Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information for

The cages, dynamics, and structuring of incipient methane clathrate hydrates

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Figures S1-S4

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Description of Movies S1, S2, and S3

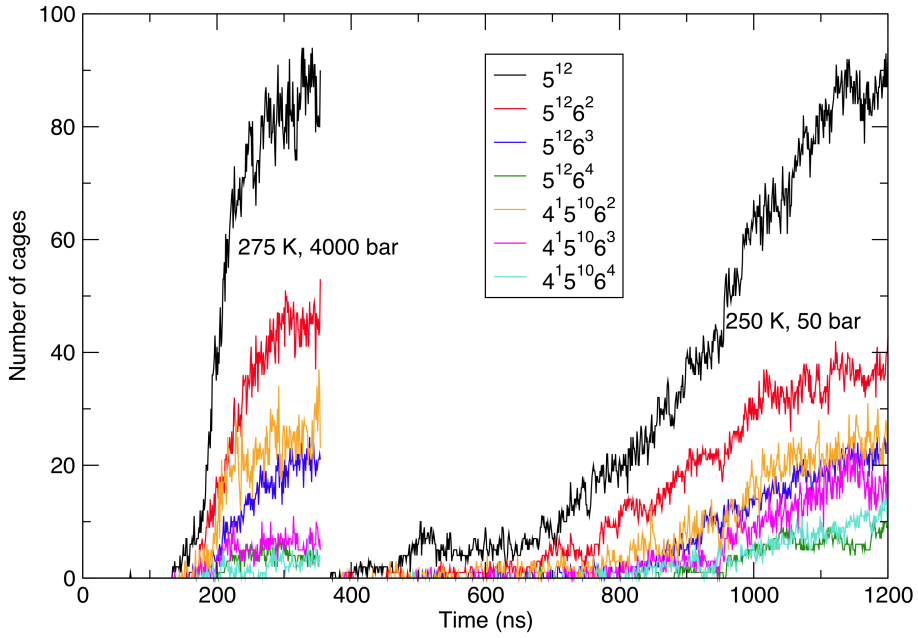

Figure S1: Evolutions in the number of cages for two trajectories at vastly different P/T conditions (275 K, 4000 bar and 250 K, 50 bar, both with spherical methane-water interfacial geometry) performed in the smaller simulation systems; the edges of the cubic simulation systems were ~ 5 nm in both cases. While the rate of growth is higher at the higher temperature (and higher concentration, due to the extreme pressure), the same trends in relative cage abundance are observed in both trajectories. As highlighted in the main text, there is some stochasticity in the growth of the nucleated hydrates, but the general trends shown in Figure 4 and in the above figure are consistent throughout all simulations (5^{12} cages are important in all simulations and $5^{12}6^n$ cages are more abundant than their $4^15^{10}6^n$ counterparts with the same coordination numbers).

