Etude par video-microscopie haute résolution de la formation et dissociation d'hydrates de cyclopentane

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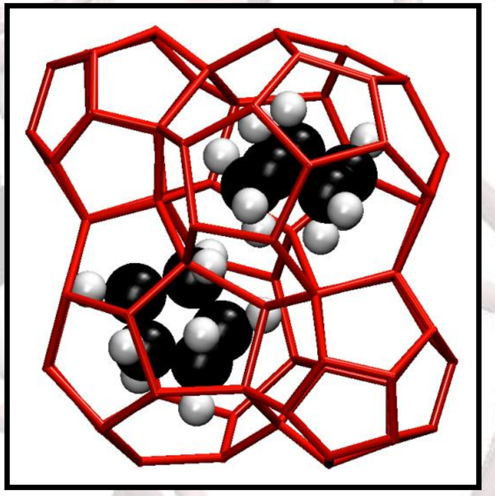
Journée HYDRATES de la SFT, 22 janvier 2016

Why cyclopentane (CP) hydrates?

Structure II

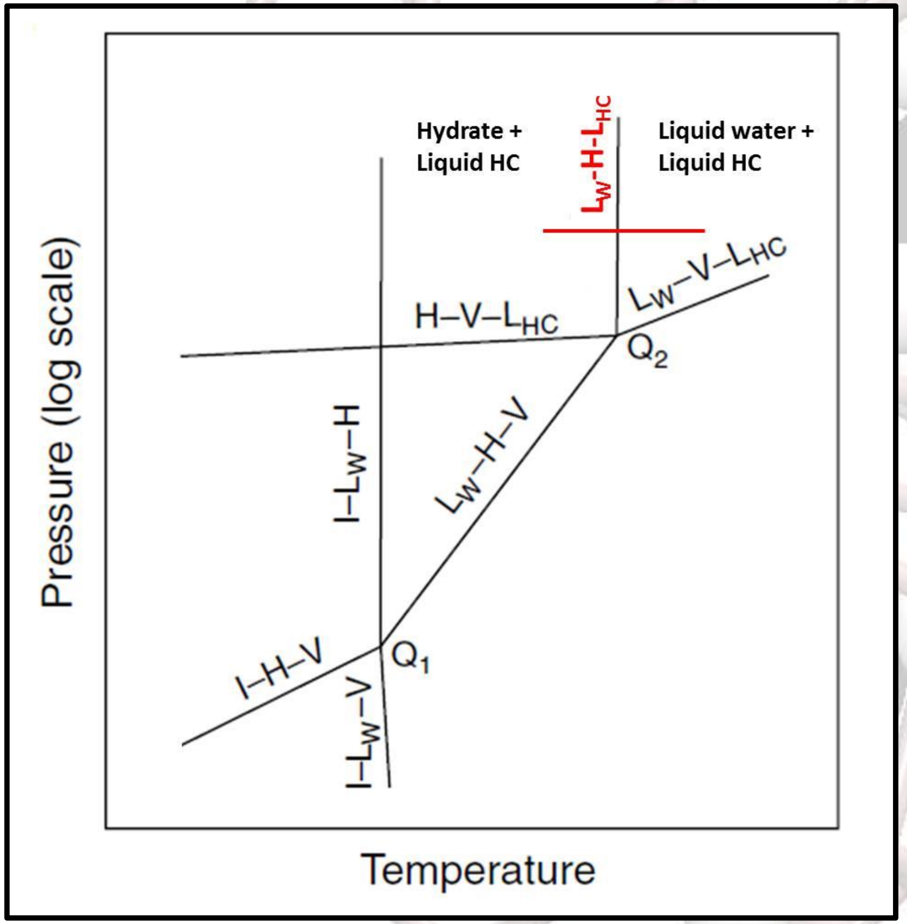


- 8 big cavities filled with CP.
- 16 small cavities: empty or small gas molecules.
- 136 H_2O molecules.

Importance:

- ✓ **Model** of natural gas hydrates (sII).
- ✓ Strongly similar phenomenology.
- ✓ T = 0 - 7°C, **P = 1bar.**
- ✓ **Well characterized:** calorimetry, spectroscopy, etc.

Phase diagramme



P-T diagram of HC-water hydrate with upper quadruple point.
Sloan and Koh, 2008

- This study: around the triple line **L_W-H-L_{HC}**
- P = constant, **T variable**
- 2 interfaces:
  - ✓ **Liquid water + Liquid CP**
  - ✓ **Hydrate – Liquid CP**

Investigations at sub-micron resolution of cyclopentane hydrate growth and melting:

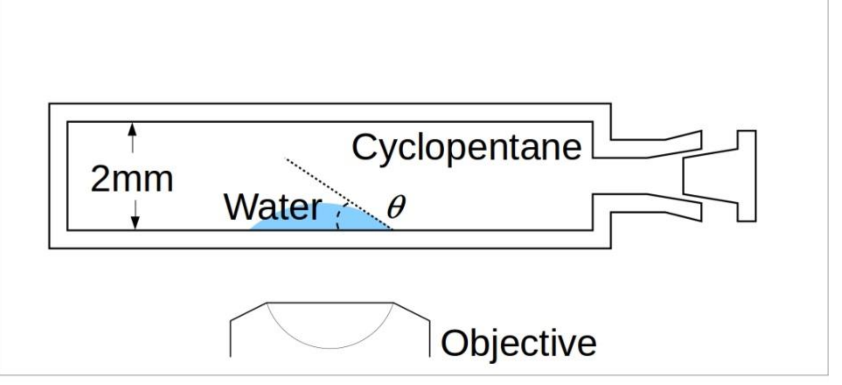
1) along water/guest interfaces

2) along a mineral substrate immersed in the guest from a 'reservoir' of water

3) in the bulk of the water phase (where guest molecules are present as an emulsion)

complex processes governed by coupled heat and mass transfers

The experimental system:



Why microscopy?

- HYDRATES WELL CHARACTERIZED:

-Crystallography
-Thermodynamics
-Macroscopic/phenomenological description of nucleation, growth, inhibitors, promoters,...

- **OPEN QUESTIONS:**

-Nearly all details (on µm scale)
-Origin of memory effect (related to emulsion)
-Interactions with the substrate

MICROSCOPY OFFERS:

High resolution

Choice of contrast modes

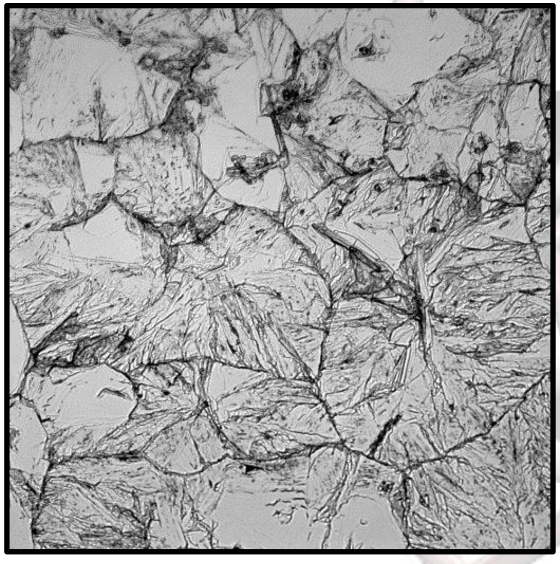
Novel for hydrate research

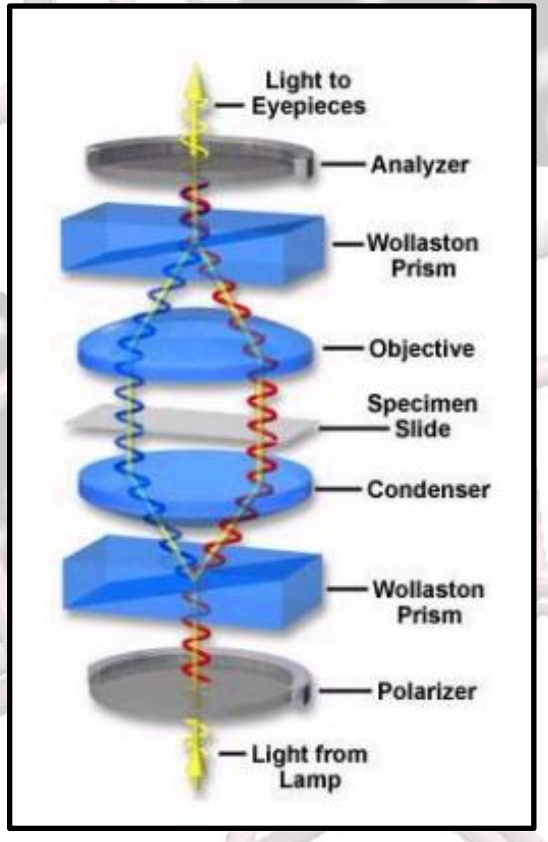
Microscopy - DIC

Differential Interference Contrast

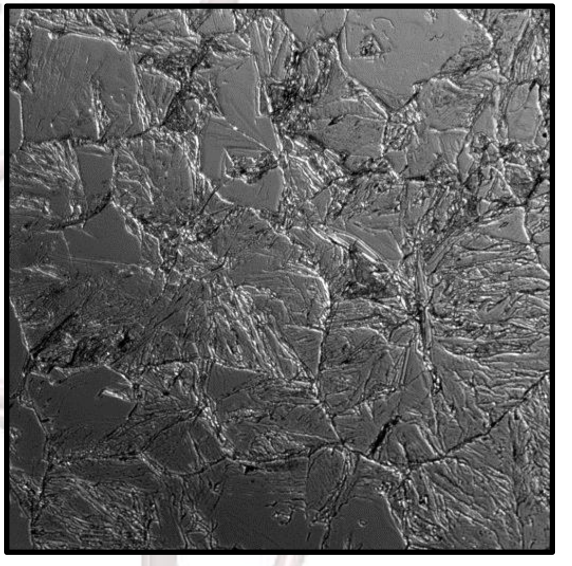
exibits variation of refractive index and thickness

