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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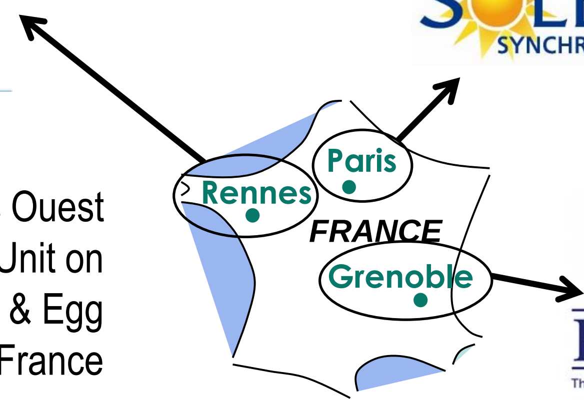
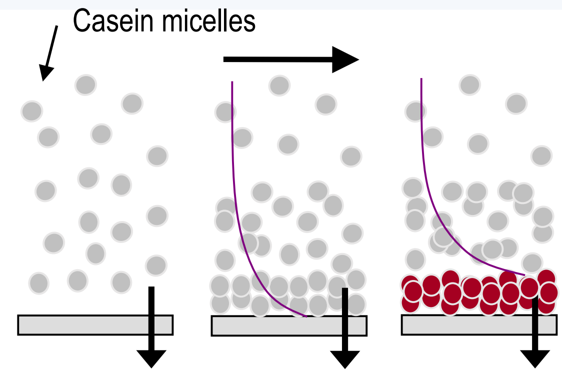


Laboratoire Rhéologie et Procédés

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

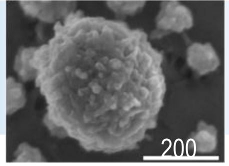
2 options

Ceramic membranes 50-53°C

Polymeric spiral wound membranes 7-12°C

	Ceramic membranes 50-53°C	Polymeric spiral wound membranes 7-12°C
Investment	--	++
Running costs	--	++
Productivity (recovery, purity of fractions)	++	-
Cleaning / disinfection	++	-

Casein micelles



SEM Image
(Dalgleish, 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

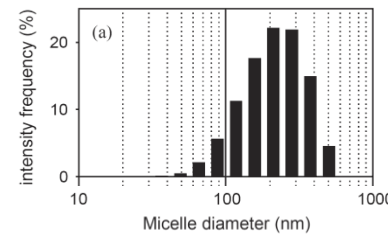
  Diameter ~ 50 -500 nm (average 200 nm)

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

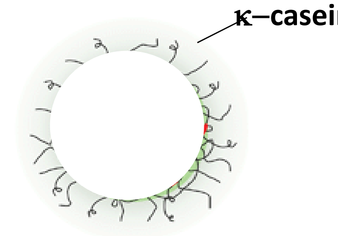
  Surface: polyelectrolyte brush κ- casein

  Content in equilibrium with the aqueous phase

Size distribution



(Regnault, IDJ, 2004)

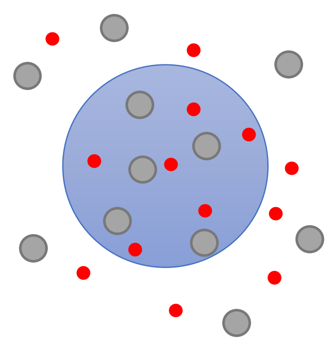


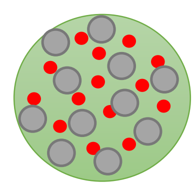
- Properties =f(temperature)

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

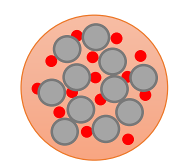
Casein (β-CN)

CaP Nanocluster





Sol/gel transition
~170-180 g/L



Objectives

→ 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 ?

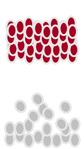
Strategy

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

Colloidal interactions, compressibility,

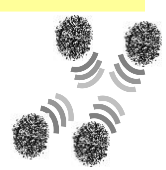
Sol-gel transition

Cohesivness and reversibility



Condensed phase

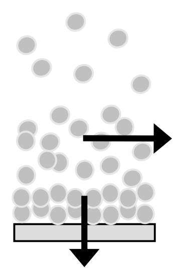
Dispersed phase



Osmotic stress
Rheology

↔

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



Concentration profile

Accumulated mass

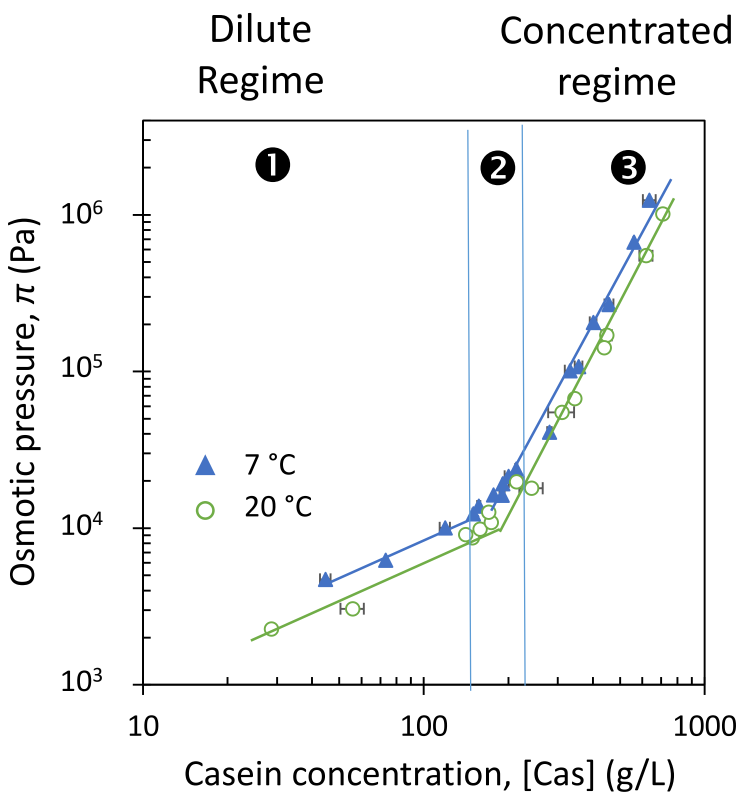
Thickness of accumulated layers and deposit (gel)

