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

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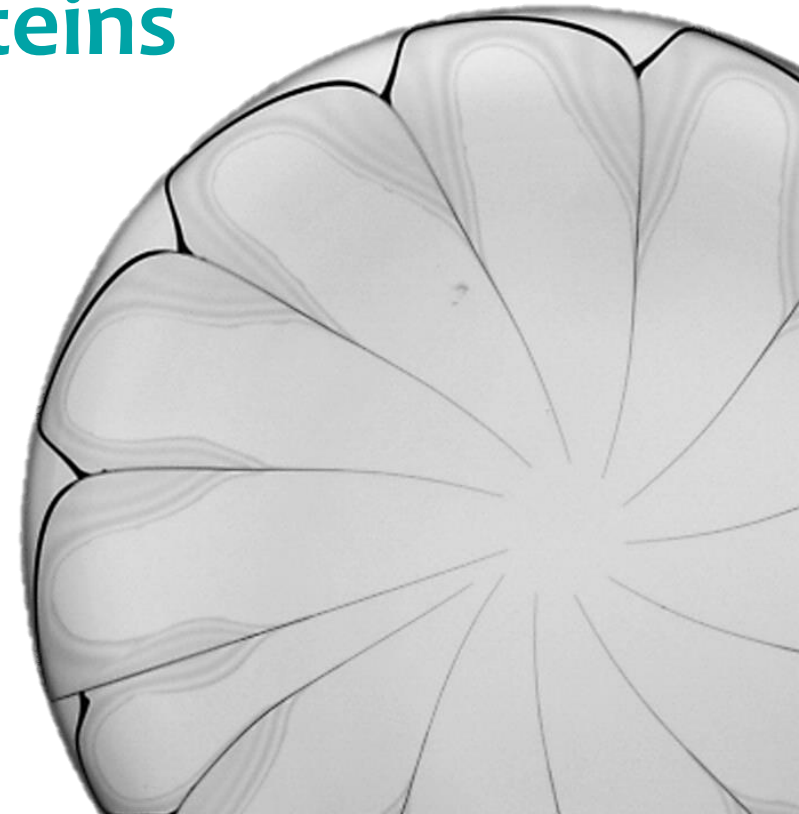
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➤ Crack patterns induced by auto-stratification in drying droplets of dairy proteins

C. Le Floch-Fouéré^a, L. Pauchard^b, L. Lanotte^a

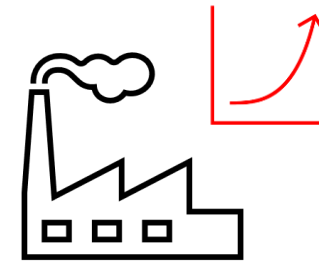
^a INRAE, Institut Agro, STLO, 35042 Rennes (France)

^b CNRS, Université Paris-Saclay, FAST, 91405 Orsay (France)



➤ 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

Infant milk
(< 6 months)



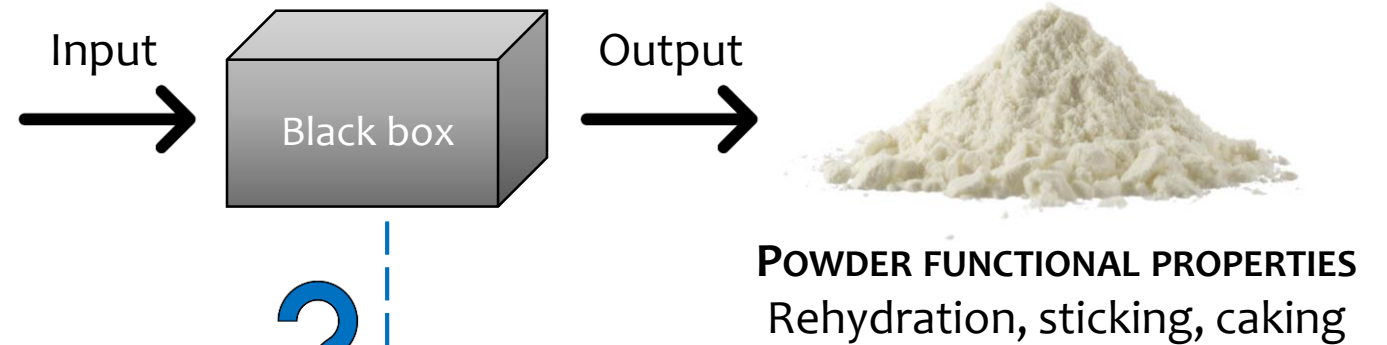
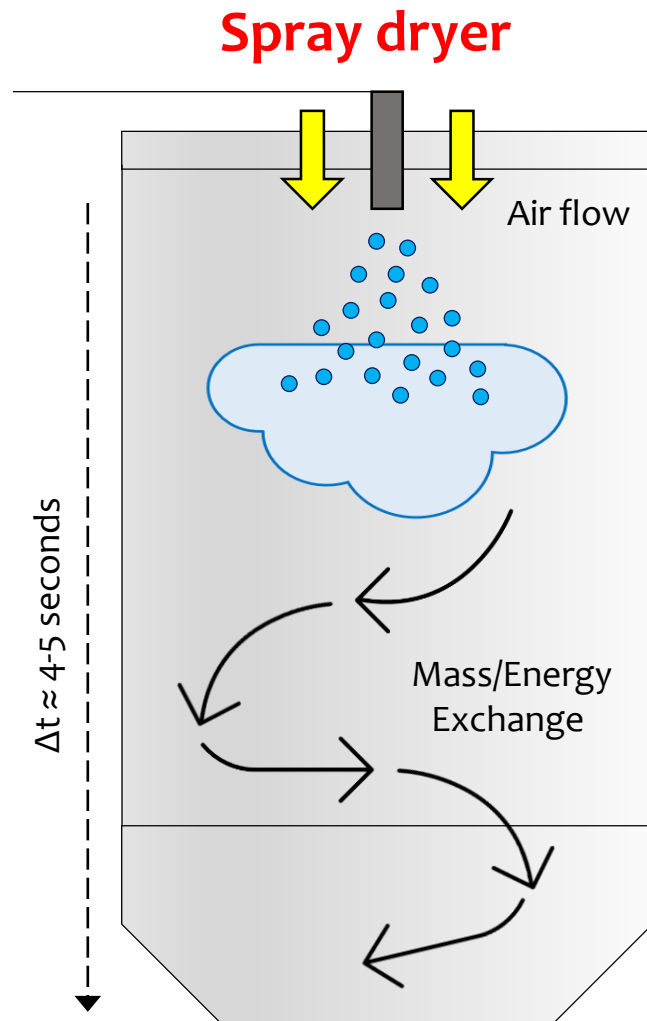
Growing-up
milk

