

# Particle formation during dairy powders production is ruled by protein mechanical properties



AGRO  
CAMPUS  
OUEST

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*Workshop Drying Days, 23-24 Mars 2017, Toulouse*

# LAB'S PRESENTATION

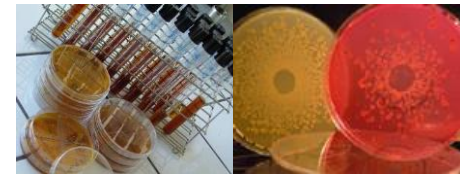


**A multidisciplinary and multiscale approach, reinforced by two high-calibre facilities:**

Dairy Platform



Biological Resource Centre



➤ **Structuration / destructuration mechanisms of food matrix:**

*from structural characterisation to digestion*

➤ **Dairy processing and cheese making:**

*toward sustainable dairy systems*

➤ **Microbial interaction:**

*food matrix and host cell*

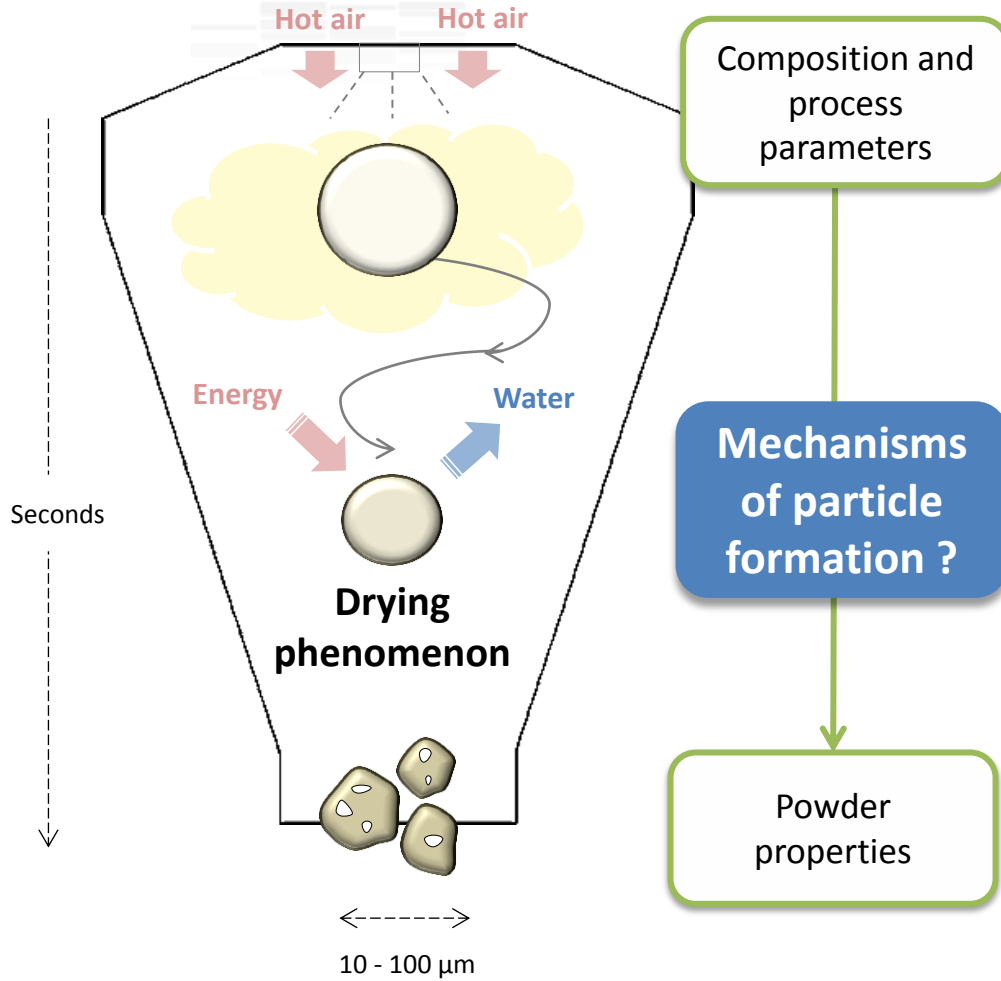


Please visit [http://www6.rennes.inra.fr/stlo\\_eng](http://www6.rennes.inra.fr/stlo_eng)

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# Scientific background

Ensure the quality of dairy powders: many challenges...



## Limits on an industrial scale

- *Fast drying kinetics*
- *Heterogeneity of samples*
- *Complexity of equipment and/or formula*
- *Costs of large scale trials*



# Strategy of the work

Question of research

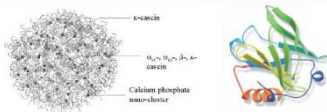
**How does the droplet become a dry particle?**



# Strategy & Objectives

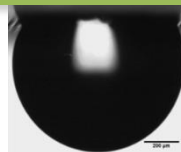
## Study of the drying process on multi-scales

### Milk proteins



- ✓ Whey protein isolates (WPI)
- ✓ Micellar casein (NPC)
- ✓ Concentration: 100g.L<sup>-1</sup>
- ✓ WPI # 10nm
- ✓ NPC # 200 nm

### Single droplet 3D / 2D



### PARTICLE FORMATION

- ✓ **Control and study** the drying kinetics
- ✓ **Record *in situ*** deformation

### Powder properties

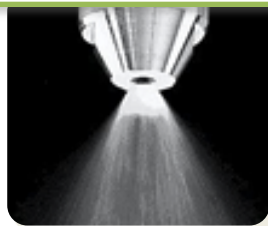
### Mono-disperse droplets



### PARTICLES PROPERTIES

- ✓ **Control** drying history
- ✓ **Get** homogenous samples
- ✓ **Analyze** physical properties

### Spraying cone of droplets



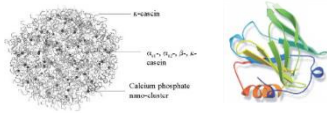
### TRANSFER OF KNOWLEDGE

- ✓ **Validate** on an industrial scale
- ✓ **Control** powder properties

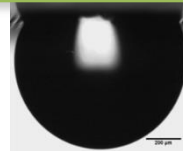
# Strategy & Objectives

## Study of the drying process on multi-scales

Milk proteins



Single droplet  
3D / 2D

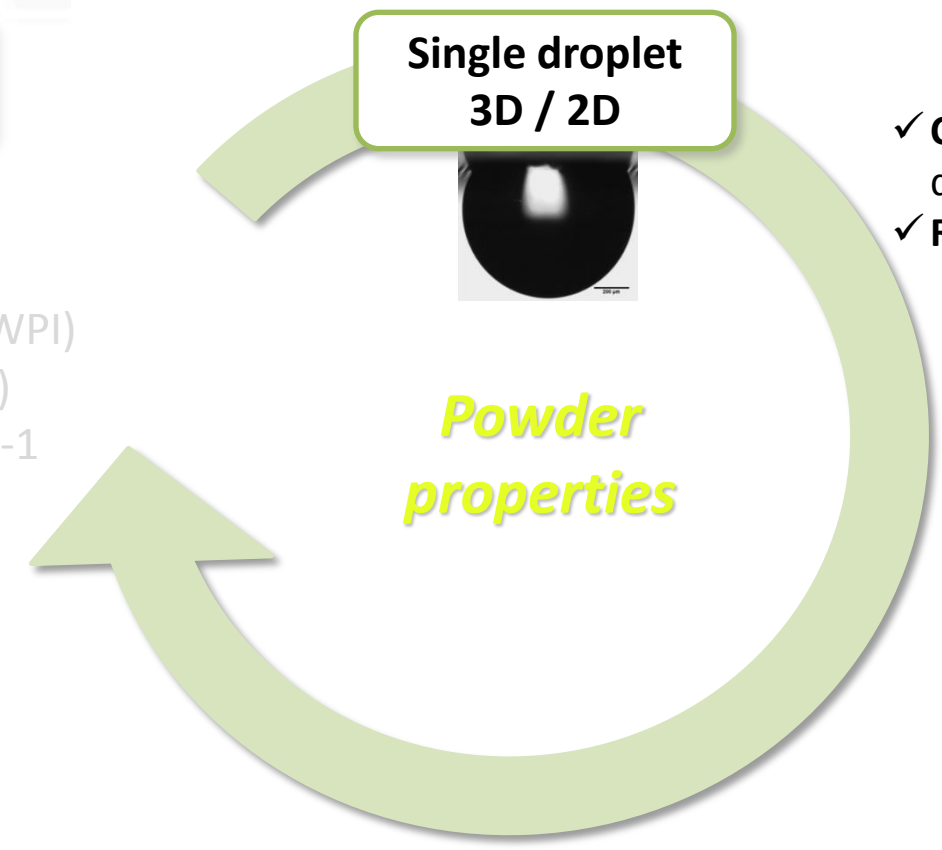


**PARTICLE FORMATION**

- ✓ Control and study the drying kinetics
- ✓ Record *in situ* deformation

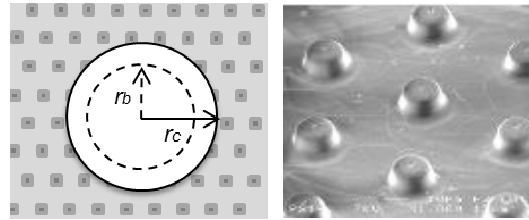
**Powder  
properties**

Whey protein isolates (WPI)  
Micellar casein (NPC)  
Concentration: 100g.L-1  
WPI # 10nm  
NPC # 200 nm



