

Supplemental Information

For

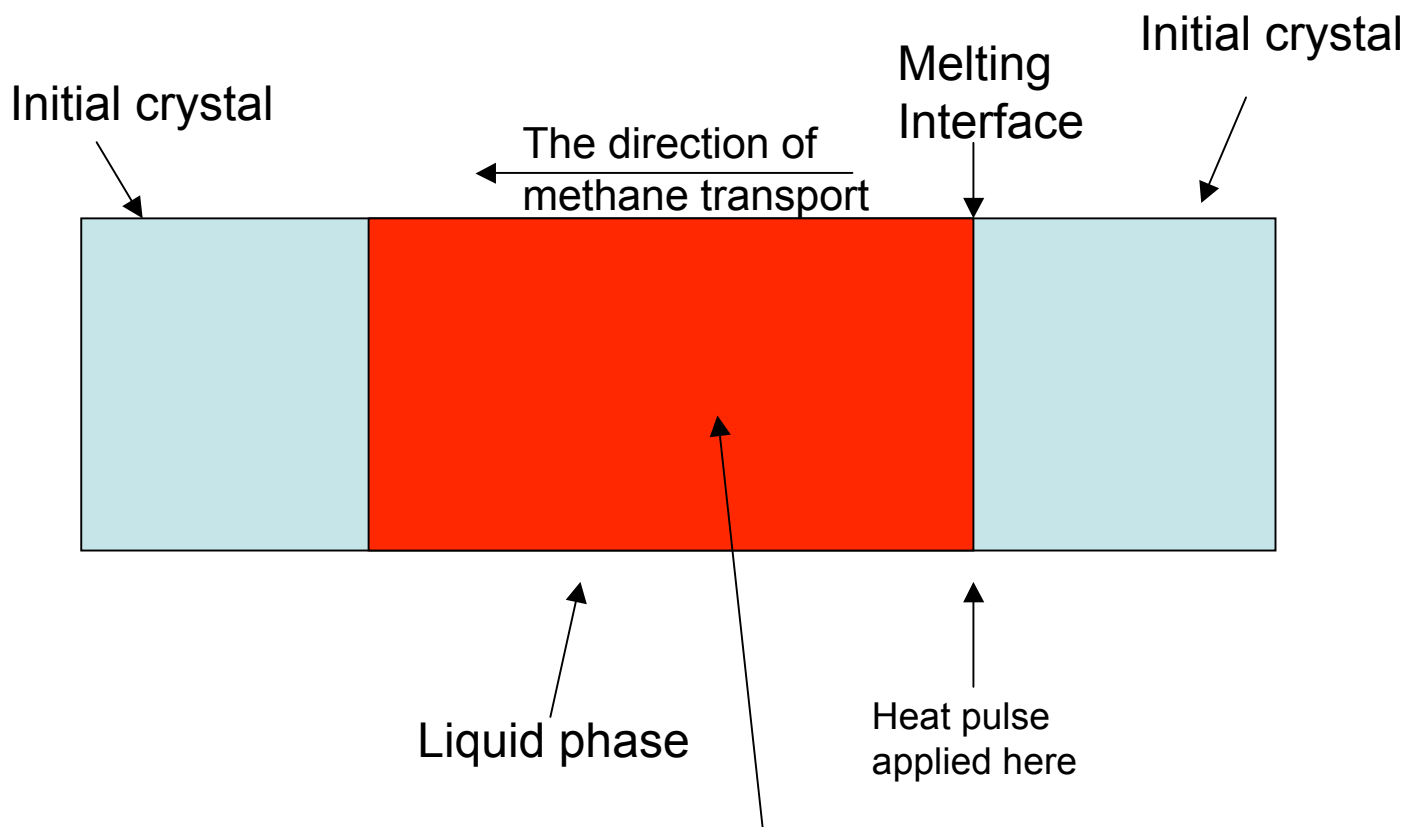
Observation of Two-Step Nucleation in Methane Hydrates

*Jenel Vatamanu and Peter G. Kusalik**

Supplemental Figure 1: The MD set-up.

Additional details regarding this MD set-up could be found in:
Vatamanu, J., Kusalik, P. G., *J. Chem. Phys.*, **2007**, *126*, 124703.

The crystal is melted at one interface, releasing methane. As the methane accumulates in solution homogeneous nucleation of a solid phase consisting of methane trapped in cages of water, is formed within 24 ns.

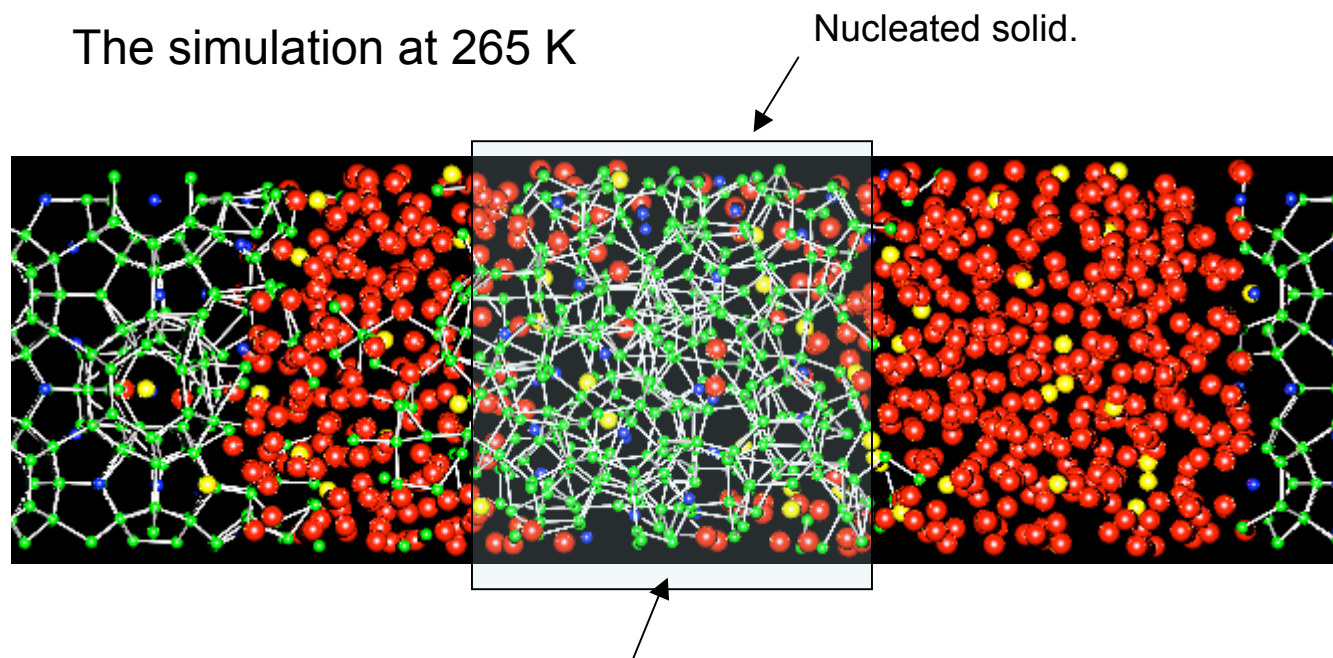


The homogeneous nucleation is initiated in the liquid phase, at a large relative distance to interfaces.

Supplemental Figure 2 (a).

Image snapshots of the nucleated solid. The green and red spheres represent the solid-like and liquid-like water molecules. The blue and yellow spheres represent the solid-like and liquid-like methane molecules, respectively.

