Non-Equilibrium Nature of Hydrates in Sediments and Consequences for Choices of Ways to Produce Hydrates Safely and Economically Feasible*

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Abstract

Hydrates can form from many different phases. The most commonly investigated is hydrate formation from gas or liquid hydrate former phase and a free water phase. But hydrate can form from dissolved solution of hydrate former in water, and solid surfaces provide several possible routes to hydrate formation and dissociation. Various routes to hydrate formation leads to several hydrate phases with varying degrees of thermodynamic stability. Thermodynamic equilibrium is impossible and the balance between thermodynamics of each phase transition (formation or dissociation), and the associated mass- and heat-transport processes needed to make the phase transition possible is implicitly linked. Hydrate phase transitions are also very fast and on nano-scale in times and space if thermodynamic driving force is sufficient but rarely exceeds microscale. It is therefore important to distinguish between the two physically well-defined processes of nucleation and growth, and the more complex onset of massive growth (induction time). Various processes can lead to extreme rate limitations and lead to misunderstood nucleation times. Various aspects of these issues are discussed with a focus on developing efficient ways to produce hydrates.

Non-Equilibrium Nature of
Hydrates in Sediments
and
Consequences for Choices of
Ways to Produce Hydrates Safely
and Economically Feasible

or:

Why cannot we as physiscists, geoscientists, chemists and others fight mathematics ???

**Life begins at 65
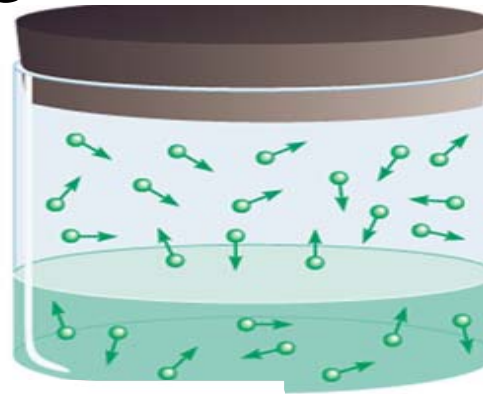and I got my freedom back
after retirement from
University of Bergen**

Professor Bjørn Kvamme

bjkvamme@gmail

CH4 and H2O outside hydrate formation
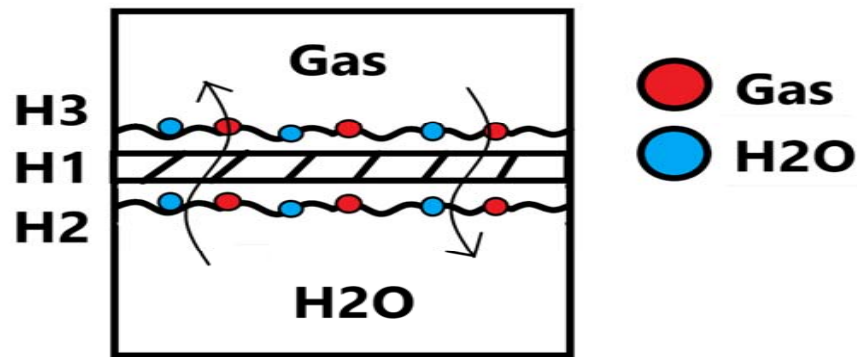
This is a trivial type Henrys law calculation.

Varables	Conserved
$x_{CH4,gas}$	$x_{CH4,gas} + x_{H2O,gas} = 1$
$x_{H2O,gas}$	$x_{CH4,water} + x_{H2O,water} = 1$
$x_{CH4,water}$	Equilibrium
$x_{H2O,water}$	$T_{gas} = T_{water}$
T_{gas}	$P_{gas} = P_{water}$
T_{water}	$\mu_{CH4,gas} = \mu_{CH4,water}$
P_{gas}	$M_{H2O,gas} = \mu_{H2O,water}$
P_{water}	
8	6

x_{CH4}

*If we provide **two independent thermodynamic variables** we can balance the difference between **all** independent thermodynamic variables and **conserved + equilibrium** conditions*
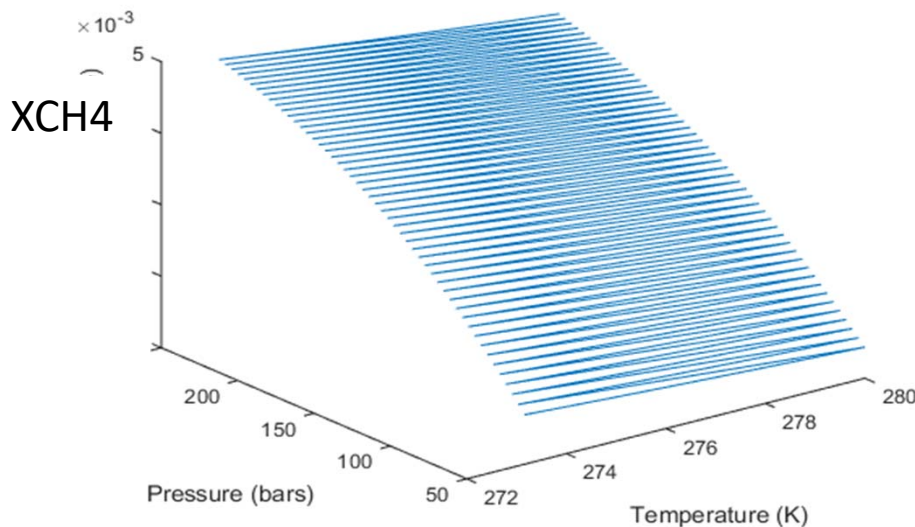
CH4 and H2O inside hydrate forming T,P

Varables	Conserved
$x_{CH4,gas}$	$x_{CH4,gas} + x_{H2O,gas} = 1$
$x_{H2O,gas}$	$x_{CH4,water} + x_{H2O,water} = 1$
$x_{CH4,water}$	$x_{CH4,hydrate} + x_{H2O,hydrate} = 1$
$x_{H2O,water}$	Equilibrium
$x_{CH4,hydrate}$	$T_{gas} = T_{water} = T_{hydrate}$
$x_{H2O,hydrate}$	$P_{gas} = P_{hydrate} = P_{water}$
T_{gas}	$\mu_{CH4,gas} = \mu_{CH4,water}$
T_{water}	$\mu_{CH4,gas} = \mu_{CH4,hydrate}$
$T_{hydrate}$	$\mu_{CH4,water} = \mu_{CH4,hydrate}$
P_{gas}	$M_{H2O,gas} = \mu_{H2O,water}$
P_{water}	$M_{H2O,gas} = \mu_{H2O,hydrate}$
$P_{hydrate}$	$M_{H2O,water} = \mu_{H2O,hydrate}$
12	11

As we all know we can now only fix 12 – 11 = 1 Independent thermodynamic variables to measure equilibrium

So if we fix **both T and P** the system is **over determined mathematically** and **equilibrium cannot be achieved** unless one of the phases disappear, and maybe not even then because we get **several different hydrate phases.** In non-equilibrium there are no rules on same chemical potentials for components in different phases

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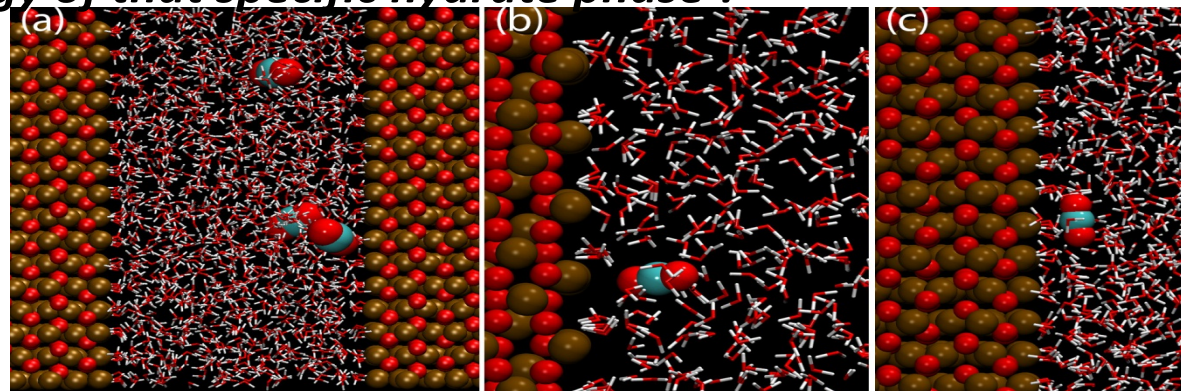
$$\mu_w^{H,i}(T,P,\vec{x}^H) = \mu_w^{H,0}(T,P) - \sum_j \nu_j \ln(1 + \sum_k h_{kj}^i)$$

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

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

Gibbs Phase Rule

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

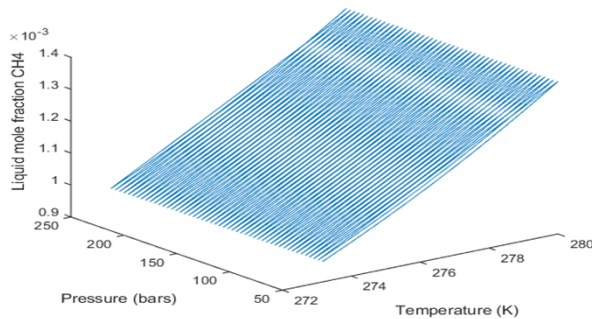No. of deg. of freedom

No. of components

No. of phases

And what about mineral surfaces in pores or surfaces of pipelines?

As we have seen Gibbs phase rule is actually very trivial. It is simply:

Number of **independent thermodynamic variables** (temperature, pressure and masses in all phases)
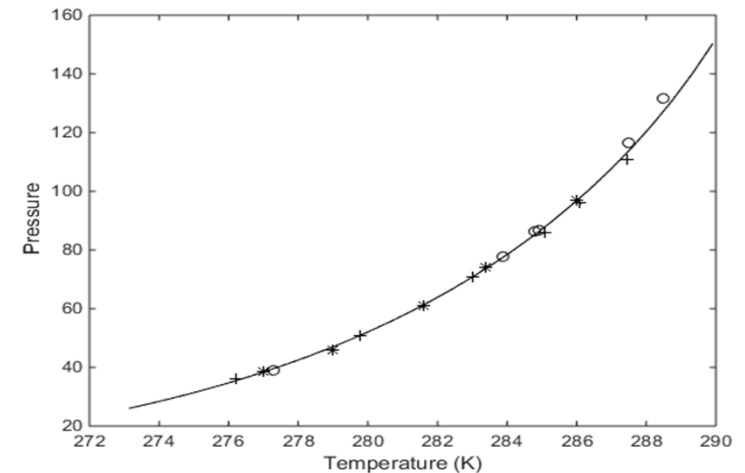
minus conservation law

minus conditions of eauilibrium

Left: Lower limits of hydrate stability concentration of CH4 in surrounding water to keep hydrate stable

Right: T-P stability limits

And it gets even more exciting in the real world

- **Solid surfaces (minerals) adds «hydrate active phases»**

  - hydrate formers adsorb and/or gets trapped in structured water
  - adsorbed/structured water cannot attach to hydrate

- **First and second law**

  - directs the dynamic hydrate formation towards formation of most stable
    hydrate first, under constraints of mass and heat transport

- **Relative thermodynamic states**

  - Some components may be supercritical and others
    have varying degrees of desire to condense/adsorb
    on liquid water, depending on thermodynamic state
    and interactions with liquid water

*CH4 and H2O in porous medium at hydrate forming
conditions are overdetermined by at least 4
independent thermodynamic variables*

