

Supporting Information for

Molecular Dynamics Study on the Nucleation of Mixed Guest Hydrate

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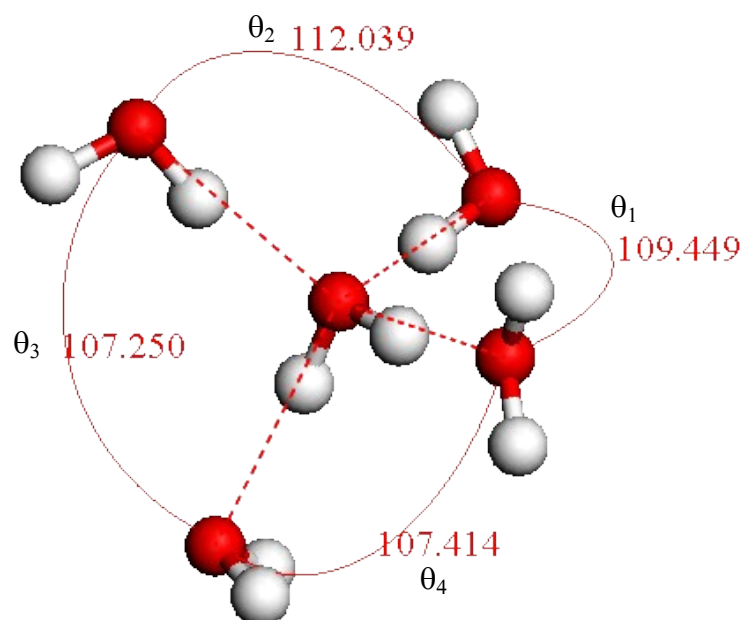


Figure S1. An illustration of 4 inclusion angles θ for determination of AOP of the central water molecule.

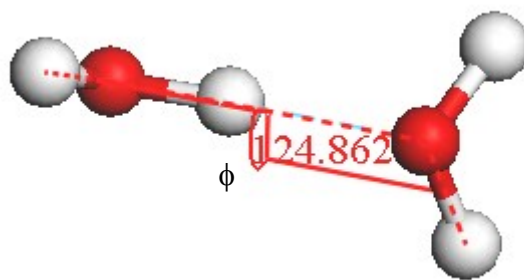


Figure S2. An illustration of the dihedral angle ϕ between two water molecules for the F4 order parameter calculation.

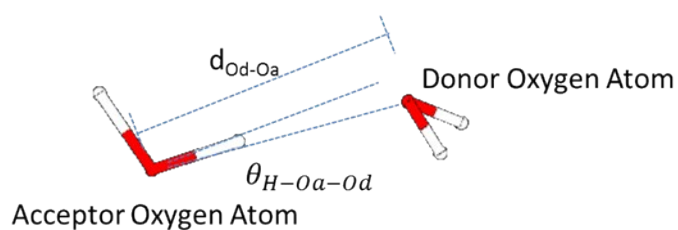


Figure S3. The definition of H-bond ($\theta_{H-O_a-O_d} < 15$ and $d_{O_d-O_a} < 3.5\text{\AA}$) used in this work

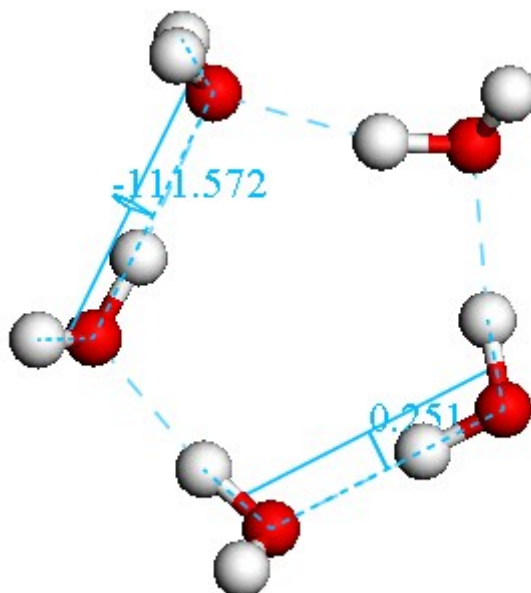


Figure S4. An example of 5-member ring structure formed by hydrogen bonds of water.

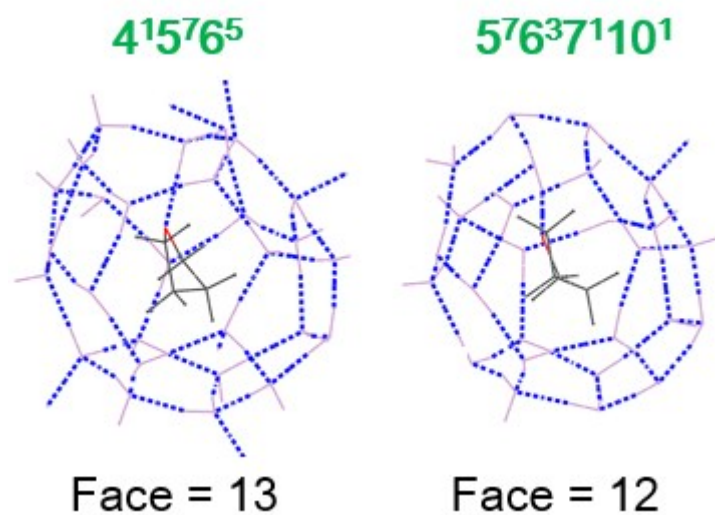


Figure S5. Two examples of water cages, i.e., a void that is surrounded by 10 or more ring structures (faces).

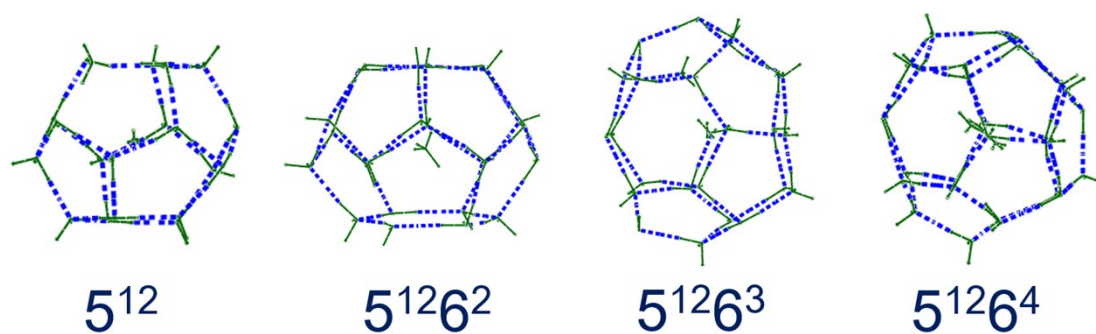


Figure S6. The illustration of the 4 regular cages: 5^{12} (pentagonal dodecahedron), $5^{12}6^2$ (tetradecahedron), $5^{12}6^3$, and $5^{12}6^4$ (hexadecahedron).

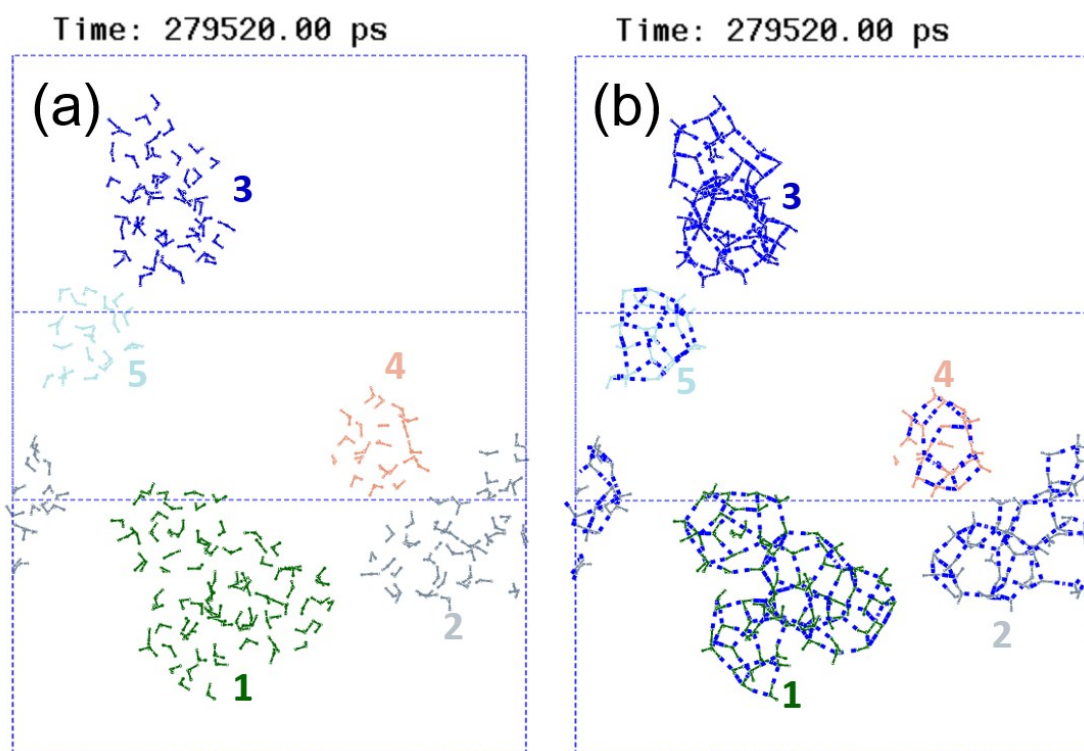


Figure S7. The Example of cage clusters without (a) and with H-bond (blue dashed lines) (b).

