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Structural organization and behaviour of casein micelles fouling layer during crossflow filtration of milk at low temperature: A Small-Angle X-Ray Scattering (SAXS), osmotic stress and rheology study

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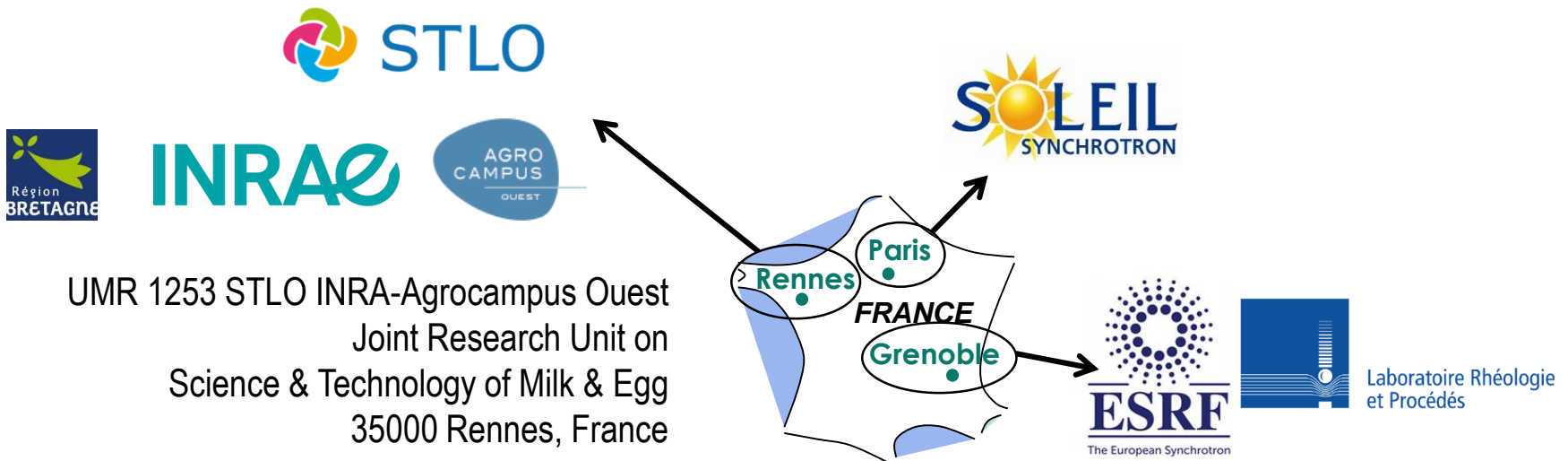
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Structural organization and behaviour of casein micelles fouling layer during crossflow filtration of milk at low temperature

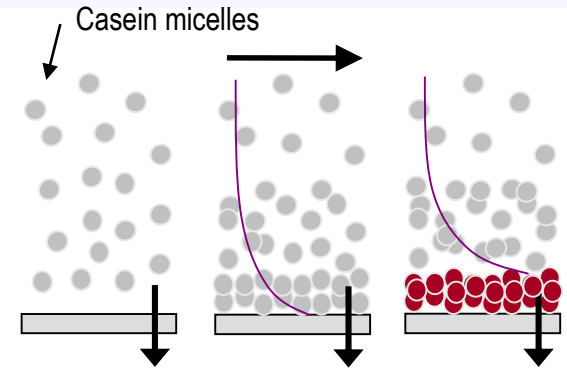
A Small-Angle X-Ray Scattering (SAXS), osmotic stress and rheology study

F. Doudiès, M. Loginov, F. Lambrouin-Garnier, N. Leconte,
N. Hengl, F. Pignon, J. Perez, **G. Gésan-Guiziu**



The skimmed milk filtration (UF & MF)

- Fouling predominantly occurs at the membrane surface
- Casein micelles = main contributor to membrane deposit
- The structure and properties of the casein micelles deposit govern the performance of the filtration



Gésan-Guiziou *et al.*, 1999, 2000

2 options

Ceramic membranes
50-53°C



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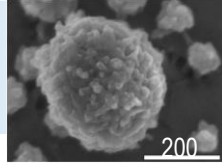
Investment
Running costs
Productivity (recovery,
purity of fractions)
Cleaning / disinfection

Polymeric spiral wound
membranes 7-12°C



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-
-

Casein micelles



SEM Image
(Dalglish, IDJ, 2004)

- Milk proteins = 80% of caseins (25 g/L)
- Composition
 - caseins** : α_{s1} , α_{s2} , β , κ (3:1:3:1)
 - minerals** : phosphate and calcium (nanoclusters)

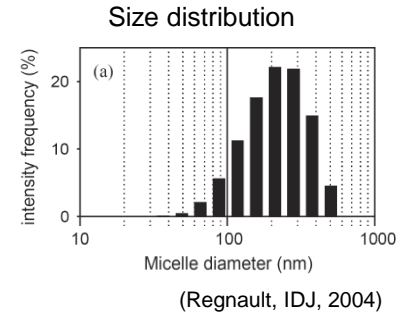
- Globular colloid

Diameter ~ 50 -500 nm (average 200 nm)

Highly deformable and hydrated structure: voluminosity 4.4 mL/g (3.7g water / g protein)

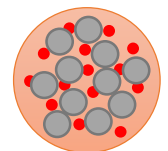
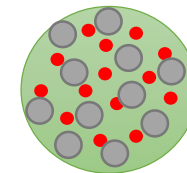
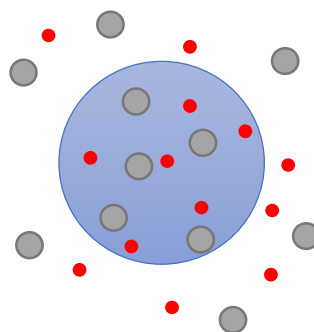
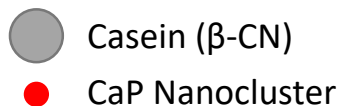
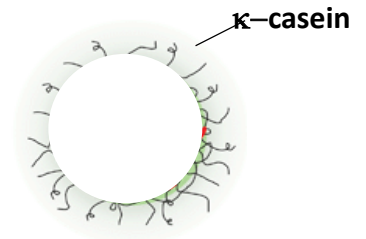
Surface: polyelectrolyte brush κ - casein

Content in equilibrium with the aqueous phase



- Properties =f(temperature)

	7 - 12 °C	20 - 25 °C	40 - 50 °C
Hydrophobic Interactions (release of Casein (β -CN))	-	+	++
Nanoclusters CaP	-	+	++
Hydration (++ internal repulsion)	+	-	--
Diameter -Voluminosity	+	-	--



Sol/gel transition
~170-180 g/L

- What are the structural organization and behavior of concentrated casein micelles at low temperature (7-12°C compared to ambient T) ?
- What are the consequences for casein micelle deposit ?

Strategy

Ex-situ characterization of concentrated dispersion in **isotropic** conditions

Colloidal interactions, compressibility,
Sol-gel transition
Cohesiveness and reversibility



Condensed phase



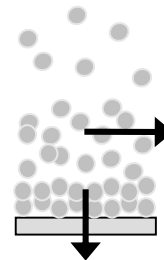
Dispersed phase



Osmotic stress
Rheology

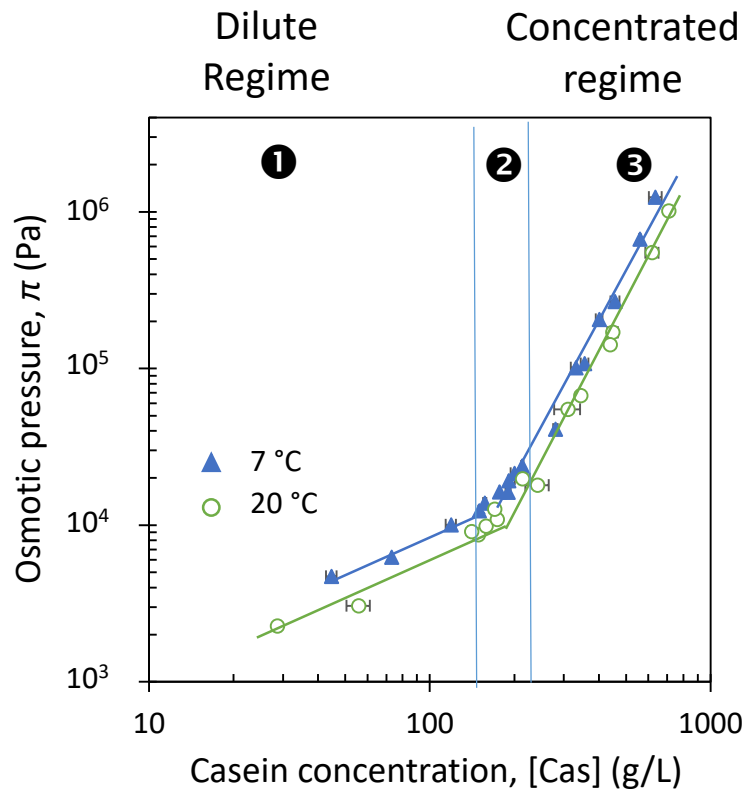
In-situ characterization of accumulated layers at nano-microscopic scale in **anisotropic** conditions

