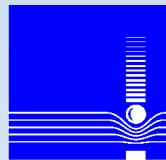


Cross flow ultrafiltration of skim milk assisted by ultrasound: multi-scale characterization



Laboratoire Rhéologie et Procédés,
UMR 5520, Grenoble, France

Hengl N, Jin Y, Baup S, Pignon F, Gondrexon N



European Synchrotron Radiation Facility,
Grenoble, France

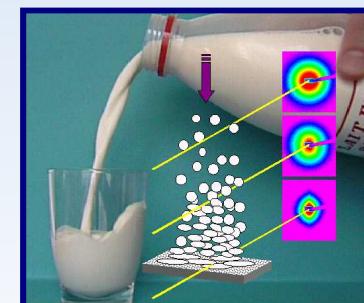


Sztucki M, Narayanan T



AGROCAMPUS OUEST, UMR 1253 STLO
Science et Technologie du Lait et de
l'Œuf, Rennes, France

Gésan-Guiziou G



OUTLINE

1) Context : Ultrafiltration-Ultrasound

2) *In-situ* characterization

Macro-scale (membrane process)

Nano-scale (SAXS measurements)

3) Effects of ultrasound

Ultrafiltration of skimmed milk under ultrasound

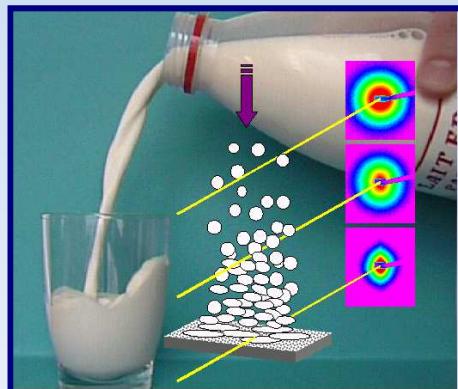
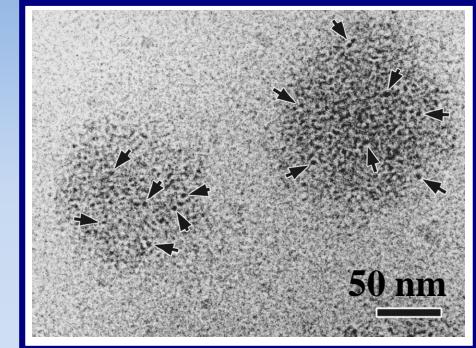
Relation between macro and nano scale observations

4) Conclusions

UNDERSTAND THE MECHANISMS INVOLVED IN ULTRAFILTRATION OF CASEIN MICELLES UNDER ULTRASOUND

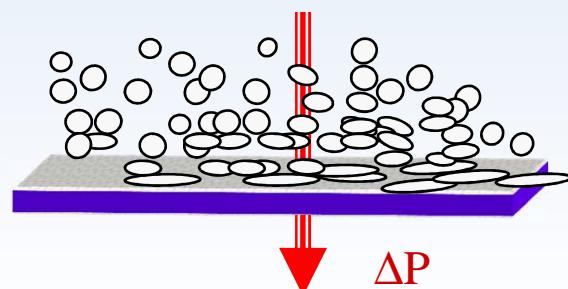
Why Casein micelles?

- Casein micelles is the main protein contained in milk.
- It plays a key role in milk processing (cheeses, yogurts, ice-creams ...) and especially in ultrafiltration processes.



Why ultrafiltration process?

- Milk production in European Union is about 43 billion € each year.
- Turnover of 117 Billion € in dairy processing.
- Concentrate species for subsequent treatments.
- Casein standardization, bacteria removal, concentrate soluble protein

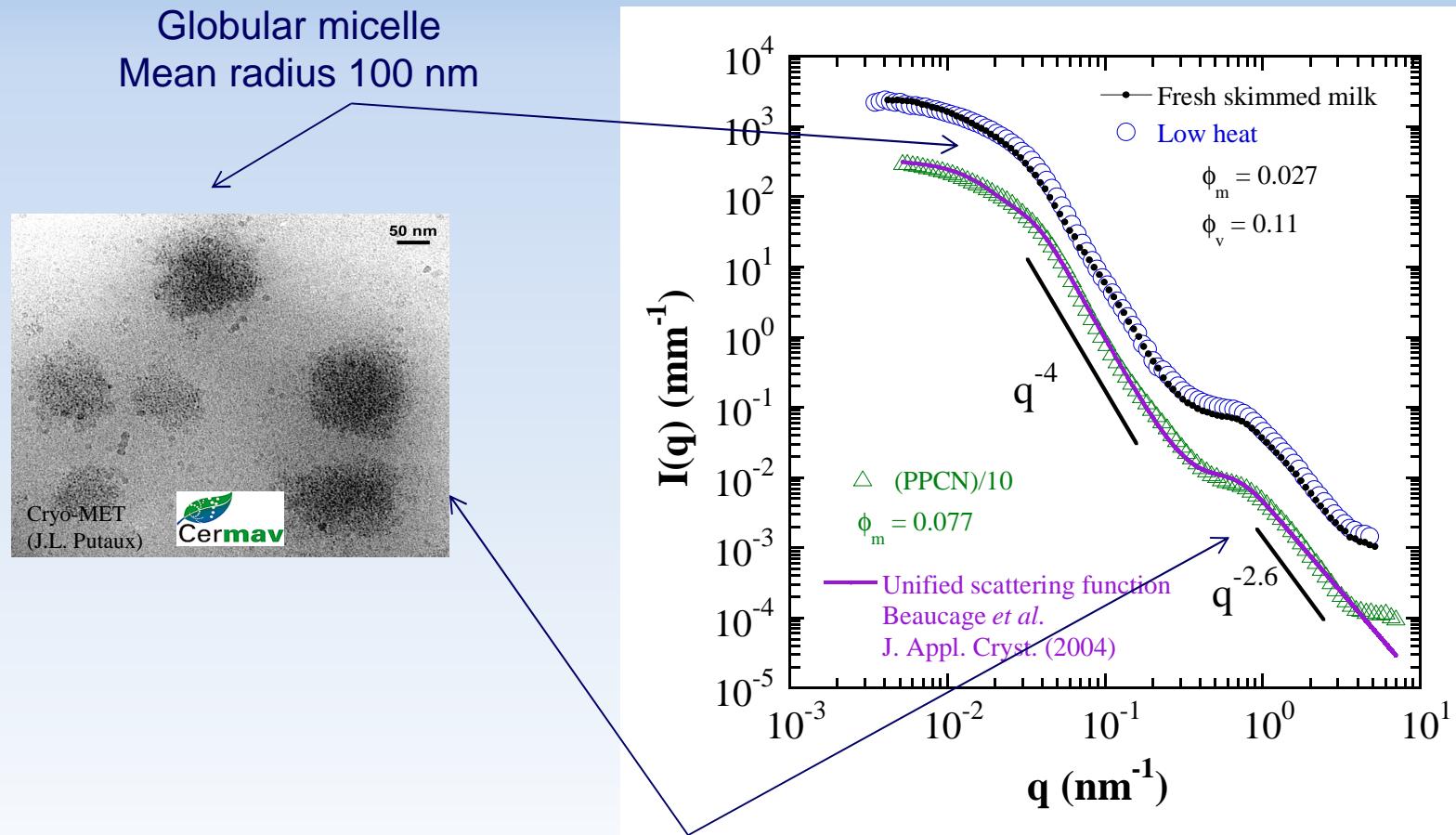


Ultrafiltration process performance is governed by the structural organization of the casein micelles accumulated on the membrane.

Casein micelle dispersions

Aggregates both heterogeneous in size and composition:
Casein (α_{s1} , α_{s2} , β et κ) + Colloidal calcium phosphate (CCP)

Skimmed milk: aqueous suspension of caseins micelles + soluble proteins + mineral and organic salts



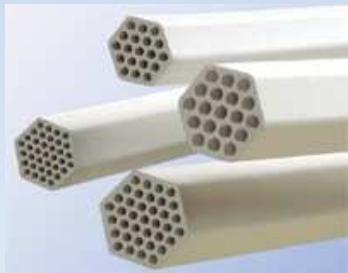
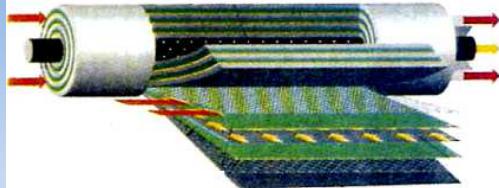
[Pignon *et al.* J. Chem. Phys. 121 (2004)]

[Marchin *et al.* J. Chem. Phys. 126 (2007)]

