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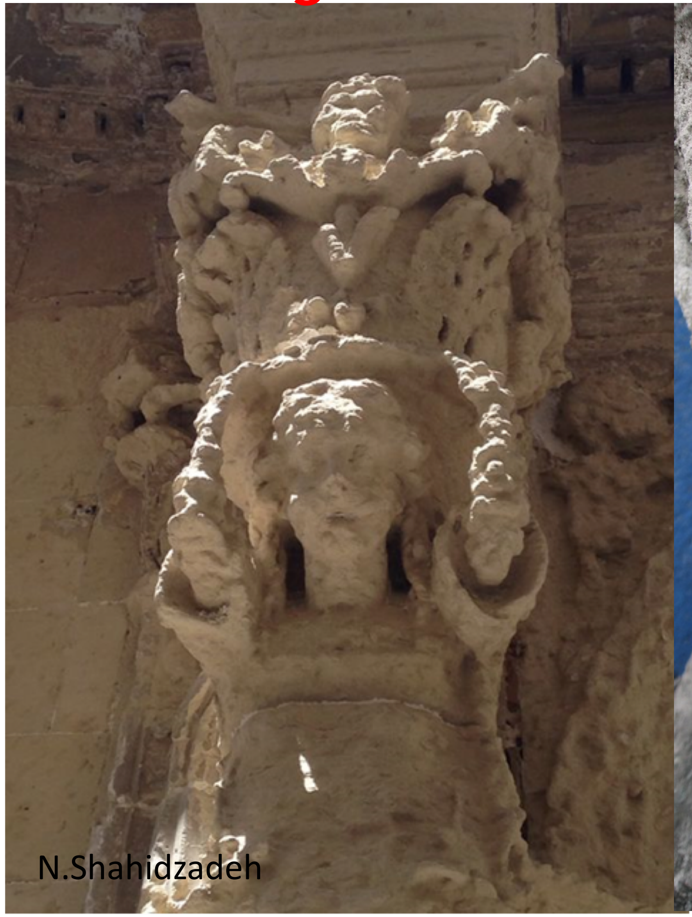
Weathering due to crystallization (Noushine Shahidzadeh)

Granular desintegration

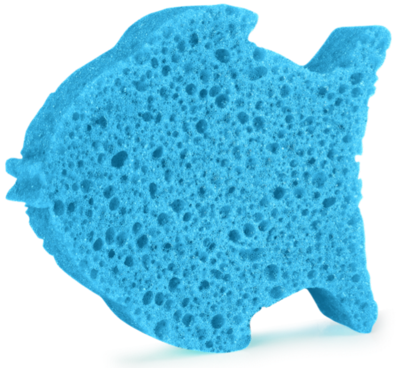


Scaling

Alveolization

ICE CRYSTALLIZATION AND MECHANICAL DAMAGE AT THE PORE SCALE

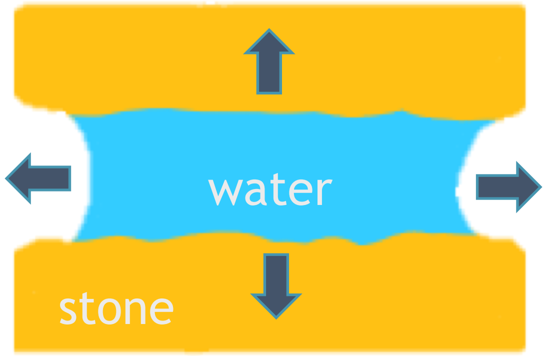
Water enters the porous system and with freeze-thaw cycles, fractures appear



Frost heave in new Hampshire (credit Tink Taylor)

Rosa Sinaasappel, Clémence Fontaine, Scott Smith, Daniel Bonn, Noushine Shahidzadeh

Why does this happen?



- Water expends when it becomes ice, this MIGHT put pressure on the walls of the porous material
- But:
  - Stones have been reported to break at saturations below 91%
  - Pores do not generally confine the water in all directions

- So, how can stones break at low saturations?
  What mechanisms are involved?

Investigate this by micro scale experiments, confirm theories by macro scale stone experiments.

MACROSCOPIC FRACTURES ARE PROBABLY DIFFERENT

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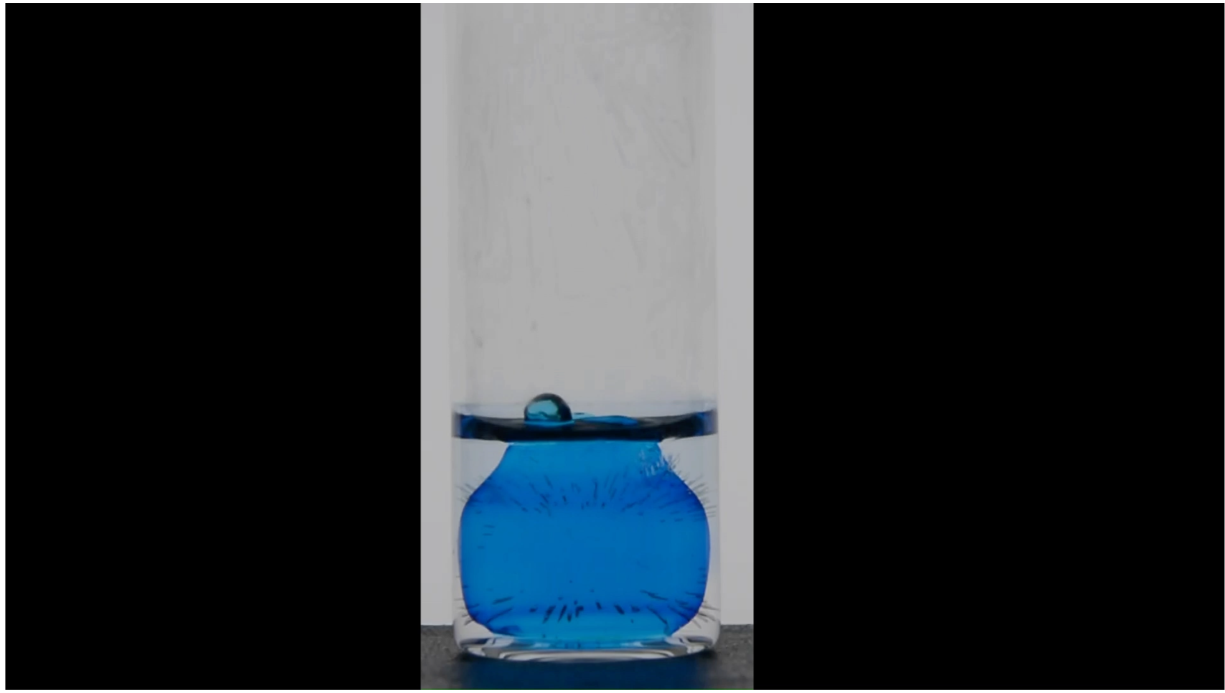
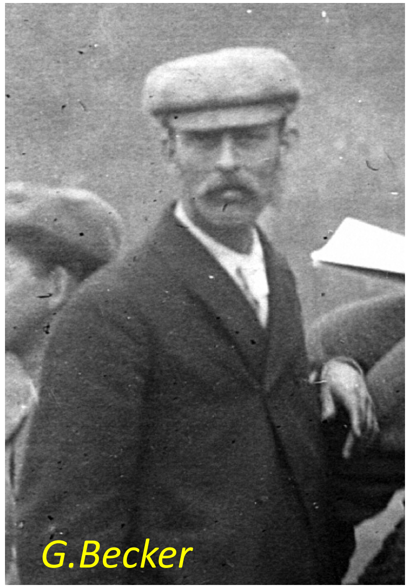


Upon freezing 9% volume increase,
However stones break at saturations (much) lower than 91%

Macroscopic-> large gradients

Microscopically: does a growing crystal exert a pressure?

A century of debate



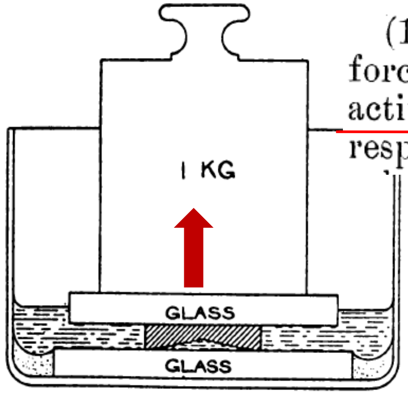


FIG. 1.—A crystal shown growing between two glass plates and lifting a heavy load. Reprinted from the paper of 1905 (*op. cit.*).

(1) A crystal will grow in a direction in which external forces oppose growth, if the surface on which the forces are acting is in contact with a solution that is supersaturated with respect to it;

Becker & Day 1905

Crystallization pressure

$$\Delta p \approx \frac{RT}{V_m} \ln \frac{C}{C_{sat}}$$

Supersaturation

From this it is seen that in addition to supersaturation and the absence of unpressed crystals there must be another condition in order that the crystal shall be able to lift a weight. This condition was pointed out in

