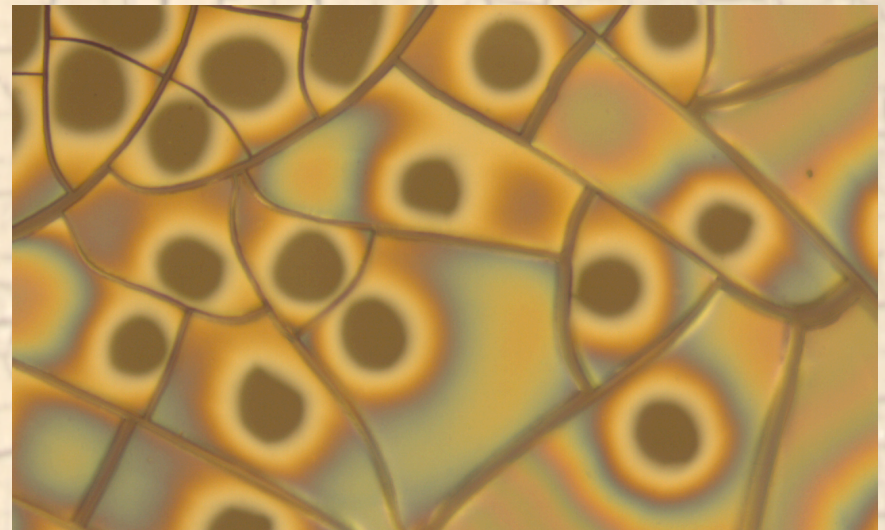
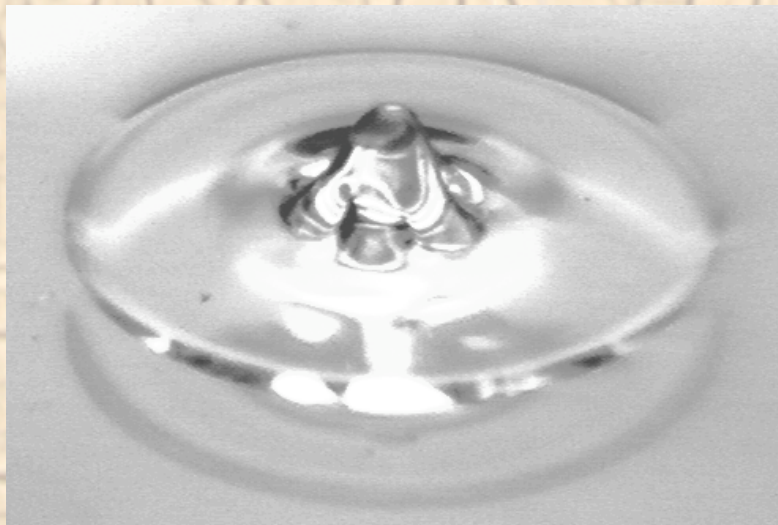


# Drying of complex fluids: Deformations and fractures

L. Pauchard  
FAST

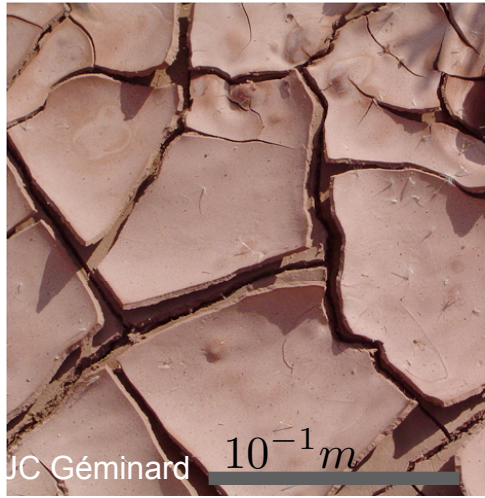
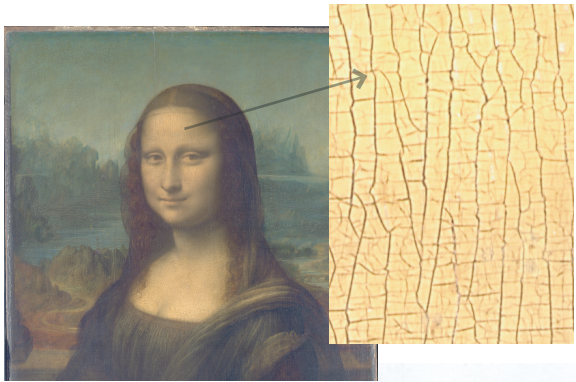




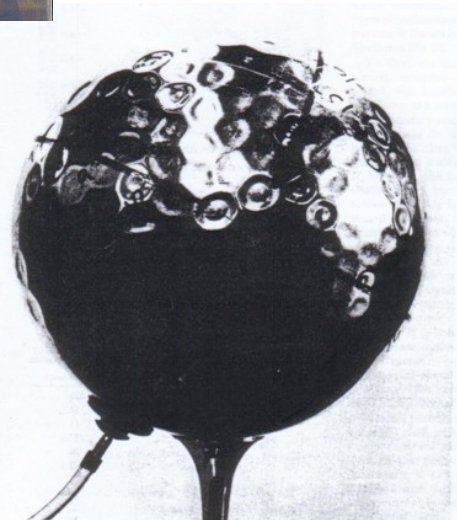
**crack patterns**

**Singularities**

**inversion of curvature in shells**

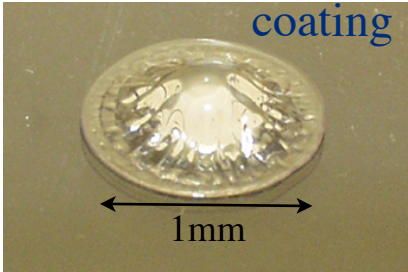
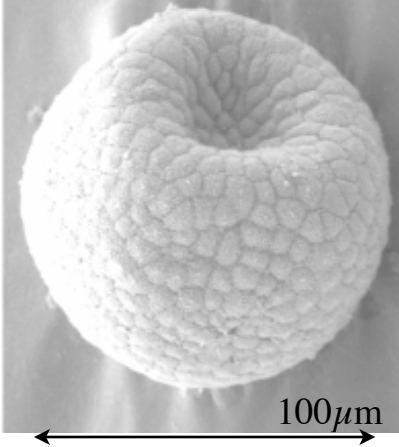


directional cracks propagation



Carlson (1967)