Internal uniform protein matrix
containing disordered CCP

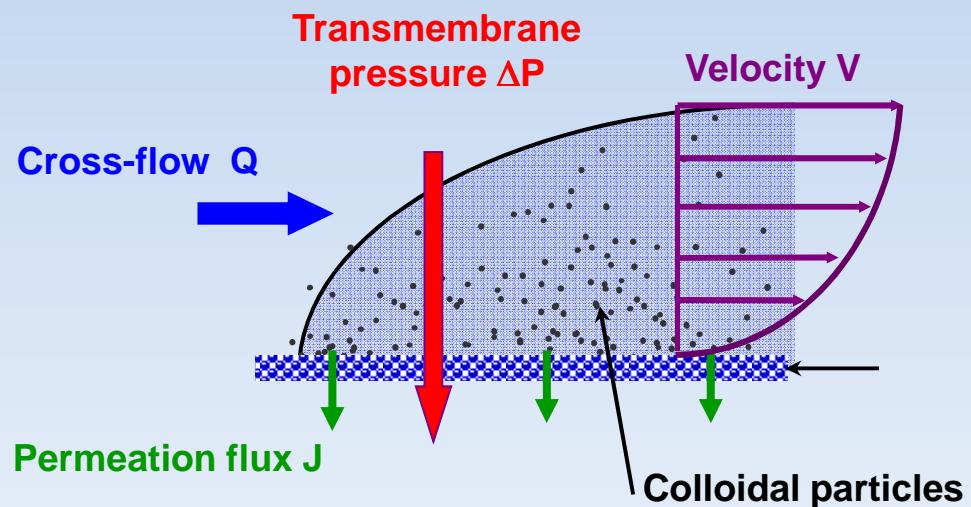
SAXS: Small Angle X-ray Scattering

CROSS-FLOW MEMBRANE ULTRAFILTRATION PROCESS



Goal

Concentrate or purify
nanoparticles dispersions



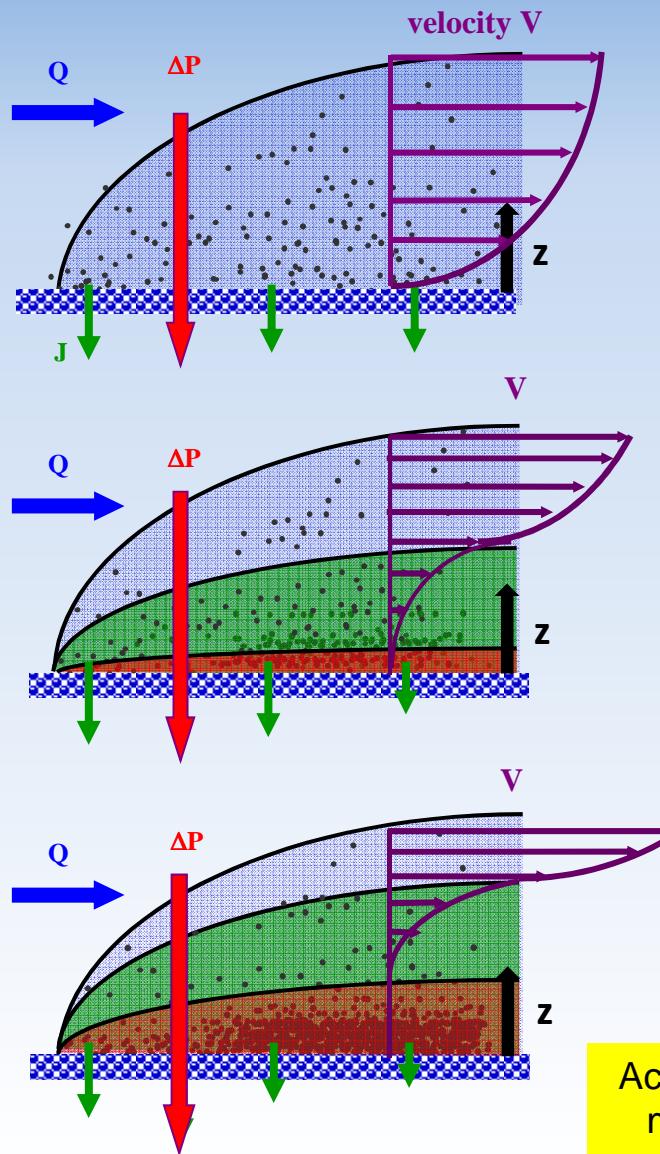
Water,
waste water
treatment

Parmaceutical
Bio-industries

Agro-industries

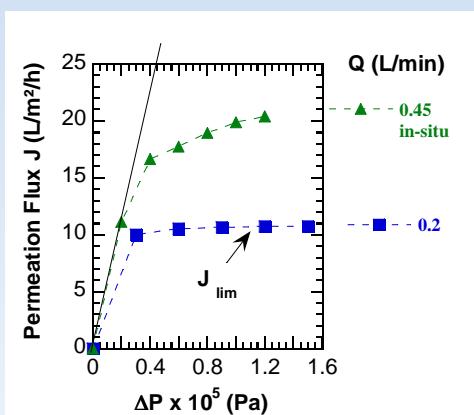
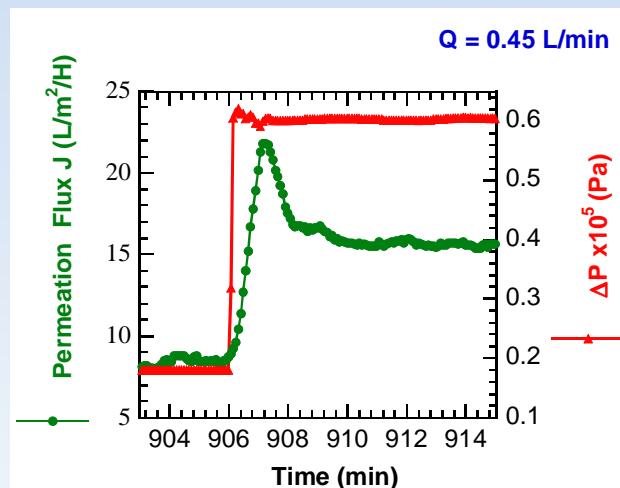
Chemical
industries

CROSS-FLOW MEMBRANE ULTRAFILTRATION PROCESS: LIMITATIONS



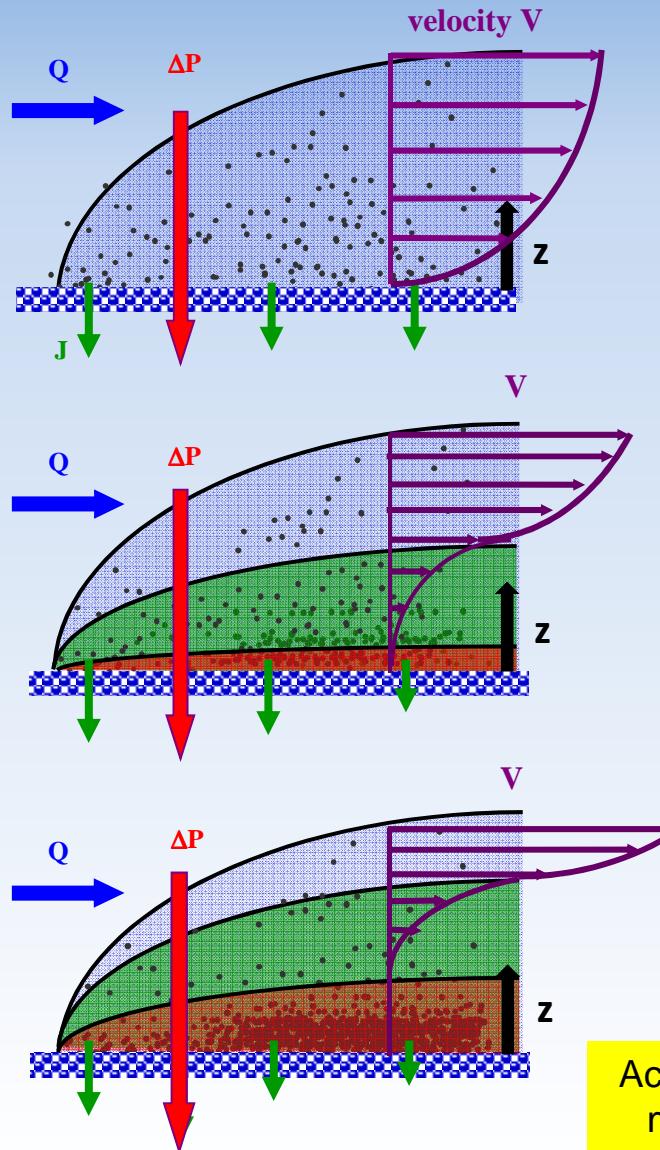
Permeation flux evolution

- Increase of particle concentration during time
- Drastic reduction of the permeation flux
- Transition from stable filtration to unstable critical regime with limiting flux J_{lim}



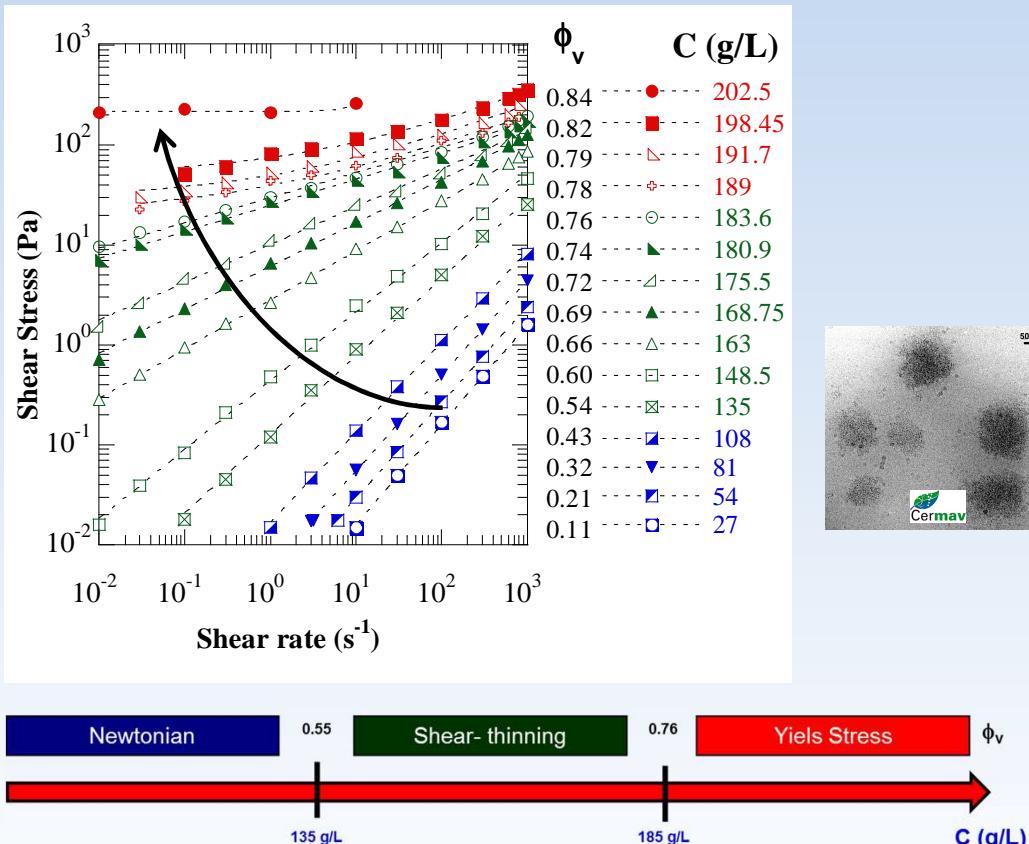
Accumulation of particles near the membrane surface during time

CROSS-FLOW MEMBRANE ULTRAFILTRATION PROCESSES: LIMITATIONS



Rheological behavior evolution

- Increase in viscosity and shear stress at increasing volume fraction (t, z) near the membrane surface
- Sol-gel transition?



