PIRE Annual Review: Hydrates thrust Introduction — Jeff Morris (CCNY)

June 19, 2018

Hydrates

- Areas of impact
  - Petroleum pipelines: flow assurance
  - Presence in permafrost, seabed:
      - harvesting for energy
      - concern over release & greenhouse effect
  - Transport operations
    - Energy transportation (stable solid for H2 or CH4)
    - Use in refrigeration systems
  - Gas separations
  - Water purification

Hydrates
history at CCNY

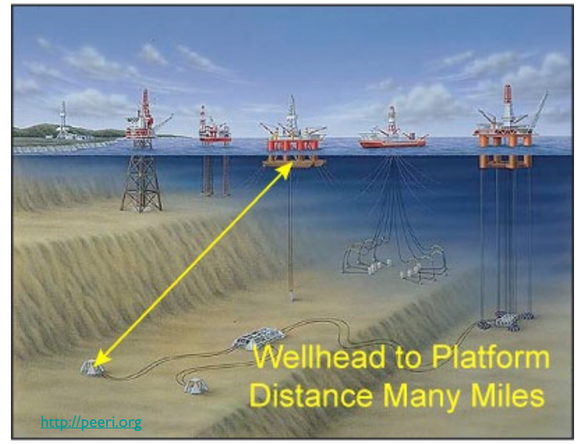
- Jeff Morris / Jae Lee (now at KAIST, South Korea)
  Flow assurance — rheological analysis
  (Chevron and BP-GOMRI)
- Jae Lee
  Ship transport of gaseous fuels in hydrate form
- Marco Castaldi (non-PIRE activities)
  Subsurface (permafrost) experimental model
  CO_2 hydrate displacement of methane hydrate

Hydrates in pipelines

Atlantis oil platform - Gulf of Mexico

Subsea transport

Flow Assurance



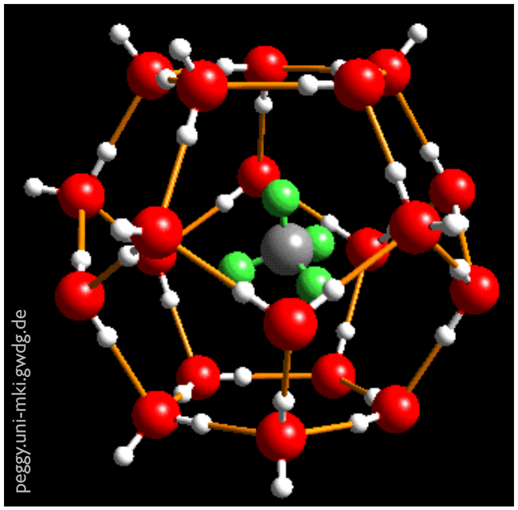
100's of miles

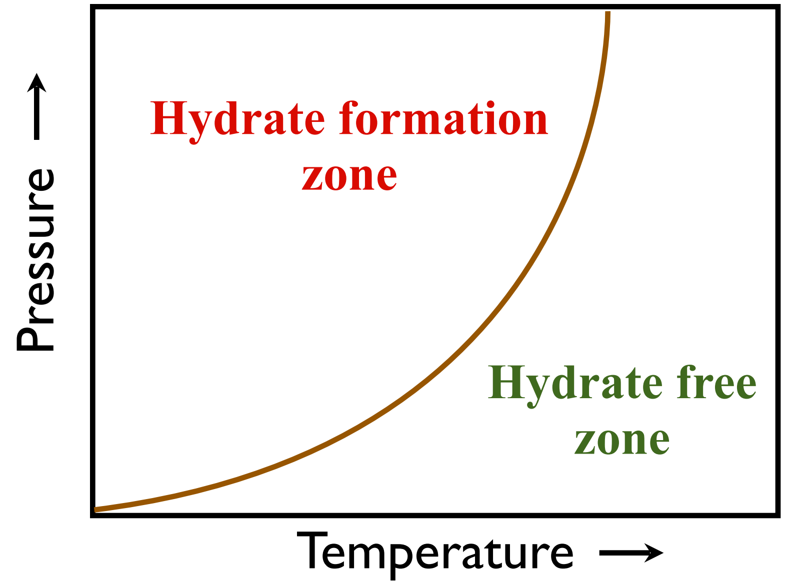
✓ Hydrate formation in oil / gas flow lines