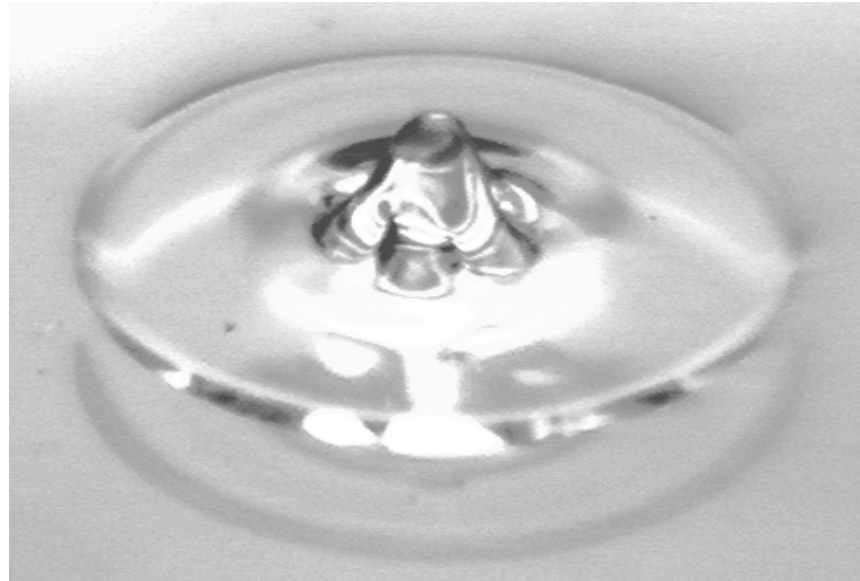
sea-urchin embryo



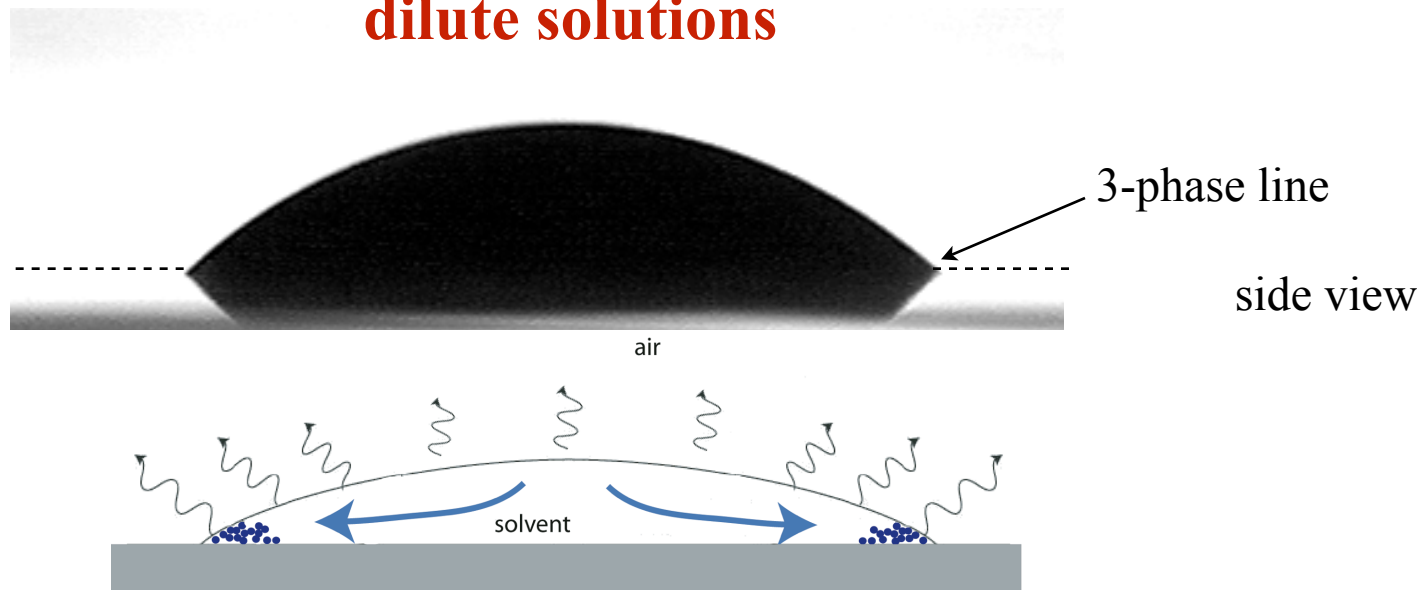
A. Davaille

# I

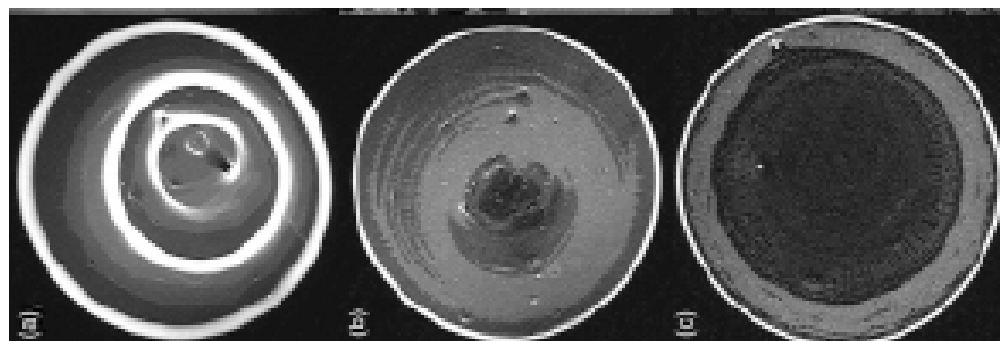
## Drying of drops of complex fluids



# Drying a sessile drop of complex liquids dilute solutions



deposition patterns left by a drop of a dilute colloidal suspension



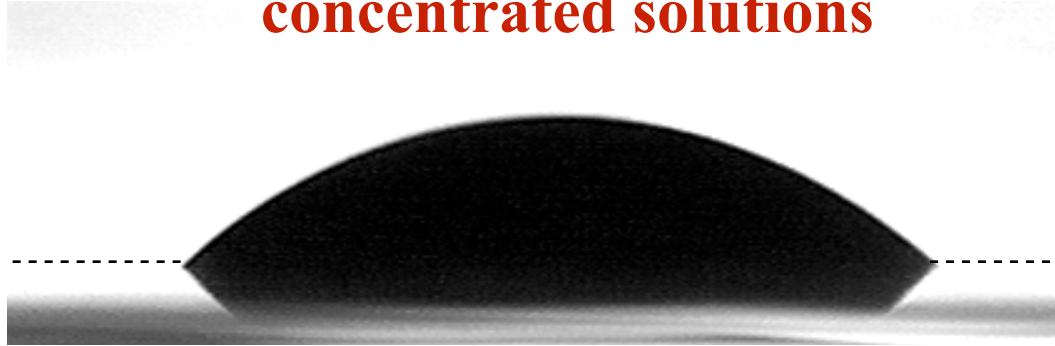
top view

Deegan, thesis (1998)

evaporation-induced flow → deposition of layers (Berteloot et al., Eur. Phys. Lett. (2008))



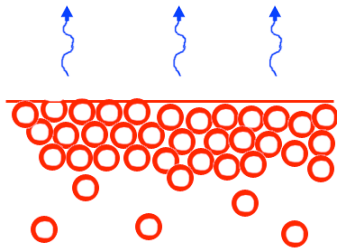
# Drying a sessile drop of complex liquids concentrated solutions



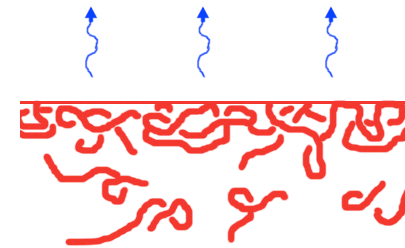
complex drop shapes due to different process

- pinning of the three-phase line
- large concentration gradients

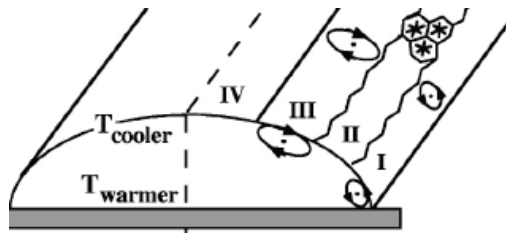
colloidal suspensions



polymer solutions



- hydrodynamic  
Rayleigh-Bénard or  
Bénard-Marangoni effects



or mechanical instabilities

# Drying a sessile drop of complex liquids concentrated solutions



importance of :

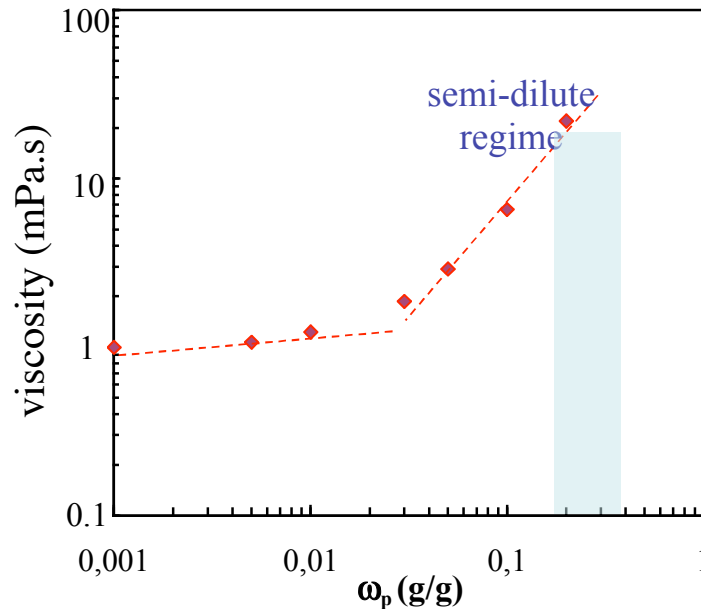
- drying conditions,
- geometry,
- physico-chemical properties of the system.



