Crack patterns induced by auto-stratification in drying droplets of dairy proteins

Cécile Le Floch-Fouéré, L. Pauchard, Luca Lanotte

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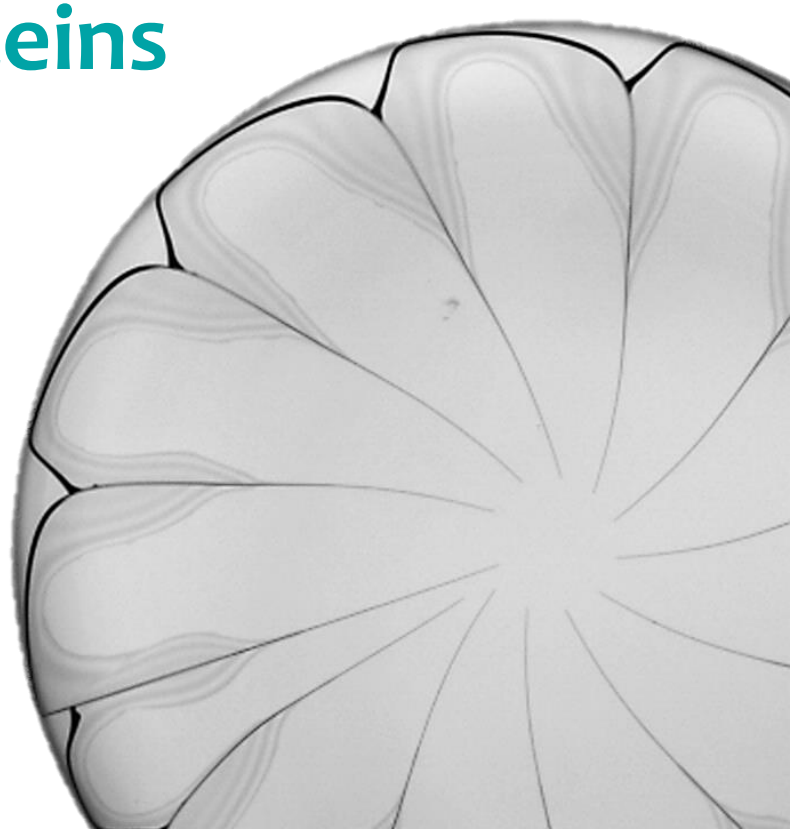
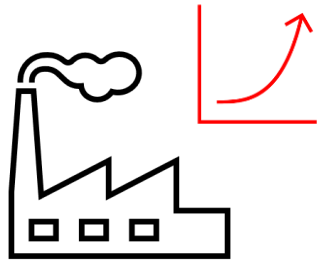


Infant Milk Formula (IMF): a challenging priority

- Globalization, economical transition, population growth
- Increasing global market: from 50.46 USD billions to predicted 109.10 USD billions by 2027 (Fortune Business Insights)
- High added value → 80% of European dairy investment since 2011



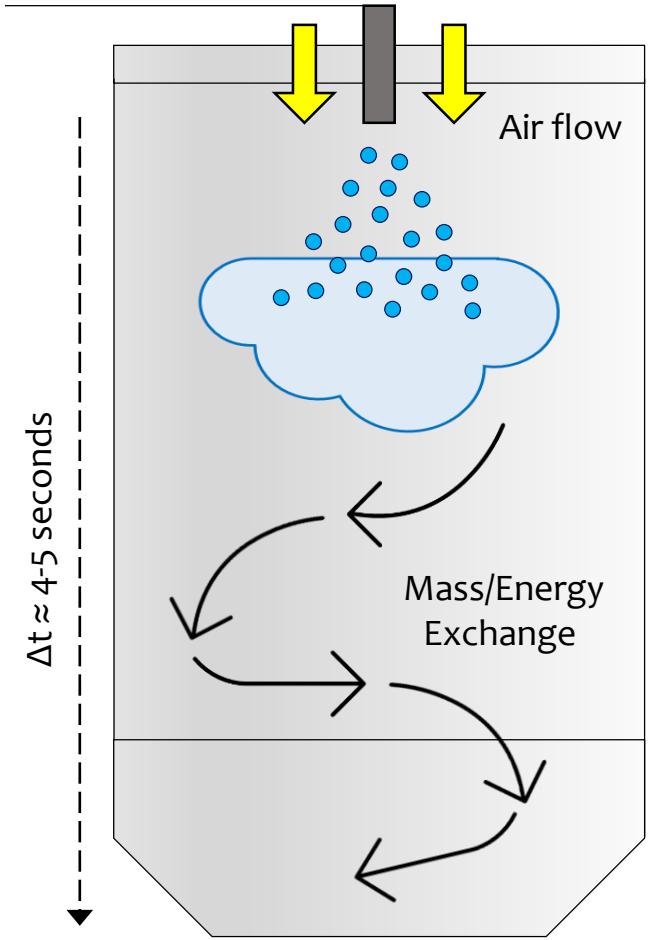
FUNCTIONAL PROPERTIES
ADAPTED TO NUTRITIONAL TARGETS

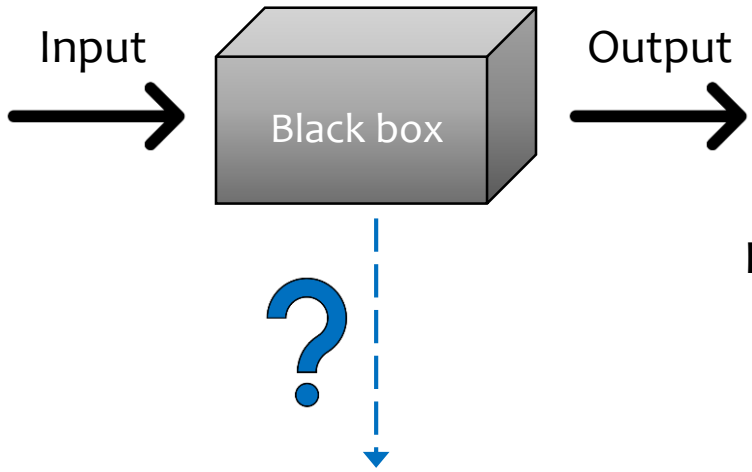
g/l	Cow milk	Human milk
Proteins	**32**	**10**
Caseins	*80%*	*35%*
WP	*20%*	*65%*
Carbohydrates	**50**	**75**
Lipids	**38**	**36**
PUFA	*2,9%*	*6,4%*