Transmission



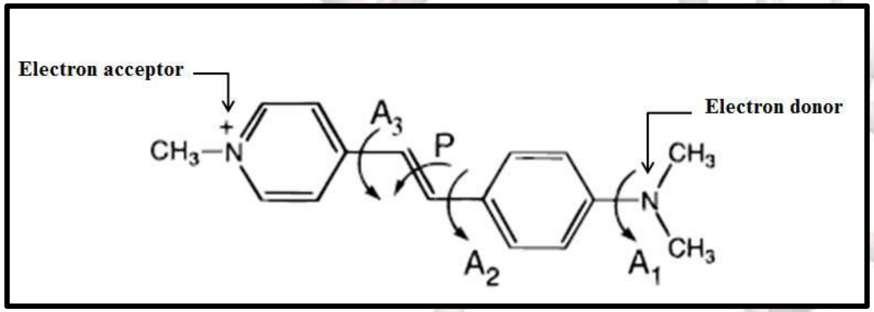


DIC

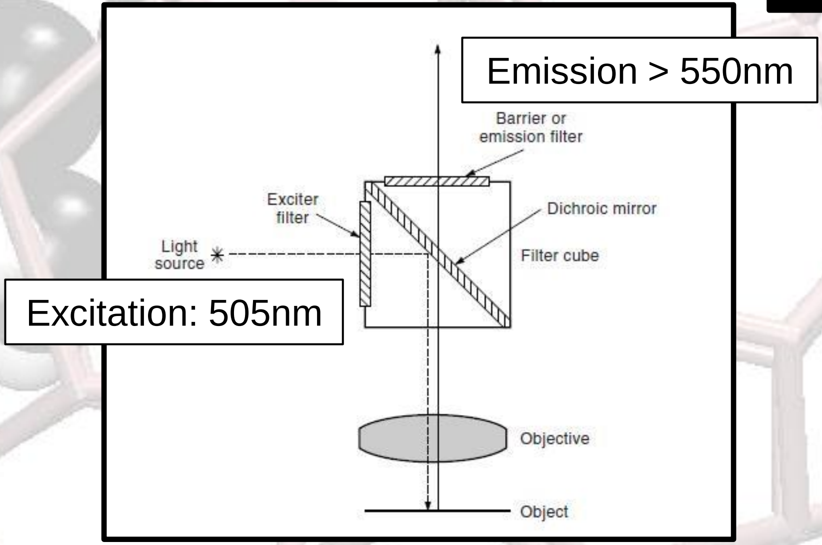


Microscopy - Fluorescence

DASPI reveals interfaces

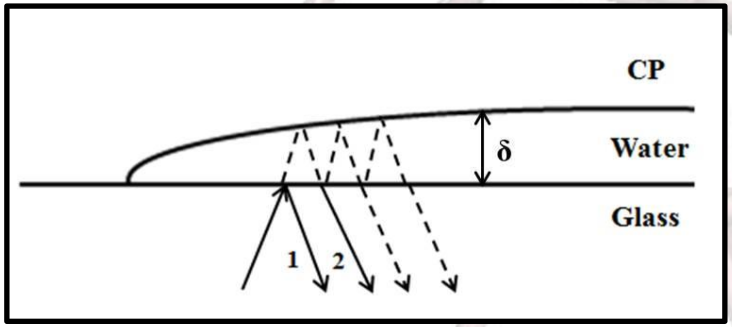


Filter cube

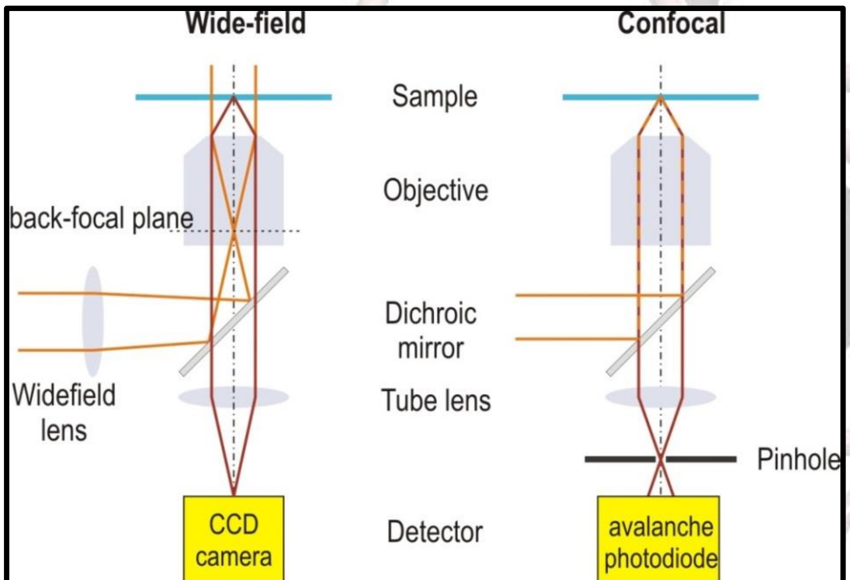


Microscopy - Confocal reflectance

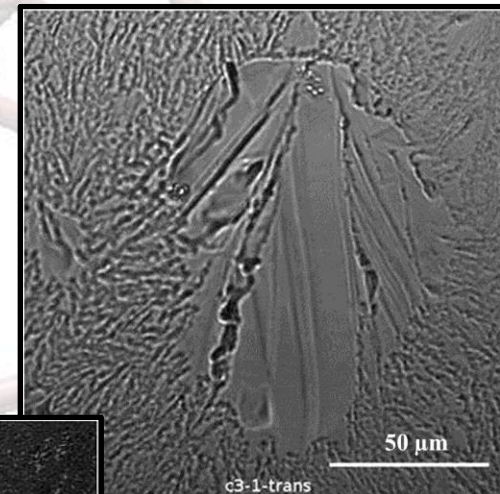
Interference of light



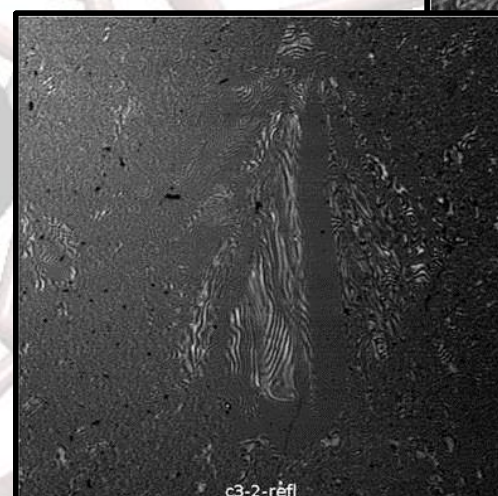
$$\Delta h = \frac{\lambda}{2n_W} = 200\ nm$$



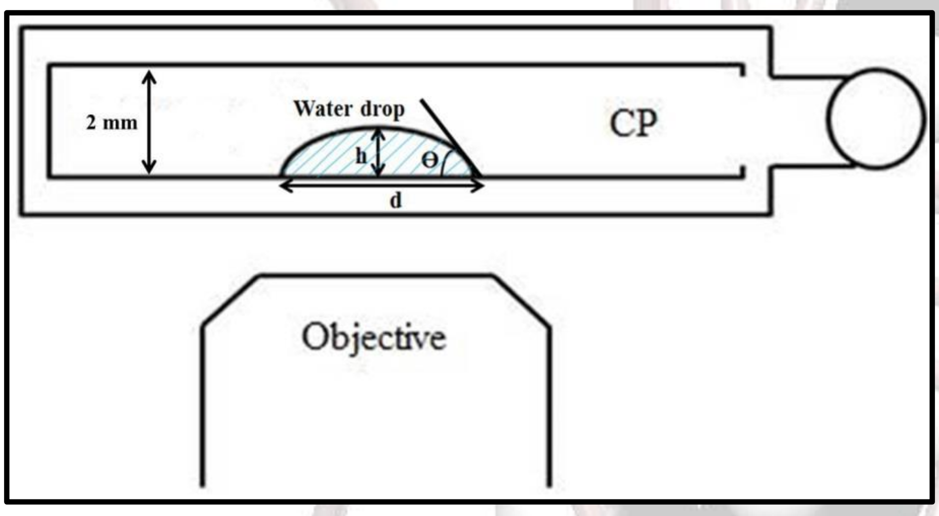
Transmission



Confocal reflectance

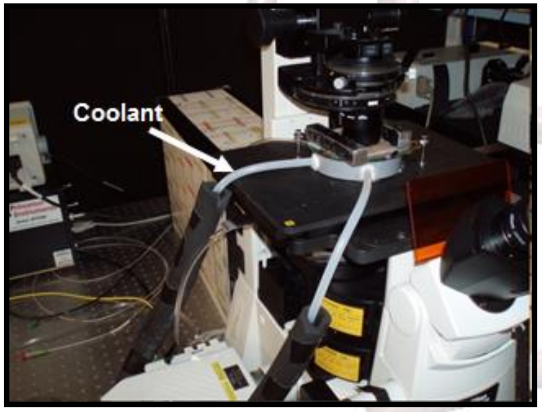


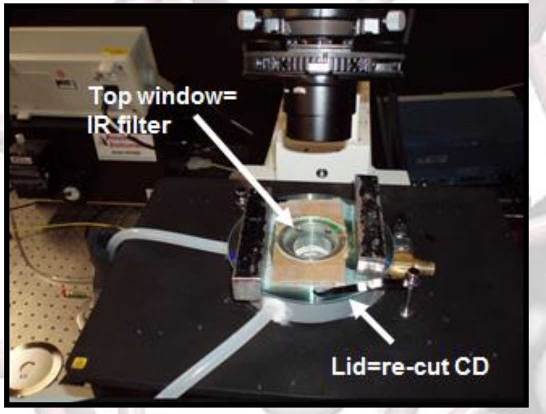
Experimental setup - Principle

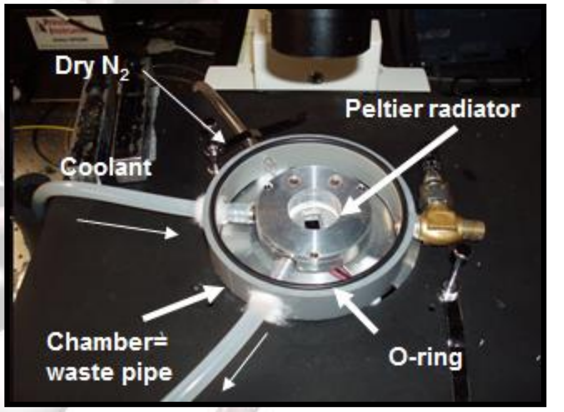


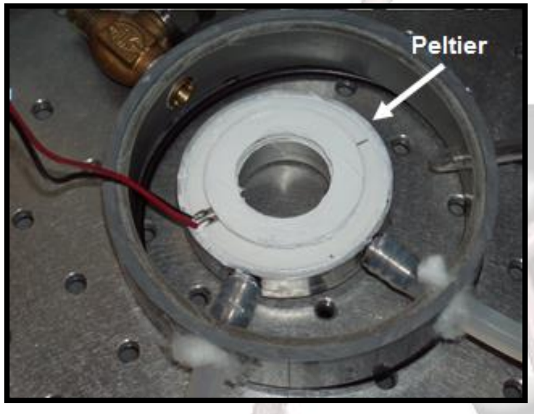
2mm Hellma cell, inside the cell holder

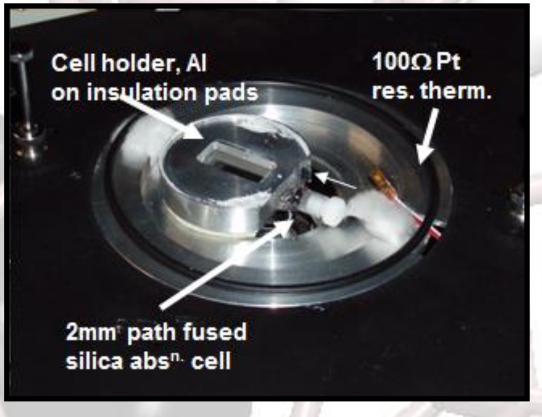
Experimental setup - Reality

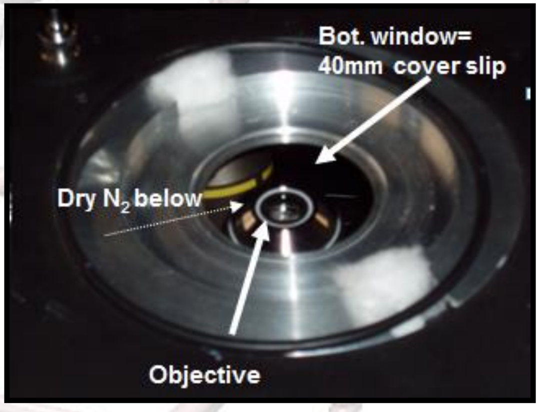












Difficulties

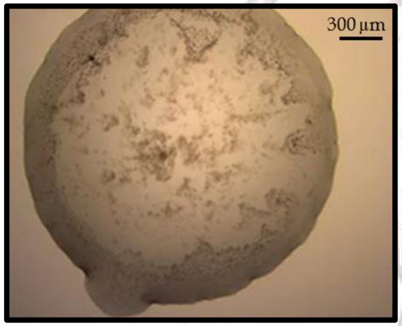
- Prevent local heating
- Prevent condensation
- Thick cell walls (1.2mm) => aberrations