# Drying a drop of polymer solution: glass transition during desiccation

polymer = dextran (hydrosoluble polysaccharide)

concentration in mass : from 20 to 40% ( $\omega_p$ )



$T_g \sim 220^\circ\text{C}$  (glass transition temperature)

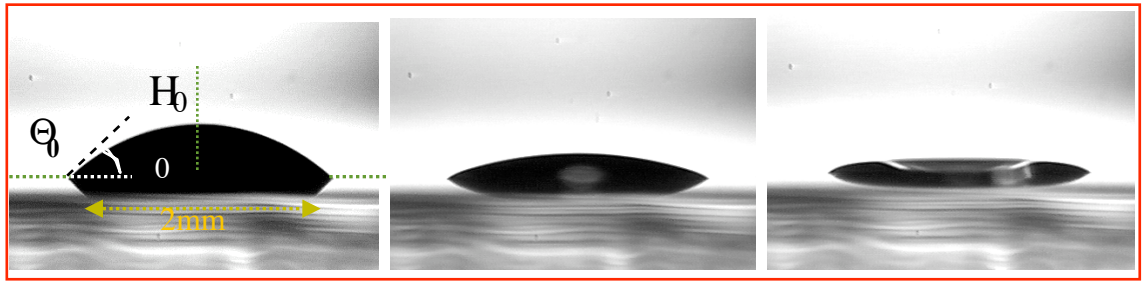
solvent loss

$\Rightarrow$  polymer concentration increases

$\Rightarrow$  medium becomes glassy

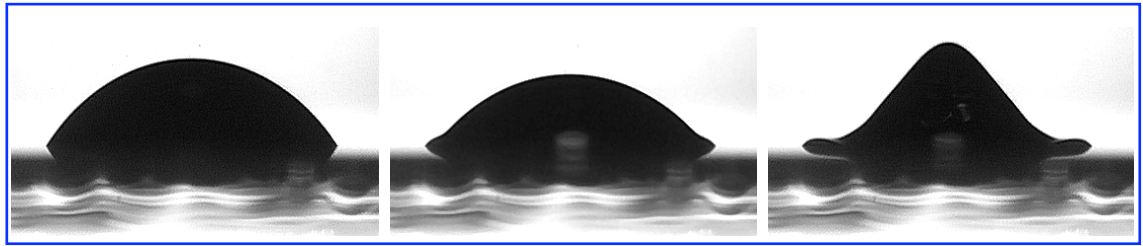
$\omega_p, RH, T : \text{constants}$

I. deformation  
polymer drop



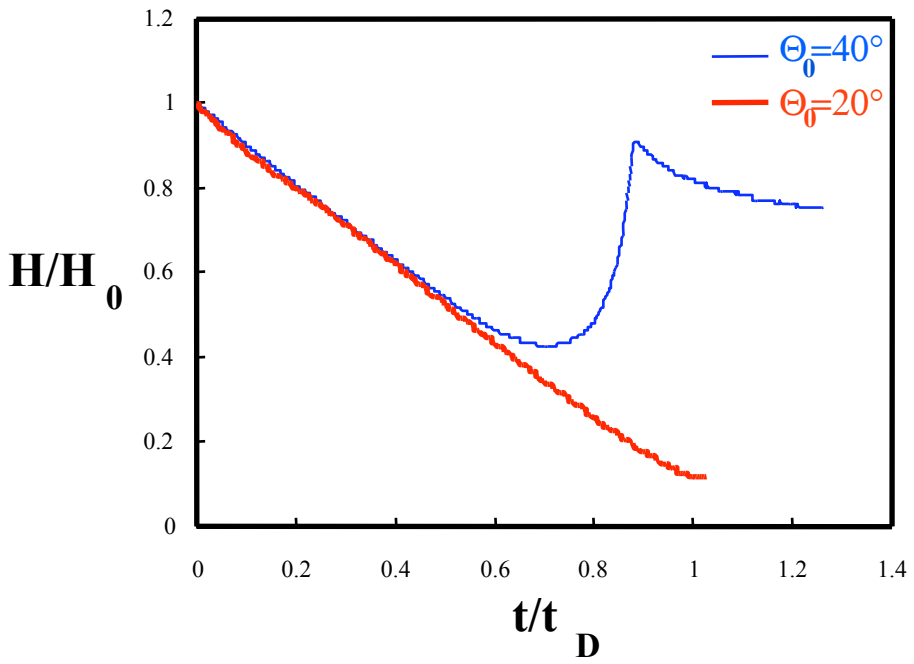
$\Theta_0 = 20^\circ$

time →



$\Theta_0 = 40^\circ$

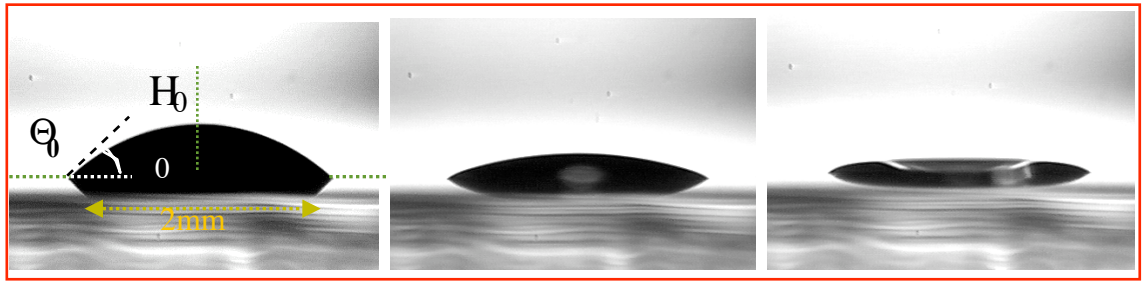
?