Concentration profile
Accumulated mass
Thickness of accumulated layers and deposit (gel)
Cohesiveness (relaxation) of accumulated layers

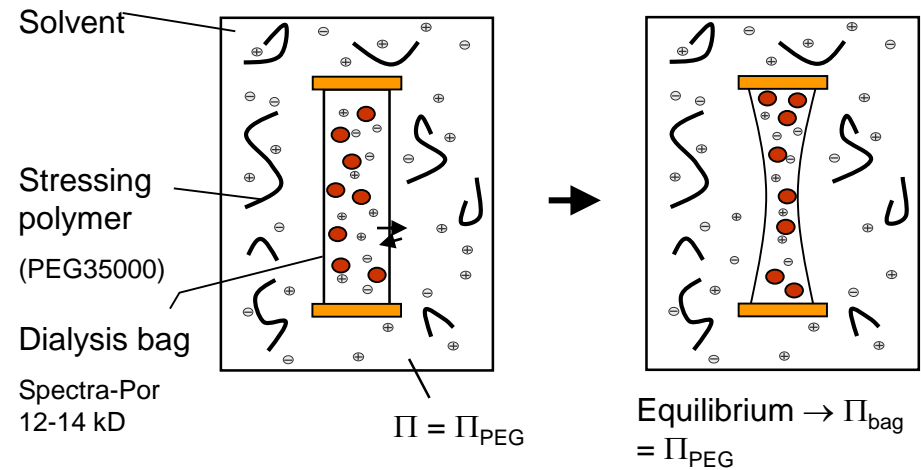


SAXS

Material : Casein micelles dispersions in native aqueous phase of milk (ultrafiltrate)

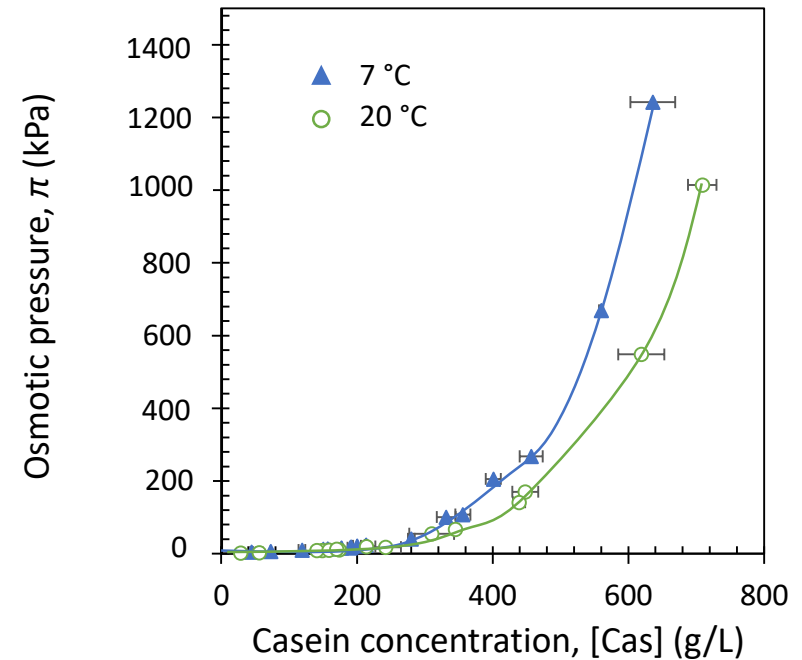
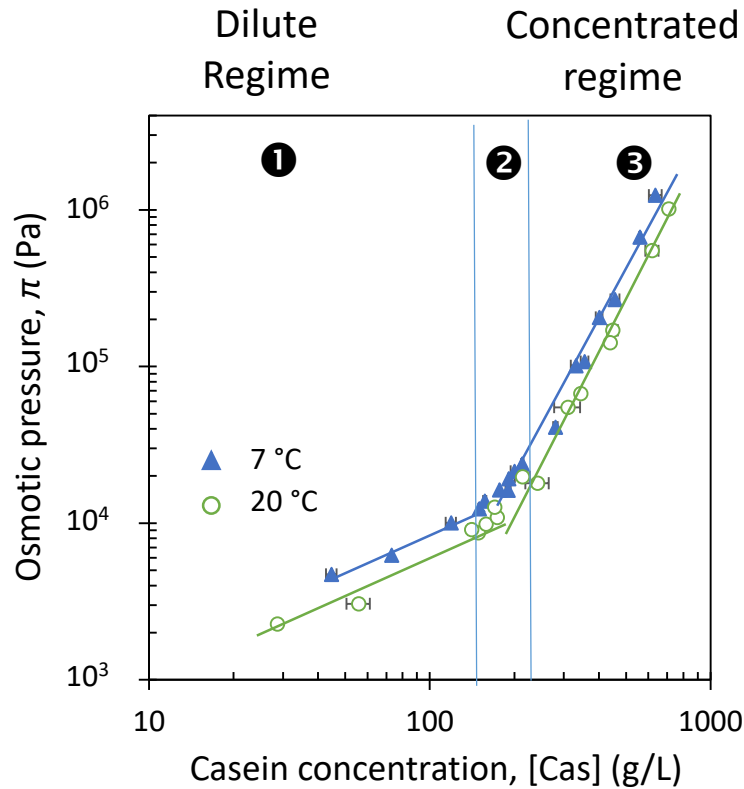


Osmotic stress technique



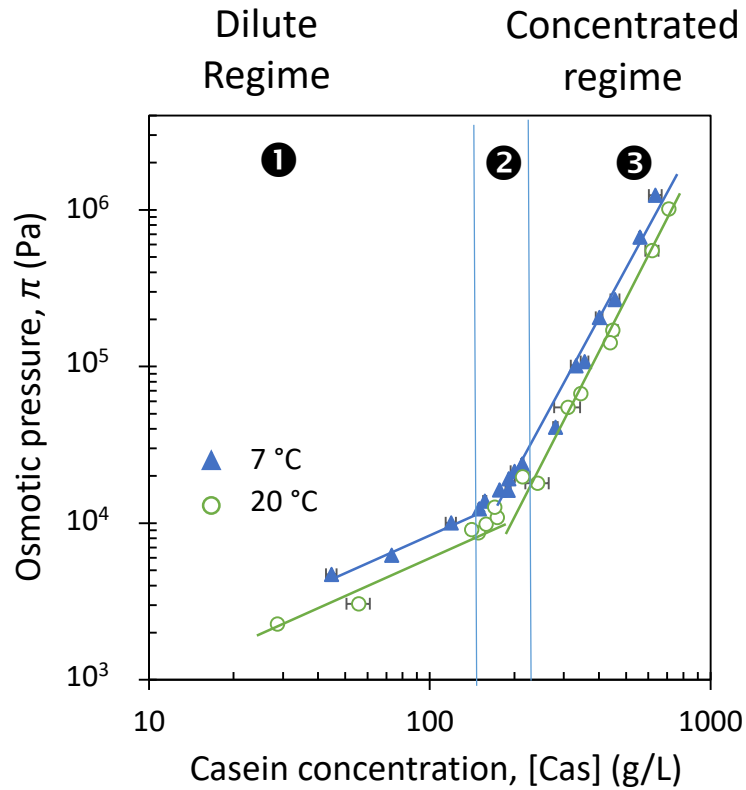
3 regimes of compression

- . Dilute regime ① -> No direct interactions
- . Transition regime ② -> Inter-micellar interactions
- . Concentrated regime ③ -> Intra-micellar interactions



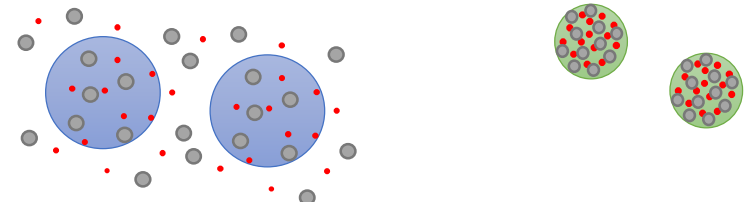
3 regimes of compression

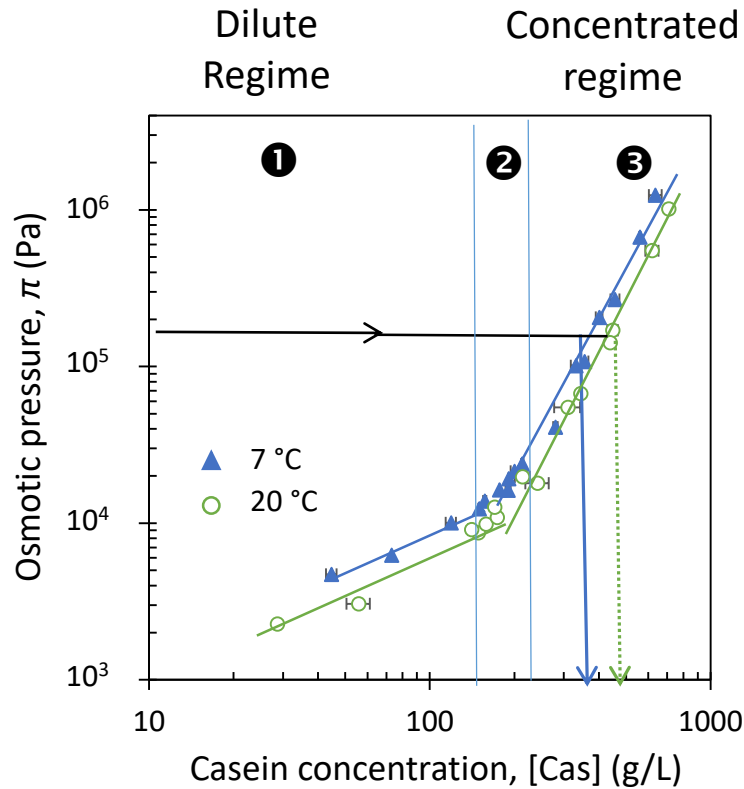
- . Dilute regime ① -> No direct interactions
- . Transition regime ② -> Inter-micellar interactions
- . Concentrated regime ③ -> Intra-micellar interactions