Solutions

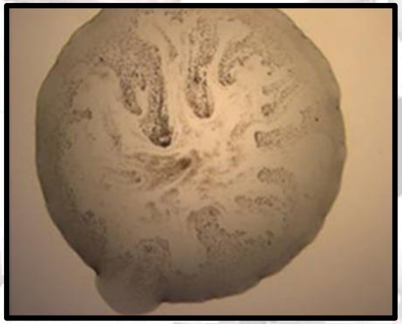
=> IR filter
=> dry N_2 flow inside and outside
=> aberration correcting objective

Nucleation sites

Nucleation in the emulsion

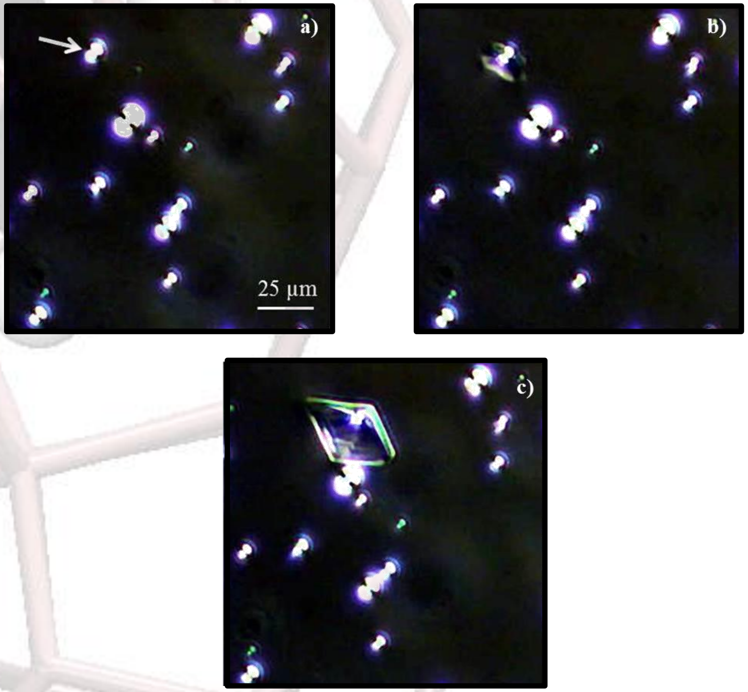


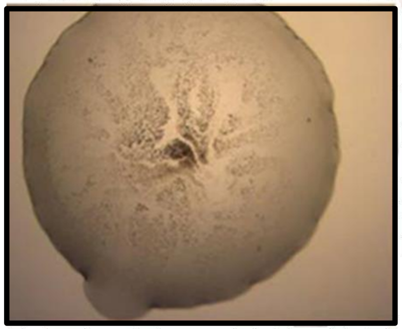
Complete dissociation of hydrate (t_0), T = 8°C



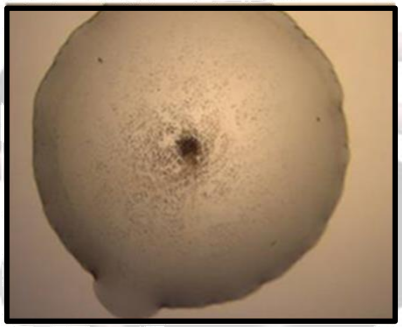
Emulsion moving towards the center
t_0 + 3 min, T = 8°C

↓T



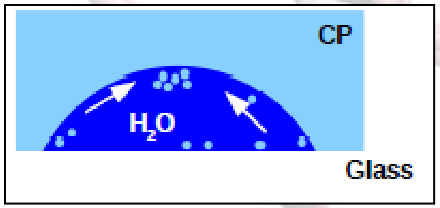


Emulsion moving towards the center
t_0 + 7.5 min, T = 8°C



Emulsion in the center
t_0 + 12 min, T = 8°C

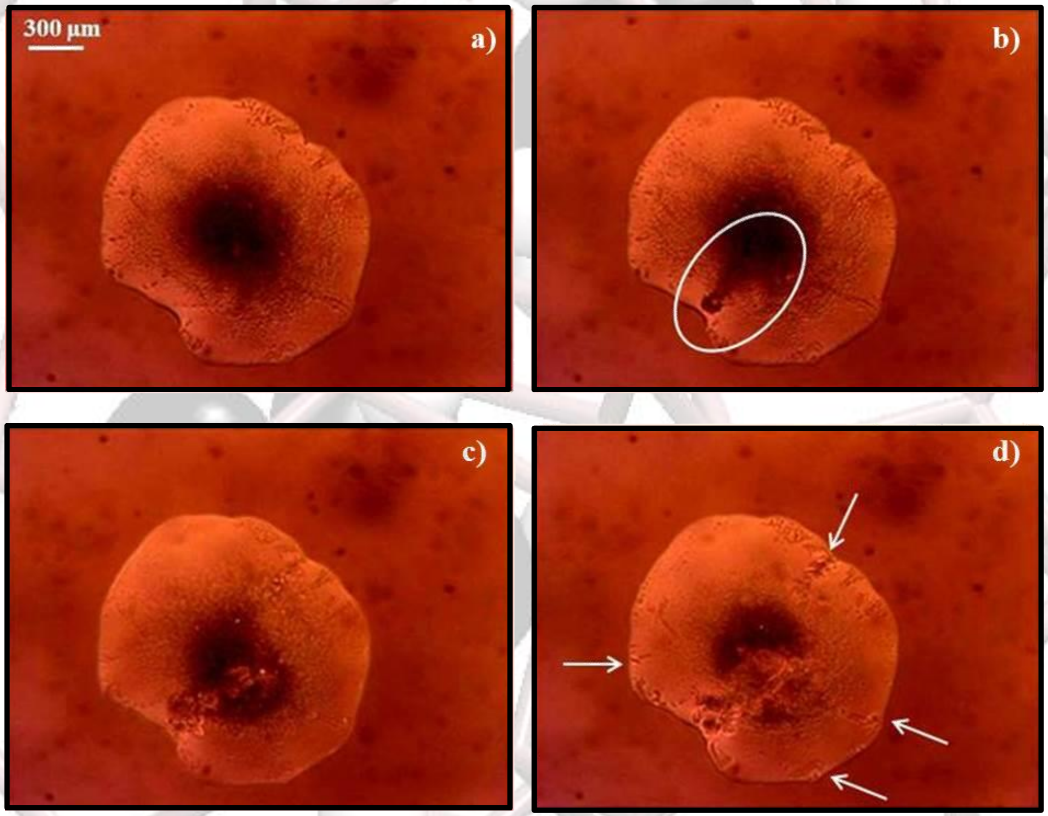
CP droplets (from the dissociation) in water



Water/CP interfaces: optimum host-guest ratio

Nucleation sites

Growing crystals are drawn to the contact line

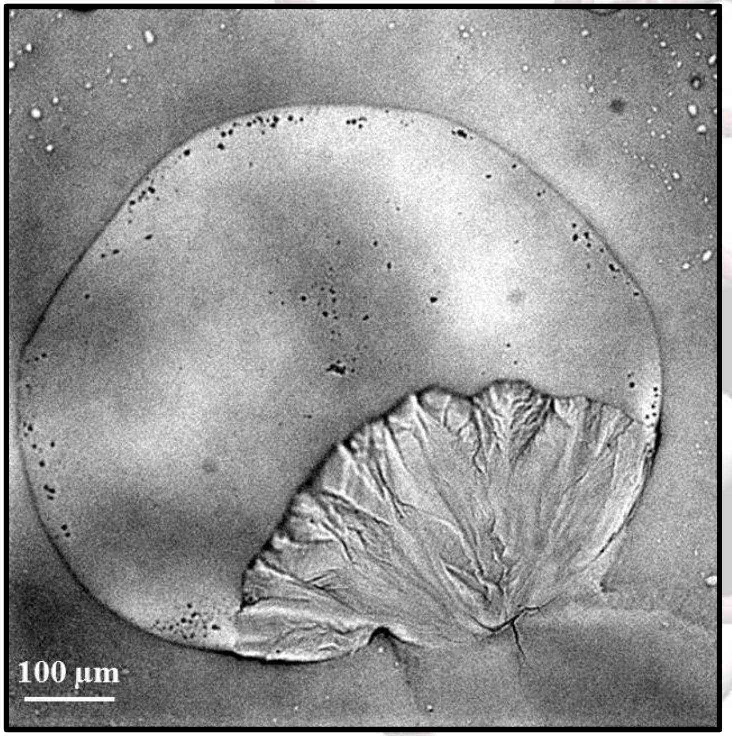


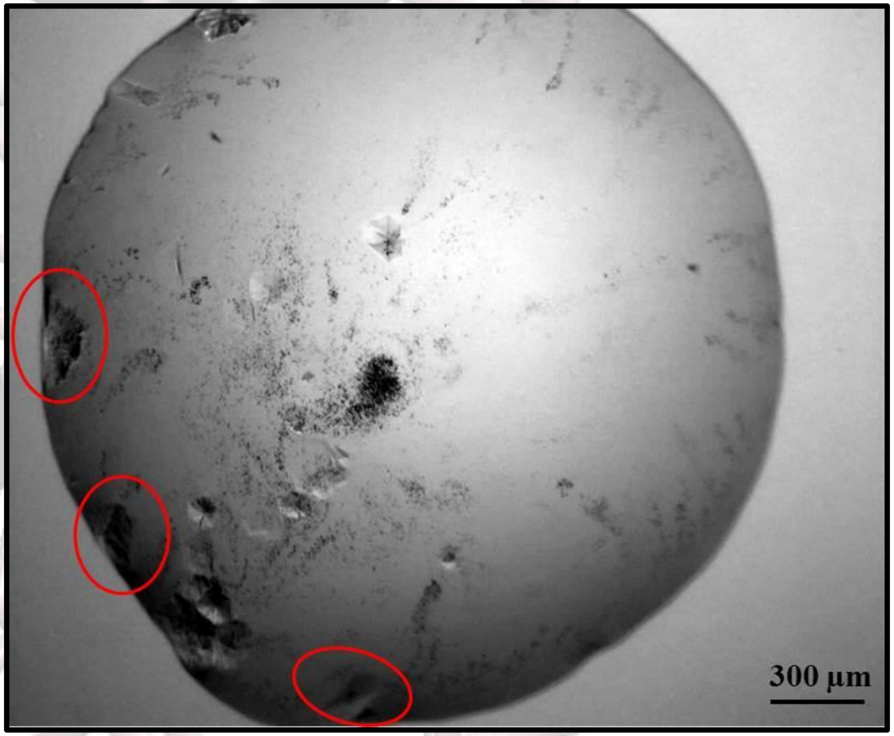
a) t_0, b) t_0 + 8 s, c) t_0 + 68 s, d) t_0 + 264 s

