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Similarity in the drying behavior between biological colloids and model colloidal dispersions



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GDR SLAMM, Hyères, 12-15 Nov. 2018

LAB'S PRESENTATION



A multidisciplinary and multiscale approach,
reinforced by two high-calibre facilities:

Dairy Platform



Biological Resource Centre



➤ **Structuration / destructuration mechanisms
of food matrix:**

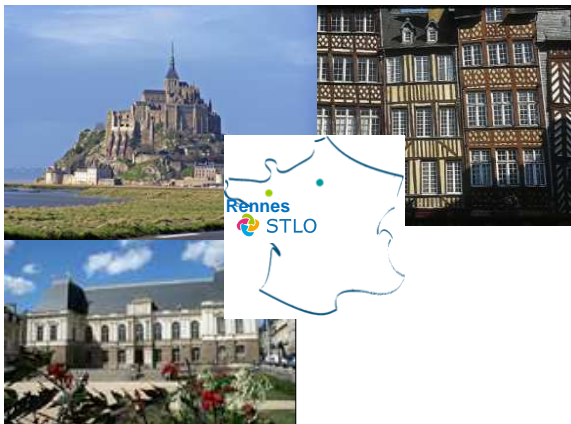
from structural characterisation to digestion

➤ **Dairy processing and cheese making:**

toward sustainable dairy systems

➤ **Microbial interaction:**

food matrix and host cell

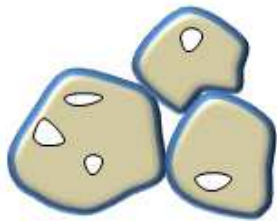


Controlling dairy powders properties

Quite challenging

Sticking & caking

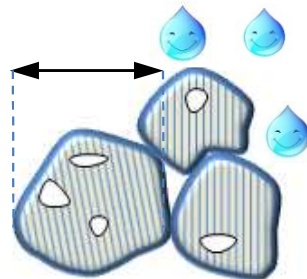
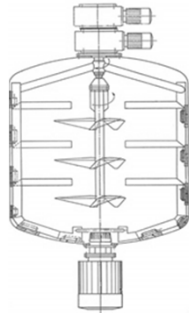
Glass transition, Hygroscopicity



SURFACE PROPERTIES

Rehydration

Surface composition & structure, Density, occluded & interstitial air, Size, Porosity



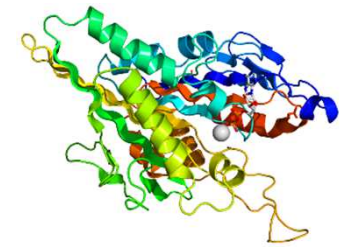
PARTICLE PHYSICAL PROPERTIES

Packing



Nutritional properties

Denaturation / aggregation rate, etc.



MOLECULAR STRUCTURE

Functional properties = f (particle intrinsic properties)
Insight on particle formation

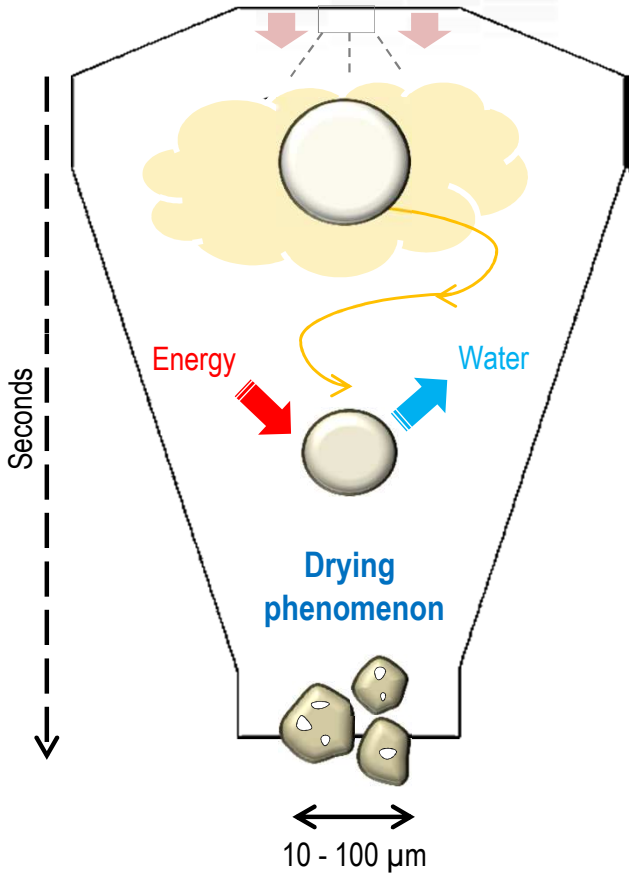
A new strategy

Sadek et al., *Langmuir*, 2013, 29, 15606-15613.
 Sadek et al., *Food Hydrocolloids*, 2015, 48, 8-16
 Sadek et al., *Food Hydrocolloids*, 2016, 52:161-166.

From the industrial scale..



