A Comprehensive Molecular-Based Study of the Stability of clathrate Hydrates

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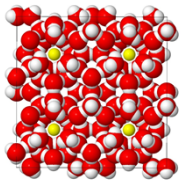
Introduction

1. Definition

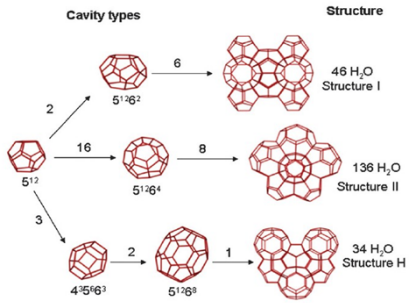
Clathrate hydrates are crystalline structures that consist of water molecules forming cages via a hydrogen-bonding network enclosing small guest molecules. Such structures normally form at a condition of high pressure and low temperature.



Yellow sphere represents the guest molecule and molecule with one red and two white spheres is represent the water.

2. Structure

Gas hydrates usually form three crystallographic cubic structures: structure I and structure II and Structure H. Each type are formed of two or three small cages:



The three common clathrate hydrate structures, including the constituent cavities. Nomenclature: $5^{12}6^8$indicates 12 pentagonal and 8 hexagonal sides in a cavity; numbers along lines indicate the number of cavities in each unit crystal structure. The rightmost numbers indicate the water molecules per crystal structure

http://www.globalspec.com/reference/55602/203279/2-what-are-natural-gas-clathrate-hydrates

Motivation

1.Solve the blockage in the oil pipelines.

The formation of clathrate hydrate becomes the main reason of blockage in the pipelines which could result in the suspension of gas and oil production.

www.radhanathswamionline.com/event

2. Recovery of huge potential energy

The global resource of methane in gas hydrate deposits in commonly cited as 20,000 trillion m^3 making gas hydrates itself contain more energy than any other forms of energies we exploit today.

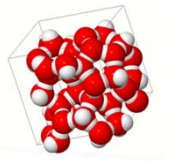
www.chem.ntnu.nononequilibrium-thermodynamicsindex522b.htm

3. Clathrate hydrate also has other applications in refrigeration, desalination and transportation.

Solid-fluid secondary refrigerants have higher energy efficiency in refrigeration. Advances are reported in several aspects of clathrate hydrate desalination fundamentals necessary to develop an economical means to produce municipal quantities of potable water from seawater. Using clathrate transport gas like H_2 would be safer and more efficient by reducing pressure and increasing temperature.

Method

1. Use harmonic analysis to find the free energy of clathrate hydrate with all cages vacant when temperature→ 0.



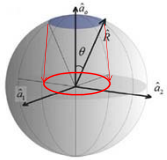
2. Introduce harmonically targeted temperature perturbation (HTTP) method to evaluate the free energy with increasing temperature.

The basic perturbation theory working equation:

$$e^{-\delta(\beta \mathrm{Ac})} = < e^{-(\beta^+ \mathrm{U}^+ - \beta U)} > \qquad U^+ = U + \frac{dU}{dT}\delta T$$

For translation: $\sum_{i=1}^{3} \frac{dU_i}{dr_i}\frac{dr_i}{dT} = \sum_{i=1}^{3} \frac{r_i}{2T}\frac{dU_i}{dr_i}$ r_i – *translation displacement*

For rotation, however, it's not so straightforward. we introduce alternative coordinates (K_1, K_2) defined in terms of the projection of the molecule's orientation R onto the plane perpendicular to a_0.in particular,



$\hat{a}_0$ = *nominal orientation*

$\hat{\mathrm{R}}$ = *molecular orientation*

$$\kappa_1 = \kappa(\hat{\mathrm{R}} \bullet \hat{a_1}) \qquad \kappa_2 = \kappa(\hat{\mathrm{R}} \bullet \hat{a_2})$$

where $\kappa = 2\sin(\theta/2)/\sin(\theta)$

So that $\sum \frac{dU_i}{d\kappa_i}\frac{d\kappa_i}{dT} = \sum \frac{\kappa_i}{2T}\frac{dU}{d\kappa_i}$