Follow-on milk
(< 36 months)

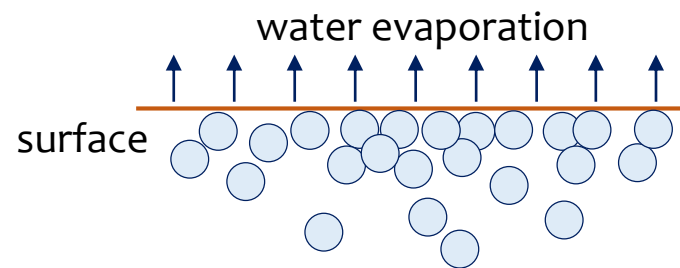
g/l	Cow milk	Human milk
Proteins	32	10
Caseins	80%	35%
WP	20%	65%
Carbohydrates	50	75
Lipids	38	36
PUFA	2,9%	6,4%

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

➤ Insights on the drying process in dairy industry

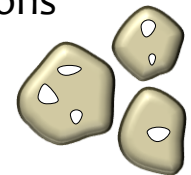


MECHANISMS GOVERNING THE DROPLET-TO-PARTICLE TRANSITION



SKIN FORMATION

- Stress-induced instabilities
- Strong deformations

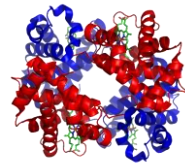


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➤ Drying of dairy protein mixes

WHEY PROTEINS (WPI)

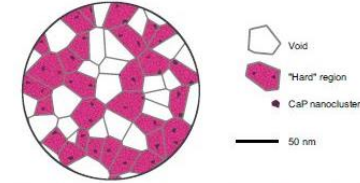
- Rigid, globular shape
- Small size (10-30 nm)



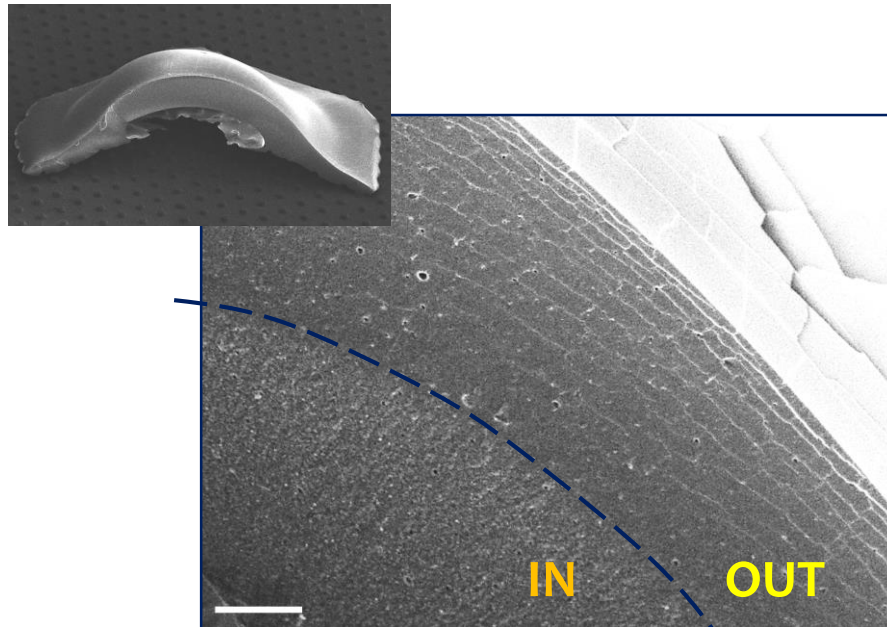
Yohko, 2012.

CASEIN MICELLES (NPC)

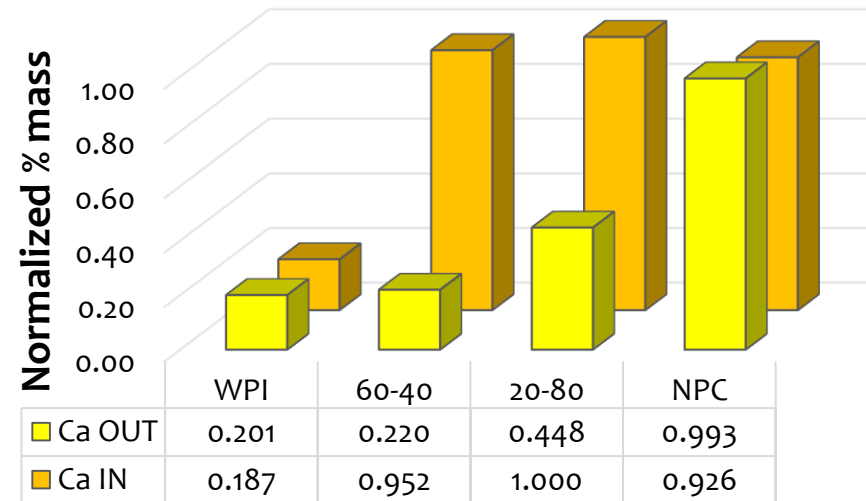
- Sponge-like, deformable structure
- Average diameter (100-300 nm)



Bouchoux, 2010.



