ESRF	**Experiment title: Time-resolved structural organization and dynamics of colloidal gels submitted to combined shear flow and ultrasound waves: break-down/build-up and diffusion phenomena**	**Experiment number**: SC-5110
Beamline: ID02	**Date of experiment**: from: 10/06/2021 to: 18/06/2021	**Date of report**: 29/04/2022
Shifts: 6	**Local contact(s)**: **T. Narayanan**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Frédéric Pignon[1*], Mathilde Challamel[1*], Emilie Guilbert[1*], Nicolas Hengl[1*], Hugues Bodiguel[1*], Bruno Jean[2*], Thomas Gibaud[3*], Sébastien Manneville[3*]

[1]*Univ. Grenoble Alpes, CNRS, Grenoble INP (Institute of Engineering Univ. Grenoble Alpes), LRP, F-38000 Grenoble, France*

[2]*Univ. Grenoble Alpes, CNRS, CERMAV, F-38000 Grenoble, France*

[3]*Univ Lyon, ENS de Lyon, Univ. Claude Bernard, CNRS, Laboratoire de Physique, F-69342 Lyon, France*

Report: The focus of this project is to study *in-situ* the combined effect of shear flow, pressure and ultrasound waves on the structural organization of colloidal suspensions with the aim of developing novel tunable nano- to micro- structured materials. Accessing a wide range of length scales, subnanometric to a few micrometers will shed light on the orientation mechanisms and structural organizations induced by the relative intensity of these external forces.

Recently, we were able to evidence the ability of the ultrafiltration processes to develop well-defined layered structures of anisometric colloidal particles aligned horizontally along the velocity direction from nanometer to micrometer length scales [1-3]. Furthermore, in our last proposal IN-1071, we discovered by using ultrasound (US) waves, it was possible to align (at nanometric length scale) the liquid crystal organization of cellulose nanocrystals (CNCs) vertically along the wave propagation direction, whereas an horizontal orientation results from the application of a shear flow along the velocity direction. By adjusting the level of shear flow and US intensity applied simultaneously to the CNC suspensions, we were then able to modulate the intensity and direction of the CNCs orientation during the process [4].

Following these initial results, our goal in this proposal SC-5110, was to study by time-resolved in situ SAXS, the time dependent mechanisms leading to orientations during ultrafiltration process in the absence or presence of ultrasounds. The final aim was to develop well controlled multi-layered cellulosic films with alternate perpendicular and parallel orientations on each successive deposited layers.

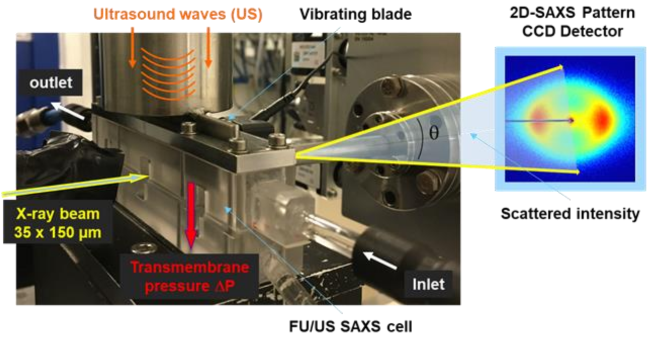

Fig. 1 : Ultrafiltration/Ultrasound-SAXS cell on ID02

A dedicated SAXS channel-type ultrafiltration/ultrasound cell was implemented at ID02 (Fig. 1) to simultaneously generate an US-induced vertical acoustic radiation force at the top of the channel and simultaneously a transmembrane pressure force at the bottom of the channel near the membrane surface.

Thanks to this set-up and in situ SAXS, typical multilayer orthotropic structuring that mimic the articular cartilage organization was achieved in one single (Frontal Ultrafiltration / Ultrasound) (FU/US) processing on CNC suspensions (Fig. 2). The three continuous structured layers (superficial, middle, and deep) regions representative of the multizonal material cartilage [5] was realized starting from an initial CNC suspension at C = 10 wt % and reaching equilibrium in a few tens of minutes.

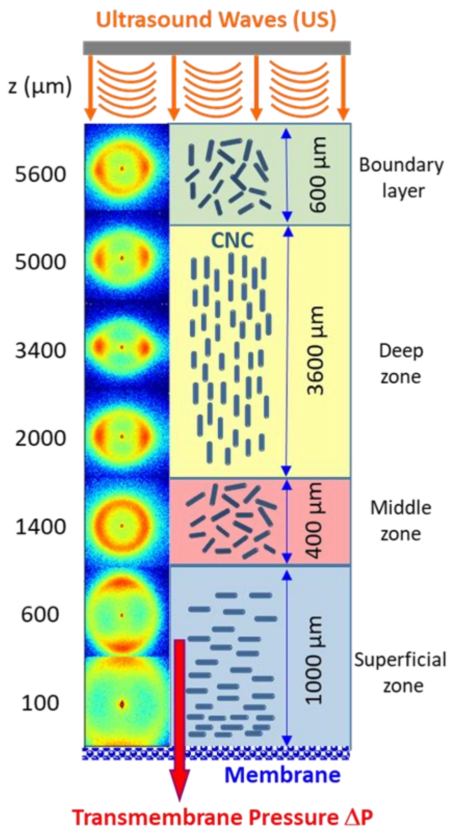

Fig. 2: Typical orthotropic organization of cartilage achieved by FU under US. 2D-SAXS patterns at t = 88 min.