# Material & Method – Single 3D droplet

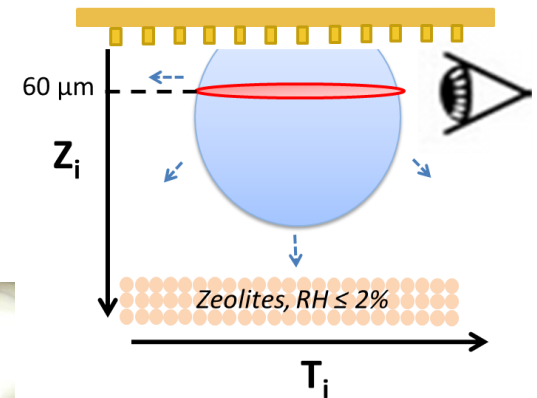
To follow the droplet distortion *in situ* and in real time



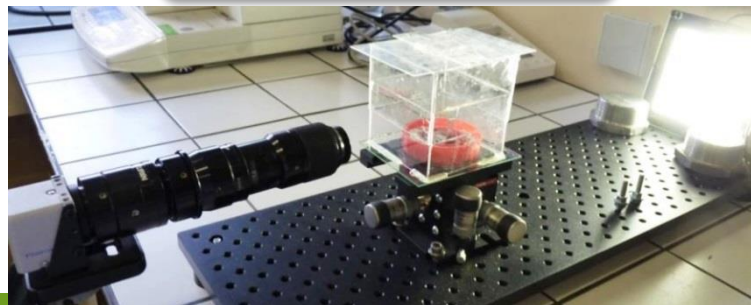
Micro-balance  
Drying kinetics



Confocal microscopy  
Internal structure



High-speed camera  
External structure



Scientific  
background

Strategy of  
work

Single  
droplet

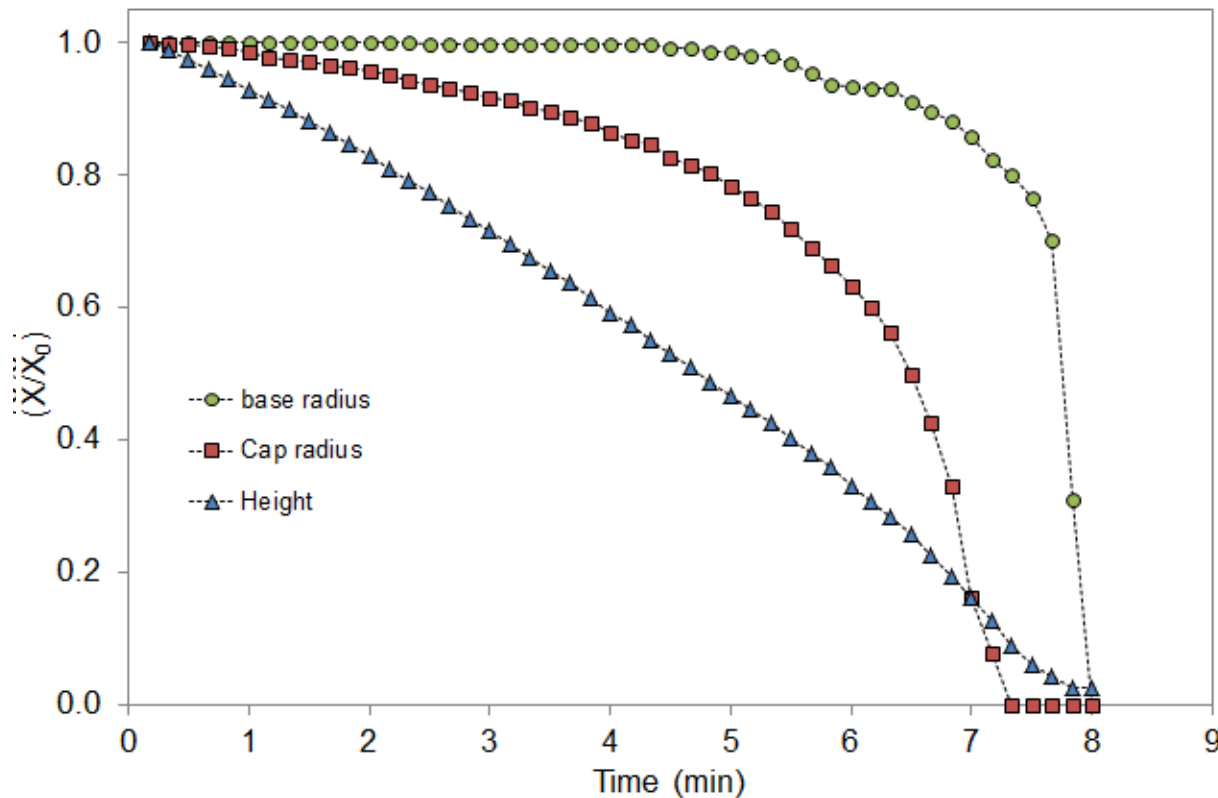
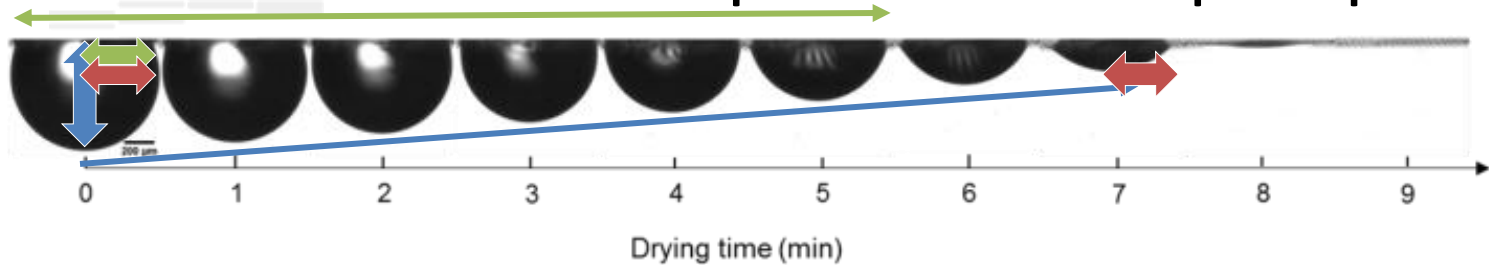
Mono-  
disperse  
droplets

Transfer of  
knowledge

General  
conclusion

# Material & Method – Single 3D droplet

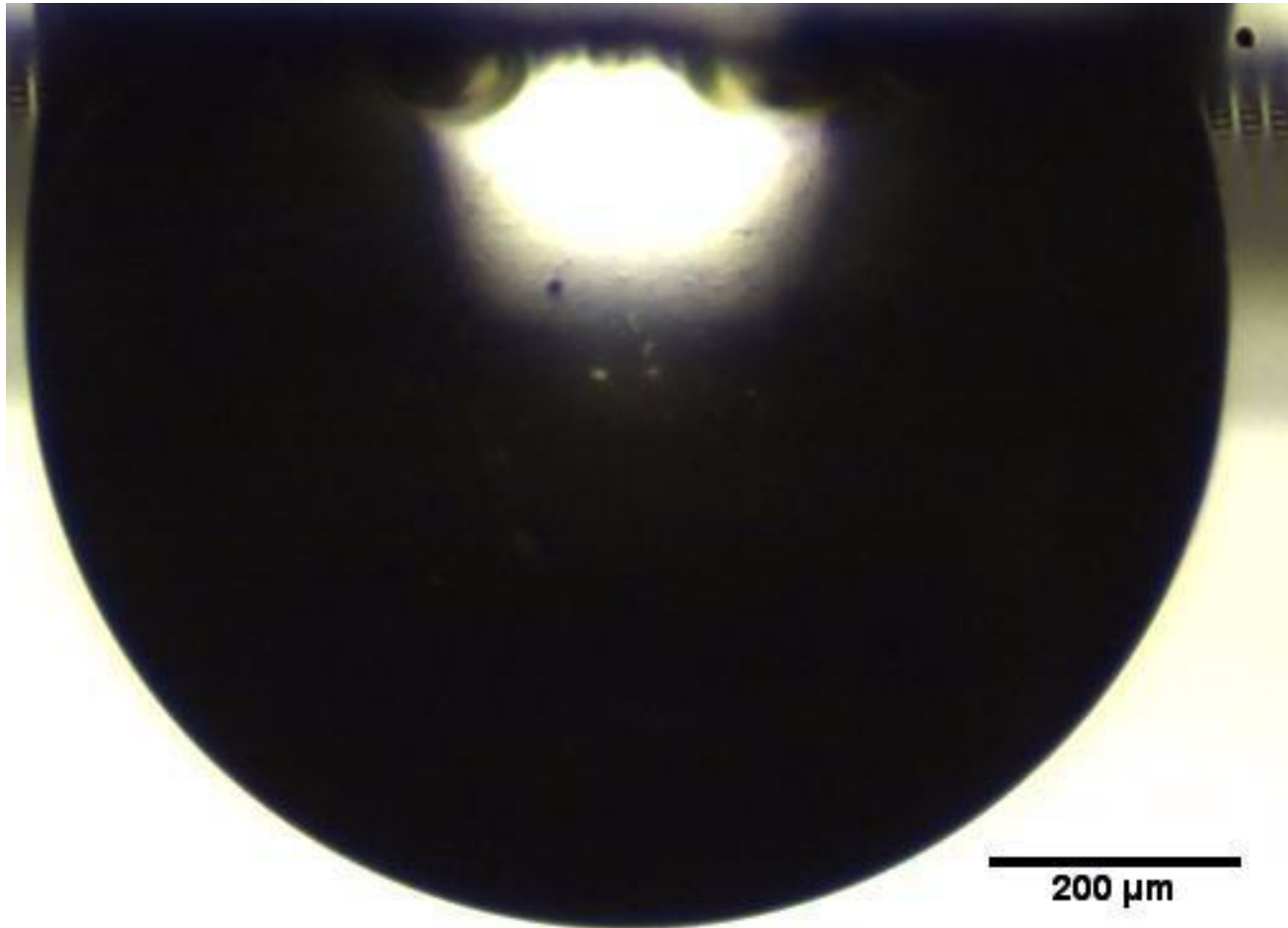
Indicators of the external shape evolution of a droplet of pure water