Water towards Calcite

Chemical potential for adsorbed water is very low

Predicte CO2 hydrate Equilibrium curve
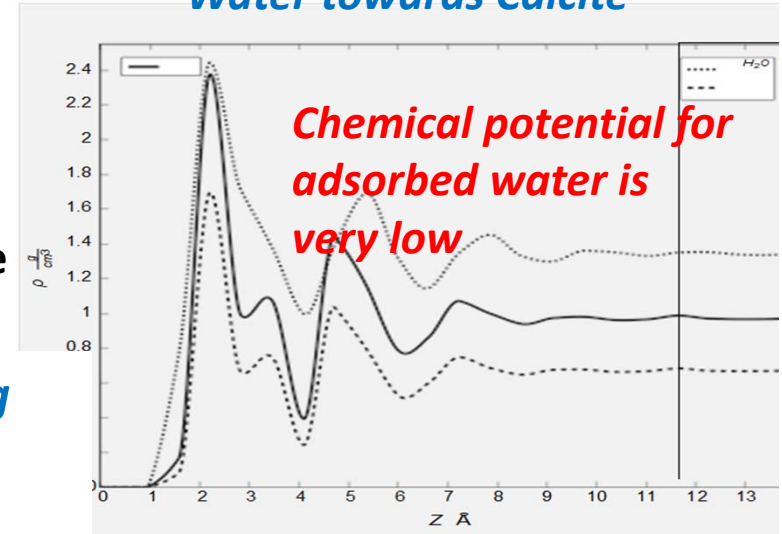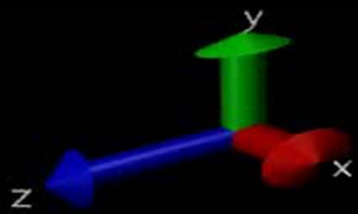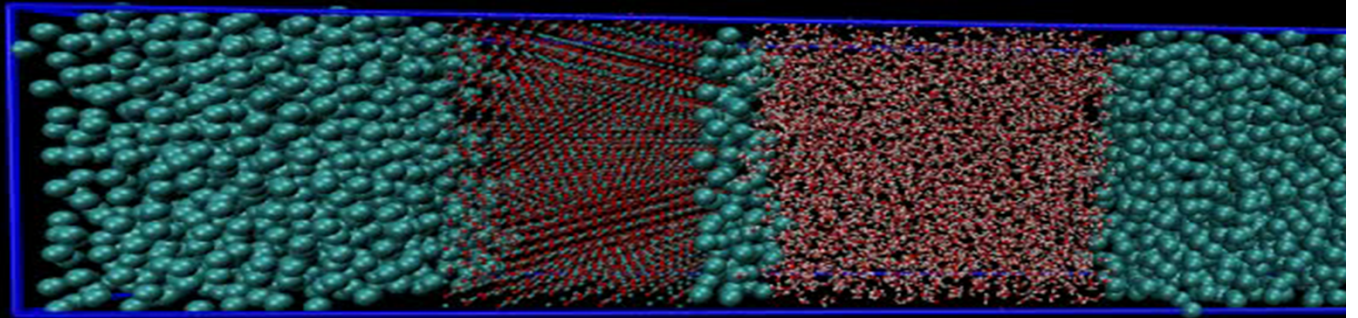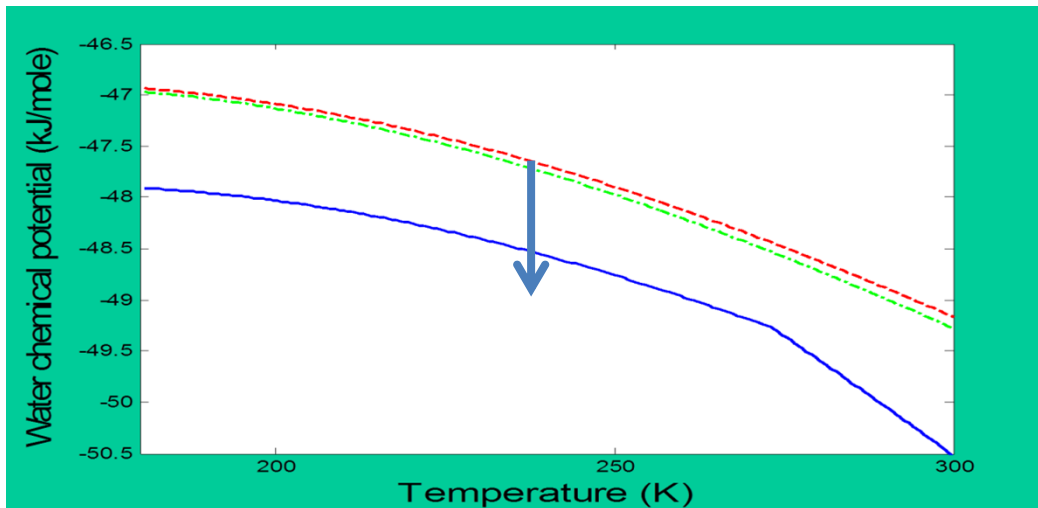
And there is **nothing** like hydrate **Quasi-equilibrium**
But
there can be *situations* of *some dynamic* processes being in a *slow* modus

But «sleeping» dynamic terms can become *very «awake»* when a *dynamic production* situation starts
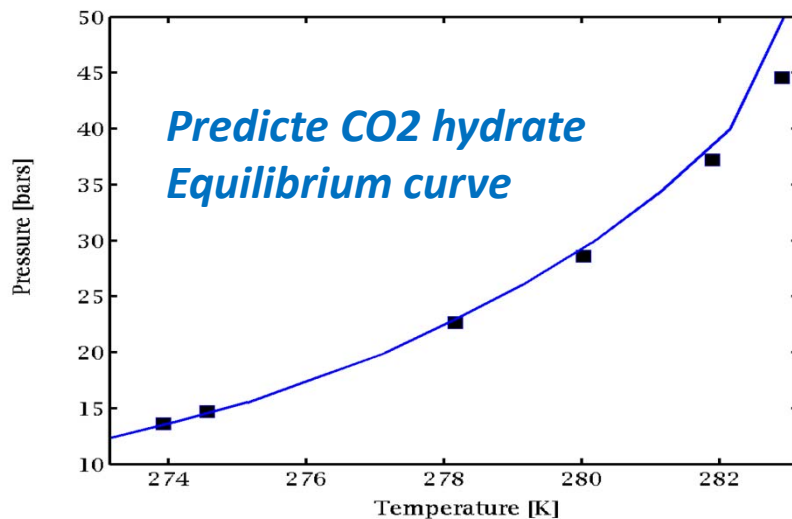
The use of residual thermodynamics (top) also for hydrate, ice and liquid water makes it easy to *analyze relative stability of co-existing hydrates and other phases* in a dynamic situation

Hydrate production philosophy

Flow: *Diffusion*
Models: Statistical mechanics, molecular dynamics
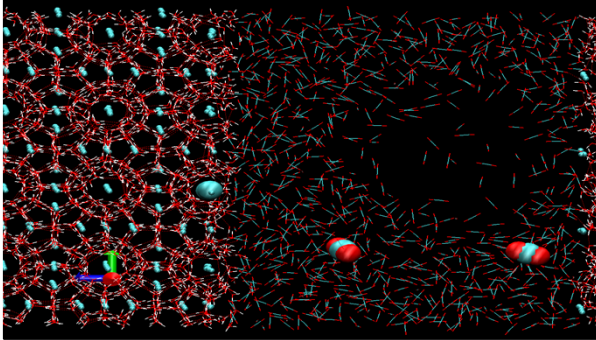
*Hydrate **phase transitions** are coupled (heat, mass, free energy) dynamic processes across a **thin (1.2 nm) interface***

*And finally (below): All pores are connected to the total reservoir flow dynamics on **scales meters to kilometers** (example is CO2 storage)*

What type of interactionlgets closest and most efficient to the phase transition dynamics on nano scale?
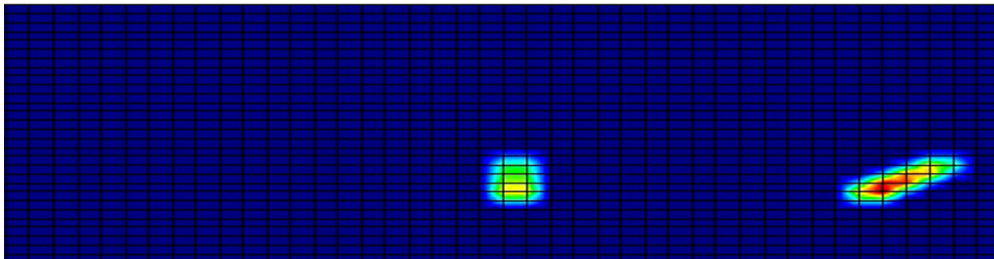
*Nano scale dynamics of phase transitions coupled to **pore scale dynamics and pore boundaries** (mineral surfaces, inlets, outlets)*

So how do we deal with non-equilibrium ?

- *Mechanical* equilibrium (pressure) and *thermal equilibrium* (temperature) can normally be assumed for systems containing hydrate phases in pores then

- Replace conditions of equal chemical ptentials with *minimization of free energy* with respect to distribution of *all component masses* over available phases for these components
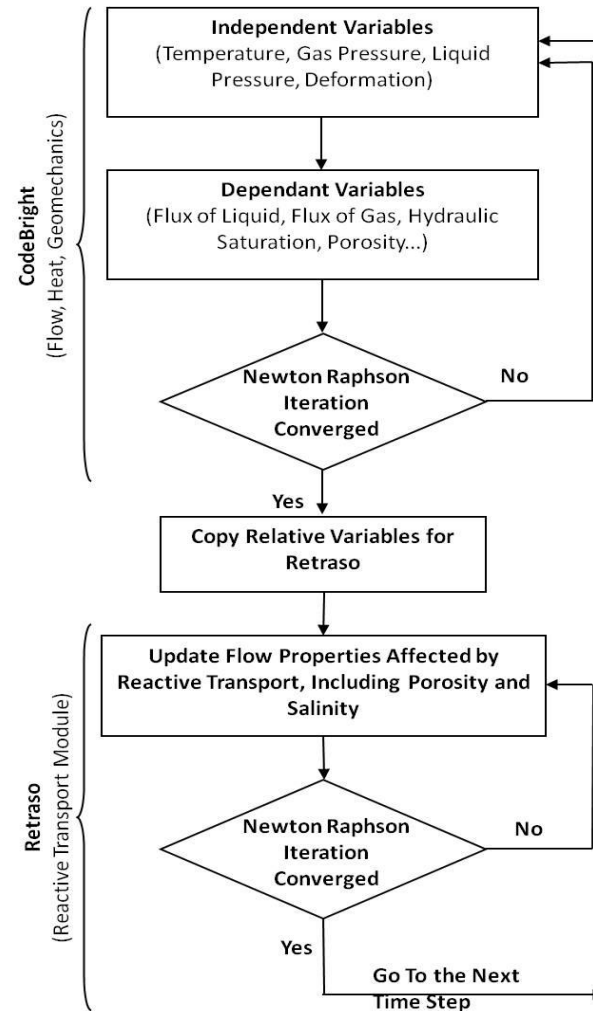
Simpllified flow-sheet for our RCB hydrate reservoir simulator

Inner cycle solves for *mass* flow, *heat* flow and *geomechanics*

Outer cycle *minimize free energy* for *distrution of masses* on various hydrate phases and fluid phases
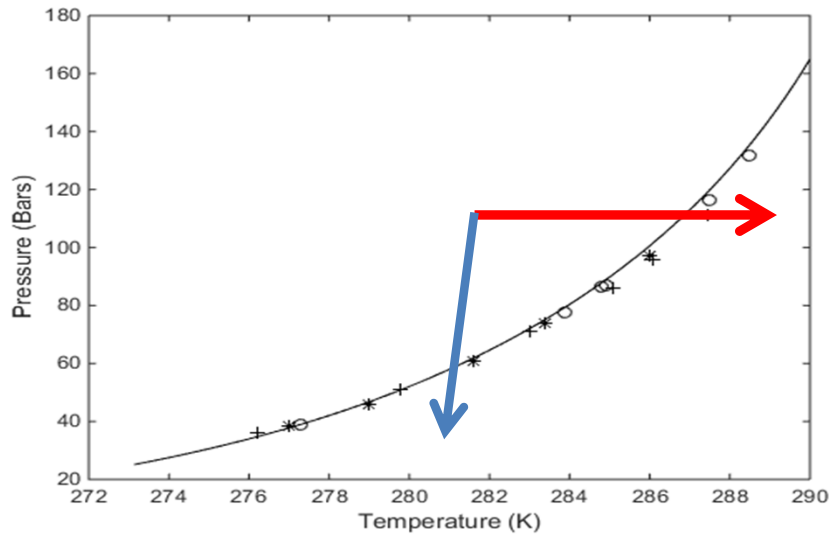
Pressure reduction or **temperature increase** ?