Cohesiveness (relaxation) of accumulated layers

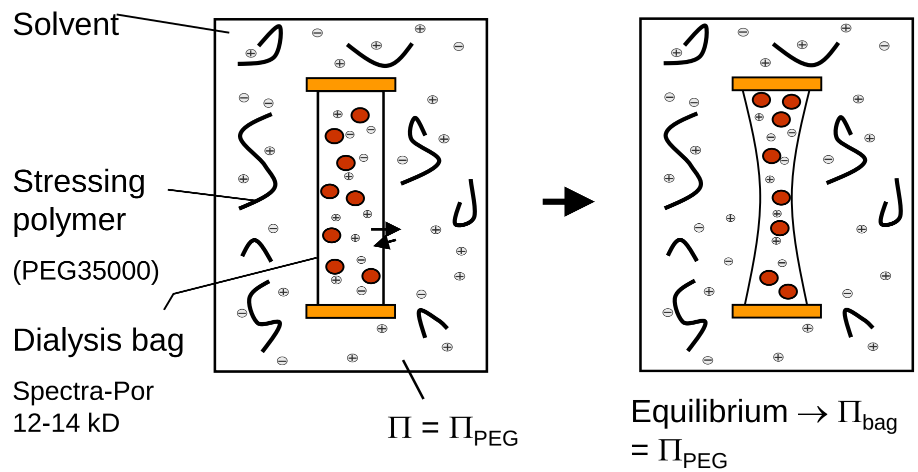
SAXS

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

Results – Colloidal interactions, compressibility



Osmotic stress technique



3 regimes of compression

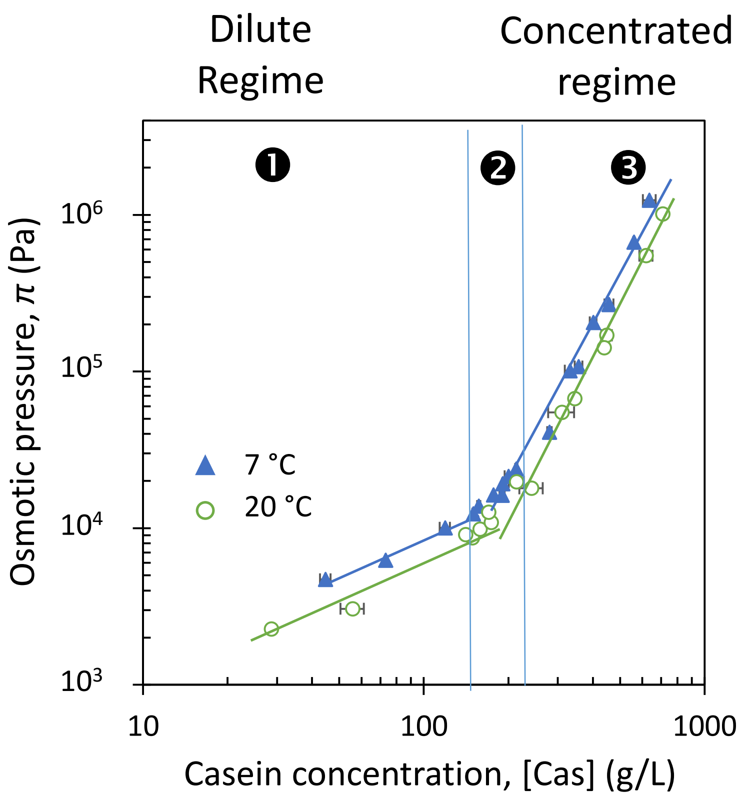
. Dilute regime ❶ -> No direct interactions

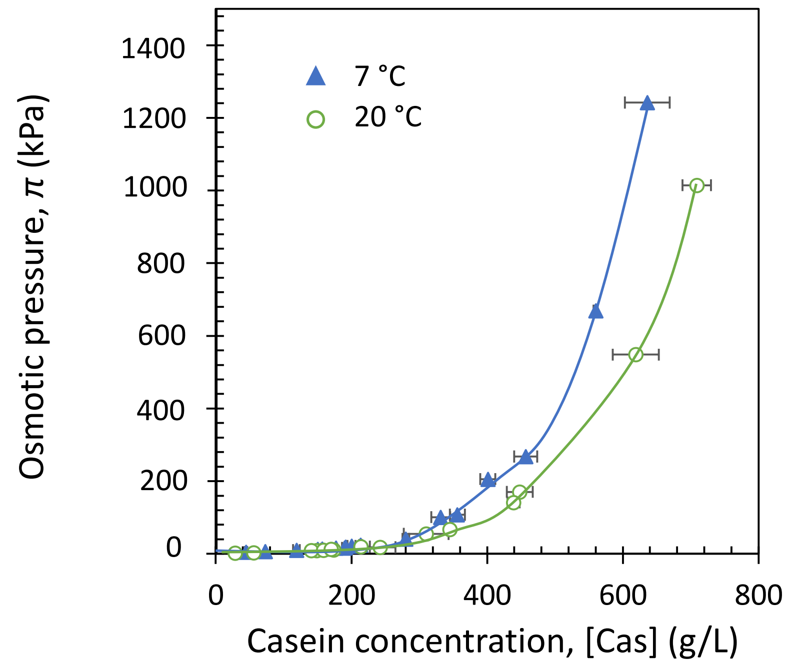
. Transition regime ❷ -> Inter-micellar interactions

. Concentrated regime ❸ -> Intra-micellar interactions

[Bouchoux et al., 2009]

Results – Colloidal interactions, compressibility





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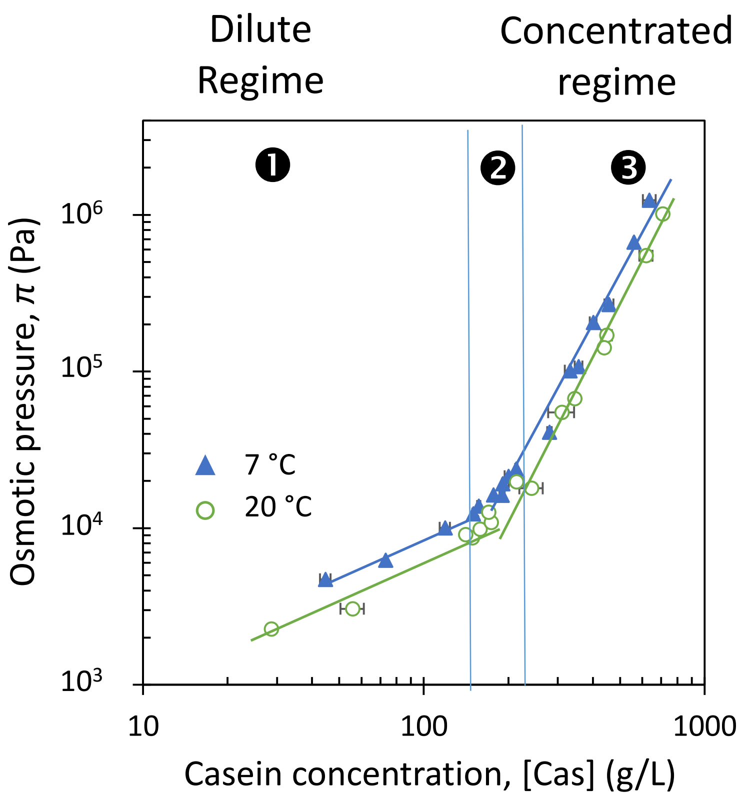
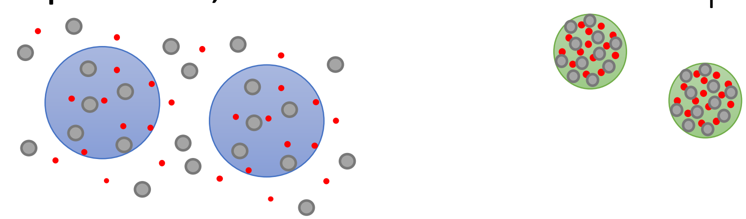
Results – Colloidal interactions, compressibility

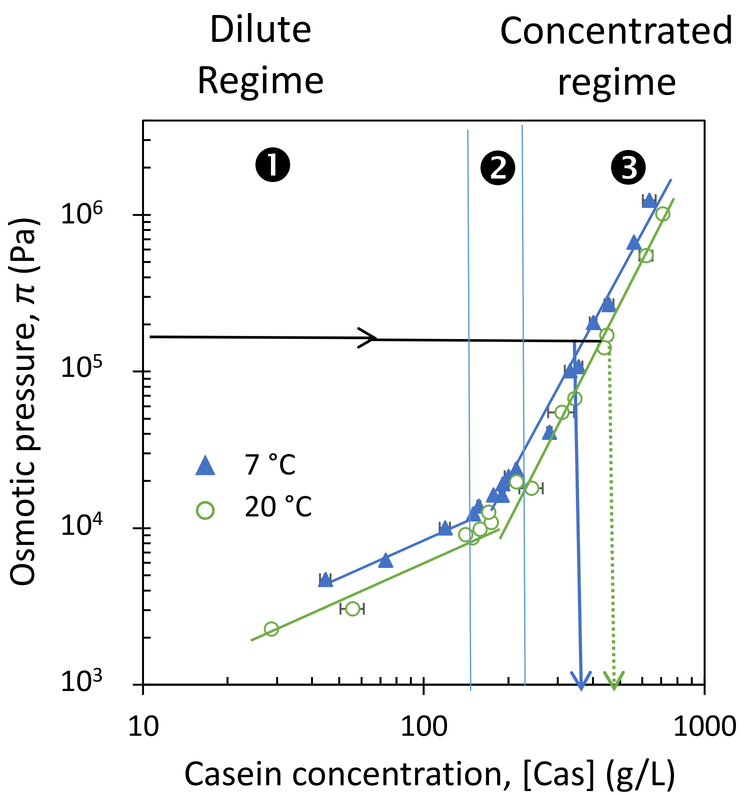


Diluted regime

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

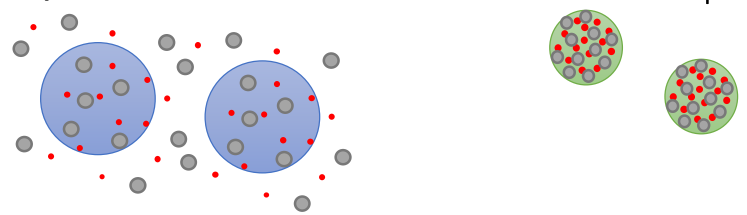


Results – Colloidal interactions, compressibility



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 : $[\text{casein}]_{7°C} < [\text{casein}]_{20°C}$