Diluted regime

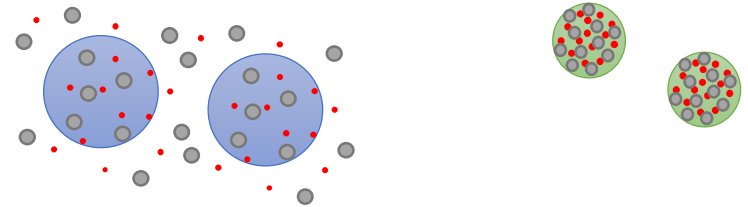
Number of particles, Van't Hoff law $\pi = RT \sum C_i$





Diluted regime

Number of particles, Van't Hoff law $\pi = RT\Sigma C_i$



Dense regime:

Higher hydration & repulsions inside the micelles



For a given value of π : $[\text{casein}]_{7^\circ\text{C}} < [\text{casein}]_{20^\circ\text{C}}$

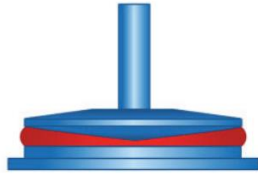
→ Casein micelle is less compressible at 7°C than at 20°C

Rheology

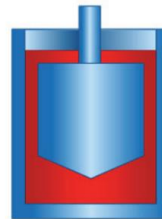
Concentrations [Cas] = 100 – 350 g/L

Rheological properties : flow and oscillatory experiments

Liquids : steady shear viscosities

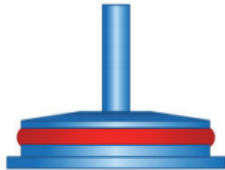


Cone-plate geometry
Diamètre 25 mm – Angle 2°
(DRH2 Rheometer)



Couette Geometry
inner-outer radii = 0.5mm
(Low Shear 400 Viscosimeter)

Gels : oscillatory experiment

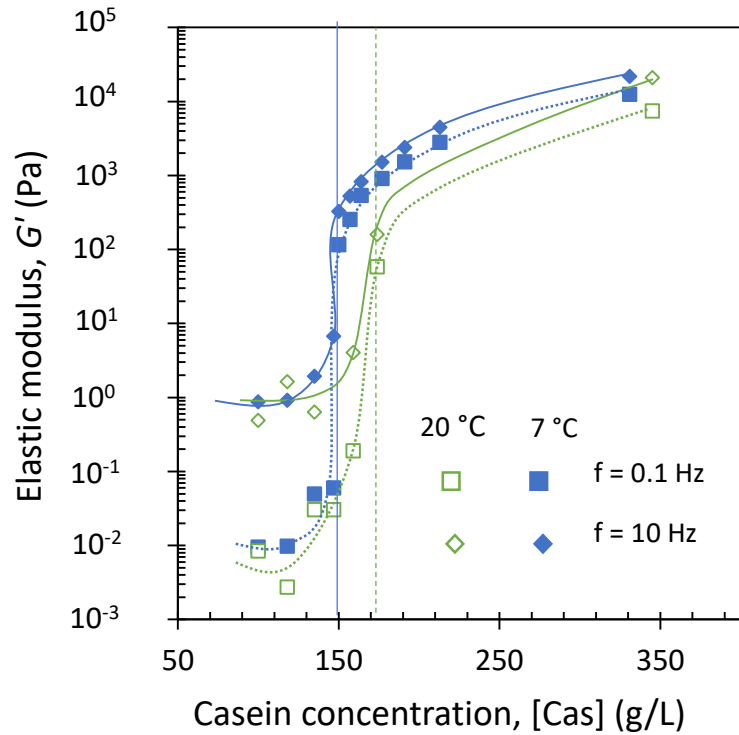


Cone-plate geometry
Parallel plated with grooved surfaces – diameter 20 mm
Gel thickness: 4 mm
(DRH2 Rheometer)



Elastic modulus G'
Loss modulus G''

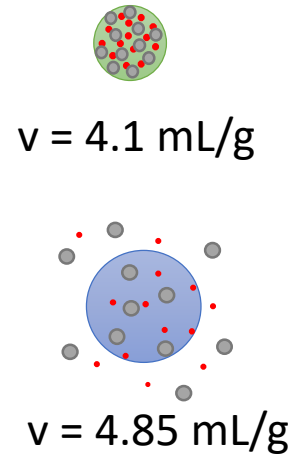
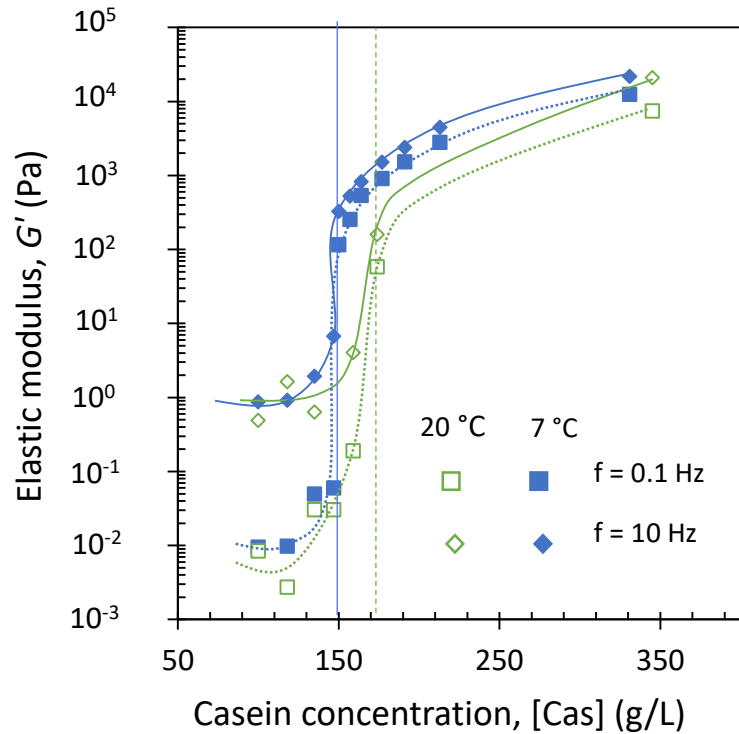
Doudiès et al., Foods 2019



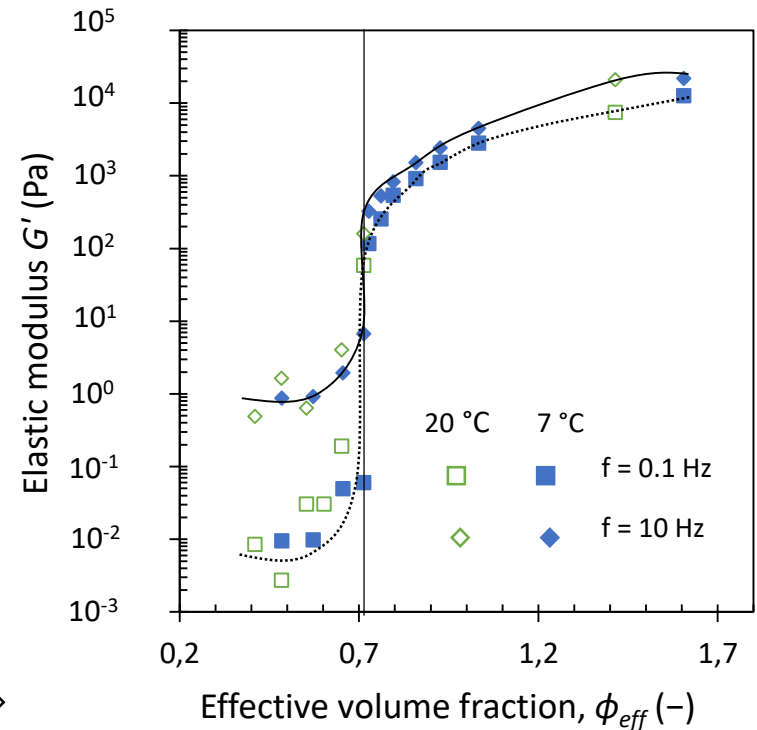
$[Cas]_{\text{sol-gel}} = 174 \text{ g/L à } 20 \text{ °C}$