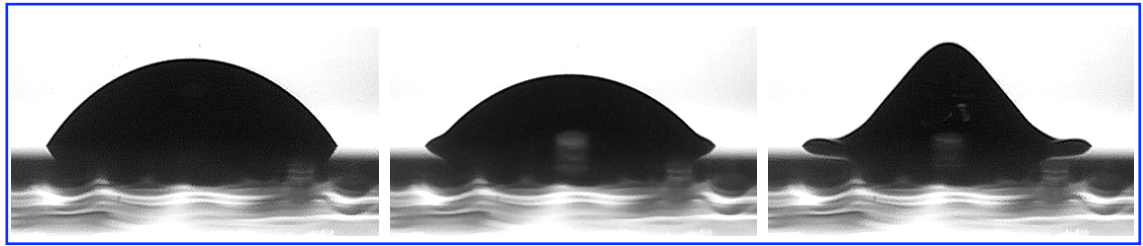
$\omega_p, RH, T : \text{constants}$

I. deformation  
polymer drop



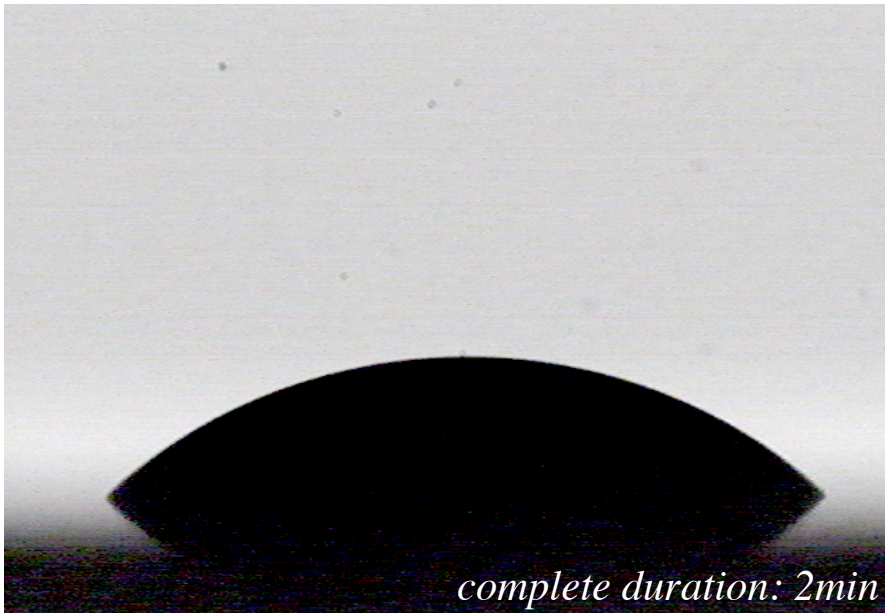
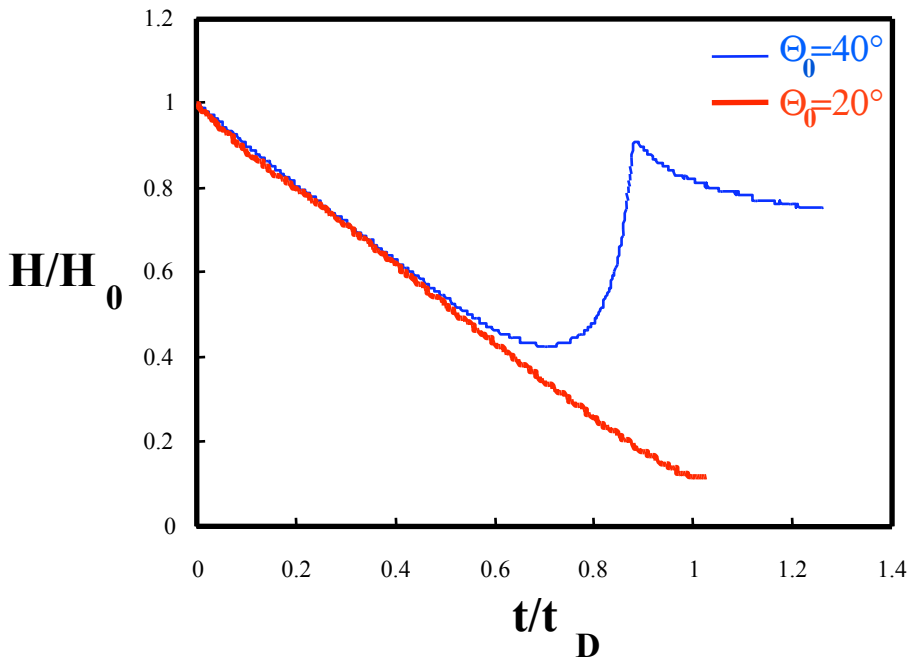
$\Theta_0 = 20^\circ$

time →

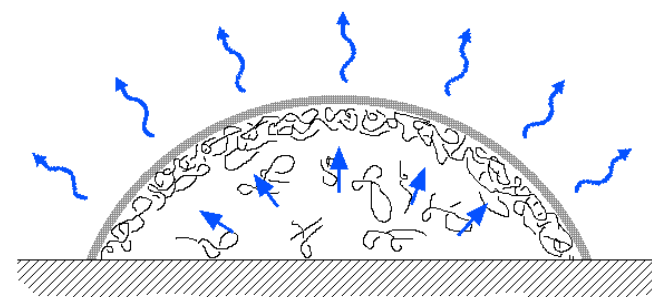
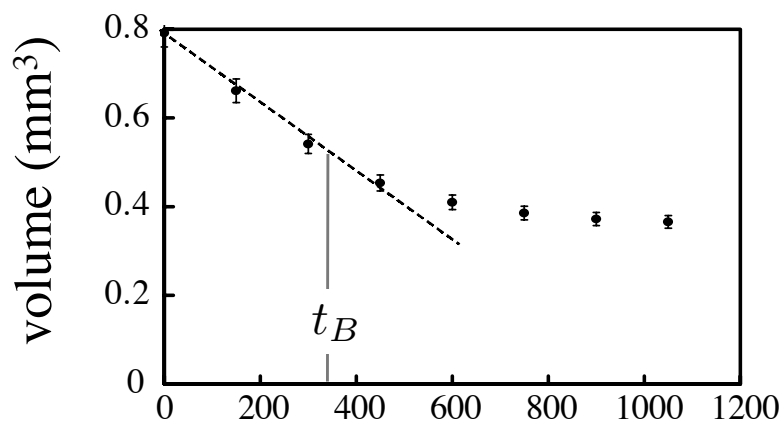
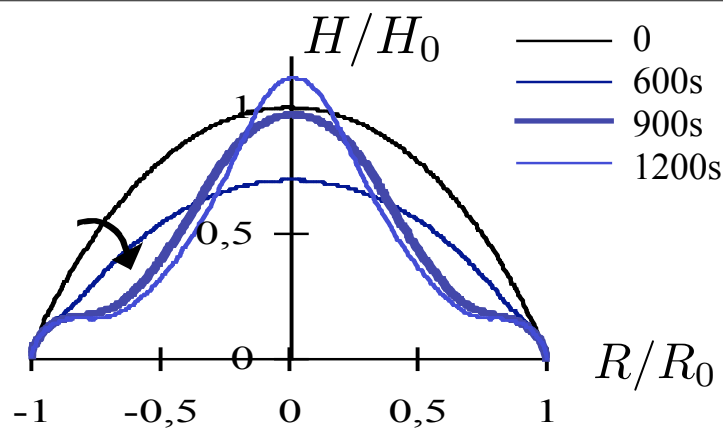


$\Theta_0 = 40^\circ$

?

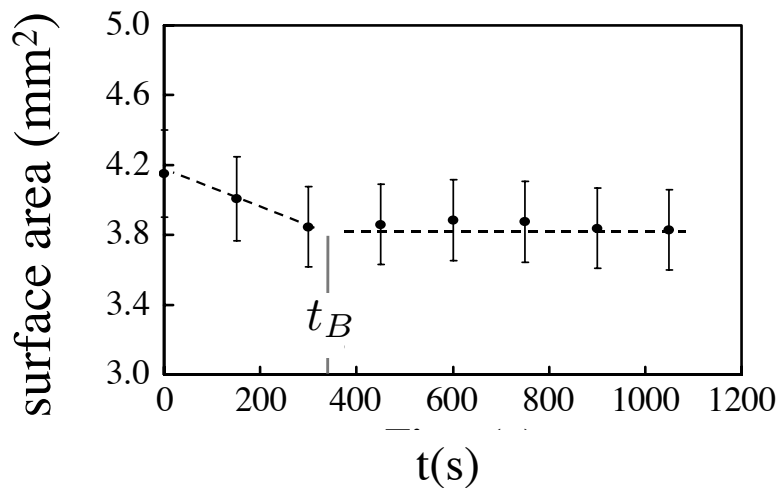


complete duration: 2min



formation of a glassy skin at the evaporation surface

deformation: buckling process





# Drop shape characterization

I. deformation  
polymer drop

Evaporation rate:

Transfer of solvent in air limited by diffusion

Solvent flux conservation at interface

Deformation criterion

$$\dot{V}_E = A(\theta_0) D_a \frac{n_{ws}(1 - RH)}{R_0}$$

$$\Rightarrow t_D = \frac{R_0}{\dot{V}_E} \cdot \frac{V_0}{R_0 S_0}$$

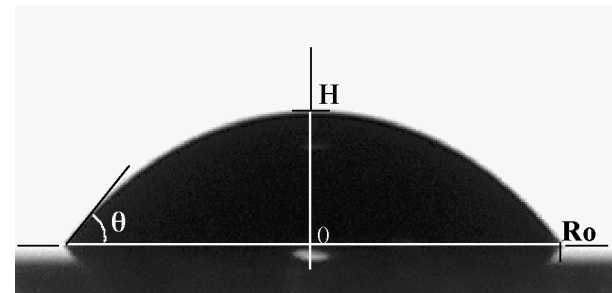
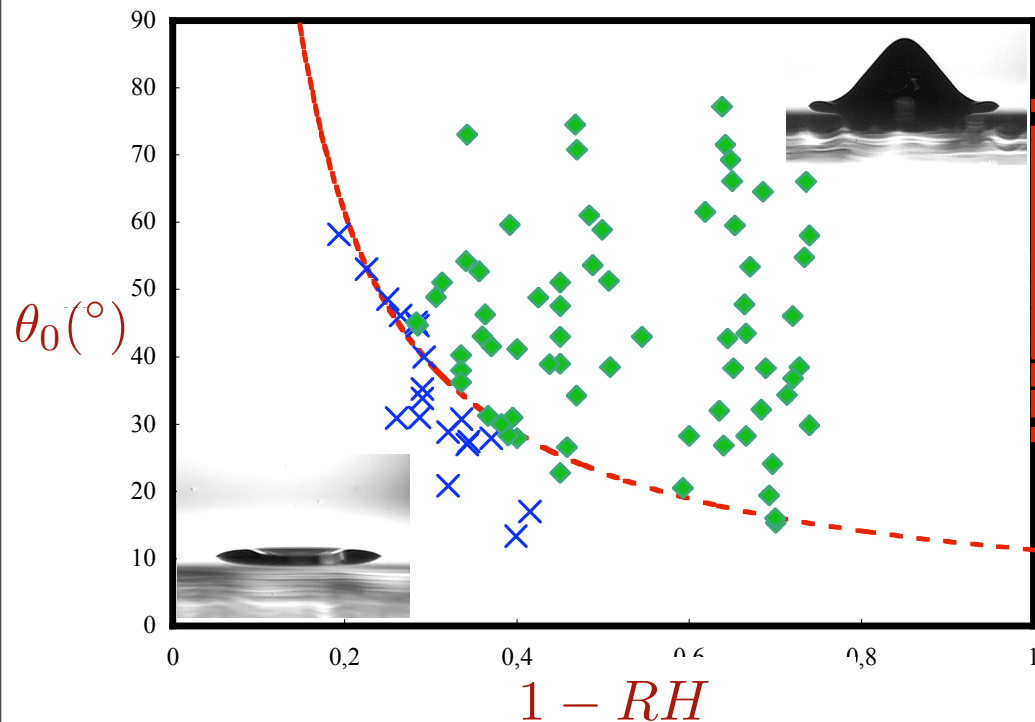
$$\dot{V}_E = D_m \cdot \nabla \phi_p$$

$$\phi_p|_{surface} = \phi_g \text{ (glassy state)}$$

$$\Rightarrow t_B = f(\theta_0, RH) \frac{R_0^2}{D_m}$$

$t_B > t_D$  : no buckling

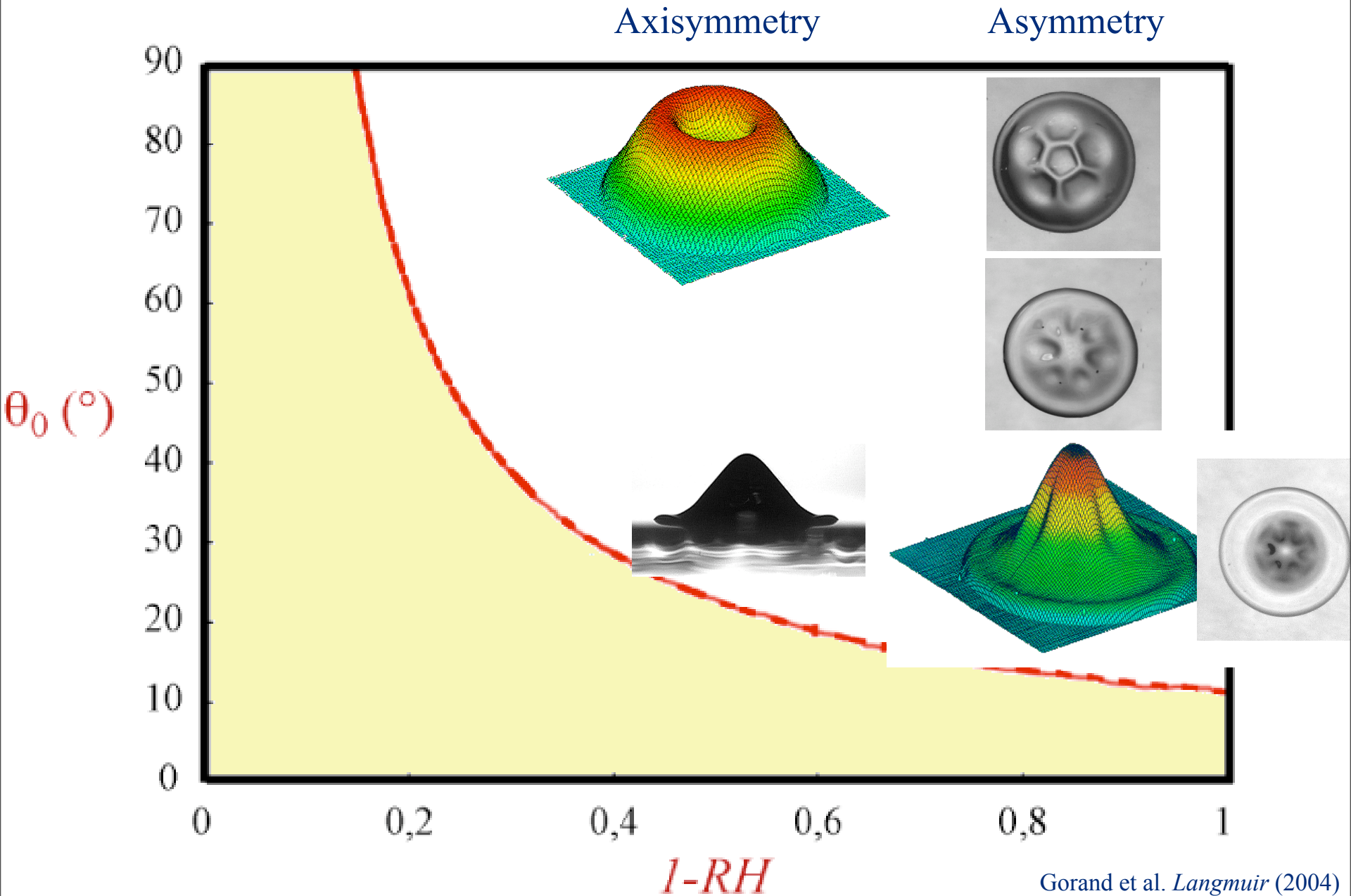
$t_B < t_D$  : buckling



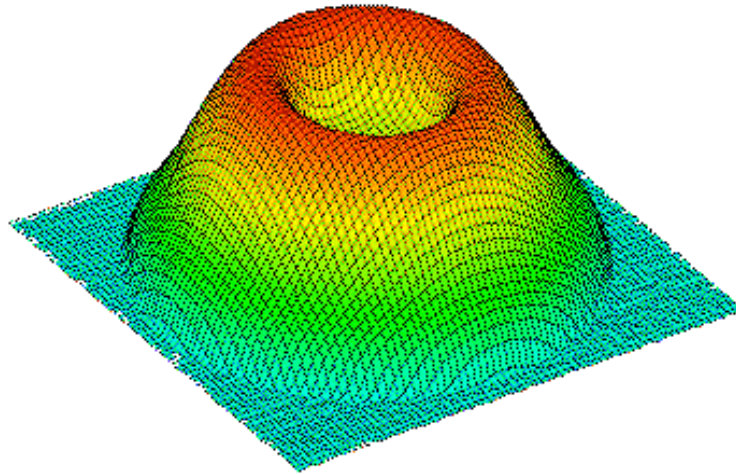
Pauchard, Allain *Europhys. Lett.* (2003)  
Pauchard, Allain *Phys. Rev. E* (2003)

