

Supplementary material for

Exploring nucleation of H₂S hydrates

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Method details

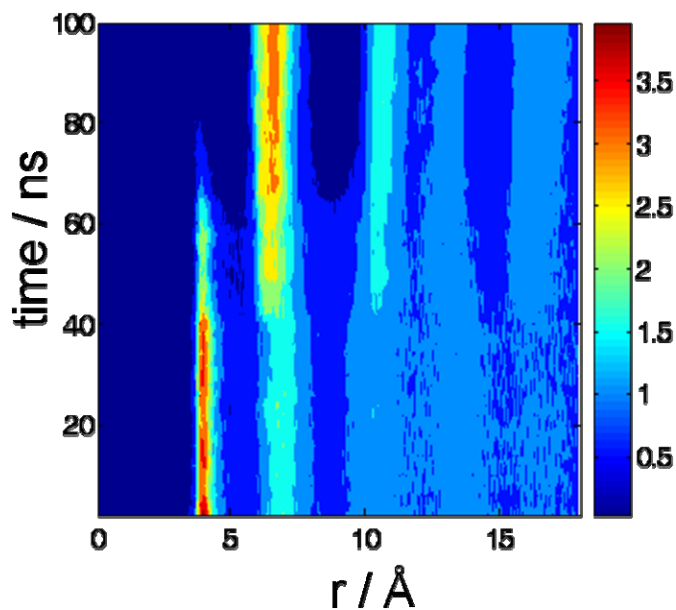
Throughout this work H₂O is represented by the TIP4P/2005 potential model^{S1}, which has been shown to reproduce a variety of thermodynamic properties of liquid and solid H₂O phases^{S1} and has recently been shown to reasonably describe density and structure of gas hydrates^{S2}. The H₂S molecules are modeled by a four-site potential model^{S3}. This model system has been successfully used in explorations of the crystal growth behavior of H₂S hydrates^{S4}.

The interactions between H₂O and H₂S molecules were calculated as the usual sums of Coulomb and Lennard-Jones potentials. The cross terms for the Lennard-Jones parameters were determined using Lorentz-Berthelot mixing rules^{S5}. The equations of motion were integrated using velocity Verlet algorithms for translations and rotations^{S6} and a time step of 2 fs was used here. A spherical cutoff of 11 Å was utilized for the short-ranged forces, while the electrostatic interactions were evaluated with the smooth particle mesh Ewald method^{S7}. The present MD methodology have been used extensively to study the crystal growth of gas hydrates and further details can be found elsewhere^{S4,8-10}.

In this work, the rate of nucleation, k , is defined by $k = \frac{n}{(Vt)}$, where n is the number of observed nucleation events, V is the volume of the simulation box, t is defined as the time needed for the F_4 order parameter of the system to reach 0.35 (i.e., about half of the system crystallized). The choice of this F_4 threshold, while somewhat arbitrary, has little effect on the calculated nucleation rate at relatively high temperatures where the transition from liquid- to solid-like behavior occurs relatively fast.

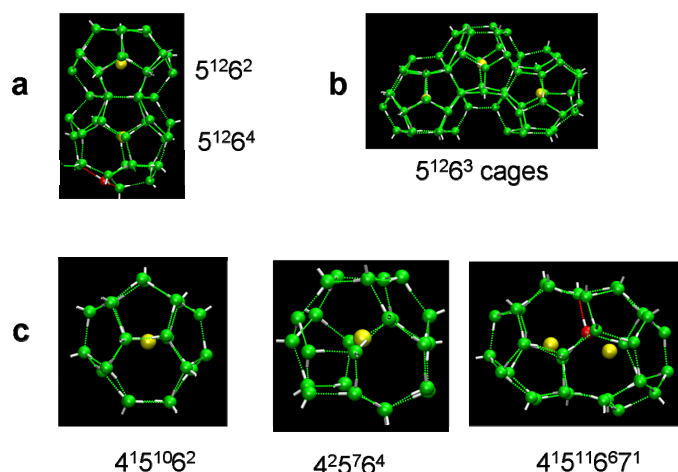
Supplementary Figure S1

Structuring of H₂S molecules in the aqueous solution. The evolution of the H₂S S-S radial distribution function, $g(r)$, is shown as a function of simulation time for the trajectory shown in Figure 1 in the main text. The colormap is provided on the right side of the figure. Initially, there is a strong peak in $g(r)$ at about 4 Å corresponds to close-contact H₂S molecules in the aqueous solution. This peak disappears as time progresses, while two relatively strong peaks appear at about 6.5 Å and 10.5 Å, indicating the ordering of the H₂S molecules consistent with hydrate cage formation.



