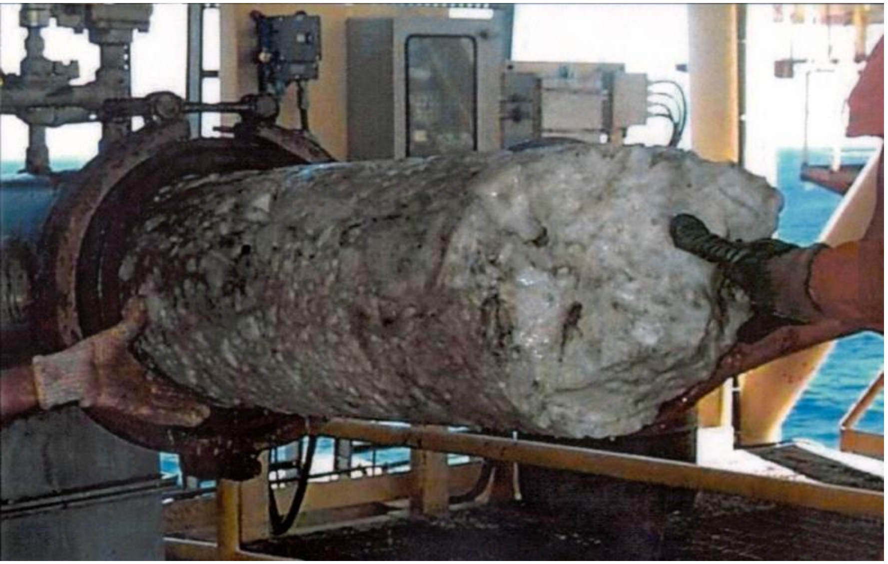
Impact of rusty pipelines on risk of hydrate formation

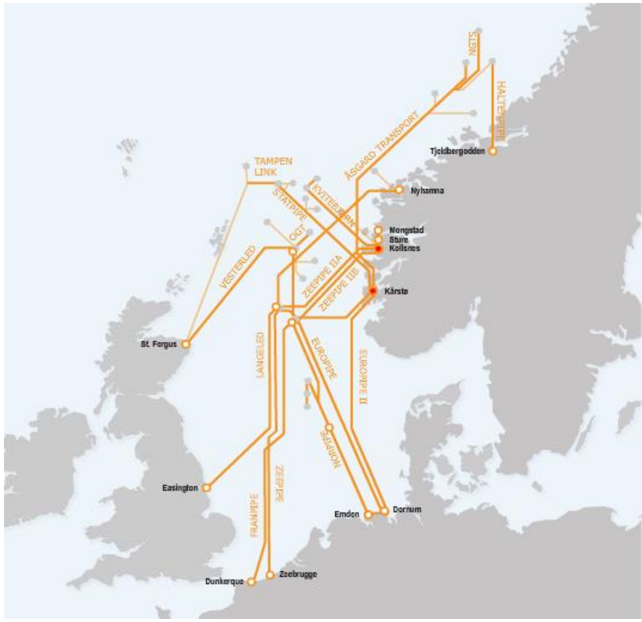
2nd World Congress on Petroleum and Refinery June 1-3, 2017



There are 7800 km of pipelines on the seafloor of the North Sea

The pipelines are rusty even before they are placed out

Hematite is one of the most stable forms of rust



Hydrate plugging is an old story and strategies for avoiding problems have changed over the decades. Bur regardles of strategy we need to understand how and how fast they form; whether we have a risk based strategy, inject chemicals or others. Picture is from internet and is a plug from a Brazil pipeline.

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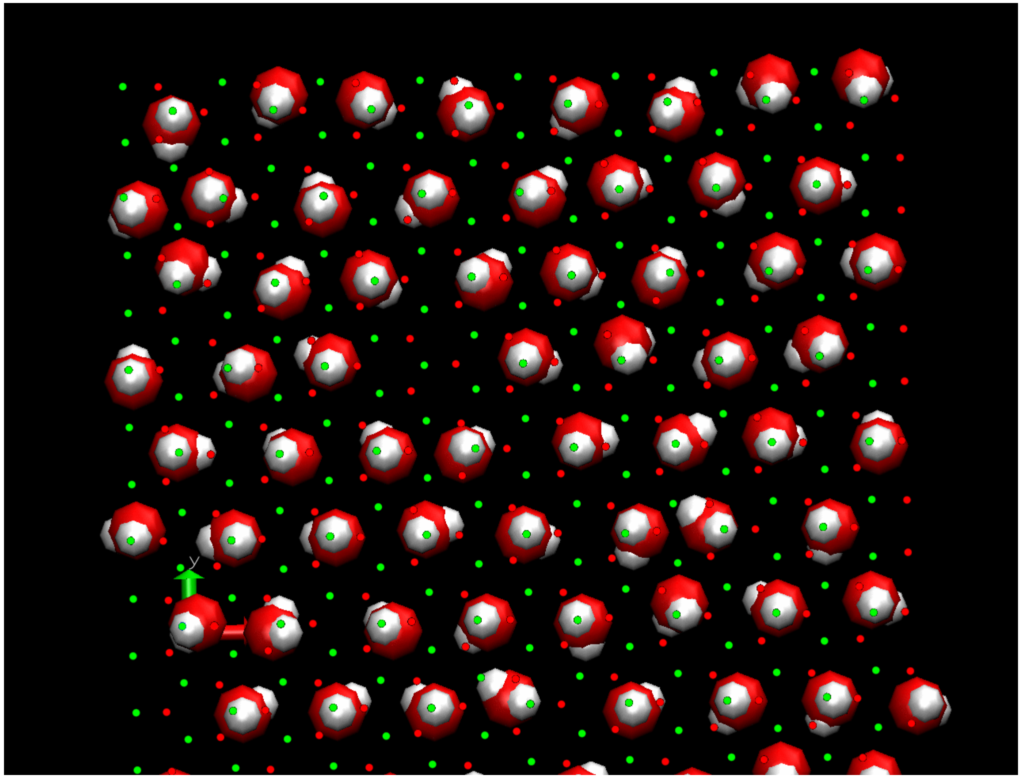
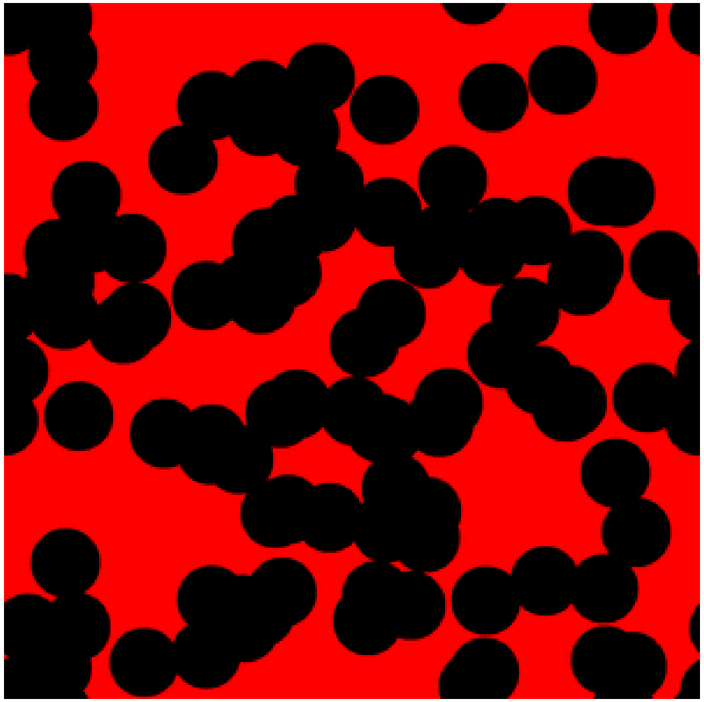
Motivation



	H2O Chemical Potential
H_2O Kluster$_{v/245K}$	-50,7 kJ/mol
H_2O Hematitt$_{v/245K}$	-54,7 kJ/mol
H_2O Kluster$_{v/278K}$	-52,8 kJ/mol
H_2O Hematitt$_{v/278K}$	-56,2 kJ/mol

Adsorbed Water chemical potential may be in the order of 3.4 kJ/mole lower than liquid water so technically it is a hydrate inhibitor

But direct and indirect (note the dynamic «pockets») adsorption of hydrate formers pluss beneficial heterogeneous hydrate nucleation makes these solid pipeline surfaces very active in hydrate phase transition dynamics

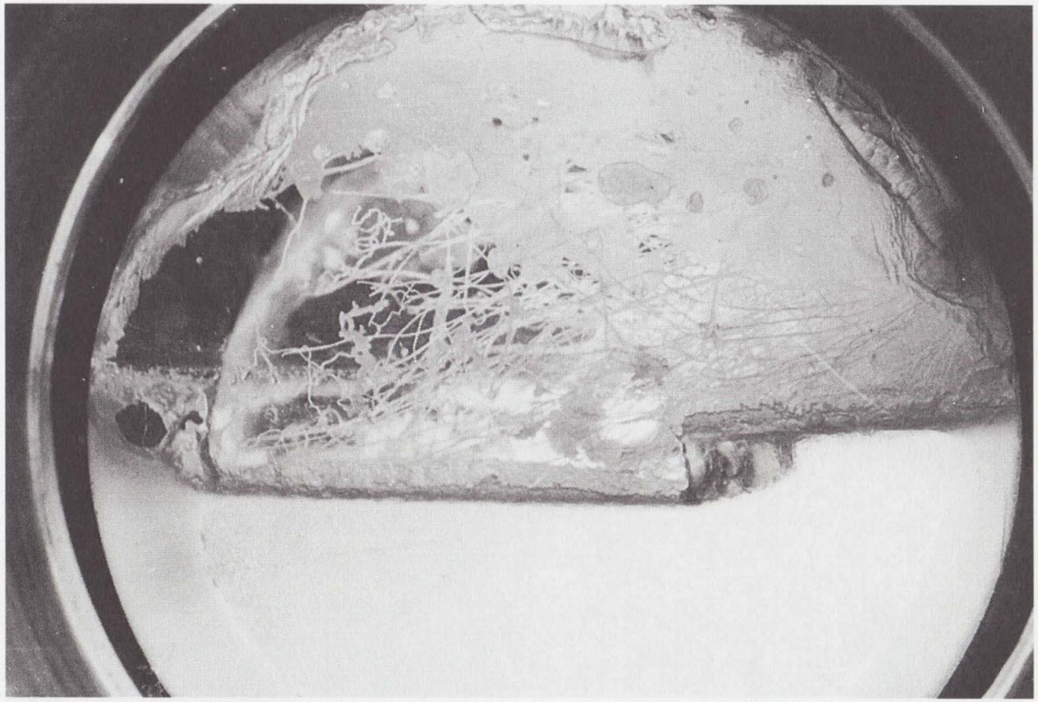


Solid surfaces promote hydrate formation on nano to micro scale though directional mass transport constraints in inclinements. Illustration (yellow) is for hydrate growing from aqueous (red) solution. Black circles are neutral particles

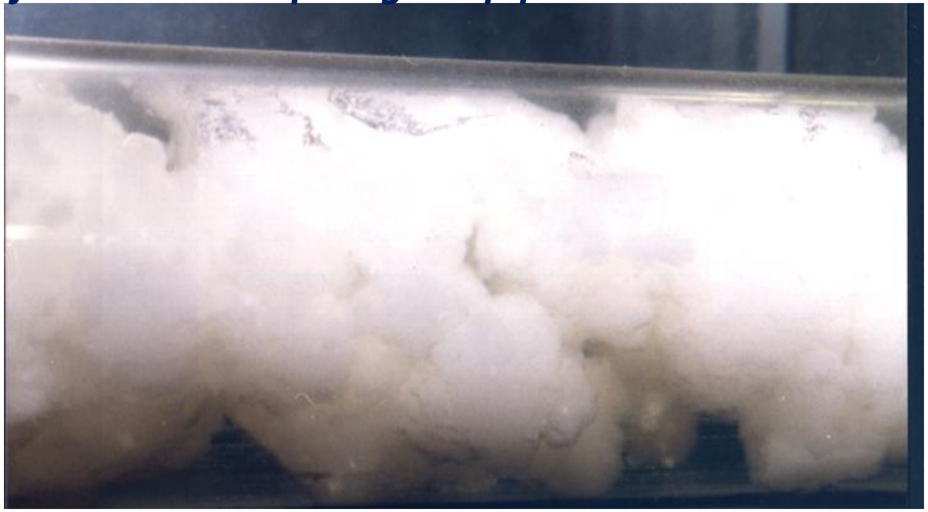
Motivation cont.

→ So if rust promotes nucleation of hydrate – can we somehow quantify the impact ?

→ Or can we circumvent the prblem with plastic coating ?



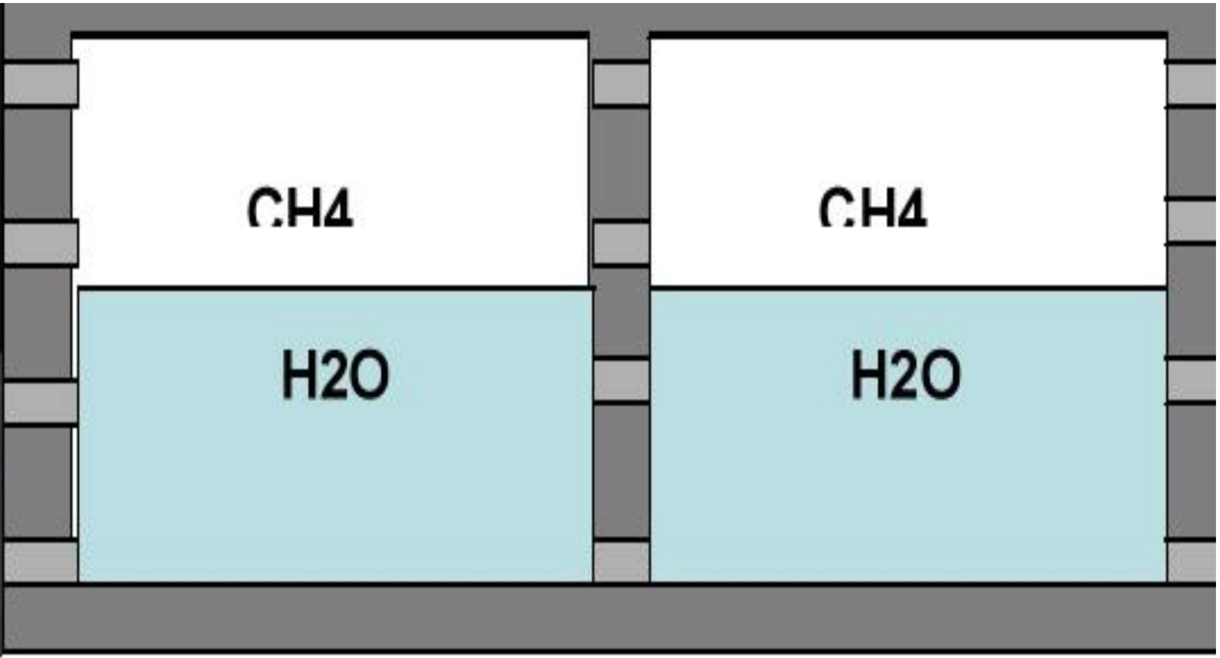
Many flow loop hydrate experiments have been conducted in plastic pipelines at low pressures using water soluble hydrate formers and as such not quite comparable Below is a snapshot from THF hydrate formation in a plexiglass pipeline



Impact of solid surfaces on hydrate formation is not new knowledge but frequently not considered. Most hydrate formation tests have been conducted using intense stirring. So where hydrate nucleate and grow on nano to micro scale is not visible/measurable directly. Illustration is from Makogan's book showing hydrate growth towards glass walls and on CH4/H2O interface.

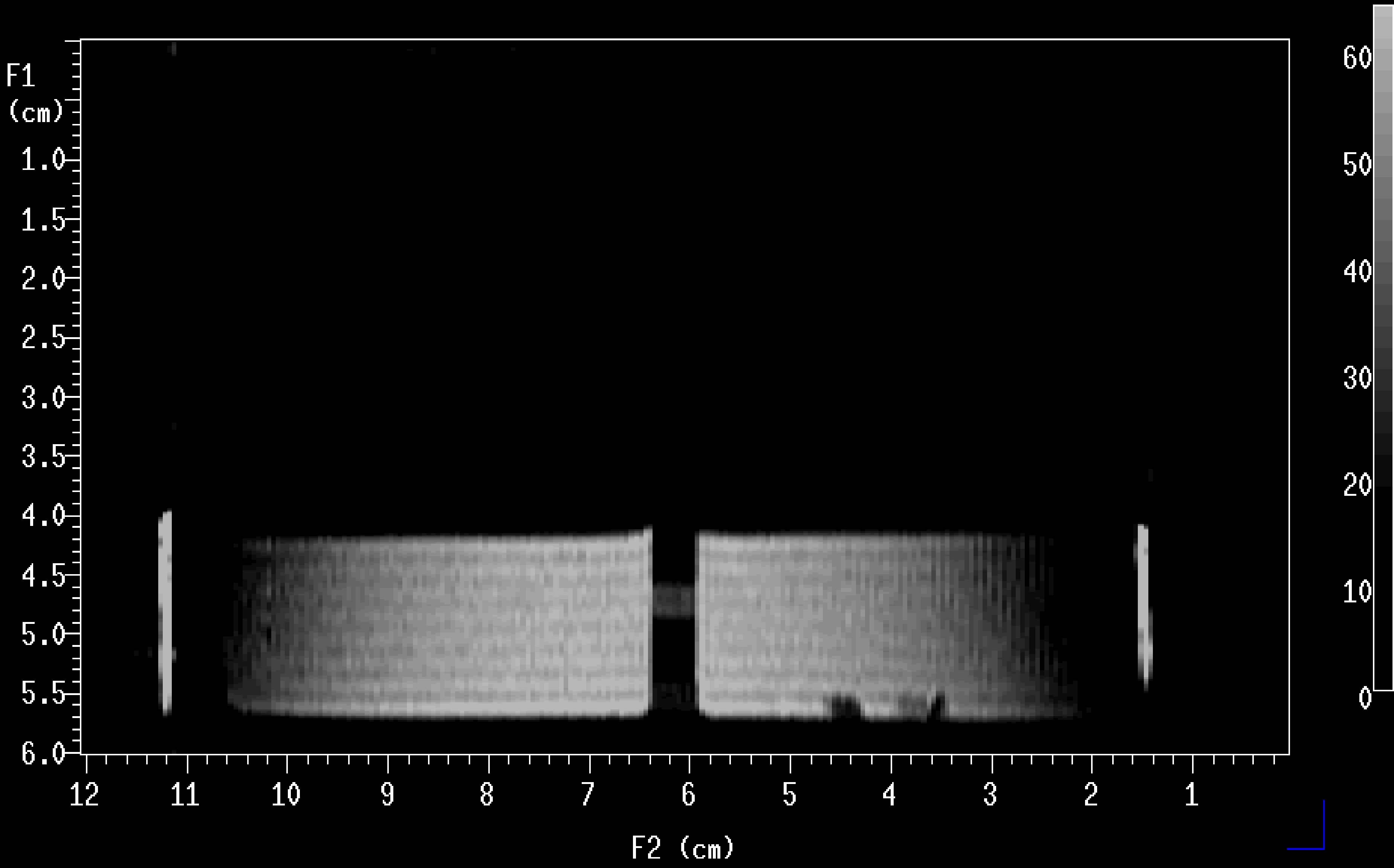
And few attempts have been made to quantify the effects in terms of variables and properties that can be used in evaluation of hydrate phase transitions

Experiments with methane and water at 83 bar and 3 C (resolution ~ 100 micrometer)



Two half cylinders of polypropylene with diameter 4 cm and lenght close to 10 cm separated by a 4 mm spacer with channels for natural fluid flow

Note that methane is the wetting component on the polypropylene, in contrast to the glass cell in which the walls are water wettening


F1
(cm)
1.0
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12
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F2 (cm)
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40
30
20
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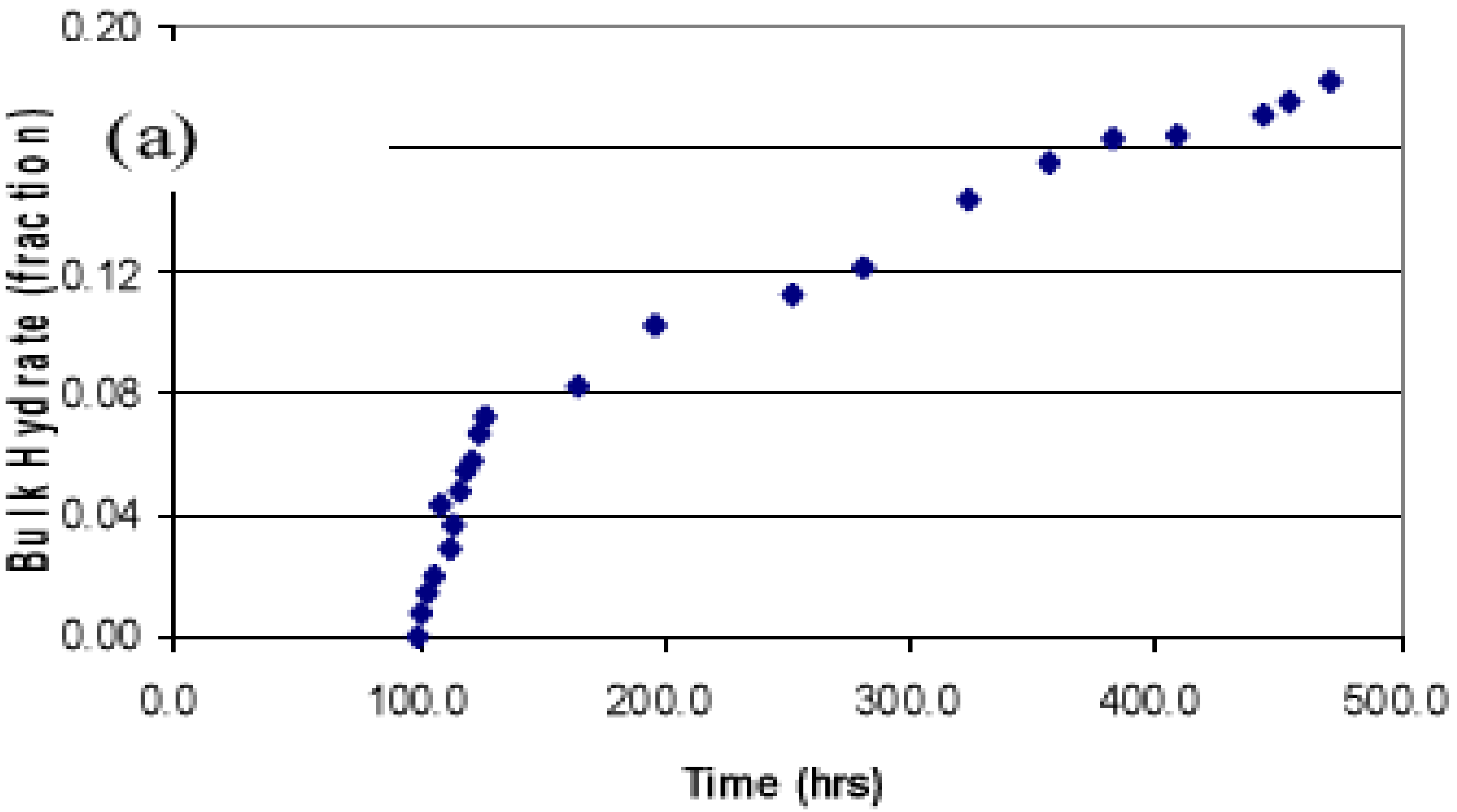
0



Why? Two primary factors:

1) A methane hydrate film will rapidly form on the water/methane interface and reduce efficiently further growth untill film penetratesdue to local competition based on first and second laws of thermodynamics

2) Methane is the wetting component of the silicone rubber and some methane will migrate along the walls downwards in the chamber due to

$$\Delta G_i = \delta\left[x_w^{H,i}\left(\mu_w^{H,i} - \mu_w^{p}\right) + x_{CH4}^{H,i}\left(\mu_{CH4}^{H,i} - \mu_{CH4}^{p}\right)\right]$$

Free energy changes for *different* phase transitions involving hydrate from CH4

Table 1. Potential hydrate phase transition scenarios for a system of carbon dioxide with impurities as relevant for transportation pipeline. The change in the free energy for any of the processes mentioned in table 1 is calculated according to equation 1. Note that the different phase transitions may involve hydrate of different composition and as such the label hydrate for the phase does not distinguish between different free energy hydrates in this table.

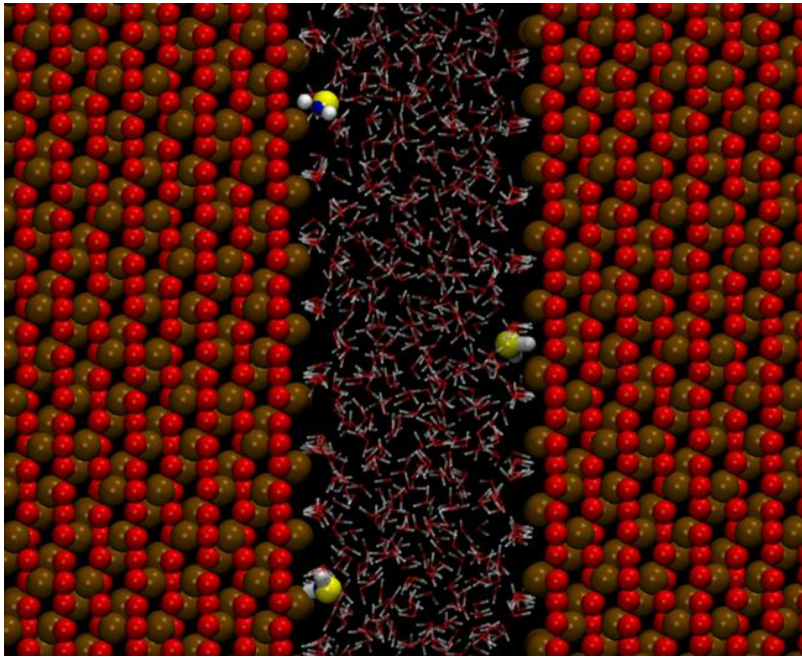
i	δ	Initial phase(s)	Driving force	Final phase(s)
1	-1	Hydrate	Outside stability in terms of local P and/or T	Gas, Liquid water
2	-1	Hydrate	Sublimation (gas under saturated with water)	Gas
3	-1	Hydrate	Outside liquid water under saturated with respect to carbon dioxide and/or other enclathrated impurities originating from the carbon dioxide phase	Liquid water, (Gas)
4	-1	Hydrate	Hydrate gets in contact with solid walls at which adsorbed water have lower chemical potential than hydrate water	Liquid water, Gas
5	+1	Gas/fluid	Hydrate more stable than water and hydrate formers in the fluid phase	Hydrate
6	+1	Gas + Liquid water	Hydrate more stable than condensed water and hydrate formers from gas/fluid	Hydrate
7	+1	Surface reformation	Non-uniform hydrate rearranges due to mass limitations (lower free energy hydrate particles consumes mass from hydrates of higher free energy)	Hydrate
8	+1	Aqueous Phase	Liquid water super saturated with carbon dioxide and/or other hydrate formers, with reference to hydrate free energy	Hydrate
9	+1	Adsorbed	Adsorbed water on rust forms hydrate with adsorbed hydrate formers.	Hydrate
10	+1	Adsorbed +fluid	Water and hydrate formers from gas/fluid forms hydrate	Hydrate

Possible competing phase transitions involving hydrate with a basis from a system of CH4 containing water. More components in the CO2 phase will not change the picture as even more hydrate phases will occur (most stable hydrate form first)

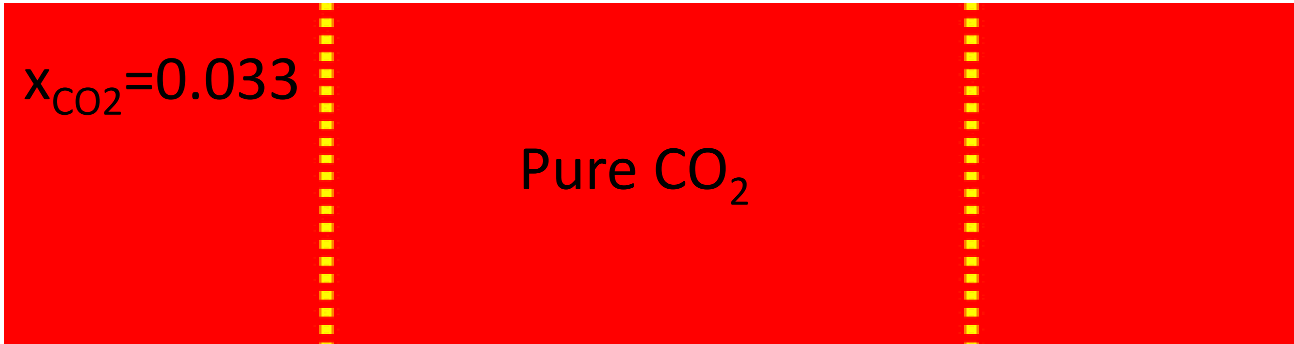
Investigating competing phase transitions in porous media (read: solid material surfaces) requires multiscale modeling approach and a free energy minimization approach. For now we limit ourselves to a few discrete routes

- Water **condense out** and forms hydrate with hydrate formers from gas phase
- Water **forms hydrate directly** from the gas mixture
- Water **adsorbs on rust** (modelled as Hematite) and liquid water slightly outside the surface (2 – 3 water layers) form hydrate with hydrate formers from gas.
- As example we consider CH4 with H2S and CO2 as impurities

H2S (yellow and greay) also adsorbs well on Hematite but not considered in this limited study



Simulation of hydrate growth dynamics on interface of a CO2 plume using PFT



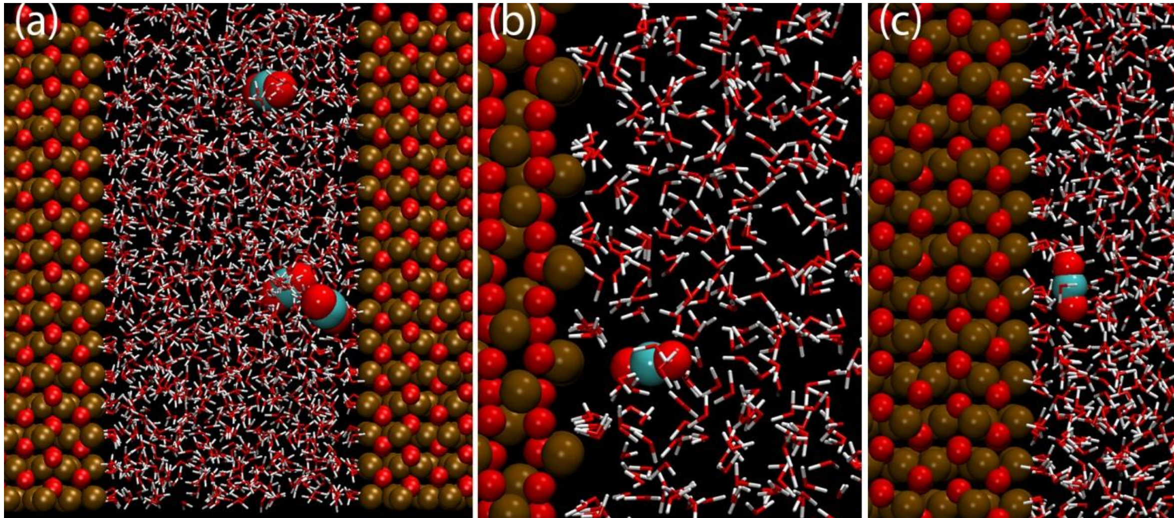
So – if the system ***cannot reach true thermodynamic equilibrium*** – then there is ***no rule that says chemical potential*** of hydrate formers ***is the same in all phases***

$$\mu_w^{H,i}(T,P,\vec{x}^H) = \mu_w^{H,0}(T,P) - \sum_j \nu_j \ln\left(1+\sum_k h_{kj}^i\right)$$

$$h_{kj}^i = e^{-\beta(\mu_{kj}^i + \Delta g_{kj}^{inclusion})}$$

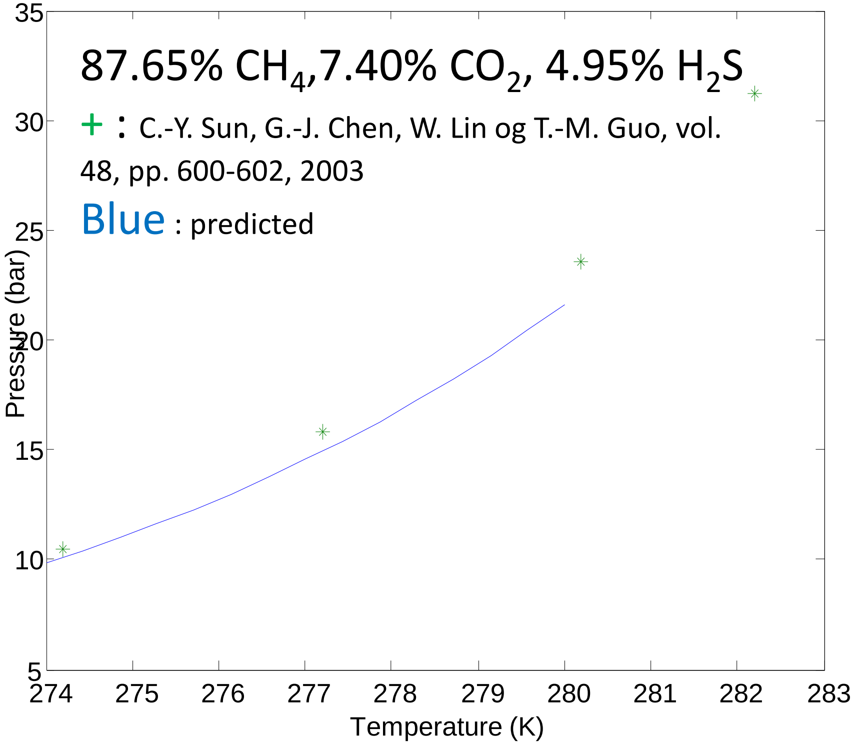
What is chemical potential for the guest in the «parent» phase ?
What is the resulting free energy of that specific hydrate phase ?

Right: CO2 (enhanced red and grey) adsorbing onto Hematite from water solution. Adsorbed CO2chemical potential: -39.21 kJ/mole at 274 K



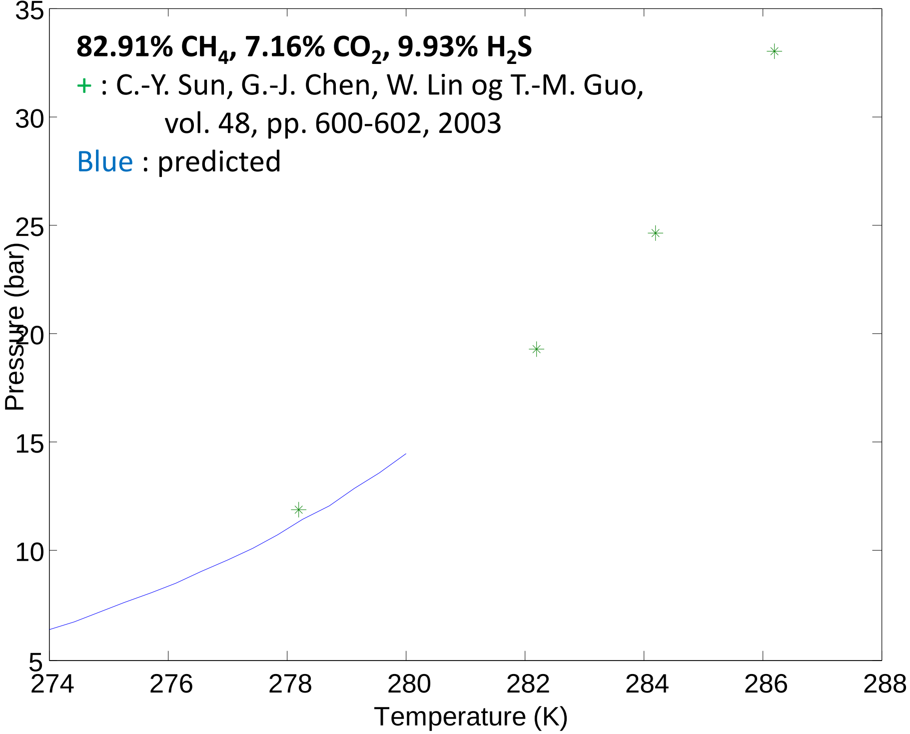
We use SRK for gas but rest of the thermodynamic properties are derived from MD using the procedure of Kvamme & Tanaka (1995). Upper temperature in estimation of free energy of inclusion was limited to 280 K

So first some few verifications of the thermodynamic model system


87.65% CH_4,7.40% CO_2, 4.95% H_2S

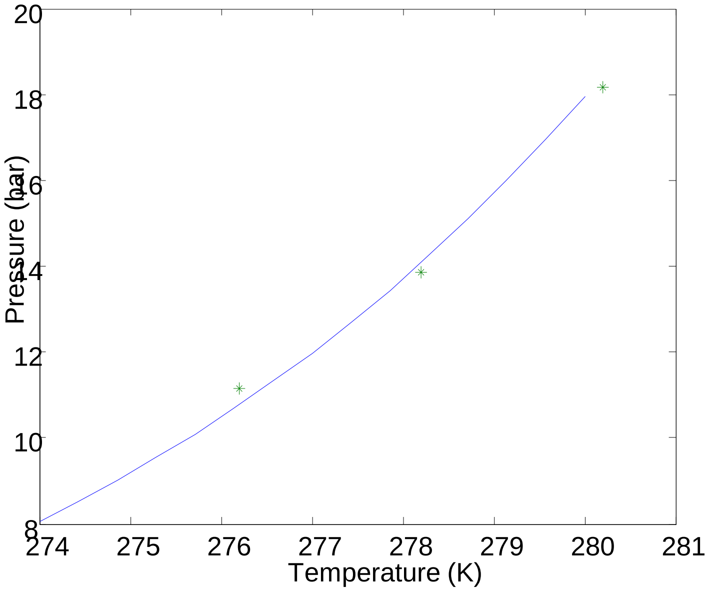
+ : C.-Y. Sun, G.-J. Chen, W. Lin og T.-M. Guo, vol. 48, pp. 600-602, 2003

Blue : predicted


82.91% CH_4, 7.16% CO_2, 9.93% H_2S

+ : C.-Y. Sun, G.-J. Chen, W. Lin og T.-M. Guo, vol. 48, pp. 600-602, 2003

Blue : predicted

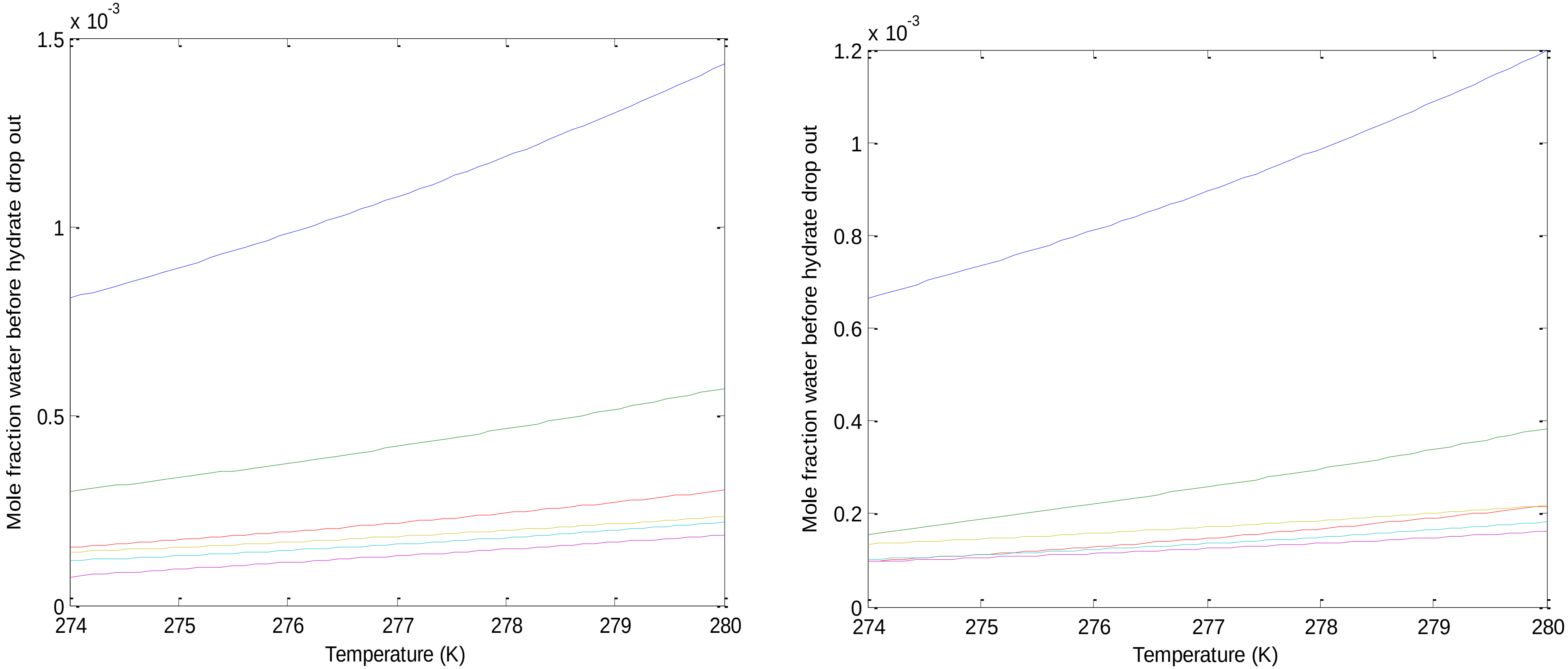


82.45% CH_4, 10.77% CO_2, 6.78% H_2S

+ : C.-Y. Sun, G.-J. Chen, W. Lin og T.-M. Guo, vol. 48, pp. 600-602, 2003

Blue : predicted

Direct formation of hydrate from water dissolved in gas. Thermodynamically considered only; what is the maximum water content before hydrate formation

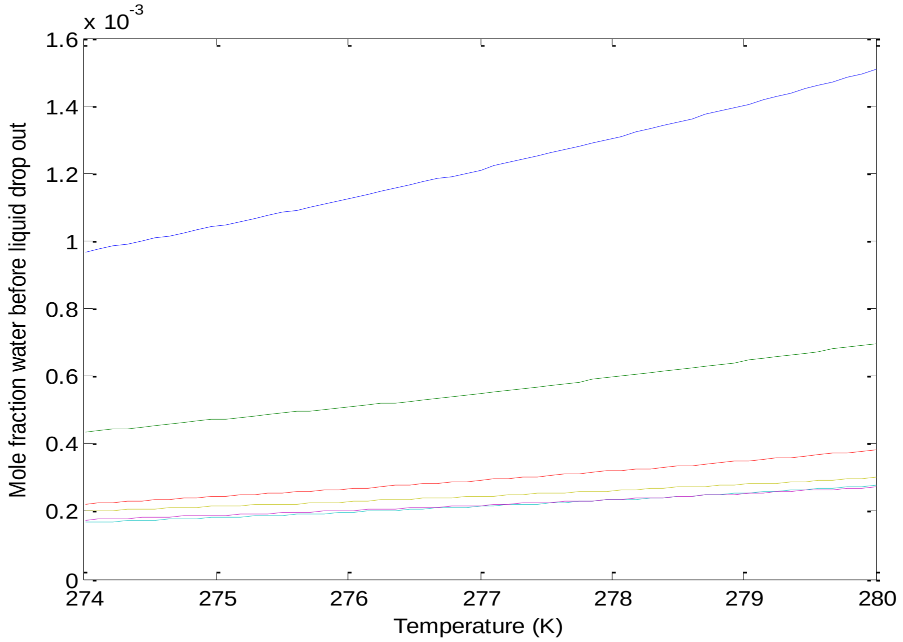


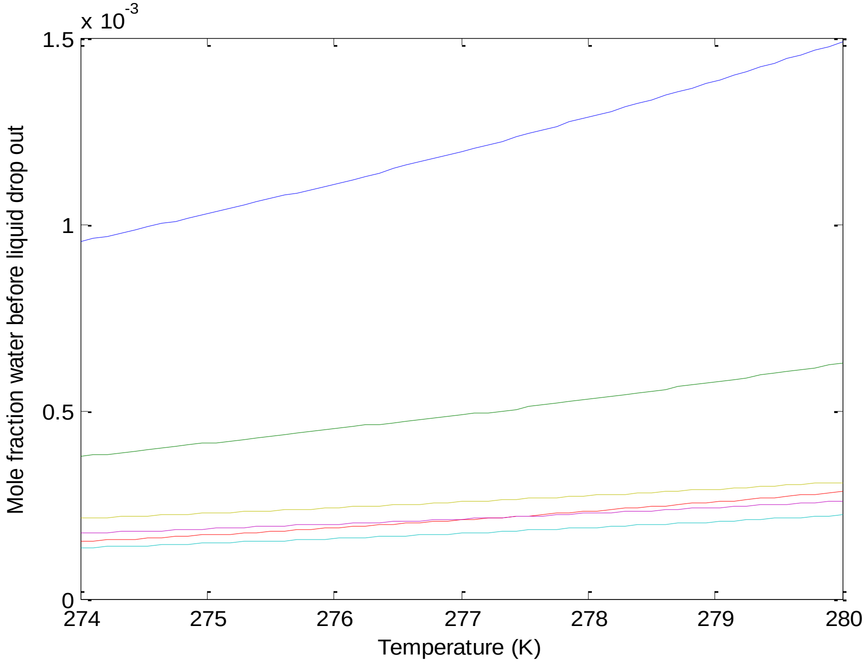
Maximum water content before hydrate drop out. Curves from top to bottom correspond to pressure 50 bar, 90 bar, 130 bar, 170 bar, 210 bar, 250 bar.

Left: mole fraction of 0.1 CO_2, 0.01 H_2S and remaining gas being CH_4
Right: mole fraction of 0.1 CO_2, 0.1 H_2S and remaining gas being CH_4

As expected even smal amounts of H2S affects the maximum permittable water content significantly. But this route is unlikely since in the order of 100 water (critical hydrate size) need to «find each other in such a dilute solution.

Water condensation (water dew-point) and subsequent hydrate formation with gas; what is the maximum water content before hydrate formation



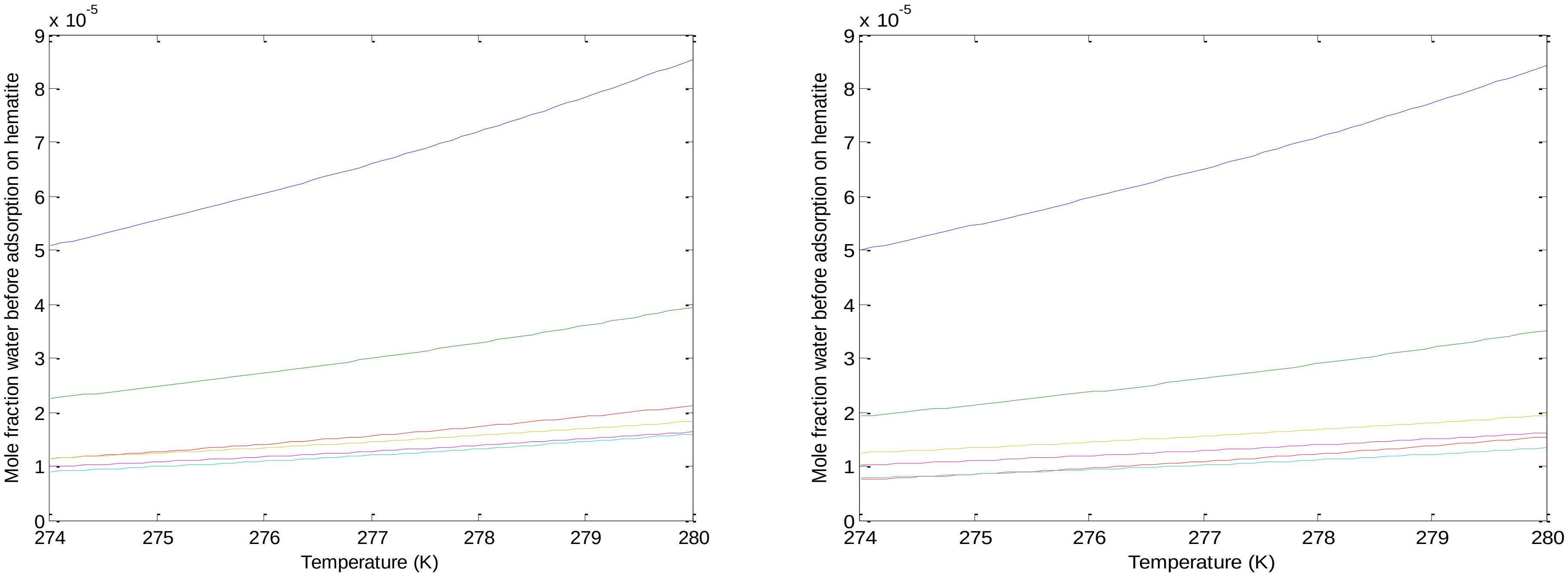


Maximum water content before hydrate drop out. Curves from top to bottom correspond to pressure 50 bar, 90 bar, 130 bar, 170 bar, 210 bar, 250 bar.

Left: mole fraction of 0.05 CO_2, 0.01 H_2S and remaining gas being CH_4
Right: mole fraction of 0.05 CO_2, 0.1 H_2S and remaining gas being CH_4

For these small H2S amounts there are even some minor differences between mole fractions 0.01 and 0.2 but hardly of practical importance. What is more important is that the maximum water content that can be tolerated according to this route is in the order of a factor of 20 less than condensation as water and subseqient hydrate formation

Water adsorbs on Hematite and subsequently liquid water form hydrate with gas; what is the maximum water content before hydrate formation ?



Maximum water content before hydrate drop out. Curves from top to bottom correspond to pressure 50 bar, 90 bar, 130 bar, 170 bar, 210 bar, 250 bar.

Left: mole fraction of 0.1 CO_2, 0.01 H_2S and remaining gas being CH_4
Right: mole fraction of 0.1 CO_2, 0.1 H_2S and remaining gas being CH_4

As expected this route is less sensitive to the changes of (the small content) H2S than the direct formation route. The change from H2S mole-fraction of 0.01 to 0.1 is noticable but hardly of any practical importance for these very small H2S contents (Notyj Sea hydrocarbon systems are generally low in H2S). For these low concentrations of H2S there is, however, limited differences in maximum water content

The bigger picture

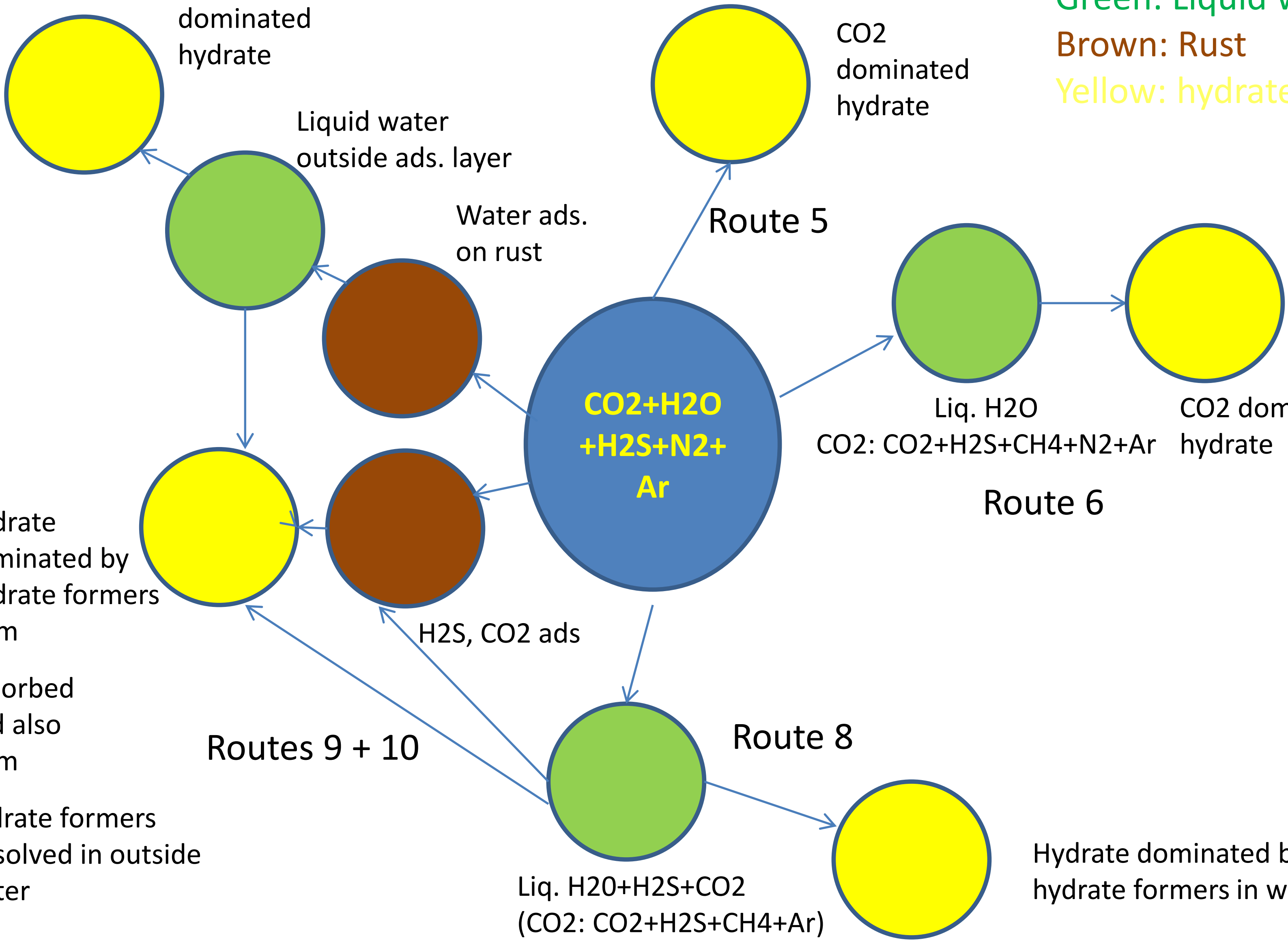
- Rust as modelled by Hematite ***dominate totally*** the ***minimum water*** that can be tolerated.
- Typical operating conditions will result in hydrate formation if liquid water becomes present along the pipe walls.
- Since ***hydrate*** cannot connect directly to the rust surface it ***will only stick to the surface if the bridging of structured water*** is strong enough compared to external stress on the formed hydrate particles.
- If the hydrate is kept towards the wall then the relevant next condition to evaluate would be ***water drop out limit as adsorbed to hydrate water***

Growth of CO2 hydrate from water solution at 150 bar, 274 K and mole fraction CO2 0.036

Favorable adsorption of H2S and partly CO2 as well liquid water solubility of these in liquid water might result in «aggresive» hydrate growth from both sides of the liquid water/gas interface

And yes CO2 is different from CH4

Blue: CO2-phase
Green: Liquid water
Brown: Rust
Yellow: hydrate



CO2+H2O +H2S+N2+ Ar

CO2 dominated hydrate

Liquid water outside ads. layer

Water ads. on rust

Route 5

CO2 dominated hydrate

Liq. H2O
CO2: CO2+H2S+CH4+N2+Ar

CO2 dominated hydrate

Route 6

H2S, CO2 ads

Hydrate dominated by Hydrate formers from

adsorbed and also from

hydrate formers dissolved in outside water

Routes 9 + 10

Route 8

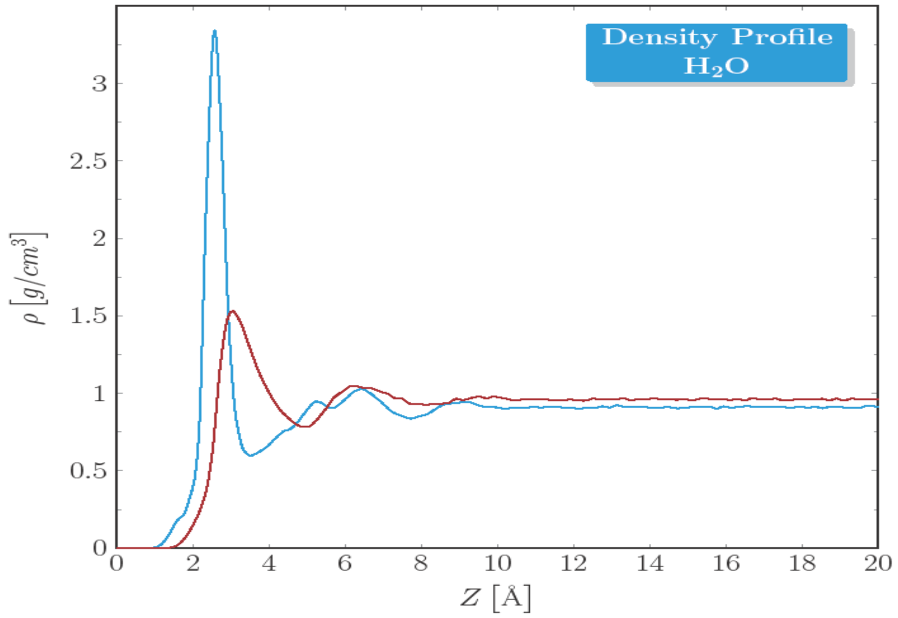
Liq. H20+H2S+CO2
(CO2: CO2+H2S+CH4+Ar)

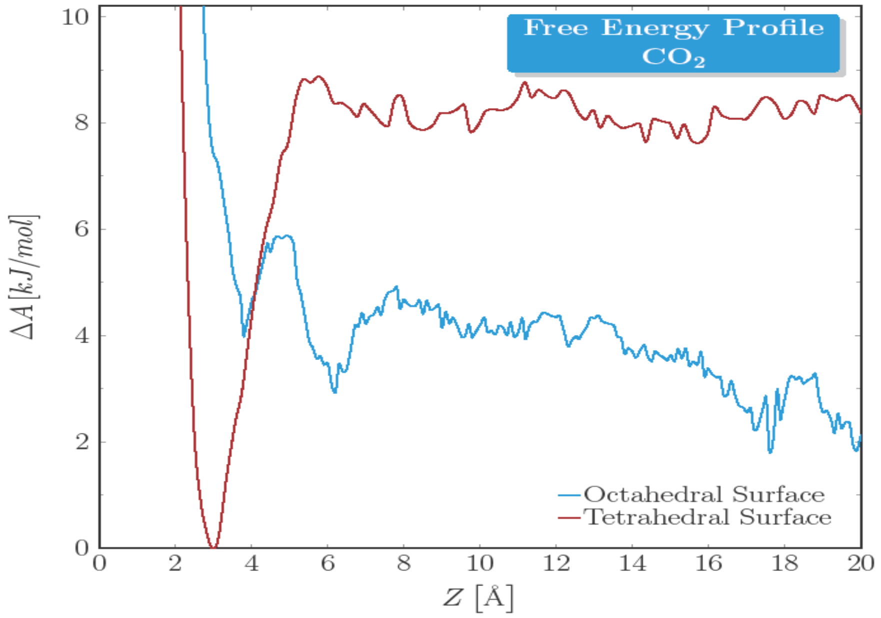
Hydrate dominated by dissolved hydrate formers in water (H2S, CO2)

CO2 adsorbs directly on some minerals like for instance Kaolinite and Calcite

- Methane essentially adsorbs indirectly in lower density «pockets» of water structure on mineral surfaces

Kaolinite is a typical Norwegian clay mineral which might be used for binding





For the tetrahedral cutting ***direct adsorption of CO2*** is feasible (see free energy change for CO2 on right figure) before first maximum for water while ***secondary adsorption*** in water density minimums might occur in both cases. Figures from Leirvik, Kvamme & Kuznetsova [1].

Another important aspect of these results is the potentially ***strong adsorption of water on the binding material***, which needs quantification in order to evaluate whether this water adsorption is too strong compared to a ***desired superior adsorption of water in the Zeolite cavities***.

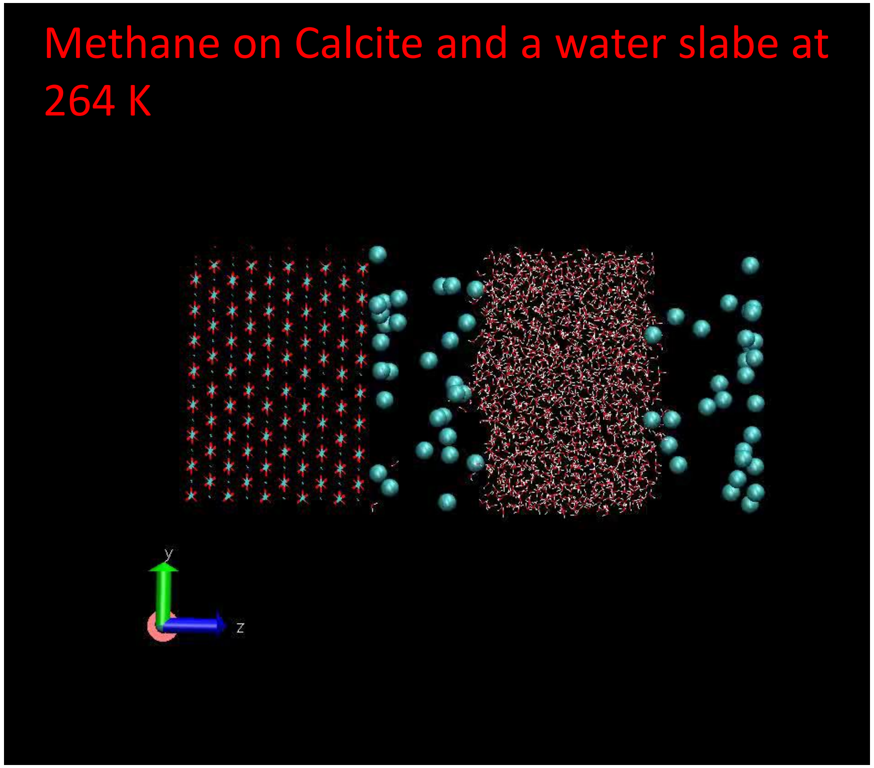
Experimental needs as support for modeling

- Adsorption of water from a gas phase dominated by methane is another story

Critical questions:

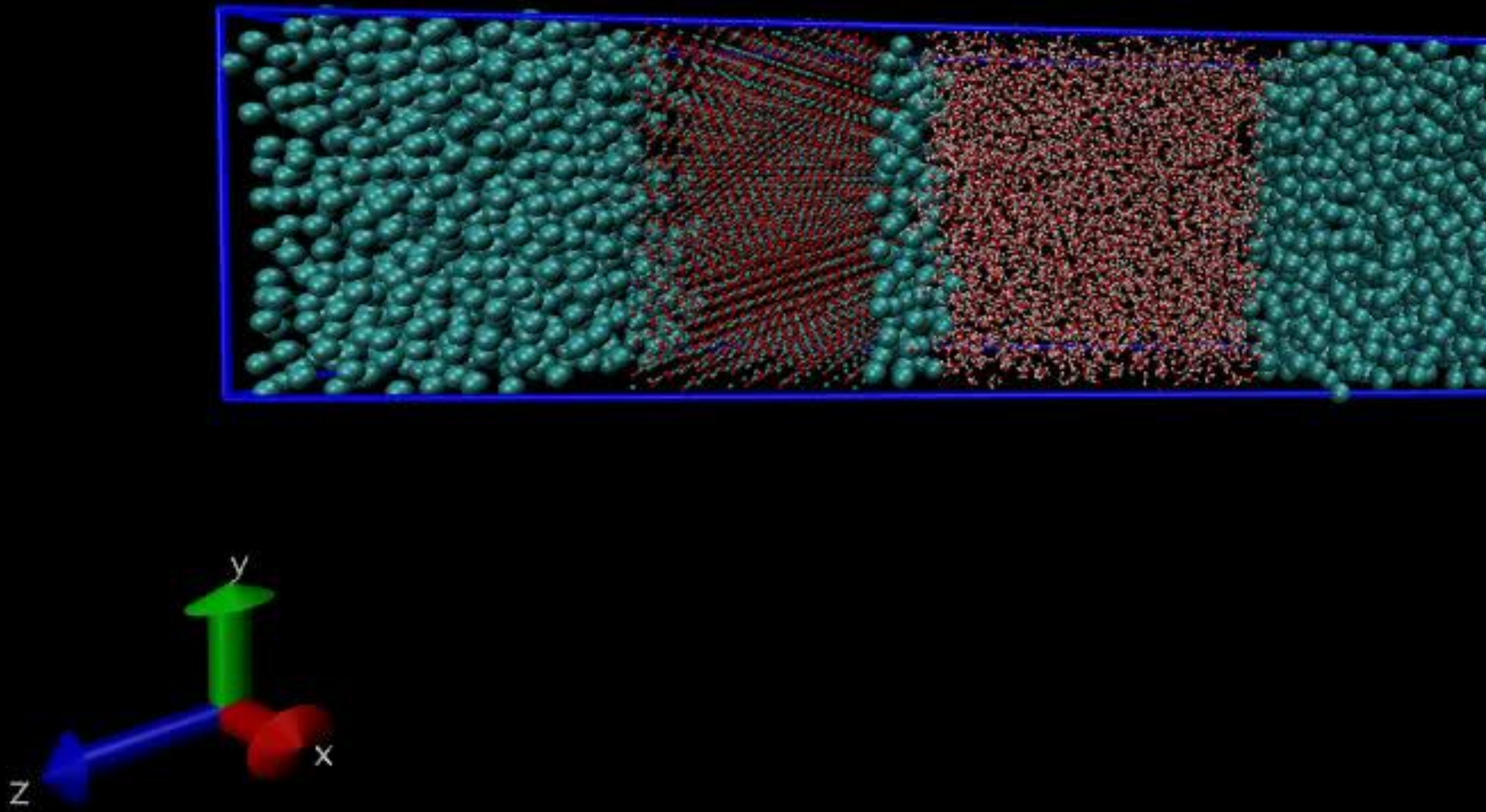
- 2 D adsorption ?
- Monolayer ?

