Laboratoire des Fluides Complexes UMR 5150

Groupe des Systèmes Dispersés

Formation/dissociation des hydrates de gaz par méthodes de gouttes, millifluidiques et de vidéo-microscopie

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Hydrate formation/dissociation from millimetric to submicronic scales

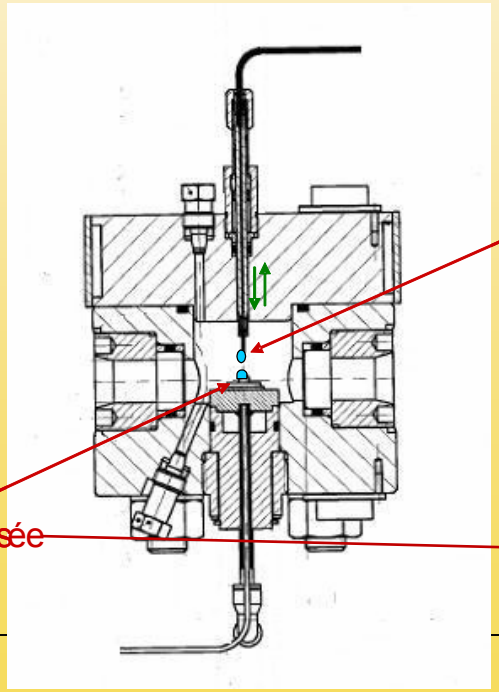
D. Daniel-David, F. Guerton, Ch. Dicharry, JP Torré

- **Drop experiments:**
  - **hydrate film growth vs. capillary-driven growth**
- **Millifluidic experiments:**
  - **insights into hydrate nucleation and memory effects**
- **Video-microscopy experiments**

Drop experiments (1/3)

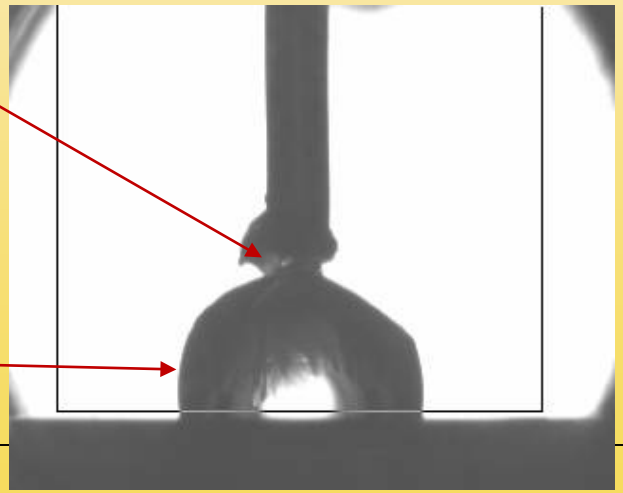
- **Hydrate growth studies at various T, P, gas compositions and water-soluble additives**
  - **Experimental setup & procedure**

T in the range of -5 to 15°C **P up to 10 MPa**



Goutte pendante cristallisée

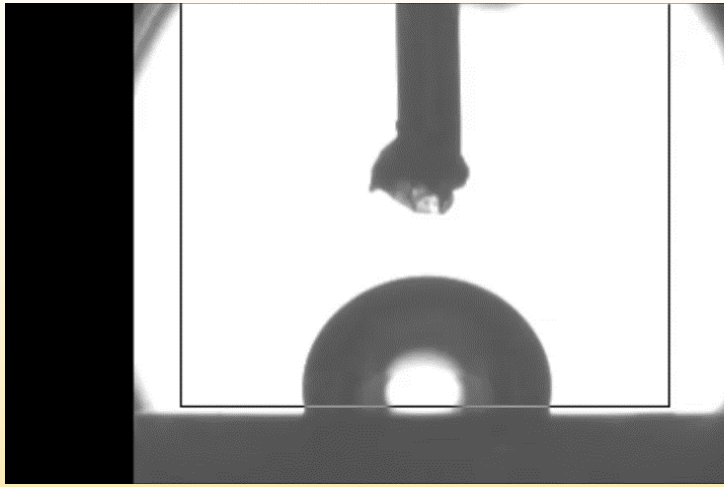
Goutte posée



Drop experiments (2/3)

- **Results with CO_2 & CH_4 hydrates: two different modes of hydrate growth**
  - Formation of a **low-permeable hydrate crust** at the water surface Ex: pure water, non-ionic surfactants, CO2
  - **Capillary-driven growth**: observed only with anionic surfactants and methane

CO2 @ 27 bar, 5°C



CH4 @ 40 bar, 0°C
500 ppm SDS

Drop experiments (3/3)

give insights into:

