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Applications of Computer Simulations to research in Sustainable Energy: what can we learn from computer simulations

(Part 2)

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Part II

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To recap:

Major techniques

- *Classical molecular dynamics*

  Classical equations of motion with given interactions

- *Monte-Carlo simulations*

  Probabilistic techniques to study statistical behaviour

- *Ab initio (total energy) calculations*

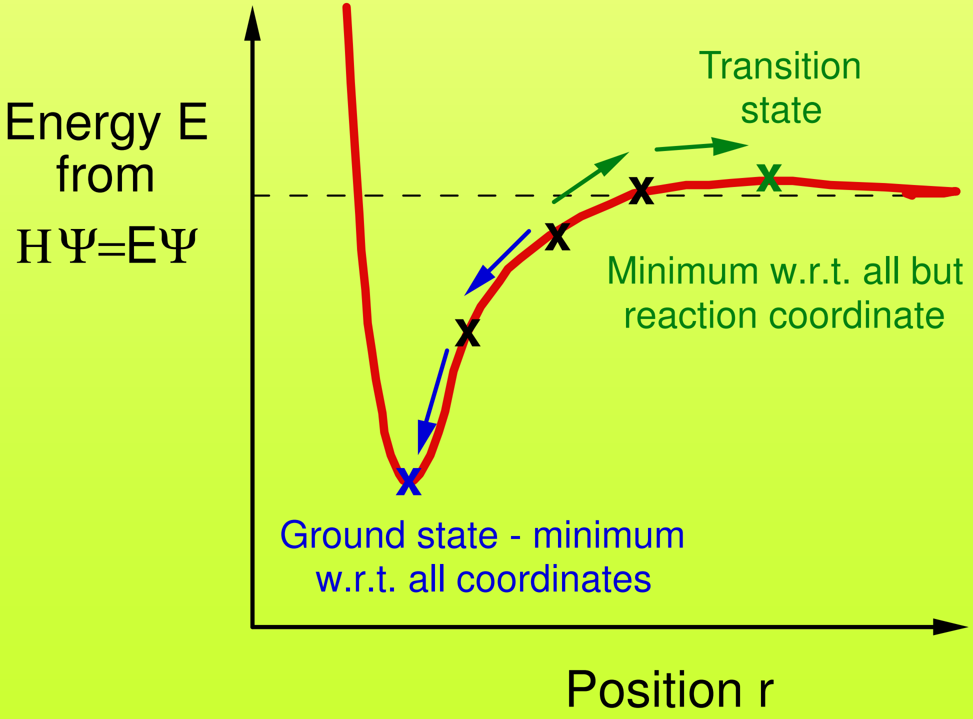
Quantum mechanical approach. Density functional theory

- *Ab initio molecular dynamics.*

  Combine computation of ab initio energy and forces with classical equations of motion for the nuclei.

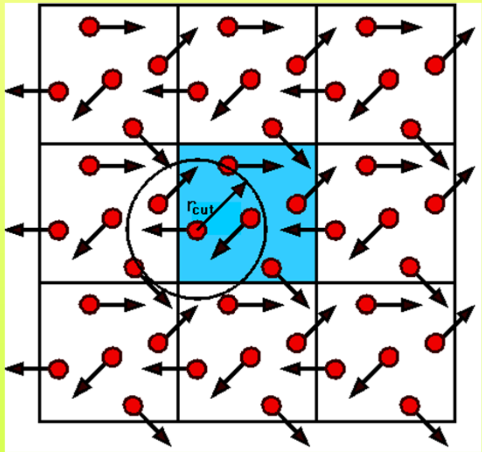
What comes out of ab initio calculations?

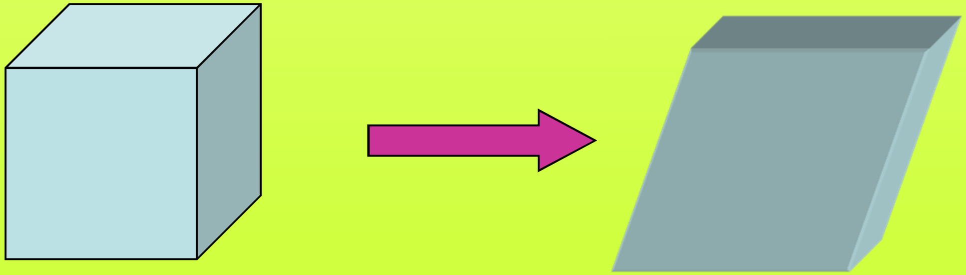
- Energies, structures optimized with respect to energy, harmonic frequencies, and other properties based on zero-kelvin electronic structures.
- Interpret with theory to get derived properties and properties at higher temperatures.



What to watch:

- *Classical molecular dynamics : Potential model*
  Length of simulation
  Monte-Carlo simulations: Potential model
- *Density functional calculations:*
  - *Plane wave cut-off*
  - *Size of the computational unit*
  - *Relaxation constraints*
  - *Appropriate technique*