Adding heat is efficient because heat transport through liquid water and hydrate is 2 – 3 orders of magnitudes faster than mass-transport

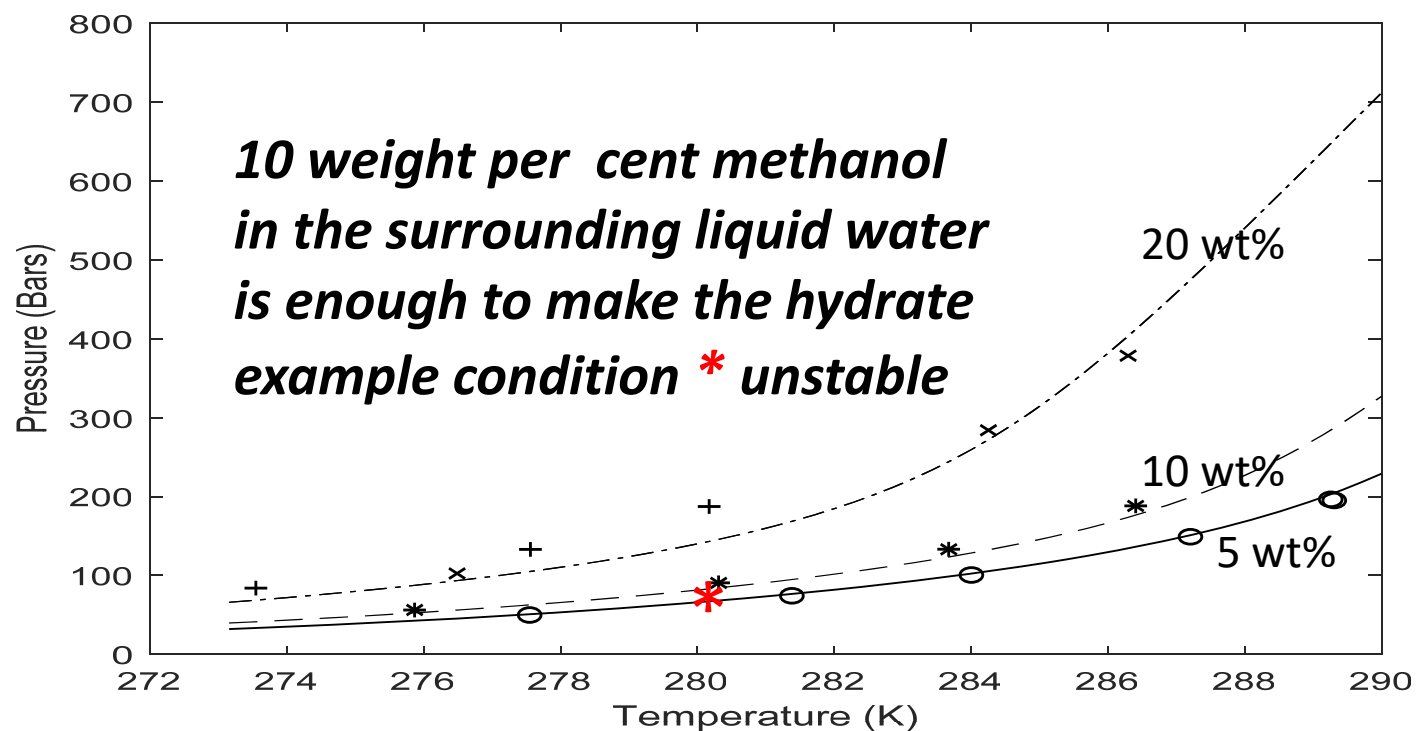**Too costly as primary action**

Pressure reduction involves dynamic chains (delays) from:
- *macro level to*
- *pore levels to*
- *nano lecel on hydrate core*
- *heat capacity and heat transport capacity of surrounding formation ???*
- *Sand production?   Water Production?   Geomechanical instabilities?*

No succesful pilots with commercial rates
**Many experiments have unrealistic heat supply**

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Adding methanol or other chemicals that reduce chemical potential for liquid water and shifts hydrate stability to higher P for given T


10 weight per cent methanol in the surrounding liquid water is enough to make the hydrate example condition * unstable

Hits hydrate Phase transition level (nano scale) efficiently **Very costly**

Why is the use of CO2 so misunderstood?

- Like hydrates in general there are frequent confusions about *nucleation, growth* and *induction times* (time for onset of massive growth)

- *Nucleation* is the *unstable* growth/deacay up to the maximum in free energy (*), and for this example roughly 2.3 nm in hydrate core radius before growth region

- After that *growth is stable* but can be substantially delayed due to *extremely slow transport of hydrate formers through hydrate films*. Diffusivities though hydrate are *8 to 10 orders of magnitude* lower than liquid diffusivities
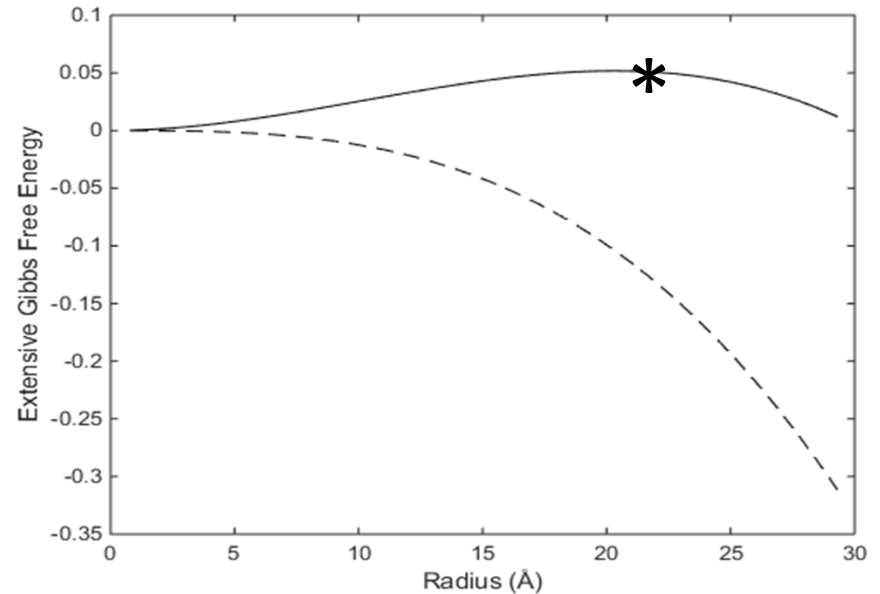
Free energy for a CH4 hydrate core as function of radius. Solid curve includes the penalty of pushing aside old phases. Dashed curve is free energy change for the phase transition. T=278 K, P=400 bar
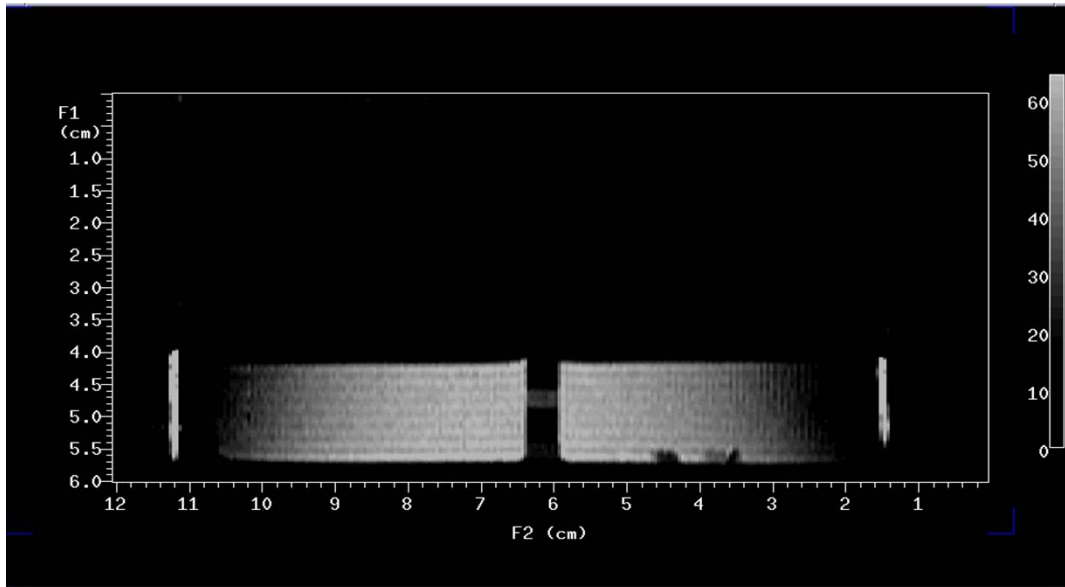
Magnetic Resonance Imaging of CH4 (black) in contact with liquid water (white) at 83 bar and 276 K. Hydrate is invisible (black).
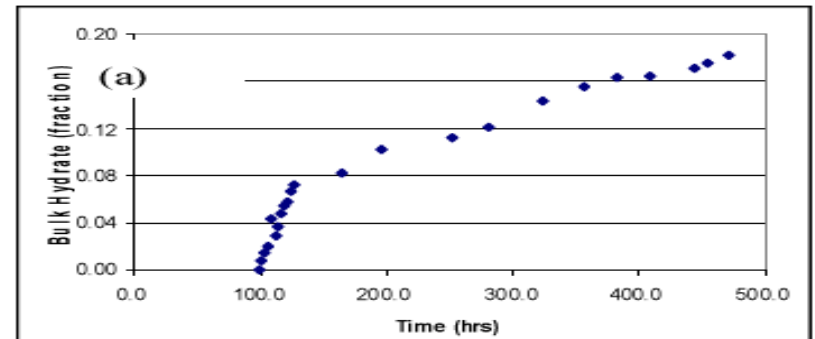
Center is a CO2 plume. Right and left outside is water containing 3.3 mole-fraction CO2. P=150 bar, T=274 K. Strongest (lowest fre energy) cores eat the weaker(PFT). In the experiment also capillary transport bring CH4 down the polypropylene walls.
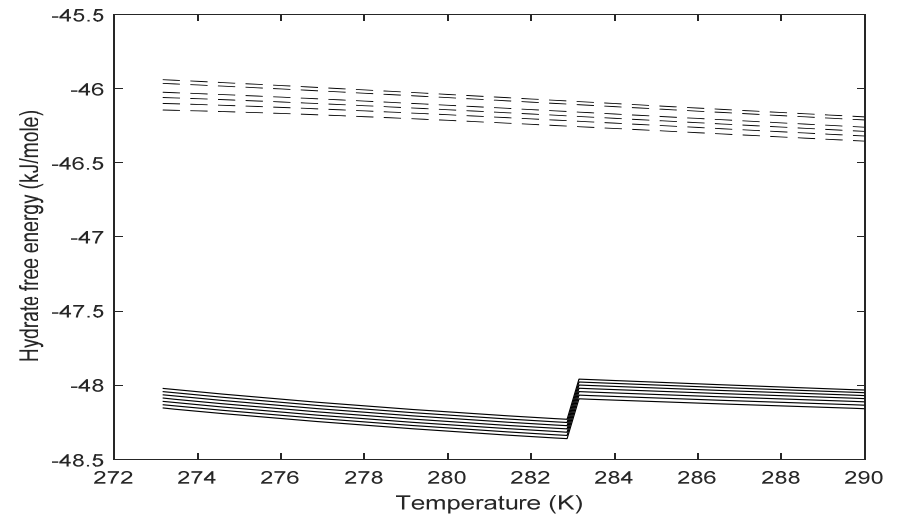
Yet some other misunderstandings