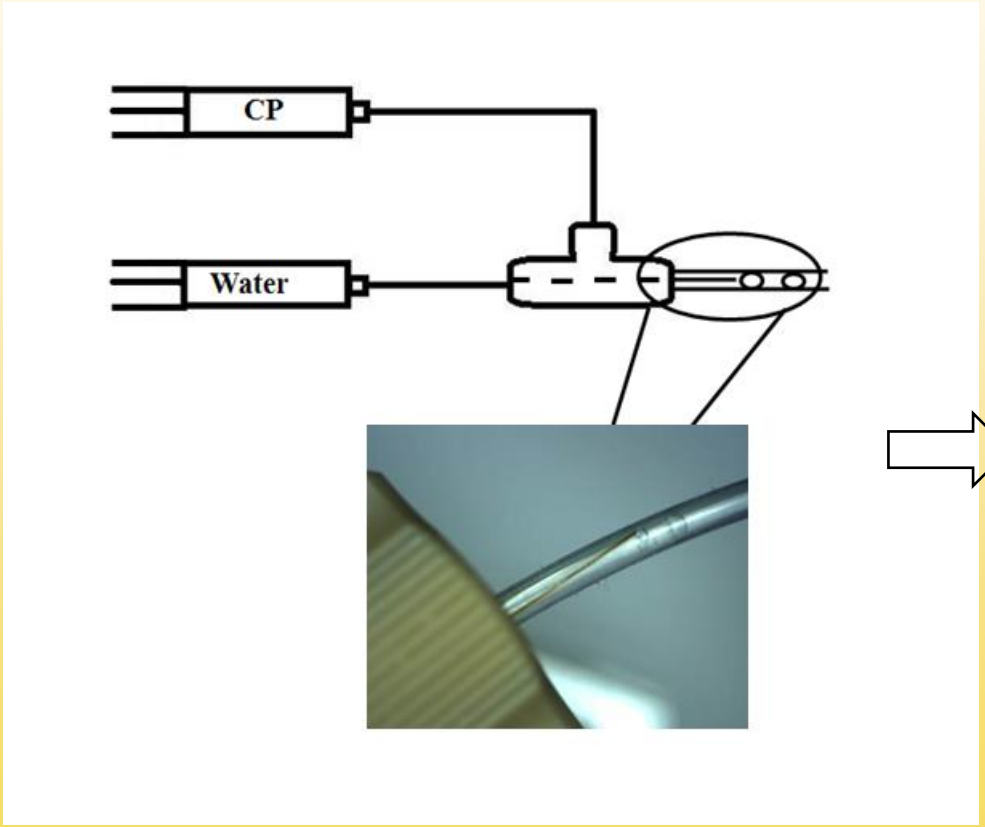
- **hydrate film morphologies**
- **hydrate film lateral velocities**
  - depend primarily on subcooling and gas solubilities
  - fairly independent of (nonionic) surfactant additives
- **mechanisms of capillary-driven growth**
  - porosity of the hydrate structure
  - pore size

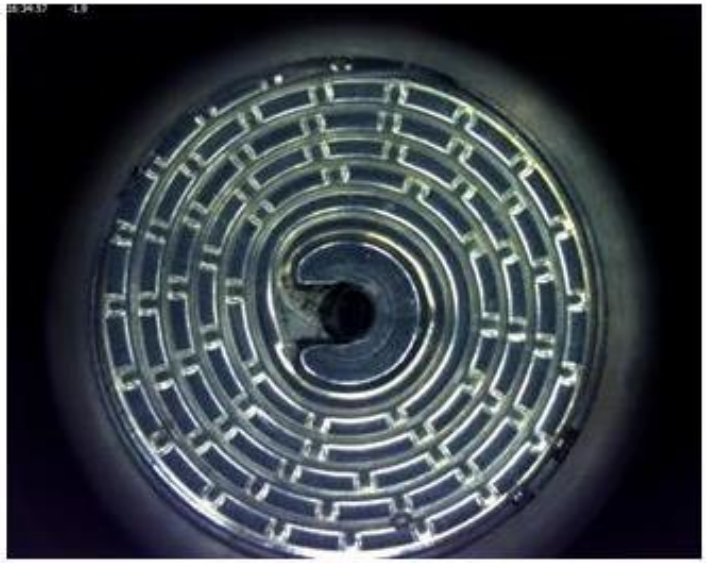
D. Daniel-David et al., Chemical Engineering & Science (submitted)

Millifluidic experiments (1/7)