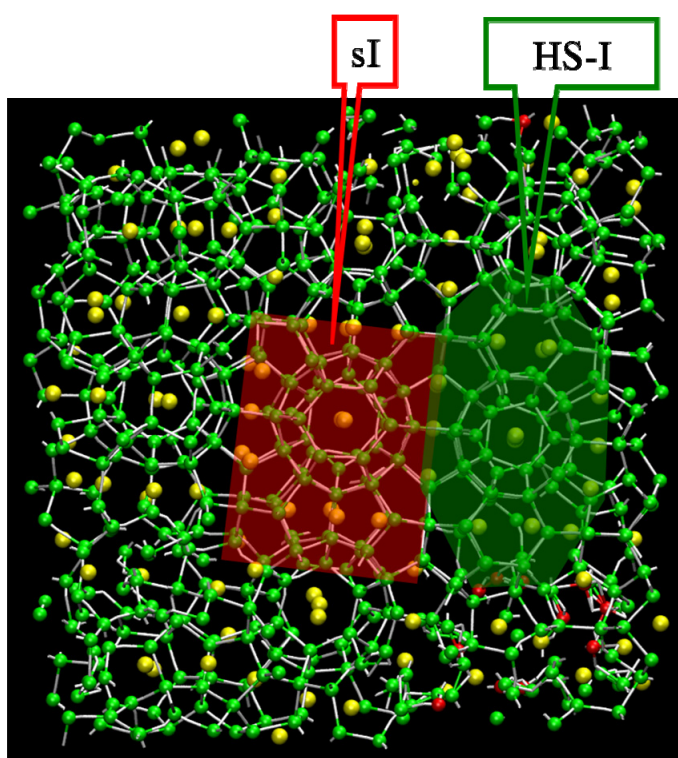
Supplementary Figure S2

Unusual arrangements of regular hydrate cages and other irregular cages in the amorphous solid. We have identified some unusual structures within the amorphous solid that initially forms. Shown are a few examples from the solid in Figure 1(IV) in the main text. (a) Direct connection of a sI $5^{12}6^2$ cage to a sII $5^{12}6^4$ cage by sharing a 6-membered ring. (b) Unusual arrangement of $5^{12}6^3$ cages, where the right cage is rotated 60° compared to the regular HS-I structure. (c) Some unusual cages, including a large cage with double guest occupancy observed in the amorphous solids. Note the $4^15^{10}6^2$ cage can potentially form as a link between sI and sH crystalline hydrates.



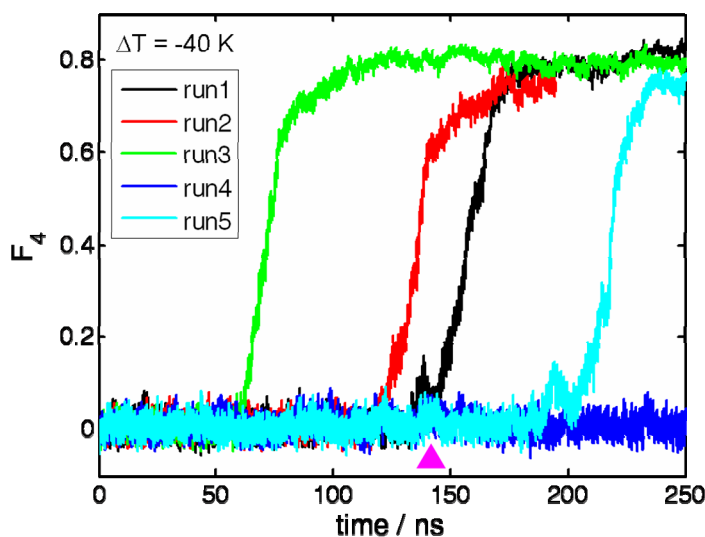
Supplementary Figure S3

Structures after annealing at an elevated temperature. Starting from the amorphous solid shown in Figure 1(IV), we performed a further 40 ns simulation at a high temperature of 265 K (25 K undercooling). The amorphous solid now shows increased crystalline order, with specific regions of sI and HS-I^{S11,12} structures can be clearly identified.