Nucleation sites

Nucleation at the triple line

Crystal replaces three interfaces by one

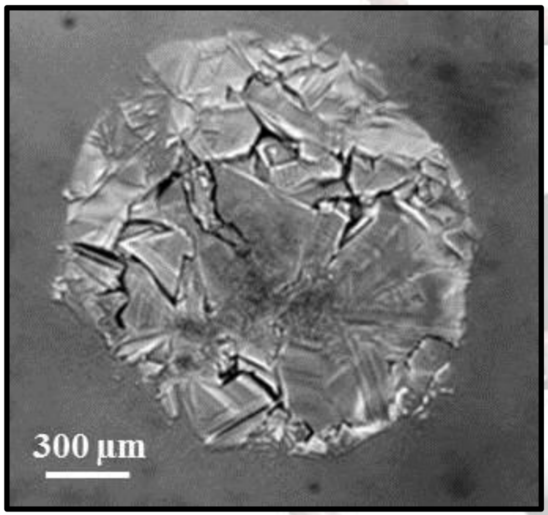




Hydrate growth and morphology

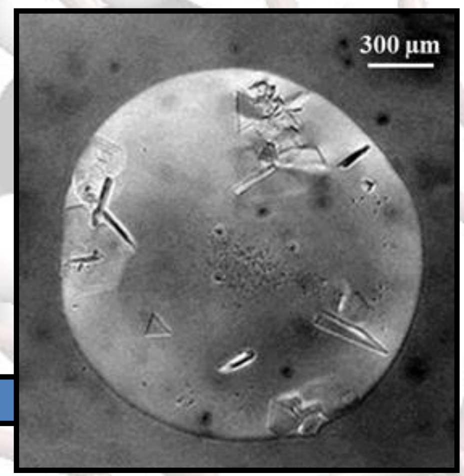
Low subcooling experiments
$\Delta T_{sub} < 3.4°C$
Growth velocity **~0.05-0.1 mm^2/min**

ΔT_{sub} = 3.4°C

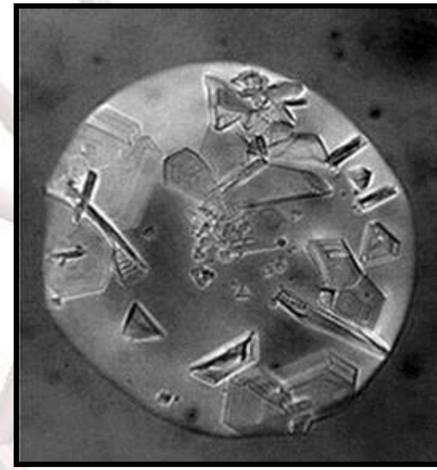


t_0 + 20 minutes

ΔT_{sub} = 1.6°C

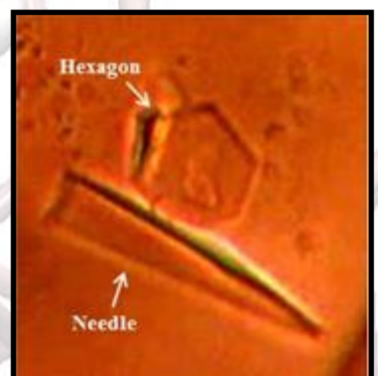


t_0 + 33 minutes



t_0 + 45 minutes

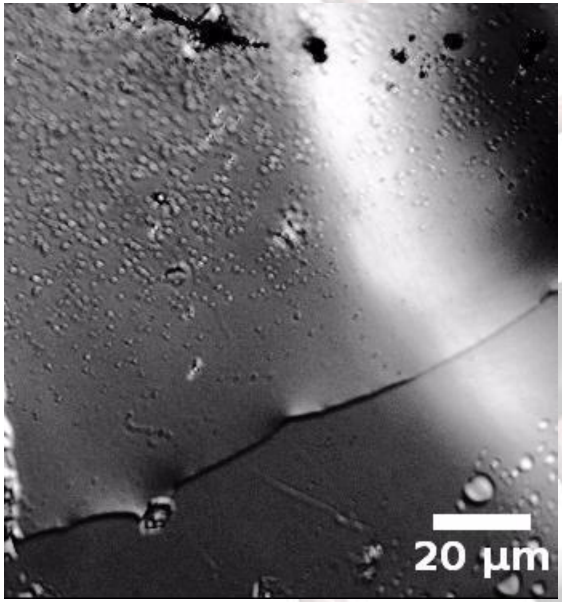
Polygonal and needle crystals

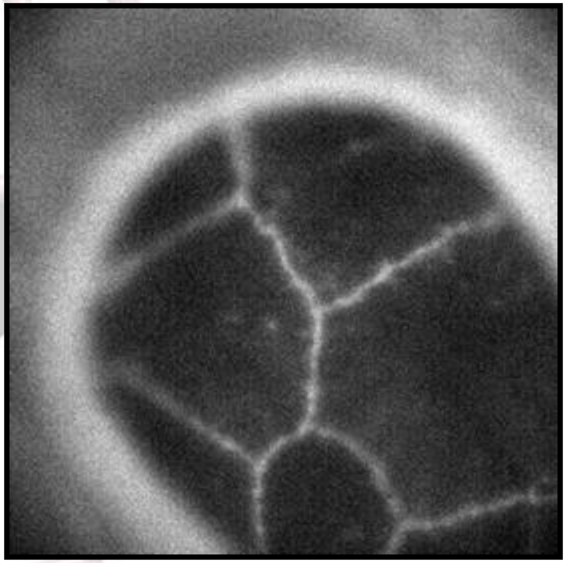


Hydrate growth and morphology

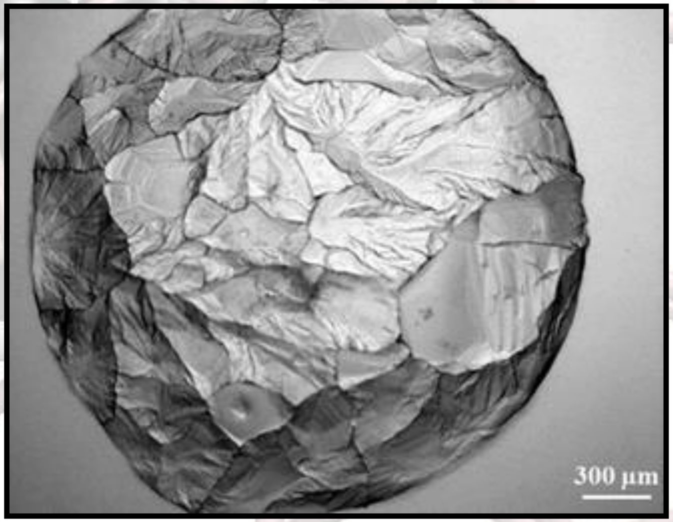
High subcooling experiments
$\Delta T_{sub} > 3.4°C$
Growth velocity **~1-1.5 mm²/min**

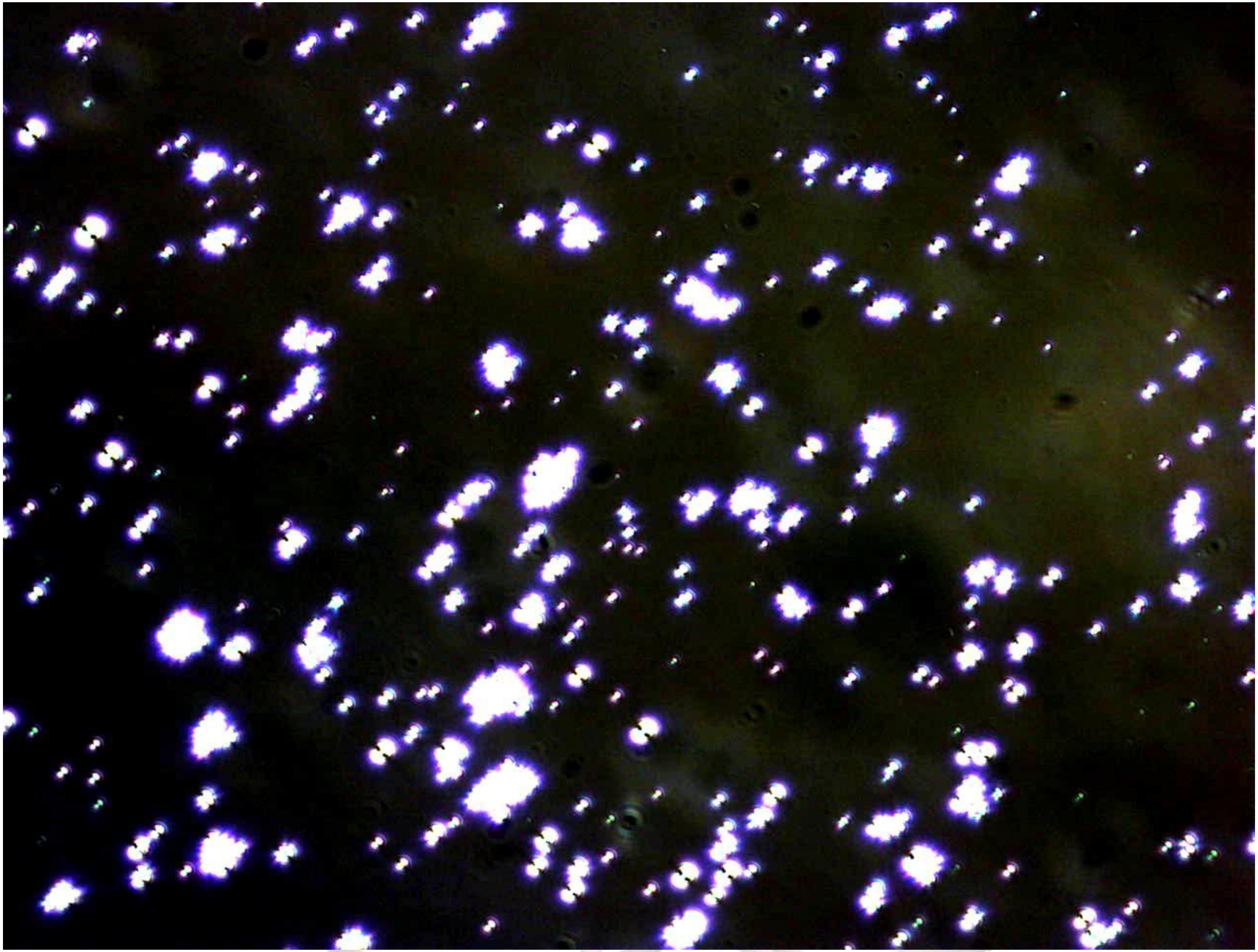
ΔT_{sub} = 7°C





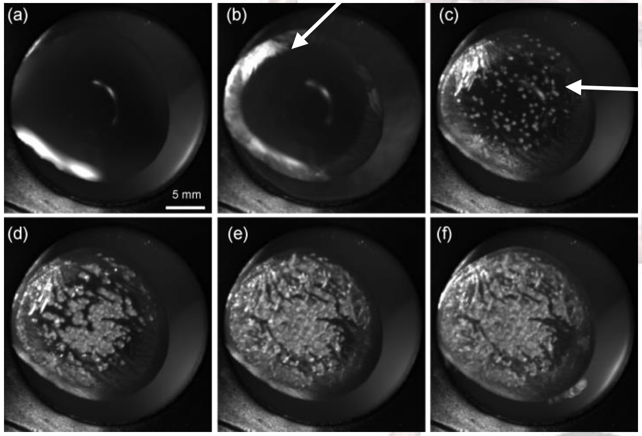
Mosaic of hydrate plates from polynucleation