CO2 hydrate has a discontinuity in the pressure-temperature stability limits
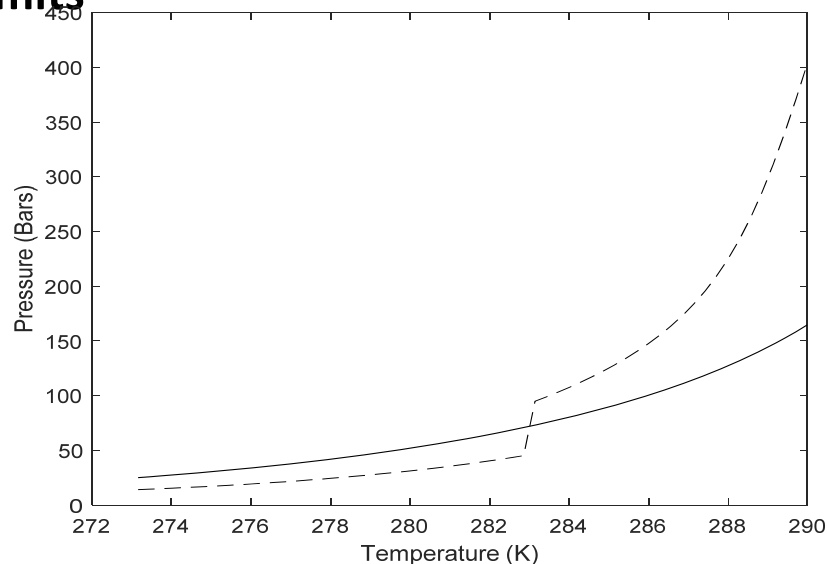
NO – there is a phase transition with very rapid change in CO2 density (dashed curve). In contrast, the supercritical CH4 has a smooth curve

CO2 hydrate is more stable than CH4 hydrate over a limited range of pressures and temperatures

NO – CO2 hydrate (solid) has 2 kJ/mole hydrate lower free energy than CH4 hydrate (dash). Curves are for varying amounts of methanol. Lowest curve for each is for pure water

Let us be very conservative and use *very slow mass transport* in Classical Nucleation Theory (CNT) to find out *how slow nucleation* actually can be

Calculated nucleation times for *heterogeneous* hydrate formation (CO2 phase + liquid water)
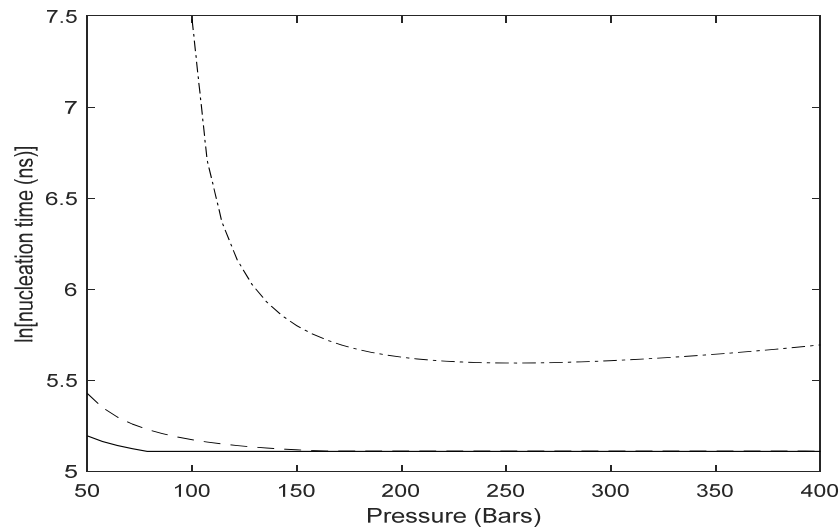
Solid is for 273.16 K, dash is for 278.16 K and dash-dot is for 283.15 K. Note the dramatic change for the condensed high T. But nucleation times are still in nano range

**Calculated nucleation times for *homogeneous* hydrate formation from CO2 dissolved in water**
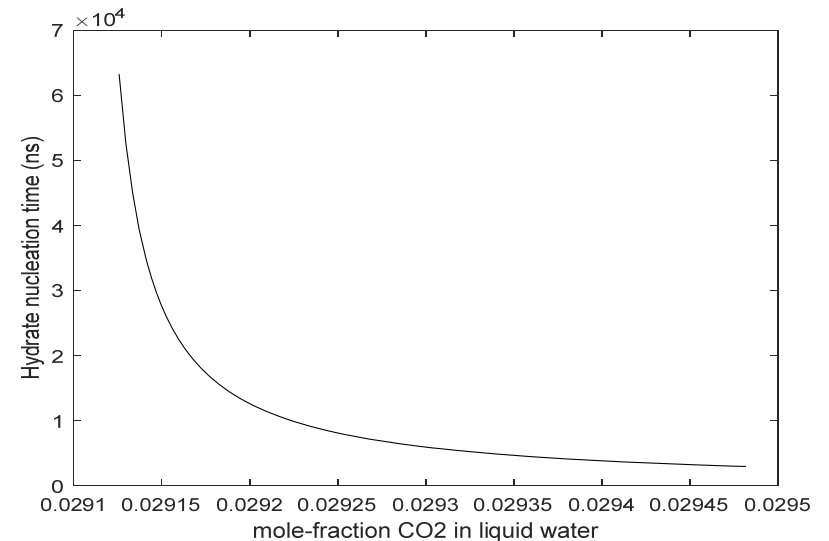
Hydrate formation from solution is very beneficial for CO2 close to liquid solubility and decrease towards lower limit for hydrate stability. T=273.16 K, P=100 bar

So then back to observable hydrates in microscope and MRI (roughly 300 micron resolution)

**Fast diffusion on liquid side of interface for CO2 hydrate**
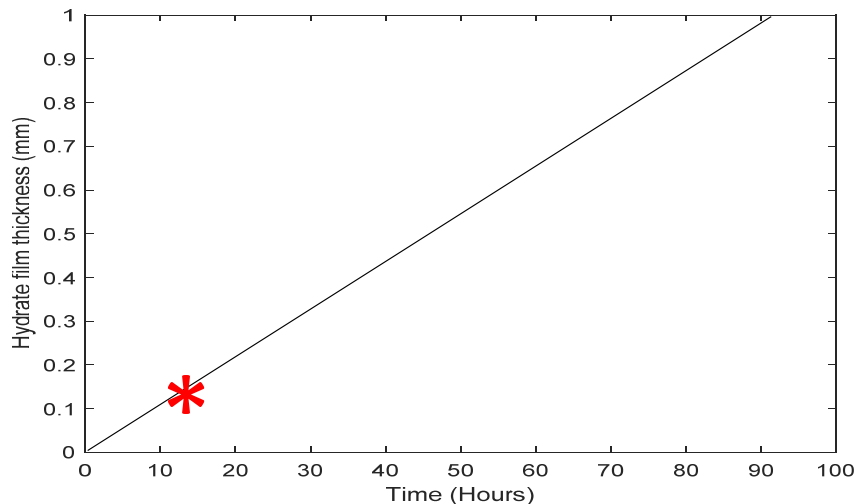
Slow diffusion on liquid side of interface for CO2 hydrate
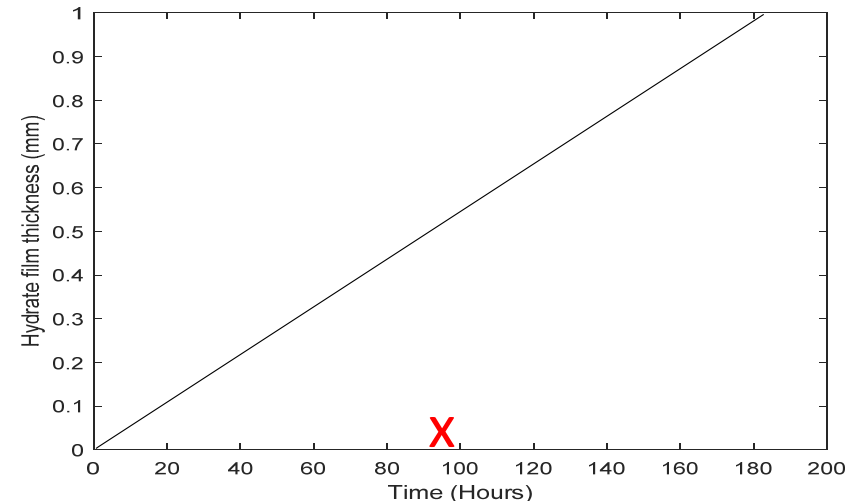
*Simplified modelling using a costant diffusion rate from hydrate side of interface and through hydrate film. * are from Uchida et. al., Journal of Crystal Growth Volumes 237–239, Part 1, April 2002, Pages 383-38. x is the experiment that I showed earlier for CH4 hydrate*

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So how does CO2 exchange with *in situ* CH4 hydrate ?