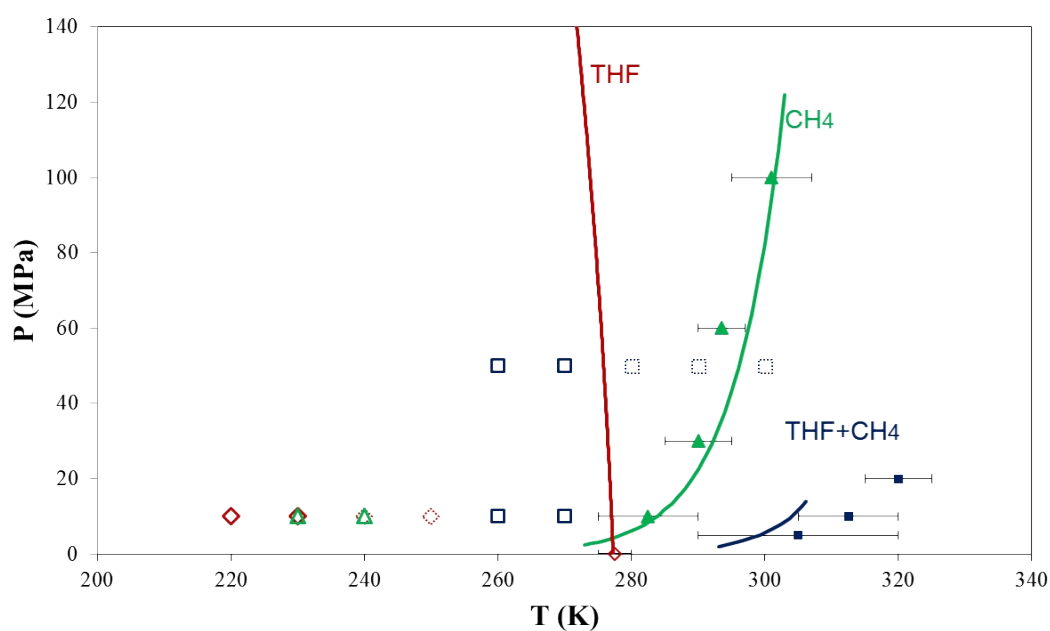


Figure S8. The dissociation temperature of CH₄¹ (green), THF² (red), and CH₄+THF³ (blue) hydrates from experiments (solid lines) and simulation (closed symbols). The open symbols are simulation conditions used to test the nucleation process. The symbols with dashed lines indicate conditions where no nucleation were observed.

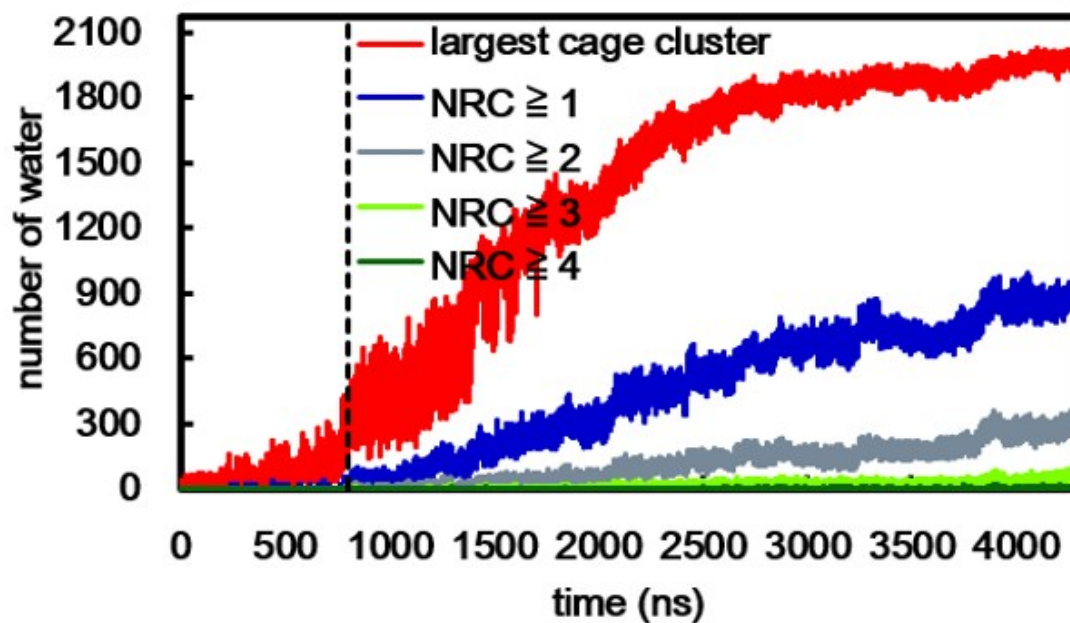


Figure S9. The time evolution of the number of water molecules in the largest cage cluster (red), the number of water molecules that belong to at least one (blue), two (grey), three (light green), or four (dark green) regular cages in $\text{CH}_4+\text{H}_2\text{O}$ system at 10 MPa and 230 K. The vertical dashed lines indicate the end of induction period, during which no cages emerge will survive until the end of the simulation.

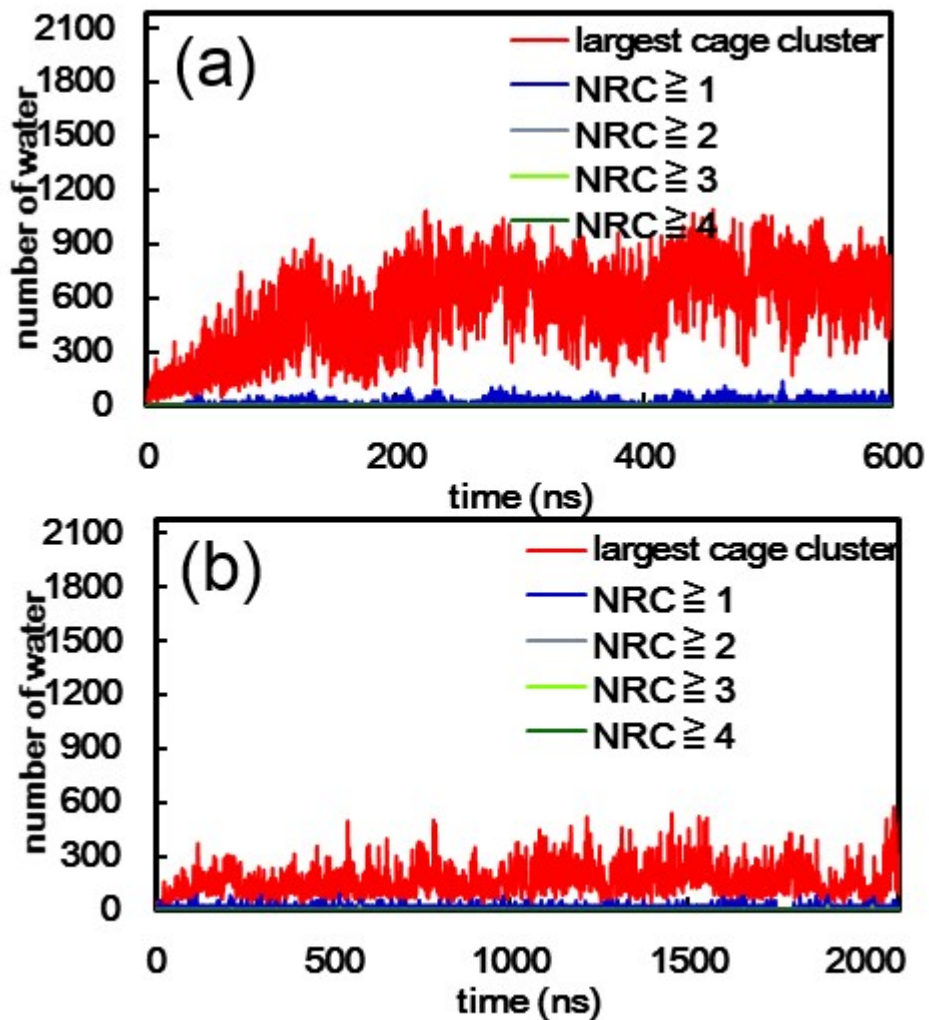


Figure S10. The time evolution of the number of water molecules in the largest cage cluster (red), the number of water molecules that belong to at least one (blue), two (grey), three (light green), or four (dark green) regular cages in THF+H₂O solution at 10 MPa and 220 K (a) and 240K(b).

