Skin formation in drying droplets of dairy proteins

Ming Yu, Romain Jeantet, Cécile Le Floch-Fouéré, Luca Lanotte

Skin formation in drying droplets of dairy colloids

PhD student: Ming Yu (11/2018-01/2022)

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

Cow milk-------White gold

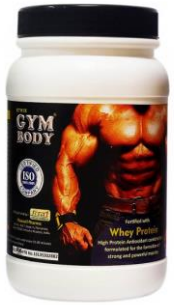
Cow milk is a nutritive food liquid

------high-quality protein source

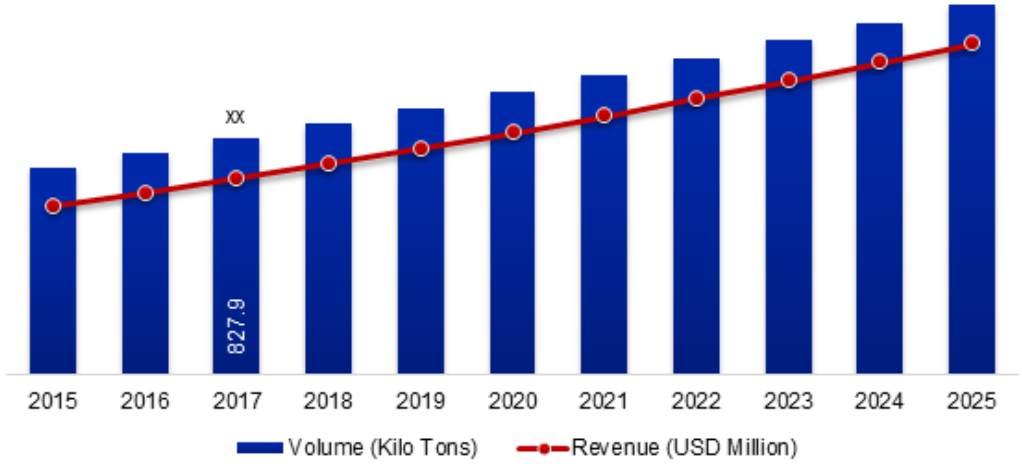
- Short quality guarantee period
- Expensive transportation cost

Dairy products

Functional products



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

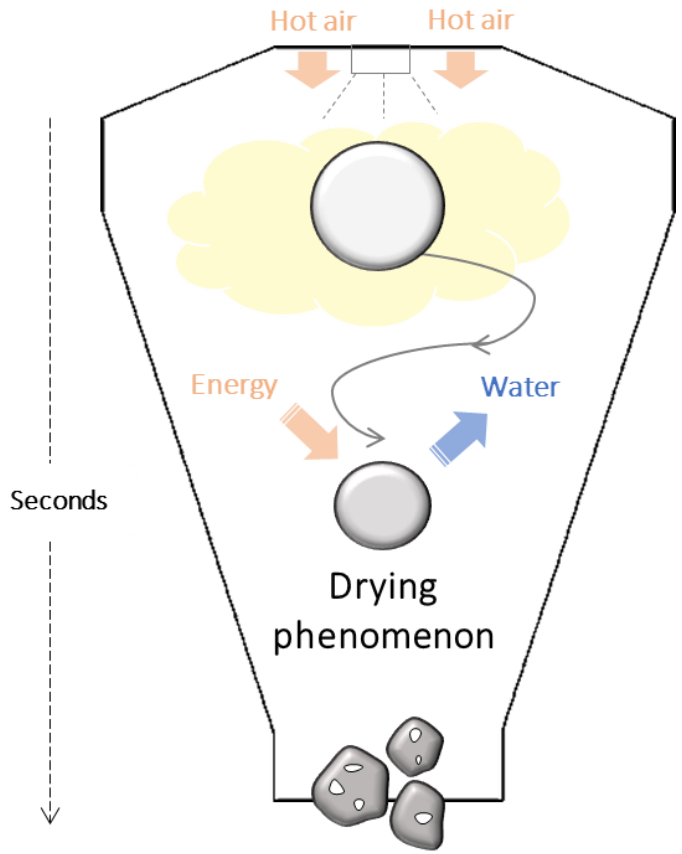
g/l	Cow milk	Human milk
Proteins	**32**	**10**
Caseins	*80%*	*35%*
WP	*20%*	*65%*
Carbohydrates	**50**	**75**
Lipids	**38**	**36**
PUFA	*2,9%*	*6,4%*