- **Physico-chemical complexity of the milk system**
- **Different composition between cow and human milk**

Insights on the drying process in dairy industry

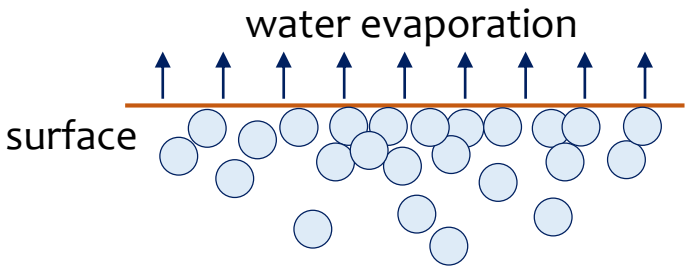
Spray dryer





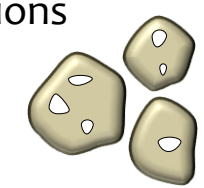
POWDER FUNCTIONAL PROPERTIES
Rehydration, sticking, caking

MECHANISMS GOVERNING THE DROPLET-TO-PARTICLE TRANSITION



SKIN FORMATION

- Stress-induced instabilities
- Strong deformations

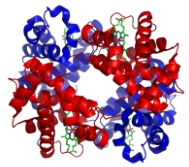


Drying of dairy protein mixes

Ming Yu
Ph.D. Thesis (2018-21)
L. Lanotte, C. Le Floch-Fouéré, R. Jeantet

WHEY PROTEINS (WPI)

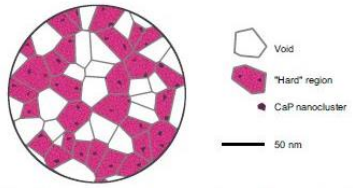
- **Rigid, globular shape**
- Small size (10-30 nm)



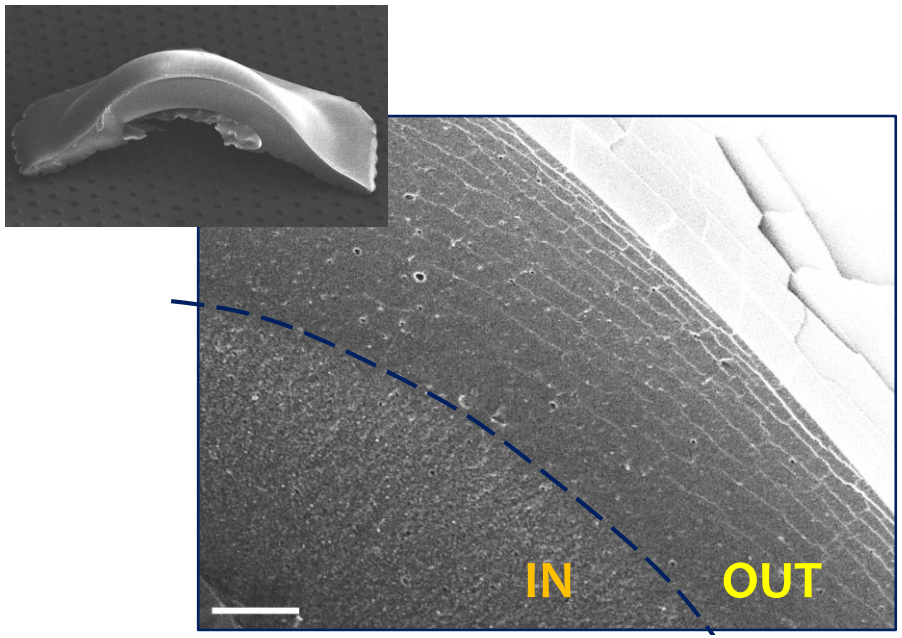
Yohko, 2012.

CASEIN MICELLES (NPC)

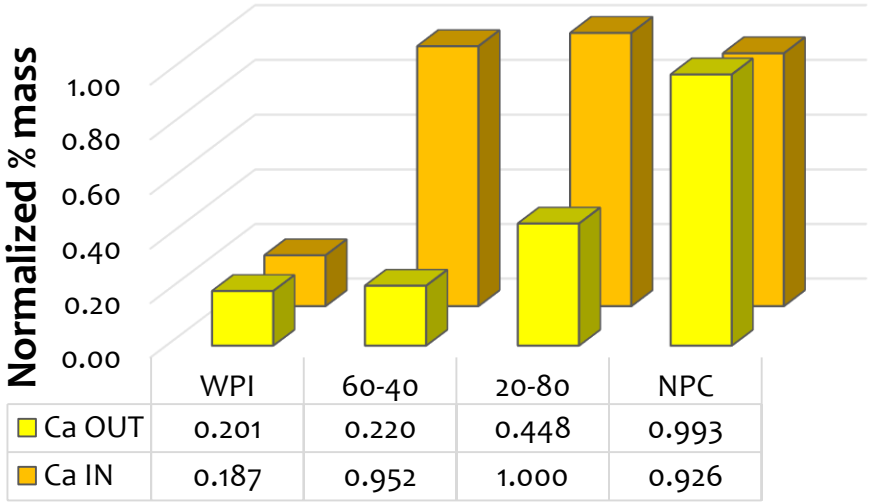
- **Sponge-like, deformable structure**
- Average diameter (100-300 nm)



Bouchoux, 2010.



