Mechanisms of drying-induced particle formation in solutions of dairy proteins:a multiscale approach

Cécile Le Floch-Fouéré, Luca Lanotte, Françoise Boissel, Ludovic Pauchard, Romain Jeantet

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CECAM, October 2019, Lausanne

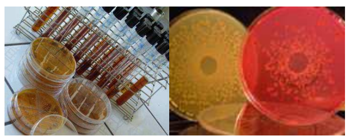
LAB'S PRESENTATION

STLO

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

Dairy Platform

Biological Resource Centre



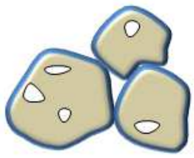
- **Structuration / destructuration mechanisms of food matrix:**
  from structural characterisation to digestion
- **Dairy processing and cheese making:**
  toward sustainable dairy systems
- **Microbial interaction:**
  food matrix and host cell

Please visit http://www6.rennes.inra.fr/stlo_eng

Controlling dairy powders properties

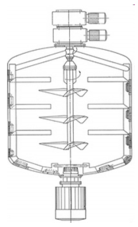
Quite challenging

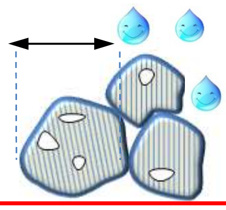
Sticking & caking
Glass transition, Hygroscopicity



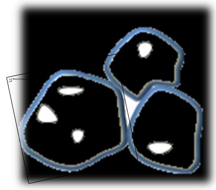
SURFACE PROPERTIES

Rehydration
Surface composition & structure, Size, Porosity





Packing
Density, occluded & interstitial air, size distribution



PARTICLE PHYSICAL PROPERTIES

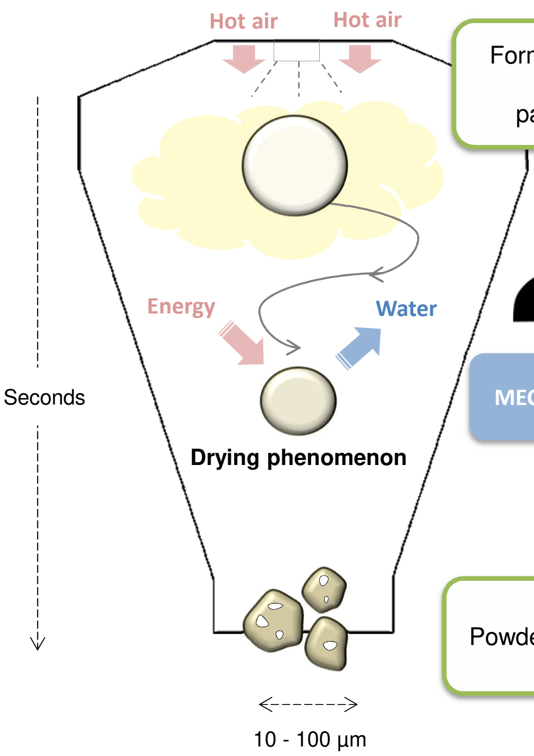
Nutritional properties
Denaturation / aggregation rate, etc.

MOLECULAR STRUCTURE

Functional properties = *f* (particle intrinsic properties)

Insight on particle formation

Ensure the quality of dairy powders: many challenges…



Formulation and process parameters

MECHANISMS ?

Particle formation ?

Powder properties

LIMITS on an industrial scale:

- *Fast drying kinetics*
- *Heterogeneity of samples*
- *Complexity of equipment*
- *Complexity of formula*
- *Costs of large scale trials*

Strategy of the work : question of research

How does the droplet become a dry particle?

Strategy of the work : innovate points of the strategy

→ Simplifying the dairy matrix

Study the drying behavior of milk proteins

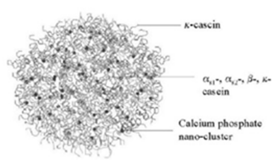
❑ Whey proteins

Yohko, 2012

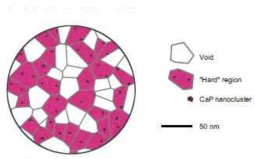
- Globular structure, D ≈ 10-20 nm

→ Reconstituted from **WP powder (Whey Protein)**

❑ Casein micelles



Holt & Horne, 1996



Bouchoux, 2010

- Micellar, dynamic and hydrated structure, D ≈ 10^{2} nm

→ Reconstituted from **NPC powder (Native PhosphoCaseinates)**

→ Study of the drying of simplified droplet systems

- **Mimic drying phenomenon with different experimental setups**
- **Variation of drying kinetics and volumes**

→ **multi-scale approach of drying process**

Experimental strategy : a multiscale approach

➢ To what extent is the formation of particles affected by the protein material **and the drying parameters**?

from **the mechanical properties of the protein material**?

Quality of industrial powder

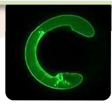
Spraying cone of droplets

Integration of knowledge

Particle properties

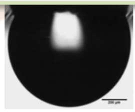
Mono-dispersed droplets

Skin formation



Confined droplet

Droplet dynamics



Pendant droplet

➢ What is the impact of particle morphology on **powder functionalities**?