The first layer (1000 µm-thick) pertaining to the superficial zone was composed of tightly packed CNCs with their directors aligned parallel to the membrane surface, and a concentration gradient reaching up to 48 wt% at the membrane surface (Fig. 3). The second intermediate layer (400 µm-thick) corresponding to the isotropic middle transitional zone of the cartilage, was located at the intersection where the vertical acoustic radiation force balanced the transmembrane pressure forces, inducing an isotropic orientation of the CNCs at a constant concentration of 13.5 wt%. The third layer (3600 µm-thick) associated to the deep region with objects arranged perpendicular to the articular surfaces, was located below the ultrasonic blade, where the ultrasound waves induced an alignment of the CNCs with their directors aligned perpendicular to the membrane surface, along the ultrasonic wave direction of propagation at a constant concentration of 13.5 wt%. In the vicinity of the ultrasonic blade a boundary layer (600 µm-thick) was highlighted with a global orientation of CNCs along the acoustic radiation and some fluctuations of the orientations at short time scale, below 1 s.

From the 2D saxs patterns, the anisotropy Principal Component Analysis (PCA) were calculated in the (0.071-0.368) nm^{-1} *q*-range, using SASET software. It allowed to follow the time dependent evolutions of the anisotropy levels of CNCs orientations inside the differents zones as a function of filtration time and distance Z from the membrane surface (Fig. 3).

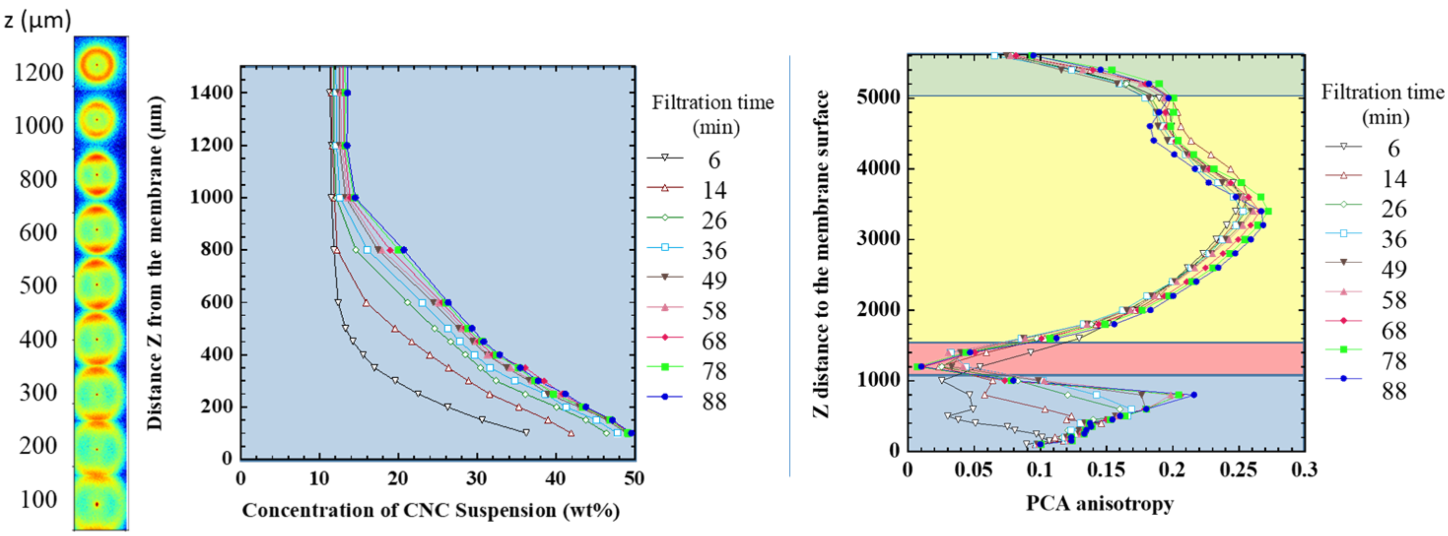

Fig. 3: Concentration profiles and PCA anisotropy of CNCs suspensions during FU/US process inside different zones. $C_{initial}$ = 10 wt%, ΔP = 1.2x10^5 Pa, Acoustic Pressure = 297 kPa

[1] Jin Y. *et al.*, Carbohydr. Polym., 124, 66-76, 2015. (doi.org/10.1016/j.carbpol.2015.01.073)
[2] Rey C. *et al.*, ACS Sust. Chem. Eng., 7, 10679-10689, 2019. (doi.org/10.1021/acssuschemeng.9b01333)
[3] Semeraro E. F. *et al.*, Colloids Surf. A, 584,124030, 2020. (doi.org/10.1016/j.colsurfa.2019.124030)
[4] Pignon F. *et al.*, J. Phys. Chem. C, 125, 18409-18419, 2021. (doi.org/10.1021/acs.jpcc.1c03506)
[5] Camarero-Espinosa S. *et al.*, Int. J. of Pharmaceutics, 523, 476–489, 2017 (doi.org/10.1016/j.ijpharm.2016.10.035)