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Mechanisms of drying-induced particle formation in solutions of dairy proteins: a multiscale approach

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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
Controlling dairy powders properties

**Surface properties**
- Sticking & caking (Glass transition, Hygroscopicity)

**Particle physical properties**
- Rehydration (Surface composition & structure, Size, Porosity)
- Packing (Density, occluded & interstitial air, size distribution)

**Molecular structure**
- Nutritional properties (Denaturation / aggregation rate, etc.)

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**Functional properties** = \( f \) (particle intrinsic properties)

*Insight on particle formation*

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

**Spray drying**
- Drying phenomenon: Hot air (Seconds)
- Formulation and process parameters
- MECHANISMS?
- Particle formation?
- Powder properties

**LIMITS on an industrial scale:**
- Fast drying kinetics
- Heterogeneity of samples
- Complexity of equipment
- Complexity of formula
- Costs of large scale trials

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**INRA SCIENCE & IMPACT**
How does the droplet become a dry particle?

### Strategy of the work: question of research

#### Scientific background

- **New strategy**

#### Strategy

- **Study of the drying of simplified droplet systems**
  - Mimic drying phenomenon with different experimental setups
  - Variation of drying kinetics and volumes

#### Results

- **Conclusion**

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### Strategy of the work: innovate points of the strategy

**→ Simplifying the dairy matrix**

**Study the drying behavior of milk proteins**

- **Whey proteins**
  - Globular structure, $D \approx 10^{-20}$ nm
  - Reconstituted from *WP powder* (Whey Protein)

- **Casein micelles**
  - Micellar, dynamic and hydrated structure, $D \approx 10^{-2}$ nm
  - Reconstituted from *NPC powder* (Native PhosphoCaseinates)

**→ Study of the drying of simplified droplet systems**

- **Holt & Horne, 1996**
- **Bouchoux, 2010**

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Yorke, 2012

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INRA SCIENCE & IMPACT
Experimental strategy: a multiscale approach

- To what extent is the formation of particles affected by the protein material and the drying parameters?

- From the mechanical properties of the protein material?

- What is the impact of particle morphology on powder functionalities?

Milk proteins

- Single or mixture
- C = 100 g.L⁻¹

Signature of milk proteins at multi-scale

Whey protein (WP)

Casein Micelles (NPC)

Drying kinetics

Particle Size

- 500 µm
- 140 µm
- 42-56 µm

Drying temperature

- 20°C
- 190°C
- 210°C

Quantity

- 1 particle
- ~ g of particles
- ~ kg of particles

Spraying cone of droplets
Experimental strategy: Skin formation / confined droplet

- Quality of industrial powder
- Spraying cone of droplets
- Skin formation
- Confined droplet

Milk proteins:
- Single or mixture
- C = 100 g.L⁻¹

How much do the final physical properties of the particles result from the mechanical properties of the protein material?

Scientific background | Strategy | Results | Conclusion

Confined droplet: investigation of the skin formation

- Confined droplet: Skin formation
- Specific properties of protein skin-layers
- Micro-indentation: Mechanical properties

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

Top view:
- Glass slides
- Spacer

Profil view:
- Fluorescence microscope

Particle morphology:
- Particle of whey proteins
- Particle of casein micelles

Micro-indentation:
- Indenter tip
- Penetration depth (p)

Graphs:
- Force (F) vs. penetration depth (p)
- Time vs. force (F)
- Creep time (s)

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Periphery length / surface area as a function of evaporation time

- **Two drying stages**: § I. isotropic shrinkage, § II. Droplet deformation (buckling)
- Buckling event occurs at different drying kinetics
- **Final shape directly results from the drying dynamics, ie the protein type**
  - WP: long shrinkage ➔ small pattern which finally fracture
  - NPC: early buckling with a fixed convex interface ➔ long and thin final pattern