Accumulation of particles near the membrane surface during time

EFFECT OF ULTRASOUND ON THE STRUCTURAL ORGANIZATION IN THE ACCUMULATED LAYERS

Acoustic streaming

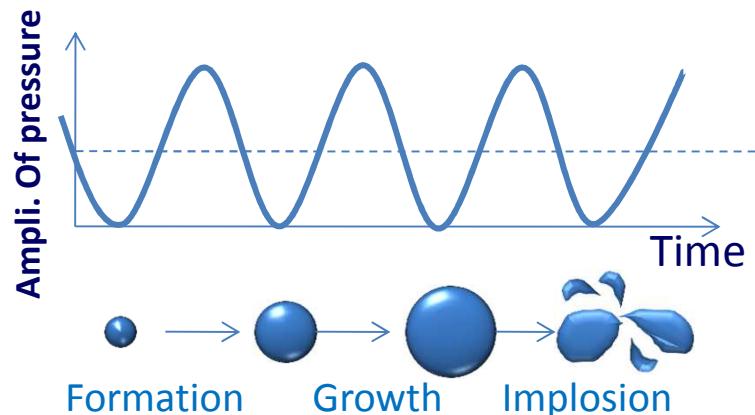


A. Nowicki et al., 1998

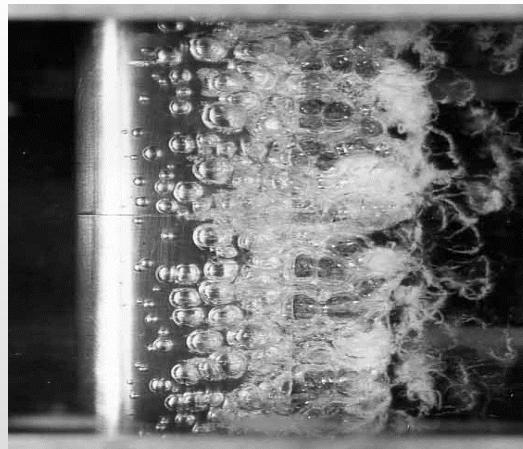


W. Dridi et al., 2007

Cavitation

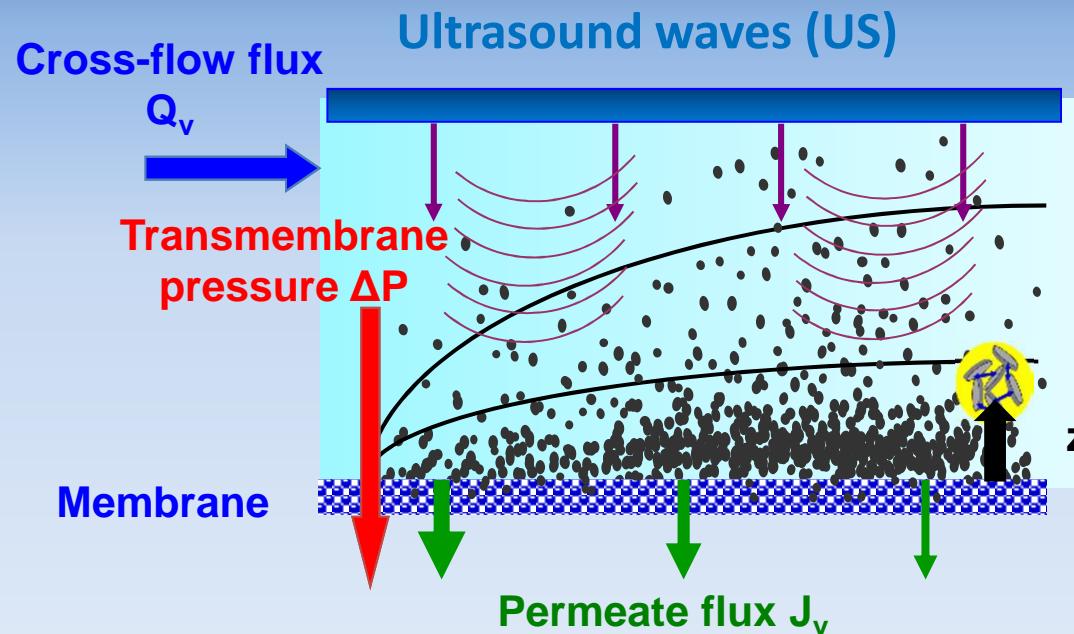


Cavitation bubbles



C. E. Brennen et al., 2000

EFFECT OF ULTRASOUND ON THE STRUCTURAL ORGANIZATION IN THE ACCUMULATED LAYERS

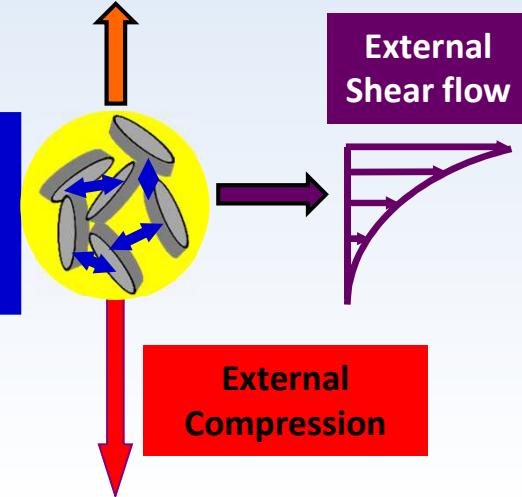


Interest of Ultrasound

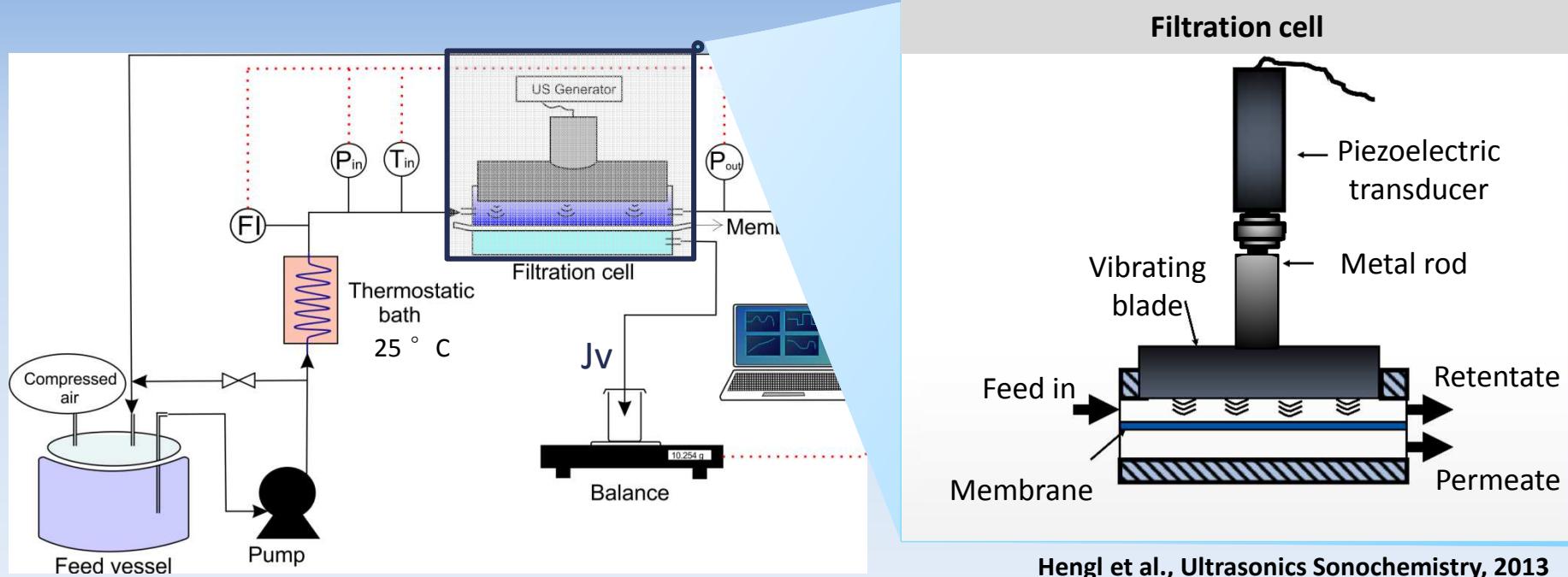
- **Control of concentrated layer formation** and aggregation of colloidal particles
- **Increase the filtration performance**
- **In-situ SAXS** is a powerful method to elucidate the structuring mechanisms involved in ultrafiltration processes

Osmotic pressure $\Pi(C, z)$

Internal colloidal interactions
Viscosity
internal stress



DEVELOPMENT OF AN INNOVATIVE SAXS CROSS-FLOW US-COUPLED FILTRATION CELL



PES membrane

Material: polyethersulfone
Cut-off: 100 kDa
Supplier: Rhodia Orelis

Characteristics of ultrasound

Frequency: 20 kHz
Amplitude: 1.6 µm
Input power: 2-10 W

EFFECT OF ULTRASOUND ON THE STRUCTURAL ORGANIZATION IN THE ACCUMULATED LAYERS (*In-situ* SAXS)