Methane on Calcite and a water slabe at 264 K



If yes on both then it is reasonable to assume ***equilibrium*** model and the following steps:

- Identify ***adsorption sites***
- ***Quantify*** adsorption sites per unit area
- Estimate ***chemical potential*** for ***water*** and ***possible pollutant (TEG)***


y
x
z

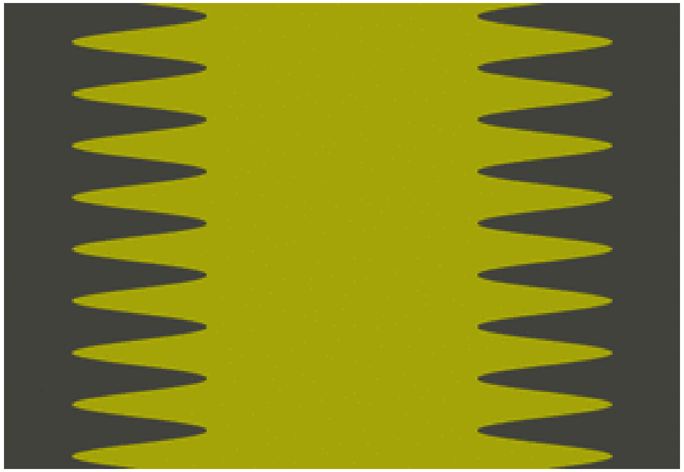
Conclusions

- Solid surfaces like for instance rust can have substantial impact on hydrate phase transition related to water following natural gas.

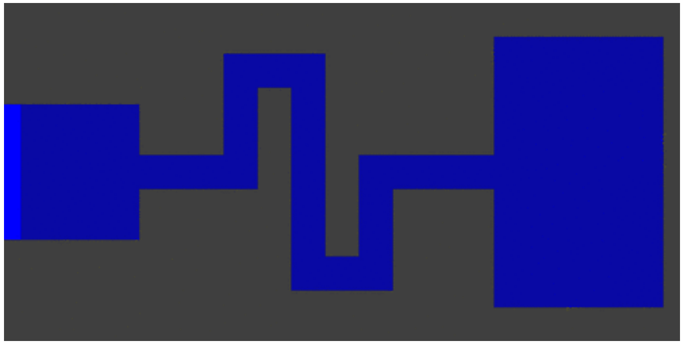
- Based on systematic studies using state of the art theoretical methods the water structure on Hematite surface results in too low water chemical potential to result in hydrate formation directly towards the Hematite surface.

- And formed hydrate cannot even connect to Hematite directly due to incompatability for surface charges on Hematite and water partial charges on hydrate

- But Hematite surfaces can actively contribute to favorable heterogeneous hydrate nucleation through direct and secondary adsorption of hydrate formers



Phase Field Theory modelling of these systems is in progress



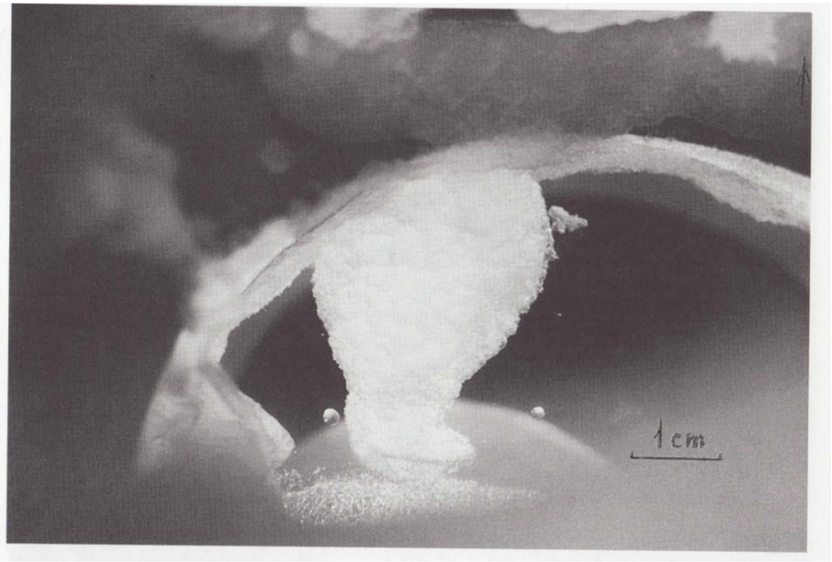
Acknowledgements

- We acknowledge the grant and support from Research Council of Norway through the following projects: SSC-Ramore, “Subsurface storage of CO2 - Risk assessment, monitoring and remediation”, Research Council of Norway, project number: 178008/I30, FME-SUCCESS, Research Council of Norway, project number: 804831. Funding from STATOIL under contract PO4502354080: “A new reservoir simulator for hydrate exploration studies” and associated funding from CLIMIT project 224857: “Safe long term storage sealing of CO2 in hydrate”

Thank you for your attention

Motivation

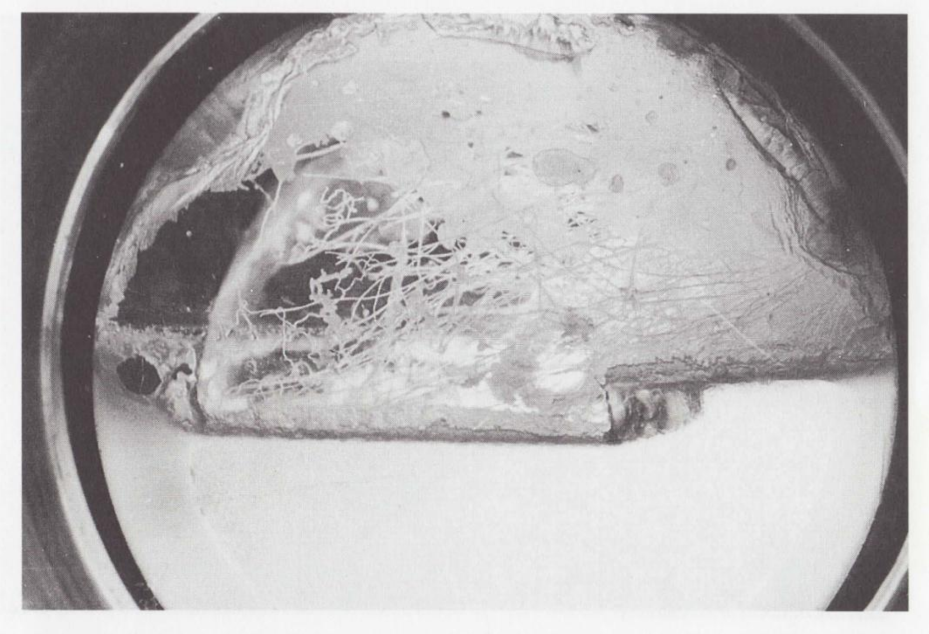
- The ***thermodynamic benefits*** for water to ***adsorb*** out onto a rusty surface may be a factor of ***5 times*** that of water ***condensing*** out as liquid water
- Benefits of rust adsorption versus condensation have been experimentally verified using Quantum Balance (Heriot-Watt, 2012, unpublished)
- Practically this implies that ***rusty pipewalls are cold*** (thermodynamic sense) surfaces. During sub-sea transport pipe walls normally ***also*** are ***zones of lowest temperatures***.



This is an illustration copied from Makogan's book showing hydrate on glass surface and on CH4/H2O interface (hydrate cannot attach directly to the surfaces but structured water bridges hydrate to solid surface)

There is a need for revision of «Best practise» for evaluation of risk for hydrate formation during transport of hydrocarbons or carbon dioxide containing water

Motivation cont.



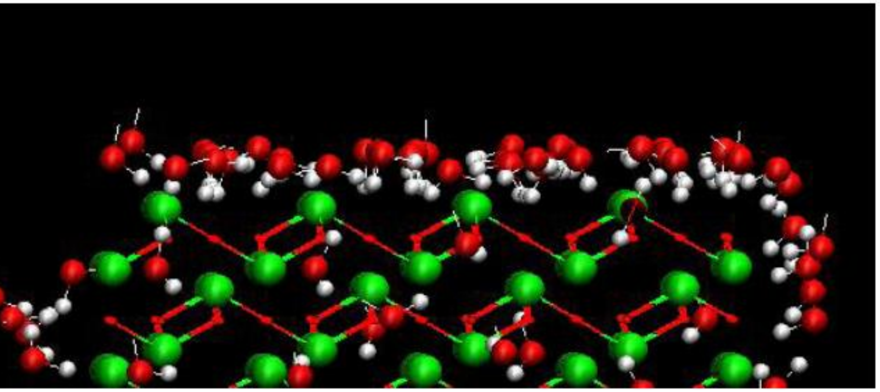
Solid surfaces can upconcentrate hydrate formers in primary and/or secondary adsorption. This will facilitate very favorable heterogeneous hydrate nucleation

Picture is from Makogan's book and shows hydrate growing on water/methane interface as well as towards glass walls

- Gibbs phase rule ***excludes*** the possibility of ***equilibrium*** since dynamic transport through the pipeline prevents some of the phases from being totally consumed.
- Rusty surfaces may play a substantial role, and two thermodynamic variables (T and P) are locally defined by mass-and heat-flow and dynamic couplings to the phase transition dynamics.
- Combined first and second laws of thermodynamics open up for ***different hydrates*** being ***formed***, depending composition of gas and phases from which phases water and hydrate former comes from

Motivation

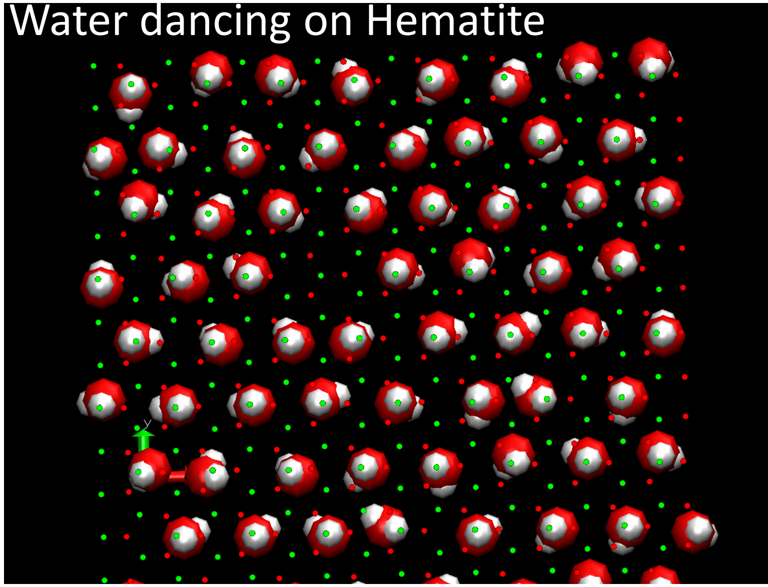
Two hydrogens on indivual water molecules creates simultaneous electrostatic bonds to ions on Hematite surface



- Relevant ***transport conditions*** in pipelines on seafloor is in the pressure regions of 50 to 250 bar and temperatures down towards zero Celcius and as such in ***risk of hydrate formation in most cases***

Water needed for hydrate formation with CO2 can come from ***condensed*** water, ***adsorbed*** water or even as water ***dissolved*** in CO2

The ditribution of water on a Hematite surface leads to locally very high densities in first adsorbed layer which gives rice to a very low chemical potential of adsorbed layer (in the order of 3.4 kJ/mole lower than liquid water) followed by a minimum that can "host" molecules like for instance methane. Note the dynamic spots of available space



Gibbs Phase Rule

No. Of deg. Of freedom →

$$\tau = N - \pi + 2$$

No. Of components

No. Of Phases

- Gibb's phase rule is the ***conservation of mass*** under the constraints of ***equilibrium***
- ***Minimum criteria*** for possibility of equilibrium but not given that all possible phases do co-exist since that also depends on chemical potentials and level of free energies of the possible phases
- For liquid H2O, CO2 and CO2 hydrate there are minimum 5 phases

  - H2O
  - CO2
  - CO2 hydrate
  - adsorbed phase on hydrate
  - adsorbed phase on Hematite

The water structuring around hydrate is totally different than the water structuring on Hematite but the two latter contribution creates a minimum distance «bridging» betweenhydrate and Hematite

So – if the system ***cannot reach true thermodynamic equilibrium*** – then there is ***no rule that says chemical potential*** of hydrate formers ***is the same in all phases***

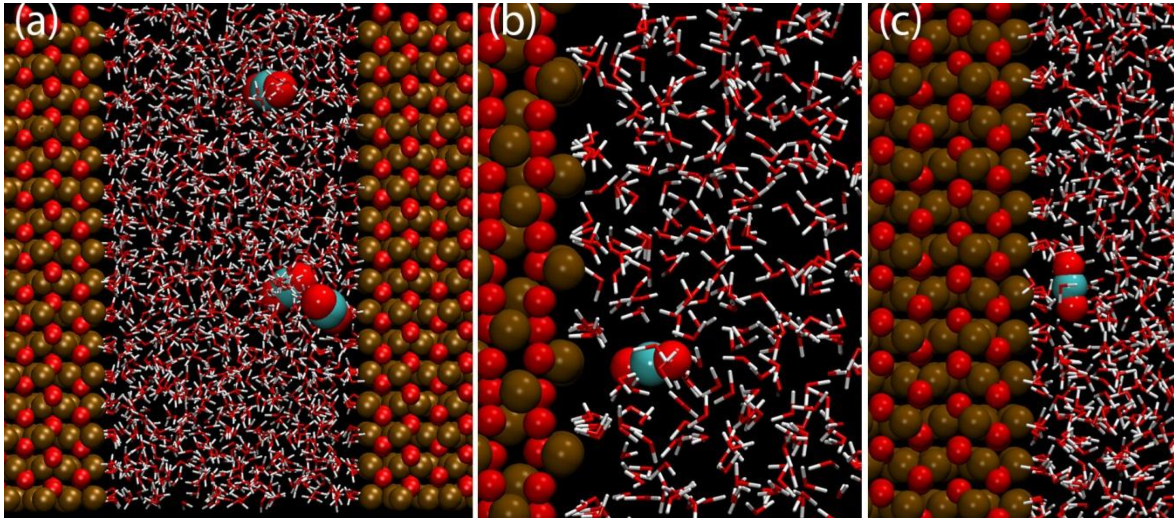
$$\mu_{w}^{H,i}(T,P,\vec{x}^{H}) = \mu_{w}^{H,0}(T,P) - \sum_{j} \nu_{j} \ln\left(1+\sum_{k} h_{kj}^{i}\right)$$

$$h_{kj}^{i} = e^{-\beta\left(\mu_{kj}^{i} + \Delta g_{kj}^{inclusion}\right)}$$

What is chemical potential for the guest in the «parent» phase ?

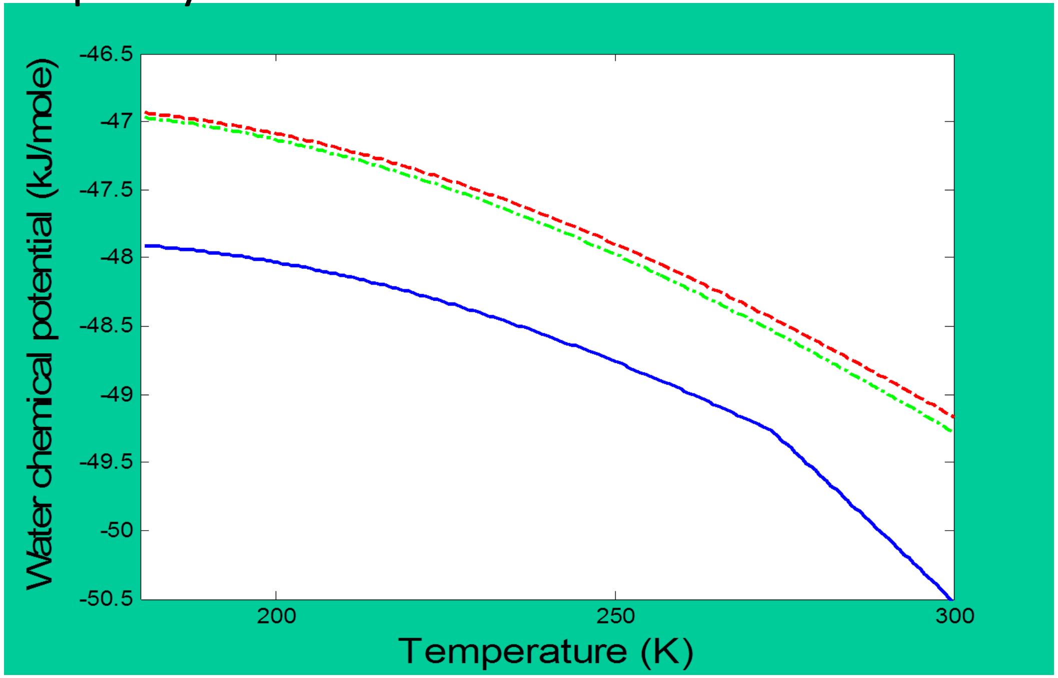
What is the resulting free energy of that specific hydrate phase ?

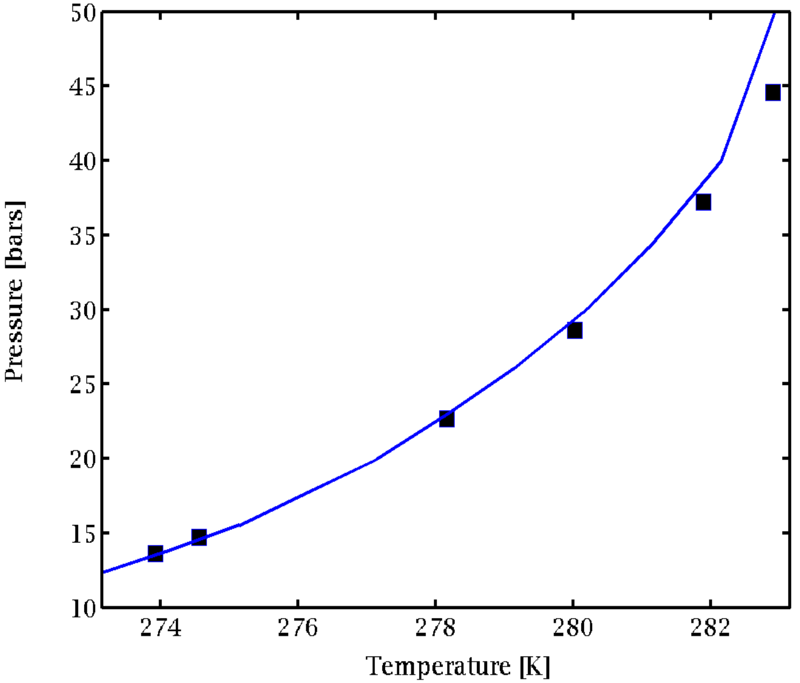
Right: CO2 (enhanced red and grey) adsorbing onto Hematite from water solution. Adsorbed CO2chemical potential: -39.21 kJ/mole at 274 K



Ideal gas as reference state for all components in all phases makes free energy comparisons between phases easier

Chemical potential for water in ice (blue up to 273.15 K) and empty clathrates of structure I and II (red and green) were derived by Kvamme & Tanaka (1995) using TIP4P model for water in Molecular Dynamics simulations. Liquid water chemical potentiall calculated using experimental heats of melting and specific heat capacity for water.

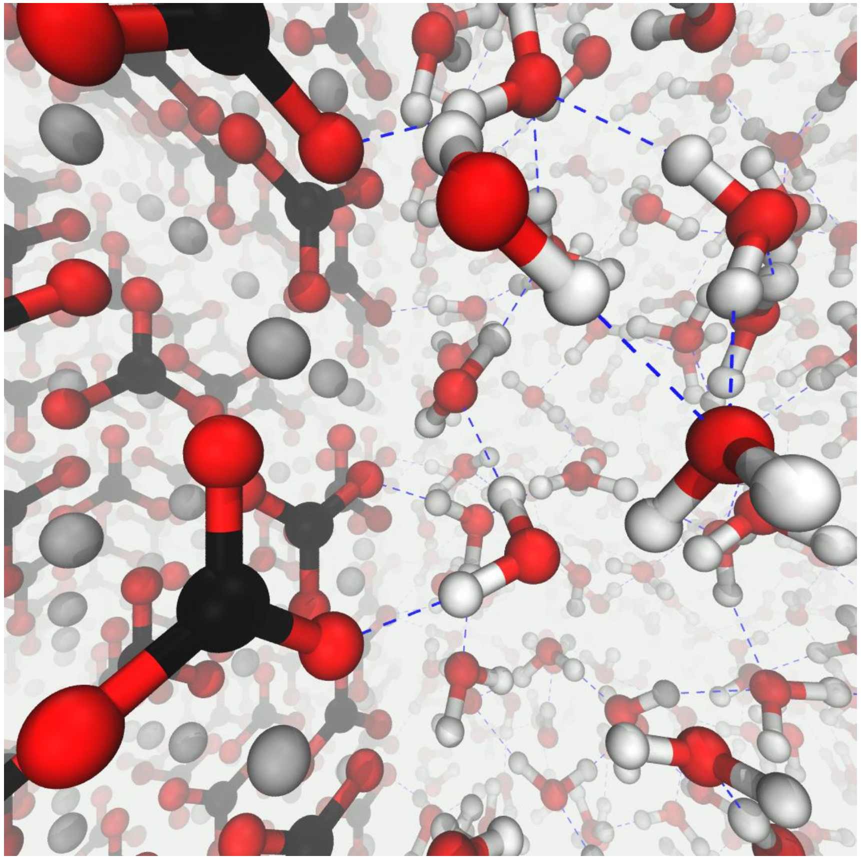




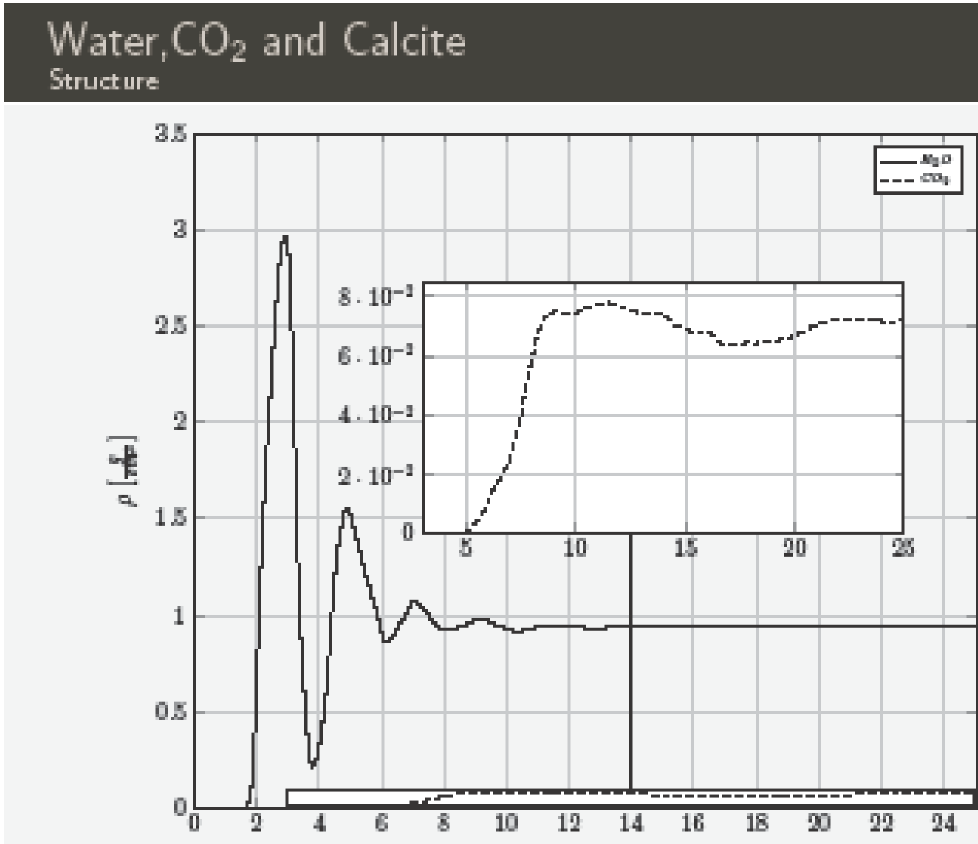
Guest molecules from gas predicted using SRK EOS while guest molecules coming from water solution are estimated using Molecular Dynamics simulations and best available models verified for water solution properties. Adsorbed chemical potential also from MD

Secondary and primary adsorption of guest molecules

Primary adsorption is adsorption directly on solid surface

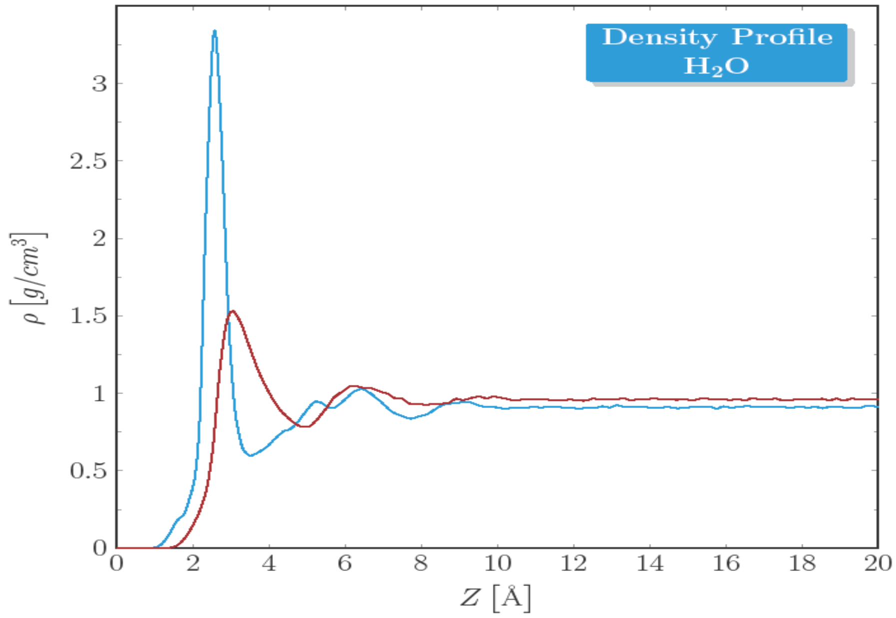


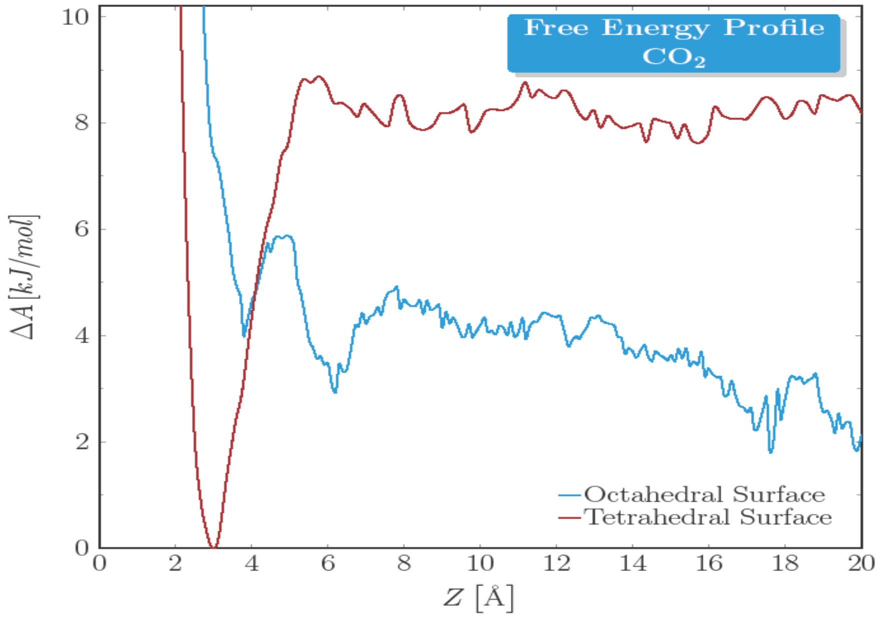
Calcite is interesting for hydrates in reservoirs
But conversion of iron oxides over times of exposure to CO2 makes the similarities to iron carbonate also makes Calcite interesting



Note the extreme density of the first adsobed water layer but also the subsequent water density minimum which gives space for trapping CO2. Simulated structure is in accordance with experimental data (IR)

Secondary adsorption is adsorption in areas («pockets») of low water density



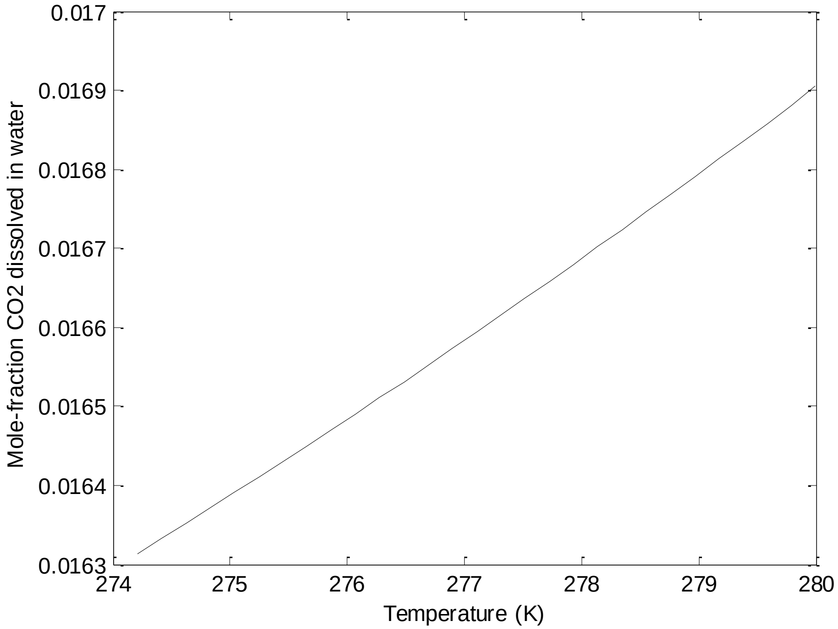


This example is for Kaolinite – which has limited direct relevance except for the similarities to some iron carbonates that can result from reactions between rust and CO2 over time. Figures from Leirvik et.al. (

The blue and brown curves are for two different cuttings of the Kaolinite crystal. Note the location of water density minimums in both curves that given possibilities for trapping and upconcentration of CO2 as basis for nucleation of hydrate.

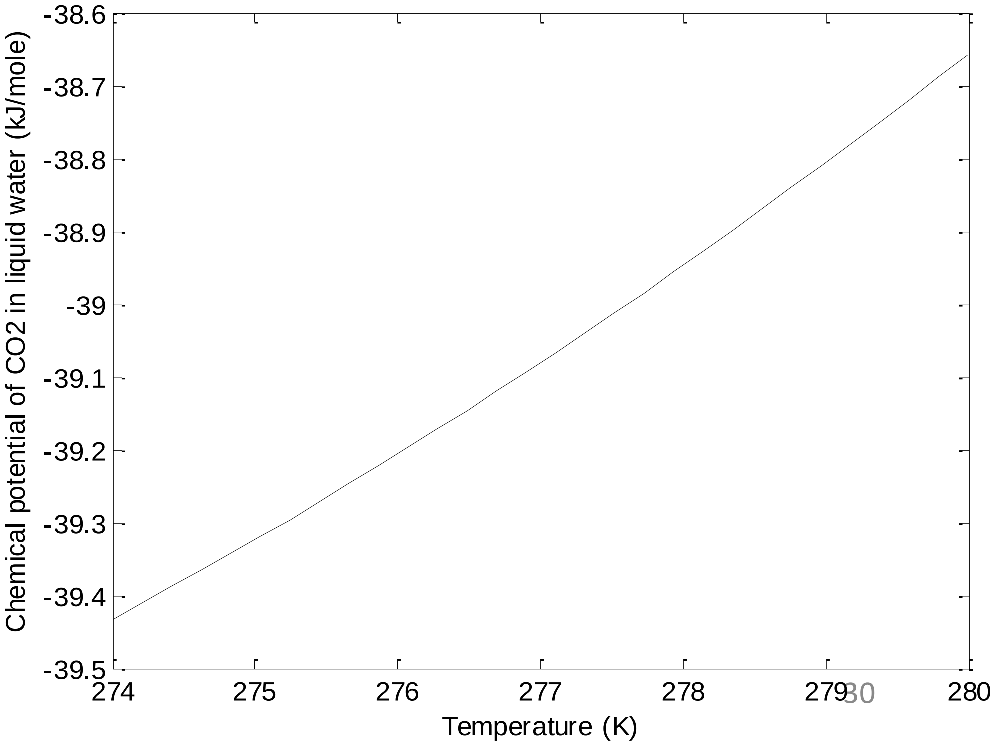
The tetrahedral durface (brown) is the least hydrophilic and also results in direct CO2 adsorption before the first water layer while the octahedral surface (blue) only gives room for secondary adsorption in water density minima.

Yet another «parent phase» for CO2 to hydrate formation; dissolved CO2 in water



Limit of CO2 hydrate stability towards CO2 mole-fraction in liquid water. Pressure dependency is very limited as long as the CO2 is dissolved (Poynting corrections on liquid and hydrate side are small and also almost cancel each other. Pressure dependency in the CO2 infinite dilution chemical potential and activity coefficient are small

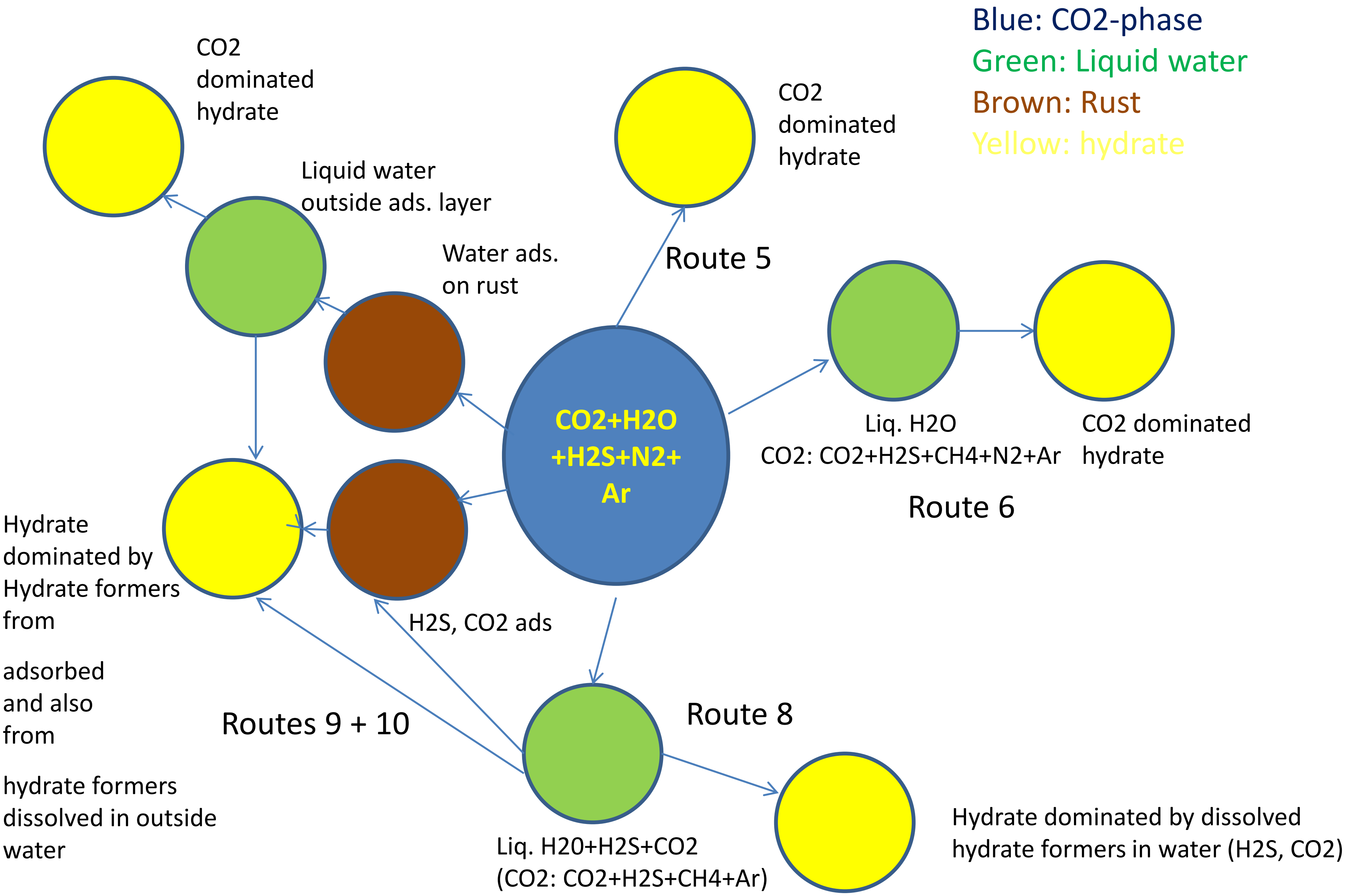
Compared to the chemical potential of adsorbed CO2 on Hematite the dissolved CO2 chemical potential at stability limit for hydrate (se figure below) is slightly lower (-39.42 kJ/mole versus -39.21 kJ/mole at 274 K)



Routes to hydrate formation

- Originally no free water – only water dissolved in CO2
- Can this water form hydrate without condensing first, or adsorbing first?
- If not – what are the concentration limits of water before dropping out as either water or adsorbed?
- And if adsorbed only 2-3 layers of water outside (less than 1 nm) needed for water to be able to form hydrate

A «map» (with reference to slide 7) of different routes that can lead to hydrate formation is given in the next overhead



Blue: CO2-phase

Green: Liquid water

Brown: Rust

Yellow: hydrate

CO2
dominated
hydrate

Liquid water
outside ads. layer

Water ads.
on rust

CO2+H2O
+H2S+N2+
Ar

Route 5

CO2
dominated
hydrate

Liq. H2O
CO2: CO2+H2S+CH4+N2+Ar

CO2 dominated
hydrate

Route 6

Hydrate
dominated by
Hydrate formers
from

adsorbed
and also
from

hydrate formers
dissolved in outside
water

H2S, CO2 ads

Routes 9 + 10

Route 8

Liq. H20+H2S+CO2
(CO2: CO2+H2S+CH4+Ar)

Hydrate dominated by dissolved
hydrate formers in water (H2S, CO2)

Summary – Gibbs phase rule analysis

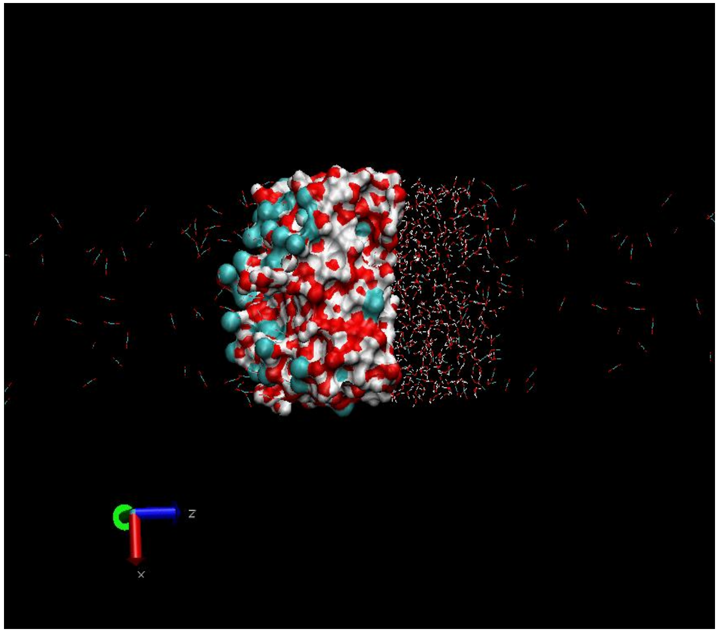
- Systems of CO2 containing water have several routes to hydrate formation and since the systems is ***unable to reach equilibrium*** chemical potentials of each component in the different phases are different and ***different hydrates have different free energies***.
- Impurities like H2S, N2, CH4 and Ar will lead to ***several different hydrate phases*** (with different free energies) since ***most stable hydrates will form first*** due to combined 1. and 2. law of thermodynamics
- ***Thermodynamic*** description needs to be ***consistent across phase boundaries*** and ideal gas as reference state for all phases is the only possibility
- ***Adsorbed*** state ***cannot be measured in terms of thermodynamic properties*** and properties must be estimated based on state of the art molecular modeling methods

A few words on the MD simulations

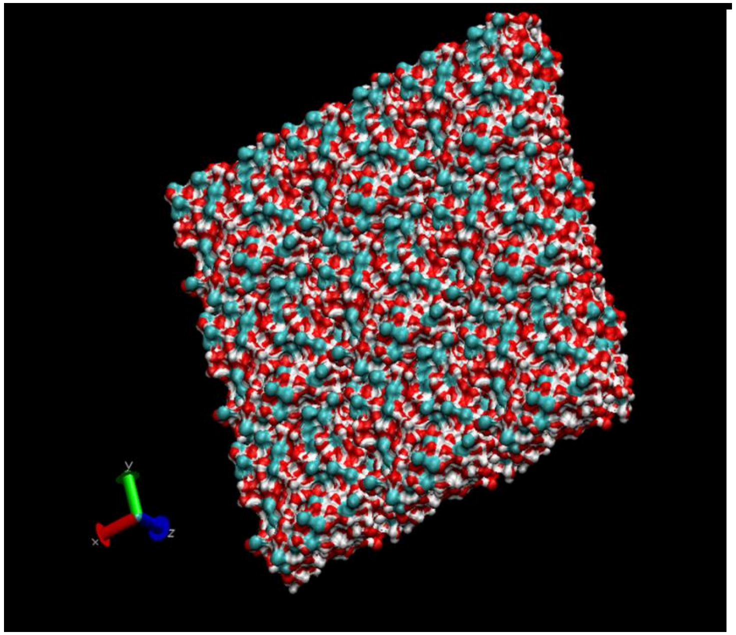
- We have applied MD43 – a software originally developed by Prof. Aatto Laaksonen at University of Stockholm more than 30 years ago and further developed and documented/verified through hundreds of publications from worldwide groups, including our group
- Sizes of simulation systems vary from 512 molecules up to 2048 depending on the system composition and need for accuracies in samplings. Corresponding volume according to experimental densities. These sizes are based on our more 30 years of experience (and corresponding publications) on size versus accuracy in sampling for these types of systems
- Standard methods for imitating infinite size systems (periodic boundary conditions) and handling of long range forces (coulombic forces due to partial charges from dipole moments) by means of Ewald summation.

A few words on the MD simulations cont.

- Most emphasis in the modeling part have been on the complex liquid region of the CO2 phase under relevant transport conditions. Specifically 100 to 200 bar and concentrations of impurities which enable modeling based on infinite dilution as reference state for impurities dissolved in CO2 and H2O respectively
- In a practical dynamic flow situation solubility of CH4, N2 and Ar into water and also adsorption of the same components onto rust are of no importance in terms of hydrate risk. They will contribute in a very standard fashion (langmuir constants, fugacities) in the chemical potential of water in hydrate during hydrate formation from CO2 phase and free liquid water. H2S is therefore the only impurity (in addition to water) which have significant implications of distribution between CO2, liquid water and rust.



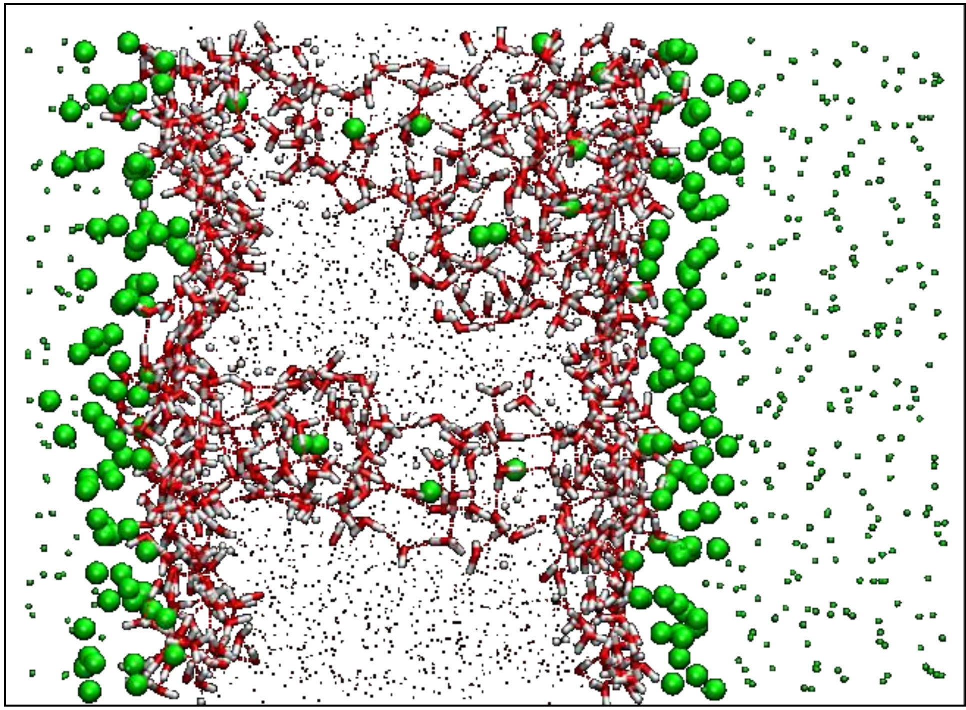
The water/CO2 interface is in the order of 1.2 Å for dense CO2 (left, 850 kg/m3) towards liquid water (rigth)



Methanol additions to water reduces the interfacial free energy between CO2 and the water phase. Snapshot of average surface waves

A few words on the MD simulations cont.

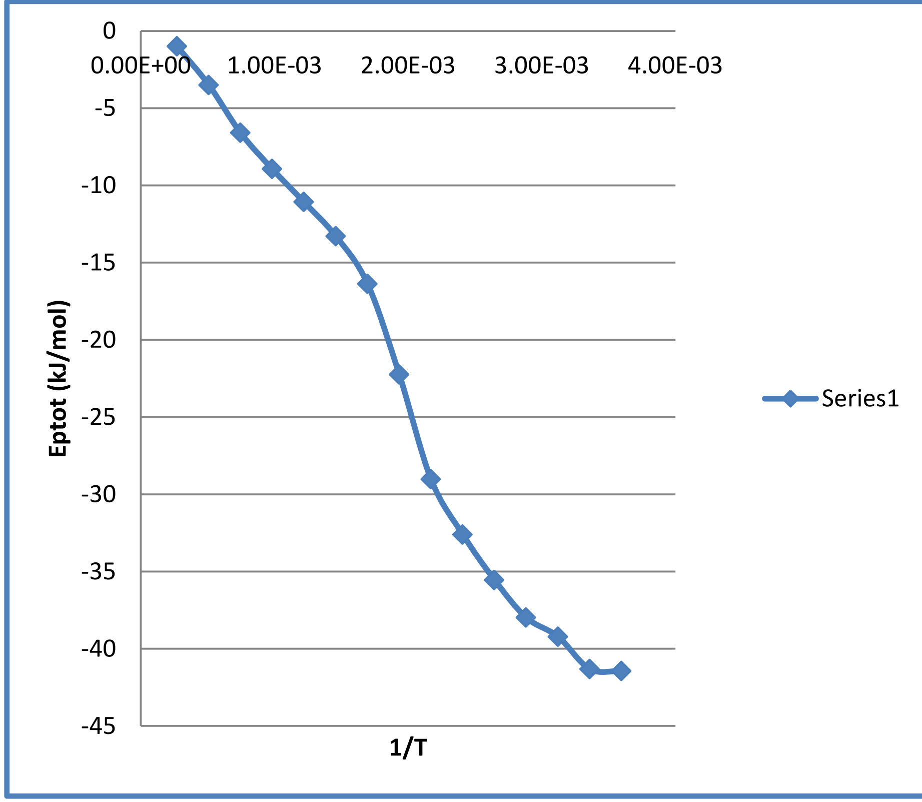
- To our knowledge there are no experiments today which can, without any dispute, claim to dissolve water as single molecules due to the particularly high strength of hydrogen bonds at these low temperature. Experimental data will therefore show a higher capacity for water uptake than a single molecule homogeneous distribution would give.



Water (red, grey) in between methane (green) will dissolve into methane as clusters of two or more waters. Experimentally an extreme challenge to dissolve water as single molecules into non-polar of slightly polar (CO2) solvents.

Experimentally observed solubility of water into CH4 or CO2 will be higher than theoretical values based on homogeneous single water distribution solubility.

Thermodynamics



- Energies and enthalpies are trivially sampled from simulations in the NVT (constant number of particles, volume and temperature) and NPT (constant number of particles, pressure and temperature)
- In ideal gas the impact of molecular interactions (the residual part in equations of state) is zero. In a molecular dynamics simulation this limit will be met when all interactions are scaled down to zero (we apply Mezei's algorithm for this). Integration of the work involved in scaling interactions from zero to full interaction gives residual free energy. This work is trivially related to corresponding energy changes by the temperature relationship between free energy and energy

Scaling the temperature and sampling the interaction energy for varying temperatures towards infinite T (3000 K is high enough for extrapolation from 1/3000 towards 0 for 1/infinite T) is equivalent to scaling interactions but error in samplings slightly higher. Figure above is for water towards hematite

Limits of water content in CO2 before drop out

- ***Several different QM charge distributions on Hematite all show consequently that water will prefer to drop out as adsorbed on Hematite and can then subsequently form hydrates heterogeneously***

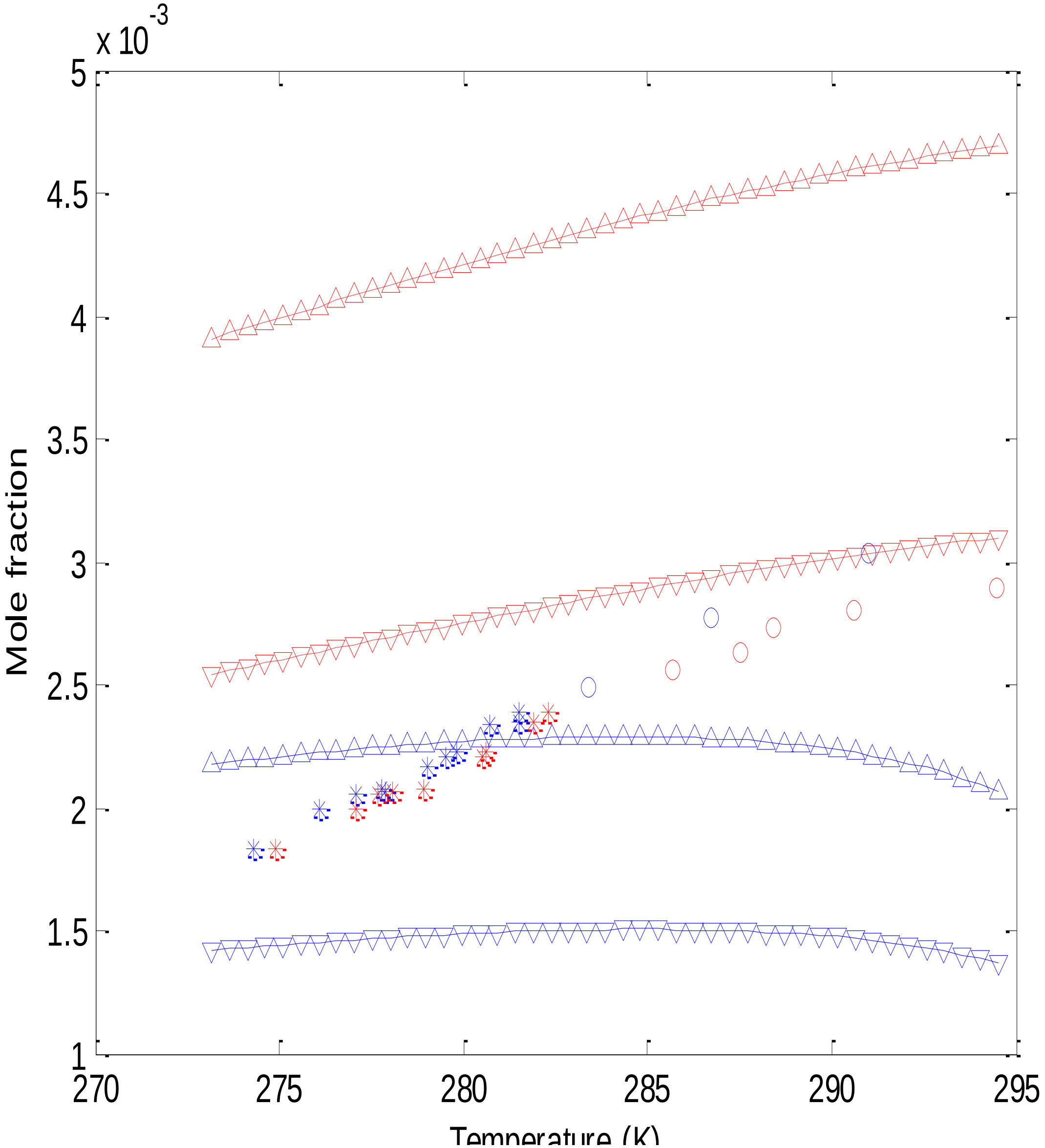


Fig. 11. Estimated maximum content of water in CO2 before dropout as adsorbed water (downward triangles) and as liquid dropout (upward triangles). Liquid water chemical potential from Kvamme and Tanaka [1] and difference between adsorbed and liquid water chemical potential from table 5 (-1.7 kJ/mole). Blue is for a pressure of 101 bar and red is for 61 bar. Same color codes for experimental data, in which stars are measured with hydrate present and circles are for liquid region.

Then what about hydrate formation as function of water mole fraction in CO2?

- ***Three layers of water outside rust water behaves liquid like and classical hydrate calculations are appropriate with the addition that also adsorbed hydrate former can form hydrate (different P,T)***

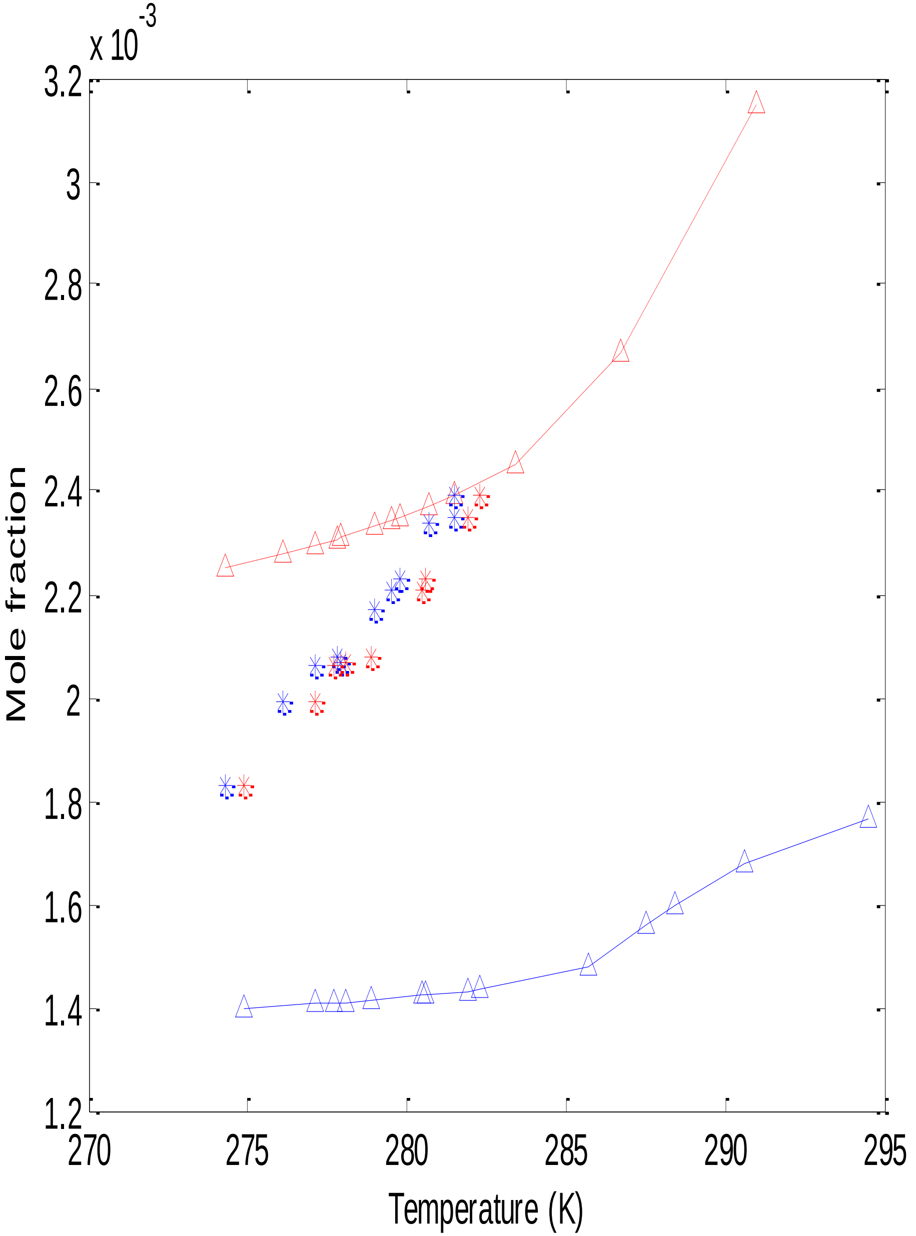


Fig. 13. Estimated content of water in CO2 in equilibrium with hydrate at two different pressures. Blue is for a pressure of 101 bar and red is for 61 bar. Stars are experimental data at 101 bar (blue) and 61 bar (red).