Lanotte et al., Colloids and Surface A, 2018.
Yu et al., Colloids and Surface A, 2021.



	WPI	60-40	20-80	NPC
Ca OUT	0.201	0.220	0.448	0.993
Ca IN	0.187	0.952	1.000	0.926

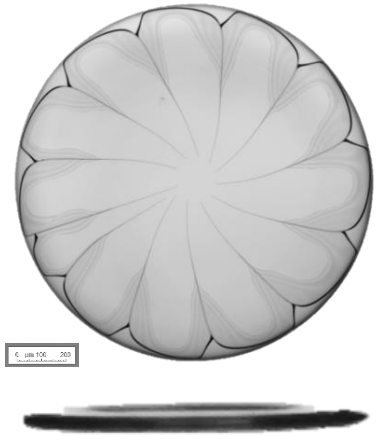
WPI accumulation on the external part of the skin (small-on-top)

Impact of protein auto-stratification on powder properties

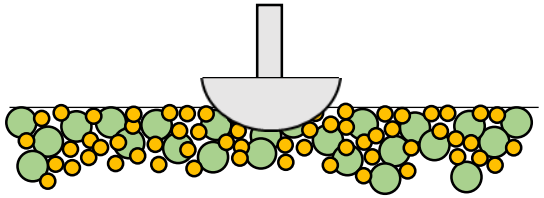
Experimental strategy

- Evaluation of colloid deposits and self-organization in WPI/NPC mixes
- Consequences of protein stratification on droplet sol-gel transition and crack patterns
- Estimation of dry droplet mechanical properties

Optical microscopy - SEM

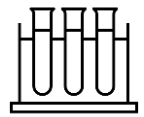


Micro-indentation tests



dry protein layer

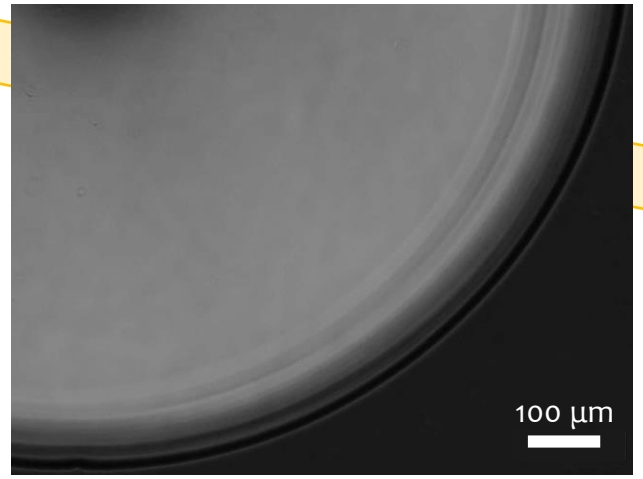
Colloid deposit and droplet morphology

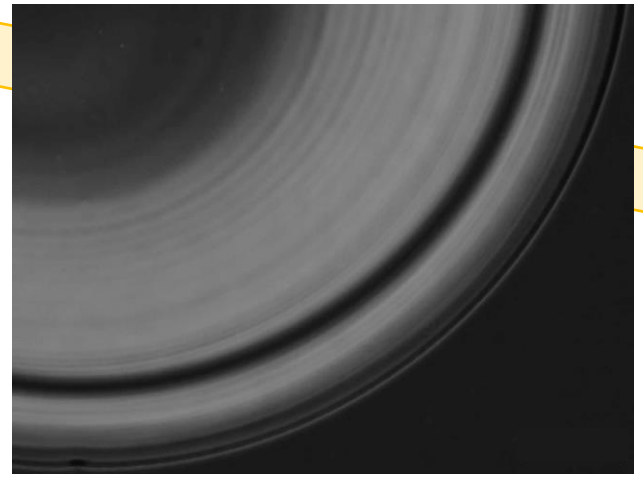


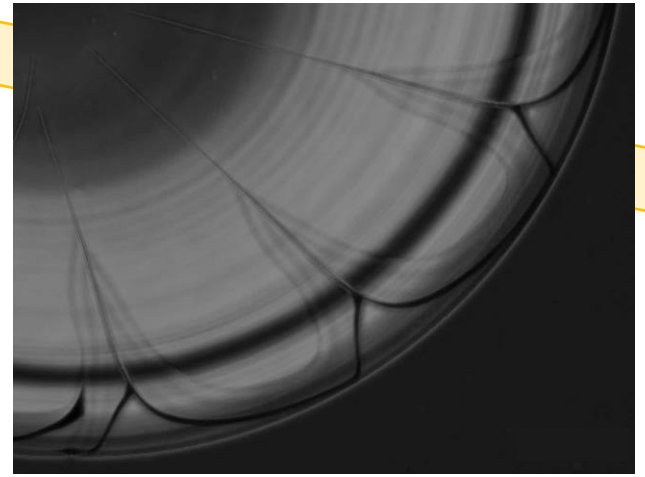
10%wt
protein concentration

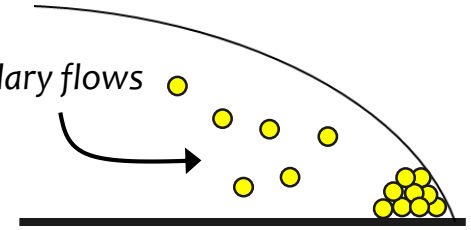
Optical microscope
(phase contrast)

Whey proteins (WPI)