$[Cas]_{\text{sol-gel}} = 150 \text{ g/L à } 7 \text{ °C}$

The concentration of sol-gel transition is lower at 7 °C than at 20 °C



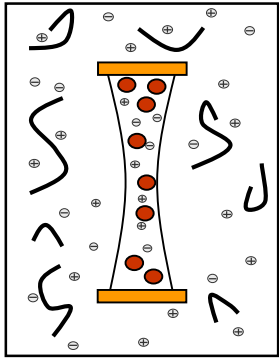
$$\phi_{eff} = [Cas] \times v$$



$[Cas]_{sol-gel} = 174$ g/L à 20 °C

$[Cas]_{sol-gel} = 150$ g/L à 7 °C

The concentration of sol-gel transition is lower at 7 °C than at 20 °C
 The sol-gel transition is fully consistent with an increase of hydration and apparent voluminosity at 7 °C compared to 20 °C (unique $\phi_{eff} = 0.71$)



Osmotic stress technique

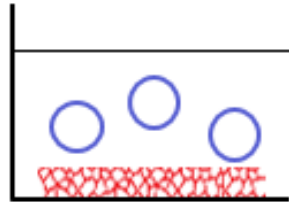
Concentrations, $[Cas] = 200 - 700 \text{ g/L}$

7 °C **20 °C**



Redispersion

7 °C **20 °C**

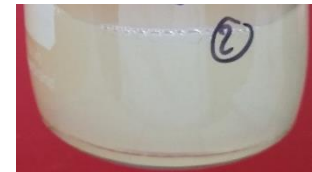


$t = 4 - 240 \text{ h}$



Hydration of residual gels

+

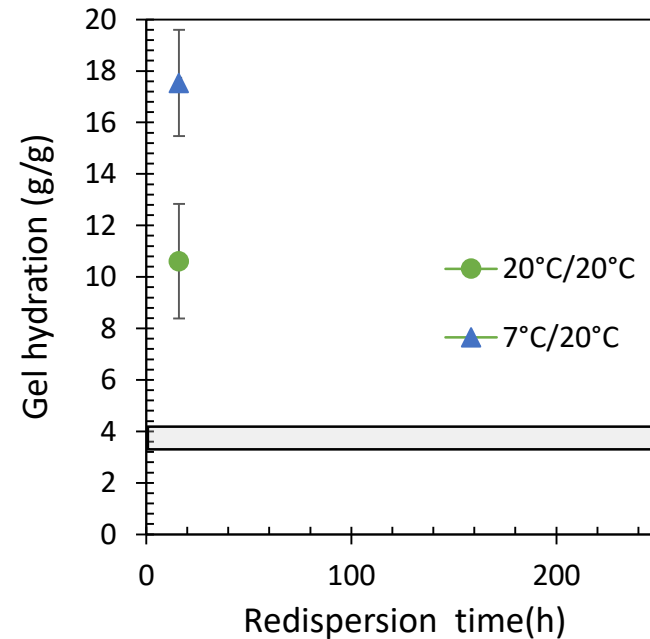
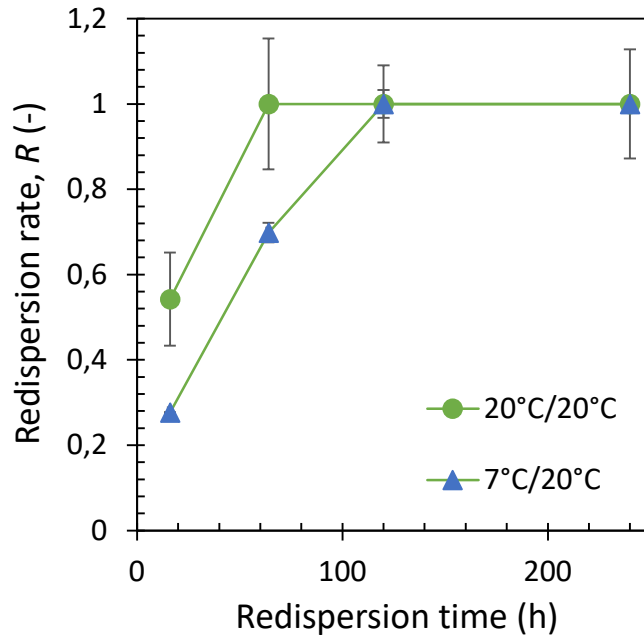


Redispersion rate, R

$$R = \frac{[Cas]_{supernatant}}{[Cas]_{total}}$$

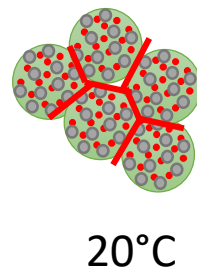
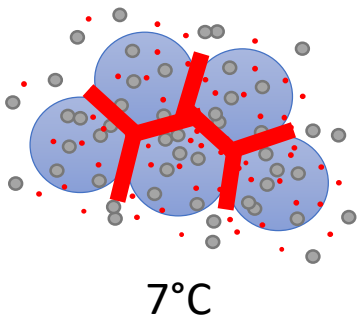
Temperature of gel production

$[Cas] = 295 \pm 21 \text{ g/L}$

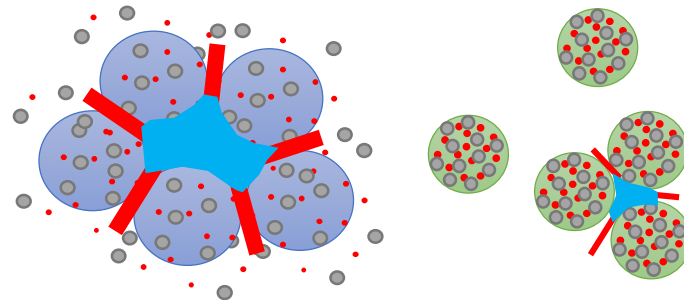


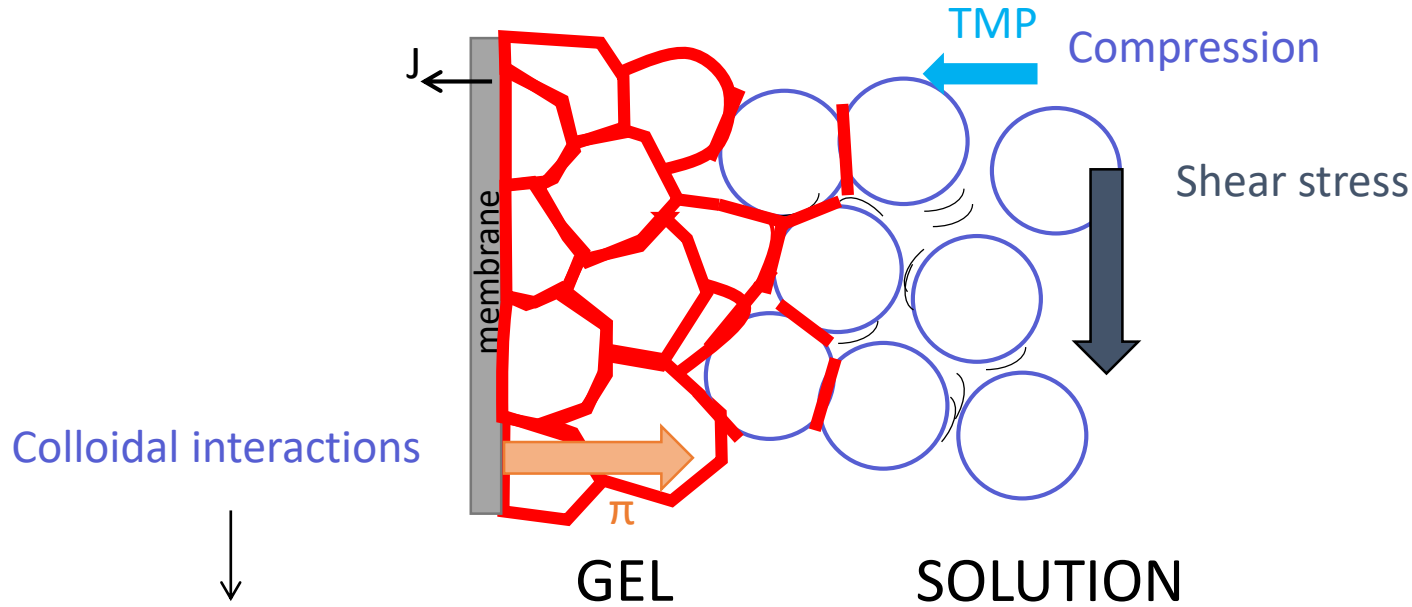
A gel prepared at 7°C is more cohesive than a gel prepared at 20°C
 A gel prepared at 7 °C is more hydrated than a gel prepared at 20°C

Concentration



Redisperion (same T)





