Microcanonical molecular simulations of methane hydrate nucleation and growth: evidence that direct nucleation to sI hydrate is among the multiple nucleation pathways

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**Fig. S1**: The cage cluster size (for CCs and FSICs), the $F_{\text{ap}}$ order parameter, and the number of solid-like water molecules for runs C and E.

**Fig. S2**: Evolution of seven dominant cage types in the simulation system for (a) run C and (b) run E.
Fig. S3: Snapshots from run C at 900 ns showing rows of face-sharing $5^{12}$ (red) and $5^{12}6^2$ cages (blue), in which the shared faces on either side of any given cage in a row are parallel.

Fig. S4: Snapshots from run C at 900 ns. Hydrogen bonds and water molecules are shown in red. Methane molecules are represented by cyan spheres. The blue box represents the system box. The box is extended according to the periodic boundary conditions, and the dashed black lines connect the axes of face-sharing rows of cages to guide the eye. Some crystal defects are also shown, including two pieces of dislocation (the row of triangles) and one methane-water fluid inclusion (circle). The upper right panel shows the hydrogen-bonded network of perfect sI hydrate.
**Fig. S5:** Resulting solid structure after nucleation and growth for run A. Red is the small $5^{12}$, blue is $5^{12}6^2$, green is $5^{12}6^3$, and gray is $5^{12}6^4$. Methane molecules are shown with cyan spheres. Hydrogen bonds are shown with black dashed lines.

**Fig. S6:** The $5^{12}6^2/5^{12}$ ratio for methane-filled cages in runs A-F. For showing the data at shorted times clearly, the ratio is not recorded until (a) the number of cages rises above 5; (b) the number of cages rises above 7.
**Fig. S7:** The local details of the resulting solid structure at 900 ns for run C in order to show the fluid inclusion (middle). $5^{12}6^n$ ($n=0, 2, 3$) cages are in blue, and other FSICs, *i.e.*, nonstandard hydrate cages, are in red. Methane molecules are shown with cyan spheres.

**Movie S1.** Visualization of the 1 μs hydrate nucleation and growth trajectory for run C. Hydrogen bonds and water molecules are shown in red and methane molecules are shown as green spheres. Molecules are trajectory-smoothed over 1 ns.

**Movie S2.** Visualization of the system in run C during the period from 590 to 700 ns. It is clear that some nonstandard hydrate cages melt first and then the sI structure grows. In addition, it is not readily seen that two $4^{15}5^{10}6^2$ cages at the upper right of the movie transform to $5^{12}6^2$ cages at 621 ns and 636 ns, respectively.