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

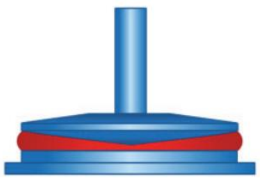
INRAE

Rheology

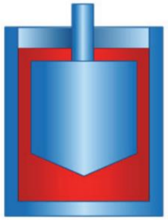
Concentrations [Cas] = 100 – 350 g/L

Rheological properties : flow and oscillatory experiments

Liquids : steady shear viscosities

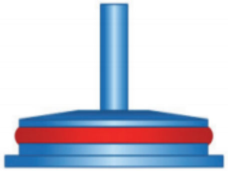


Cone-plate geometry
Diamètre 25 mm – Angle 2°
(DRH2 Rheometer)



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

Gels : oscillatory experiment

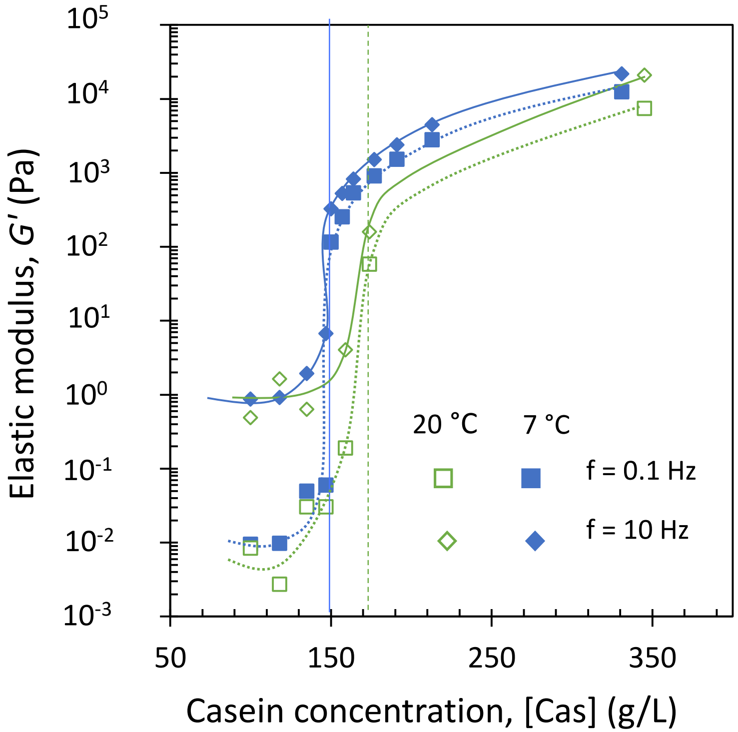


Cone-plate geometry
Parallel plated with grooved surfaces – diameter 20 mmm
Gel thickness: 4 mm
(DRH2 Rheometer)

Elastic modulus G'
Loss modulus G''

Doudiès et al., Foods 2019

Results – Sol-gel transition

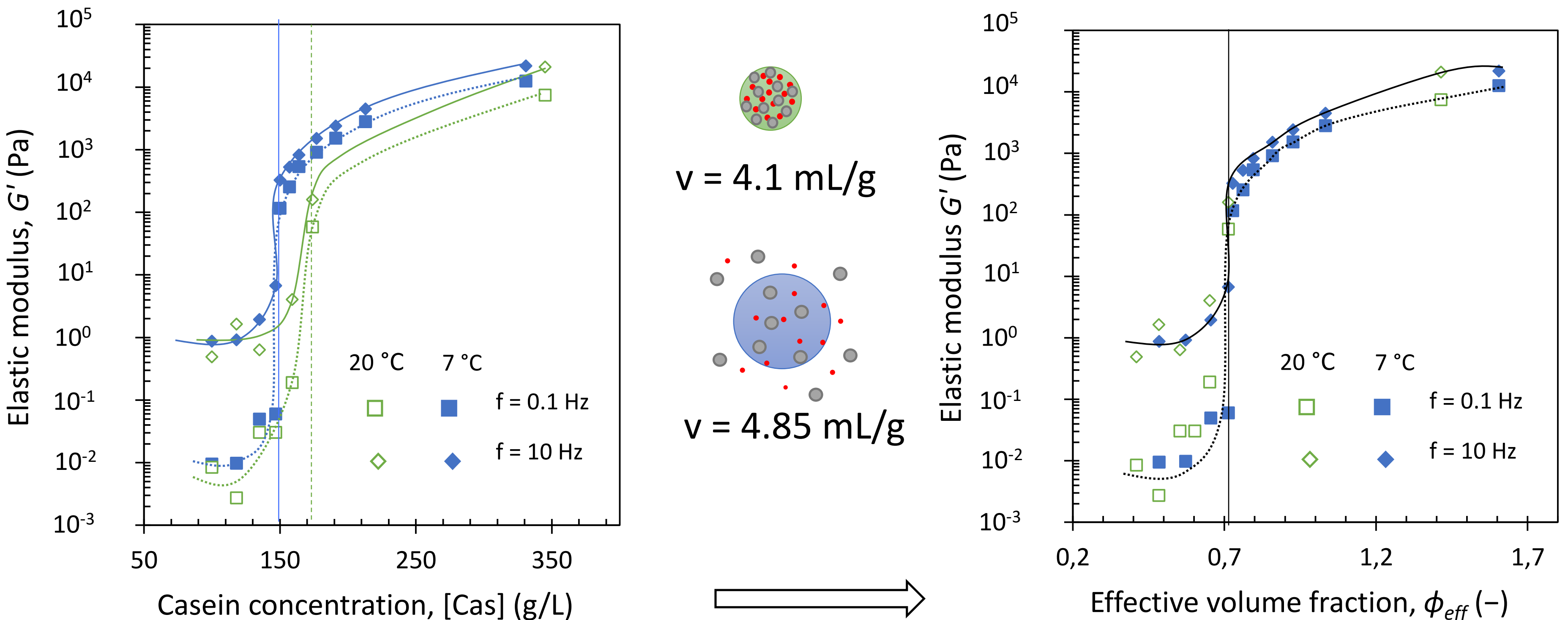


$[Cas]_{sol\text{-}gel}$ = 174 g/L à 20 °C

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

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

Results – Sol-gel transition

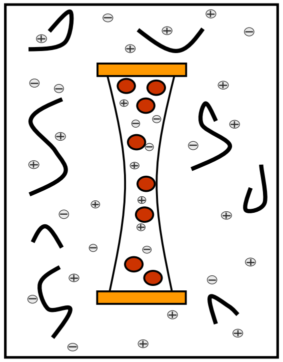


ϕ_{eff} = [Cas] x v

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

$[Cas]_{sol\text{-}gel}$ = 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 ϕ_{eff} = ***0.71***)