Most critical flow assurance issue

Rapid formation rate

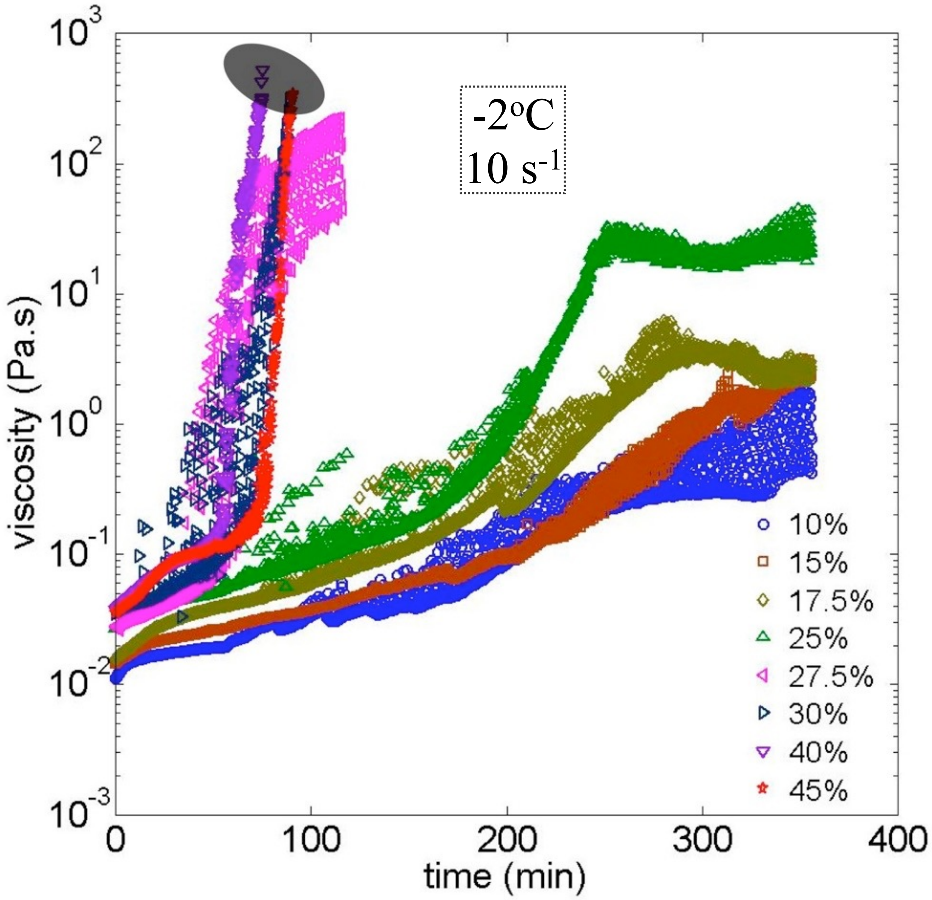
Hydrate structure and thermodynamics

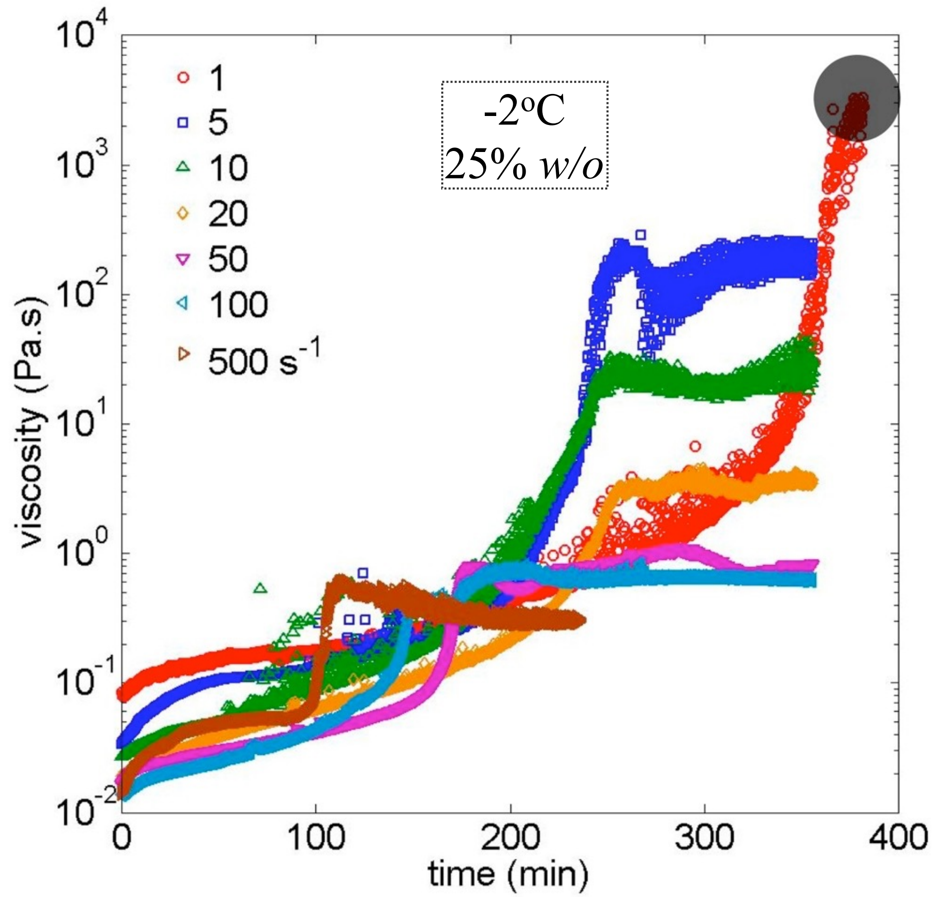




- Solid *crystalline* compounds
- Entrapped guest molecules, *e.g.* methane, ethane, CO_2, H_2
- Stable at low T (< 20°C) and high P (> 30 bar)
- Cyclopentane (CP): hydrate former at atmospheric pressure
  $T_{diss} = 7^oC$ — reduced for CP mixed with other oil (CP activity controls