Correns, 1949

Scherer 2004, Steiger 2005, Flatt et al. 2007

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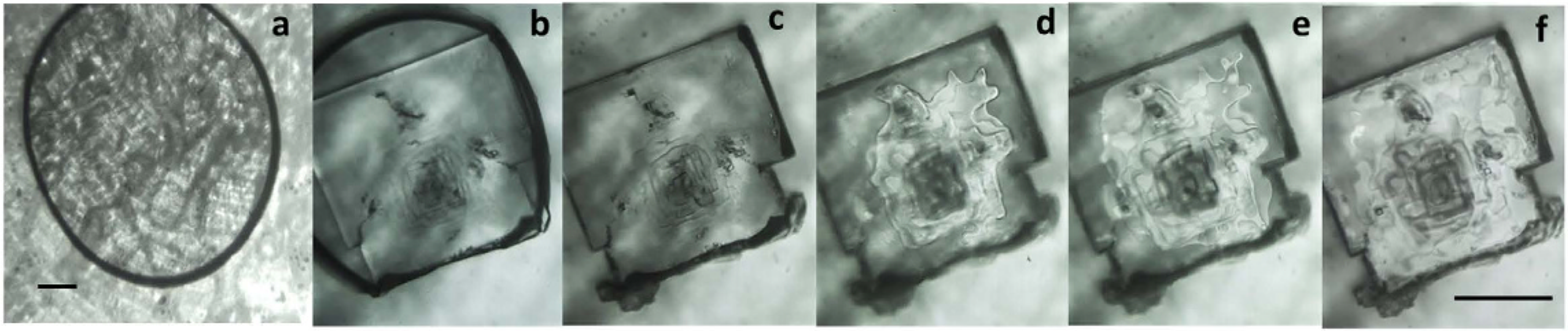
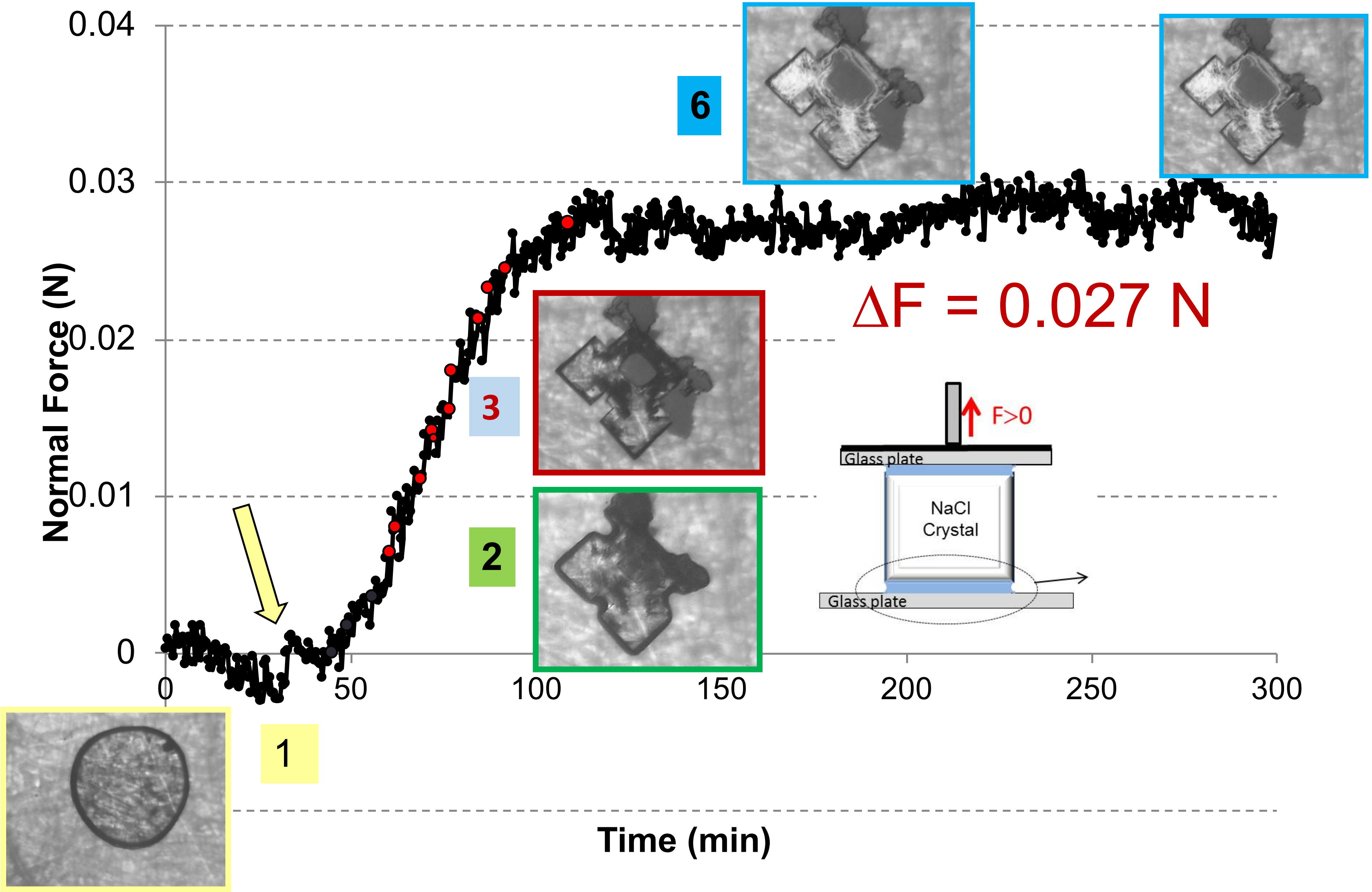
NaCl growth between glass plates

$[NaCl]_0$=5,9M
Gap=50 μm

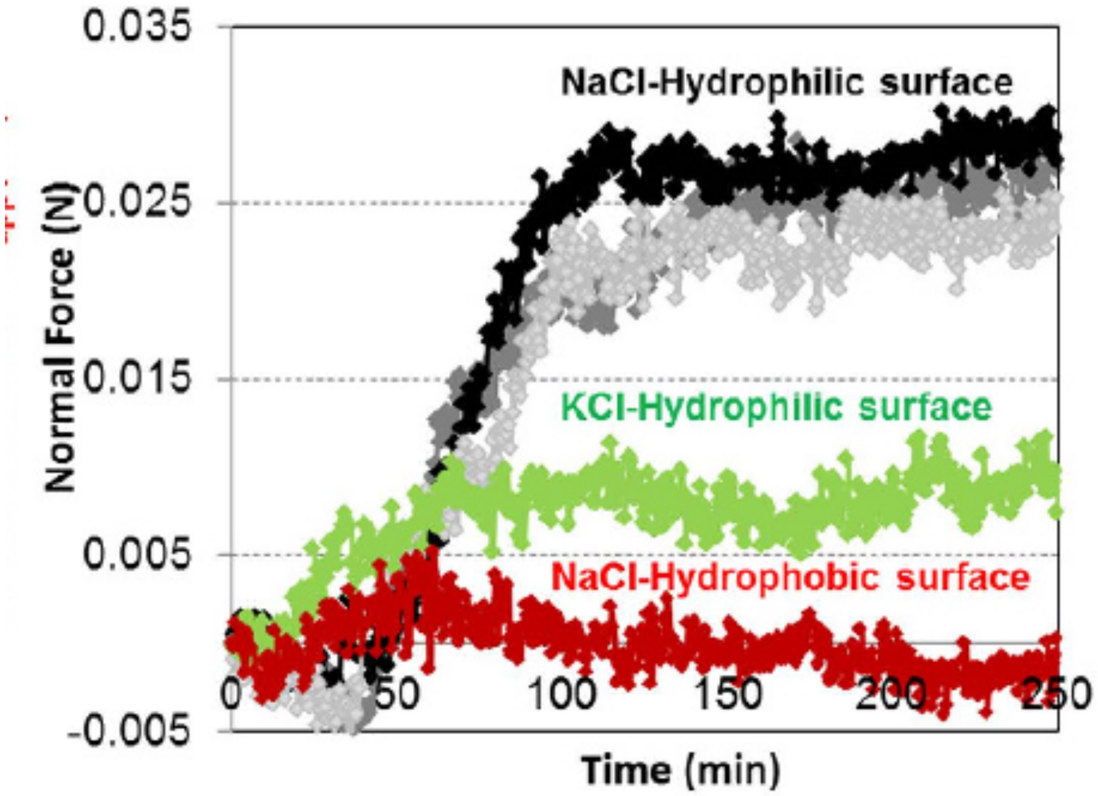
200 μm



Force measurement during NaCl growth



No film, no force……



Film

No film

[The Pressure induced by salt crystallization in confinement]
J Desarnaud, D Bonn, N Shahidzadeh Scientific Reports 6, 30856 (2016)

AND WATER/ICE IN A POROUS MEDIUM??

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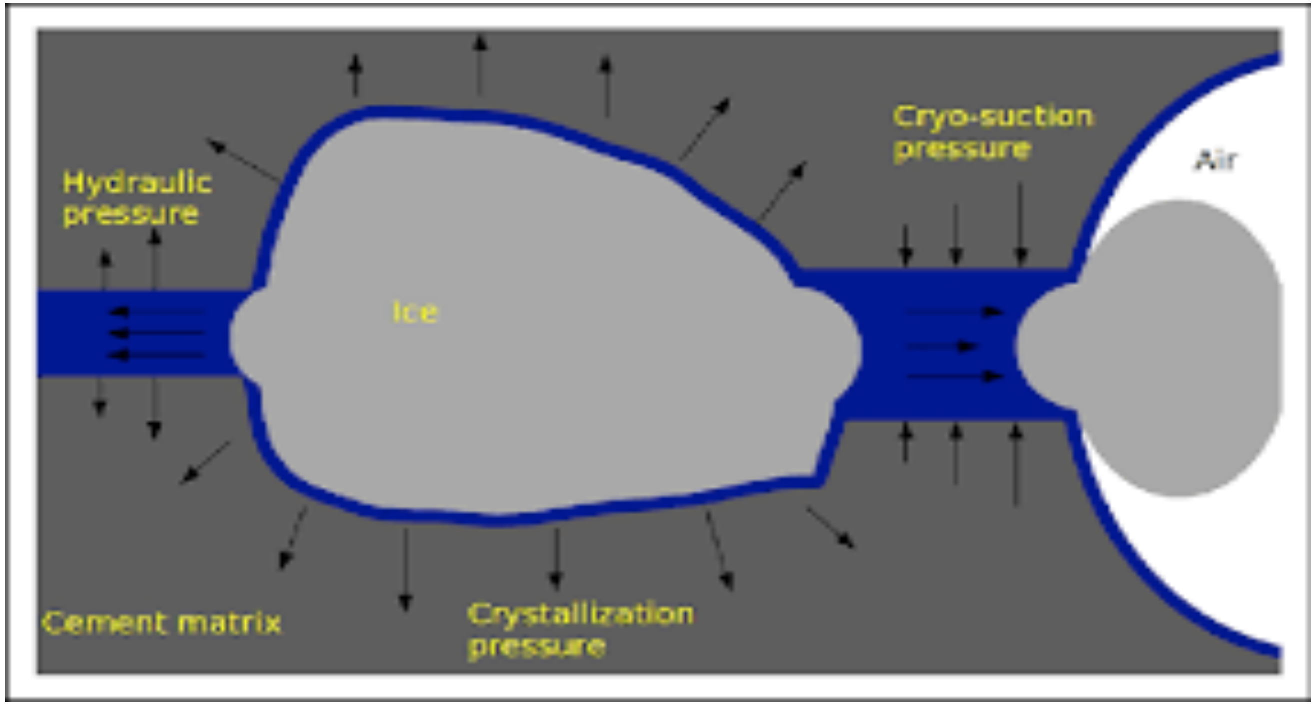


Hydraulic pressure

Ice lensing

Thermal expansion of the ice during the cycling?