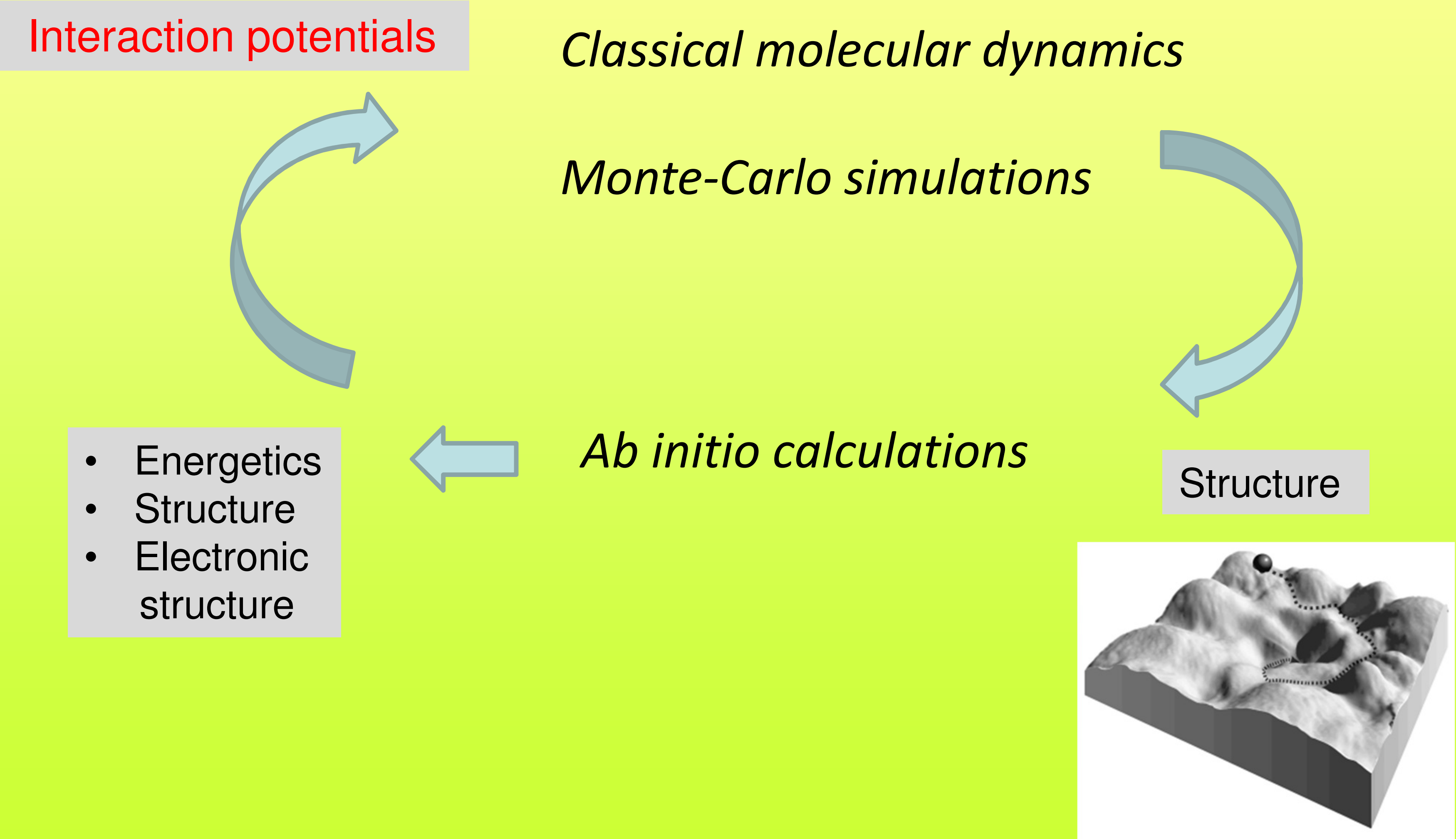




Shape
Symmetry →

Structural phase change

To recap:



Interaction potentials

Classical molecular dynamics

Monte-Carlo simulations

Ab initio calculations

Structure

- Energetics
- Structure
- Electronic structure

Monte Carlo Simulation

Helmholtz free energy F=E-TS for a system of N (rigid) molecules with positions r_i *and orientations* Ω_i *in a volume V interacting through a potential function* $U(\mathrm{r}_1,\ldots\ldots,\mathrm{r}_N,\Omega_1,\ldots,\Omega_N)$ **is, apart from trivial factors, given by:**

$$F(N,V,T) = -k_B T \ln Q(N,V,T)$$

T *is the temperature and* k_B *is Boltzman's constant*

Q(N,V,T) *is the configurational integral*:

$$Q(N,V,T) = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \int d\mathbf{\Omega}_1 \cdots d\mathbf{\Omega}_N e^{-\beta U}$$

$\beta=(k_B T)^{-1}$

Monte Carlo Simulation

Configurations of the system are distributed according the Boltzman factor:

$$P\left(\mathbf{r}_1,\cdots,\mathbf{r}_N;\mathbf{\Omega}_1,\cdots,\mathbf{\Omega}_N\right) \propto \exp\left(-\beta U\left(\mathbf{r}_1,\cdots,\mathbf{r}_N;\mathbf{\Omega}_1,\cdots,\mathbf{\Omega}_N\right)\right)$$

Thermodynamic quantities are averages over the Boltzman distribution, e.g.

$$\left\langle U\right\rangle = \int d\mathbf{r}_1\cdots d\mathbf{r}_N\int d\mathbf{\Omega}_1\cdots d\mathbf{\Omega}_N U\left(\mathbf{r}_1,\cdots,\mathbf{r}_N;\mathbf{\Omega}_1,\cdots,\mathbf{\Omega}_N\right)P\left(\mathbf{r}_1,\cdots,\mathbf{r}_N;\mathbf{\Omega}_1,\cdots,\mathbf{\Omega}_N\right)$$

A chain of configurations is generated on the computer with the probability of a configuration given by the Boltzman distribution. Thermodynamic quantities are computed as averages over this chain of configurations.

- **To recap**:

Intercalation compounds

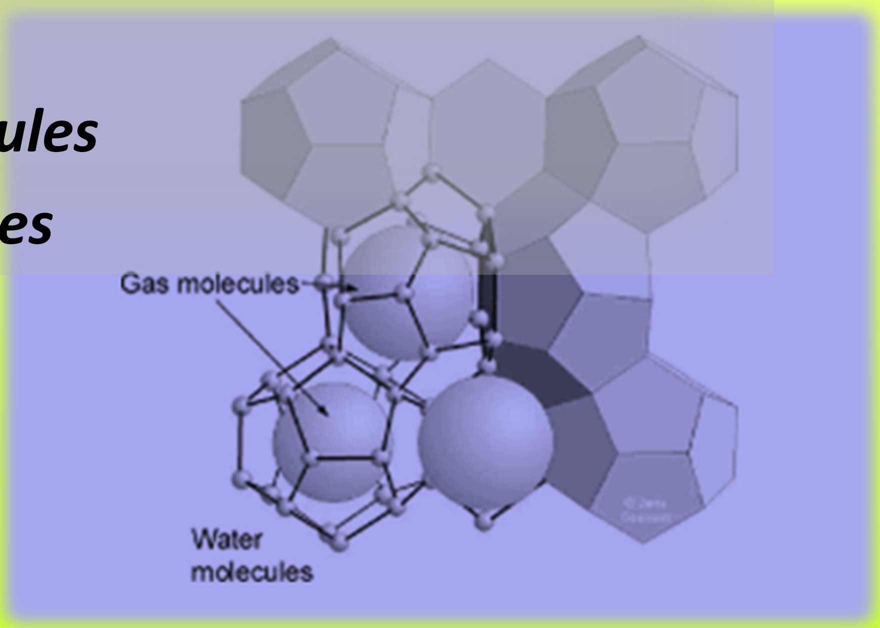
- Reversible uptake of guest ions
- Interactions between the host and the guest: charge transfer. Hence distortions of the host, phase transformations
- Goals: high concentrations of intercalated ions;
  fast kinetics

Output of calculations:

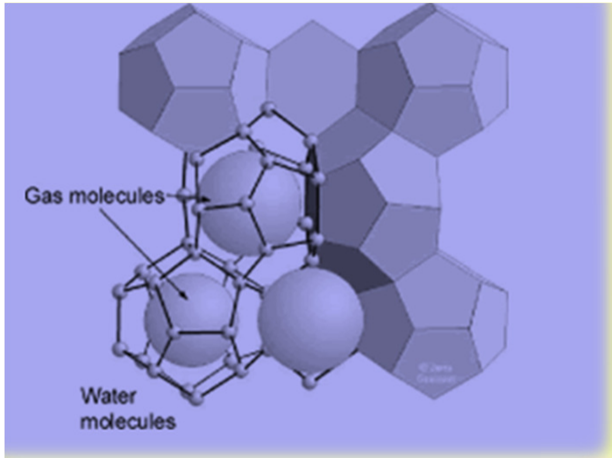
- max insertion concentration
- structure and phase transformations
- electronic structure
- Frequencies
- Quantities of interest (for instance, voltage)

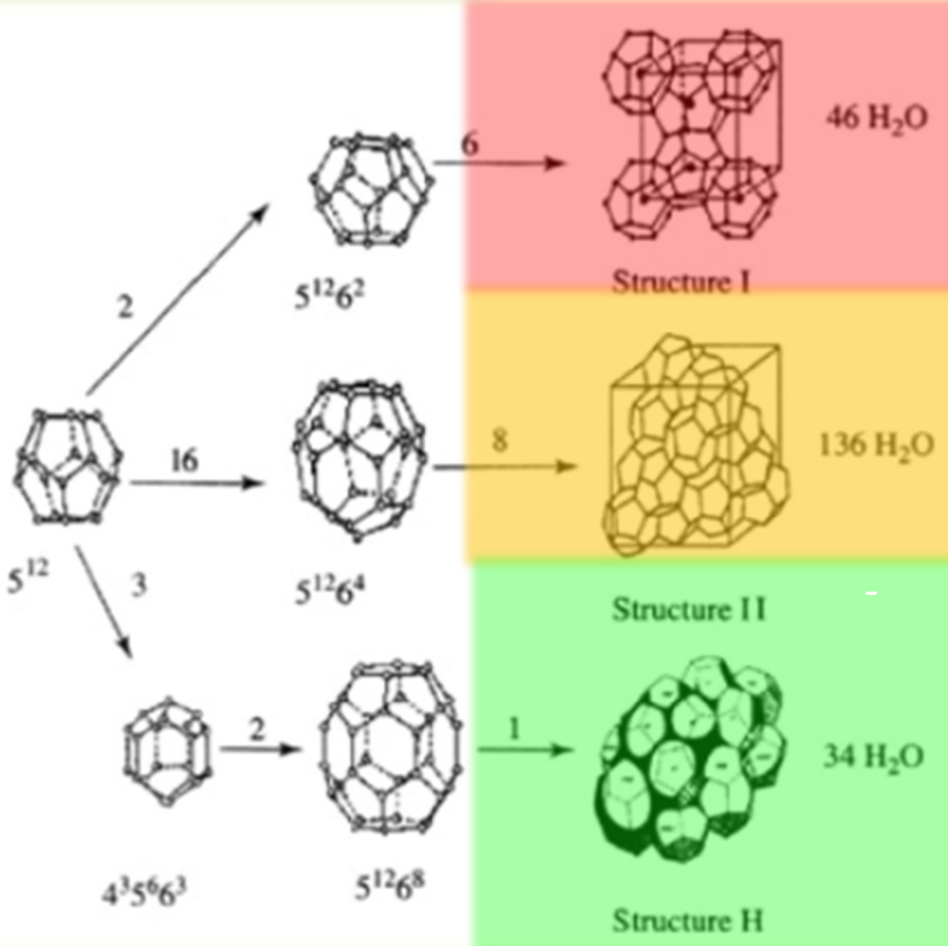
Modelling of hydrogen storage in clathrate hydrates

- *Inclusion compounds with a cage structure*
- *Hydrogen bonded network of H_2O*
- *Ice rules*
- *One or more guest molecules*
- *Contain different size cages*



Clathrate hydrates: known Structures





Cubic;

two types of cages;

most common small guest molecules (CH_4)

Cubic;

two types of cages;

larger guest molecules in large cages (C_2H_6, CH_3OCH_3,THF)