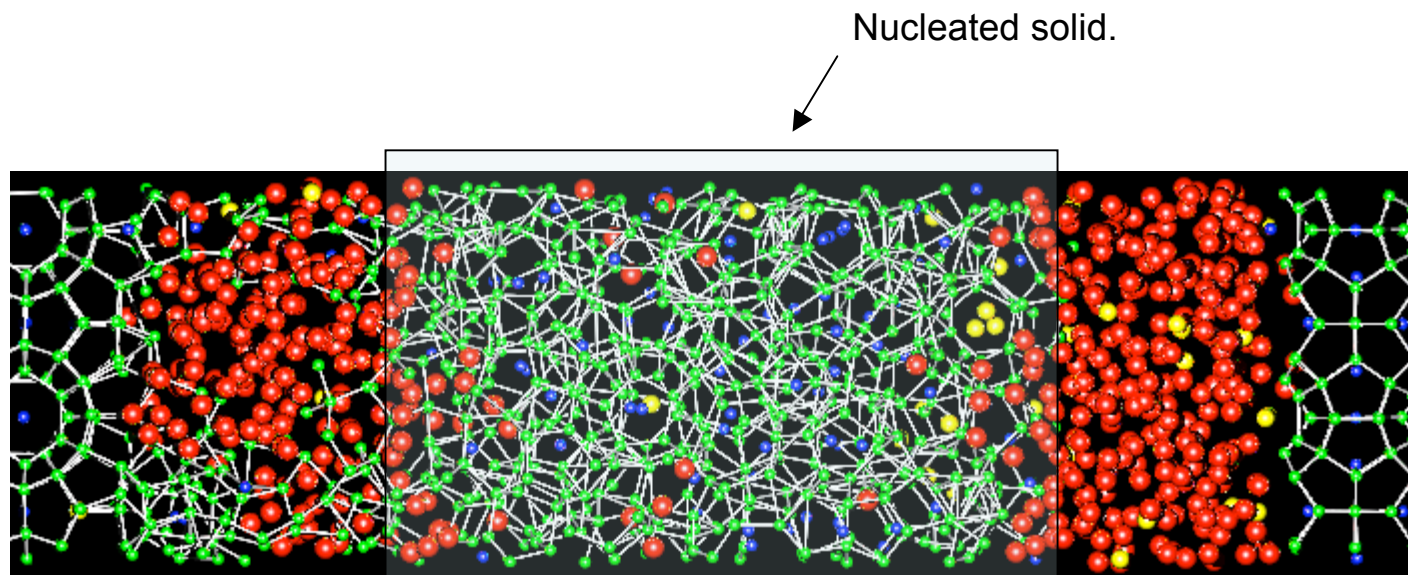
While water structuring around methane in solutions has been previously reported, (see: (a) Moon, C., Taylor, P. C., Rodger, P. M., *J. Am. Chem. Soc.* **2003**, *125*, 4706 and (b) Moon, C., Hawtin, R. W., Rodger, P. M., *Faraday Discussions*, **2007**, *136*, 367) the nucleation of a solid-phase methane hydrate from bulk aqueous phase was, prior to this work, unreported.



A solid-like area, which resembles the structure of hydrate cages, is nucleated. Both methane and water were identified to have very little translational motion, hence they were identified as solid-like.

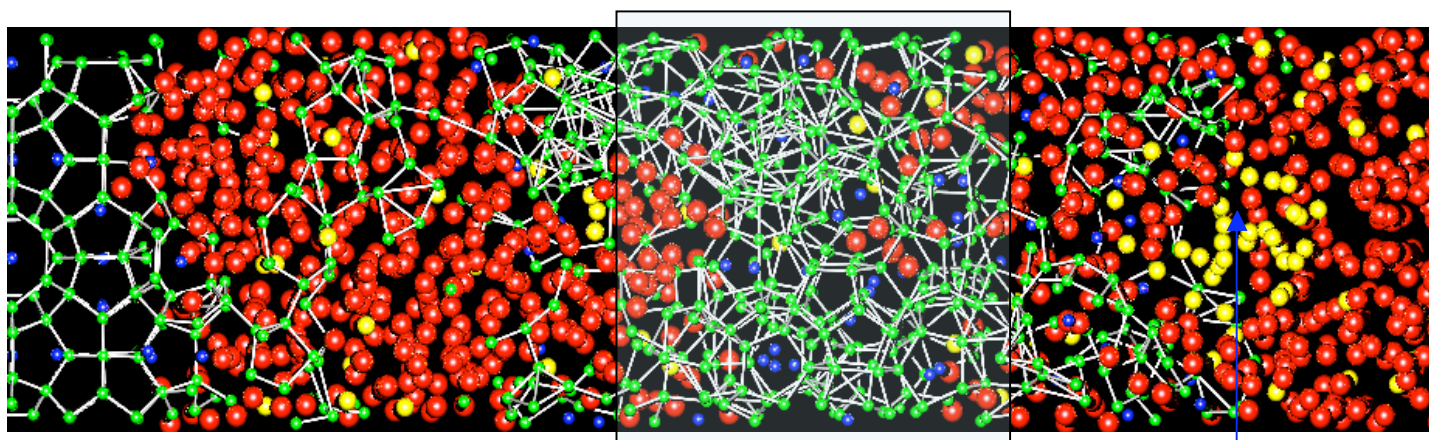
Supplemental Figure 2 (b).

Image snapshots of the nucleated solid at 255 K.



Supplemental Figure 2 (c).

Image snapshots of the nucleated solid at 270K.



The yellow spheres are liquid-like methane which are close to phase separation (demixing).

Supplemental Figure 3 (a).

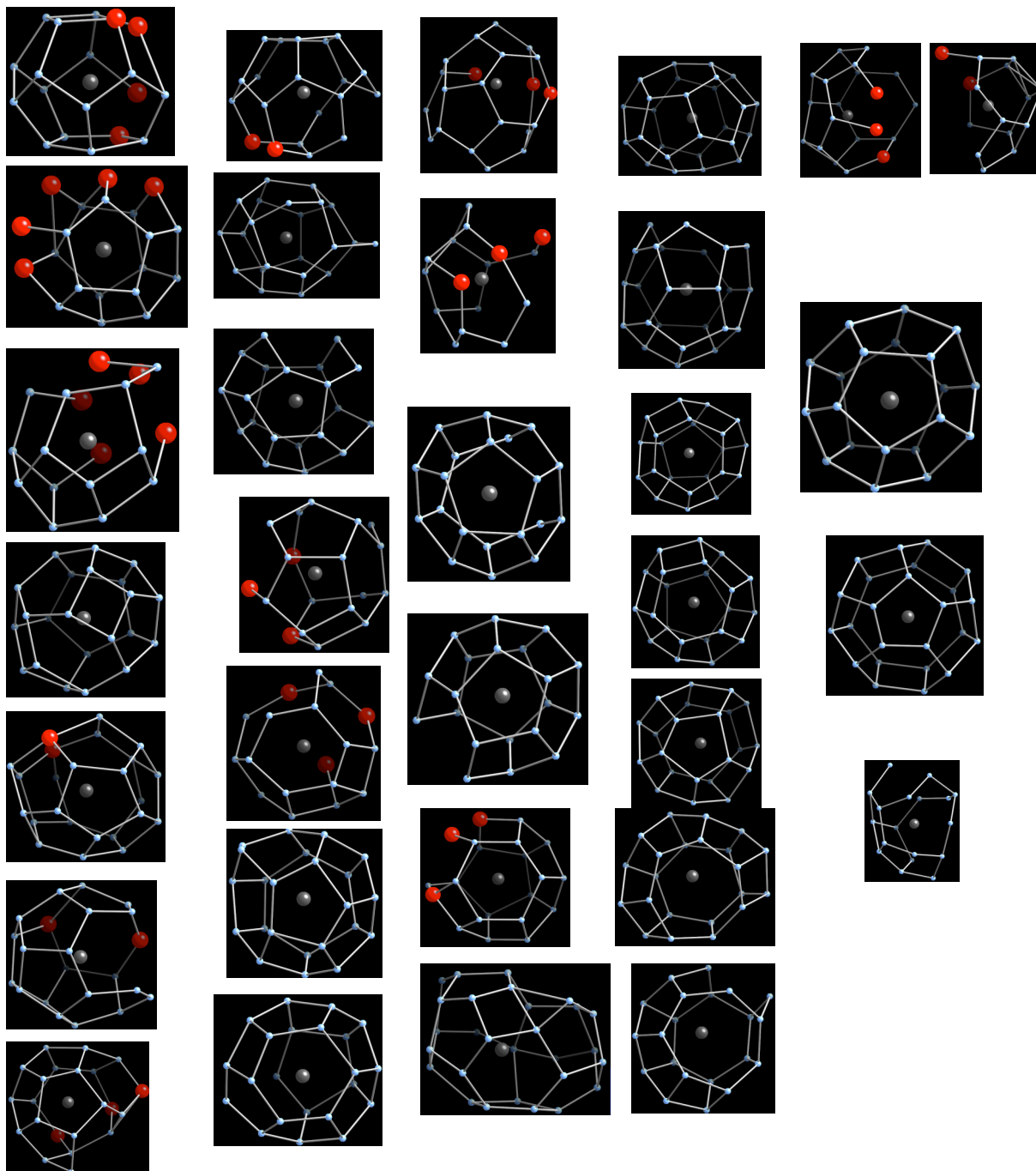
Cage structures found in the nucleated solid at 270K.