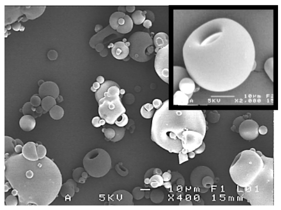
Milk proteins

- ✓ Single or mixture
- ✓ C = 100 $g.L^{-1}$

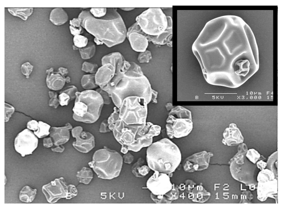
Signature of milk proteins at multi-scale

Spraying cone of droplets

Whey protein (WP)



Casein Micelles (NPC)



Drying kinetics → **~1 s**

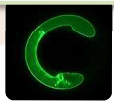
Particle Size	*500 µm*	*140 µm*	*42-56 µm*
Drying temperature	*20°C*	*190 °C*	*210 °C*
Quantity	***1 particle***	***~ g of particles***	***~ kg of particles***

Experimental strategy : Skin formation / confined droplet

Milk proteins

- ✓ Single or mixture
- ✓ C = 100 g.L^{-1}

Skin formation



Confined droplet

Quality of industrial powder

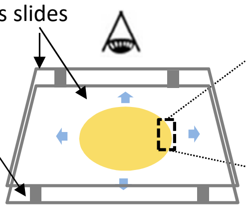
Spraying cone of droplets

➢ How much do the final physical properties of the particles result from **the mechanical properties of the protein material**?

Confined droplet : investigation of the skin formation

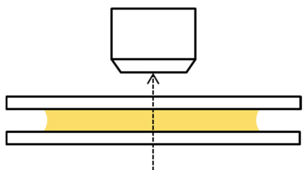
Confined droplet Skin formation

Top view

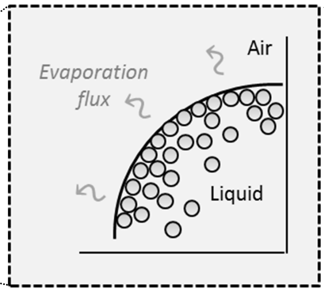


Profil view

Fluorescence microscope

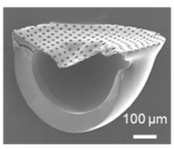


Specific properties of protein skin-layers

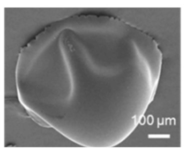


Particle morphology

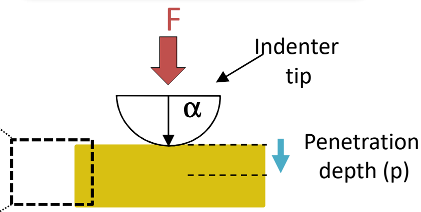
Particle of whey proteins

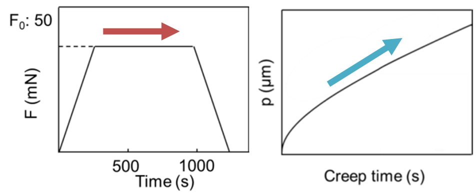


Particle of casein micelles



Micro-indentation Mechanical properties



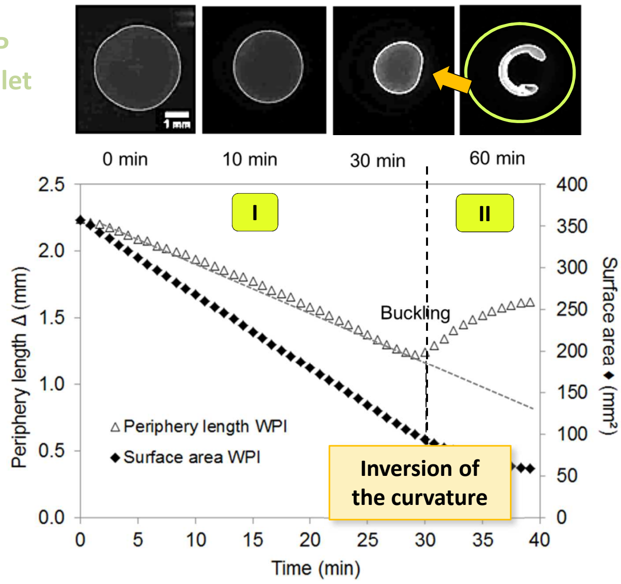


Experimental conditions:

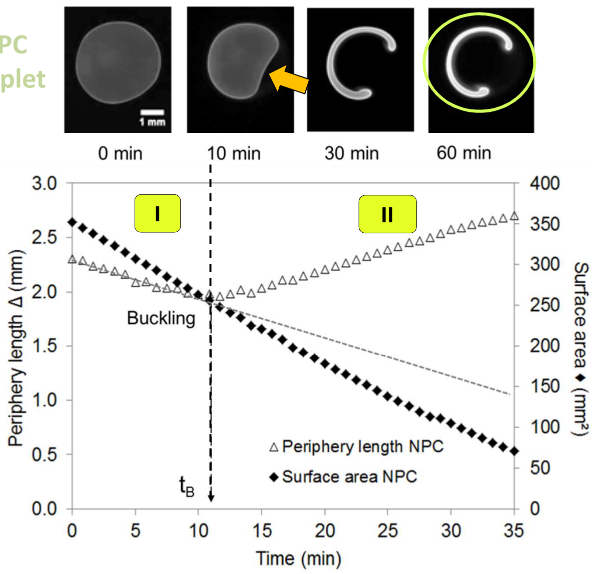
- ➢ Temperature: 20°C
- ➢ Relative humidity: 40%