Adapted to their nutritional target

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

Controlled functional end-use properties

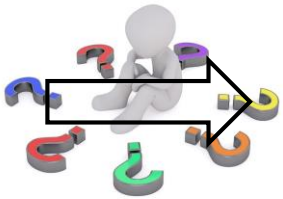
Spray drying



Drying condition

- Initial solution
- Temperature
- Air flow velocity

black box

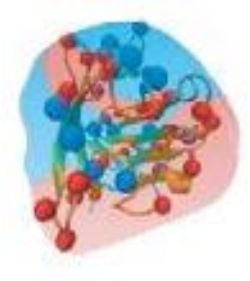


UNDERSTANDING THE DROPLET-TO-PARTICLE TRANSITION

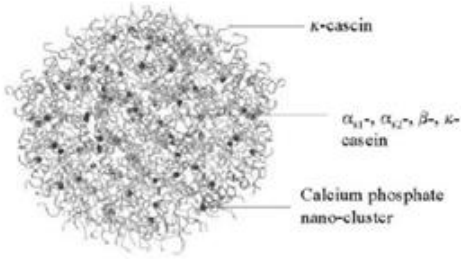
Powder property

- size
- surface
- structure

Materials



Whey protein isolates
(WPI)



Native phosphocaseinates
(NPC)

- Globular structure
- D ≈ 10 nm

Yohko, 2012

- Micellar, dynamic and hydrated structure
- D ≈ 200 nm

Holt & Horne, 1996

Bouchoux, 2010

Concentration: 8wt.%

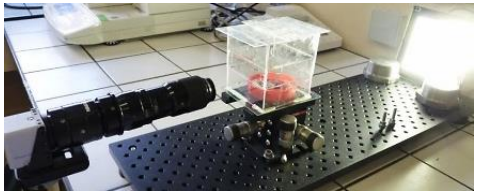
WPI relative percentage($WPI\%_R$):
0, 20, 50, 80 and 100%

Drying conditions

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

Methods

Single droplet drying setup



Micro-balance
Drying kinetics

Scanning Electron Microscope

Parameters:

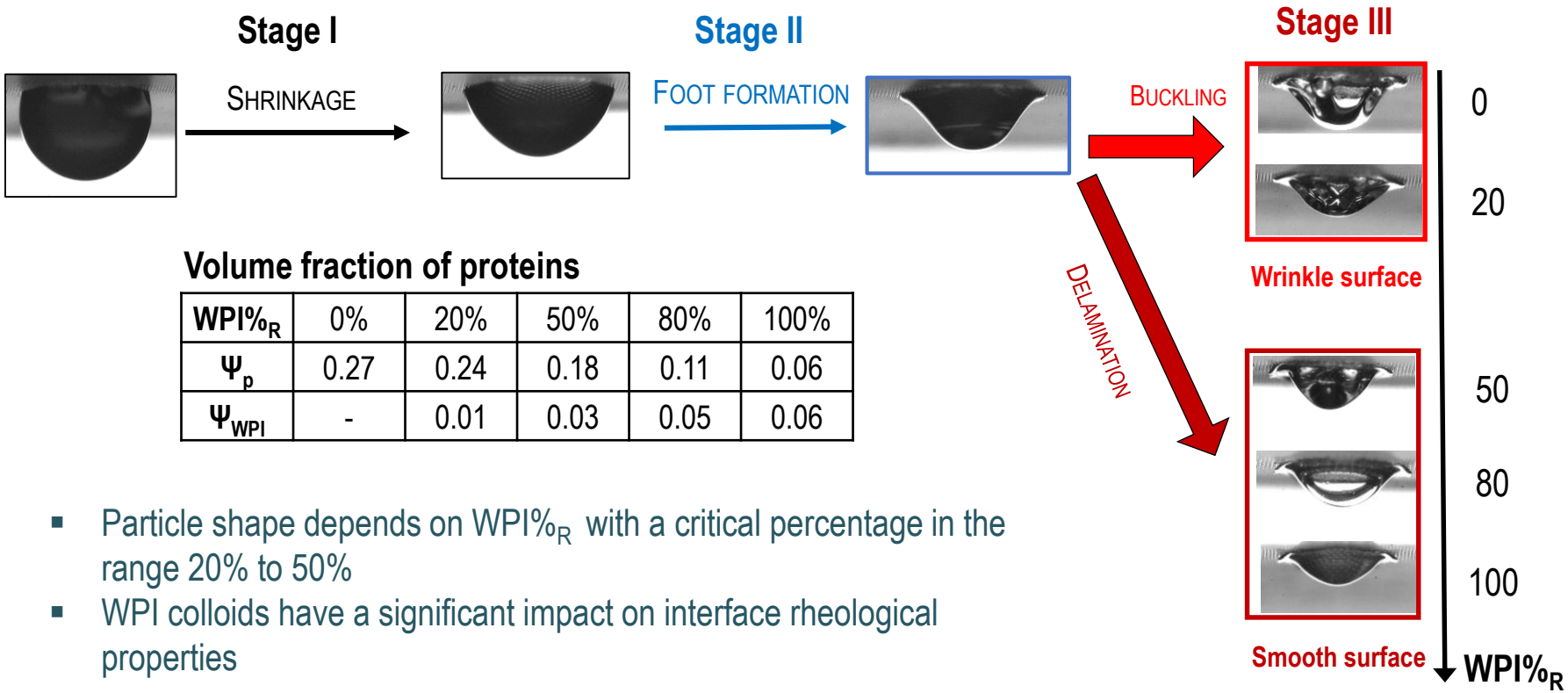
- Voltage: 5kV
- Work distance: 10mm

Interfacial adsorption and rheometry

Parameters:

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

Droplet morphology evolution during the drying process



Volume fraction of proteins

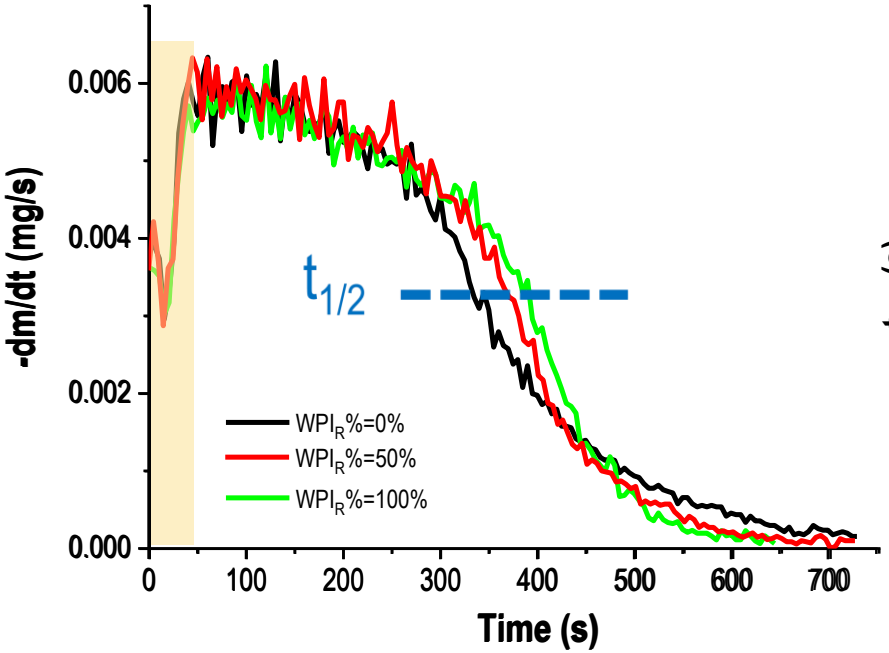
$WPI\%_R$	0%	20%	50%	80%	100%
Ψ_p	0.27	0.24	0.18	0.11	0.06
Ψ_{WPI}	-	0.01	0.03	0.05	0.06