ML Martinez de Banos, O. Carrier, P. Bouriat

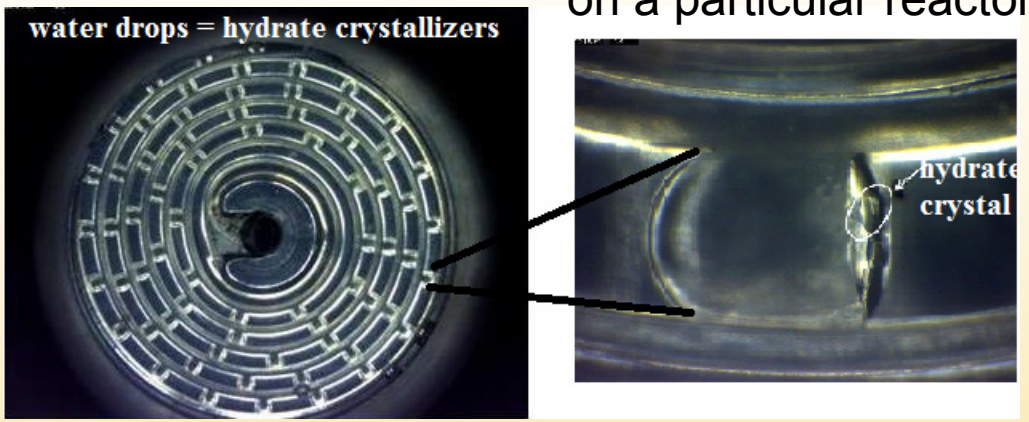
Memory effects in cyclopentane hydrate formation
Study of the guest-in-water emulsion



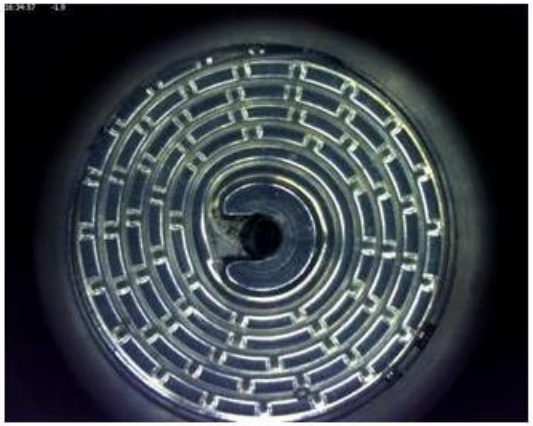


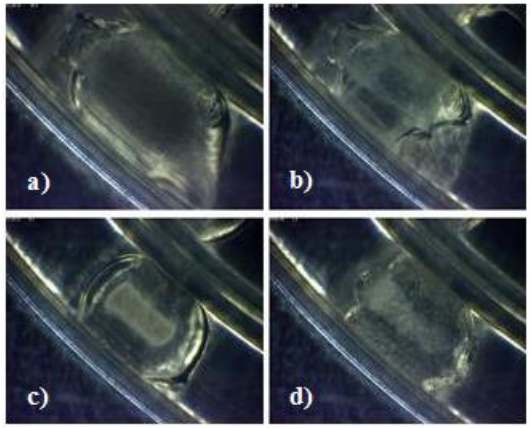
each water drop is a reactor for hydrate formation