Periphery length / surface area as a function of evaporation time

❑ WP droplet



❑ NPC droplet



- **Two drying stages** : §I. isotropic shrinkage, §II. Droplet deformation (buckling)
- Buckling event occurs at different drying kinetics
- **Final shape directly results from the drying dynamics, ie the protein type**
  - ➢ WP: long shrinkage ➔ small pattern which finally fracture
  - ➢ NPC: early buckling with a fixed convex interface ➔ long and thin final pattern

Sol gel transition / mechanical properties of WP & NPC skin layers

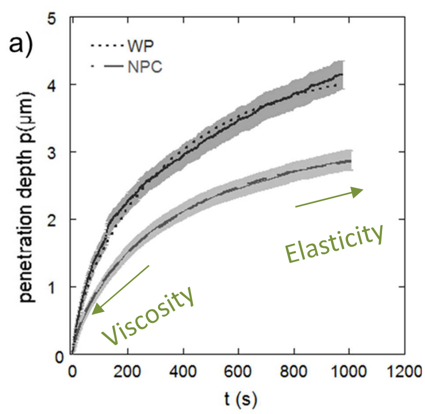
❑ Estimation of the concentration at the buckling time

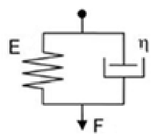
	Concentration at $t_{buckling}$ ($g.L^{-1}$)	Concentrations published at sol-gel transition ($g.L^{-1}$)	Ref
WP	**414**	540	Parker et al., 2005
		500 - 600	Brownsey et al., 2003
NPC	**156**	130	Bouchoux et al., 2009
		148 - 170	Dahbi et al., 2010

➢ **At the interface:** buckling instability is occurring at a concentration compatible with sol-gel transition

	Viscosity, η (GPa.s)	Young's modulus, E (GPa)	$\frac{\eta}{E}(s)$	Yield stress, σ_y (MPa)
WP	136 ± 0.6	0.29 ± 1.10^{-3}	469 ± 0.6	52
NPC	238 ± 0.3	0.48 ± 6.10^{-4}	496 ± 0.3	30

❑ Mechanical properties of protein skin layers



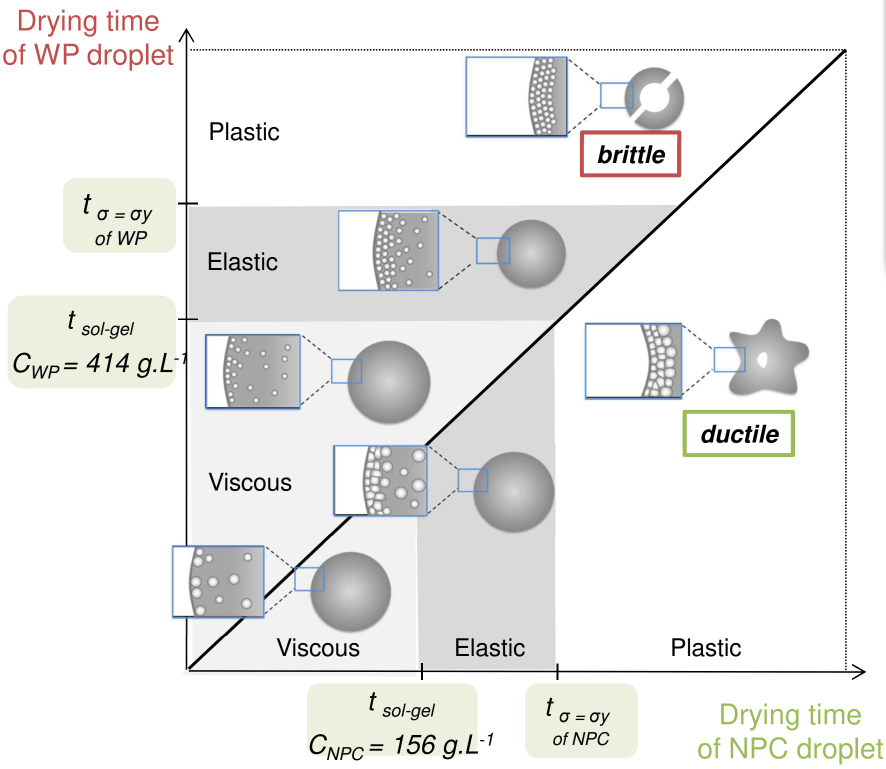


=> Kelvin-Voigt model

➢ Viscous effect more pronounced for casein micelle material

➢ Casein micelle skin reaches the plasticity well before whey protein material

Possible skin formation mechanisms



WP

- Long shrinkage ($t_{buckling} \sim 1/2\ t_{drying}$)
- plastic state → keeps spherical shape but cracks

Brittle plastic material

NPC

- Early gelled layer ($t_{buckling} \sim 1/3\ t_{drying}$)
- plastic state → surface invaginations