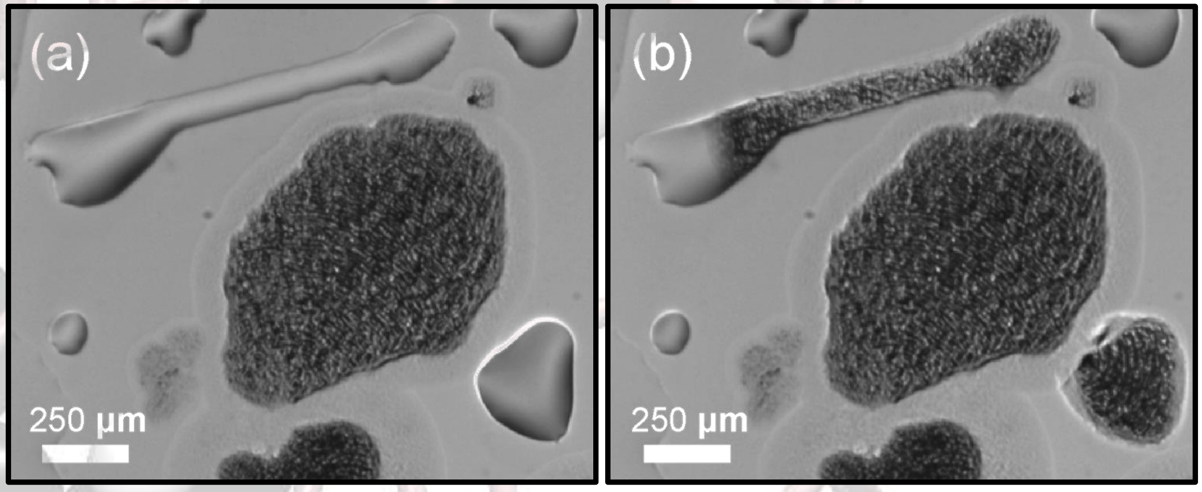


Hydrate and the mineral substrate

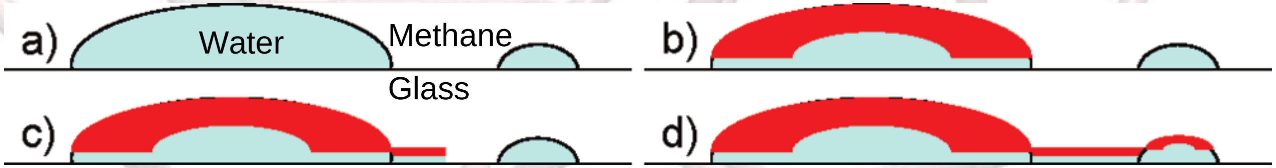
NUCLEATION AT 3-LINE



NUCLEATION AT CH_4-LIQ. INTERFACE



Morphological investigation of methane-hydrate films formed on a glass surface
Juan G. Beltrán & Phillip Servio
Cryst. Growth. Des. **10** (2010) 4339-4347



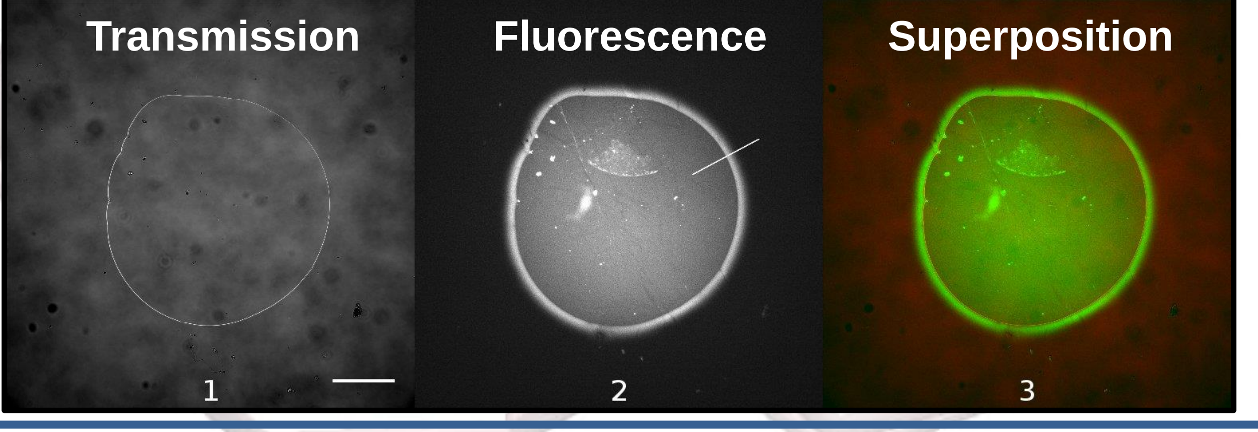
Water source - Precursor water film

Strongly hydrophilic (freshly plasma-treated) glass

Beginning of the experiment

- Water drop + 2· 10^{-6} M DASPI (water-soluble fluorescent)
- Contact angle θ ≈ 1° $\tan(\theta) = \frac{d \cdot h}{\left(\frac{d}{2}\right)^2 - h^2}$

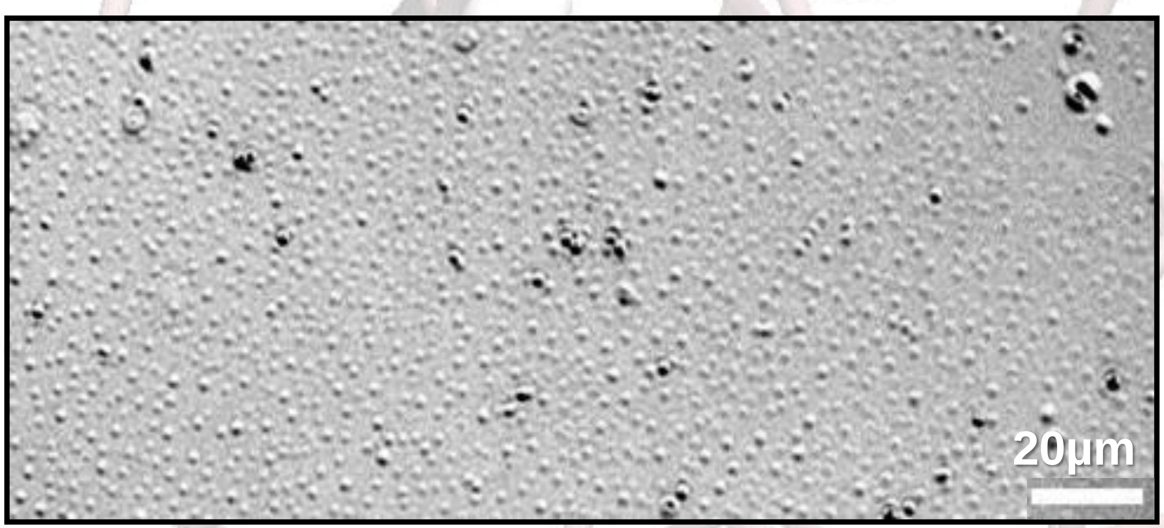
Strongly fluorescent ring (width ≈ 50 µm) outside the contact line => **thin (precursor) film** on the substrate (expected for a system exhibiting pseudo-partial wetting).



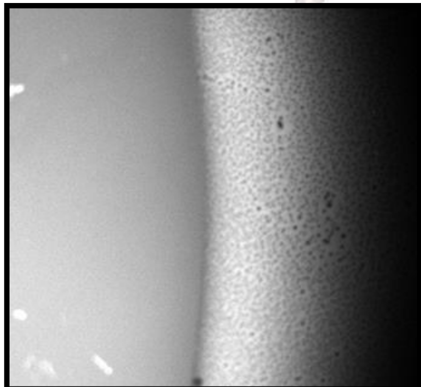
Water source - 'Breath figure' droplets

Cooling down to ~ -15°C

- CP-rich phase becomes cloudy. Strong decrease of solubility in CP => Rain droplets.
- Microdroplets form **'breath figures'** on the substrate. They coexist with the precursor film.