Legend:

Red spheres: liquid-like water

Green/blue spheres: solid-like water

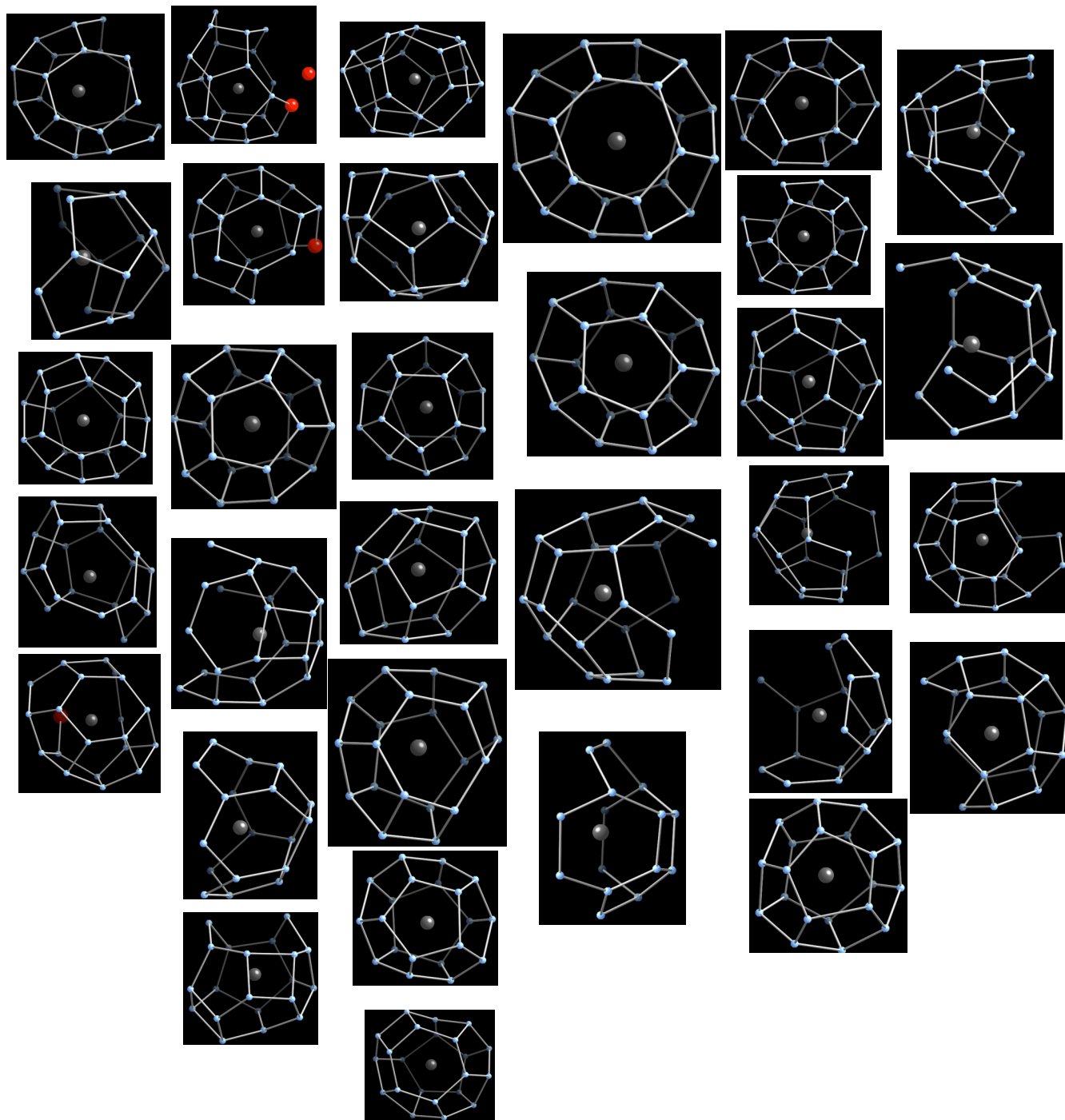
Grey spheres: methane molecule



Supplemental Figure 3 (b).

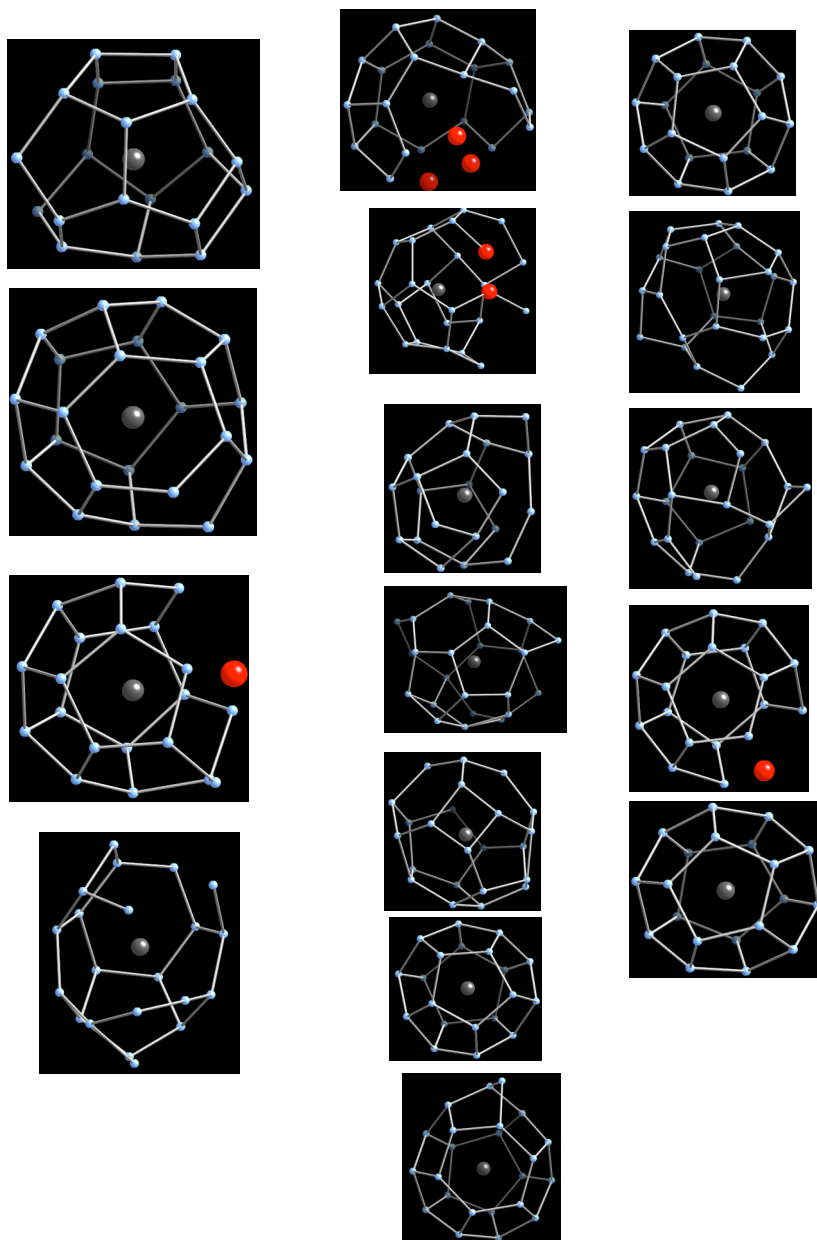
Cage structures found in the nucleated solid at 270K.

The nucleated solid was an inclusion compound where methane was hosted in various kinds of cages. Regular cages of gas hydrate structures can be identified.