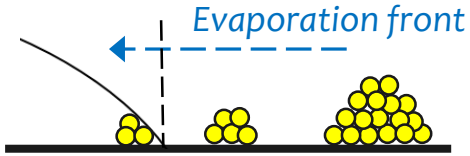






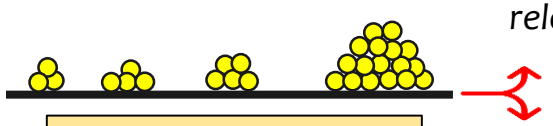


Corona formation



Stick-slip motion

Centripetal stress release



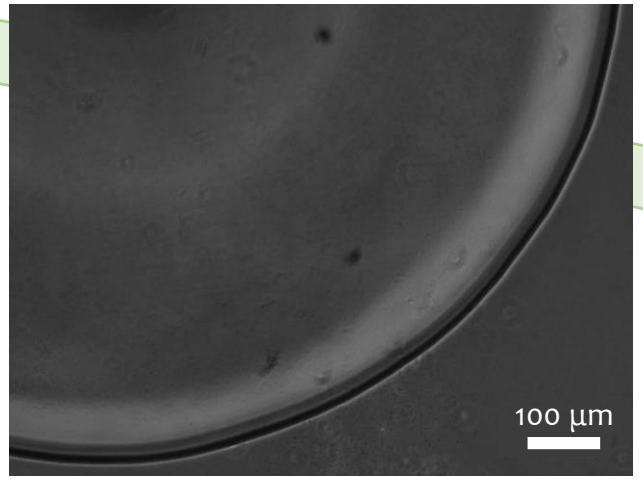
Crack formation

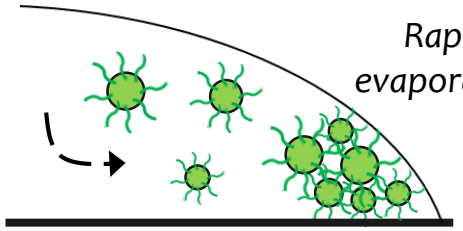
Colloid deposit and droplet morphology

10%wt
protein concentration

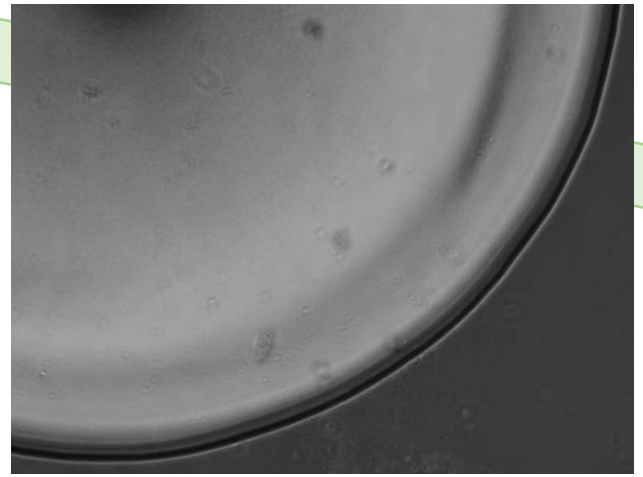
Optical microscope
(phase contrast)

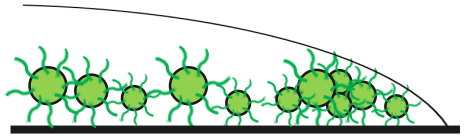
Casein micelles (NPC)



