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➤ **Skin formation in drying droplets of dairy colloids**

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Supervisors: Romain Jeantet, Cécile Le Floch-Fouéré, Luca Lanotte

Cow milk-----White gold



Cow milk is a nutritive food liquid
-----high-quality protein source



- Short quality guarantee period
- Expensive transportation cost

Dairy products



Functional products

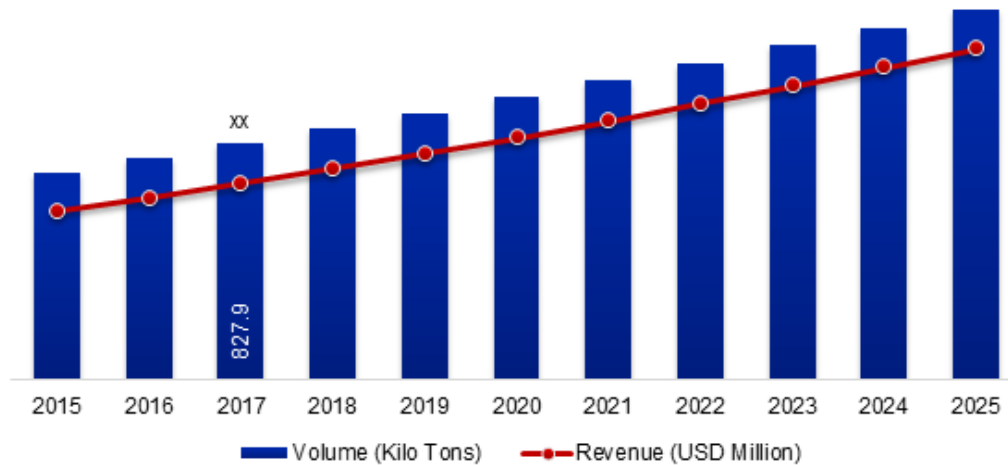


GAULLAC 365
BREPRO+ FORMULAS



Gauliac 365 BrePro+ is a nutritionally balanced formula designed to satisfy the nutritional requirements of your baby where breast feeding is not available.

Infant milk formula powder (IMF): high value & fast growing market



<https://www.adroitmarketresearch.com/industry-reports/baby-infant-formula-market>

1. Economic growth
2. Increasing spend on premium nutrition
3. Baby population

Mimicking breast milk

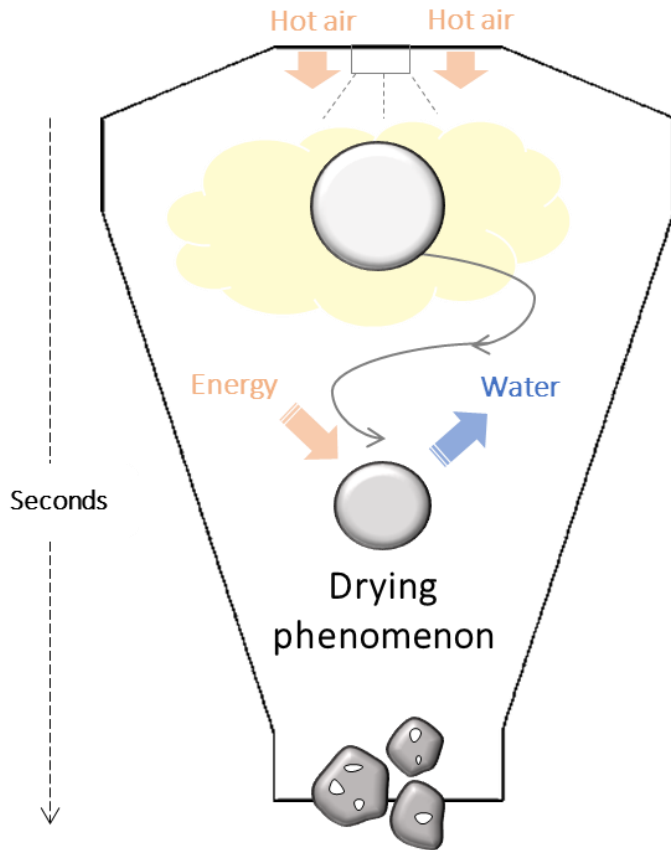
g/l	Cow milk	Human milk
Proteins	32	10
Caseins	80%	35%
WP	20%	65%
Carbohydrates	50	75
Lipids	38	36
PUFA	2,9%	6,4%