Options for industrial applications of non-equilibrium analysis

- Step one is a trivial ellimination of all phase transitions that are impossible because of positive free energy changes or too small free energy change to overcome the barrier of interface free energy related to pushing aside «old phases»
- Each possible phase transition can be evaluated separately in order to quantify which one of them are the most feasible in terms of free energy changes for the different steps leading to hydrate in each route.
- A simple kinetic analysis using Classical theory or MDIT theory (Kvamme, 2002, 2003) is easy to implement and computationally fast
- More advanced theories can be used as tools for better qualification of kinetic rate limitations. Phase Field Theory is one option
- University of Bergen (Kvamme's group) will be happy to contribute in implementation into industrial codes through follow up projects
- Advanced kinetic modeling as a tool for implementation of kinetics as well is also interesting and can include impact of kinetic hydrate inhibitors

Routes to hydrate formation

- As a conservative analysis skipping possible re-dissociation of formed hydrate by contact with undersaturated phases is a good option
- Some routes to hydrate formation may be going in parallell at different kinetic rates
- Some routes to hydrate formation might even result in competing hydrate formations since H2S is an aggresive hydrate former and H2S dominated hydrate might form parallell to CO2 dominated hydrate

Route 5: Hydrate formation from water dissolved in CO2

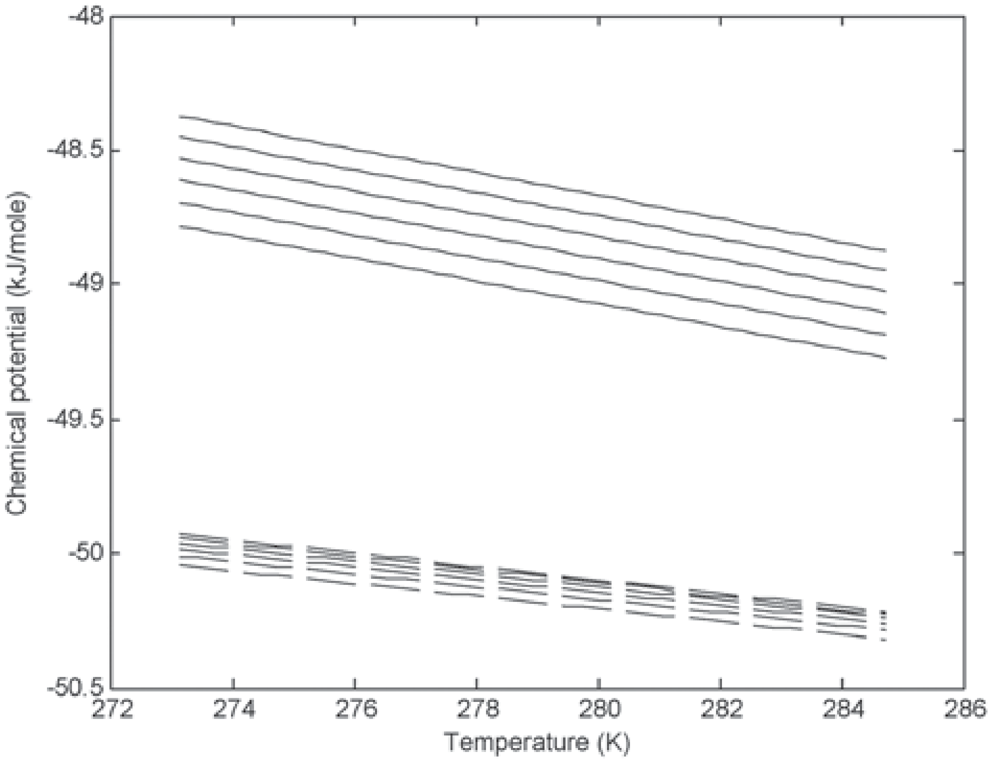


Fig. 6 Estimated chemical potentials of water that drop out in either liquid water or hydrate form. The same mole-fractions and conditions as in Fig. 5. Pressures are, from bottom to top, 100, 120, 140, 160, 180 and 200 bar. Solid lines are conditions for drop out as liquid water. Dashed lines are the corresponding estimated conditions for drop-out directly as hydrate from CO2 solution

- This option has been investigated and published in a paper prior to this project. ***Hydrate formation directly from water dissolved in CO2 is possible*** but with low water concentrations the question is whether it is realistic or not (PFT modeling is one way to investigate)

Water would like to drop out from CO2 as hydrate rather than as liquid water at all conditions in the range investigated. Benefit is around 1.5 kJ/mole for hydrate versus liquid water

Route 6: Hydrate forming from liquid water and fluid phase

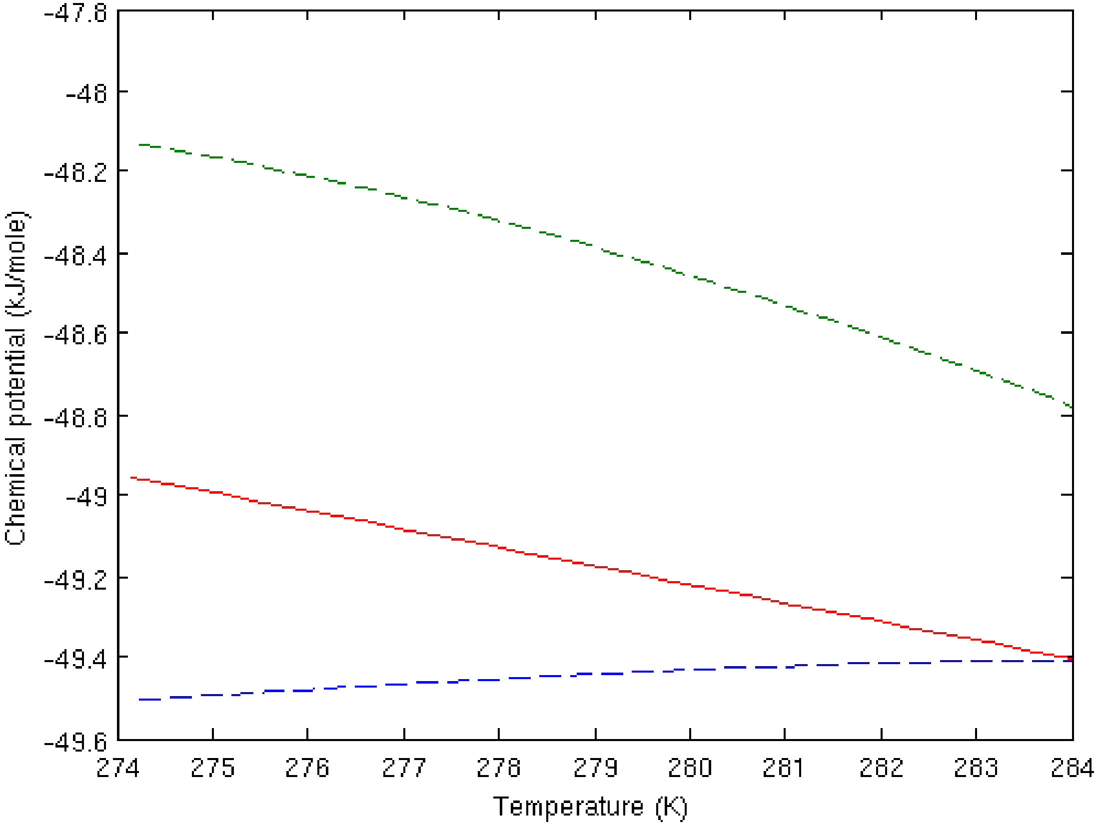


Figure 4 Chemical potential for liquid water (solid), water in hydrate formed from a mixture of 0.001 mole-fraction H_2S dissolved in CO_2 at 200 bar (lower dashed curve) and water in hydrate formed by the H_2S alone (upper dashed curve).

- As we already know CO2 hydrate will surely form at the conditions in consideration but a critical question is whether H2S dissolved in CO2 can stablize a competing hydrate dominated by H2S, which it is not able to under concentrations of 0.001 H2S in CO2

Route 6/8: Hydrate forming from liquid water with dissolved H2S and fluid CO2 phase

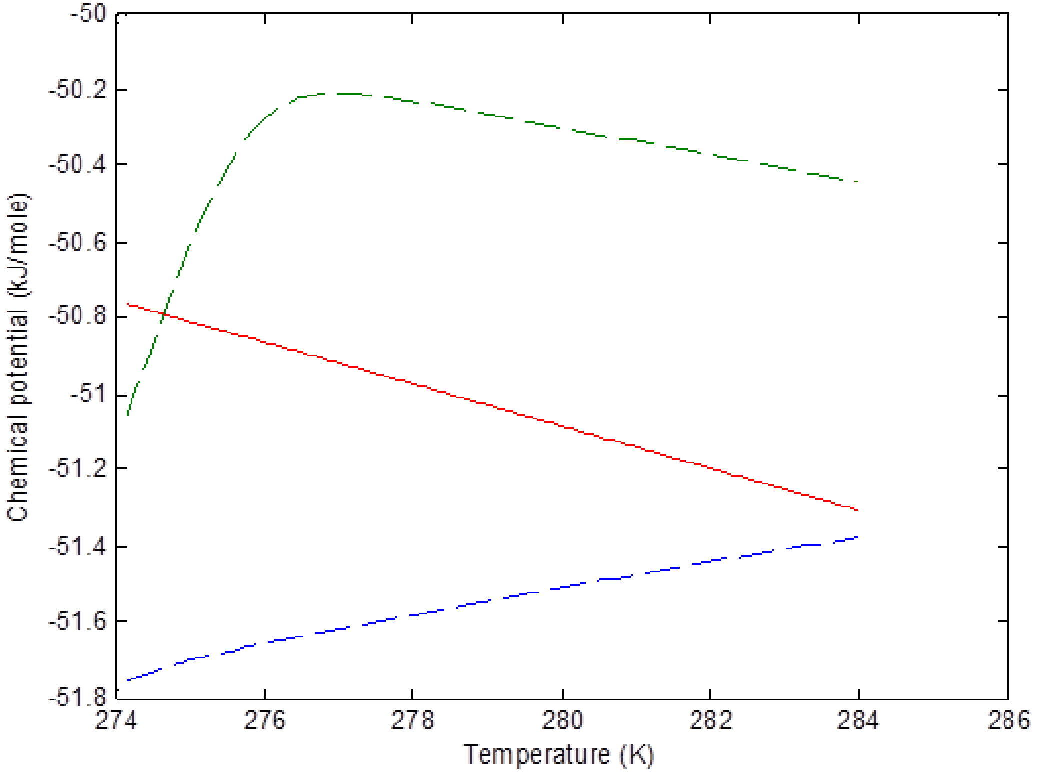
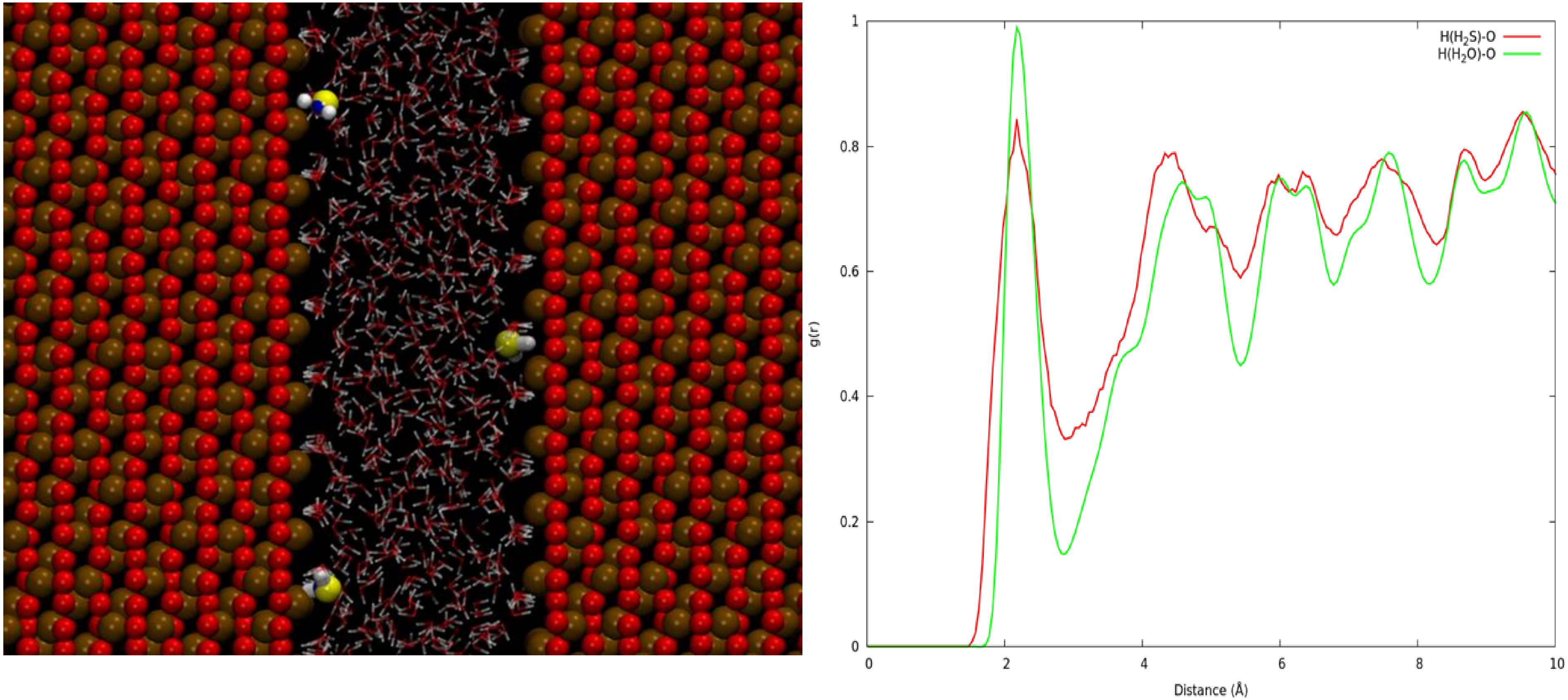


Figure 17. Chemical potential of water as liquid (solid) and in hydrate only stabilised by dissolved H_2S (upper dashed curve) and stabilised by dissolved H_2S in water and CO_2 from fluid (lower dashed curve). Pressure equal to 100 bar and H_2S mole-fraction in CO_2 0.001

- This will be an aggressive hydrate formation since it can grow from both sides of an initial hydrate film (H2S dominated hydrate from water side and CO2 dominated on fluid side)

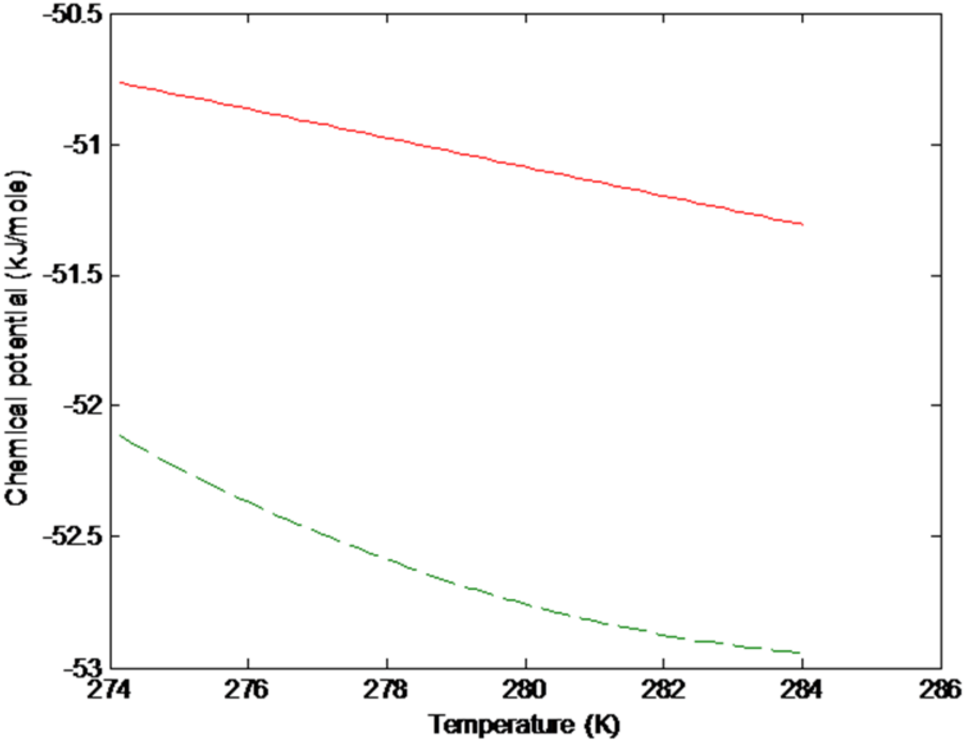
Hydrate formation involving adsorbed hydrate former (enriched on the rust surface)



Snapshot of H2S (enhanced molecules) adsorption on Hematite in competition with water (left) and pair correlation functions for oxygen in hematite and hydrogen in hydrogen sulfide (green) and water (red) (right)

H2S adsorption is highly favorable

Route 9: Hydrate forming from liquid like water (roughly 1.3 nm outside Hematite) or bulk water and adsorbed H2S

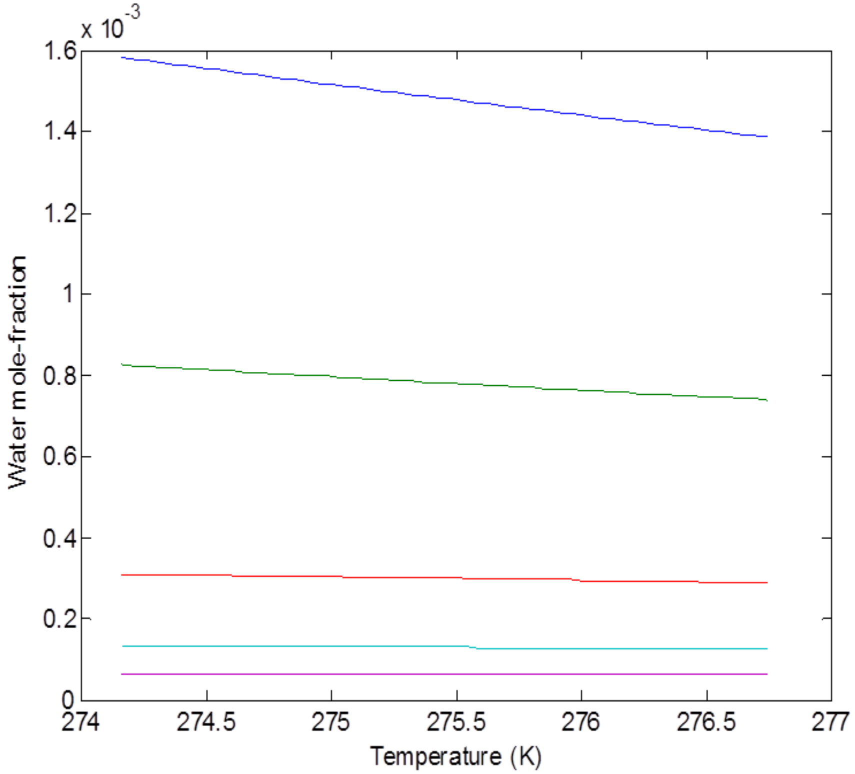


Chemical potential for water in hydrate (dashed) as stabilized from adsorbed H2S at 100 bar and liquid water chemical potential (solid) at same conditions.

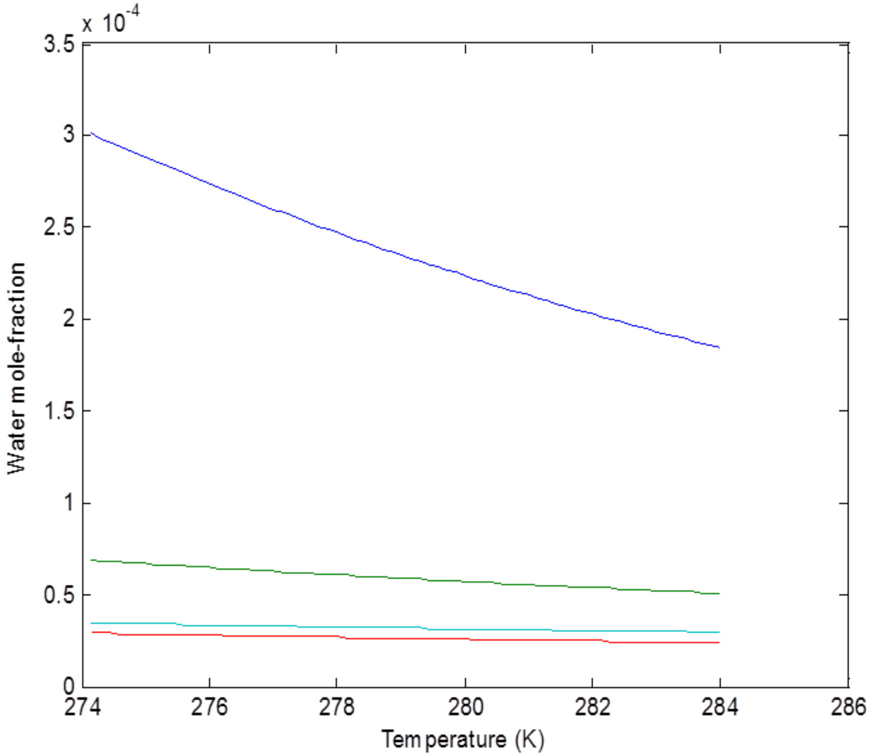
Hydrate formation from adsorbed H2S is highly facilitated and togther with previous slides very aggreasive hydrate formation can occur from adsorbed H2S and H2S dissolved outside the adsorbed layers in parallell to CO2 dominated hydrate towards the CO2 phase.

Limits of water content in CO2

Estimated water dew-point concentrations in carbon dioxode solution. Curves are, from top to bottom, for pressures 110 bars, 120 bars, 135 bars, 150 bars and 200 bars.



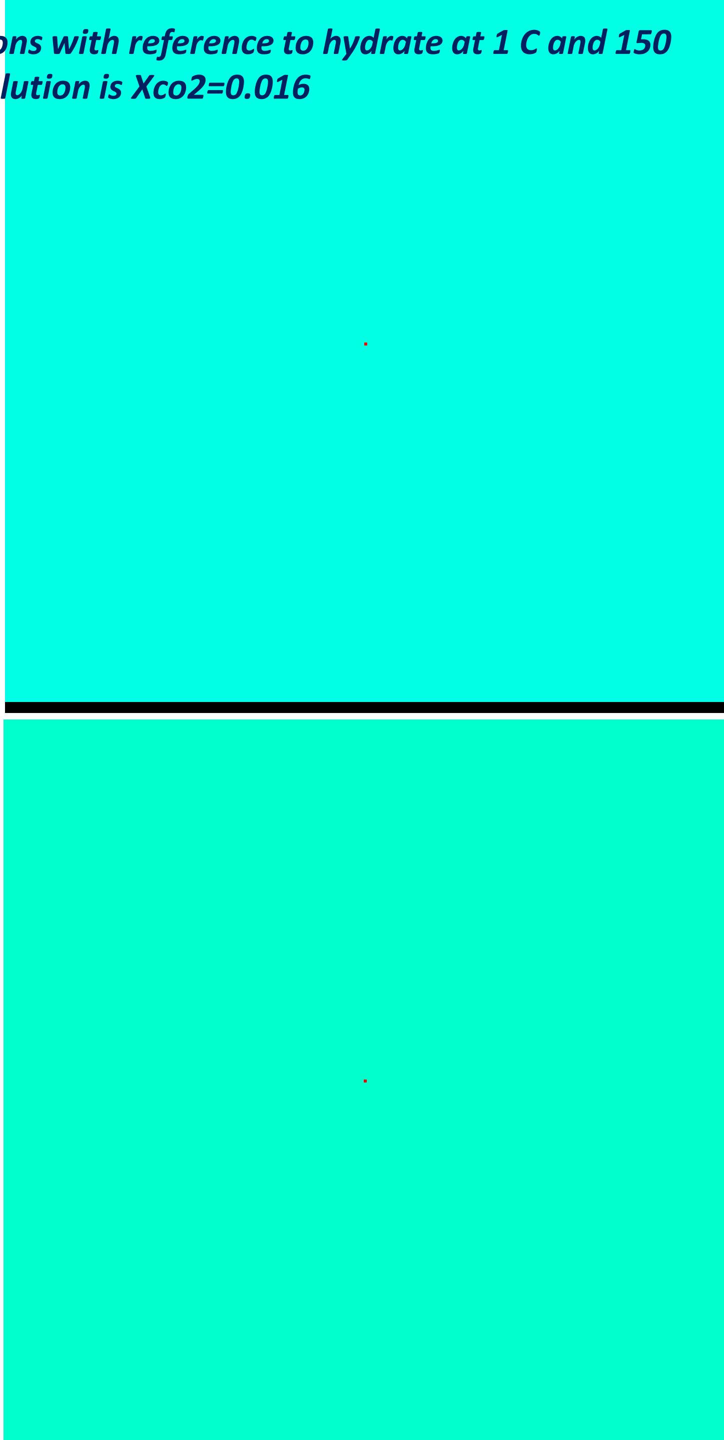
Limits of water mole-fraction in CO_2 before drop-out as adsorbed on Hematite. Upper curve is for 125 bars followed by 150 bars, 175 bars and 200 bars (bottom curve).



These estimated values for single molecule uniform distribution (formal thermodynamics) is lower (<u>more conservative</u>) than experimental measurements, which are likely to overestimate amount of water in CO2

Kinetics

Hydrate growing from two supersaturations with reference to hydrate at 1 C and 150 bar. Lowest limit coexisting with aqous solution is Xco2=0.016
Right: Xco2=0.032
Bottom right: Xco2=0.036



- A limit ***does not mean that liquid water drop out instantly*** at that concentration for given P and T

- Citical droplet size is in the order of 2.5 – 3 nm so ***more than 100 waters need to find each other*** (in a fixed T,P situation). Long nucleation time and even longer induction time (onset of massive, visible phase change)

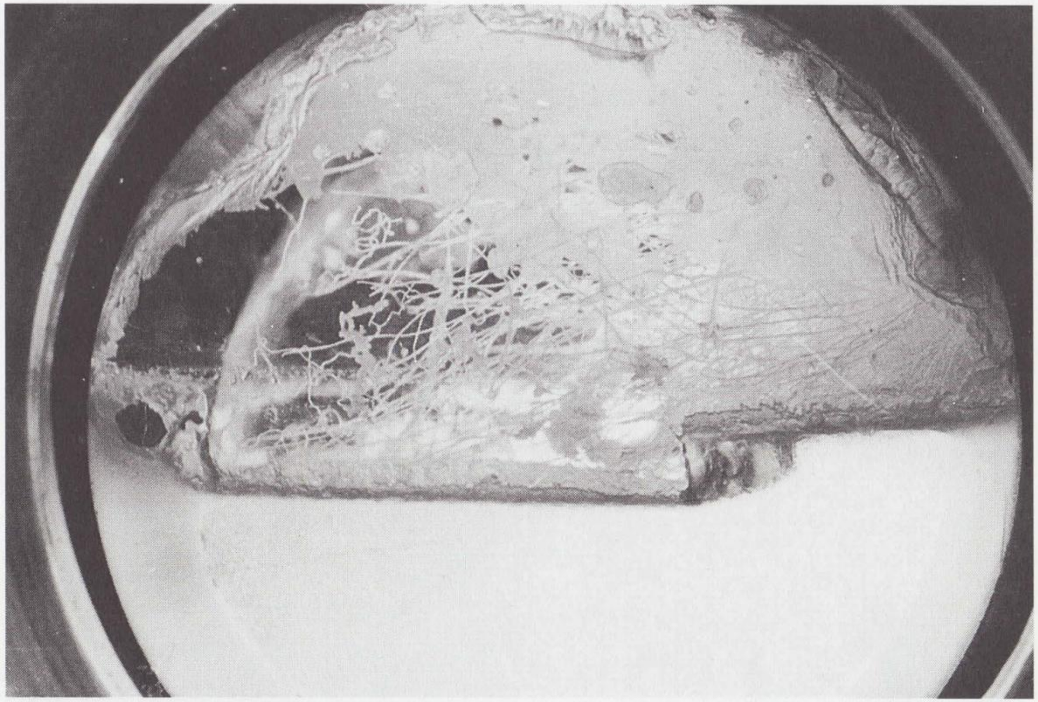
- And at exactly dew-point there is ***NO net driving force*** to deposit liquid water at all

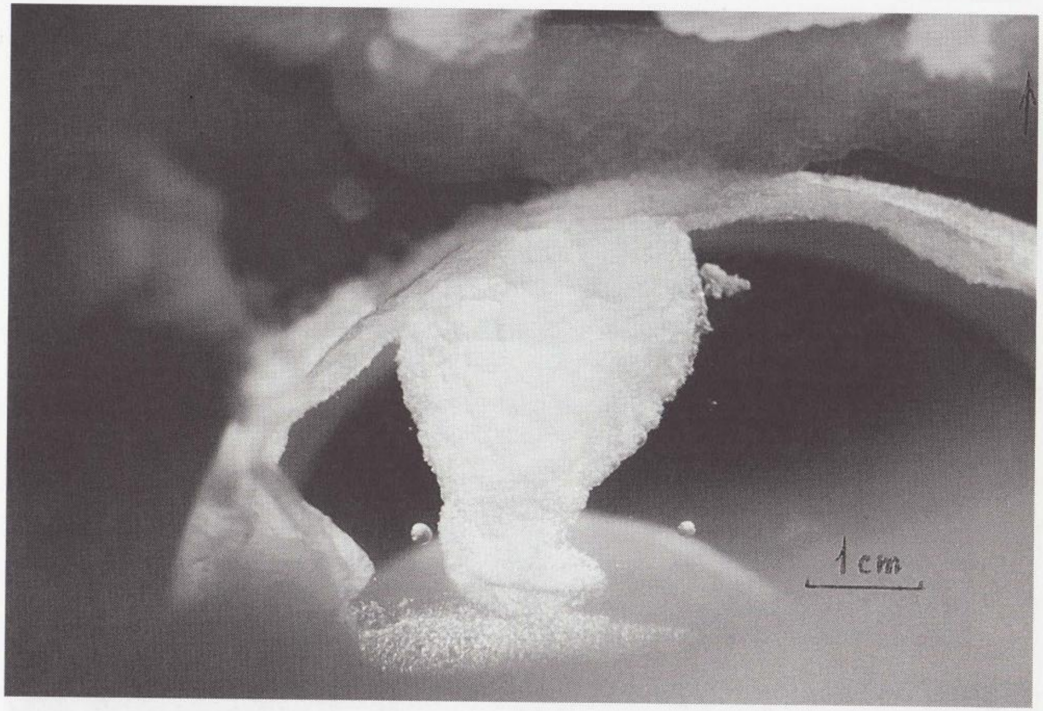
- Minimum free energy difference must ***also overcome interface free «penalty»***. So a significant driving force (higher concentration of water) and an extra free energy proportional to area of a critical size droplet times interface free energy (we have values for that)

Can this lead to pipeline blocking?

- Thickness of hydrate layer on wall is not limited since – when hydrate forms it is the lowest free energy water phase.
- And hydrate is water wettening so further adsorption of water and hydrate former onto hydrate will ensure continued growth according to supply of mass, unless exposed to under saturated CO2 for long enough periods of time.

Note the white hydrate growing from water/CH4 interface and connecting to hydrate growing from adsorbed layers on the glass wall in this PVT cell experiments at 1 Celsius and 150 bar





Conservative values?

- Yes – but conservative because we did not discuss ***driving forces needed*** (higher concentrations) for drop-up (equilibrium takes infinite time to reach !)
- And we did only briefly mention that ***kinetics will limit drop-out rates*** and might ***even prevent drop-out from happening*** before substantial super-saturation
- And we skipped all processes that can ***redissosiate*** hydrate and as such reduce net impact

Conclusions

- Transport of carbon dioxide with water and other impurities will not be able to establish equilibrium due to Gibbs phase rule
- Non-equilibrium analysis of possible competing phase transitions requires consistent thermodynamic properties for all phases, which can be accomplished using ideal gas as reference state for all components in all phases.
- Routes to hydrate formation that involves adsorbed phases dominate in terms of thermodynamic preferences

Conclusions continued

- Estimated limits of solubility are generally lower than experimental values at these low temperatures. This trend is expected since dissolution of water into CO2 as single monomers in this low T range (strong hydrogen bonds) is an almost impossible challenge. Observed uptakes of water will consequently be higher than solubility in a true thermodynamic sense (uniform distribution of single water molecules)

- Regardless of further processing of the data to fit into existing modeling software (process-, transport- and other) the infite estimated infinite dilution data and free energies are unique and not available from any other open source

Conclusions continued

- Routes towards hydrate formation that involves solid surfaces have never been been quantified before this study and the presence of H2S implies dramatic changes in the nature of hydrate formation, in which hydrates can efficiently form for adsorbed and water dissolved hydrate formers parallell to water/CO2 interface growth. This implies a much more aggressive growth with small induction (if any at all within a second scale in time)

Thank you for the attention !

Smoking is not permitted at UoB so it cannot be me in the picture

Acknowledgements

- We acknowledge the grant and support from Research Council of Norway through the following projects: SSC-Ramore, “Subsurface storage of CO2 - Risk assessment, monitoring and remediation”, Research Council of Norway, project number: 178008/I30, FME-SUCCESS, Research Council of Norway, project number: 804831. Funding from STATOIL under contract PO4502354080: “A new reservoir simulator for hydrate exploration studies” and associated funding from CLIMIT project 224857: “Safe long term storage sealing of CO2 in hydrate”

One possible way forward: Kinetic modeling and two experimental approaches for hydrate formation in pipelines

- Phase Field Theory (PFT) is state of he art kinetic modeling of hydrate kinetics and is free of adjustable empirical parameters.
- PFT can serve as a platform for development of simplified models for use in industrial models
- Complementary experiments (loops at CMR) could be possible using three detection principles:

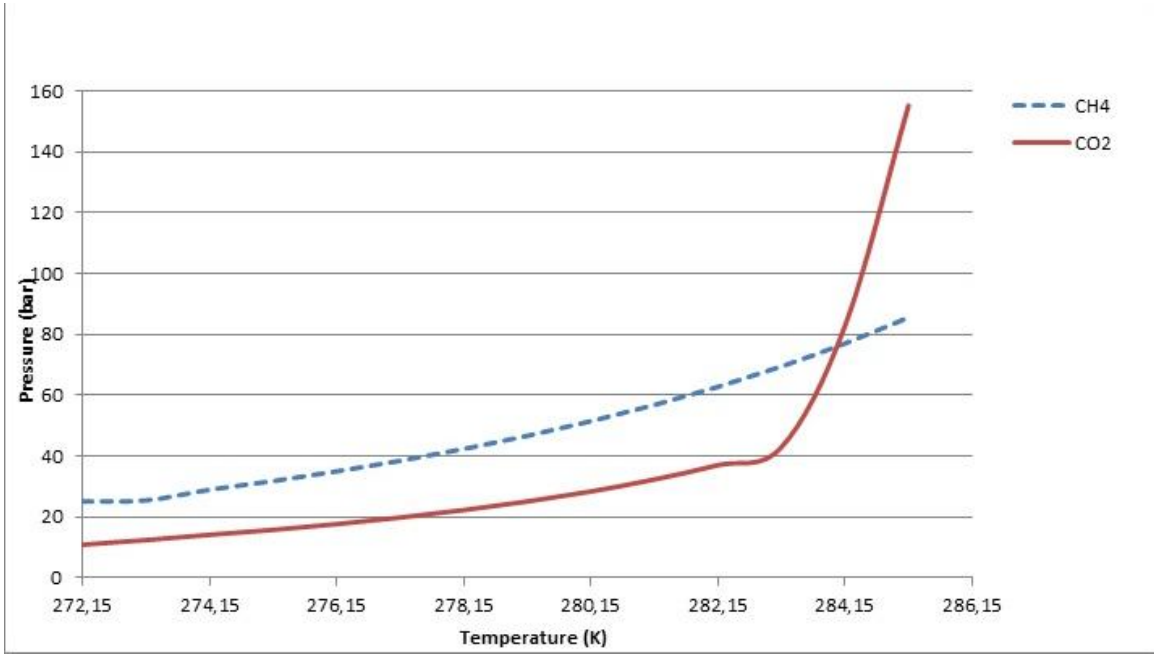
  - Gamma- or X-ray tomography (Prof. Geir Anton Johansen)
  - Ultrasound (Prof. Per Lunde)

One possible way forward: Kinetic modeling and two expreimental approaches for hydrate formation in pipelines

- Inclusion of studies on the impact of knetic inhibitors using molecular modeling is possible and feasible

- Phase Field Theory (PFT)
-
- With example from hydrate exchange process in which original CH4 hydrate is converted to a mixed hydrate through injection of CO2

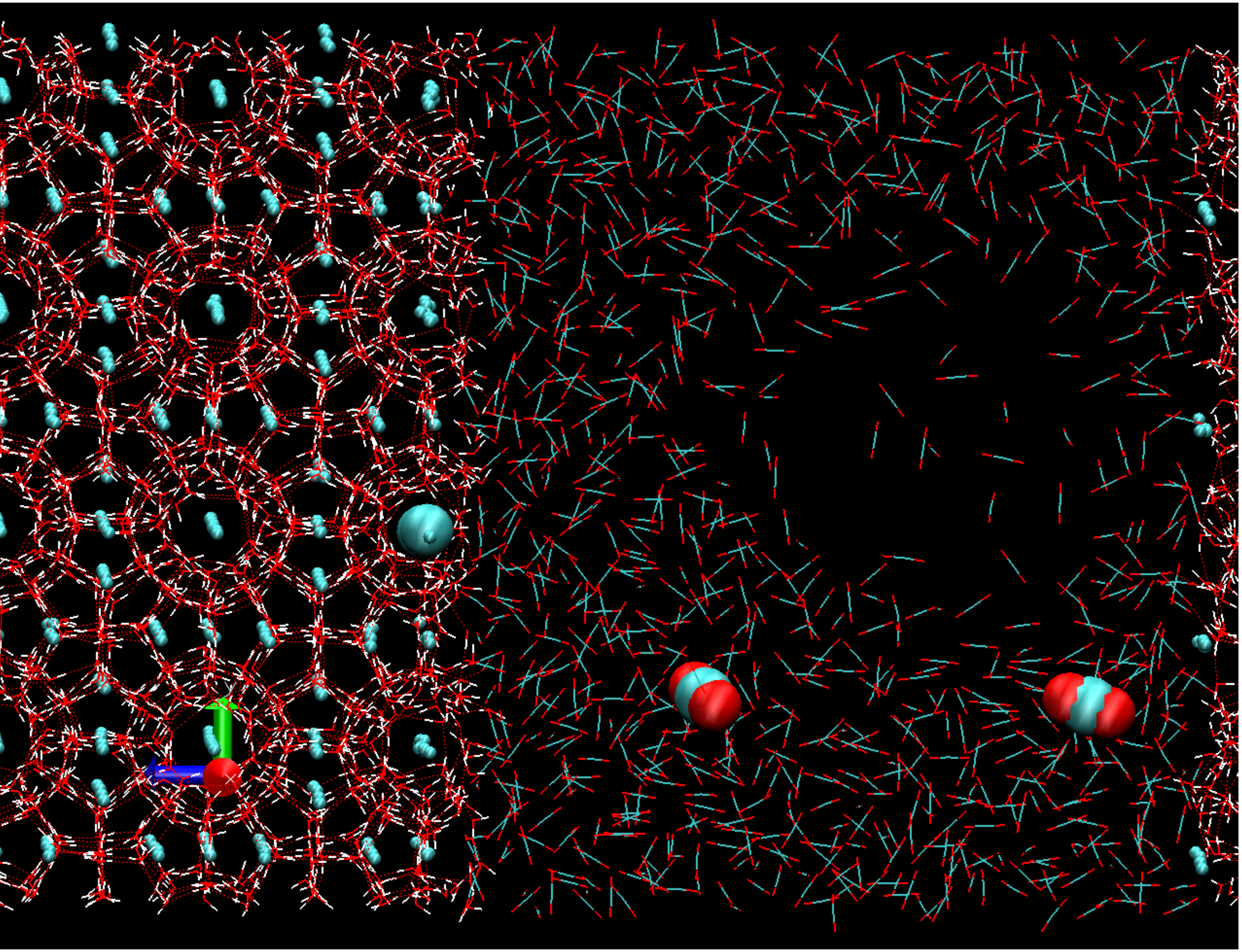
Part 2



Regions of hydrate stability for pure CH4 and pure CO2 hydrates. Mixed hydrate in which CO2 fills the large cavities and CH4 fills the small is more stable over all regions of pressure and temperature

Two primary mechanisms: 1) Solid state conversion and 2) Sequences of new CO2 hydrate and subsequent CH4 hydrate dissociation due to released heat from the hydrate formation.

Conversion: the movie



Solid state conversion is slow, with diffusivity coefficient in the order of 10^-16 m^2/s

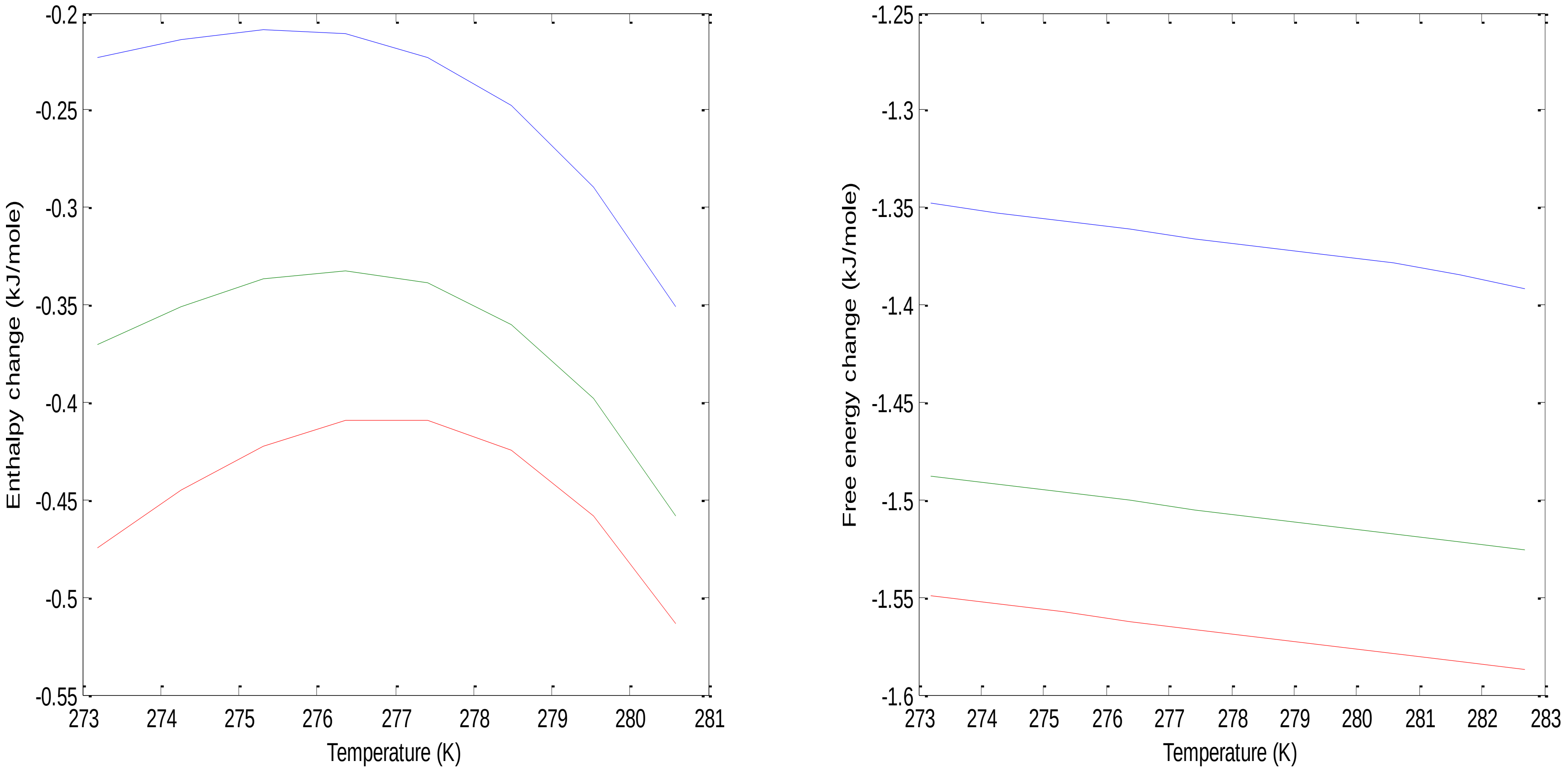
The process in entropy dominated (see next slide)

The relative impact of this mechanism will increase with lower free water in pores

The second mechanism is much faster and in the rate order of liquid water transport but requires advanced theory to investigate due to complex dynamic couplings between mass transport and heat transport

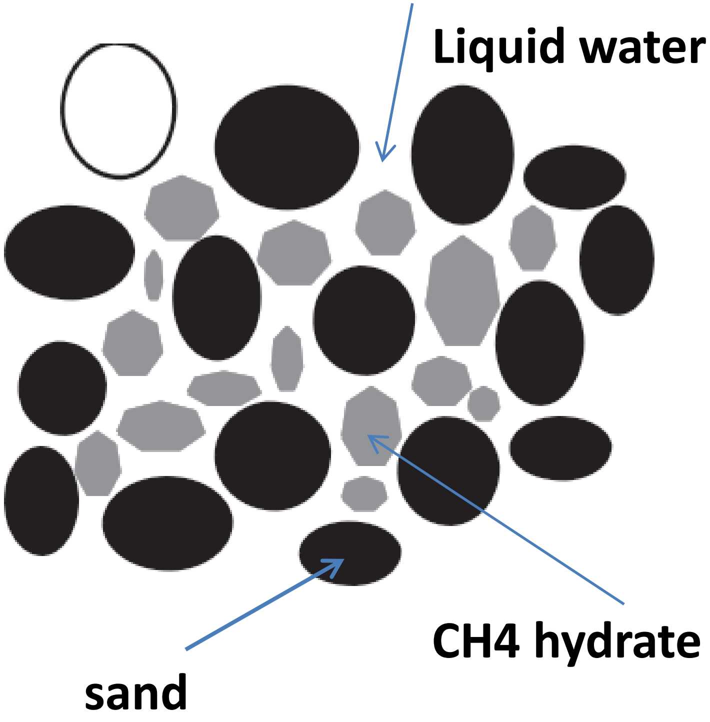
Free energy and enthalpy changes for conversion from pure methane hydrate to pure carbon dioxide hydrate

Blue: 43 bar, **Green: 83 bar**, **Red: 120 bar**



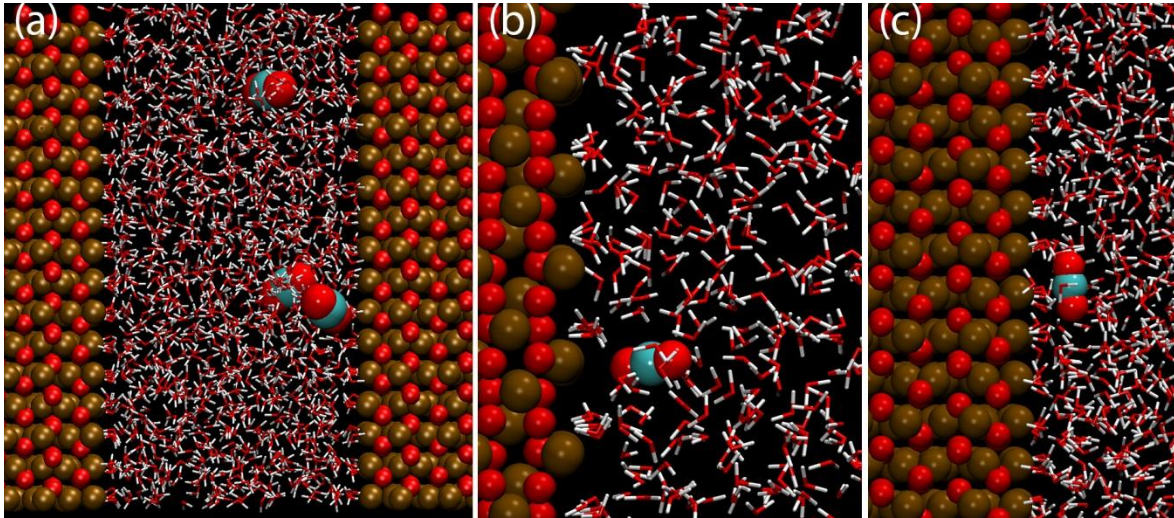
Free energy chage for the water in the structure is not large. CO2 change is also limited since it comes from a fairly dense phase and have reasonable filling. But CH4 will benefit from the entropy change of getting released.

2: Injected CO2 can form new hydrate and released heat from that process can dissociate ***in situ*** CH4 hydrate



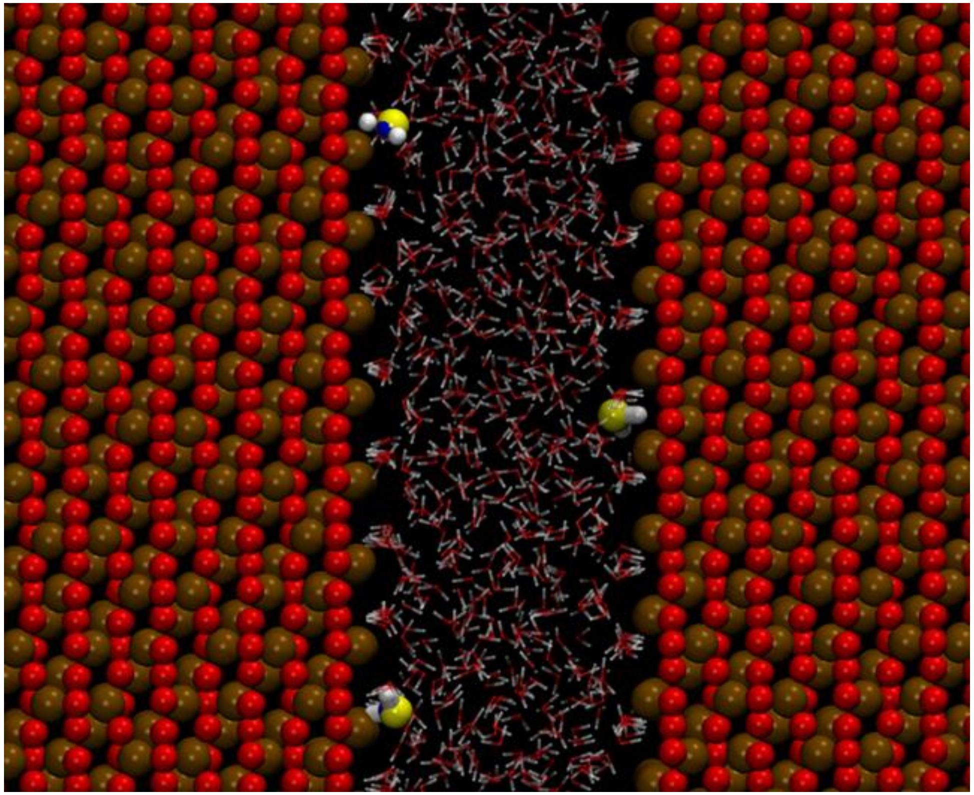
- *The new hydrate can nucleate from water/CO2 interface*
- *or*
- *From adsorbed CO2 on mineral surface*
- *or*
- *From CO2 adsorbed on CH4 hydrate surface*

Right: CO2 (enhanced red and grey) adsorbing onto Hematite from water solution. Adsorbed CO2chemical potential: -39.21 kJ/mole



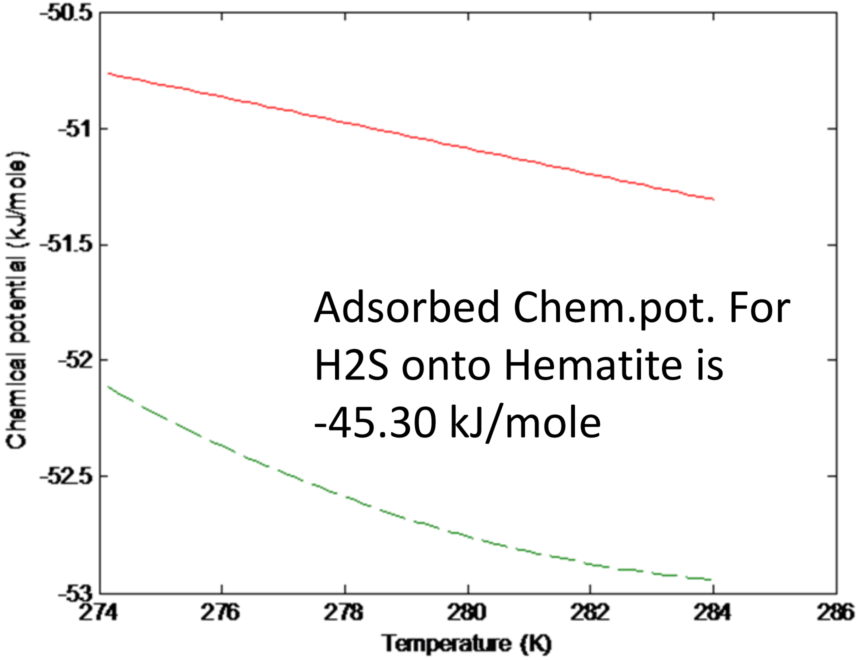
Possible Remaing H2S following injected CO2 will enhance new hydrate formation

We need a theoretical approach that can model all of these options and «decide» by itself how the system should progress as function of time and space



Top: Snapshot of H2S (enhanced molecules) adsorption on Hematite in competition with water (left) and pair correlation functions for oxygen in hematite and hydrogen in hydrogen sulfide (green) and water (red) (right)

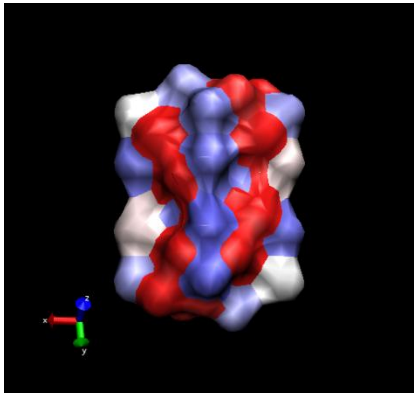
Below:Chemical potential for water in hydrate (dashed) as stabilized from adsorbed H2S at 100 bar and liquid water chemical potential (solid) at same conditions.



Adsorbed Chem.pot. For H2S onto Hematite is -45.30 kJ/mole

Investigating competing phase transitions in porous media (read: solid material surfaces) requires multiscale modeling approach

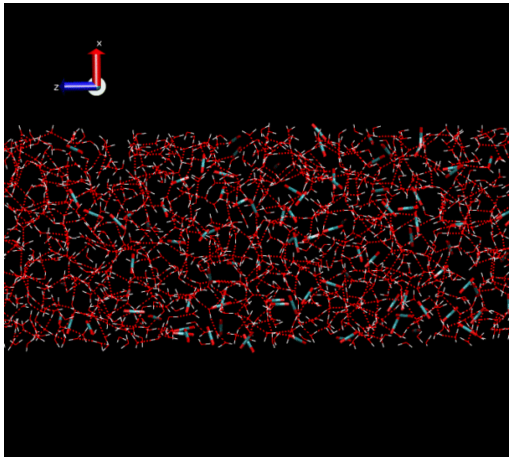
Charge distribution for hematite by Gaussian03



from

quantum (characterisation of charge distribution in model molecules, from below nano in scale)

MD for Studies of mechanisms, thermodyn, interface properties and parametrisation



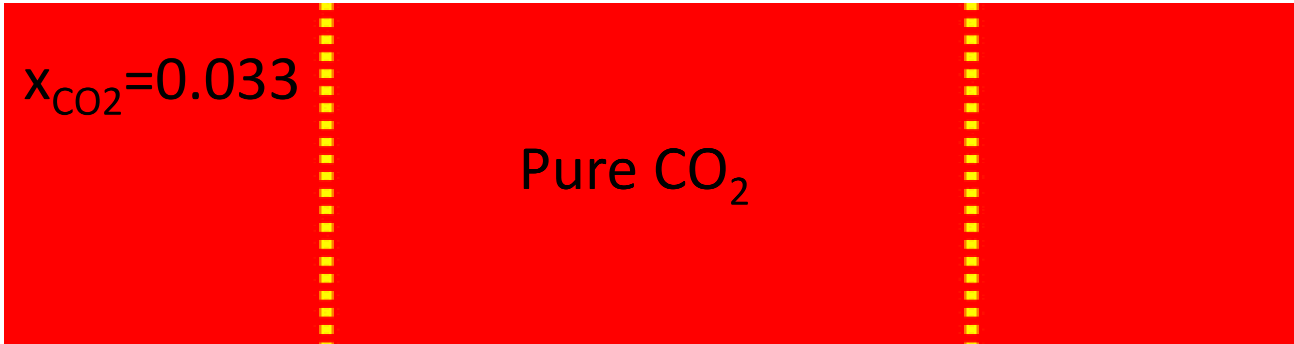
to

nano (Molecular Dynamics simulations, MD)

and

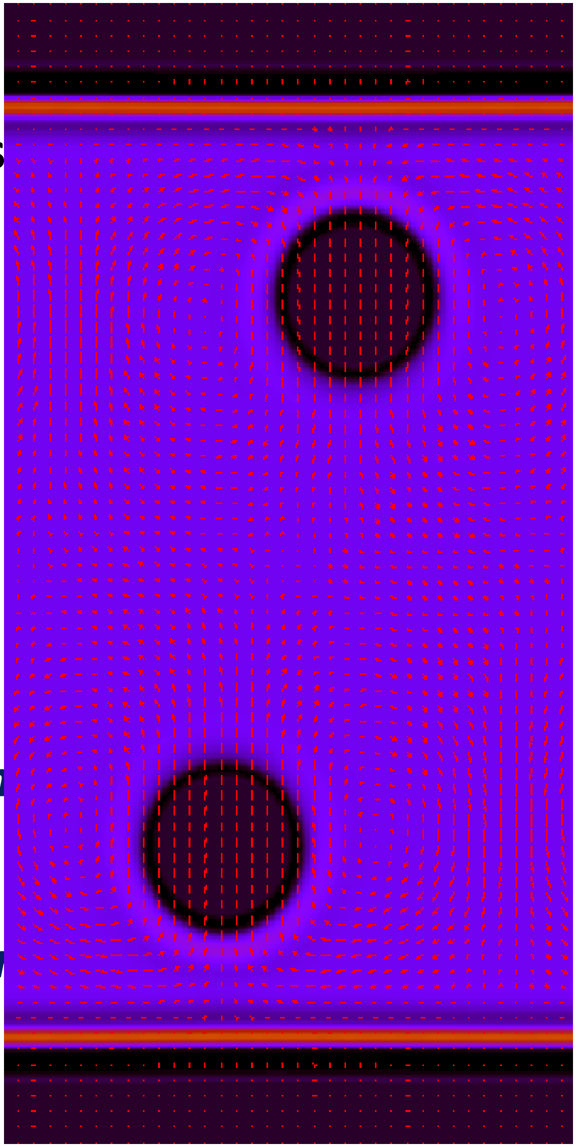
micro (Phase Field Theory)

Simulation of hydrate growth dynamics on interface of a CO2 plume using PFT



So what is phase field theory (qualitatively)?

- ***Phase Field Theory (PFT) is similar to Density Functional Theory (DFT) in the sense that the*** **structural changes** ***in DFT is replaced by the*** **corresponding free energies** ***in PFT***
- ***Practically PFT simulations can be considered as local and global*** **free energy minimalisation** ***under the*** **constraints of mass and heat transport dynamics*****.***
- ***In contrast to DFT, PFT is*** **free of any volumetric scale limitations** ***although*** **interface free energy flucttutations** ***(upcoming slides) are on nano scale and needs to be evaluated at least o an*** **average impact fashion** ***for the pronlem/system in consideration***



Phase-field theory simulation of a simplified binary alloy phase transition in gradients of T (decreases towards centre in heigth direction) and gravity field (increases outwards, up and down from centre. Arrows are directions of velocity fields for mass transport

Phase Field Theory Model

$$F = \int d\underline{r} \left(\boxed{\frac{\varepsilon_{\phi}^{2}}{2} T(\nabla\phi)^{2} + \sum_{i,j=1}^{3} \frac{\varepsilon_{xi,j}^{2}}{4} T\rho\left(x_i \nabla x_j - x_j \nabla x_i\right)^{2}} + f_{bulk}(\phi, x_1, x_2, x_3, T) \right)$$

Free energy changes due to phase transition (ϕ is 0 for solid and 1 for fluid)

Free energy changes due to concentration gradients across the interface

Ɛ is unique for each component according to distribution profile across the interface but as an average value it may not be very different from the similar parameter for the phase transition so setting them equal is a first approximation which makes at least numerical solutions feasible

- Free energy due to thermal fluctuation across the interface
- Function of interface
  - Thickness
  - Free energy of interface
  - Interface structure(available from interface density profile for all components)

Model Parameters

Estimated to 8.5 Å for hydrate/liquid water (Kvamme et.al. (2007))

$$d = \left(\frac{\varepsilon^2 T}{2}\right)^{1/2} \int_{0.05}^{0.95} d\xi \left\{\Delta f[\xi, \vec{\mathrm{x}}(\xi)]\right\}^{-1/2}$$

Phase Field Theory parameter ***w*** is in the free energy *f* (previous slide) as the barrier for transition over to the new phase

where $\Delta f = f - f_0$, and

$$\gamma_\infty = (\varepsilon^2 T)^{1/2} \int_0^1 d\xi \left\{\Delta f[\xi, \vec{\mathrm{x}}(\xi)]\right\}^{1/2}$$

ξ is the interface profile

$$f_0 = G_L(\vec{\mathrm{x}}_L^{eq}) + \sum_{i=1}^{n} \frac{\partial \mu_{i,L}}{\partial x_{i,L}}\bigg|_{\vec{x}_L^{eq}} (x_{i,L} - x_{i,L}^{eq})$$

$$f_S = G_S(\vec{\mathrm{x}}_S^{eq}) + \sum_{i=1}^{n} \frac{\partial \mu_{i,S}}{\partial x_{i,S}}\bigg|_{\vec{x}_S^{eq}} (x_{i,S} - x_{i,S}^{eq})$$

Phase Field Theory parameter ε

Interface free energy ≈ liquid water/ice 29 mJ/m^2 – (S.C.Hardy, Philos. Mag. 35 (1977)471)

(Different methods for estimation of hydrate/water interrface free energy is currently being investigated, including cleaving and capillary wave theory)

Interface thickness d and interface free energy fixes the two model parameters *w* and ε. The extension over to the multi-components case in current use follows

Phase Field Theory Model

$$F = \int d\underline{r} \left(\frac{\varepsilon_{\phi}^{2}}{2} T(\nabla\phi)^{2} + \sum_{i,j=1}^{3} \frac{\varepsilon_{xi,j}^{2}}{4} T\rho\left(x_i \nabla x_j - x_j \nabla x_i\right)^{2} + f_{bulk}(\phi, x_1, x_2, x_3, T) \right)$$

$$f_{bulk} = WTg(\phi) + \left(1 - p(\phi)\right) f_S(x_1, x_2, x_3, T) + p(\phi) f_L(x_1, x_2, x_3, T)$$

g(Φ) is assumed symmetric quadratic
p(Φ) is the propablity distribution of phases across the interface as sampled from MD

$$f_s = G_H \rho_m^H \quad , \quad f_L = G_L \rho_m^L$$

$$\frac{\partial\phi}{\partial t} + (\vec{v}.\nabla)\phi = -M_{\phi}(\phi, x_1, x_2, x_3) \frac{\delta F}{\delta\phi}$$

$$\frac{\partial x_i}{\partial t} + (\vec{v}.\nabla)x_i = \nabla.\left(M_{xi}(\phi, x_1, x_2, x_3) \nabla \frac{\delta F}{\delta xi} \right)$$

Mobilities across the interface are complex but in the simplest approximation diffusivity constants are applied

Hydrodynamics

$$\frac{\partial\rho}{\partial t} = -\rho_m \nabla.\vec{v}$$

$$\rho \frac{\partial\vec{v}}{\partial t} + \rho(\vec{v}.\nabla)\vec{v} = \rho\vec{g} + \nabla.P$$

PFT with Hydrodynamics

Total stress tensor

$$P = \mathfrak{z} + \Pi$$

Heat transport Model

Primary contributions to heat transport is conduction and convection are lumped into an "efficient" conductivity →

$$\left(\frac{\Delta H}{\Delta t}\right)_i = k_i A_i \Delta T_i$$

Rearrangements of water involves significant ***enthalpy*** *and* ***entropy*** *changes which affects structuring and rearrangements into new phases like for instance ice and/or hydrate.*

These enthalpies are evaluated directly from the ***free energy of each grid*** block

$$H_i = -RT^2 \left(\frac{\left(\frac{G_i}{RT}\right)_{T+\Delta T} - \left(\frac{G_i}{RT}\right)_T}{\Delta T} \right)$$

$$k_i = (1 - p(\phi)) k_{S,i}(T, P, \vec{x}_{S,i}) + p(\phi) k_{L,i}(T, P, \vec{x}_{L,i})$$

Substantial room for improvements on this part but at least a convenient starting point for illustration purposes

Density calculations

$$\rho_m^{L,Fluid} = \frac{1}{\overline{V}_L^{Fluid}}$$

$$\rho_m^{L,aqueous} = \frac{1}{\overline{V}_L^{aqueous}}$$

$$\overline{V}_L^{Fluid} = \sum_{i=1}^{3} x_i \overline{V}_i$$

$$\overline{V}_L^{aqueous} = \sum_{i=1}^{3} x_i \overline{V}_i + x_3 \overline{V}_3^{\,0}$$

Approximated to average molar volume of pure water

Estimated from MD using first shell approximation in integration over pair correlation functions

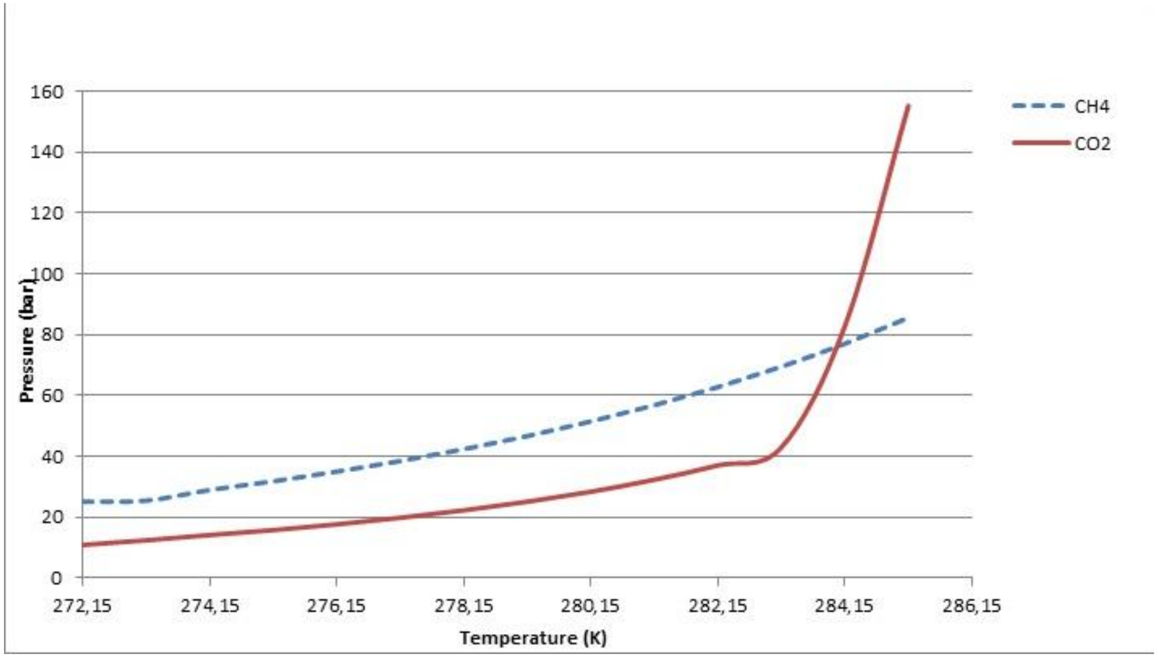
$$\overline{V}_i = \frac{ZRT}{p} + \frac{nRT}{p}\left(\frac{\partial Z}{\partial n_i}\right)_{p,T,n_{i\neq j}}$$

Partial molar volume for ***water in hydrate*** is trivially calculated from the ***unit cell dimensions and compositions***, see for instance Sloan et al. (2008), 3rd edition, CRC Press for examples. ***Guest molecule partial molar volumes*** evaluated by ***Monte Carlo*** (Kvamme & Lund, 1993).

$$\rho_m^{Hyd}$$

Example from Hydrate exchange

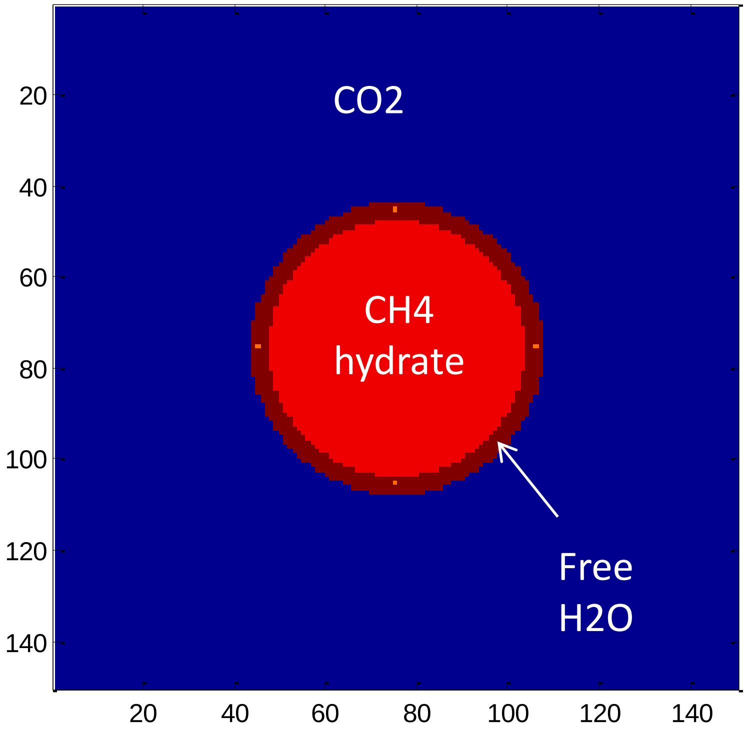
- The conversion process have been known theoretically for several decades, intensively investigated through different experiments but there are still some confusions about the process



Regions of hydrate stability for pure CH4 and pure CO2 hydrates. Mixed hydrate in which CO2 fills the large cavities and CH4 fills the small is more stable over all regions of pressure and temperature

Two primary mechanisms: 1) Solid state conversion and 2) Sequences of new CO2 hydrate and subsequent CH4 hydrate dissociation due to released heat from the hydrate formation.