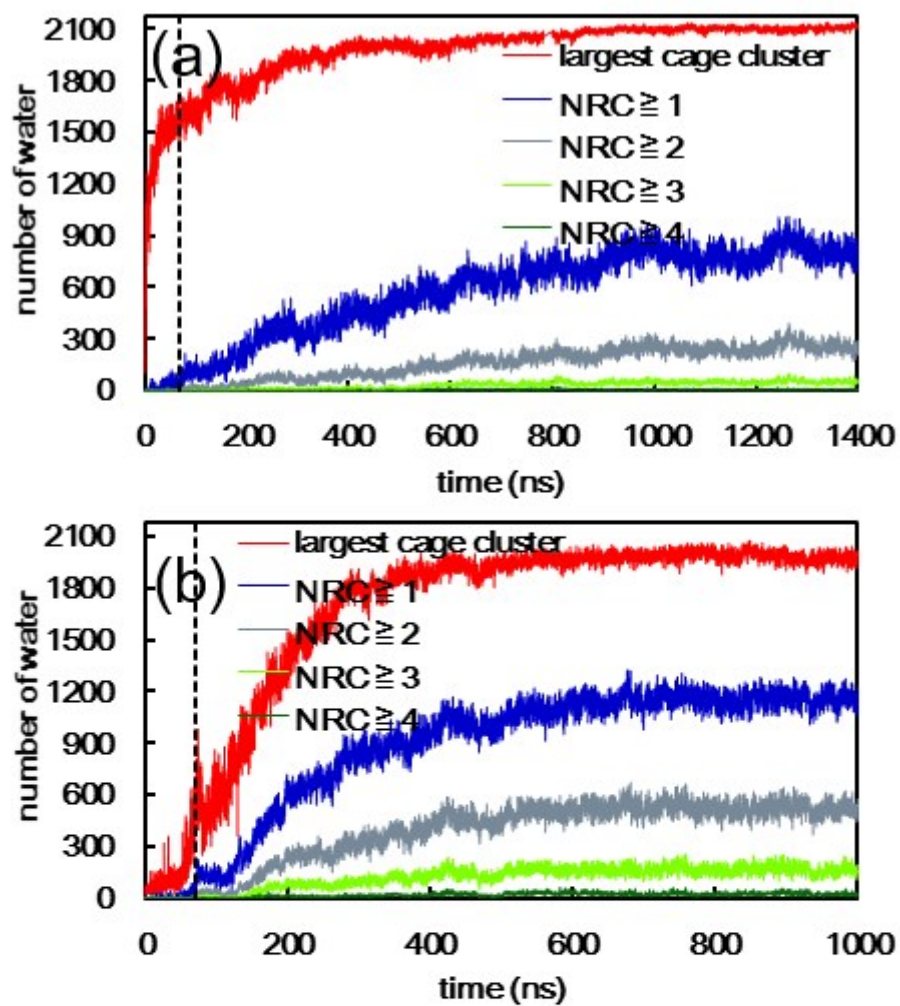


Figure S11. The time evolution of the number of water molecules in the largest cluster of cages (red curve), the number of water molecules that belong to at least one (blue), two (grey), three (light green), or four (dark green) regular cages in $\text{CH}_4+\text{THF}+\text{H}_2\text{O}$ system at 10 MPa and 240 K (a) and 260 K (b). The vertical dashed lines indicate the end of induction period.

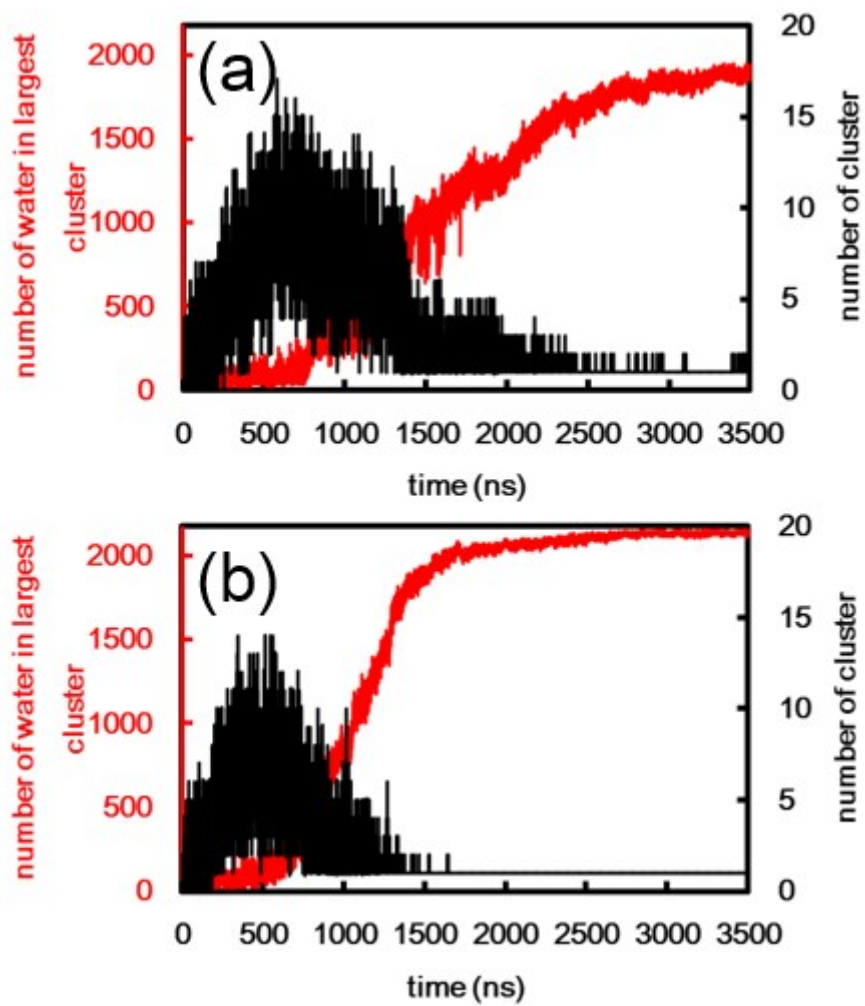


Figure S12. The time evolution of the size of largest cluster (red curve) and the number of clusters in the CH₄ hydrate nucleation simulation at 10 MPa and 230 K (a) and 240 K(b).

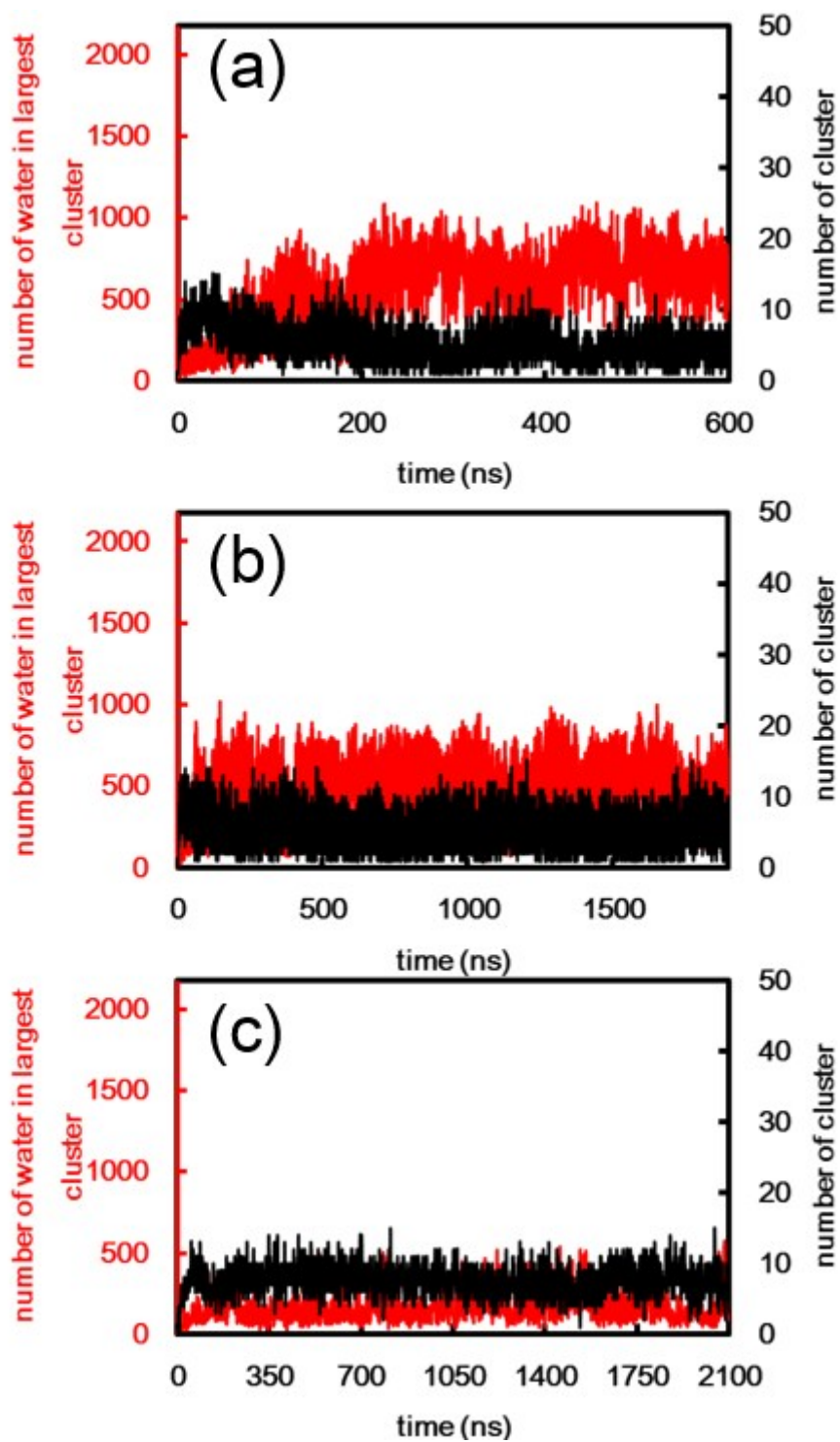


Figure S13. The time evolution of the size of largest cluster (red curve) and the number of clusters in the THF hydrate nucleation simulation at 10 MPa and 220 K (a), 230 K (b) and 240 K (c).

