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

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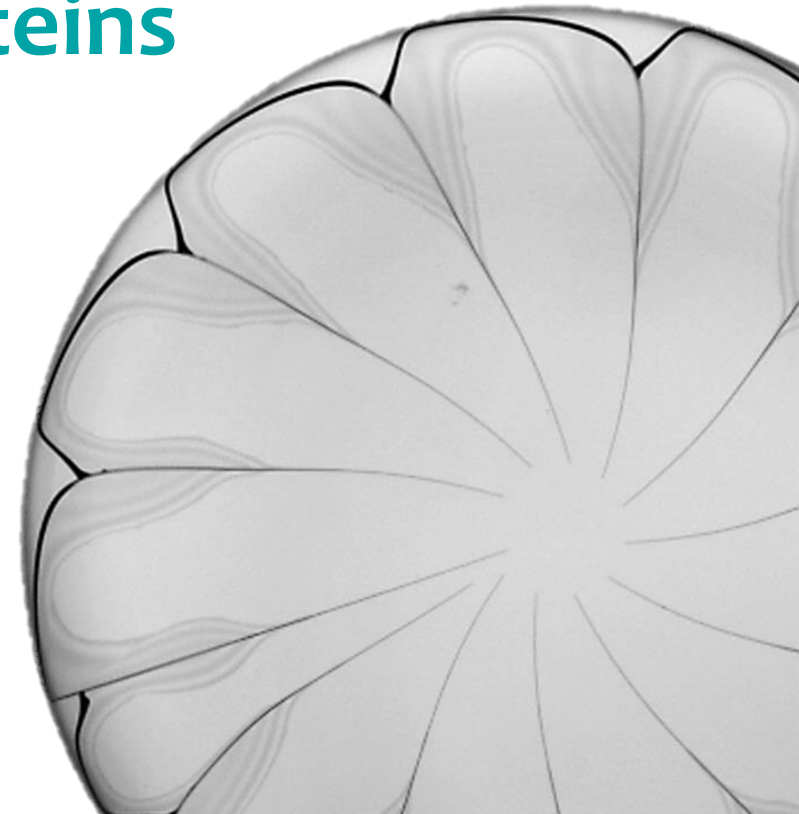
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# ➤ Crack patterns induced by auto-stratification in drying droplets of dairy proteins

C. Le Floch-Fouéré<sup>a</sup>, L. Pauchard<sup>b</sup>, L. Lanotte<sup>a</sup>

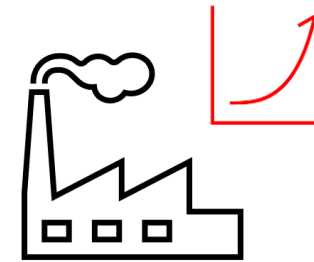
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<sup>b</sup> CNRS, Université Paris-Saclay, FAST, 91405 Orsay (France)



# ➤ 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)



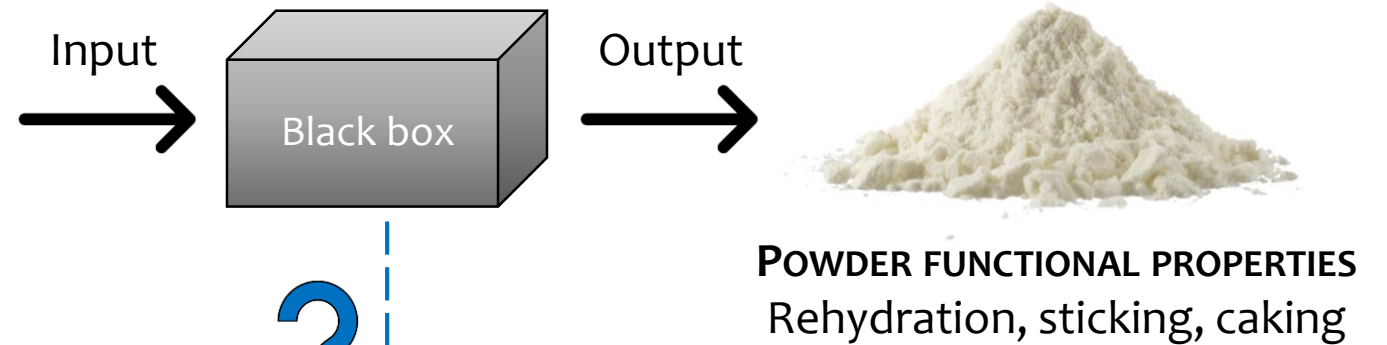
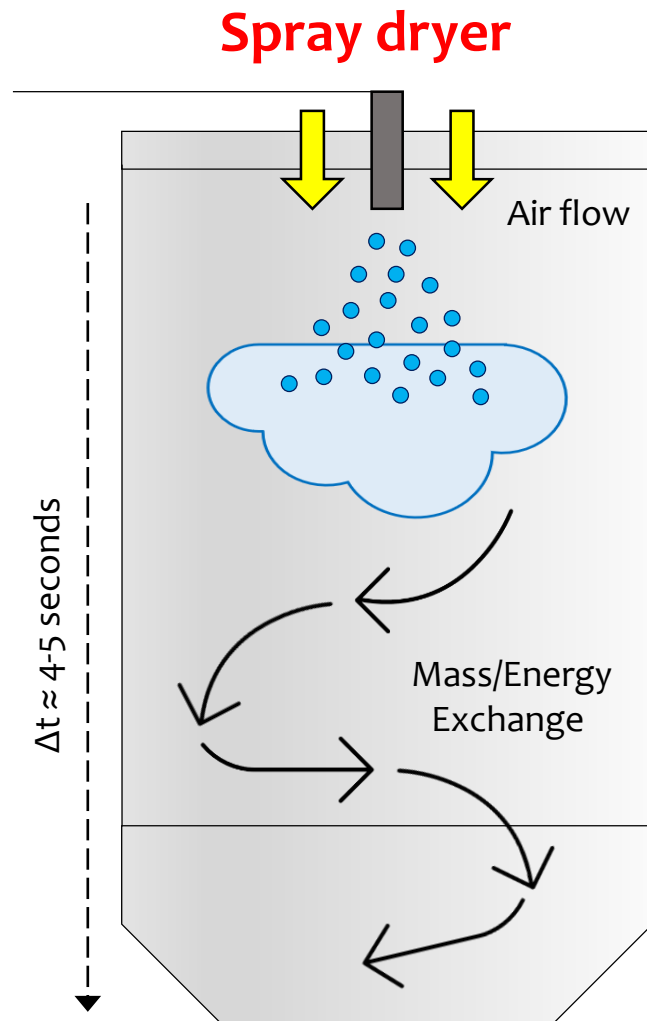
Growing-up  
milk