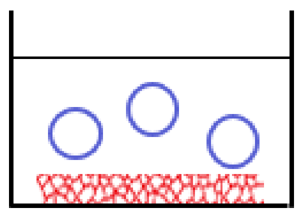
Osmotic stress technique

Concentrations, [Cas] = 200 – 700 g/L

7 °C , 20 °C

Redispersion

7 °C 20 °C



t = 4 – 240 h

Hydration of residual gels

+

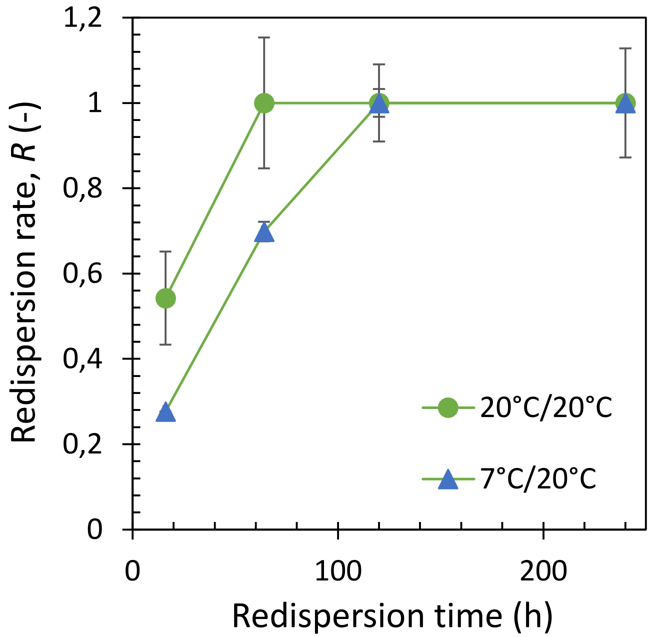
Redispersion rate, R

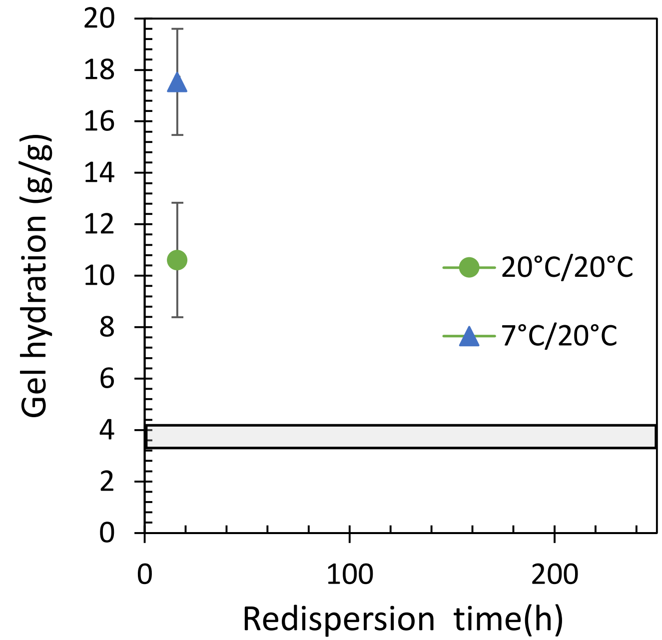
$$R = \frac{[Cas]_{supernatant}}{[Cas]_{total}}$$

Results – Cohesivness

[Cas] = 295 ± 21 g/L

Temperature of gel production

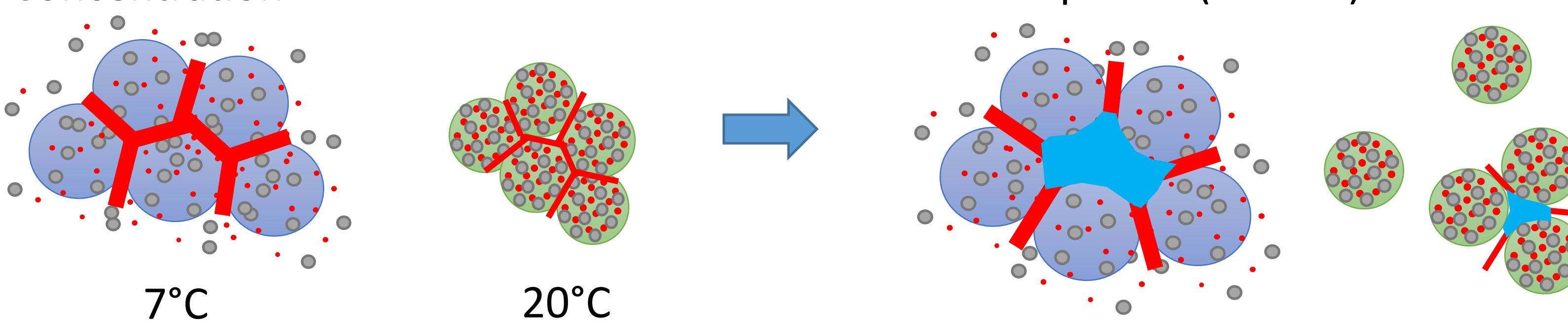




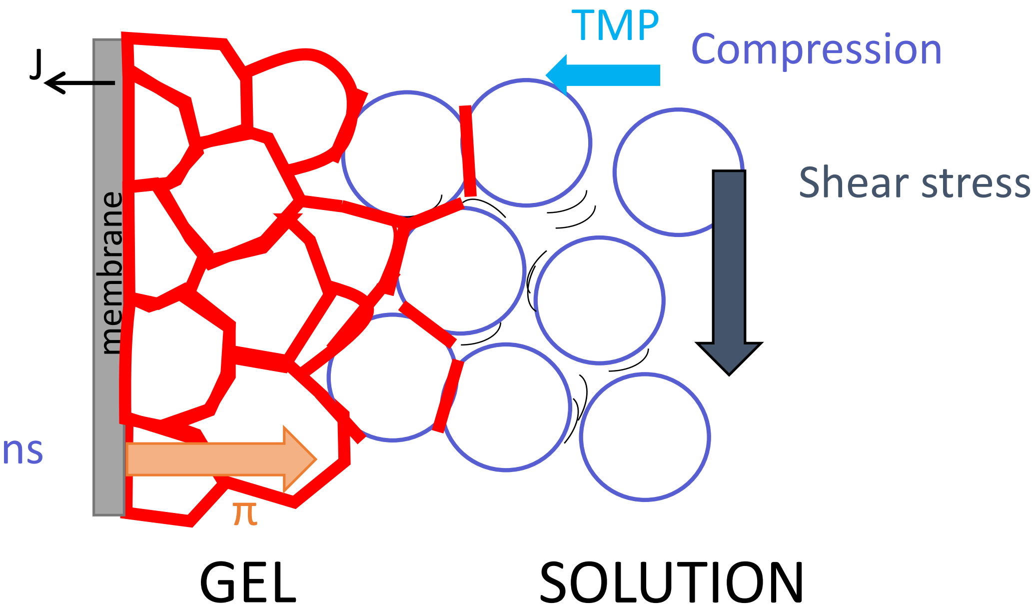
A gel prepared at 7°C is more cohesive than a gel prepared at 20°C
A gel prepared at 7 °C is more hydrated than a gel prepared at 20°C

Concentration

Redisperion (same T)



Summary – Properties of concentrated casein micelles at 7°C / 20°C



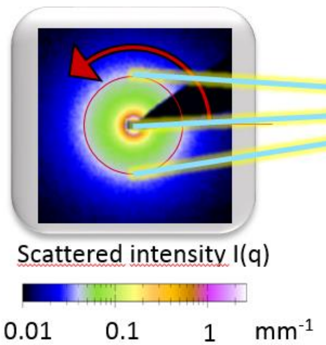
Colloidal interactions

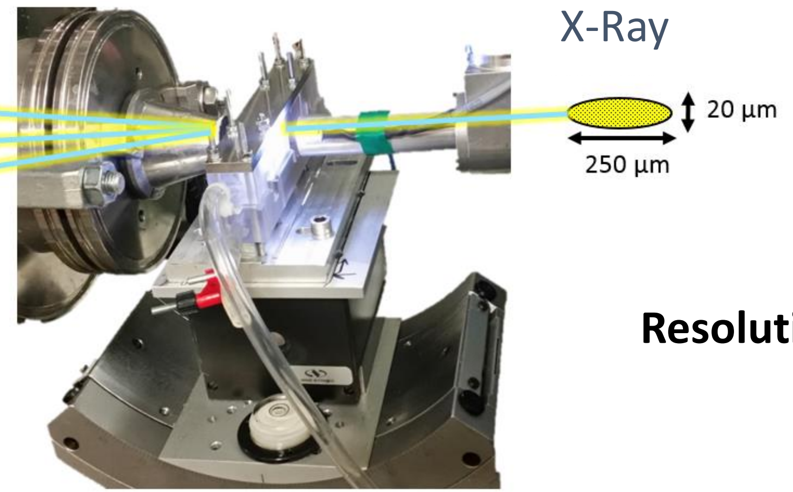
↓

Osmotic pressure, π	Rheology	Cohesivness
Casein micelles are less compressible at 7°C / 20 °C	$[Cas]_{sol\text{-}gel}$ is lower at 7 °C /20 °C	Gel of casein micelles obtained at 7 °C is more cohesive/ 20°C