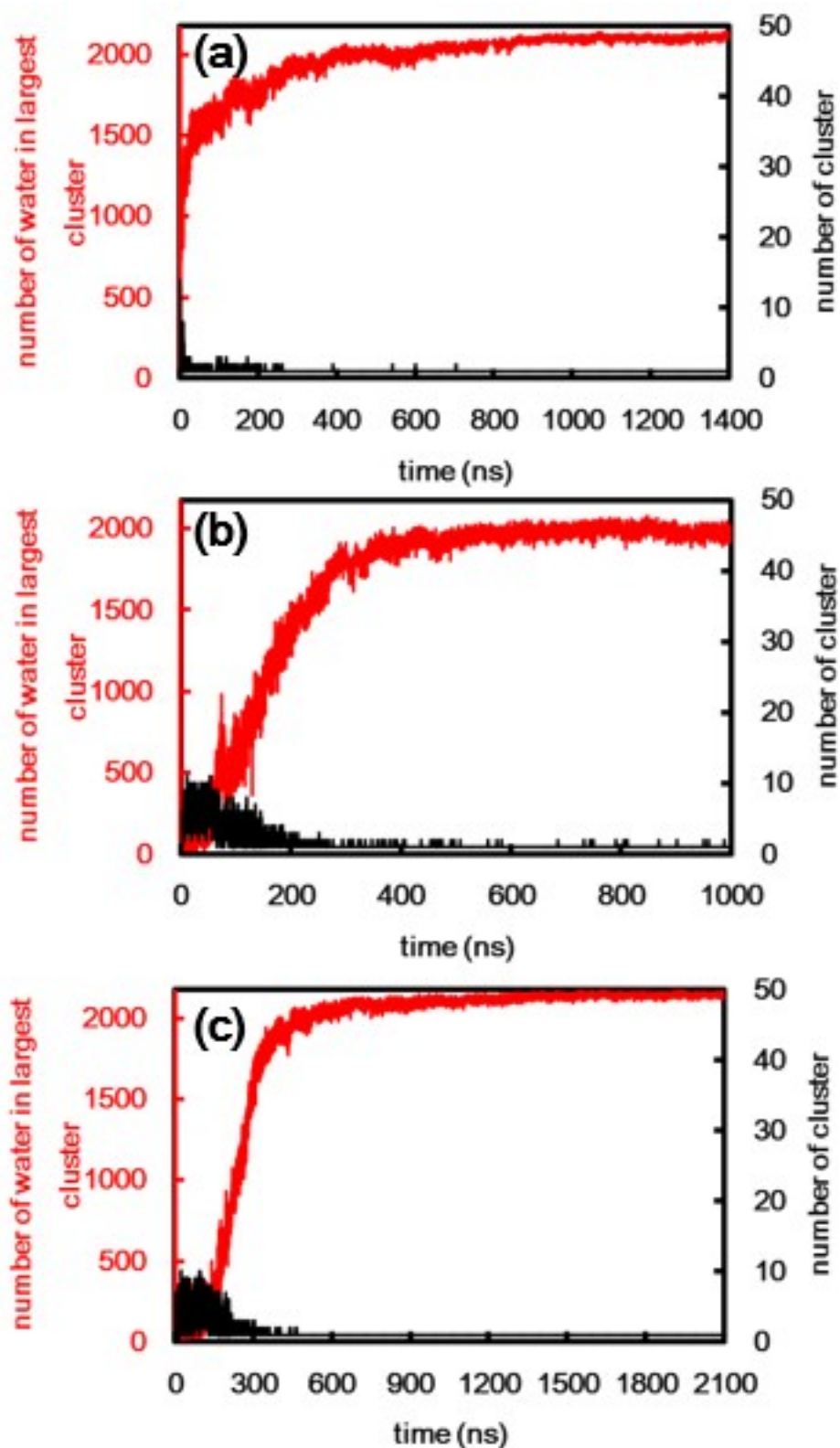


Figure S14. The time evolution of the size of largest cluster (red curve) and the number of clusters in the CH_4+THF hydrate nucleation simulation at 10 MPa and 240 K (a), 260 K (b) and 270 K (c).

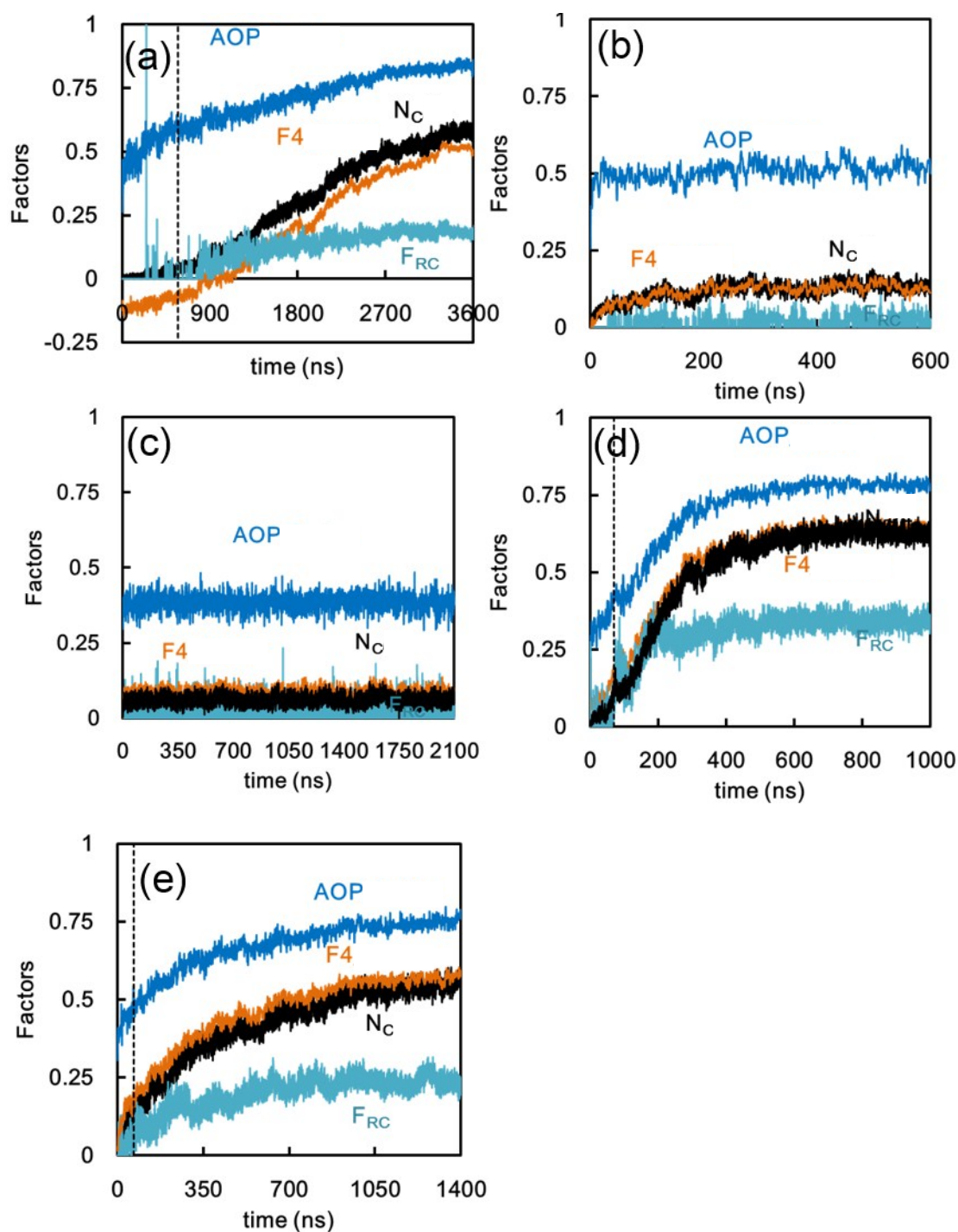


Figure S15. The time evolution of rescaled order parameters AOP (blue), F4 (brown), $\langle N_c \rangle$ (black), and F_{RC} (cyan) for the nucleation process of CH_4 hydrate nucleation at 10 MPa and 230 K (a), THF hydrate nucleation at 10 MPa and 220 K (b), and 230 K (c), CH_4 +THF nucleation at 10 MPa and 260 K (d) and 240 K (e). The rescaled $AOP = (AOP - 0.823) / (0.066 - 0.823)$ and rescaled $F4 = (F4 - 0.0013) / (0.9616 - 0.0013)$ for THF, CH_4 +THF hydrate cases, and $(F4 - 0.0013) / (0.8936 - 0.0013)$ for CH_4 hydrate case. The rescaled $\langle N_c \rangle = \langle N_c \rangle / 4$. The dash line shows the induction time of the

corresponding simulation.