possibility of zooming
on a particular reactor

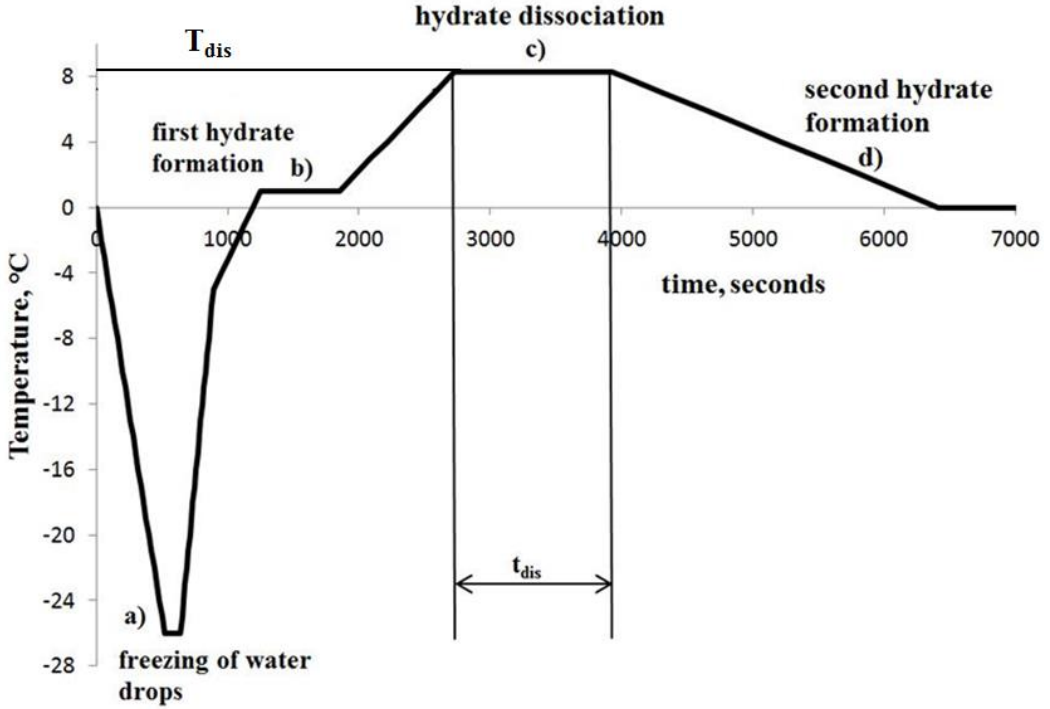


Investigation of memory effects: procedure



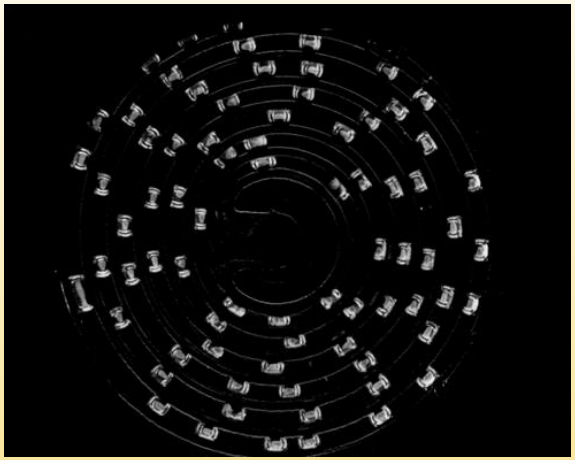


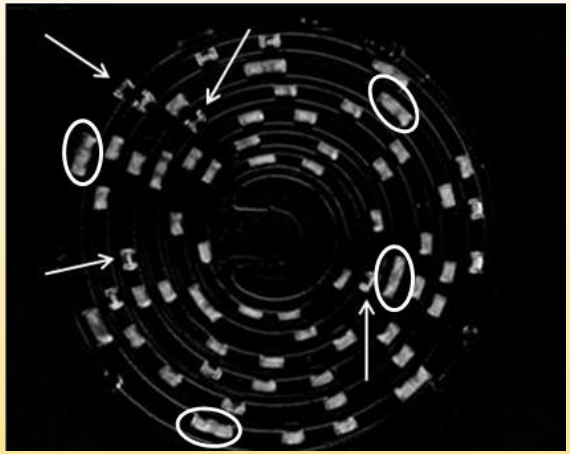
sequence of temperature variation



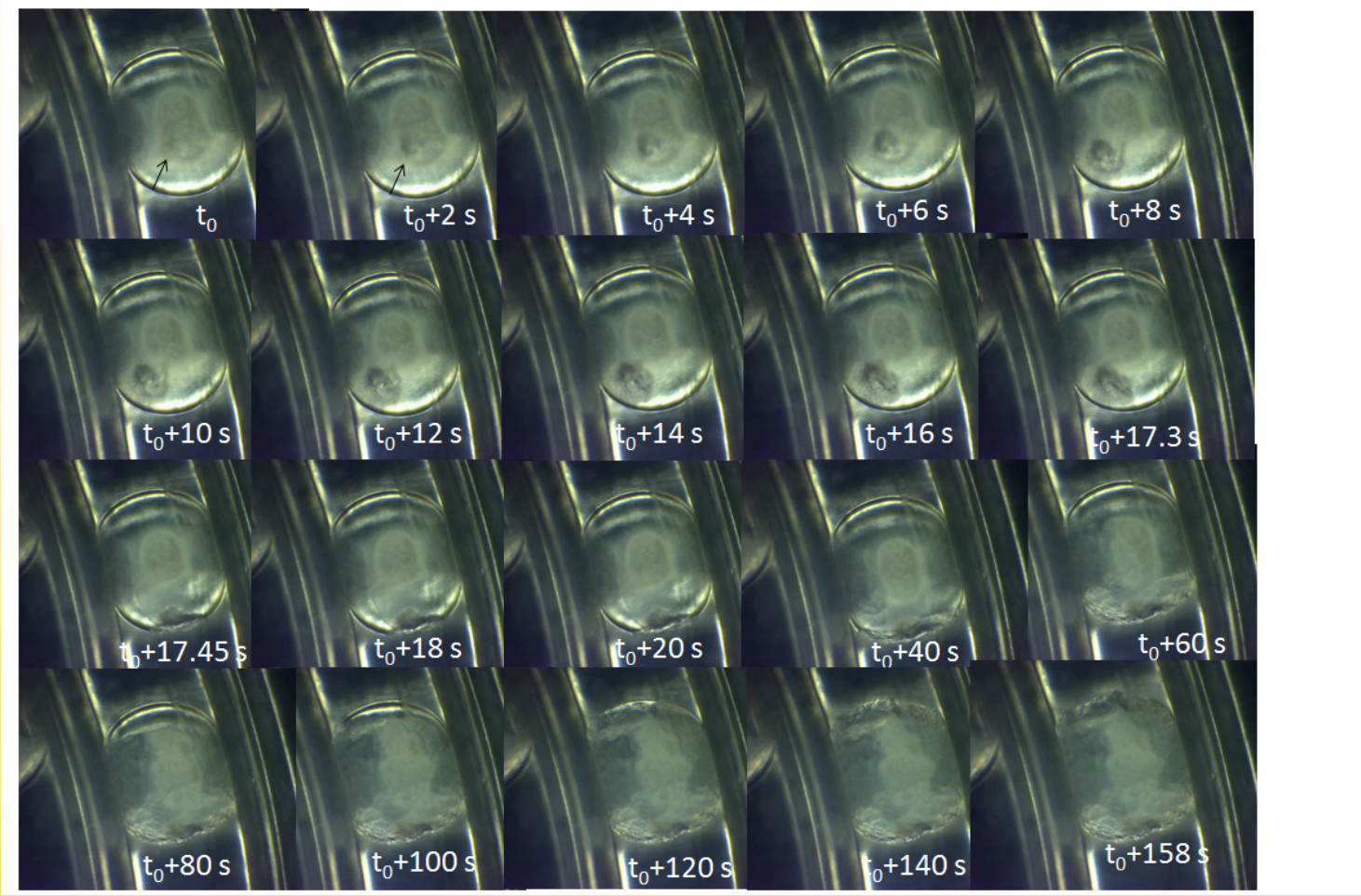
Investigation of memory effects: procedure