Non Equilibrium Challenge



- Part of this work (exchange processes)
  - ***Initially 3 phases*** (CH4 Hydrate, Aqueos, CO2 Fluid)
  - ***3 components*** (CO2,CH4,H2O)
  - ***Degree of freedom is 2*** with P,T defined, minimum criteria is fullfilled
  - ***Non equilibrium*** due to initial ***difference (negative) in chemical potentials*** of CO2 in hydrate and fluid

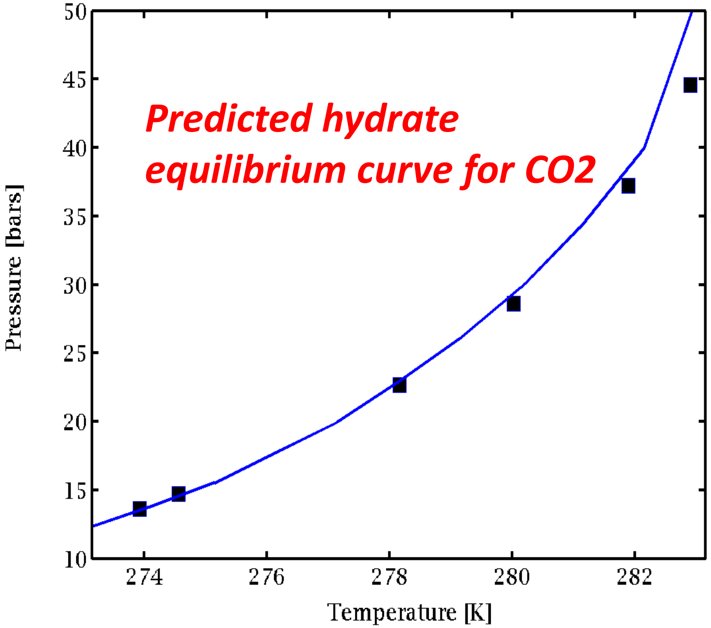
Details of the thermodynamics will be skipped but overheads are included here for completenes

- Thermodynamics for fluid-phases (aqeous and other) are continuously described and straightforward
- Thermodynamics for hydrate is related to adsorption theory and linked to equilibrium conditions so needs to be extended to outside equilibrium – we apply series expansion for this – details given elsewhere (publications available and slides available for specially interested)

Non Equilibrium Challenge

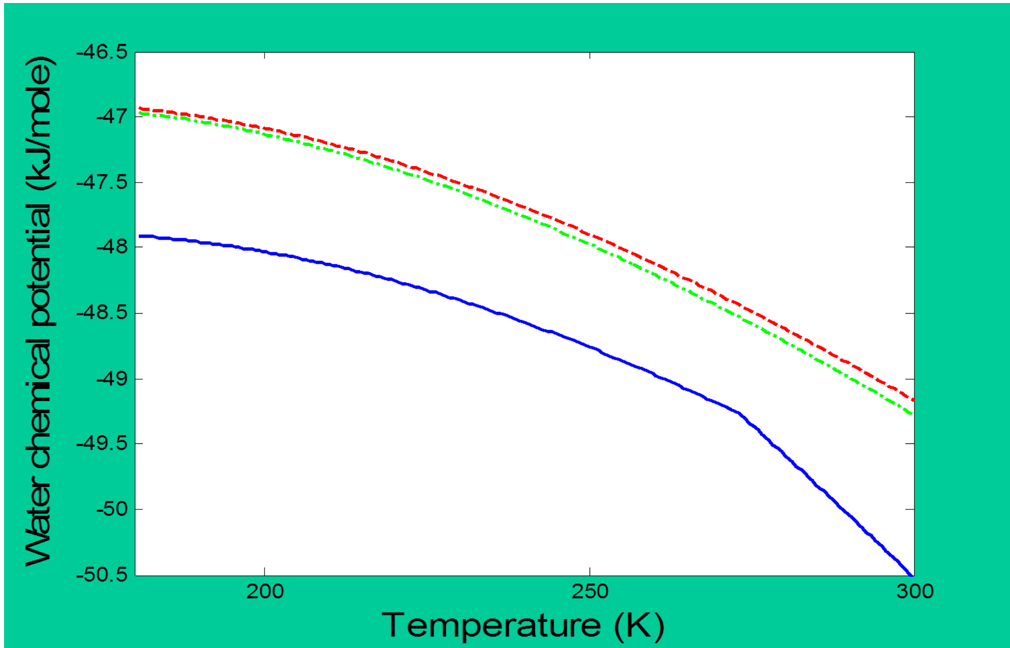
Accurate and consistent model for free energy of the different co-existing phases

- A critical basis for ***Phase Field Modeling***
- Free energies for individual (Aqueous, Fluid and Hydrate) phases are used here
  - Revised adsorption theory (Kvamme & Tanaka, 1995) for hydrate
  - TIP4P simulated chemical potential for ice, liquid water, and empty hydrate



Predicted hydrate equilibrium curve for CO2

Solid line for ice or liquid water, dash line for SI empty hydrate and dash-dotted line for SII empty hydrate.



Hydrate Thermodynamics

$$\mu_j^H = \Delta g_{ji}^{inc} + RT\ln\left(h_{ij}\right)$$

$$\mu_w^H(T,P,\vec{\theta}) = \mu_w^{0,H}(T,P_0) - \sum_i RTv_i \ln\left(1+\sum_j h_{ij}\right)$$

$\mu_w^{0,H}(T,P_0)$ = Chemical potential for water in an empty hydrate structure

$$h_{ij} = e^{\beta\left(\mu_j^H - \Delta g_{ji}^{inc}\right)}$$

Cavity partition function of component j in cavity type i

Δg_{ji}^{inc} = Free energy of inclusion in cavity by ”classical” langmuir integration or harmonic oscillator approach (Kvamme & Tanaka, 1995)

Hydrate Thermodynamics

$$G_H^{EXP} = G^{EQ} + \sum_r \frac{\partial G_H}{\partial x_r}\bigg|_{P,V,T,x_{i\neq r}} (x_r^{act} - x_r^{EQ}) + \frac{\partial G_H}{\partial P}\bigg|_{T,V,\vec{x}} (P^{act} - P^{EQ}) + \frac{\partial G_H}{\partial T}\bigg|_{P,V,\vec{x}} (T^{act} - T^{EQ})$$

$$\frac{\partial G_H}{\partial x_r} = x_c \frac{\partial \mu_c^H}{\partial x_r} + x_m \frac{\partial \mu_m^H}{\partial x_r} + x_w \frac{\partial \mu_w^H}{\partial x_r} + \mu_r \frac{\partial x_r}{\partial x_r}$$

$$\mu_k^H = Aln(x_k) + B, \qquad \frac{\partial \mu_k^H}{\partial x_r} = \{0, r \neq k\}$$

$$\frac{\partial G_H}{\partial x_w} = \sum_r x_r \frac{\partial \mu_r^H}{\partial x_w} + \mu_w^H$$

- Mole fractions are ***conserved within the Phase Field Theory***

Hydrate Thermodynamics

$$\frac{\partial G_H}{\partial P} = x_c \frac{\partial \mu_c^H}{\partial P} + x_m \frac{\partial \mu_m^H}{\partial P} + x_w \frac{\partial \mu_w^H}{\partial P} + \mu_c \frac{\partial x_c}{\partial P} + \mu_m \frac{\partial x_m}{\partial P} + \mu_w \frac{\partial x_w}{\partial P}$$

$$\frac{\partial \mu_r^H}{\partial P} = \overline{V}_r$$

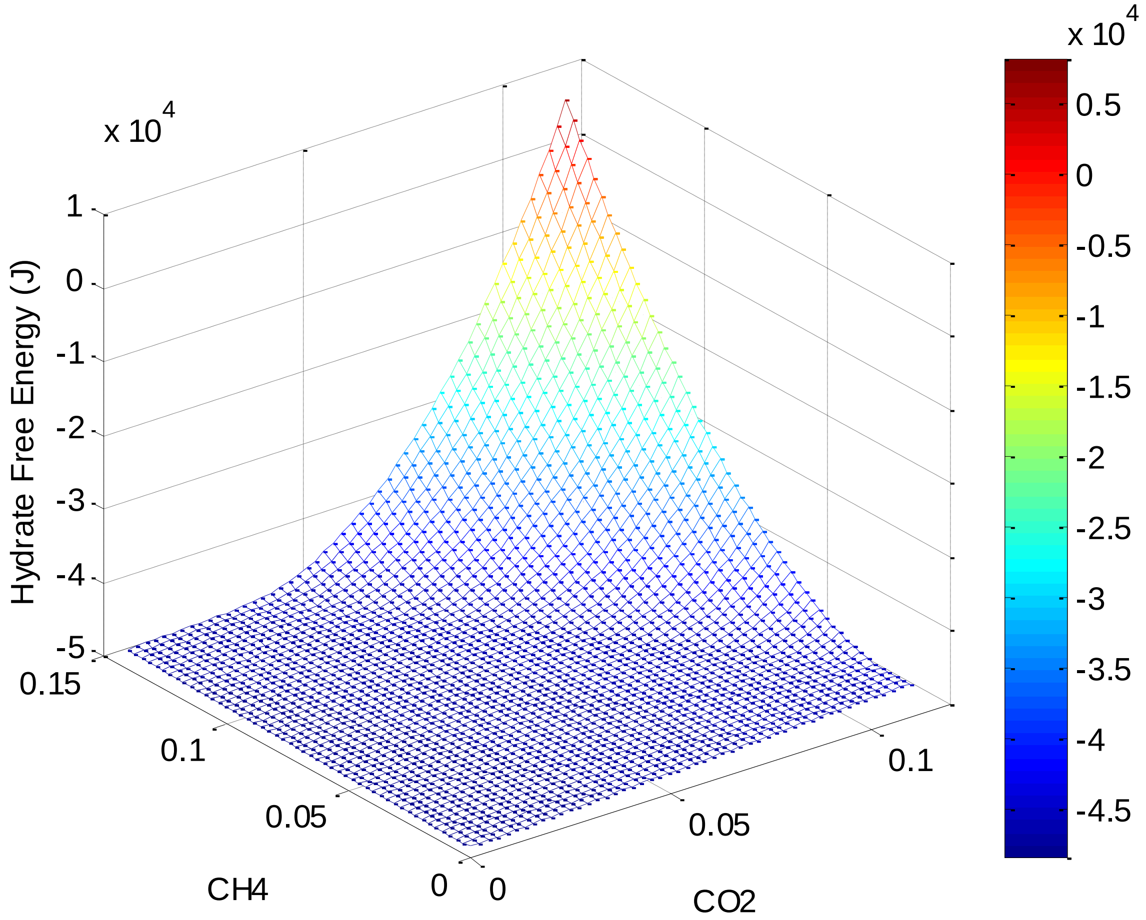
$$\frac{\partial G_H}{\partial P} = x_c \overline{V}_c + x_m \overline{V}_m + x_w \overline{V}_w + \mu_c^H \frac{\partial x_c}{\partial P} + \mu_m^H \frac{\partial x_m}{\partial P} + \mu_w^H \frac{\partial x_w}{\partial P}$$

$$\overline{V}^{clath} = x_c . \overline{V}_c + x_m . \overline{V}_m + x_w . \overline{V}_w$$

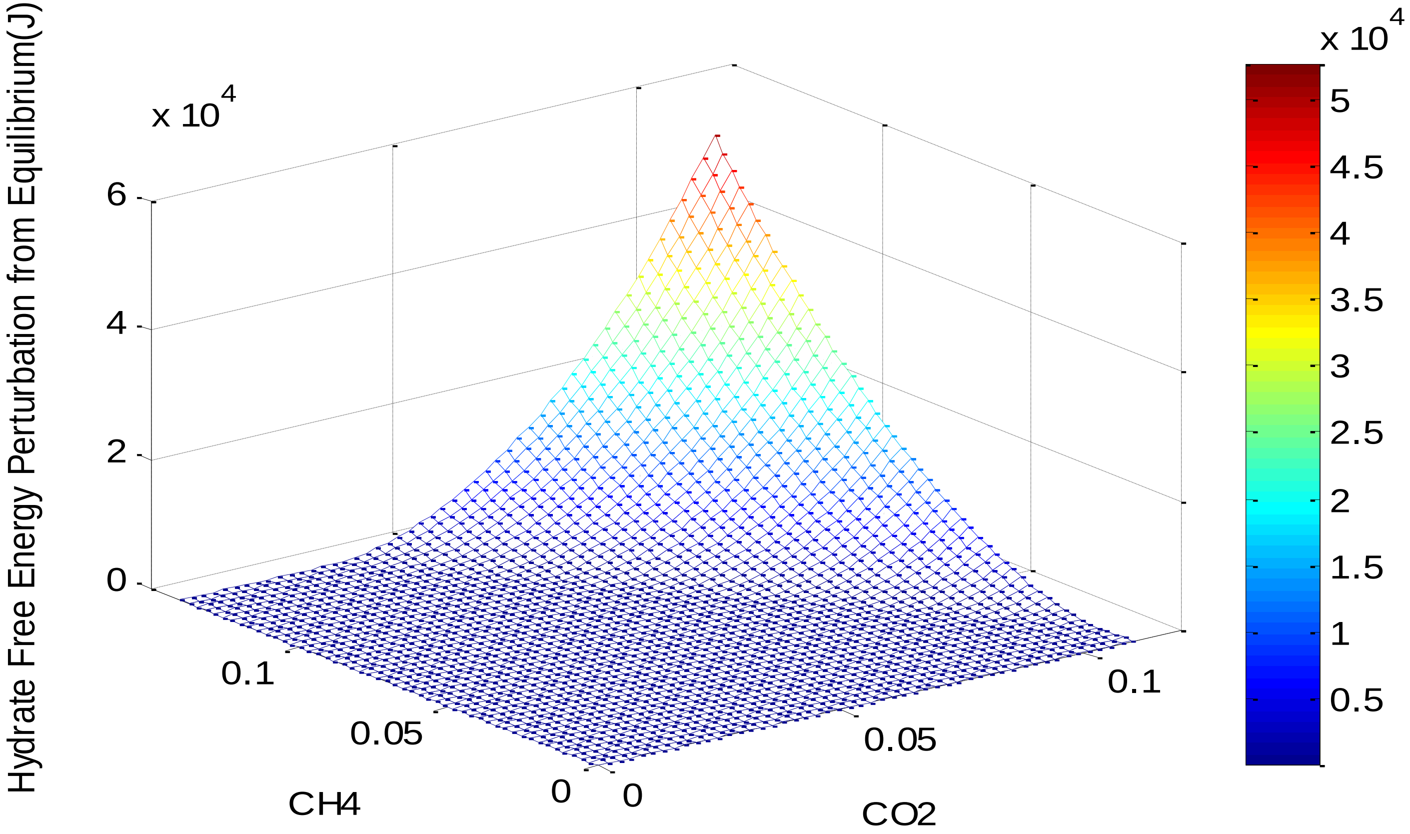
$$\frac{\partial G_H}{\partial P} = \overline{V}^{clath} + \mu_c^H \frac{\partial x_c}{\partial P} + \mu_m^H \frac{\partial x_m}{\partial P} + \mu_w^H \frac{\partial x_w}{\partial P}$$

$$\left[\frac{\partial G_H}{\partial P}\right]_{T,V,\vec{x}} = \overline{V}^{clath}$$

$$-\frac{\partial}{\partial T}\left[\frac{G}{T}\right]_{P,\vec{x}} = \frac{\overline{H}}{T^2}$$



Hydrate free energy of mixed hydrate at 3°C and 40 bars.



Difference due to pressure, temperature and composition gradients in hydrate free energy from equilibrium at 3°C and 40 bars.

Fluid Thermodynamics

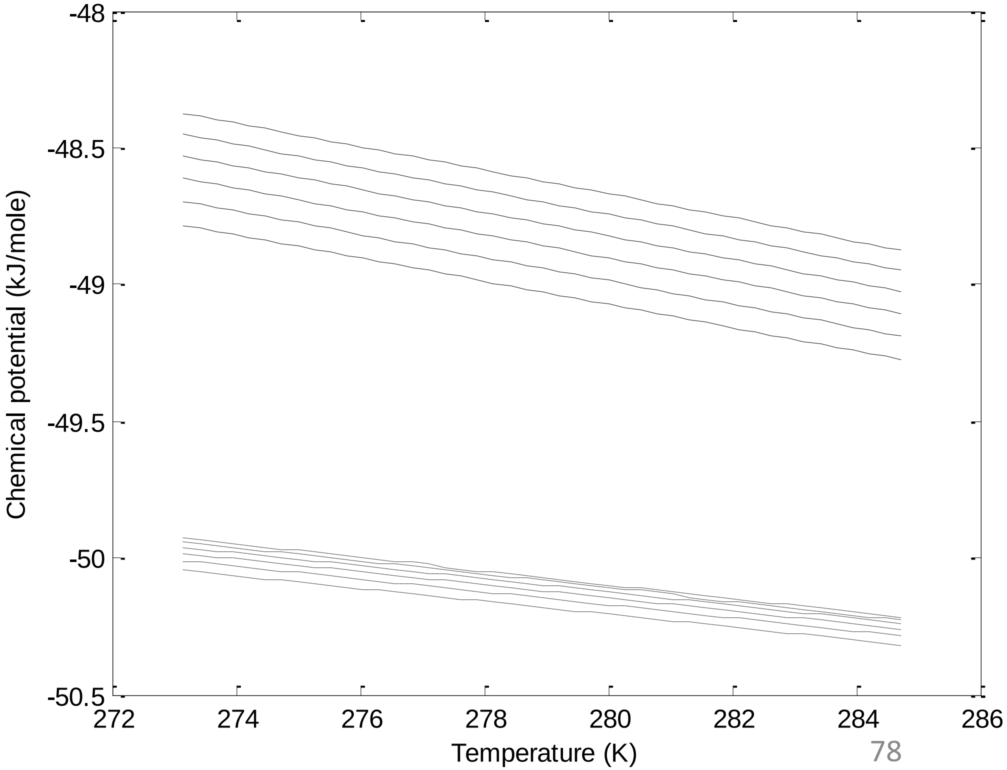
$$\mu_i^{Fluid} = \mu_i^{id.gas,pure} + RT\ln(y_i) + RT\ln\varphi_i(T,P,\bar{y})$$

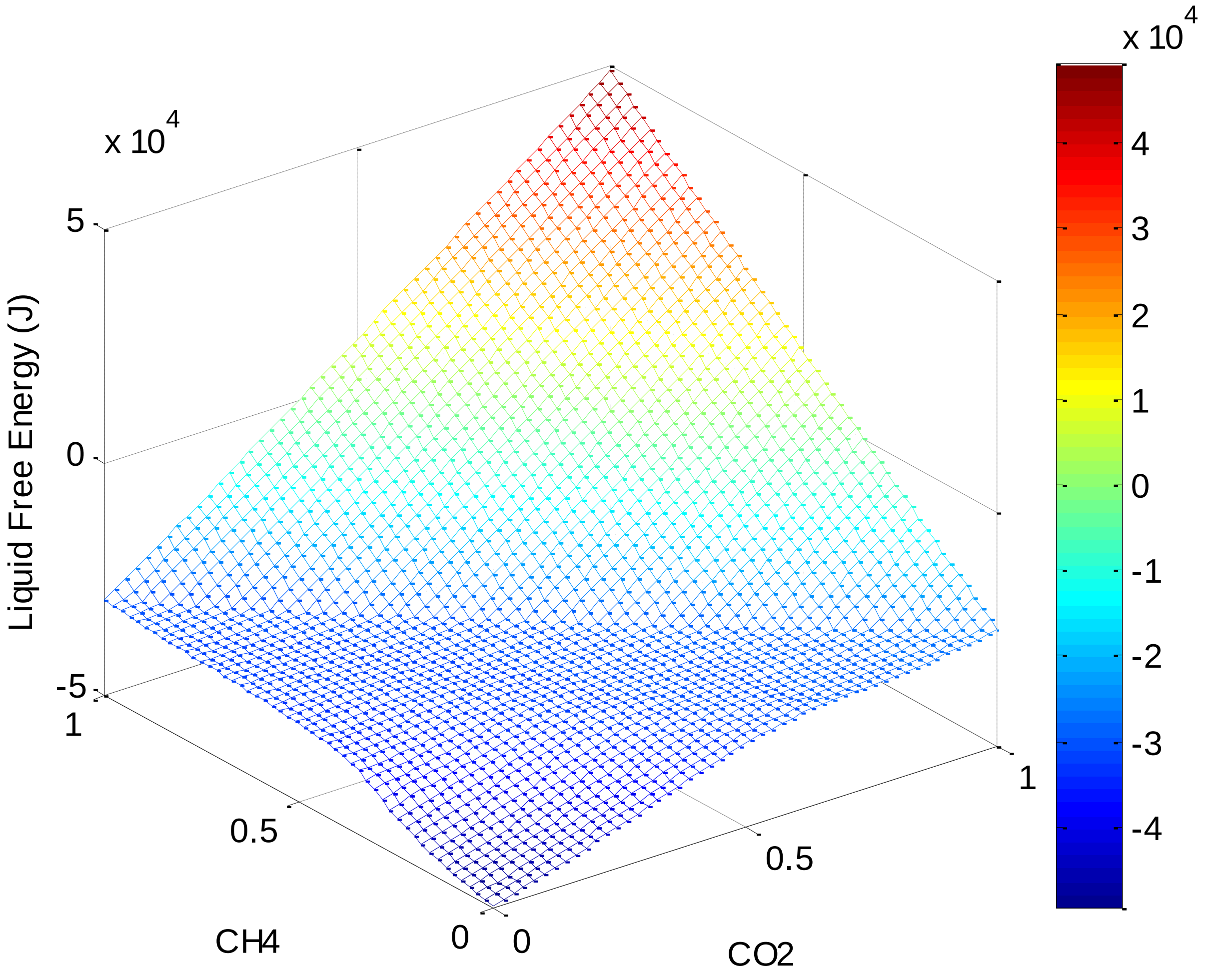
$$\mu_w^{Fluid} = \mu_w^{ideal\ gas}(T,P) + RT\ln(y_w)$$

Accurate enough approximation For the special example since hydrate formation from gas is unimportant in this problem/system

$$y_w = \frac{x_w\gamma_w(T,P,\bar{x})P_w^{sat}(T)}{\varphi_w(T,P,\bar{y})}$$

Estimated chemical potentials of water that drop out from CO2 solution in either liquid water or hydrate form. Same mole-fractions and conditions as in figure 5. Pressures are, from bottom to top, 100, 120, 140, 160, 180 and 200 bar. Solid lines are conditions for drop out as liquid water. Dashed lines are corresponding estimated conditions for drop-out directly as hydrate from CO2 solution.





Liquid Gibbs free energy as function of mole fraction at 3°C and 40 bars.

Aqueous Thermodynamics

$$\mu_w = \mu_w^{\text{pure liquid}}(T) + RT\ln(x_w\gamma_w) + v_w(P - P_0)$$

$$\mu_i = \mu_i^{\infty}(T) + RT\ln\left(x_i\gamma_i^{\infty}\right) + v_i^{\infty}(P - P_o)$$

where,

$$\left.\begin{aligned} \gamma_i^{\infty} &= \frac{f_i^{\infty}}{k_H(T)} \\ f_i^{\infty} &= e^{\left(-\beta\mu_i^{\infty}\right)} \\ k_H(T) &= k_H^{\ominus} e^{\left(\frac{-\Delta_{soln}H}{R}\left(\frac{1}{T}-\frac{1}{T^{\ominus}}\right)\right)} \end{aligned}\right\}$$

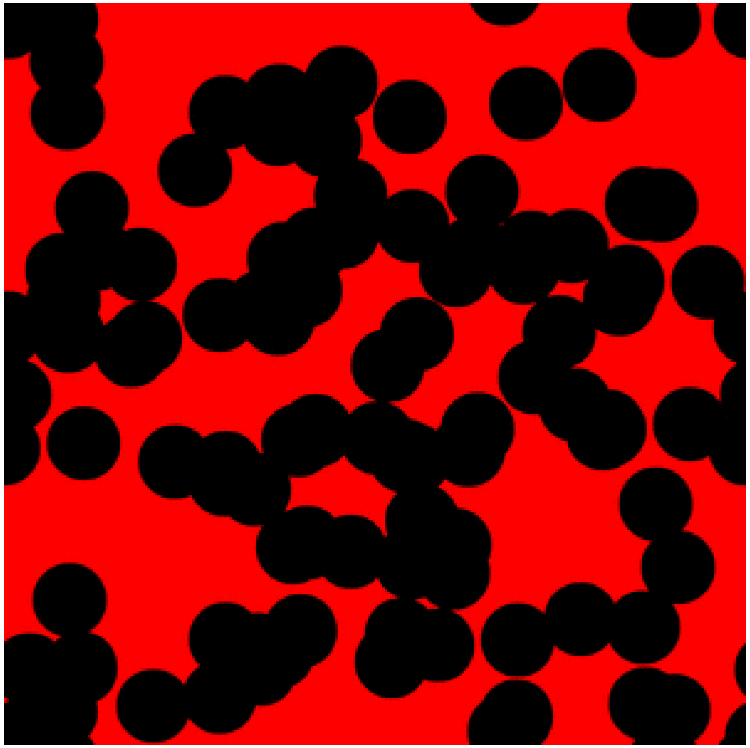
R. Sander, Surv. Geophys, 20, 1(2009)

Constants	CO2	CH4
$k_H^{\ominus}$ (M/atm)	0.036	0.0013
$\frac{\Delta_{soln}H}{R}$ (K)	2200	1800

D. Q. Zheng, T. M. Guo, and H. Knapp, Fluid Phase Equilib, 129 , 197 (1997)

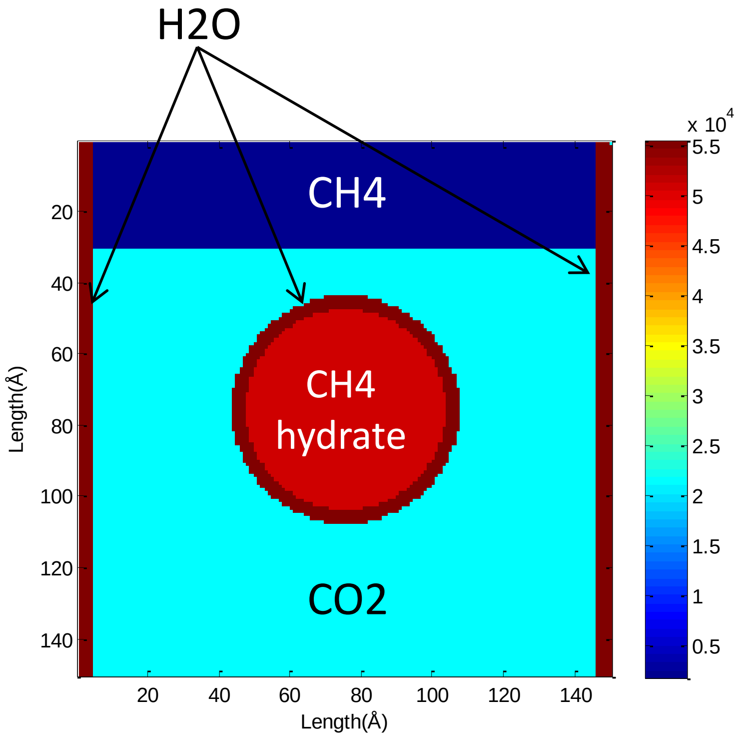
Example related to a real case of pore phase distribution as interpreded from different methods

- The relative fraction of different phases (hydrate, water, free gas) given
- An unknown parameter here is the distribution of water around mineral versus around hydrate during injection of CO2
- Free gas (CH4) assumed initially to be at top of pore due to density
- At this stage there are no mineral surfaces in the system but work is in progress on implementation of that



Solid surfaces without thermodynamic properties (excluded volume) is trivial and have a triggering function in nucleation preferences in inclinements. See yellow CO2 hydrate nucleation from solution of CO2 in water. Addition of surface thermodynamics (adsorbed chemical potentials) in progress

Simulation setup

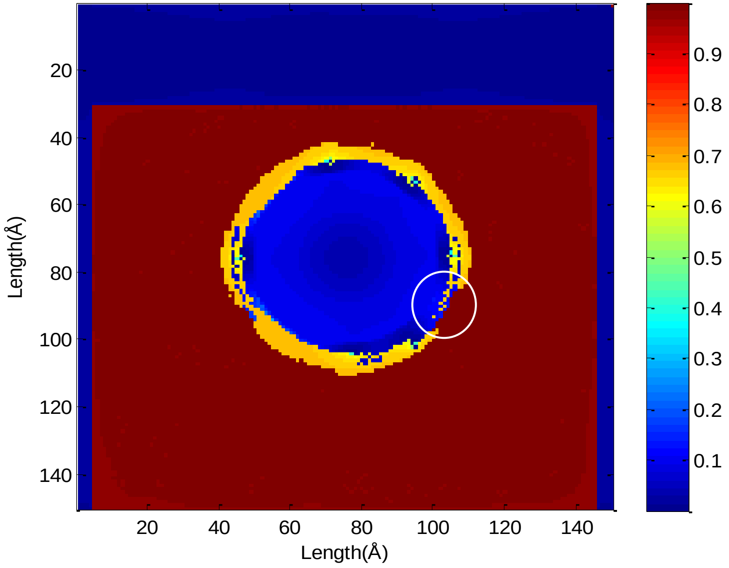


Distribution is based on average liquid water saturation, free gas saturation and hydrate saturation of a ***real reservoir***

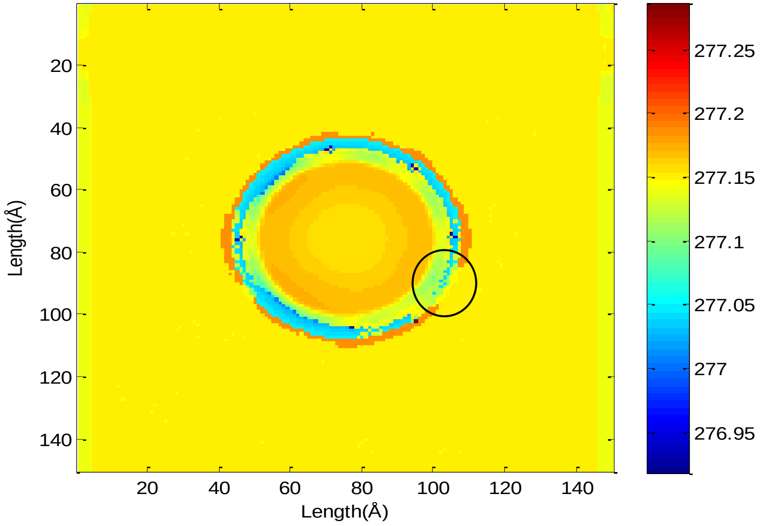
The different sizes will have different contact areas between hydrate and the CO2 phase

- ***Three different hydrate systems*** sizes were considered
  - (150 Å×150 Å, 500 Å×500 Å and 5000 Å×5000 Å)
  - Hydrate radii are ***28 Å, 114 Å and 1136 Å***
- Injection of CO2 into the pore
  - Will displace some of the water surrounding the hydrate because the ***minerals*** will normally have a ***higher thermodynamic benefit*** from the water than the hydrate
  - The examples here are for 1.2 nm liquid water surrounding hydrate. Several other distributions of water around hydrate versus on mineral is running
- Initial methane saturation is 20 %
- CH4 mole fraction in hydrate: 0.14 (max)

Smallest system



CO2 filling in hydrate after 3 ns

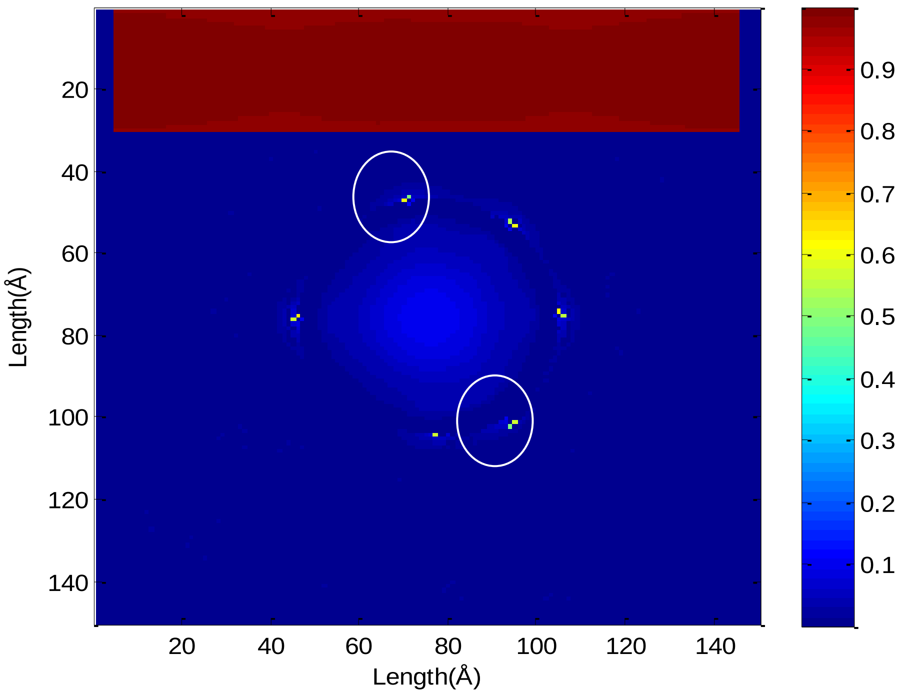


Temperature (Kelvin) after 3 ns

- ***CO2 in hydrate results in hydrate lower free energy*** versus CH4 hydrate
  - ***Drives the exchange*** process
- Exchange is fast initially
  - Due to heat released from formation of new CO2 hydrate
- Encircled region is an ***escape region for dissociating methane***
- Inner parts of hydrate are cooled down

Bubble formation

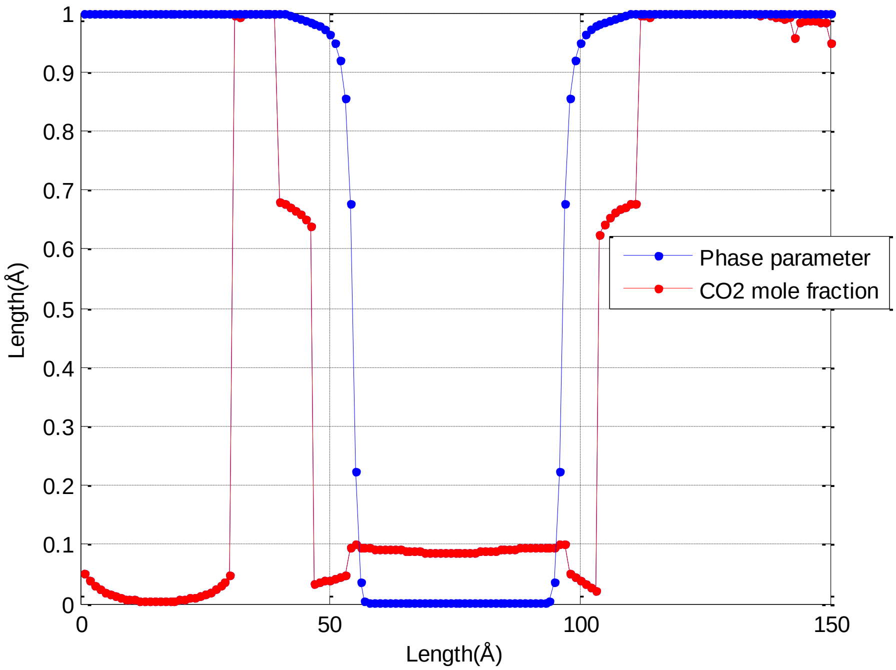
- Methane will exist as a ***free gas near the interface***
  - If the surrounding fluid is incapable to dilute the released methane
  - The bubble may ***merge*** after colliding with each other
  - Will eventually dissolve into CO2 but the hydrodynamically controlled escape (buyouncy) from the surface keep the CO2/hydrate «clean» from CH4 pollution



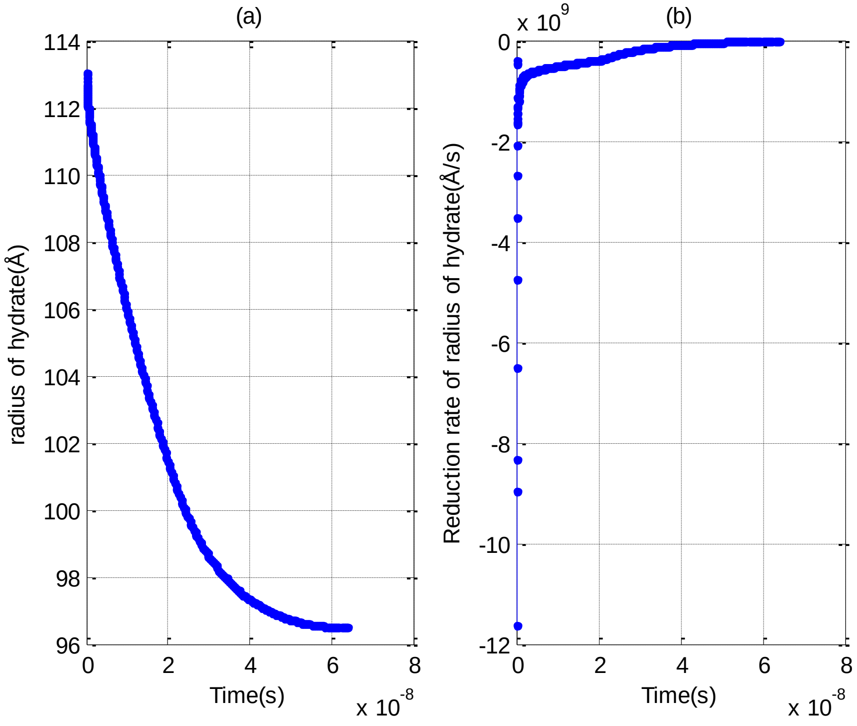
Snapshot of methane mole fraction in entire system after 3 ns

Unstable mix hydrate

- Exchange til 5.6 ns
-
- After 5.6 ns, Mix hydrate could not be sustained and melted very quickly due to unfavorable chemical potential gradients for water and CH4
  - Larger systems are more stable (coming results)



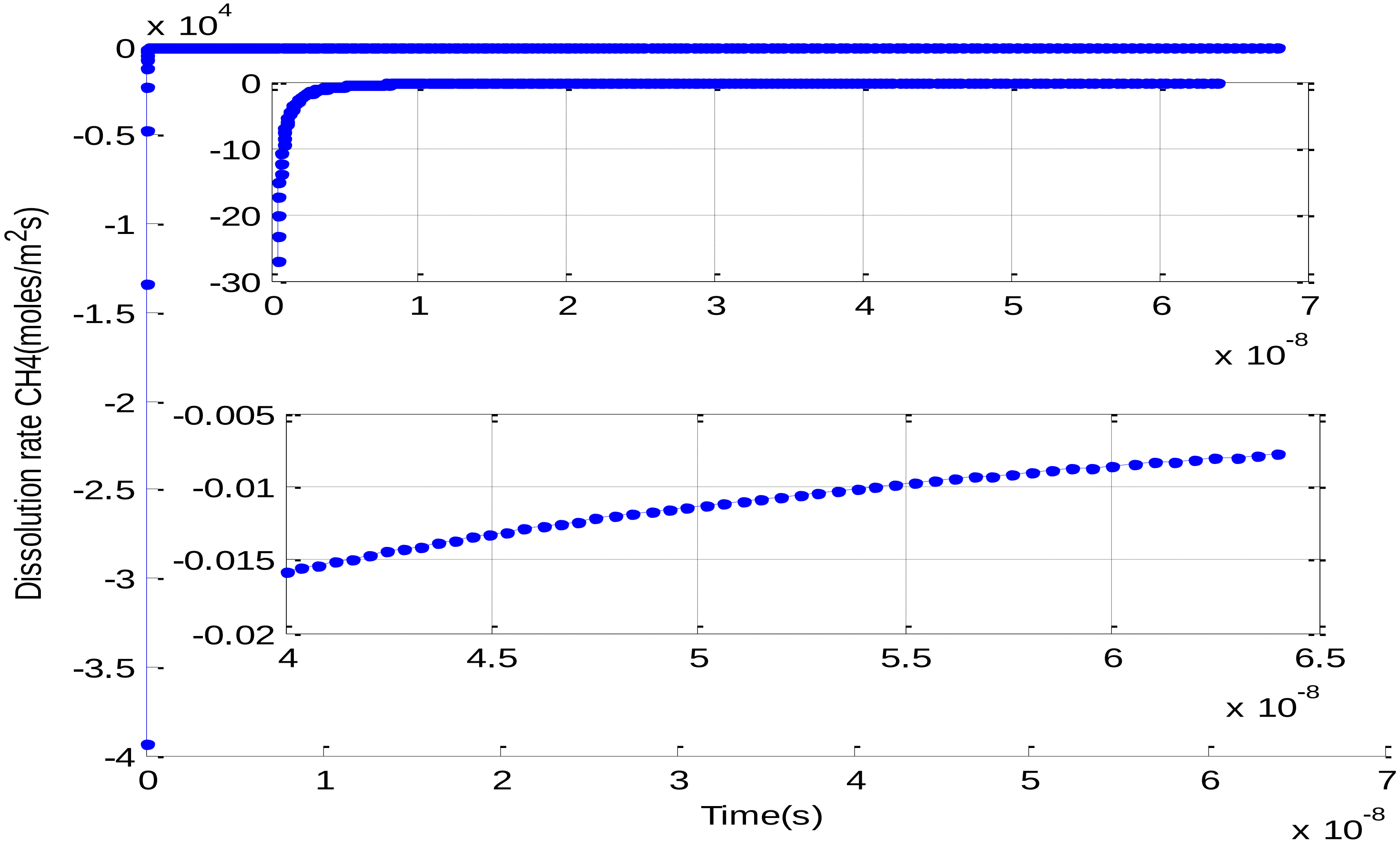
Intermediate size



Intermediate system (500Å×500Å) system: Radius of circular hydrate and its reduction rate shows convergence to a stable mixed hydrate as function of time

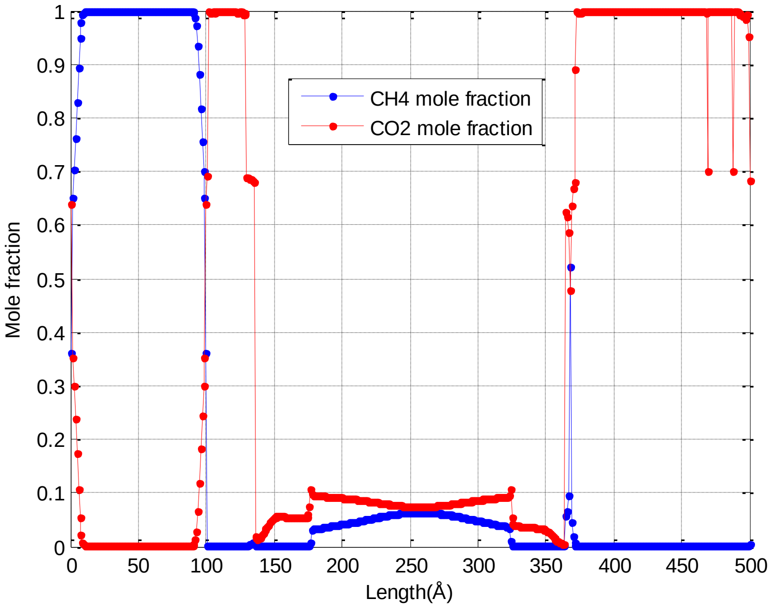
- Initially exchange and dissociation ***processes are rapid***
  - Due to ***heat release*** from formation of ***new hydrate***
- As time progress
  - Dissociation process slows down
  - Slower direct conversion which is ***solid state transport limited***
- Less loss of hydrate core
- Form more stable mix hydrate than smallest size

Intermediate size

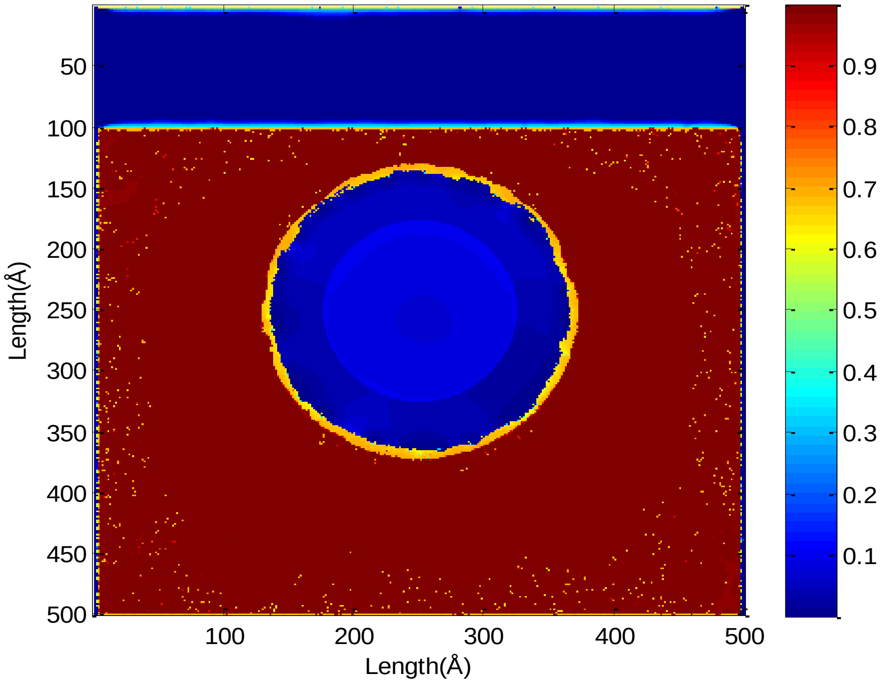


- Flux of dissociating methane also become small with time
  - Conversion which is ***solid state transport limited***
  - CH4 dissolution rate shows the system approaching stability

Results

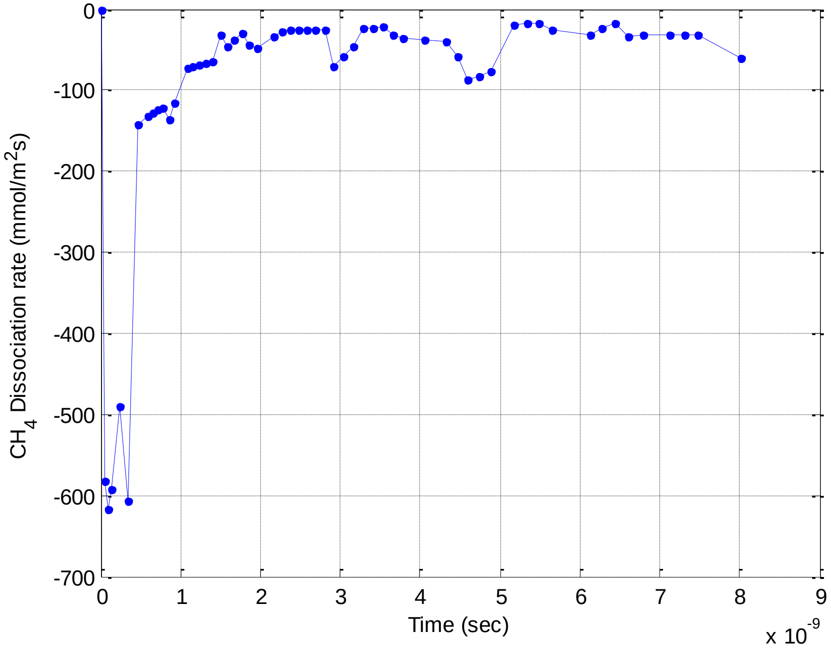


CH4 and CO2 mole fraction after 64 ns

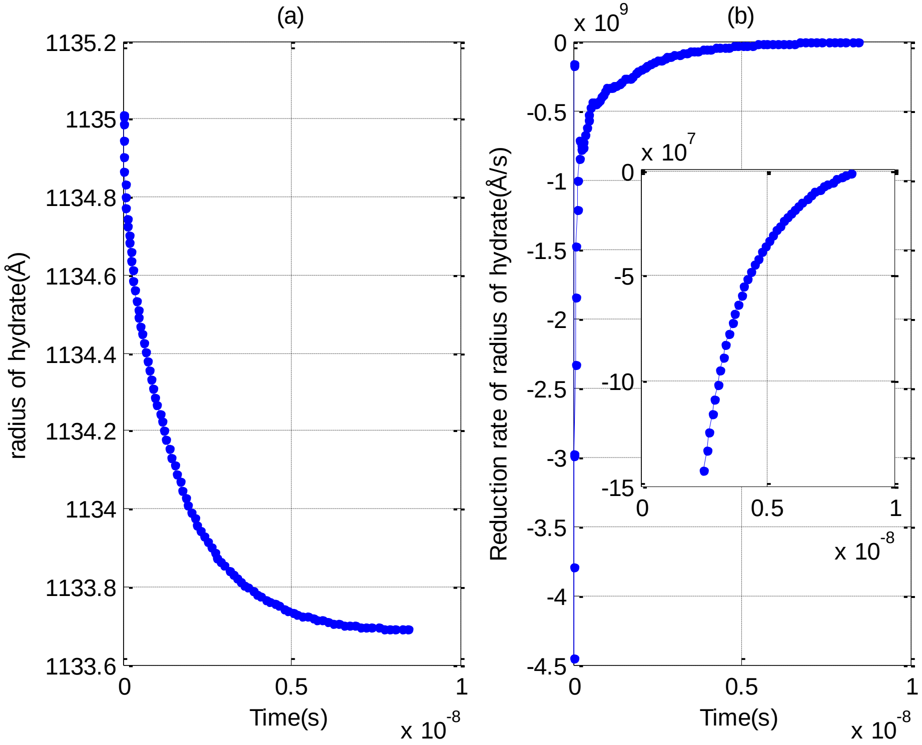


CO2 mole fraction after 64 ns

Largest system



Methane flux



hydrate core as function of time

- Largest system achieves a stable mixed hydrate faster
- Least loss of hydrate core
- Results are only available up to 8.4 ns
- Methane is still ***releasing after 8.4 ns***
  - Due to the exchange process in favor of CO2 occupation of large cavities
- System seem to be entering a ***stationary slow progress***

Conclusions and discussion

- Phase Field Theory (PFT) model extended with hydrodynamics
  - Free methane gas ***bubbles are observed*** on the interface
    - ***Dissociation is faster*** than rate of dissolution into the surrounding water
      - separate gas bubbles will form
    - ***Fluxes of releasing methane are changed*** as dissociation kinetics are affected
- Thermodynamic properties for hydrate outside of equilibrium have also been derived
  - Implicit implementation
  - Heat transport dynamics can then be incorporated

Conclusions and discussion

- Heat released due to formation of mix hydrate
  - Which make the initial exchange process fast
  - Later limited by solid state transport
- CH4 hydrate surrounded by CO2 converted into a mixed hydrate
  - In accordance with experimental and theoretical evidence from open literature
- The effect of the initial size of hydrate system on the stability of the mix hydrate has been studied
  - Larger systems form more stable mix hydrate

Conclusions and discussion

- This is the first kinetic theory for hydrate/water/fluid which is able to model kinetic progress in non-equilibrium systems relevant for hydrates
  - in porous media
  - transport of CO2 or CH4 in pipelines
  - other situations of hydrate phase transitions under non-equilibrium conditions

Part 3 – Kvasi equilibrium calculations

- Each individual phase transition can be evaluated in terms of ***free energy changes*** and compared in order to evaluate which ones are ***impossible due to positive free energy*** change or free energy change that are favorable (negative) but ***too small to overcome the penalty of pushing*** away the surroundings to give room for the new phase
- All these other phase transitions can be implemented in any hydrate code and can supplement the current basis for hydrate risk evaluation
- BUT the phase transitions are complex kinetic processes so even if driving forces says «possible» kinetic may be too slow so even simple kinetic models should be implemented as a minimum. Classical theory or better MDIT theory (Kvamme, 2002, 2003)

The non equilibrium challenge

$$\mu_{w}^{H,i}(T,P,\vec{x}^{H}) = \mu_{w}^{H,0}(T,P) - \sum_{j} \nu_{j} \ln\Big(1+\sum_{k} h_{kj}^{i}\Big)$$

$$\mathbf{h}_{\mathbf{kj}}^{\mathbf{i}} = \mathbf{e}^{-\beta(\mu_{kj}^{i} + \Delta g_{kj}^{inclusion})}$$

$$\theta_{kj}^{i} = \frac{h_{kj}^{i}}{1+\sum_{k} h_{kj}^{i}}$$

- ***Chemical potential***

  of guest molecules from different phases are different and

  - results in different filling fractions

  - different hydrate free energies

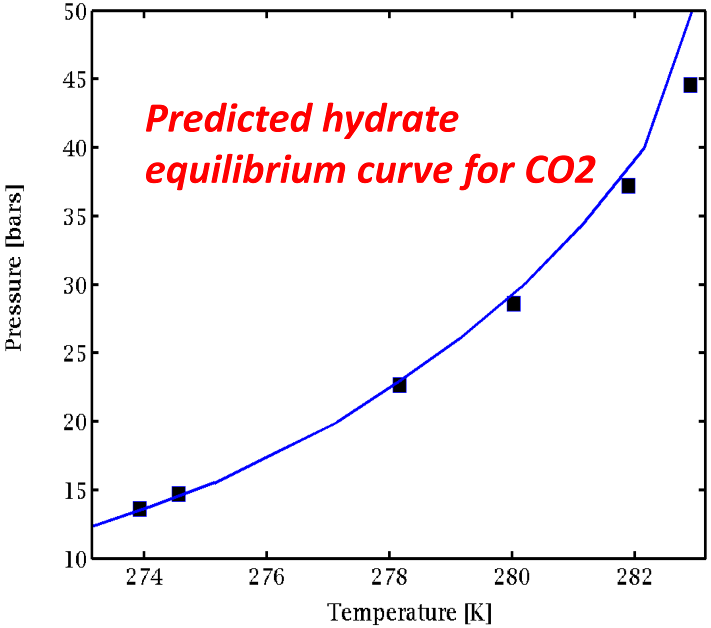
  - different hydrate kinetics

$\mu_{w}^{H,i}$	Water chemical potential in hydrate phase i
$\Delta g_{kj}^{inclusion}$	Free energy of inclusion in cavity by ”classical” langmuir integration or harmonic oscillator approach (Kvamme & Tanaka, 1995)

Non Equilibrium Challenge

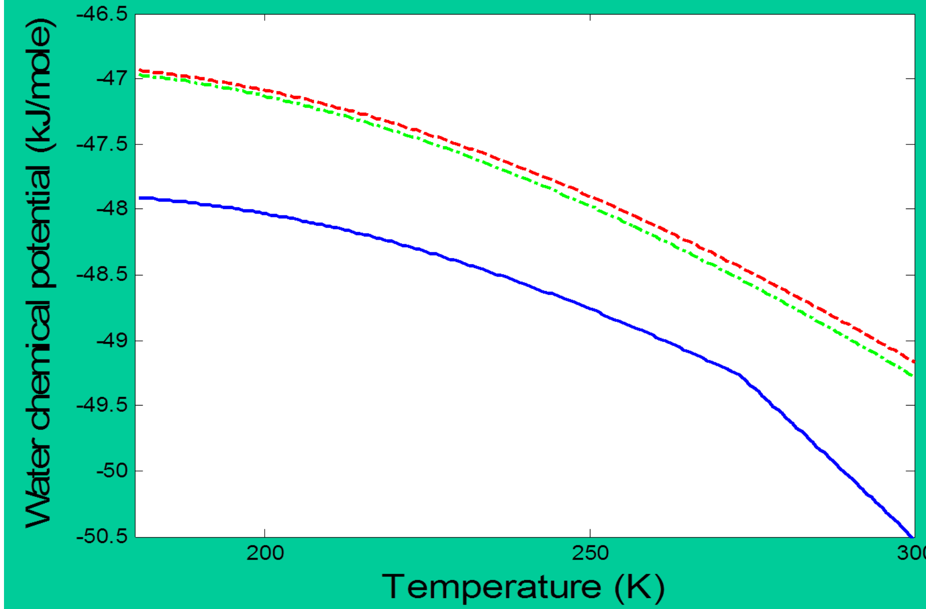
Accurate and consistent model for free energy of the different co-existing phases

- A critical basis for ***Phase Field Modeling***
- Free energies for individual (Aqueous, Fluid and Hydrate) phases are used here
  - Revised adsorption theory (Kvamme & Tanaka, 1995) for hydrate
  - TIP4P simulated chemical potential for ice, liquid water, and empty hydrate



Predicted hydrate equilibrium curve for CO2

Solid line for ice or liquid water, dash line for SI empty hydrate and dash-dotted line for SII empty hydrate.



Kvasi equilibrium models

- We use chemical potential of empty hydrate from MD (Kvamme and Tanaka, 1995) to avoid 5 empirically fitted parameters for a fundamental property like a change in chemical potential

- For each possible phase transition assume equilibrium can be reached for the actual phase transition at current local P and T
- Calculate chmical potential for the actuall guests in the phase they come from
- Calculate water chemical potential and solve for the unknown

Hydrate risk analysis in systems of CO2 containing water and impurities

Professor Bjørn Kvamme

Department of Physics and Technology

University of Bergen

Acknowledgements

- We acknowledge the grant and support from ***Research Council of Norway*** through the following projects:

- - SSC-Ramore, “Subsurface storage of CO2– risk assessment, mon-itoring and remediation”, project number: 178008/I30.
- - FME-SUCCESS, project number: 804831.- PETROMAKS, “CO2injection for extra production”,
- - CLIMIT “Safe long term sealing of CO2in hydrate”, project number: 224857.
- - PETROMAKS “CO2injection for stimulated production of naturalgas”, project numbers: 175968 and 230083.