Osmotic pressure, π

Rheology

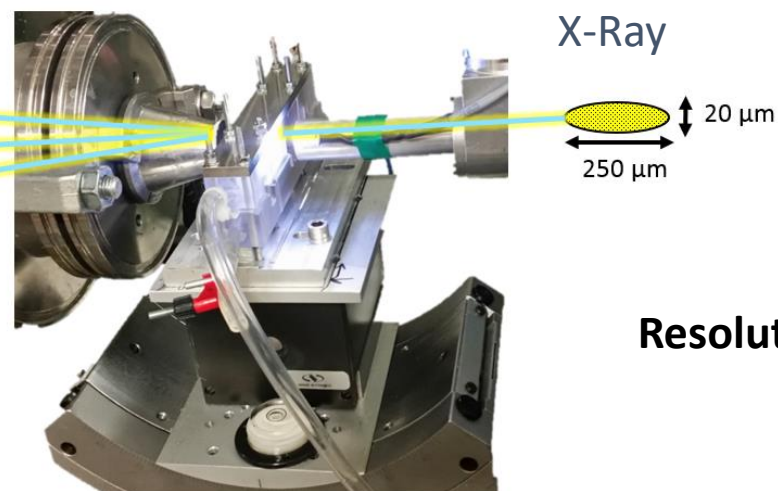
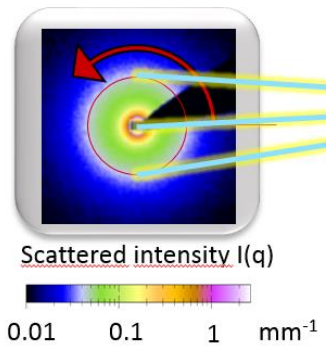
Cohesiveness

Casein micelles are less compressible at 7°C / 20°C

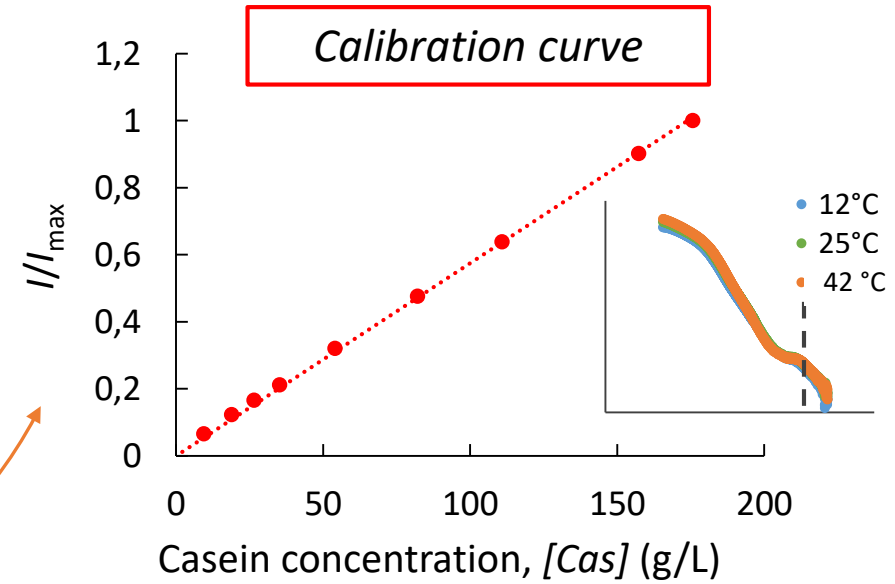
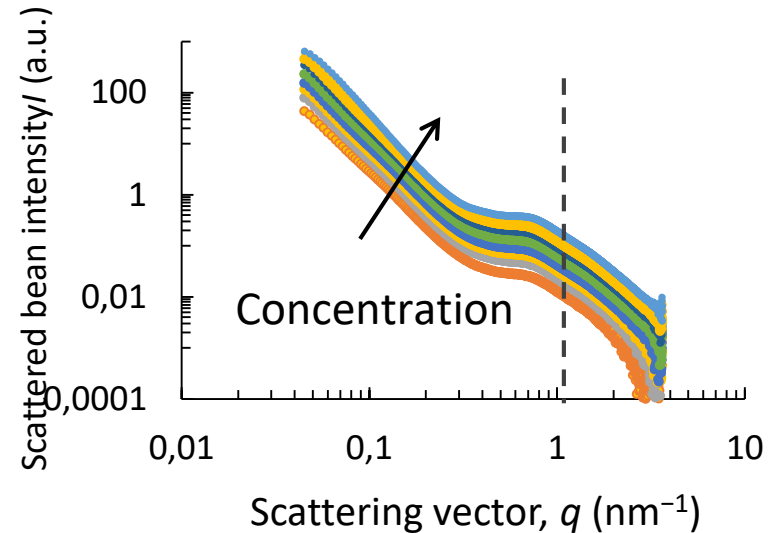
$[Cas]_{sol-gel}$ is lower at 7°C / 20°C

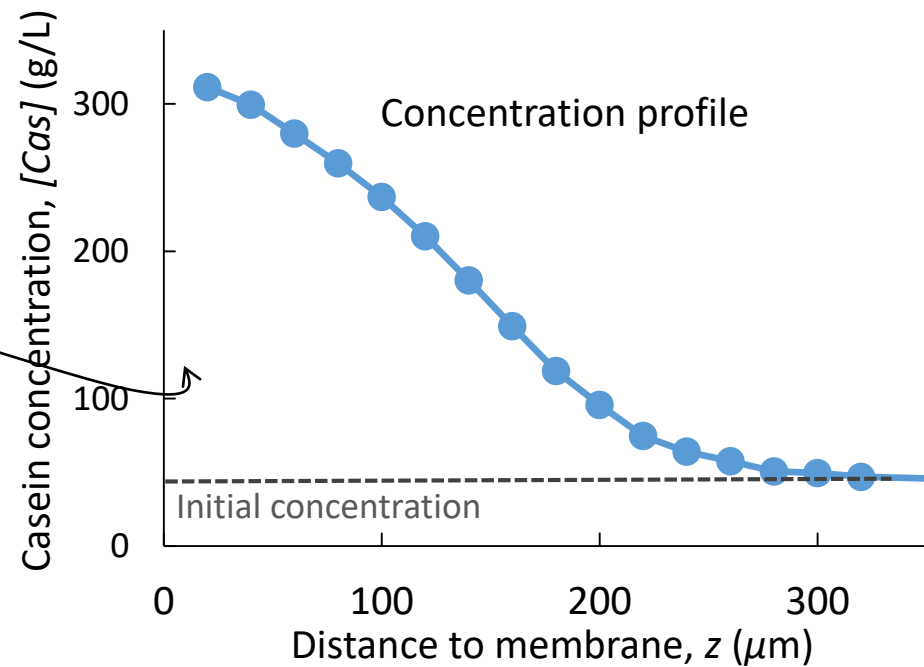
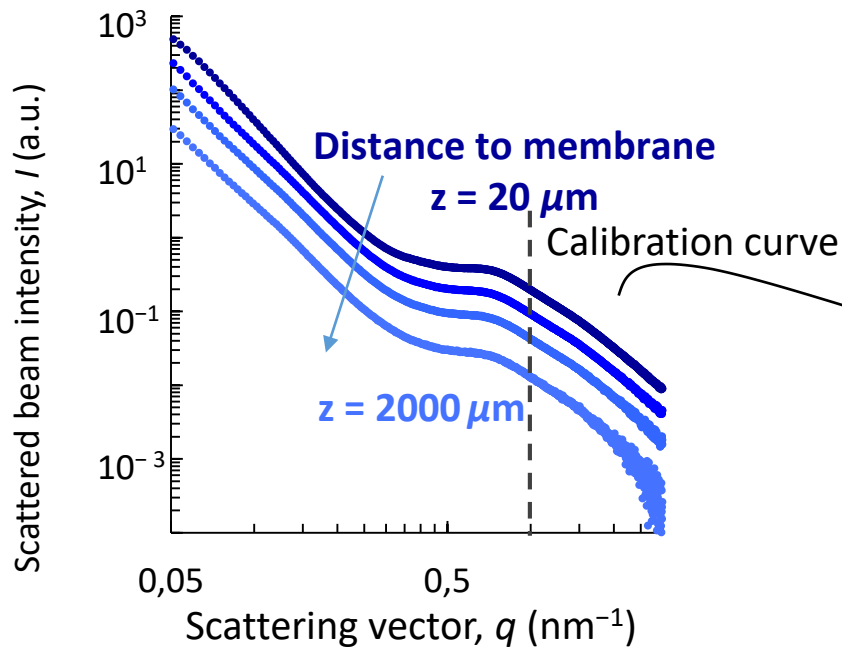
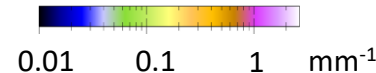
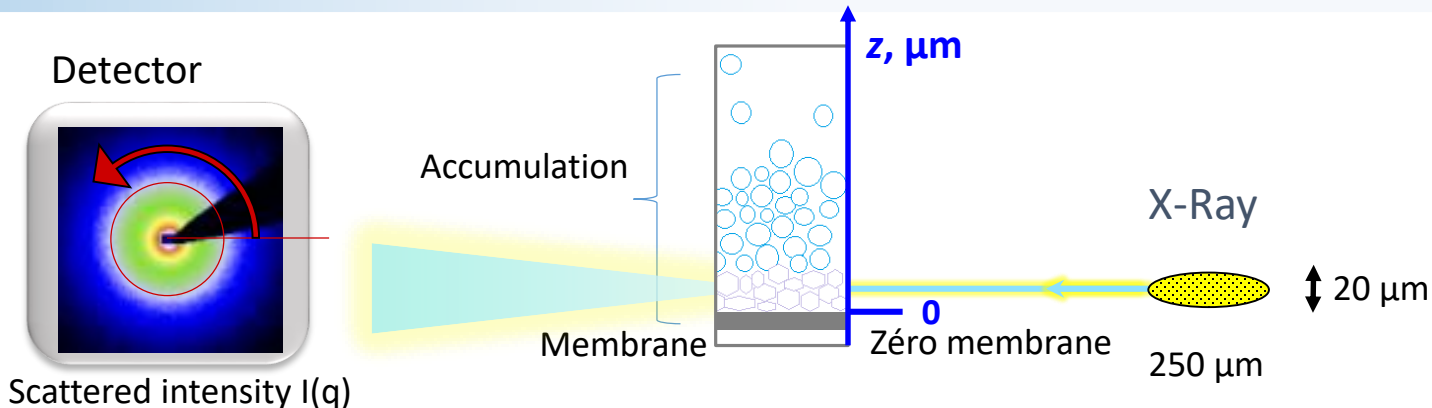
Gel of casein micelles obtained at 7°C is more cohesive/ 20°C