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



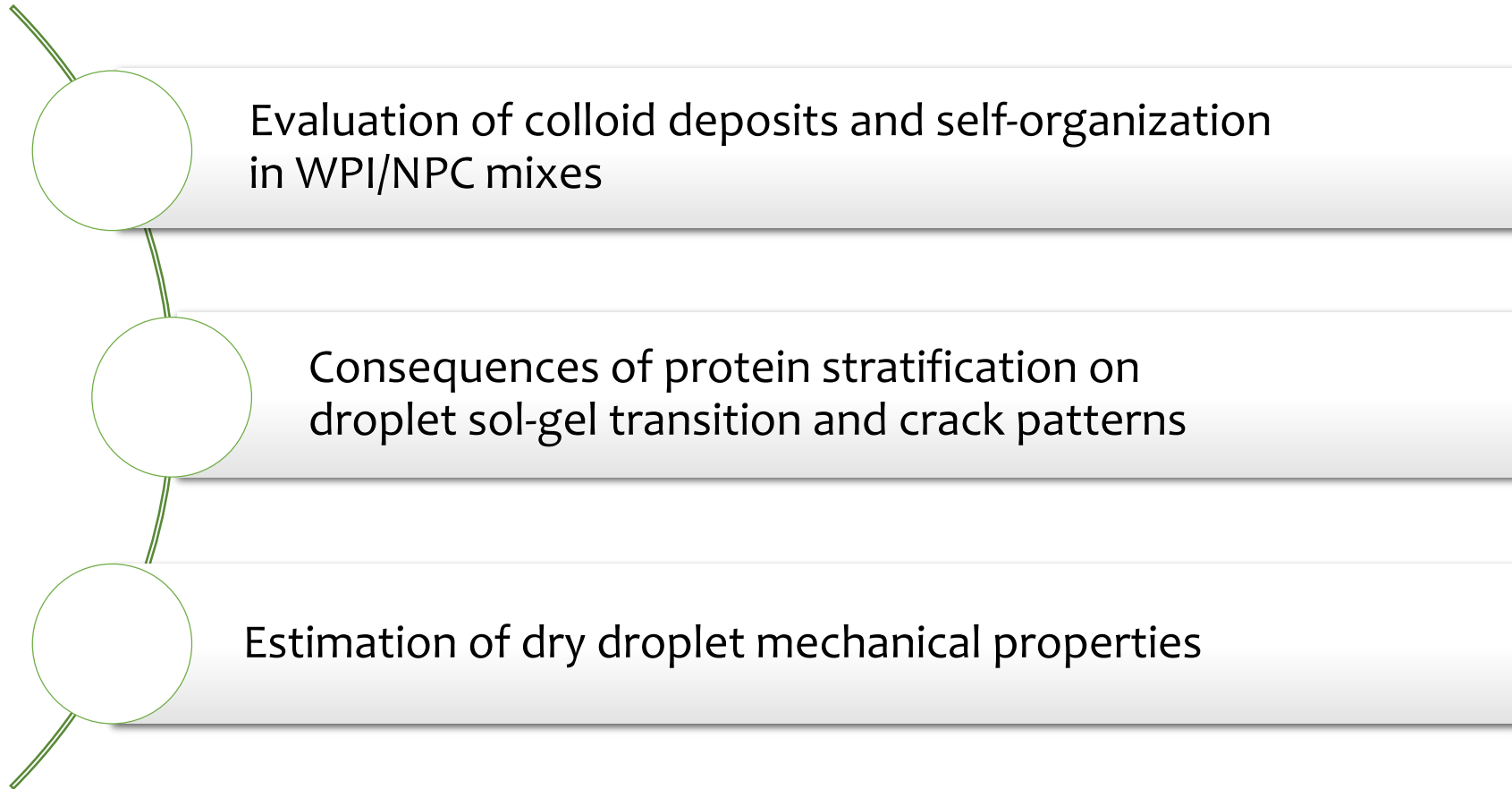
**WPI accumulation
on the external part of the skin
(small-on-top)**



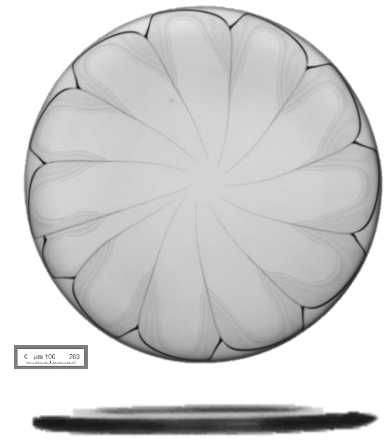
➤ Impact of protein auto-stratification on powder properties



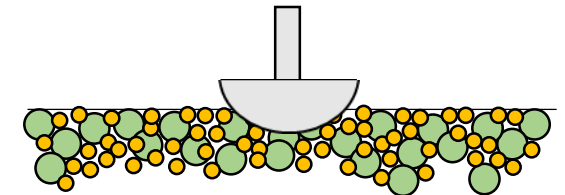
Experimental strategy



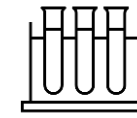
Optical microscopy - SEM



Micro-indentation tests



➤ Colloid deposit and droplet morphology

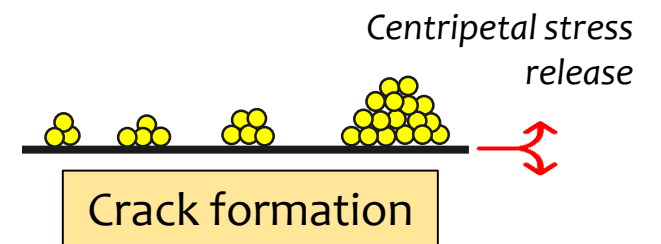
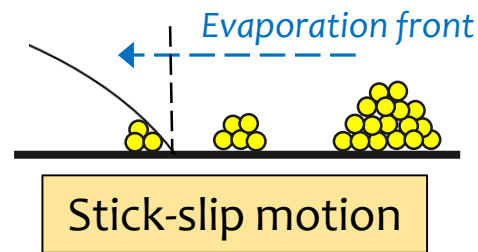
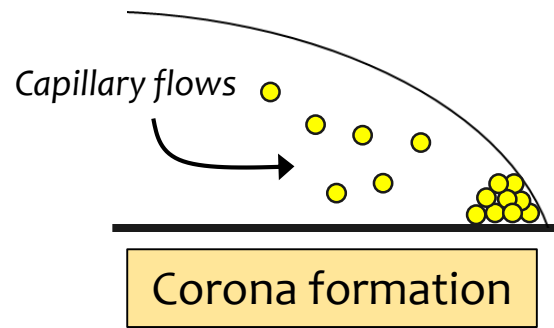
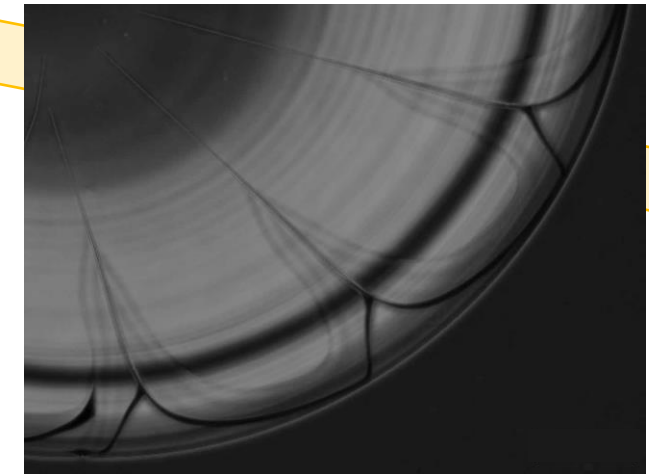
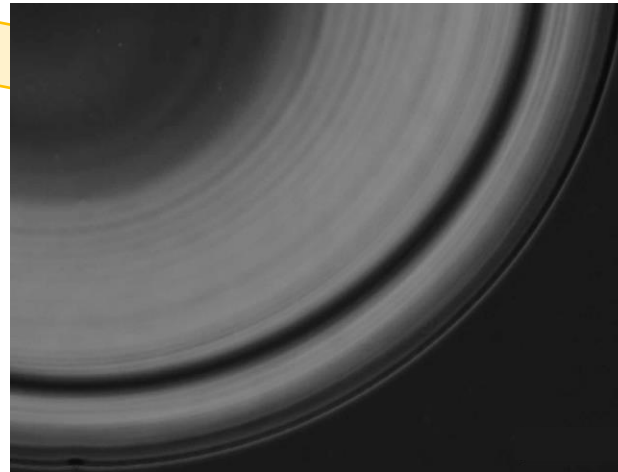
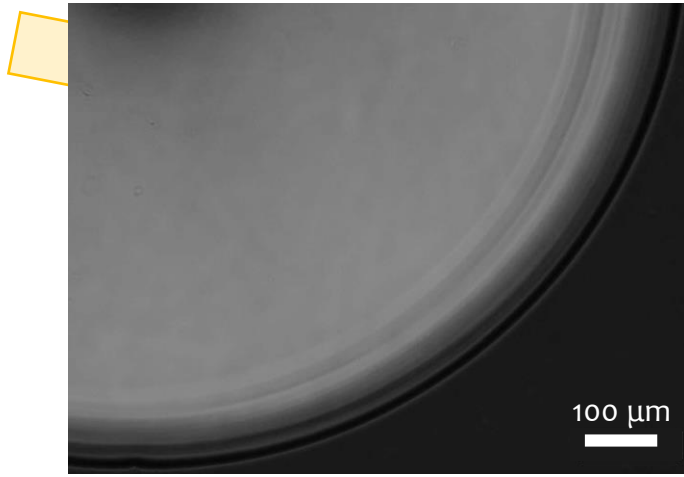