- ***STATOIL***, under contract 4502354080

- ***Experimental work*** described under slides 10 -26 conducted by Prof. Arne Graue and PhD students Geir Ersland (now UiB) and Jarle Husebø (now STATOIL) in collaboration with ConocoPhillips (Special thanks to James Howard)

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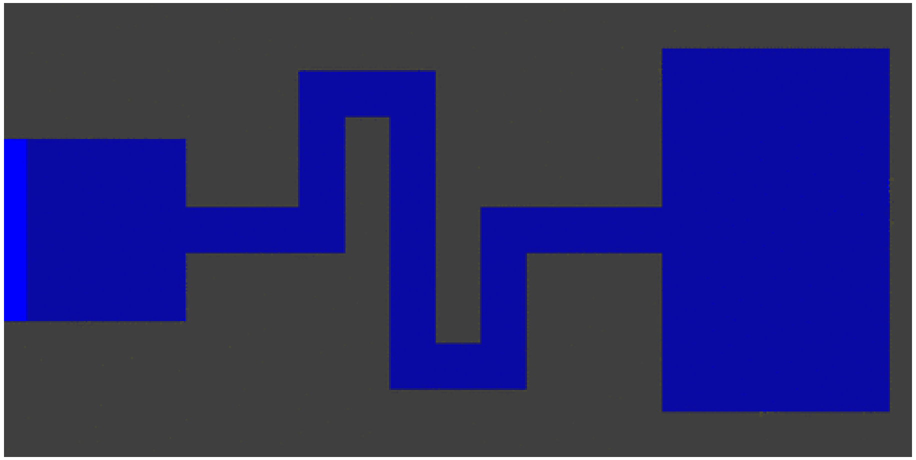
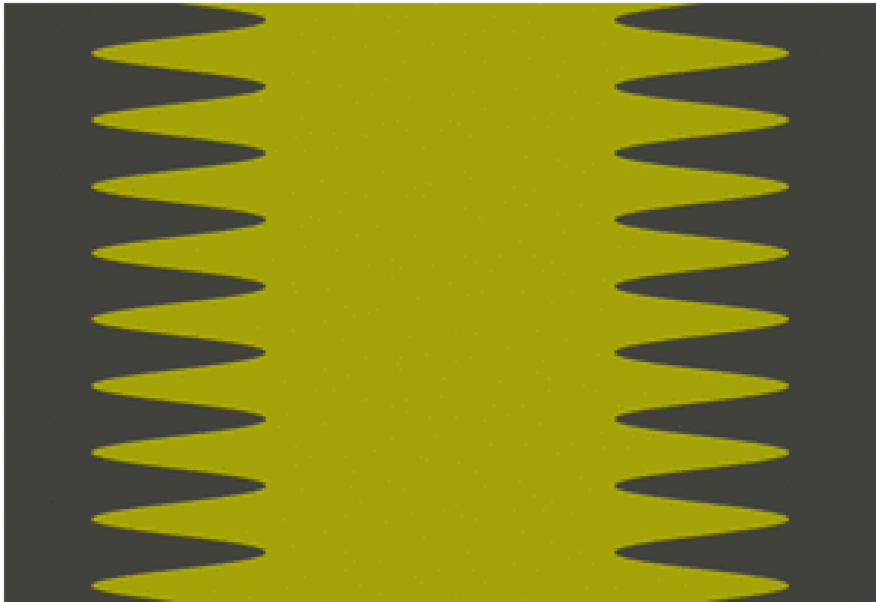
- *Pilvi-Helina Kivela* (hydrate reformation kinetics)
- *Ashok Chejara* (hydrate phase transitions dynamics in reservoirs)
- *Mohammad Taghi Vafaei* (hydrate sealing effects in cold reservoirs during CO2 storage)
- *Khaled Jemai* (hydrate dynamics in reservoirs)
- *Khuram Baig* (hydrate phase transitions)
- *Bjørnar Jensen* (mineral/fluid reactions during CO2 storage)
- *Sara Sjøblom* (corrosion modeling)
- *Khadijeh Qorbani Nashaqi* (Non-equilibrium termodynamics in hydrate reservoir modeling)
- *Richard Olsen* (Fundamentals of water separation from natural gas in Zeolite membranes)
- *Kim Nes Leirvik* (Quantum and classical molecular modeling of hydrate phase transitions in porous media)
- *Mojdeh Zarifi* (Phase Field Theory modeling of phase transition kinetics). From April 2014

9 MSc students

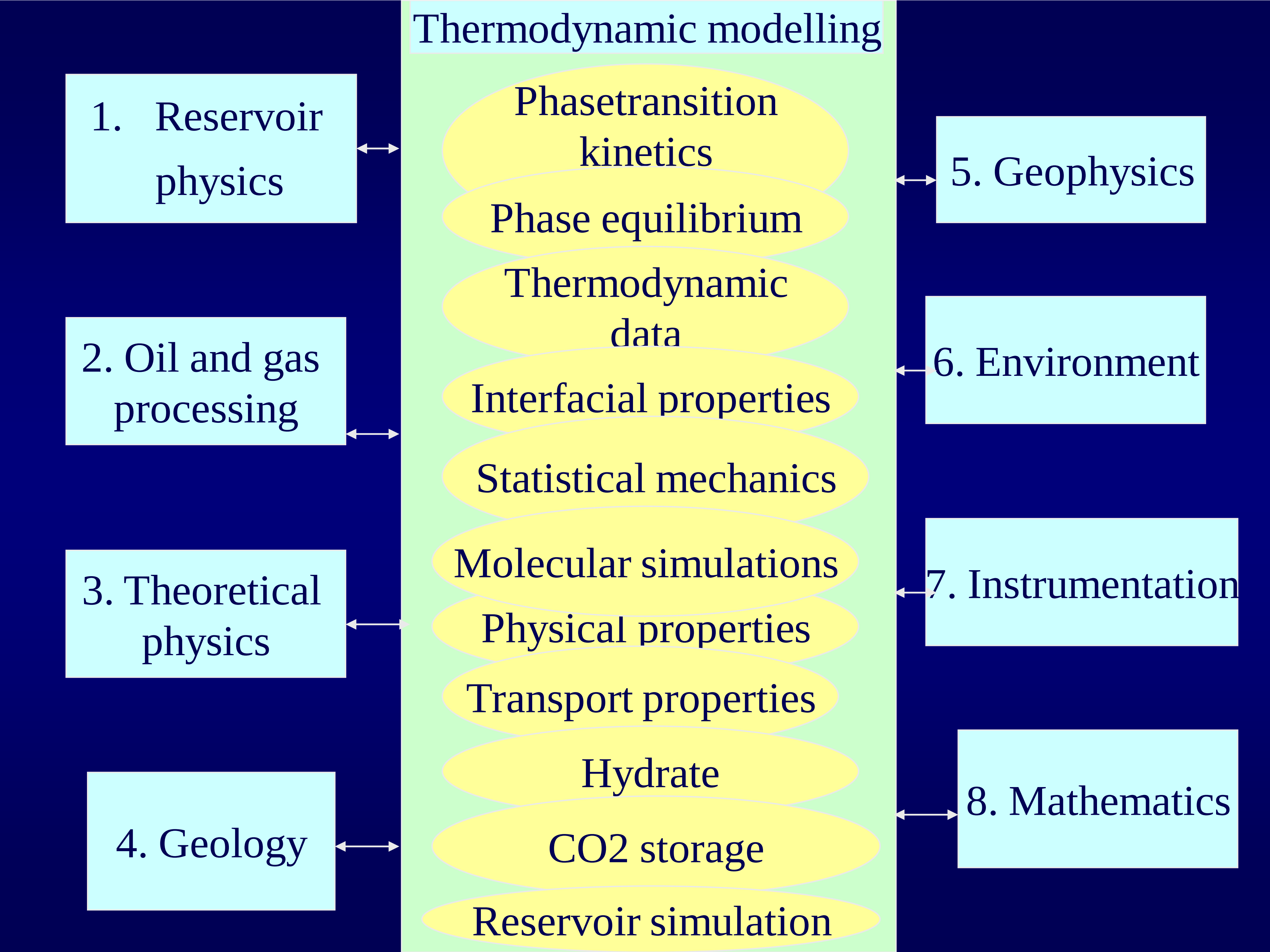
Guest researchers and guest students



Liquid/solid phase transition in prsence of inert solid walls



Thermodynamic modelling



1. Reservoir physics
2. Oil and gas processing
3. Theoretical physics
4. Geology

Phasetransition kinetics

Phase equilibrium

Thermodynamic data

Interfacial properties

Statistical mechanics

Molecular simulations

Physical properties

Transport properties

Hydrate

CO2 storage

Reservoir simulation

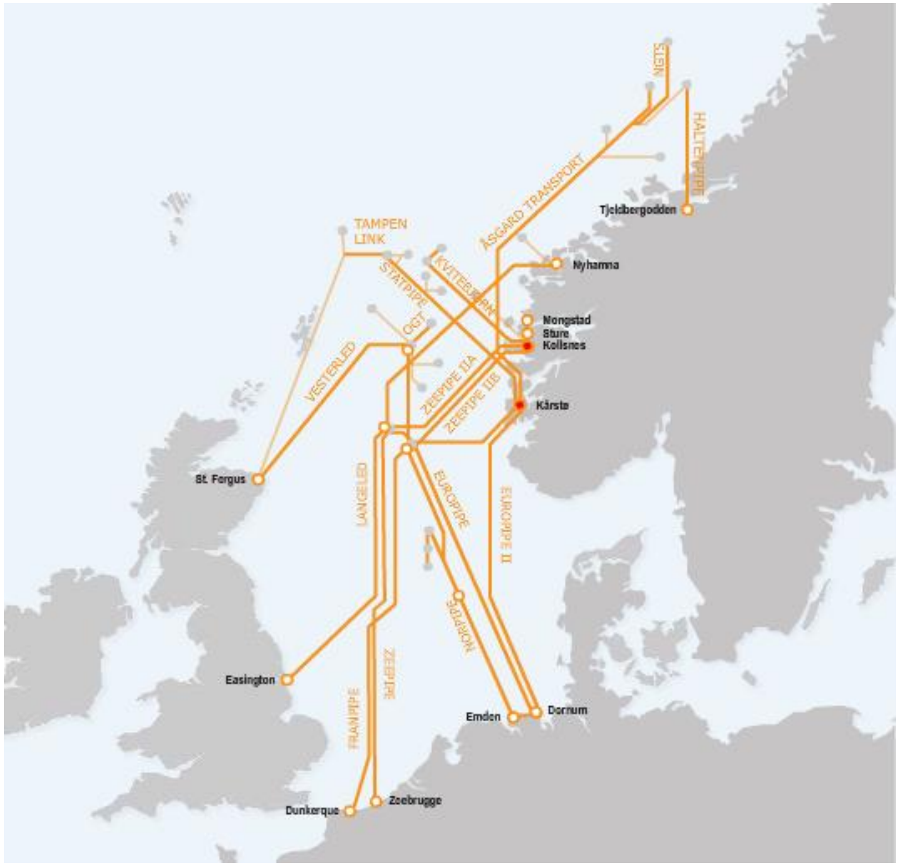
5. Geophysics
6. Environment
7. Instrumentation
8. Mathematics

Motivation

- The ***thermodynamic benefits*** for water to ***adsorb*** out onto a rusty surface may be a factor of ***5 times*** that of water ***condensing*** out as liquid water
- Benefits of rust adsorption versus condensation have been experimentally verified using Quantum Balance (Heriot-Watt, 2012, unpublished)
- Practically this implies that ***rusty pipewalls are cold*** (thermodynamic sense) surfaces. During sub-sea transport the pipe walls are normally ***also*** the ***zones of lowest temperatures***.

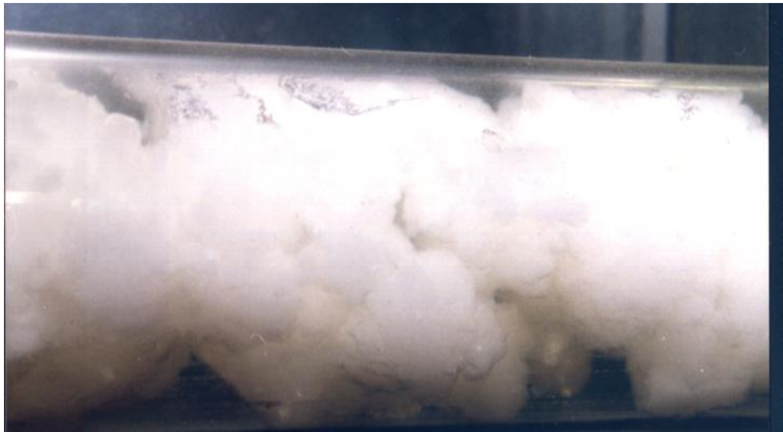
There is a need for revision of «Best practise» for evaluation of risk for hydrate formation during transport of hydrocarbons or carbon dioxide containing water

Motivation cont.



- Gibbs phase rule ***excludes*** the possibility of ***equilibrium*** since dynamic transport through the pipeline prevents some of the phases from being totally consumed and rusty surfaces may play a substantial role
- Combined first and second laws of thermodynamics open up for ***different hydrates*** being ***formed***, depending composition of gas and phases from which phases water and hydrate former comes from

- **There are 7800 km of pipelines on the seafloor of the North Sea (temperatures : 0-6°C)**
- **94,5 billions Sm^3 gas transported in2008**
- **Entrance pressures 175-200 bar.**



Motivation cont.

- Any scheme that applies ***free energy minimization*** in order to search for most likely events of phase transitions ***needs a common level of reference*** for all components in all phases in order to evaluate gradients of free energy changes due to phase transitions. There is a need for absolute (reference: ***ideal gas***) thermodynamic properties.
- Industry will prefer simple extensions of existing risk evaluation tools
- Some phase transitions that involves ***impact of solid surfaces cannot be measured experimentally*** in terms of the values that is needed for verifications. This abscence of experiments call for higher degree of rigor in development of theoretical models and evaluation tools.

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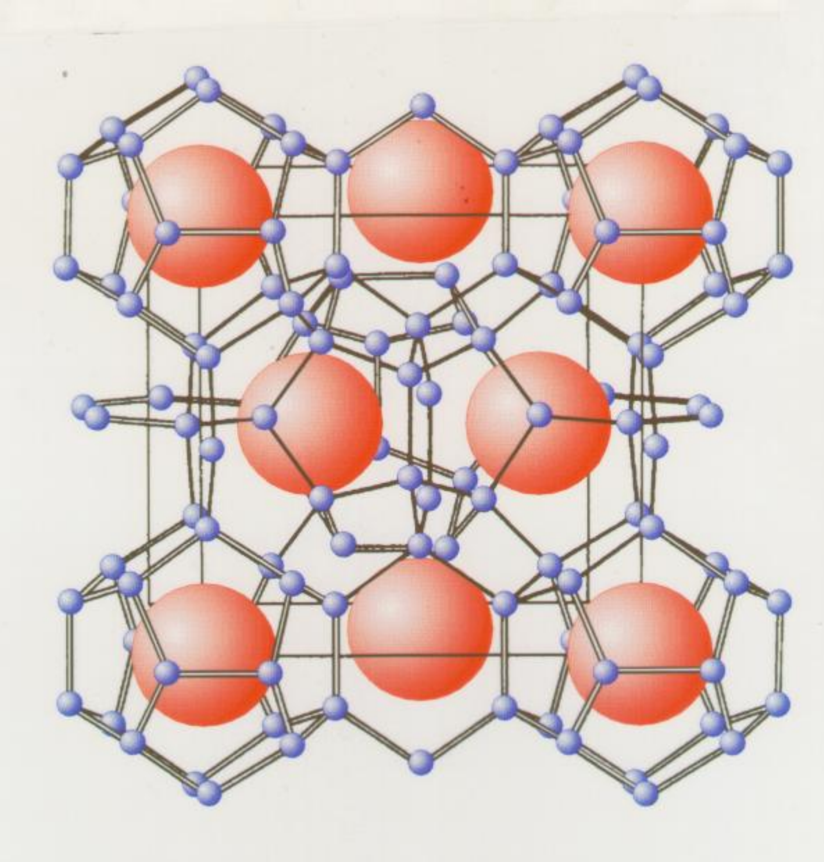
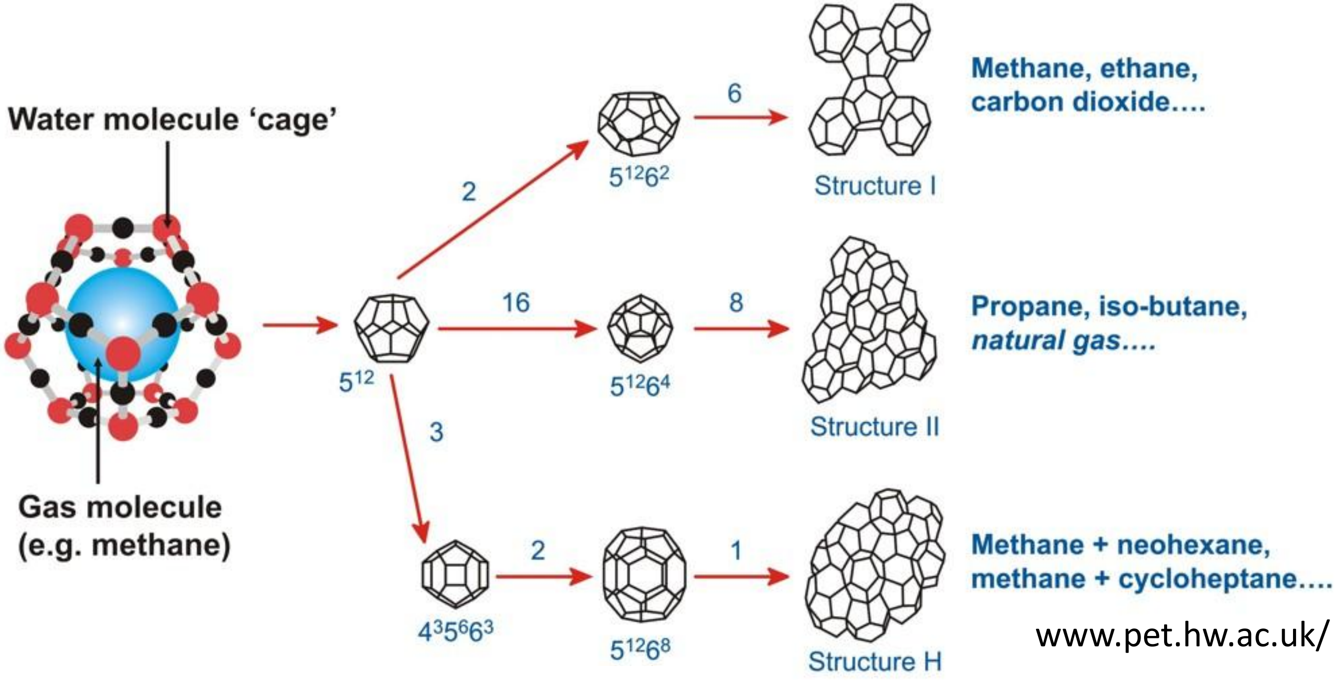
- Phase transitions are ***nano scale*** processes which are ***coupled dynamically to processes of longer range*** and a multi-scale strategy is needed



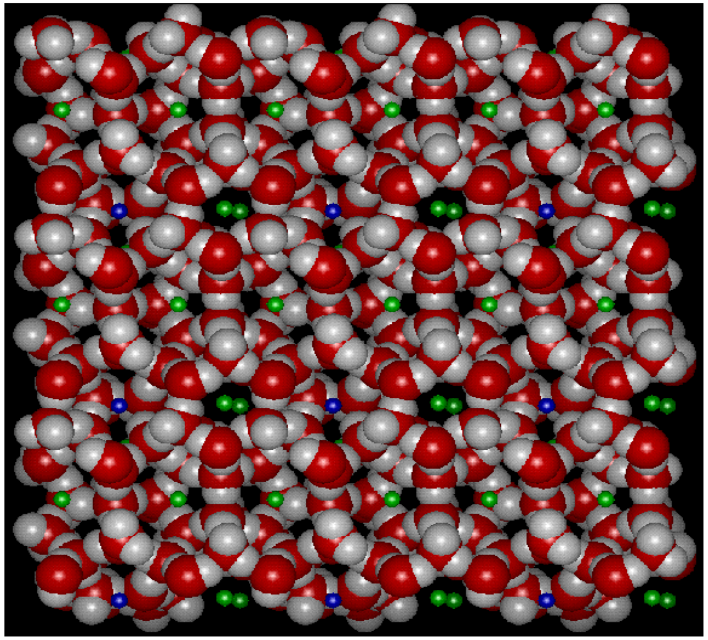
The smallest symmetric hydrate unit cell of structure I is cubic and inside the cube (see fig.) contains 46 water (downscaled blue points) connected by hydrogen bonds (grey lines) creating 2 small cavities with 20 waters (see corners) and 6 larger (24 water)

OUTLINE

- Definition of problem
- Gibbs phase rule and non-equilibrium analysis
- Representative results from different routes to hydrate formation
- Conclusions
- Part 2 (optional). Advanced kinetic modelling as a strategy towards development of simplified kinetic models for industrial use



www.pet.hw.ac.uk/



Red is oxygen and grey is hydrogen in water. Ethane in large cavities (green) and methane in small cavities (blue) of structure I is scaled down. Volume of water in hydrate is roughly 10% larger than in liquid water.

Definition of problem

- Transport of CO2 containing water and other impurities like H2S, N2, Ar and CH4 at seafloor controlled conditions (typically 0 – 6 degrees minimum)
- Pressures ranging from 50 to 250 bars
- What are the limits of water content that will be acceptable in view of possible events that can lead to hydrate formation?

Gibbs Phase Rule

No. Of deg. Of freedom →

$$\tau = N - \pi + 2$$

No. Of components

No. Of Phases

- Gibb’s phase rule is the ***conservation of mass*** under the constraints of ***equilibrium***
- ***Minimum criteria*** for possibility of equilibrium but not given that all possible phases do co-exist since that also depends on chemical potentials and level of free energies of the possible phases

- Even for the simplest system of only CO2 and H2O with fixed T and P in a flow:
- ***Equilibrium*** *can be achieved* ***when hydrate forms from CO2 dissolved in water*** *if there is no free CO2 phase and no impact of solid surfaces*
- ***Equilibrium cannot*** *be achieved* ***when hydrate forms from a separate CO2 phase and water unless one of the fluid phases is consumed and*** *there is no impact of solid surfaces (not relevant since there is continuous feed of new mass*
- ***Equilibrium*** *can be achieved* ***when hydrate forms from water dissolved in CO2*** *if there is no free water phase and no impact of solid surfaces. Strongly rate limited by low water concentrations*

The non equilibrium challenge

Details are not important in this context – the message is that it is obvious from statistical mechanics that we will get different hydrates – and it has been experimentally verified

$$\mu_w^{H,i}(T,P,\vec{x}^H) = \mu_w^{H,0}(T,P) - \sum_j \nu_j \ln\left(1 + \sum_k h_{kj}^i\right)$$

$$h_{kj}^i = e^{-\beta\left(\mu_{kj}^i + \Delta g_{kj}^{\text{inclusion}}\right)}$$

$$\theta_{kj}^i = \frac{h_{kj}^i}{1 + \sum_k h_{kj}^i}$$

- ***Chemical potential of guest molecules from different phases are different and***

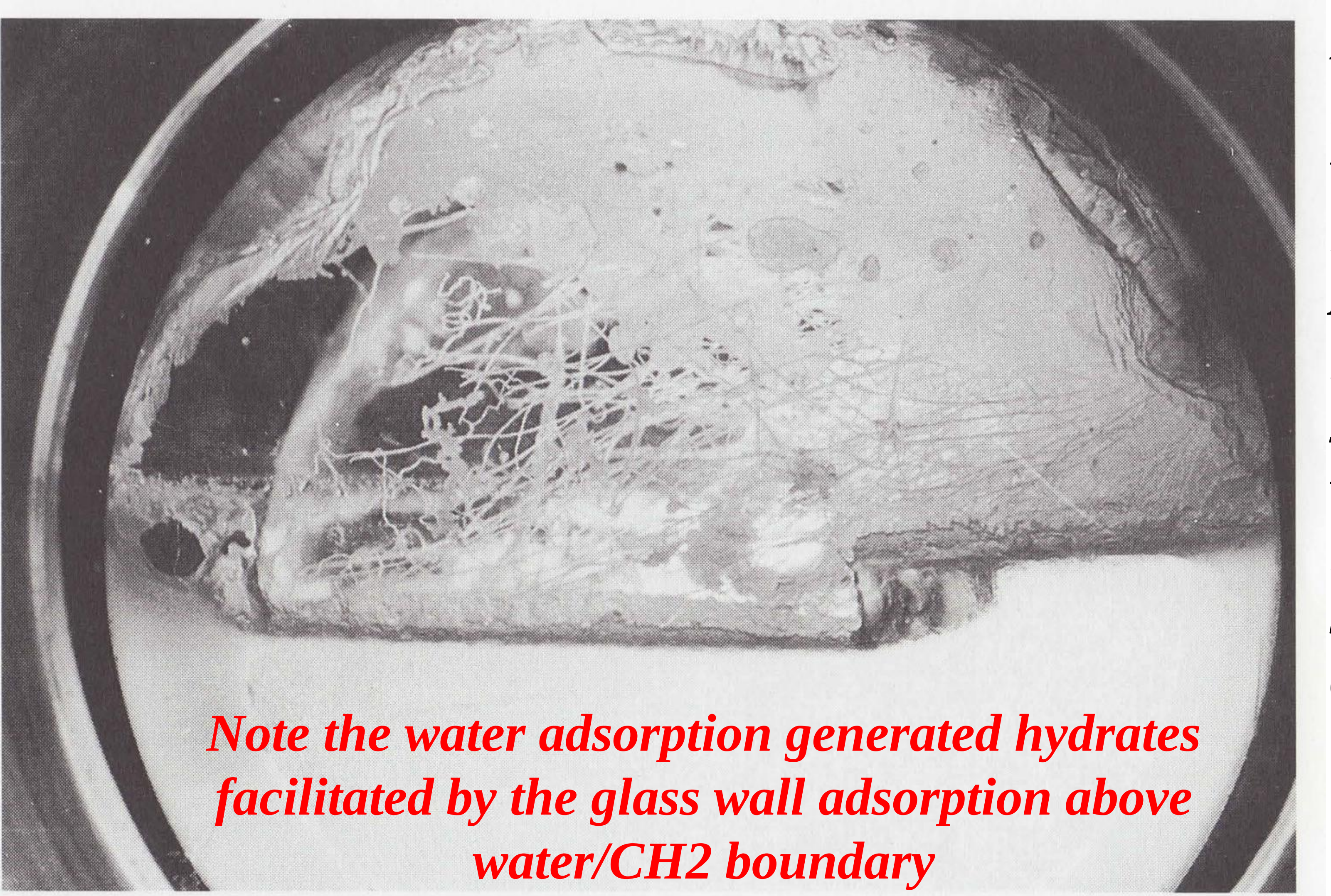
  - results in different filling fractions

  - different hydrate free energies

  - different hydrate kinetics

$\mu_w^{H,i}$	Water chemical potential in hydrate phase i
$\Delta g_{kj}^{\text{inclusion}}$	Free energy of inclusion in cavity by ”classical” langmuir integration or harmonic oscillator approach (Kvamme & Tanaka, 1995)

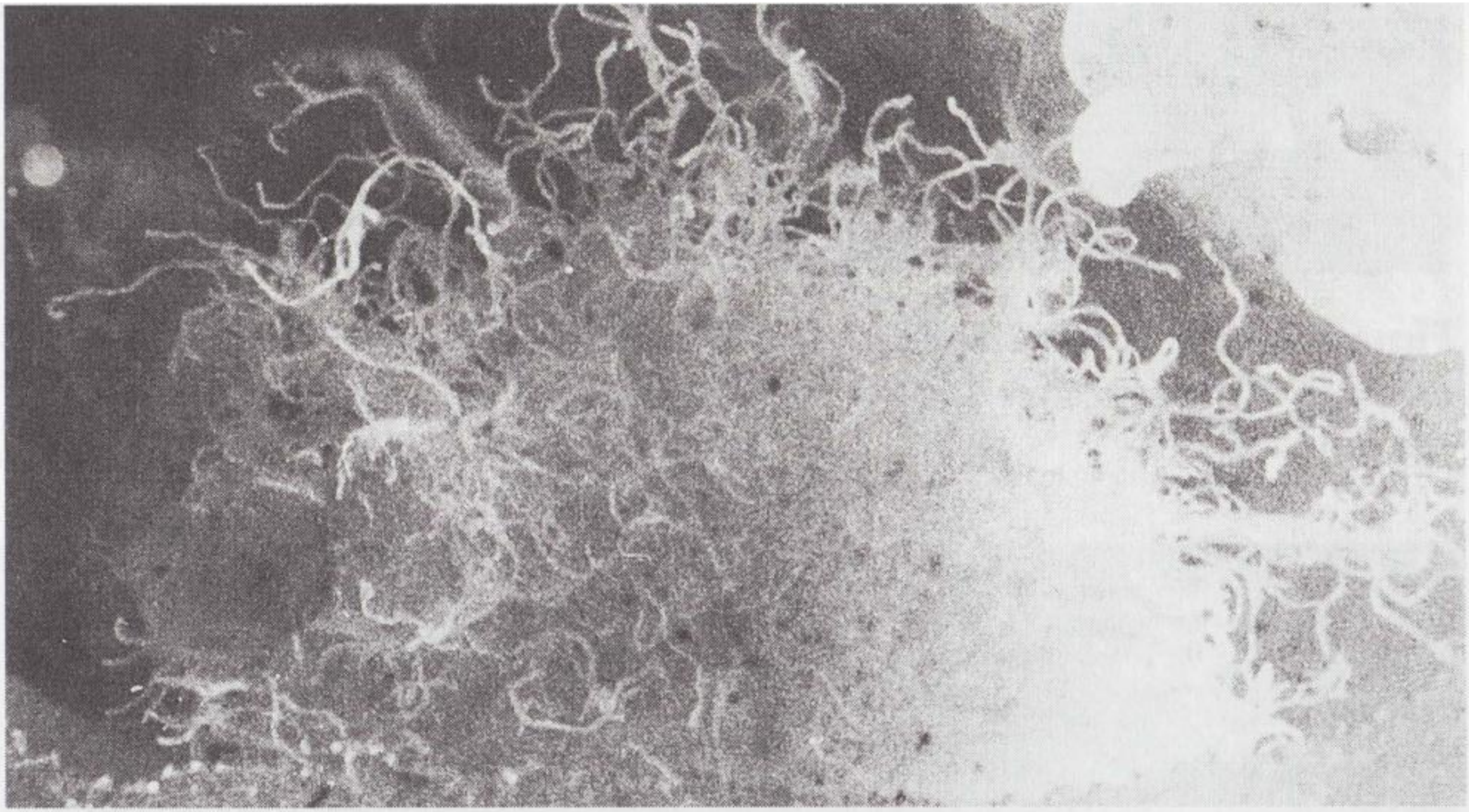
Some snapshots of multiple hydrate phases from Makogan's book

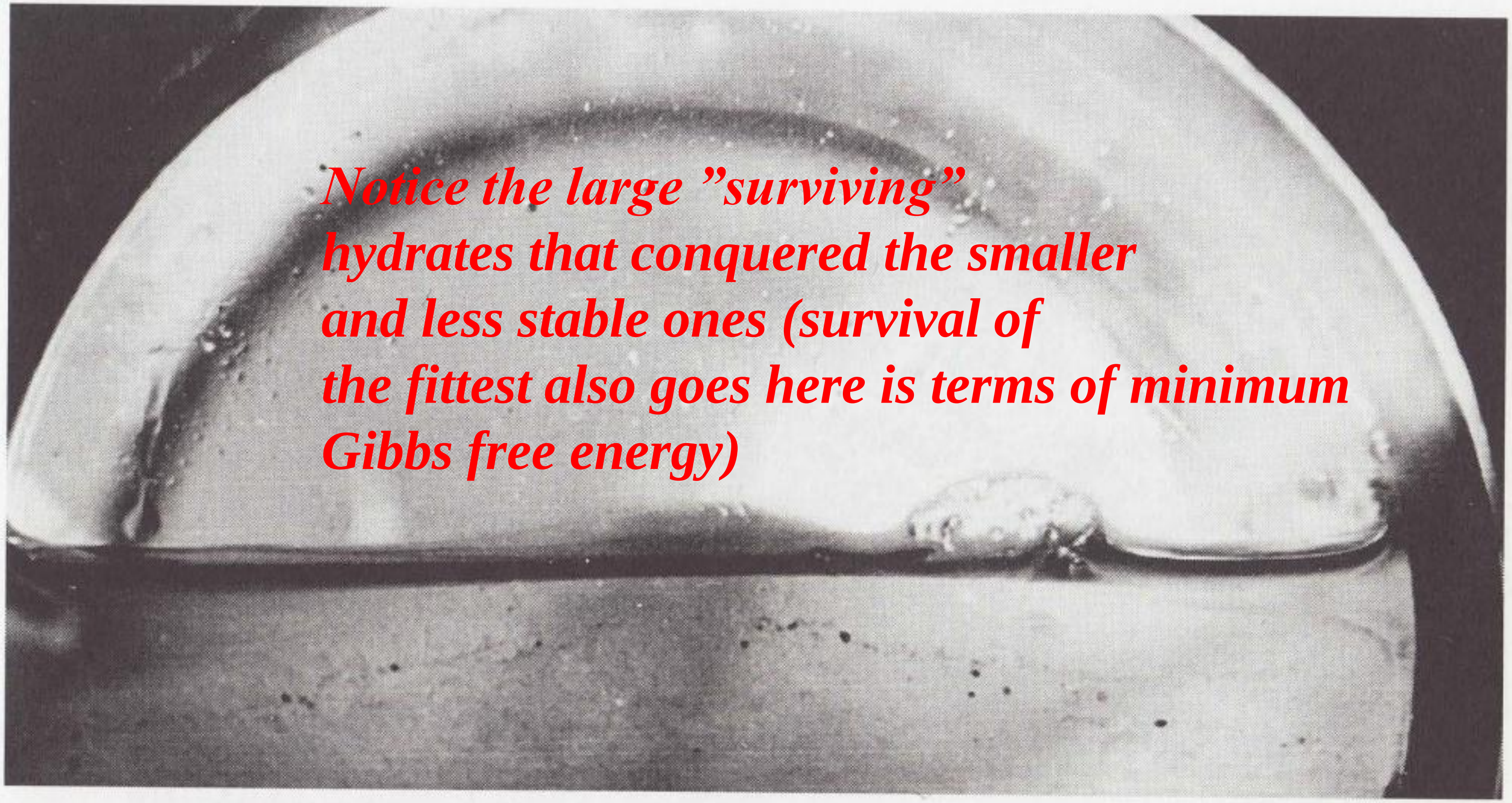


His laboratory was also his office And with methane at 200 bar it was not norwegian standards of rules

Note the water adsorption generated hydrates facilitated by the glass wall adsorption above water/CH2 boundary

Nice illustration of Growth connection from Wall hydrate through gas Section to top of liquid water hydrate





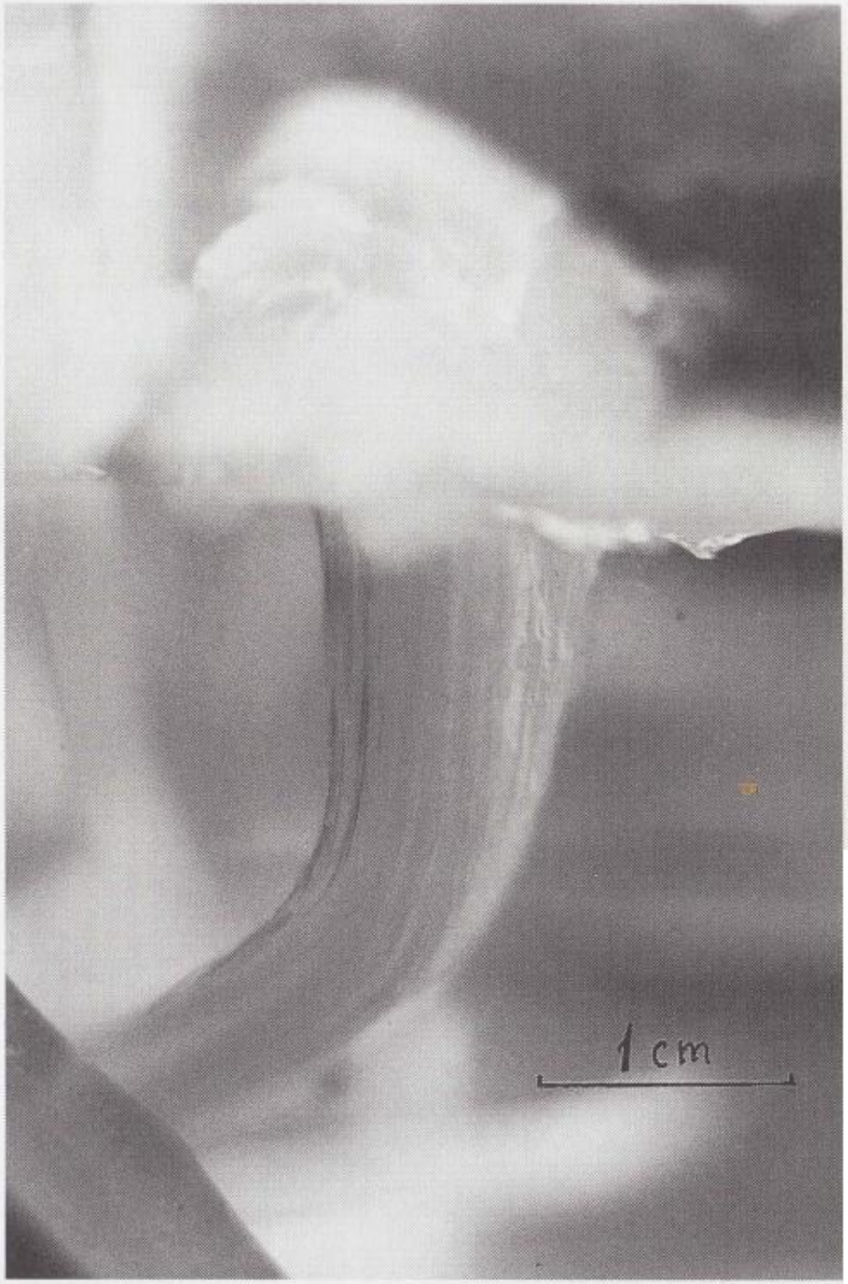
Notice the large ”surviving” hydrates that conquered the smaller and less stable ones (survival of the fittest also goes here is terms of minimum Gibbs free energy)

(a)

(d)

(e)

Figure 3-42a–e

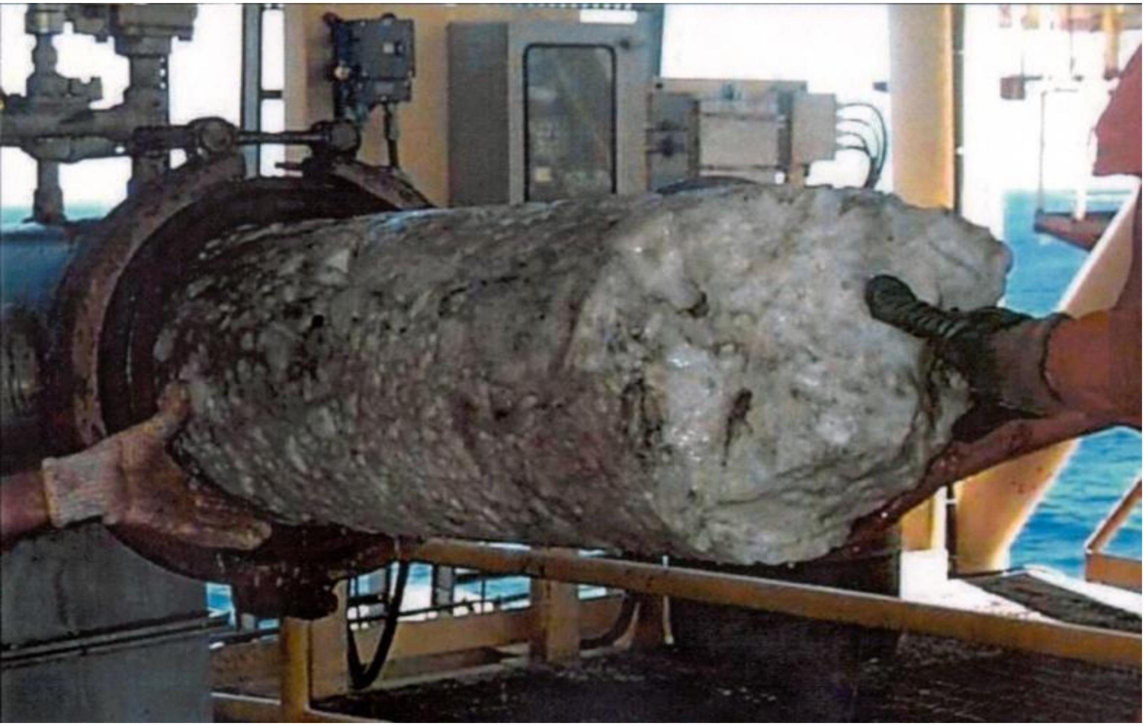


Beautiful hydrate flower growing from adsorbed towards interface through aqeous column containg dissolved methane

So unfortunately the hydrate world is not a very simple two dimensional P,T projection in nature – or in prosessing and transport for that matter …

Hetrogeneous hydrate formation is facilitated through 2-dimensional mass transport control versus 3-dimensional for homogeneous. But solid surfaces will also serve as adsorption sites for hydrate formers

Gibbs Phase Rule cont.

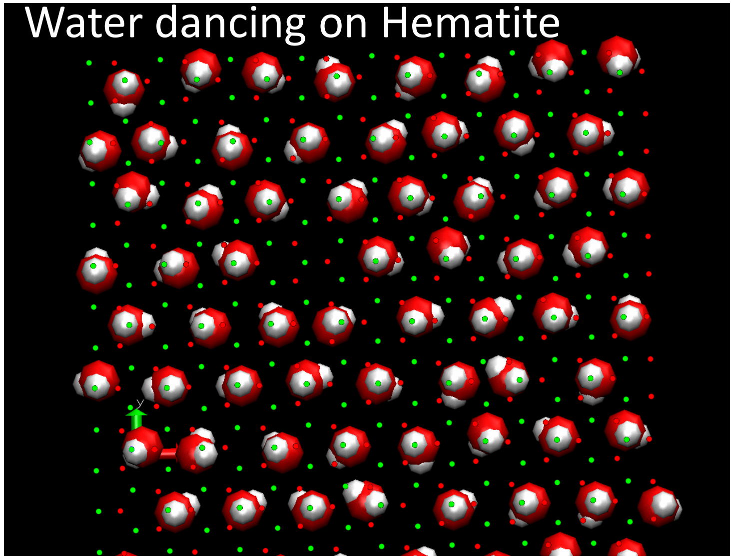


- In addition to the hydrate risk CO2 and H2S will promote corrosion and conversion of iron oxides to iron carbonates and other components

- ***But it is a challenge that the thermodynamic properties of adsorbed phases can not be measured***

- Molecules adsorbed on solid surfaces are unique phases since the ***density, structure and composition*** are uniquely different from the other phases in the system.

- ***Rust is a mixture of iron oxides*** and the relative ratio between the different oxides change over time. ***Hematite***, Fe2O3 is ***one of the most stable forms*** from a thermodynamic point of view



Water dancing on Hematite

Adsorbed structures

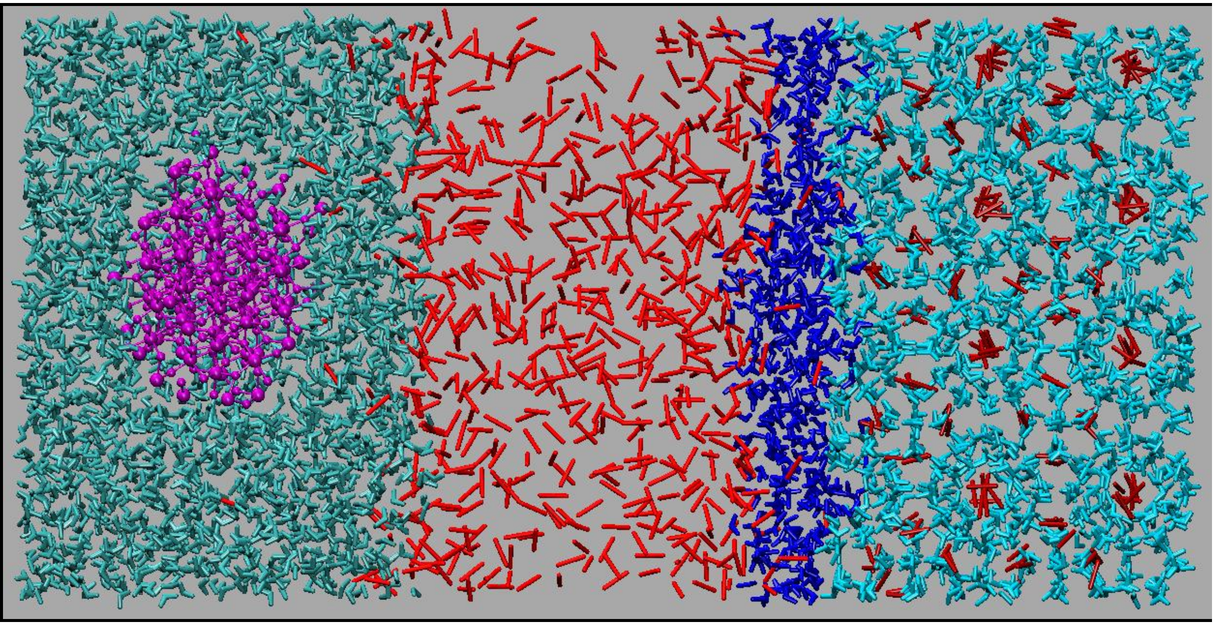


Fig. 1. The final configuration of a composite simulation system consisting of hydrate (left), water, carbon dioxide and liquid water with a small hematite crystal (red is oxygen and green is iron) 5.6 ns after the start of the simulation

Details of these simulations are not important in the context of this discussion but the composition profiles illustrate the adsorbed phases on hydrate and hematite respectively

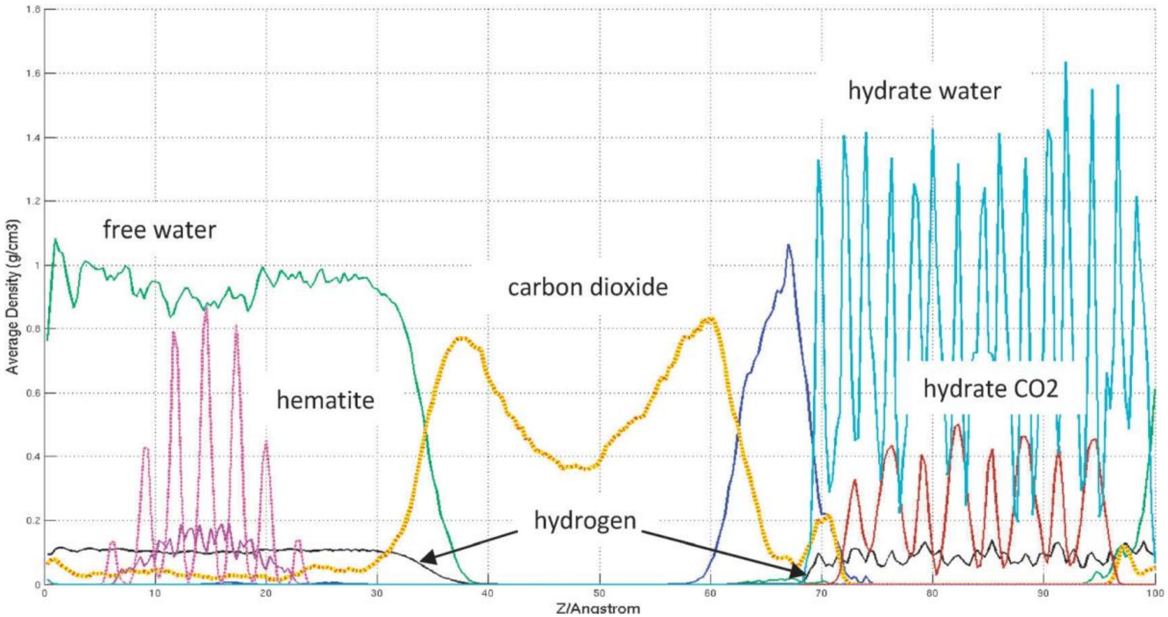
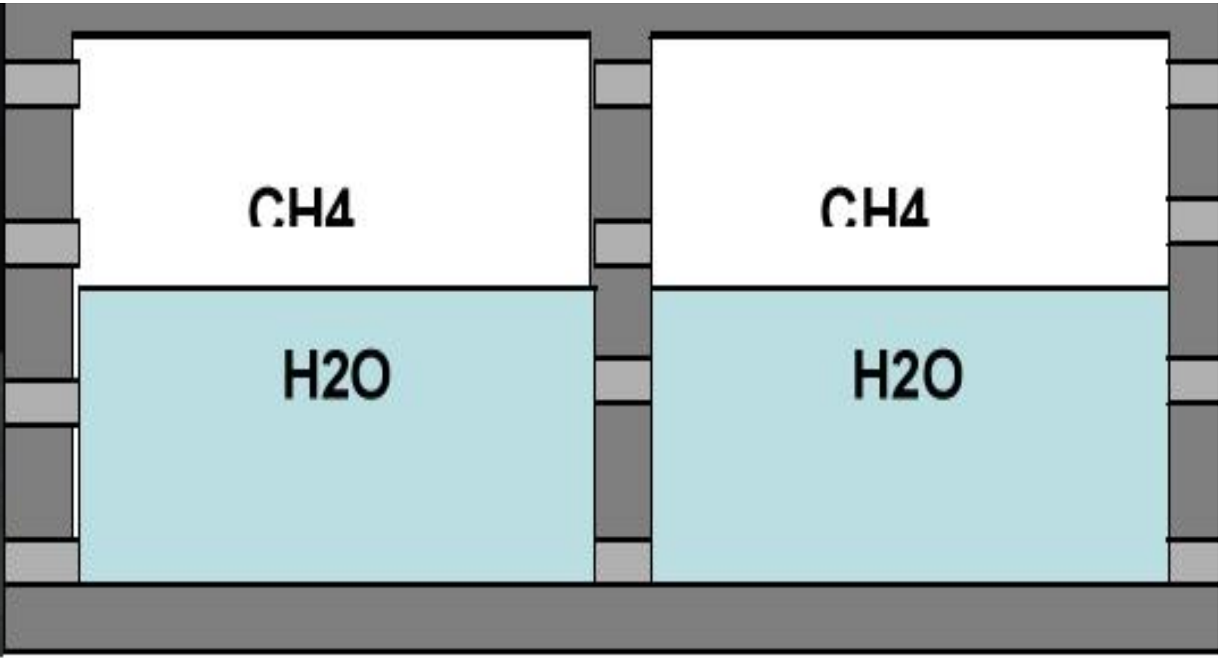


Fig. 2. Average density profile (grams/cm^3) for different molecules and atoms in the composite system of fig. 8 Yellow curve: all free CO_2 (sum of all three atoms at carbon centre), the green and blue curves are the two free water layers. Light magenta curve is iron, darker, black-dotted, line represents oxygen. Cyan: hydrate water, red: CO_2 hydrate. Black: hydrogen in water.

Hydrate nucleation, growth and induction

- ***Nucleation***: Given ”reasonable” driving forces nucleation occurs on water/hydrate former interface on nanoscale in time and critical size is in the order of 3 nm diameter
- ***Growth*** is stable unless competition from other particles consumes less stable particles due to mass limitations
- ***Induction*** time is ”onset of massive growth” and identification depends on resolution of detection method

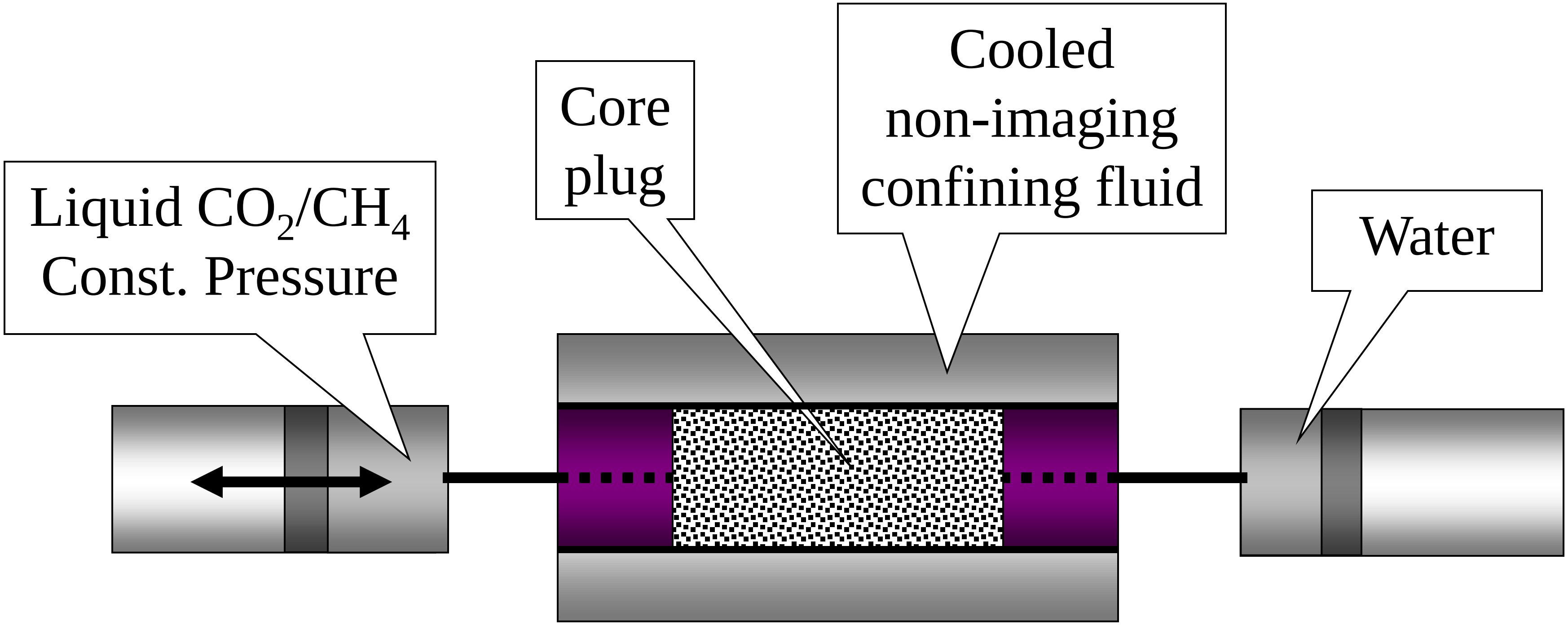
Experiments with methane and water at 83 bar and 3 C (resolution ~ 100 micrometer)



Two half cylinders of polypropylene with diameter 4 cm and lenght close to 10 cm separated by a 4 mm spacer with channels for natural fluid flow

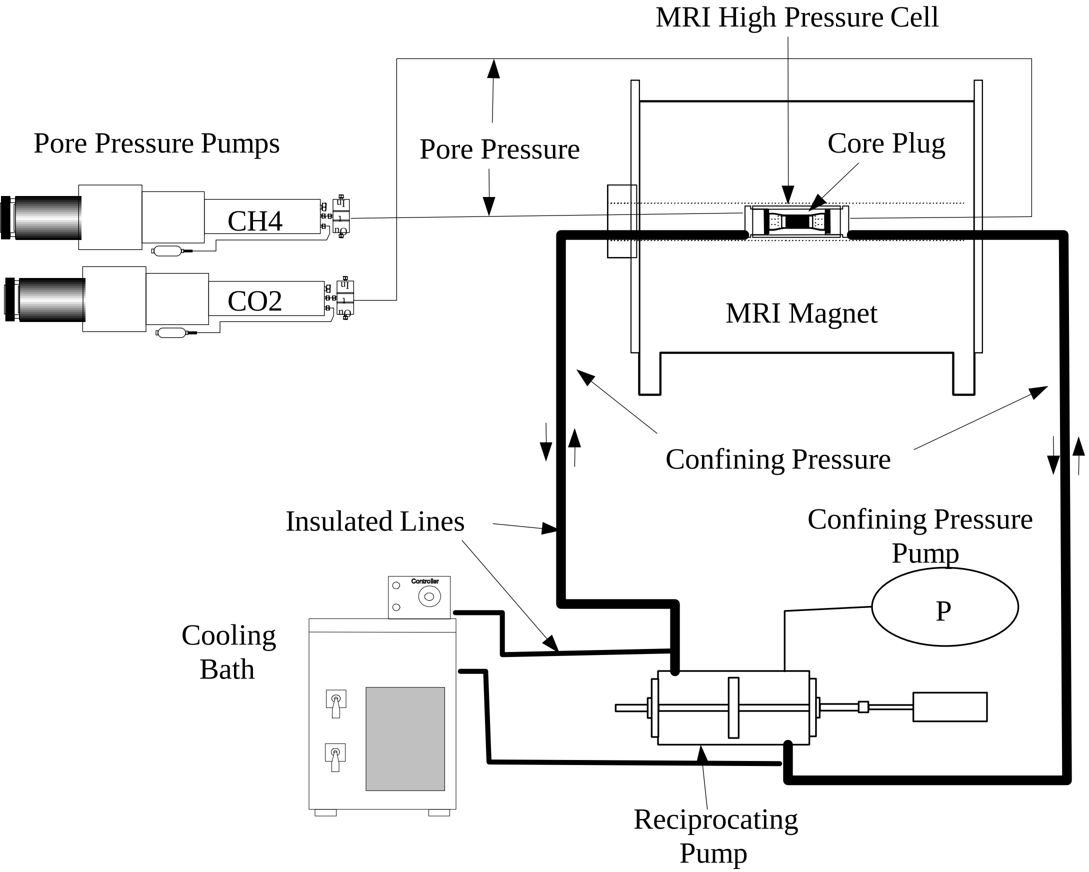
Note that methane is the wetting component on the polypropylene, in contrast to the glass cell in which the walls are water wettening

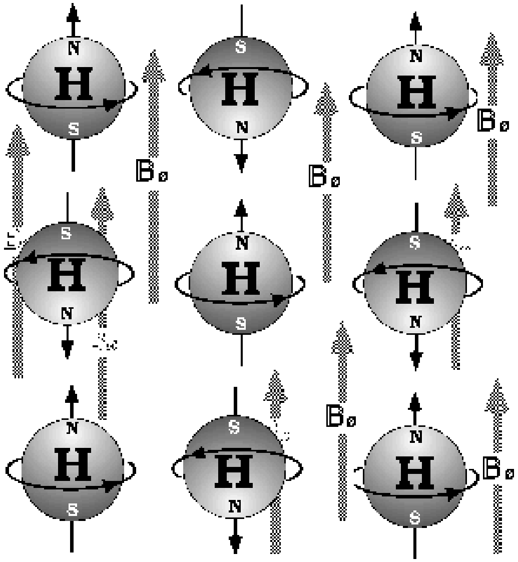
Hydrate Experiments Setup



Acknowledgements to Prof. Arne Graue and PhD students, and ConocoPhillips staff, with James Howard as coordinator at CoP, for conducting this experiment.

Experimental Setup



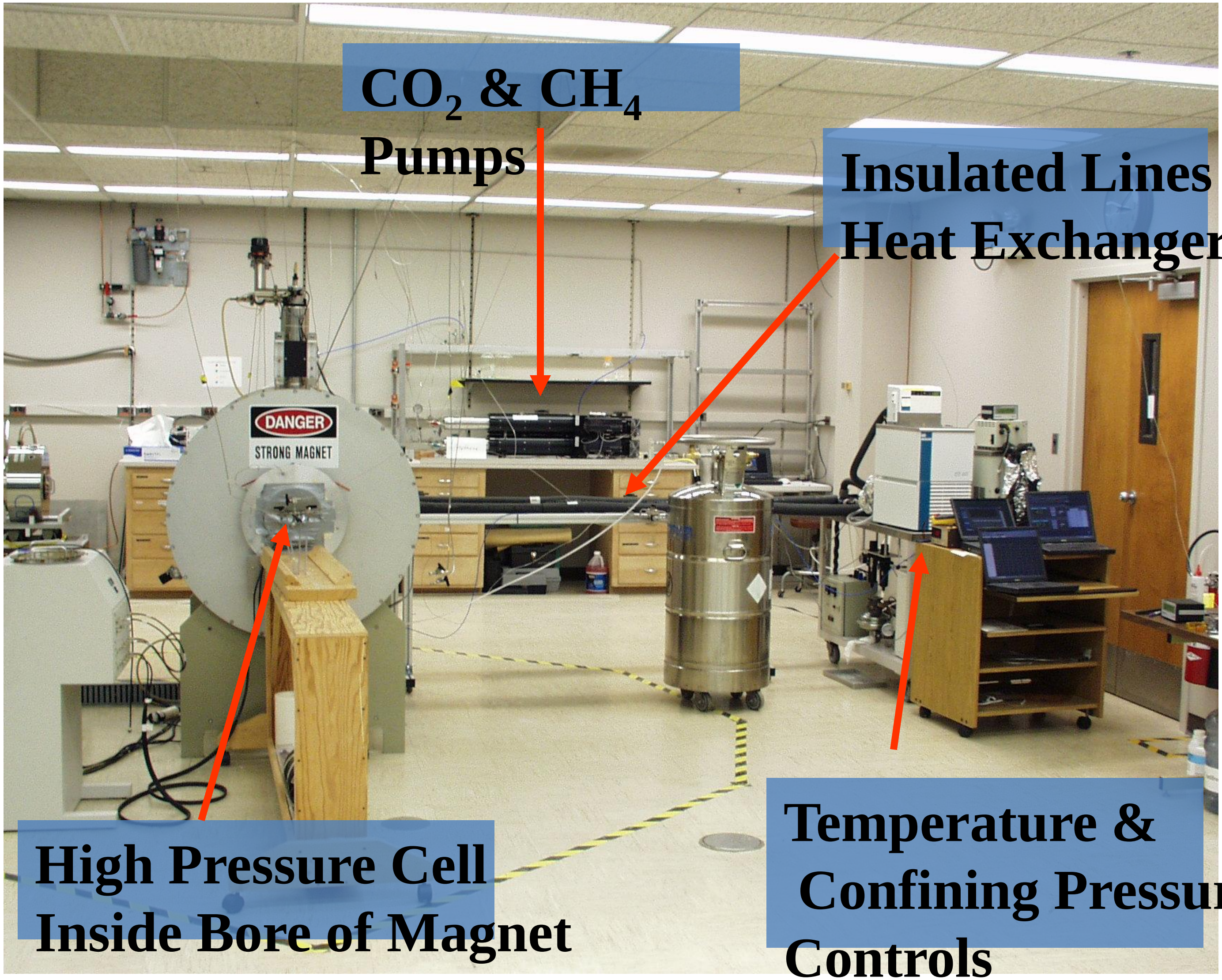


Spinning protons acts like Magnets.

The spin in hydrogen liquid water differs from that of hydrogen in hydrate water.