Filtration
Retentate
Concentration polarization layer
Membrane
Permeate



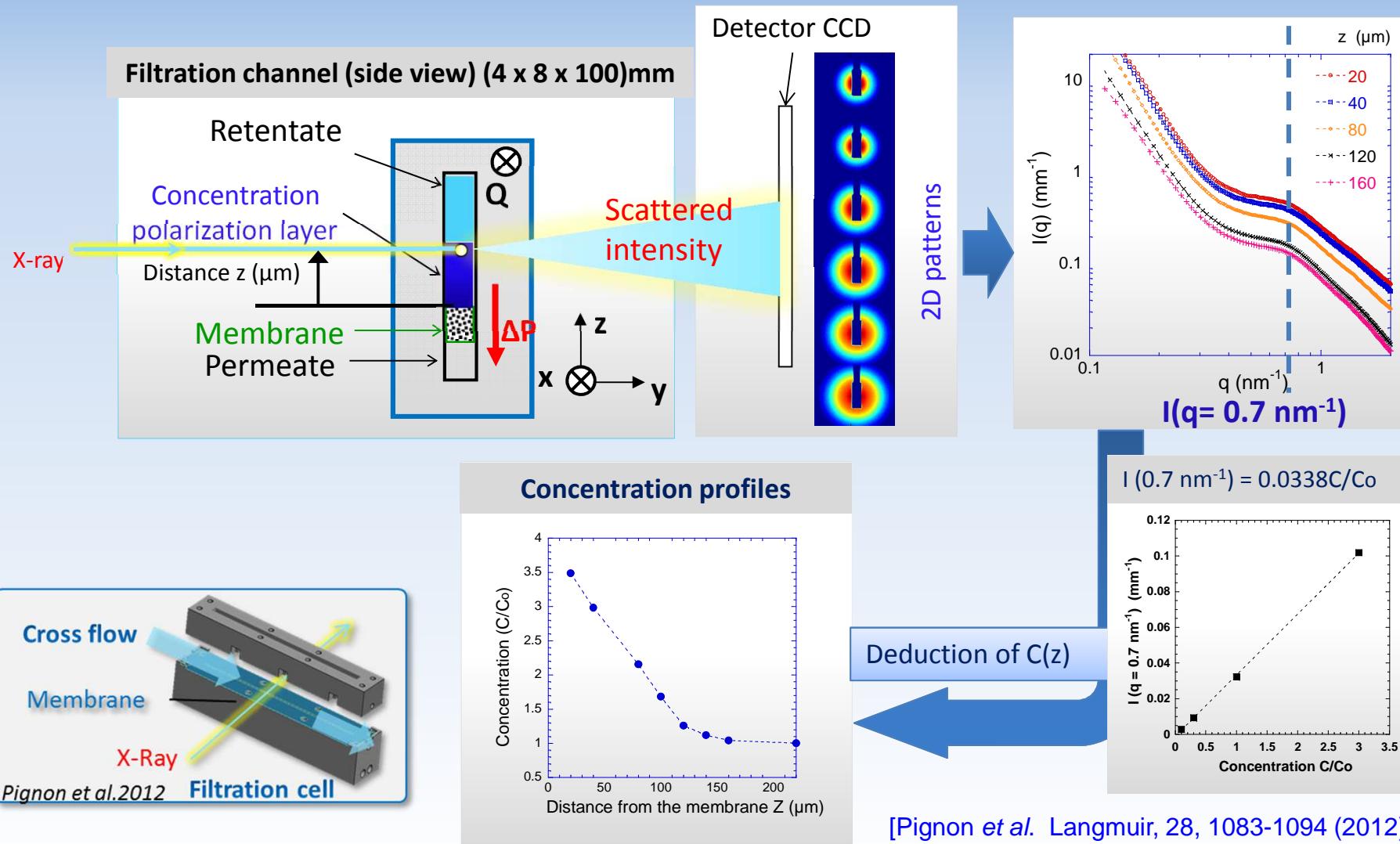
ID02 High Brilliance beamline, ESRF

Wavelength: 0.1 nm

Beam size: 20 µm vertical, 200 µm horizontal



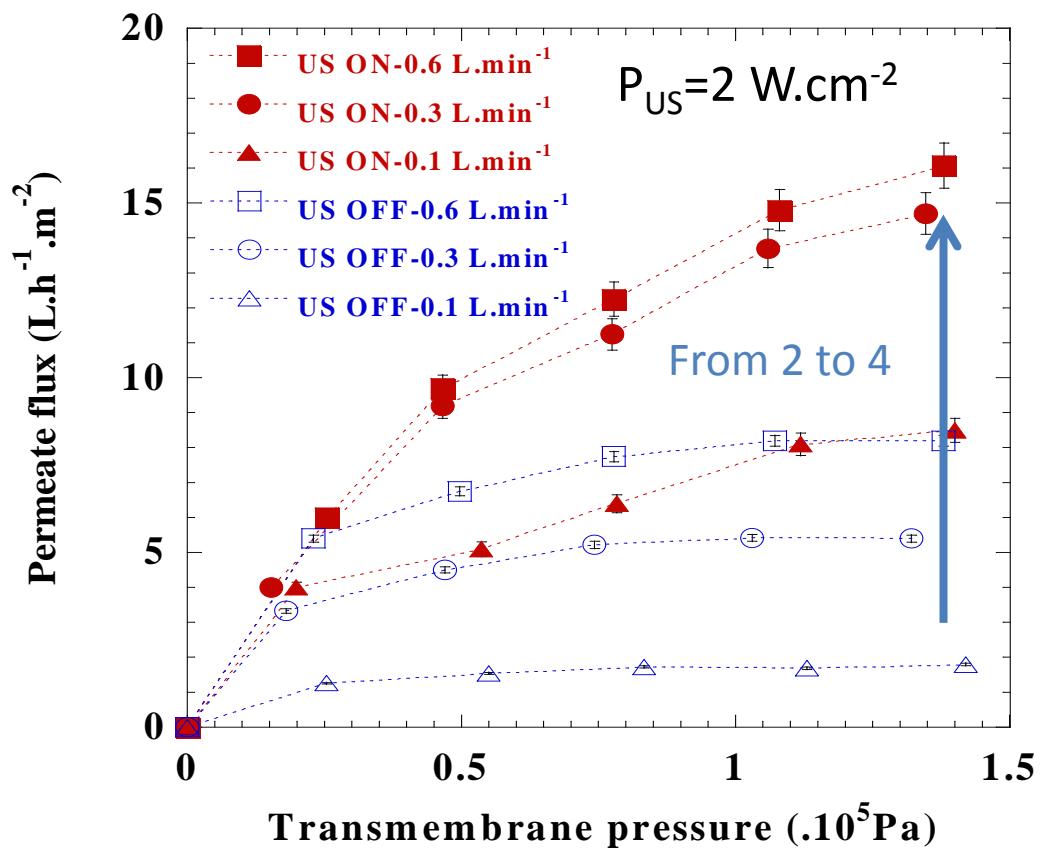
DETERMINATION OF CONCENTRATION PROFILE FROM *IN-SITU* SAXS



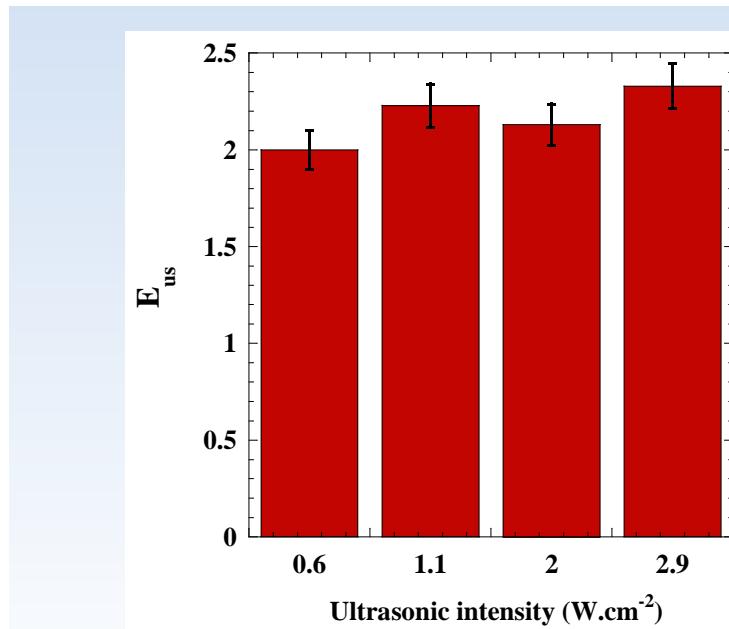
ULTRAFILTRATION OF SKIMMED MILK UNDER ULTRASOUND: MACRO-SCALE APPROACH

C_o = casein micelle concentration of standard skim milk (27 g.L^{-1})

Skimmed milk concentration: $C = C_o$, $\text{pH} = 6.7$, $T = 25 \pm 1^\circ\text{C}$. Ultrasound: 20 kHz

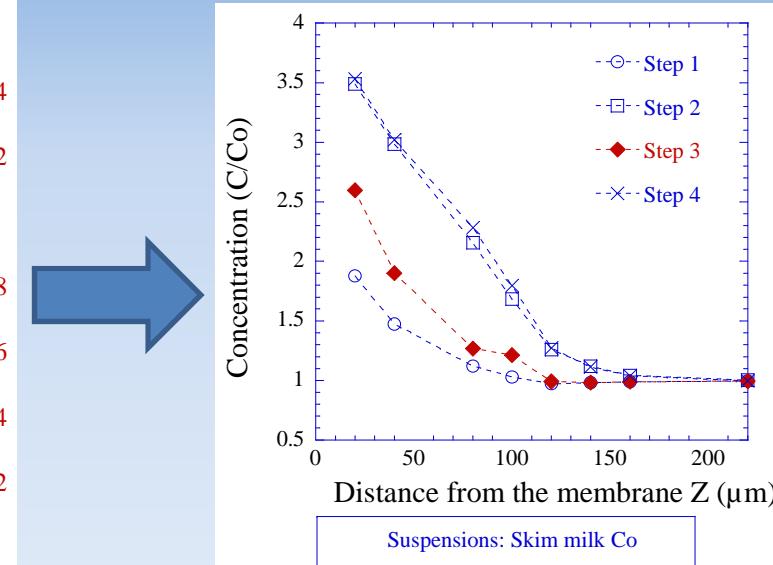
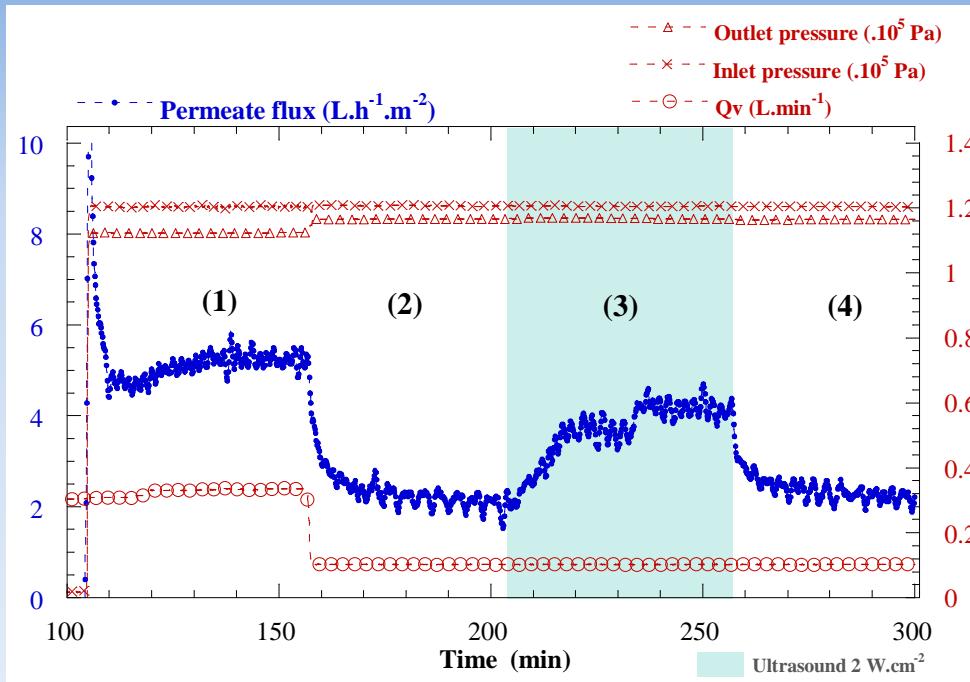


Filtrations	Re	Membrane permeability ($\times 10^{-5} \text{ L.h}^{-1} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1}$)		$\text{TR}_{\text{caseins}}$
		Before UF	After UF	
US ON 0.6 $\text{L} \cdot \text{min}^{-1}$	/	92.6	81.5	99.9%
US OFF 0.6 $\text{L} \cdot \text{min}^{-1}$	902			99.7%
US ON 0.3 $\text{L} \cdot \text{min}^{-1}$	/	75.5	62.7	99.2%
US OFF 0.3 $\text{L} \cdot \text{min}^{-1}$	451			99.8%
US ON 0.1 $\text{L} \cdot \text{min}^{-1}$	/	99.7	85.2	99.8%
US OFF 0.1 $\text{L} \cdot \text{min}^{-1}$	150			99.0%



$$\text{TMP} = 1.1 \times 10^5 \text{ Pa}, Q_v = 0.3 \text{ L} \cdot \text{min}^{-1}$$