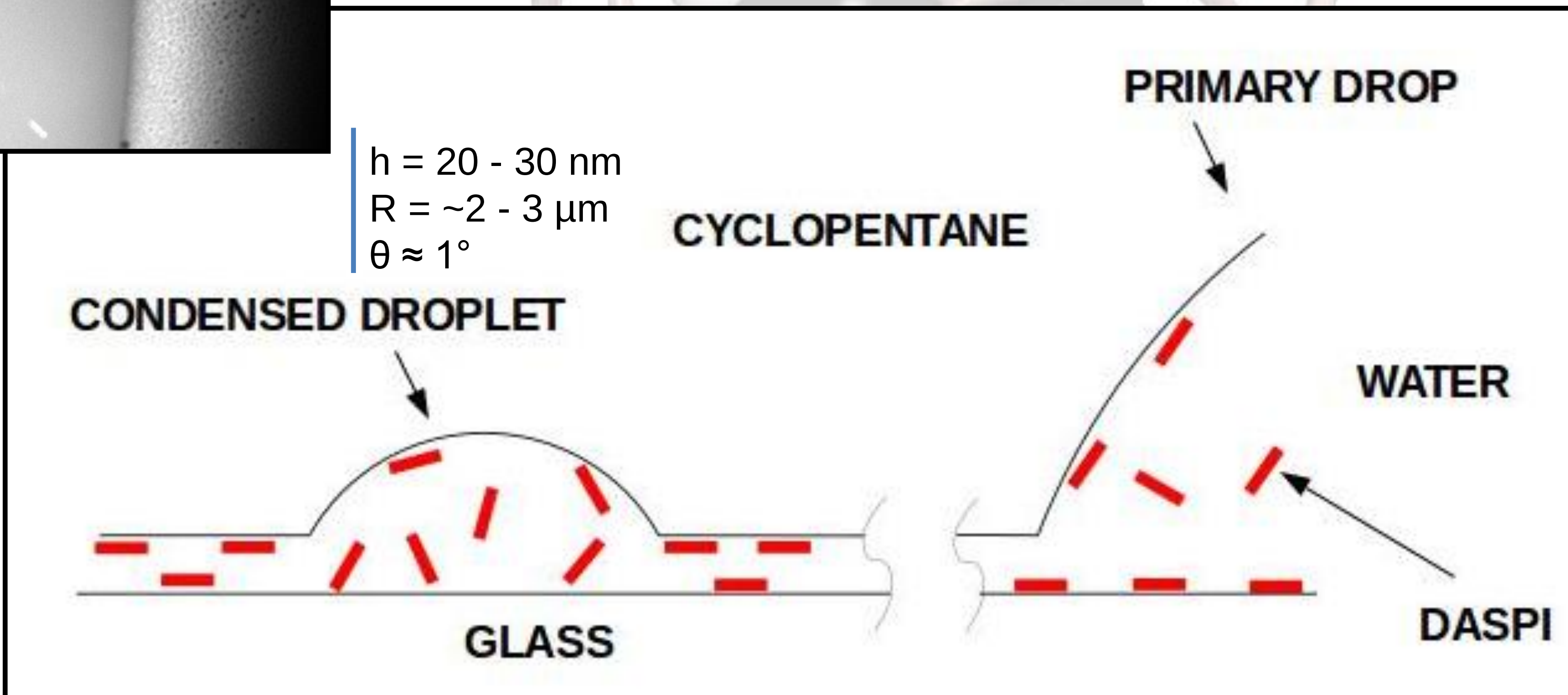


Physical picture



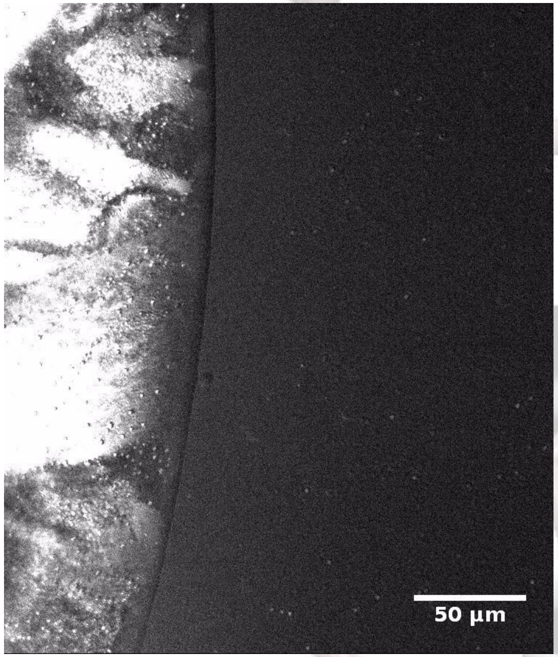
h = 10 µm
R = 1000 µm
θ ≈ 1°

h = 20 - 30 nm
R = ~2 - 3 µm
θ ≈ 1°

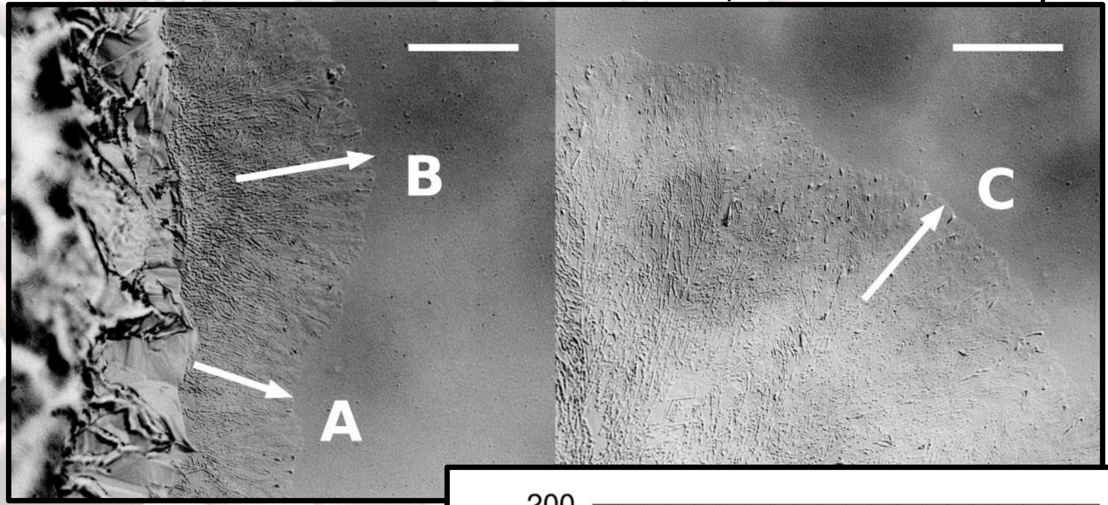


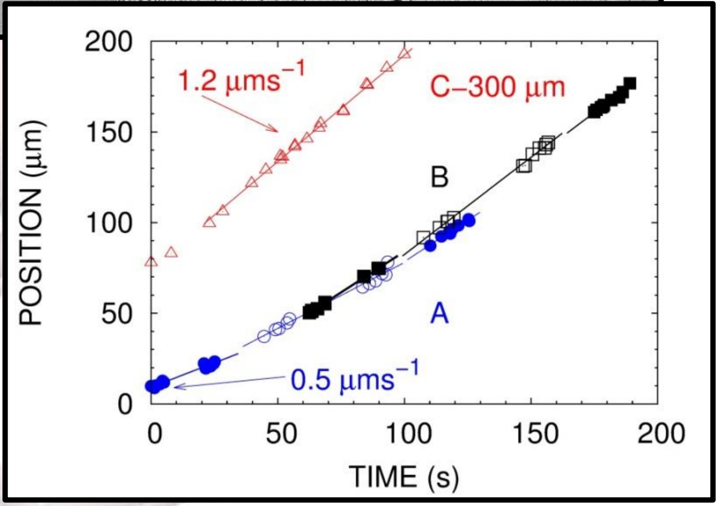
Halo growth – 1st formation

Growth of the 1st CP hydrate halo



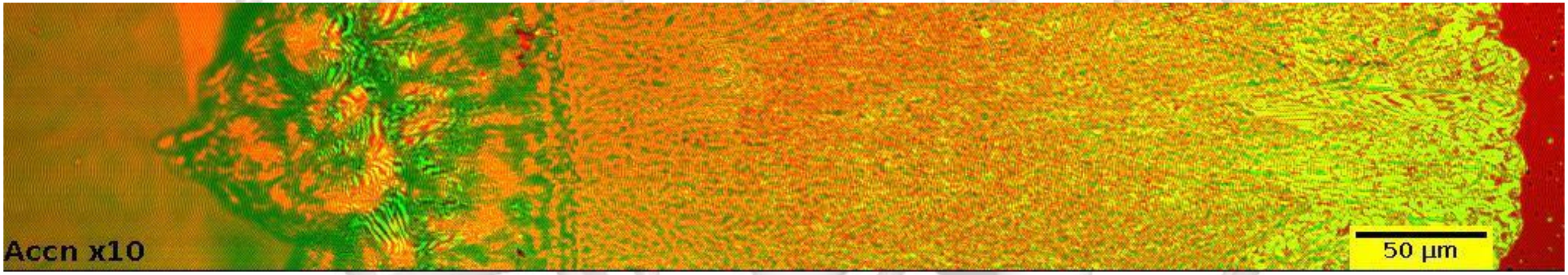
Inverted DIC, scale bar 100µm

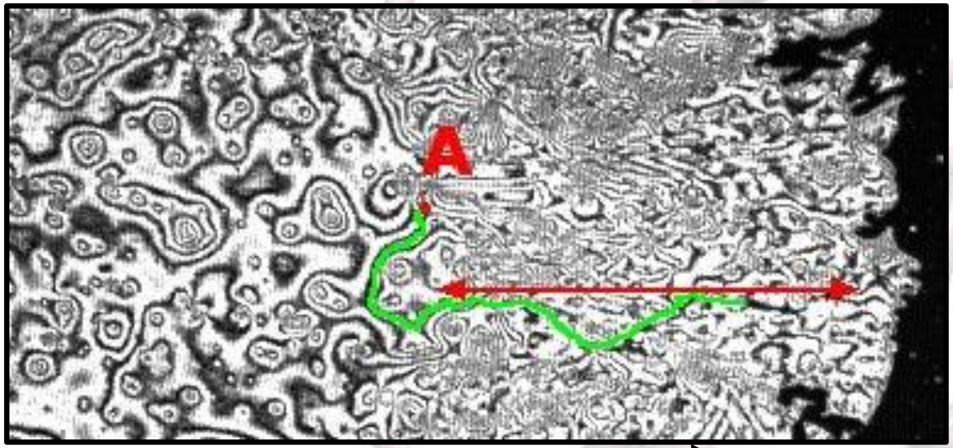




Halo growth accelerates away from the contact line: ~ 0.5 – 2 µm/s

Halo melting - Confocal reflectance fringes





~0.5 µm/s

Path to A = 5 - 6 fringes =>1--1.2 µm

A is 100 µm / 0.5 µm/s = 200s behind the front

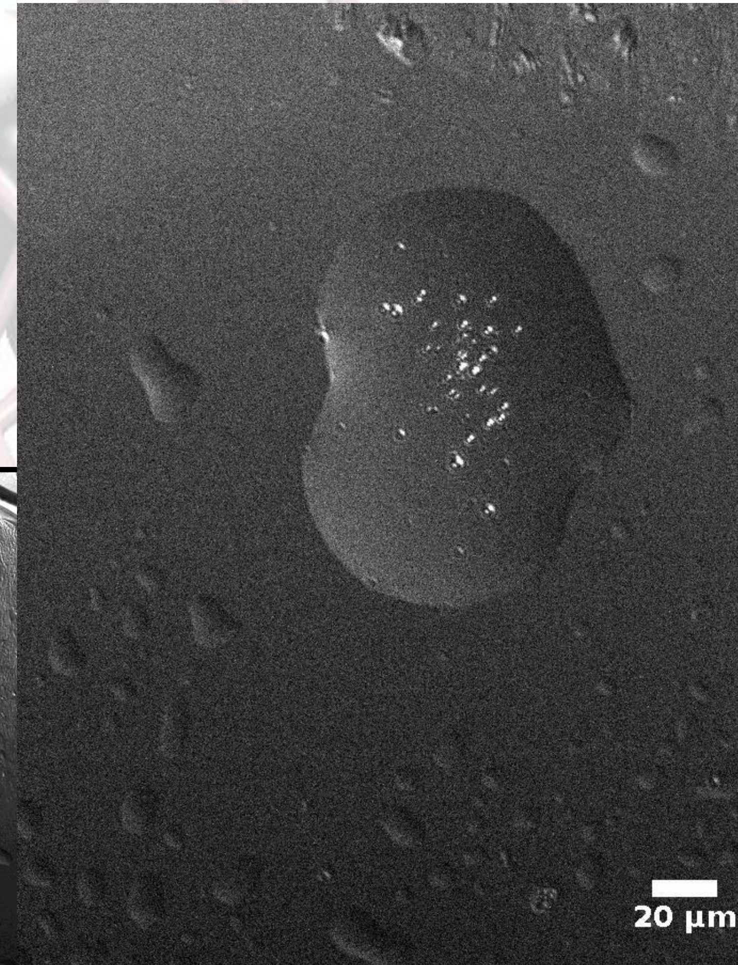
Halo thickens at 1µm / 200s = **5 nm/s**