Sol gel transition / mechanical properties of WP & NPC skin layers

- **Estimation of the concentration at the buckling time**

<table>
<thead>
<tr>
<th></th>
<th>Concentration at $t_{\text{buckling}}$ (g.L$^{-1}$)</th>
<th>Concentrations published at sol-gel transition (g.L$^{-1}$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>WP</td>
<td>414</td>
<td>540</td>
<td>Parker et al., 2005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500 - 600</td>
<td>Brownsey et al., 2003</td>
</tr>
<tr>
<td>NPC</td>
<td>156</td>
<td>130</td>
<td>Bouchoux et al., 2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>148 - 170</td>
<td>Dahbi et al., 2010</td>
</tr>
</tbody>
</table>

- **At the interface**: buckling instability is occurring at a concentration compatible with sol-gel transition

<table>
<thead>
<tr>
<th></th>
<th>Viscosity, $\eta$ (GPa.s)</th>
<th>Young’s modulus, $E$ (GPa)</th>
<th>$\frac{\eta}{E}$ (s)</th>
<th>Yield stress, $\sigma_y$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WP</td>
<td>$136 \pm 0.6$</td>
<td>$0.29 \pm 1.1 \times 10^{-2}$</td>
<td>$469 \pm 0.6$</td>
<td>52</td>
</tr>
<tr>
<td>NPC</td>
<td>$238 \pm 0.3$</td>
<td>$0.48 \pm 6 \times 10^{-4}$</td>
<td>$496 \pm 0.3$</td>
<td>30</td>
</tr>
</tbody>
</table>

- Viscous effect more pronounced for casein micelle material
- Casein micelle skin reaches the plasticity well before whey protein material
Possible skin formation mechanisms

WP
- Long shrinkage ($t_{buckling} \sim \frac{1}{2} t_{drying}$)
- Plastic state $\rightarrow$ keeps spherical shape but cracks

Brittle plastic material

NPC
- Early gelled layer ($t_{buckling} \sim \frac{1}{3} t_{drying}$)
- Plastic state $\rightarrow$ surface invaginations

Ductile plastic material

Signature of milk proteins

Whatever the drying kinetics, same morphological behavior
- Specific signatures of WP and NPC proteins on the particle formation
- Different kinds of drying behavior
  - Whey proteins = brittle material
  - Casein micelles = ductile material

To what extent is the formation of particles affected by the protein material and its mechanical properties?

Studying model colloidal solutions for understanding more complicated biological systems
Experimental strategy: use of model colloids

Can model colloids contribute to the better understanding of the physical mechanisms taking place throughout the evaporation of droplets of milk colloids?

Coupling cracks dynamics and micro-indentation

Investigation of mechanical behaviors

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

Milk proteins

- Single or mixture
- C = 100 g.L⁻¹

Specific properties of protein skin-layers

Micro-indentation

Mechanical properties

- Indenter tip
- Penetration depth (p)
- F (mN)
- Time (s)
- Creep time (s)
Drying behavior of milk proteins and colloidal systems

- **Whey proteins**
  - Globular structure, $D \approx 10-20 \text{ nm}$
  - Reconstituted from **WP powder** (Whey Proteins, 100 g.L$^{-1}$)

- **Casein micelles**
  - Micellar, dynamic, hydrated structure, $D \approx 10^2 \text{ nm}$
  - Reconstituted from **NPC powder** (Native PhosphoCaseinates, 100 g.L$^{-1}$)

- **Dispersion of silica colloidal particles**
  - Ludox TM50: $\varnothing = 22 \text{ nm} \pm 2$
  - (weight fraction in silica particles = 0.40)

- **Polymer chains on TM particles**
  - Ludox TM50 + PVP (40kDa)
  - (weight concentration of PVP = 0.1%)
  - PVP owns high affinity for silica surfaces

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Drying process of sessile drops (WP / TM50)

**Experimental conditions:**
- Temperature: 20°C
- Relative humidity: 40%
- Initial contact angle: 31° ± 2°
- $2 R_0 = 8 \text{ mm}$
- Evaporation rate: $8.10^{-8} \text{ m.s}^{-1}$

**Comparable behavior**

Formation of radial fractures in the solid periphery
Crack dynamics and delay time before cracking

Similar time evolution of the drying front location obtained for WP and TM50

Similar statistics of duration elapsed before crack propagation:
- 334 ± 41 s for WP
- 311 ± 61 s for TM50

Drying process of sessile drops (NPC / TM50 + PVP)