New: pore scale experiments, glass capillaries as a simplified model

Disjoining pressure

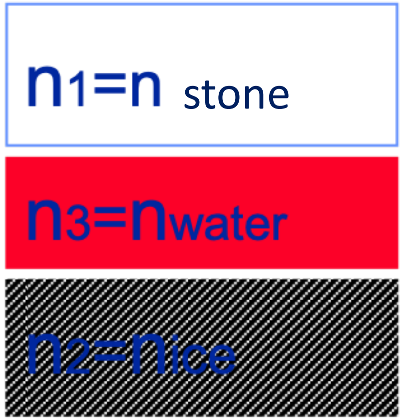
Israelachvili, J., Intermolecular and Surface Forces, Academic Press (London, 1985), p.145

$$W = W_{\nu=0} + W_{\nu>0}$$

$$W_{\nu=0} = \frac{3}{4} kT \left(\frac{\varepsilon_1(0)-\varepsilon_3(0)}{\varepsilon_1(0)+\varepsilon_3(0)}\right)\left(\frac{\varepsilon_2(0)-\varepsilon_3(0)}{\varepsilon_2(0)+\varepsilon_3(0)}\right)$$

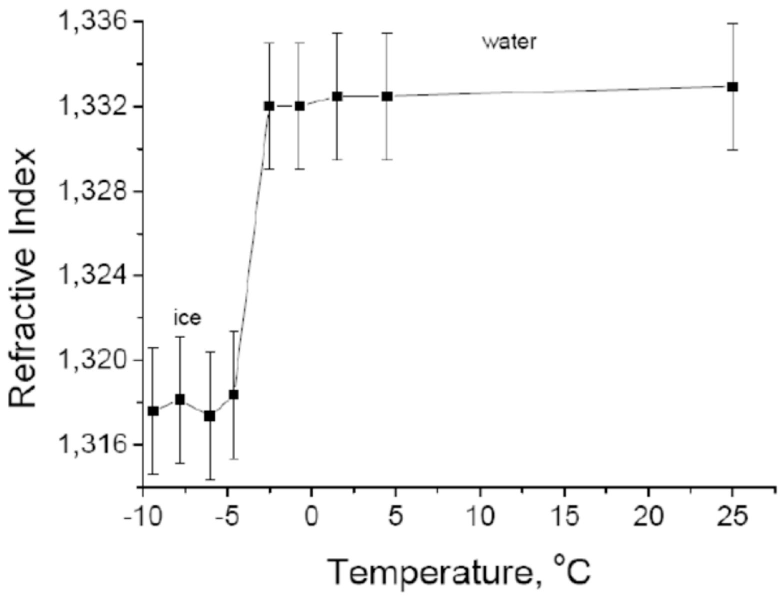
and

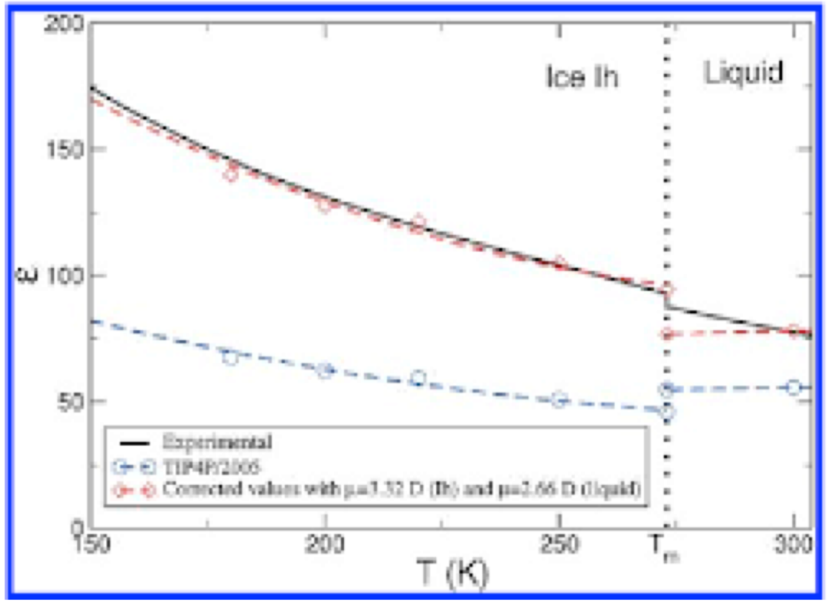
$$W_{\nu>0} = \frac{3h\nu_e}{8\sqrt{2}} \frac{(n_1^2-n_3^2)\boxed{(n_2^2-n_3^2)}}{(n_1^2+n_3^2)^{1/2}(n_2^2+n_3^2)^{1/2}\{(n_1^2+n_3^2)^{1/2}+(n_2^2+n_3^2)^{1/2}\}}$$



W negative -> disjoining pressure pressure tends to separate the two surfaces -> wetting film

$\Pi_{vdW}(l) = -dV_{vdW}/dl = -W/6\pi l^3$: Disjoining pressure





$n_3 > n_2$: *WATER DOES NOT WET ICE*

Small differences, large absolute value: probably irrelevant contribution

Israelachvili, J., Intermolecular and Surface Forces, Academic Press (London, 1985), p.145

$$W = W_{\nu=0} + W_{\nu>0}$$

$$W_{\nu=0} = \frac{3}{4} kT \left(\frac{\varepsilon_1(0)-\varepsilon_3(0)}{\varepsilon_1(0)+\varepsilon_3(0)}\right)\left(\frac{\varepsilon_2(0)-\varepsilon_3(0)}{\varepsilon_2(0)+\varepsilon_3(0)}\right)$$

and

$$W_{\nu>0} = \frac{3h\nu_e}{8\sqrt{2}} \frac{(n_1^2-n_3^2)\boxed{(n_2^2-n_3^2)}}{(n_1^2+n_3^2)^{1/2}(n_2^2+n_3^2)^{1/2}\{(n_1^2+n_3^2)^{1/2}+(n_2^2+n_3^2)^{1/2}\}}$$

W<0: Wetting!

CAPILLARY EXPERIMENTS: SETUP

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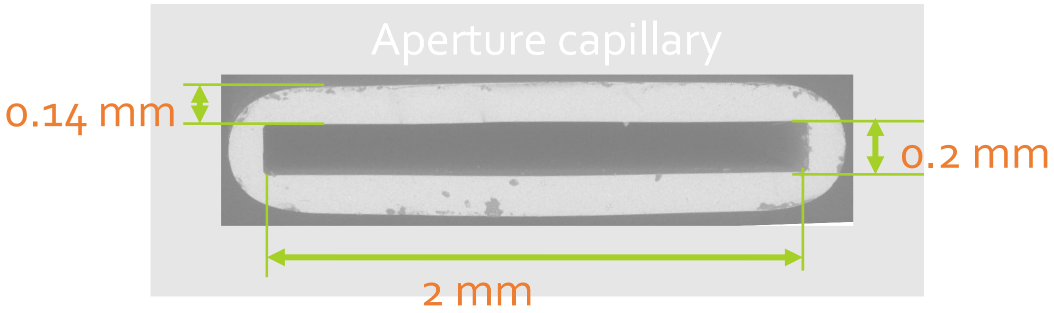