Follow-on milk  
(< 36 months)

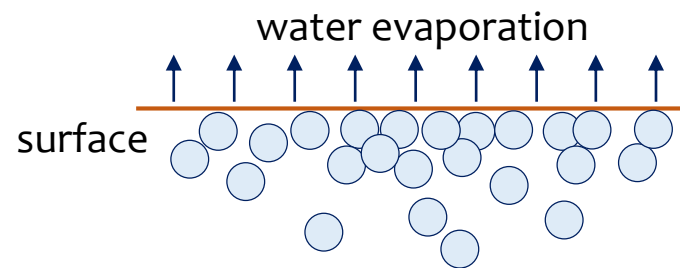
g/l	Cow milk	Human milk
<b>Proteins</b>	<b>32</b>	<b>10</b>
Caseins	80%	35%
WP	20%	65%
<b>Carbohydrates</b>	<b>50</b>	<b>75</b>
<b>Lipids</b>	<b>38</b>	<b>36</b>
PUFA	2,9%	6,4%

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

# ➤ Insights on the drying process in dairy industry

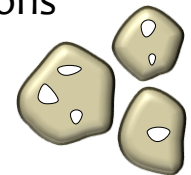


## MECHANISMS GOVERNING THE DROPLET-TO-PARTICLE TRANSITION



### SKIN FORMATION

- Stress-induced instabilities
- Strong deformations



# ➤ Drying of dairy protein mixes

## WHEY PROTEINS (WPI)

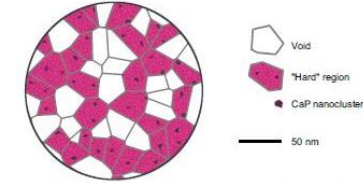
- Rigid, globular shape
- Small size (10-30 nm)



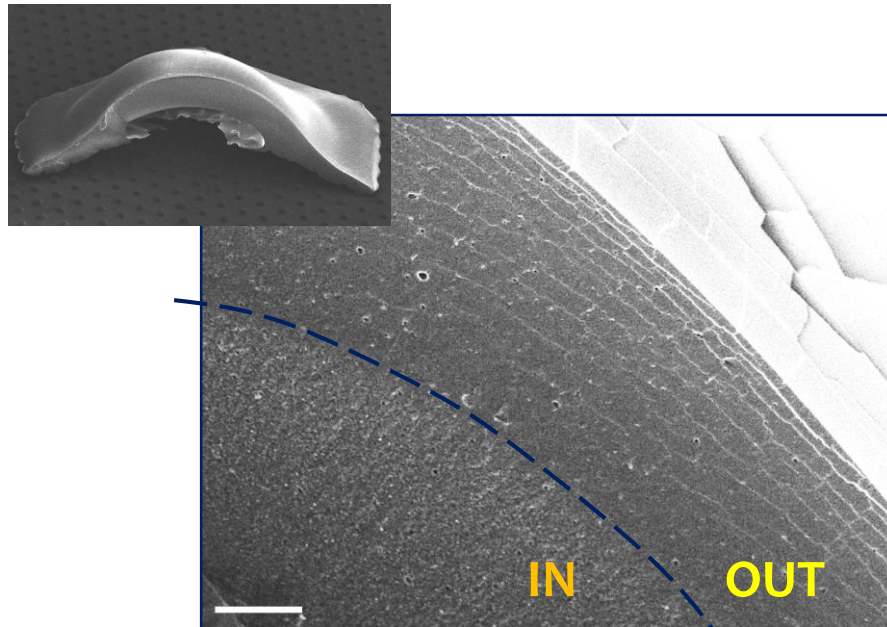
Yohko, 2012.

## CASEIN MICELLES (NPC)

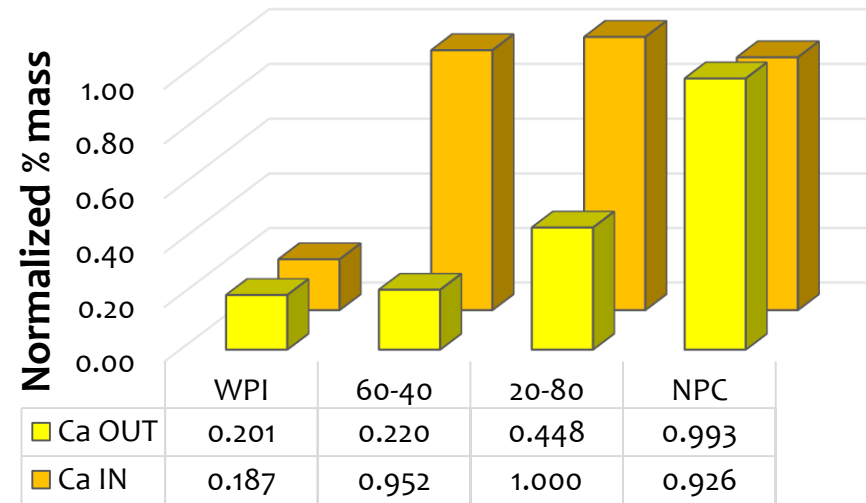
- Sponge-like, deformable structure
- Average diameter (100-300 nm)



Bouchoux, 2010.