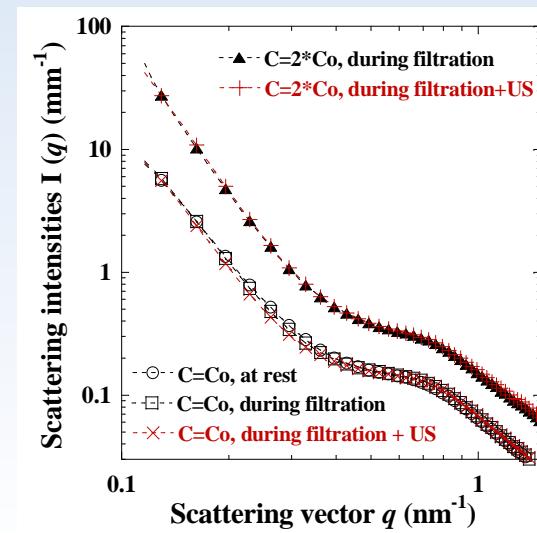
ULTRAFILTRATION OF SKIMMED MILK UNDER ULTRASOUND: COMBINATION OF MACRO-SCALE RESULTS AND NANO-SCALE OBSERVATIONS



Experiment details

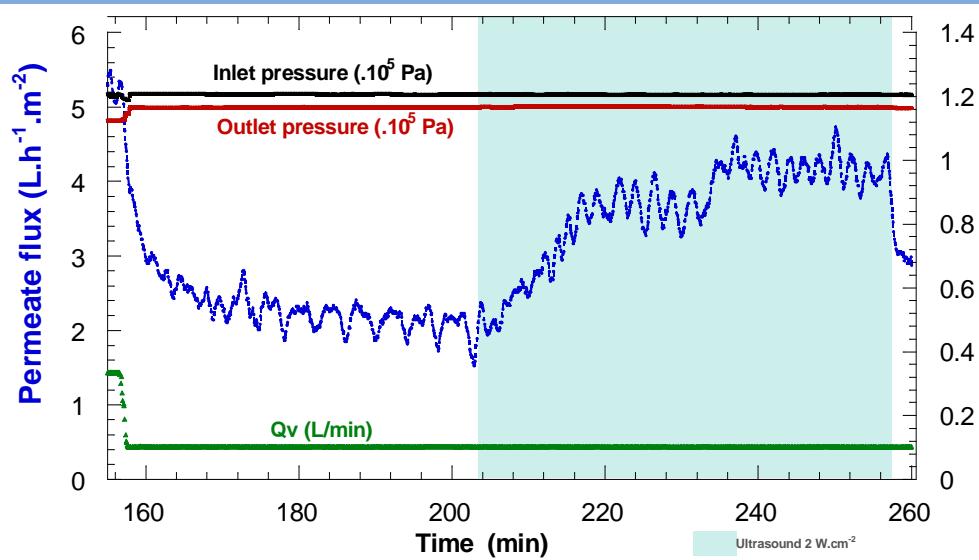
Casein Micelles $C = C_0 = 27 \text{ g/L}$
 Ultrafiltration à $1.2 \times 10^5 \text{ Pa}$, $Q_v = 0.3$ and $0.1 \text{ L} \cdot \text{min}^{-1}$
 Ultrasound: 20 kHz , 2 W.cm^{-2} ; $T = 25 \pm 1 \text{ }^\circ\text{C}$

- Partial disruption of the accumulated particle layers
- No influence of ultrasonication on structural organization at these length scales

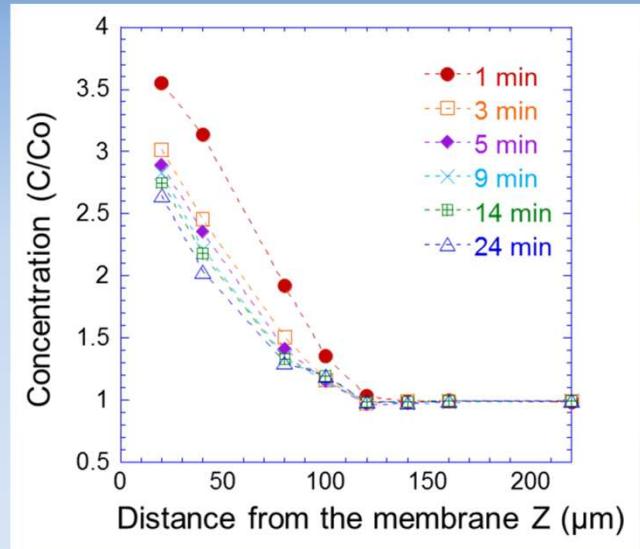


ULTRAFILTRATION OF SKIMMED MILK UNDER ULTRASOUND: EFFECT OF CURATIVE AND PREVENTIVE MODE

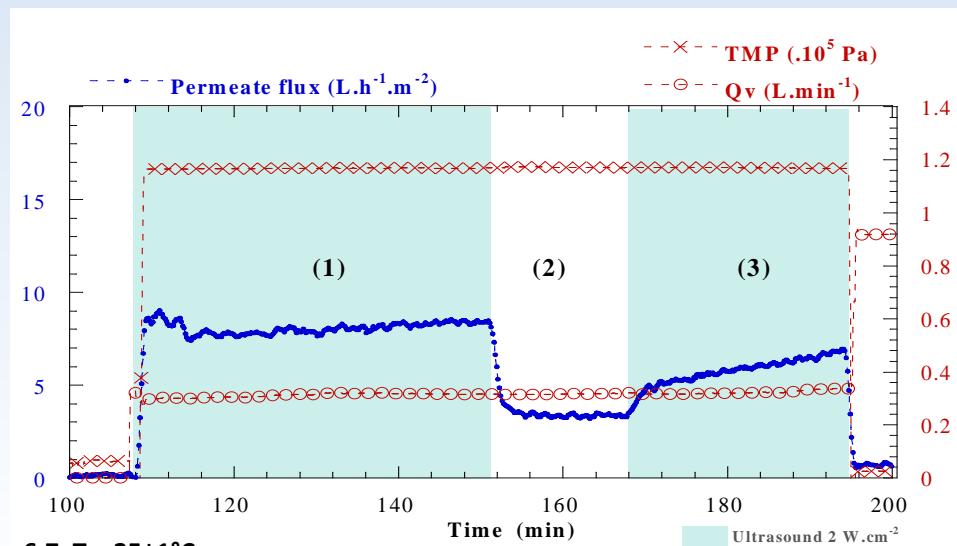
Curative mode



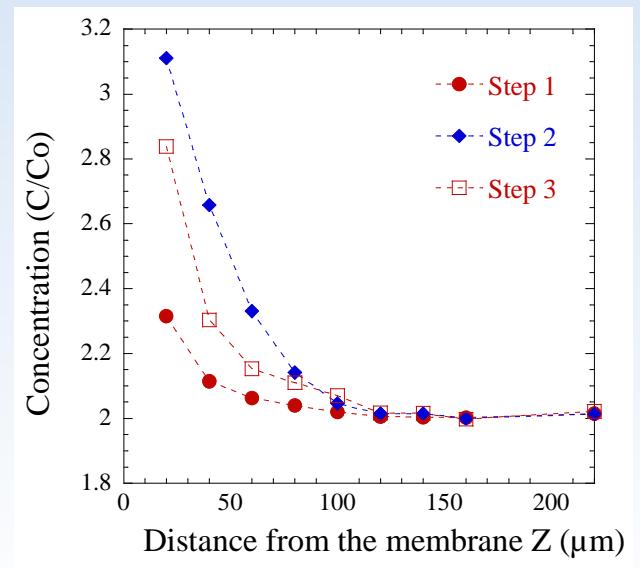
$C = C_0$, $\text{pH} = 6.7$, $T = 25 \pm 1^\circ\text{C}$.
Ultrasound: 2 W.cm^{-2} , 20 kHz



Preventive mode



$C = 2*C_0$, $\text{pH} = 6.7$, $T = 25 \pm 1^\circ\text{C}$.
Ultrasound: 2 W.cm^{-2} , 20 kHz

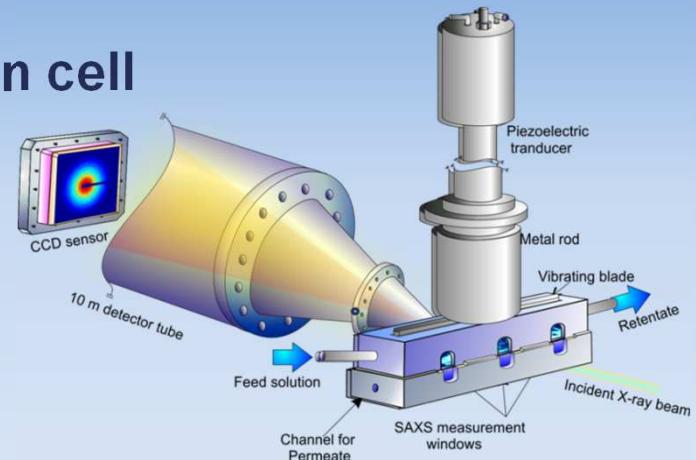


Skim milk $2*C_0$

Conclusions

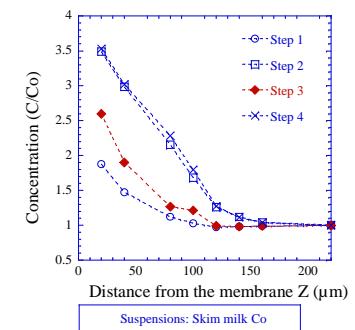
Development of an innovative US filtration cell

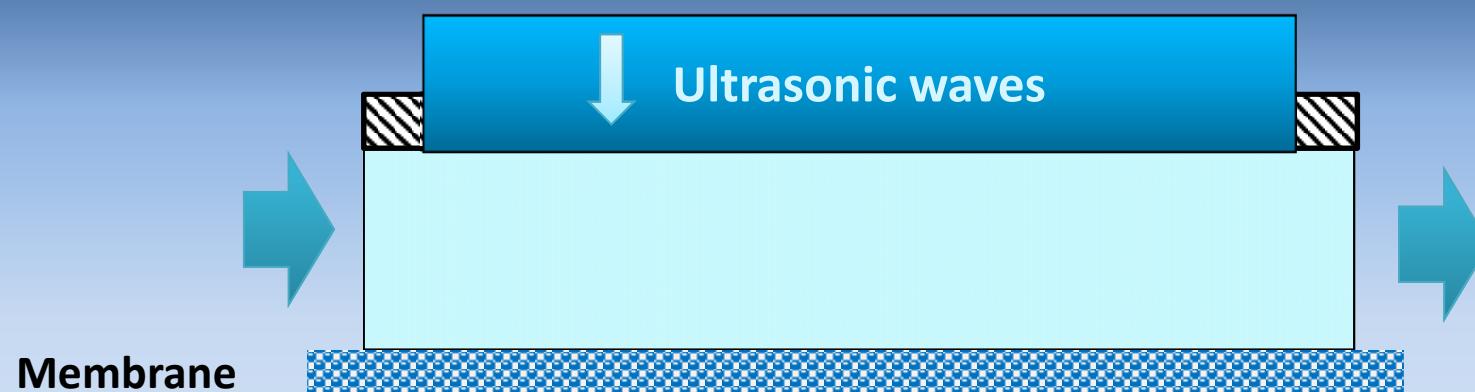
- ✓ Access to *in-situ* characterization by SAXS of concentrated layers during ultrafiltration process.