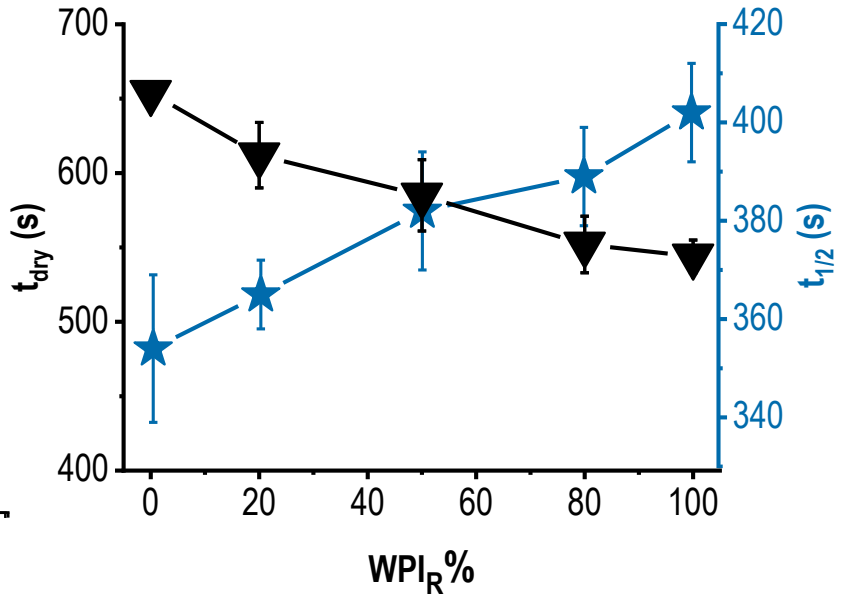
- Particle shape depends on $WPI\%_R$ with a critical percentage in the range 20% to 50%
- WPI colloids have a significant impact on interface rheological properties

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

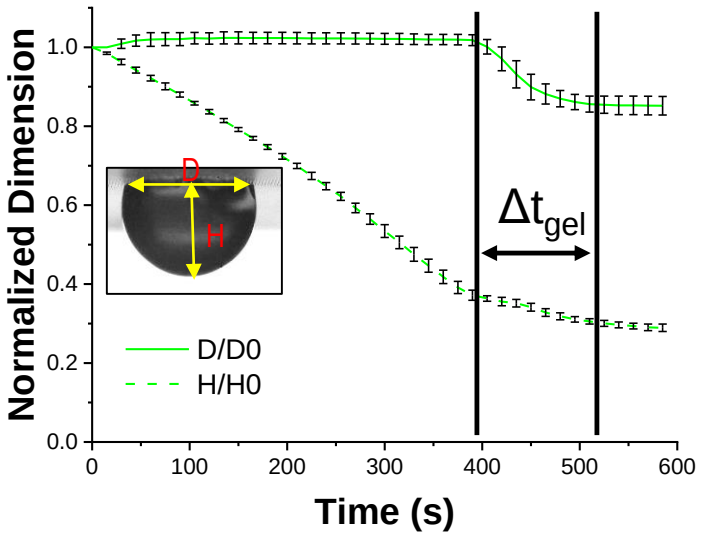
- **$T_{1/2}$ ↑ with $WPI\%_R$:** NPC(large particle) favors the sol-gel transition occurrence (NPC:16wt.%,WPI:41wt/%)
- **T_{dry} ↓ with $WPI\%_R$:** NPC molecule 'traps' water during the drying process