# Different patterns

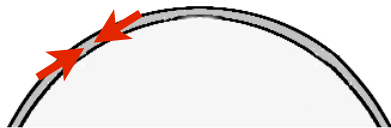
I. deformation  
polymer drop



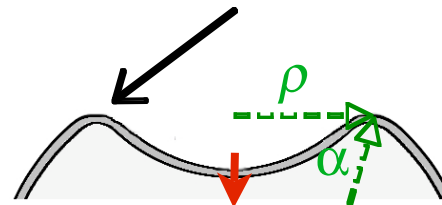
# Inversion of curvature



in-plane deformation



out-of-plane deformation



$$h \sim \frac{\alpha^2}{\rho}$$

$$\sim \frac{(400 \cdot 10^{-6})^2}{2 \cdot 10^{-3}}$$

$$= 100 \mu\text{m}$$

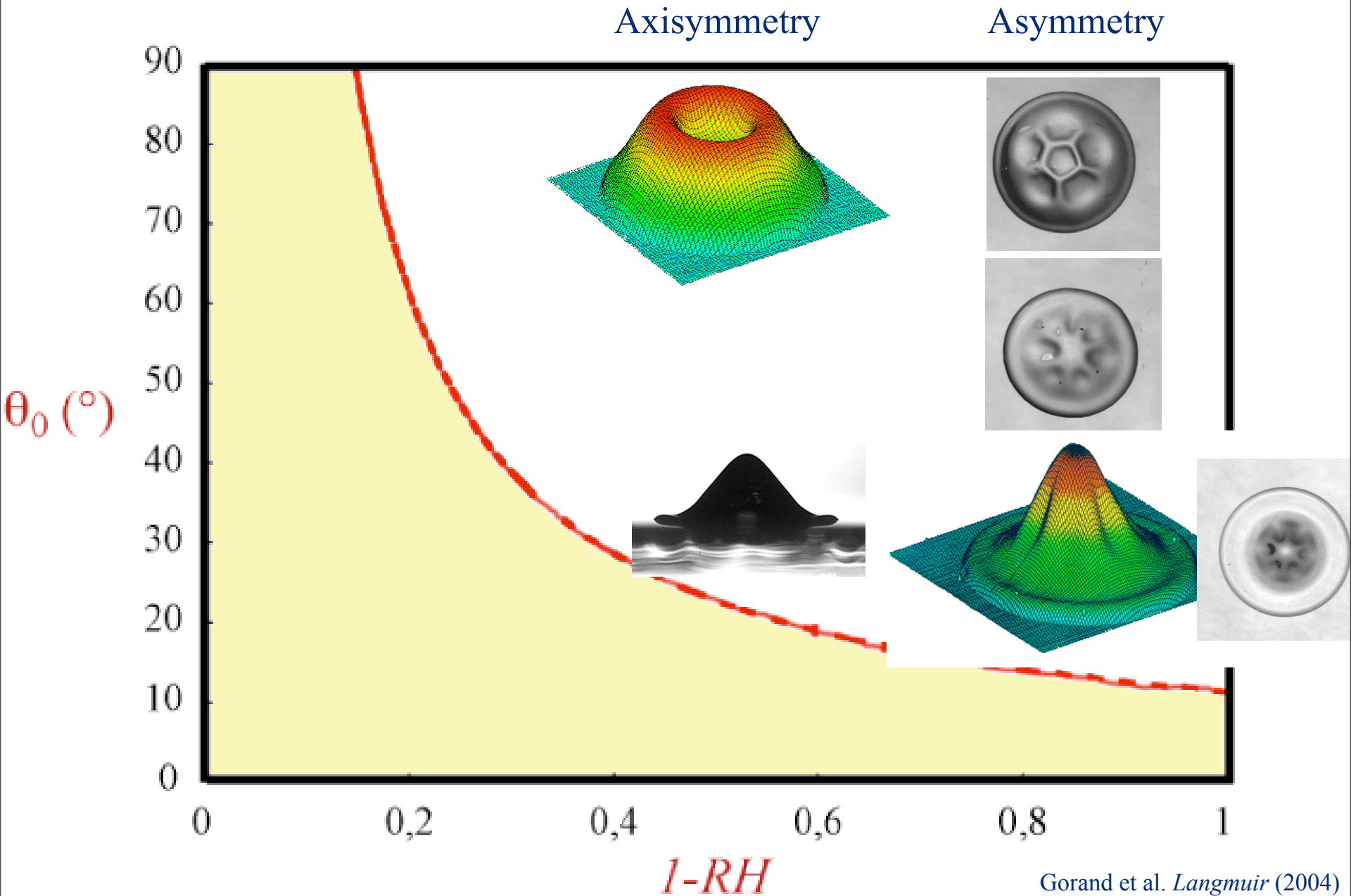
$$U_{\text{compression}} = C_2 \frac{Eh}{R} \delta^3$$

$$U_{\text{fold}} = C_1 \frac{Eh^{5/2}}{R} \delta^{3/2}$$

elastic energy  $U = Eh \int \left[ \frac{h^2}{24(1-\nu^2)} H^2 + 1/8 (\Delta^{-1} K)^2 \right] ds$  Föppl (1907)

# Different patterns

I. deformation  
polymer drop





# Drying a drop of colloidal suspension

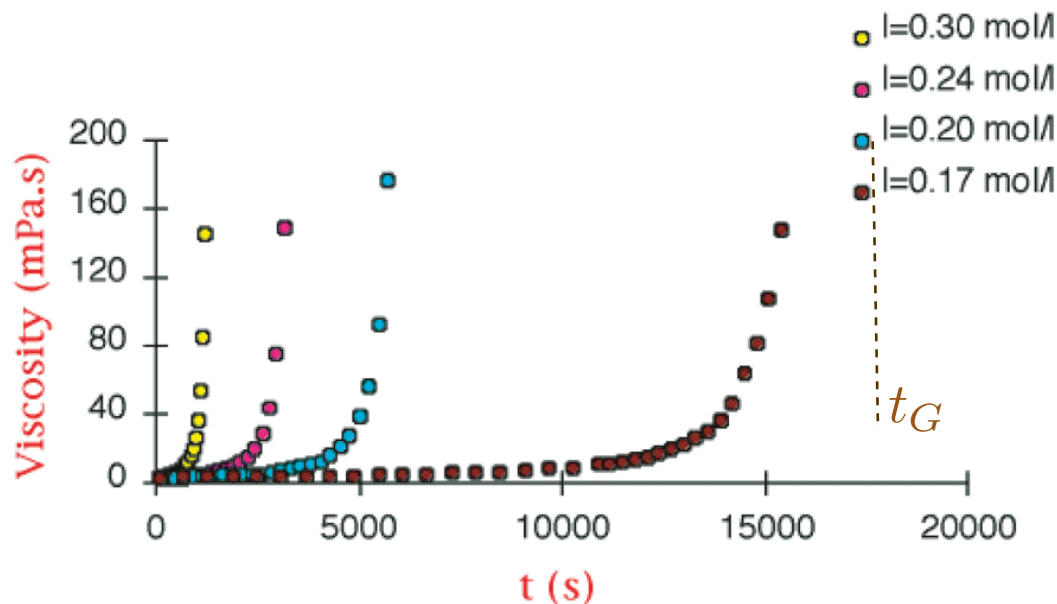
2 coupled effects in the sol-gel transformation (case of a silica dispersion)

