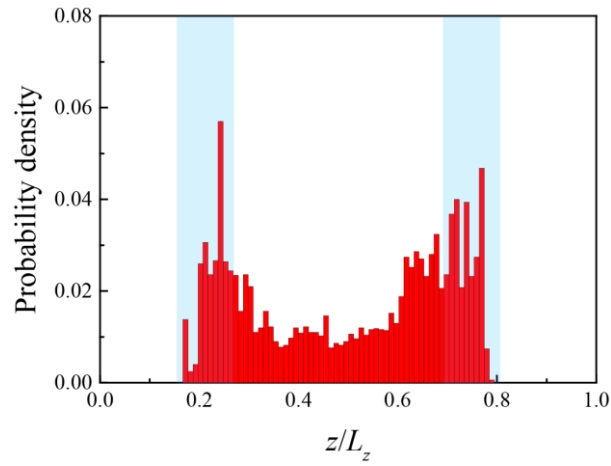


Fig. S16 The same as Fig. S15 but for the trajectory SPP-1 from 0 to 100 ns.