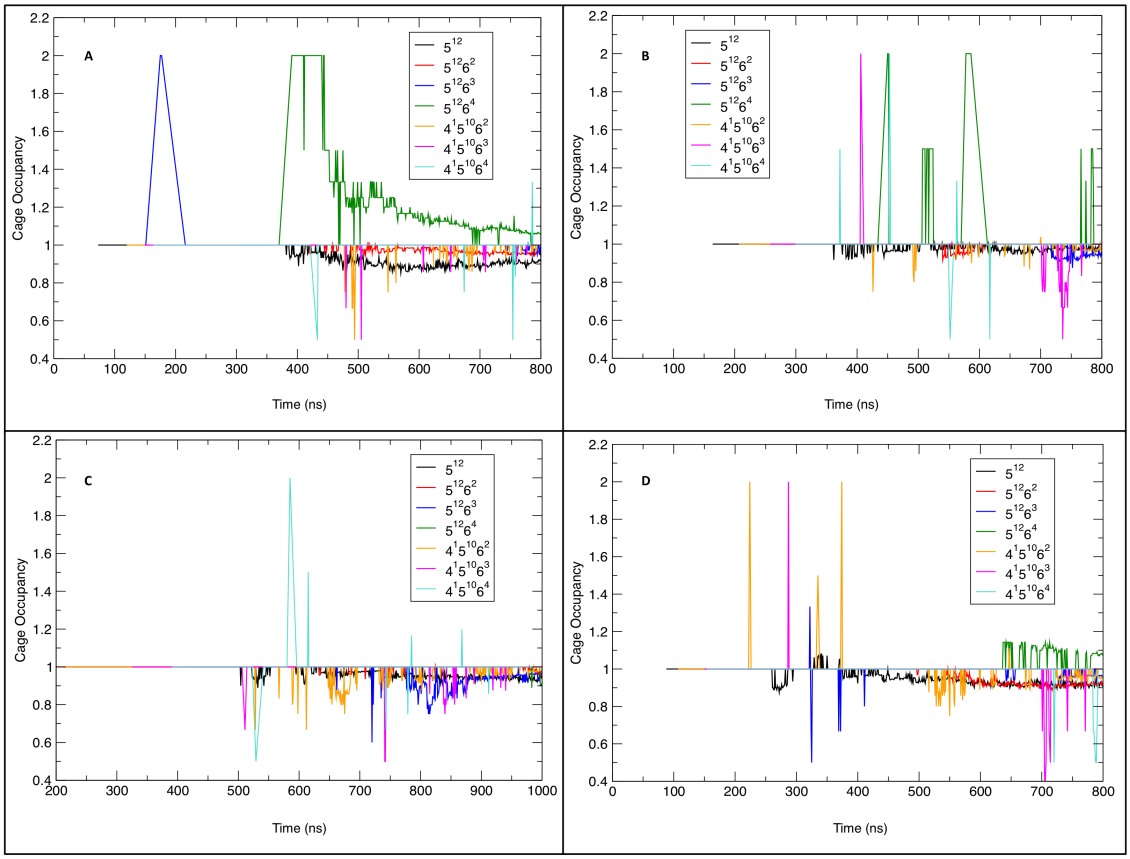

Figure S2: Average occupancies of the dominant seven cages for simulations *A*, *B*, *C*, and *D* from Figure 4 from the main text. The colouring scheme for cage occupancies used is the same as for the cages in Figure 4. Most cages are singly occupied by methane guests, though the average occupancy of the cages falls to ~ 90-95 % towards the end of the simulations. One example of sustained double occupancy is seen in the $5^{12}6^4$ cages in Part A.

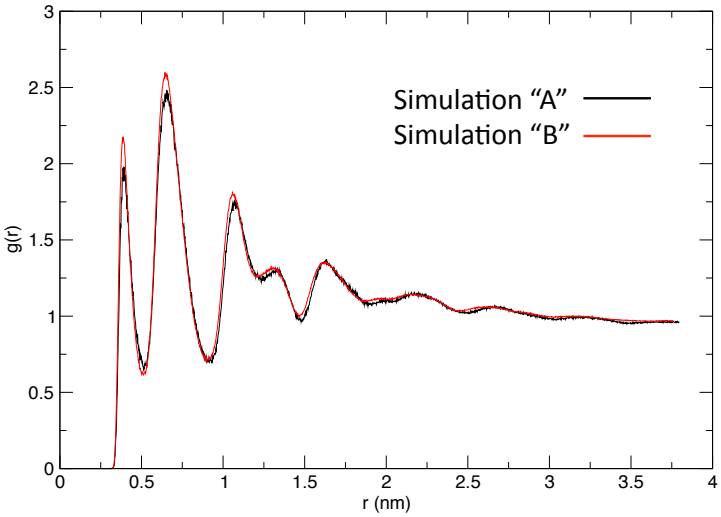

Figure S3: Methane-methane RDF’s calculated from the configurations used to generate the histograms shown in Figures 7b-7e; the peak at < 0.5 nm is from residual unenclathrated methane after nucleation and growth.