**Small-Angle
X-Ray
Scattering
SAXS**



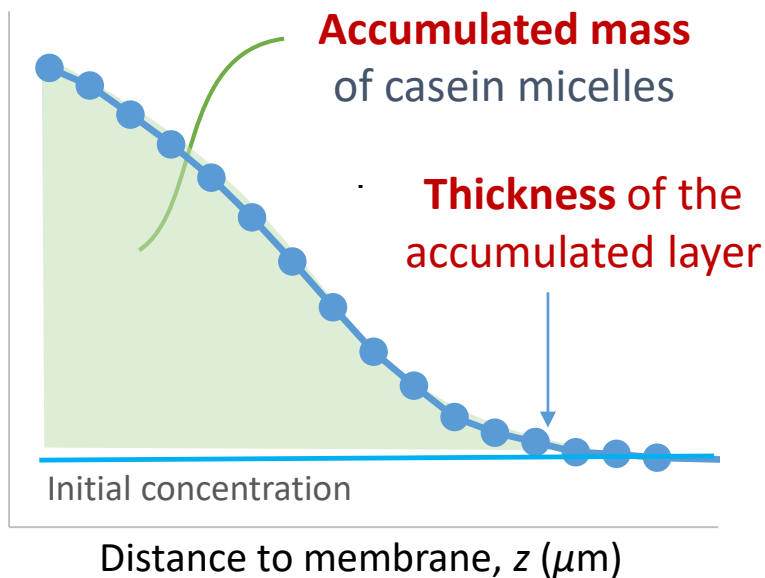
Resolution 20 μm



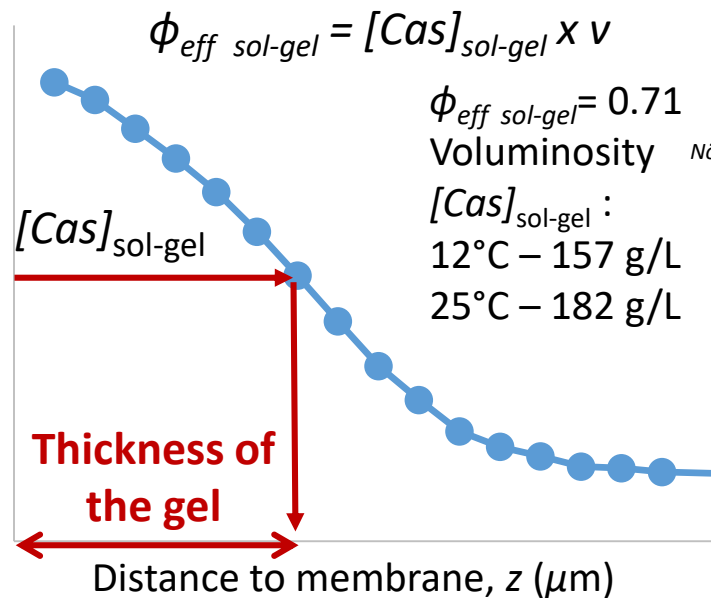


0.1 1

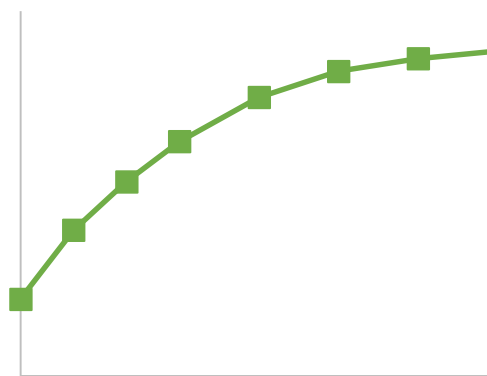
Casein concentration, [Cas] (g/L)



Casein concentration, [Cas] (g/L)



Accumulated mass (g/m²)
Thickness of the gel (μm)

