Skin Formation in Drying Droplets of Dairy Proteins

M. Yu, C. Le Floch-Fouéré, F. Boissel, L. Pauchard, A. Saint-Jalmes, R. Jeantet, L. Lanotte

[1] INRAE, UMR 1253 Science and Technology of Milk and Eggs, France

[2] Institut Agro, UMR 1253 Science and Technology of Milk and Eggs, France

[3] Université Paris-Saclay, CNRS, FAST, France

[4] Univ. Rennes, CNRS, IPR, France

RÉPUBLIQUE FRANÇAISE
Liberté
Égalité
Fraternité

INRAE

Infant Milk Formula (IMF): Mimicking breast milk

Dairy Industry Challenge

- 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

Adapted to Nutritional Targets

Infant milk (< 6 months)

Growing-up milk

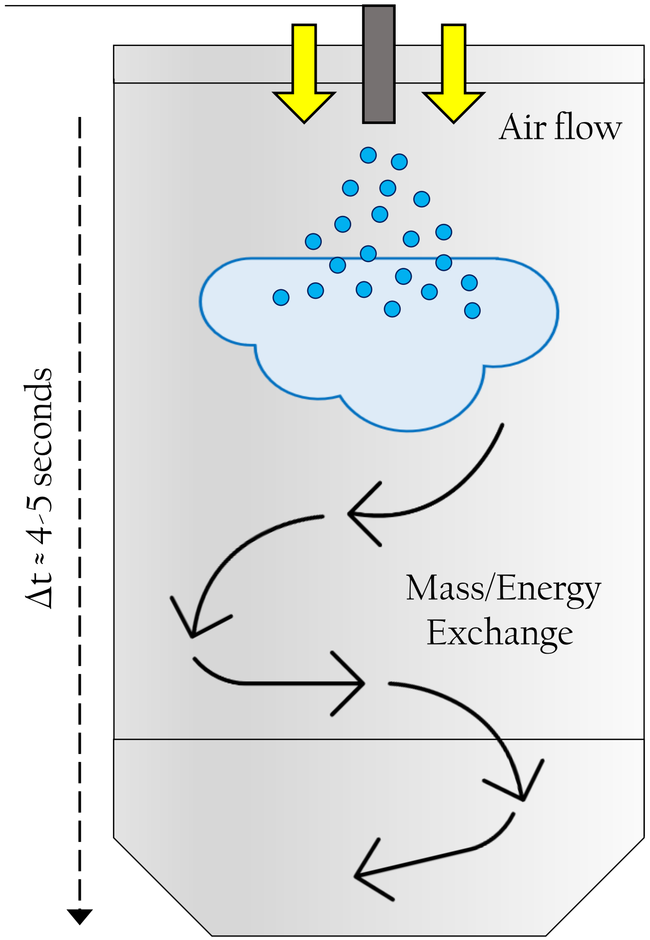
Follow-on milk (< 36 months)