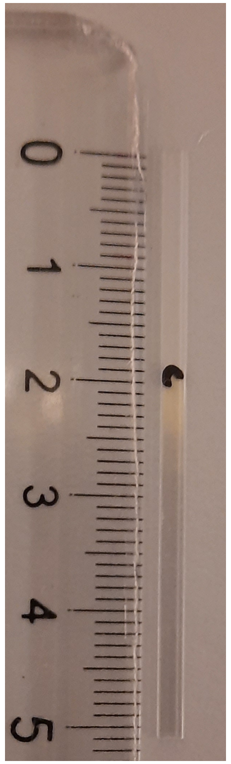

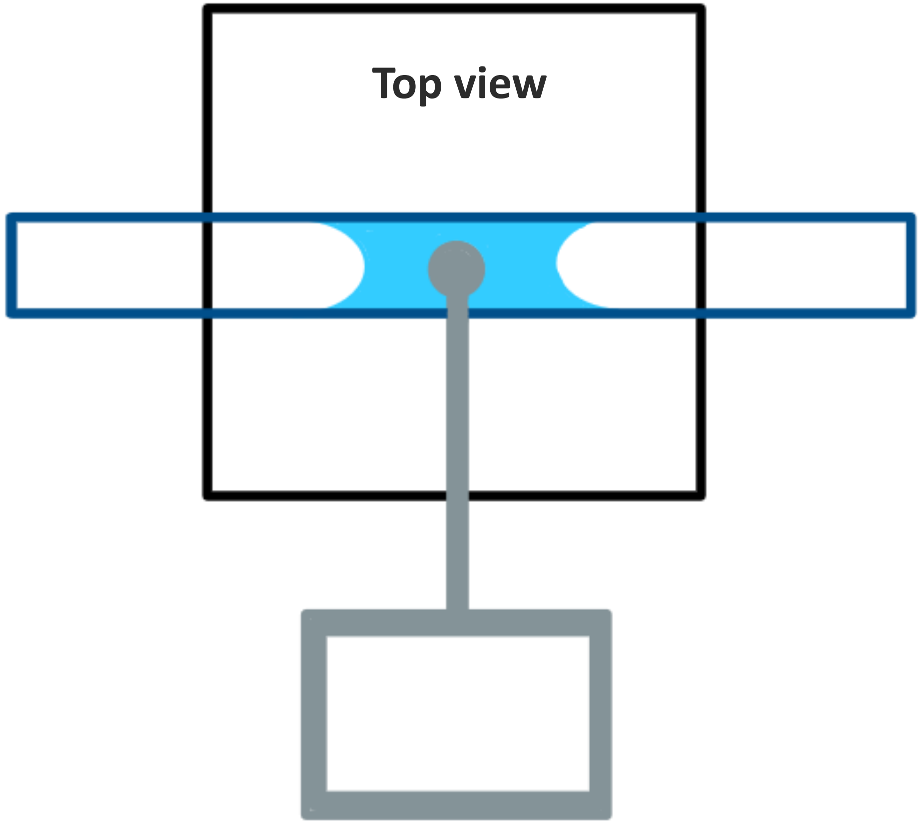

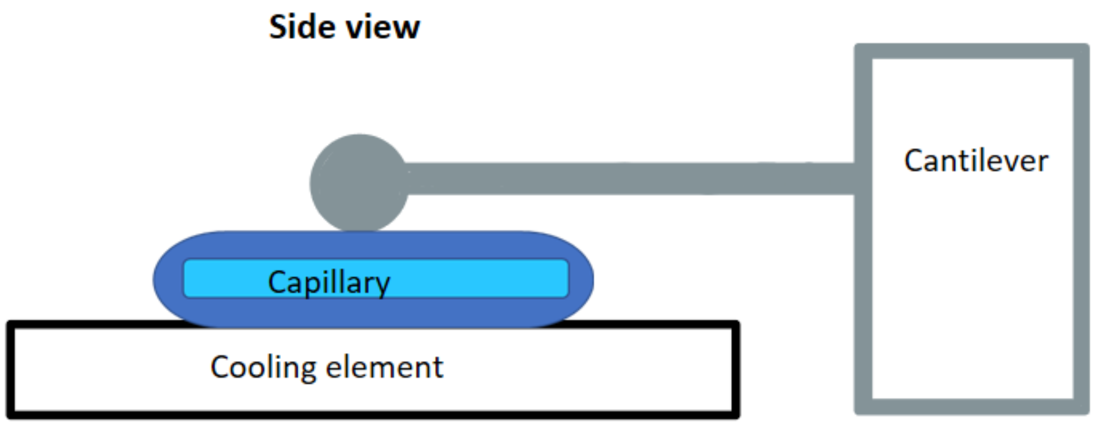

PRESSURE MEASUREMENTS

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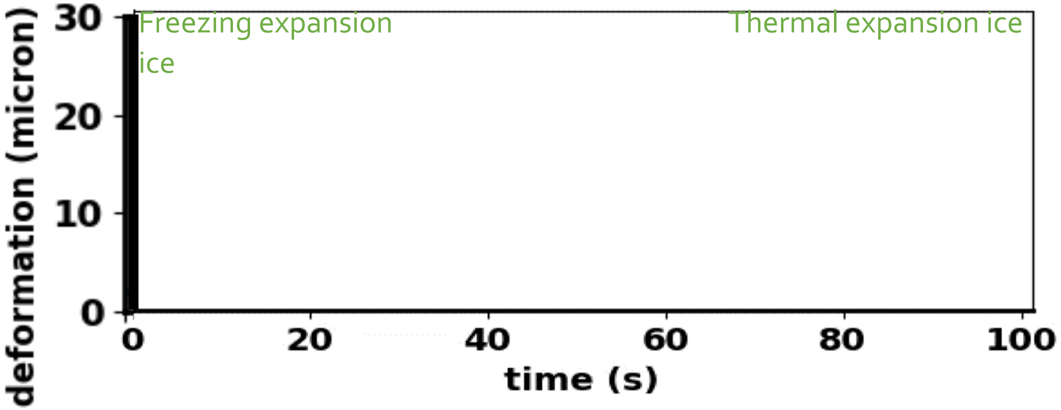