## Gelation kinetics

influence of the ionic strength  $I$ :  
screening charges borne by particles

suspension viscosity increases as aggregates form

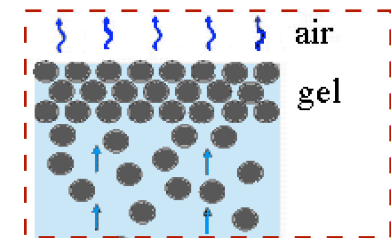
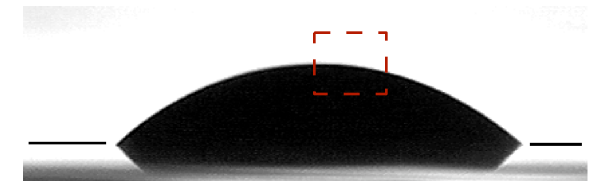
⇒ colloidal gel = solid porous matrix saturated by solvent



gelation time  $t_G$

## Drying kinetics

evaporation of solvent

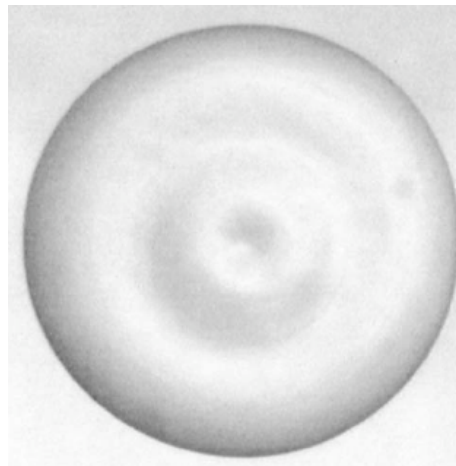
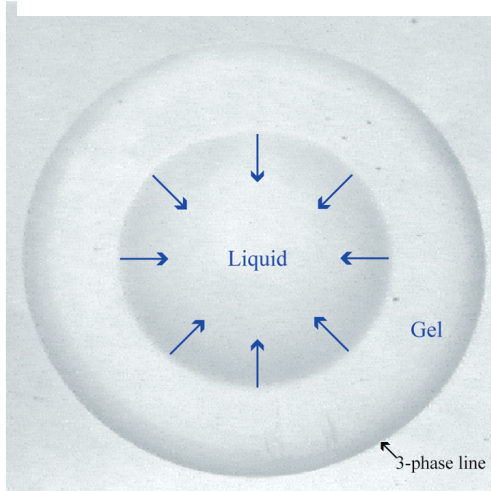
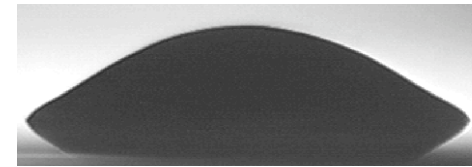
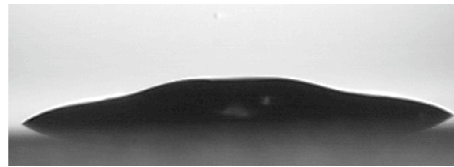
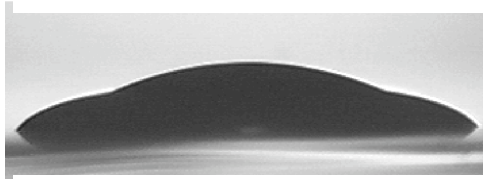
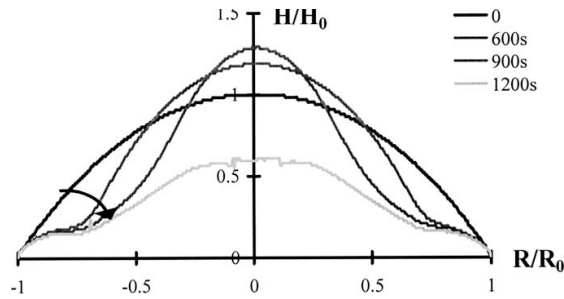


drying time  $t_D = \frac{R_0}{\dot{V}_E} \cdot \frac{V_0}{R_0 S_0}$

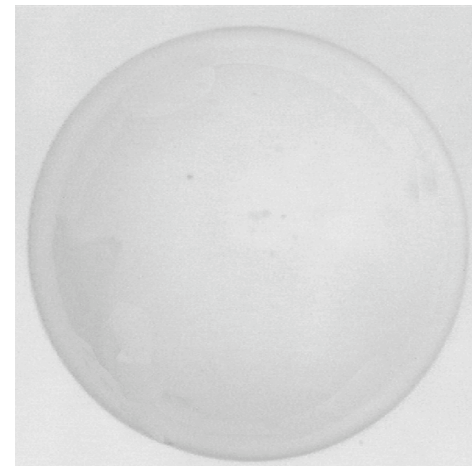
$t_G/t_D > 10^2$   
drying

$10^{-1} < t_G/t_D < 10$   
drying + gelation

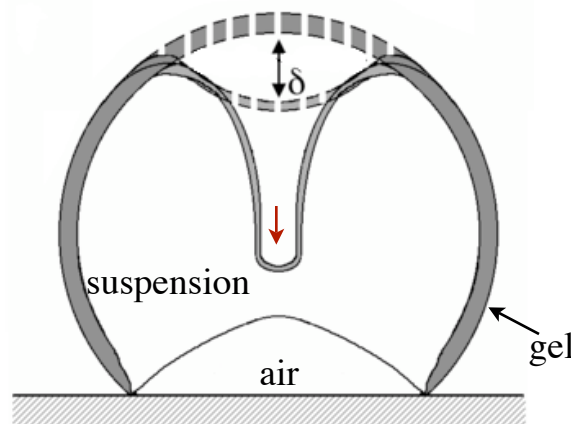
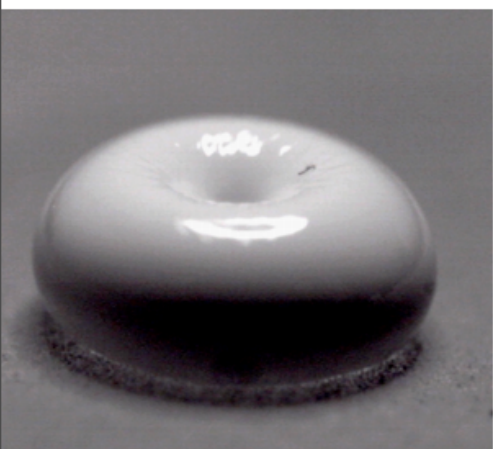
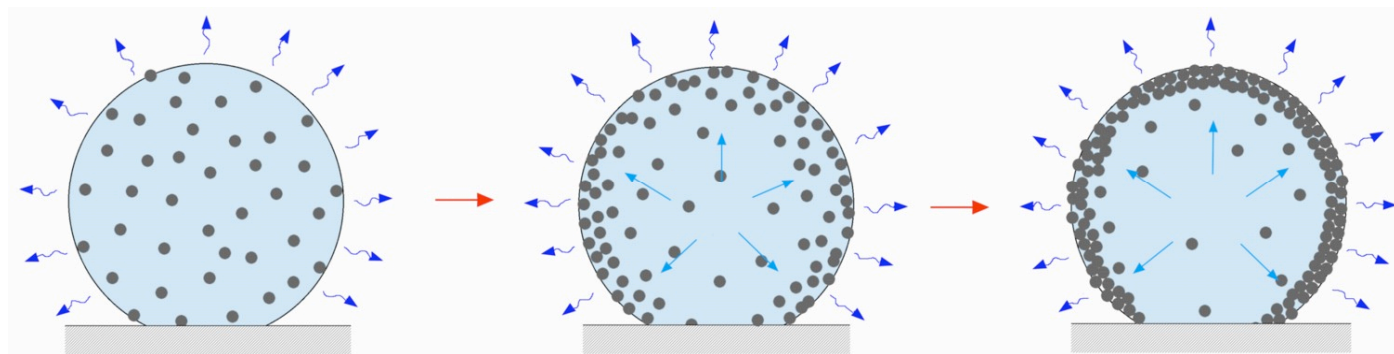
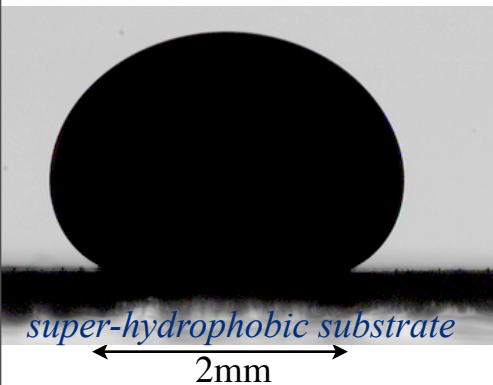
$t_G/t_D < 10^{-2}$   
gelation