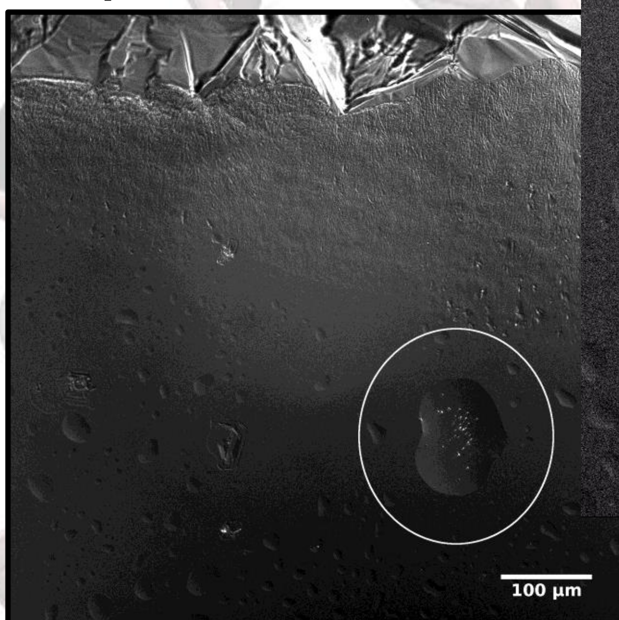
Halo growth - 2nd and later cycles

<u>Growth of the 2nd CP hydrate halo</u>

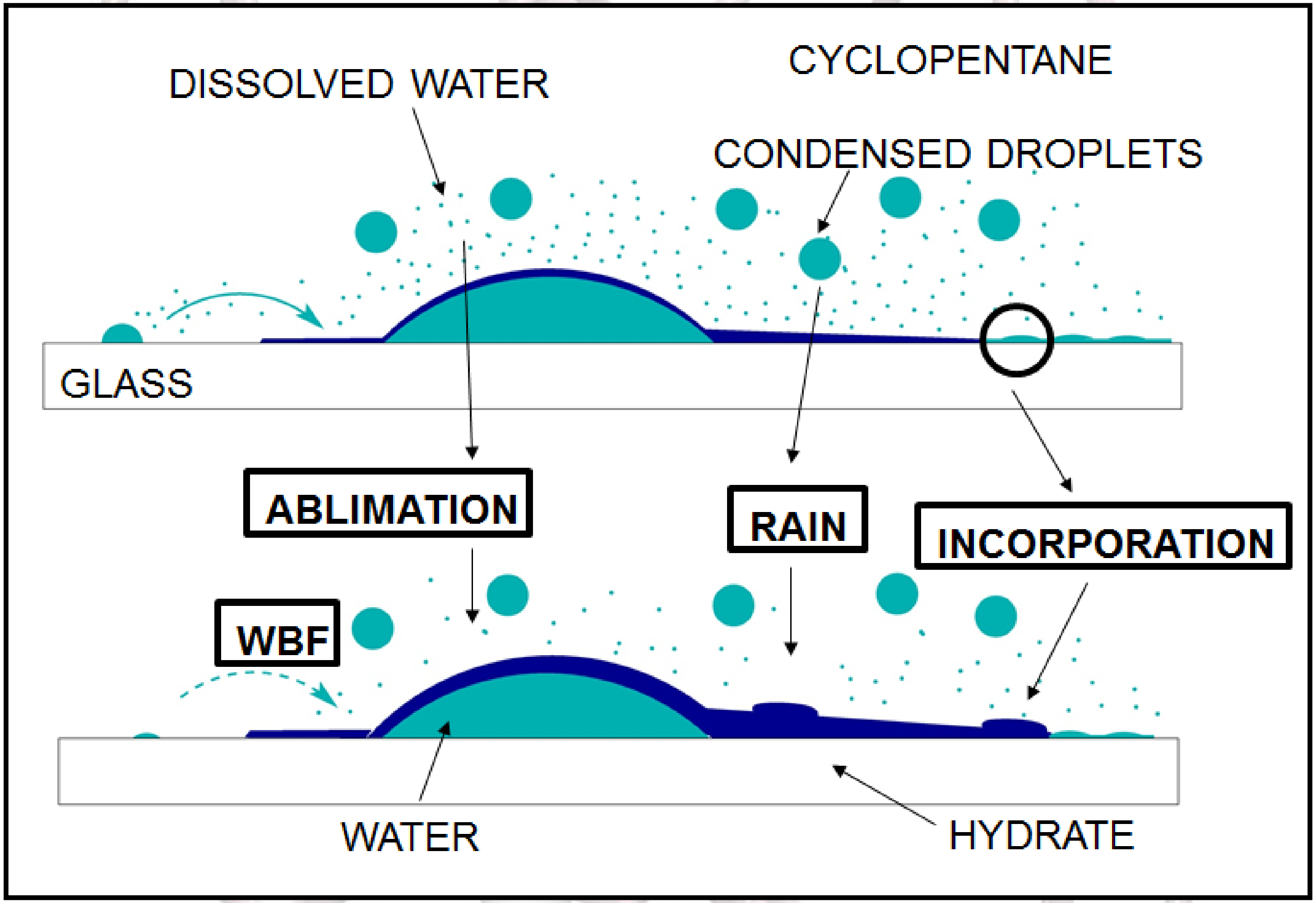
'Leap-frog' acceleration of growth

-Halo sucks in a secondary drop
-Regurgitates it with a crust
-Continues
-Halo crust grows at **~10µm/s**