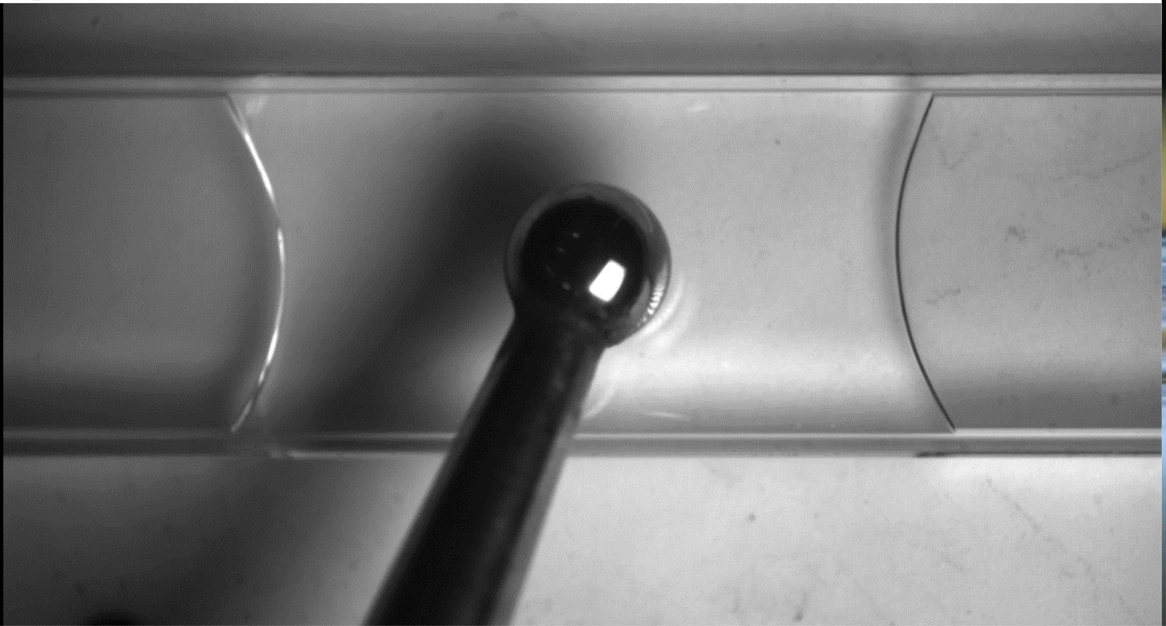

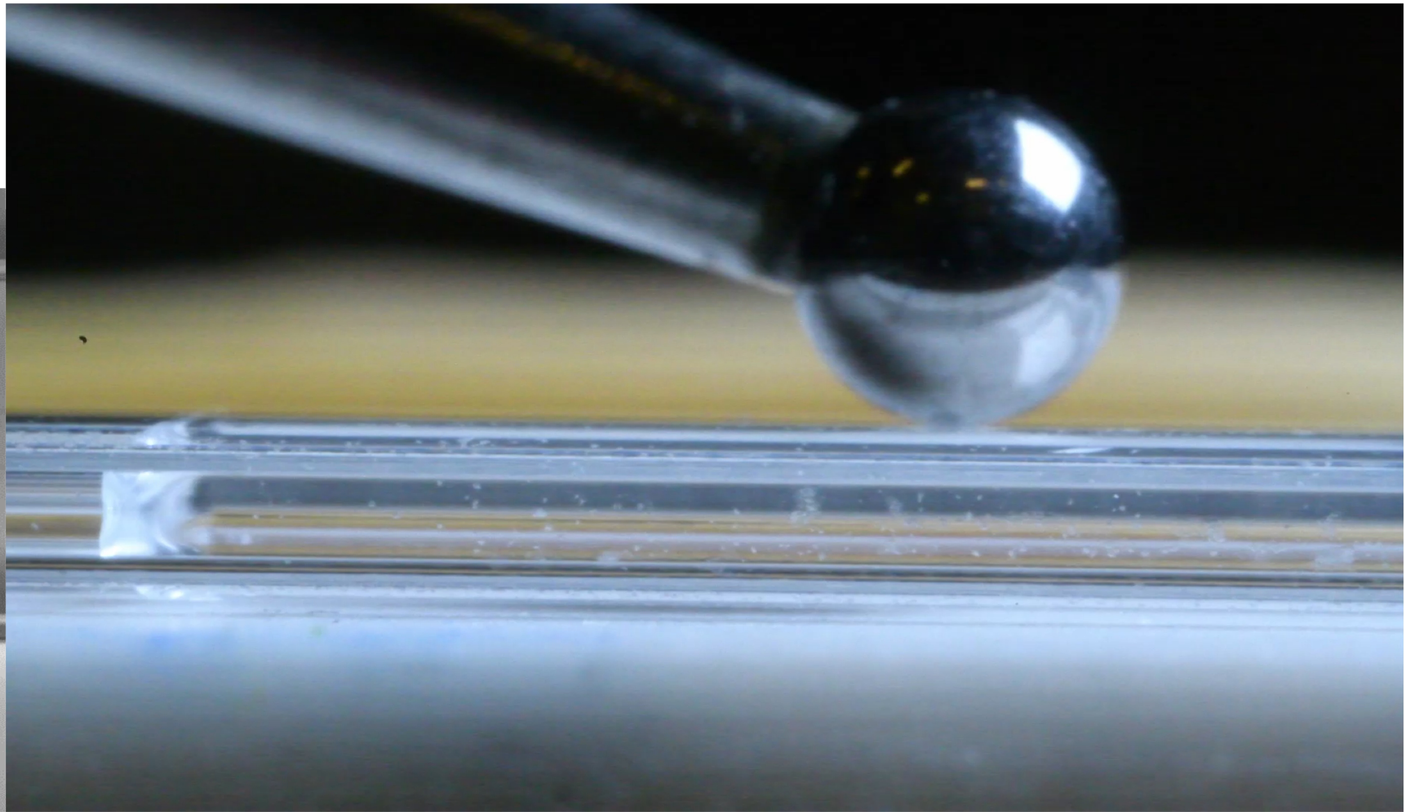

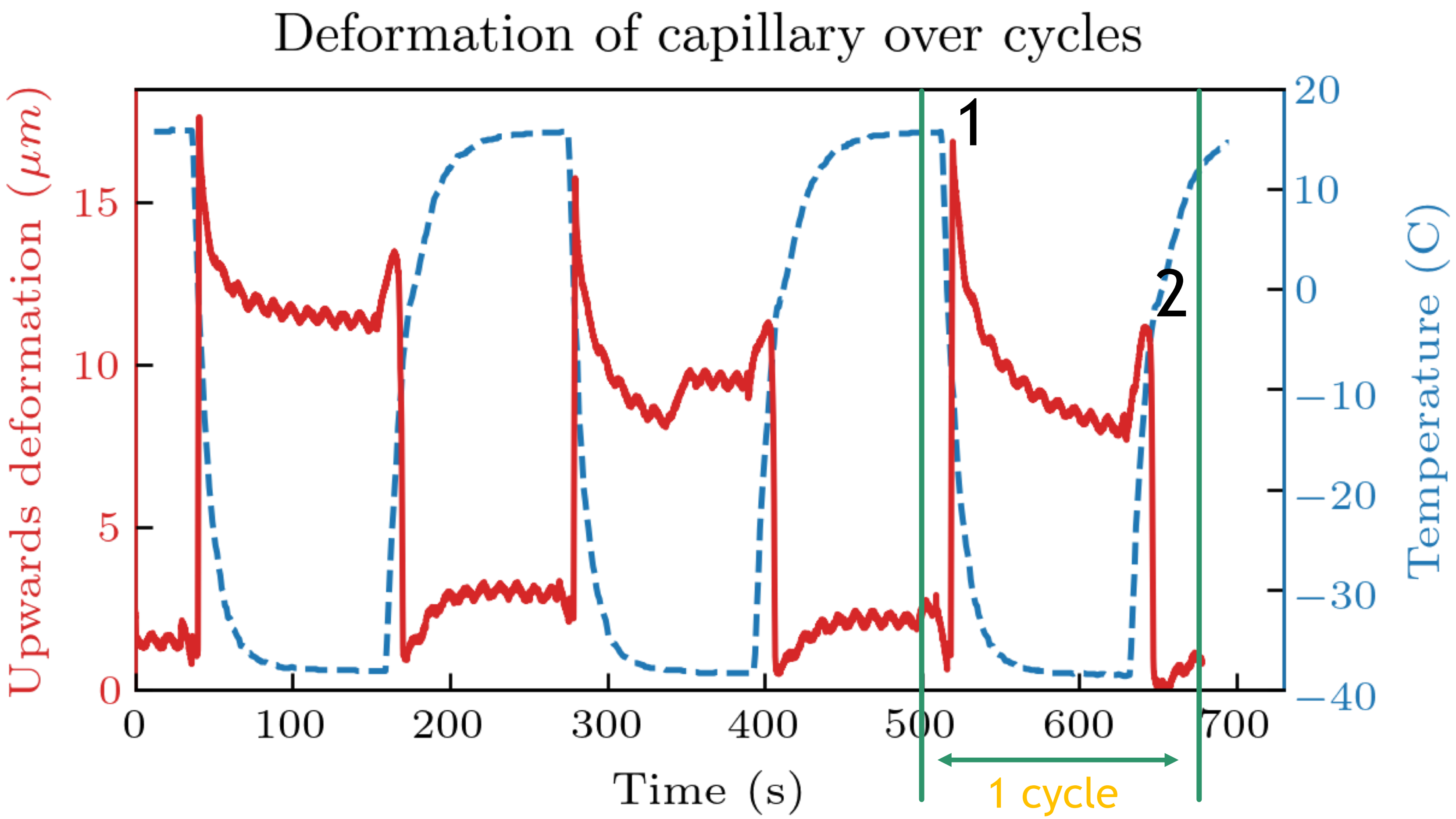

1=freezing expansion peak
2=thermal expansion of ice peak

CALIBRATION WITH COMSOL

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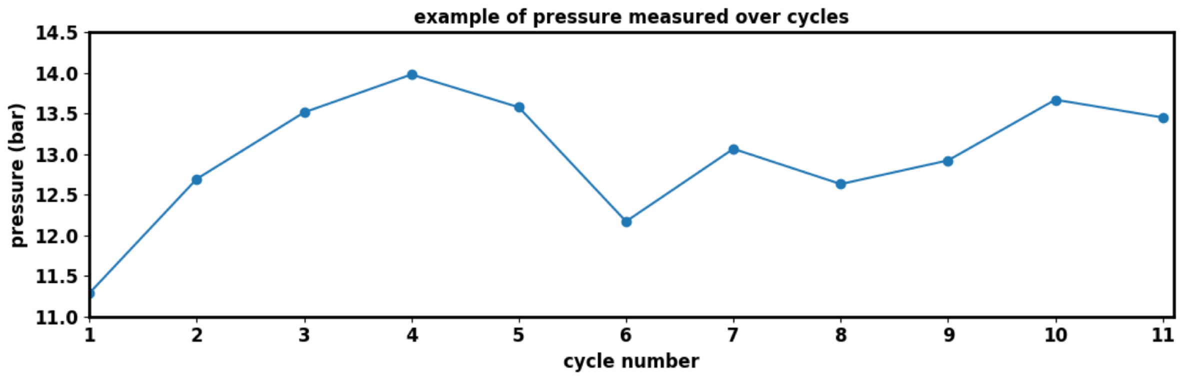
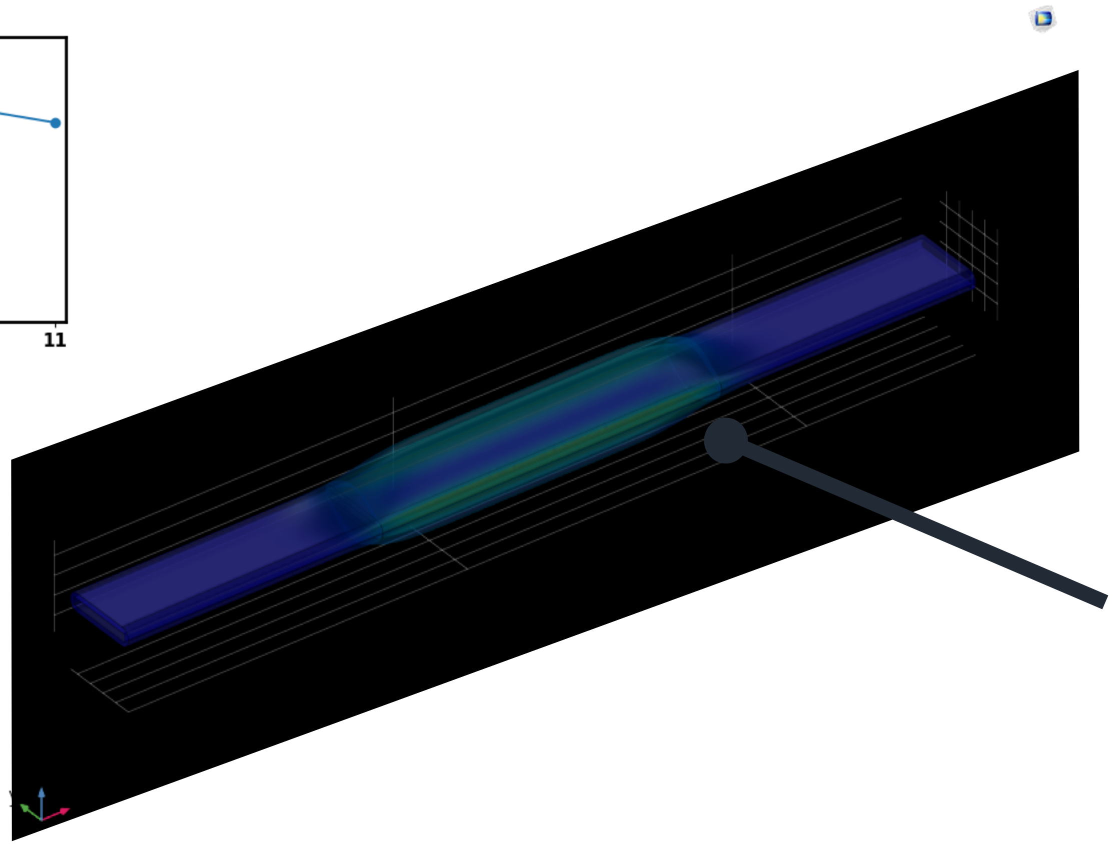
Deformation to pressure with finite element modeling (Comsol)
Pressures turn out to be at the order of 0.1 to 25 Mpa (1 to 25 bar)



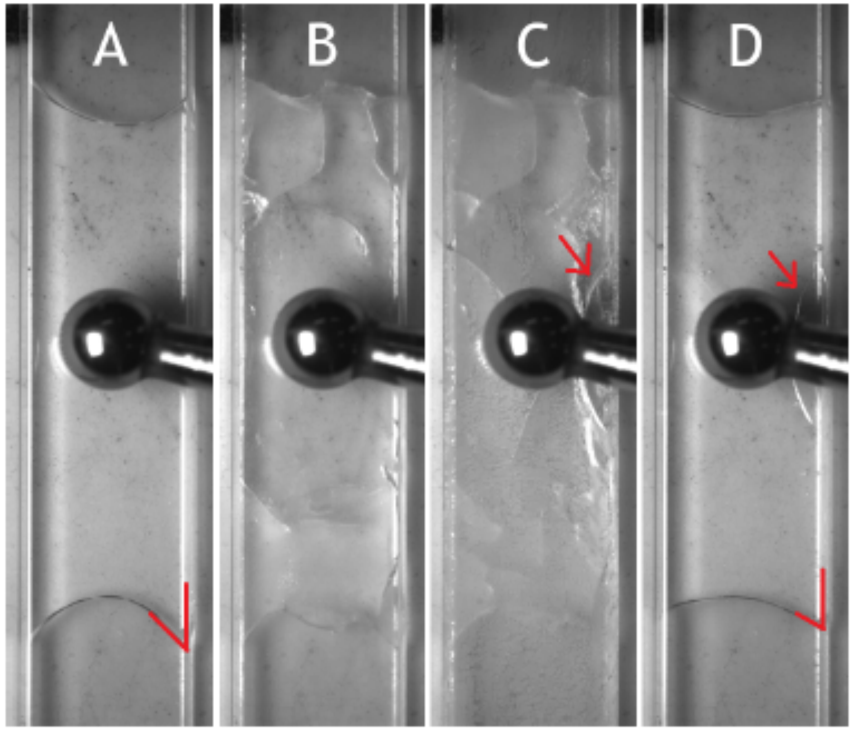


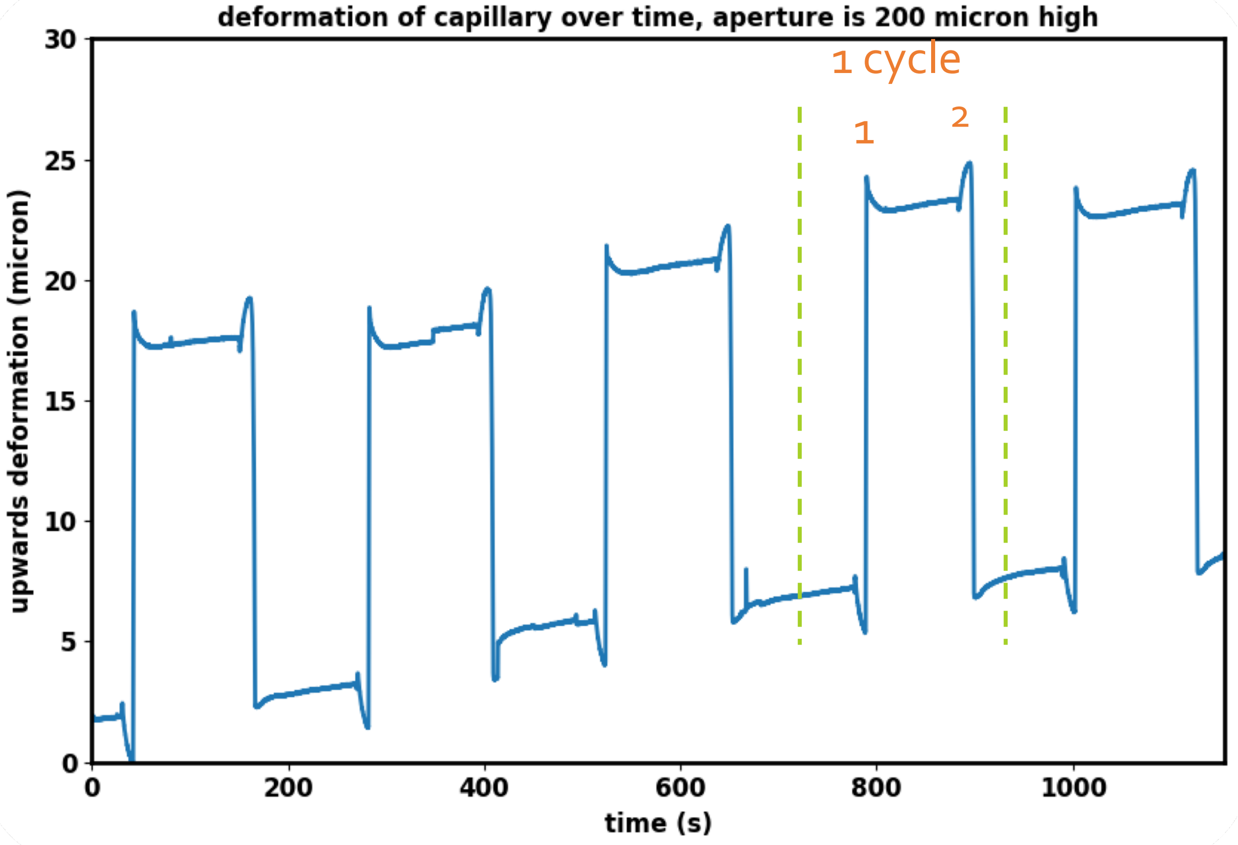
Crystallisation pressure: 1.2 Mpa per degree of undercooling (Scherer 1998)