Experimental conditions:
- Temperature: 20°C
- Relative humidity: 40%
- Initial contact angle: 35 ± 2°
- 2 R₀ = 8 mm
- Evaporation rate: 8.10⁻⁸ m.s⁻¹

Comparable behavior
Later nucleation of a few, random fractures
Crack dynamics and delay time before cracking

Similar time evolution of the drying front location obtained for NPC and TM50 + PVP

Similar statistics of duration elapsed before crack propagation:
- $834 \pm 50$ s for NPC
- $855 \pm 40$ s for TM50

Mechanical behavior & viscoelastic relaxation time

<table>
<thead>
<tr>
<th></th>
<th>Viscosity $\eta$ (GPa.s)</th>
<th>Elastic modulus $E_2$ (GPa)</th>
<th>Viscoelastic relaxation time, $t_\eta$(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WP</td>
<td>99 ± 5</td>
<td>$3.50 \pm 1.10^{-3}$</td>
<td>28 ± 2</td>
</tr>
<tr>
<td>TM50</td>
<td>82 ± 5</td>
<td>$3.20 \pm 1.10^{-3}$</td>
<td>26 ± 2</td>
</tr>
<tr>
<td>NPC</td>
<td>119 ± 5</td>
<td>$0.96 \pm 1.10^{-3}$</td>
<td>124 ± 5</td>
</tr>
<tr>
<td>TM50 + PVP</td>
<td>115 ± 5</td>
<td>$0.98 \pm 1.10^{-3}$</td>
<td>129 ± 5</td>
</tr>
</tbody>
</table>

- Penetration depth deeper for NPC and TM50 + PVP than for WP layer and TM50
- Values of viscoelastic relaxation time are similar between WP / TM50 and NPC / TM50 + PVP
Conclusion: How does the droplet become a dry particle?

- The protein kind influences the **drying dynamics** of the single droplet under controlled spray drying conditions
  - The **skin formation** originates from a buckling instability at sol-gel transition
  - The **mechanical properties** of the skin condition the final particle shape
  - **Specific signatures** of WP and NPC
- Interest of the approach with **model colloidal solutions**
  - Numerous analogies between dairy and the corresponding model systems

OUTLOOK

Gathering conceptual tools of the physical chemistry of interfaces and the physics of soft matter

- What about the permeability of the skin?
- What about the evaporation in a binary colloidal solution?
- What is the impact of the WP/NPC ratio on the onset of sol-gel transition and skin formation mechanisms?
- Is the skin representative of the bulk composition?
Gradients of protein concentration near the edge of the droplet

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

**Diffusion length $\lambda$**

$$\lambda = \frac{D}{J}$$

**Fluorescence profile**

More information
- Sadek et al., 2014, *Drying Technol*, 32, 1540-1551
- Sadek et al., 2015, *Food Hydrocolloids*, 48, 8-16
- Sadek et al., 2016, *Food Hydrocolloids*, 52, 161-166

Thank you for your attention
**Drying stress and poro-elasticity**

- **Drying stress at the film/air interface:**
  \[ \sigma(z = h) \sim \frac{E t}{t_D} \]
  where \( t_D \) is the evaporation timescale \( (h/V_E) \)

- **Max stress leading to crack when:**
  \[ \sigma(z = h) \approx -P_{cap} \approx 5 \frac{\gamma_{air/water}}{r_{pore}} \]

Hypothesis: delay time before stress reaches max stress: **viscoelastic timescale** \( t_\eta \)

\[ \frac{E t_\eta}{t_D} \approx: 5 \frac{\gamma_{air/water}}{r_{pore}} \Rightarrow r_{pore} \]

 estimation of the pore size in the solid state: \( r_{pore\ (WP)} / r_{pore\ (NPC)} \sim 2 \)

**Results in concordance with drying behavior:**

NPC more deformable than WP

---

**Thickness of PVP Coating**

- **Average value of ~ 8 nm for thickness of the PVP shell**

  In accordance with Yu et al. (2017, 2018) but without a clearly core-shell structure

- **Ellipsometry measurements**

  Thickness of the PVP coating ~ 65 nm (whole structure including the possible PVP core–shell and the outer polydisperse polymer brush)