Controlled functional end use properties

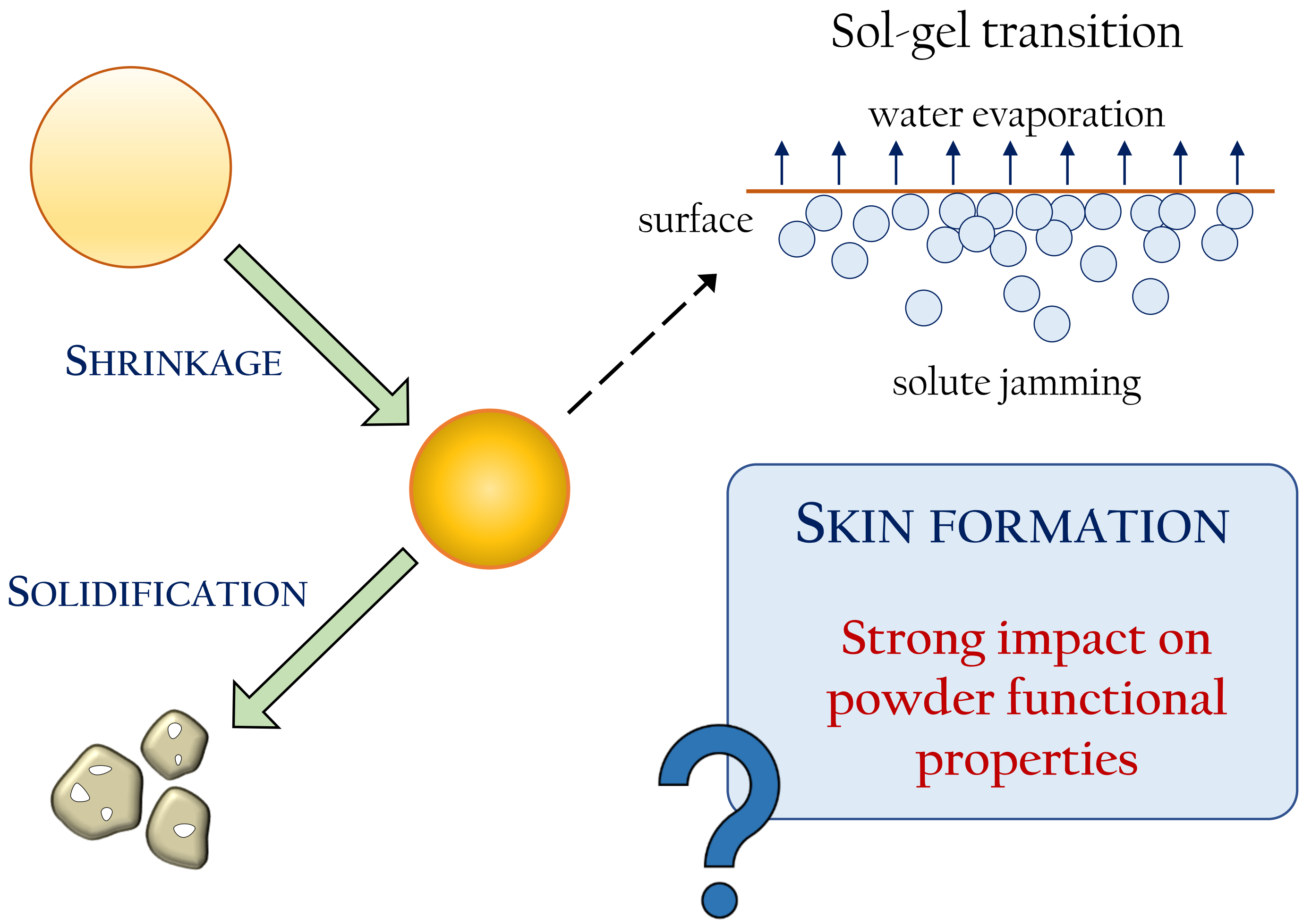
g/l	Cow milk	Human milk
Proteins	32	10
Caseins	80%	35%
WP	20%	65%
Carbohydrates	50	75
Lipids	38	36
PUFA	2,9%	6,4%

The drying process in dairy industry

Spray dryer

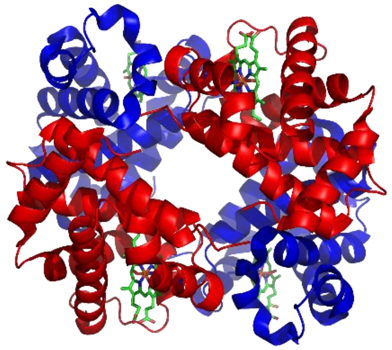


Droplet scale



Simplified model: mixes of dairy proteins

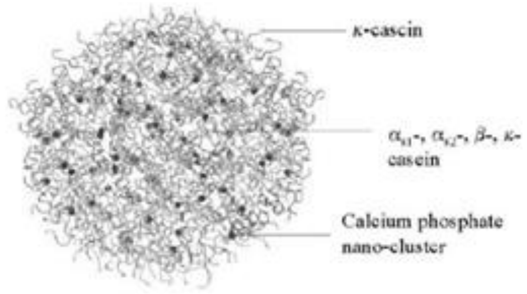
WHEY PROTEINS (WPI)



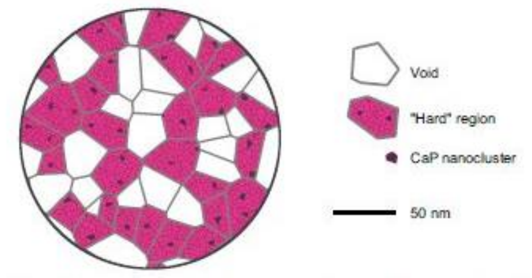
Yohko, 2012.

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

CASEIN MICELLES (NPC)



Holt and Horne, 1996.



Bouchoux, 2010.

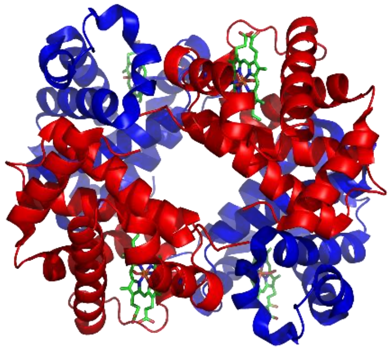
- **Sponge-like, deformable structure**
- Average diameter (100-300 nm)

WHICH PARAMETERS INFLUENCE SKIN DEVELOPMENT?