There is a very slow mechanism which has been proven in the *ice range of temperatures*
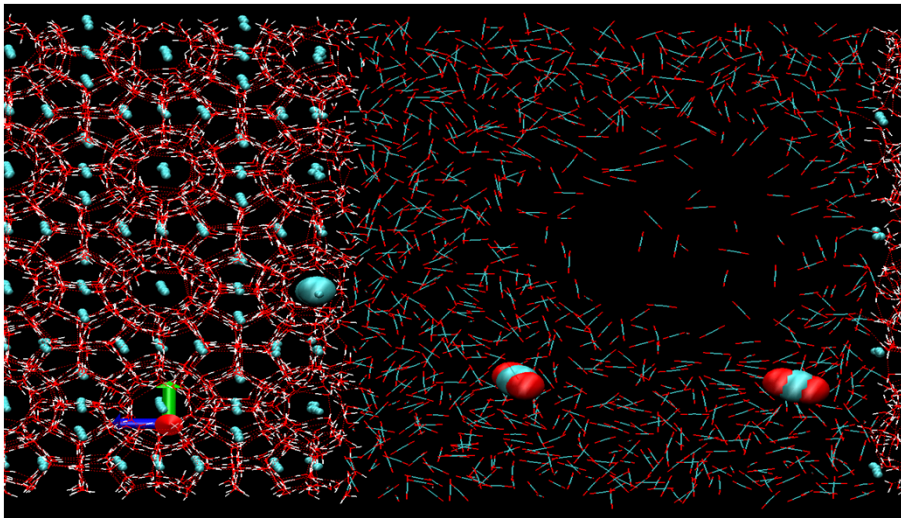
CO2 destabilize neighboring empty cavities and also the disturbs CH4 filled cavities and CH4 escapes. Extremely slow but not relevant for relevant te,peratures above zero

When there is *free water available* a new CO2 hydrate tilms forms fast (nano seconds) but then hydrate blocks the further progress
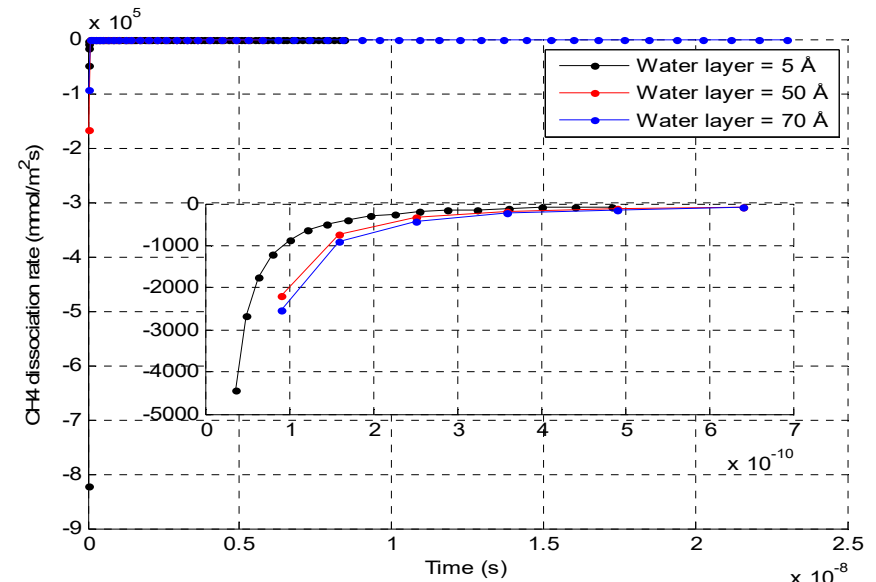

The more liquid water around CH4 hydrate – the longer time before slow mechanism

The fast mechanism consists of two elements:
1) Formation of new CO2 hydrate **releases heat** and
2) **Increased ion concentrations** in remaining water dissociate CH4
hydrate first
(CO2 hydrate is more stable and has even 2 kJ/mole hydrate lower free energy)

Enthalpies of CH4 hydrate formation along the hydrate T, P stability curve
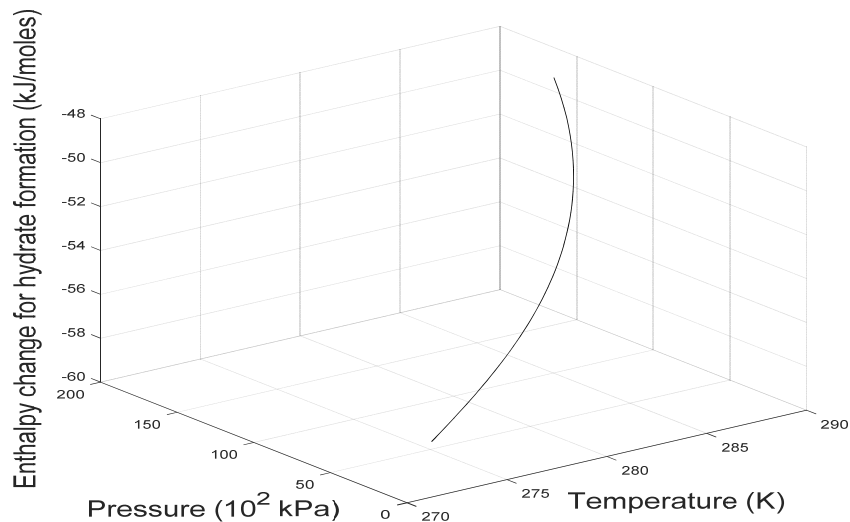
Enthalpies of CO2 hydrate formation along the hydrate T, P stability curve
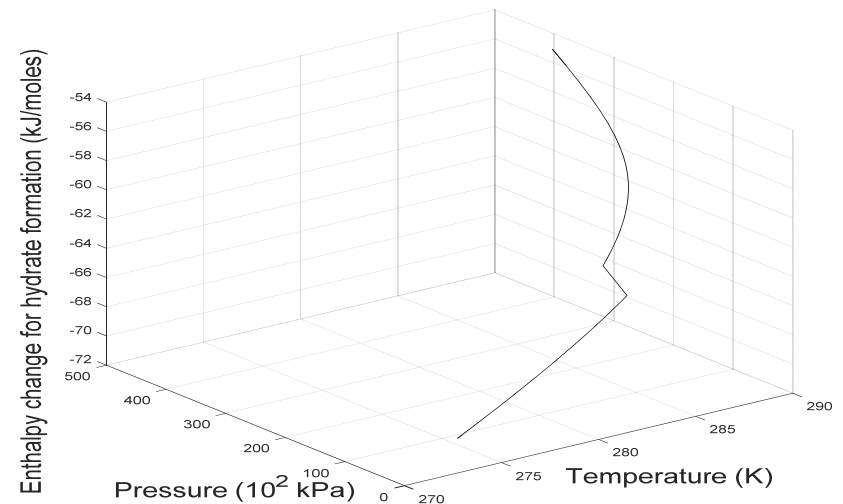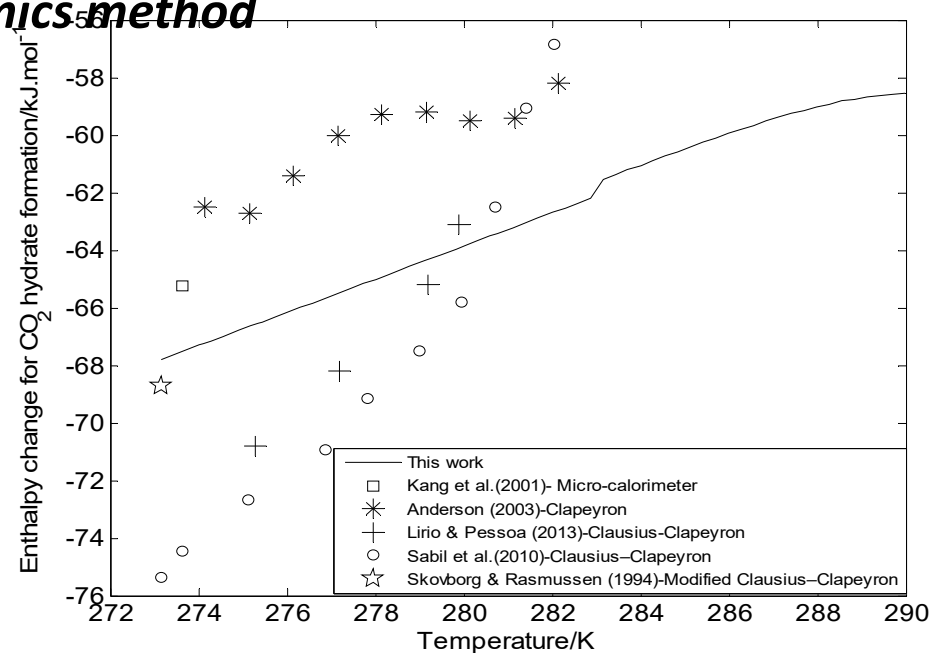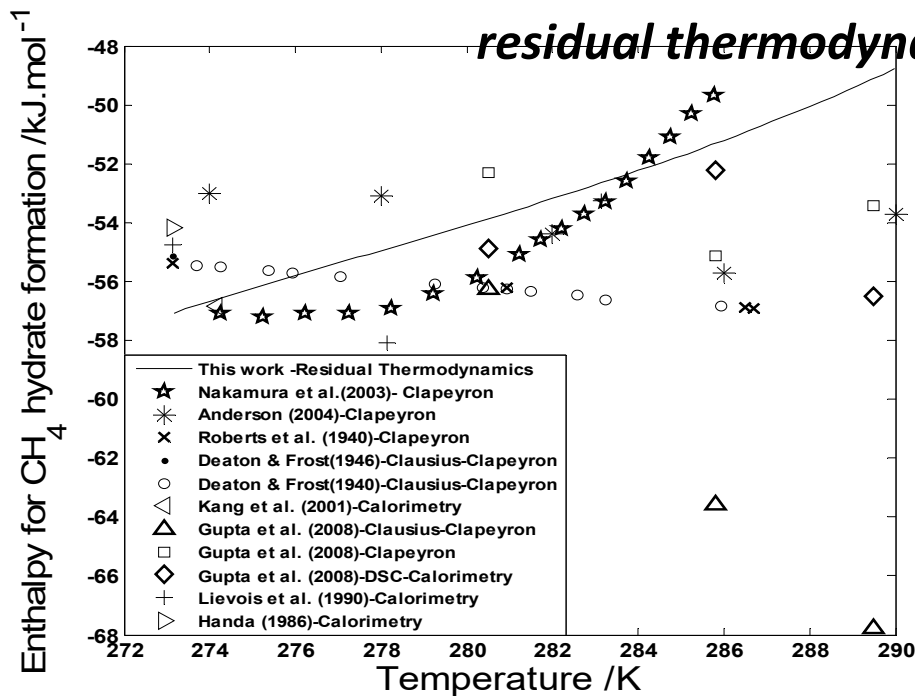
The heat release from hydrate formation for CO2 hydrate is roughly 10 kJ/mol hydrate former higher than corresponding number for CH4 hydrate

Evaluating experimental data was very hard work since important pieces (composition, pressure etc.) of information was lacking in most cases