10%wt
protein concentration



Optical microscope
(phase contrast)

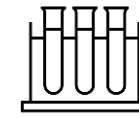
Whey proteins (WPI)



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➤ Colloid deposit and droplet morphology

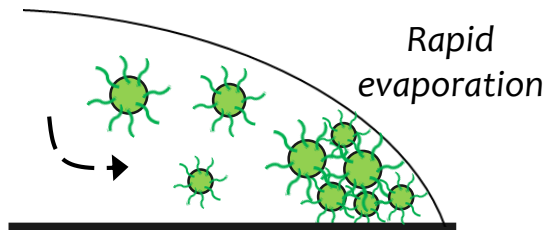
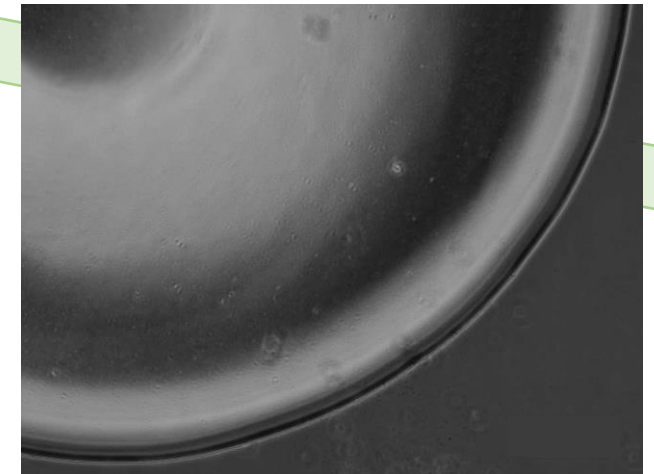
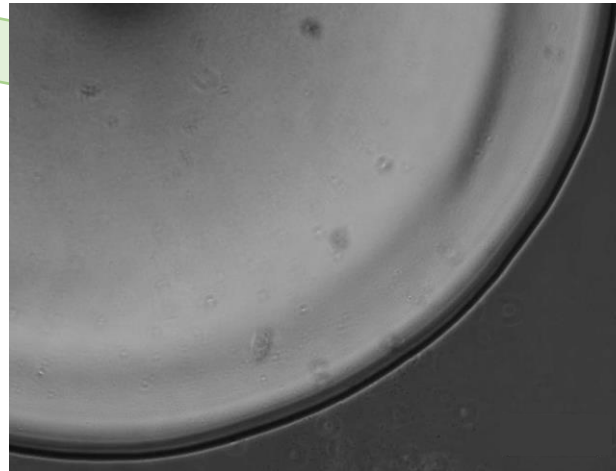
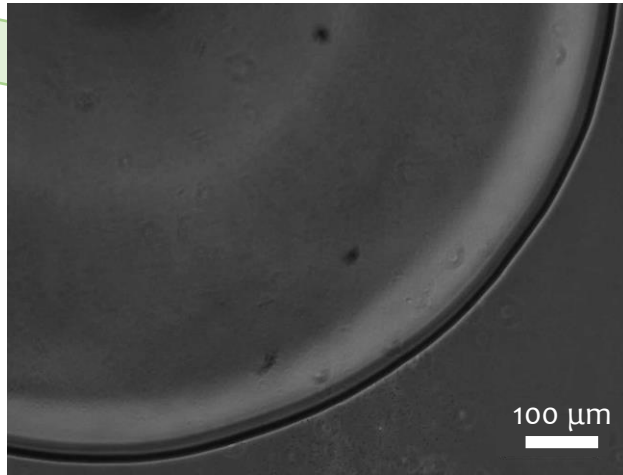


10%wt
protein concentration

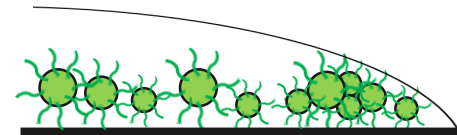


Optical microscope
(phase contrast)

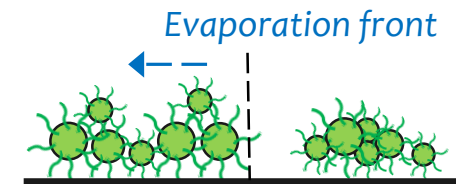
Casein micelles (NPC)