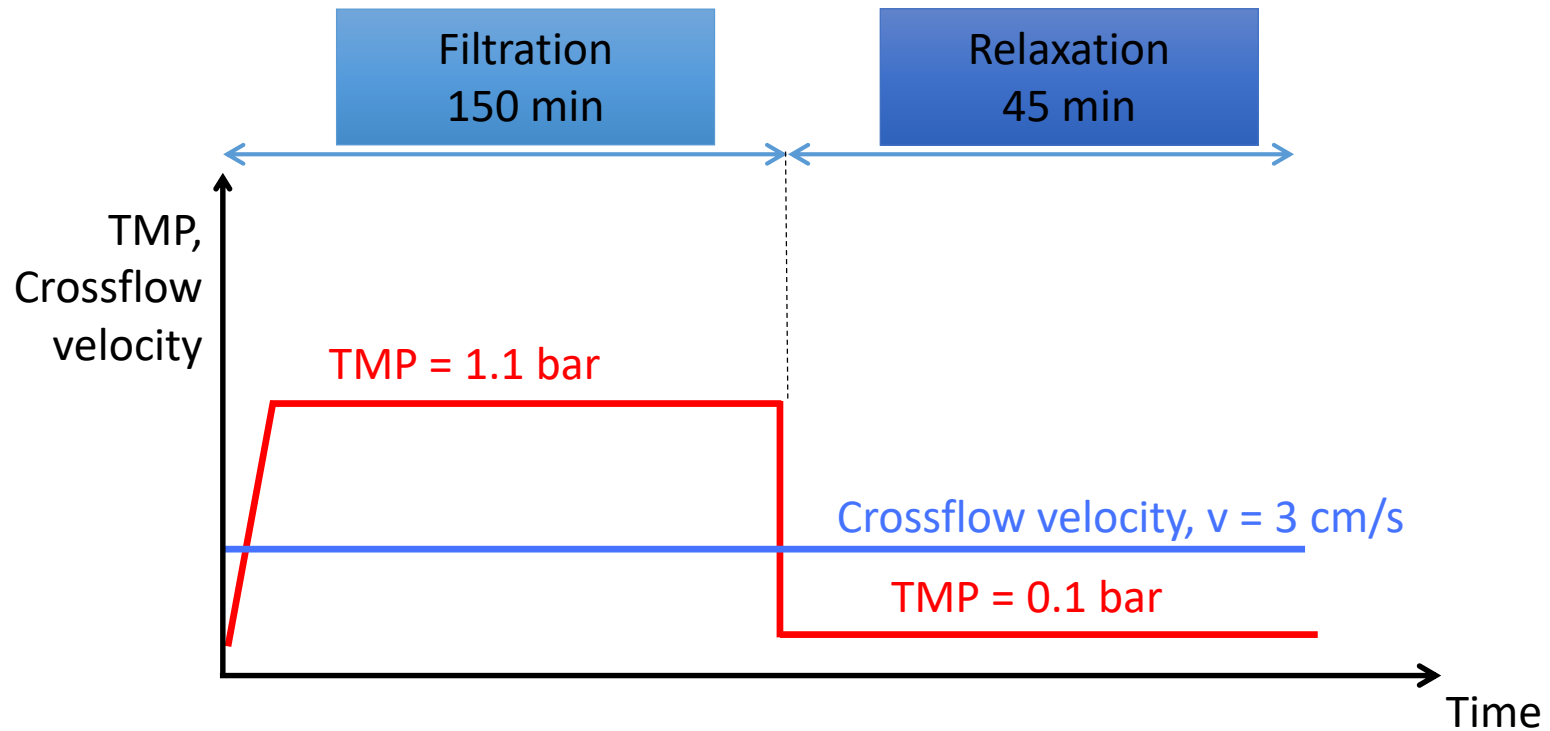


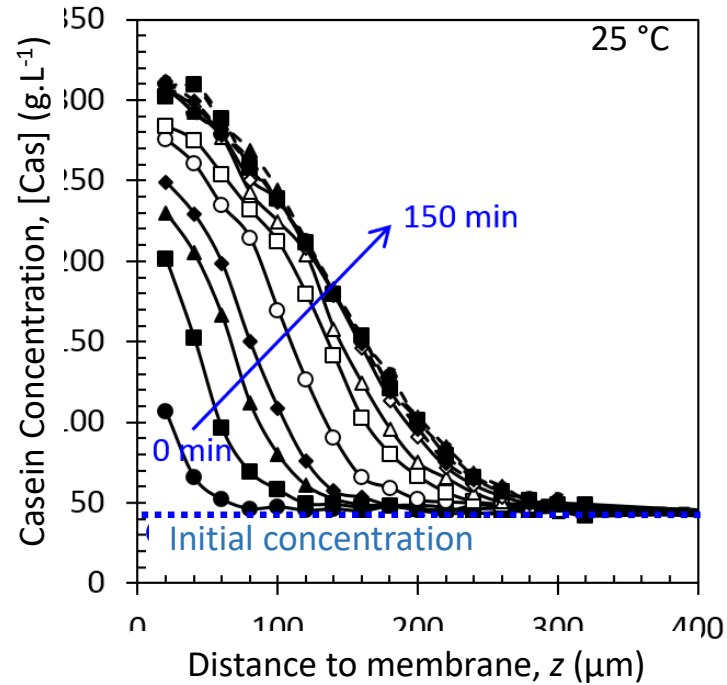
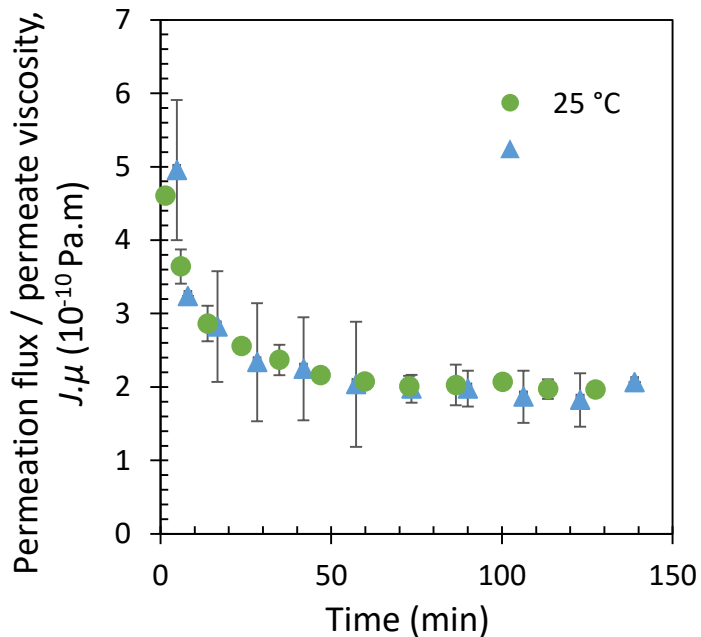
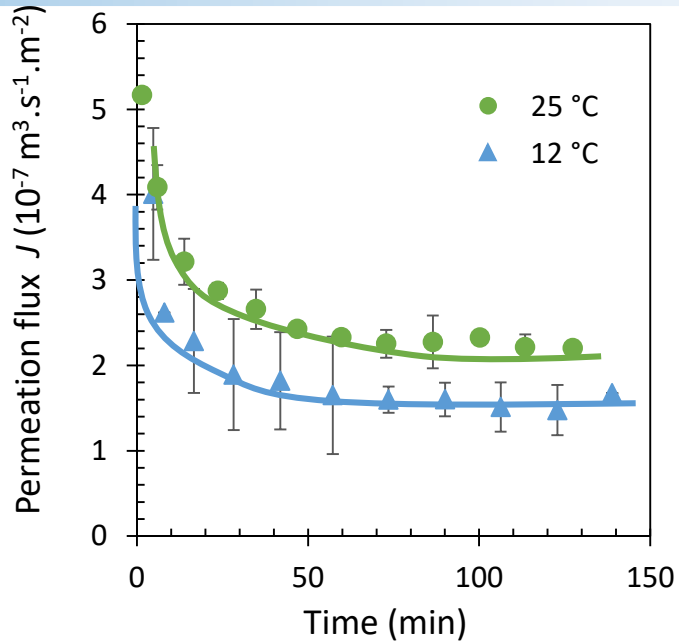
Time (min)

Casein micelle dispersion : 50 g/L

Membrane: Polyethersulfone 100 kDa (Orelis, France)

Temperature: 12 and 25 °C

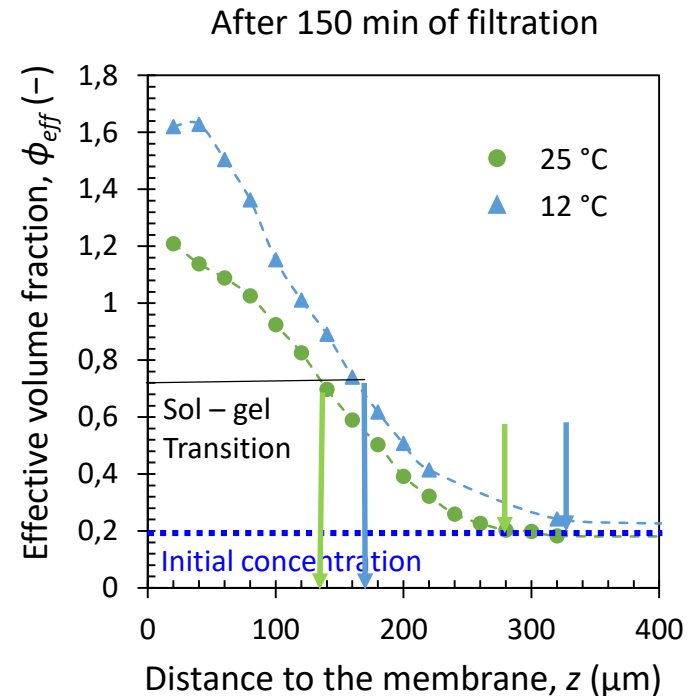
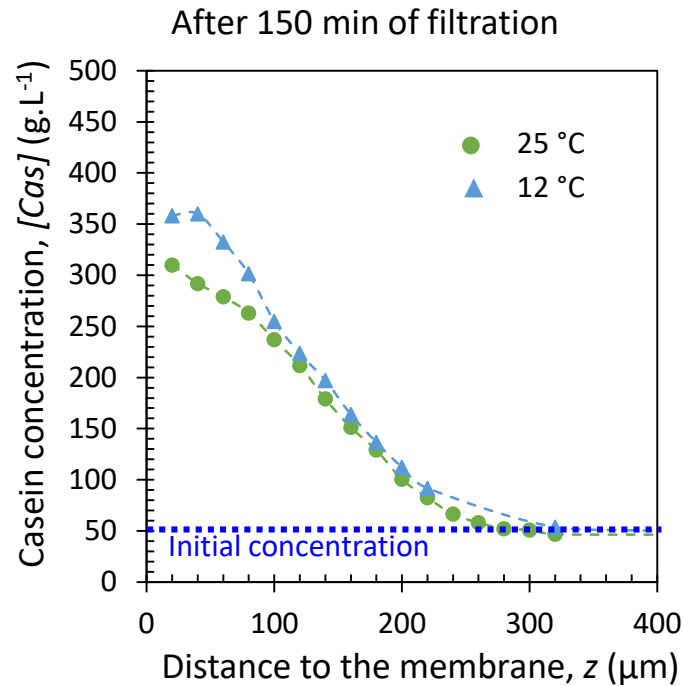




TMP = 1,1 bar
V = 3 cm/s

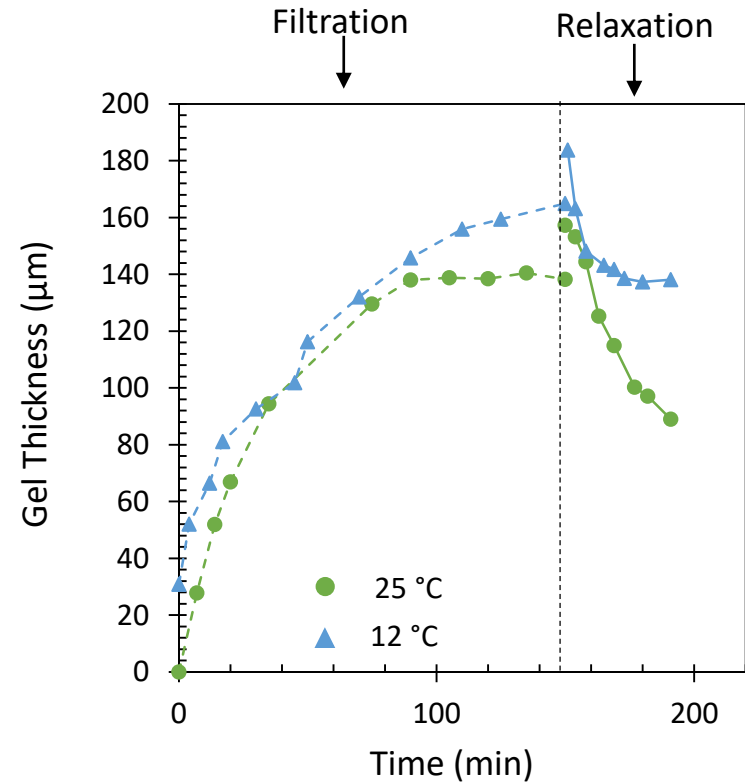
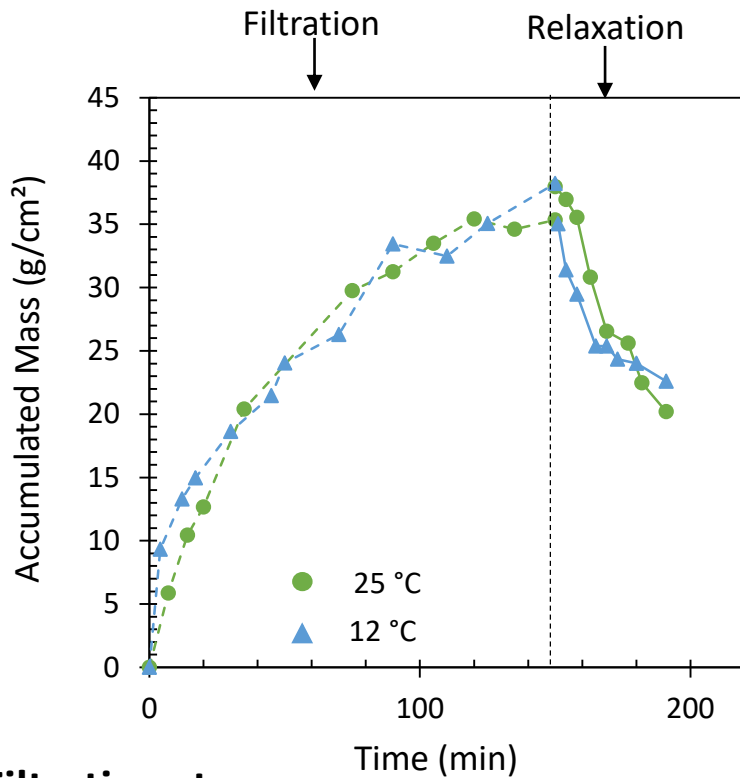
- Decrease of $J = f(t) \rightarrow$ accumulation of casein micelles at the membrane surface
- $J_{12^\circ\text{C}} < J_{25^\circ\text{C}} \rightarrow$ Increase of permeate viscosity at low temperature