# Results – Single 3D droplet

## Drying behaviour of the whey proteins



### WPI droplet dynamics

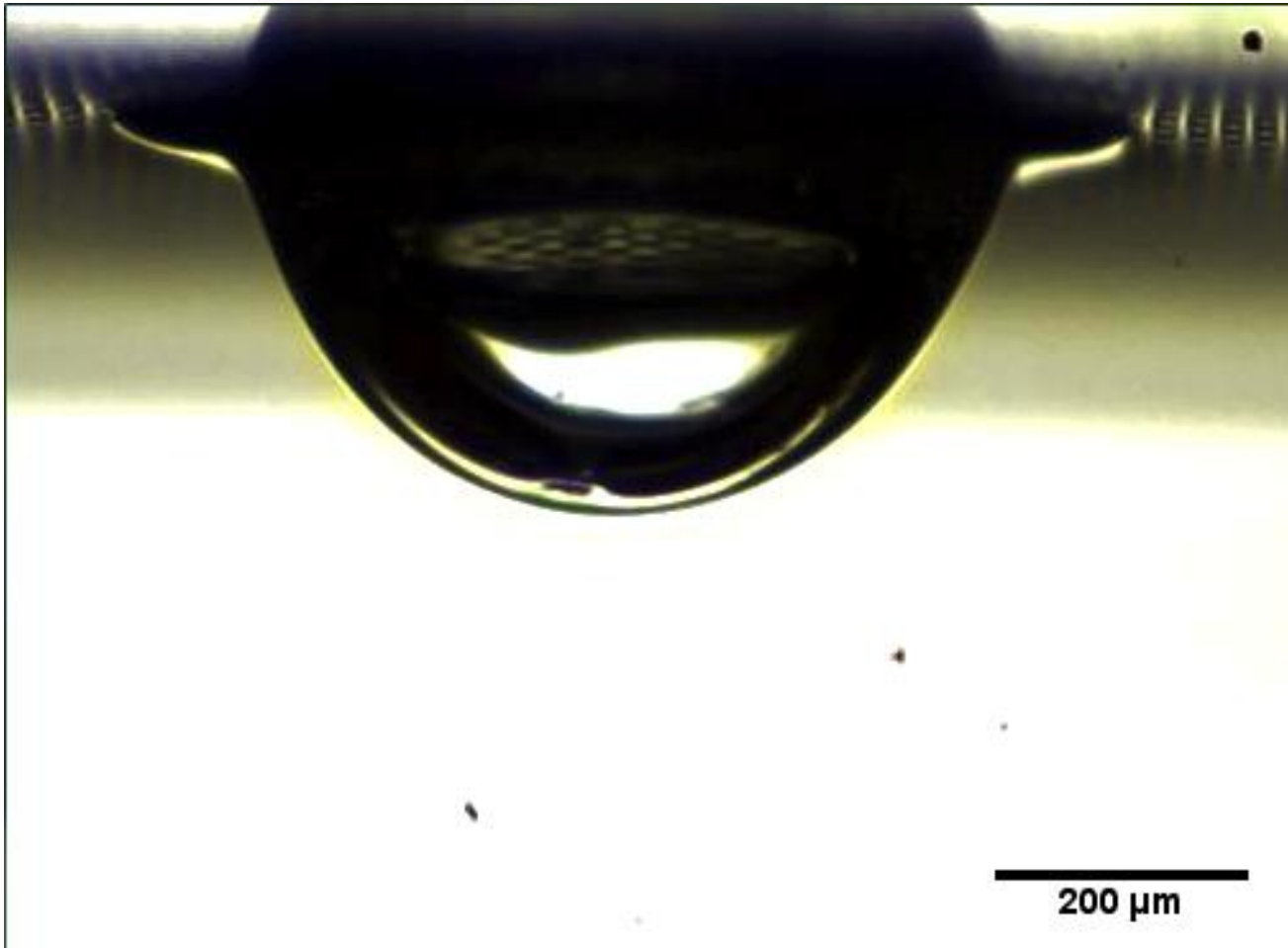
- **STAGE I**  
Isotropic shrinkage
- **STAGE II**  
Buckling instability
- **STAGE III**  
Vacuole nucleation

→ Spherical & hollow cap shape

Frame rate : 1 image/30s

# Results – Single 3D droplet

## Drying behaviour of the whey proteins



### WPI droplet dynamics

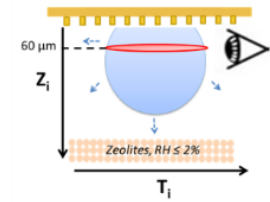
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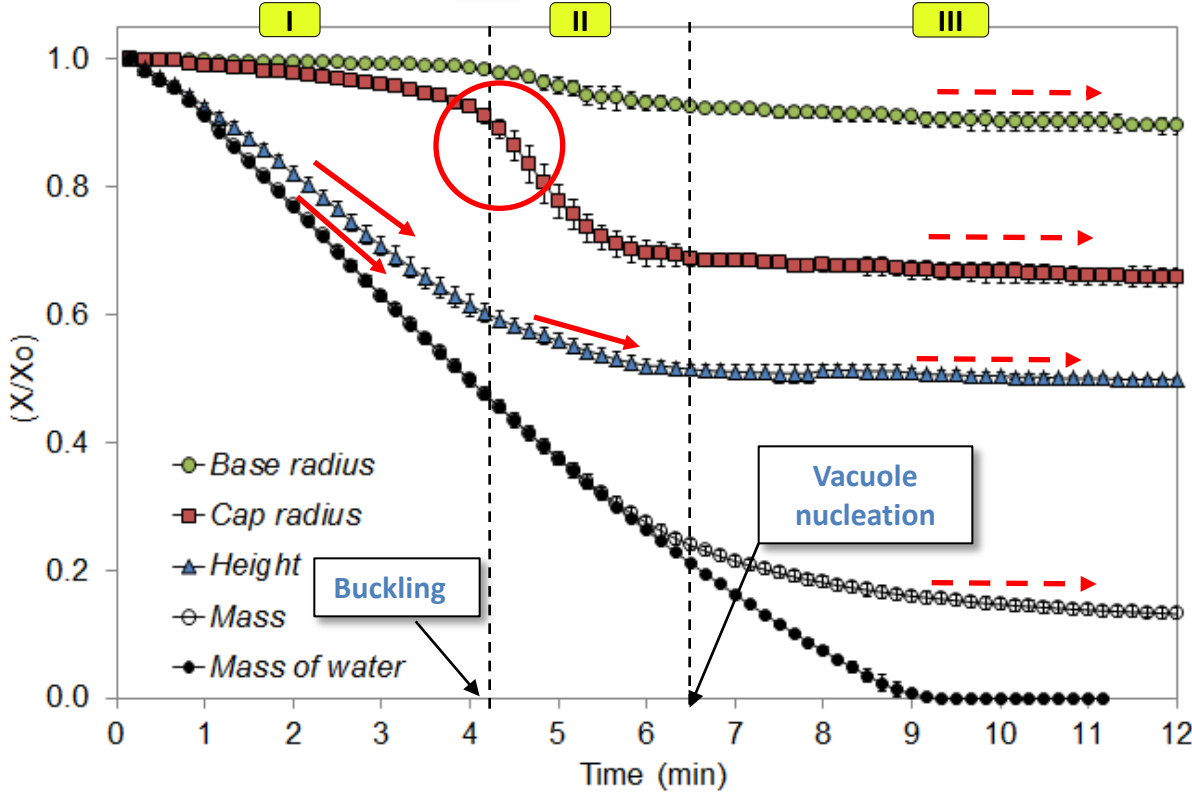
Frame rate : 1 image/30s