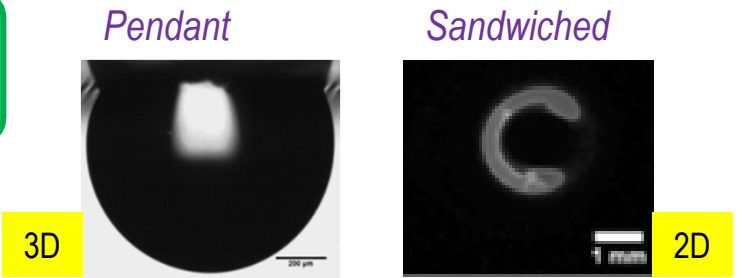
..to the droplet approach



- Fast drying kinetics
- Complexity and costs



SINGLE DROPLET



- Kinetics of particle formation
- Material mechanical properties

FLYING DROPLETS



Validation at Δ scale
 (size, temperature, time)
Powder properties determination

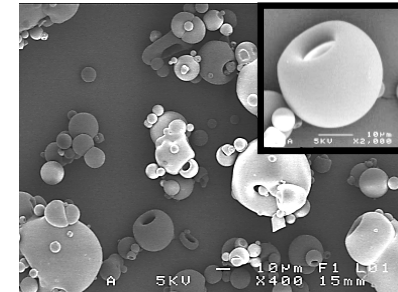
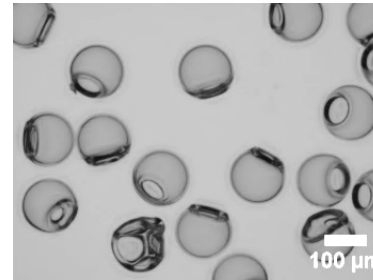
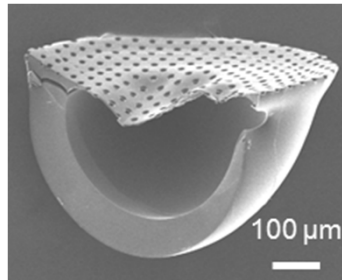
Signature of milk proteins at multi-scale

Single,
Pendant droplet →

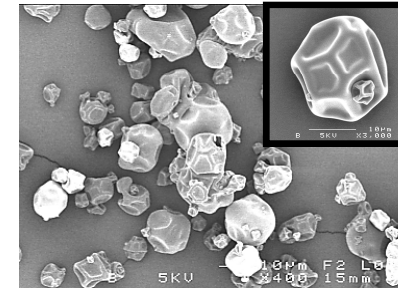
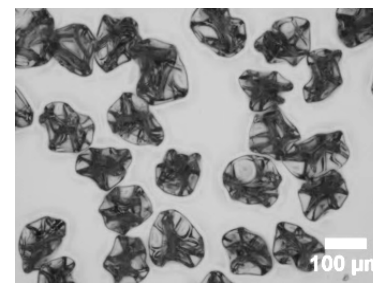
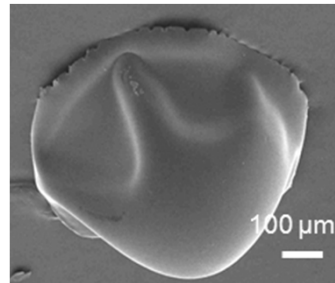
Mono-dispersed
droplets →

Spraying cone
of droplets

Whey protein
(WP)



Casein
Micelles
(NPC)



Drying kinetics

Particle Size

10 min

500 μm

140 μm

→ ~1 s

42-56 μm

Drying temperature

20 °C

190 °C

210 °C

Quantity

1 particle

~ g
of particles

~ kg
of particles

Signature of milk proteins at multi-scale

Whatever the drying kinetics, same morphological behavior

- **Specific signatures** of WP and NPC proteins on the particle formation
- **Different kinds of drying behavior**
 - ✓ **Whey proteins = brittle material**
 - ✓ **Casein micelles = ductile material**



To what extent is the formation of particles affected by the protein material and its mechanical properties ?

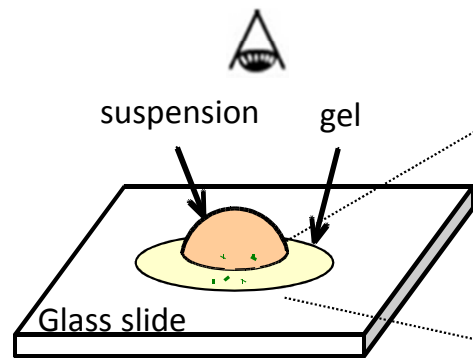


Studying model colloidal solutions for understanding more complicated biological systems

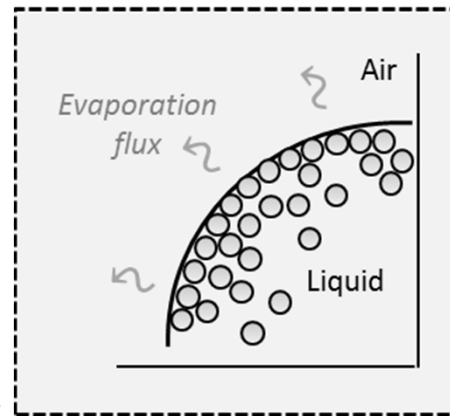
Material & Method : investigation of mechanical behaviors