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



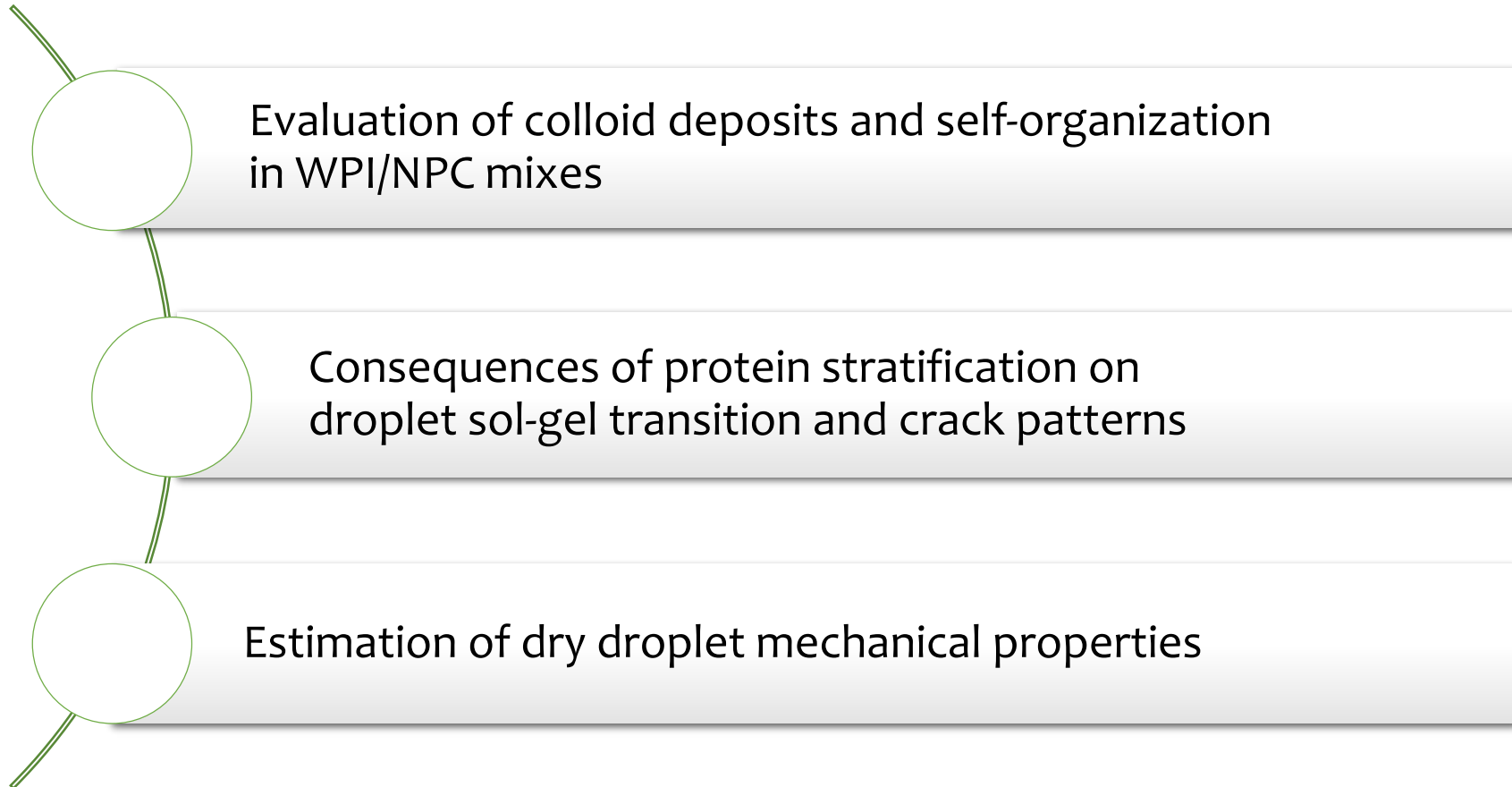
**WPI accumulation  
on the external part of the skin  
(small-on-top)**



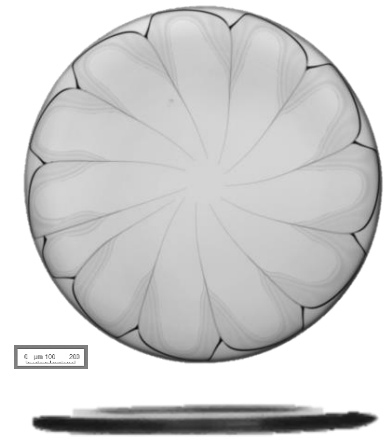
# ➤ Impact of protein auto-stratification on powder properties



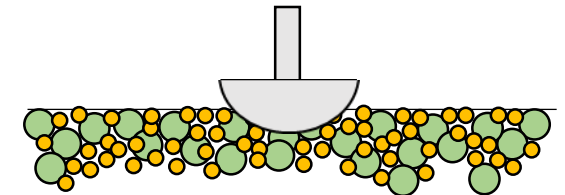
## Experimental strategy



Optical microscopy - SEM



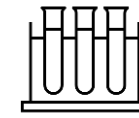
Micro-indentation tests



dry protein layer



# ➤ Colloid deposit and droplet morphology

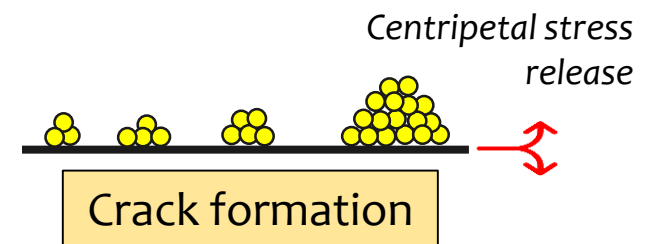
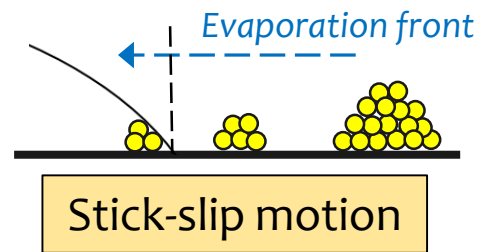
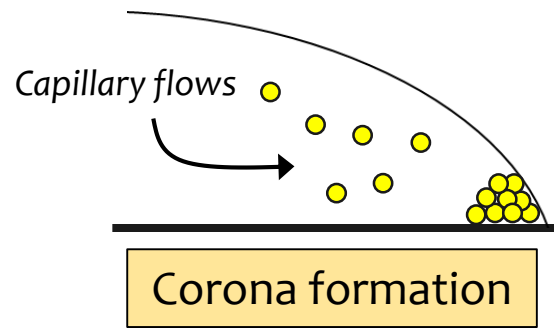
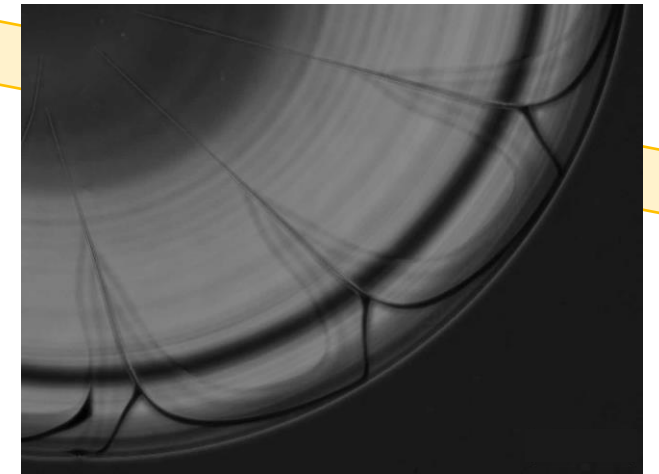
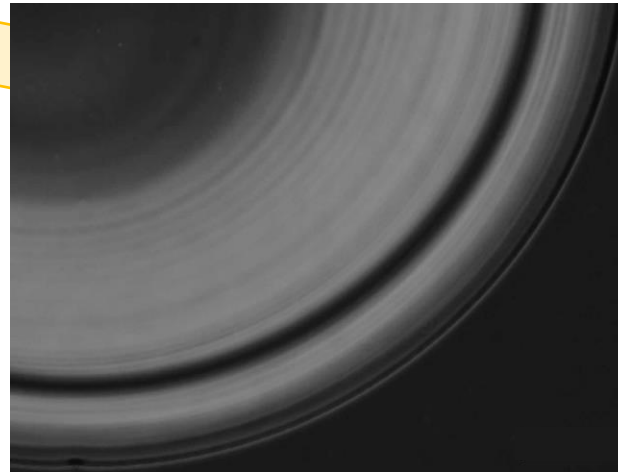
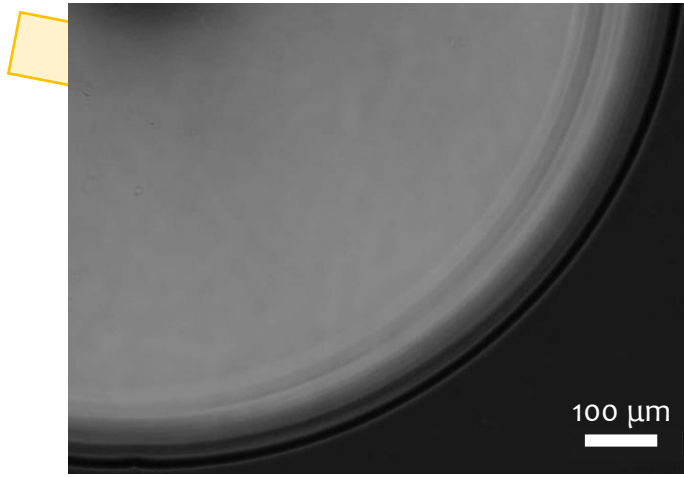