# Results & Discussion– Single 3D droplet

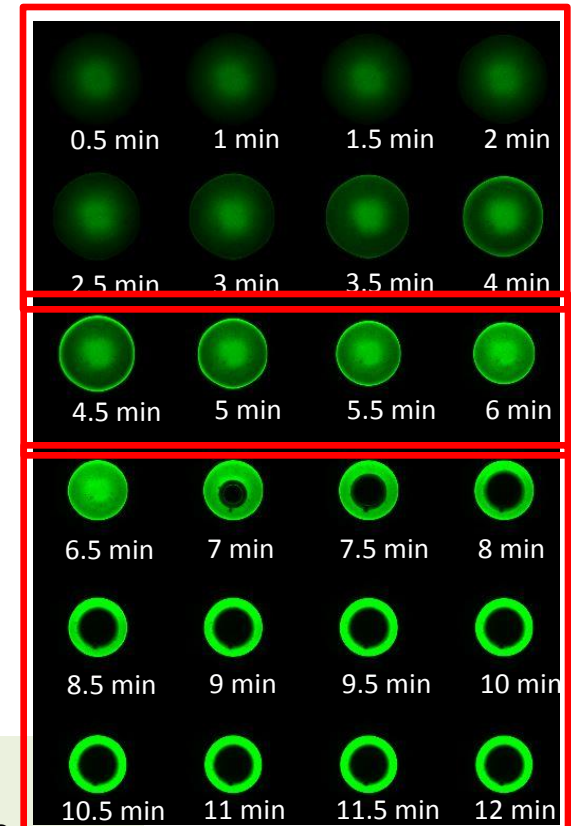
## Drying behaviour of the whey proteins



### Evolution of shape indicators and drying kinetics of a WPI droplet



### Time lapse of a WPI droplet section (z: 60μm) during drying



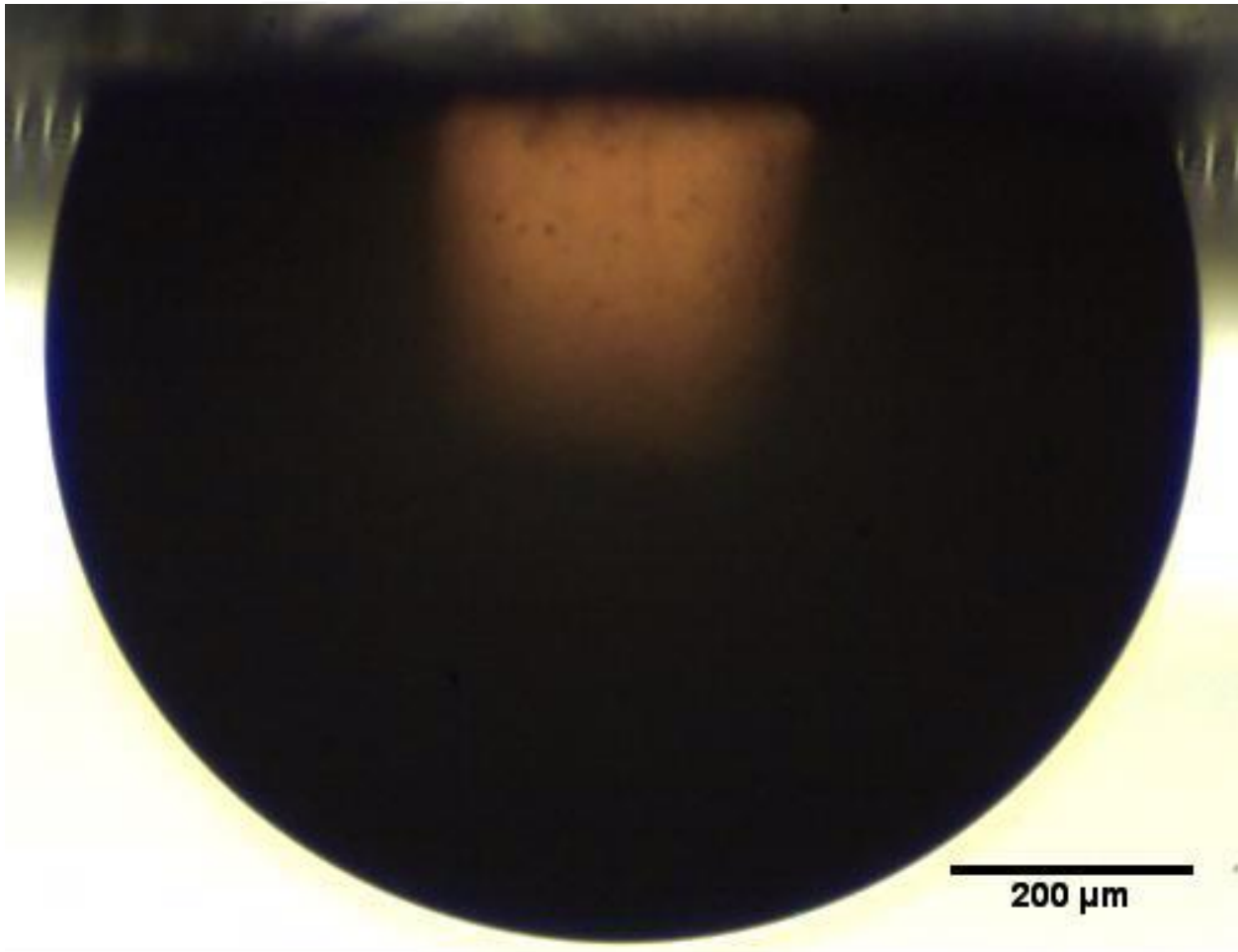
§ I : Constant shrinkage of the droplet

§ II : **Buckling instability** and a progressive **skin formation** at the surface

§ III : Maintain of the **spherical shape** and nucleation of the **internal vacuole**

# Results – Single 3D droplet

## Drying behaviour of the casein micelles proteins



### NPC droplet dynamics

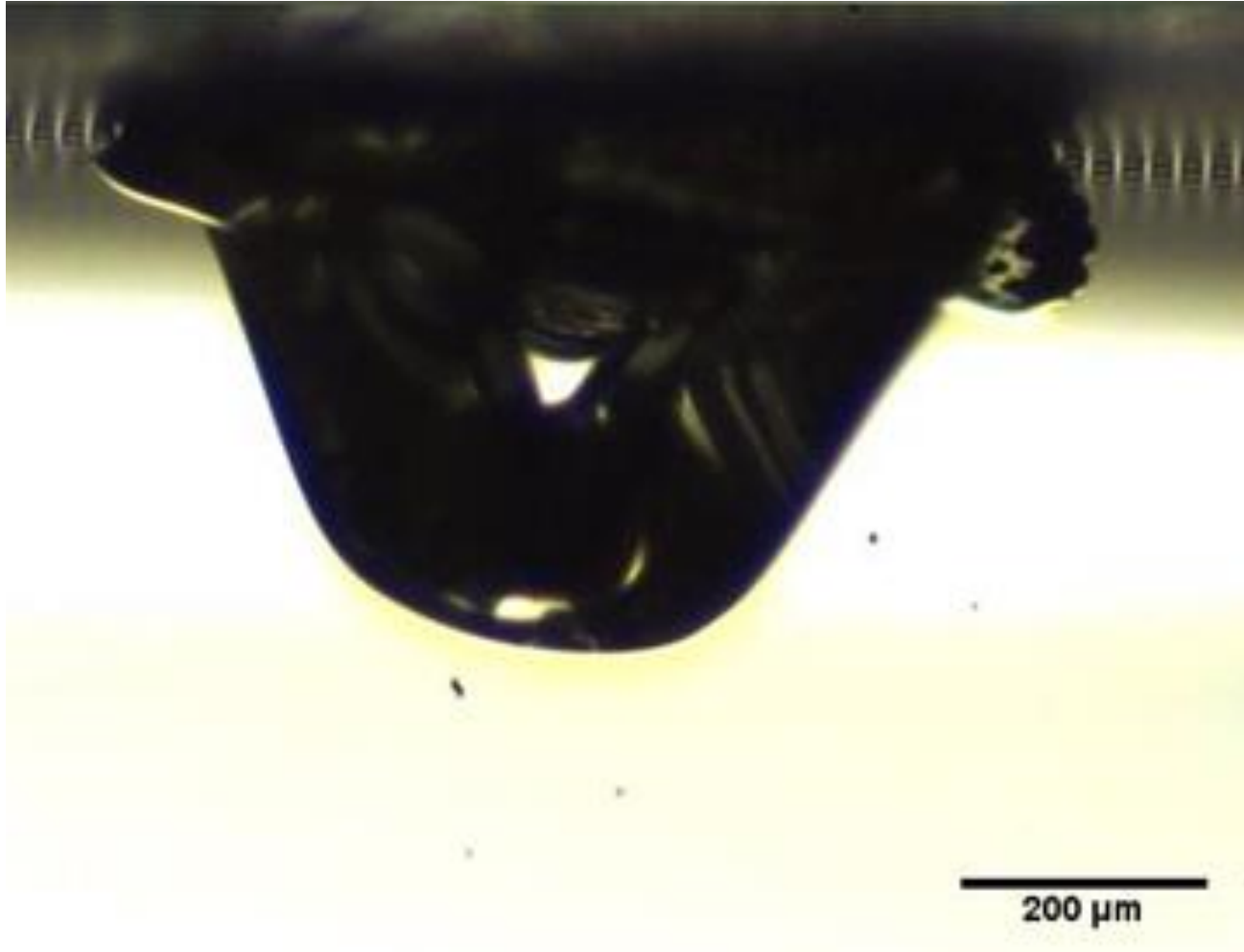
- **STAGE 1**  
Isotropic shrinkage
- **STAGE 2**  
Asymmetric / Buckling instability
- **STAGE 3**  
Invagination instability