Coupling cracks dynamics and micro-indentation

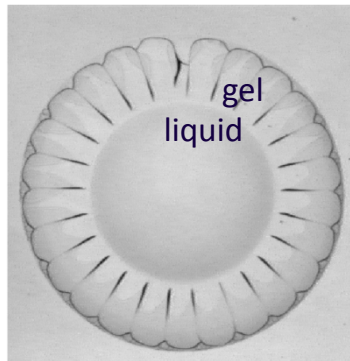
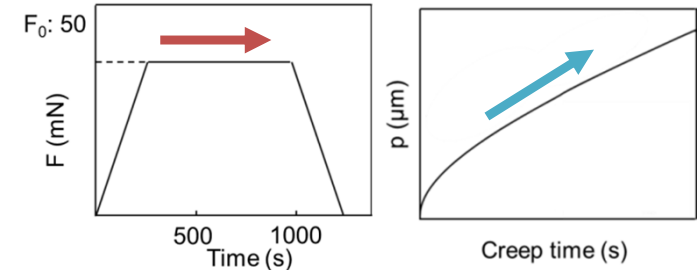
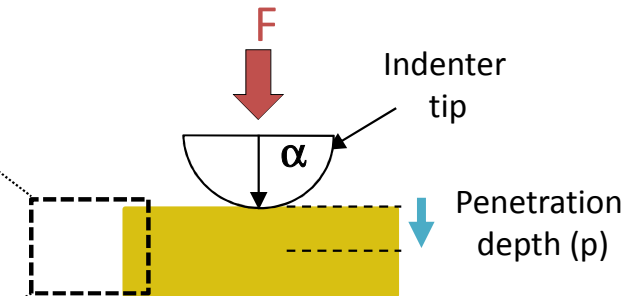
Sessile droplet Cracks formation



Specific properties of concentrated phases



Micro-indentation Mechanical properties



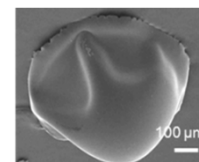
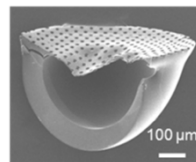
8 mm
top view



Particle morphology

Particle of whey proteins

Particle of casein micelles



Experimental conditions:

- Temperature: 20°C
- Relative humidity: 40%

Material & Method : milk proteins and colloidal systems

Study the drying behavior of **milk proteins** and **model colloidal systems**

□ Whey proteins

- Globular structure, $D \approx 10\text{-}20\text{ nm}$
- Reconstituted from **WP powder** (**Whey Proteins, 100 g.L^{-1}**)



Yohko, 2012

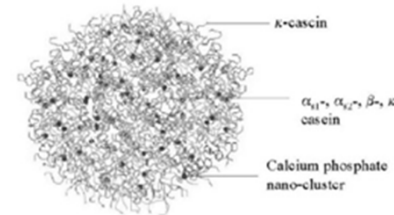


□ Dispersion of silica colloidal particles

- Ludox TM50 : $\varnothing = 22\text{ nm} \pm 2$
(weight fraction in silica particles = 0.40)

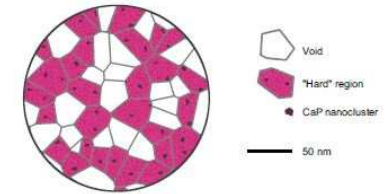
□ Casein micelles

- Micellar, dynamic and hydrated structure, $D \approx 10^2\text{ nm}$
- Reconstituted from **NPC powder** (**Native PhosphoCaseinates, 100 g.L^{-1}**)