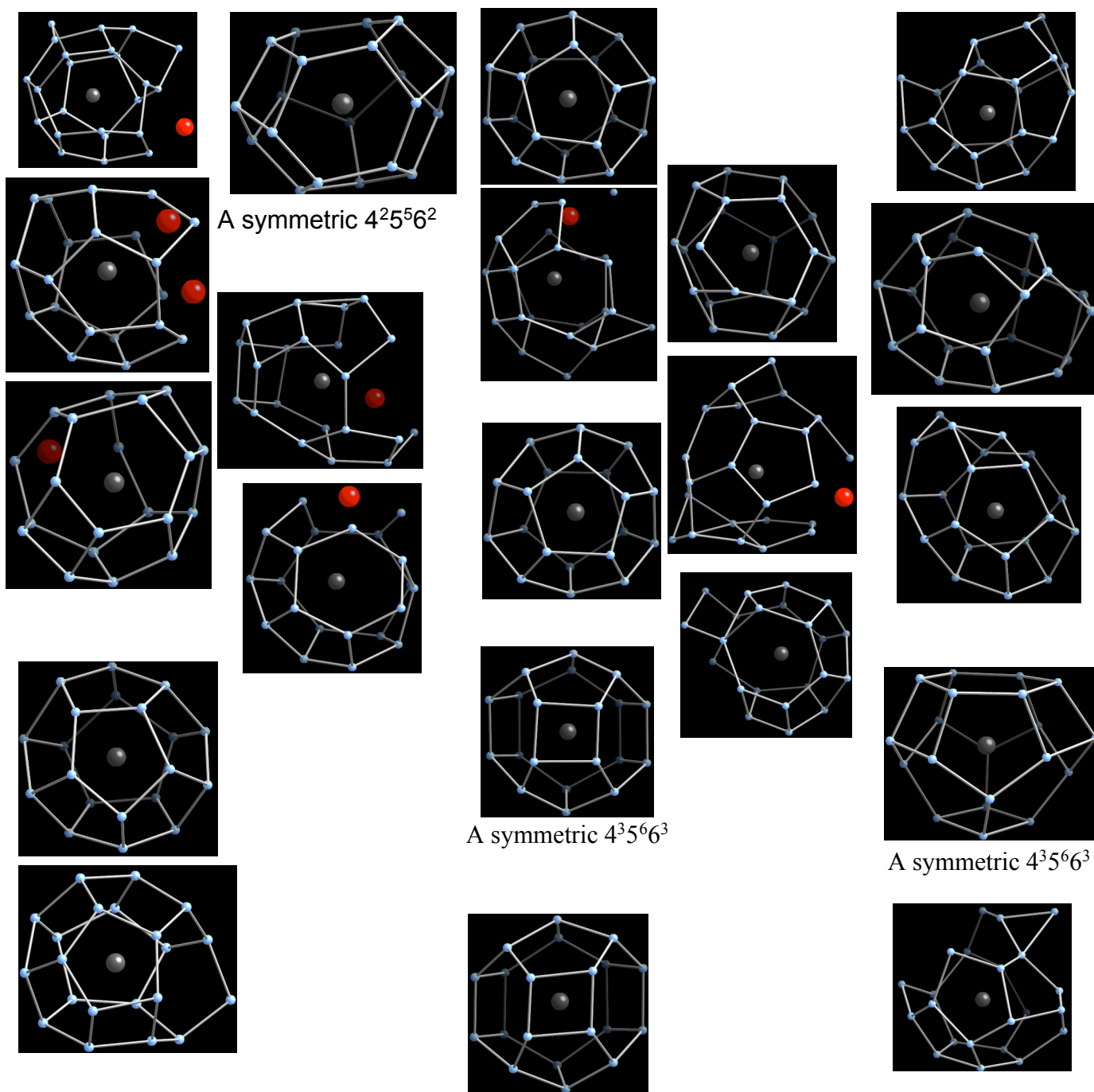
Supplemental Figure 4.

Cages found in the nucleated solid at 265K.



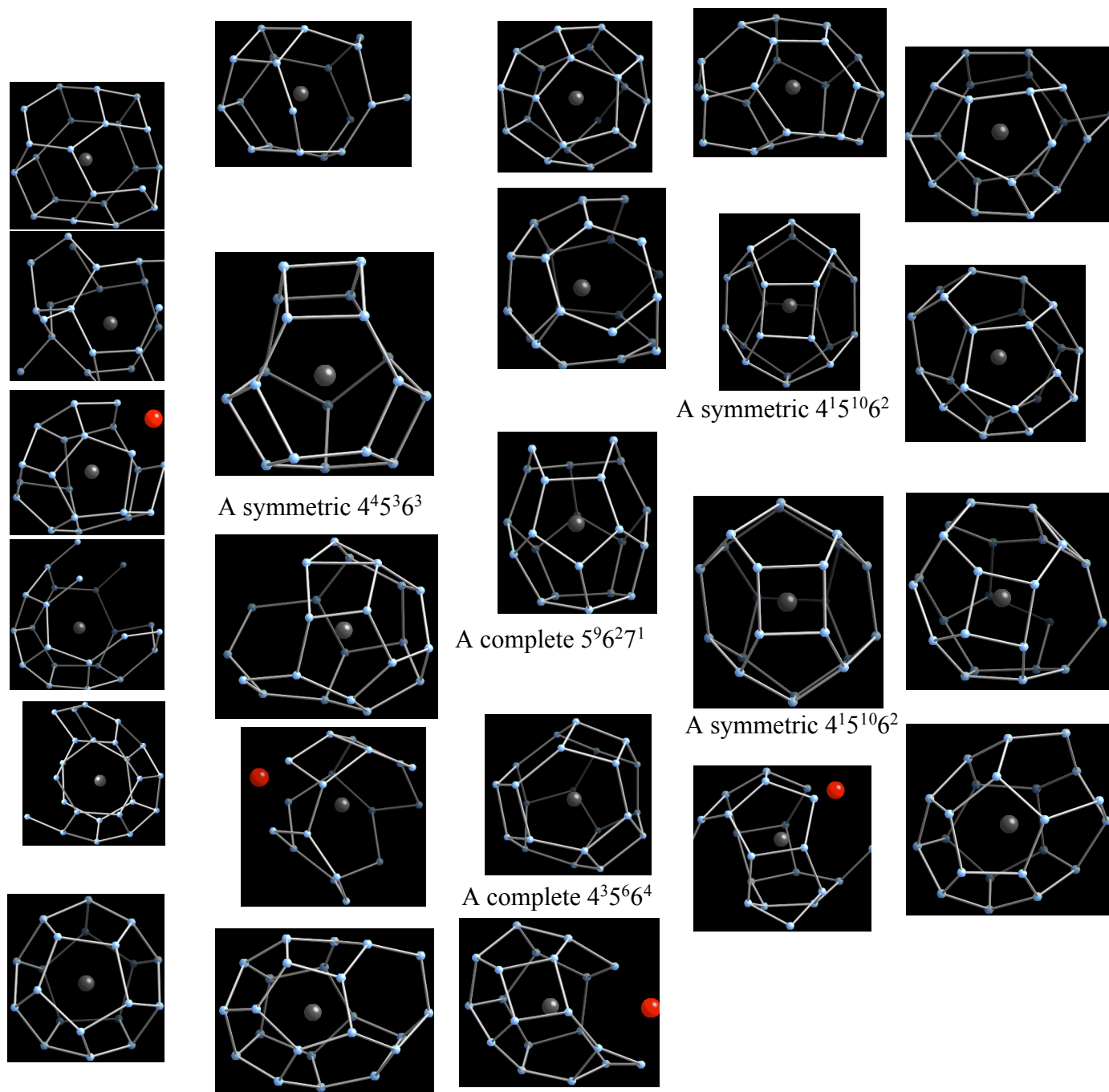
Supplemental Figure 5 (a).

Cages found in the nucleated solid at 255K.



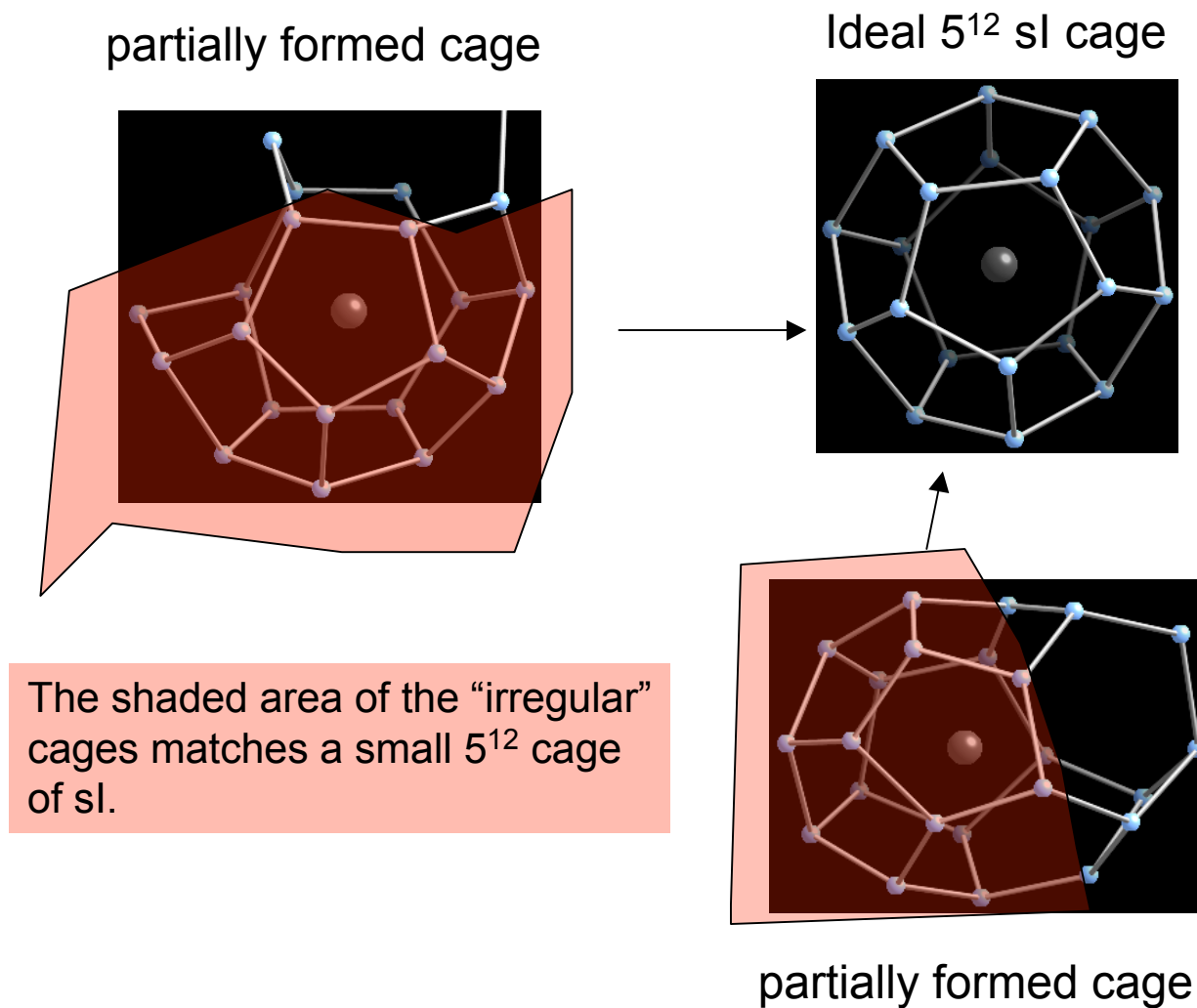
Supplemental Figure 5 (b).