Corona formation



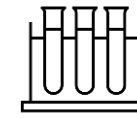
Homogeneous sedimentation



Inward migration

➤ Colloid deposit and droplet morphology

Signature of each protein in WPI/NPC mixes

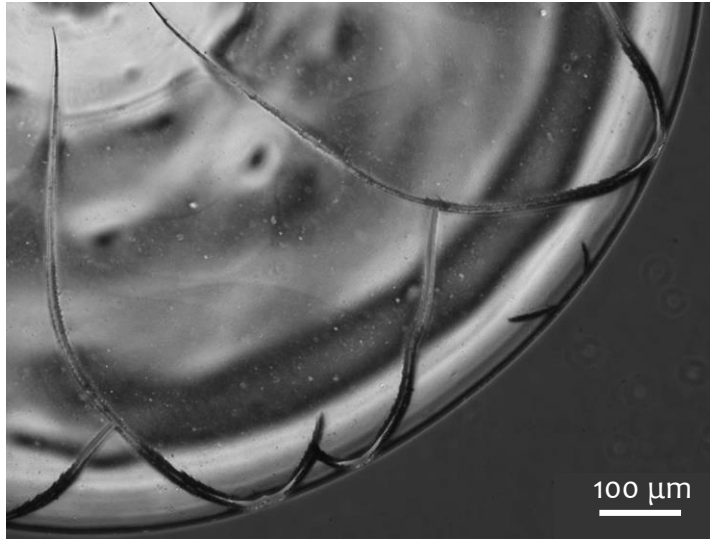


10%wt
protein concentration

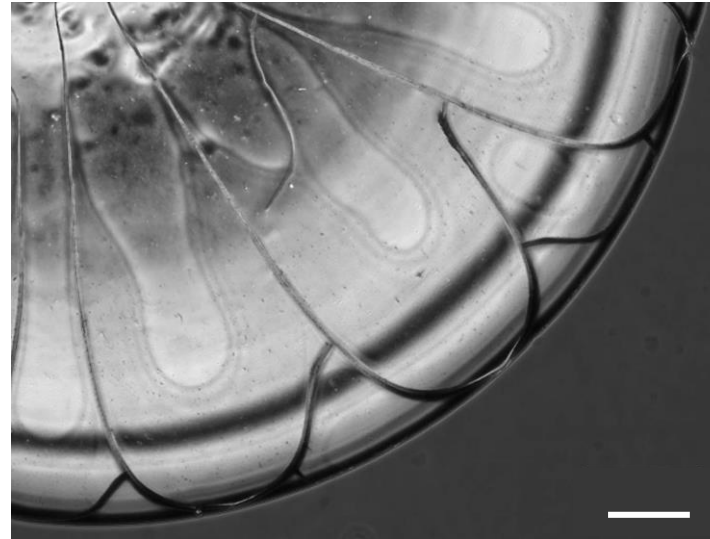
$$\text{WPI}\%_R = \frac{m_{\text{WPI}}}{m_{\text{solute}}}$$



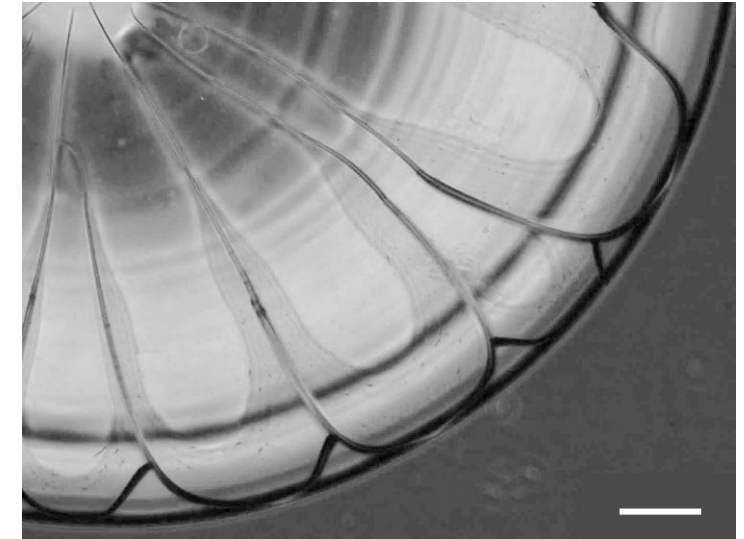
Optical microscope
(phase contrast)



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)

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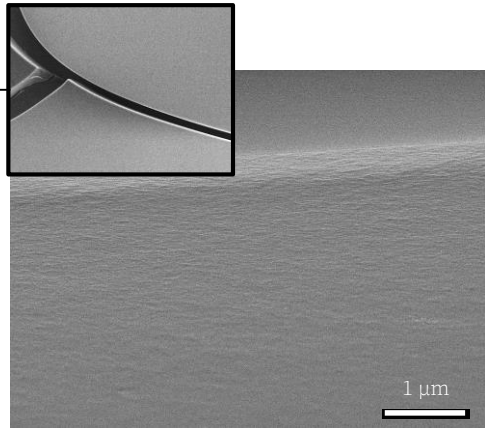
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➤ Observation of protein segregation in dry droplets

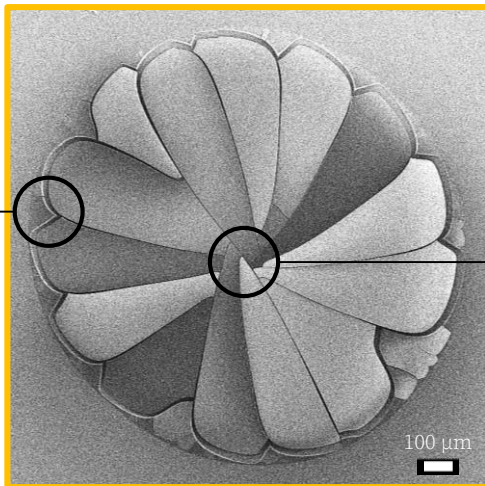
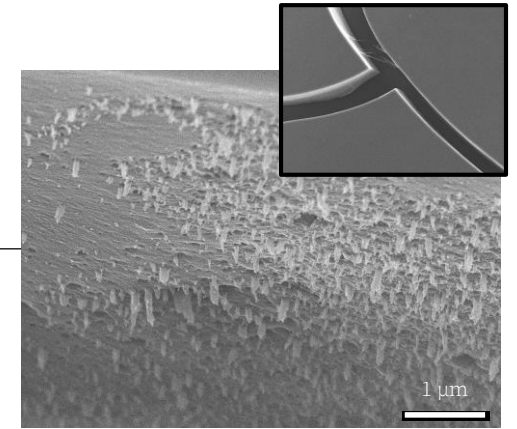


