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Effect of Solubility and Guest Size on Hydrate Nucleation

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Abstract

Our goal is to explore the feasibility of concurrently achieving energy recovery and carbon sequestration through replacing methane with CO₂ in naturally occurring gas hydrate. Toward this goal, one must understand the mechanisms of hydrate formation and particularly their variations with the change in the thermodynamic conditions.

In this research an advanced molecular simulation tool is used to understand how the size and solubility of the guest (gas) molecule would affect the nucleation mechanisms and kinetics at the molecular level.

Background

- Gas Hydrates are crystalline ice-like solids that consist of a particular gas molecule trapped within the frozen cages of water molecules (Fig. 1.)
- They form under low temperatures (<-300K) and elevated pressures (<-1000 bar).
- They are a vast energy resource: methane hydrate constitutes the world's most abundant reservoir of fossil fuels

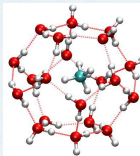


Fig. 1. Molecular structure of methane hydrate

Applications

- Potential energy resource
- Energy storage and transportation
- Hazards in petroleum industry: Methane hydrates form inside oil/gas pipelines causing severe safety and environmental concerns
- Climate change: methane is a green-house gas

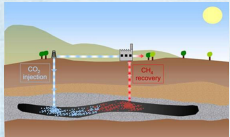


Fig. 2. Carbon sequestration
<http://www.themixolandwater.com>



Fig. 3. methane hydrate formation in oil pipeline
<http://www.rschem.com/solutions/flow-assurance-services>

Methodology

Yuanfei Bi and Tianshu Li, *Journal of Physical Chemistry B* 118, 13324 (2014)

1. Molecular Dynamics (MD)

- A computational approach to mimic molecules' behavior
- Experimental approach is not too effective: Nucleation occurs in a scale of **picoseconds** and **nanometers**

2. Forward Flux Sampling (FFS) (Allen et al., JCP 124, 024102 (2006))

- Accelerate brute-force MD
- Nucleation of clathrate from liquid to solid phase under a supercooled state is a rare event in nature. A nucleus needs to develop into a critical size before the crystallization process is energetically favorable

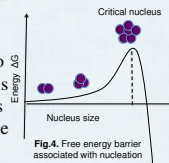


Fig. 4. Free energy barrier associated with nucleation

- Rate of nucleation:

$$k_{AB} = \frac{1}{\tau} P(n | 0)$$

3. Coarse-grained mW water model

(Moliner and Moore, *J. Phys. Chem. B* 113, 4008 (2009))

- Improves computational efficiency
- H₂O is modeled as a single particle favoring tetrahedral-bonded network.
- Guest size and solubilities are expressed in the model as medium (M) and large (L). Methane and carbon dioxide molecules are represented by (M) and (L) respectively.

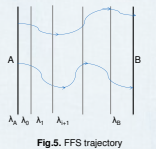


Fig. 5. FFS trajectory

Results

1. Nucleation Rate

Constant Pressure 500 bar	Medium (CH ₄)	Large (CO ₂)
270 K	*	7.20 ± 4.87 × 10 ²⁷
220 K	6.12 ± 2.56 × 10 ²⁷	*

*The nucleation rate at 270 K for the methane hydrate would be significantly smaller than that of CO₂ hydrate

2. Critical Size

- Represents the size where there is 50% of probability to grow.
- For the Large model at 270K the critical nucleus contains 370 water molecules.

3. Crystal Structure

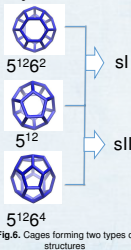
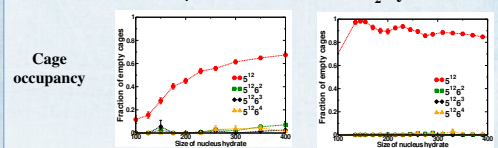


Fig. 6. Cages forming two types of structures

Results (continued)

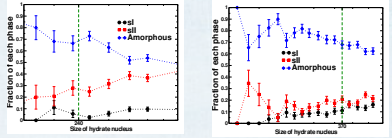
CH₄ hydrate

CO₂ hydrate



The occupancy of CO₂ in cages is significantly higher in hydrate nucleus than that in CH₄ hydrate.

Evolution of hydrate structure



The nucleation of both CO₂ and CH₄ hydrates proceeds with the formation of an amorphous nucleus, followed by a gradual transition to crystalline phase, which supports the two-step nucleation mechanism.

Conclusion

1. We have investigated the spontaneous nucleation of hydrates containing the large and soluble guest molecules by employing a novel computational approach recently developed in our group.
2. The nucleation behaviors of the L-hydrates were found to be at variance from that of methane hydrate, as a result of the enhanced solubility and size of the guest molecules.
3. Our work implies that the production of a specific gas hydrate phase may be potentially tuned through varying the solubility of the gas species in aqueous solution through controlling thermodynamic conditions.

Future Work

We will carry out molecular simulation to understand the kinetics of carbon sequestration and energy production, through gas replacement in hydrate.

Acknowledgement

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