10%wt  
protein concentration



Optical microscope  
(phase contrast)

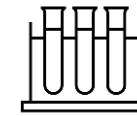
Whey proteins (WPI)



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# ➤ Colloid deposit and droplet morphology

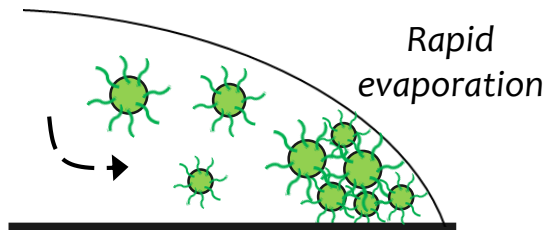
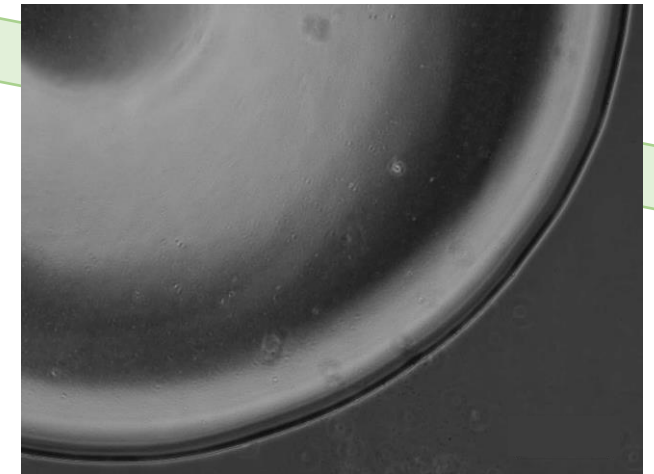
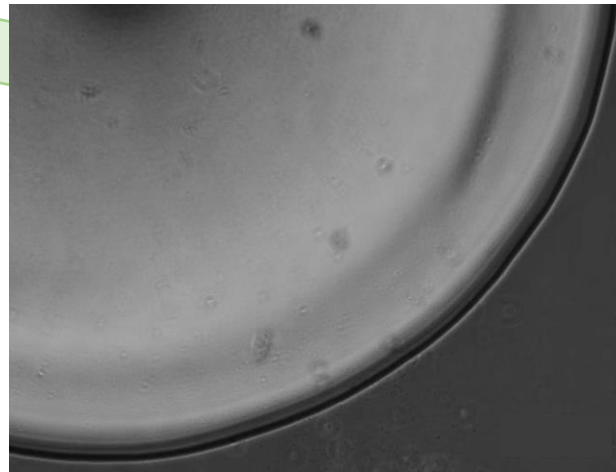
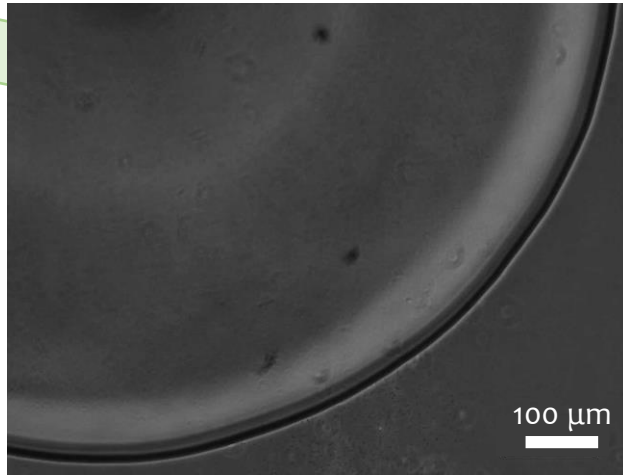


10%wt  
protein concentration

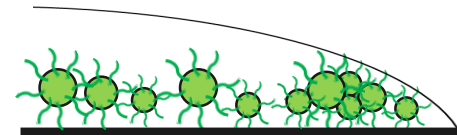


Optical microscope  
(phase contrast)

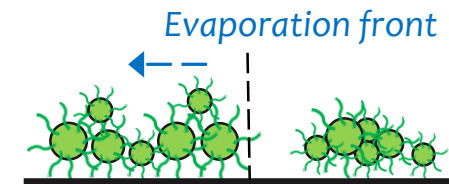
Casein micelles (NPC)