Skim milk under UF assisted by US

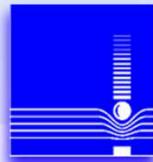
- ✓ Characterization of the phenomena induced by the US:
 - Disaggregation of accumulated particles near the membrane surface
 - Take into consideration the curative and preventive mode for industrial applications
- ✓ Better performance of filtration with US, with a factor from 2 to 4 on permeation fluxes.





Thank you for your attention

Acknowledgments



M. Karrouch
D. Blésès
H. Galliard
F. Hugenell

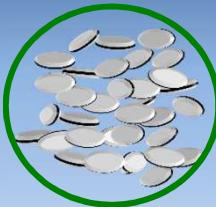


J. Gorini
SC 2409 and SC 3483
beam time allocation of ESRF



UMR 1253 STLO
INRA-Agrocampus Ouest
G. Gésan-Guizou

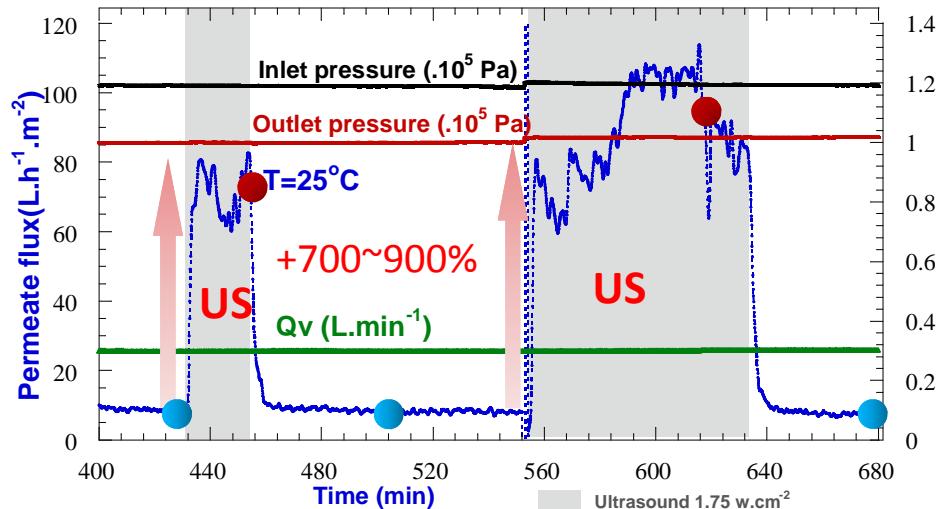
6% tspp



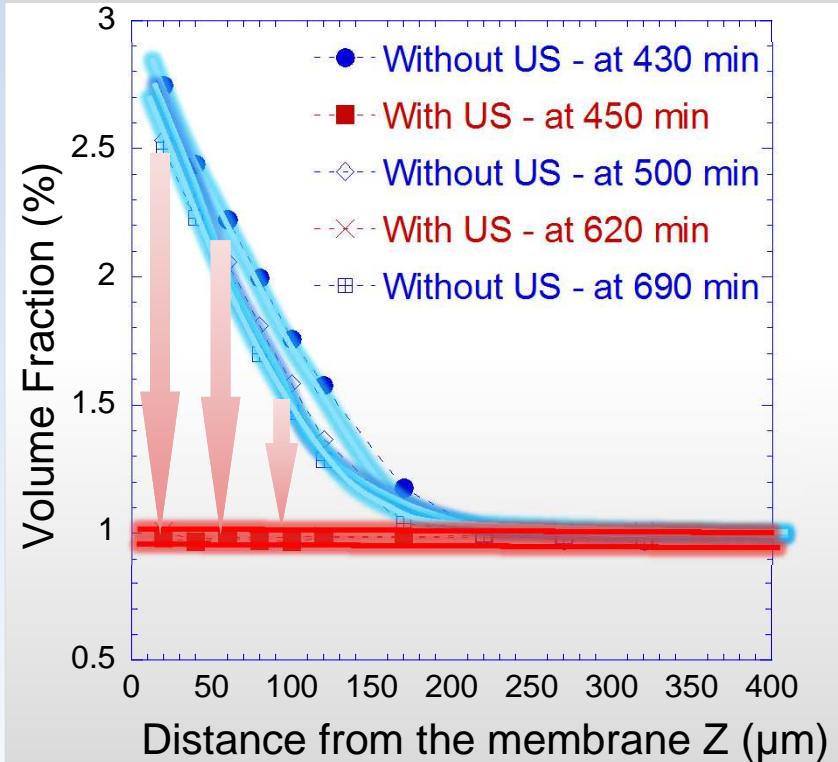
Effect of US at steady state in Laponite dispersions with tspp

- Removal of concentrated layer by US
- Disaggregation from the membrane surface

Macro-scale



Nano-scale (via SAXS)



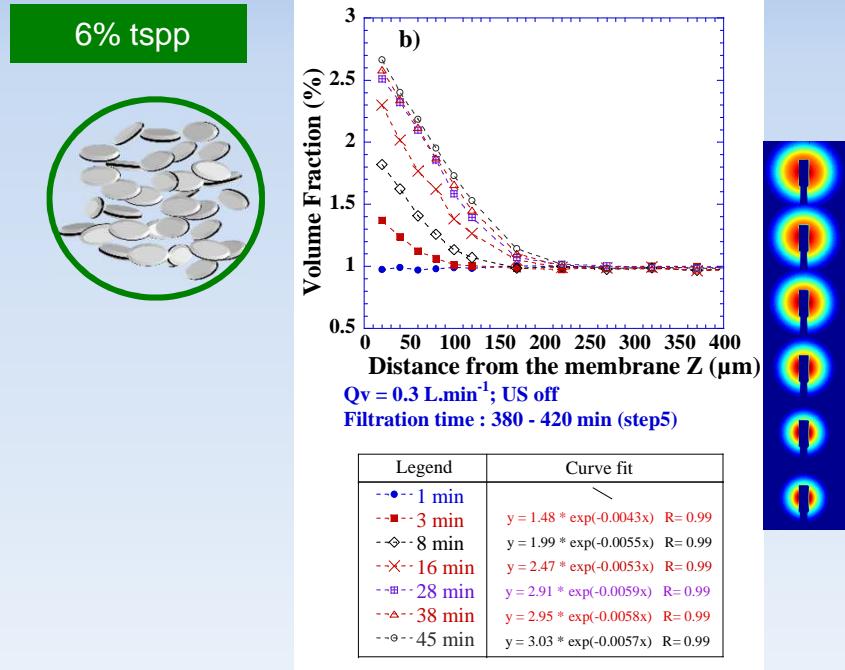
Experiment details

Laponite 1 vol%, 6% tspp, 12 days ;
Ultrafiltration at $1.1 \times 10^5 \text{ Pa}$, $Q_v = 0.3 \text{ L} \cdot \text{min}^{-1}$;
Ultrasound: 20kHz, $1.75 \text{ w} \cdot \text{cm}^{-2}$; $T = 25 \pm 1^\circ\text{C}$

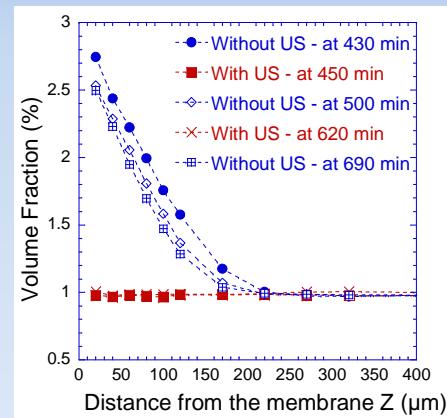
[Jin et al. J. Membrane Sci. 453, 624-635 (2014)]

Structural organization during ultrafiltration of Laponite dispersions

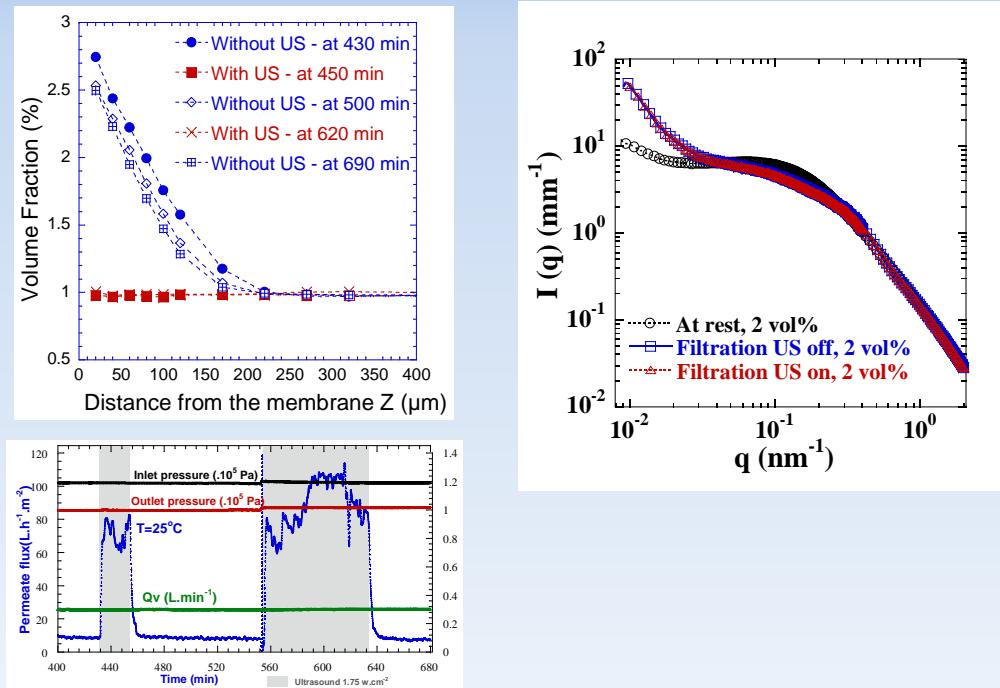
Concentration under cross-flow ultrafiltration