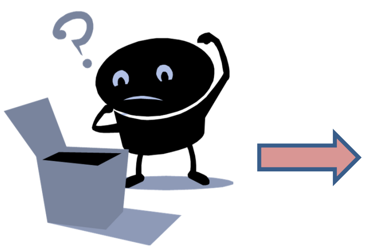
Ductile plastic material

Signature of milk proteins

<u>Whatever the drying kinetics, same morphological behavior</u>

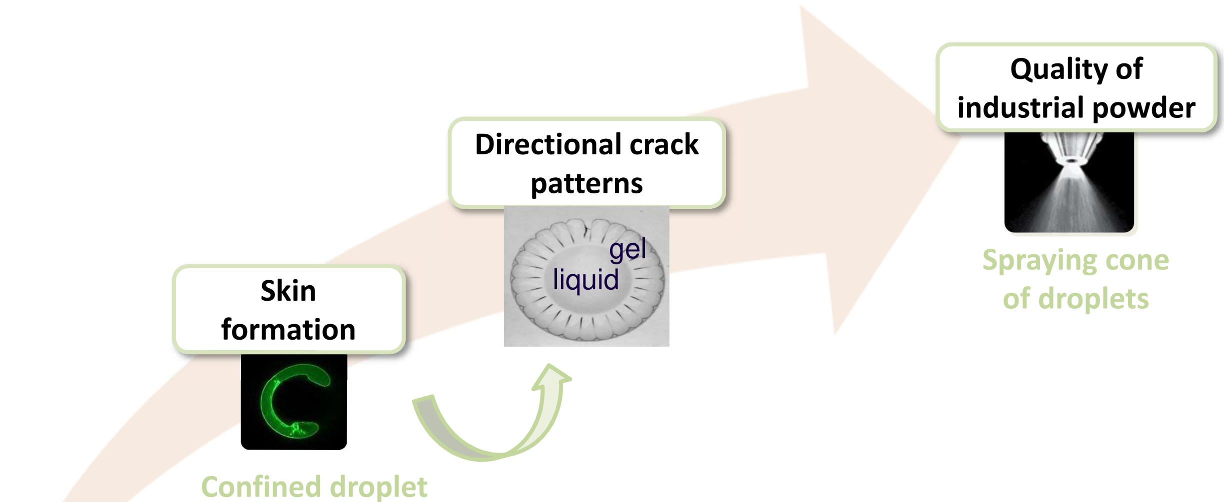
- **Specific signatures** of WP and NPC proteins on the particle formation
- Different **kinds of drying behavior**
  - ✓ **Whey proteins = brittle material**
  - ✓ **Casein micelles = ductile material**

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

Experimental strategy : use of model colloids



Milk proteins

- ✓ Single or mixture
- ✓ C = 100 $g.L^{-1}$

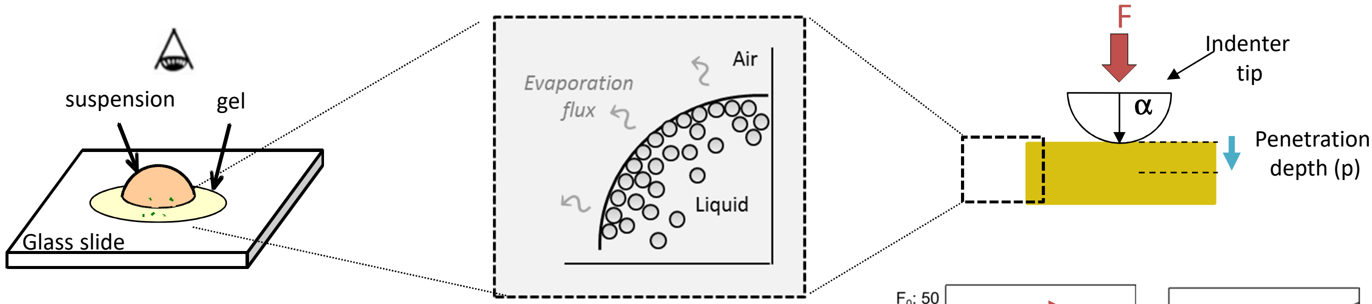
Can model colloids contribute to the better understanding of the physical mechanisms taking place throughout the evaporation of droplets of milk colloids ?

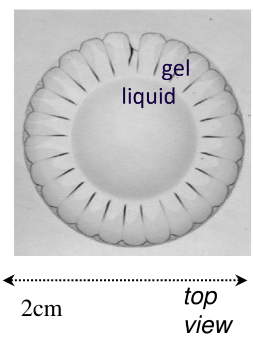
Coupling cracks dynamics and micro-indentation

Sessile droplet Cracks formation

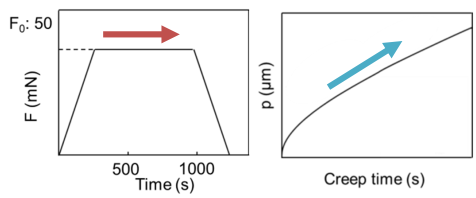
Specific properties of protein skin-layers

Micro-indentation Mechanical properties





Investigation of mechanical behaviors



Experimental conditions:

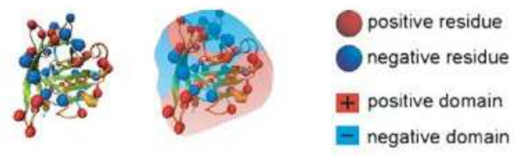
- Temperature: 20°C
- Relative humidity: 40%

Drying behavior of milk proteins and colloidal systems

❑ Whey proteins

- Globular structure, D ≈ 10-20 nm

→ Reconstituted from **WP powder (Whey Proteins, 100 g.L^{-1})**



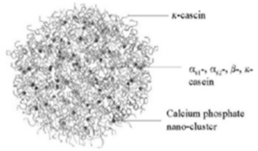
Yohko, 2012

❑ Casein micelles

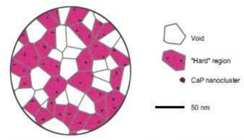
- Micellar, dynamic, hydrated structure, D ≈ 10^2 nm

→ Reconstituted from **NPC powder (Native PhosphoCaseinates, 100 g.L^{-1})**

Internal structure not known



Holt & Horne, 1996



Bouchoux, 2010

❑ Dispersion of silica coloidal particles

Ludox TM50 : ∅ = 22 nm ± 2
(weight fraction in silica particles = 0.40)

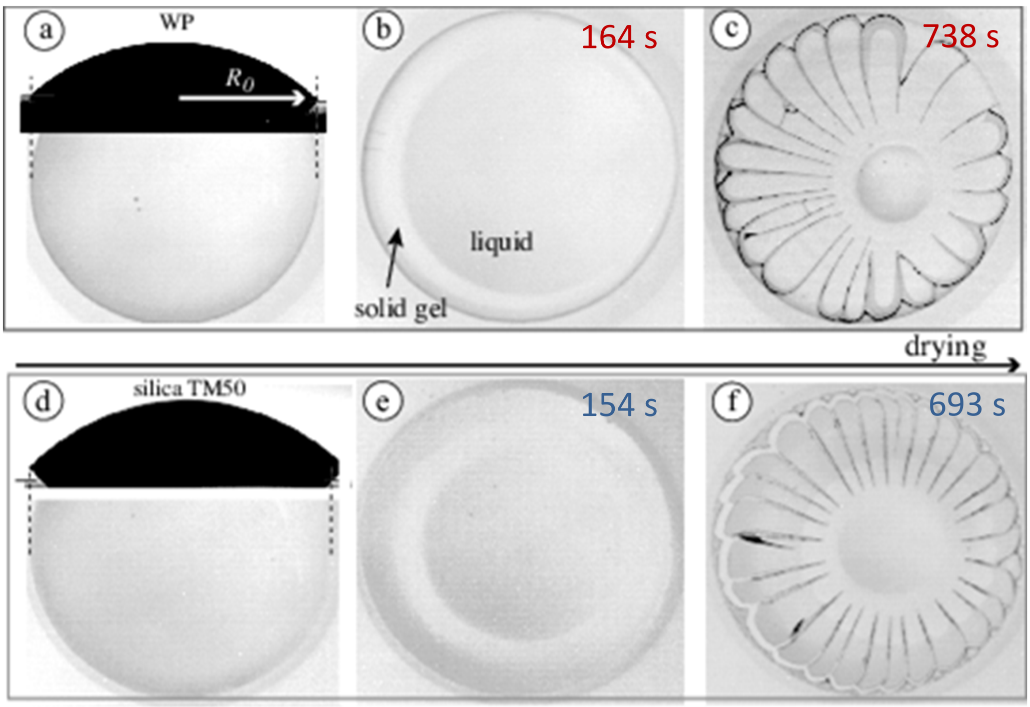
❑ Polymer chains on TM particles

Ludox TM50 + PVP (40kDa)

(weight concentration of PVP = 0.1%)

⇒ PVP owns high affinity for silica surfaces

Drying process of sessile drops (WP / TM50)



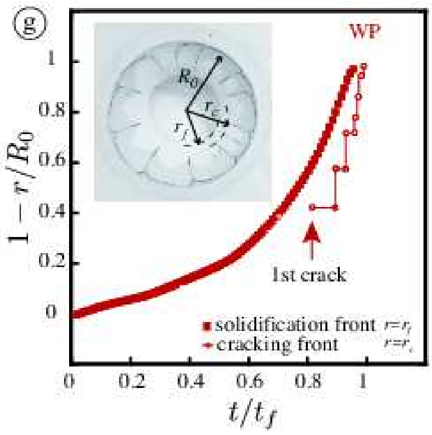
Experimental conditions:

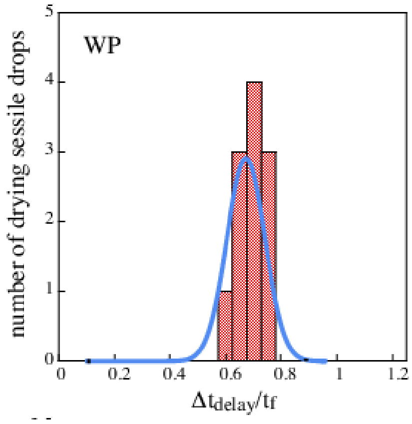
- Temperature: 20°C
- Relative humidity: 40%
- Initial contact angle : 31 ± 2°
- 2 R_0 = 8 mm
- Evaporation rate : 8.10^{-8} m.s^{-1}