Cages found in the nucleated solid at 255K.



Supplemental Figure 6(a).

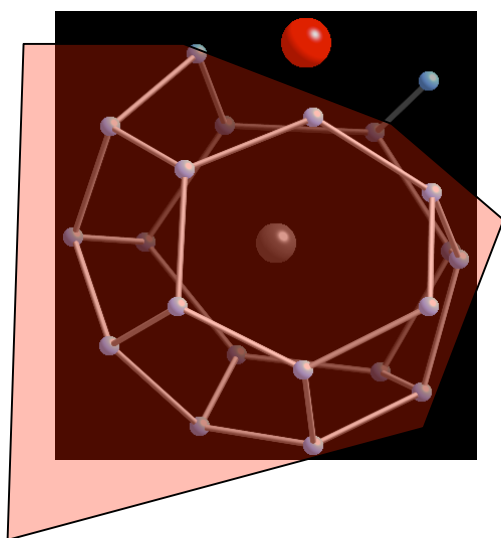
Partial symmetry in cages. Some asymmetric cages resemble the structures of more symmetric sl counterparts.



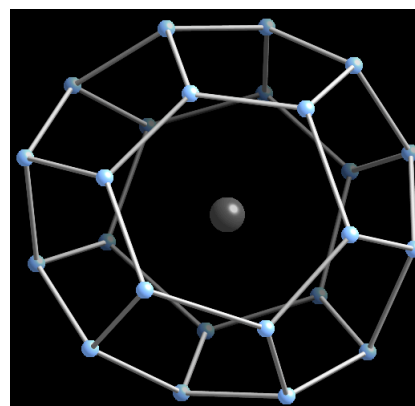
Supplemental Figure 6(b).

Partial symmetry in cages. Some asymmetric cages resemble the structures of more symmetric sl counterparts.

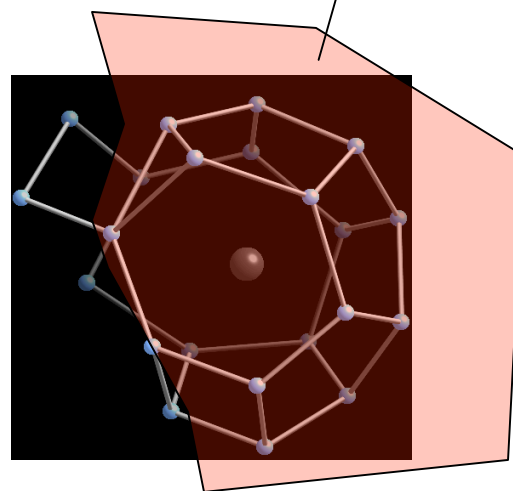
partially formed cage



Ideal sl large
 $5^{12}6^2$ cage

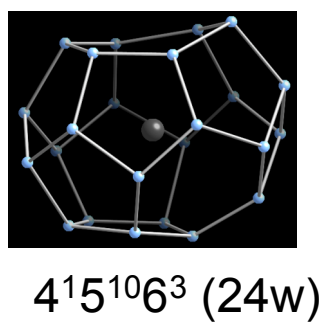
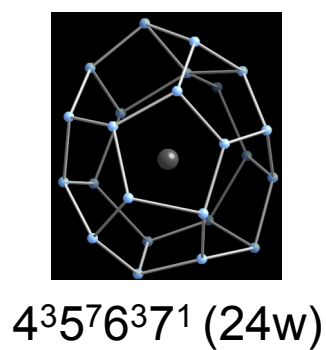
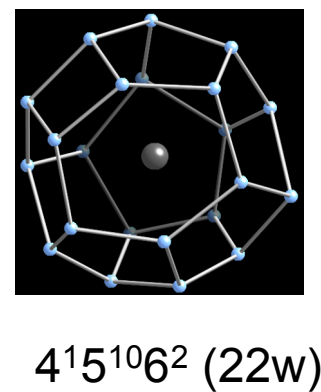
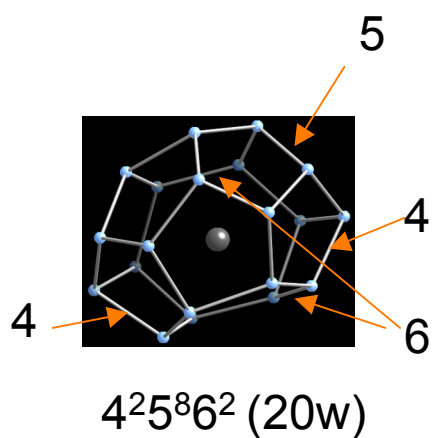
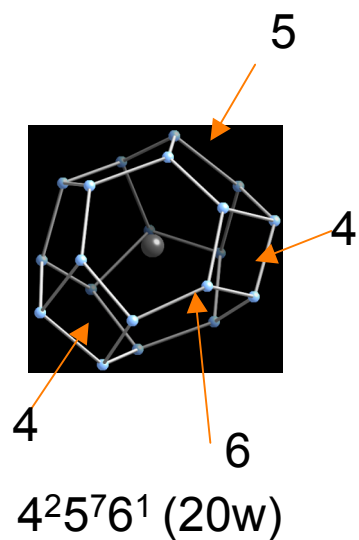


The shaded area of the “irregular” cages matches a sl large $5^{12}6^2$ cage of sl.

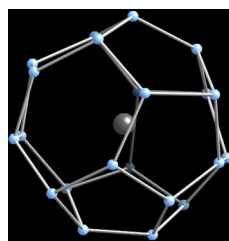
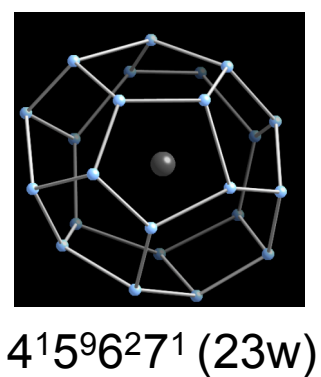
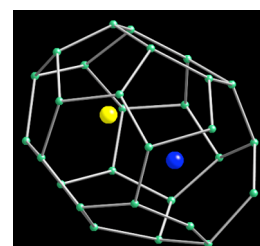


partially formed cage

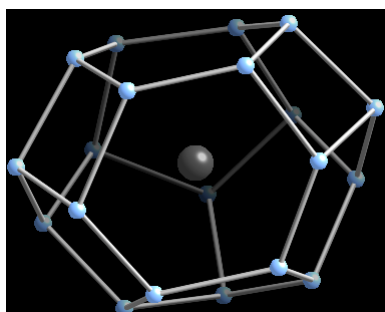
Supplemental Figure 7. Irregular cages: a closer look.