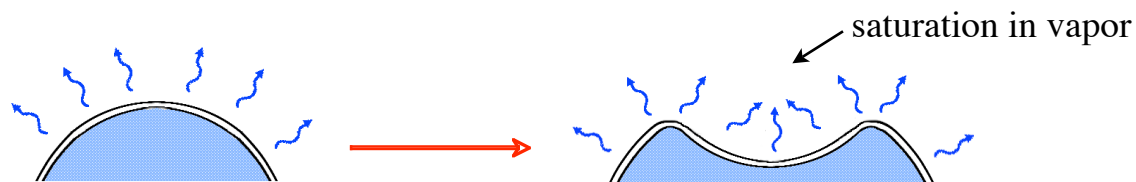
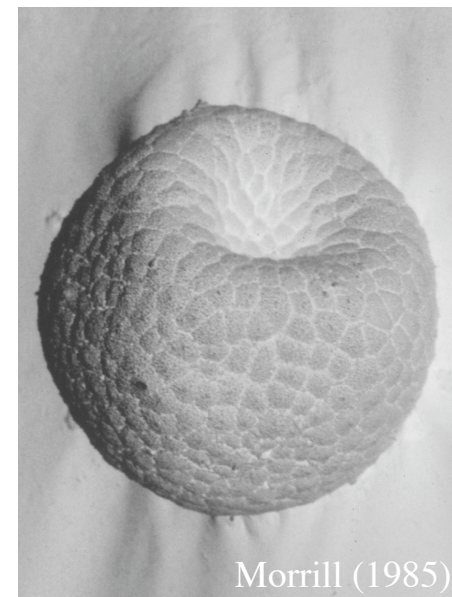
skin formation  
buckling process



# Invagination during the collapse of an inhomogeneous spheroidal shell

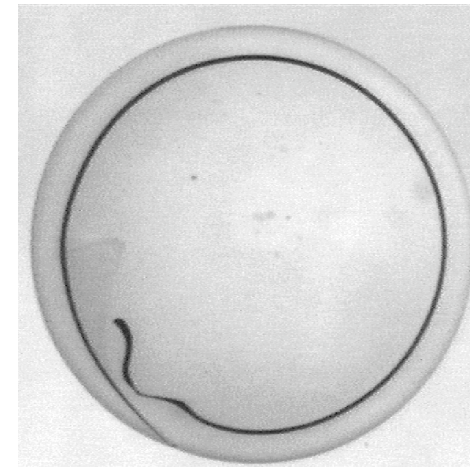
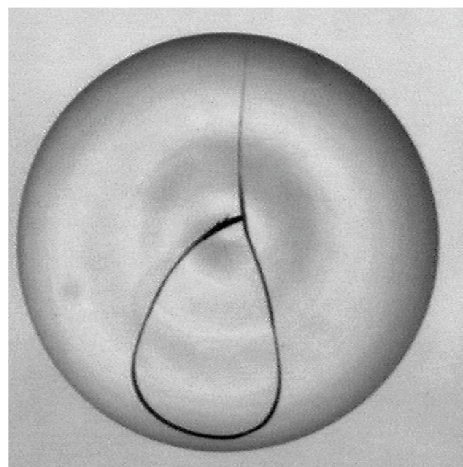
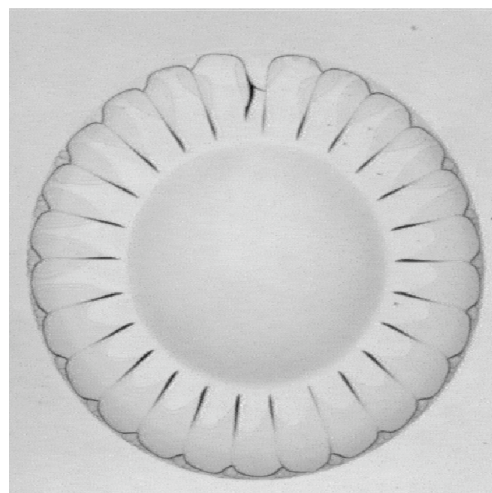
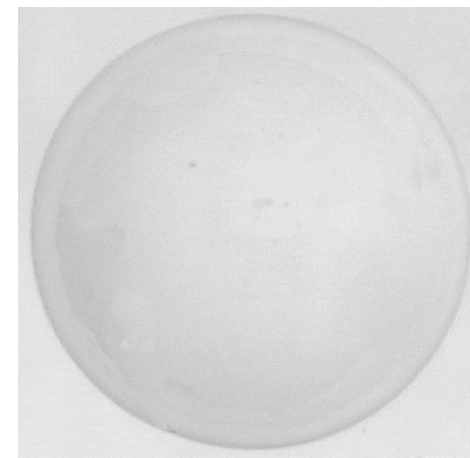
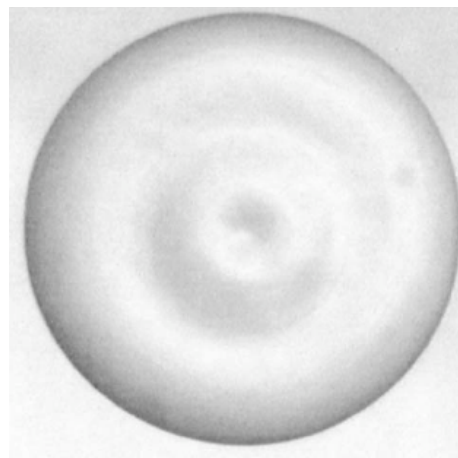
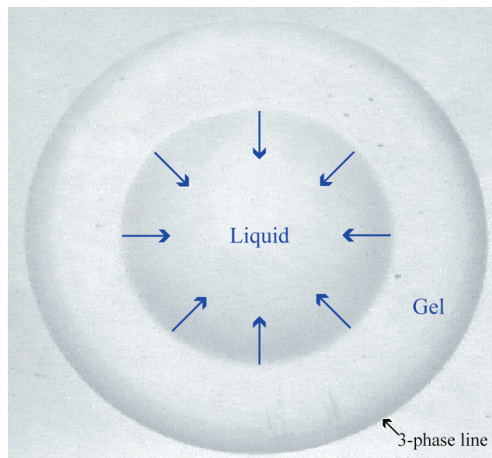


*invagination in sea-urchin embryo*





# Crack patterns induced by desiccation





## Conclusion

**examples of problems coupling physico-chemical properties and mechanical properties**

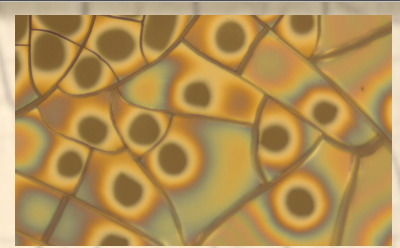
large domain of elasticity

brittle domain

stress relaxation  $\Rightarrow$  modifications internal structures

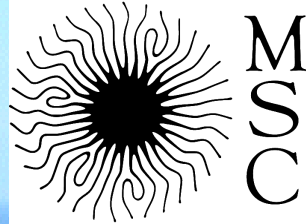
$\Rightarrow$  deformations (wrinkles, fractures)

successive generations of cracks induced by residual stresses

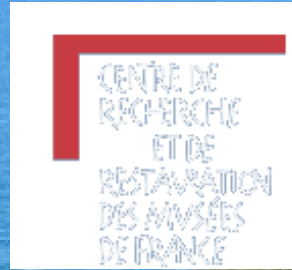




C. Allain  
G. Gauthier  
V. Lazarus  
L. Pauchard  
F. Parisse



B. Abou  
JC Bacri  
F. Elias  
K. Sekimoto



G. Aitken  
C. Lahanier



M. Adda-Bedia  
Y. Couder