Shear rheology





Hydrate seeding at t= 0, T = -2°C

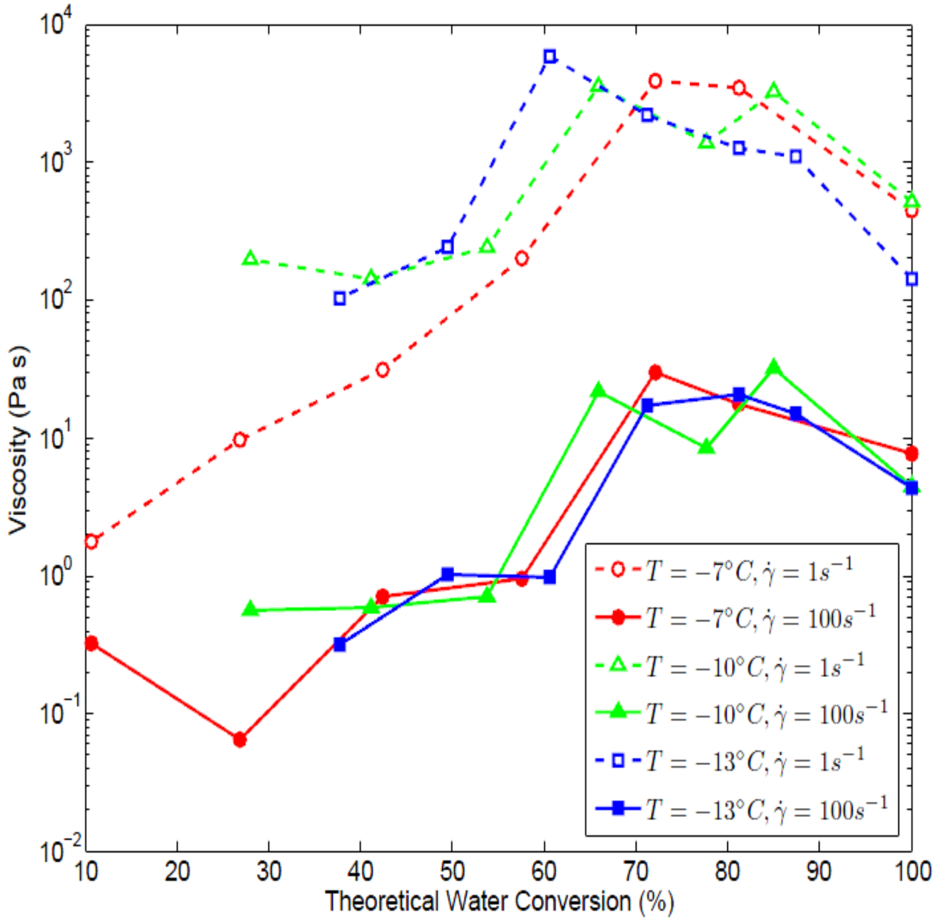
Transition stochastic without seeding

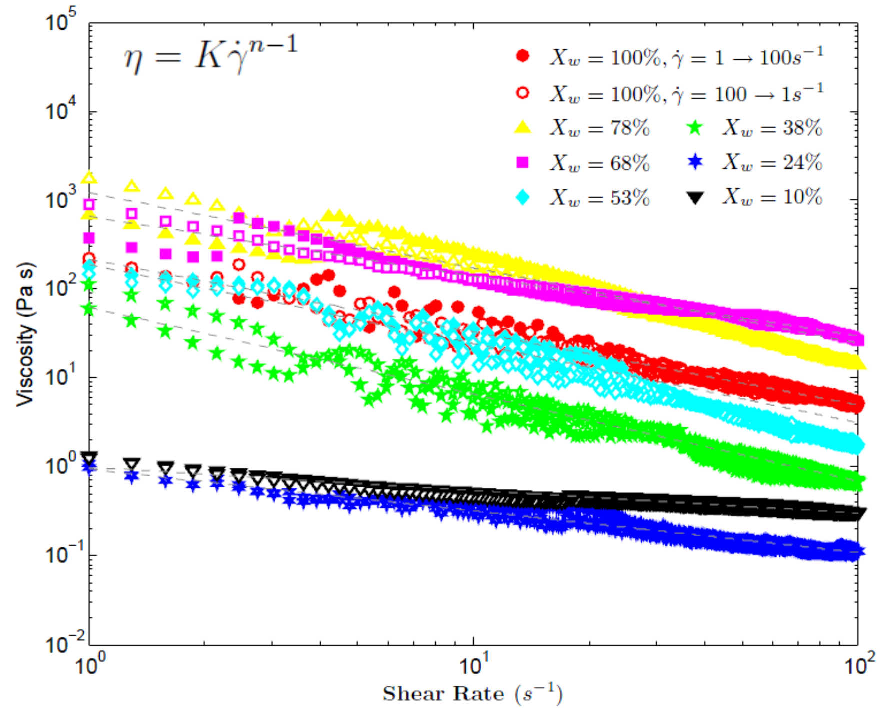
Peixinho *et al. Langmuir* 2010,

Karanjkar, Abuja *et al. Rheol. Acta* 2016

Final Viscosity

Zylyftari, Lee & Morris *Chem Eng Sci* 2013



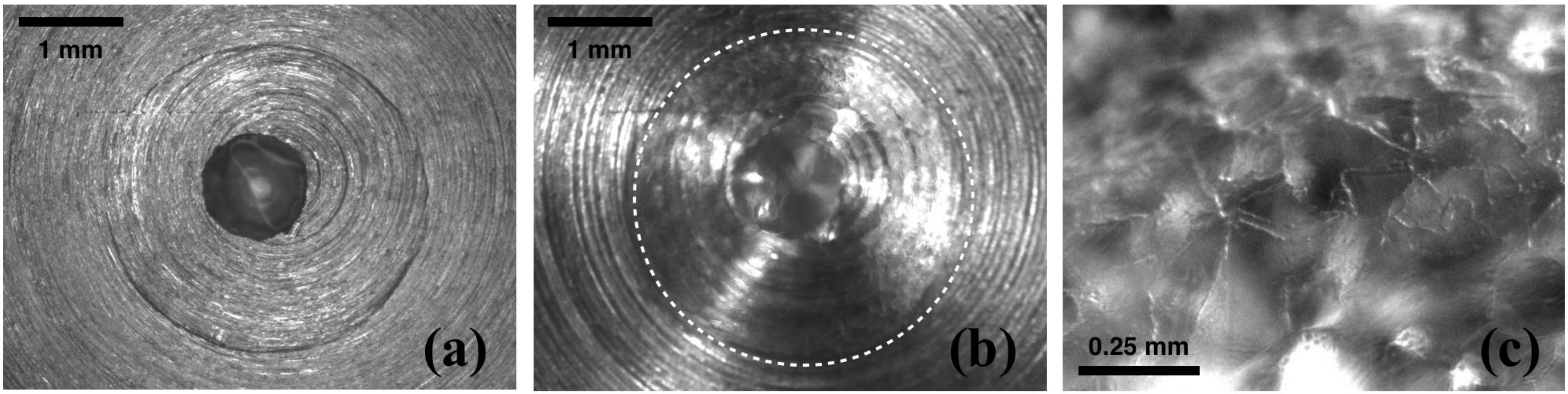


- Maximum viscosity is observed at 60-80% water to hydrate conversion (salt controlled).