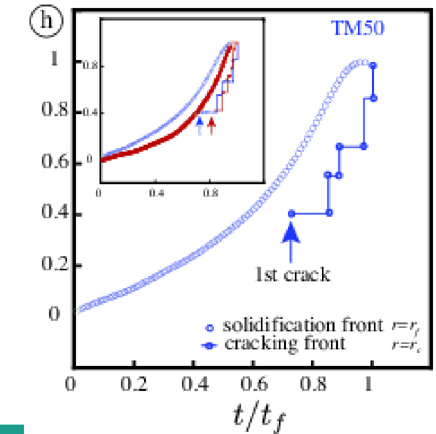
Comparable behavior

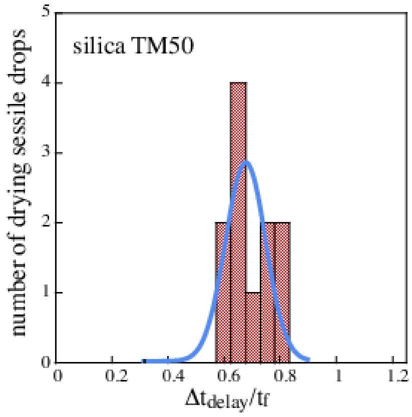
Formation of radial fractures in the solid periphery

Crack dynamics and delay time before cracking





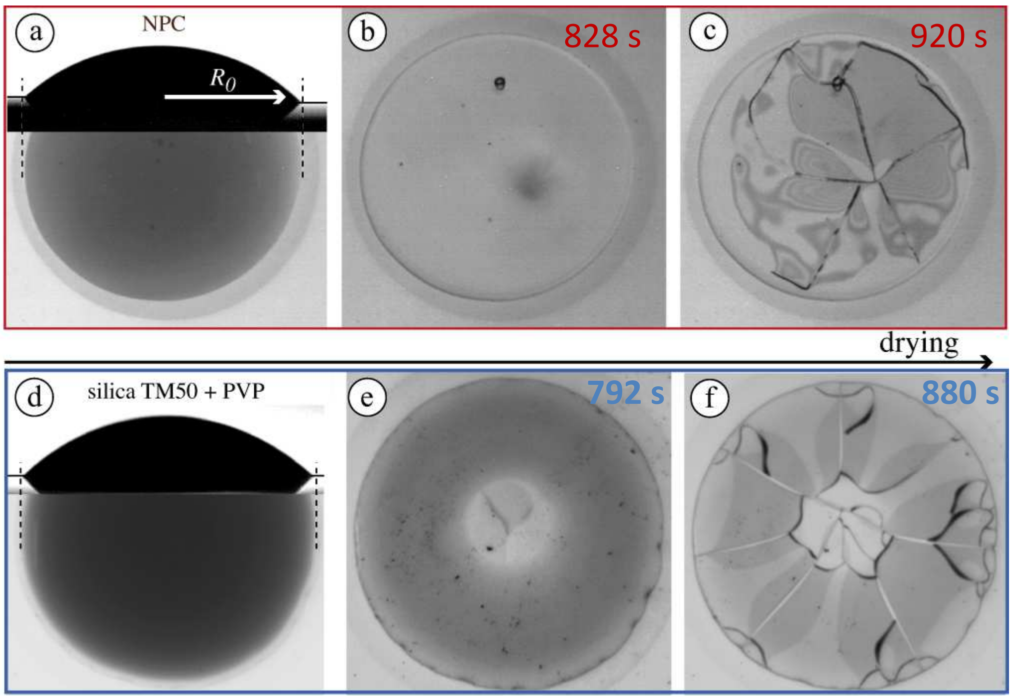




- **Similar time evolution of the drying front location obtained for WP and TM50**

- **Similar statistics of duration elapsed before crack propagation :**
  - ✓ **334 ± 41 s for WP**
  - ✓ **311 ± 61 s for TM50**

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



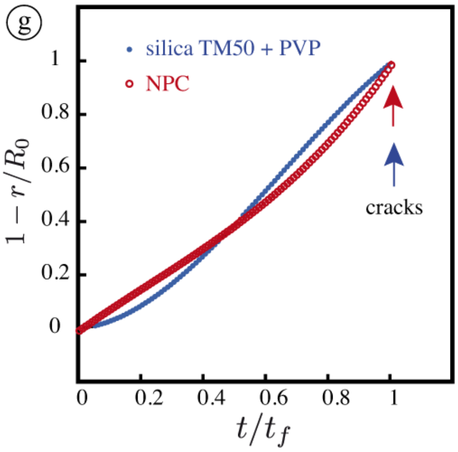
Experimental conditions:

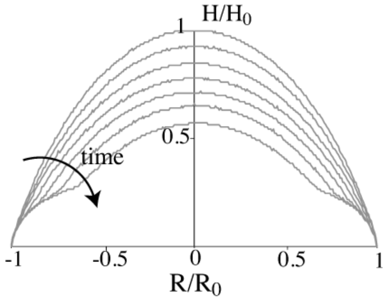
- Temperature: 20°C
- Relative humidity: 40%
- Initial contact angle : 35 ± 2°
- 2 R_0 = 8 mm
- Evaporation rate : 8.10^{-8} m.s^{-1}