CH4 hydrate

Solid curves are calculated using my residual thermodynamics method
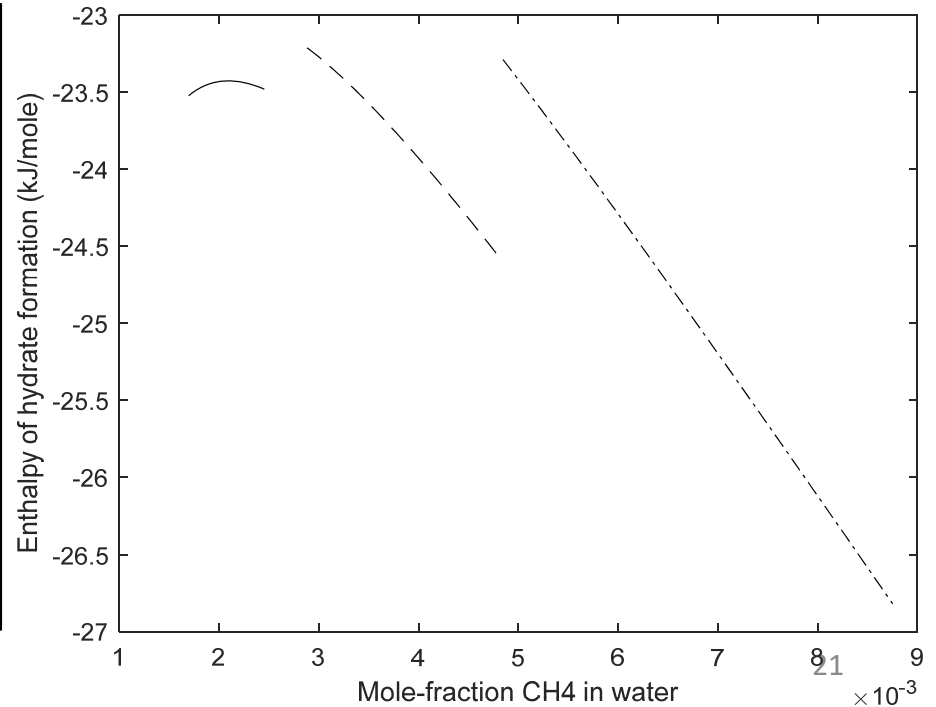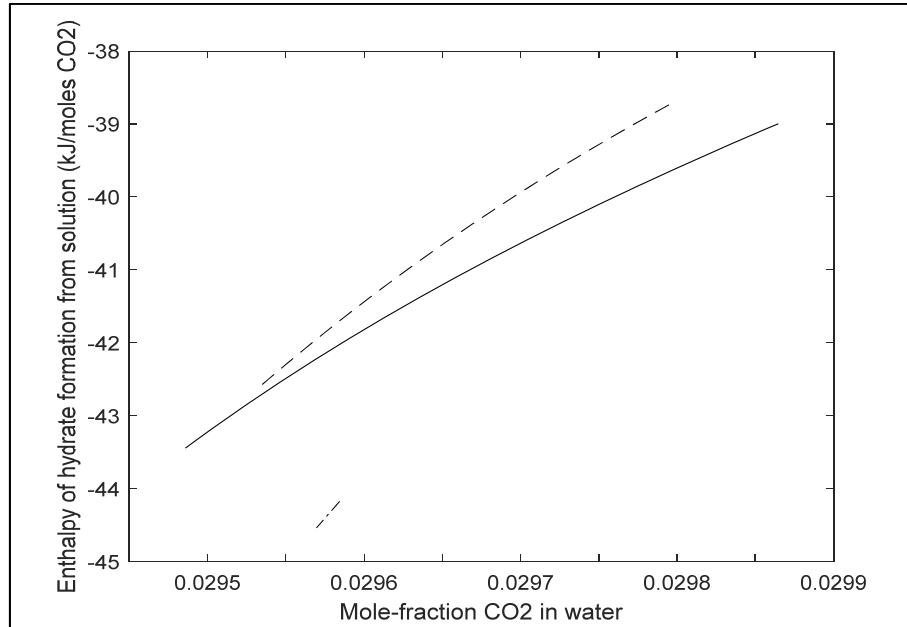
CO2 hydrate

Heat release from hydrate formation in liquid water is smaller because changes in guest enethalipes are limited

CO2 hydrate at three different T. Solid is for 273.16 K, dashed is for 278.16 K and dash-dot is for 283.16 K

CH4 hydrate at three different T. Solid is for 273.16 K, dashed is for 278.16 K and dash-dot is for 283.16 K

So how to get around these instantly (macroscale) forming films of CO2 hydrate?

- The key is to add something that keeps the CO2/water *interface hydrate free.*

- Any alcohol will up-concentrate on the interface between water and a non-polar (or slightly polar) phase.

- Methanol used as example here because it is well known experimentally and theoretically, so lots of information to compare with

- Example with CH4 used here because a methanol research activity was funded by a project. Qualitatively the effects with CO2 will be the same.
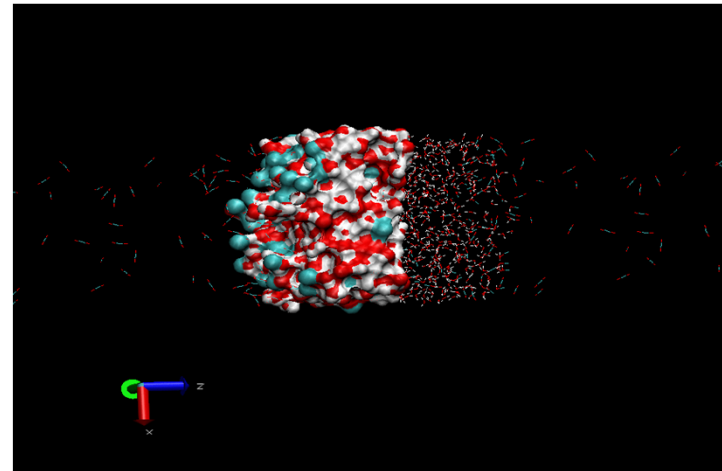
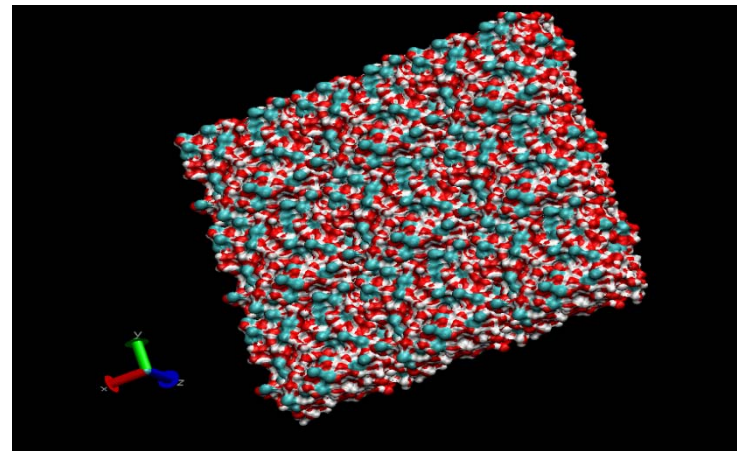*Liquid water slab exposed to CO2 at 83 bars and 276 K. CO2 phase to the right (but hard to see).*

Fairly thick (roughly 1.2 nm) and dynamic interface.

Supersaturation and dynamic mass and heat transport in the interface are important in nucleation

Presenting the details of the Molecular Dynamics simulation study will be far too time consuming here. I will be happy to distribute the original paper:
Bjørn Kvamme, Juri Selvåg, Navid Saeidi, Tatiana Kuznetsova, Methanol as a hydrate inhibitor and hydrate activator, Phys. Chem. Chem. Phys., 2018, 20, 21968

Methanol will upconcentrate on the interface and lead to:

Snapshot of Capillary waves on an interface between CO_2 and Water with methanol

- Hydrate free interface

- Fast transport of CO2 into the water interface

- Higher concentration of CO2 below the methanol enriched layer

- Very fast nucleation of hydrate particles below methanol

- Many hydrate particles formed per unit time leads to efficient growth and agglomeration/reformation to larger.

Diffusivities for bulk liquid can be calculated from the auto velocity correlation functions or mean square displacements

- For the interface transport we use Fick's law and sample fluxes across the interface and the concentration gardients across the interface

$$D_{CH_4}(z,t) = - \frac{J_{CH_4}(z,t)}{\left[\dfrac{\partial C_{CH_4}(z,t)}{\partial z} \right]}$$

Water/methane system

Sampled rate $3.7 \cdot 10^{-16} kg / s$

$$D_{CH_4} = (4.3 \pm 0.3) \times 10^{-8} cm^2/s$$
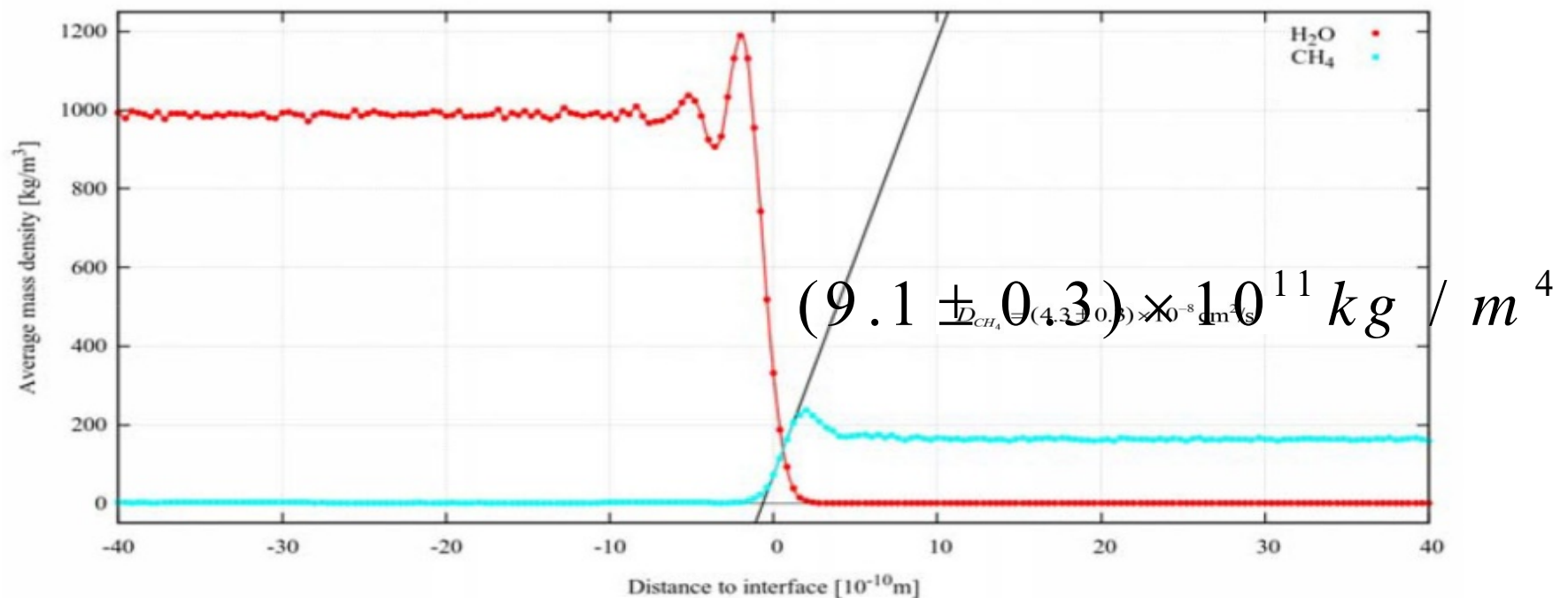

$$(9.1 \pm 0.3) \times 10^{11} kg / m^4$$

Figure 3. Density profile of H_2O and CH_4 in H_2O/CH_4 system after 10.0 ns, as function of the distance to the interface (negative and positive values represent the aqueous and gas phases respectively). Gradient of methane density at the interface is indicated by black tangent line.