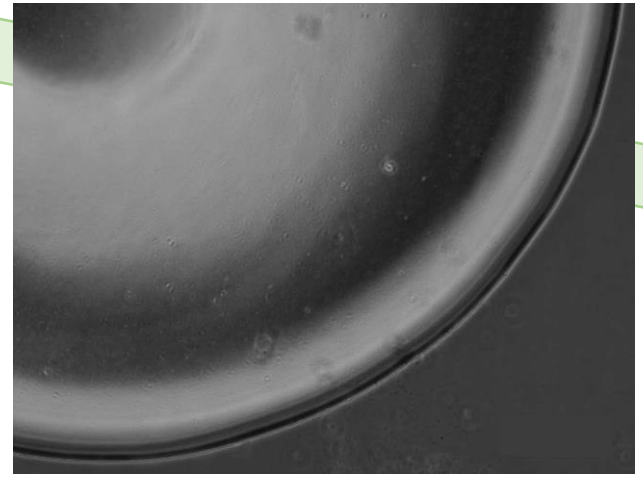


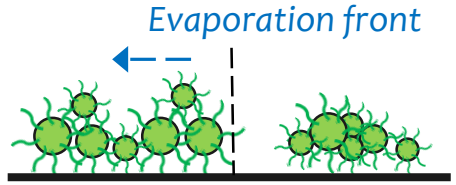
Corona formation





Homogeneous sedimentation





Inward migration

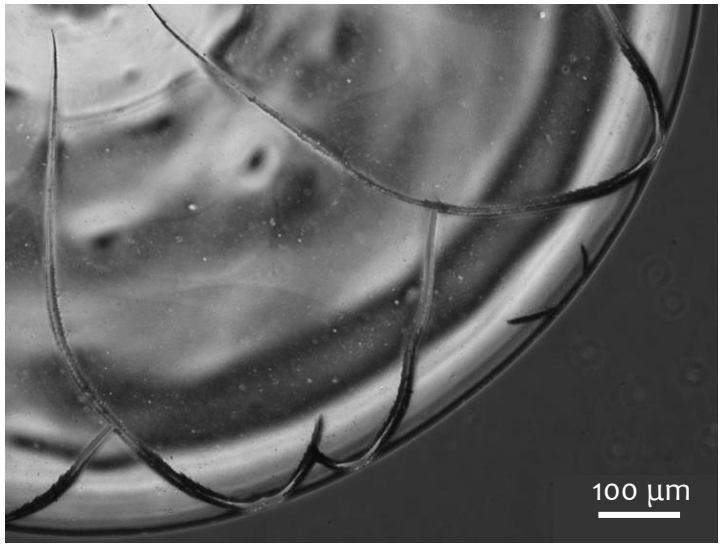
Colloid deposit and droplet morphology

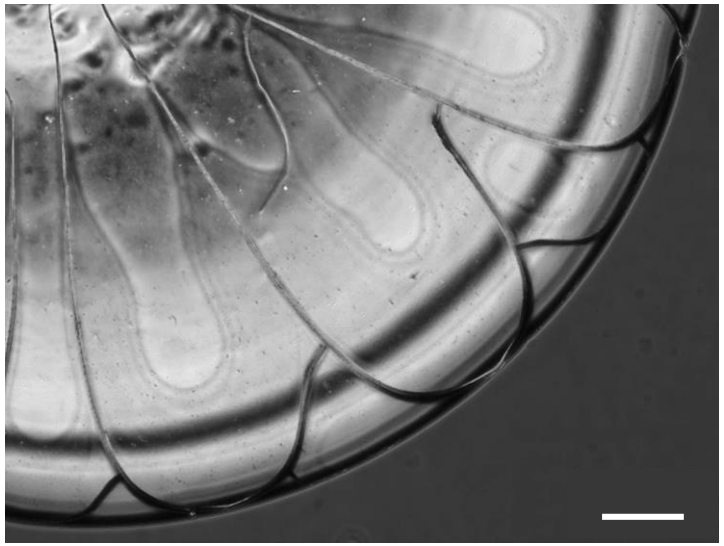
Signature of each protein in WPI/NPC mixes

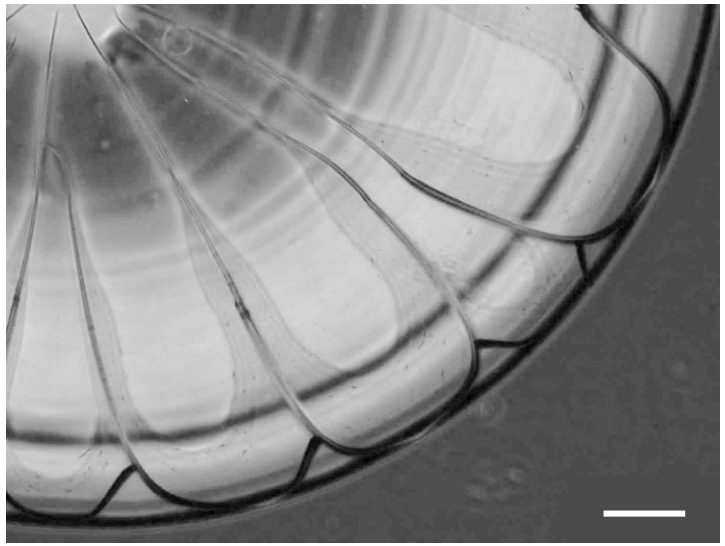
10%wt
protein concentration

$$WPI\%_R = \frac{m_{WPI}}{m_{solute}}$$

Optical microscope
(phase contrast)







20 50 80 $WPI\%_R$

- Gradual transition from NPC to WPI-like morphology with increasing $WPI\%_R$
- **WPI segregation** in the vicinity of droplet edge and crack formation; NPC accumulation in the middle

WPI is always a minor component in terms of volume fraction

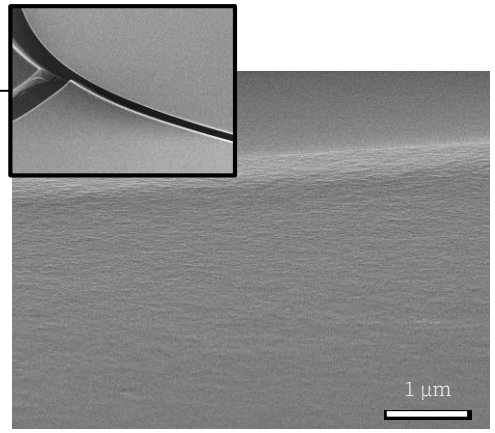
Voluminosity: WPI (0.74 ml/mg) - NPC (4.4 ml/mg)

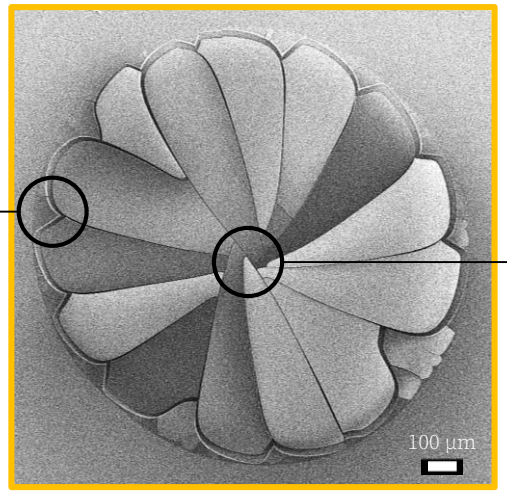
Observation of protein segregation in dry droplets

SEM Microscopy

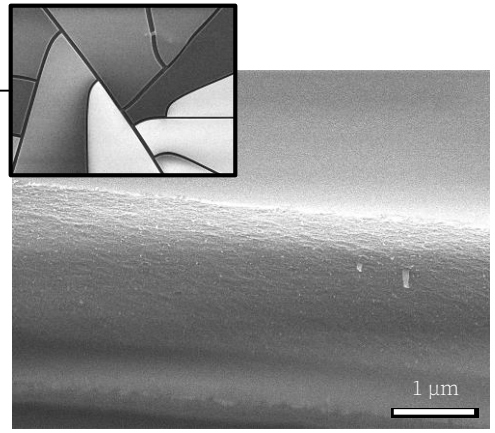
WPI%$_R$=100%
Smooth and packed colloid self-organization

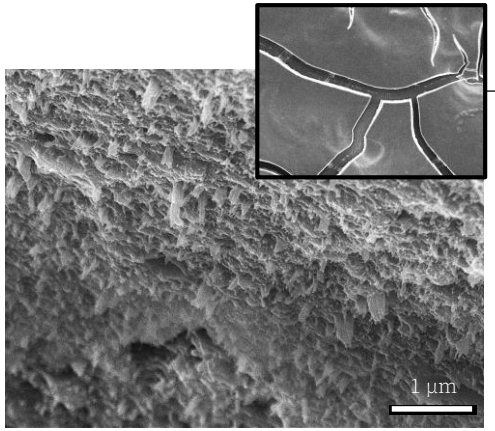
WPI%$_R$=80%
Net of debris, transition from compact (borders) to highly porous structure (center)
Presence of micelles at the borders?