Supplementary Figure S4

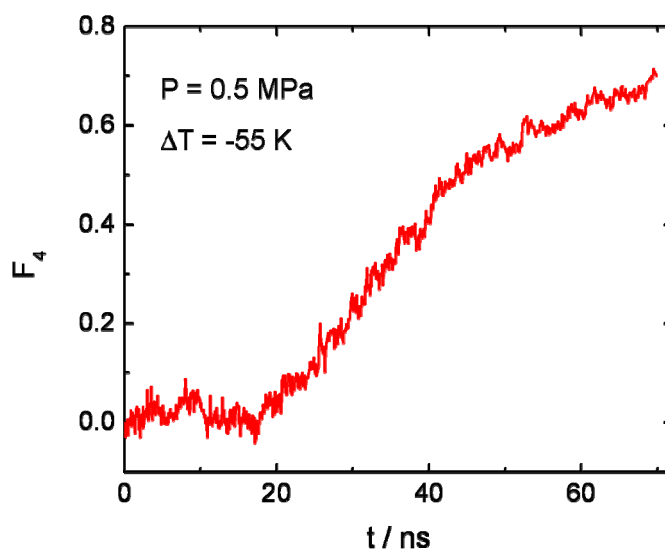
Extension of the simulations for sys-A at high temperatures. The five simulations for sys-A at $\Delta T = -40$ K and $\Delta T = -35$ K were extended to 250 ns. Three more trajectories at $\Delta T = -40$ K resulted in nucleation, as shown below. None of the five simulations at $\Delta T = -35$ K were observed to nucleate within 250 ns.



On several occasions during the induction period of simulations at 250 K ($\Delta T = -40$ K), we observe fluctuations involving larger clusters of solid-like H_2O molecules (e.g., the cluster formed around 140 ns in run5, as indicated by the pink triangle). No solid-like clusters that failed to nucleate have been observed with a size larger than 100 molecules, suggesting a critical nucleus size of about 100 molecules under the present simulation conditions and this size is comparable to the estimates by other groups^{S13-15}. A more precise determination of the critical size of the nucleus would require identification of the key order parameters for nucleation and perhaps the use of other techniques, e.g. path-sampling^{S16}, meta-dynamics^{S17}.

Supplementary Figure S5

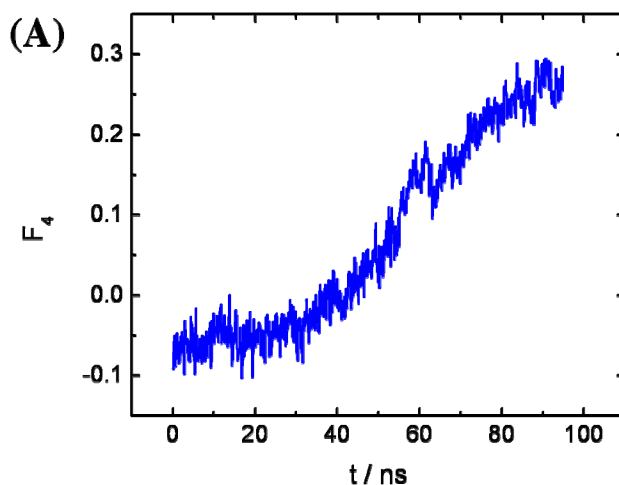
Simulation at low pressures. A simulation of sys-A at a pressure of 0.5 MPa and $\Delta T = -55$ K was performed. The F_4 structural order parameter as a function of the simulation time is shown. The system nucleates after 20 ns, suggesting that the applied pressure has little influence on the nucleation behavior.