- ❑ Experimental conditions (T, RH)
- ❑ Protein overall concentration (c_p)
- ❑ SAMPLE COMPOSITION ($WPI\%_R$)

Simplified model: mixes of dairy proteins

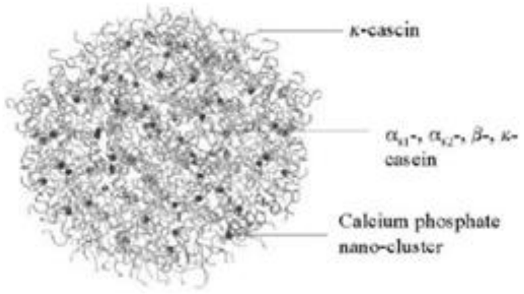
WHEY PROTEINS (WPI)



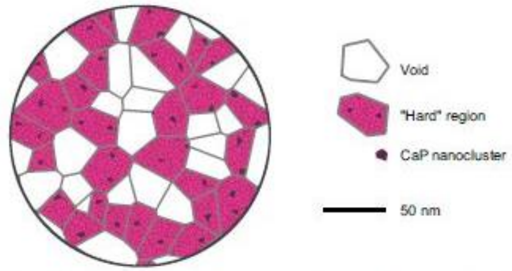
Yohko, 2012.

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

CASEIN MICELLES (NPC)



Holt and Horne, 1996.



Bouchoux, 2010.

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

Dispersion characteristics

1. Protein overall concentration =8%wt.
2. Relative concentration

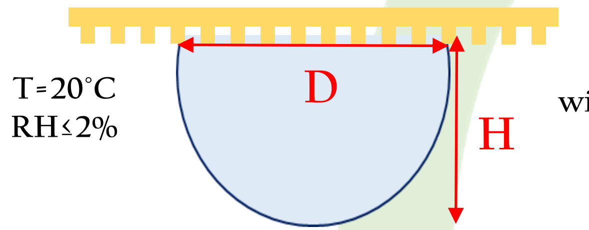
$$WPI\%_R = \frac{m_{WPI}}{m_{solute}}$$

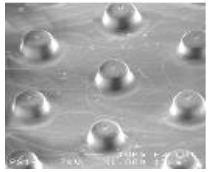
$WPI\%_R$	0%	20%	50%	80%	100%
φ_p	0.27	0.24	0.18	0.11	0.06
φ_{WPI}	-	0.01	0.03	0.05	0.06

WPI IS ALWAYS THE MINOR COMPONENT IN TERMS OF VOLUME FRACTION

Experimental strategy

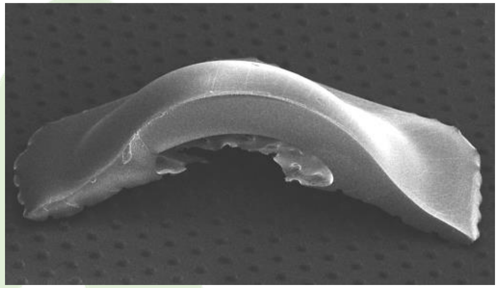
Single droplet approach
(Hydrophobic support)



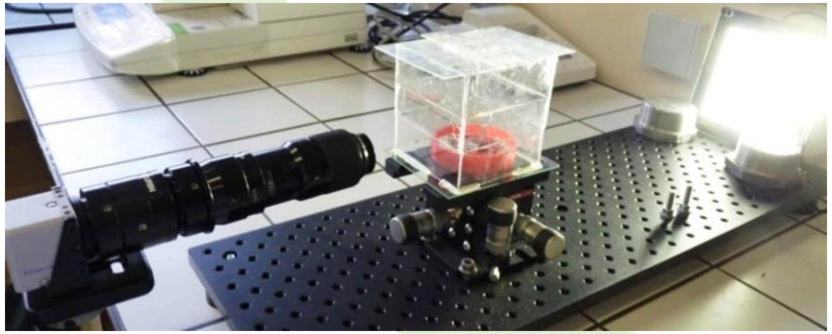


PDMS patterned
with cylindrical pillars

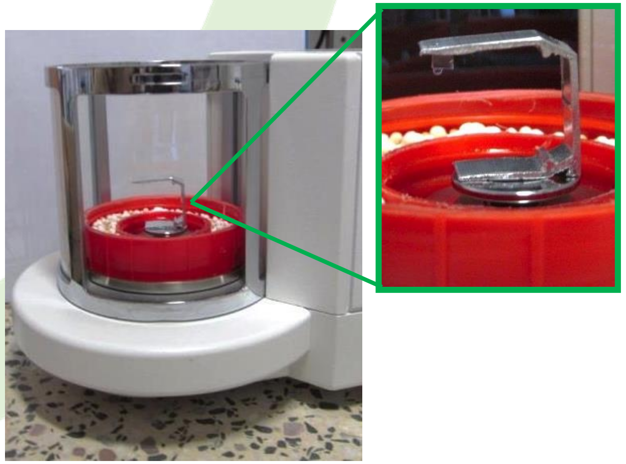
Skin structure
(Scanning Electron Microscopy)