- **Image treatment: for each time or T, count the fraction of reacted drops**



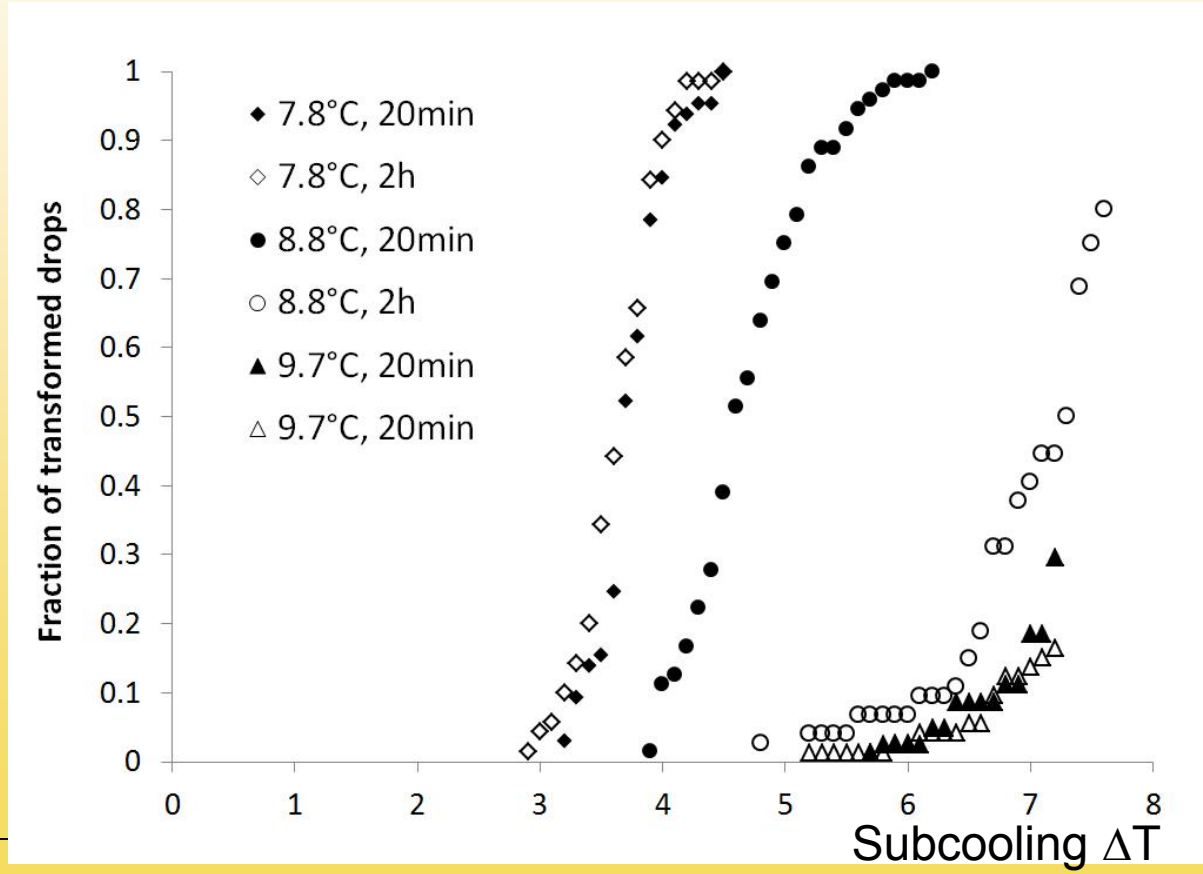


2nd hydrate formation and growth in a single drop:



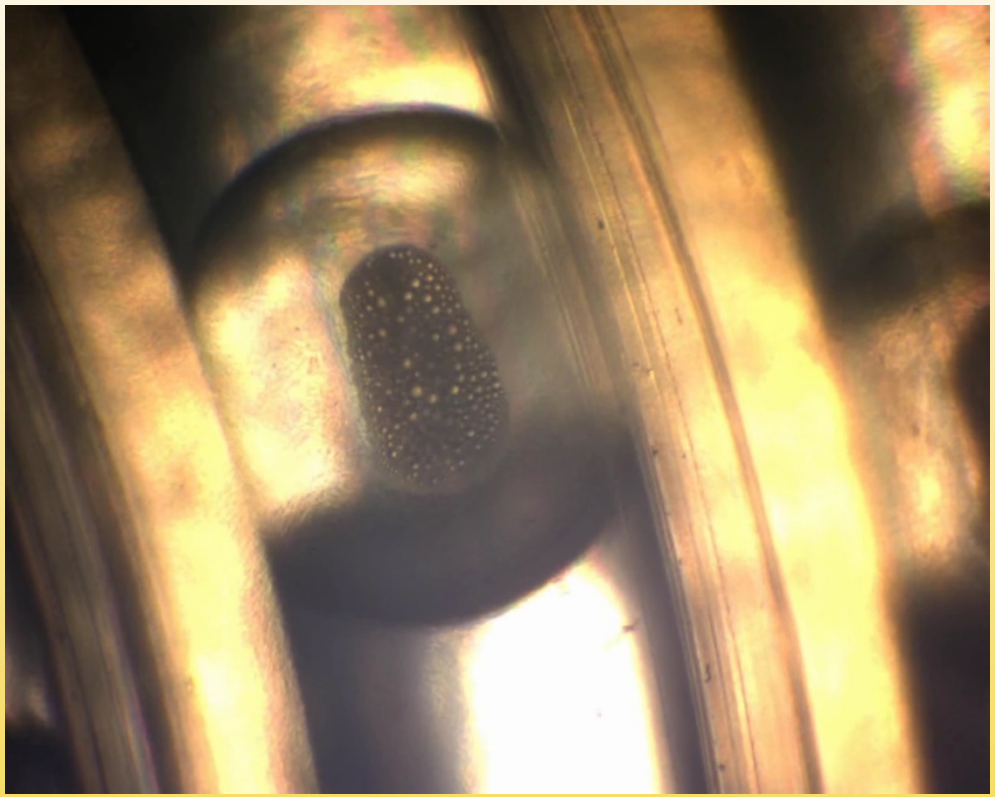
Investigation of memory effects: results

- **2nd hydrate formation strongly depends on the previous history of formation/dissociation**



Investigation of memory effects: results

- **2nd hydrate formation: role of the guest-in-water emulsion?**

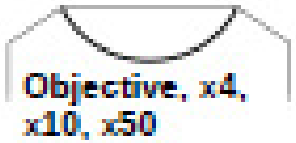


Chemical Engineering & Science, in press.

Video-microscopy experiments

ML Martinez de Banos, P. Bouriat, R. Brown

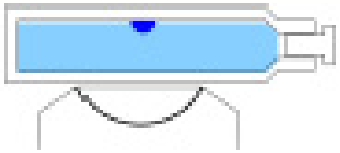
METHODS



Widefield video

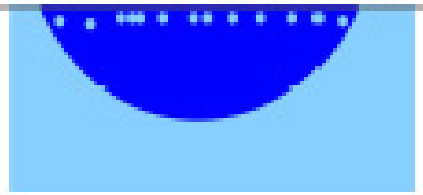
- ** transmission*
- ** DIC phase contrast*
- ** dark field*

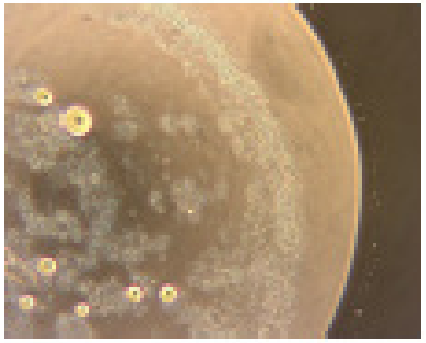
+ fluorescence microscopy

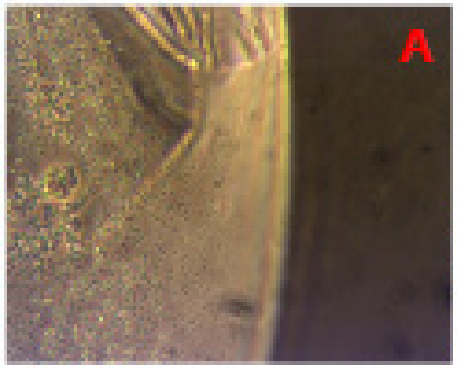


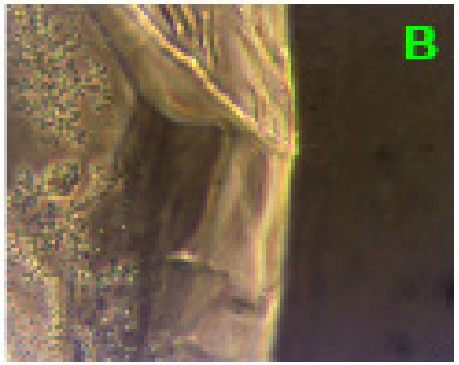
NEW Hydrophilic sub-strate, hanging drop