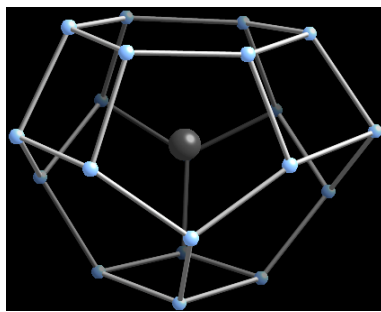
“Very large” cage with
2 methane inside



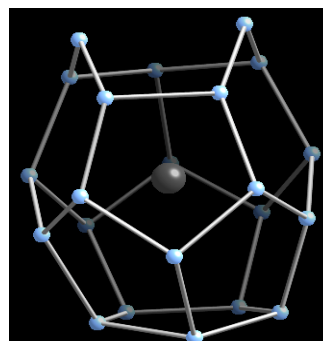
Supplemental Figure 8. Cages with internal symmetry, which had not been previously identified in any known methane-hydrate crystal structure.



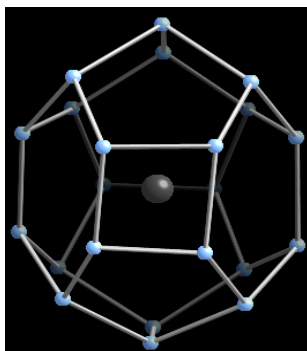
(a) $4^2 5^5 6^2$



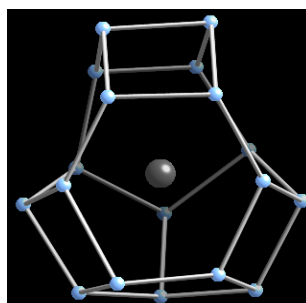
(b) $4^3 5^6 6^3$



(c) $5^9 6^2 7^1$



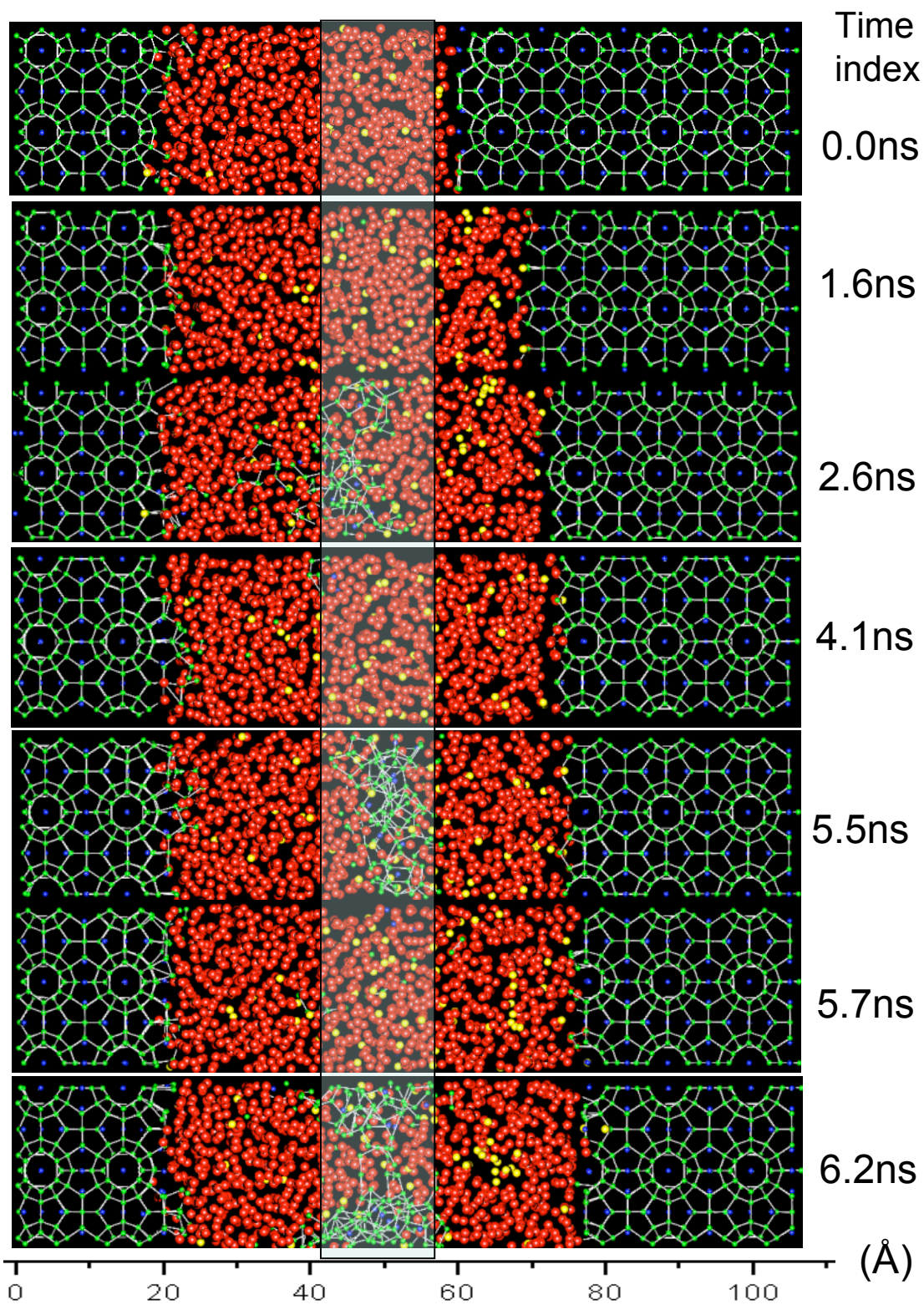
(d) $4^1 5^{10} 6^2$



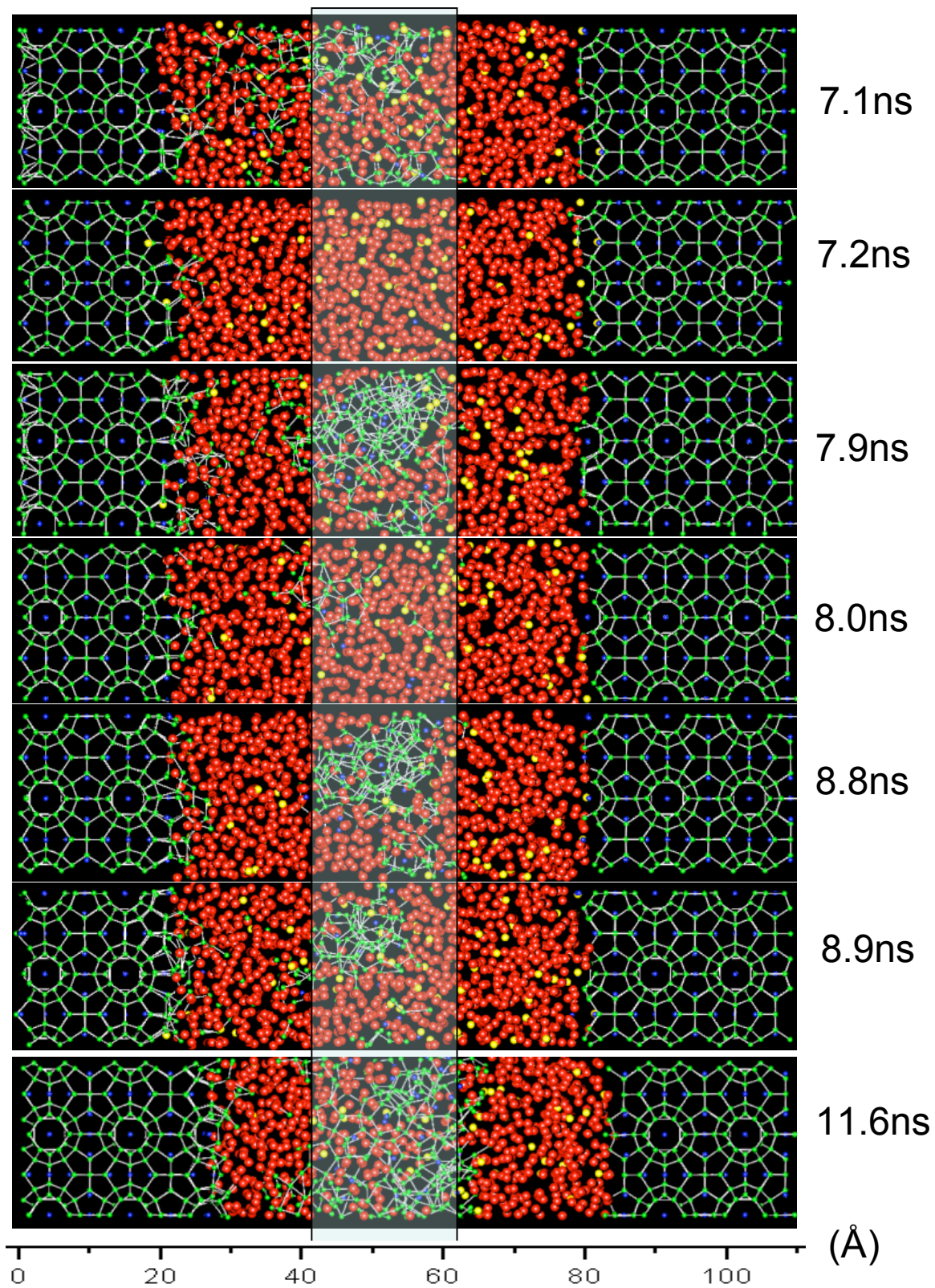
(e) $4^4 5^3 6^3$

Supplemental Figure 9.