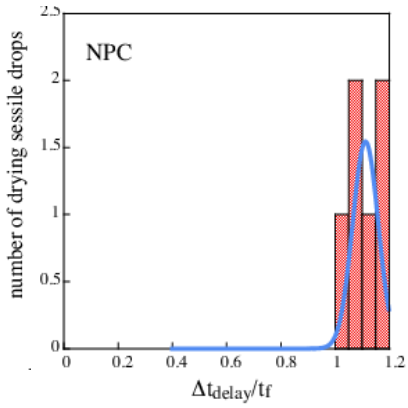
<u>Comparable behavior</u>

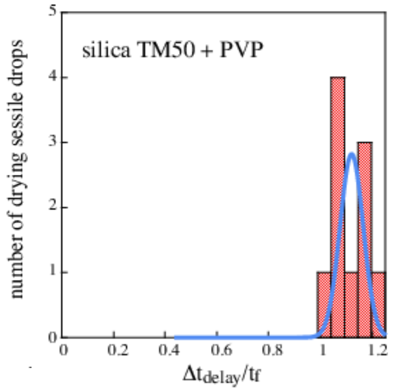
Later nucleation of a few, random fractures

Crack dynamics and delay time before cracking





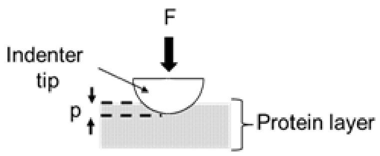


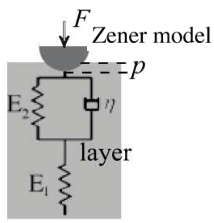


- **Similar time evolution of the drying front location obtained for NPC and TM50 + PVP**

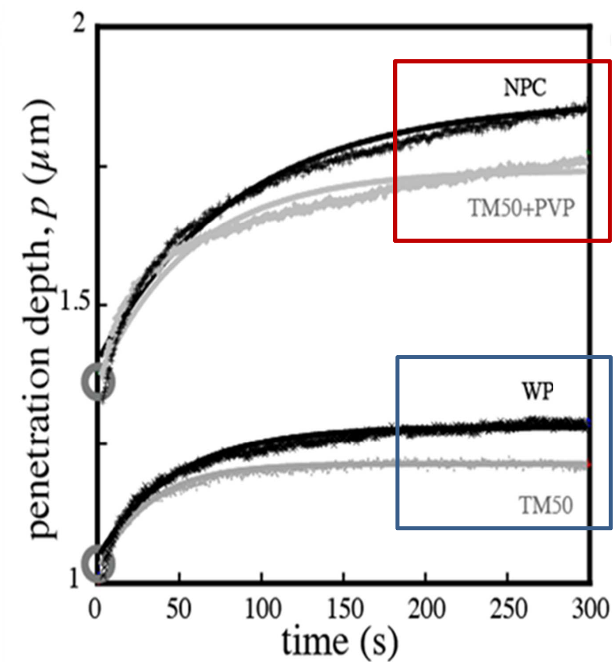
- **Similar statistics of duration elapsed before crack propagation:**
  - ✓ **834 ± 50 s for NPC**
  - ✓ **855 ± 40 s for TM50**

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**

Conclusion : How does the droplet become a dry particle?

- The protein kind influences the **drying dynamics** of the single droplet under controlled spray drying conditions

  - ✓ The **skin formation** originates from a buckling instability at **sol-gel transition**
  - ✓ The **mechanical properties** of the skin **condition the final particle shape**
  - ✓ **Specific signatures** of WP and NPC

- Interest of the approach with **model colloidal solutions**

  - ✓ **Numerous analogies between dairy and the corresponding model systems**

OUTLOOK

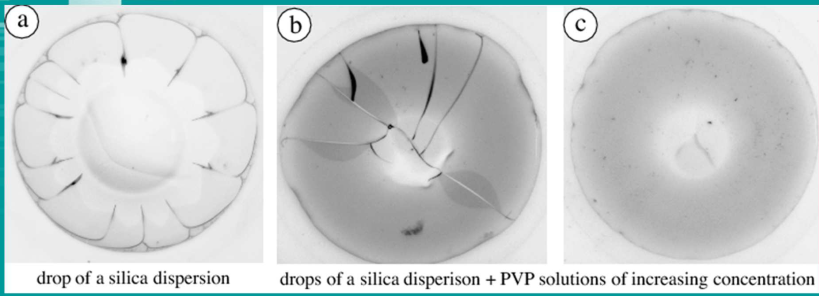
Gathering conceptual tools of the physical chemistry of interfaces and the physics of soft matter

What about the permeability of the skin ?

What about the evaporation in a binary colloidal solution ?

What is the impact of the WP/NPC ratio on the onset of sol-gel transition and skin formation mechanisms ?

Is the skin representative of the bulk composition ?