Corona formation



Homogeneous sedimentation

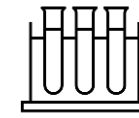


Inward migration



# ➤ Colloid deposit and droplet morphology

Signature of each protein in WPI/NPC mixes

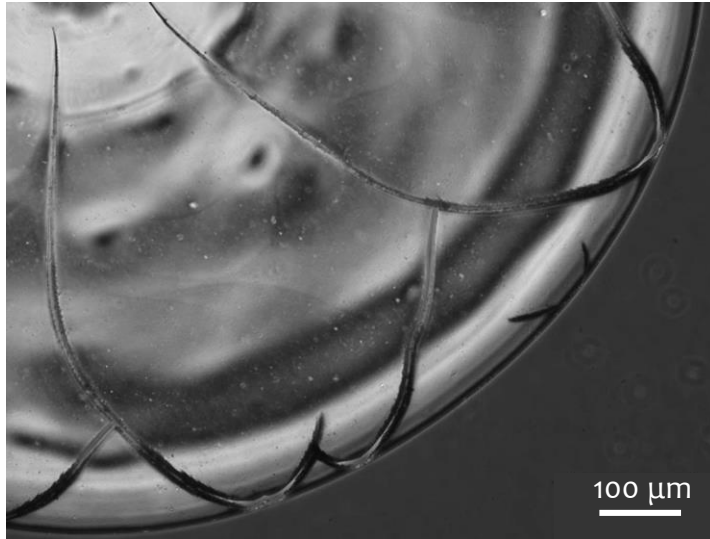


10%wt  
protein concentration

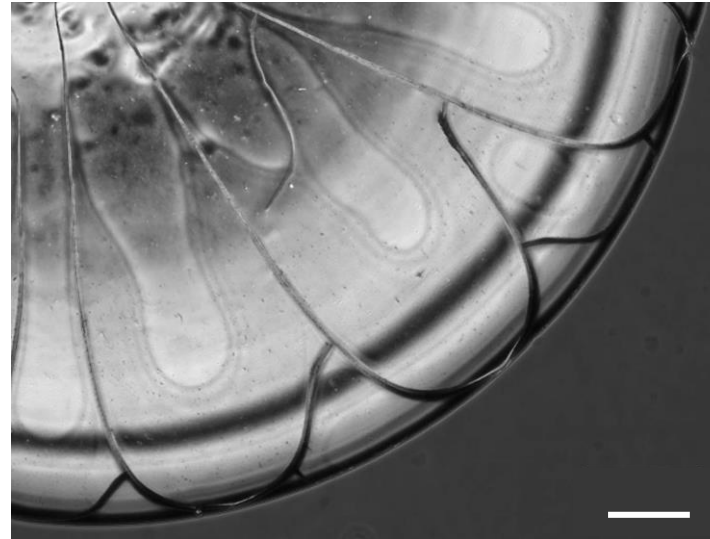
$$\text{WPI}\%_R = \frac{m_{\text{WPI}}}{m_{\text{solute}}}$$



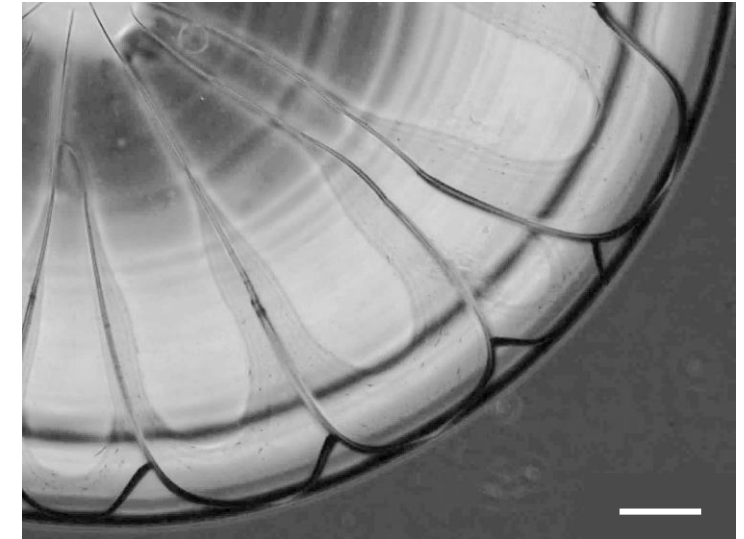
Optical microscope  
(phase contrast)



20



50



80

WPI%<sub>R</sub>

- Gradual transition from NPC to WPI-like morphology with increasing WPI%<sub>R</sub>
- **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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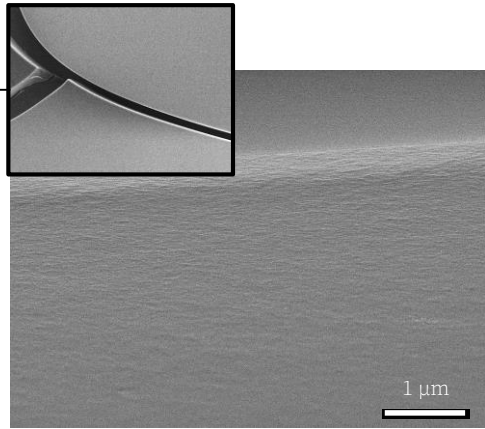
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# ➤ Observation of protein segregation in dry droplets

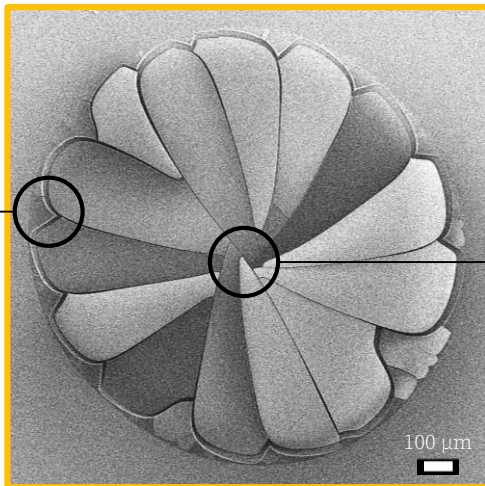
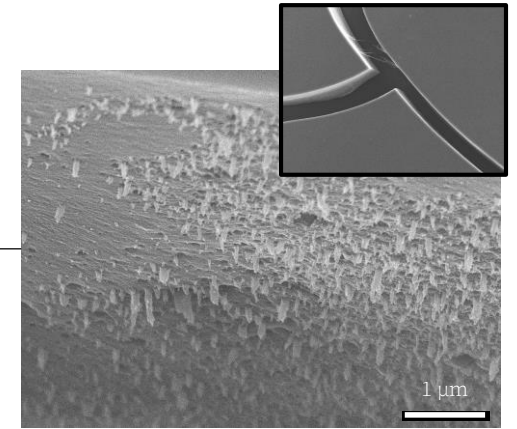