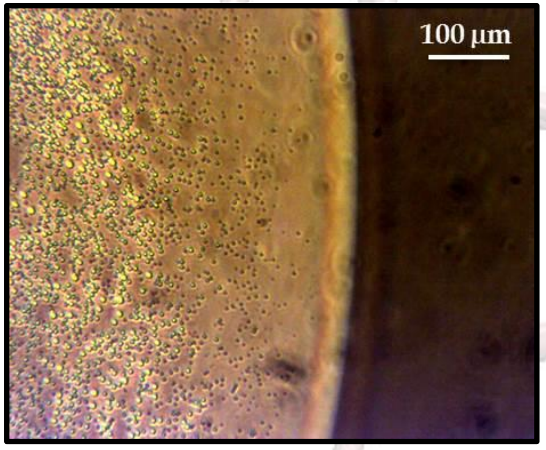


Summary of water sources

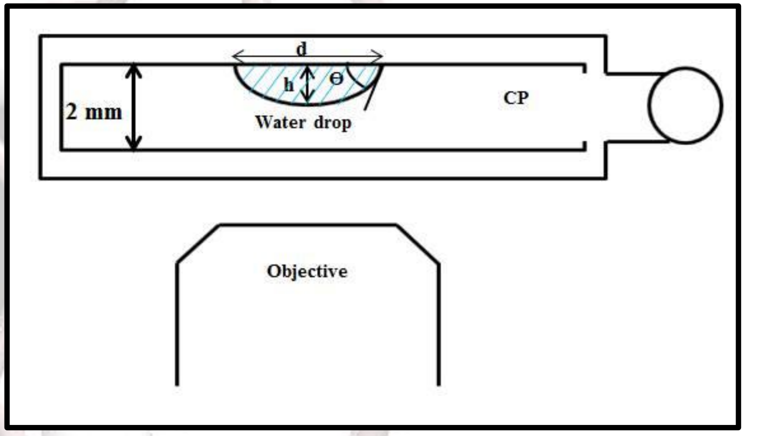


PROCESSES CONTRIBUTING TO HALO/CRUST THICKNESS

Crystallization in a 2D emulsion

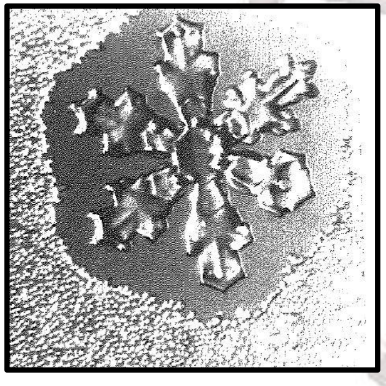


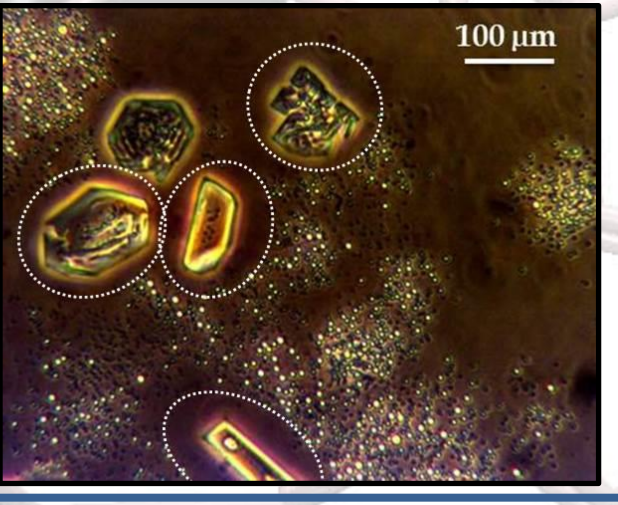
2D CP-in-water emulsion

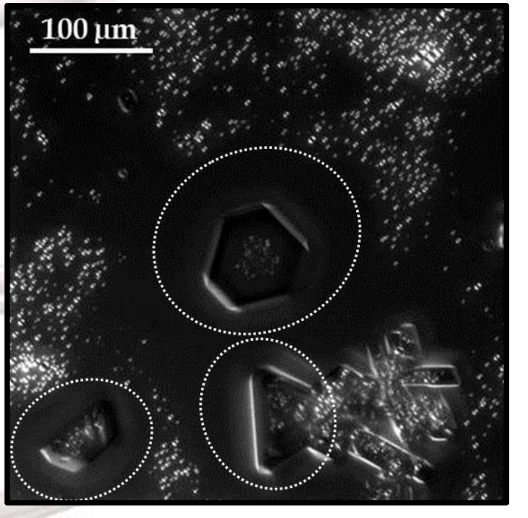


Conventional hydrate crystallization

Wegener – Bergeron – Findeisen process

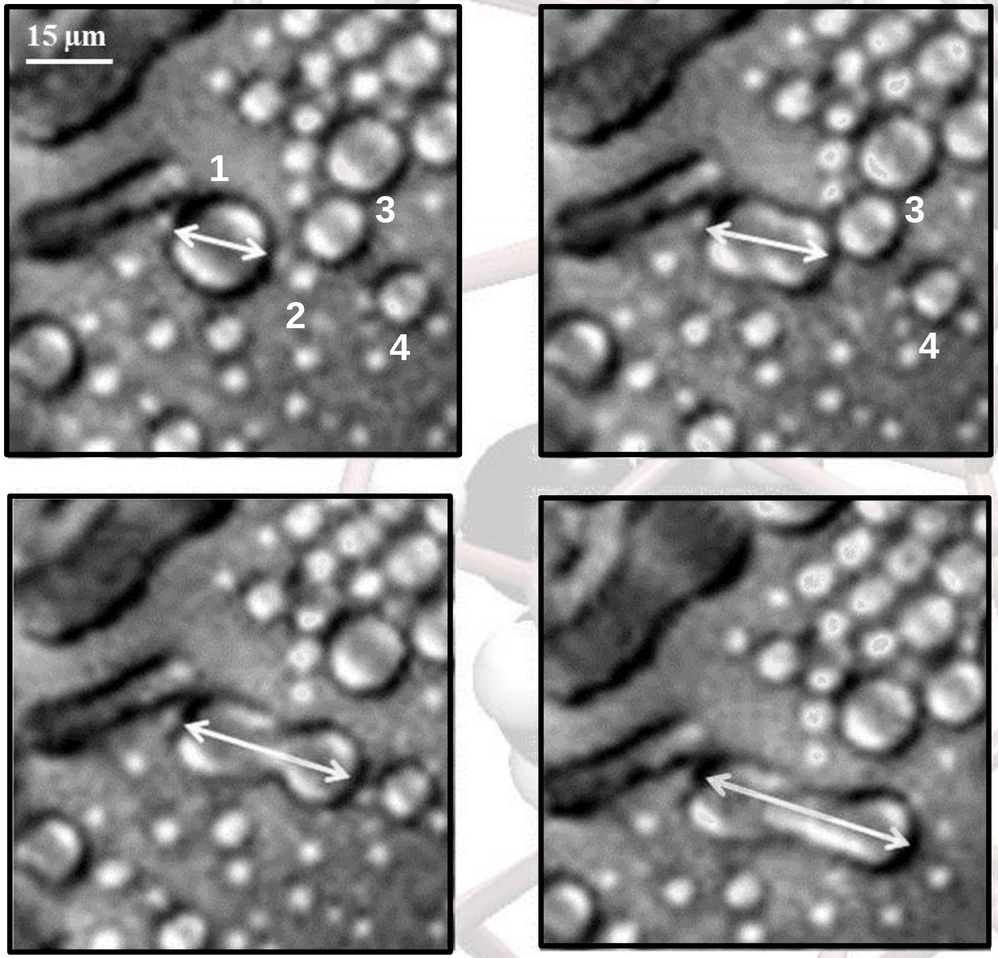




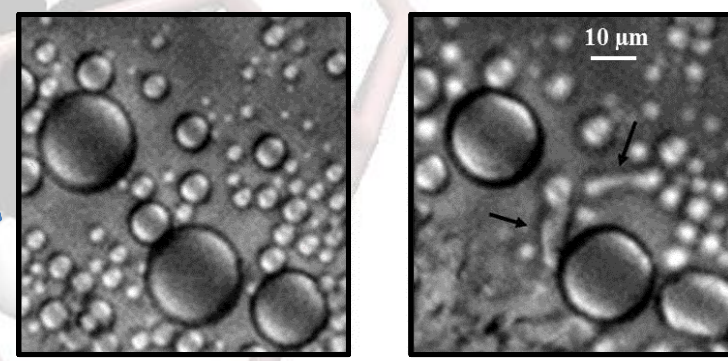


Crystallization in a 2D emulsion

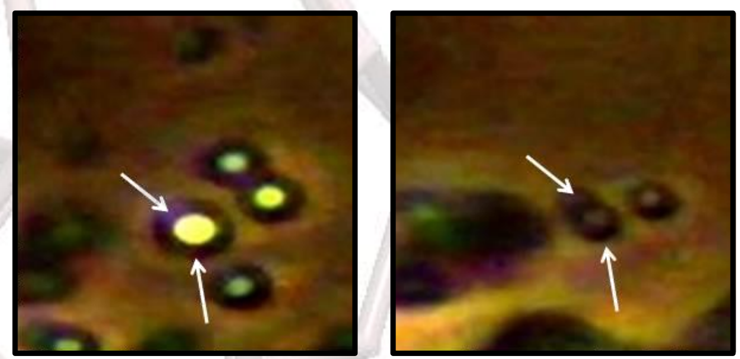
Percolation-like crystallization in the emulsion



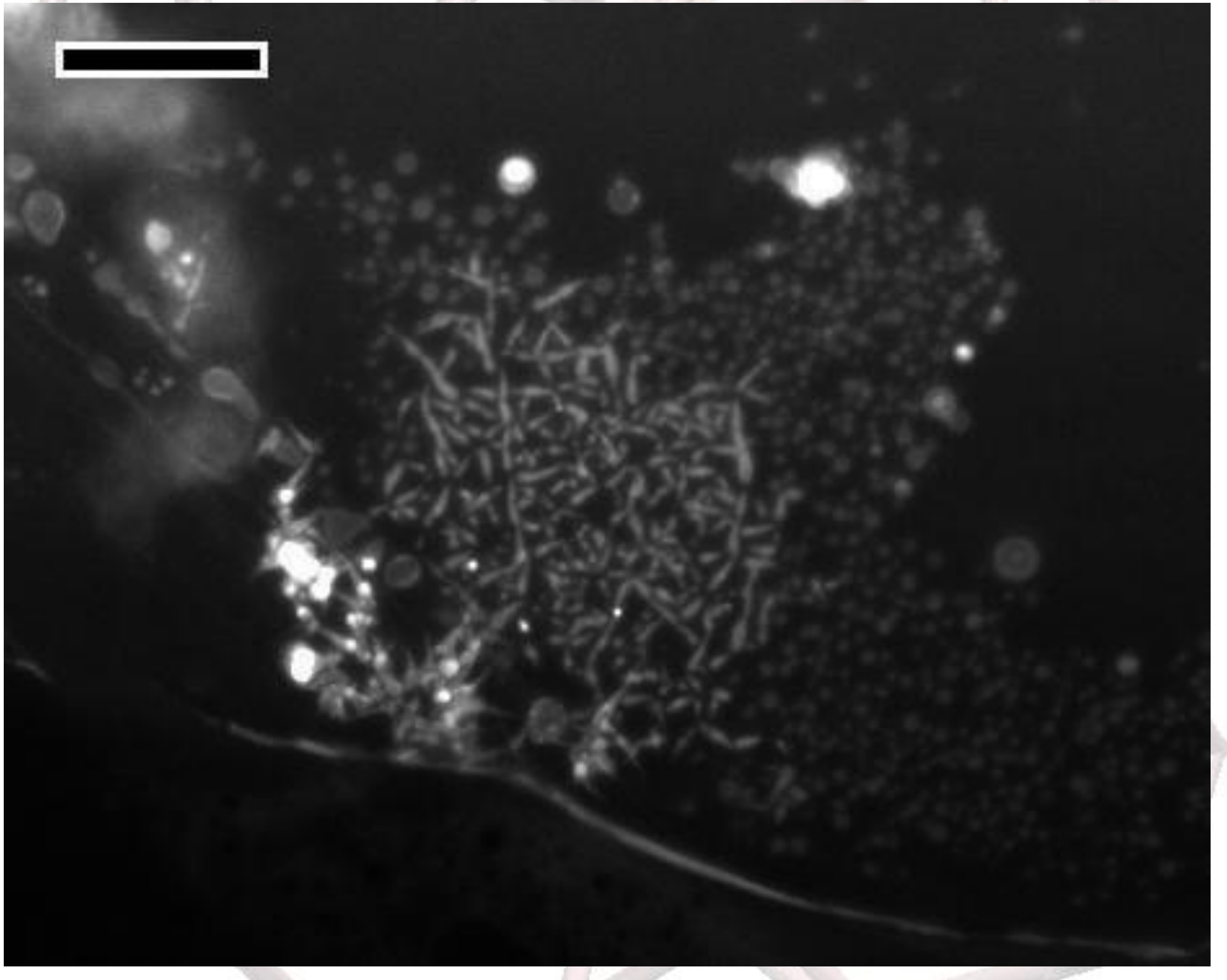
'Bridging process'



Dissolution process



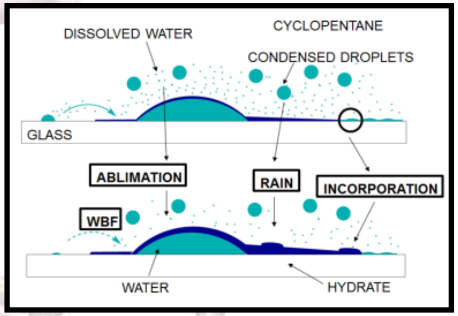
Percolation aggregate film



Conclusions and perspectives

Main conclusions obtained with CP hydrate, a close analogue of natural gas hydrate

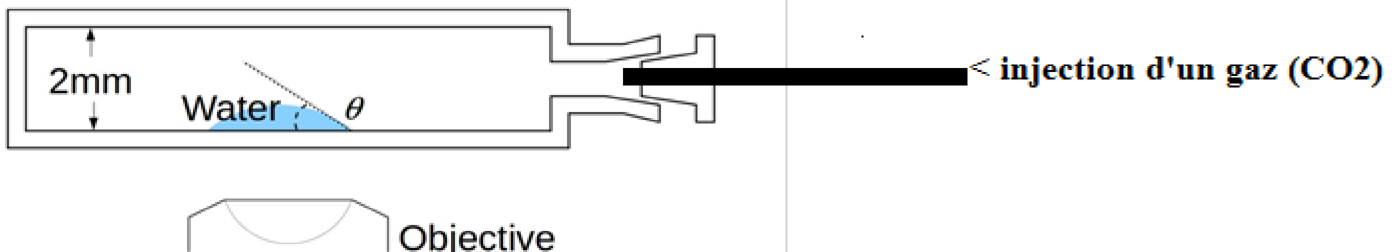
- Hydrate nucleation occurs in the emulsion and at triple lines (CP/water/substrate)
- Halo growth (0°C):
  - lateral 1 – 2 µm/s
  - leap-frog 10 µm/s
  - thickening 5 nm/s
- Halo feeds on external water.
- Novel, percolation-type hydrate growth process.



Conclusions and perspectives

Perspectives

- modelling the effects of coupled heat and mas transfers
- go to higher pressures/gas hydrates (CO_2 & CH_4 hydrates)



- other geometries: glass capillaries. Coupling with other characterization methods (e.g., Raman: coll with ISM Bordeaux)
- Interaction with other substrates/behavior in porous media.

- extend techniques to other systems: salt effluorescence, etc.

MERCI DE VOTRE ATTENTION