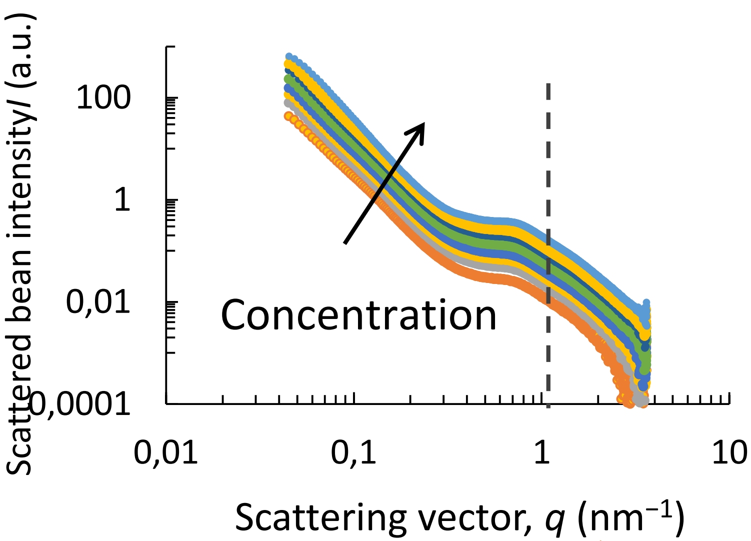
Results – In-situ characterization of casein micelles deposit by SAXS