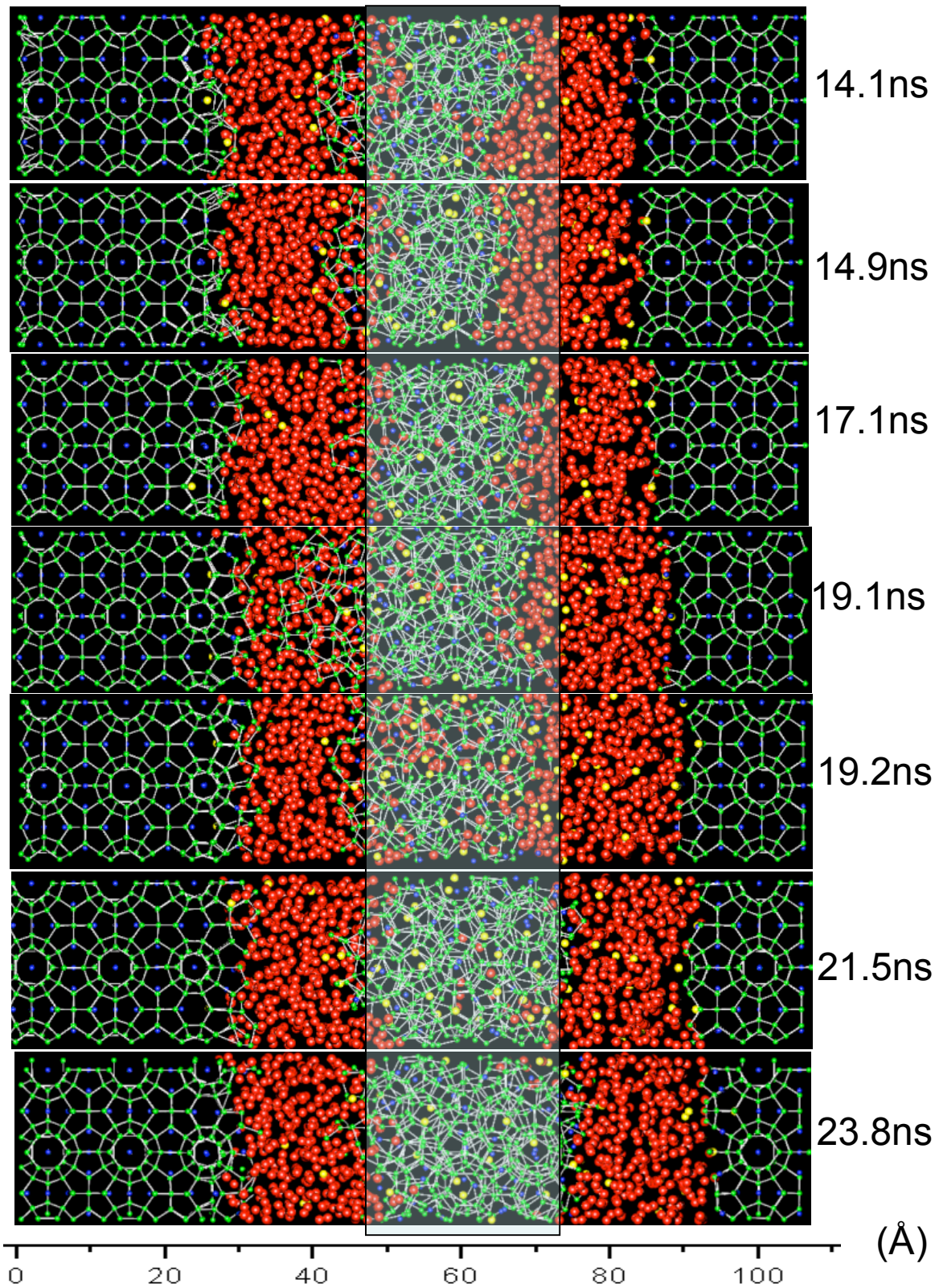
A sequence of system configurations showing fluctuations of an increasing degree of order in the system that leads eventually to nucleation. The shaded area represents the area where nucleation is initiated. The systems are represented as in Figure 2.



Supplemental Figure 9 (continued).



Supplemental Figure 9 (continued).



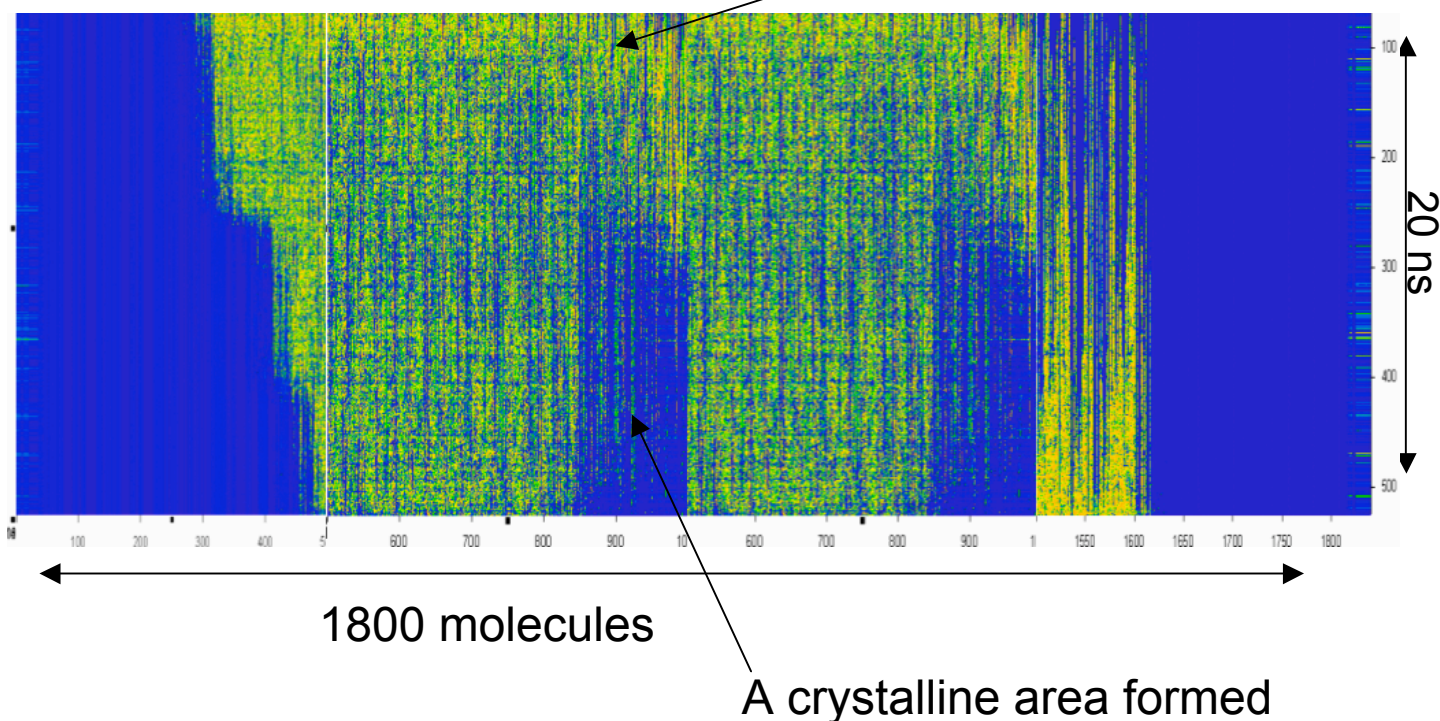
Supplemental Figure 10.

Tracking of molecular history through the time dependence of potential energy of all water molecules in the simulation.