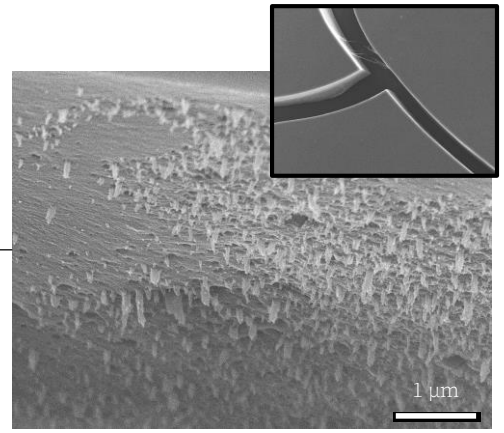


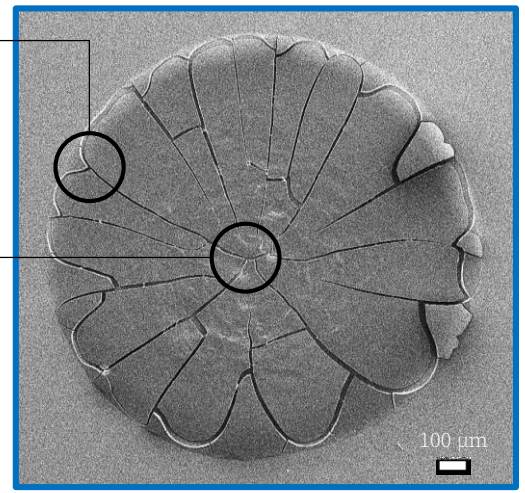


WPI%$_R$=100%



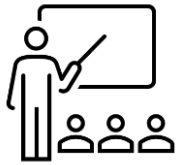






WPI%$_R$=80%

Conclusions I



❑ PROTEIN VOLUMINOSITY PLAYS A ROLE ON THE INTERNAL FLOWS

WPI
Dilute regime

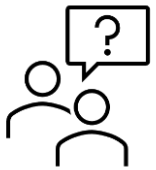
NPC
Crowd conditions

❑ SEGREGATION NOT ONLY IN THE SKIN BUT ALSO IN THE CORONA/SUBSTRATE

- Which is the driving force? (internal flows, osmotic pressure, diffusiophoresis)
- Which adimensional number could characterize this phenomenon?

SKIN FORMATION → PÉCLET NUMBER (EVAPORATION VS DIFFUSION)

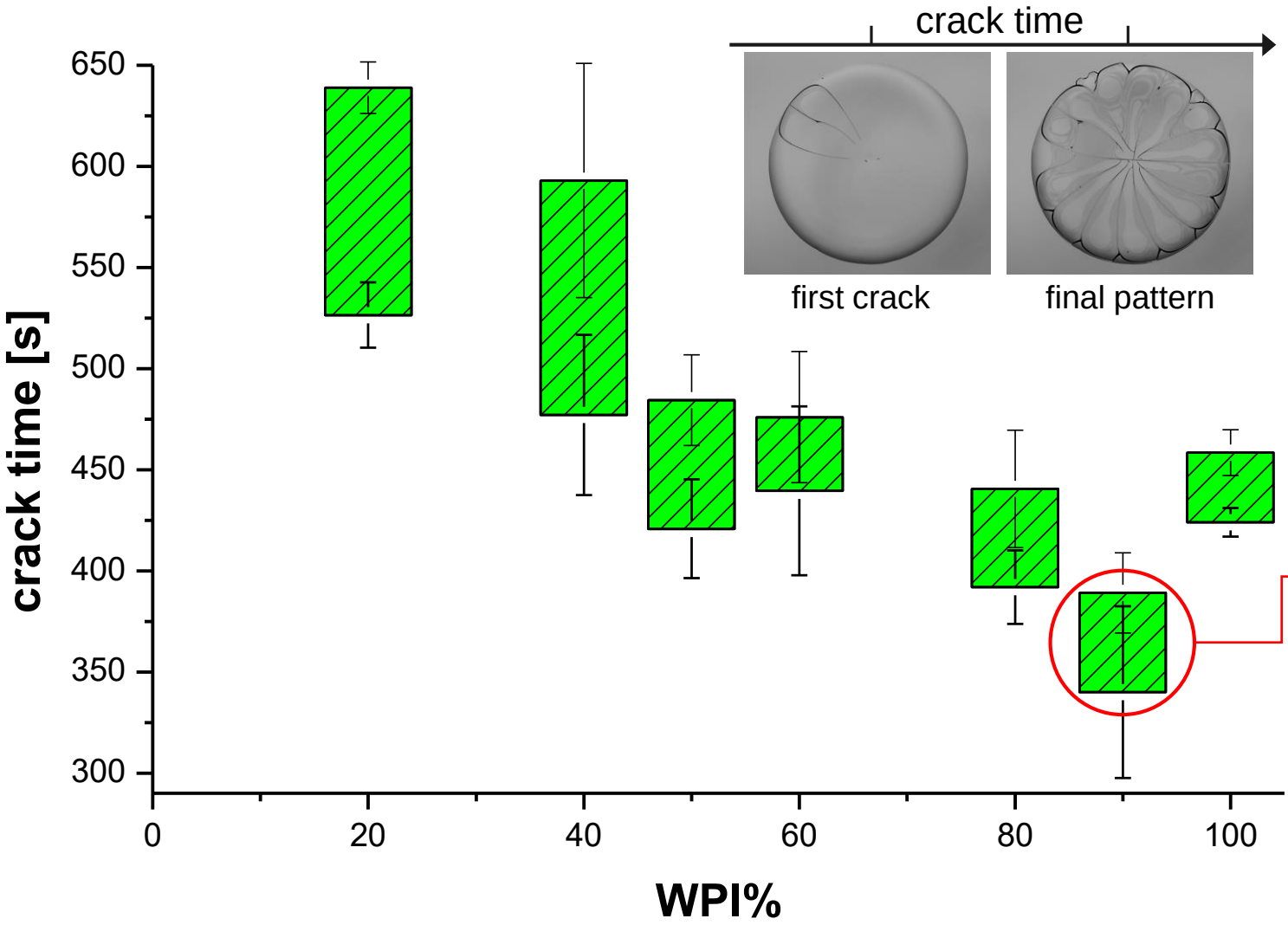
Zhou et al., PRL 2017; Sear and Warren, PRE 2017; Schulz and Keddie, Soft matter 2018.