SEM Microscopy

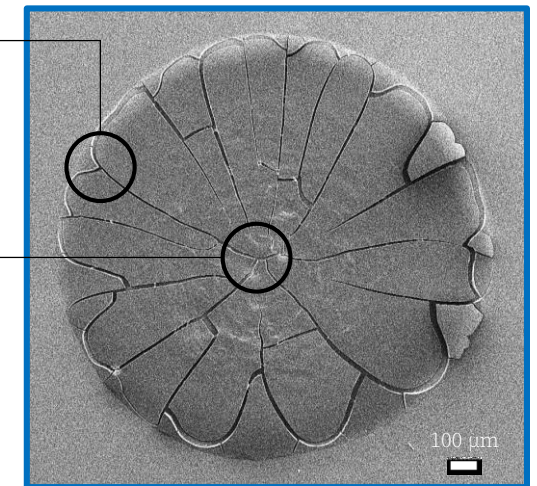
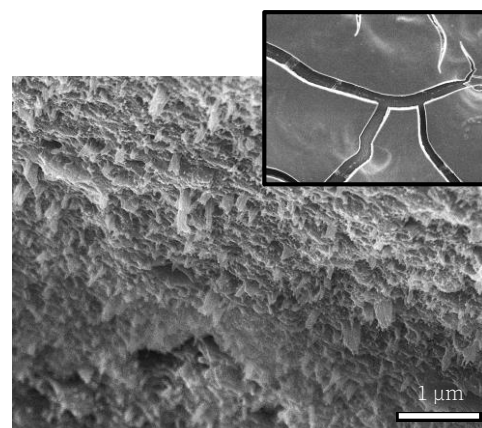
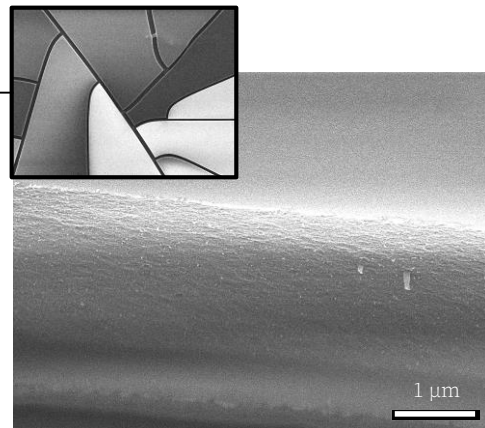


WPI%<sub>R</sub>=100%  
Smooth and packed colloid self-organization

WPI%<sub>R</sub>=80%  
Net of debris, transition from compact (borders) to highly porous structure (center)  
*Presence of micelles at the borders?*