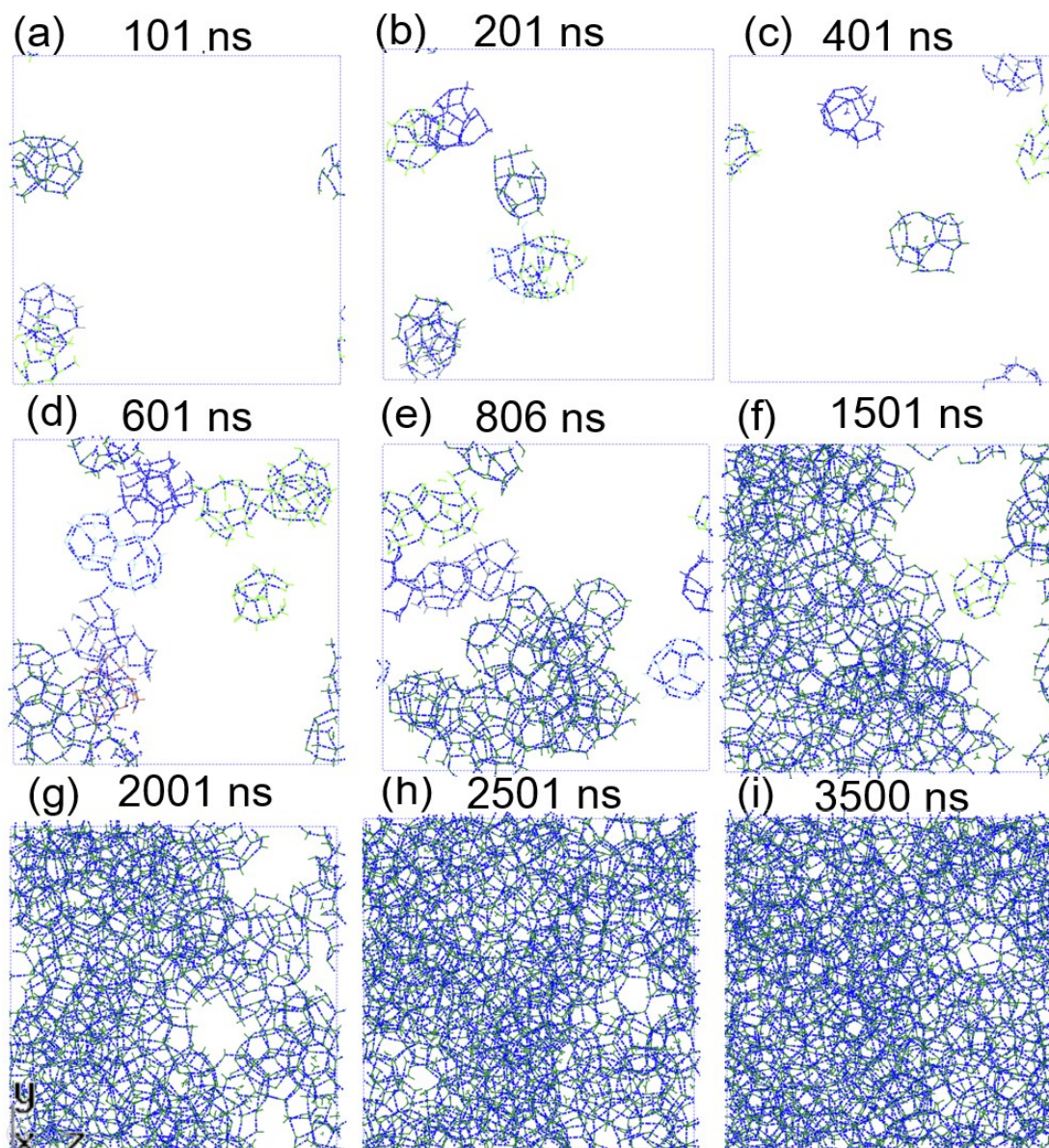


Figure S16. The development of cluster of cages for CH₄ hydrate nucleation at 10 MPa and 230 K.

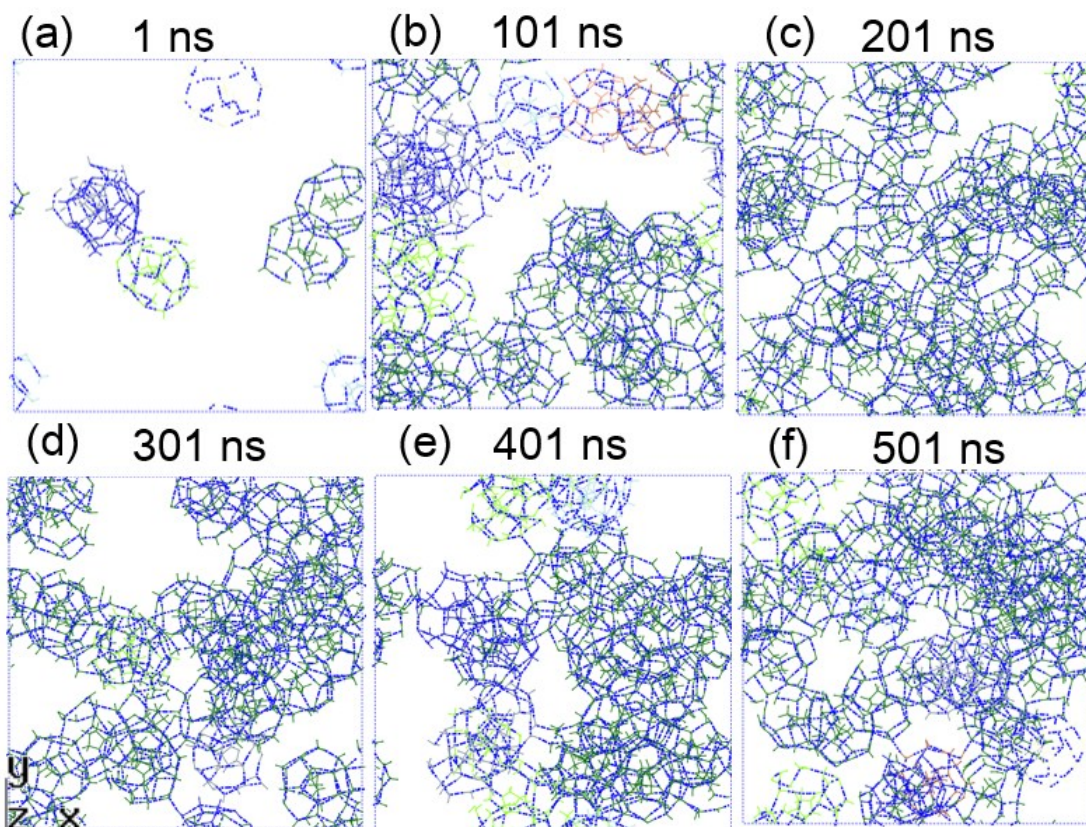


Figure S17. The development of cluster of cages for THF hydrate nucleation at 10 MPa and 220 K.

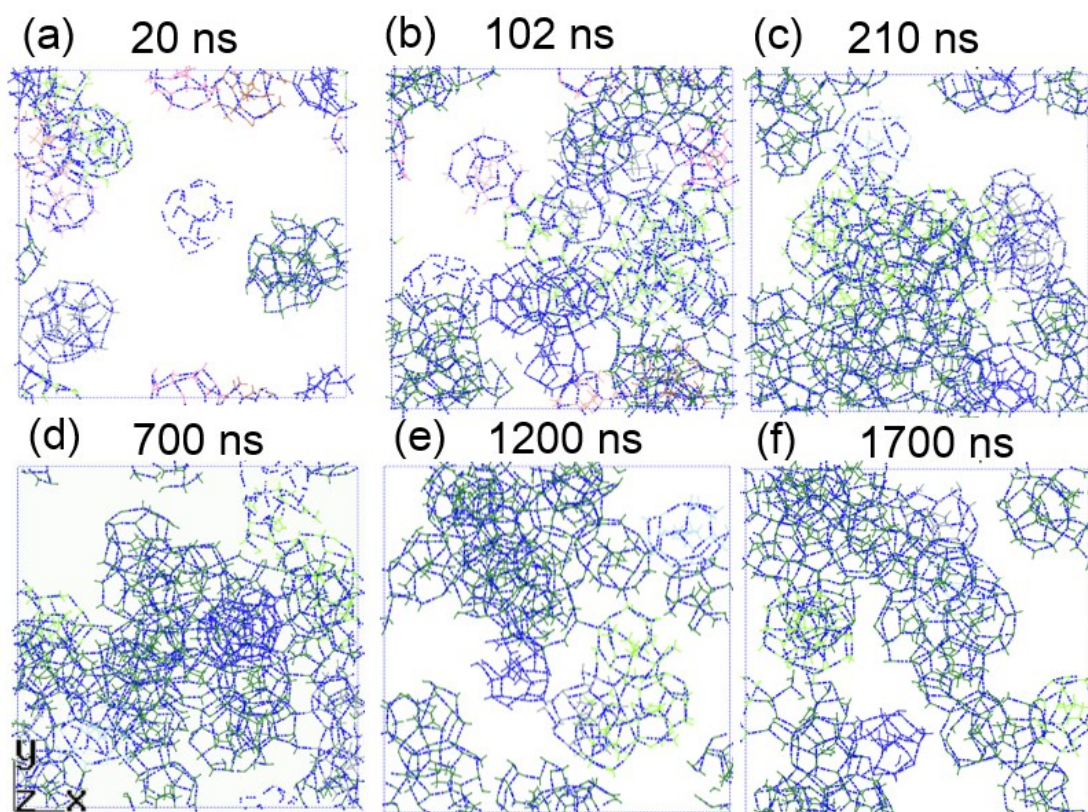


Figure S18. The development of cluster of cages for THF hydrate nucleation at 10 MPa and 230 K.