Water/methanol (5%)/CH4

Sampled rate $4.9 \cdot 10^{-16} \, kg \, / \, s$

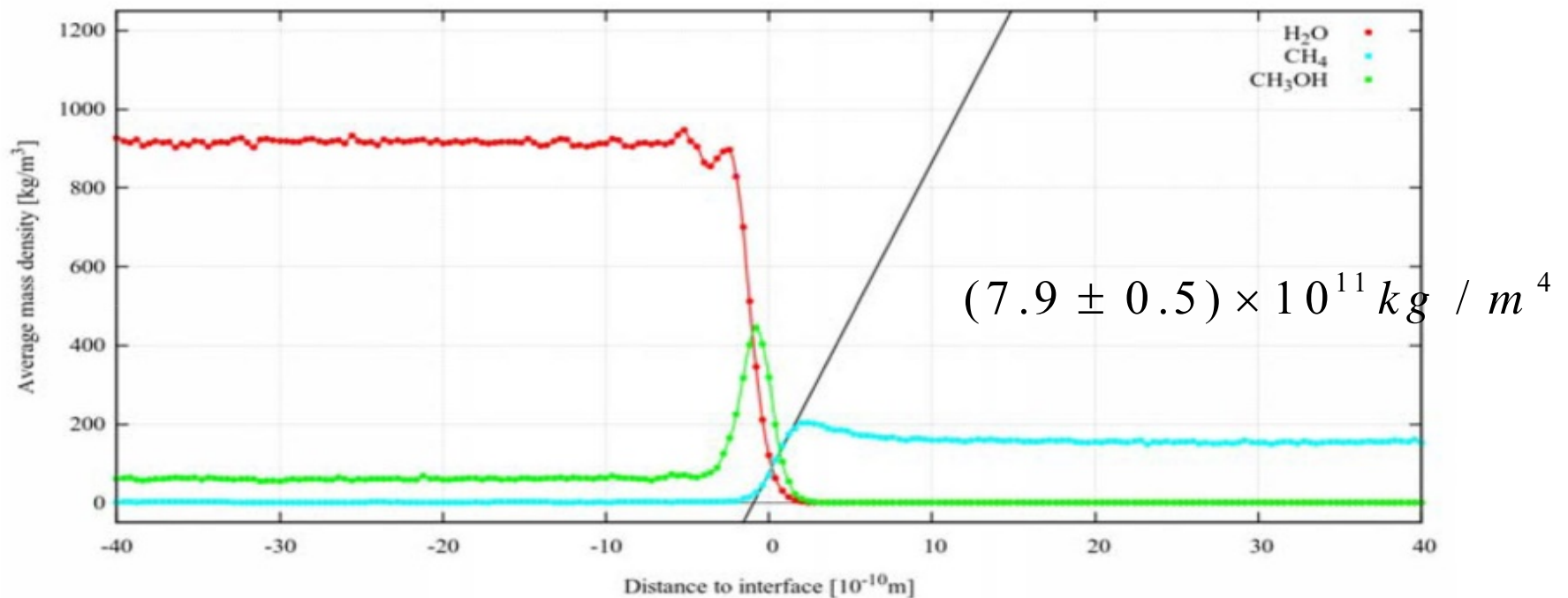$$D_{CH_4} = (6.2 \pm 0.4) \times 10^{-8} \, \text{cm}^2/\text{s}$$

$$(7.9 \pm 0.5) \times 10^{11} \, kg \, / \, m^4$$

Figure 4. Density profile of H_2O, CH_4 and CH_3OH in $H_2O/CH_4/CH_3OH$ system after 10.0 ns, as function of the distance to the interface (negative and positive values represent the aqueous and gas phases respectively). Gradient of methane density at the interface is indicated by black tangent line.

A few snapshots for CO2 with N-Acetyl Morpholine (NAM) as surface active substance

- Selvåg, J., Kuznetsova, T., Kvamme, B., *Molecular Dynamics Study of Morpholines at Water - Carbon Dioxide Interfaces,* FPE, [Volume 485](#), 15 April 2019, Pages 44-60

- Selvåg, J., Kuznetsova, T., Kvamme, B., *Molecular dynamics study of surfactant-modified water–carbon dioxide systems,* Molecular Simulation, 2018, Volume 44, 128-136

- NAM is not by itself interesting because it is too ***expensive*** and ***not environmentally*** friendly

- But this class of CO2/water surface active components do have some very interesting features which makes them serve as ***reference components*** (performance) in search for ***low MW natural components (low price, environmental friendly***
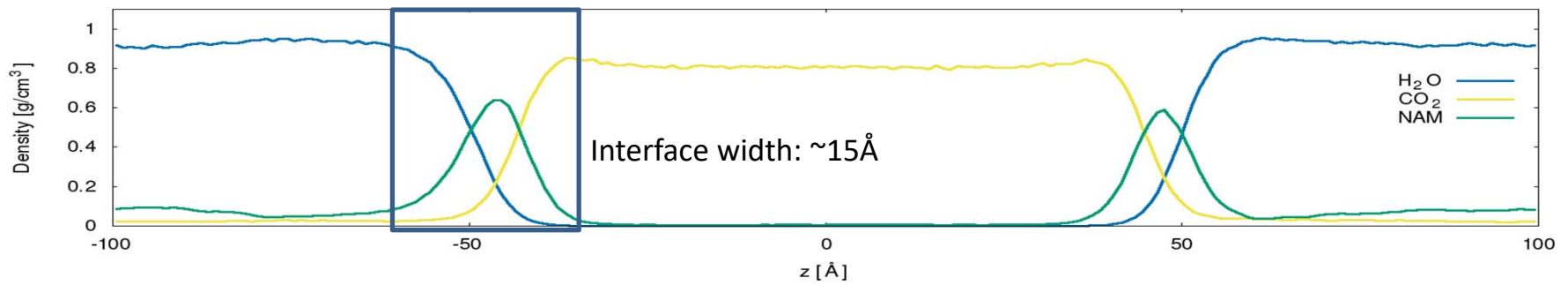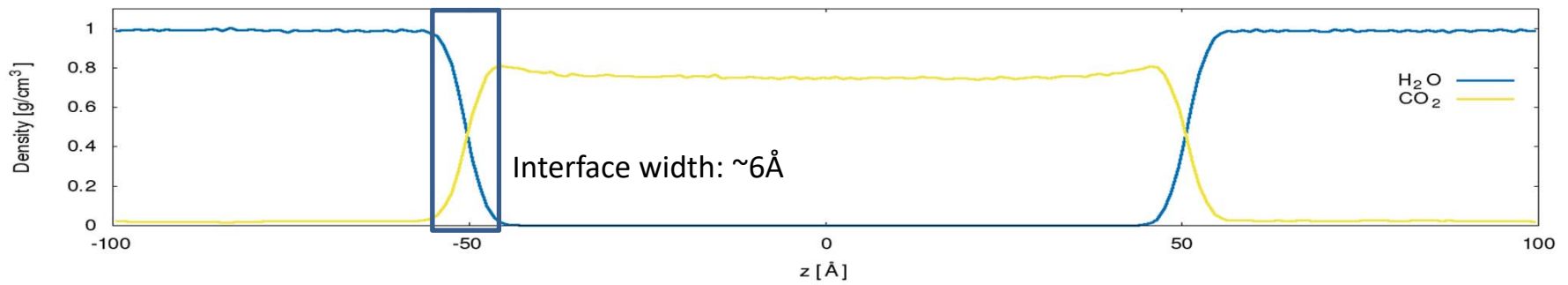
Binary H$_2$O/CO$_2$ System
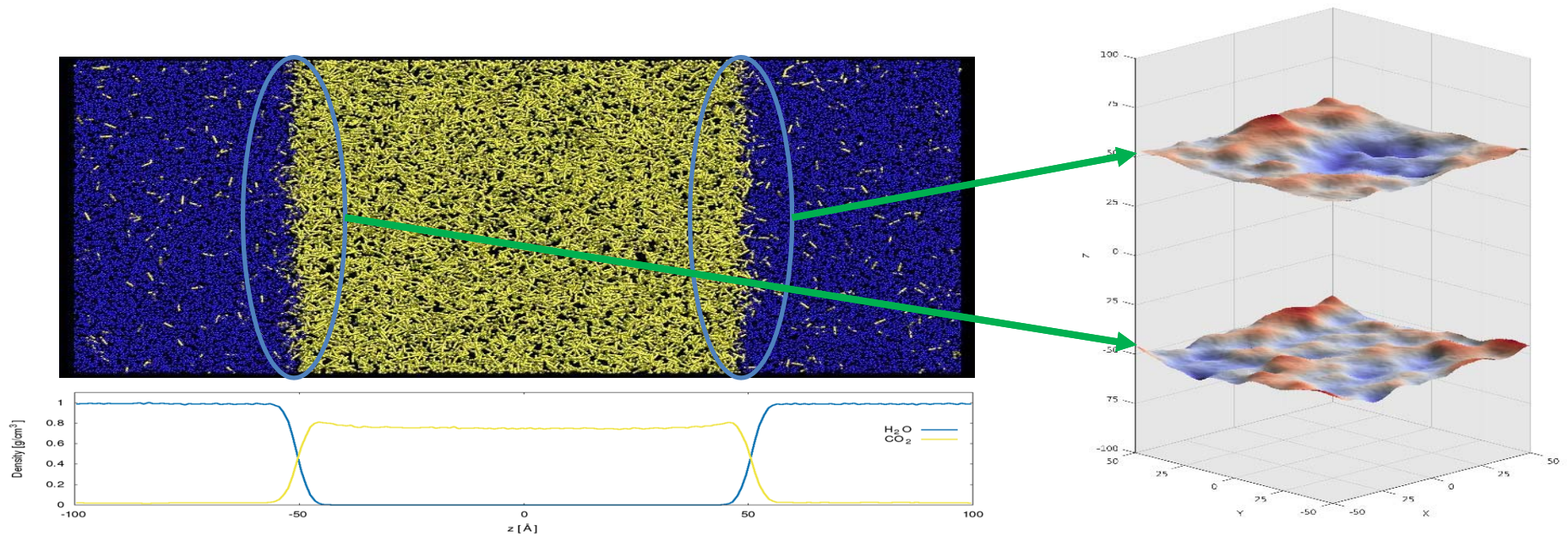
H$_2$O/CO$_2$+NAM System
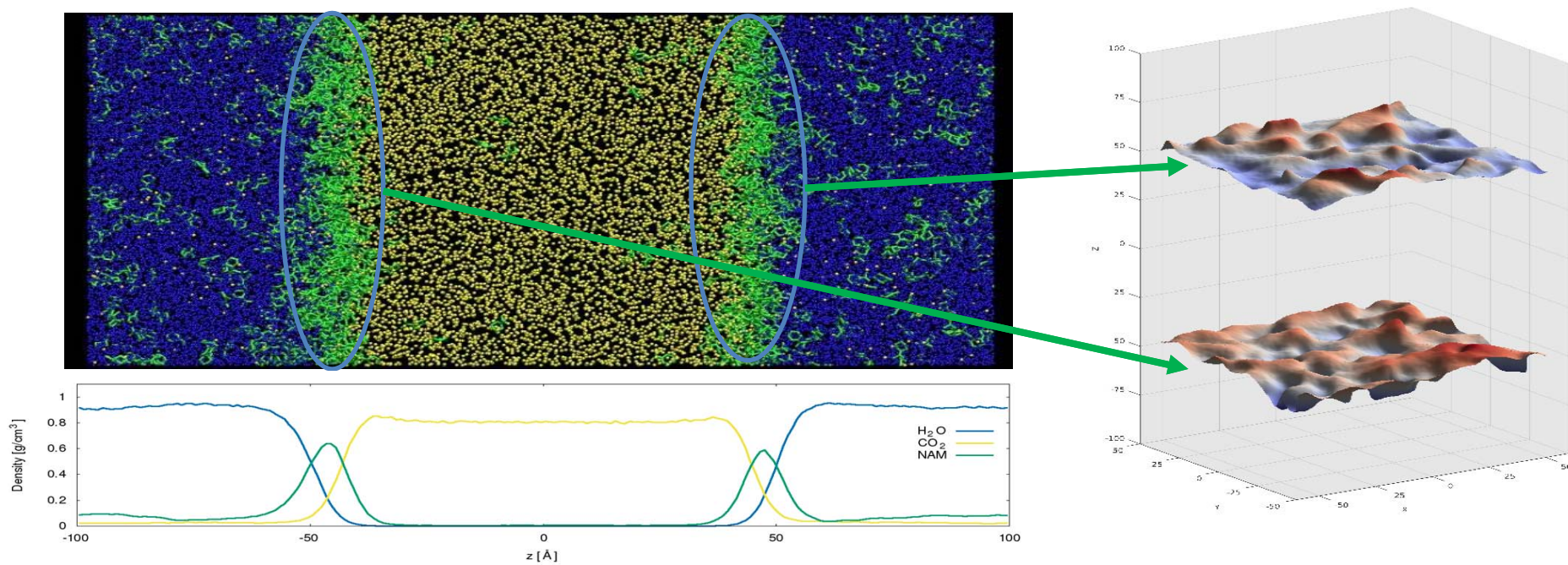
H$_2$O/CO$_2$ vs H$_2$O/CO$_2$+NAM