Droplet profile evolution
(High-speed camera)



Drying kinetics
(Ultra precision micro-balance)

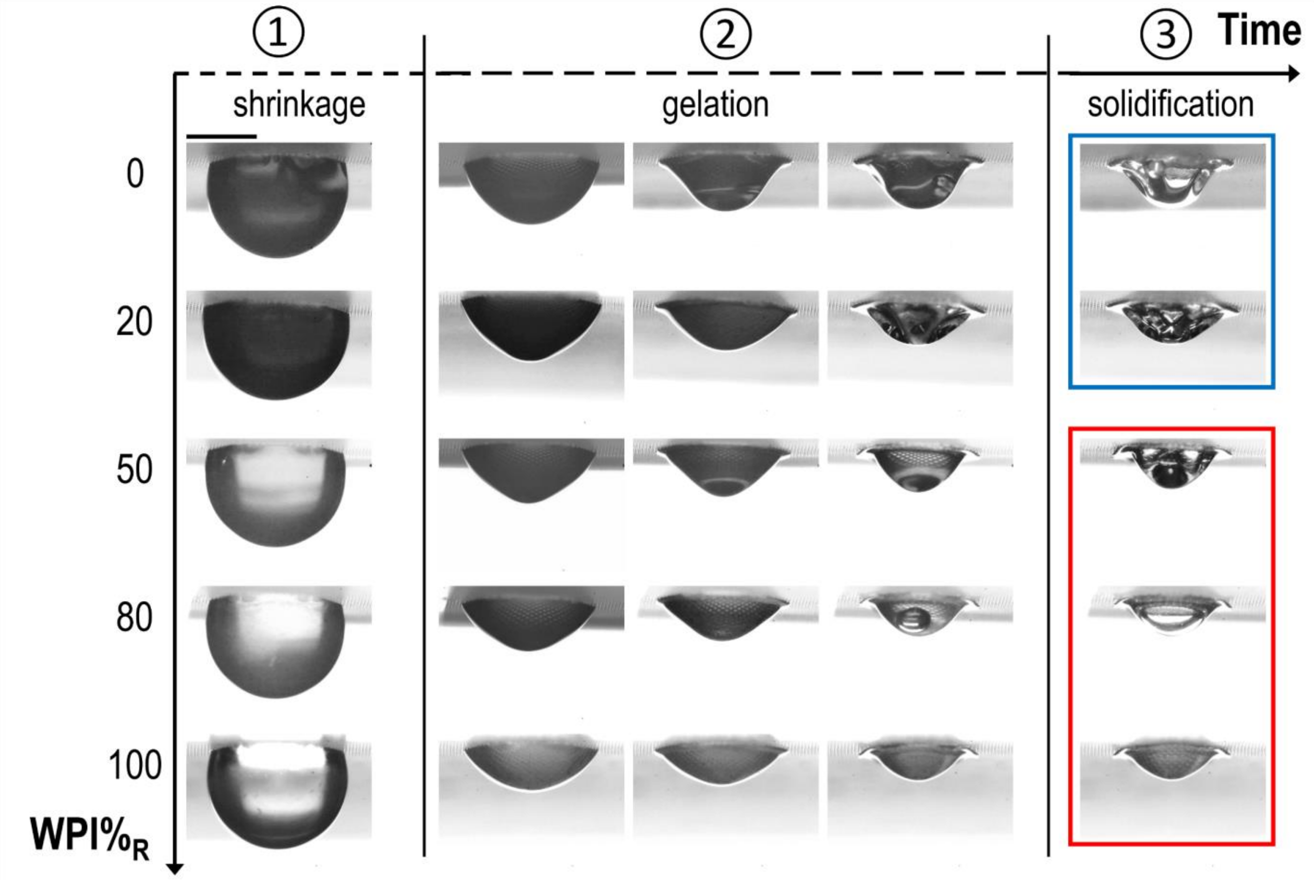


Droplet shape evolution with time

Main drying stages

Agreement with studies on single protein dispersions

(Sadek *et al.*, Langmuir 2013; Sadek *et al.*, Food Hydrocoll. 2015.)



Yu *et al.*, Colloids and Surface A 2021.