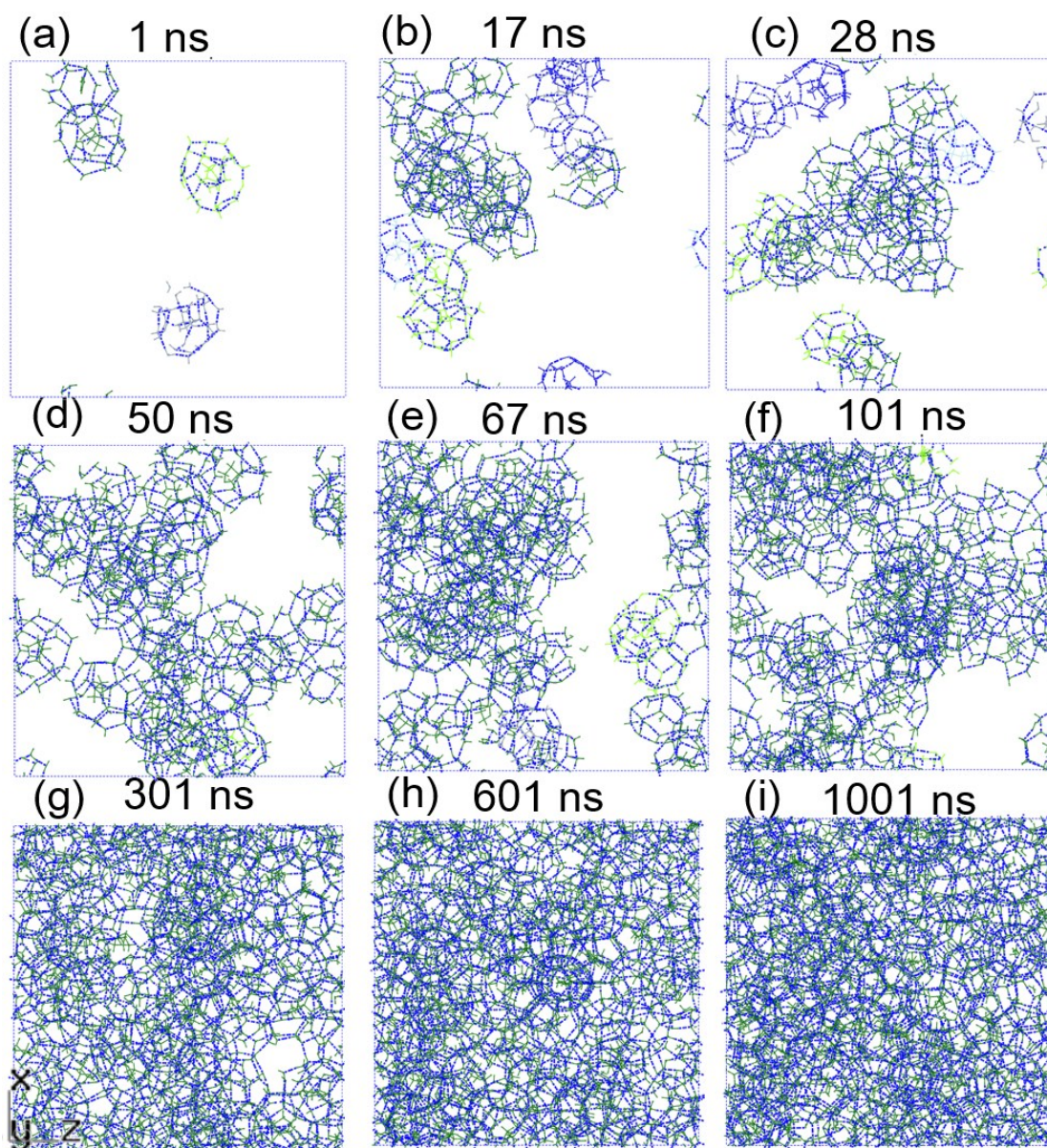


Figure S19. The development of cluster of cages for CH_4 +THF hydrate nucleation at 10 MPa and 240 K.

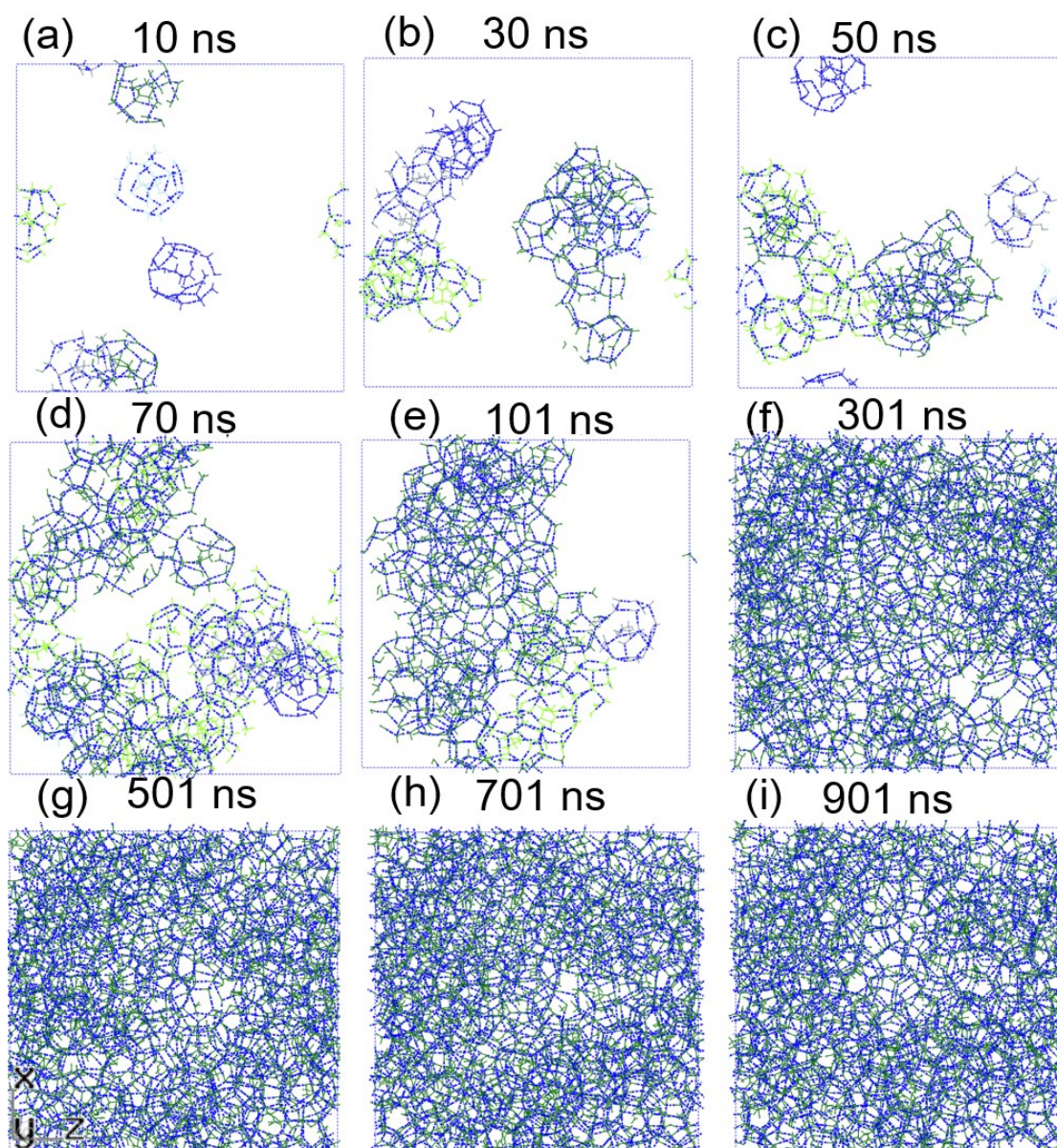


Figure S20. The development of cluster of cages for CH_4+THF hydrate nucleation at 10 MPa and 260 K.