How does WPI external segregation affect droplet mechanical behavior?

CRACK PATTERN FORMATION

Sol-gel transition: crack occurrence

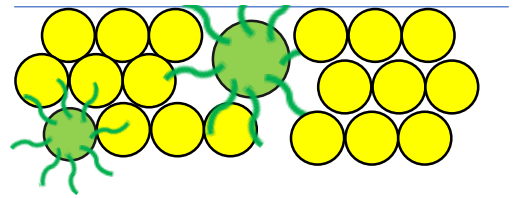


Water removal + Colloid arrangement

Increasing internal stress

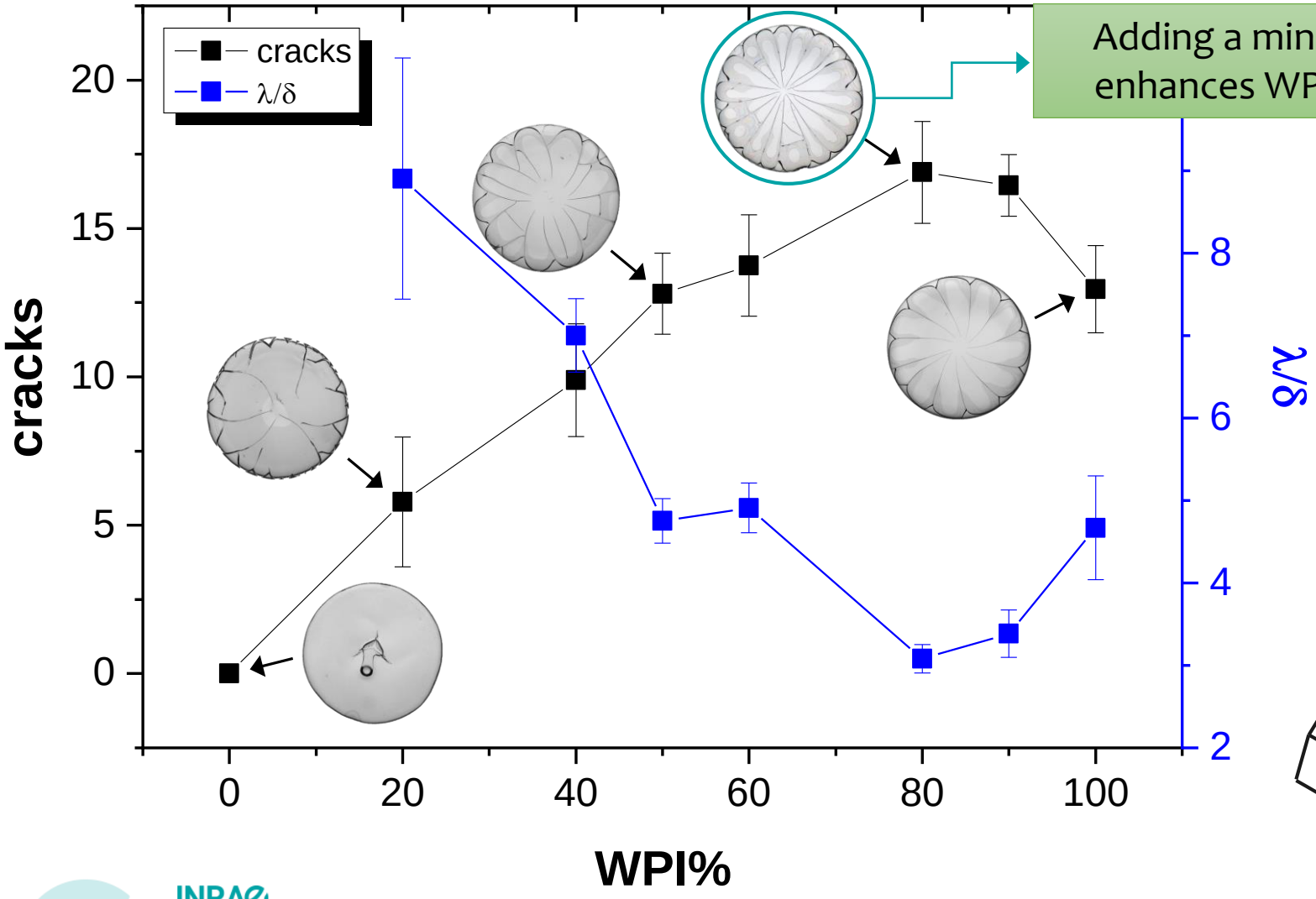
Crack occurrence

Lowered threshold for stress release
(favored crack occurrence)

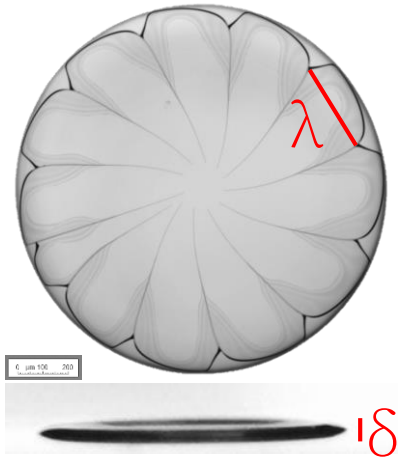


NPC makes the packing less regular (polydispersity, deformability)