1 IMPACT OF SAMPLE COMPOSITION

Buckling (No border delamination) → $WPI\%_R$ → Rigid shell (significant delamination)

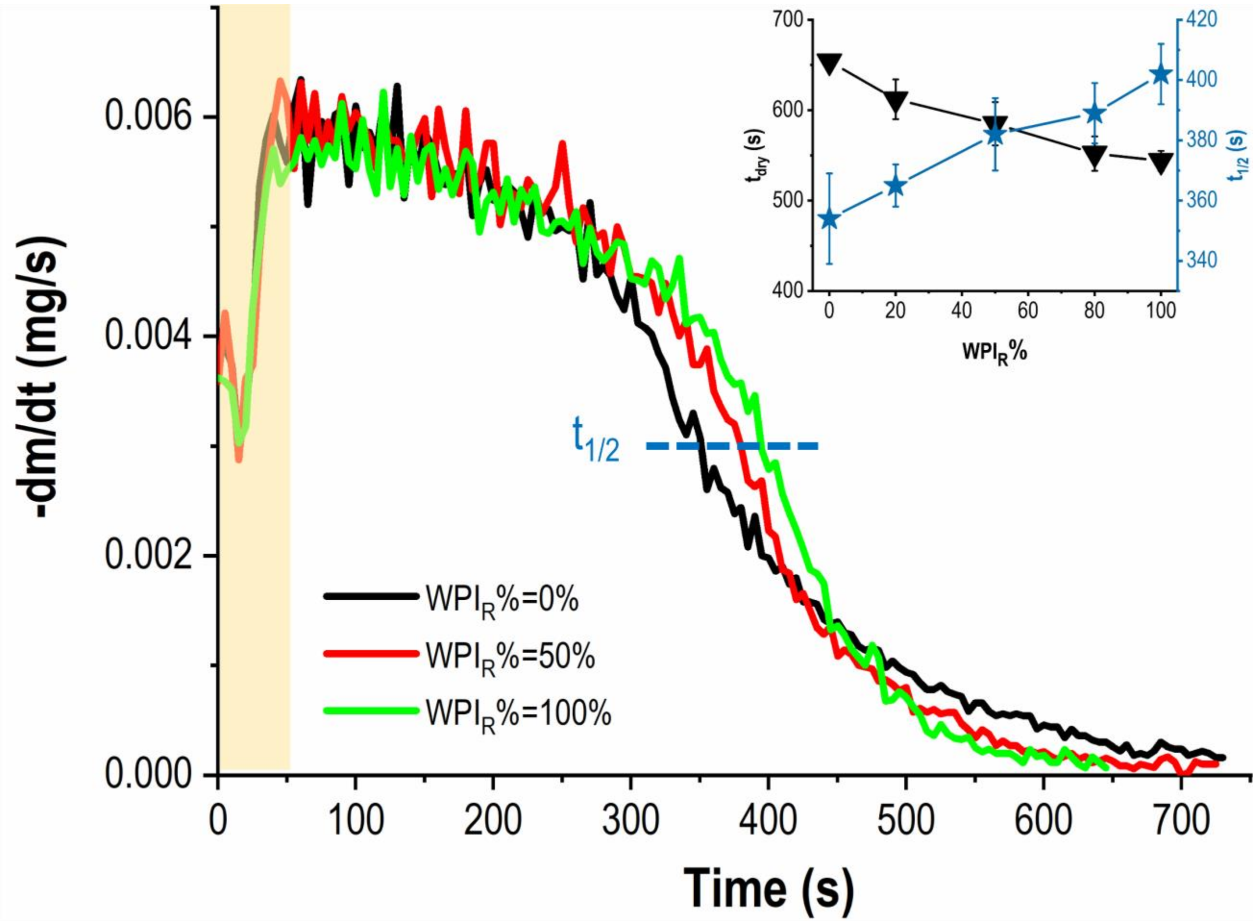
Shape transition
$WPI\%_{Rc}$=20-50%

2 WPI KEY ROLE ON DROPLET SHAPE

despite low φ

Is droplet shape depending on colloid concentration or on any interfacial organization?

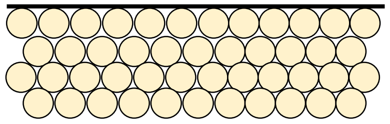
Drying kinetics



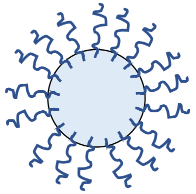
Yu *et al.*, Colloids and Surface A 2021.

