



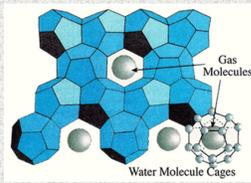
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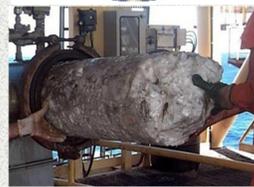
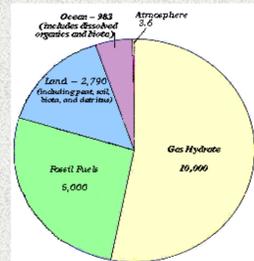
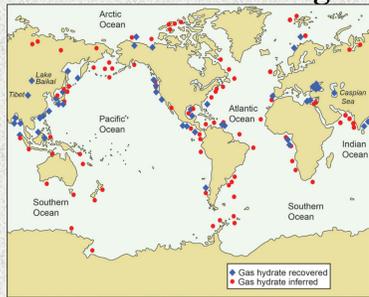
In this study, we present an advanced computational strategy integrating forward flux sampling, backward flux sampling, and P_B histogram analysis to investigate hydrate nucleation.¹ Through this strategy, we pursue a quantitative, “first-principle” description of the free energy landscape and molecular pathways of hydrate formation. The calculated distribution profile was found to fit reasonably well against the classical nucleation theory. Structural analysis of the obtained ensemble of nucleation pathways obtained clearly suggests that, on an average, hydrate formation is facilitated through a “two-step” like, amorphous to crystal transition. However the analysis also clearly reveals the structural diversity in nucleation pathways, particularly the existence of the direct crystallization trajectories without going through the amorphous stage.

Introduction

Gas hydrates are solid compounds composed of water and guest molecules (CH_4 , CO_2 , etc).



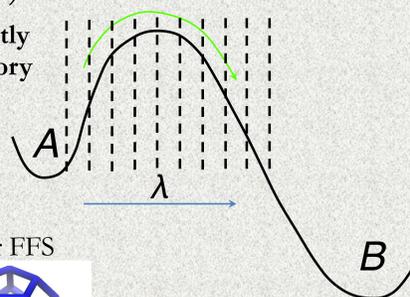
- Future energy
- Major carrier of carbon
- Flow assurance
- Global climate change



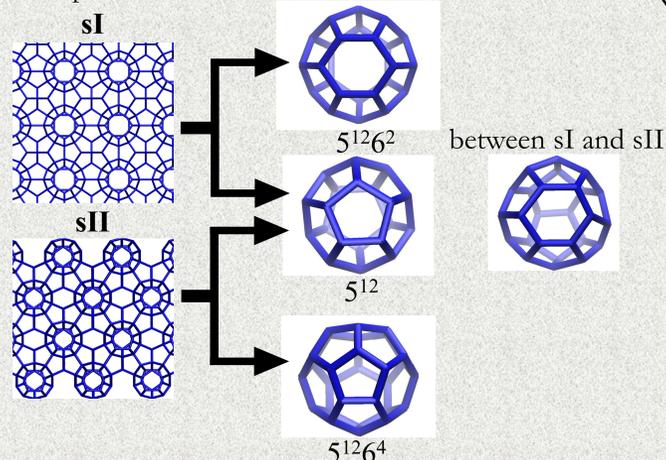
Objective: To obtain methane hydrate nucleation mechanisms supported by sufficient statistical sampling.

Methods

- Molecular Dynamics (MD) simulation
 - obtain molecular details of hydrate nucleation
 - insufficient temporal and spatial experimental resolution
- Forward Flux Sampling (FFS) method²
 - obtain rate constant k_{AB} explicitly
 - Independent of nucleation theory
 - High efficiency (closer to realistic conditions)
 - Sufficient sampling (various nucleation trajectories)

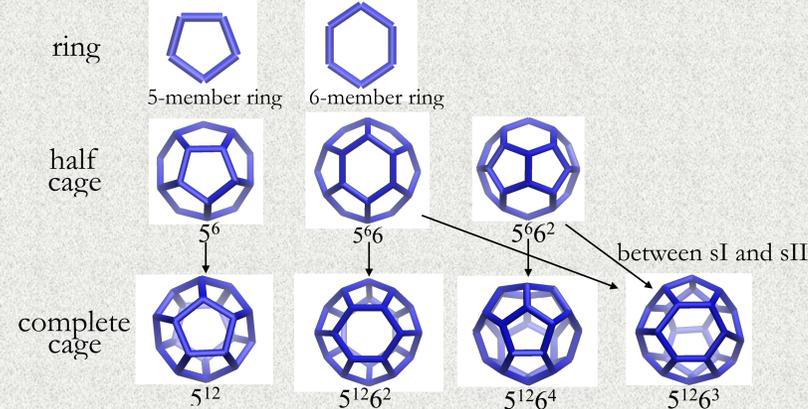


An order parameter λ is needed for FFS



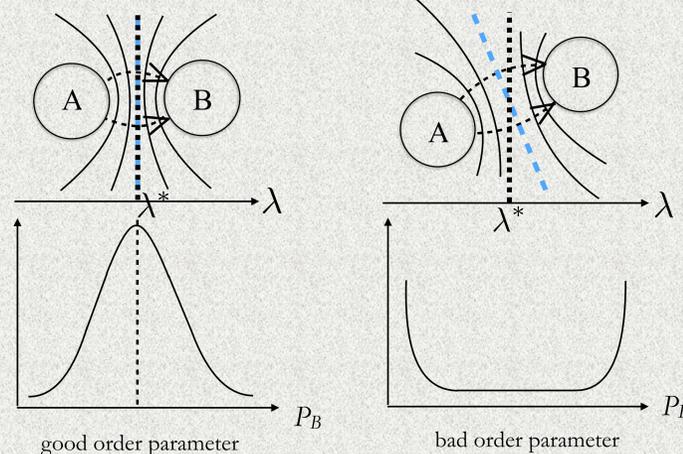
Methods (Cont.)