Effect of US on concentration



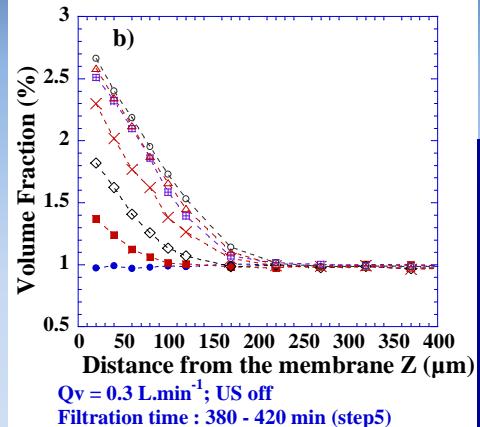
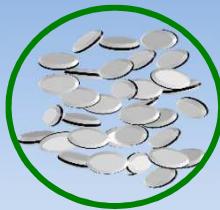
Effect of US on structural organization



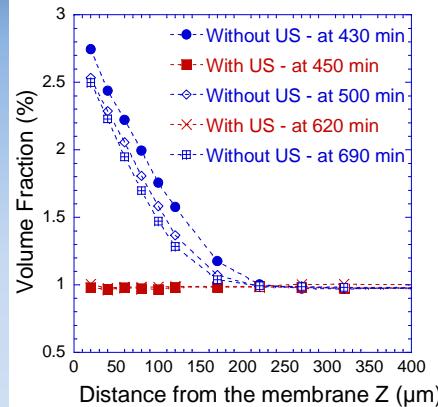
Structural organization during ultrafiltration of Laponite dispersions

Concentration under cross-flow ultrafiltration

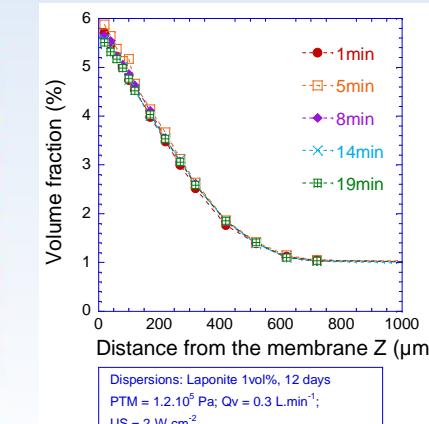
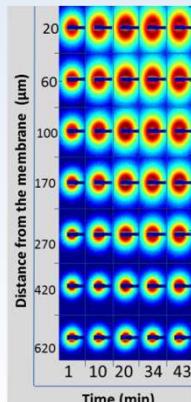
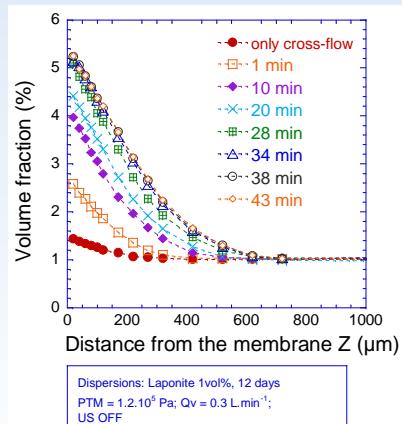
6% tspp



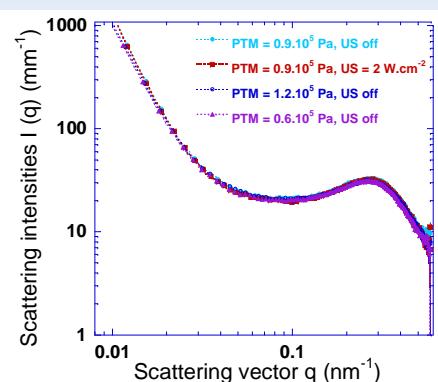
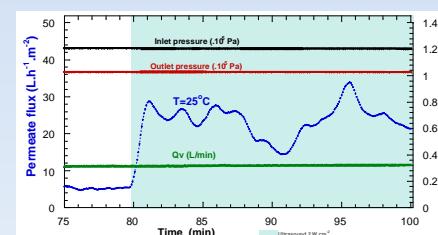
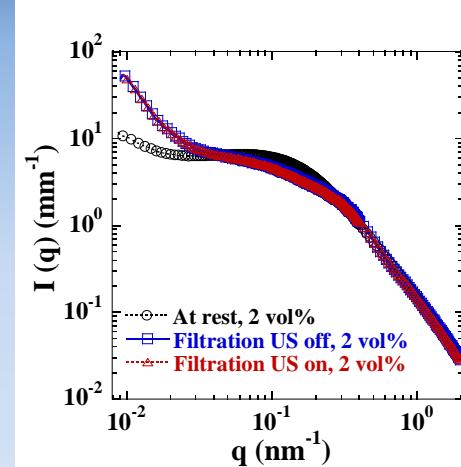
Effect of US on concentration



0% tspp



Effect of US on structural organization

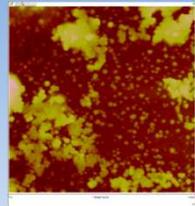


Dispersions: Laponite 1vol%, 12 days
 $Q_v = 0.3 \text{ L} \cdot \text{min}^{-1}$,
Sample position: $z = 80 \mu\text{m}$;
Experiment time: 140 - 220 min

Structural organization during ultrafiltration of SNC and CNC dispersions

Concentration under cross-flow ultrafiltration

Starch Nanocrystals

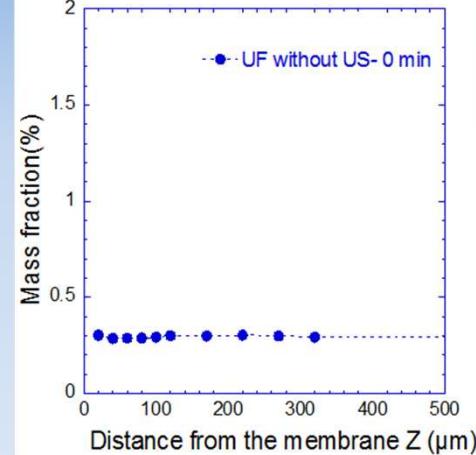


Highly heterogeneous suspensions
Individual nanocrystals
(≈ 100 nm)

Aggregates of starch nanocrystals (≈ 400 nm)
Intact starch granules
(≈ 1 μ m)

Nano-scale (via SAXS)

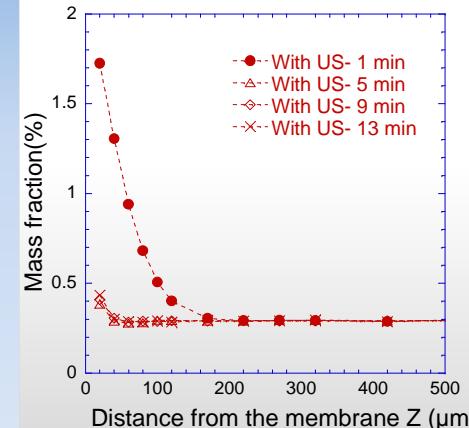
Growth of concentration layer



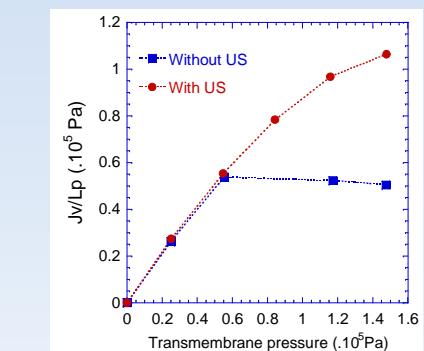
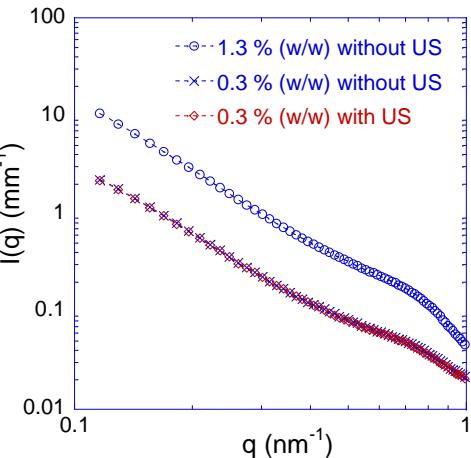
Effect of US on concentration

Nano-scale (via SAXS)

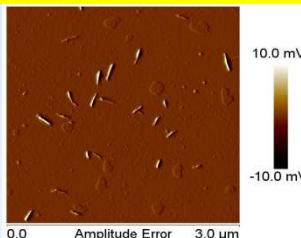
Break-up of concentration layer



Effect of US on structural organization

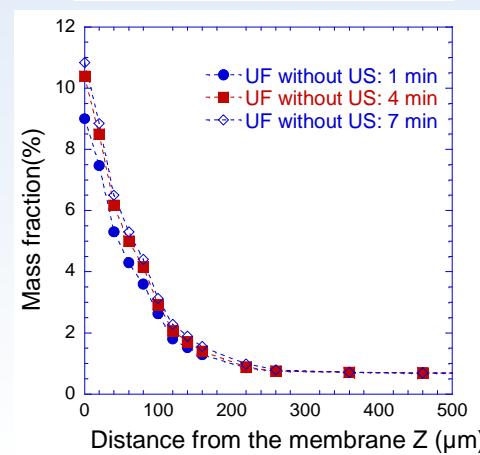
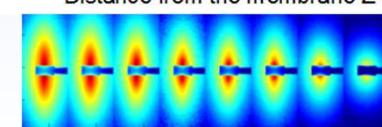
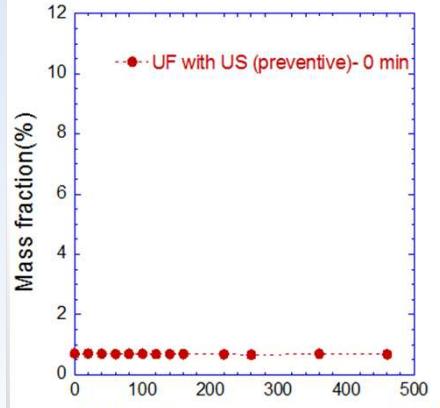


Cellulose Nanocrystals



Nano-scale (via SAXS)

Growth of concentration layer

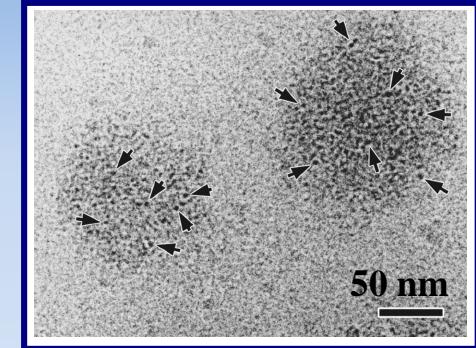


A. Romdhane
E. Mauret
A. Guillet
R. Bardet
J. Bras

Understand the mechanisms involved in ultrafiltration of casein micelles

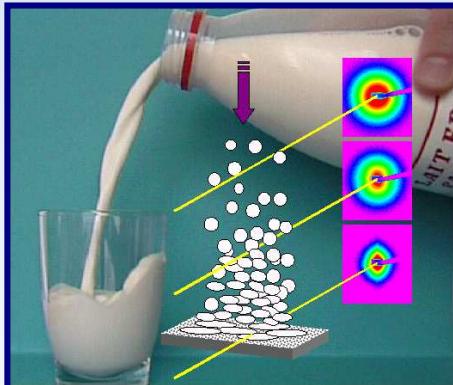
Why Casein micelles?