1 DIFFERENT WPI AND NPC SKIN STRUCTURE

WPI



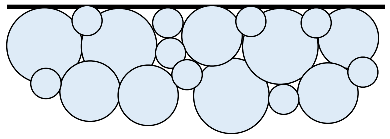
Compact ordered layer



Higher packing

- Polydispersity
- Squeezing
- Chemical bonds

NPC



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

2 SIMILAR BEHAVIOR WHEN $WPI\%_R \geq 50\%$

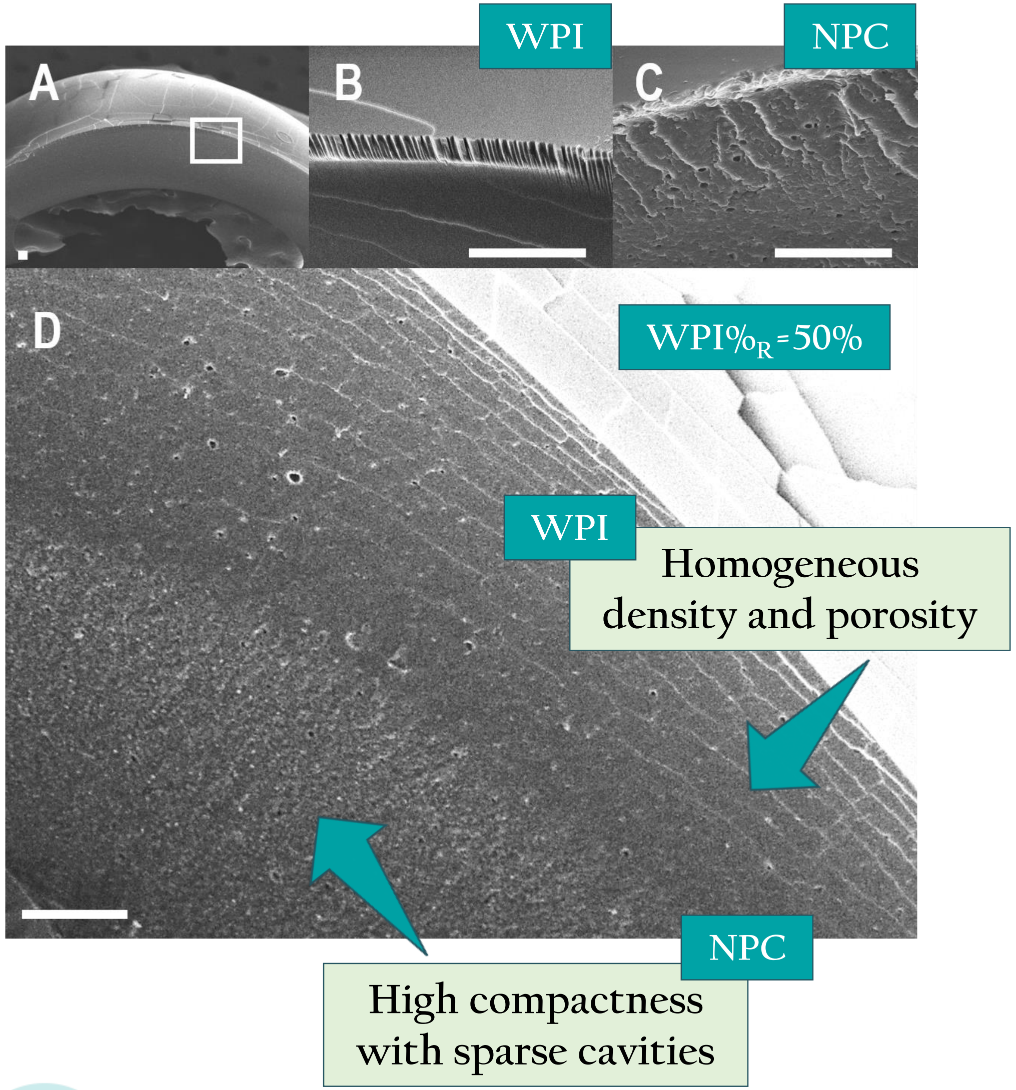
- Skin rigidity
- Limiting kinetics factor

PROTEIN STRATIFICATION

Schulz and Keddie, Soft matter 2018.
Nunes *et al.*, Prog. Org. Coat. 2014.

WPI ACCUMULATED ON TOP SURFACE?

Small-on-top stratification



Péclet Number

$$Pe = \frac{\tau_{ev}}{\tau_d} = \frac{\text{evaporation}}{\text{diffusion}}$$

$Pe_{WPI} \approx 6$

$Pe_{NPC} \approx 100$

The evaporation should favor NPC accumulation at the surface

SMALL-ON-TOP THEORY

1. Colloid size ratio, α
2. Péclet number, Pe
3. Volume fraction, φ

OSMOTIC PRESSURES
Zhou *et al.*, PRL 2017.

$$\alpha^2(1 + Pe_{WPI})\varphi_{WPI} > 1$$

DIFFUSIOPHORESIS
Sear and Warren, PRE 2017.