Former case is only for linear and for nonlinear molecules like water, we need to use the same idea in 4D quaternion space:

$$\hat{\mathrm{R}} = q_0 + q_1\hat{i} + q_2\hat{j} + q_2\hat{k} \qquad \text{or} \qquad \hat{\mathrm{R}} = \cos\theta + \sin\theta\hat{u}$$

in which θ is **half** of the **overall rotation angle** α $(\theta = \alpha/2)$

$$\kappa_1 = \kappa(\hat{\mathrm{R}} \bullet \hat{a_1}) \quad \kappa_2 = \kappa(\hat{\mathrm{R}} \bullet \hat{a_2}) \quad \kappa_3 = \kappa(\hat{\mathrm{R}} \bullet \hat{a_3}) = \kappa q_3$$

where $\kappa = \sqrt[3]{\frac{3}{4}(2\theta - \sin 2\theta)/\sin\theta}$

Combining the translation and rotation and a long calculation

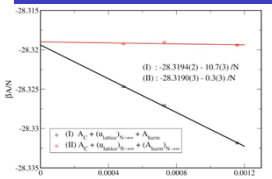
$$\frac{\delta(\beta \mathrm{A_c})}{\delta T} = -<\frac{U}{kT^2} + \frac{\sum \vec{F_i} \bullet \vec{r_i}}{2kT^2} - \frac{3}{2kT^2}\frac{\alpha - \sin\alpha}{1 - \cos\alpha}\frac{dU}{d\alpha}>$$

3. Conduct additional molecular simulations to gauge the dependence on composition and/or pressure by integration along μ_S

4. With the knowledge of free energy we can identify the stable crystalline form and locate the conditions where phase transitions occur.

$d(\beta N_w \mu_w)$=Hd$\beta - \beta dP - N_s d\beta\mu_s + \beta\mu_w dN_s$

Advantages



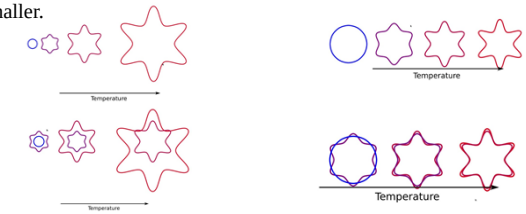
1. few system size dependence

Dependence of free-energy contributions on the size of the simulated

Tan, T. B.; Schultz, A. J.; Kofke, D. A., *J. Chem. Phys.* **2011,** *135* (4), 044125.

2. Much more precise than FEP theory

When temperature is 0, we could do the harmonic analysis (configuration space is circle). But when temperature get higher, system become enharmonic(not circle) and configuration space increases rapidly with temperature. If we do the scaling, difference would be smaller.



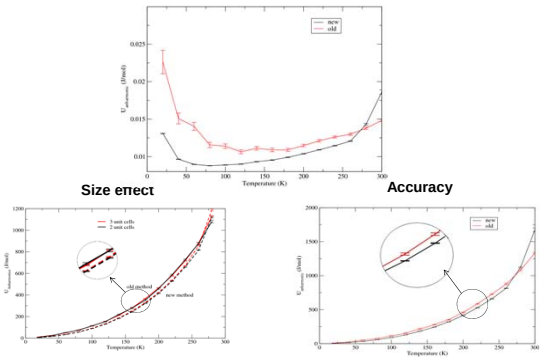
Temperature perturbation method. Measuring ΔβA with perturbation fails

http://rheneas/~andrew/http/HTTP.xhtml

HTTP method. Scale out the change in size we expect

http://rheneas/~andrew/http/HTTP.xhtml

Preliminary Result



References

1. Tan Tai Boon, A. J. Schultz, and D. A. Kofke, 'Efficient Calculation of - and -Nitrogen Free Energies and Coexistence Conditions Via Overlap Sampling with Targeted Perturbation', *Journal of Chemical Physics*, 135 (2011), 044125 (13 pp.).

2. T. B. Tan, A. J. Schultz, and D. A. Kofke, 'Efficient Calculation of Temperature Dependence of Solid-Phase Free Energies by Overlap Sampling Coupled with Harmonically Targeted Perturbation', *Journal of Chemical Physics*, 133 (2010).

Acknowledgements

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