Capillaries break at 1.3-2.0 Mpa (depending on glass weathering) confirmed by independent measurement

CYCLES AND BREAKING GLASS

Universiteit van Amsterdam





Ice breaks most of the times, capillaries break sometimes, mostly at the 1st peak; probability is higher when:

- Contact angles are high
- Volume is small
- Multiple cycles have happened

QUANTITATIVE RESULTS

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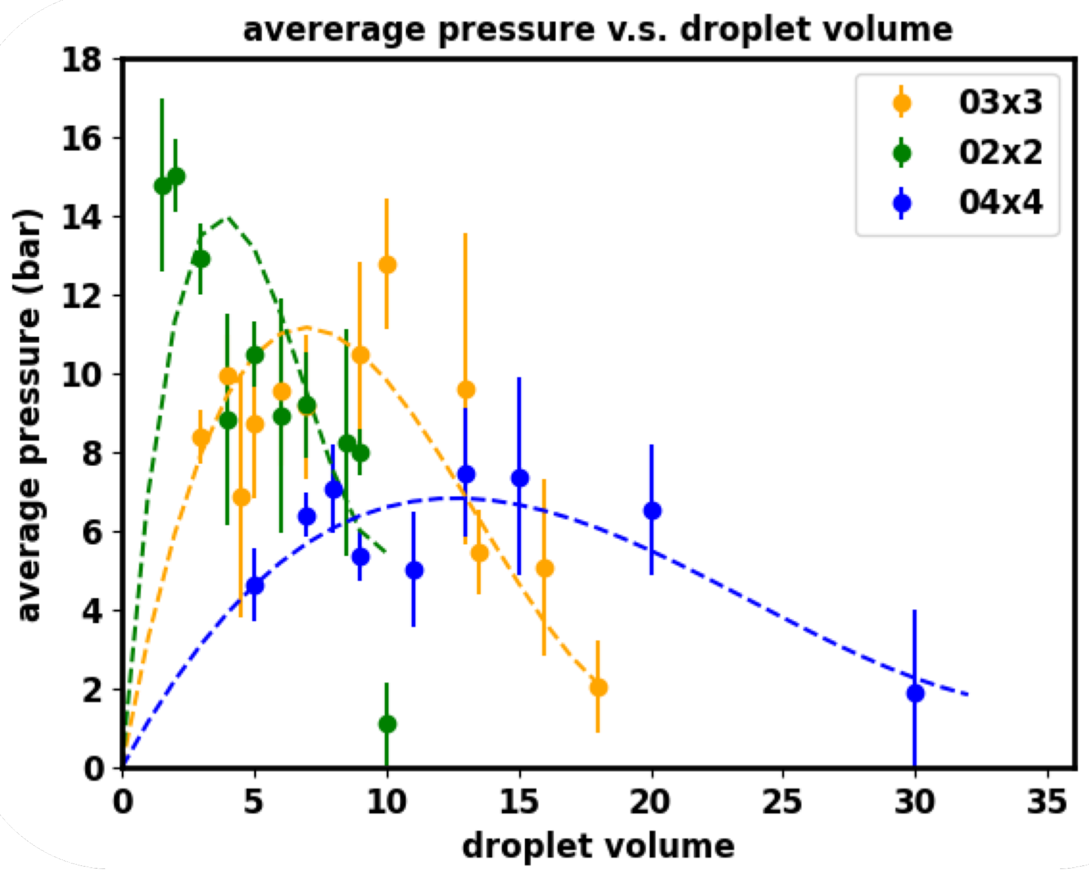
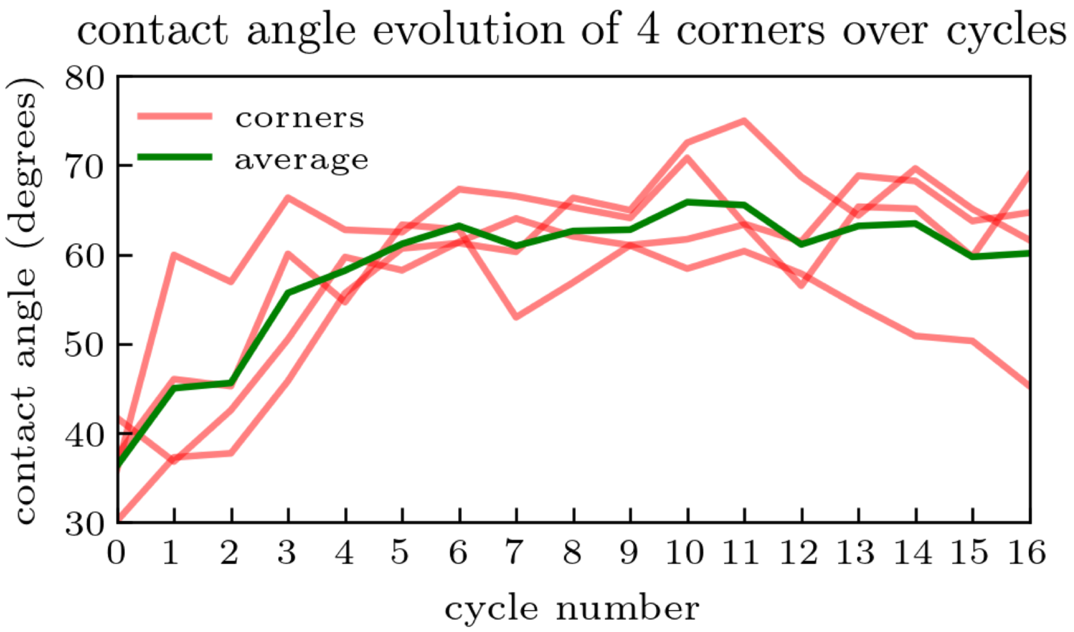


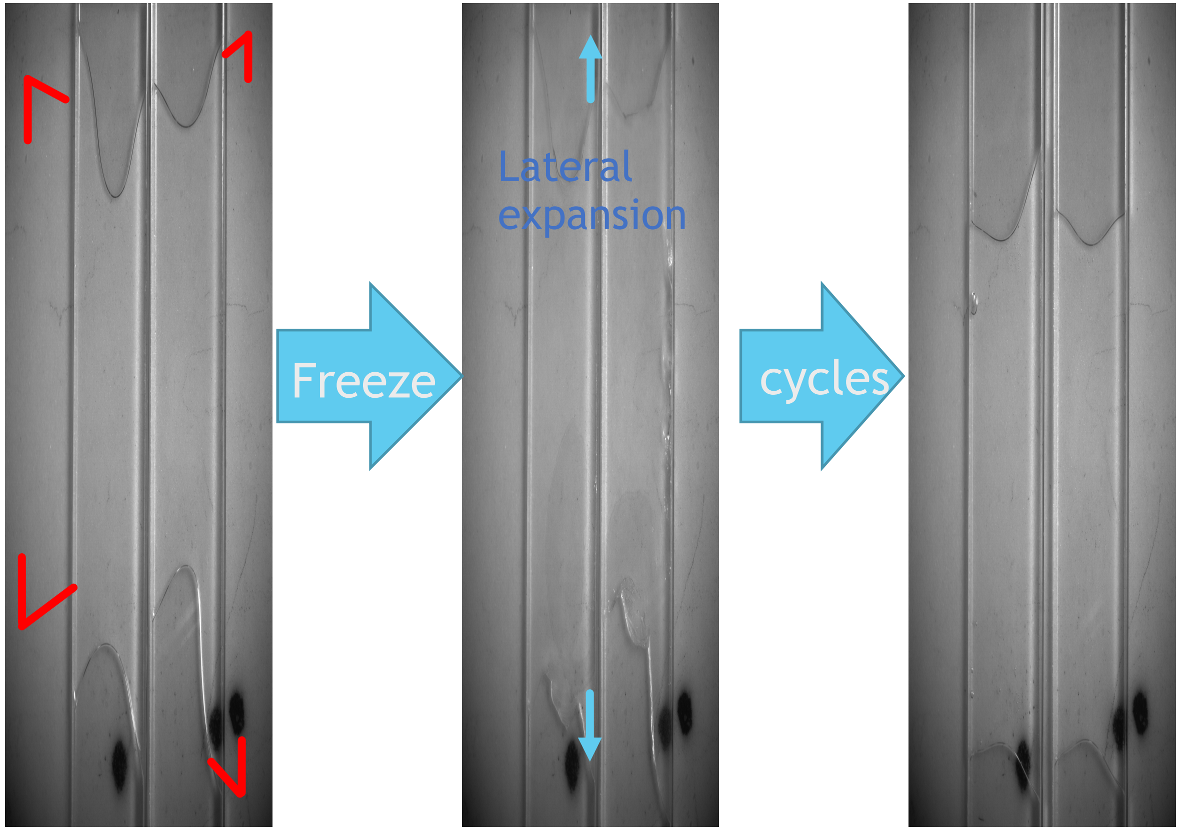
To small: not enough pressure

To large: deviated to the sides

The smaller the pore, the larger the pressure, showing importance of confinement by surface tension