Hexagonal;

large, medium and small cages

***large molecules** in medium and large cages (THF, dodecane)*

***small molecules** (H_2, CH_4) in small,*
medium and large cages

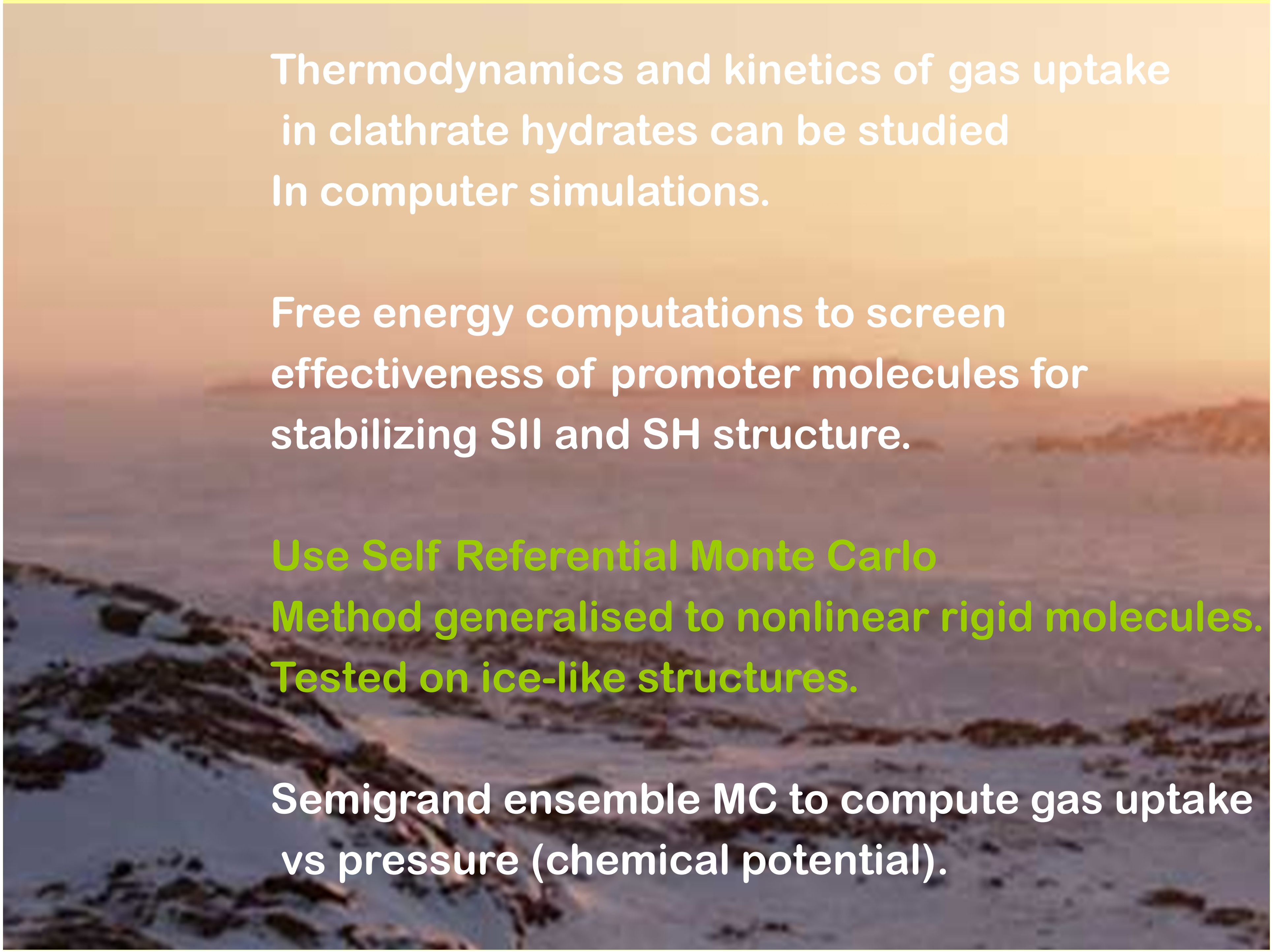
Natural occurence

Natural clathrate hydrates store methane and carbon dioxide in Siberia (permafrost) and in Ocean bed

Technological Relevance

- The major problem in offshore energy development.
- Storage of gas (biofuels (methane)), CO_2 sequestration
- Hydrogen storage:

only at extremely high pressure (>180 Mpa)
or stabilized by 2nd guest (promoter) molecule (e.g. THF).
However, large hydrogen content (> 5% wgt) and environmentally friendly.

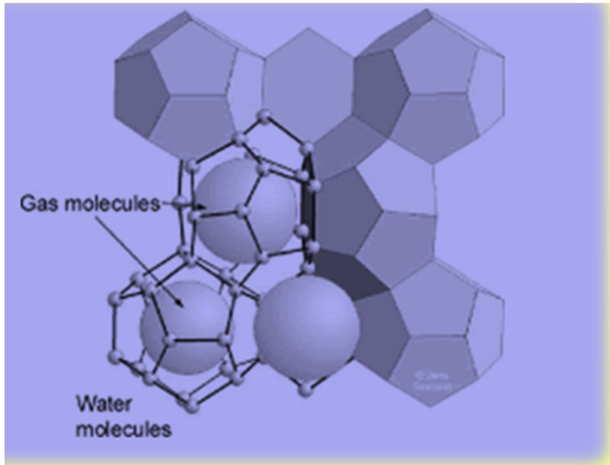


Thermodynamics and kinetics of gas uptake
in clathrate hydrates can be studied
In computer simulations.

Free energy computations to screen
effectiveness of promoter molecules for
stabilizing SII and SH structure.

Use Self Referential Monte Carlo
Method generalised to nonlinear rigid molecules.
Tested on ice-like structures.

Semigrand ensemble MC to compute gas uptake
vs pressure (chemical potential).



Open questions

Stability of clathrate structures

energy minimization, vibrational properties
how many guest molecules are required to stabilize lattice

Optimal promoter molecule

THF extensively studied, are there other possibilities?
For sII THF appears the best promoter!