Summary

- The *use of CO2* for combined safe CO2 storage and release of in situ CH4 from hydrate is frequently very *misunderstood*

- It is actually *one of the fastest mechanisms* for producing hydrate because CO2 hydrate forms instantly and releases heat, BUT *formed hydrate films blocks* the pores *unless surface active chemicals are added* in small amounts

- Since only a very limited pressure difference between injection well(s) and producing wells is needed there are likely very *limited sand* production and *water* production

- And since the mechanism goes through formation of a *new CO2 dominated hydrate* from injection gas, in front of the CH4 hydrate, it is not expected that significant amounts of CO2 should end up in the produced gas

Ignik Sikumi pilot
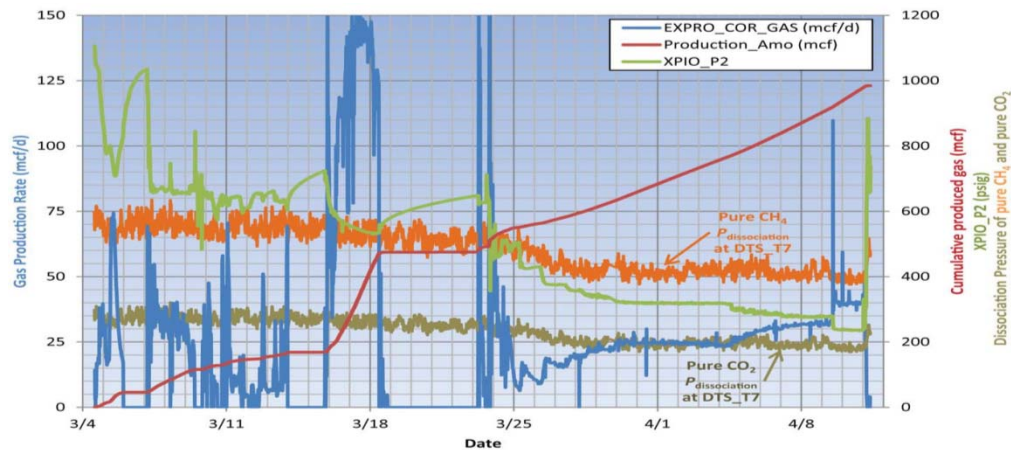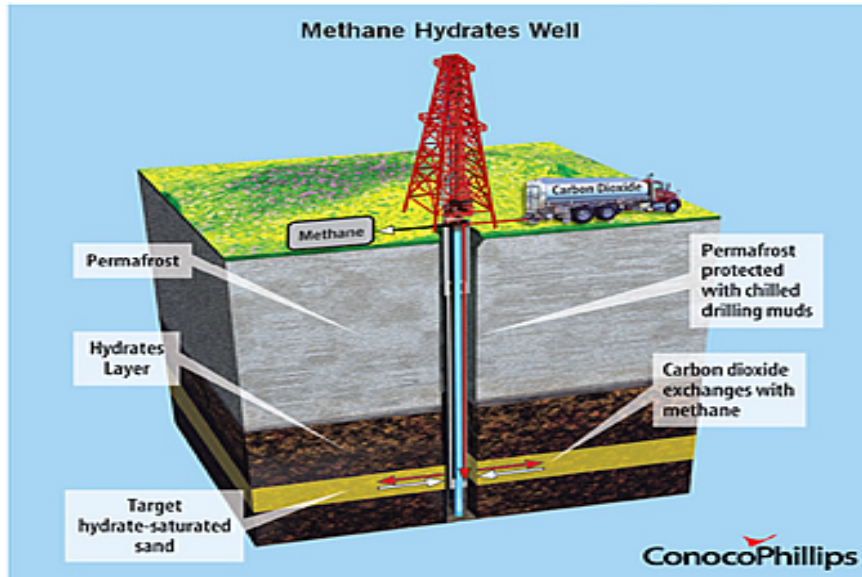
- 22.5 per cent by volume CO2 in N2

- «Huff and puff», with sampled accumulated released gas in solid red curve below

- CO2 will distribute as dissolved in groundwater, adsorbed and potentially limited amounts of injected CO2 converted to hydrate but thermodynamic benefits very limited for these dilute mixtures (see next overhead)
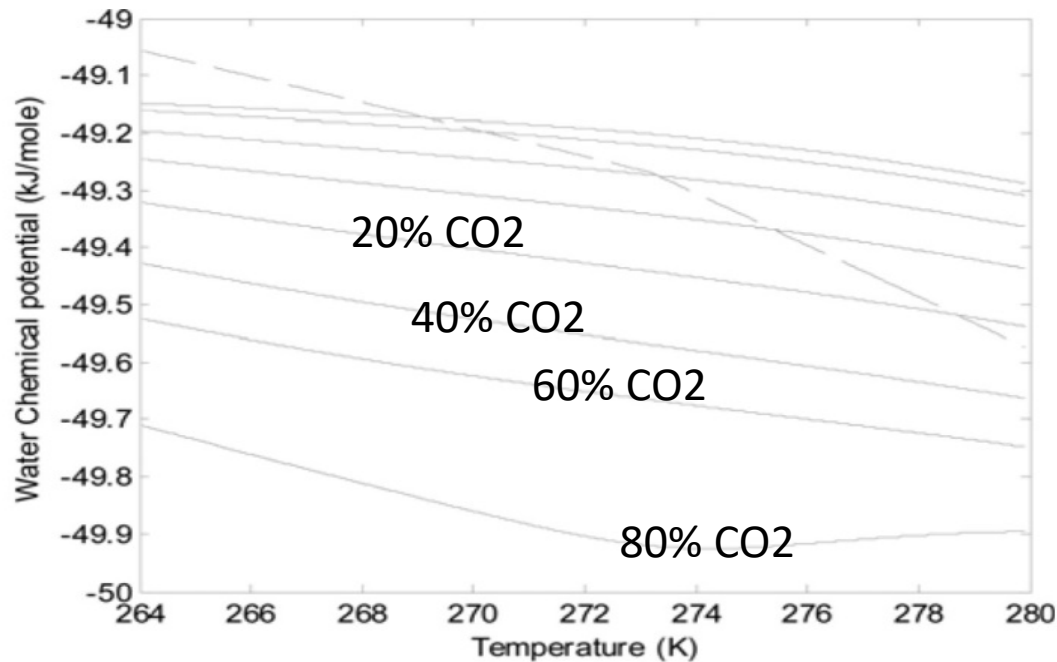
Limits for hydrate formation

Figure 7. Estimated water chemical potential in hydrate (solid) and liquid water (dash) as a function of temperature for 85 bar and CO_2 mole-fractions of 0.80, 0.6, 0.4, 0.2, 0.1, 0.05, 0.02, 0.01, with 0.80 mol-fraction curve lowest and 0.01 mol-fraction curve on top.

Chemical potential for *water (solid) in hydrate* must to be *lower than liquid water chemical* potential (dashed) for the formation of a new CO2 dominated hydrate.

This is the only feasible mechanism for CO2/CH4 swap:

- *CO2* makes a *new hydrate*

- *Associated heat* assist in *dissociating in situ hydrate*

But CO2 dissolves in water, adsorbs on minerals and potentially makes a small amount of new hydrate but not enough to be responsible for the results

Conclusions

The only feasible mechanism for CO_2/CH_4 hydrate exchange goes through formation of a new CO_2 dominated hydrate

Addition of limited amounts of N_2 is feasible, but small amounts of CO_2/water surface active component i the key

Injection of flue gas may not facilitate formation of new CO_2 hydrate but selective chemicals can assist

The snapshots to the right is just an example case for CO_2 injection into CH_4 hydrate using our hydrate reservoir simulator RCB Hydrate. No details given but a thesis with papers can be handed out
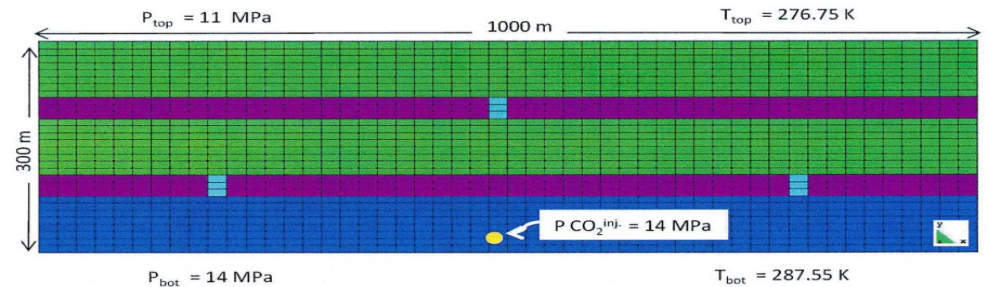

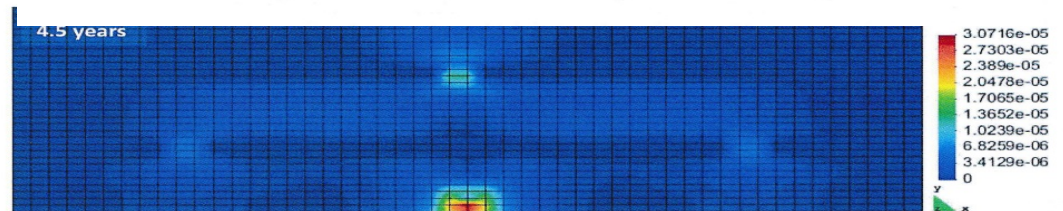Figure 1—The reservoir model with one injection well within the aquifer.

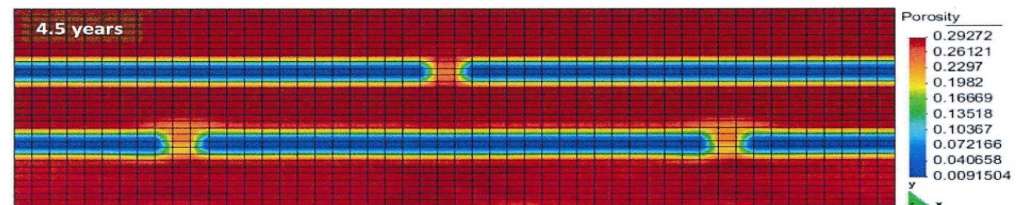Figure 2—CO2 gas flux after 4.5 years of CO2 injection.

Figure 3—Porosity started to decrease as a result of hydrate formation after CO2 has reached to the CH4 hydrate layers, where the CO2 hydrate formation condition is suitable, results after 4.5 years of CO2 injection.
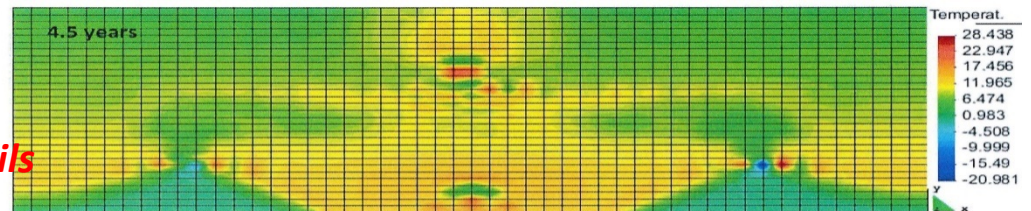
Figure 4—Temperature changes as a result of CO2 hydrate formation after 4.5 years of CO2 injection.

Acknowledgements

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