Adapted to their nutritional target

- First stage < 6 months
- Follow up < 36 months

Controlled functional end-use properties

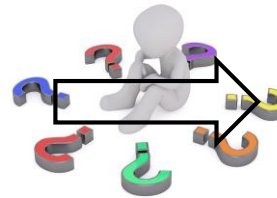
Spray drying



Drying condition

- Initial solution
- Temperature
- Air flow velocity

black box

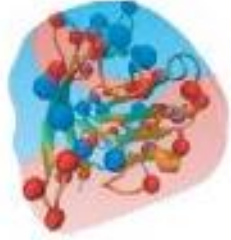


UNDERSTANDING THE DROPLET-TO-PARTICLE TRANSITION

Powder property

- size
- surface
- structure

Materials



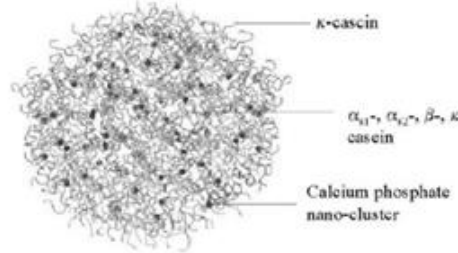
**Whey protein isolates
(WPI)**

- Globular structure
- $D \approx 10 \text{ nm}$

Yohko, 2012

Concentration: 8wt.%

WPI relative percentage(WPI%_R):
0, 20, 50, 80 and 100%



**Native phosphocaseinates
(NPC)**

- Micellar, dynamic and hydrated structure
- $D \approx 200 \text{ nm}$

Holt & Horne, 1996

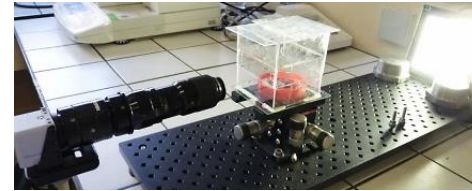
Bouchoux, 2010

Drying conditions

- Temperature: 20 °C
- Initial size: 0.5 μL
- Relative Humidity: < 2 %

Methods

Single droplet drying setup



Micro-balance
Drying kinetics

Scanning Electron Microscope

Parameters:

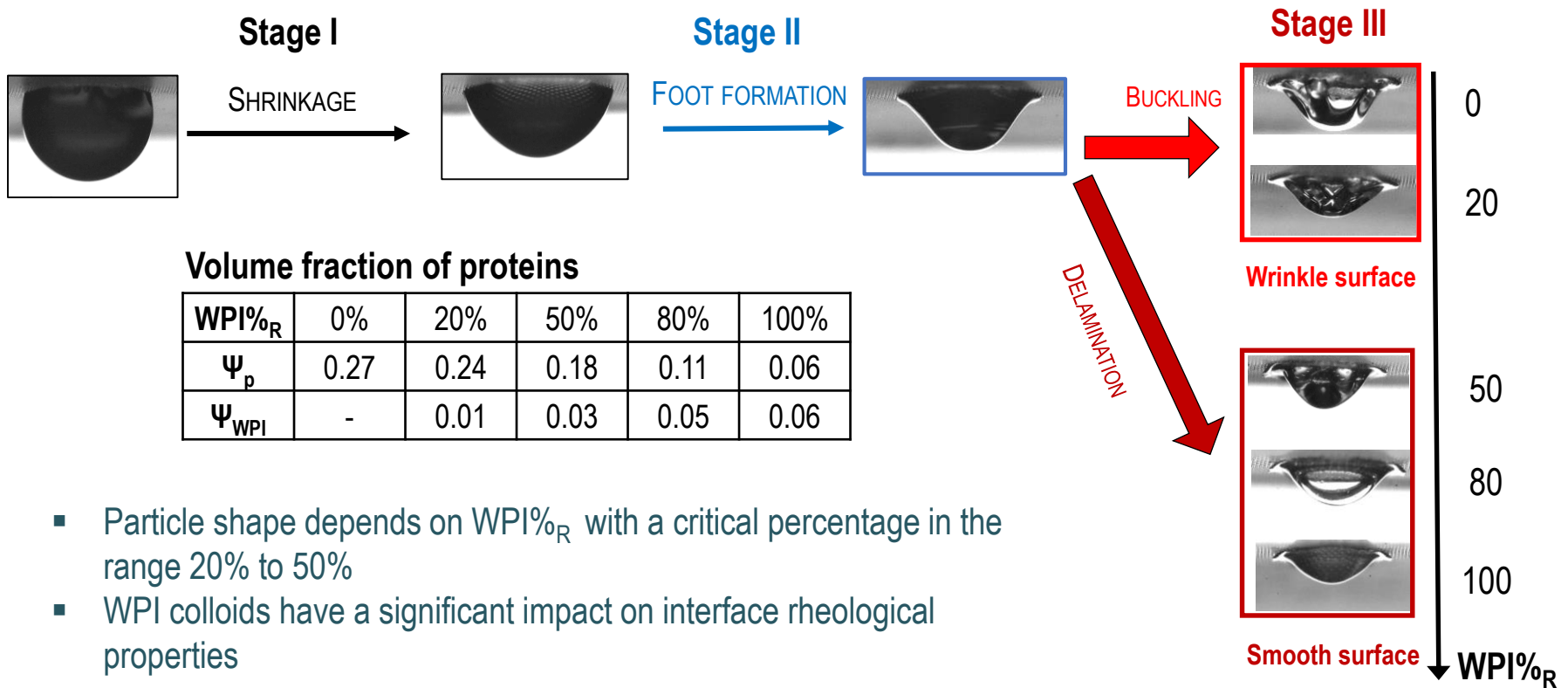
- Voltage: 5kV
- Work distance: 10mm

Interfacial adsorption and rheometry

Parameters:

- Initial volume: 8 μL
- Amplitude: 1 μL
- Period: 30 s

Droplet morphology evolution during the drying process

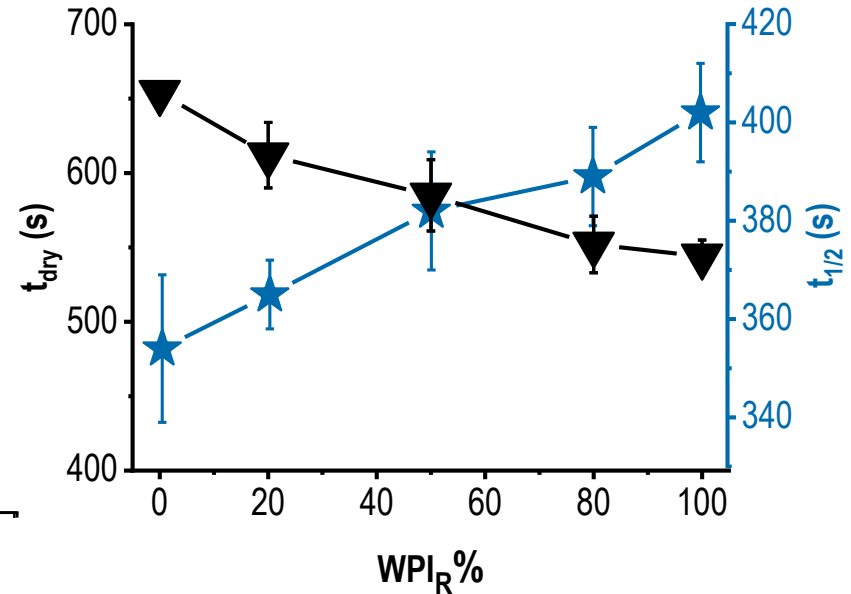
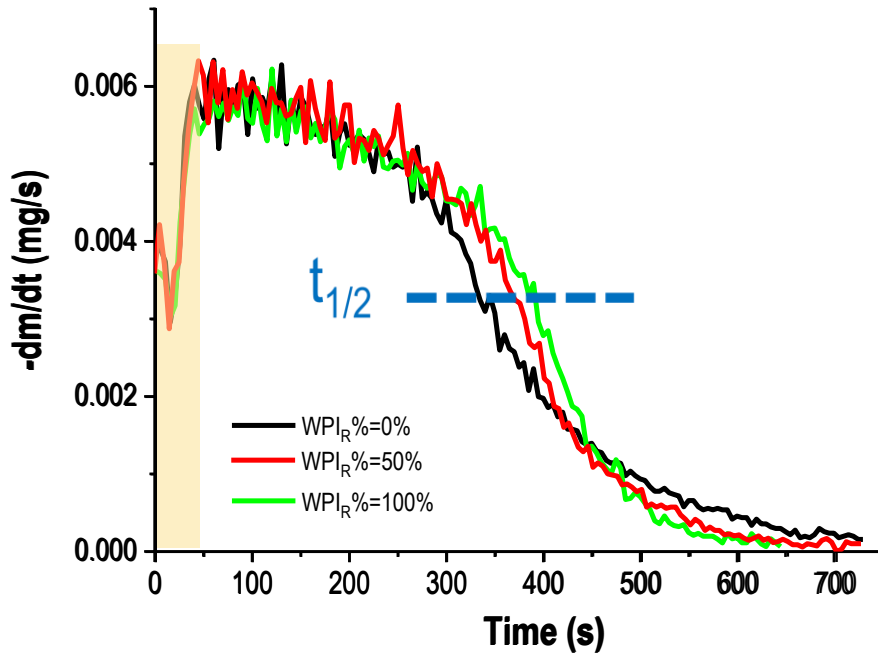