SEM Microscopy

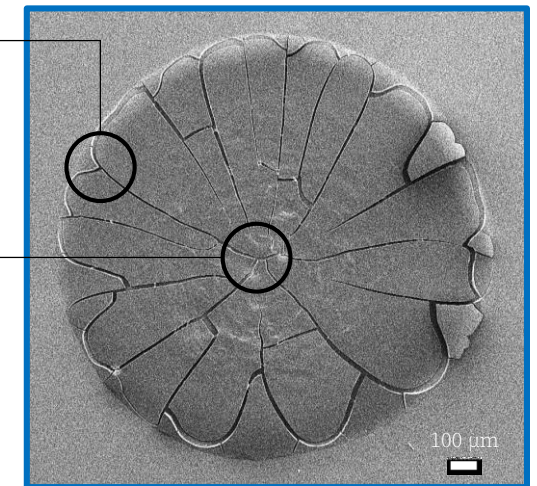
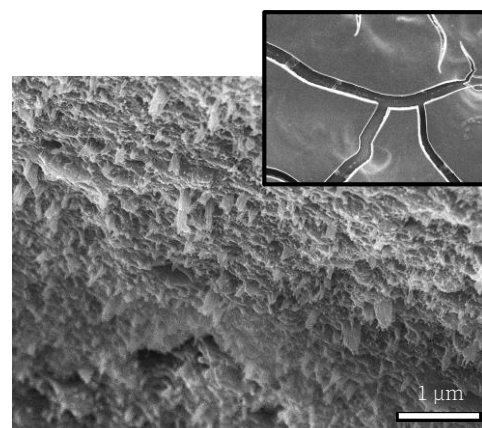
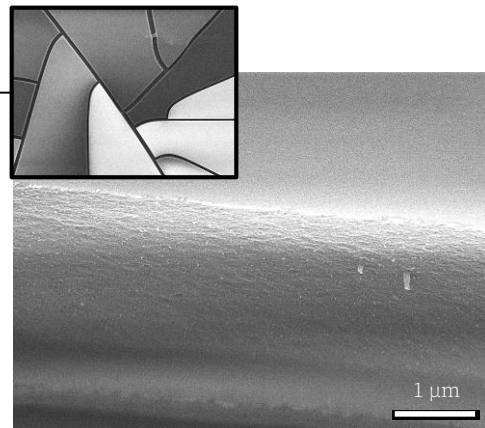