We have developed a new order parameter half-cage order parameter (H-COP) the # of water molecules of the largest hydrate-like cluster³

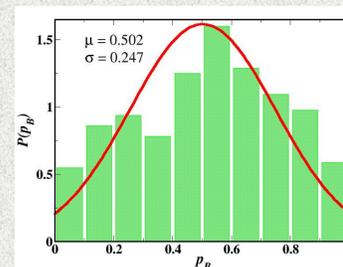


Results

p_B histogram test of H-COP order parameter

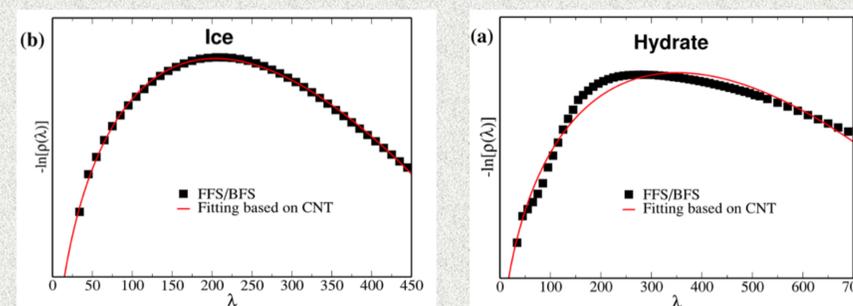


p_B histogram of H-COP order parameter can be reasonably fitted by Gaussian distribution



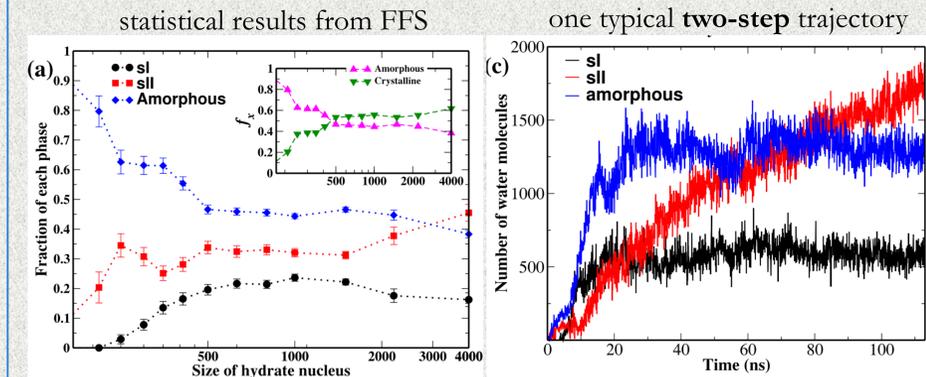
H-COP is capable of describing hydrate nucleation pathway well!

Free energy profile of hydrate nucleation

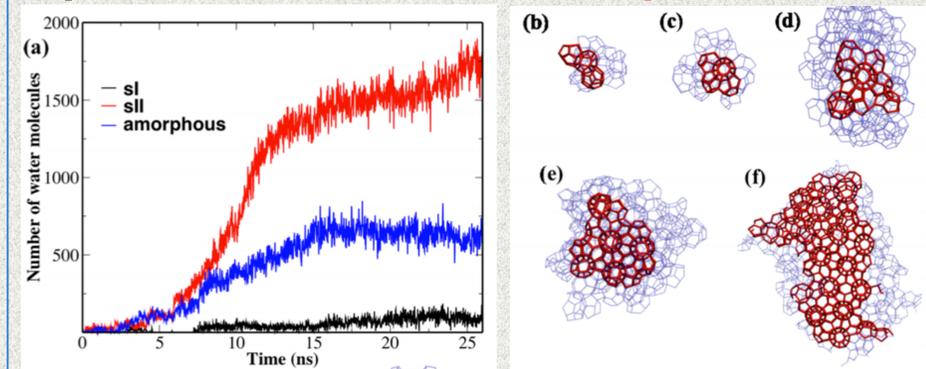


Results (Cont.)

Co-existence of multiple nucleation pathways

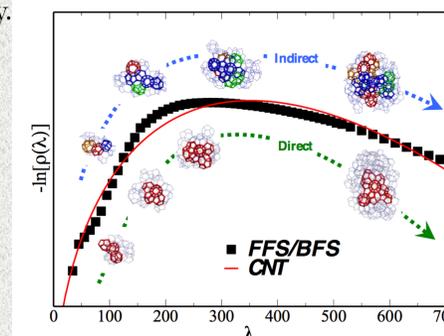


Importantly, there also do exist one-step nucleation pathways!



Conclusions

- We developed a new computational strategy that allows obtaining both the free energy profile and transition pathway of hydrate nucleation, independent of any nucleation theory.
- The validity of our strategy was verified by rigorous p_B histogram analysis.
- Intriguingly the free energy profile of hydrate nucleation was shown to be classical-like, regardless of the overall non-classical molecular pathway.
- We propose a new mechanism for hydrate nucleation: **It is an entropically driven, kinetic process that proceeds via multiple pathways with nearly degenerate free energy profiles.**



References

- [1]: Yuanfei Bi Anna Porras and Tianshu Li, J. Chem. Phys. 145.21 (2016): 211909
- [2]: Rosalind.J. Allen, Daan. Frenkel, and Peter. R. ten Wolde, J. Chem. Phys. 124, 024102 (2006)
- [3]: Yuanfei Bi and Tianshu Li, J. Phys. Chem. B. 118, 167402 (2014)