TMP = 1.1 bar
V = 3 cm/s



At the end of the 150 min filtration,
 the **casein concentration** at the membrane surface
 the **effective volume fraction** at the membrane surface
 the **thickness of the accumulated layer**
 the **thickness of the gel**
 are higher at 12°C compared to 25°C

TMP = 0.1 bar
V = 3 cm/s

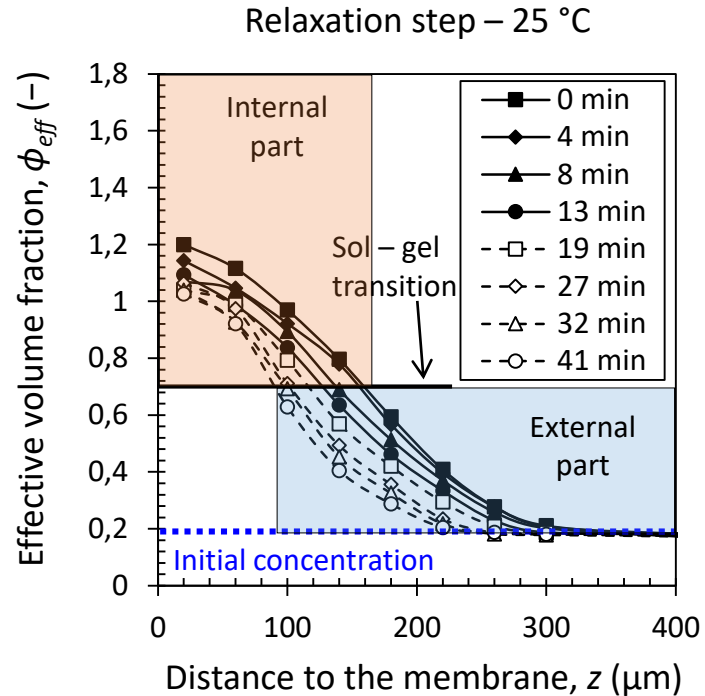
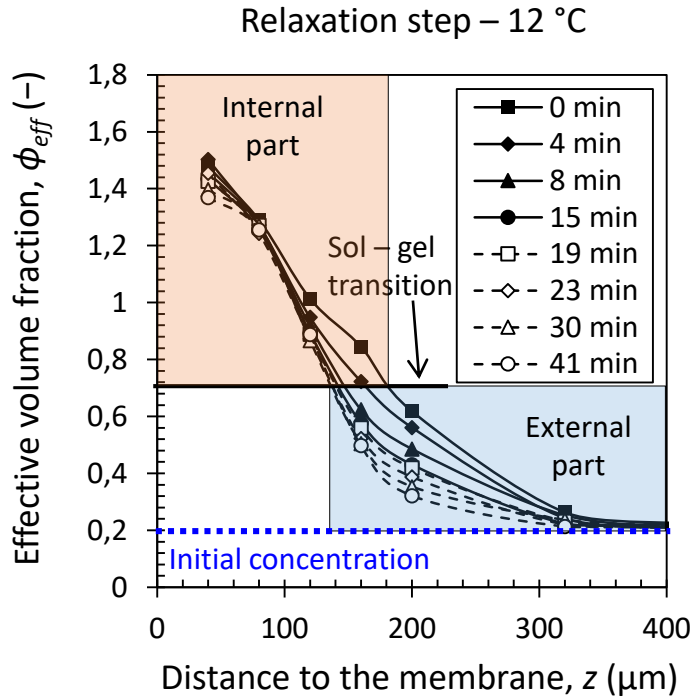


Filtration step

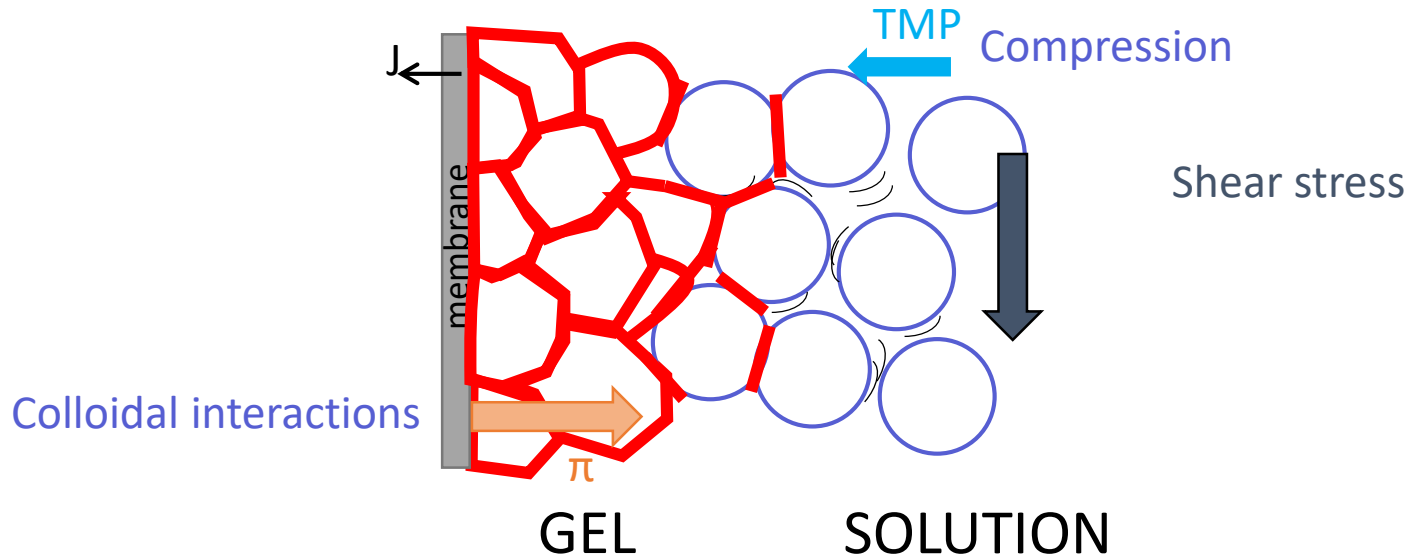
'Similar' accumulated mass at 12 and 25°C
The gel thickness is higher at 12 °C, compared to 25 °C

Relaxation step

The removal of gel is easier at 25°C compared to 12°C
(very limited at 12°C)



- . Gels of casein micelles are more cohesive at 12 °C compared to 25°C
- . At 12°C, the gel with $\phi_{eff} > 0.71$ is not removed
- . At 25°C the whole accumulated matter (below and above $\phi_{eff} = 0.71$) swells and redisperses



Osmotic pressure, π

Casein micelles are less compressible at 7°C / 20°C

The thickness of the accumulated layer is higher at 12°C compared to 25°C

Rheology

$[Cas]_{sol-gel}$ is lower at 7°C / 20°C

The thickness of the gel is higher at 12°C compared to 25°C

Cohesiveness

Gel of casein micelles obtained at 7°C are more cohesive/ 20°C

The deposit is more cohesive at 12°C compared to 25°C

- . UF/ MF of skimmed milk using polymeric membranes are hindered by the properties of casein micelle at low temperature
- . Osmotic stress experiments (π , redispersion) and rheology = useful to predict the behavior of colloidal dispersions during filtration

Thank you for your attention!