WPI%_R=100%
Smooth and packed colloid self-organization

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



WPI%_R=100%

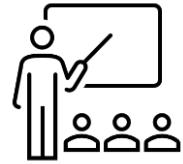


WPI%_R=80%

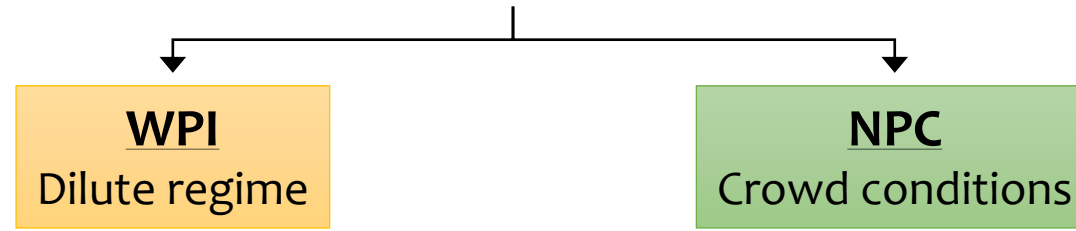


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➤ Conclusions I



❑ PROTEIN VOLUMINOSITY PLAYS A ROLE ON THE INTERNAL FLOWS

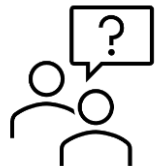


❑ SEGREGATION NOT ONLY IN THE SKIN BUT ALSO IN THE CORONA/SUBSTRATE

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

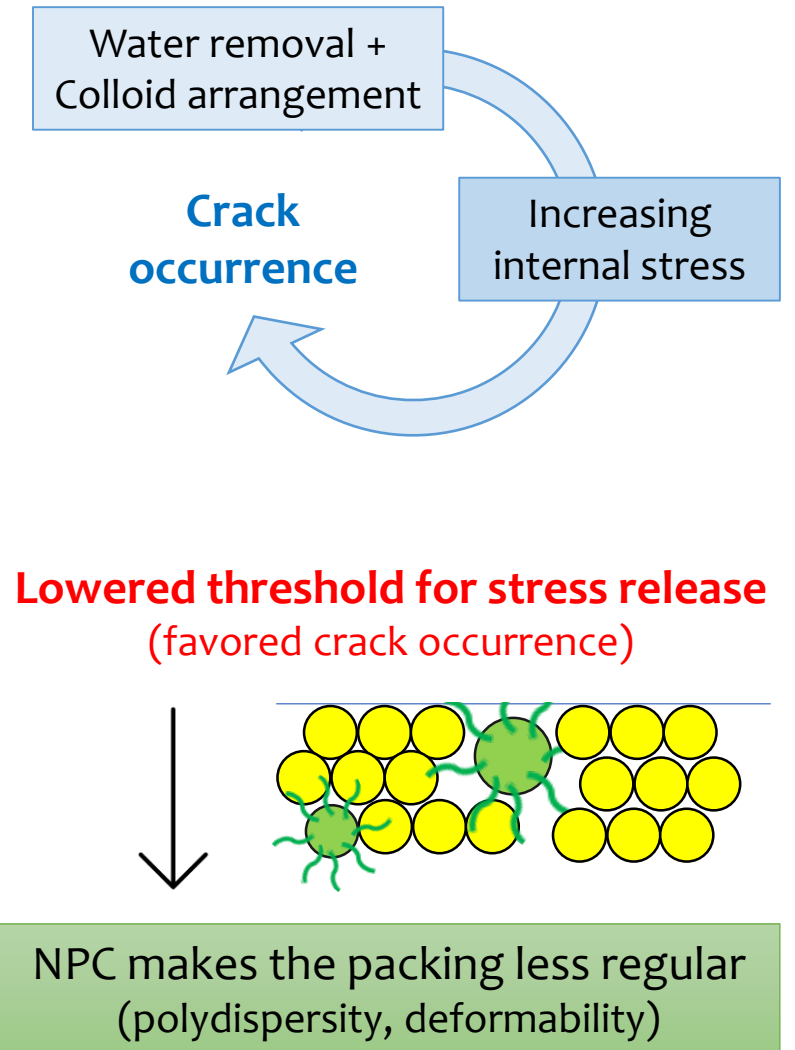
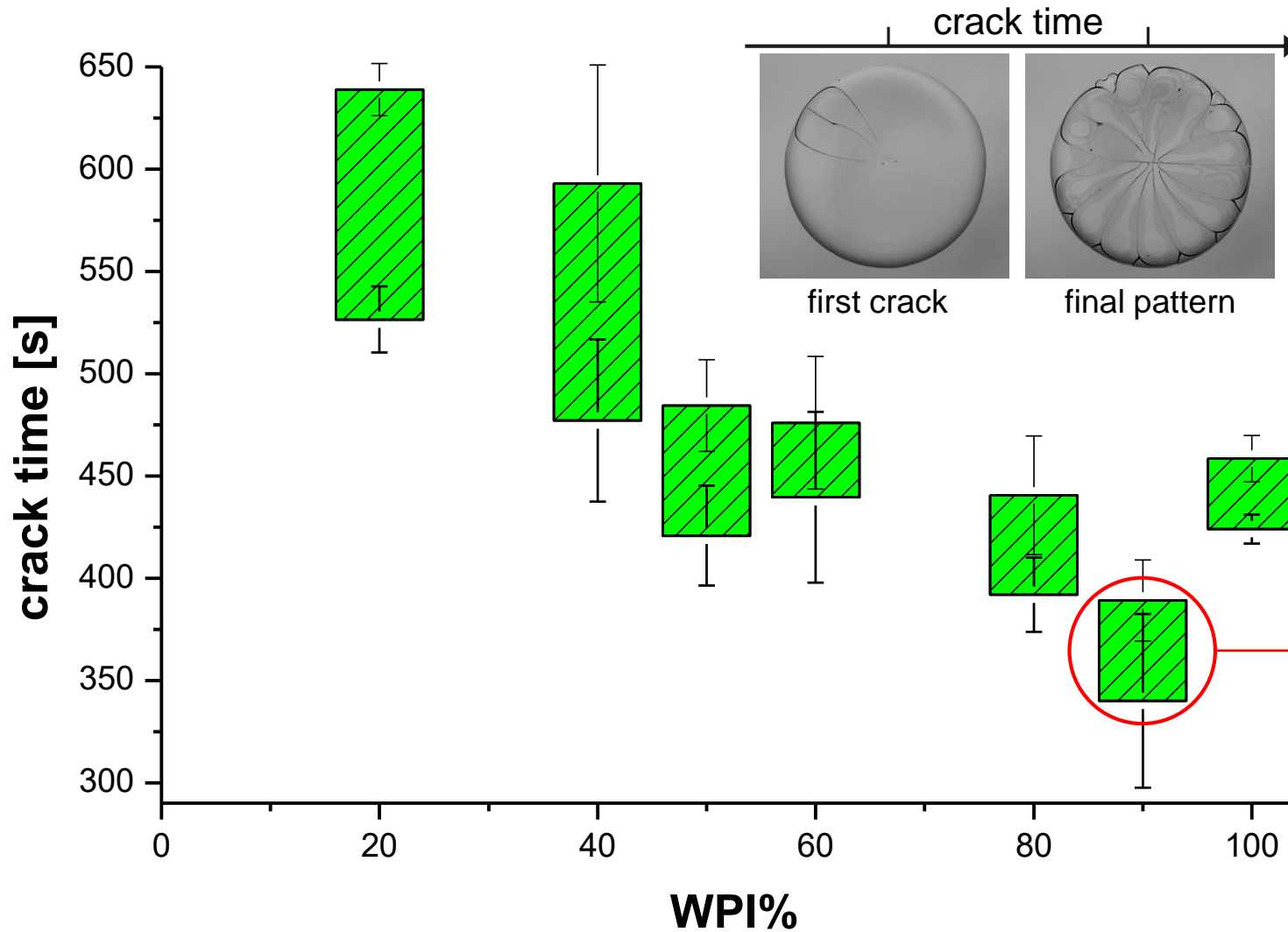
SKIN FORMATION → PÉCLET NUMBER (EVAPORATION VS DIFFUSION)