→ Deflated particle shape

Frame rate : 1 image/30s

# Results – Single 3D droplet

## Drying behaviour of the casein micelles proteins



### NPC droplet dynamics

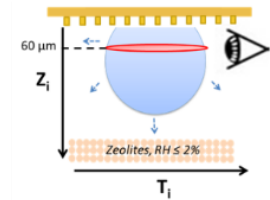
- **STAGE 1**  
Isotropic shrinkage
- **STAGE 2**  
Asymmetric / Buckling instability
- **STAGE 3**  
Invagination instability

→ **Deflated particle shape**

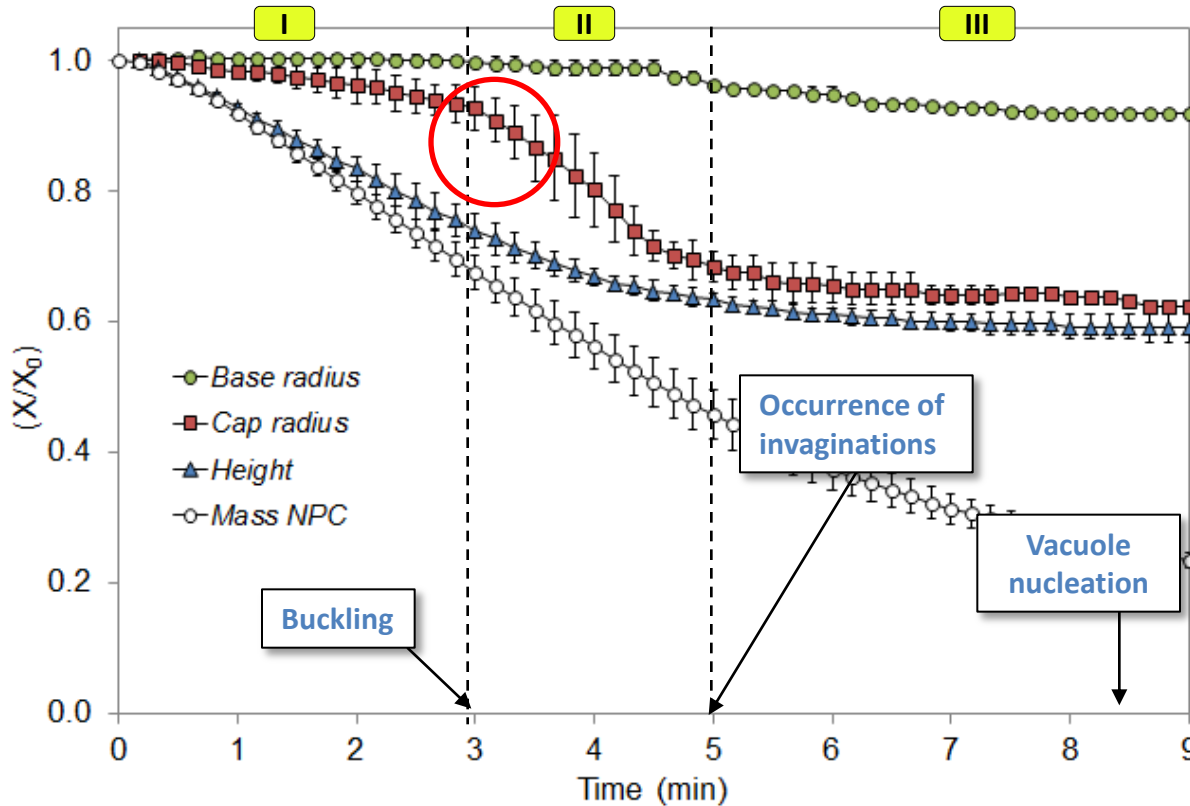
Frame rate : 1 image/30s

# Results – Single 3D droplet

## Drying behaviour of the casein micelles proteins



### Evolution of shape indicators and drying kinetics of a NPC droplet

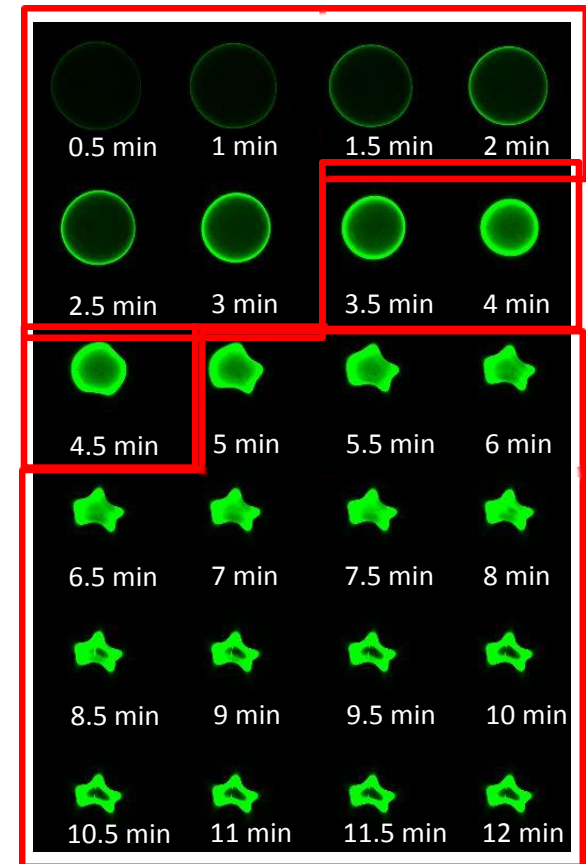


§ I : Same constant shrinkage as WPI droplet

§ II : Rheological changes at the surface appear much **earlier**

§ III : After buckling instability occurs **invagination instability**

### Time lapse of a NPC droplet section (z: 60μm) during drying

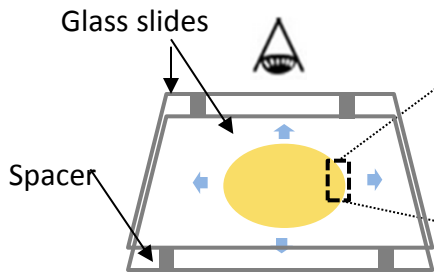


# Material & Method – Single 2D droplet

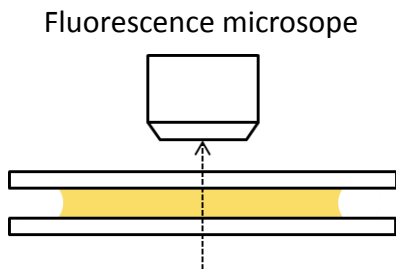
## To investigate the skin formation and mechanical properties

### Confined droplet Skin formation

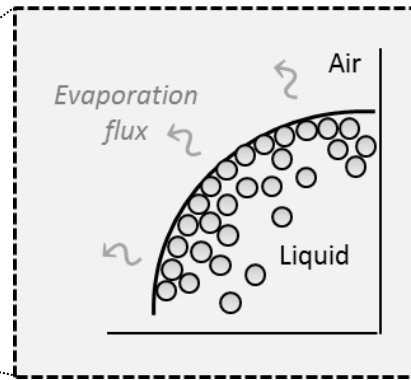
#### Top view



#### Profile view



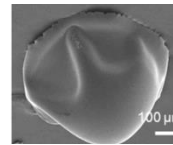
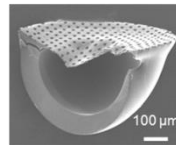
### Specific properties of protein skin-layers