Tuning the magnetic field and sampling reflections will locate regions of hydrate and liquid water respectively

Experimental Setup

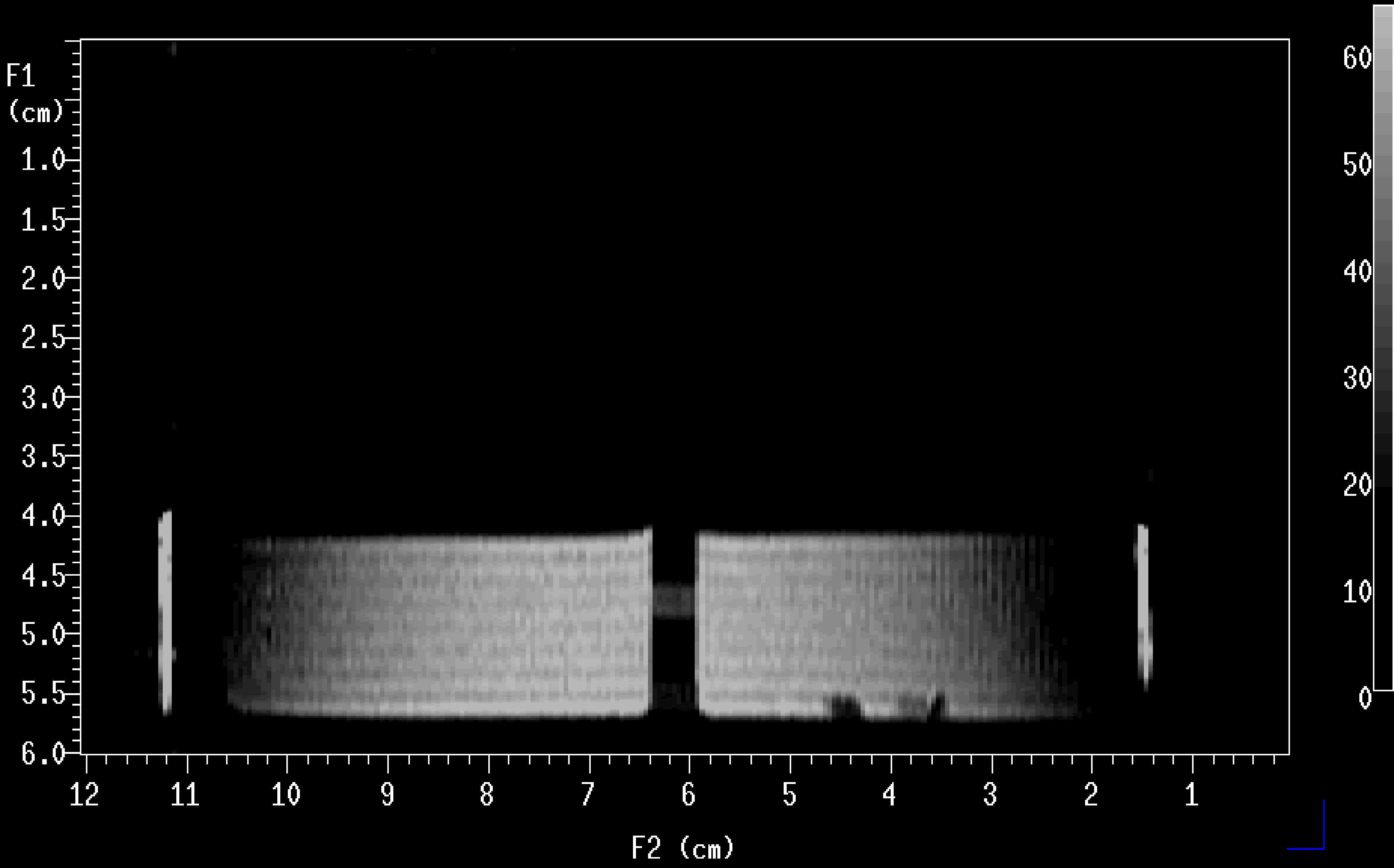


CO_2 & CH_4 Pumps

Insulated Lines & Heat Exchanger

High Pressure Cell Inside Bore of Magnet

Temperature & Confining Pressure Controls


F1
(cm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
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12
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9
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F2 (cm)
60
50
40
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10
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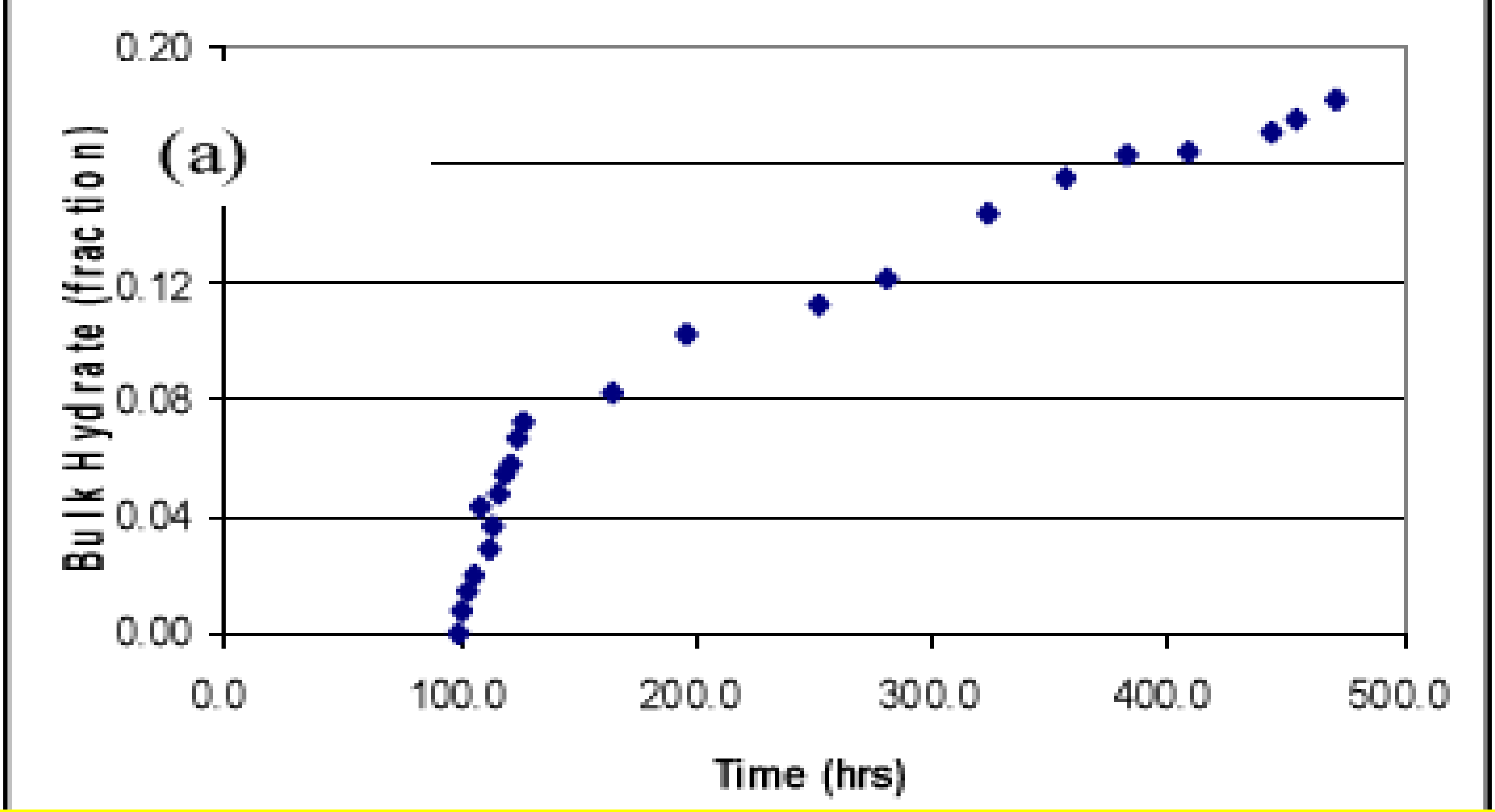


Why? Two primary factors:

1) A methane hydrate film will rapidly form on the water/methane interface and reduce efficiently further growth untill film penetratesdue to local competition based on first and second laws of thermodynamics

2) Methane is the wetting component of the silicone rubber and some methane will migrate along the walls downwards in the chamber due to

Free energy changes for *different* phase transitions involving hydrate from CH4

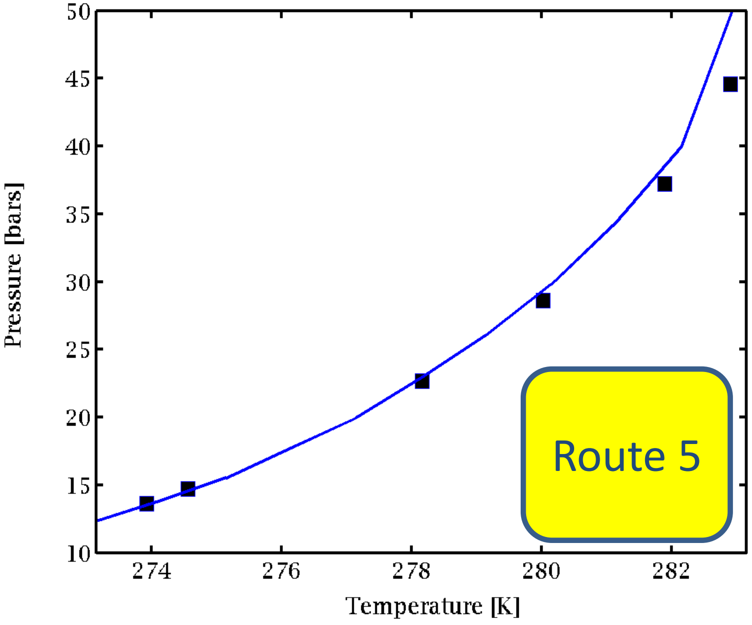
$$\Delta G_i = \delta\left[x_w^{H,j}\left(\mu_w^{H,j} - \mu_w^{p}\right) + x_{CH4}^{H,j}\left(\mu_{CH4}^{H,j} - \mu_{CH4}^{p}\right)\right]$$

Table 1. Potential hydrate phase transition scenarios for a system of carbon dioxide with impurities as relevant for transportation pipeline. The change in the free energy for any of the processes mentioned in table 1 is calculated according to equation 1. Note that the different phase transitions may involve hydrate of different composition and as such the label hydrate for the phase does not distinguish between different free energy hydrates in this table.

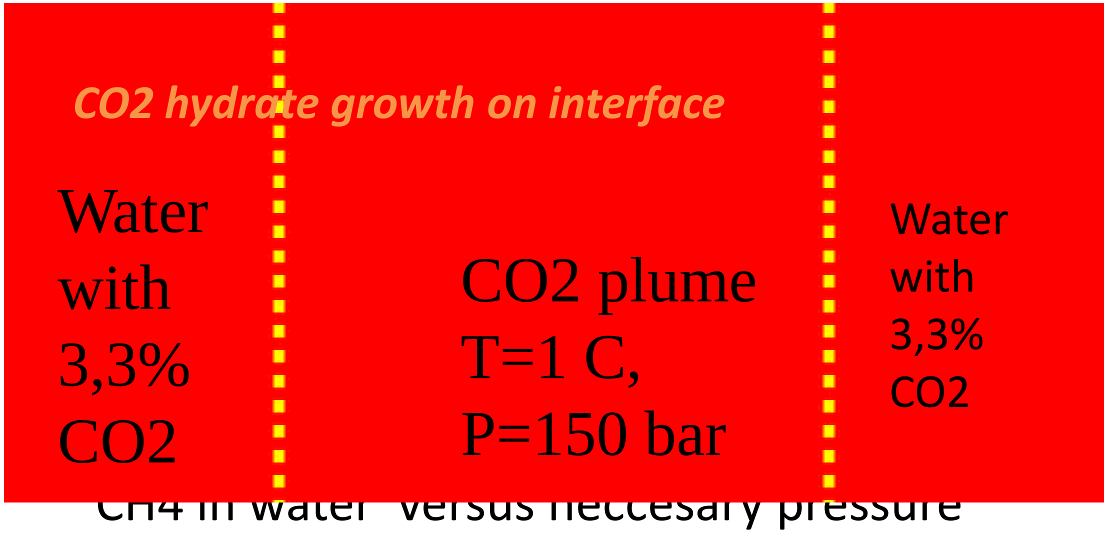
i	δ	Initial phase(s)	Driving force	Final phase(s)
1	-1	Hydrate	Outside stability in terms of local P and/or T	Gas, Liquid water
2	-1	Hydrate	Sublimation (gas under saturated with water)	Gas
3	-1	Hydrate	Outside liquid water under saturated with respect to carbon dioxide and/or other enclathrated impurities originating from the carbon dioxide phase	Liquid water, (Gas)
4	-1	Hydrate	Hydrate gets in contact with solid walls at which adsorbed water have lower chemical potential than hydrate water	Liquid water, Gas
5	+1	Gas/fluid	Hydrate more stable than water and hydrate formers in the fluid phase	Hydrate
6	+1	Gas + Liquid water	Hydrate more stable than condensed water and hydrate formers from gas/fluid	Hydrate
7	+1	Surface reformation	Non-uniform hydrate rearranges due to mass limitations (lower free energy hydrate particles consumes mass from hydrates of higher free energy)	Hydrate
8	+1	Aqueous Phase	Liquid water super saturated with carbon dioxide and/or other hydrate formers, with reference to hydrate free energy	Hydrate
9	+1	Adsorbed	Adsorbed water on rust forms hydrate with adsorbed hydrate formers.	Hydrate
10	+1	Adsorbed +fluid	Water and hydrate formers from gas/fluid forms hydrate	Hydrate

Possible competing phase transitions involving hydrate with a basis from a system of CO2 containing water. More components in the CO2 phase will not change the picture as even more hydrate phases will occur (most stable hydrate form first)

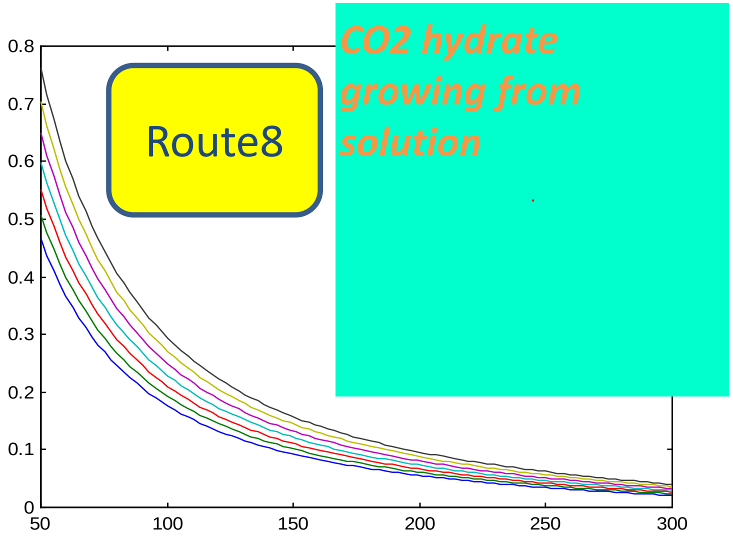
Most hydrate evaluation software only focus on route 5



Hydrate from CO2 and liquid water given only T fixed and P dependent variable. (Kvamme & Tanaka,1995)



CH4 in water versus neccesary pressure (horisontal axis) to produce hydrate (upper curve for 6 C and lower for 0 C)



Kvamme, Bjørn. *Initiation and growth of hydrate from nucleation theory*. International Journal of Offshore and Polar Engineering 2002; 12:256-262

Kvamme, Bjørn. *Droplets of dry ice and cold liquid CO2 for self transport to large depths*. International Journal of Offshore and Polar Engineering 2003; 13(1):1-8

Impact of solid surfaces on hydrate phase transitions

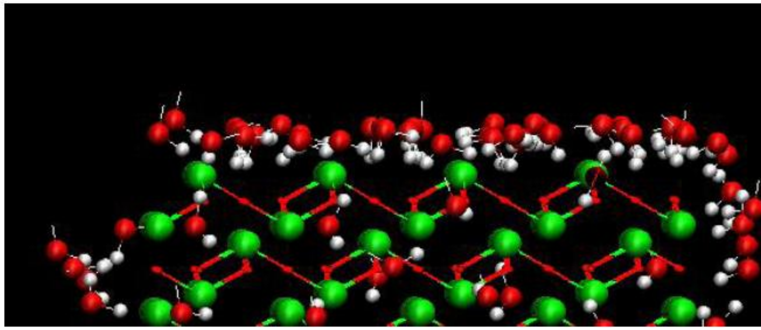
Geometrical aspects

Red is saturated CO2 in aqueous solution at 150 bar and 3 C

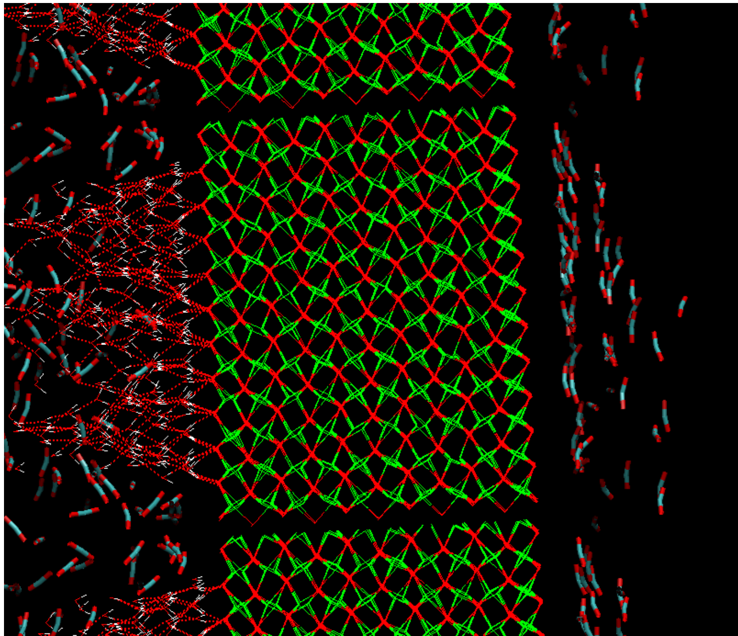
Hydrate (yellow) will preferentially nucleate and grow from inclinements (black circles are inert partcles)

Interface thermodynamics

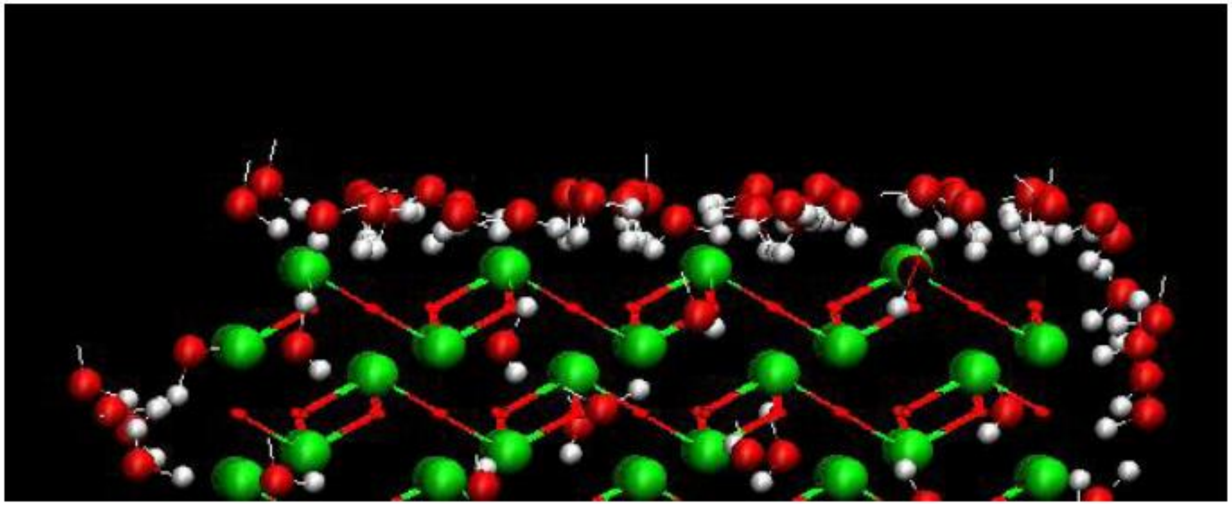
Water chemical potential adsorbed on hematite surfaces are 2 to 4 kJ/mole lower than as liquid

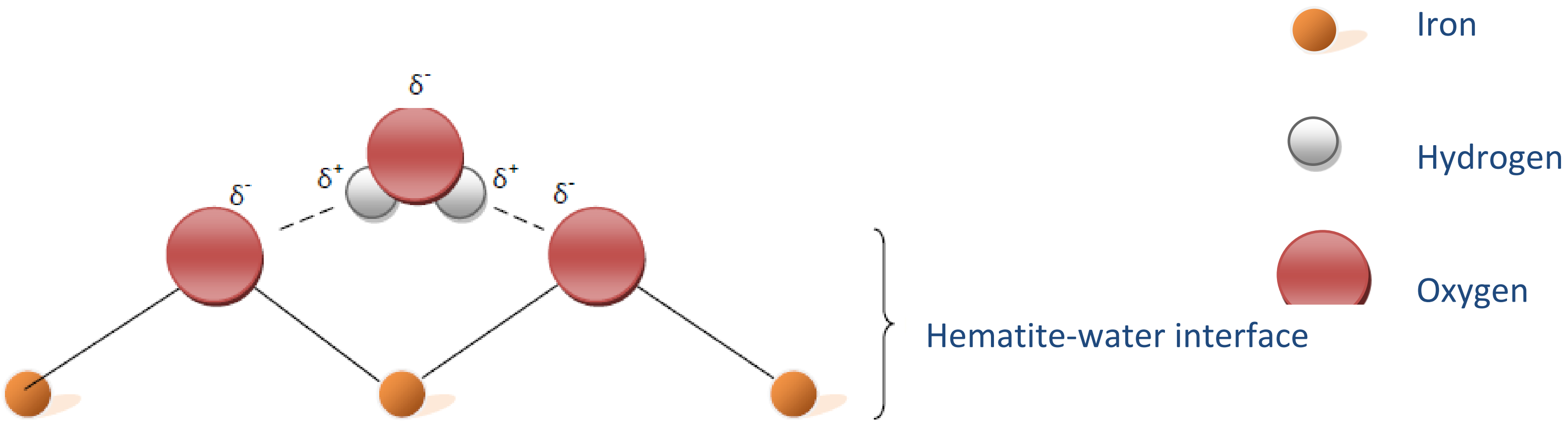


Selective adsorption of water and hydrate formers on mineral surfaces are unique for each mineral and hydrate former and can "catalyst" hydrate formation (enrichment and heteogeneous nucleation)

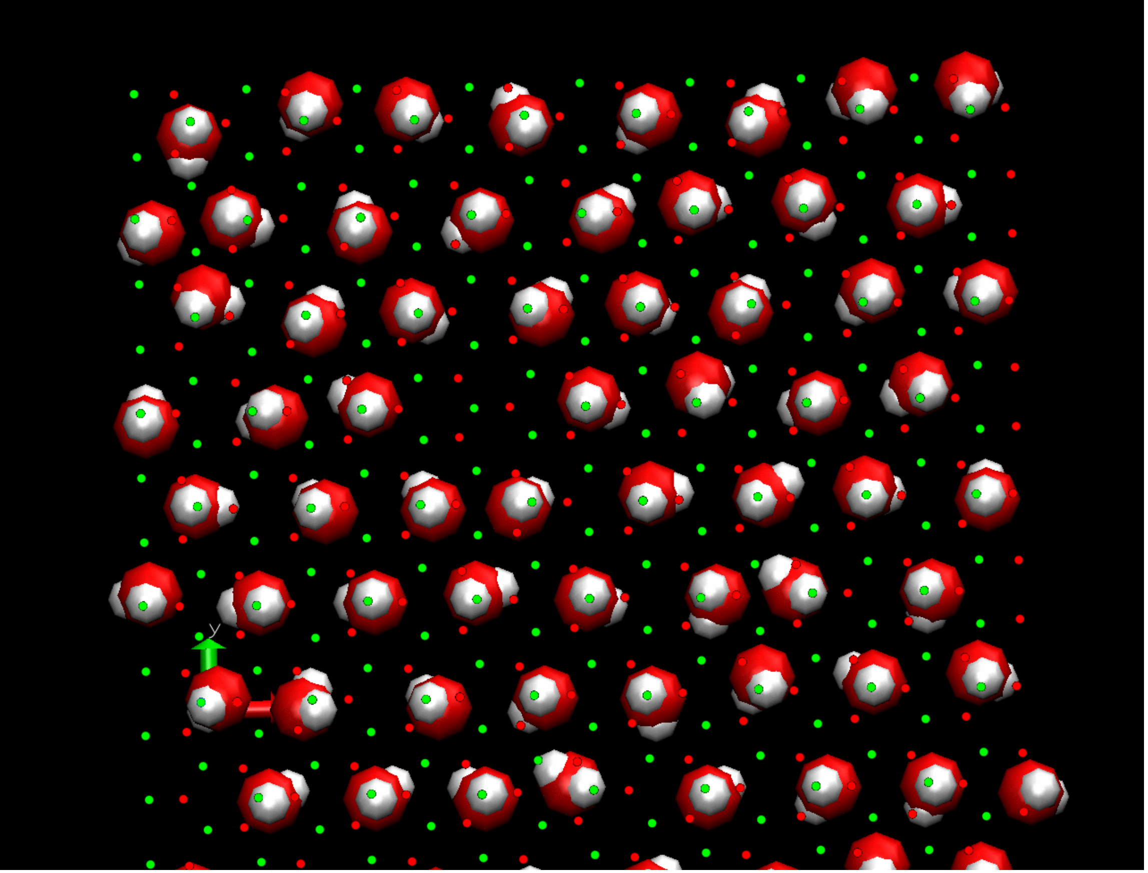


Water restructuring





Hematite-water interface



Adsorbed water is ”inhibited” compared to liquid water ***but structuring of water*** and ***enriched hydrate former concentration*** will facilitate heterogeneous hydrate formation and/or reformation slightly outside the adsorbed water layer (1.5 – 2 nm)

	Excess bidrag	**Ideell gass**	**Reell**
H_2O Kluster$_{v/245K}$	-20,3350 kJ/mol	-30,3201 kJ/mol	-50,7 kJ/mol
H_2O Hematitt$_{v/245K}$	-24,3775 kJ/mol	-30,3201 kJ/mol	-54,7 kJ/mol
H_2O Kluster$_{v/278K}$	-17,4894 kJ/mol	-35,2802 kJ/mol	-52,8 kJ/mol
H_2O Hematitt$_{v/278K}$	-20,8985 kJ/mol	-35,2802 kJ/mol	-56,2 kJ/mol

Here we are back to the thermodynamic «competition» between adsorbed and condensed, which is the Boltzmann factor of adsorbed minus cluster, which in simplified nucleation theories (classical) is the relative thermodynamic benefit, which is around 4.4 with these data

Summary – Gibbs phase rule analysis

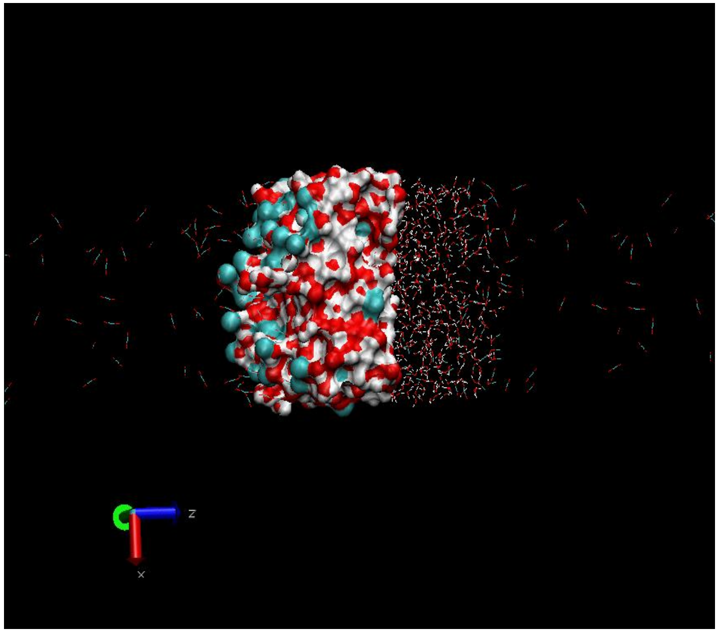
- Systems of CO2 containing water have several routes to hydrate formation, and since the systems is ***unable to reach equilibrium*** chemical potentials of each component in the different phases are different and hydrate formation from different routes results in different filling fractions, and ***different filling of hydrates results in different free energies***.
- Impurities like H2S, N2, CH4 and Ar will lead to ***several different hydrate phases*** (with different free energies) since ***most stable hydrates will form first*** due to combined 1. and 2. law of thermodynamics
- ***Thermodynamic*** description needs to be ***consistent across phase boundaries*** and ideal gas as reference state for all phases is the only feasible possibility
- ***Water wettening surfaces*** will thermodynamically favor adsorption of water relative to condensation as liquid. These surfaces will also benefit from favorable heterogeneous hydrate nucleation. ***Non-polar surfaces adsorb*** methane and other ***non-polar components*** and can play a role in hydrate nucleation and growth but condensation will be favorable over adsorption for non-polar walls.
- ***Adsorbed*** state ***cannot be measured in terms of thermodynamic properties*** and properties must be estimated based on state of the art molecular modeling methods (Quantum mechanics and molecular dynamics simulations)

A few words on the MD simulations

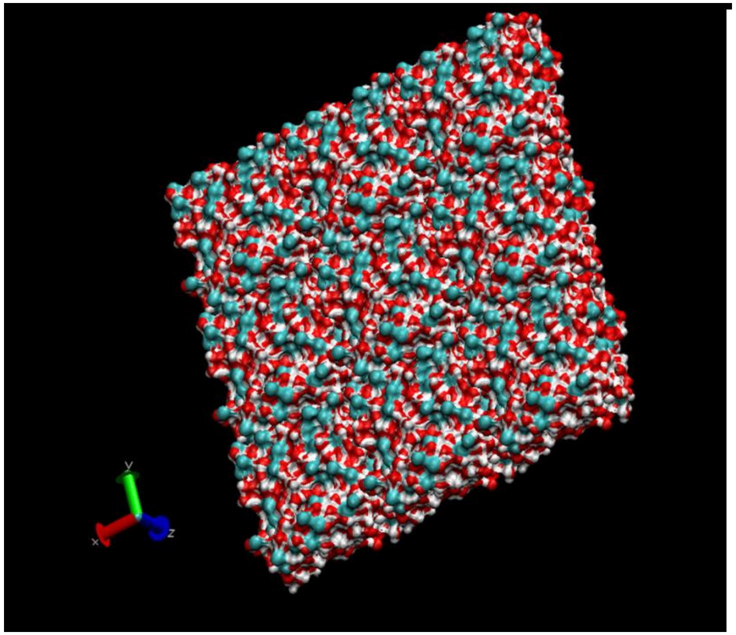
- We have applied MD43 – a software originally developed by Prof. Aatto Laaksonen at University of Stockholm more than 30 years ago and further developed and documented/verified through hundreds of publications from worldwide groups, including our group
- Sizes of simulation systems vary from 512 molecules up to 2048 depending on the system composition and need for accuracies in samplings. Corresponding volume according to experimental densities. These sizes are based on our more 30 years of experience (and corresponding publications) on size versus accuracy in sampling for these types of systems
- Standard methods for imitating infinite size systems (periodic boundary conditions) and handling of long range forces (coulombic forces due to partial charges from dipole moments) by means of Ewald summation.

A few words on the MD simulations cont.

- Most emphasis in the modeling part have been on the complex liquid region of the CO_2 phase under relevant transport conditions. Specifically 100 to 200 bar and concentrations of impurities which enable modeling based on infinite dilution as reference state for impurities dissolved in CO_2 and H_2O respectively
- In a practical dynamic flow situation solubility of CH_4, N_2 and Ar into water and also adsorption of the same components onto rust are of no importance in terms of hydrate risk. They will contribute in a very standard fashion (langmuir constants, fugacities) in the chemical potential of water in hydrate during hydrate formation from CO_2 phase and free liquid water. H_2S is therefore the only impurity (in addition to water) which have significant implications of distribution between CO_2, liquid water and rust.



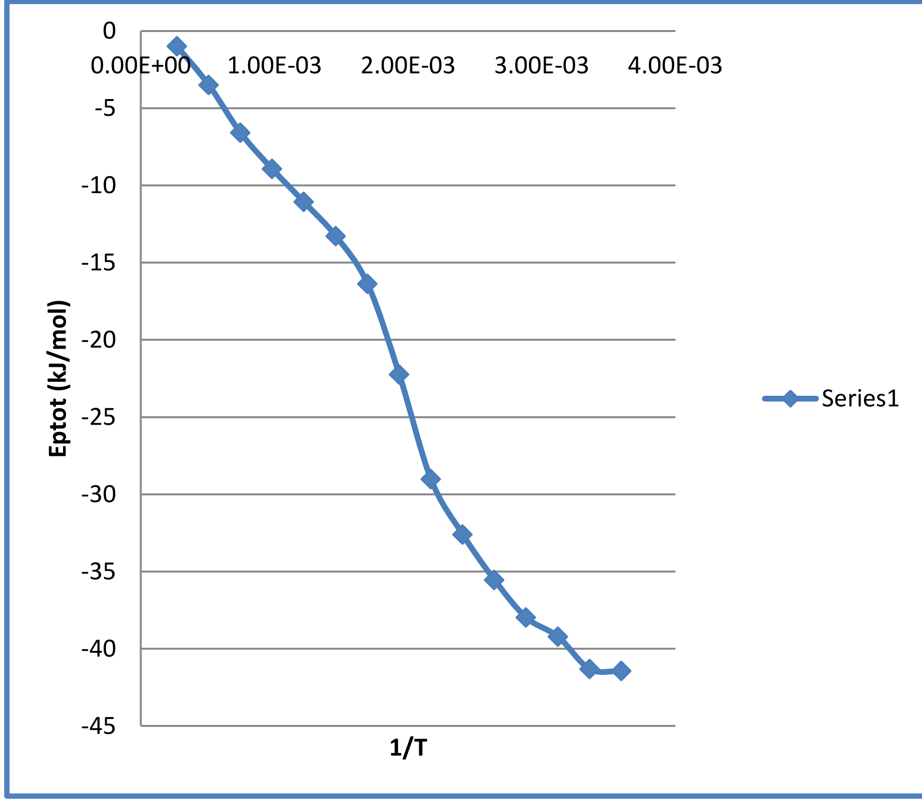
The water/CO2 interface is in the order of 1.2 Å for dense CO2 (left, 850 kg/m3) towards liquid water (rigth)



Methanol additions to water reduces the interfacial free energy between CO2 and the water phase. Snapshot of average surface waves

Thermodynamics

- Energies and enthalpies are trivially sampled from simulations in the NVT (constant number of particles, volume and temperature) and NPT (constant number of particles, pressure and temperature)
- In ideal gas the impact of molecular interactions (the residual part in equations of state) is zero. In a molecular dynamics simulation this limit will be met when all interactions are scaled down to zero (we apply Mezei's algorithm for this). Integration of the work involved in scaling interactions from zero to full interaction gives residual free energy. This work is trivially related to corresponding energy changes by the temperature relationship between free energy and energy



Scaling the temperature and sampling the interaction energy for varying temperatures towards infinite T (3000 K is high enough for extrapolation from 1/3000 towards 0 for 1/infinite T) is equivalent to scaling interactions but error in samplings slightly higher. Figure above is for water towards hematite

Thermodynamics cont.

Free energy and Gibbs-Duhem

By definition:

$$\underline{G} = \sum_{i=1}^{n} N_i \mu_i(T, P, \vec{x})$$

And by consistency of the combined 1. and 2. laws:

$$d\underline{G} = \sum_{i=1}^{n} N_i d\mu_i(T, P, \vec{x}) = 0$$

at constant T and P

These are trivially applied to a binary system and also Trivial (but more equations to solve simultaneously) for more components.

Example:

$$G(T,P,\vec{x}) = x_{H_2S,CO_2}\mu_{H_2S,CO_2}(T,P,\vec{x}) + (1 - x_{H_2S,CO_2})\mu_{CO_2,CO_2}(T,P,\vec{x})$$

$$\frac{dG(T,P,\vec{x})}{dx_{H_2S,CO_2}} = \mu_{H_2S,CO_2}(T,P,\vec{x}) - \mu_{CO_2,CO_2}(T,P,\vec{x})$$

$$\mu^{\infty}_{H_2S,CO_2}(T,P,\vec{x}) = G(T,P,x_{H_2S,CO_2} \to 0) + \lim\left[\frac{dG(T,P,\vec{x})}{dx_{H_2S,CO_2}}\right]_{x_{H_2S,CO_2} \to 0}$$

Infinite dilution chemical potentials in liquid CO2 and H2O

$$\mu_i(T,P,\vec{x}) - \mu_i^{\infty}(T,P,\vec{x}) = RT\ln\left[x_i\gamma_i^{\infty}(T,P,\vec{x})\right]$$

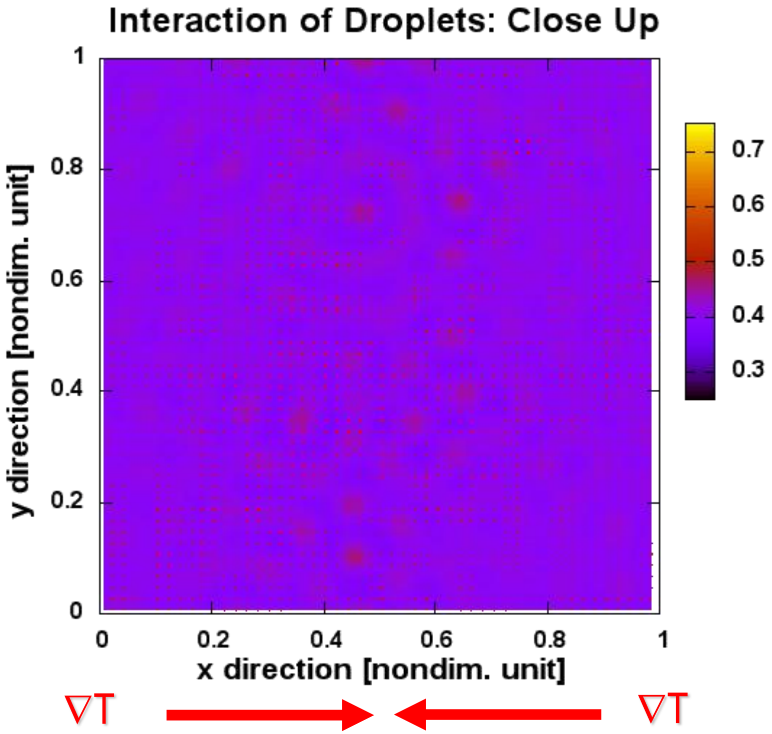
$$\lim(\gamma_i^{\infty}) = 1.0 \quad \text{when } x_i \rightarrow 0$$

		Infinite dilution chemical potentials with Liquid CO_2 as solvent		Infinite dilution chemical potentials with Liquid H_2O as solvent	
T(K)	P(bar)	H2S (kJ/mole)	H2O (kJ/mole)	H2S (kJ/mole)	CO2 (kJ/mole)
274.15	100.	-61.16	-55.71	-56.90	-58.02
278.15	100.	-58.83	-55.80	-56.39	-57.86
283.15	100.	-56.00	-55.91	-55.80	-57.68
274.15	150.	-53.89	-53.09	-56.78	-56.41
278.15	150.	-53.73	-53.58	-56.28	-56.17
283.15	150.	-53.54	-54.18	-55.68	-55.89
274.15	200.	-46.61	-43.46	-58.11	-54.80
278.15	200.	-46.46	-43.96	-57.54	-54.48
283.15	200.	-46.27	-44.56	-56.85	-54.09

The total chemical potential for each component at given T and P can be derived from the sampled free energies and Gibbs-Duhem. This again gives a basis for modeling the activity coefficients as function of concentration and temperature and pressure. A simple modeling is given in the report while waiting for implementation into the companies own «favorite» activity models for these types of systems. But as such the infinite chemical potentials above can also be used as a reference state for fitting activity coefficients to experimental data using equilibrium measurements. BUT: as discussed in the report snd here: expect a bias since hydrogen bondings makes it almost impossible to distribute waters and maybe also H2S as single molecules uniformly distributed. Binary clusters, ternary clusters and so on will lead to over-estimates of amounts dissolved relative to true thermodynamics of uniform solutions.

So why do we use molecular modeling and not acitivity coefficient models for water phase and CO2 liquid phase with water and impurities?

- In a non-equilibrium situation we need schemes of calculation that are ***based on same reference state*** so that free energy minimization can be applied according to ***1. + 2. law, to decide which phases that can form,*** and the ***distribution of the different phases***.
- PFT (Phase field theory is an example – part 2 available if audience is interested)



Spontaneous nucleation and growth from Solution, in gravity and temperature field

Extended adsorbtion Theory

$$G^H = \left[\mu_w^H x_w^H + \sum_{guests} \mu_{guest}^H x_{guest}^H \right]$$

- Single cavity integration (small guest molecules)
- Harmonic oscillator approach (large guest molecules)

$$\mu_w = \mu_w{}^0 - \sum_i v_i RT \ln(1 + \sum_j a_{ij})$$

$$\overset{\pi}{a} = \exp\left[\beta\left(\mu + \beta^{-1} \ln b\right)\right]$$

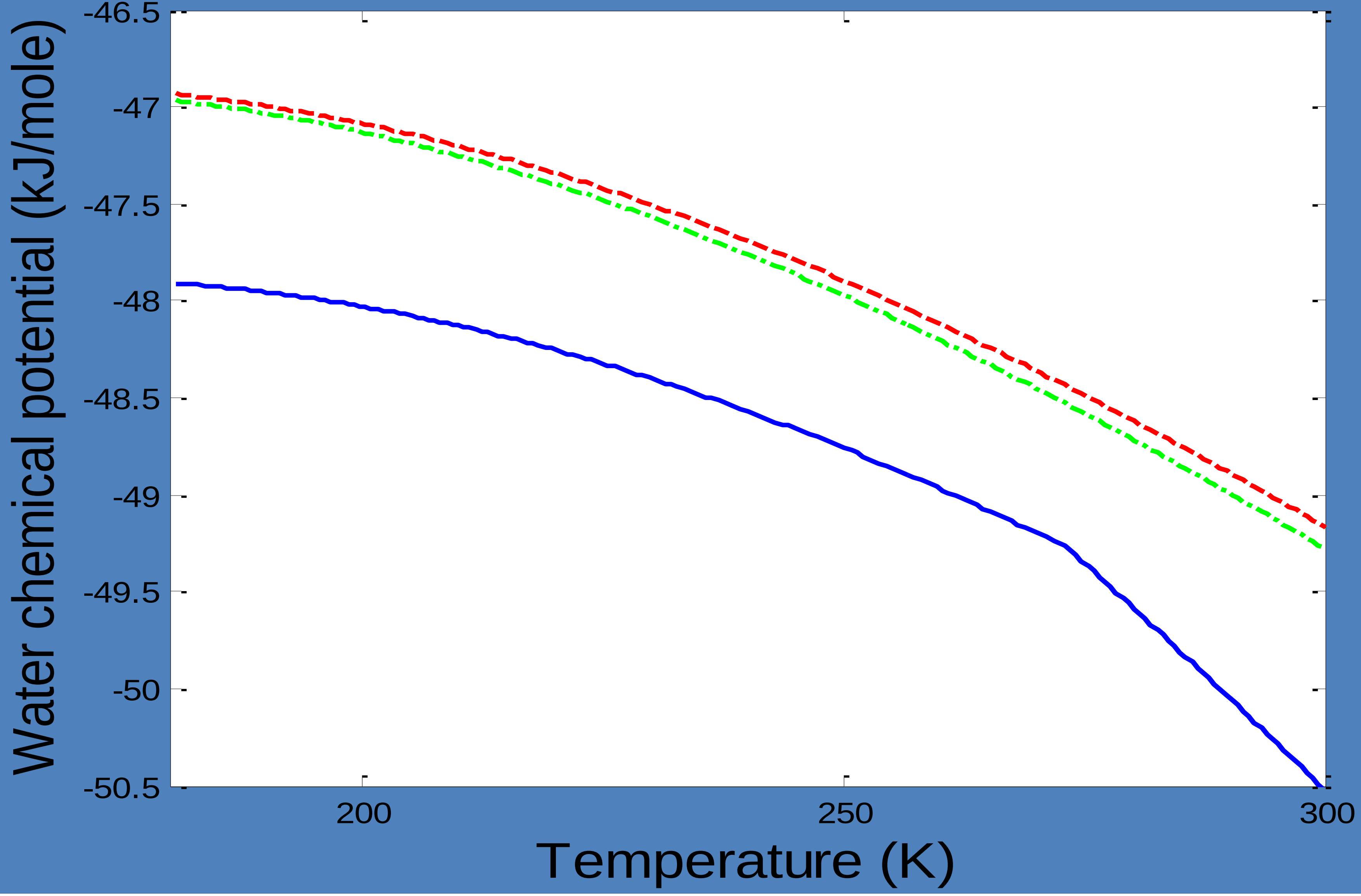
$$b = (m / \beta 2 \pi \hbar^2)^{3/2}$$

$$\int_{V_{cage}} \exp[-\beta w(v)] dv$$

$$a = \exp\left[\beta\left(\mu - \Delta g - u\right)\right]$$

$$g = \int \ln(\beta h \omega) h(\omega) d\omega$$

$$\beta = 1 / k_B T$$

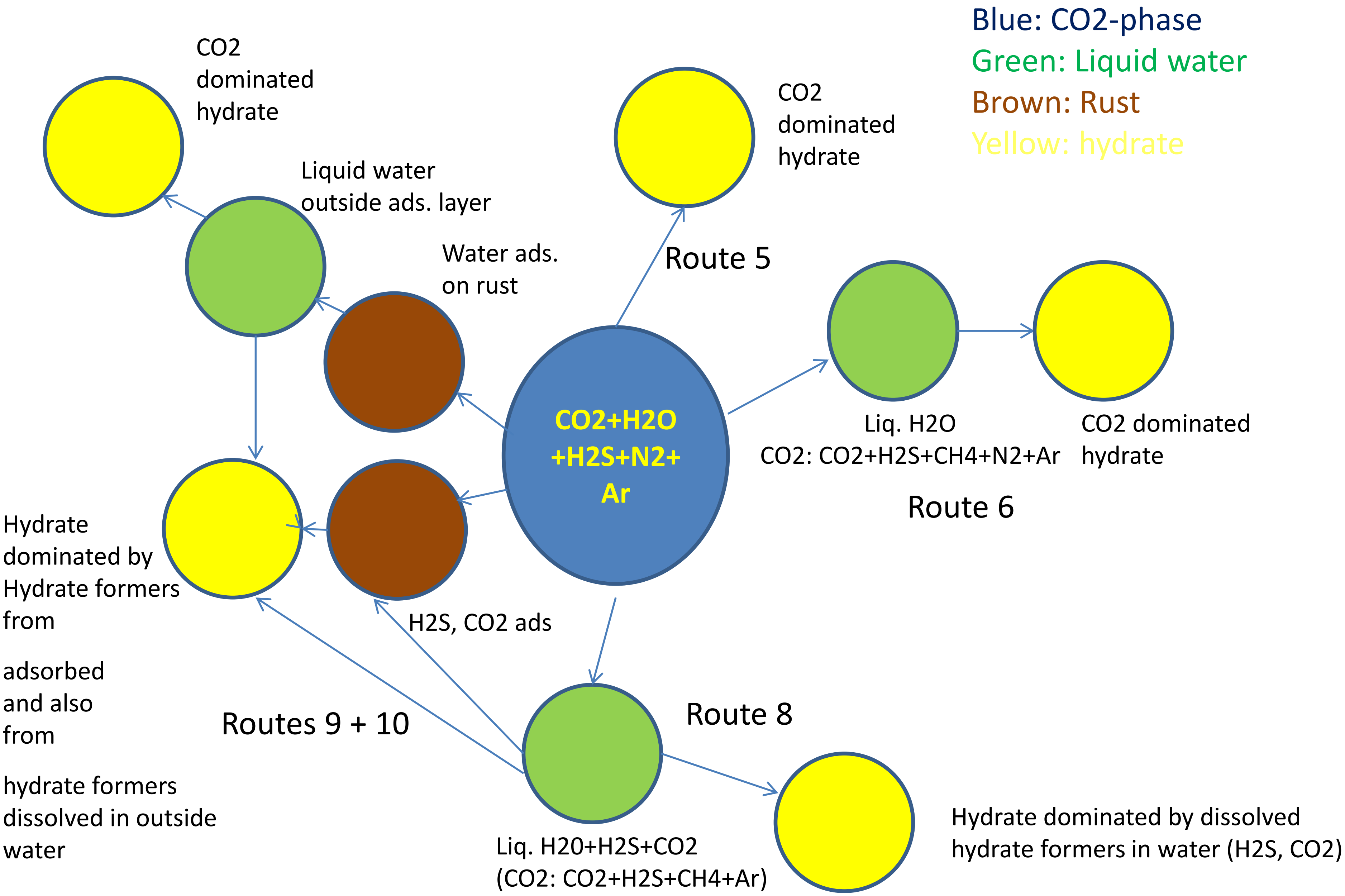


Residual Chemical potential for TIP4P model. Solid line for ice or liquid water, dash line for SI empty hydrate and dash-dotted line for SII empty hydrate.

Routes to hydrate formation

- Originally no free water – only water dissolved in CO2
- Can this water form hydrate without condensing first, or adsorbing first?
- If not – what are the concentration limits of water before dropping out as either water or adsorbed?
- And if adsorbed only 2-3 layers of water outside (less than 1 nm) needed for water to be able to form hydrate
- In a conservative evaluation we might skip all possible routes that can lead to redissociation of hydrate (routes 1 – 4 in the table in slide 7)

A «map» (with reference to slide 7) of different routes that can lead to hydrate formation is given in the next overhead



Blue: CO2-phase

Green: Liquid water

Brown: Rust

Yellow: hydrate

CO2 dominated hydrate

Liquid water outside ads. layer

Water ads. on rust

CO2 dominated hydrate

Route 5

CO2+H2O +H2S+N2+ Ar

Liq. H2O
CO2: CO2+H2S+CH4+N2+Ar

CO2 dominated hydrate

Route 6

Hydrate dominated by Hydrate formers from

adsorbed and also from

hydrate formers dissolved in outside water

H2S, CO2 ads

Routes 9 + 10

Route 8

Liq. H20+H2S+CO2
(CO2: CO2+H2S+CH4+Ar)

Hydrate dominated by dissolved hydrate formers in water (H2S, CO2)

Limits of water content in CO2 before drop out

- ***Several different QM charge distributions on Hematite all show consequently that water will prefer to drop out as adsorbed on Hematite and can then subsequently form hydrates heterogeneously***

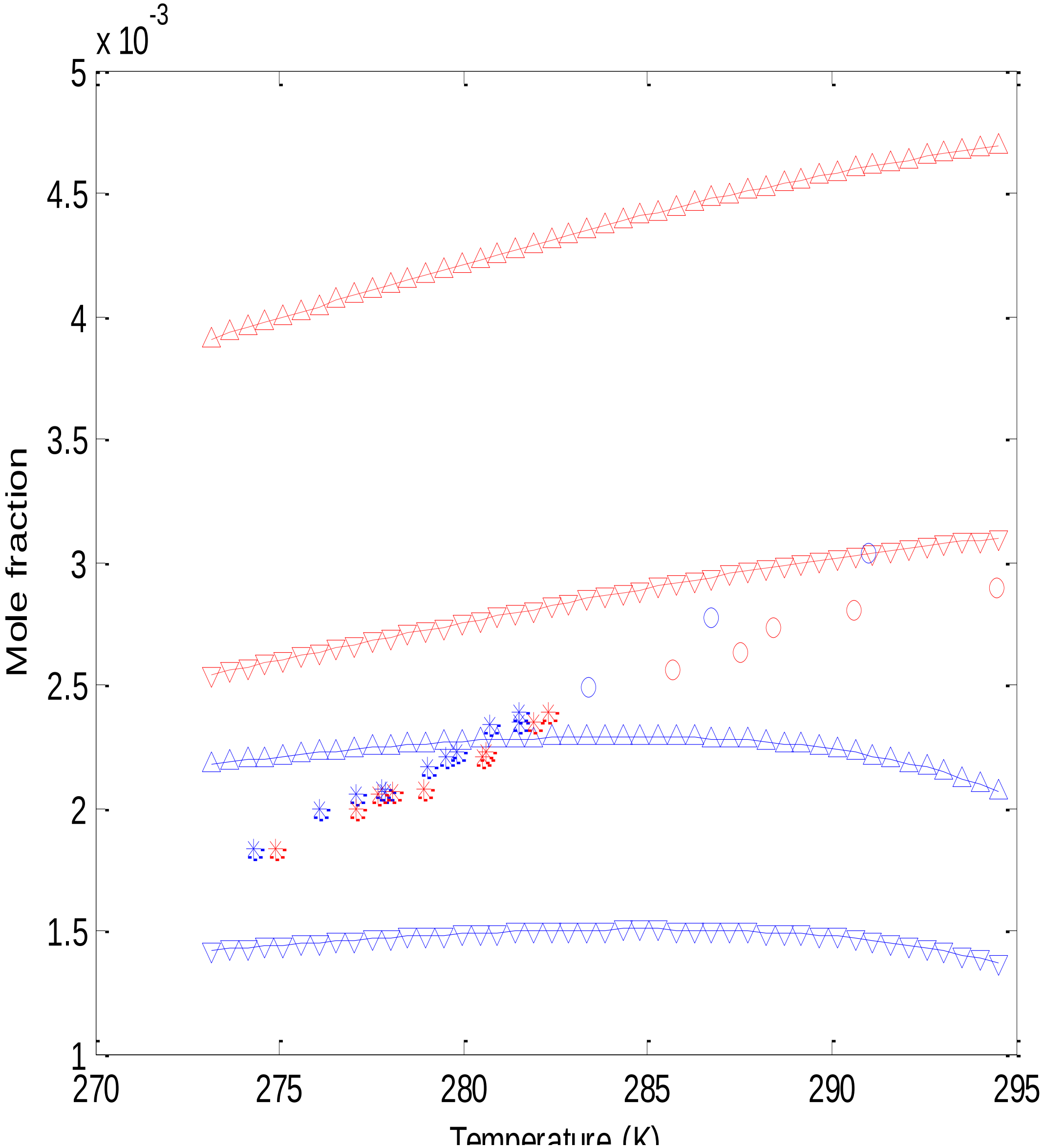


Fig. 11. Estimated maximum content of water in CO2 before dropout as adsorbed water (downward triangles) and as liquid dropout (upward triangles). Liquid water chemical potential from Kvamme and Tanaka [1] and difference between adsorbed and liquid water chemical potential from table 5 (-1.7 kJ/mole). Blue is for a pressure of 101 bar and red is for 61 bar. Same color codes for experimental data, in which stars are measured with hydrate present and circles are for liquid region.

hydrate formation as function of water mole fraction in CO2?

- ***Three layers of water outside rust water behaves liquid like and classical hydrate calculations are appropriate with the addition that also adsorbed hydrate former can form hydrate (different P,T)***

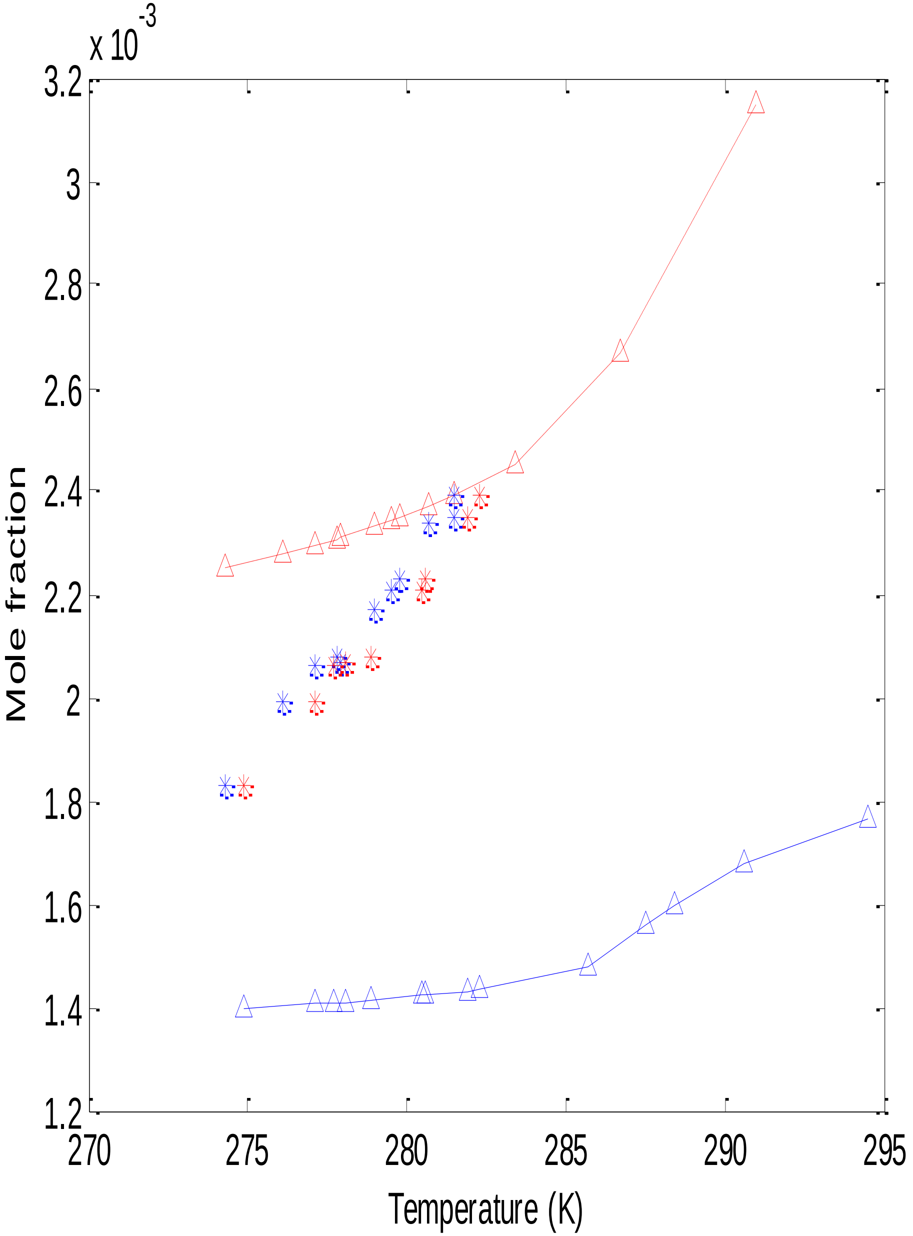


Fig. 13. Estimated content of water in CO2 in equilibrium with hydrate at two different pressures. Blue is for a pressure of 101 bar and red is for 61 bar. Stars are experimental data at 101 bar (blue) and 61 bar (red).

Options for industrial applications of non-equilibrium analysis

- Step one is a trivial ellimination of all phase transitions that are impossible because of positive free energy changes or too small free energy change to overcome the barrier of interface free energy related to pushing aside «old phases»
- Each possible phase transition can be evaluated separately in order to quantify which one of them are the most feasible in terms of free energy changes for the different steps leading to hydrate in each route.
- A simple kinetic analysis using Classical theory or MDIT theory (Kvamme, 2002, 2003) is easy to implement and computationally fast
- More advanced theories can be used as tools for better qualification of kinetic rate limitations. Phase Field Theory is one option
- Advanced kinetic modeling as a tool for implementation of kinetics as well is also interesting and can include impact of kinetic hydrate inhibitors

Routes to hydrate formation

- As a conservative analysis skipping possible re-dissociation of formed hydrate by contact with undersaturated phases is a good option
- Some routes to hydrate formation may be going in parallell at different kinetic rates
- Some routes to hydrate formation might even result in competing hydrate formations since H2S is an aggresive hydrate former and H2S dominated hydrate might form parallell to CO2 dominated hydrate

Route 5: Hydrate formation from water dissolved in CO2

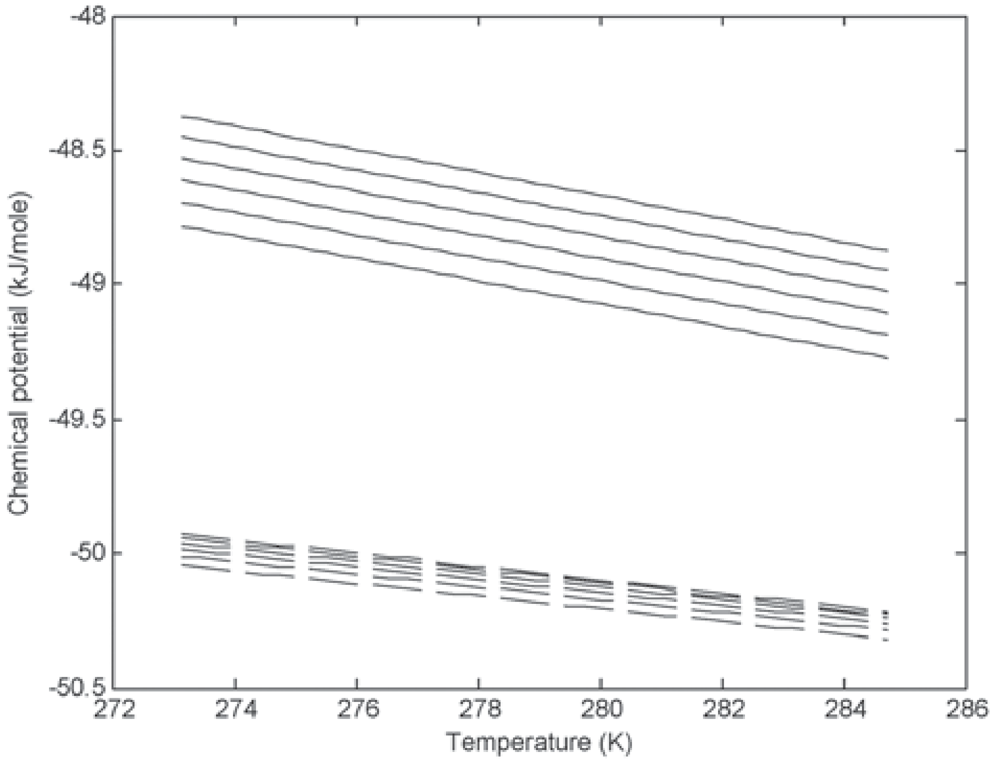


Fig. 6 Estimated chemical potentials of water that drop out in either liquid water or hydrate form. The same mole-fractions and conditions as in Fig. 5. Pressures are, from bottom to top, 100, 120, 140, 160, 180 and 200 bar. Solid lines are conditions for drop out as liquid water. Dashed lines are the corresponding estimated conditions for drop-out directly as hydrate from CO2 solution

- This option has been investigated and published in a paper prior to this project. ***Hydrate formation directly from water dissolved in CO2 is possible*** but with low water concentrations the question is whether it is realistic or not (PFT modeling is one way to investigate)

Water would like to drop out from CO2 as hydrate rather than as liquid water at all conditions in the range investigated. Benefit is around 1.5 kJ/mole for hydrate versus liquid water

Route 6: Hydrate forming from liquid water and fluid phase

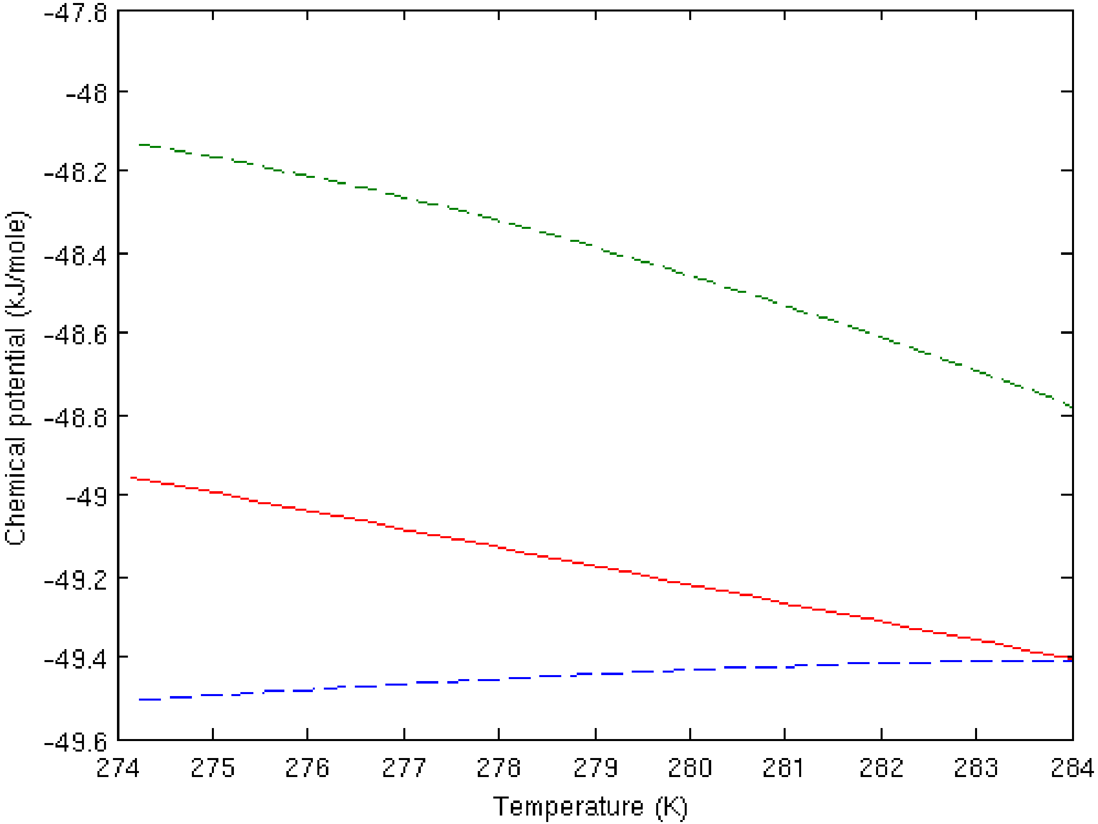


Figure 4 Chemical potential for liquid water (solid), water in hydrate formed from a mixture of 0.001 mole-fraction H_2S dissolved in CO_2 at 200 bar (lower dashed curve) and water in hydrate formed by the H_2S alone (upper dashed curve).