Optimal composition

Monte Carlo simulation to determine occupancy vs. P,T

New structures with “ice-rules”

Thermodynamic integration

Non-ideal part of the free energy of a crystalline solid composed of N particles is given by:

$$F = -k_B T \ln(Q(N,V,T)) = -k_B T \ln\left(\frac{\int_{V'} d\mathbf{r}^{N-1} \exp(-\beta U(\mathbf{r}^N))}{N} \right)$$

Thermodynamic integration: energy *U* depends on a parameter *λ.* e.g. ***$U=U_0+\lambda U_1$***. Then:

$$\left(\frac{\partial F(\lambda)}{\partial \lambda} \right) = \frac{1}{\beta} \frac{\partial}{\partial \lambda} \ln(Q(N,V,T,\lambda)) = \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{\lambda}$$

and the free energy change if *λ* changes from ***λ_o*** to ***λ_f*** is:

$$\boxed{\Delta F = F(\lambda_f) - F(\lambda_o) = \int_{\lambda_0}^{\lambda_f} d\lambda \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{\lambda}}$$

Self Referential Monte Carlo Method

Free energy is extensive: **$G(2N)=2G(N)$**

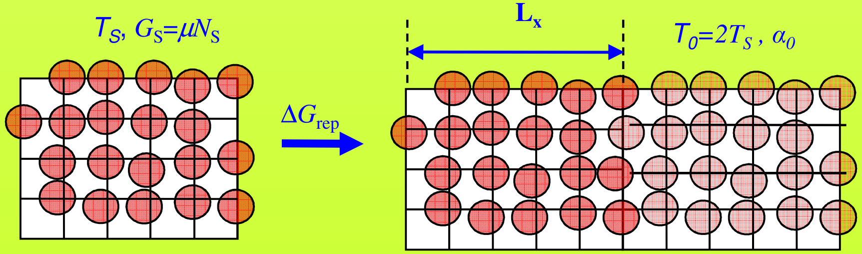
In SR Monte Carlo a path is constructed from a system of size N to a system of size 2N, so that **$G(2N)-G(N)$** *can be calculated and hence* **$G(N)$**

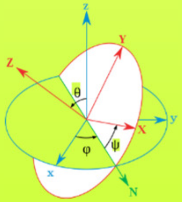
Two stages: **replication** *and* **relaxation**

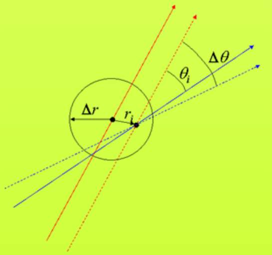
Replication

produces a 'self-similar' constrained double-sized system at a temperature ***$2T_S$*** *by doubling the* ***size*** *and the* ***number of particles*** *in the simulation.*

$$r_i = \left|\left(\mathbf{r}_{i+N_s} - \mathbf{L}_x\right) - \mathbf{r}_i\right| \le \Delta r$$







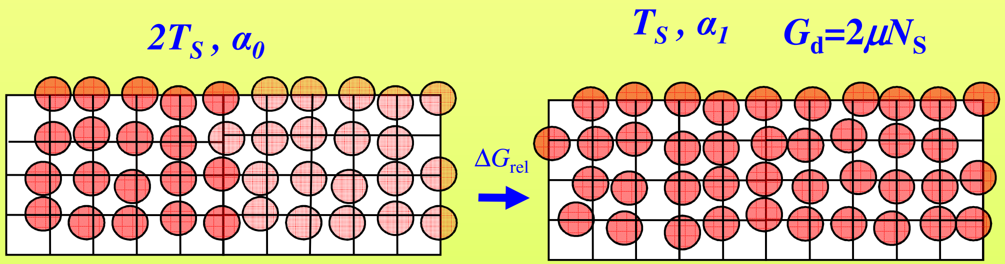
$$0 \le \phi \le 2\pi \quad -\pi \le \varphi_i \le \pi$$

$$\left|\phi_i\right| \le \Delta\phi \quad \theta_i \le \Delta\theta$$

Self Referential Monte Carlo Method

Relaxation

allows the coordinates of the newly created particles to relax fully from their initial highly constrained values, while also reducing temperature back to T_S



$$G_s = G_d - G_s = \Delta G_{rep} + \Delta G_{rel}$$

*The relaxation is controlled by a parameter α, which increases gradually from a value α_1 to α_m in a number of steps. As α increases the temperature decreases from **$2T_s$** to **T_s**. At the same time the positional and orientational constraints are relaxed to a stage, where they are no longer '**felt**' by the system.*

Self Referential Monte Carlo Method

Calculations are performed in the canonical ensemble (NVT)
Application to nonlinear rigid molecules using thermodynamic integration

$$\Delta\beta F = (\Delta\beta F)_{rep} + (\Delta\beta F)_{rel}$$

The free energy change $\Delta(\beta F)_{\mathrm{rep}}$ *due to the replication can be calculated analytically if the temperature of the constrained double-sized system is* $2T_s$*:*

$$\Delta(\beta F)_{rep} = \frac{F_{\alpha_1}}{k_B T_{\alpha_1}} - \frac{F_s}{k_B T_s} = -\ln\left(\frac{Q_{\alpha_1}}{Q_s}\right) = -N_s \ln\left(\frac{V_{r_1}\hat{\eta}_1\hat{\kappa}_1}{8\pi^2}\right)$$

Q_d *and* Q_s *are the configurational integrals of the double and single sized systems respectively,* $\hat{\eta}_1, \hat{\kappa}_1$ *are the initial constraints on the orientational angles and* $V_{r_1} = 4\pi\alpha_1^3/3$

Self Referential Monte Carlo Method

The free energy change $\Delta(\beta F)_{rel}$ *is obtained through thermodynamic integration:*

$$(\Delta\beta F)_{rel} = \int_{\alpha_0}^{\alpha_1} d\alpha \frac{d(\beta F(\alpha))}{d\alpha} = \int_{\beta_s/2}^{\beta_s} d\beta \langle H \rangle + (\Delta\beta F)_r + (\Delta\beta F)_\theta + (\Delta\beta F)_\varphi$$