Tracing the individual trajectories of all molecules, we can identify that all water and methane molecules involved in nucleation had liquid-like character prior to nucleation. In the figure the molecules are sorted along the horizontal axis by their final position in simulation box. The blue points represent molecules with lower (solid-like) potential energies and the yellow-green points identify molecules with higher (liquid-like) potential energies. All individual molecules identified in the nucleated solid (labeled in the figure) were found to have liquid-like character for 2-5 ns prior to solidification.

Blue crystal;
yellow: liquid

Molecules that formed the
crystalline area were
initially liquid like.



Supplemental Figure 11.

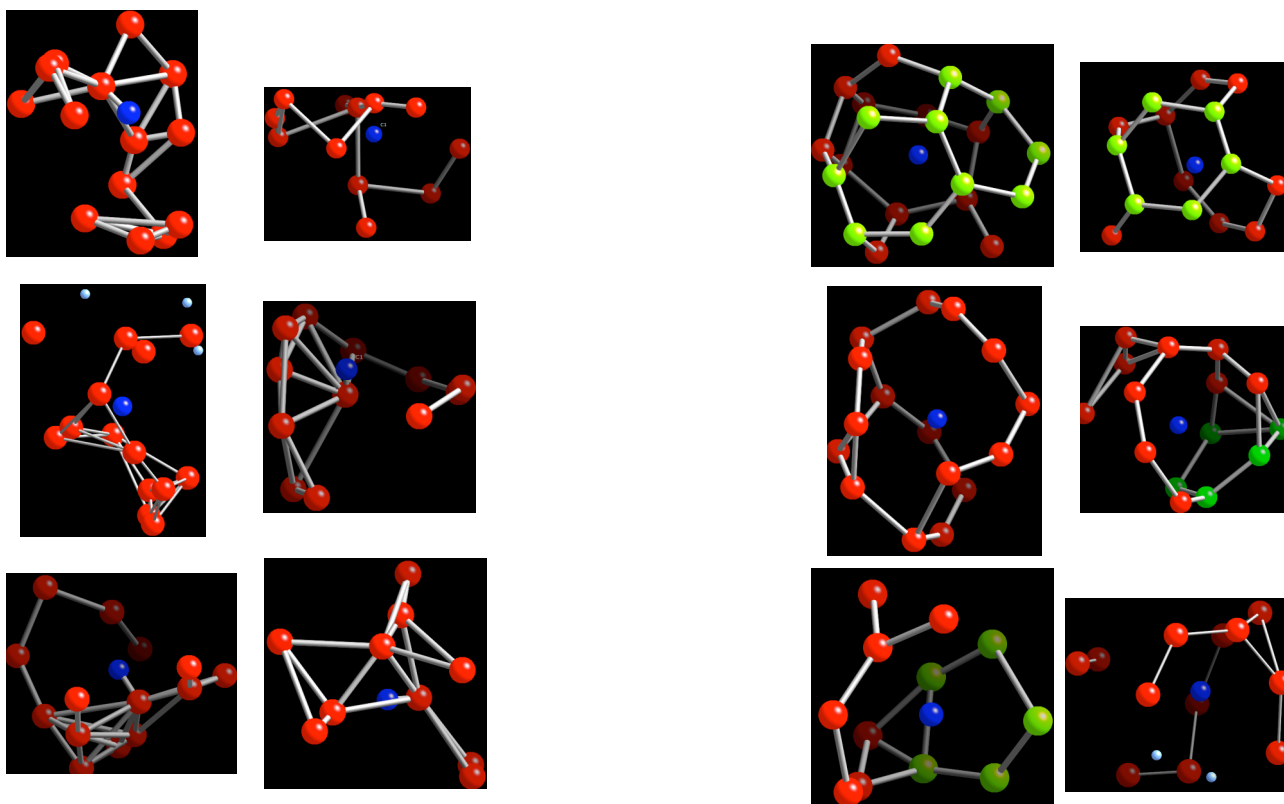
Averaged configurations representing water/methane local environments at (a) 370 K and (b) 270 K.

At high temperatures (370 K) an essentially random pattern is observed, indicating that specific local water/methane arrangements (structures) are not retained over 50 ps at 370 K.

In contrast, at 270 K (33-35 K undercooled) pentagonal/hexagonal water (ring) structures are seen to survive for hundreds of picoseconds (obvious here in configurations averaged over 50 ps).

It is also important to note that, in such long-lived ring structures the water molecules have their molecular motion slightly retarded and they were identified as solid-like.

The green spheres represent the water molecules making up specific ring structures around methane.



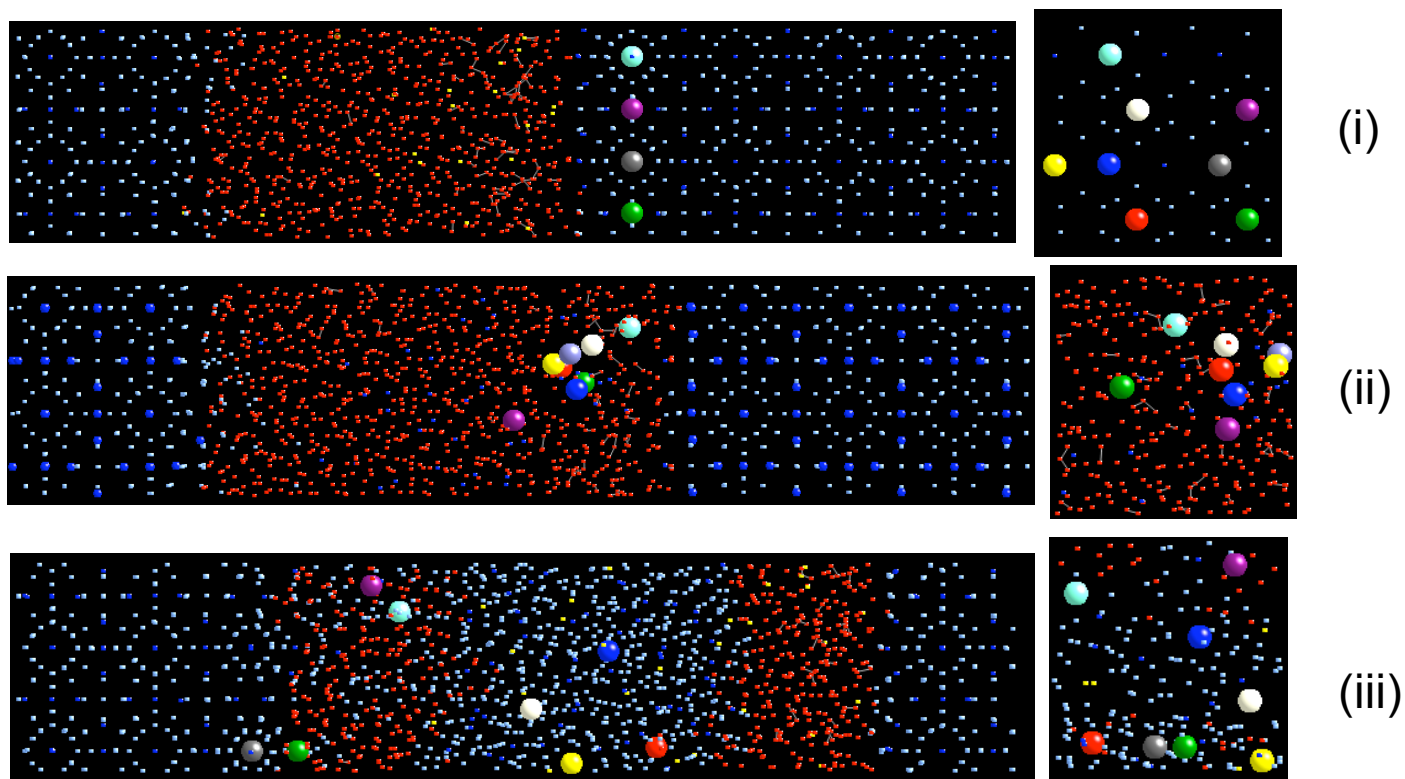
(a) T=370 K

(b) T=270 K

Supplemental Figure 12.

System configurations tracking the evolution of a selected set of methane molecules which were initially located in the same cross-section (xy) plane.

The methane molecules of interest are represented by large spheres of various colors.



(i) The initial configuration showing the planar distribution of a selected set of methane molecules, (ii) the configuration 500 ps after the heat pulse encounters the initial position of the methane molecules, and (iii) the final configuration after nucleation. The left panels are views perpendicular to xy plane.

These images also capture the randomization of the positions of the methane molecules, and hence the loss of any memory of their initial crystalline structure.