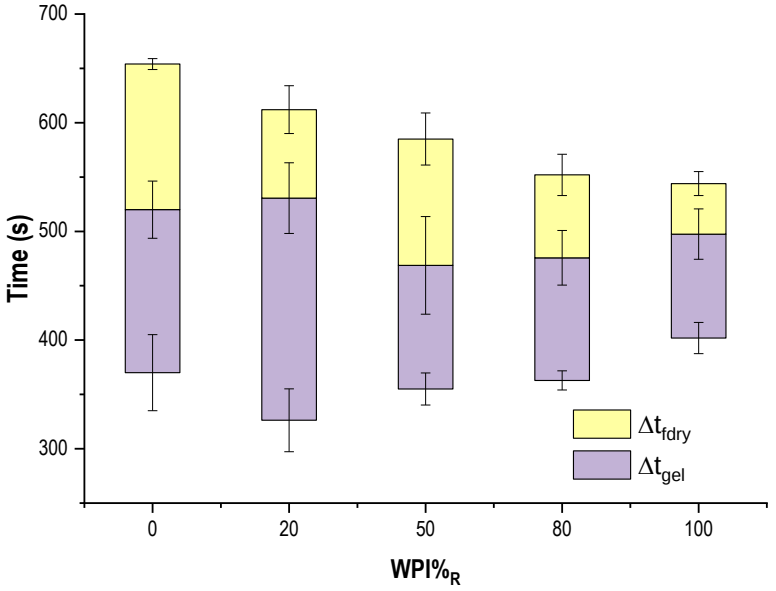
C. Sadek, 2013 *Bouchoux, 2010*

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%
Δt_{gel}(s)	156±27	204±47	114±47	113±27	107±8
$\Delta t_{fdry(s)}$	130±20	100±39	126±42	76±15	42±11

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

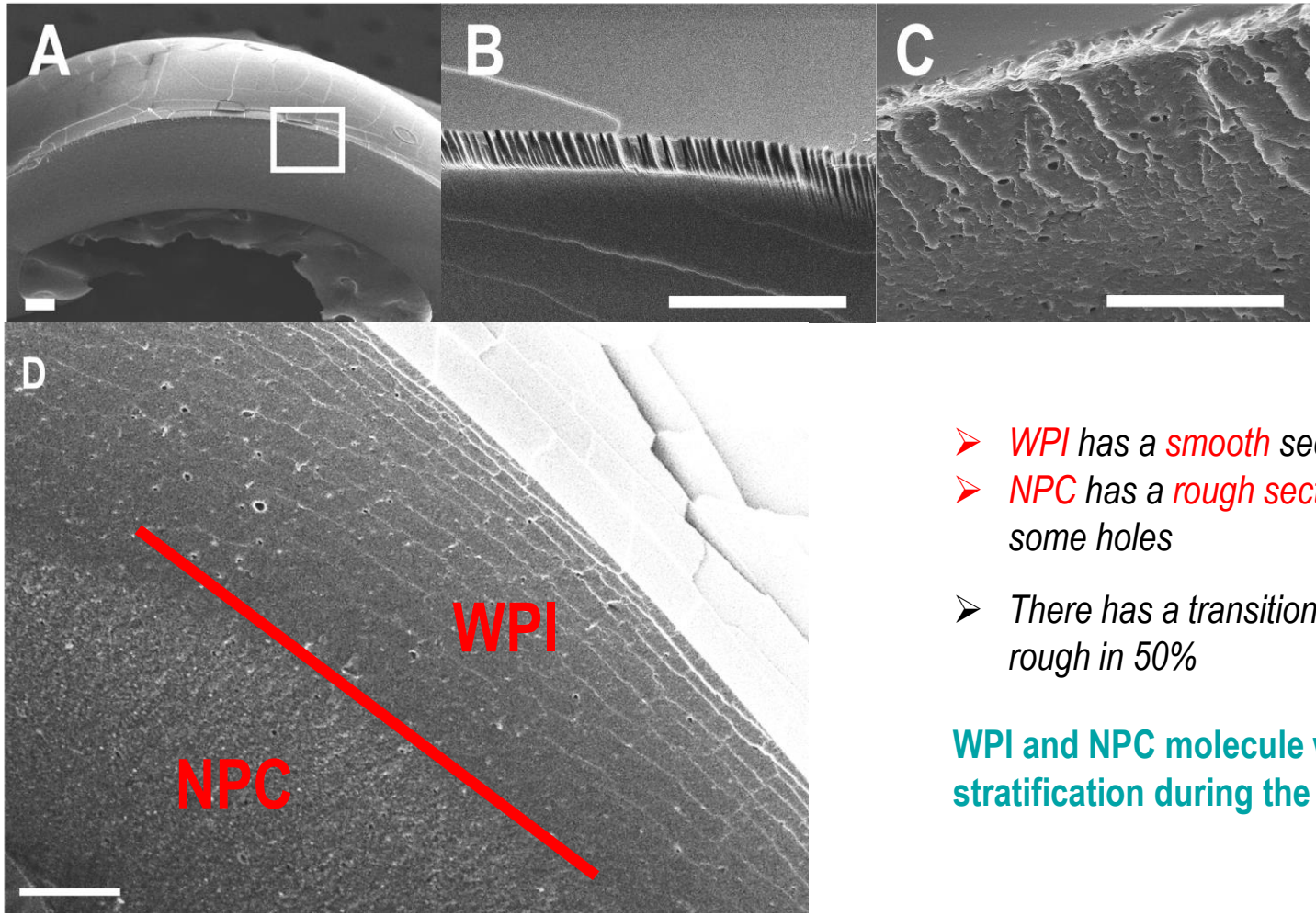
Δt_{gel} reflects the duration of surface **buckling** or border **delamination**