Evaluating the different contributions we obtain:

$$\Delta(\beta F_{rel}) = \int_{\beta_s/2}^{\beta_s} d\beta_\alpha \langle U_\alpha \rangle - 4\pi N_s \int_{\ln(\hat{r}_1)}^{\ln(\hat{r}_m)} d\ln(\hat{r}) g_r(\hat{r},\hat{r})\hat{r}^3 - N_s \int_{\ln(\hat{\eta}_1)}^{\ln(\hat{\eta}_m)} d\ln(\hat{\eta}) g_\xi(1-\hat{\eta},\hat{\eta})\hat{\eta} -$$

$$N_s \int_{\ln(\hat{\kappa}_1)}^{\ln(\hat{\kappa}_m)} d\ln(\hat{\kappa}) g_\kappa(\hat{\kappa},\hat{\kappa})\hat{\kappa}$$

The g's are distribution functions for pairs of replica's. $g_r(r',\hat{r})$ *is the probability of finding a replica pair at a reduced distance* $r' = |\Delta\mathbf{r} - \mathbf{L}_x|$ *when the positional constraint is* $\hat{r}(\alpha)$.

Similarly $g_\xi(1-\eta,\hat{\eta})$ *and* $g_\kappa(\vartheta,\hat{\kappa})$ *are probability distribution for their relative orientations* $\eta = \cos\xi$ *and* ϑ*, when the constraints are* $\hat{\eta}$ *and* $\hat{\kappa}$ *respectivily.*

Simulation details

Monte Carlo simulations for free energy in NVT ensemble:

- Cubic ice
- Hexagonal ice
- Ice VII
- empty/full sI
- sII (THF + H2)
- sH

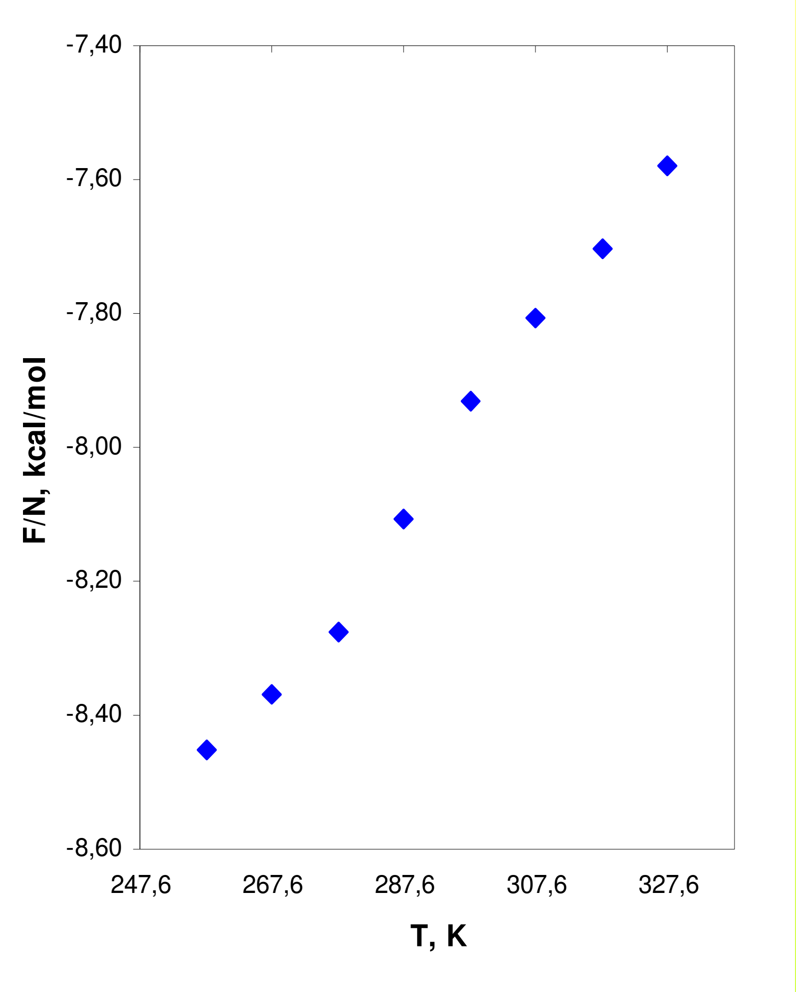
Interaction energy: Lennard-Jones+ Electrostatic between sites

$$U = 4\sum_{i>j}^{N}\sum_{ab}\varepsilon_{ab}\left[\left(\frac{\sigma_{ab}}{r_{ij}^{ab}}\right)^{12} - \left(\frac{\sigma_{ab}}{r_{ij}^{ab}}\right)^{6}\right] + \sum_{i>j}\sum_{ab}\frac{q_i^a q_j^b}{4\pi\varepsilon_0 r_{ij}^{ab}}$$

$r_{ij}^{ab} = \left|\mathbf{r}_i^a - \mathbf{r}_j^b\right|$ *is the distance between site* ***a*** *on molecule* ***i*** *and site* ***b*** *on molecule* ***j.***

Long range electrostatic interactions are treated using Ewald sums

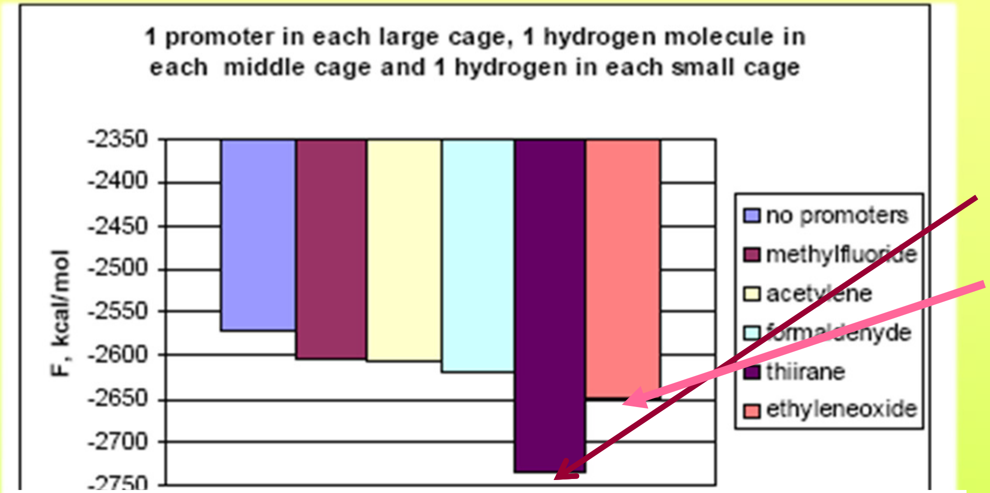
Free energy of sII filled with THF and H_2