-Emulsion all over interface

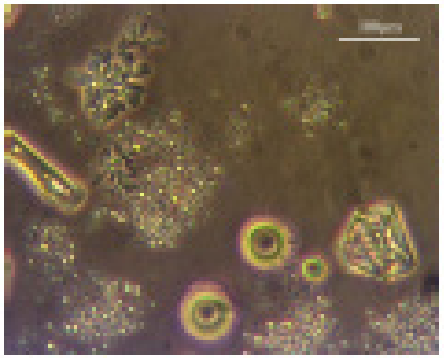


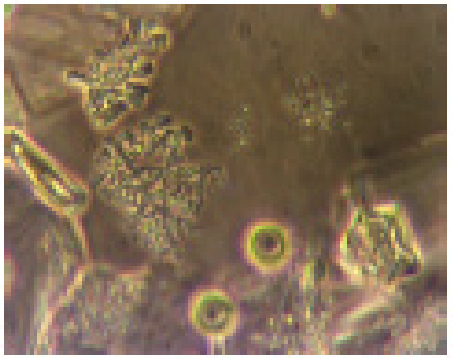




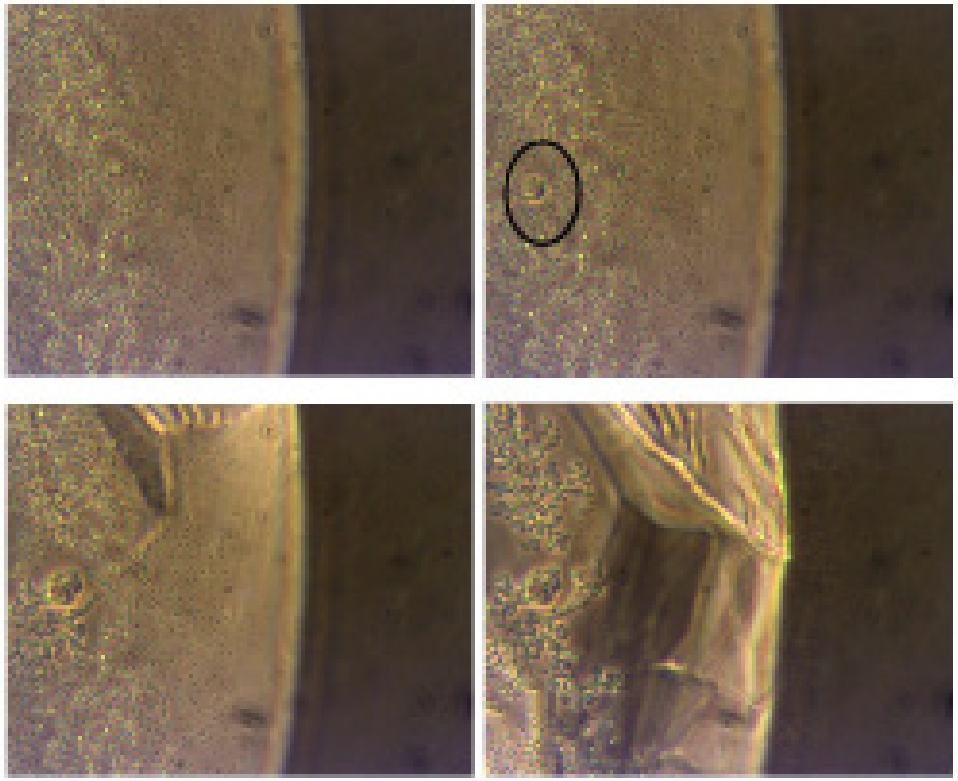


-Inverted 'igloo'
-Dendritic growth on glass

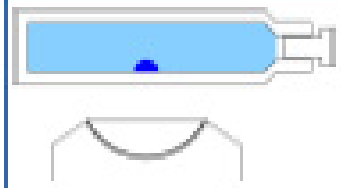




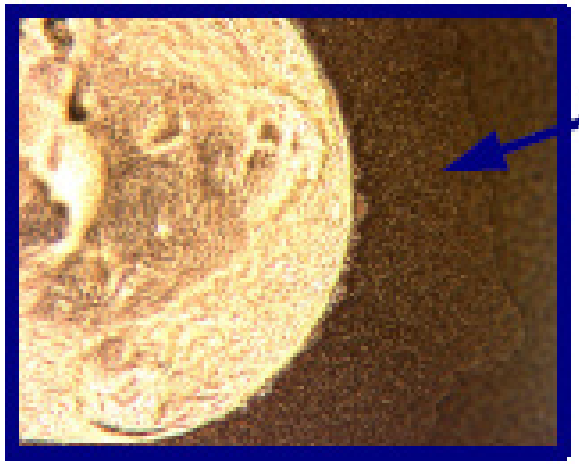
-CP depletion around growing crystal, cf. Ostwald ripening