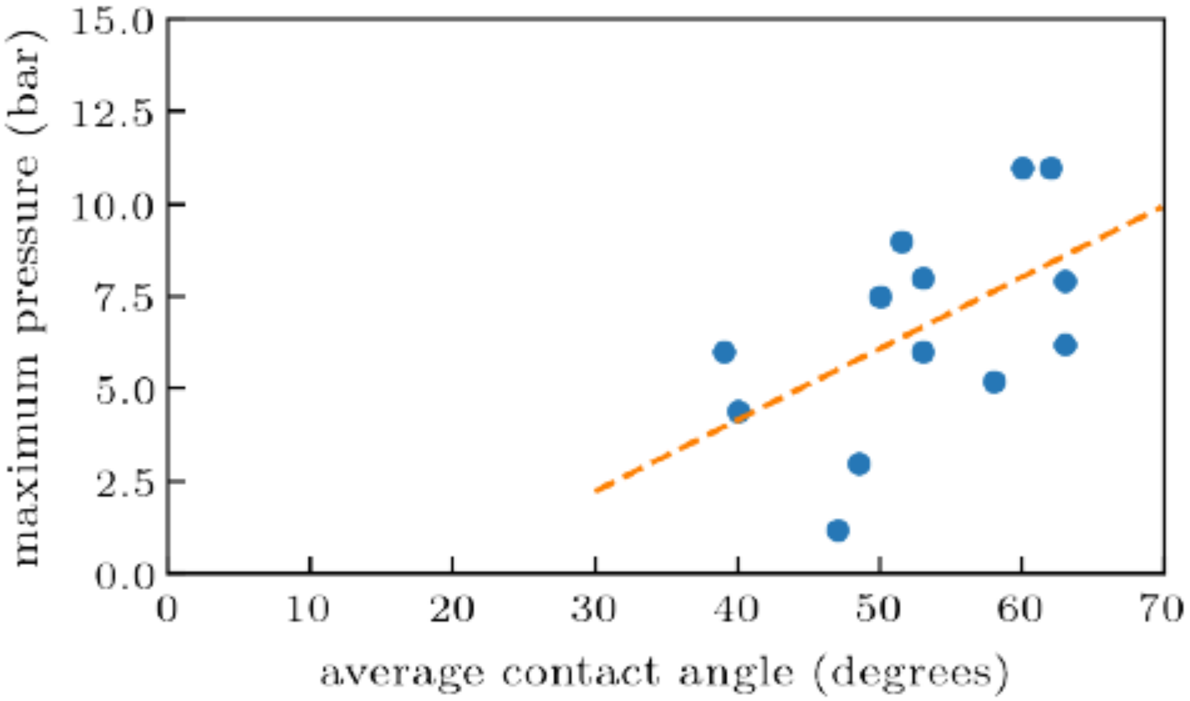
Contact angle evolution





Effect of contact angle on pressure

- There appears to be a correlation
- Mostly capillaries that show contact angle evolution break



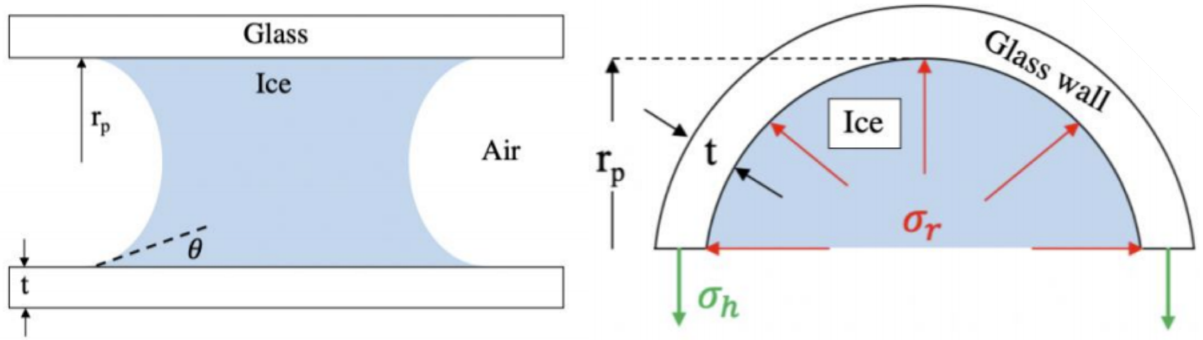
Effect of contact angle

using Crystallisation pressure: 1.2 Mpa per degree of undercooling (Scherer 1998)

- Hoop stress as found :

$$\sigma_h = \left(E_{comp}^{ice}(0.04)\sin(\theta) - \frac{\gamma_{air-ice}\cos\theta}{r_p}\right)\left(\frac{2r_p^2+2r_pt+t^2}{2r_pt+t^2}\right)$$

- When the contact angle is low, the pressure might dissipate into the corners



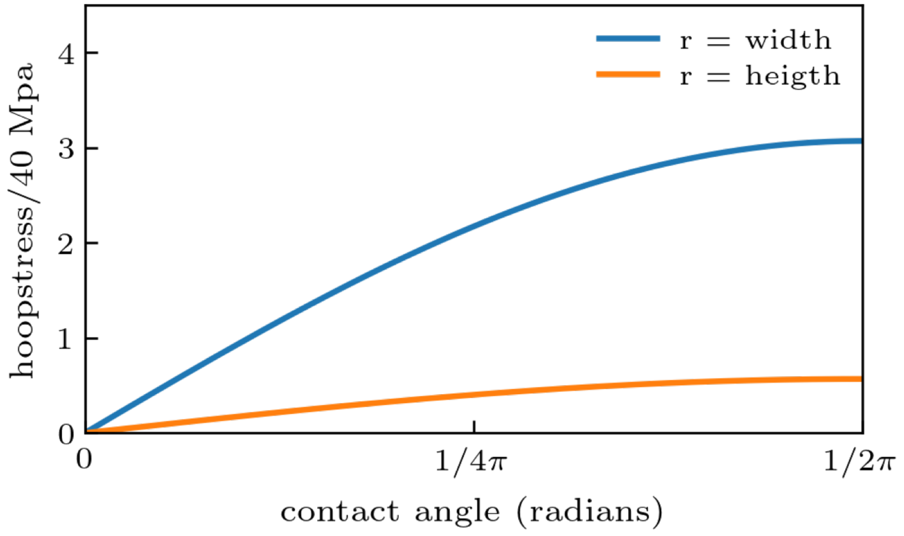
The better the meniscus is at confining the droplet, the higher the pressure

Certain optimum in droplet volume

Smaller capillaries give higher pressures

Higher contact angle gives higher pressure

Cycling increases the contact angle



AND SO WHAT ABOUT REAL STONES?

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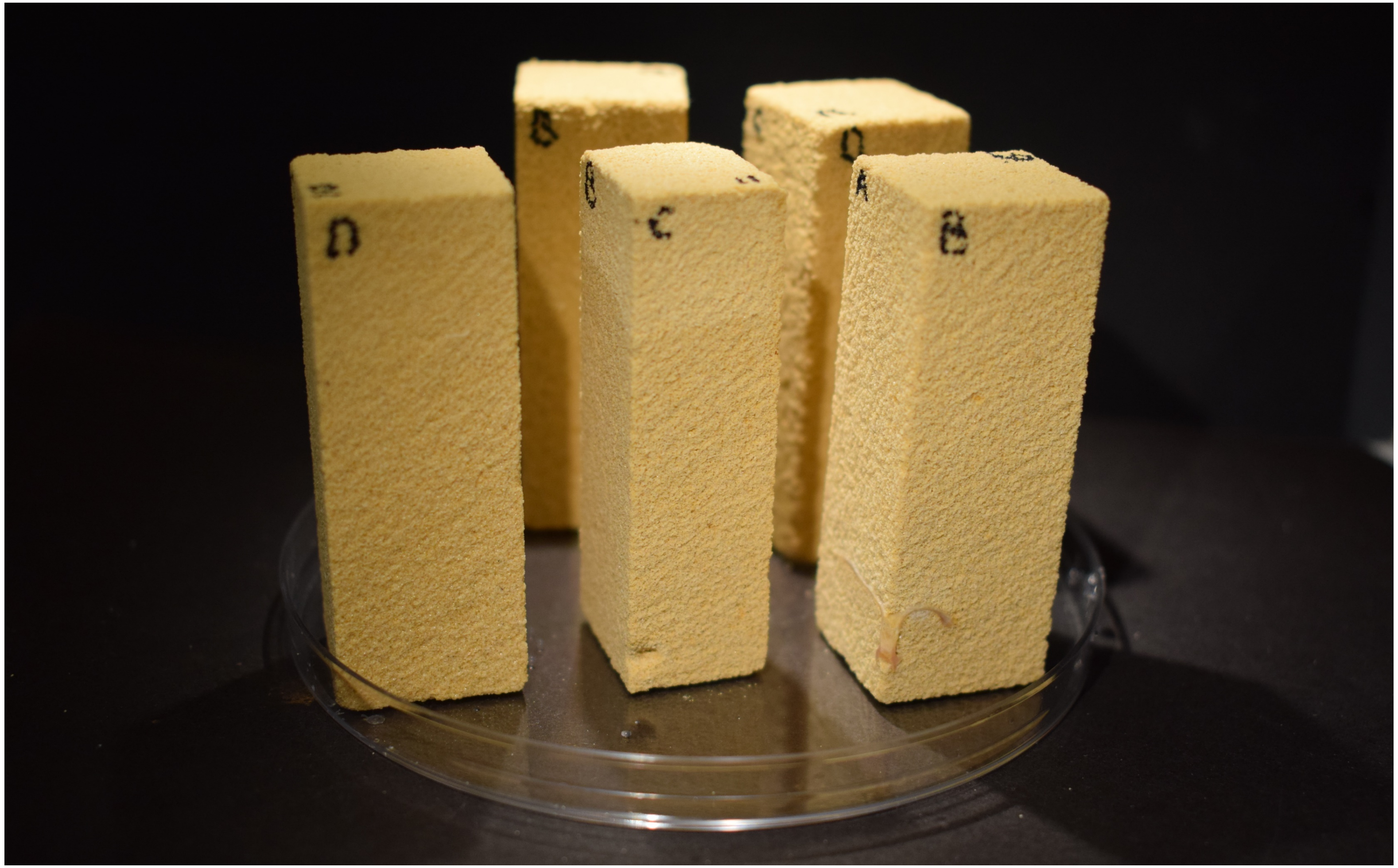
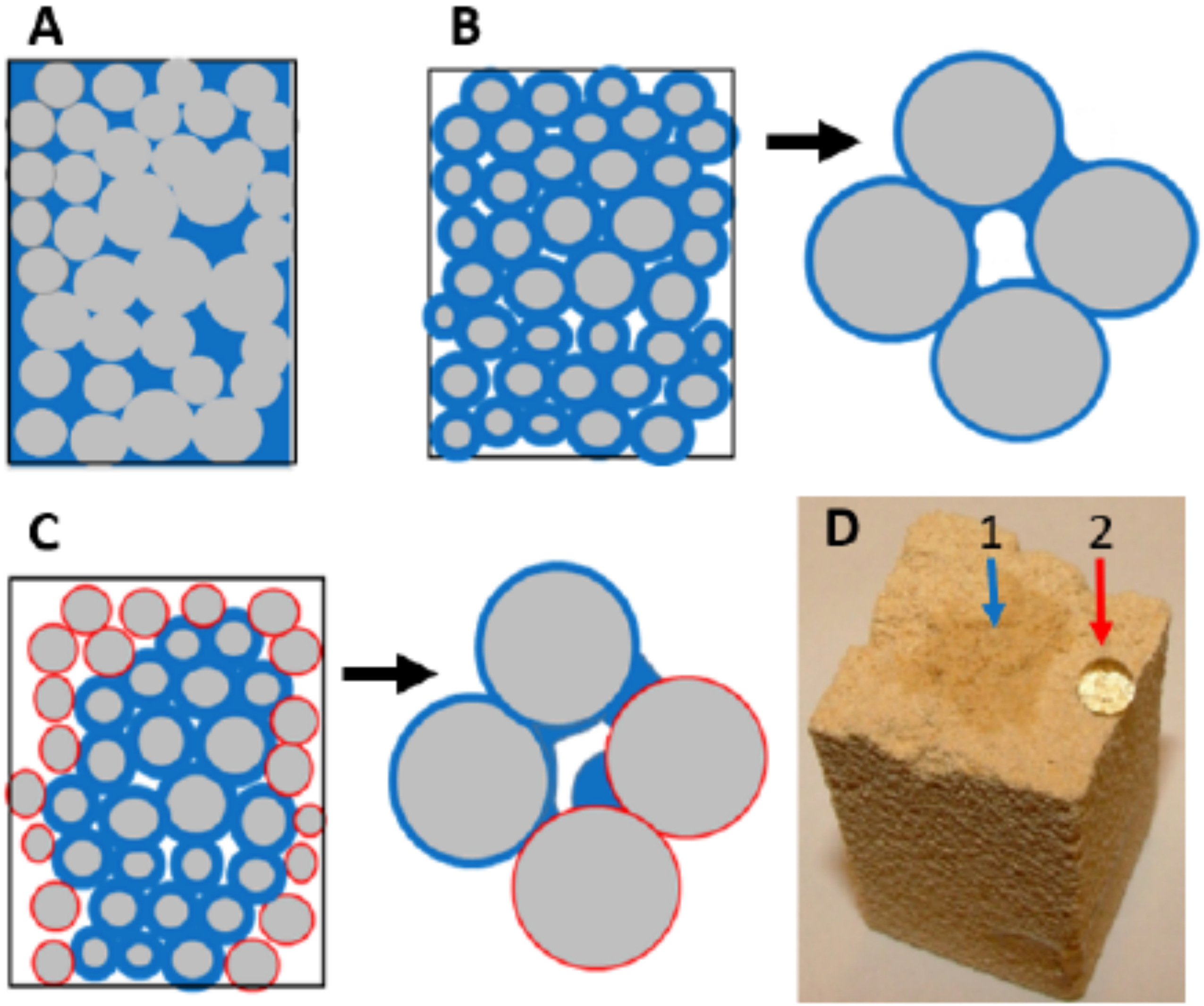