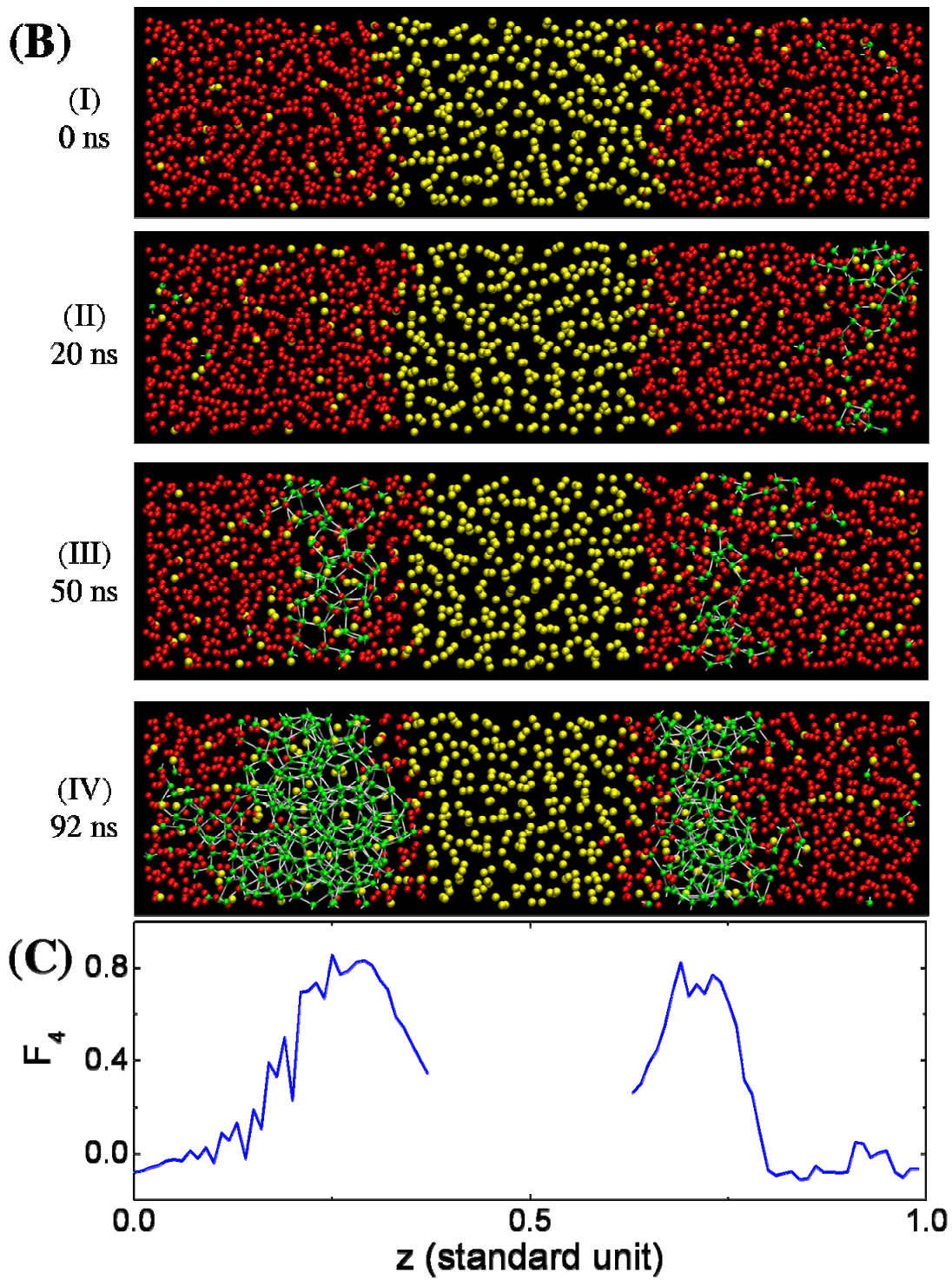


Supplementary Figure S6

Nucleation in a system with a liquid H₂S slab. A simulation of sys-C (with a liquid H₂S slab) at a pressure of 50 MPa and $\Delta T = -60$ K was performed. Below we show (A) the evolution of the F_4 order parameter of the system, (B) some representative configurations from the trajectory where the molecules are colored as in Figure 1 of the main text, and (C) the profile of F_4 order parameters along the z-coordination (the axis vertical to the H₂S/H₂O interfaces) as averaged over the last 2 ns (90–92 ns) of the simulation. The nucleation behavior is very similar to that seen for sys-A and sys-B (see main text), although with a lower H₂S concentration in the aqueous solution (see table 1 in the main text), sys-C tends to nucleate with a longer induction time.

We observe the formation of some solid-like clusters in the “bulk” solution (an example is shown in (B), 20ns), however these clusters do not survive. The successful nucleation events were observed to occur very close to both of the H₂S/H₂O interfaces (as shown in (B), 50 ns and 92 ns). The appearance of amorphous solids at both interfaces forms an effective barrier to mass transfer, hence further crystal growth is rather slow. The hydrate nucleation at both interfaces can also be seen clearly from the F_4 order parameter profile along the z-coordination, as shown in (C).





References

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