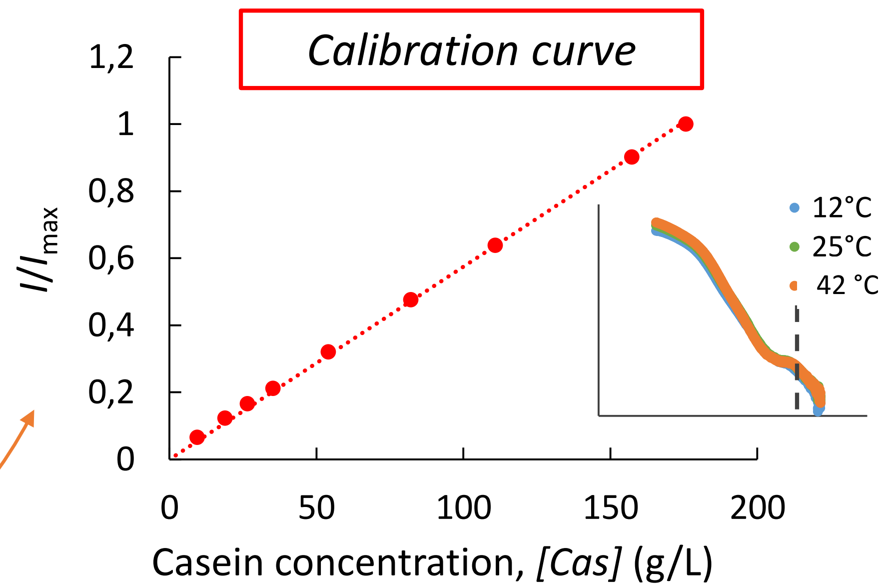
Small-Angle X-Ray Scattering SAXS





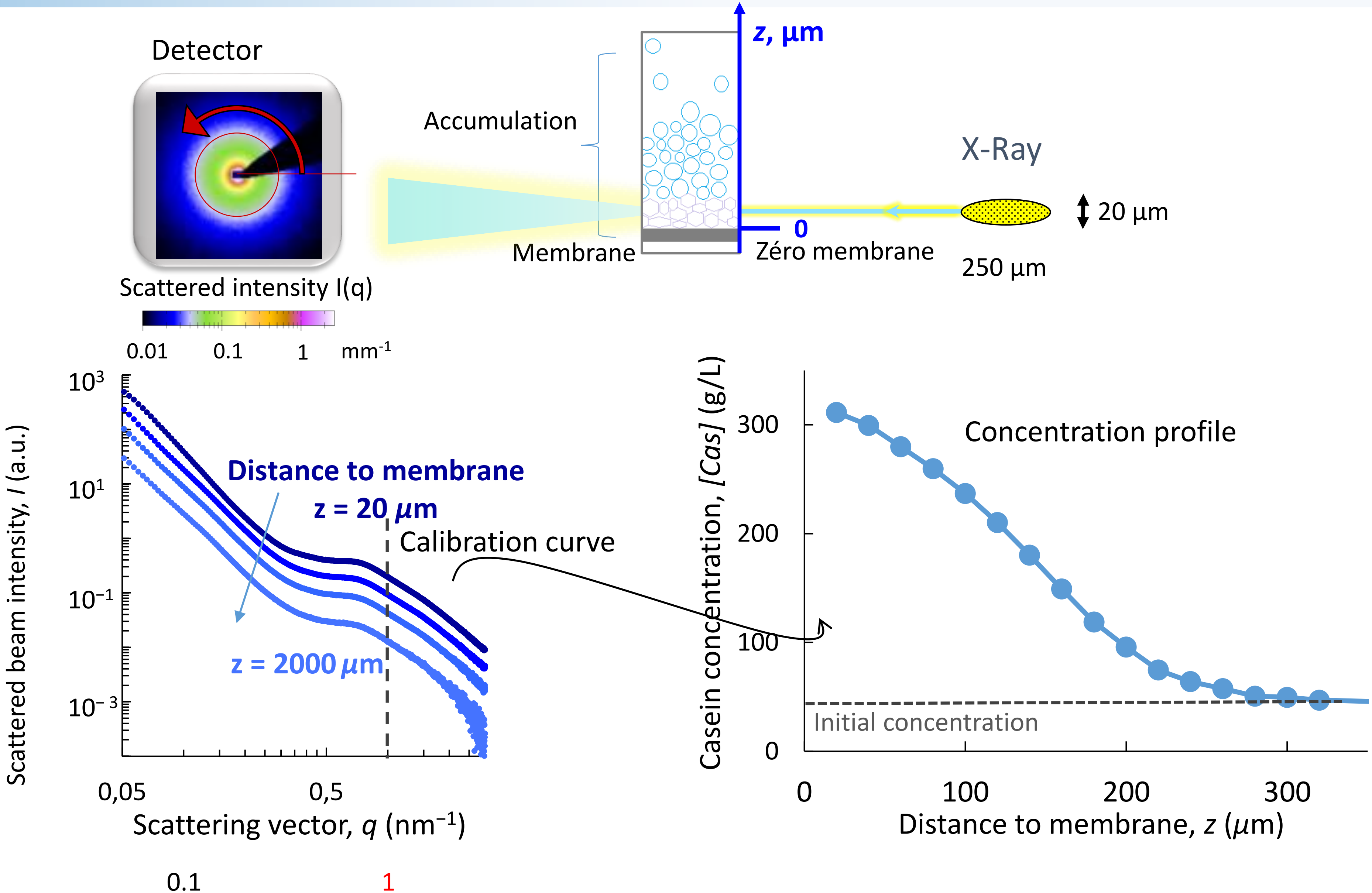
Resolution 20 µm



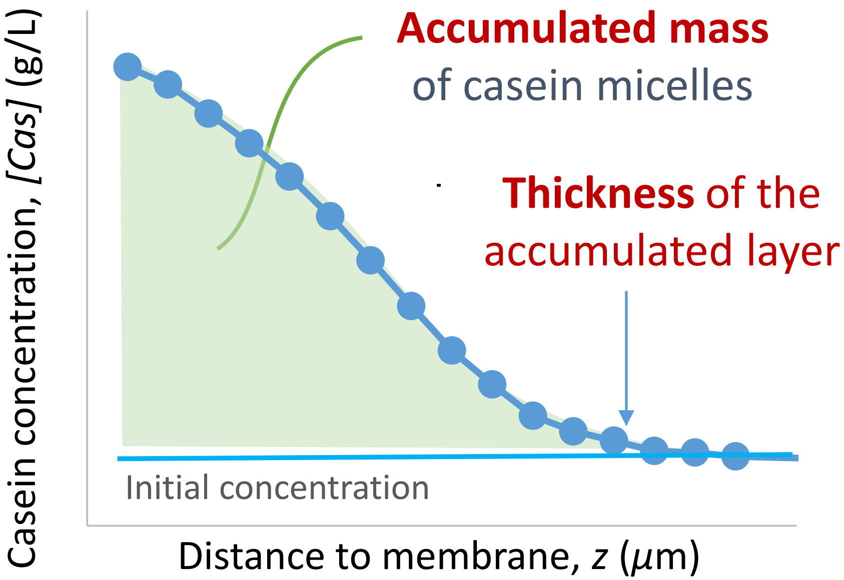


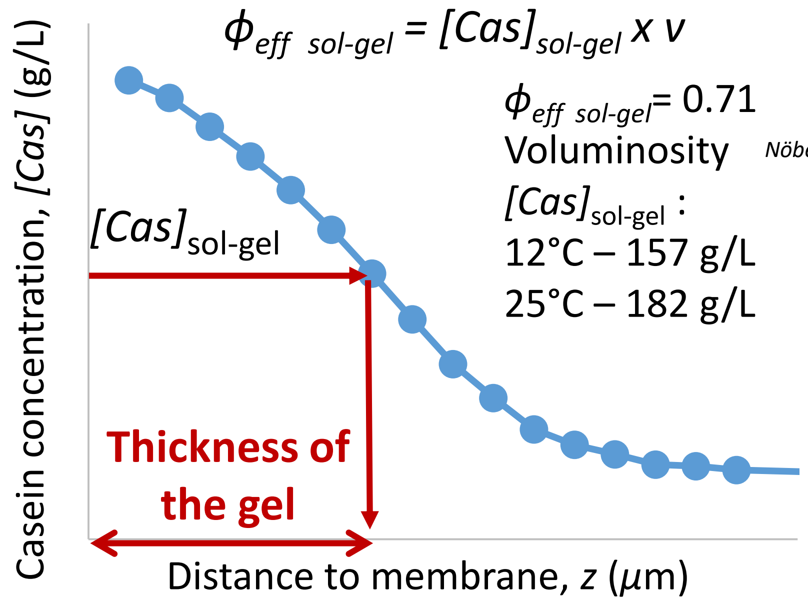
David et al. 2004
Jin et al., 2014

Results – *In-situ* characterization of casein micelles deposit by SAXS



Results – *In-situ* characterization of casein micelles deposit by SAXS





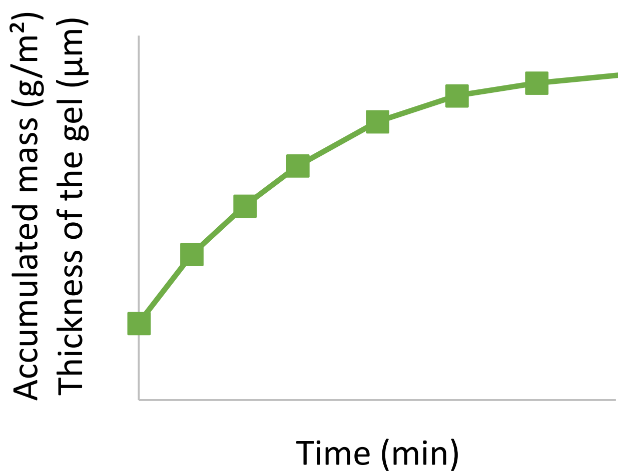
$\phi_{eff\ sol\text{-}gel}$ = 0.71

Voluminosity *Nöbel et al., 2012; 2016*

$[Cas]_{sol\text{-}gel}$:

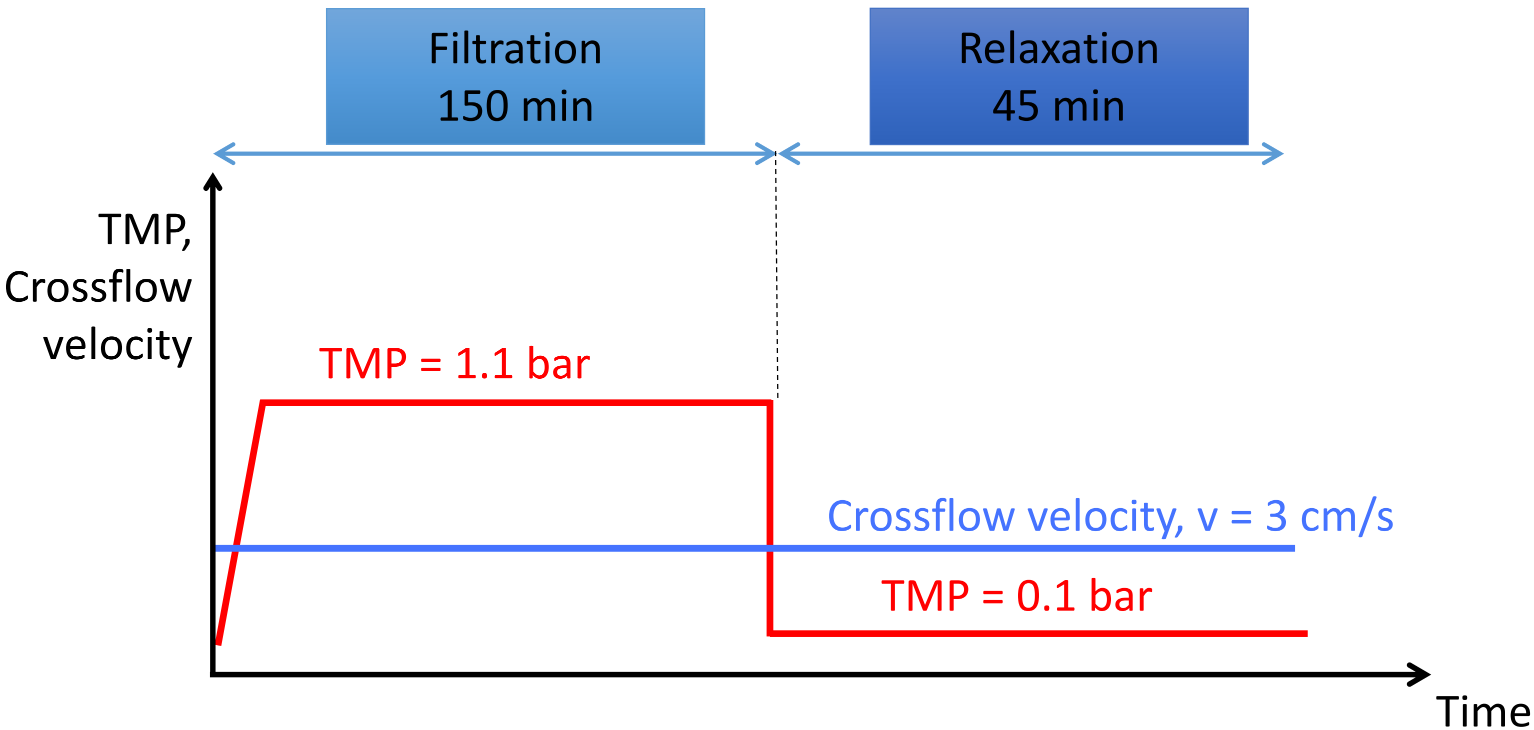
12°C – 157 g/L

25°C – 182 g/L

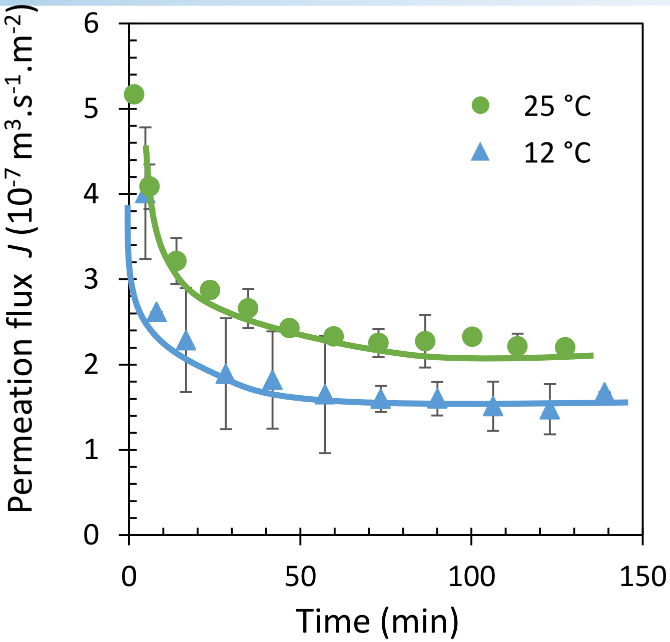


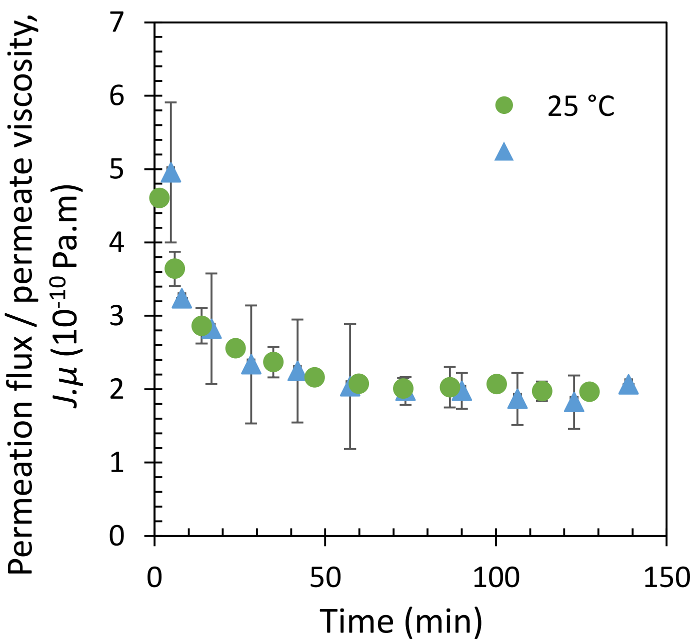
Results – *In-situ* characterization of casein micelles deposit by SAXS

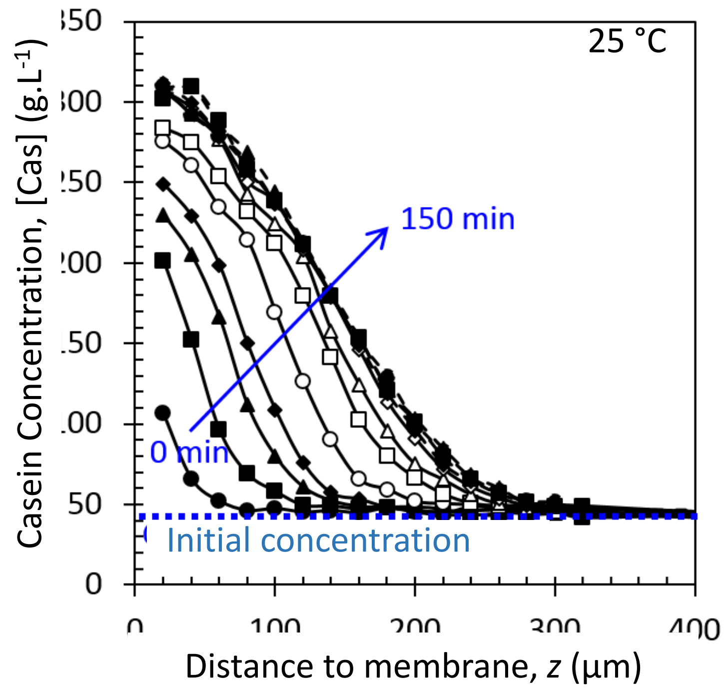
Casein micelle dispersion : 50 g/L
Membrane: Polyethersulfone 100 kDa (Orelis, France)
Temperature: 12 and 25 °C



Results – Permeation flux - SAXS



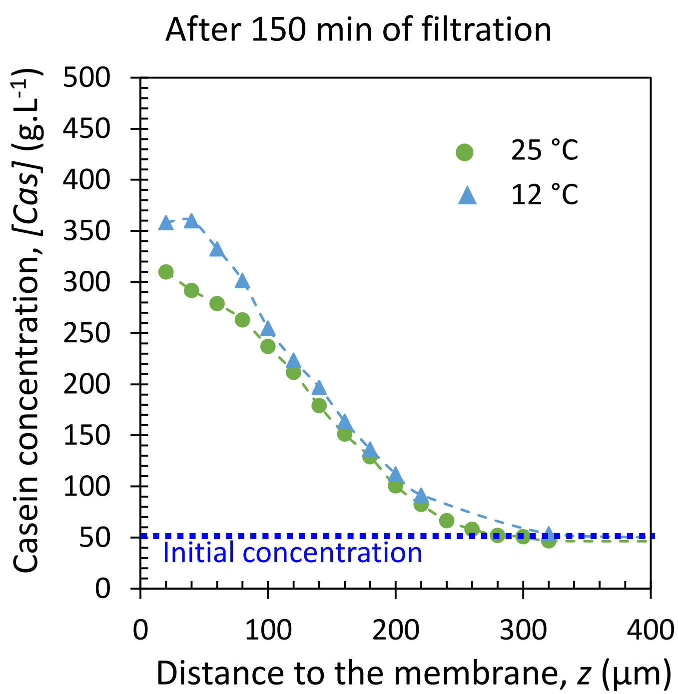


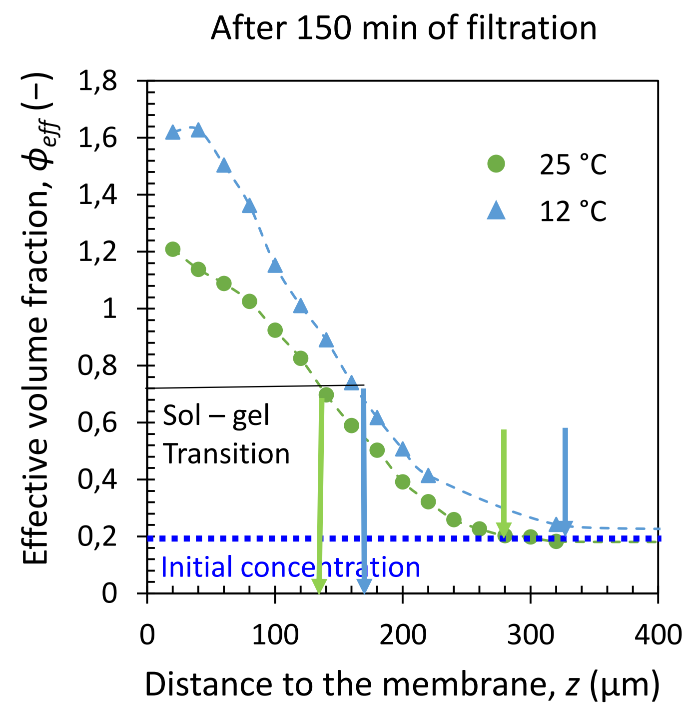


TMP = 1,1 bar
V = 3 cm/s

. Decrease of J =f(t) → acumulation of casein micelles at the membrane surface
. $J_{12°C} < J_{25°C}$ → Increase of permeate viscosity at low temperature