*Temperature dependence of the free energy of **sII** with **THF** promoters in **big** cages and **hydrogen** molecules in **small** cages*

Screening promoters for sH

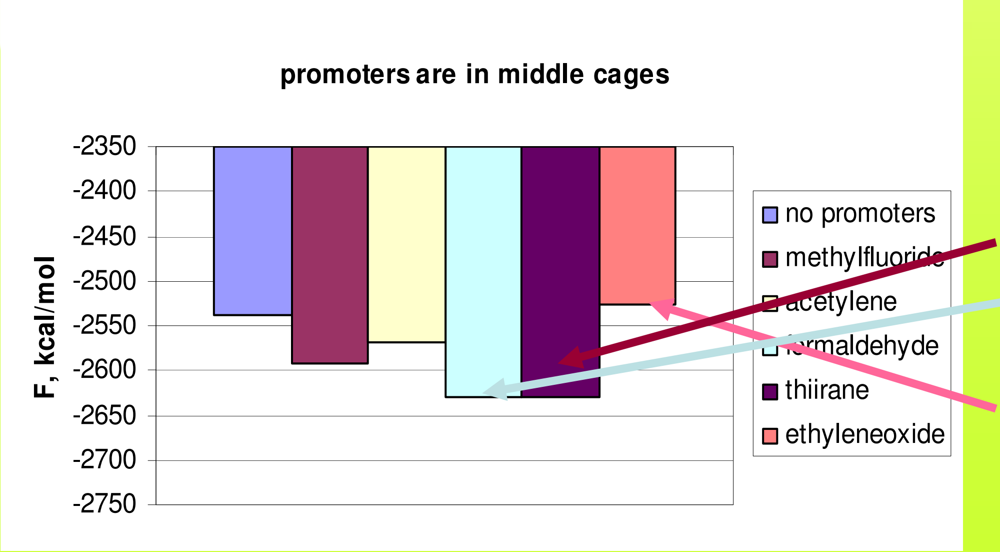
Free energies of sH clathrate hydrate filled in part with hydrogen (in small and medium or large cages) at ***T=253 K*** *and* ***P=50 MPa***



Large cages filled with promoters

Thiirane *performs best.*

Ethyleneoxide *(CH_3OCH_3) 2nd best*



Middle cages filled with promoters

Thiirane *and* ***formaldehyde*** *perform equally well.*

Ethyleneoxide *(CH_3OCH_3) not so good.*

Free energy of partially filled clathrates

In ***semigrand*** *Monte Carlo simulations*

temperature ***T***
pressure ***P***
number of water molecules N_w
guest molecule chemical potential μ_p

are fixed

The number of guest (promoter, hydrogen) molecules N_p *is determined by the chemical potential* μ_p

The chemical potential of water is obtained through the ***Gibbs-Duhem*** *relation.*

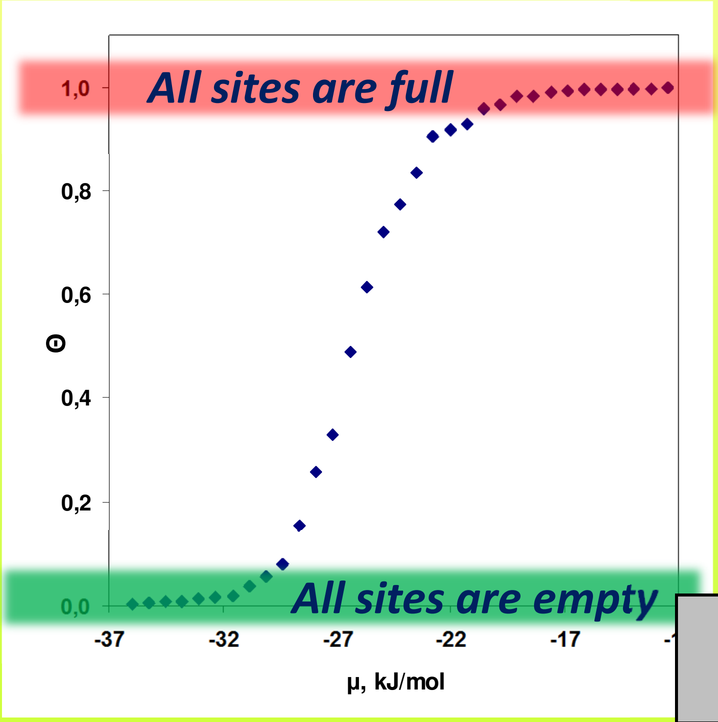
$$-SdT + VdP - N_p d\mu_p - N_w d\mu_w = 0 \quad \Rightarrow$$

$$\mu_w = \mu_w^0 - \frac{1}{N_w} \int_{\mu_p^0}^{\mu_p} N_p \, d\mu'_p \qquad \text{at constant } \boldsymbol{T,P}$$

Free energy of partially filled clathrates

Free energy is given by:

$$F = \mu_p N_p + \mu_w N_w = \mu_p N_p + \mu_w^0 N_w - \int_{\mu_p^0}^{\mu_p} N_p \, d\mu_p^{'}$$