- Final viscosity attains a peak at 80% conversion when temperature is varied.
- Similar for yield stress.
- Consistent with mechanism described by Colorado School of Mines researchers.

Interfacial morphology

A water drop in cyclopentane (No surfactant) : 0.2°C

Faceted - *joining numerous facets together*



water drop | hydrate ball | enlarged view

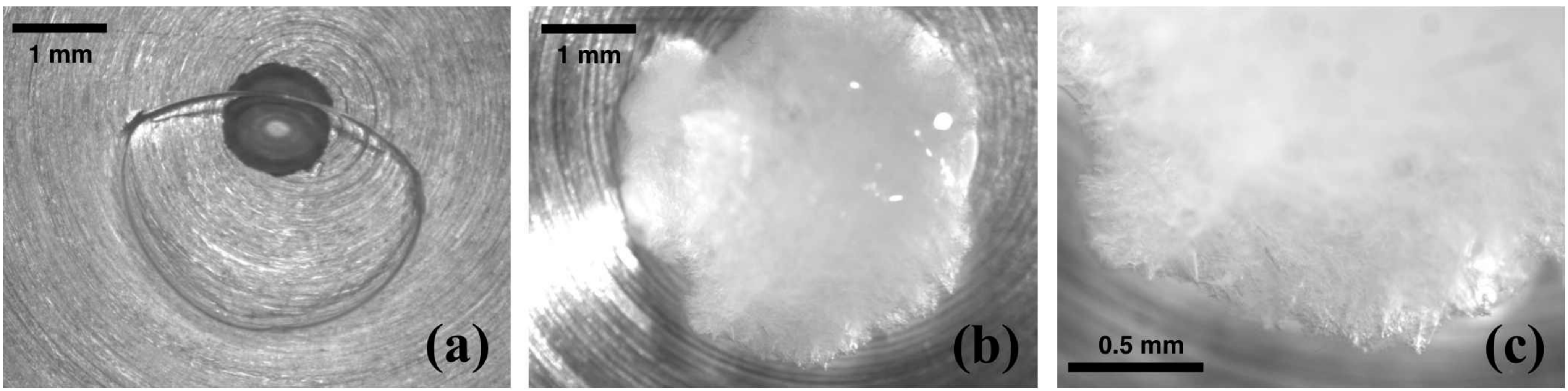
“Nucleation - Surface growth”