Late evaporation stage: crack patterns

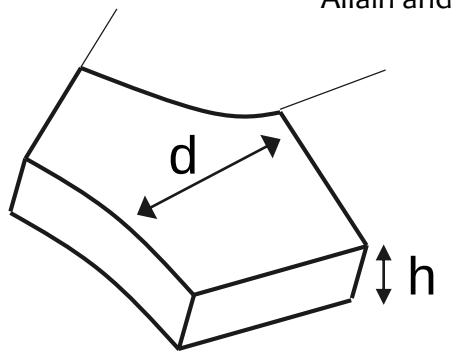


Adding a minor amount of NPC enhances WPI brittle character



Link between crack formation and structure permeability

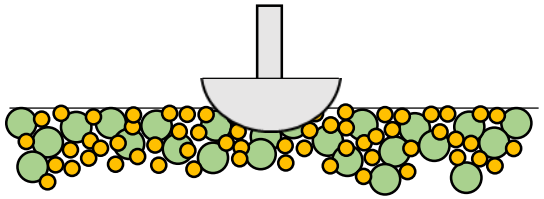
Allain and Limat, PRL, 1995.



Elastic energy of the material = Energy necessary to "create" a new surface

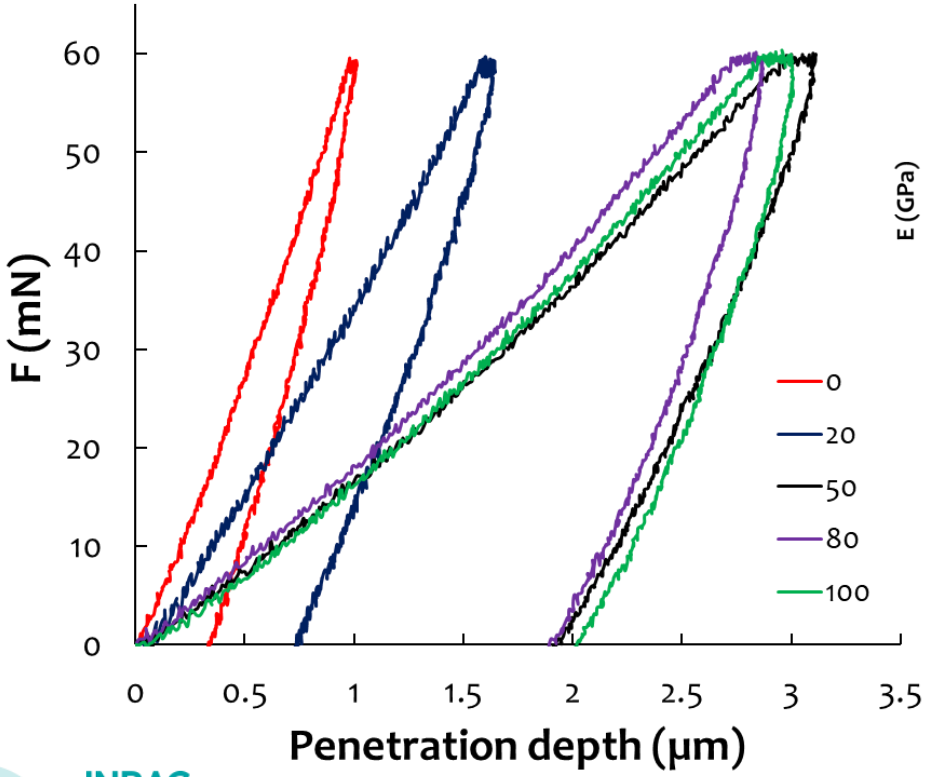
Mechanical properties of dry WPI/NPC structure

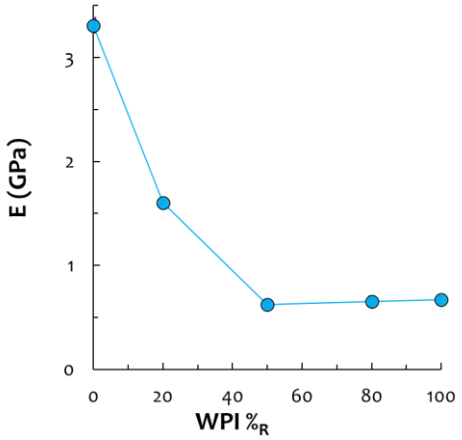
Micro-indentation tests on dry films



dry protein layer

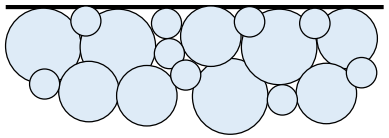
Dry droplet structure in the radial direction ⟷ Stratified layer of WPI/NPC films





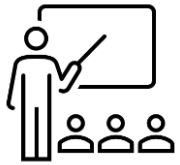
Elastic modulus

- **Evidence of protein auto-stratification for WPI%$_R$≥50%**
- **WPI-rich samples are brittle and with low elasticity**
- **NPC-rich samples exhibit higher rigidity**



Bouchoux *et al.*, Biophys. J. 2010.

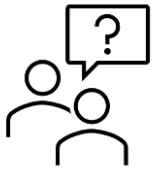
Conclusions II



❑ Similar mechanical behavior in WPI-rich mixes due to protein auto-stratification

Crack occurrence and patterns, mechanical response to indentation

WPI strongly affects the drying process when sufficiently represented in the samples

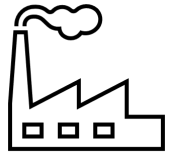


Are these results useful to tune dairy powder functional properties?

From the laboratory..

Monodisperse spray drying

..to the industrial scale



Thank you for your attention!

Ming Yu

Romain Jeantet

Cécile Le Floch-Fouéré

Ludovic Pauchard

STLO

FAST
Fluides, Automatique et Systèmes Thermiques