- Particle shape depends on WPI%_R with a critical percentage in the range 20% to 50%
- WPI colloids have a significant impact on interface rheological properties

C. Sadek, 2015, C. Sadek, 2016

To understand the skin layer formation in the WPI/NPC droplet drying, and consequently the evolution of surface mechanical properties

Drying kinetics



- Drying kinetics curves correspond to the morphology evolution stages
- WPI_R%=50% curve close to pure WPI

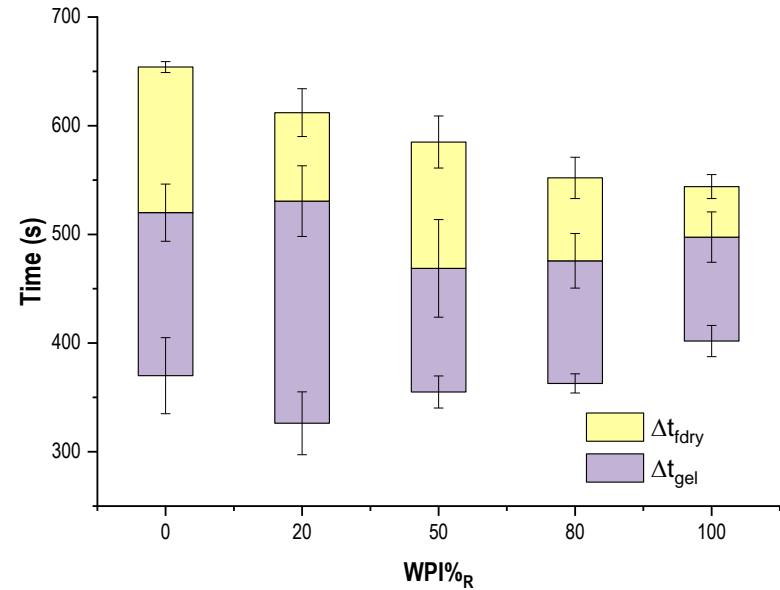
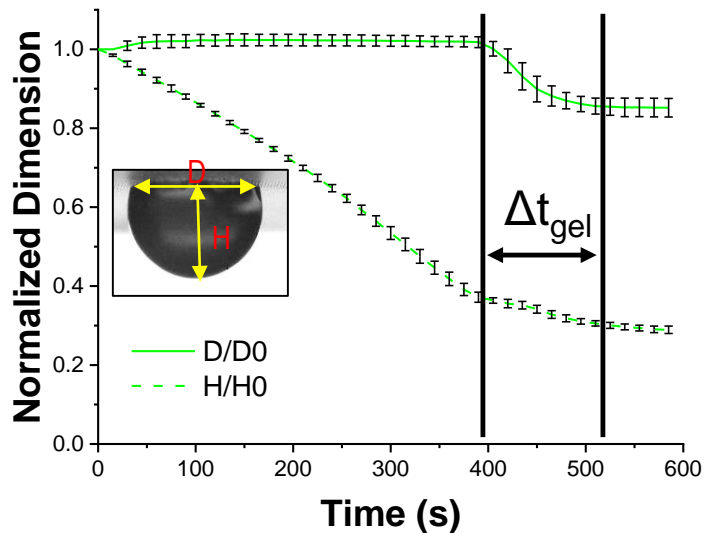
- $T_{1/2} \uparrow$ with WPI_R%: NPC (large particle) favors the sol-gel transition occurrence (NPC:16wt%, WPI:41wt%)
- $T_{dry} \downarrow$ with WPI_R%: NPC molecule 'traps' water during the drying process

C. Sadek, 2013 Bouchoux, 2010

How protein physico-chemical properties affect skin structure and mechanical properties?