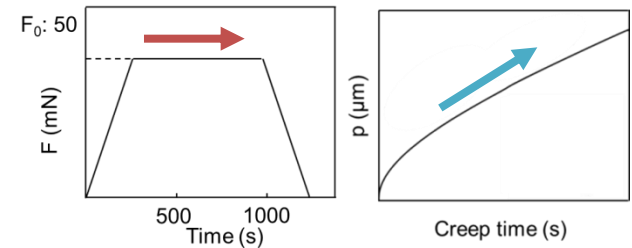
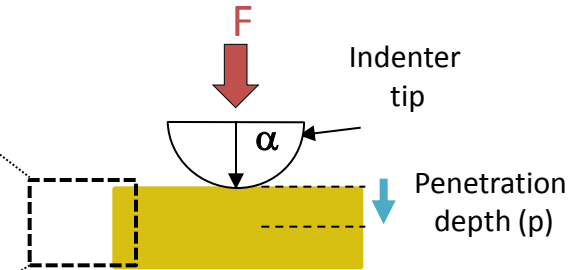
### Particle skin formation

Particle of whey proteins

Particle of casein micelles



### Micro-indentation on the final dry protein film



#### Experimental conditions:

- Temperature: 20°C
- Relative humidity: 40%

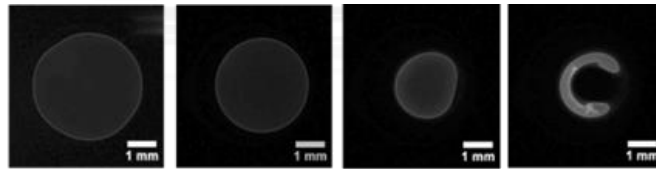


# Results – Single 2D droplet

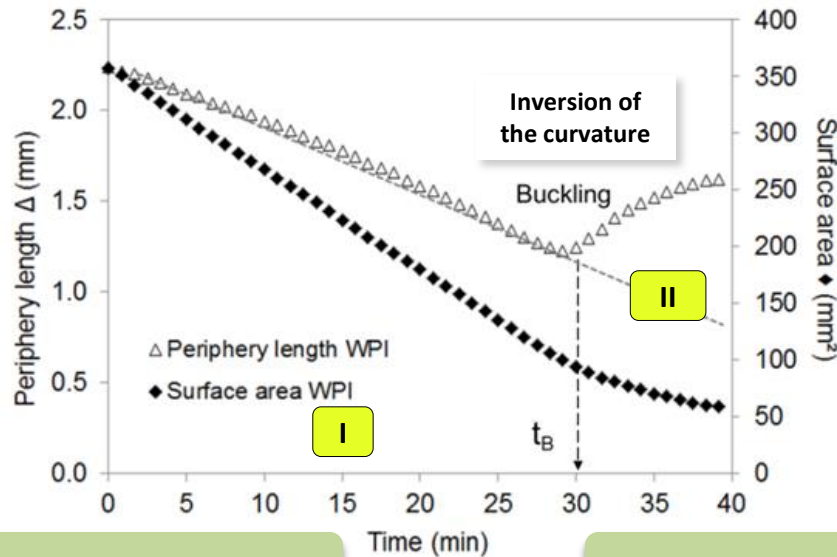
## Evolution of the shape

Periphery length and surface area as a function of evaporation time

WPI  
proteins



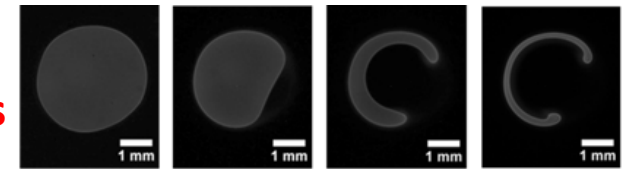
0 min    10 min    30 min    60 min



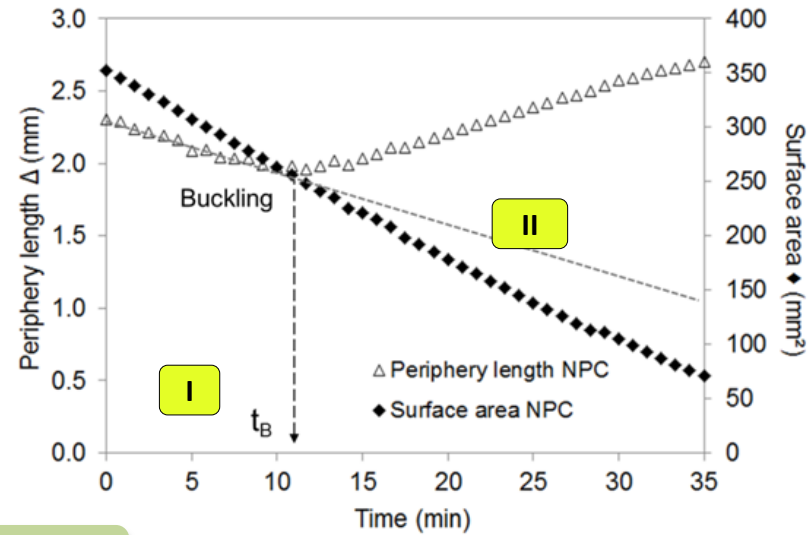
I : Isotropic shrinkage

II : Invagination deformation

NPC  
proteins



0 min    10 min    30 min    60 min



Final shape directly resulting from the drying dynamics, *ie* the protein type

- WPI: long shrinkage → small pattern which finally cracked
- NPC: early distortions with a fixed convex interface → long and thin final pattern

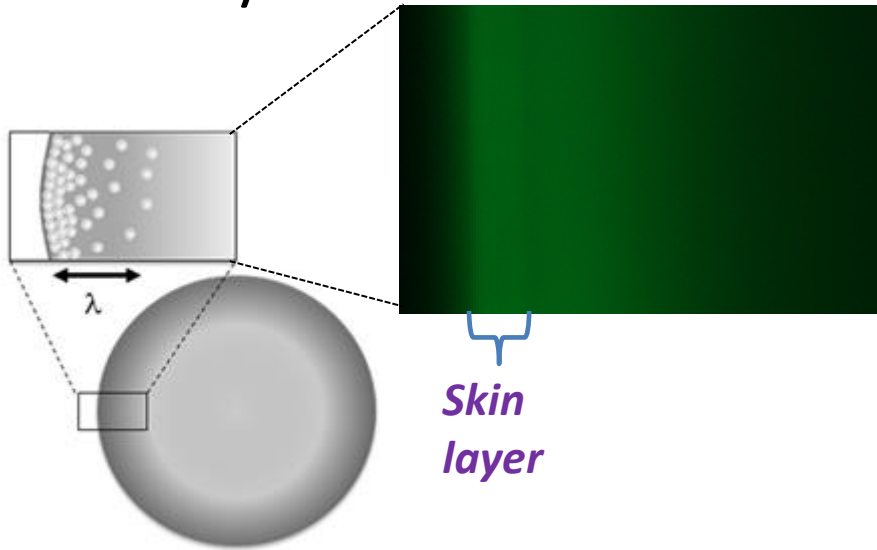


# Results – Single 2D droplet Skin formation

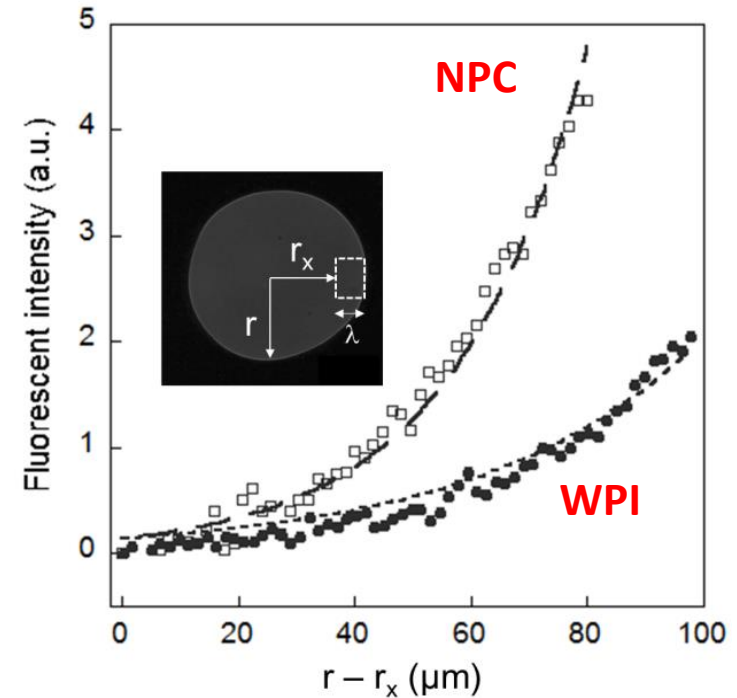
## Gradients of protein concentration near the edge of the confined droplet

### □ Diffusion length $\lambda$

$$\lambda = D / J$$



### □ Fluorescence profile



- Evaporation flux  $J$  toward the surface
- Protein accumulation at the interface
- Skin formation