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

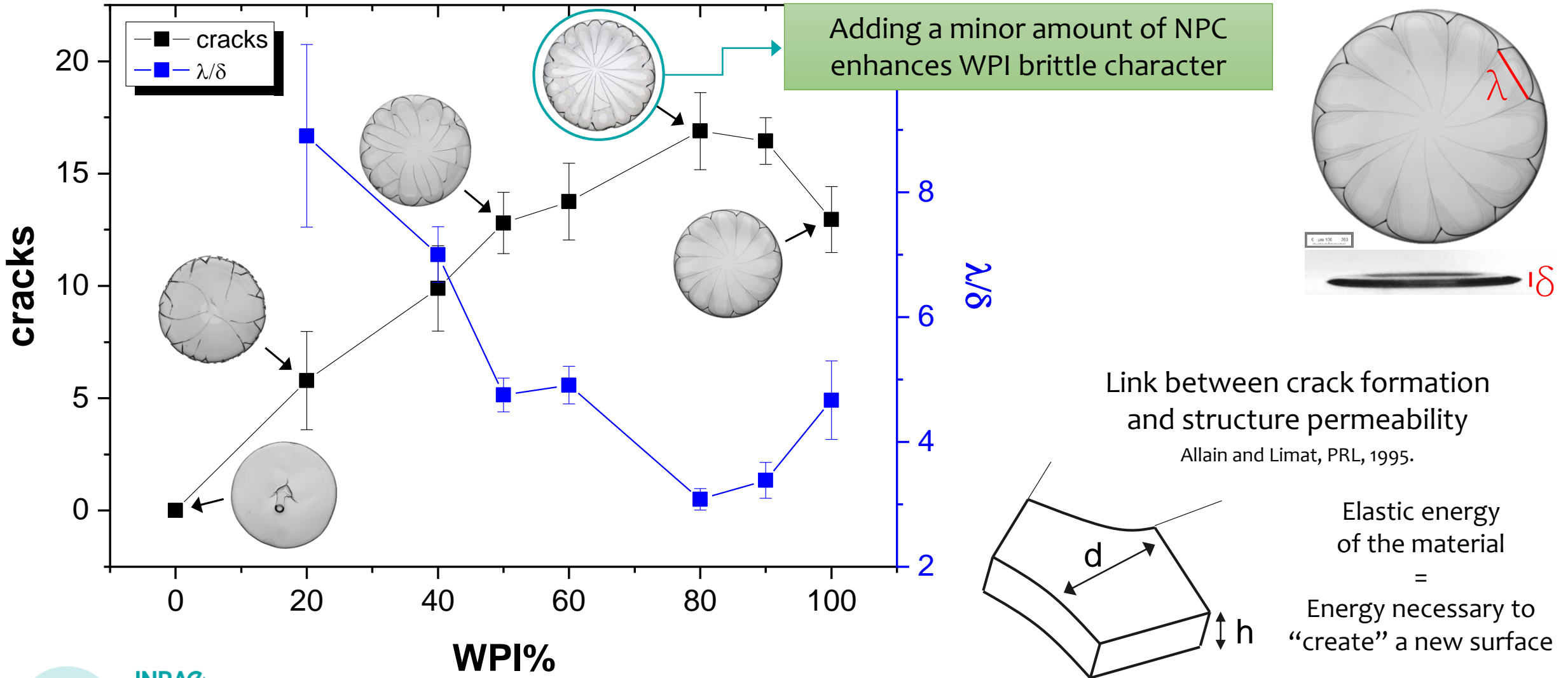


**How does WPI external segregation affect droplet mechanical behavior?
CRACK PATTERN FORMATION**

➤ Sol-gel transition: crack occurrence

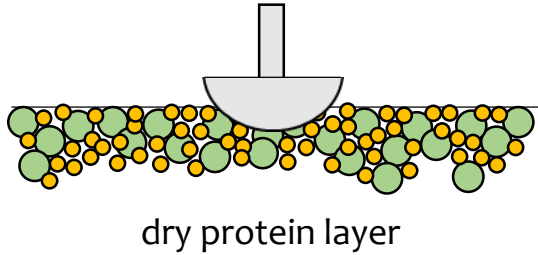


➤ Late evaporation stage: crack patterns

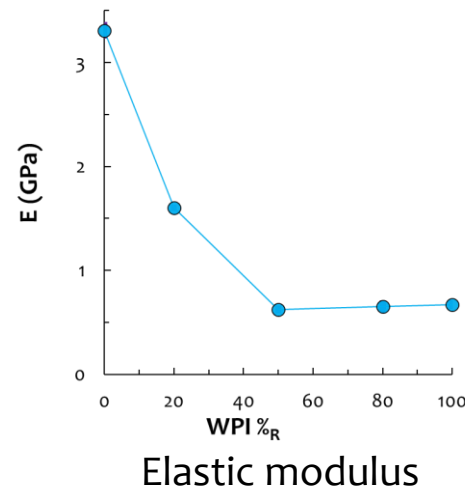
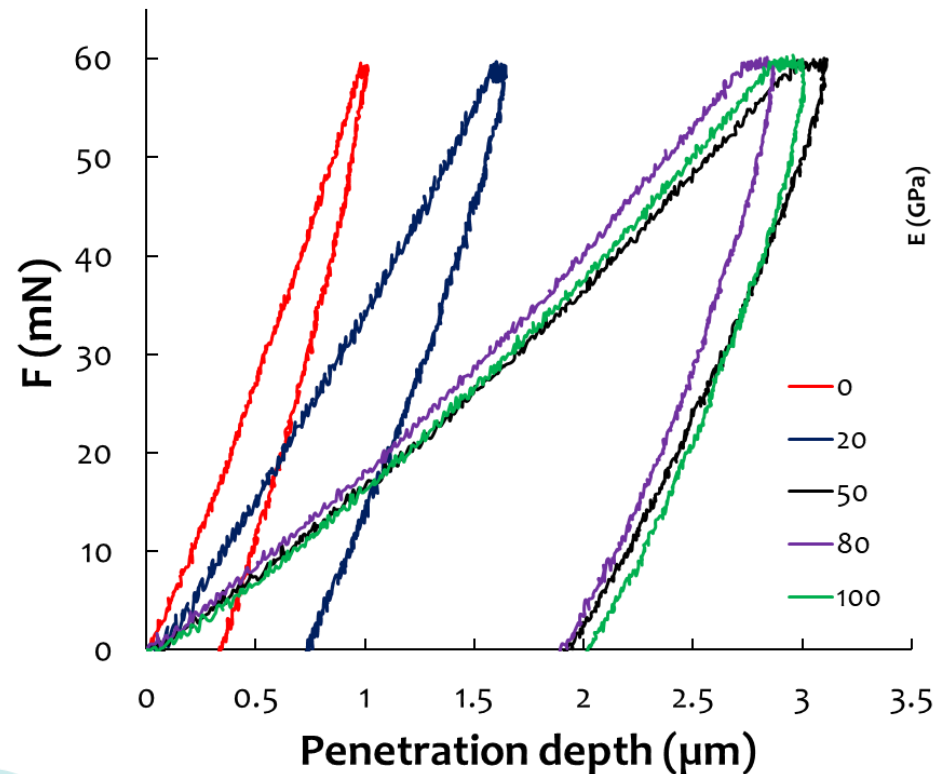


➤ Mechanical properties of dry WPI/NPC structure

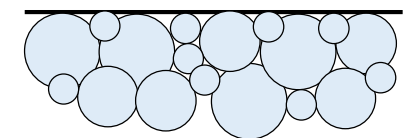
Micro-indentation tests on dry films



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

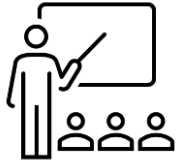


- Evidence of protein auto-stratification for $WPI\%_R \geq 50\%$
- WPI-rich samples are brittle and with low elasticity
- NPC-rich samples exhibit higher rigidity



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

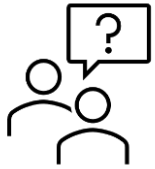
> Conclusions II



□ 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



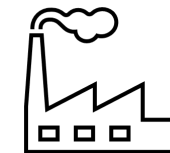
Are these results useful to tune dairy powder functional properties?

From the laboratory..

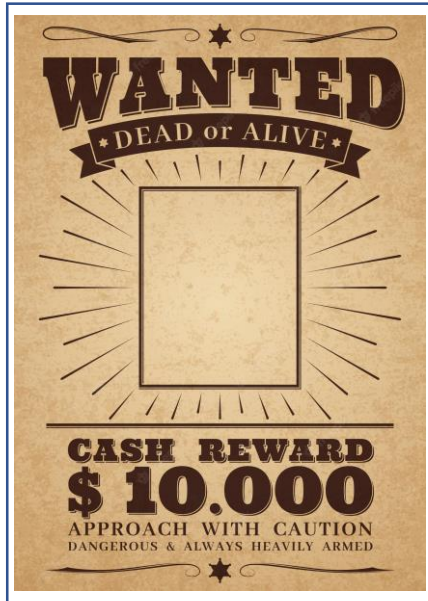


MONODISPERSE SPRAY DRYING

..to the industrial scale



➤ Thank you for your attention!



Ming Yu

Romain Jeantet Cécile Le Floch-Fouéré

Ludovic Pauchard



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