WPI molecules randomly dispersed **OR** spatial stratification

Sol-gel transition



Duration of drying time and sol-gel transition time

WPI% _R	0%	20%	50%	80%	100%
$\Delta t_{gel}(s)$	156±27	204±47	114±47	113±27	107±8
$\Delta t_{dry}(s)$	130±20	100±39	126±42	76±15	42±11

WPI and NPC segregated during sol-gel transition → WPI accumulates on the outer layer ????

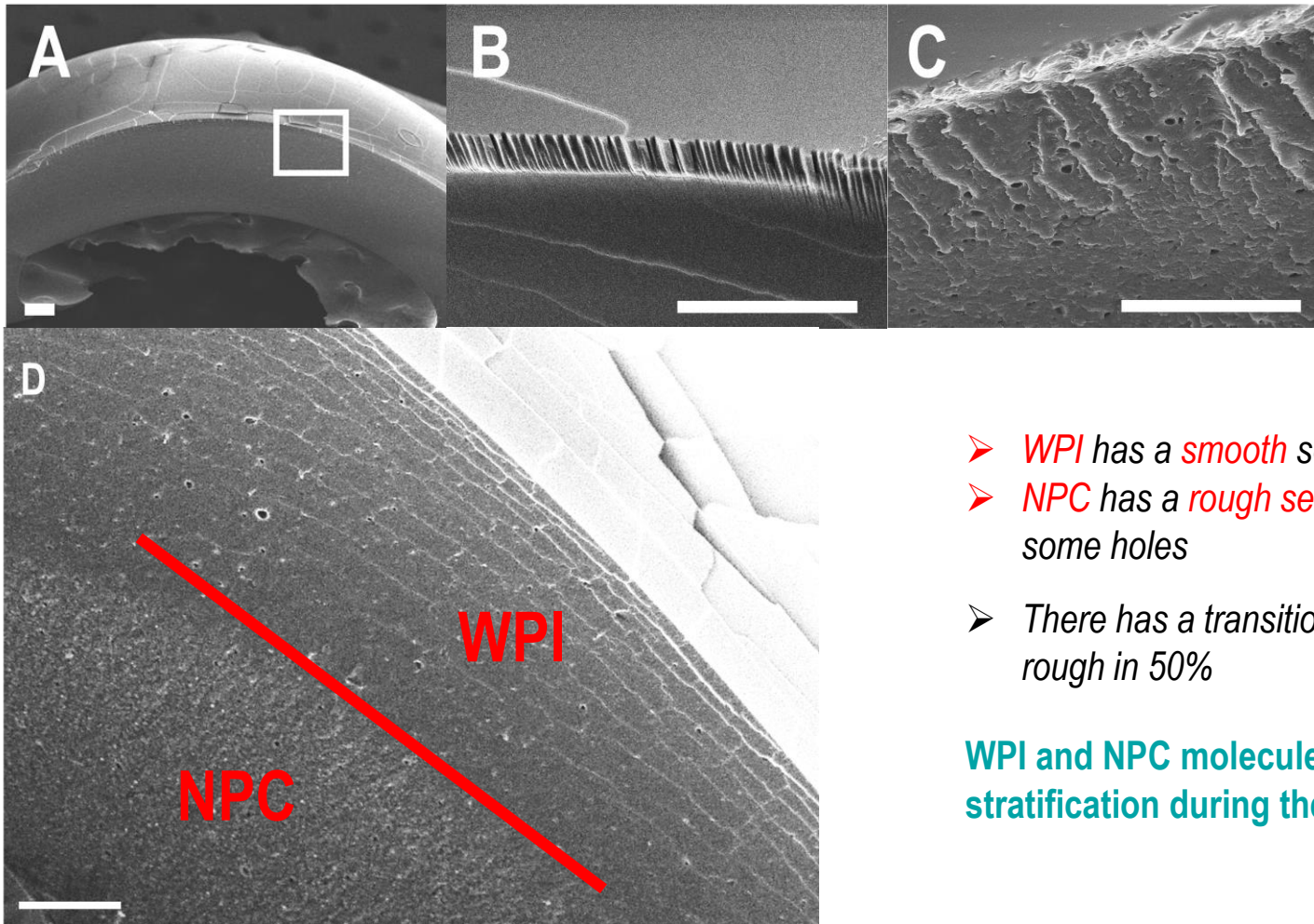
Δt_{gel} reflects the duration of surface **buckling** or border **delamination**