WPI%<sub>R</sub>=100%

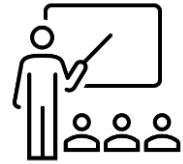


WPI%<sub>R</sub>=80%

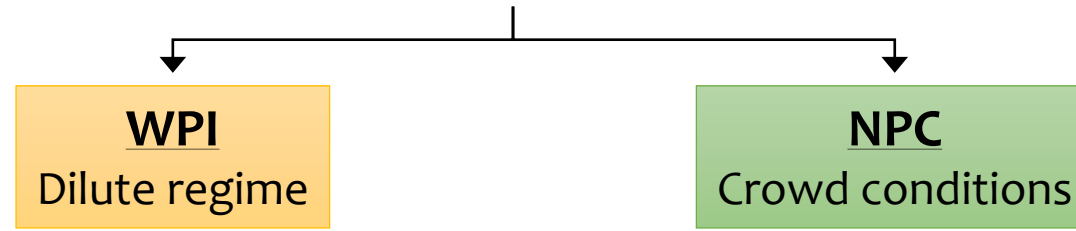


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# ➤ Conclusions I



## ❑ PROTEIN VOLUMINOSITY PLAYS A ROLE ON THE INTERNAL FLOWS

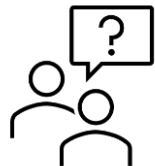


## ❑ SEGREGATION NOT ONLY IN THE SKIN BUT ALSO IN THE CORONA/SUBSTRATE

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

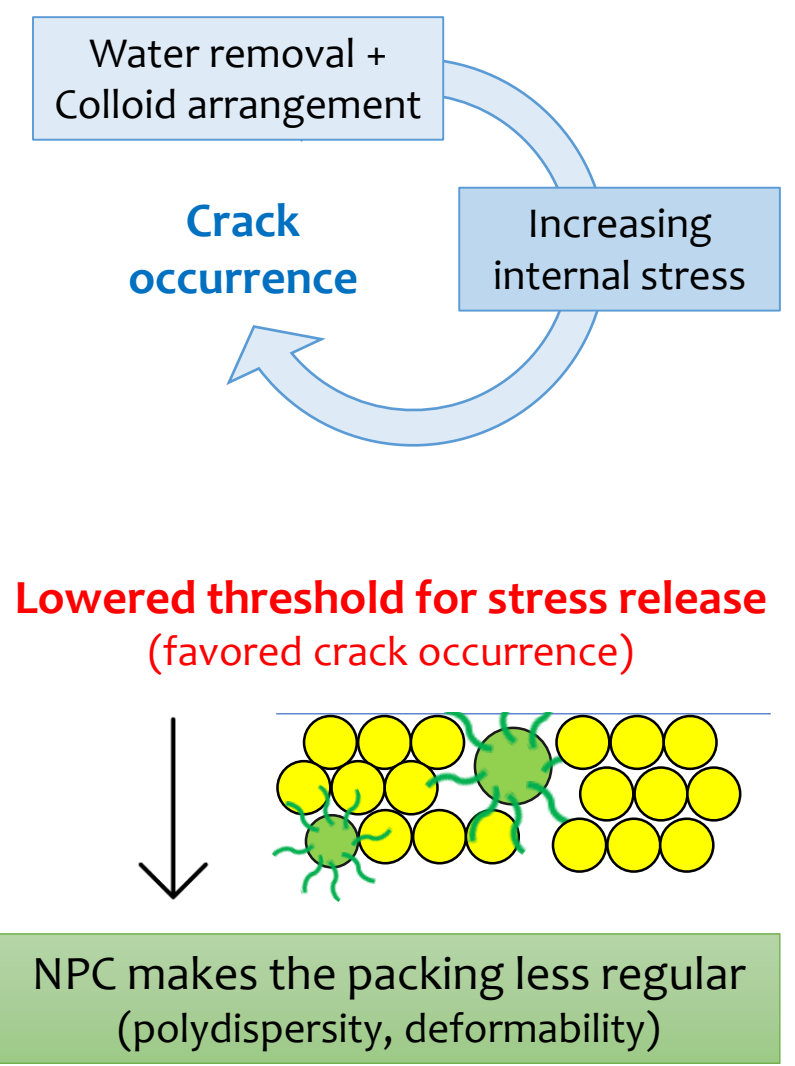
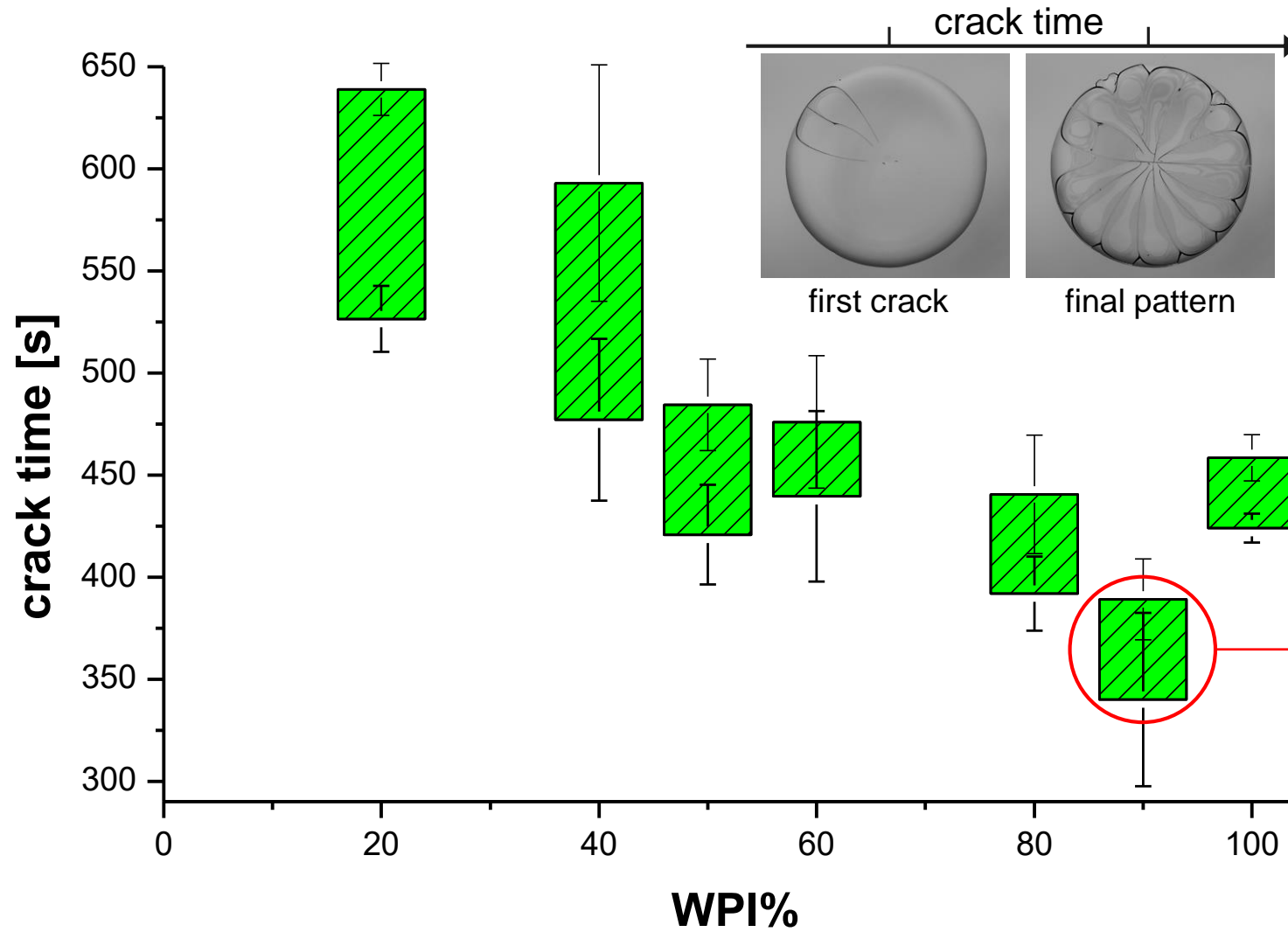
**SKIN FORMATION → PÉCLET NUMBER (EVAPORATION VS DIFFUSION)**