# Results – Single 2D droplet Skin formation

## Gradients of protein concentration near the edge of the confined droplet

### □ Diffusion length $\lambda$

$$\lambda = D / J$$

$\lambda$ ( $\mu\text{m}$ )	
WPI	$37 \pm 0.3$
NPC	$23 \pm 0.1$



### □ Concentration at buckling / sol gel transition

	Concentration at $t_{\text{buckling}}$ ( $\text{g.L}^{-1}$ )	Published data ( $\text{g.L}^{-1}$ )	Ref
WPI	<b>414</b>	540 500 - 600	Parker et al., 2005 Brownsey et al., 2003
NPC	<b>156</b>	130 148 - 170	Bouchoux et al., 2009 Dahbi et al., 2010

Shorter diffusion length for NPC proteins

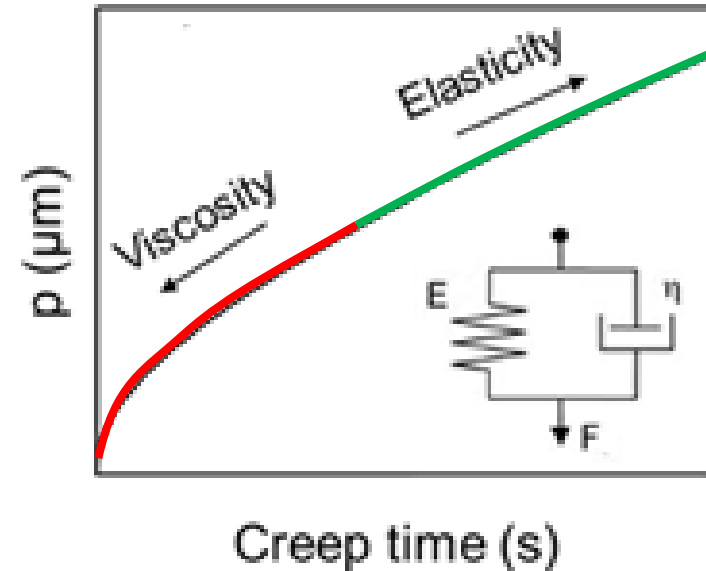
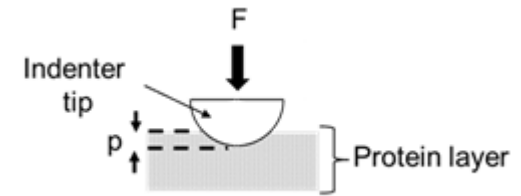
→ Lower surface concentration needed to induce buckling instability for NPC than for WPI

Buckling instability is occurring at a concentration compatible with sol-gel transition

# Results – Single 2D droplet

## Mechanical properties of WPI and NPC skin layers

	Viscosity $\eta$ (GPa.s)	Elastic modulus $E$ (GPa)	Yield stress, $\sigma_y$ (MPa)
WPI	$136 \pm 0.6$	$0.29 \pm 1.10^{-3}$	52
NPC	<b><math>238 \pm 0.3</math></b>	<b><math>0.48 \pm 6.10^{-4}</math></b>	<b>30</b>



- NPC skin is **harder and stiffer** than WPI
  - NPC **yield stress is twice lower**
- NPC material leaves earlier the linear elastic regime and reaches the plasticity well before WPI material

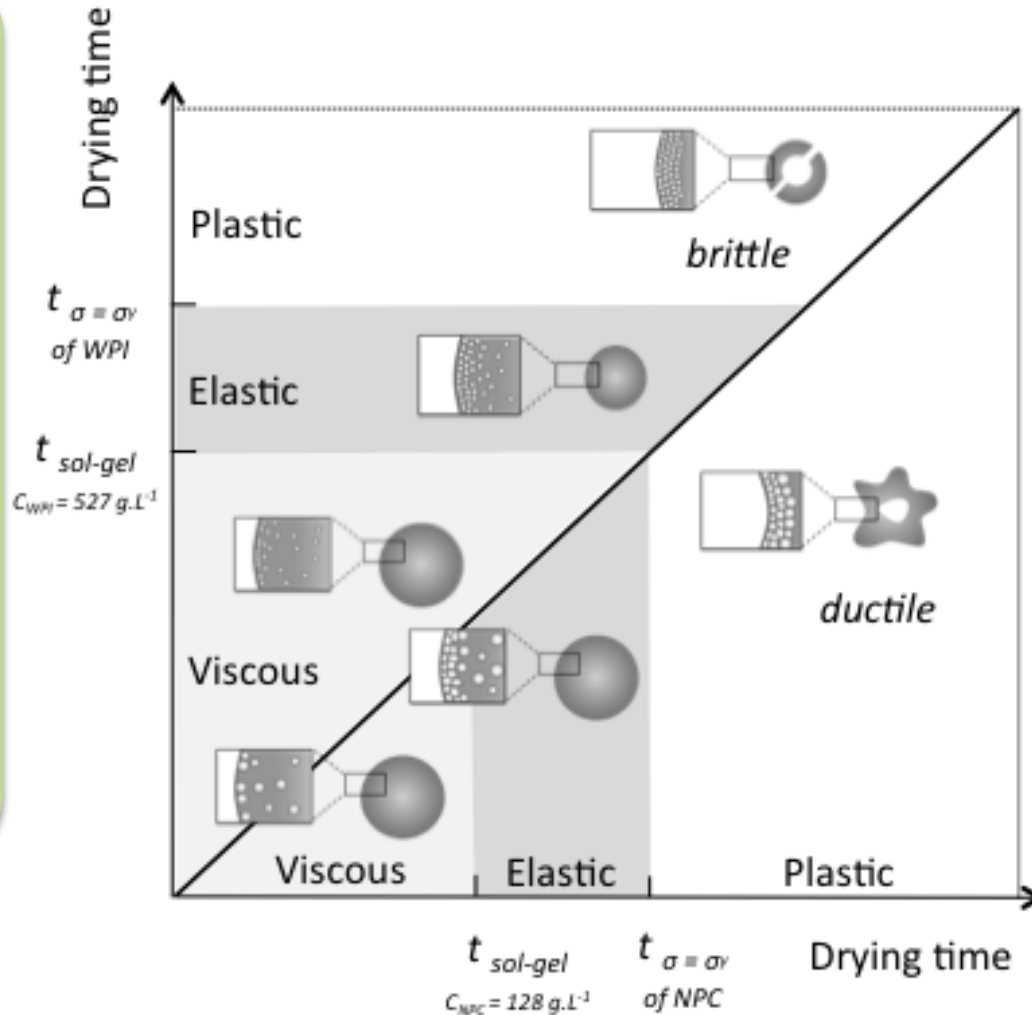
# Results & Discussion– 2D droplet

## Possible skin formation mechanisms

### WPI

- Long shrinkage ( $t_{\text{buckling}} \sim 1/2 t_{\text{drying}}$ )
- plastic state  $\rightarrow$  keeps spherical shape but cracks

**Brittle plastic material**



### NPC

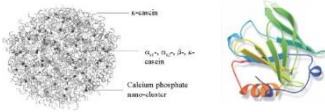
- Early gelled layer ( $t_{\text{buckling}} \sim 1/3 t_{\text{drying}}$ )
- plastic state  $\rightarrow$  surface invaginations

**Ductile plastic material**

# Strategy & Objectives

## Study of the drying process on multi-scales

### Milk proteins



Whey protein isolates (WPI)  
Micellar casein (NPC)  
Concentration: 100g.L-1  
WPI # 10nm  
NPC # 200 nm

### Single droplet 3D / 2D



### PARTICLE FORMATION

- ✓ Control and study the drying kinetics
- ✓ Record *in situ* deformation

### Powder properties

### Mono-disperse droplets



### PARTICLES PROPERTIES

- ✓ **Control** drying history
- ✓ **Get** homogenous samples
- ✓ **Analyze** physical properties

Scientific  
background

Strategy of  
work

Single  
droplet

Mono-  
disperse  
droplets

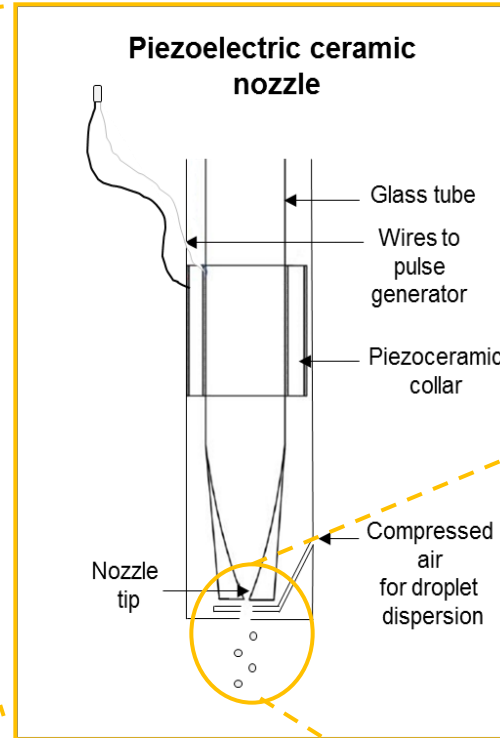
Transfer of  
knowledge

General  
conclusion

.021

# Material & Method – Mono-disperse droplets

To produce homogenous droplets having the same trajectory



- Experimental conditions:**
- $\varnothing$  nozzle : 100  $\mu\text{m}$
  - $T_{\text{int}}$  : 193  $^{\circ}\text{C}$
  - $T_{\text{out}}$  : 108  $^{\circ}\text{C}$
  - 25g of powder