- WPI%_R ≤ 20%: deformable skin layer → buckling
- WPI%_R ≥ 50%: rigid skin layer → delamination

Δt_{dry} : final drying time

- Skin solidification ≠ drying finished

Structure of dry droplet section



- *WPI* has a *smooth* section
- *NPC* has a *rough section* and exists some holes
- There has a transition from smooth to rough in 50%

WPI and NPC molecule were subjected to stratification during the drying process

Small-on-top theory -----ZJD model

Small-on-top theory: In a binary system, small size colloids prefer to accumulate on the external skin layer in the drying process [Zhou et al. - 2017](#)

Main condition for particles segregation

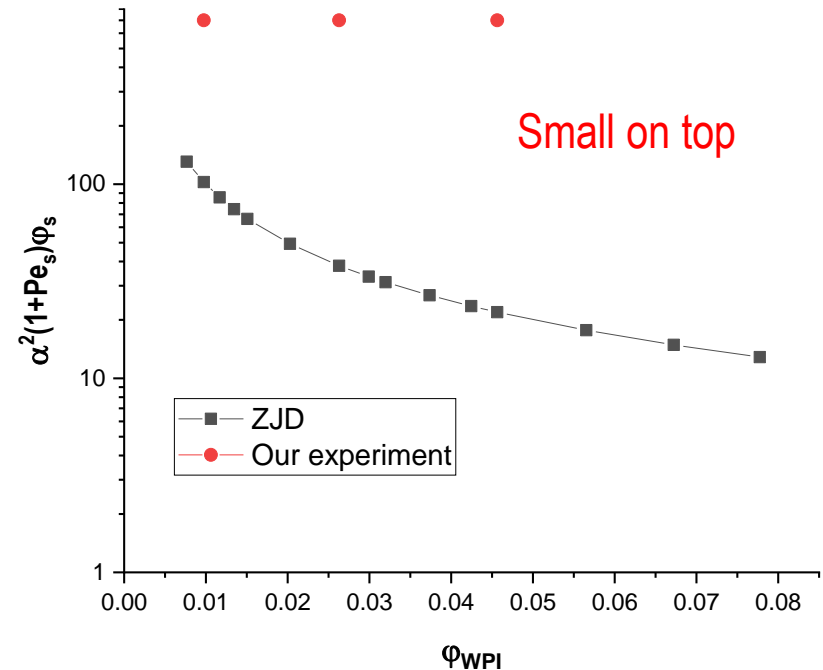
$$\alpha^2 (1 + Pe_s)\varphi_s = C$$

$\alpha=10$: Size ratio of big and small particle

$Pe_s=6$: Péclet number

φ_s : Volume fraction of small particle

WPI% _R	20%	50%	80%
Ψ_{WPI}	0.01	0.03	0.05



ZJD model prediction showed good agreement with our experiment: in the skin layer, WPI colloid are localized on the top of NPC micelles

Summary

- In **droplet of mixes**, the $WPI\%_R$ leads the morphology showing **two shape categories**:
surface **buckling** ($WPI\%_R \leq 20\%$) or **rigid convex shell** ($WPI\%_R \geq 50\%$)
- The drying kinetics and the drying time of mixes samples are governed by whey proteins if the $WPI\%_R \geq WPI\%_{Rc}$ ($20\% \leq WPI\%_{Rc} \leq 50\%$)
- In the mixed sample, **WPI molecules** tend to accumulate on the particle **outer layer** (**SEM image, confirmed by ZJD modelling**)
- Whey proteins have a significant influence on the interfacial rheology properties if $WPI\%_R \geq WPI\%_{Rc}$

Thanks for your attention

Merci



谢谢