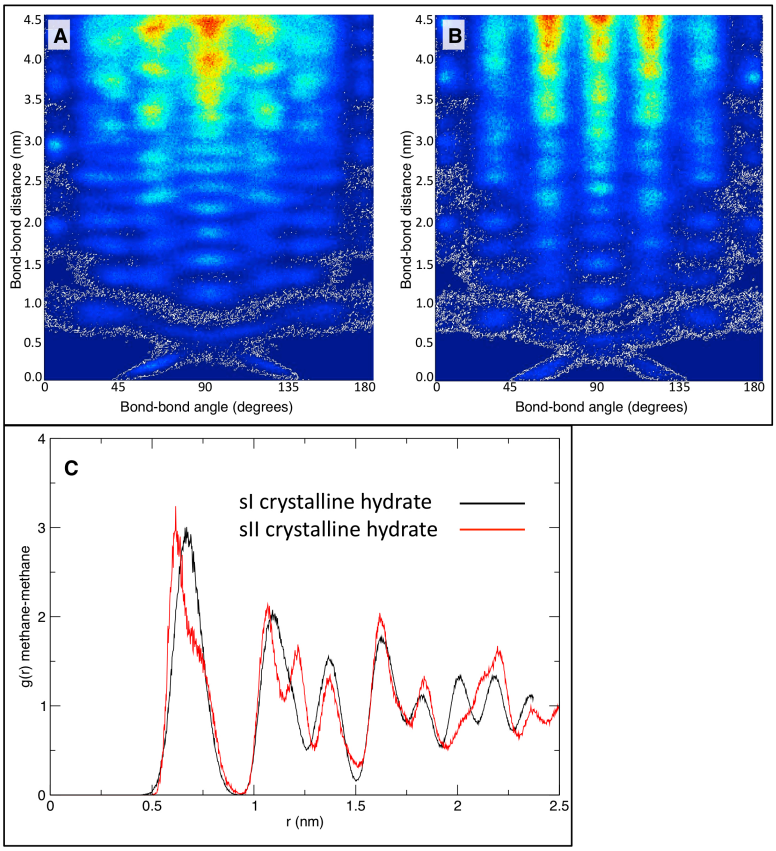

Figure S4: BBDBBA histograms and RDF's calculated from reference crystals: **A)** and **B)** BBDBBA histograms calculated on reference sI and sII hydrate, respectively. **C)** Methane-methane RDF's for sI and sII hydrate (sI methane-methane RDF in black, sII methane-methane RDF in red).

Table S1: Thermodynamic conditions for the nucleation trajectories analyzed in this study. Multiple simulations were performed at conditions of lower concentration without observing nucleation on the time and volume scales used.

Temperature (K)	Interfacial Geometry	Barostat Pressure (bar)	Concentration Range (methane mole frac.)	Nucleation events analyzed
275	Sphere	3,000-4,000	0.034-0.039	2
250	Cylinder and Sphere	50-300	0.025-0.035	19
250	Flat	NVT equilibrated at 2,000 bar	0.022	1
245	Flat	2,000	0.02-0.024	3

Table S2: Cage diameters of the dominant seven cages, calculated from simulation data. The entries in the middle column (*Max Internal Diameter*) correspond to the smallest sphere that would fully encompass each cage, while the entries in the right-hand column (*Cavity Diameter*) correspond to the max internal diameter value minus the approximate diameter of water (0.28 nm).

Cage Type	Max Internal Diameter (nm)	Cavity Diameter (nm)
5^{12}	0.85	0.57
$4^1 5^{10} 6^2$	0.90	0.62
$5^{12} 6^2$	0.95	0.67
$5^{12} 6^3$	0.98	0.70
$5^{12} 6^4$	1.00	0.72
$4^1 5^{10} 6^3$	0.98	0.70
$4^1 5^{10} 6^4$	0.99	0.71

Movie S1: Visualization of the formation of a $4^1 5^{10} 6^2$ cage from a 5^{12} cage via a water-pair insertion. The guest is CH_4 and is indicated by the green sphere. The hydrogen bonds are shown as grey lines between water oxygen atoms, also shown in grey. The two inserting waters are shown in red (oxygen) and white (hydrogen). The positions of the molecules are smoothed with a running average of 2 ns. The transformation requires approximately 9 ns to complete.

Movie S2: Visualization of the formation of a $5^{12} 6^2$ cage from a $4^1 5^{10} 6^3$ cage via a hydrogen-bond rotation. The guest is CH_4 and is indicated by the green sphere. The hydrogen bonds are shown as grey lines between water oxygen atoms, also shown in grey. The two active (rotating) water molecules are shown in red (oxygen) and white (hydrogen). The positions of the molecules are smoothed with a running average of 2 ns. The transition requires approximately 5 ns to complete.

Movie S3: Visualization of coupling of transitions between neighboring cages, involving both insertion/deletion and rotation transformations. Hydrogen bonds are shown as grey lines, methane molecules are shown as green spheres, and waters (except for the four highlighted waters) are shown in red (oxygen) and white (hydrogen). Multiple T1 transitions can be seen involving the four water molecules that are highlighted in blue. The positions of the molecules are smoothed with a running average of 2 ns, and ~1300 ns are shown in the movie.