Very slow radial growth - diffusion of cyclopentane through hydrate shell

Interfacial morphology
w/ surface-active agents in oil

A water drop in cyclopentane + 0.1% Span 80 : 0.2°C

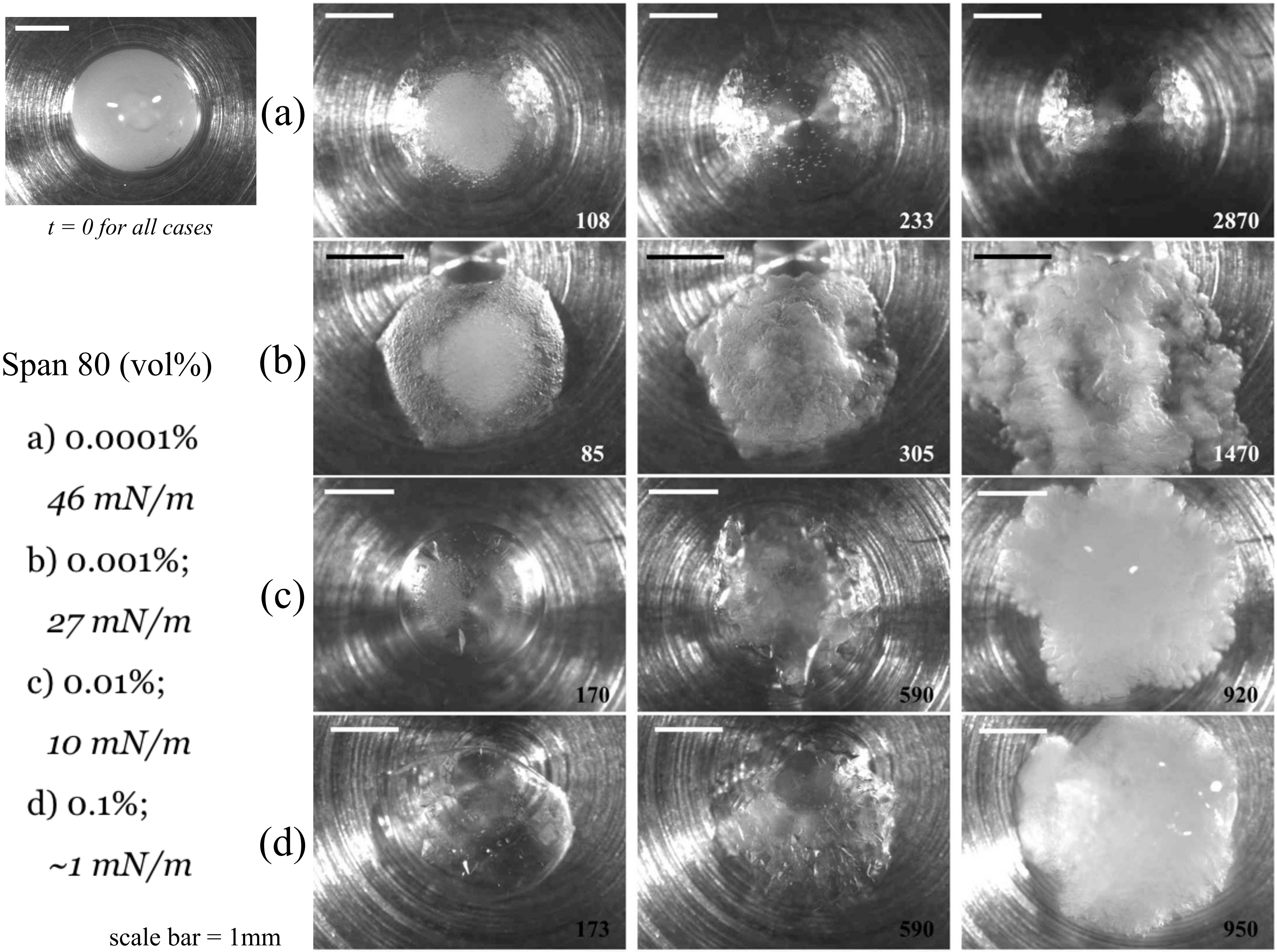
“dendritic” crystals — induces porosity



water drop hydrate ball enlarged view

“Nucleation - Surface growth - Radial growth”

Karanjkar et al., Proceedings 7th International Conference on Gas Hydrates (ICGH), Scotland, UK July 2011


t = 0 for all cases
(a)
108
233
2870
(b)
85
305
1470
(c)
170
590
920
(d)
173
590
950
Span 80 (vol%)
a) 0.0001%
46 mN/m
b) 0.001%;
27 mN/m
c) 0.01%;
10 mN/m
d) 0.1%;
~1 mN/m
scale bar = 1mm

Summary & what's up next

- Hydrate formation in emulsions:
  Interfacial phenomenon - water drop/oil interface

  Interfacial properties govern:
  — wetting in water / oil / hydrate system (***Fanny Thomas***)
  — hydrate crystal morphology

- Hydrates research:
  —SINTEF (Norway): ***Harald Linga*** (for ***Martin Fossen***)
  —French ANR proposal: ***Didier Dalmazzone*** (ENSTA ParisTech)
  —IRSTEA hydrates research:
  Anthony Delahaye (overview)
  Laurence Fournaison (secondary refrigeration)