- Casein micelles is the main protein contained in milk.
- It plays a key role in milk processing (cheeses, yogurts, ice-creams ...) and especially in ultrafiltration processes.



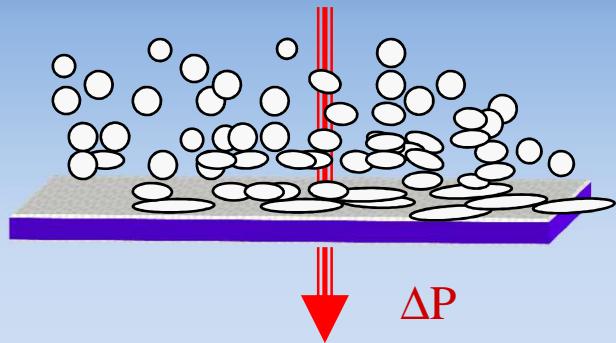
Why ultrafiltration process?

- Milk production in European Union is about 43 billion € each year.
- Turnover of 117 Billion € in dairy processing.
- Ultrafiltration process performance is governed by the structural organization of the casein micelles accumulated on the membrane.



In-situ SAXS is a powerful method to elucidate the structuring mechanisms involved in ultrafiltration processes.

Ultrafiltration Process of Casein Micelles suspensions



- Concentrate species for subsequent treatments.
- Casein standardization, bacteries removal, concentrate soluble protein.

Good agreement between experiments and models at macroscopic length scale

- Optimizing ultrafiltration process require a better understanding of the structure of the casein micelles in the accumulated layers near the membrane at the pertinent nanometer length scales.

- Are casein micelles organized and deformed in deposits?
- How casein micelles concentrate in deposits?
- What is the rheological behavior of deposited layers?

- *In-situ local probe by small angle X-ray scattering*

Casein Micelles Suspensions

Skimmed milk: aqueous suspension of caseins micelles + soluble protein + mineral and organic salts

Casein micelles = heterogeneous in size and composition

mean hydrodynamic radius of 100 nm

Casein (α_{s1} , α_{s2} , β and κ)
19 000 à 25 000 g/mol

+

**Colloidal calcium phosphate (CCP)
Complexe of phosphate, calcium
citrate and magnesium**

- Industrial skimmed milk powder (Promilk 852 B)

with high protein content (84.5 % of native micellar casein)

Dispersed in dimeneralized water

- 0.2 g/l sodium azide, pH = 7.2
- C_0 = Casein micelle content of skimmed milk = 29 g/L, ϕ_m = 0.028

$$1 < C/C_0 < 7$$

$$0.028 < \text{Mass fraction } \phi_m < 0.19$$

$$0.085 < \text{Volume fraction } \phi_v < 0.64$$

Structure of Casein Micelle by SAXS and USAXS

➤ Exceptionally wide range of scattering vector 3×10^{-3} to 7 nm^{-1}

Micelles length scale

Low q branch



Globular micelle

$R_{g1} = 100 \text{ nm}$

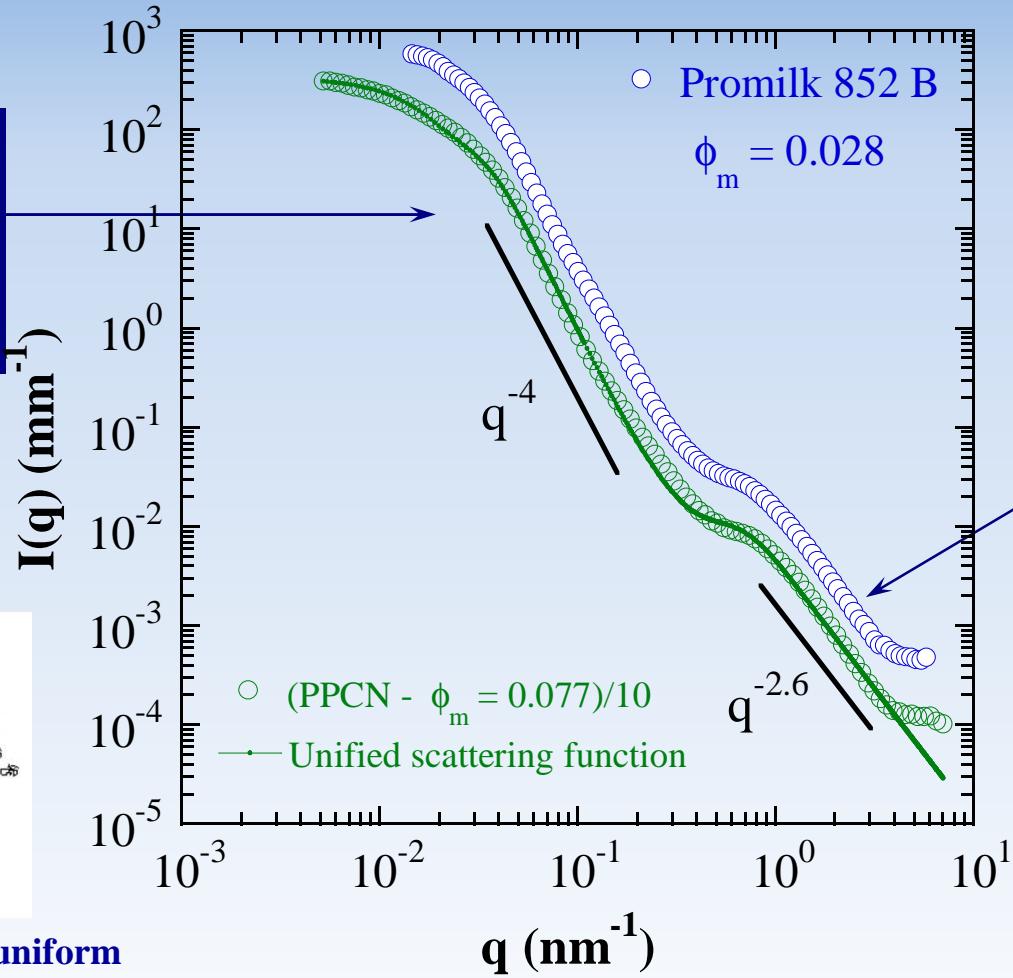
➤ Size, shape interaction



✓ Suit well with model of uniform protein matrix

de Kruif, J Dairy Sci, 1998

Holt *et al.*, Col. Surface A, 2003



Casein length scale

High q region

$R_{g2} = 5 \text{ nm}$

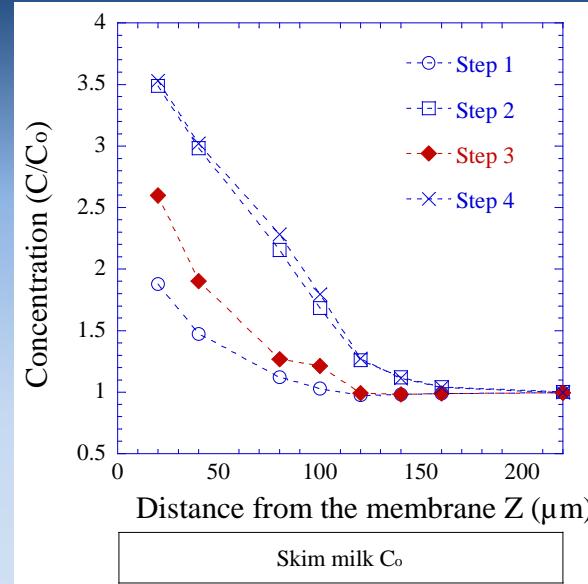
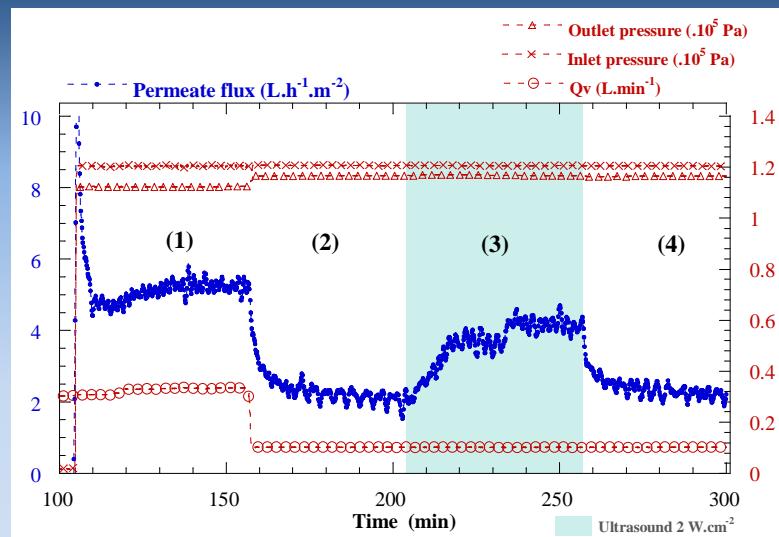
$I(q)$ exhibit a plateau



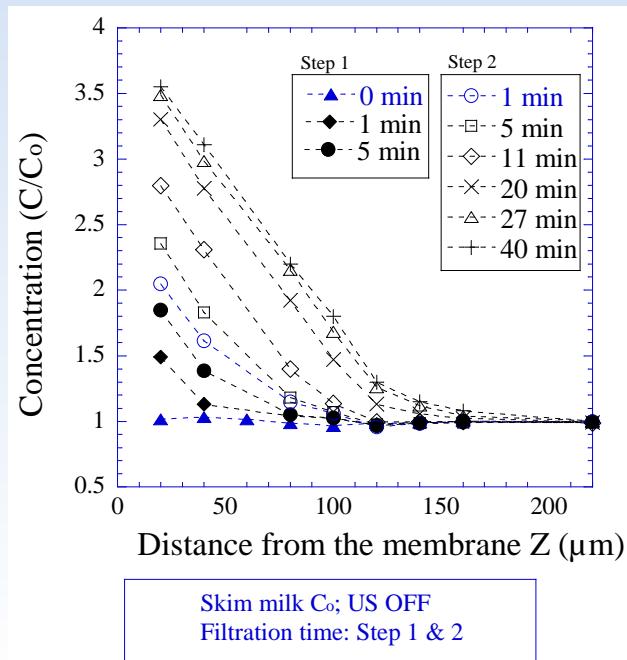
Non globular internal structure

➤ Casein micelles concentration

▪ Pignon *et al.* J. Chem. Phys. 121 8138 (2004)



BUILT UP OF THE CONCENTRATED LAYER



DESTRUCTURATION OF THE CONCENTRATED LAYER