- $WPI\%_R \leq 20\%$: deformable skin layer → buckling
- $WPI\%_R \geq 50\%$: rigid skin layer → delamination

Δt_{fdry} : 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

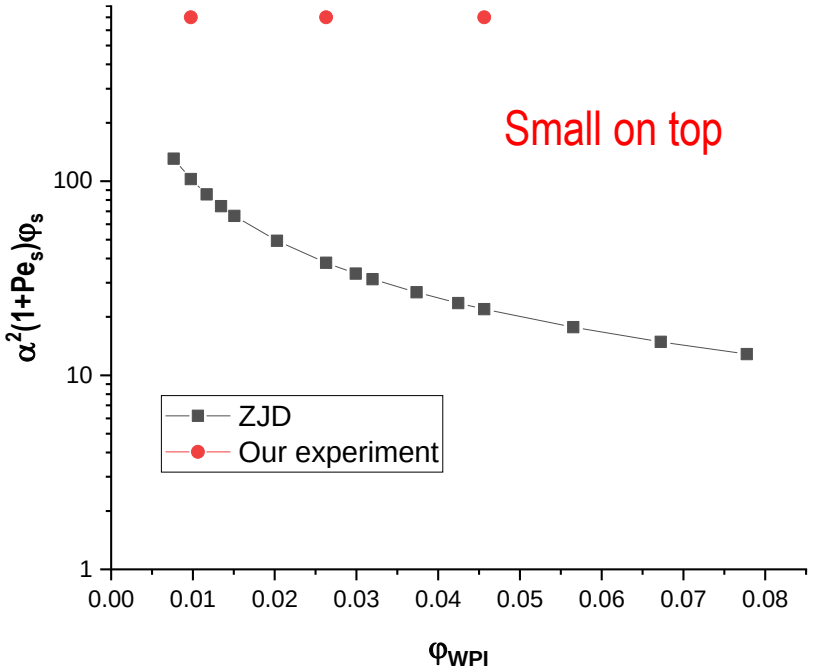
$$\alpha^2 (1 + Pes)\varphi_s = C$$

α=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