RESULTS

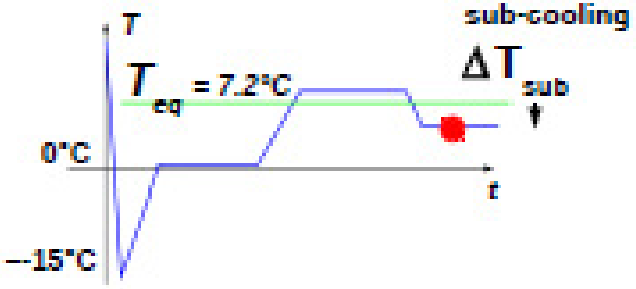


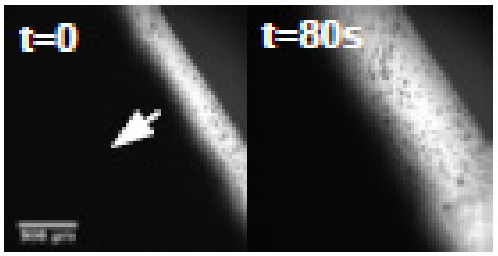
Hydrophilic substrate, sitting drop

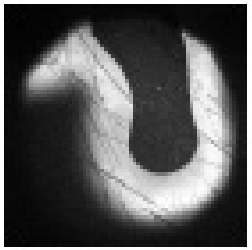


KNOWN Hydrate halo spreading on substrate (Beltran et al 2010)

NEW water precursor film present under CP at $t=0^+$







DASPI, fluorescent marker of liquid/solid interfaces.

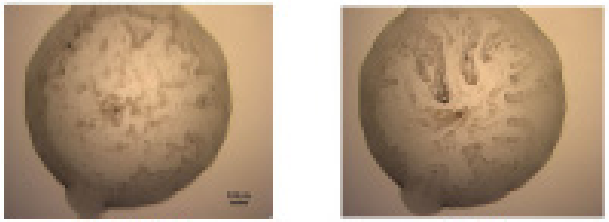
DASPI/H_2O on coverslip

DASPI/H_2O/cyclopentane in cuvette

NEW -H_2O drop spreads to edge of halo at each melting

-Halo growth faster with repeated cycling

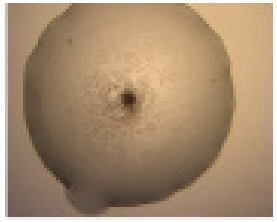
VN Melting hydrate makes an emulsion of CP in H_2O



t=0, T=8°C

t=3min

t=7.5min

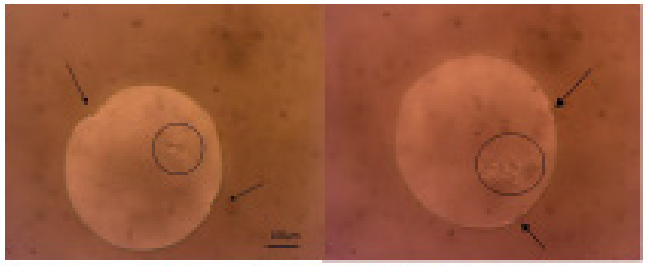


t=12min

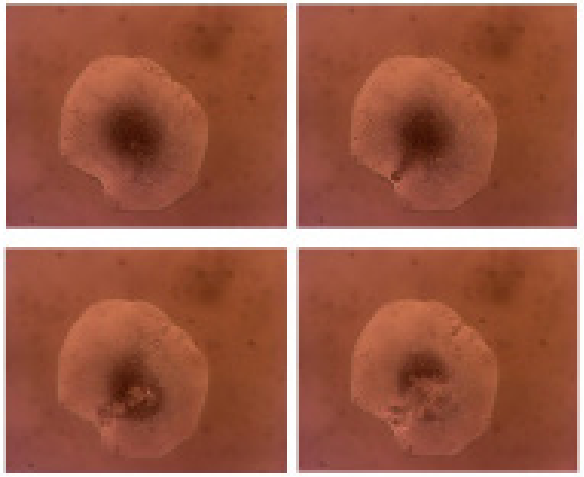
NEW Emulsion collects at top of drop

Glass

NEW Hydrate 2nd formation $=f(\Delta T_{sub})$



Large ΔT_{sub} (T=0°C): nucleation in emulsion and at triple line



Small ΔT_{sub} (T=5°C): -nucleation in emulsion
-migration to triple line
-growth

Summary & conclusions & prospects

- « There is plenty of room at the bottom » (Feynman, 1959), also in hydrate research!

- at scales from the mm to below 1 µm: key for the elucidation of hydrate formation & growth mechanisms and of the effects of additives (promoters, inhibitors)

- milli- & micro-fluidic methods: a mature technology, still in its infancy in the field of hydrate research!

- extension to higher pressures (real hydrates): ongoing and future work (thesis A. Touil)