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

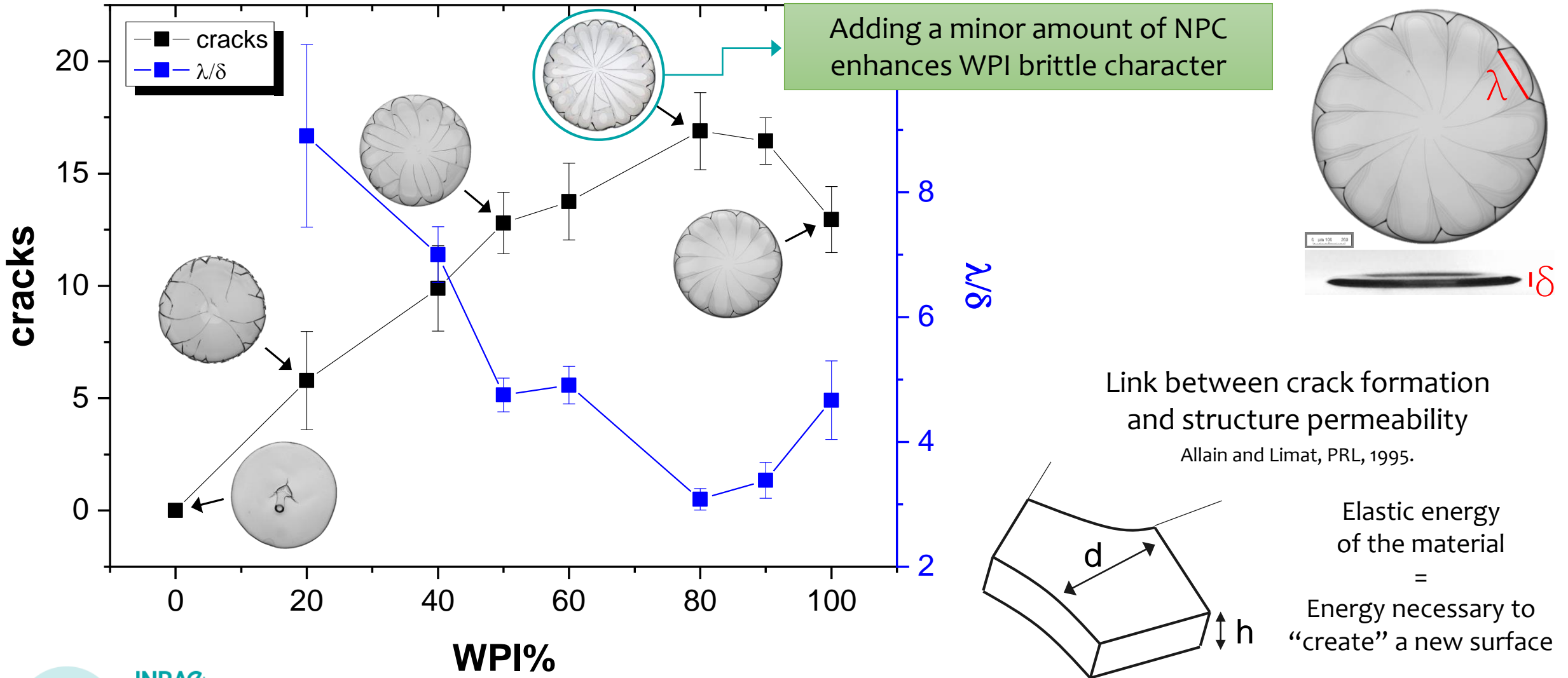


**How does WPI external segregation affect droplet mechanical behavior?  
CRACK PATTERN FORMATION**

# ➤ Sol-gel transition: crack occurrence

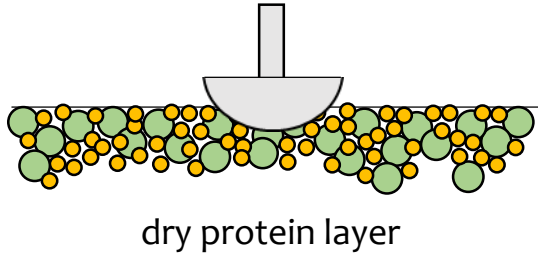


# ➤ Late evaporation stage: crack patterns

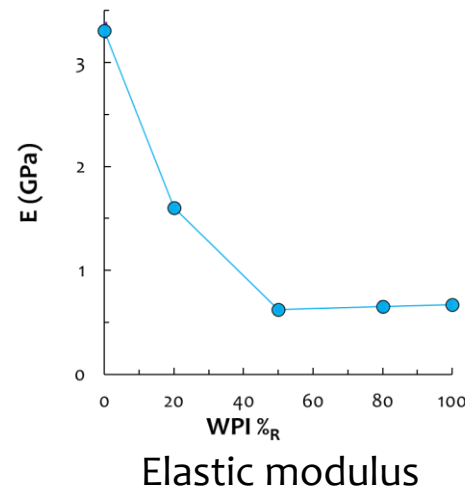
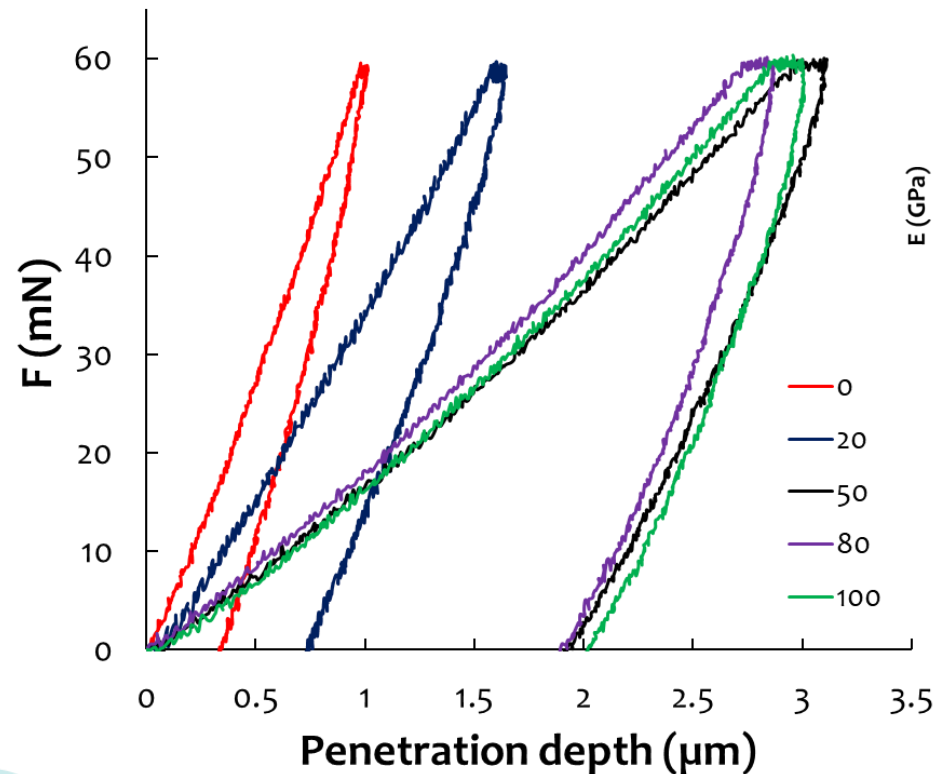


# ➤ Mechanical properties of dry WPI/NPC structure

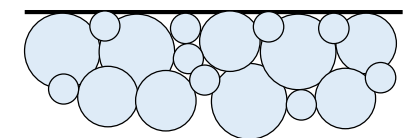
## Micro-indentation tests on dry films



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

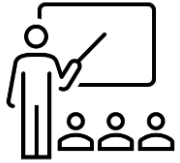


- Evidence of protein auto-stratification for  $WPI\%_R \geq 50\%$
- WPI-rich samples are brittle and with low elasticity
- NPC-rich samples exhibit higher rigidity



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

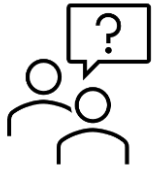
## > Conclusions II



### □ 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..*

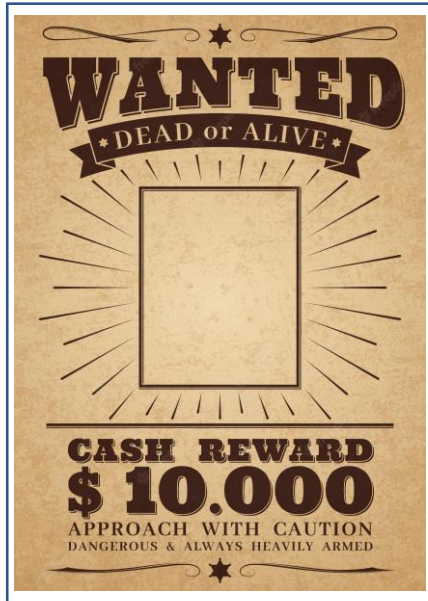


**MONODISPERSE SPRAY DRYING**

*..to the industrial scale*



➤ Thank you for your attention!



Ming Yu

Romain Jeantet Cécile Le Floch-Fouéré

Ludovic Pauchard



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