Merci

Thank you for your attention

More information

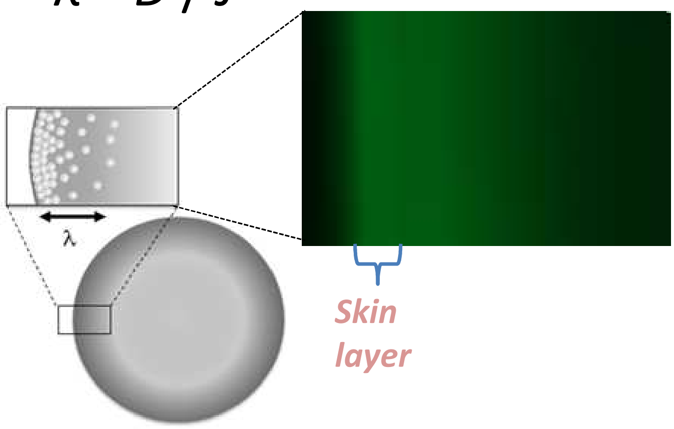
- **Sadek et al., 2013, Langmuir, 29, 15606-15613**
- **Sadek et al., 2014. Drying Technol,32, 1540-1551**
- **Sadek et al., 2014, Dairy Sci Technol, 95, 771-794**
- **Sadek et al., 2015, Food Hydrocolloids, 48, 8-16**
- **Sadek et al., 2016, Food Hydrocolloids, 52, 161-166**
- **Lanotte et al., 2018, Col. Surf. A, 553, 20-27**
- **Le Floch-Fouéré et al., 2019, Soft Matter, 15, 6190**

CECAM, October 2019, Lausanne

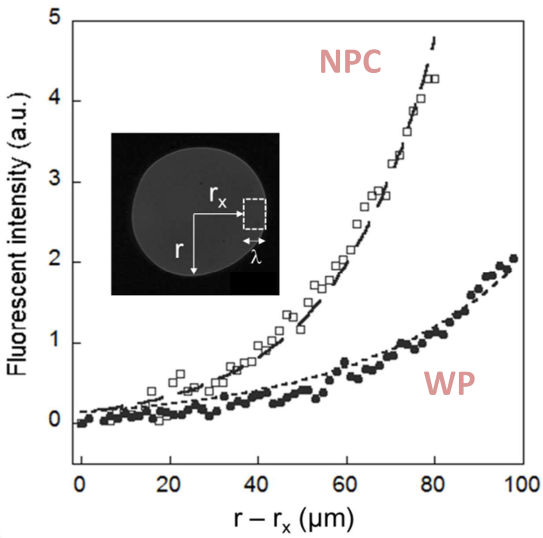
Gradients of protein concentration near the edge of the droplet

❑ Diffusion length λ

$$\lambda = D / J$$



❑ Fluorescence profile



- **Evaporation flux *J* toward the surface**
- **Protein accumulation** at the interface
- **Skin formation**

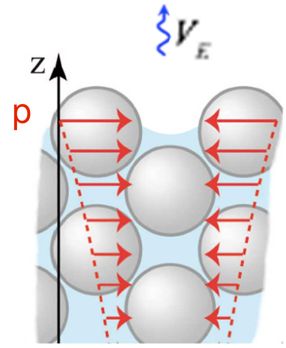
Drying stress and poro-elasticity

- **Drying stress at the film/air interface :**

$$\sigma(z=h) \sim E\frac{t}{t_D}$$ where t_D 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)

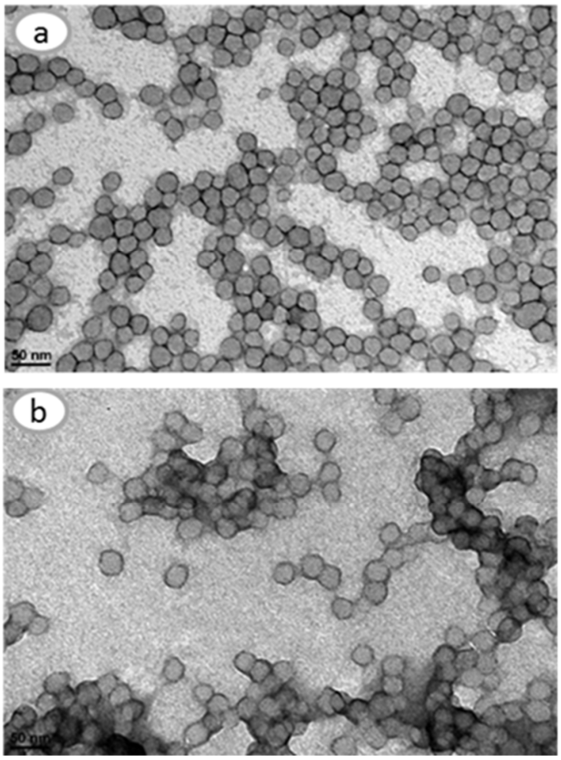
Hypothesis: delay time before stress reaches max stress **: viscoelastic timescale** t_η

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

estimation of the pore size in the solid state : **$r_{pore\ (WP)}$ / $r_{pore\ (NPC)}$ ~ 2**

Results in concordance with drying behavior :
NPC more deformable than WP

Thickness of PVP Coating



TEM images of silica nanoparticles (a) and hybrid PVP–silica nanoparticles (b)

Average value of ~ 8 nm for thickness of the PVP shell

In accordance with Yu et al. (2017, 2018)
but without a clearly core-shell structure

Ellipsometry measurements

Thickness of the PVP coating ~ 65 nm
(whole structure including the possible PVP core–shell and the outer polydisperse polymer brush)