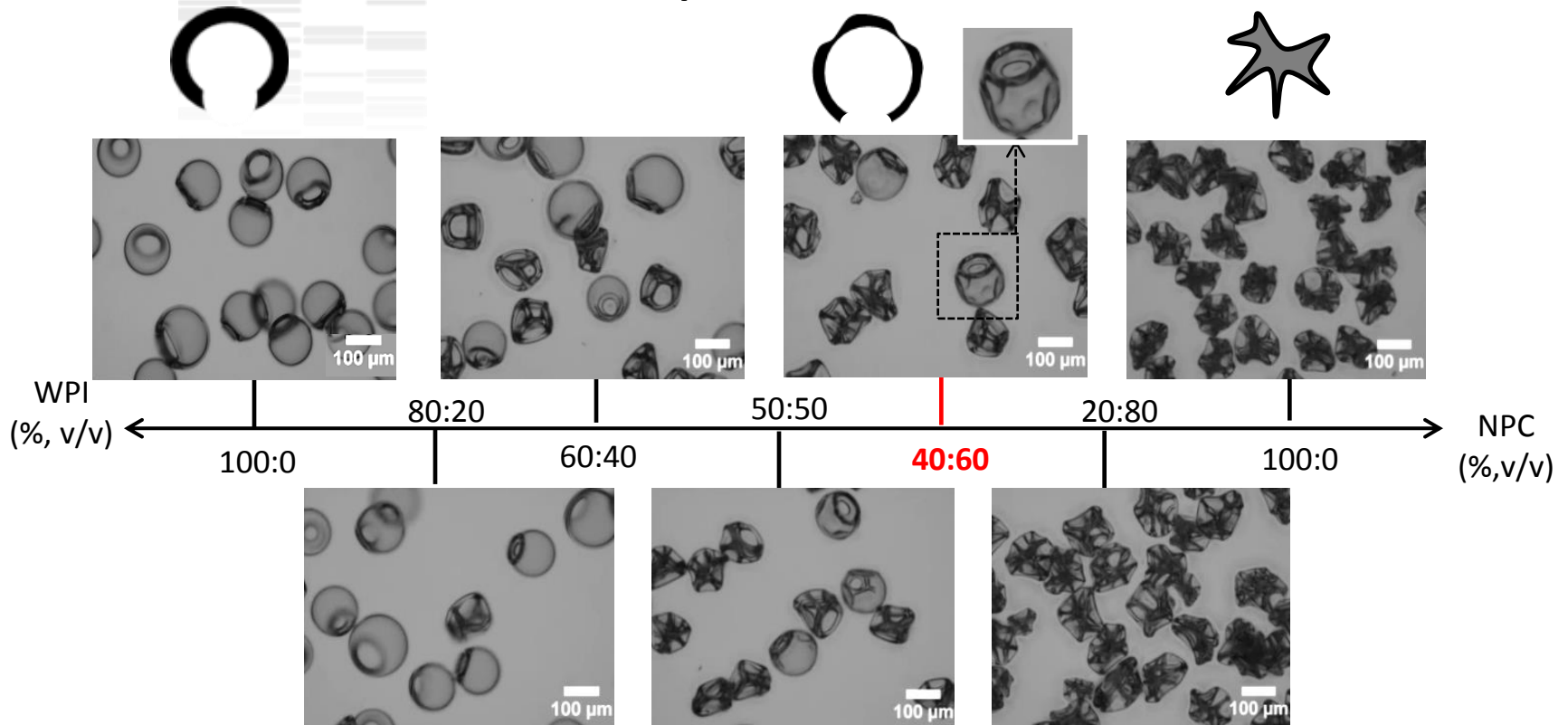


- Uniform droplets
- Same trajectory
- ➔ **Same drying history**
- ➔ **Homogeneous samples**

**MDSD-Mark II,**  
Dong-Concept New Material Technology Co.

# Results – Mono-disperse droplets

## Particle shapes of WPI:NPC mixtures



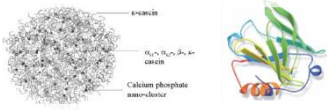
Under controlled drying parameters :

- **Specific signatures** of WPI and NPC proteins
- Different **morphological distributions of particles** according to WPI:NPC ratios
- The drying of WPI:NPC mixtures induces **three reproducible morphologies**

# Strategy & Objectives

## Study of the drying process on multi-scales

### Milk proteins



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Concentration: 100g.L-1  
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### PARTICLE FORMATION

- ✓ Control and study the drying kinetics
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## Powder properties

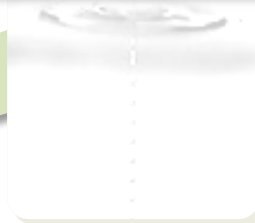
### Spraying cone of droplets



### TRANSFER OF KNOWLEDGE

- ✓ **Validate** on an industrial scale
- ✓ **Control** powder properties

### Mono-disperse droplets



### PARTICLES PROPERTIES

- ✓ **Control** drying history
- ✓ **Get** homogenous samples
- ✓ **Analyze** physical properties



# Material & Method – Spraying cone of droplets

To validate on an industrial scale and transfer of knowledge



## TRANSFER OF KNOWLEDGE

- ✓ **Validate** on an industrial scale
- ✓ **Optimization** of formula
- ✓ **Control** product quality



### Experimental conditions:

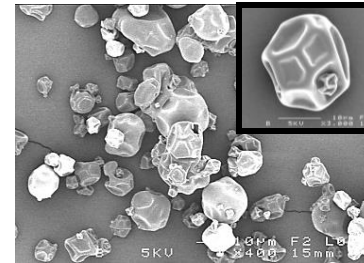
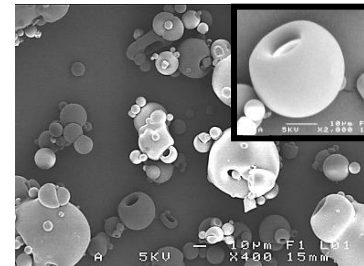
- $\varnothing$  droplets : 10-500  $\mu\text{m}$
- $T_{\text{int}}$  : 210 °C
- 30-80 kg/h of powder

# Transfer of knowledge

## Signature of milk proteins at multi-scale



Spraying cone  
of droplets



Whey protein  
Isolates  
(WPI)

Casein  
Micelles  
(NPC)

### Drying kinetics

Particle Size

500 µm

140 µm

42-56 µm

Drying temperature

20 °C

190 °C

210 °C

→ ~1 s

Quantity

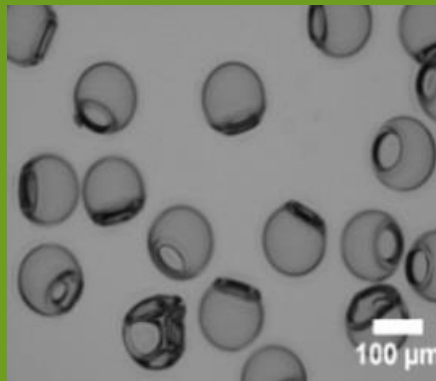
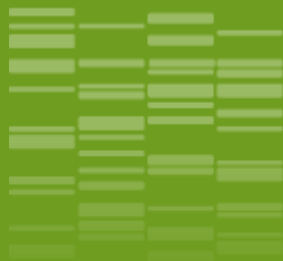
1 particle

~ g  
of particles

~ kg  
of particles

# Conclusions - Studying the drying of milk proteins on multi-scales

- ❑ The protein kind influences the **drying dynamics** of the single droplet
  - ❑ The **skin formation** is marked by a buckling instability at **sol-gel transition**
  - ❑ The **mechanical properties** of the skin **condition the final particle shape**
- ❑ Under controlled spray drying conditions
  - ❑ **Specific signatures** of WPI and NPC
  - ❑ **Morphological distribution** depending on **WPI:NPC ratio**
  - ❑ *Future insight on the hybrid shape at 40:60 WPI:NPC ratio*
- ❑ Interest of a **single droplet approach** of the spray drying
  - ❑ Gain in knowledge about the **skin and particle formation** → **control the particle properties**
  - ❑ *Future outlook on model colloids / coupling with micro-indentation*
    - *Permeability of the skin*
    - *Drying modelling and prediction*



*Merci*

*Thank you for your attention*



#### More information

- Sadek et al., 2013, [Langmuir](#), **29**, 15606-15613
- Sadek et al., 2014. [Drying Technol](#),**32**, 1540-1551
- Sadek et al., 2014, [Dairy Sci Technol](#), **95**, 771-794
- Sadek et al., 2015, [Food Hydrocolloids](#), **48**, 8-16
- Sadek et al., 2016, [Food Hydrocolloids](#), **52**, 161-166



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