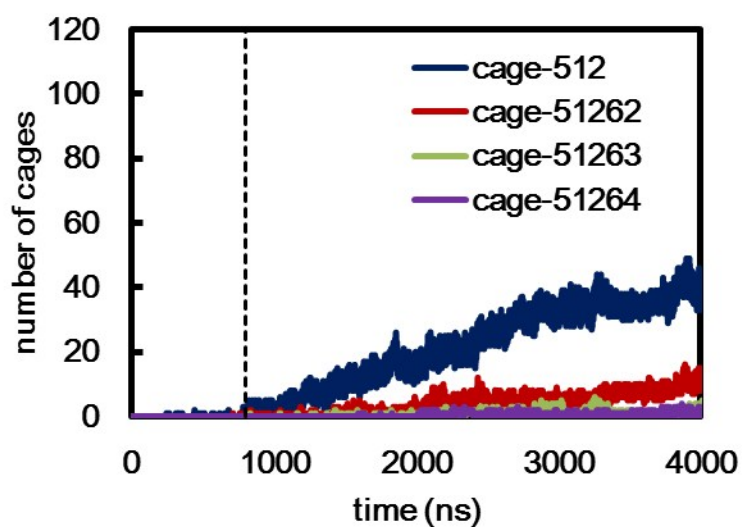


Figure S21. The number of regular cages (5^{12} , $5^{12}6^2$, $5^{12}6^3$, $5^{12}6^4$) from CH_4 hydrate nucleation simulation at 10 MPa and 230 K.

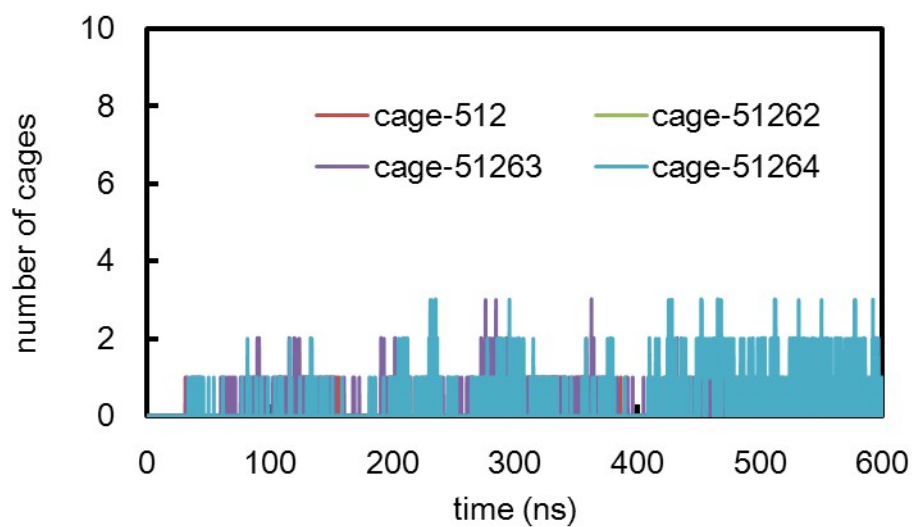


Figure S22. The number of regular cages (5^{12} , $5^{12}6^2$, $5^{12}6^3$, $5^{12}6^4$) from THF hydrate nucleation simulation at 10 MPa and 220 K.

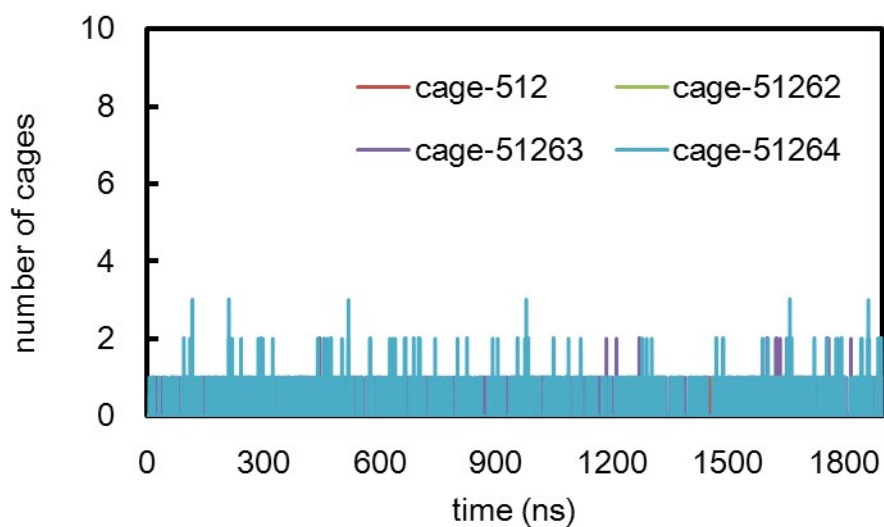


Figure S23. The number of regular cages (5^{12} , $5^{12}6^2$, $5^{12}6^3$, $5^{12}6^4$) from THF hydrate nucleation simulation at 10 MPa and 240 K.

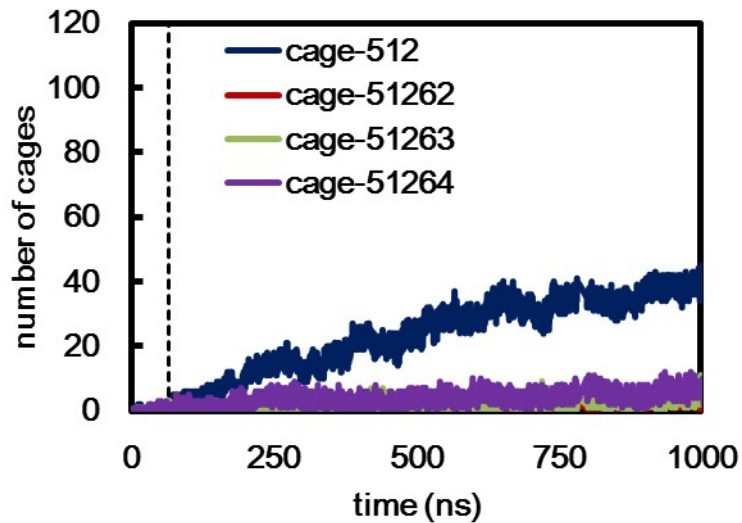


Figure S24. The number of regular cages (5^{12} , $5^{12}6^2$, $5^{12}6^3$, $5^{12}6^4$) from CH₄+THF hydrate nucleation simulation at 10 MPa and 240 K.

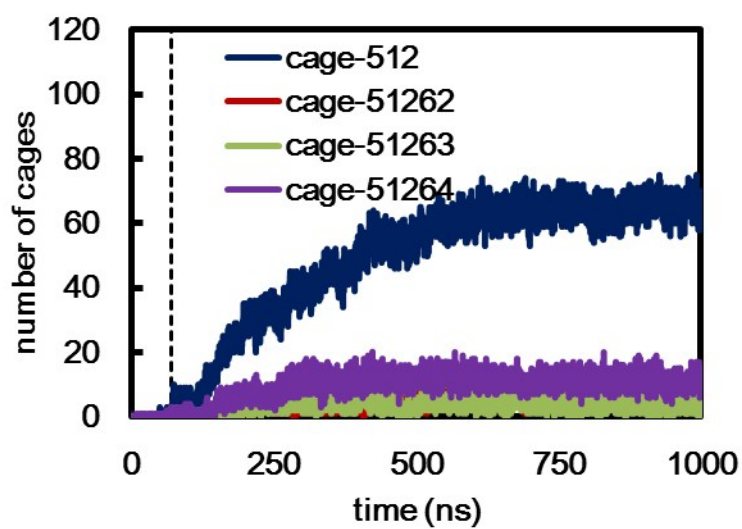


Figure S25. The number of regular cages (5^{12} , $5^{12}6^2$, $5^{12}6^3$, $5^{12}6^4$) from CH_4 +THF hydrate nucleation simulation at 10 MPa and 260 K.