- As we already know CO2 hydrate will surely form at the conditions in consideration but a critical question is whether H2S dissolved in CO2 can stablize a competing hydrate dominated by H2S, which it is not able to under concentrations of 0.001 H2S in CO2

Route 6/8: Hydrate forming from liquid water with dissolved H2S and fluid CO2 phase

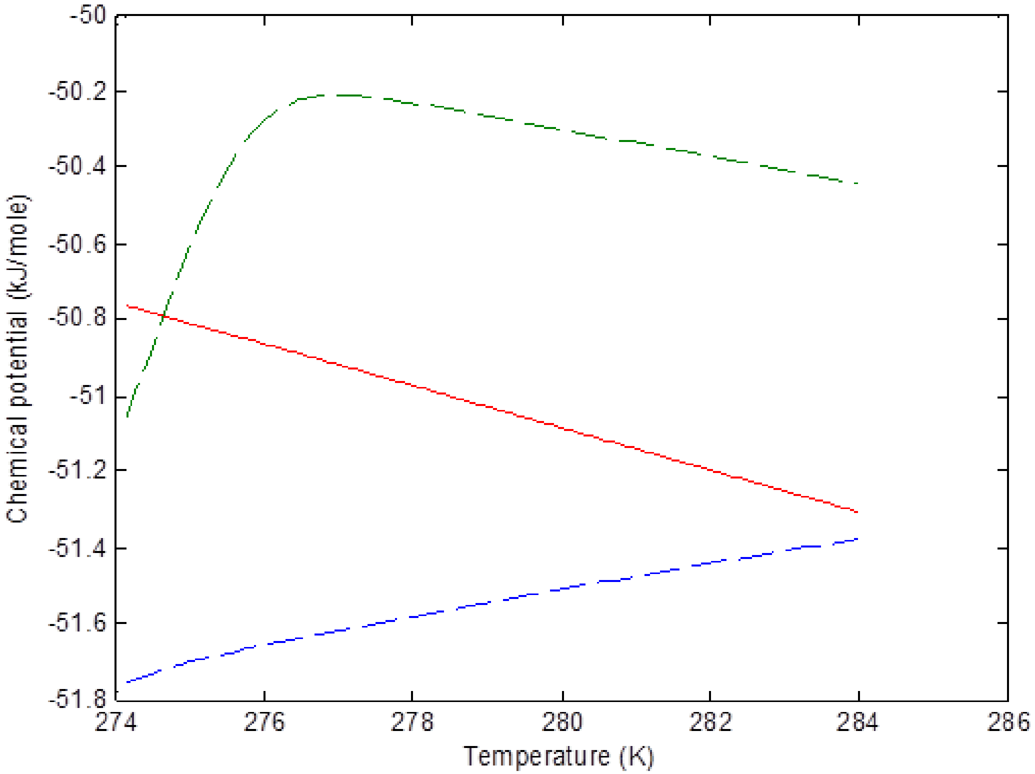
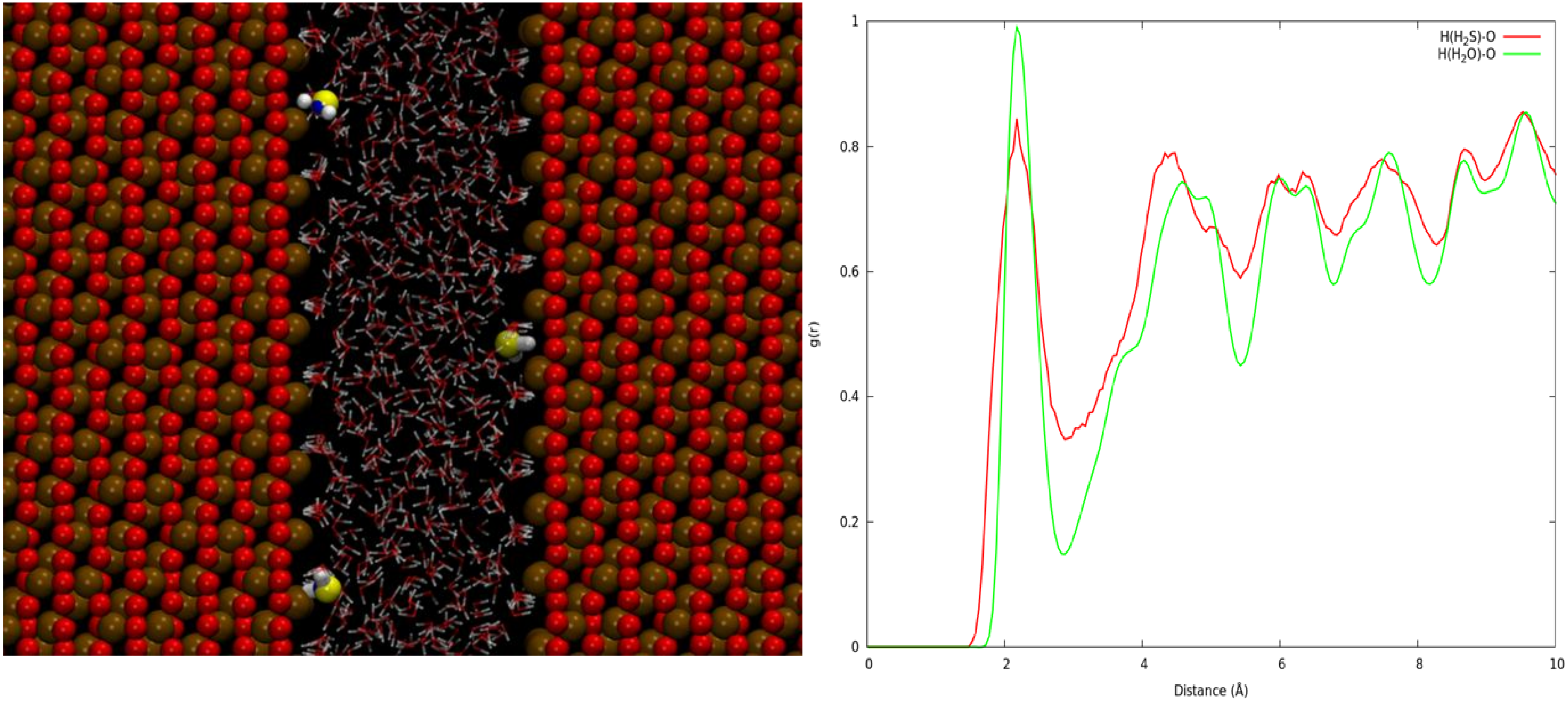


Figure 17. Chemical potential of water as liquid (solid) and in hydrate only stabilised by dissolved H_2S (upper dashed curve) and stabilised by dissolved H_2S in water and CO_2 from fluid (lower dashed curve). Pressure equal to 100 bar and H_2S mole-fraction in CO_2 0.001

- This will be an aggressive hydrate formation since it can grow from both sides of an initial hydrate film (H2S dominated hydrate from water side and CO2 dominated on fluid side)

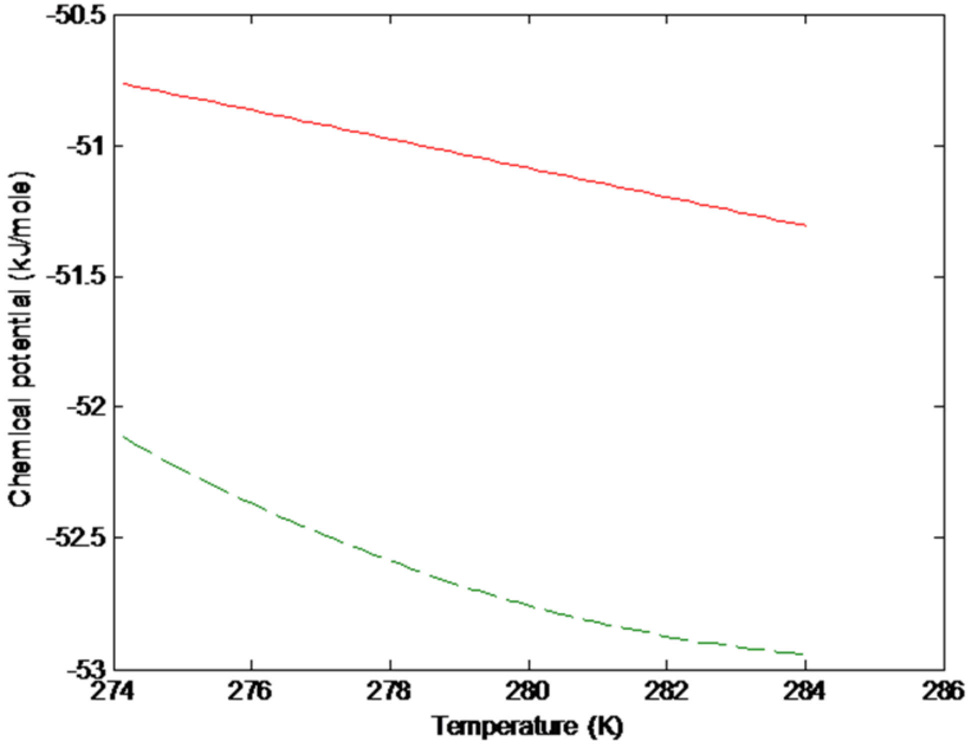
Hydrate formation involving adsorbed hydrate former (enriched on the rust surface)



Snapshot of H2S (enhanced molecules) adsorption on Hematite in competition with water (left) and pair correlation functions for oxygen in hematite and hydrogen in hydrogen sulfide (green) and water (red) (right)

H2S adsorption is highly favorable

Route 9: Hydrate forming from liquid like water (roughly 1.3 nm outside Hematite) or bulk water and adsorbed H2S

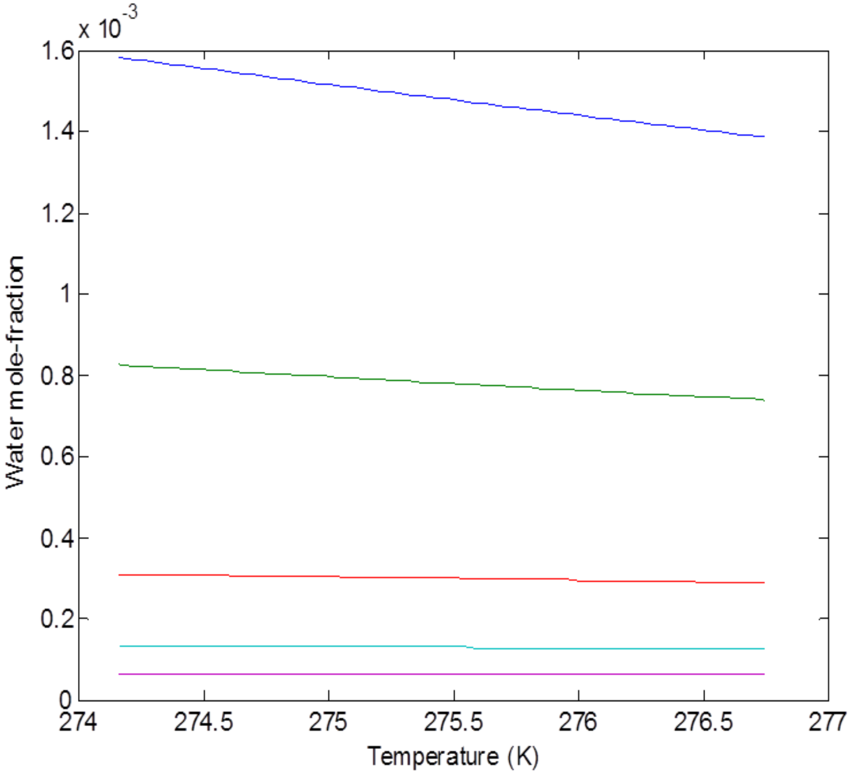


Chemical potential for water in hydrate (dashed) as stabilized from adsorbed H2S at 100 bar and liquid water chemical potential (solid) at same conditions.

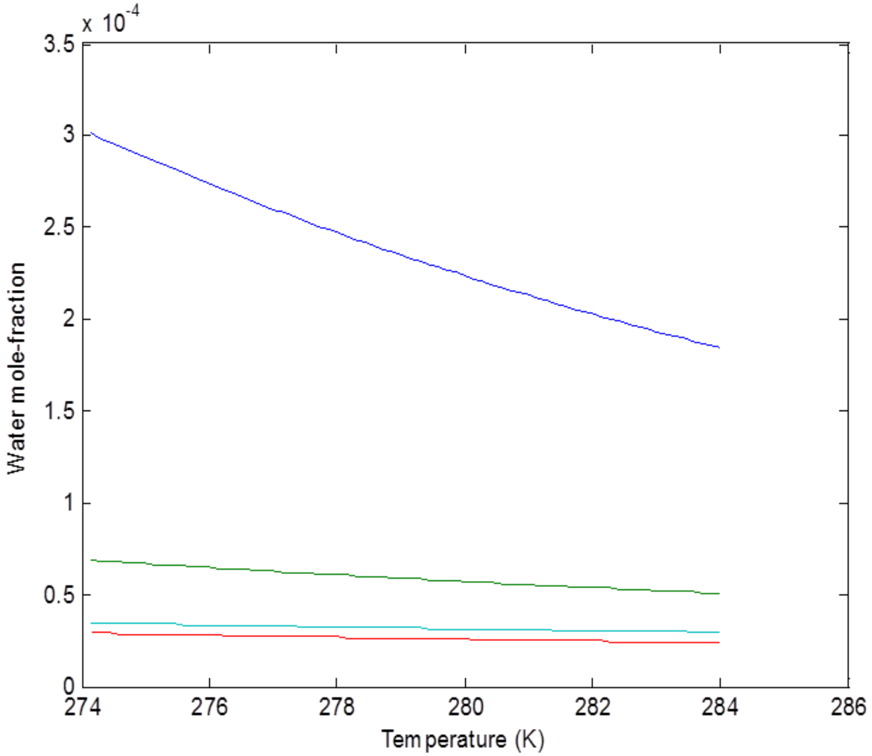
Hydrate formation from adsorbed H2S is highly facilitated and togther with previous slides very aggreasive hydrate formation can occur from adsorbed H2S and H2S dissolved outside the adsorbed layers in parallell to CO2 dominated hydrate towards the CO2 phase.

Limits of water content in CO2

Estimated water dew-point concentrations in carbon dioxode solution. Curves are, from top to bottom, for pressures 110 bars, 120 bars, 135 bars, 150 bars and 200 bars.



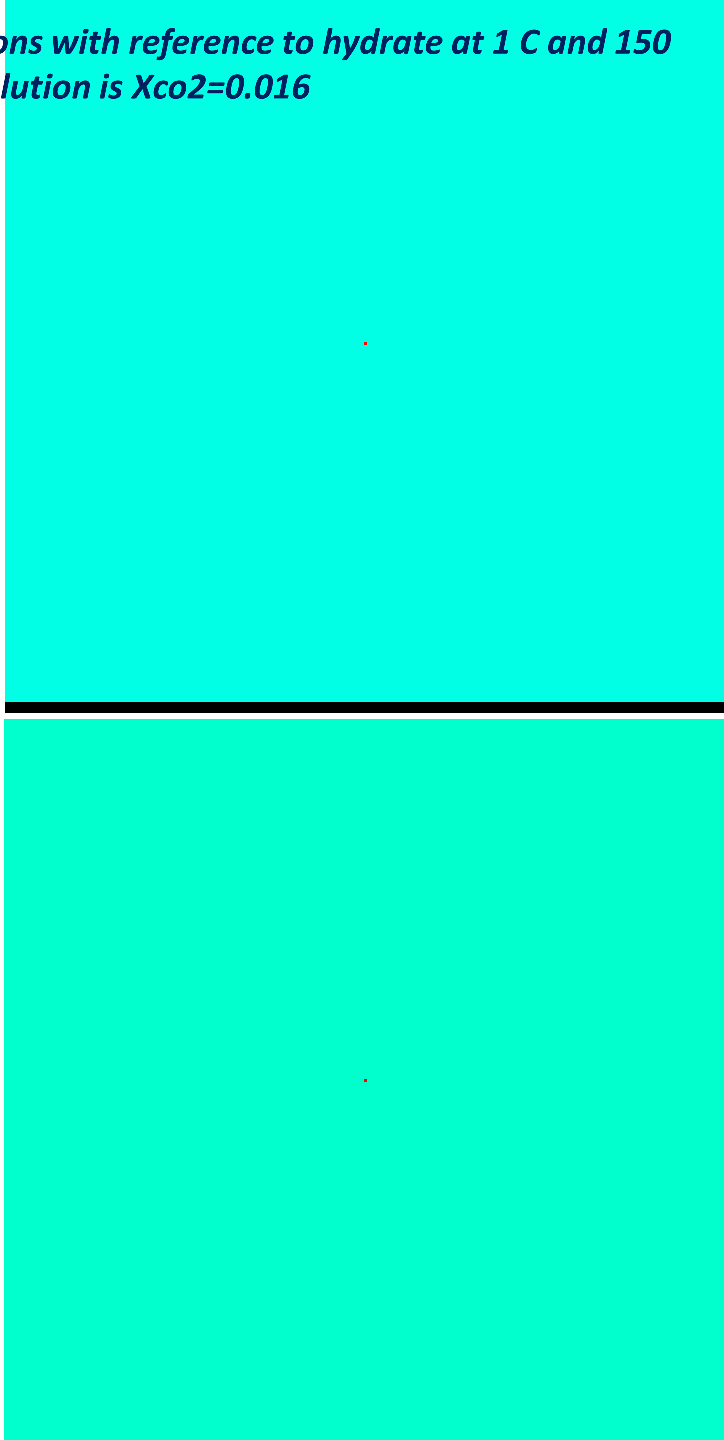
Limits of water mole-fraction in CO_2 before drop-out as adsorbed on Hematite. Upper curve is for 125 bars followed by 150 bars, 175 bars and 200 bars (bottom curve).



These estimated values for single molecule uniform distribution (formal thermodynamics) is lower (<u>more conservative</u>) than experimental measurements, which are likely to overestimate amount of water in CO2

Kinetics

Hydrate growing from two supersaturations with reference to hydrate at 1 C and 150 bar. Lowest limit coexisting with aqous solution is Xco2=0.016
Right: Xco2=0.032
Bottom right: Xco2=0.036

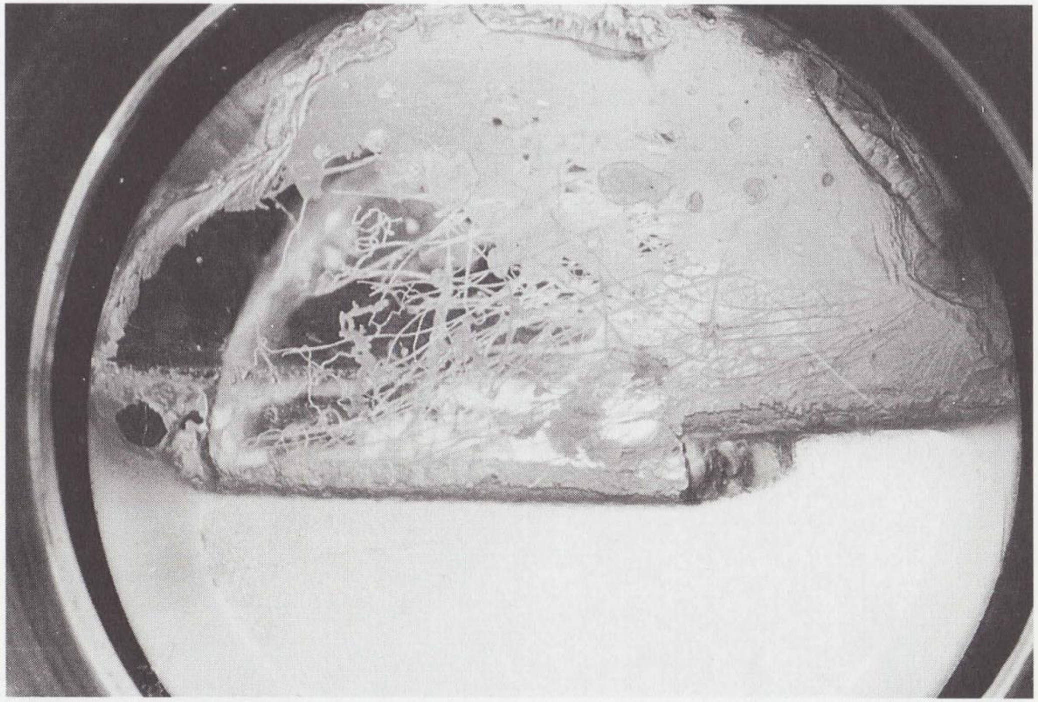


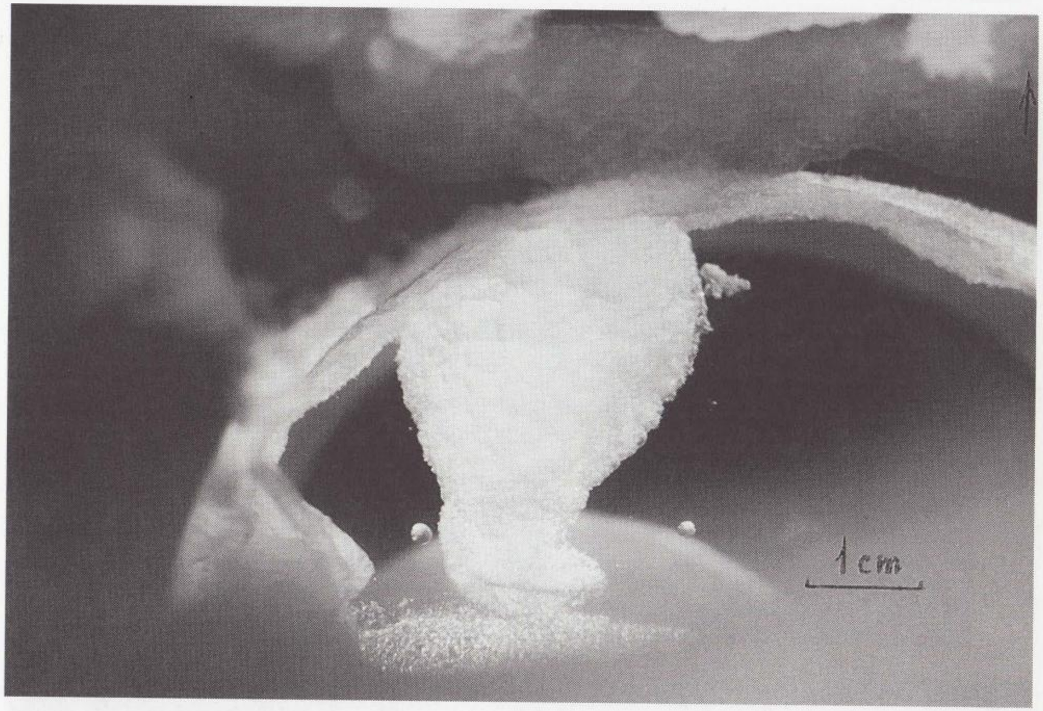
- A limit ***does not mean that liquid water drop out instantly*** at that concentration for given P and T
- Citical droplet size is in the order of 2.5 – 3 nm so ***more than 100 waters need to find each other*** (in a fixed T,P situation). Long nucleation time and even longer induction time (onset of massive, visible phase change)
- And at exactly dew-point there is ***NO net driving force*** to deposit liquid water at all
- Minimum free energy difference must ***also overcome interface free «penalty»***. So a significant driving force (higher concentration of water) and an extra free energy proportional to area of a critical size droplet times interface free energy (we have values for that)

Can this lead to pipeline blocking?

- Thickness of hydrate layer on wall is not limited since – when hydrate forms it is the lowest free energy water phase.
- And hydrate is water wettening so further adsorption of water and hydrate former onto hydrate will ensure continued growth according to supply of mass, unless exposed to under saturated CO2 for long enough periods of time.

Note the white hydrate growing from water/CH4 interface and connecting to hydrate growing from adsorbed layers on the glass wall in this PVT cell experiments at 1 Celsius and 150 bar





This is *NOT* the classical solubility of water into CO2 because hydrate water have the lowest water chemical potential when hydrate is formed. This will control water chemical potential also for water entering CO2

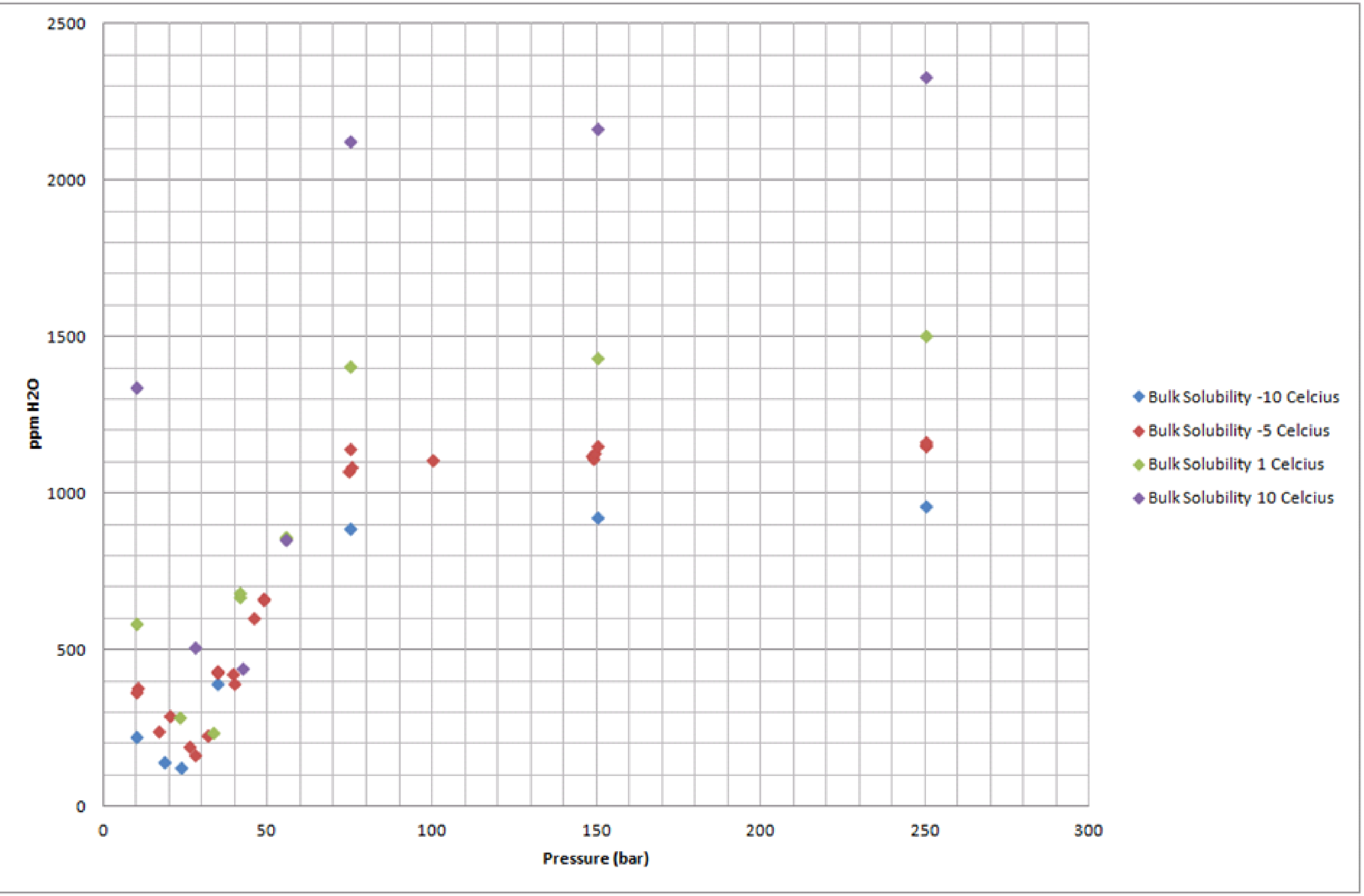


Figure 2: Measured solubility of water in CO_2 in presence of excess hydrates as a function of pressure for temperatures between -10°C and 10°C.

Conservative values?

- Yes – but conservative because we did not discuss ***driving forces needed*** (higher concentrations) for drop-up (equilibrium takes infinite time to reach !)
- And we did only briefly mention that ***kinetics will limit drop-out rates*** and might ***even prevent drop-out from happening*** before substantial super-saturation
- And we skipped all processes that can ***redissosiate*** hydrate and as such reduce net impact

Conclusions

- Transport of carbon dioxide with water and other impurities will not be able to establish equilibrium due to Gibbs phase rule
- Non-equilibrium analysis of possible competing phase transitions requires consistent thermodynamic properties for all phases, which can be accomplished using ideal gas as reference state for all components in all phases.
- Routes to hydrate formation that involves adsorbed phases dominate in terms of thermodynamic preferences

Conclusions continued

- Estimated limits of solubility are generally lower than experimental values at these low temperatures. This trend is expected since dissolution of water into CO2 as single monomers in this low T range (strong hydrogen bonds) is an almost impossible challenge. Observed uptakes of water will consequently be higher than solubility in a true thermodynamic sense (uniform distribution of single water molecules)
- Regardless of further processing of the data to fit into existing modeling software (process-, transport- and other) the infite estimated infinite dilution data and free energies are unique and not available from any other open source

Conclusions continued

- Routes towards hydrate formation that involves solid surfaces have never been been quantified before this study and the presence of H2S implies dramatic changes in the nature of hydrate formation, in which hydrates can efficiently form for adsorbed and water dissolved hydrate formers parallell to water/CO2 interface growth. This implies a much more aggressive growth with small induction (if any at all within a second scale in time)
- Since these results cannot be verified special care is needed. Work is in progress on examining different models for H2S and we also search for a master student to conduct combined Quantum and classical simulations (Carr-Parinello type). We also expect to be able to fund a follow-up PhD study

Thank you for the attention !

Smoking is not permitted at UoB so it cannot be me in the picture

One possible way forward: Kinetic modeling and two expreimental approaches for hydrate formation in pipelines

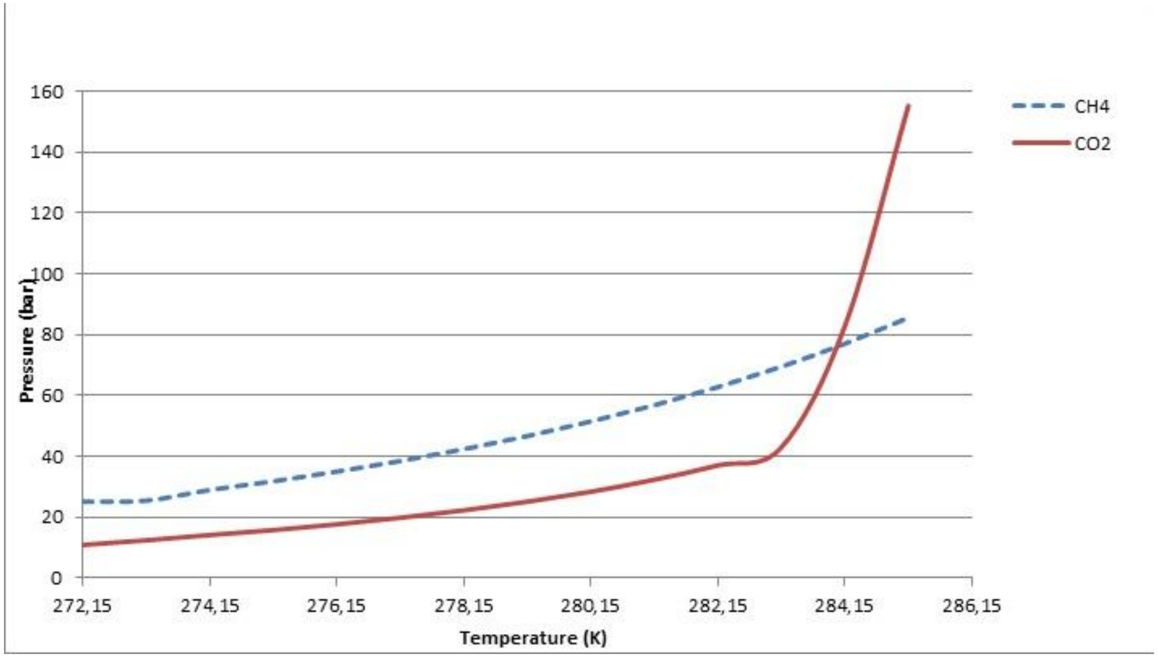
- Phase Field Theory (PFT) is state of he art kinetic modeling of hydrate kinetics and is free of adjustable empirical parameters.
- PFT can serve as a platform for development of simplified models for use in industrial models
- Complementary experiments (loops at CMR) could be possible using three detection principles:

  - Gamma- or X-ray tomography (Prof. Geir Anton Johansen)
  - Ultrasound (Prof. Per Lunde)

- Phase Field Theory (PFT)

Part 2

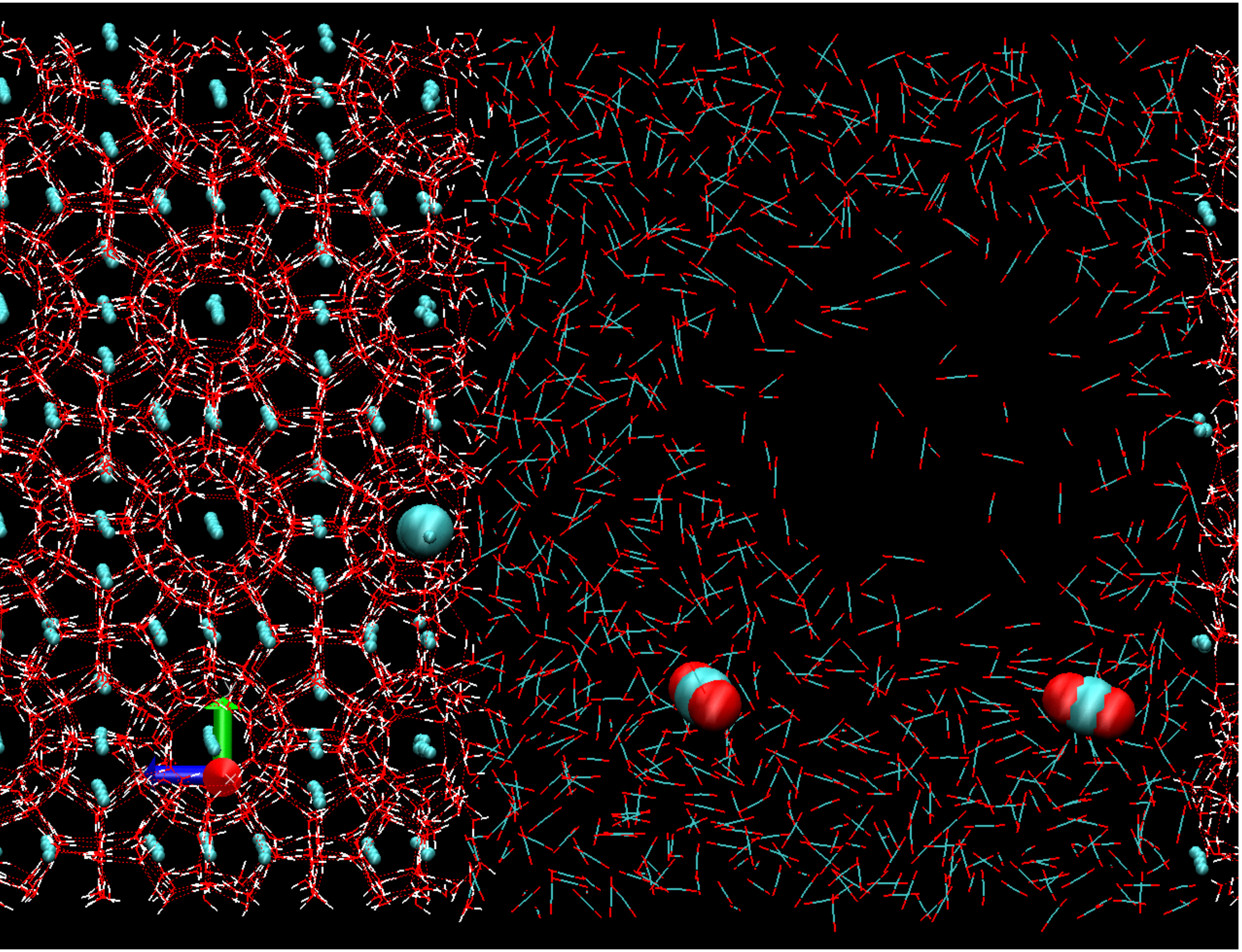
- With example from hydrate exchange process in which original CH_4 hydrate is converted to a mixed hydrate through injection of CO_2



Regions of hydrate stability for pure CH_4 and pure CO_2 hydrates. Mixed hydrate in which CO_2 fills the large cavities and CH_4 fills the small is more stable over all regions of pressure and temperature

Two primary mechanisms: 1) Solid state conversion and 2) Sequences of new CO_2 hydrate and subsequent CH_4 hydrate dissociation due to released heat from the hydrate formation.

Conversion: the movie



Solid state conversion is slow, with diffusivity coefficient in the order of 10^-16 m^2/s

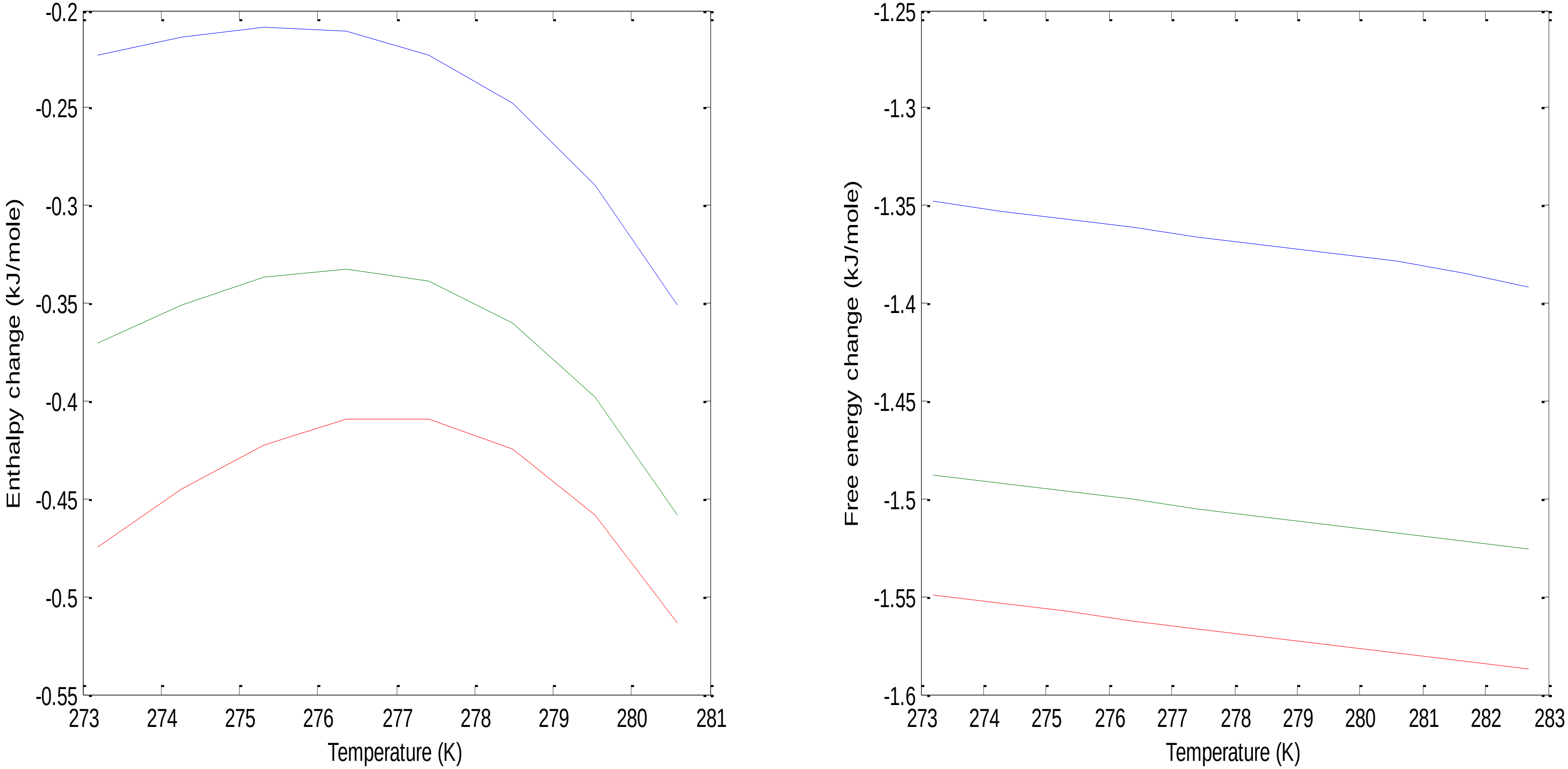
The process in entropy dominated (see next slide)

The relative impact of this mechanism will increase with lower free water in pores

The second mechanism is much faster and in the rate order of liquid water transport but requires advanced theory to investigate due to complex dynamic couplings between mass transport and heat transport

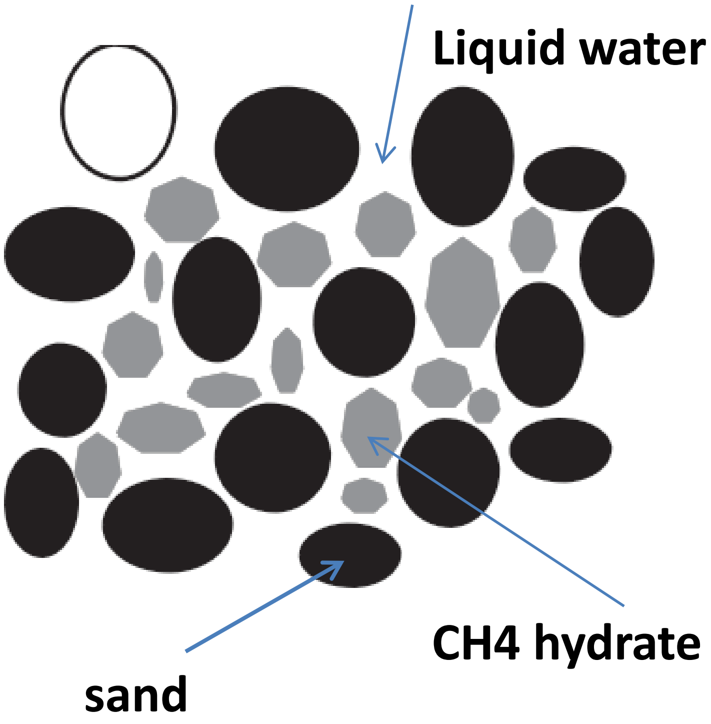
Free energy and enthalpy changes for conversion from pure methane hydrate to pure carbon dioxide hydrate

Blue: 43 bar, **Green: 83 bar**, **Red: 120 bar**



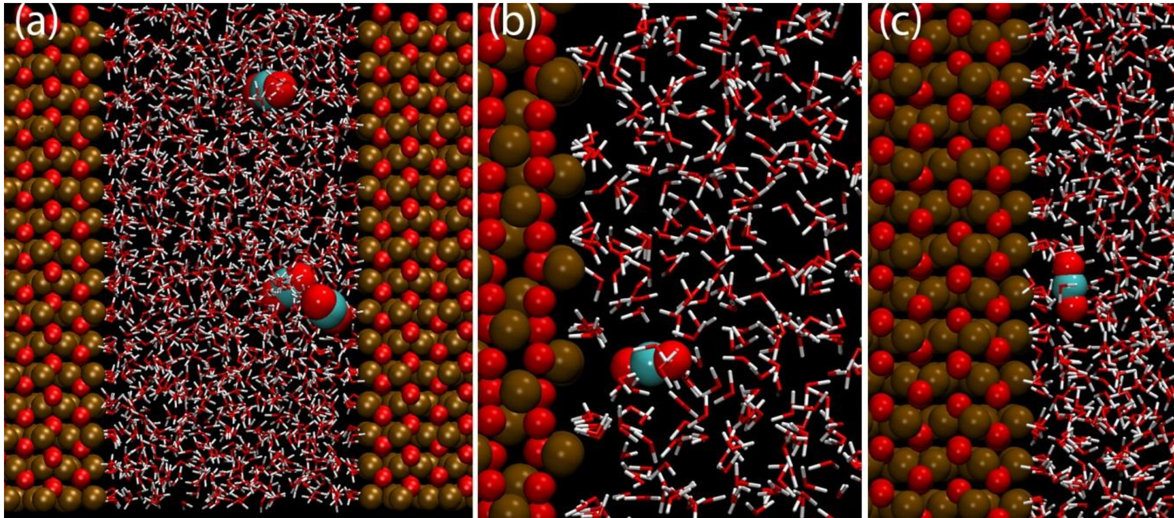
Free energy chage for the water in the structure is not large. CO2 change is also limited since it comes from a fairly dense phase and have reasonable filling. But CH4 will benefit from the entropy change of getting released.

2: Injected CO2 can form new hydrate and released heat from that process can dissociate ***in situ*** CH4 hydrate



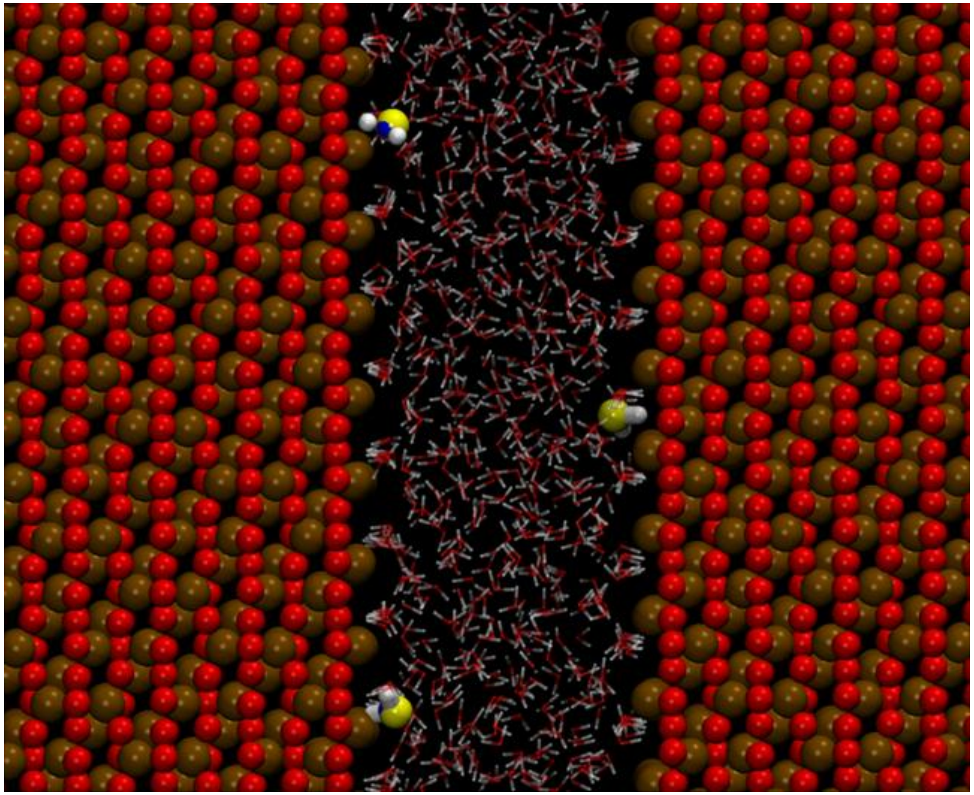
- *The new hydrate can nucleate from water/CO2 interface*
- *or*
- *From adsorbed CO2 on mineral surface*
- *or*
- *From CO2 adsorbed on CH4 hydrate surface*

Right: CO2 (enhanced red and grey) adsorbing onto Hematite from water solution. Adsorbed CO2chemical potential: -39.21 kJ/mole



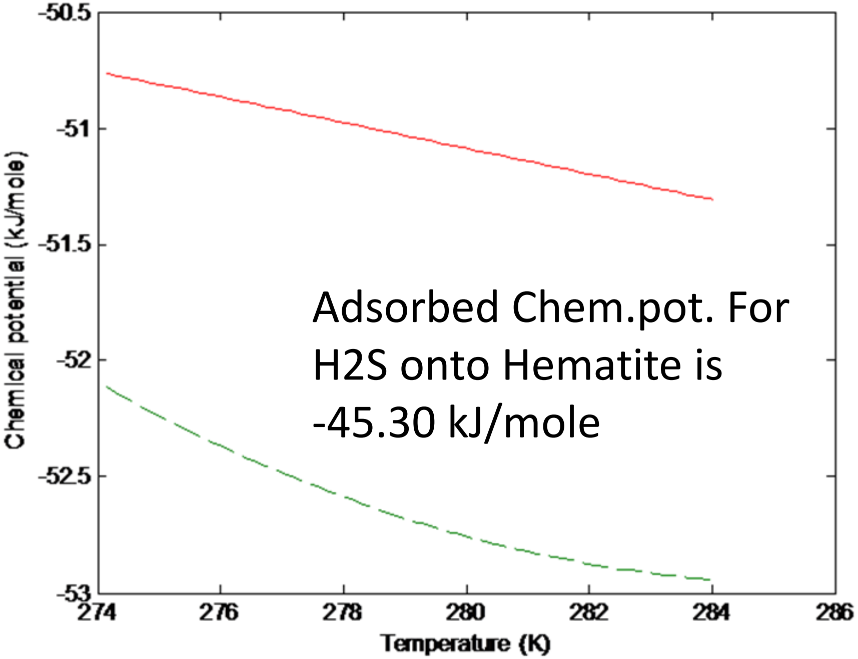
Possible Remaing H2S following injected CO2 will enhance new hydrate formation

We need a theoretical approach that can model all of these options and «decide» by itself how the system should progress as function of time and space



Top: Snapshot of H2S (enhanced molecules) adsorption on Hematite in competition with water (left) and pair correlation functions for oxygen in hematite and hydrogen in hydrogen sulfide (green) and water (red) (right)

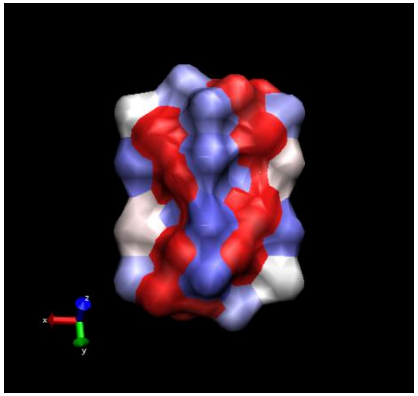
Below:Chemical potential for water in hydrate (dashed) as stabilized from adsorbed H2S at 100 bar and liquid water chemical potential (solid) at same conditions.



Adsorbed Chem.pot. For H2S onto Hematite is -45.30 kJ/mole

Investigating competing phase transitions in porous media (read: solid material surfaces) requires multiscale modeling approach

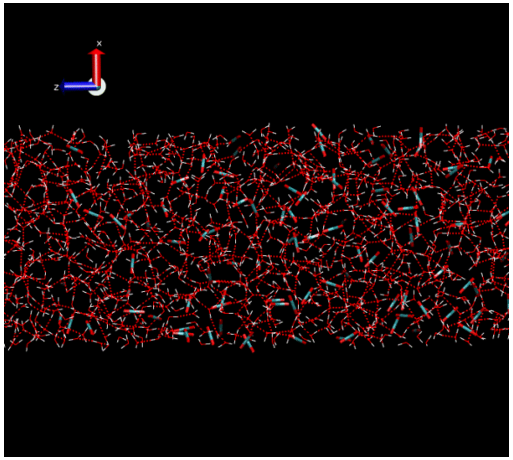
Charge distribution for hematite by Gaussian03



from

quantum (characterisation of charge distribution in model molecules, from below nano in scale)

MD for Studies of mechanisms, thermodyn, interface properties and parametrisation



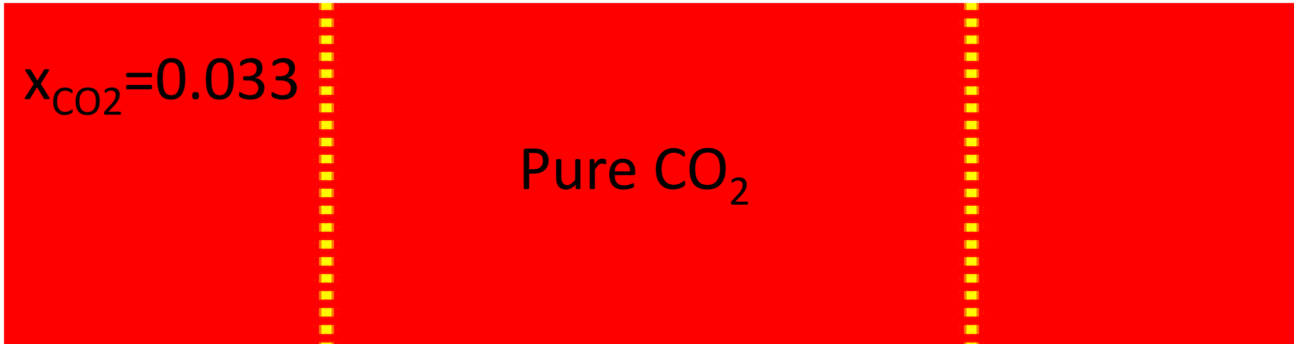
to

nano (Molecular Dynamics simulations, MD)

and

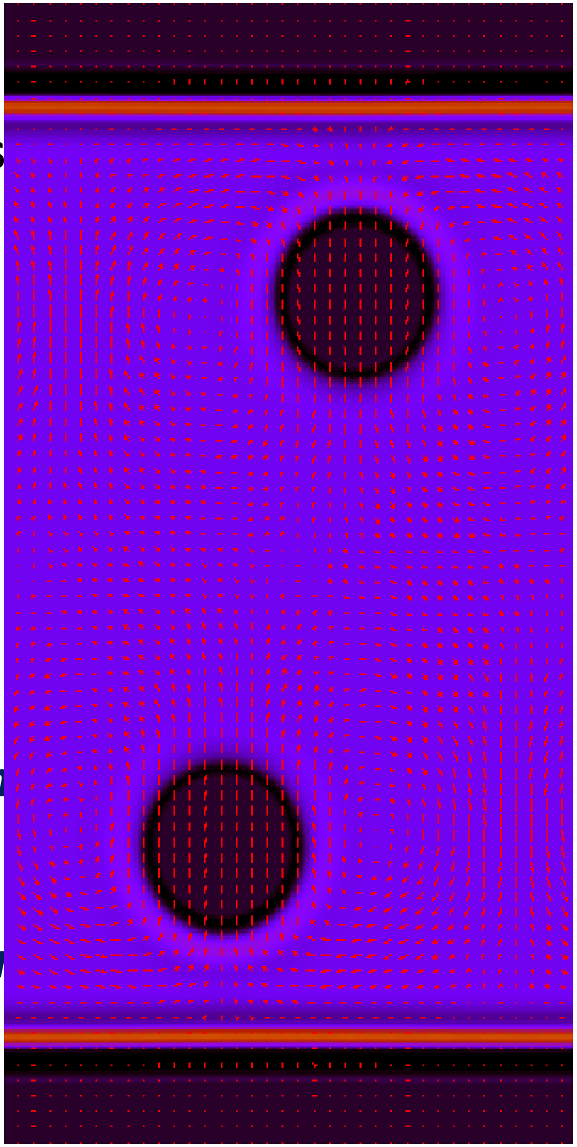
micro (Phase Field Theory)

Simulation of hydrate growth dynamics on interface of a CO2 plume using PFT



So what is phase field theory (qualitatively)?