Holt & Horne, 1996

Internal structure not known



Bouchoux, 2010

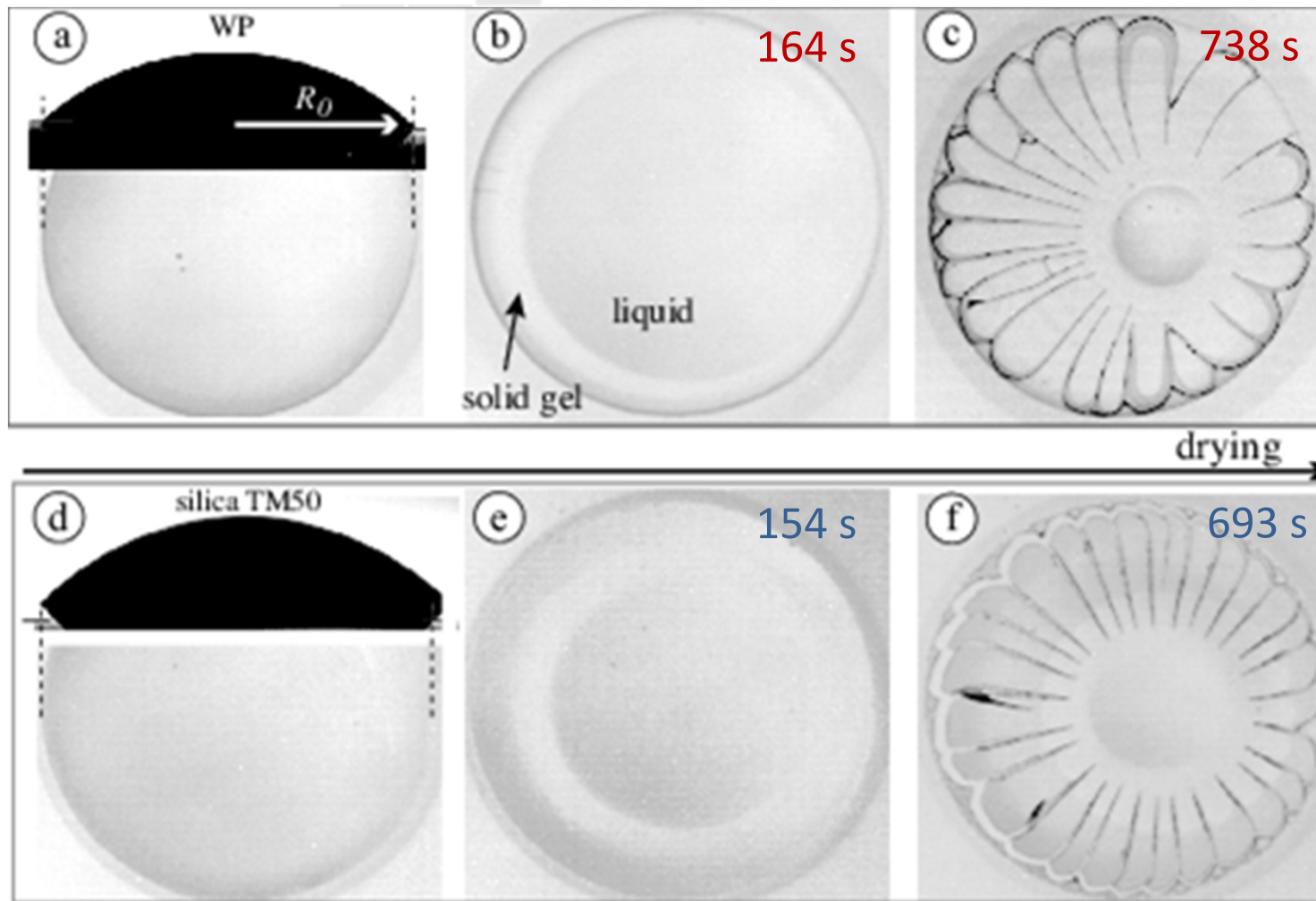


□ Polymer chains on TM particles

- Ludox TM50 + PVP (40kDa)
(weight concentration of PVP = 0.1%)

→ PVP owns high affinity for silica surfaces

Results – Drying process of sessile drops (WP / TM50)



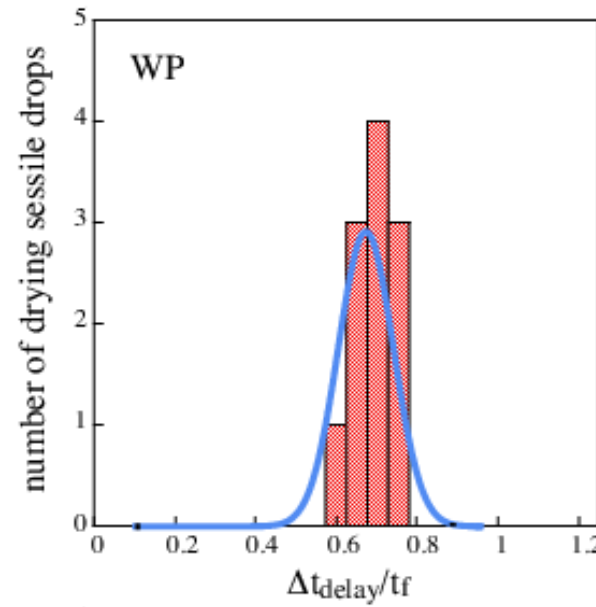
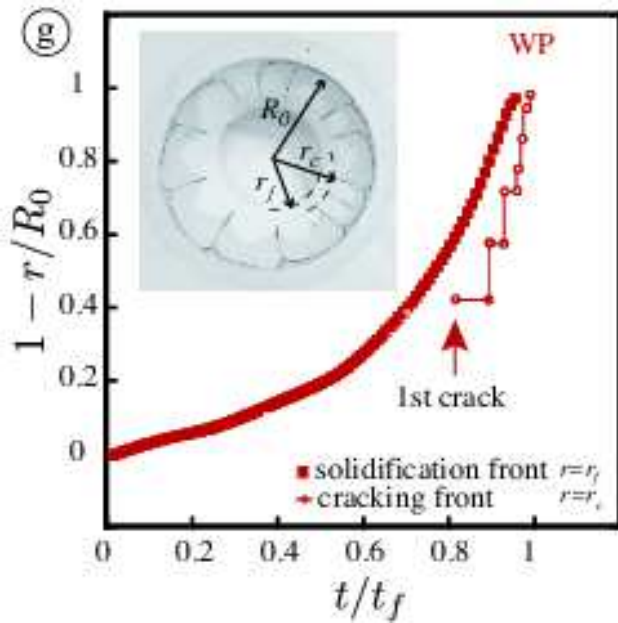
Experimental conditions:

- Temperature: 20°C
- Relative humidity: 40%
- Initial contact angle : $31 \pm 2^\circ$
- $2 R_0 = 8 \text{ mm}$
- Evaporation rate : $8 \cdot 10^{-8} \text{ m} \cdot \text{s}^{-1}$