TMP = 1.1 bar
V = 3 cm/s

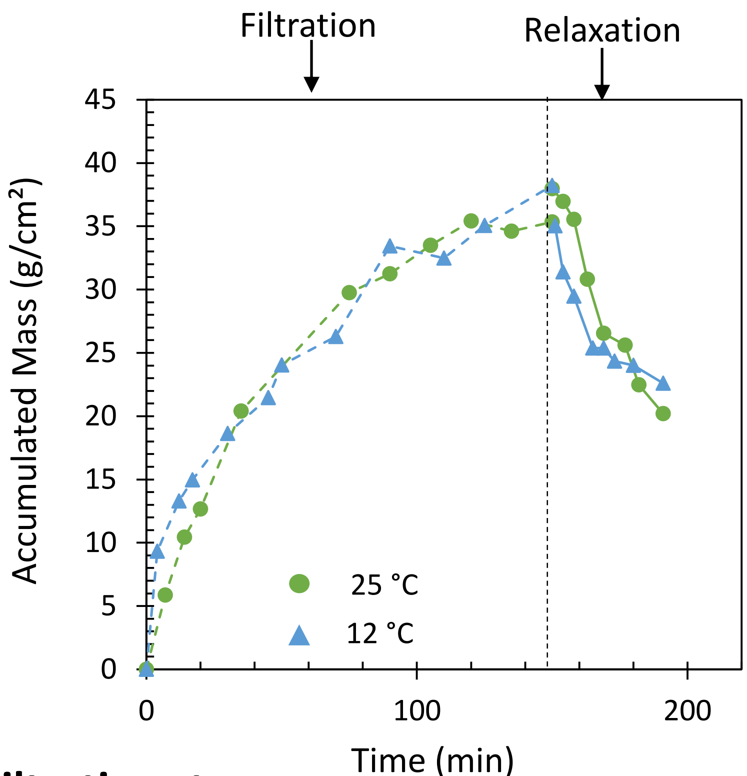


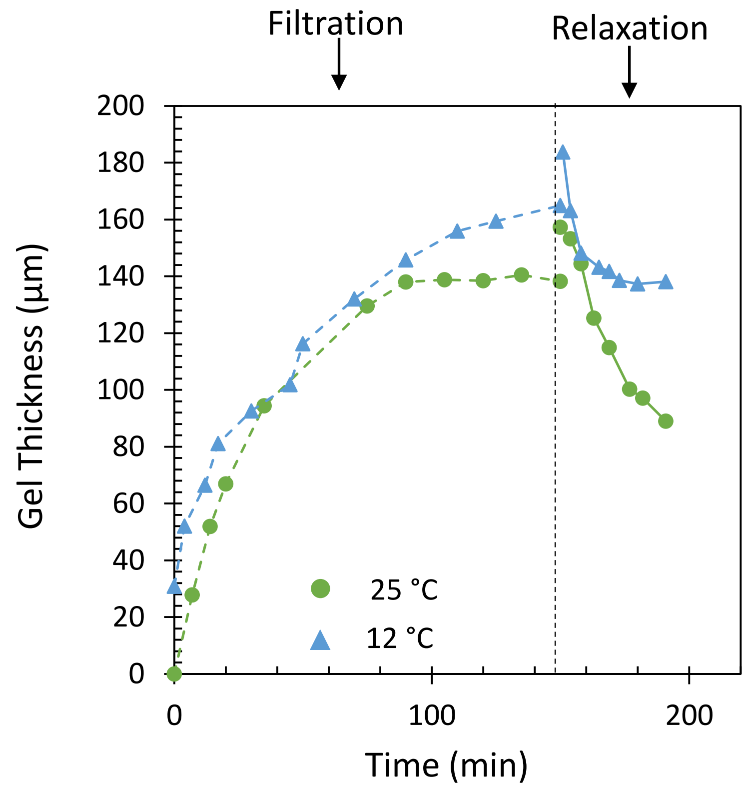


At the end of the 150 min filtration,
the **casein concentration** at the membrane surface
the **effective volume fraction** at the membrane surface
the **thickness of the accumulated layer**
the **thickness of the gel**
are higher at 12°C compared to 25°C

Results – Accumulated mass and gel thickness - SAXS

TMP = 0.1 bar
V = 3 cm/s





Filtration step

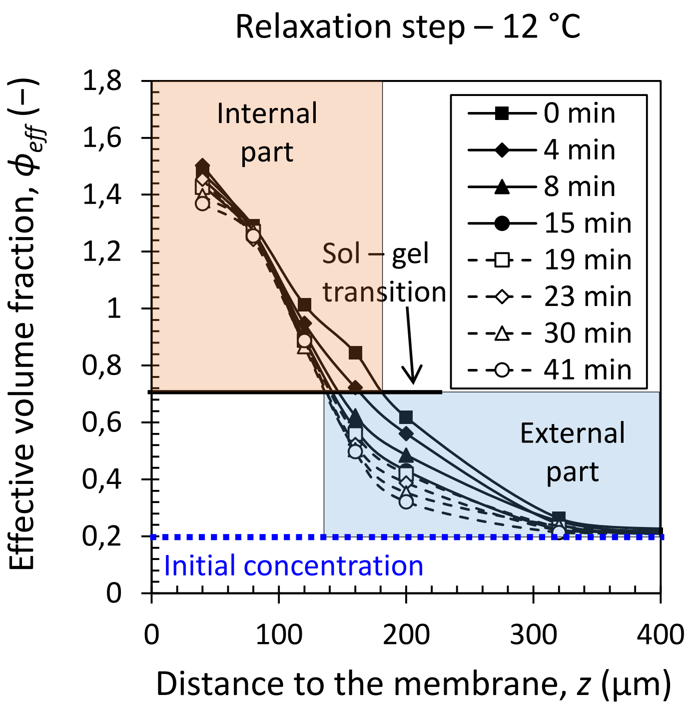
'Similar' accumulated mass at 12 and 25°C
The gel thickness is higher at 12 °C,compared to 25 °C

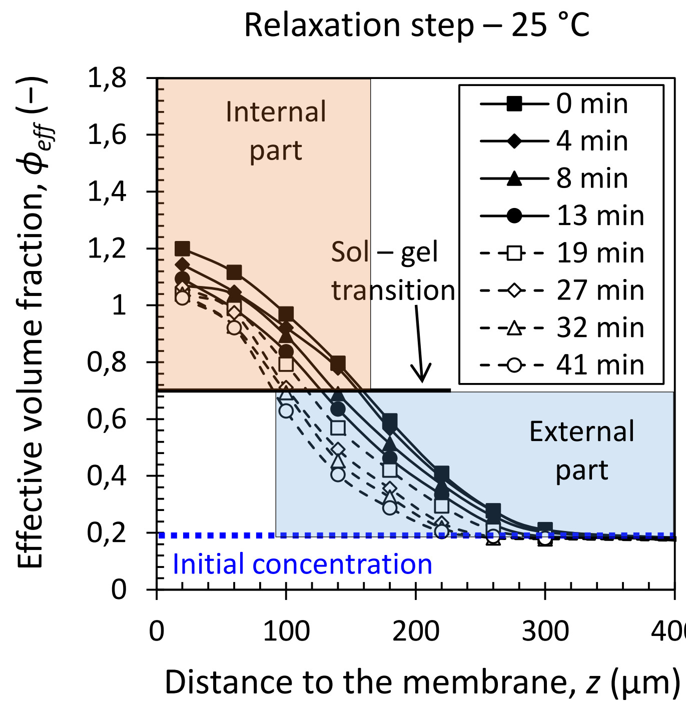
Relaxation step

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

Results – Cohesivness of gel - SAXS

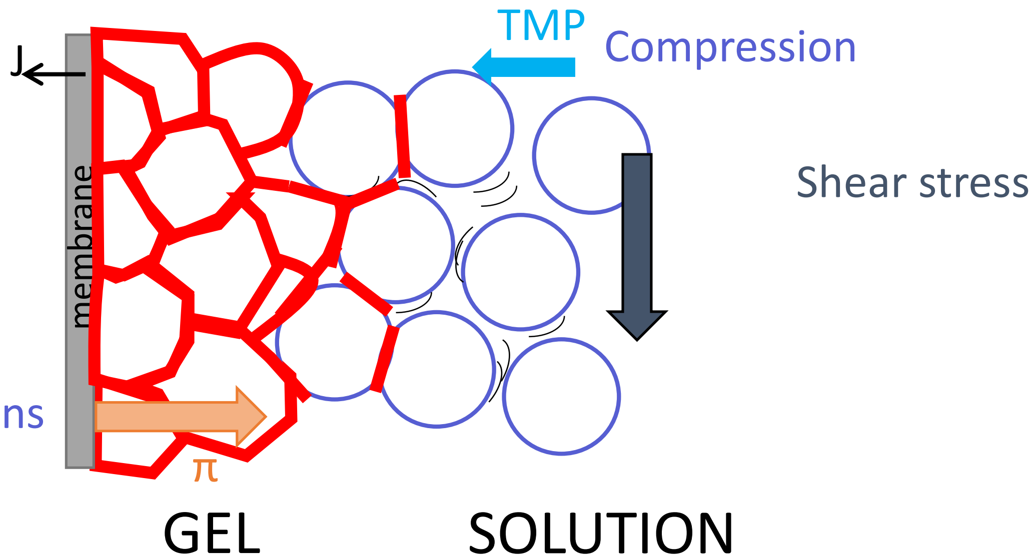
TMP = 0.1 bar
V = 3 cm/s





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

Conclusions



Osmotic pressure, π	Rheology	Cohesivness
Casein micelles are less compressible at 7°C / 20 °C	$[Cas]_{sol\text{-}gel}$ is lower at 7 °C /20 °C	Gel of casein micelles obtained at 7 °C are more cohesive/ 20°C
The thickness of the accumulated layer is higher at 12°C compared to 25°C	The thickness of the gel is higher at 12°C compared to 25°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!