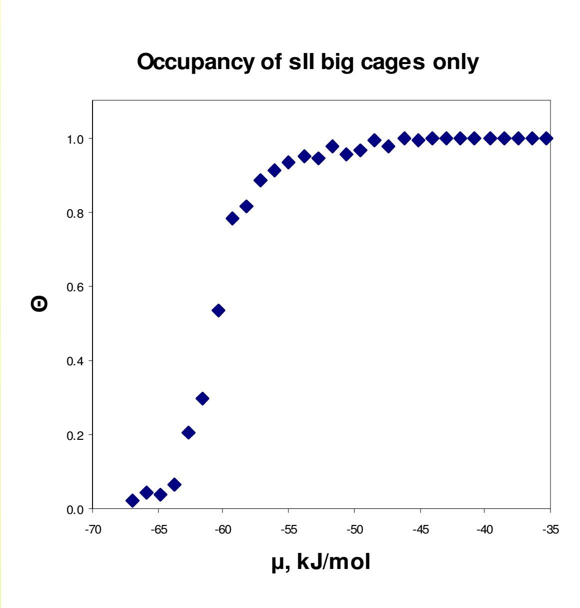


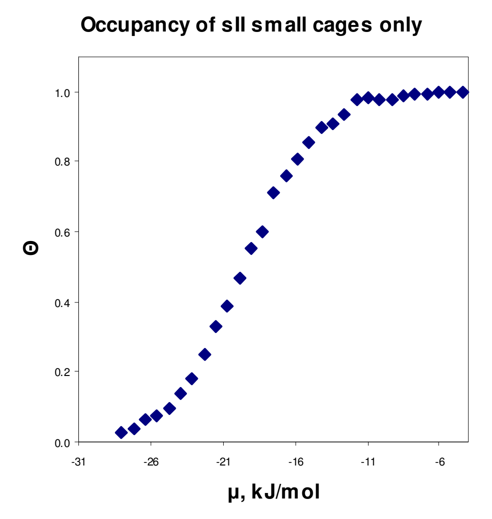
Fractional occupancy of the sI methane hydrate vs. chemical potential from a semigrand ensemble simulation at ***T=241.5 K*** *and* ***P=102.9 bar****.*

Free energy at end points computed with Self Referential method.

	F/N, kJ/mol Our results	F/N, kJ/mol Monson's results*
zero ocupancy sI hydrate (SR)	-38.81±0.05	-38.66(6)
full hydrate (SR)	-35.63±0.06	-35.70(5)
full hydrate (TI)	-35.57±0.04	-35.67(5)

Free energy of sII filled with THF and H2

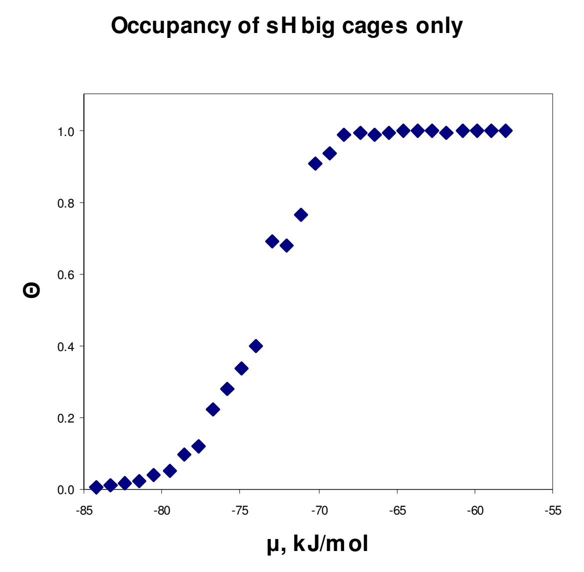


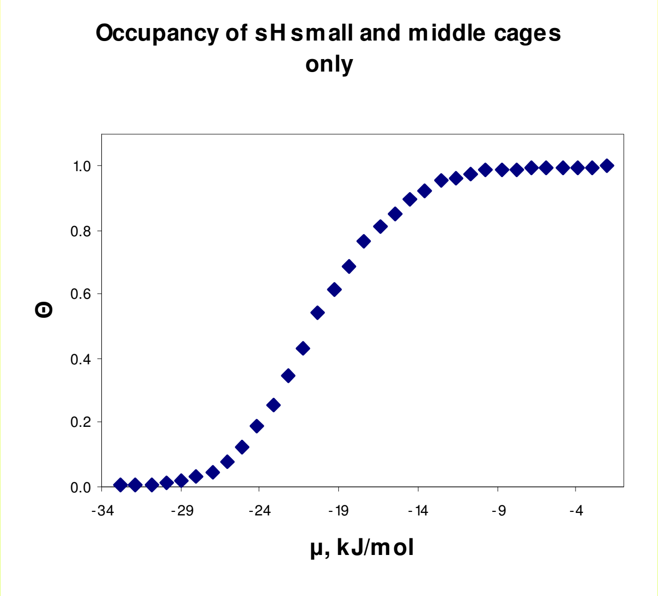


Fractional occupancy for the sII hydrate vs the chemical potential at ***T=253 K*** *and* ***P=100 bar***

	F, kJ/mol
zero ocupancy sII hydrate (SR)	-4420.00±6.8
full hydrate (TI)	-5204.21±6.8

Free energy of sH filled with thiirane and H_2





Fractional occupancy for the sH hydrate vs the chemical potential at ***T=273.15 K*** *and* ***P=500 bar***

	F, kJ/mol
zero ocupancy sH hydrate (SR)	-10078.46±10.88
full hydrate (TI)	-11316.46±13.6

Conclusions

- the SR technique is adapted to rigid nonlinear molecules
- good agreement with existing reference
- the method is applied to clathrate hydrate structures containing hydrogen and/or second guest molecules
- for SII hydrate THF appears to be the best promoter
- thiirane stabilizes the large cages the best. When the small and large cages are filled with hydrogen, thiirane and formaldehyde perform roughly equaly as promoters
- semigrand Monte Carlo technique was tested on sI and applied to sII and sH to determine hydrogen uptake.

Ab initio simulations in combination with statistical treatment is a powerful technique to investigate materials for sustainable energy applications.

Simulations are complimentary to the experimental and theoretical studies, so that considerable interactions are requiered!