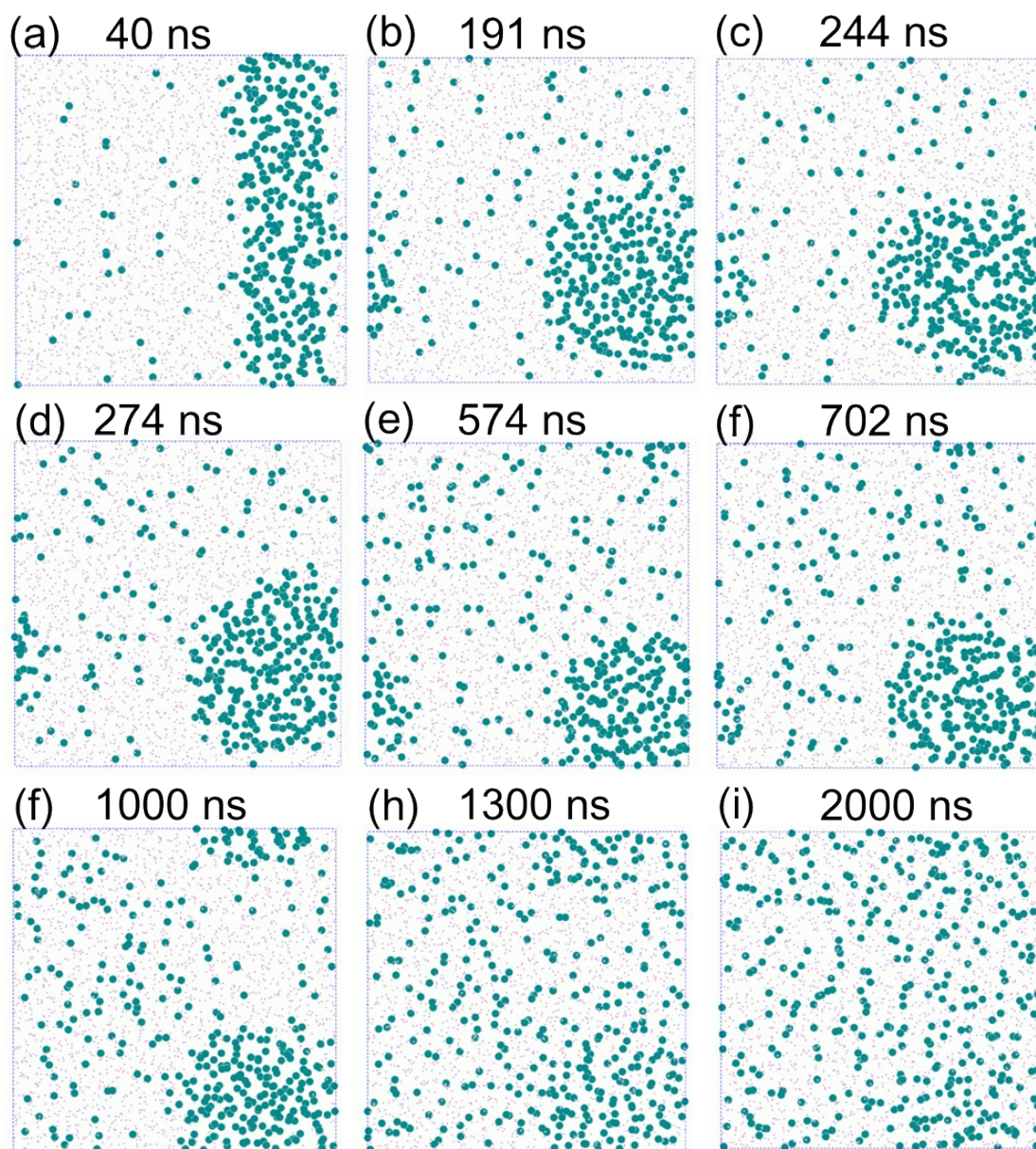


Figure S26. The distribution of CH₄ molecules (green spheres) during CH₄ hydrate nucleation simulation at 10 MPa and 240 K.

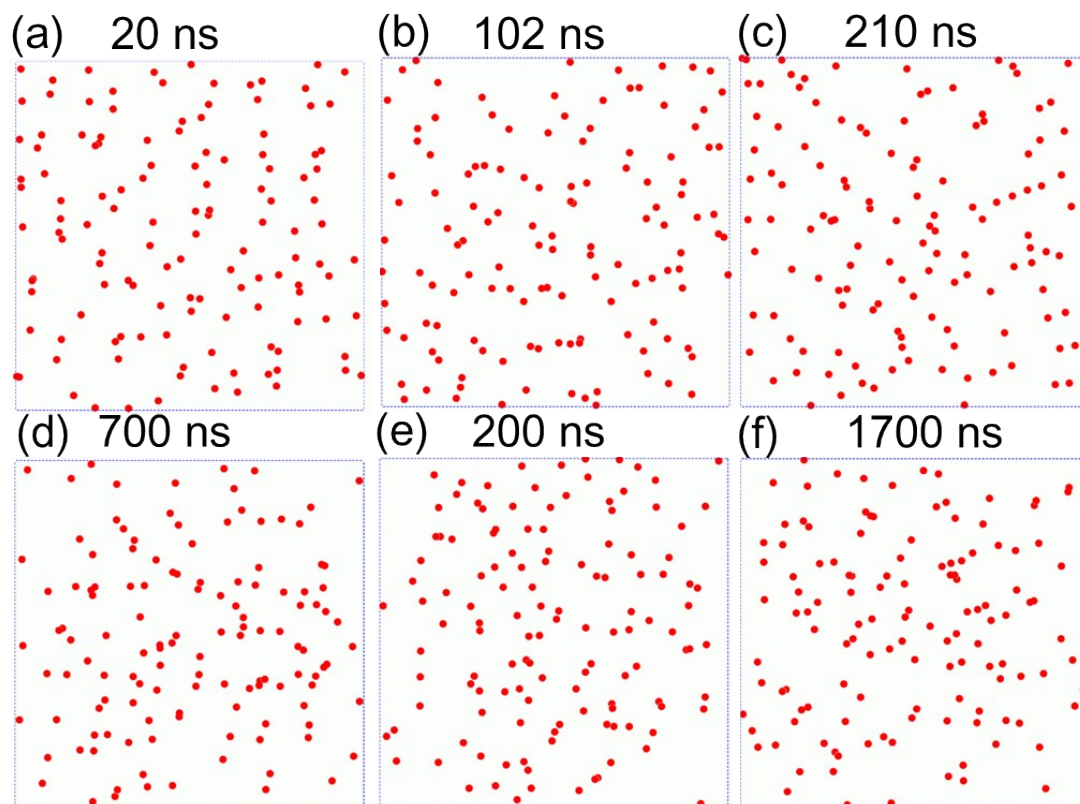


Figure S27. The distribution of THF molecules (red spheres) during THF hydrate nucleation simulation at 10 MPa and 230 K.

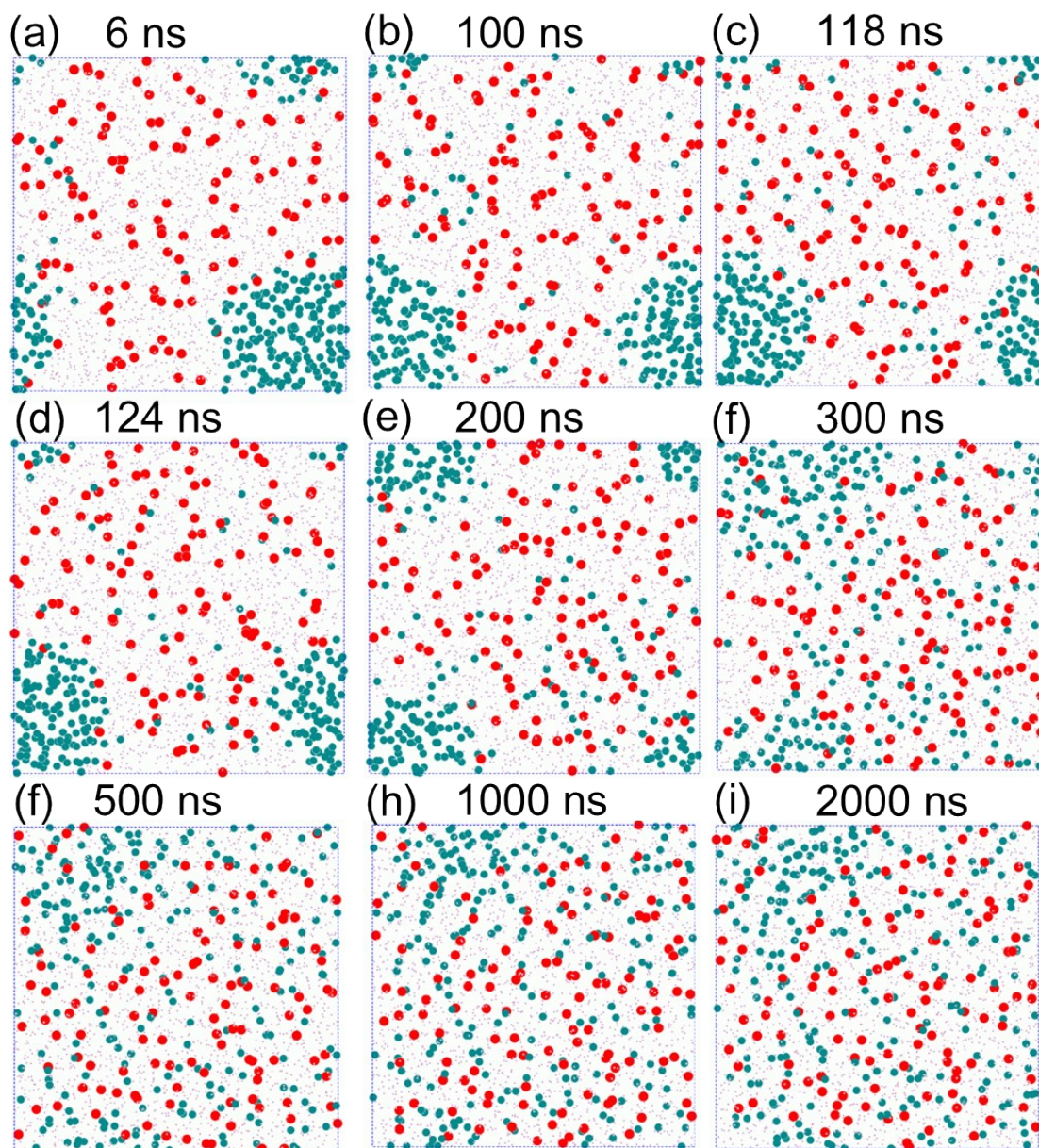


Figure S28. The distribution of CH₄ (green spheres) and THF (red spheres) during CH₄+THF hydrate nucleation simulation at 10 MPa and 270 K.

References:

1. C. A. Koh and J. E. Dendy Sloan, *Clathrate Hydrates of Natural Gases*, 3rd edn., CRC Press: Boca Raton, FL, 2008.
2. S. R. Gough and D. W. Davidson, *Canadian Journal of Chemistry*, 1971, **49**, 2691-2699.
3. R. M. de Deugd, M. D. Jager and J. D. Arons, *AIChE Journal*, 2001, **47**, 693-704.