GOOD AGREEMENT WITH EXPERIMENTAL RESULTS
Yu *et al.*, Colloids and Surface A 2021.

Colloid stratification exclusively induced by drying?

SURFACE AGEING
- Adsorption
- Local concentration gradients

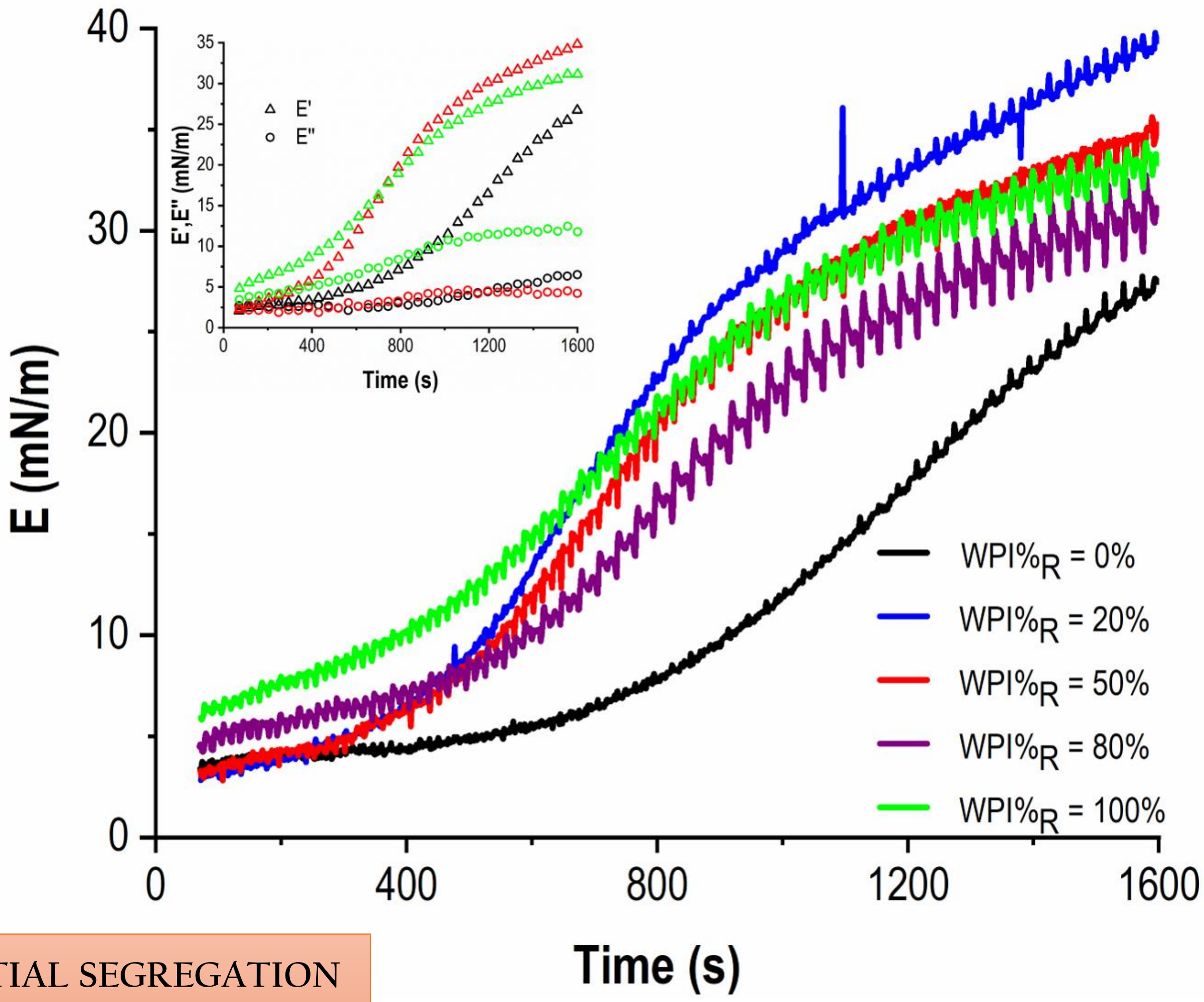
→ Osmotic pressure

→ **Protein stratification**

INTERFACIAL RHEOLOGY
Oscillatory droplet tests

- Similar behavior when $WPI\%_R \geq 50\%$
- Unexpected response for $WPI\%_R = 20\%$