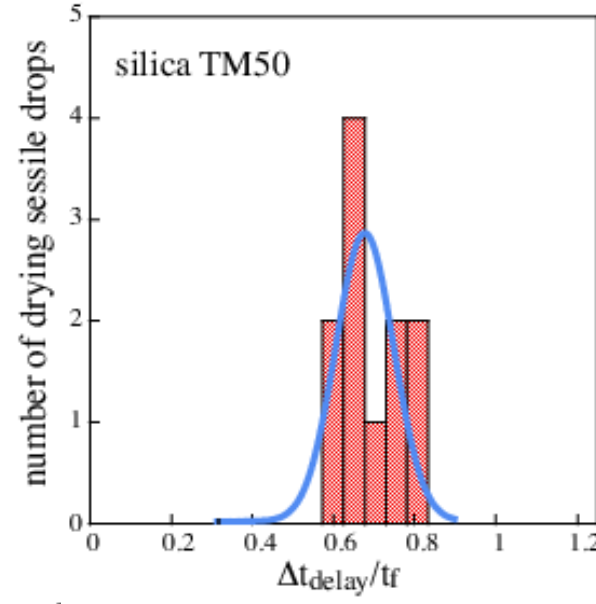
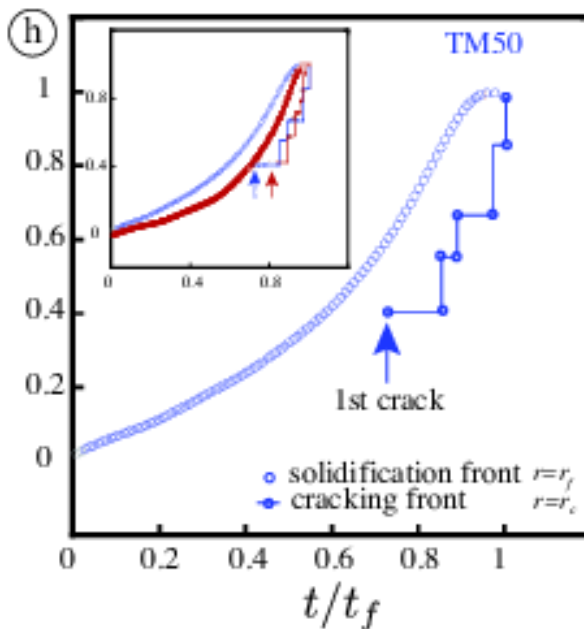
Comparable behavior

Formation of radial fractures in the solid periphery

Results – Crack dynamics and delay time before cracking



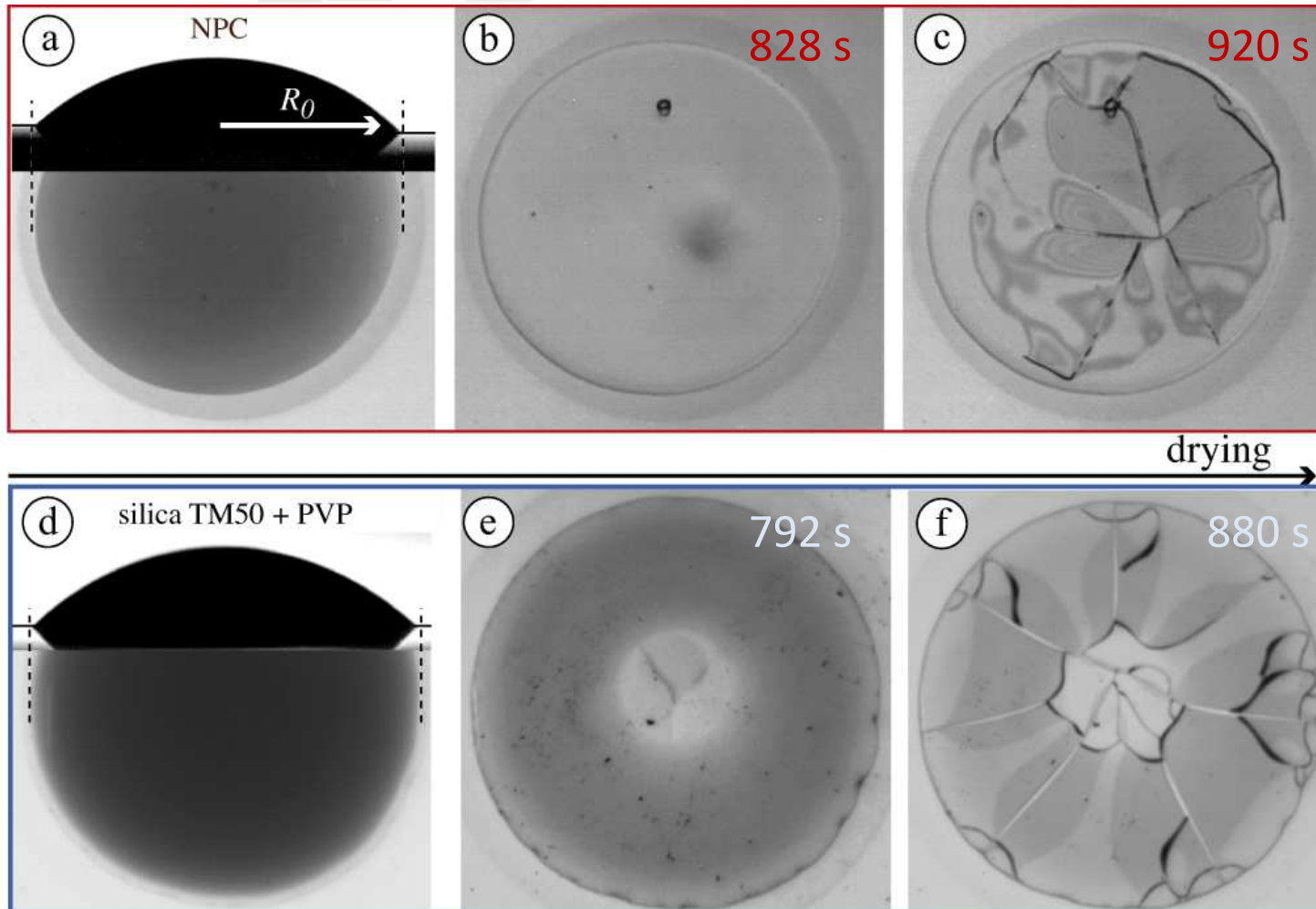
➤ Similar time evolution of the drying front location obtained for WP and TM50