- ***Phase Field Theory (PFT) is similar to Density Functional Theory (DFT) in the sense that the*** **structural changes** ***in DFT is replaced by the*** **corresponding free energies** ***in PFT***
- ***Practically PFT simulations can be considered as local and global*** **free energy minimalisation** ***under the*** **constraints of mass and heat transport dynamics*****.***
- ***In contrast to DFT, PFT is*** **free of any volumetric scale limitations** ***although*** **interface free energy fluctutations** ***(upcoming slides) are on nano scale and needs to be evaluated at least on an*** **average impact fashion** ***for the pronlem/system in consideration***



Phase-field theory simulation of a simplified binary alloy phase transition in gradients of T (decreases towards centre in heigth direction) and gravity field (increases outwards, up and down from centre. Arrows are directions of velocity fields for mass transport

Phase Field Theory Model

$$F = \int d\underline{r} \left(\boxed{ \frac{\varepsilon_{\phi}^{2}}{2} T (\nabla\phi)^{2} + \sum_{i,j=1}^{3} \frac{\varepsilon_{xi,j}^{2}}{4} T\rho \left(x_i \nabla x_j - x_j \nabla x_i \right)^{2} } + f_{bulk}(\phi, x_1, x_2, x_3, T) \right)$$

Free energy changes due to phase transition (ϕ is 0 for solid and 1 for fluid)

Free energy changes due to concentration gradients across the interface

Ɛ is unique for each component according to distribution profile across the interface but as an average value it may not be very different from the similar parameter for the phase transition so setting them equal is a first approximation which makes at least numerical solutions feasible

- Free energy due to thermal fluctuation across the interface
- Function of interface
  - thickness
  - free energy of interface
  - interface structure(available from interface density profile for all components)

Model Parameters

Estimated to 8.5 Å for hydrate/liquid water (Kvamme et.al. (2007))

$$d = \left(\frac{\varepsilon^2 T}{2}\right)^{1/2} \int_{0.05}^{0.95} d\xi \{\Delta f[\xi, \vec{x}(\xi)]\}^{-1/2}$$

Phase Field Theory parameter ***w*** is in the free energy *f* (previous slide) as the barrier for transition over to the new phase

where $\Delta f = f - f_0$, and

$$\gamma_\infty = (\varepsilon^2 T)^{1/2} \int_0^1 d\xi \{\Delta f[\xi, \vec{x}(\xi)]\}^{1/2}$$

ξ is the interface profile

$$f_0 = G_L(\vec{x}_L^{eq}) + \sum_{i=1}^{n} \frac{\partial \mu_{i,L}}{\partial x_{i,L}}\bigg|_{\vec{x}_L^{eq}} (x_{i,L} - x_{i,L}^{eq})$$

$$f_S = G_S(\vec{x}_S^{eq}) + \sum_{i=1}^{n} \frac{\partial \mu_{i,S}}{\partial x_{i,S}}\bigg|_{\vec{x}_S^{eq}} (x_{i,S} - x_{i,S}^{eq})$$

Phase Field Theory parameter ε

Interface free energy ≈ liquid water/ice 29 mJ/m^2 – (S.C.Hardy, Philos. Mag. 35 (1977)471)

(Different methods for estimation of hydrate/water interrface free energy is currently being investigated, including cleaving and capillary wave theory)

Interface thickness d and interface free energy fixes the two model parameters *w* and ε. The extension over to the multi-components case in current use follows

Phase Field Theory Model

$$F = \int d\underline{r}\left(\frac{\varepsilon_{\phi}^{2}}{2}T(\nabla\phi)^{2} + \sum_{i,j=1}^{3}\frac{\varepsilon_{xi,j}^{2}}{4}T\rho\left(x_i\nabla x_j - x_j\nabla x_i\right)^{2} + f_{bulk}(\phi, x_1, x_2, x_3, T)\right)$$

$$f_{bulk} = WTg(\phi) + \left(1 - p(\phi)\right)f_{S}(x_1, x_2, x_3, T) + p(\phi)f_{L}(x_1, x_2, x_3, T)$$

g(Φ) is assumed symmetric quadratic p(Φ) is the propablity distribution of phases across the interface as sampled from MD

$$f_s = G_H\rho_m^H \quad , \quad f_L = G_L\rho_m^L$$

Mobilities across the interface are complex but in the simplest approximation diffusivity constants are applied

$$\frac{\partial\phi}{\partial t} + (\vec{v}.\nabla)\phi = -M_{\phi}(\phi, x_1, x_2, x_3)\frac{\delta F}{\delta\phi}$$

$$\frac{\partial x_i}{\partial t} + (\vec{v}.\nabla)x_i = \nabla.\left(M_{xi}(\phi, x_1, x_2, x_3)\nabla\frac{\delta F}{\delta xi}\right)$$

PFT with Hydrodynamics

Hydrodynamics

$$\frac{\partial\rho}{\partial t} = -\rho_m\nabla.\vec{v}$$

$$\rho\frac{\partial\vec{v}}{\partial t} + \rho(\vec{v}.\nabla)\vec{v} = \rho\vec{g} + \nabla.P$$

Total stress tensor

$$P = \mathfrak{z} + \Pi$$

Heat transport Model

Primary contributions to heat transport is conduction and convection are lumped into an “efficient” conductivity ⟶

$$\left(\frac{\Delta H}{\Delta t}\right)_i = k_i A_i \Delta T_i$$

These enthalpies are evaluated directly from the ***free energy of each grid*** block

$$H_i = -RT^2 \left(\frac{\left(\frac{G_i}{RT}\right)_{T+\Delta T} - \left(\frac{G_i}{RT}\right)_T}{\Delta T} \right)$$

Rearrangements of water involves significant enthalpy and entropy changes which affects structuring and rearrangements into new phases like for instance ice and/or hydrate.

$$k_i = (1 - p(\phi))k_{S,i}(T, P, \vec{x}_{S,i}) + p(\phi)k_{L,i}(T, P, \vec{x}_{L,i})$$

Substantial room for improvements on this part but at least a convenient starting point for illustration purposes

Density calculations

$$\rho_m^{L,Fluid} = \frac{1}{\overline{V}_L^{Fluid}}$$

$$\rho_m^{L,aqueous} = \frac{1}{\overline{V}_L^{aqueous}}$$

$$\overline{V}_L^{Fluid} = \sum_{i=1}^{3} x_i \overline{V}_i$$

$$\overline{V}_L^{aqueous} = \sum_{i=1}^{3} x_i \overline{V}_i + x_3 \overline{V}_3^{0}$$

Approximated to average molar volume of pure water

Estimated from MD using first shell approximation in integration over pair correlation functions

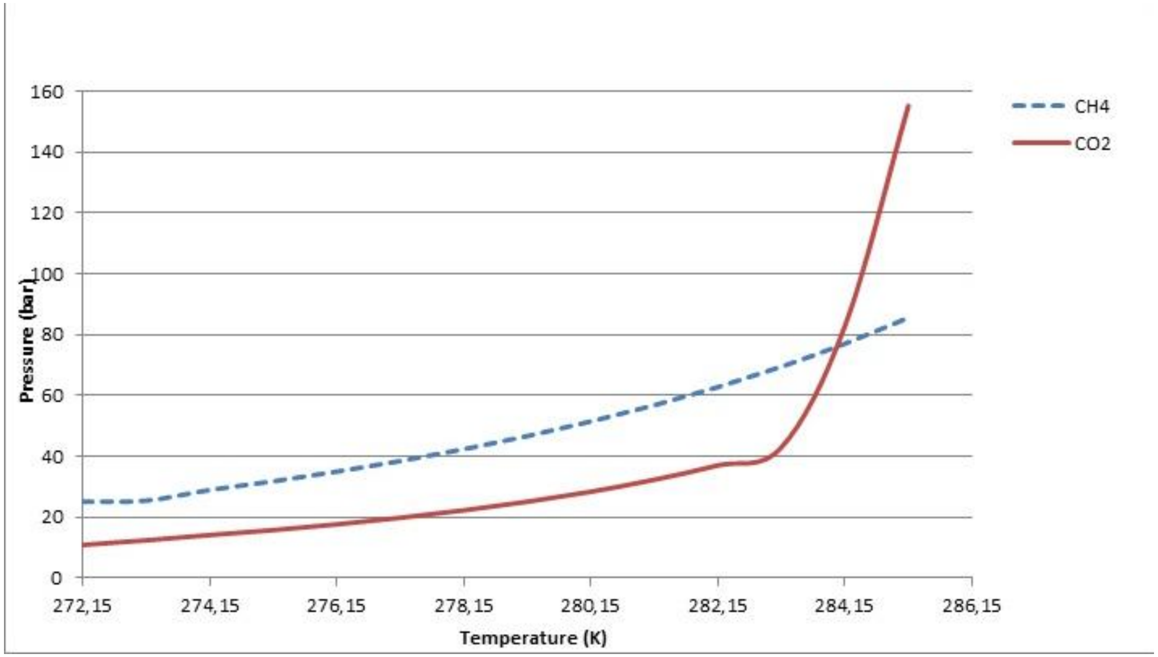
$$\overline{V}_i = \frac{ZRT}{p} + \frac{nRT}{p}\left(\frac{\partial Z}{\partial n_i}\right)_{p,T,n_{i\neq j}}$$

Partial molar volume for ***water in hydrate*** is trivially calculated from the ***unit cell dimensions and compositions***, see for instance Sloan et al. (2008), 3rd edition, CRC Press for examples. ***Guest molecule partial molar volumes*** evaluated by ***Monte Carlo*** (Kvamme & Lund, 1993).

$$\rho_m^{Hyd}$$

Example from Hydrate exchange

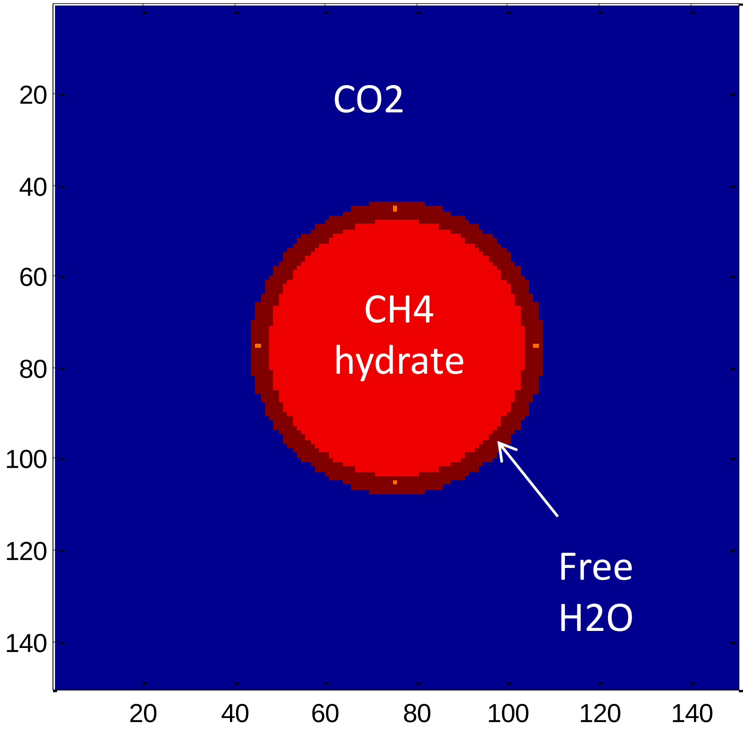
- The conversion process have been known theoretically for several decades, intensively investigated through different experiments but there are still some confusions about the process



Regions of hydrate stability for pure CH4 and pure CO2 hydrates. Mixed hydrate in which CO2 fills the large cavities and CH4 fills the small is more stable over all regions of pressure and temperature

Two primary mechanisms: 1) Solid state conversion and 2) Sequences of new CO2 hydrate and subsequent CH4 hydrate dissociation due to released heat from the hydrate formation.

Non Equilibrium Challenge



- Part of this work (exchange processes)
  - ***Initially 3 phases*** (CH4 Hydrate, Aqueos, CO2 Fluid)
  - ***3 components*** (CO2,CH4,H2O)
  - ***Degree of freedom is 2*** with P,T defined, minimum criteria is fullfilled
  - ***Non equilibrium*** due to initial ***difference (negative) in chemical potentials*** of CO2 in hydrate and fluid

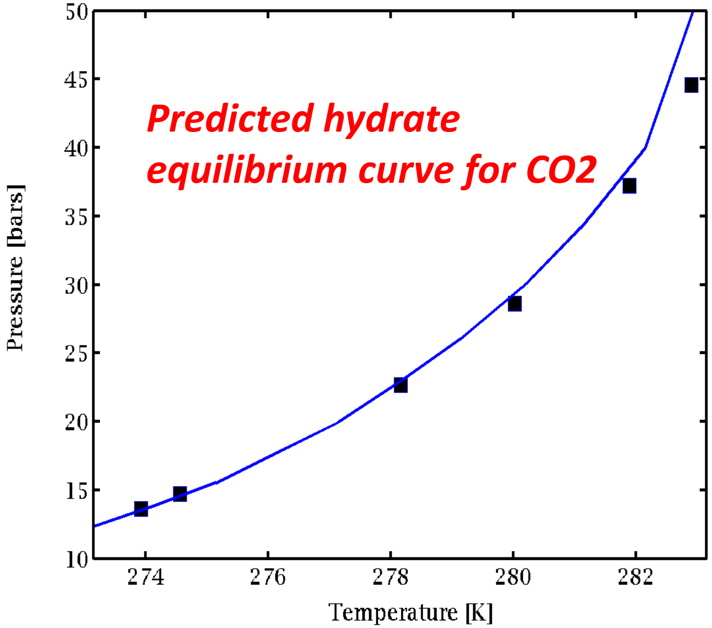
Details of the thermodynamics will be skipped but overheads are included here for completenes

- Thermodynamics for fluid-phases (aqeous and other) are continuously described and straightforward
- Thermodynamics for hydrate is related to adsorption theory and linked to equilibrium conditions so needs to be extended to outside equilibrium – we apply series expansion for this – details given elsewhere (publications available and slides available for specially interested)

Non Equilibrium Challenge

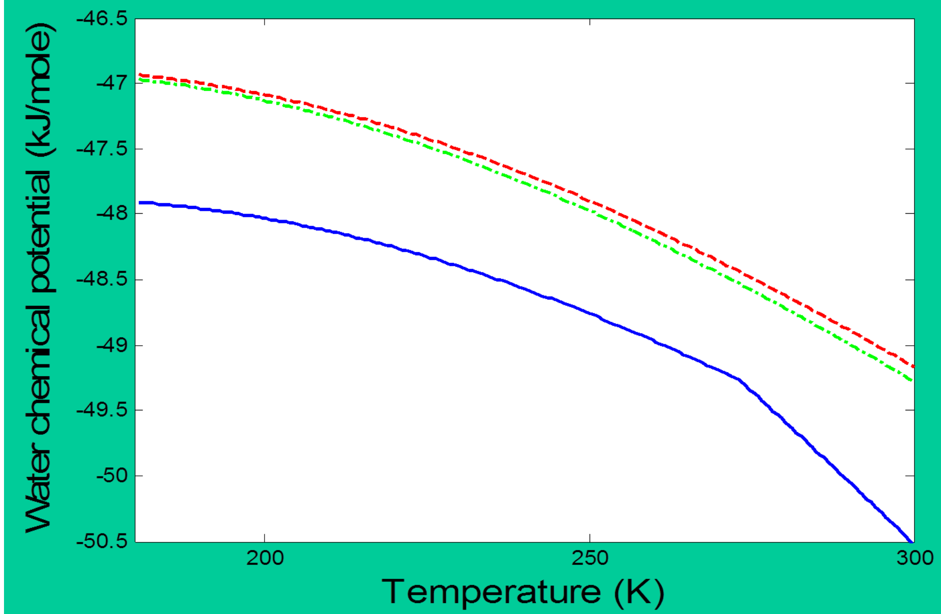
Accurate and consistent model for free energy of the different co-existing phases

- A critical basis for ***Phase Field Modeling***
- Free energies for individual (Aqueous, Fluid and Hydrate) phases are used here
  - Revised adsorption theory (Kvamme & Tanaka, 1995) for hydrate
  - TIP4P simulated chemical potential for ice, liquid water, and empty hydrate



Predicted hydrate equilibrium curve for CO2

Solid line for ice or liquid water, dash line for SI empty hydrate and dash-dotted line for SII empty hydrate.



Hydrate Thermodynamics

$$\mu_j^H = \Delta g_{ji}^{inc} + RT\ln\left(h_{ij}\right)$$

$$\mu_w^H\left(T,P,\vec{\theta}\right) = \mu_w^{0,H}(T,P_0) - \sum_i RTv_i\ln\left(1+\sum_j h_{ij}\right)$$

$\mu_w^{0,H}(T,P_0)$ = Chemical potential for water in an empty hydrate structure

$$h_{ij} = e^{\beta\left(\mu_j^H - \Delta g_{ji}^{inc}\right)}$$

Cavity partition function of component j in cavity type i

Δg_{ji}^{inc} = Free energy of inclusion in cavity by ”classical” langmuir integration or harmonic oscillator approach (Kvamme & Tanaka, 1995)

Hydrate Thermodynamics

$$G_H^{EXP} = G^{EQ} + \sum_r \frac{\partial G_H}{\partial x_r}\bigg|_{P,V,T,x_{i\neq r}} (x_r^{act} - x_r^{EQ}) + \frac{\partial G_H}{\partial P}\bigg|_{T,V,\vec{x}} (P^{act} - P^{EQ}) + \frac{\partial G_H}{\partial T}\bigg|_{P,V,\vec{x}} (T^{act} - T^{EQ})$$

$$\frac{\partial G_H}{\partial x_r} = x_c \frac{\partial \mu_c^H}{\partial x_r} + x_m \frac{\partial \mu_m^H}{\partial x_r} + x_w \frac{\partial \mu_w^H}{\partial x_r} + \mu_r \frac{\partial x_r}{\partial x_r}$$

$$\mu_k^H = A ln(x_k) + B, \qquad \frac{\partial \mu_k^H}{\partial x_r} = \{0, r \neq k\}$$

$$\frac{\partial G_H}{\partial x_w} = \sum_r x_r \frac{\partial \mu_r^H}{\partial x_w} + \mu_w^H$$

- Mole fractions are ***conserved within the Phase Field Theory***

Hydrate Thermodynamics

$$\frac{\partial G_H}{\partial P} = x_c \frac{\partial \mu_c^H}{\partial P} + x_m \frac{\partial \mu_m^H}{\partial P} + x_w \frac{\partial \mu_w^H}{\partial P} + \mu_c \frac{\partial x_c}{\partial P} + \mu_m \frac{\partial x_m}{\partial P} + \mu_w \frac{\partial x_w}{\partial P}$$

$$\frac{\partial \mu_r^H}{\partial P} = \overline{V}_r$$

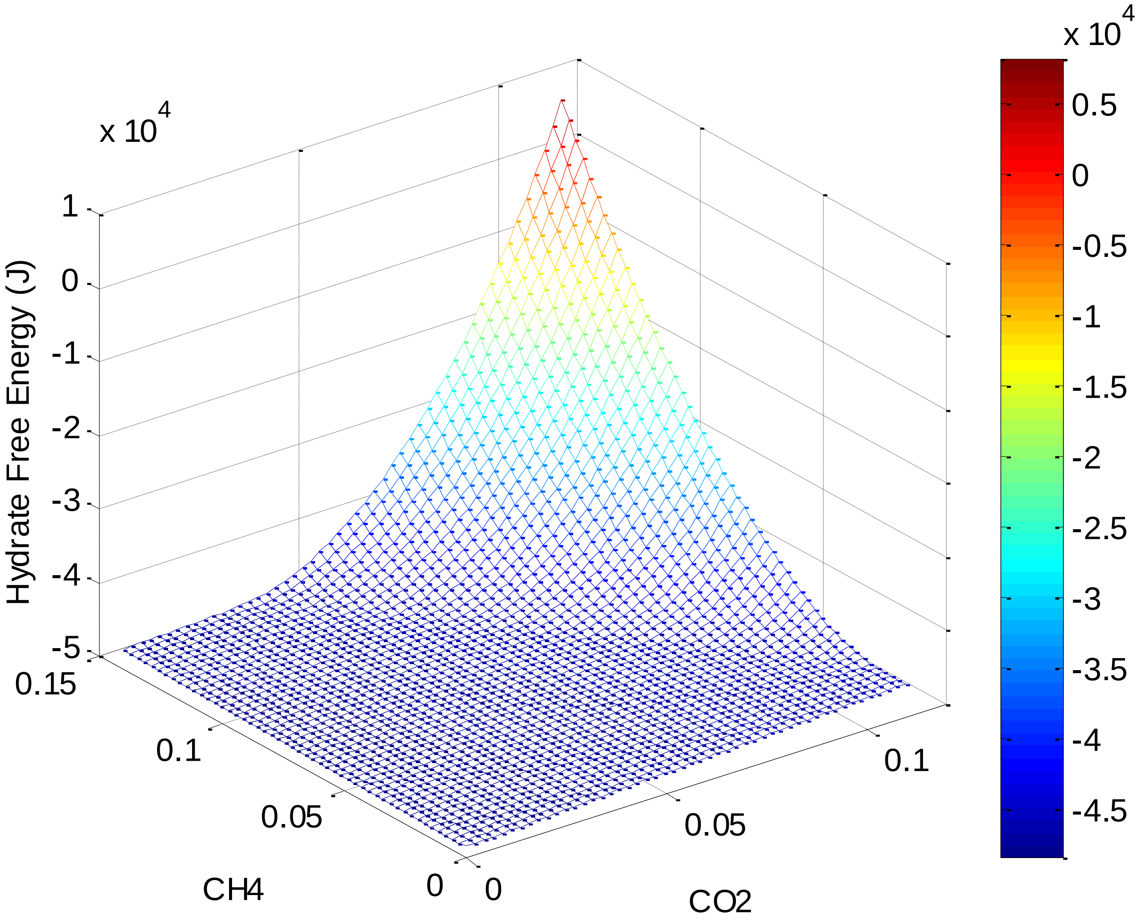
$$\frac{\partial G_H}{\partial P} = x_c \overline{V}_c + x_m \overline{V}_m + x_w \overline{V}_w + \mu_c^H \frac{\partial x_c}{\partial P} + \mu_m^H \frac{\partial x_m}{\partial P} + \mu_w^H \frac{\partial x_w}{\partial P}$$

$$\overline{V}^{clath} = x_c . \overline{V}_c + x_m . \overline{V}_m + x_w . \overline{V}_w$$

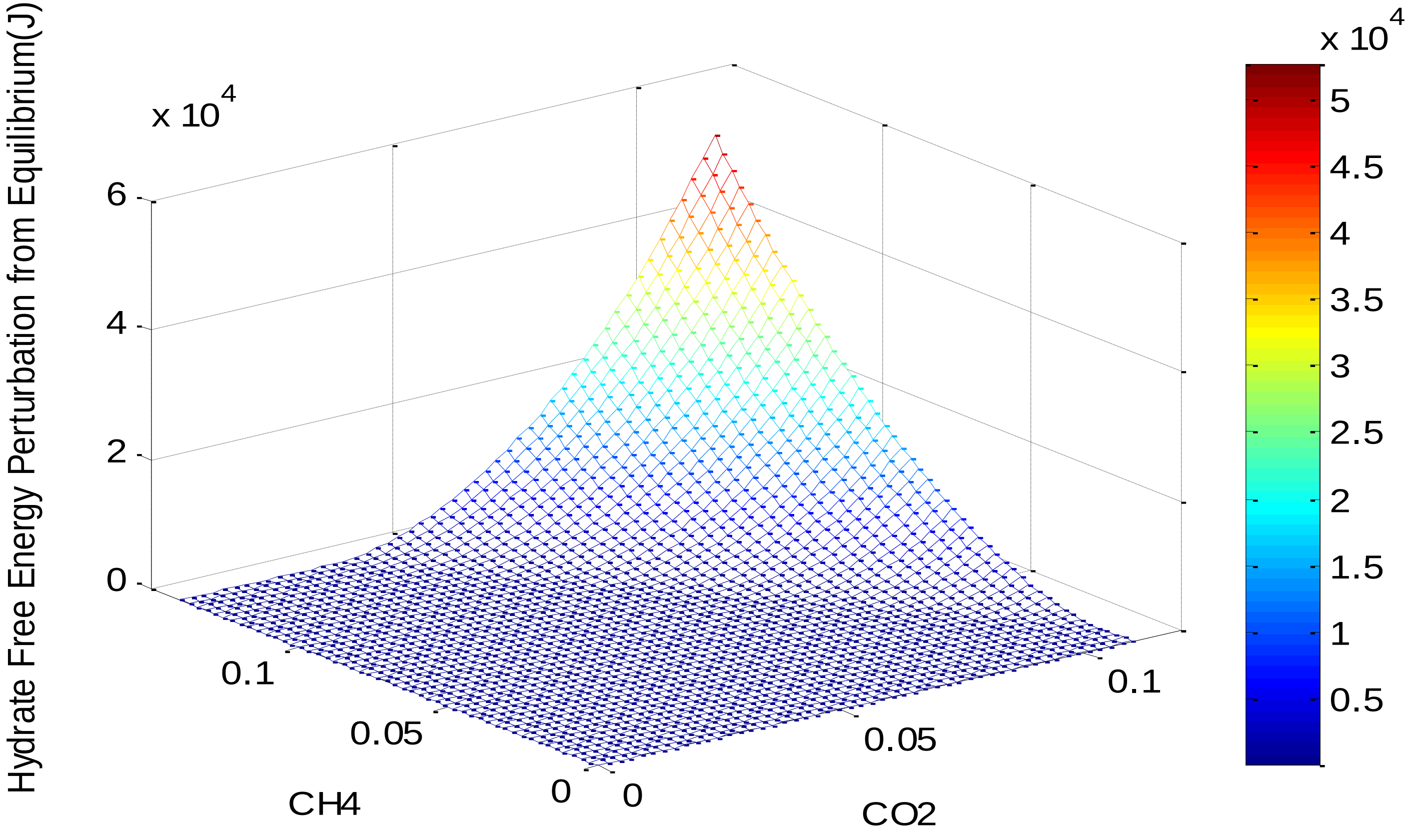
$$\frac{\partial G_H}{\partial P} = \overline{V}^{clath} + \mu_c^H \frac{\partial x_c}{\partial P} + \mu_m^H \frac{\partial x_m}{\partial P} + \mu_w^H \frac{\partial x_w}{\partial P}$$

$$\left[\frac{\partial G_H}{\partial P}\right]_{T,V,\vec{x}} = \overline{V}^{clath}$$

$$-\frac{\partial}{\partial T}\left[\frac{G}{T}\right]_{P,\vec{x}} = \frac{\overline{H}}{T^2}$$



Hydrate free energy of mixed hydrate at 3°C and 40 bars.



Difference due to pressure, temperature and composition gradients in hydrate free energy from equilibrium at 3°C and 40 bars.

Fluid Thermodynamics

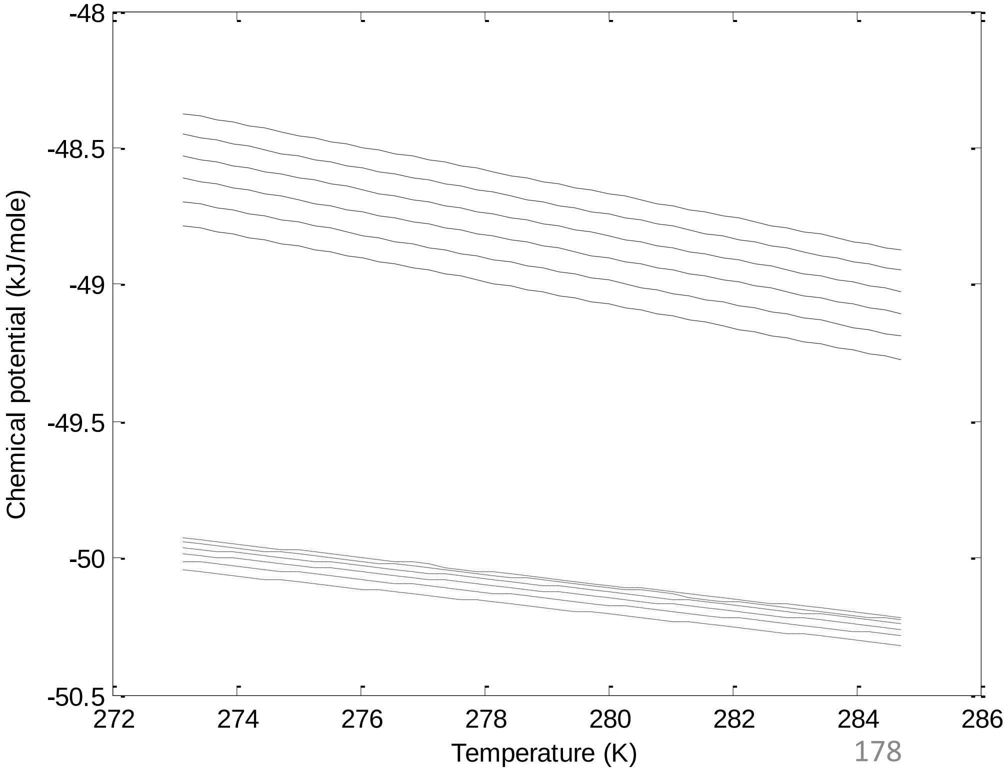
$$\mu_i^{Fluid} = \mu_i^{id.gas,pure} + RT\ln(y_i) + RT\ln\varphi_i(T,P,\bar{y})$$

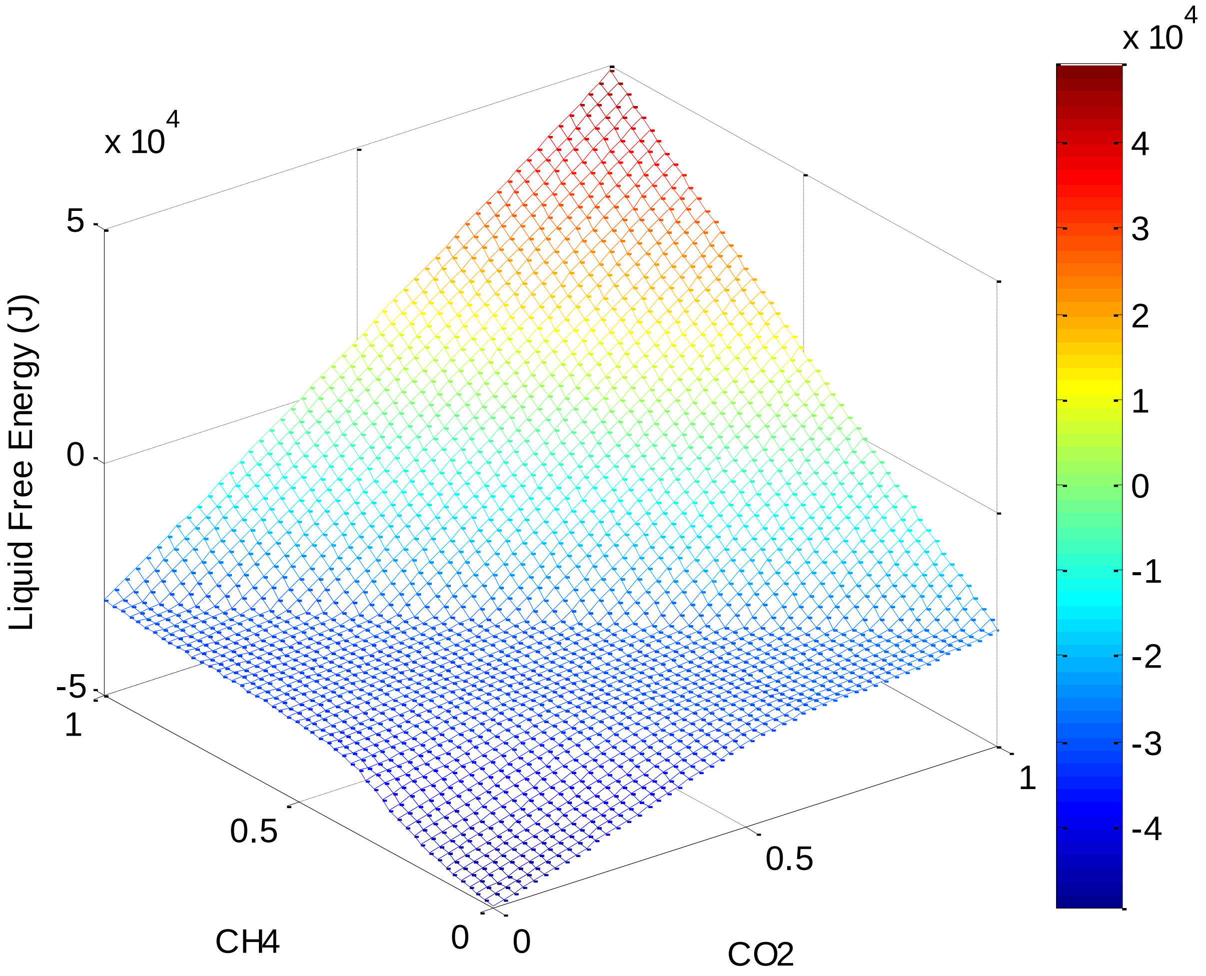
$$\mu_w^{Fluid} = \mu_w^{ideal\ gas}(T,P) + RT\ln(y_w)$$

Accurate enough approximation For the special example since hydrate formation from gas is unimportant in this problem/system

$$y_w = \frac{x_w\gamma_w(T,P,\bar{x})P_w^{sat}(T)}{\varphi_w(T,P,\bar{y})}$$

Estimated chemical potentials of water that drop out from CO2 solution in either liquid water or hydrate form. Same mole-fractions and conditions as in figure 5. Pressures are, from bottom to top, 100, 120, 140, 160, 180 and 200 bar. Solid lines are conditions for drop out as liquid water. Dashed lines are corresponding estimated conditions for drop-out directly as hydrate from CO2 solution.





Liquid Gibbs free energy as function of mole fraction at 3°C and 40 bars.

Aqueous Thermodynamics

$$\mu_w = \mu_w^{\text{pure liquid}}(T) + RT\ln(x_w\gamma_w) + v_w(P - P_0)$$

$$\mu_i = \mu_i^{\infty}(T) + RT\ln\left(x_i\gamma_i^{\infty}\right) + v_i^{\infty}(P - P_o)$$

where,

$$\gamma_i^{\infty} = \frac{f_i^{\infty}}{k_H(T)}$$

$$f_i^{\infty} = e^{(-\beta\mu_i^{\infty})}$$

$$k_H(T) = k_H^{\ominus} e^{\left(\frac{-\Delta_{soln}H}{R}\left(\frac{1}{T}-\frac{1}{T^{\ominus}}\right)\right)}$$

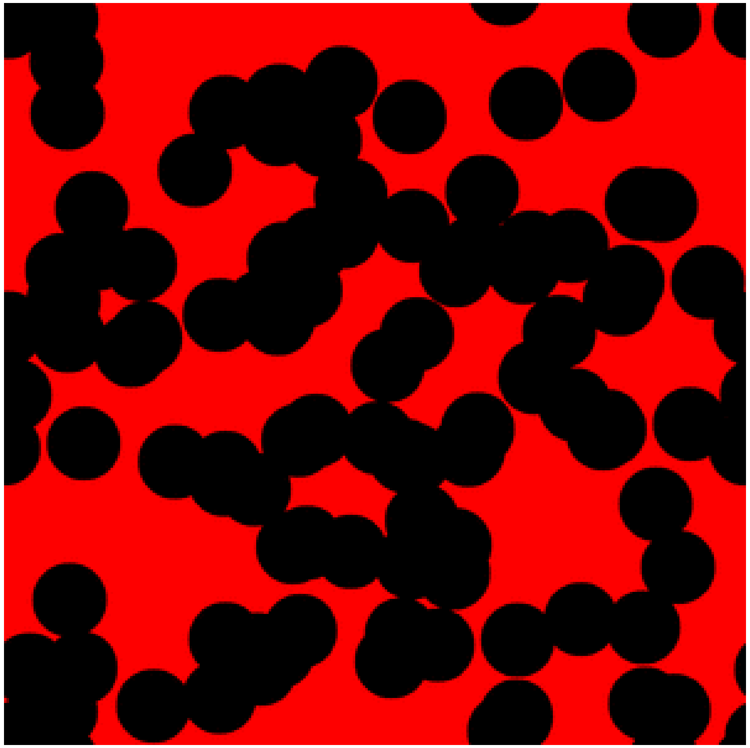
R. Sander, Surv. Geophys, 20, 1(2009)

Constants	**CO2**	**CH4**
$k_H^{\ominus}$ (M/atm)	0.036	0.0013
$\frac{\Delta_{soln}H}{R}$ (K)	2200	1800

D. Q. Zheng, T. M. Guo, and H. Knapp, Fluid Phase Equilib, 129 , 197 (1997)

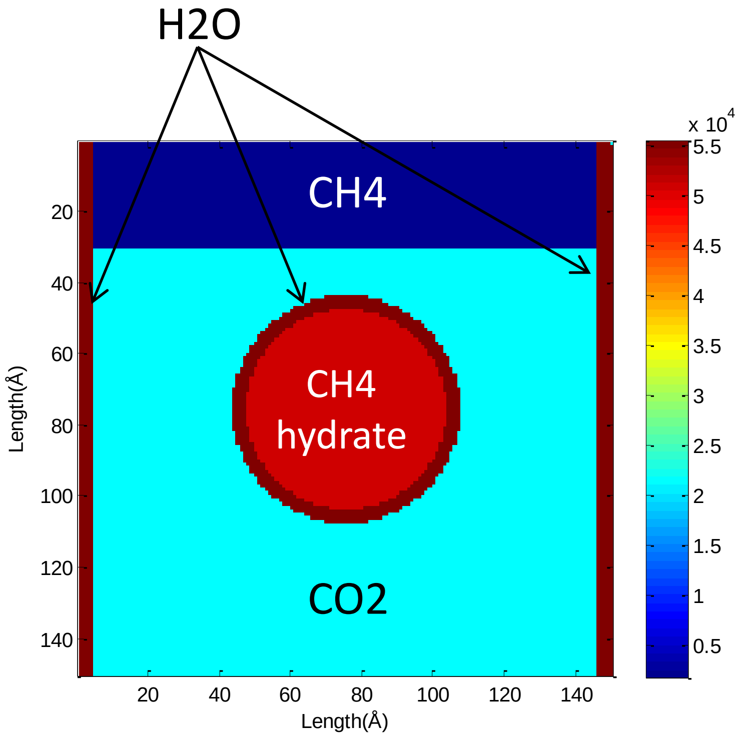
Example related to a real case of pore phase distribution as interpreded from different methods

- The relative fraction of different phases (hydrate, water, free gas) given
- An unknown parameter here is the distribution of water around mineral versus around hydrate during injection of CO2
- Free gas (CH4) assumed initially to be at top of pore due to density
- At this stage there are no mineral surfaces in the system but work is in progress on implementation of that



Solid surfaces without thermodynamic properties (excluded volume) is trivial and have a triggering function in nucleation preferences in inclinements. See yellow CO2 hydrate nucleation from solution of CO2 in water. Addition of surface thermodynamics (adsorbed chemical potentials) in progress

Simulation setup

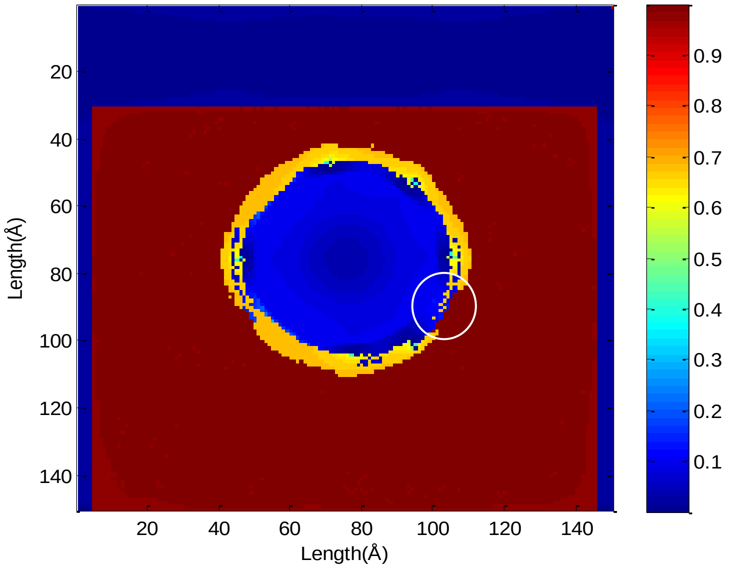


Distribution is based on average liquid water saturation, free gas saturation and hydrate saturation of a ***real reservoir***

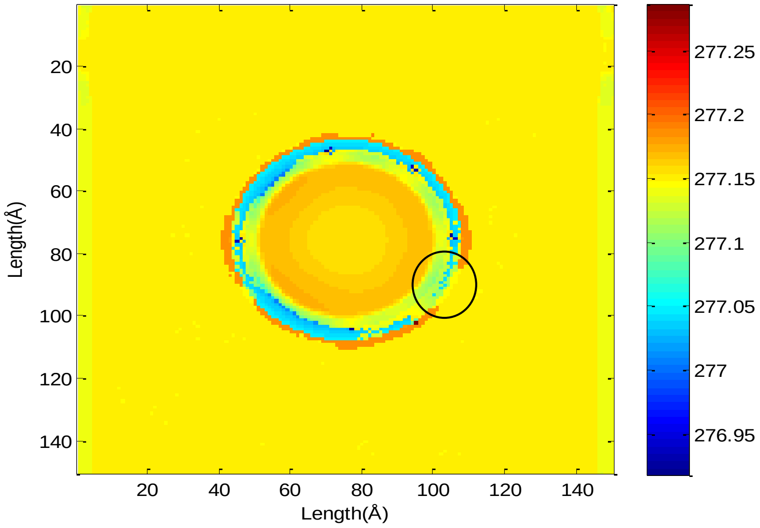
The different sizes will have different contact areas between hydrate and the CO2 phase

- ***Three different hydrate systems*** sizes were considered
  - (150 Å×150 Å, 500 Å×500 Å and 5000 Å×5000 Å)
  - Hydrate radii are ***28 Å, 114 Å and 1136 Å***
- Injection of CO2 into the pore
  - Will displace some of the water surrounding the hydrate because the ***minerals*** will normally have a ***higher thermodynamic benefit*** from the water than the hydrate
  - The examples here are for 1.2 nm liquid water surrounding hydrate. Several other distributions of water around hydrate versus on mineral is running
- Initial methane saturation is 20 %
- CH4 mole fraction in hydrate: 0.14 (max)

Smallest system



CO2 filling in hydrate after 3 ns

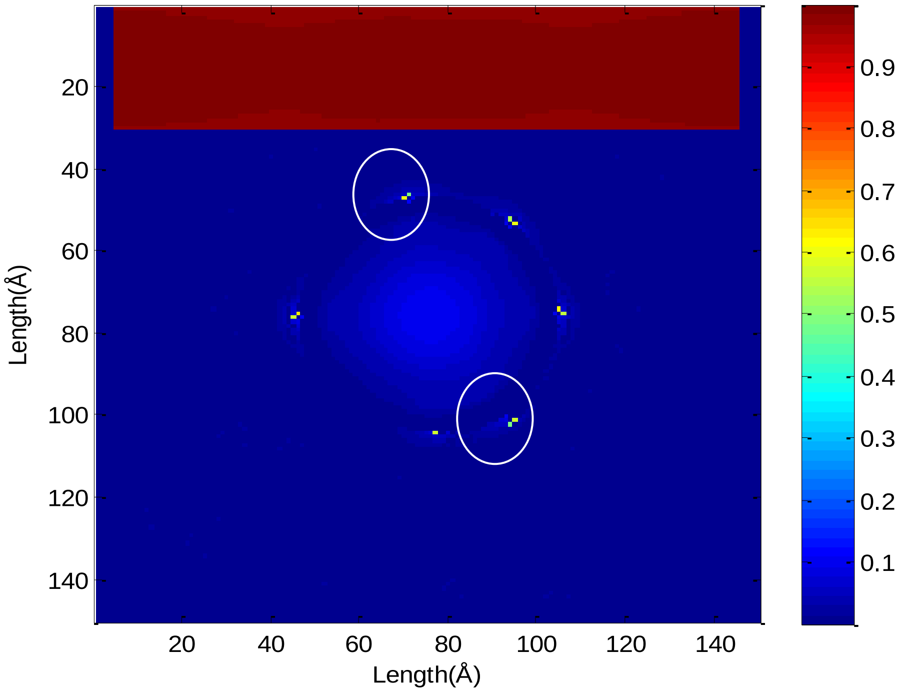


Temperature (Kelvin) after 3 ns

- ***CO2 in hydrate results in hydrate lower free energy*** versus CH4 hydrate
  - ***Drives the exchange*** process
- Exchange is fast initially
  - Due to heat released from formation of new CO2 hydrate
- Encircled region is an ***escape region for dissociating methane***
- Inner parts of hydrate are cooled down

Bubble formation

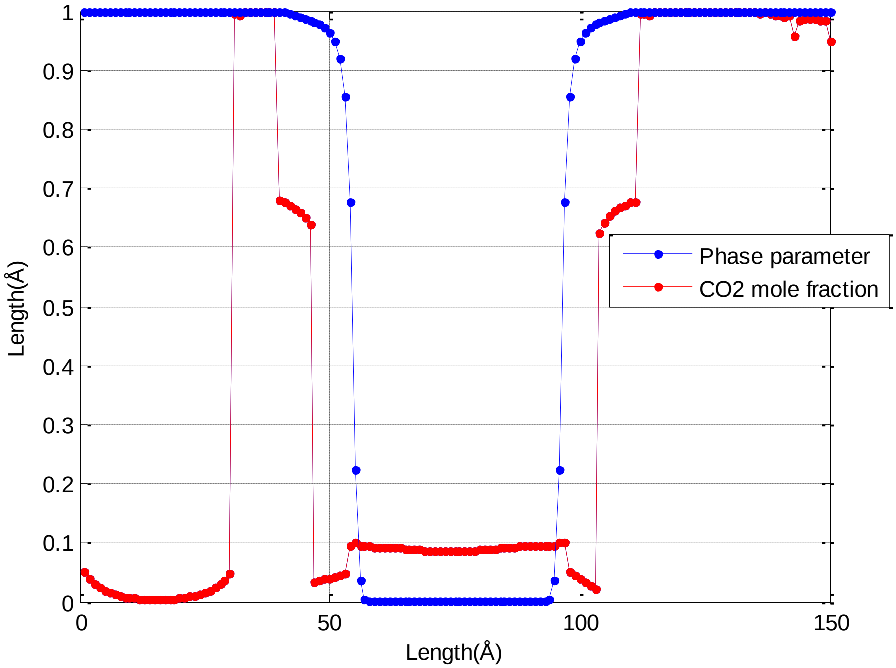
- Methane will exist as a ***free gas near the interface***
  - If the surrounding fluid is incapable to dilute the released methane
  - The bubble may ***merge*** after colliding with each other
  - Will eventually dissolve into CO2 but the hydrodynamically controlled escape (buyouncy) from the surface keep the CO2/hydrate «clean» from CH4 pollution



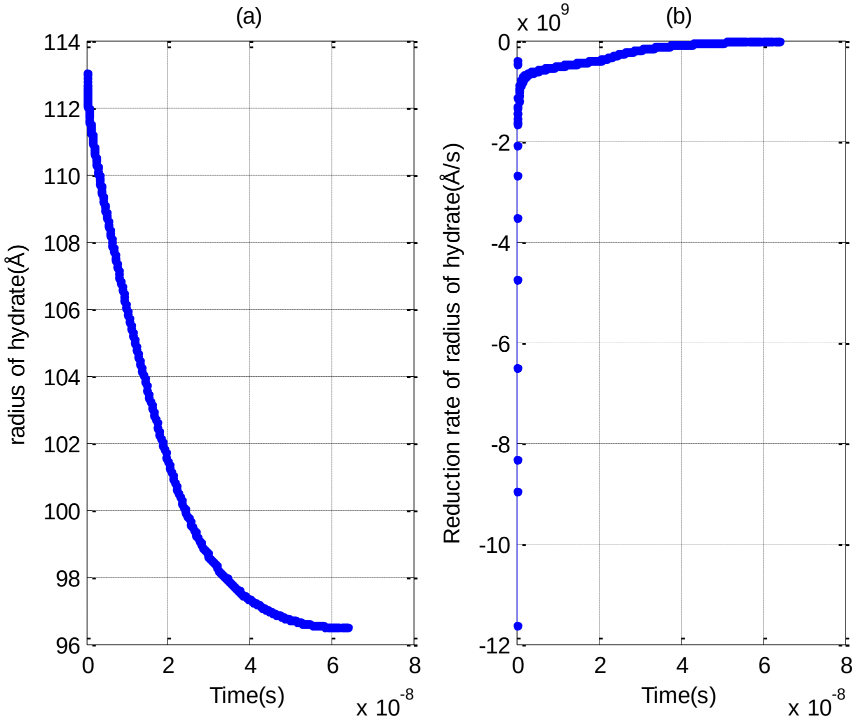
Snapshot of methane mole fraction in entire system after 3 ns

Unstable mix hydrate

- Exchange til 5.6 ns
- After 5.6 ns, Mix hydrate could not be sustained and melted very quickly due to unfavorable chemical potential gradients for water and CH4
  - Larger systems are more stable (coming results)



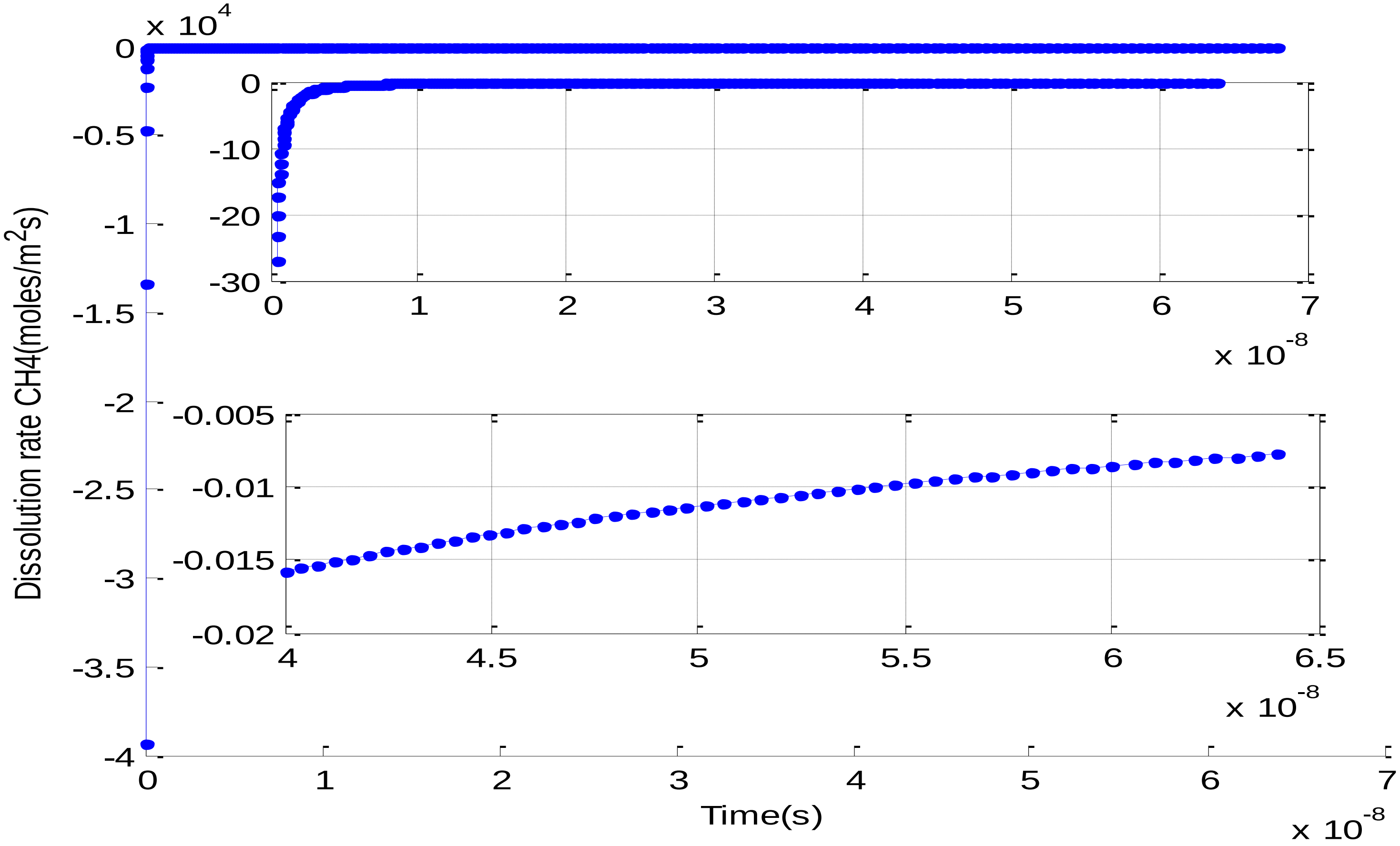
Intermediate size



Intermediate system (500Å×500Å) system: Radius of circular hydrate and its reduction rate shows convergence to a stable mixed hydrate as function of time

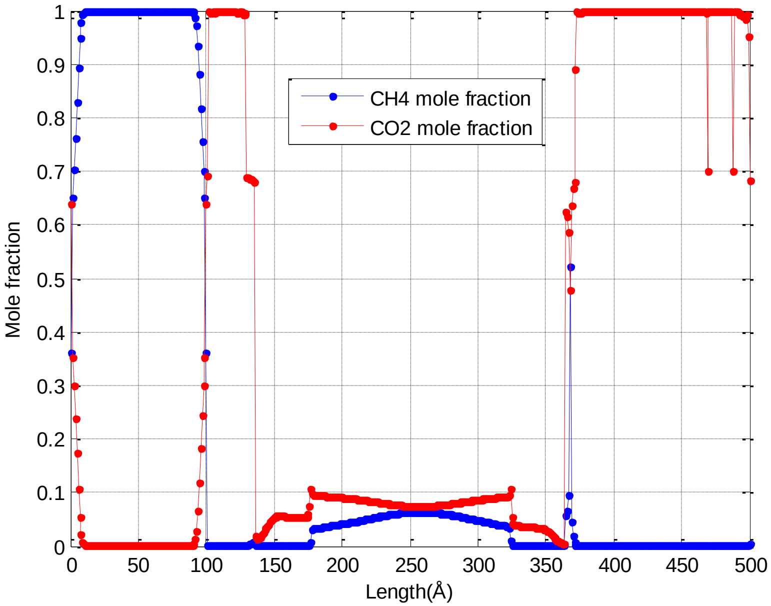
- Initially exchange and dissociation ***processes are rapid***
  - Due to ***heat release*** from formation of ***new hydrate***
- As time progress
  - Dissociation process slows down
  - Slower direct conversion which is ***solid state transport limited***
- Less loss of hydrate core
- Form more stable mix hydrate than smallest size

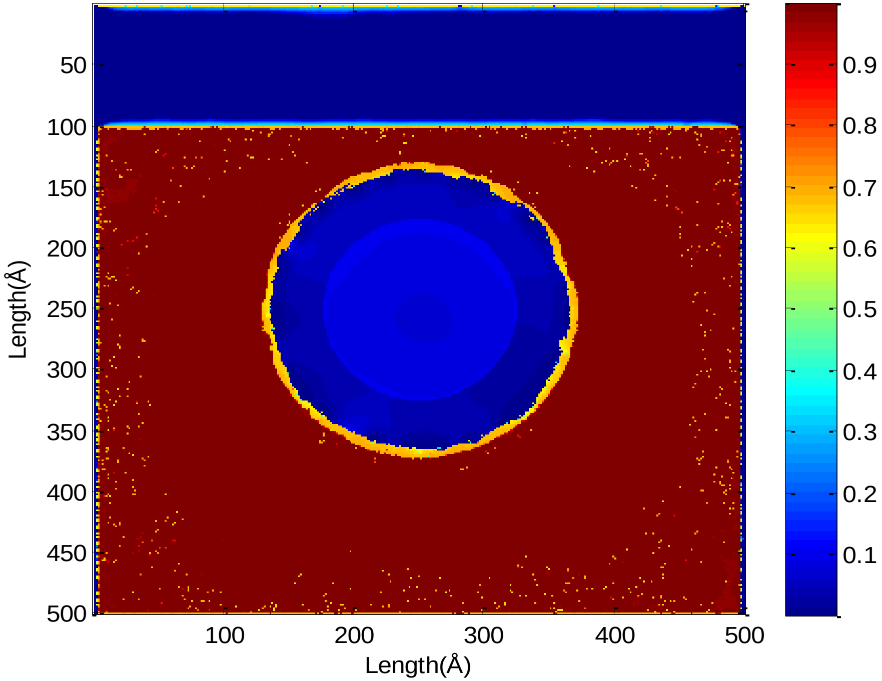
Intermediate size



- Flux of dissociating methane also become small with time
  - Conversion which is ***solid state transport limited***
  - CH4 dissolution rate shows the system approaching stability

Results

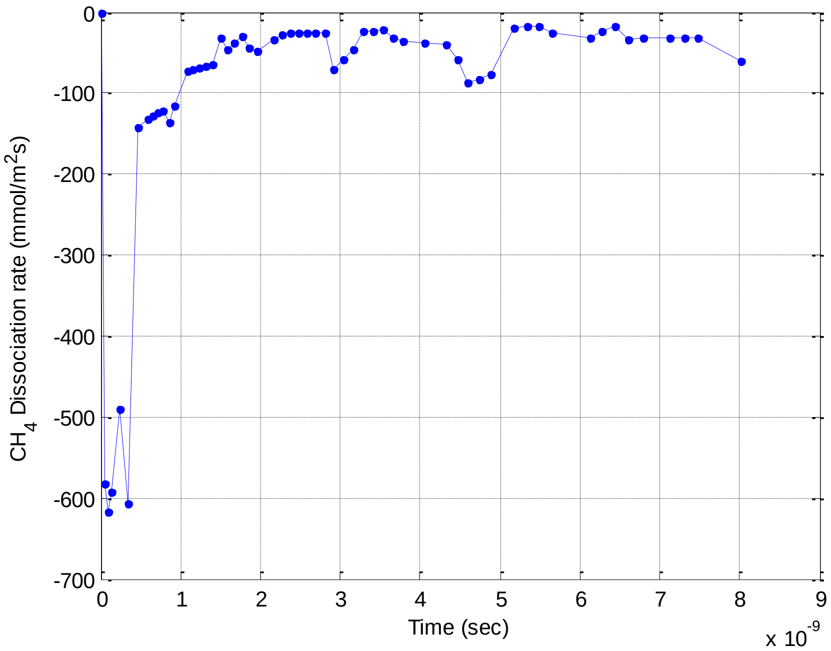




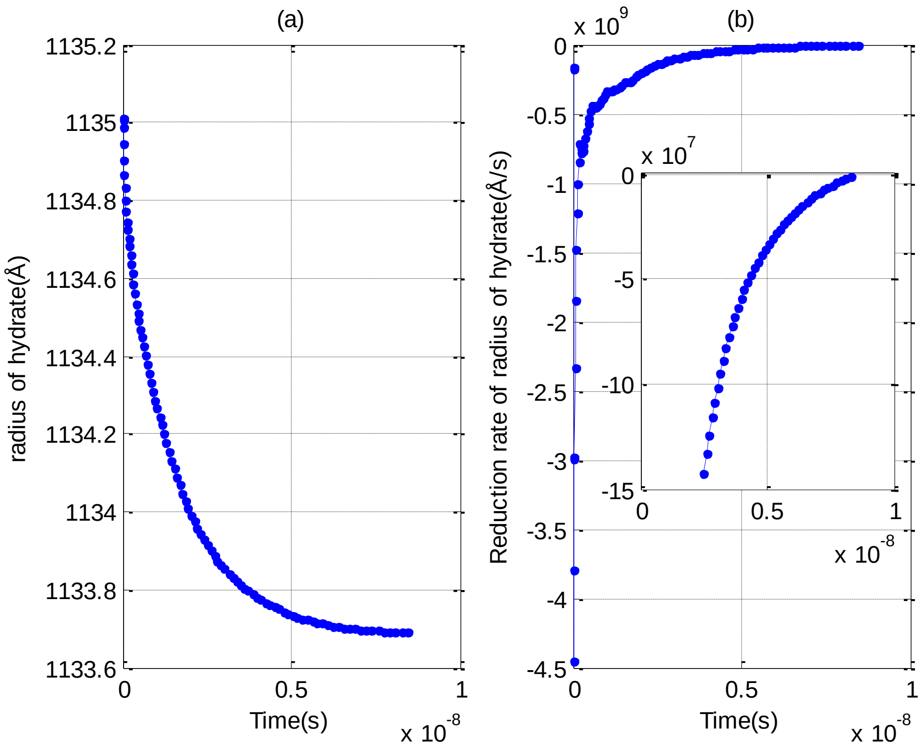
CH4 and CO2 mole fraction after 64 ns

CO2 mole fraction after 64 ns

Largest system



Methane flux



hydrate core as function of time

- Largest system achieves a stable mixed hydrate faster
- Least loss of hydrate core
- Results are only available up to 8.4 ns
- Methane is still ***releasing after 8.4 ns***
  - Due to the exchange process in favor of CO2 occupation of large cavities
- System seem to be entering a ***stationary slow progress***

Conclusions and discussion

- Phase Field Theory (PFT) model extended with hydrodynamics
  - Free methane gas ***bubbles are observed*** on the interface
    - ***Dissociation is faster*** than rate of dissolution into the surrounding water
      - separate gas bubbles will form
    - ***Fluxes of releasing methane are changed*** as dissociation kinetics are affected
- Thermodynamic properties for hydrate outside of equilibrium have also been derived
  - Implicit implementation
  - Heat transport dynamics is incorporated through a simplified «lumped» conduction model. More refined models will be implemented in the future (we applied for 5 new PhD grants but got only 3)

Conclusions and discussion

- Heat released due to formation of mix hydrate
  - Which make the initial exchange process fast
  - Later limited by solid state transport
- CH4 hydrate surrounded by CO2 converted into a mixed hydrate
  - In accordance with experimental and theoretical evidence from open literature
- The effect of the initial size of hydrate system on the stability of the mix hydrate has been studied
  - Larger systems form more stable mix hydrate

Conclusions and discussion

- This is the first kinetic theory for hydrate/water/fluid which is able to model kinetic progress in non-equilibrium systems relevant for hydrates
  - in porous media
  - transport of CO2 or CH4 in pipelines
  - other situations of hydrate phase transitions under non-equilibrium conditions

Conclusions and discussion

- Impact of solid surfaces is fairly straightforward once adsorbed chemical potentials are available (some estimates are available for a start)
- There is no limit in how large the simulation system is but in present form the resolution is limited by the free energy related to thermal fluctuations. A practical limit with our Cray supercomputer is micrometer in 2D and less for 3D. So pore scale modeling is within reach

Part 3 – Kvasi equilibrium calculations

- Each individual phase transition can be evaluated in terms of ***free energy changes*** and compared in order to evaluate which ones are ***impossible due to positive free energy*** change or free energy change that are favorable (negative) but ***too small to overcome the penalty of pushing*** away the surroundings to give room for the new phase
- All these other phase transitions can be implemented in any hydrate code and can supplement the current basis for hydrate risk evaluation
- BUT the phase transitions are complex kinetic processes so even if driving forces says «possible» kinetic may be too slow so even simple kinetic models should be implemented as a minimum. Classical theory or better MDIT theory (Kvamme, 2002, 2003)

The non equilibrium challenge

$$\mu_w^{H,i}(T,P,\vec{x}^H) = \mu_w^{H,0}(T,P) - \sum_j \nu_j \ln\left(1+\sum_k h_{kj}^i\right)$$

$$h_{kj}^i = e^{-\beta\left(\mu_{kj}^i + \Delta g_{kj}^{\mathrm{inclusion}}\right)}$$

$$\theta_{kj}^i = \frac{h_{kj}^i}{1+\sum_k h_{kj}^i}$$

- ***Chemical potential of guest molecules from different phases are different and***

  - results in different filling fractions

  - different hydrate free energies

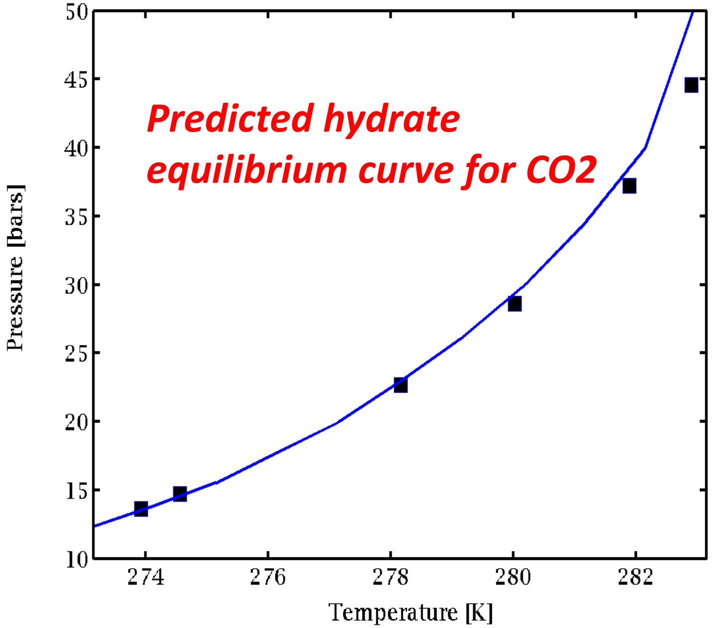
  - different hydrate kinetics

$\mu_w^{H,i}$	Water chemical potential in hydrate phase i
$\Delta g_{kj}^{\mathrm{inclusion}}$	Free energy of inclusion in cavity by ”classical” langmuir integration or harmonic oscillator approach (Kvamme & Tanaka, 1995)

Non Equilibrium Challenge

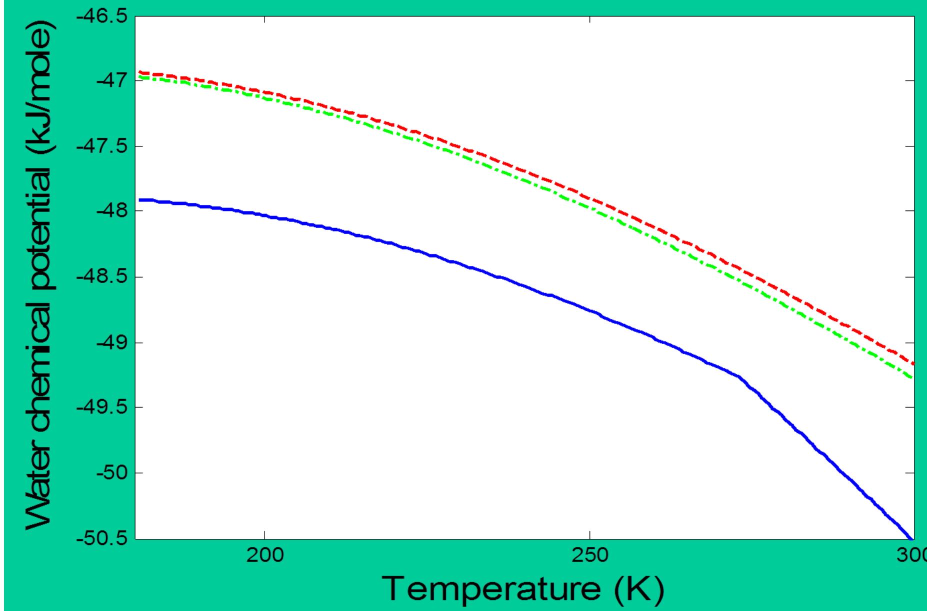
Accurate and consistent model for free energy of the different co-existing phases

- A critical basis for ***Phase Field Modeling***
- Free energies for individual (Aqueous, Fluid and Hydrate) phases are used here
  - Revised adsorption theory (Kvamme & Tanaka, 1995) for hydrate
  - TIP4P simulated chemical potential for ice, liquid water, and empty hydrate



Predicted hydrate equilibrium curve for CO2

Solid line for ice or liquid water, dash line for SI empty hydrate and dash-dotted line for SII empty hydrate.



Kvasi equilibrium models

- We use chemical potential of empty hydrate from MD (Kvamme and Tanaka, 1995) to avoid 5 empirically fitted parameters for a fundamental property like a change in chemical potential

- For each possible phase transition assume equilibrium can be reached for the actual phase transition at current local P and T
- Calculate chmical potential for the actuall guests in the phase they come from
- Calculate water chemical potential and solve for the unknown