Sandstone samples 1,5 x 1,5 x 5 cm

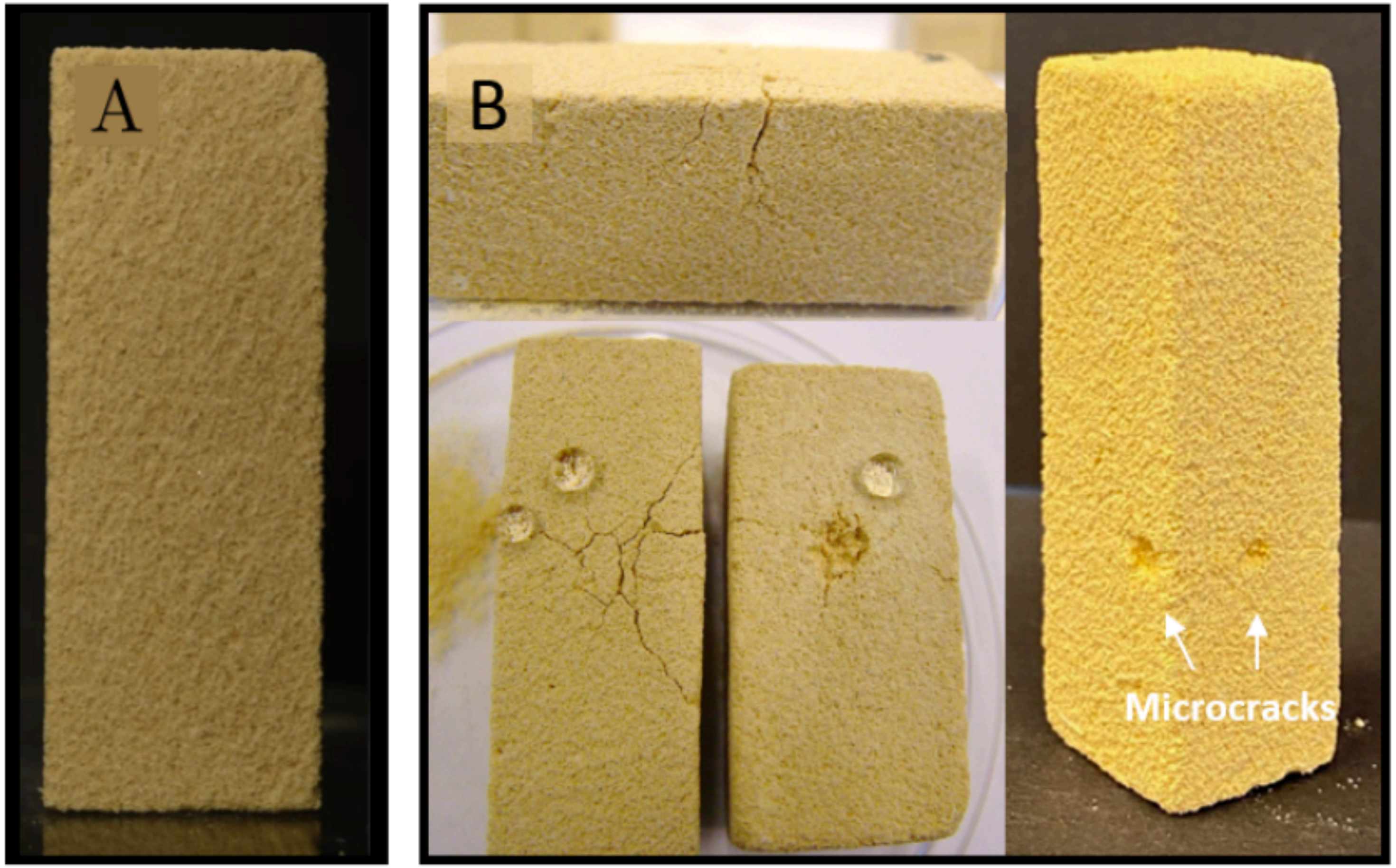


Very hydrophilic sandstone:
Small contact angles

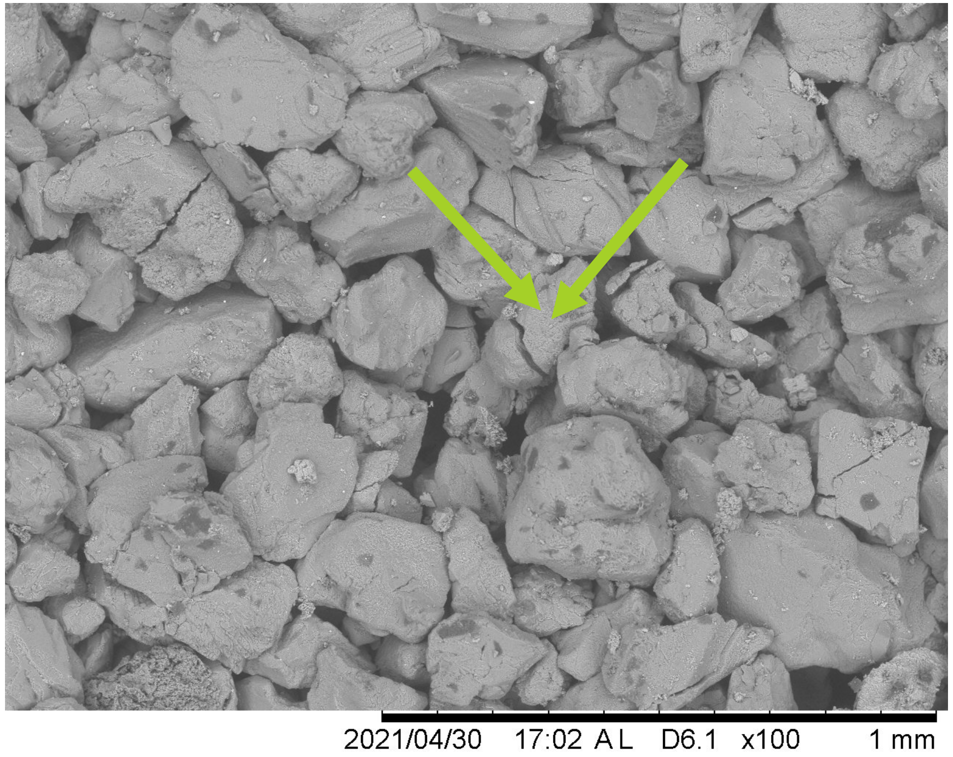
Less hydrophilic sandstone:
Large contact angles

Very hydrophilic sandstone:
No damage

Less hydrophilic sandstone:
Severe damage



EVEN THE INDIVIDUAL GRAINS BREAK



CONCLUSIONS

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Crystallisation pressure explains most observations with a small additional effect of thermal expansion

Surface tension confines droplet laterally, fracture happens if confinement is sufficient

Explains fractures at saturation lower than 91%