➤ Similar statistics of duration elapsed before crack propagation :

- ✓ 334 ± 41 s for WP
- ✓ 311 ± 61 s for TM50

Results – Drying process of sessile drops (NPC / TM50 + PVP)



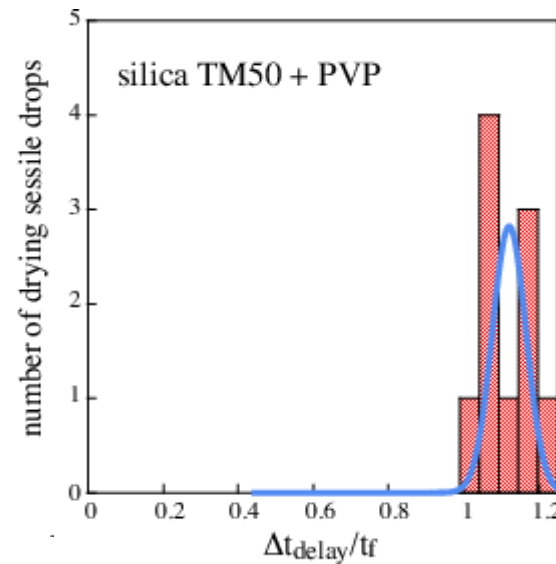
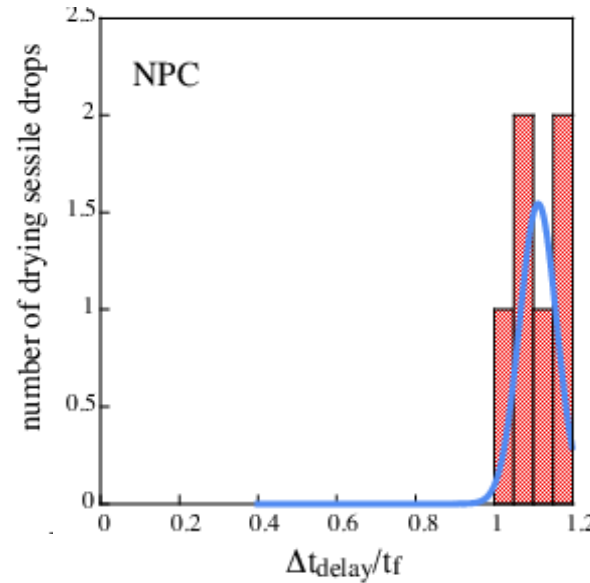
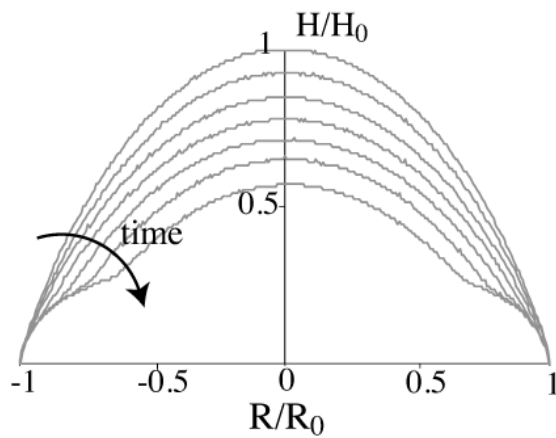
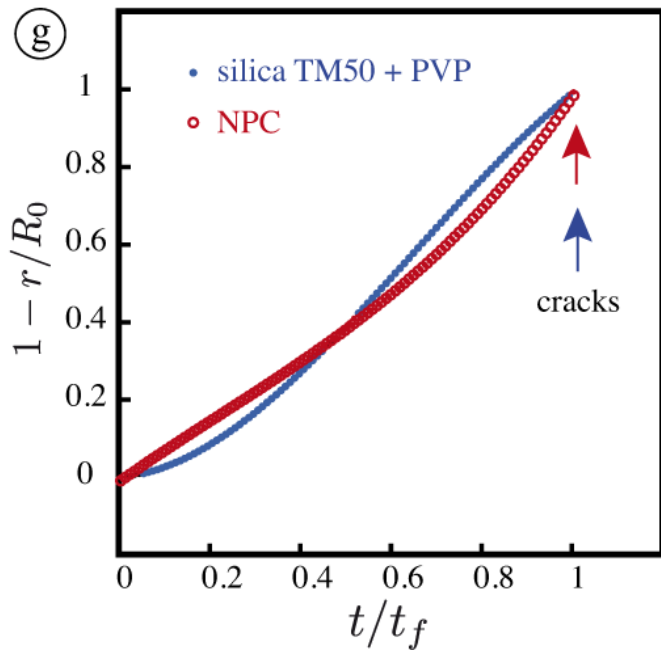
Experimental conditions:

- Temperature: 20°C
- Relative humidity: 40%
- Initial contact angle : $35 \pm 2^\circ$
- $2 R_0 = 8 \text{ mm}$
- Evaporation rate : $8 \cdot 10^{-8} \text{ m} \cdot \text{s}^{-1}$

Comparable behavior

Later nucleation of a few, random fractures

Results – Crack dynamics and delay time before cracking

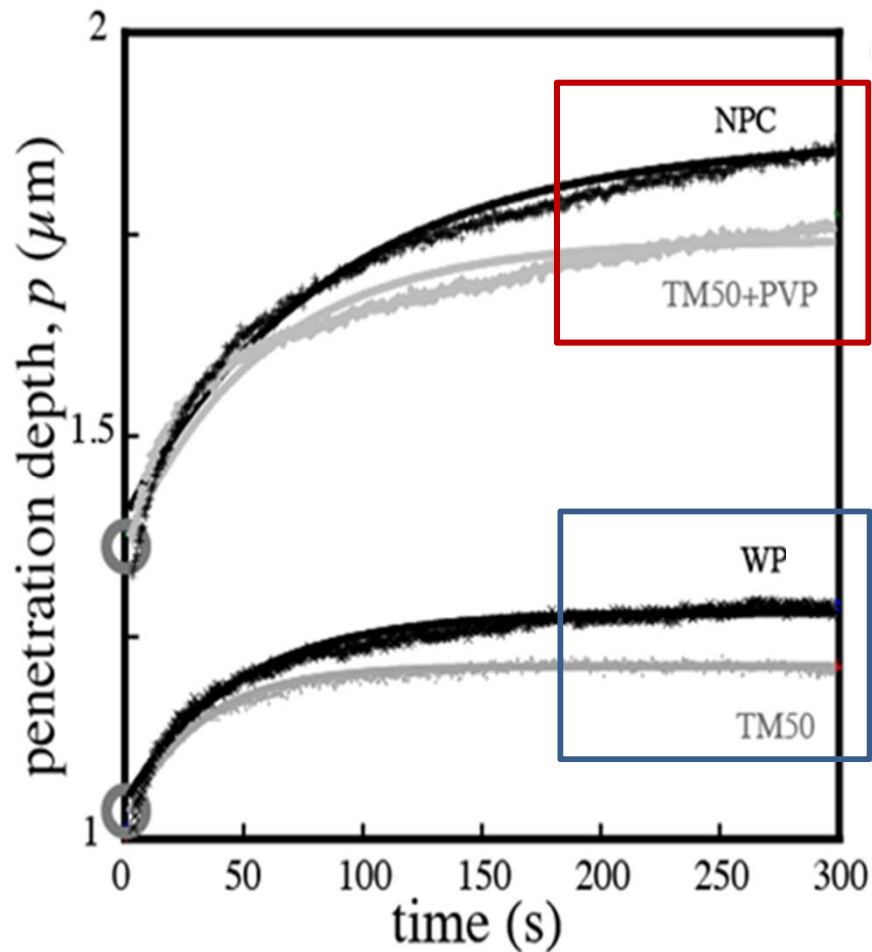
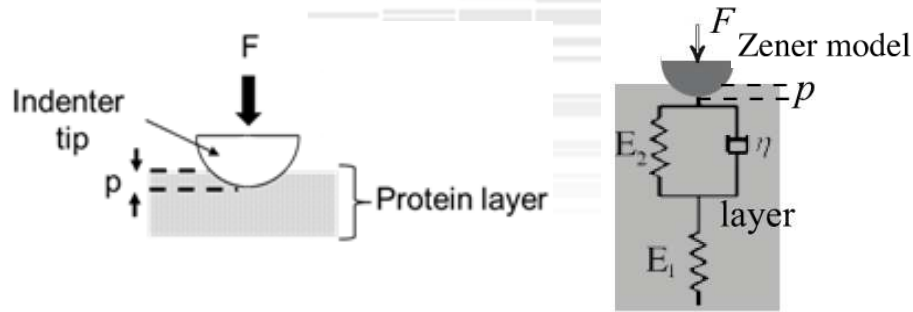


➤ Similar time evolution of the drying front location obtained for NPC and TM50 + PVP

➤ Similar statistics of duration elapsed before crack propagation:

- ✓ 834 ± 50 s for NPC
- ✓ 855 ± 40 s for TM50

Results – Mechanical behavior & viscoelastic relaxation time



	Viscosity η (GPa.s)	Elastic modulus E_2 (GPa)	Viscoelastic relaxation time, $t\eta$ (s)
WP	99 ± 5	3.50 ± 1.10^{-3}	28 ± 2
TM50	82 ± 5	3.20 ± 1.10^{-3}	26 ± 2
NPC	119 ± 5	0.96 ± 1.10^{-3}	124 ± 5
TM50 + PVP	115 ± 5	0.98 ± 1.10^{-3}	129 ± 5

- Penetration depth deeper for NPC and TM50 + PVP than for WP layer and TM50
- Values of viscoelastic relaxation time are similar between WP / TM50 and NPC / TM50 + PVP

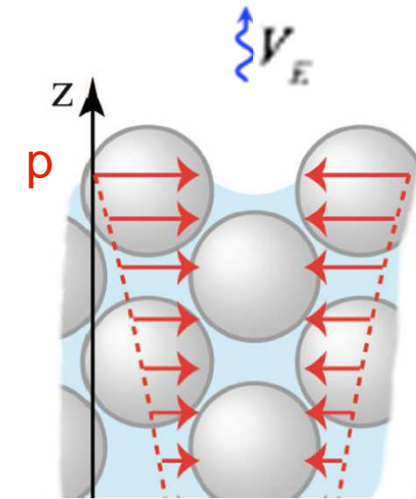
Results – Drying stress and poro-elasticity

- Drying stress at the film/air interface :

$$\sigma(z = h) \sim E \frac{t}{t_D} \quad \text{where } t_D \text{ is the evaporation timescale } (h/V_E)$$

- Max stress leading to crack when:

$$\sigma(z = h) \approx -P_{cap} \approx 5 \frac{\gamma_{air/water}}{r_{pore}}$$



poroelasticity, Biot (1941)

Hypothesis: delay time before stress reaches max stress : viscoelastic timescale t_η

$$E \frac{t_\eta}{t_D} \sim 5 \frac{\gamma_{air/water}}{r_{pore}} \Rightarrow r_{pore}$$



estimation of the pore size in the solid state :

$$r_{pore} (WP) / r_{pore} (NPC) \sim 2$$

Results in concordance with drying behavior (NPC more deformable than WP)

Conclusion

To what extent is the formation of particles affected by the protein material and its mechanical properties ?



Coupling cracking time (direct measurements) and indentation (indirect measurements of mechanical properties)

WP : analogous mechanical behavior with TM50

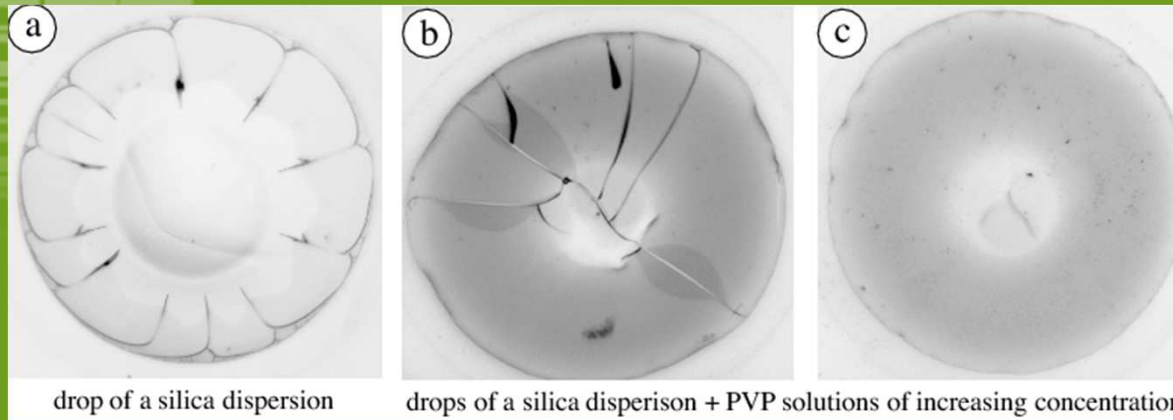
→ **Brittle plastic** property of skin layer similar to non-interacting **hard sphere colloids**

NPC : similar mechanical behavior with TM50 + PVP

→ **Ductile plastic** characteristics of skin layer similar to **soft colloids**

OUTLOOK

Modelling approach to control the phase transition in the drop leading to skin or cracking
→ better link between the physicochemical milk properties and the drying kinetics.



Merci

Thank you for your attention



More information

- Sadek et al., 2013, [Langmuir](#), **29**, 15606-15613
- Sadek et al., 2014. [Drying Technol](#), **32**, 1540-1551
- Sadek et al., 2014, [Dairy Sci Technol](#), **95**, 771-794
- Sadek et al., 2015, [Food Hydrocolloids](#), **48**, 8-16
- Sadek et al., 2016, [Food Hydrocolloids](#), **52**, 161-166
- Lanotte et al., 2018, [Col. Surf. A](#), **553**, 20-27

GDR SLAMM, Hyères, 12-15 Nov. 2018