→ WPI PREFERENTIAL SEGREGATION ON TOP SURFACE



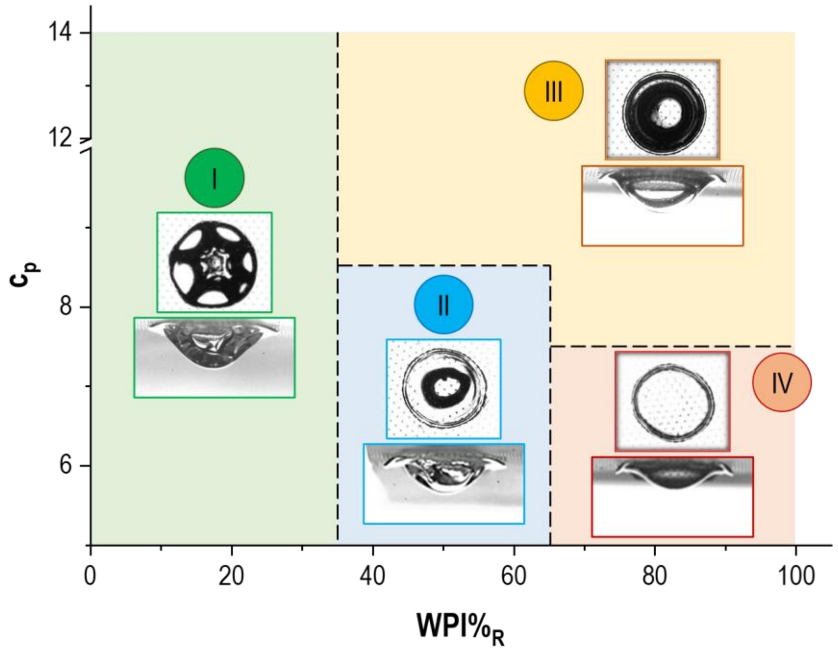
Yu *et al.*, Colloids and Surface A 2021.

Conclusions

- ❑ Investigation of drying dynamics in dairy protein mixes.
  Difference in terms of size, structure, mechanical properties
- ❑ When sufficiently represented in the samples ($WPI\%_R \geq 50\%$), WPI proteins strongly affect droplet skin rigidity and drying kinetics.
- ❑ The key role played by WPI proteins depend on their preferential segregation at top surface.
  Stratification by size → "small-on-top" theory
- ❑ WPI stratification can be induced even by ageing phenomena.
  Agreement between drying and ageing outcomes

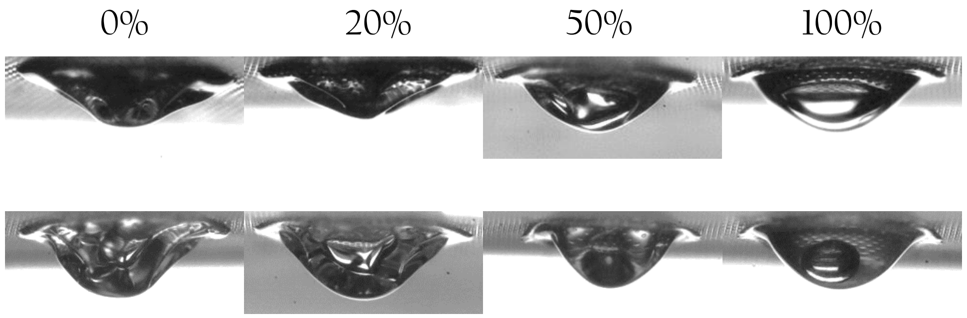
Current works

1 Impact of Protein concentration



Prediction of dairy mix particle shape starting from initial suspension characteristics

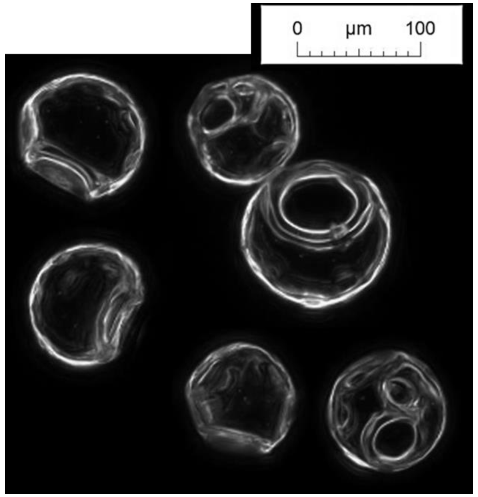
2 Investigation of other kind of proteins



Influence of protein physico-chemical properties on surface self-organization

3 Stratification in Monodisperse Drying

$WPI\%_R$=50%
(phase contrast microscopy)
Hybrid shape



Thank you for your attention