	Experiment title: Development of controlled oriented nano-structured biomaterials concentrated near membrane surface by simultaneous shear flow and transmembrane pressure.	**Experiment number**: SC 4177
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Report: The goal of this project is to use a membrane separation process coupled to *in-situ* SAXS monitoring to develop controlled oriented nano-structured biomaterials.

An important aspect for developing novel tuneable nanostructured composites is to reach a deep understanding and control of the organization induced during their processing, one of the main difficulties being to properly balance external forces (shear flow, pressure) and internal (colloidal) ones. Contrary to other processes (extrusion, injection molding, film casting) that implement suspensions of nanocharges at initial concentrations equivalent to the final concentration of the manufactured product, membrane separation processes has the advantage of working with initial concentrations in the dilute domain. Consequently, the material can be designed at low volume fraction when the external shear flow and pressure forces are higher than colloidal interactions. This allows a regular deposition and concentration of the well-oriented colloids near the membrane surface.

Thanks to specific cross-flow ultrafiltration SAXS cells, we have studied the relative effect of colloidal interaction and external shear-flow /transmembrane pressure applied during ultrafiltration to optimize the oriented organizations of colloidal particles deposited on the membrane surface.

Several aqueous colloidal suspensions have been studied: i) plate-like cellulose nanocrystals (270 nm x 10 nm), plate-like natural clays with a high aspect ratio, Wyoming T2 Montmorillonite (250 nm x 1 nm), Nontronite (460 nm x 60 nm) and disk-like clay particles Beidellite (280 nm x 1 nm), Laponite (30 nm x 1 nm).

We have evidenced in this work, that the simultaneous effects of shear and pressure resulted in the formation of highly regularly oriented colloidal layers (a few hundreds of µm thick), with concentration levels 10 to 15 times higher than the initial concentration in solution. In terms of orientation properties, an exponential decay of anisotropy as a function of the distance to the membrane surface could be further observed (Fig. 1 and 2).

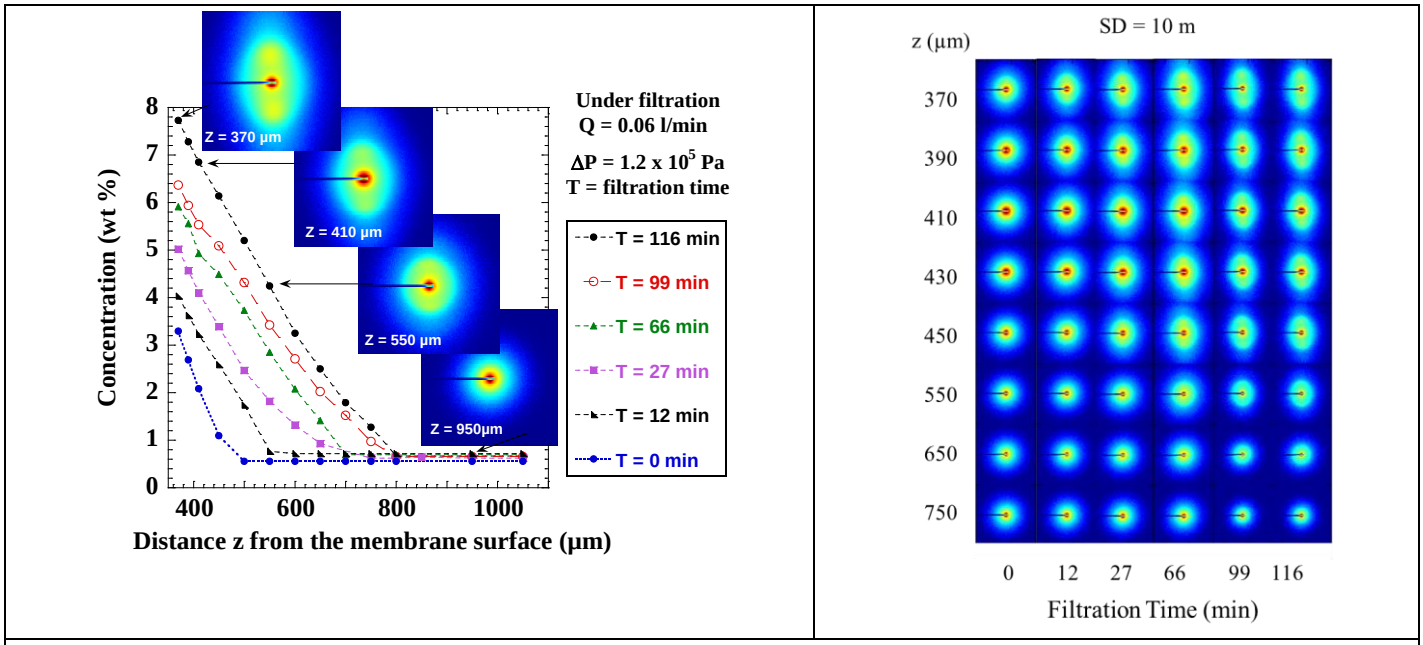

Fig. 1: concentration profiles and anisotropic organization (2D-SAXS patterns) deduced from *in-situ* SAXS during cross-flow ultrafiltration of cellulose nanocrystal dispersions. The distance z from the membrane surface has been corrected according to the lowering membrane phenomenon detailed thereafter.

In this work we have also explored the effect of cessation of cross-flow and transmembrane pressure. At the end of the filtration when the cross-flow is stopped and the pressure is released, it has been shown that the particles diffuse from the upper layers near the membrane surface which leads to a decrease of the oriented state achieved under filtration. This relaxation process is established on timescales of about 30 min (Fig. 2). In the next future we will find a way to freeze the oriented architectures achieved under filtration.

Another drawback that has been emphasis during this experiment is a lowering of the membrane in the permeate canal due to the effect of transmembrane pressure. This has been well characterized thanks to the *in-situ* SAXS measurements, following the relaxation of the deposit after cessation of the pressure. It has been evidenced that the membrane lowering is about 350 µm, has shown in fig. 2 a) and c). The consequences of this observation is twofold: firstly it has allowed us to evidence that the first layers deposited near the membrane surface during filtration, reach higher concentration levels and better orientated states than expected, which is a good point for the intended purpose. Secondly, it has allowed us to improve the ultrafiltration cell set-up. Recently we have found the way to avoid

lowering membrane phenomenon, designing a rigid porous support positioned between the membrane and the permeate canal. By *in-situ* µPIV measurements performed at the Rheology laboratory, we have shown that this phenomenon no longer takes place and is now overcome. We will use this new equipment in future investigations.

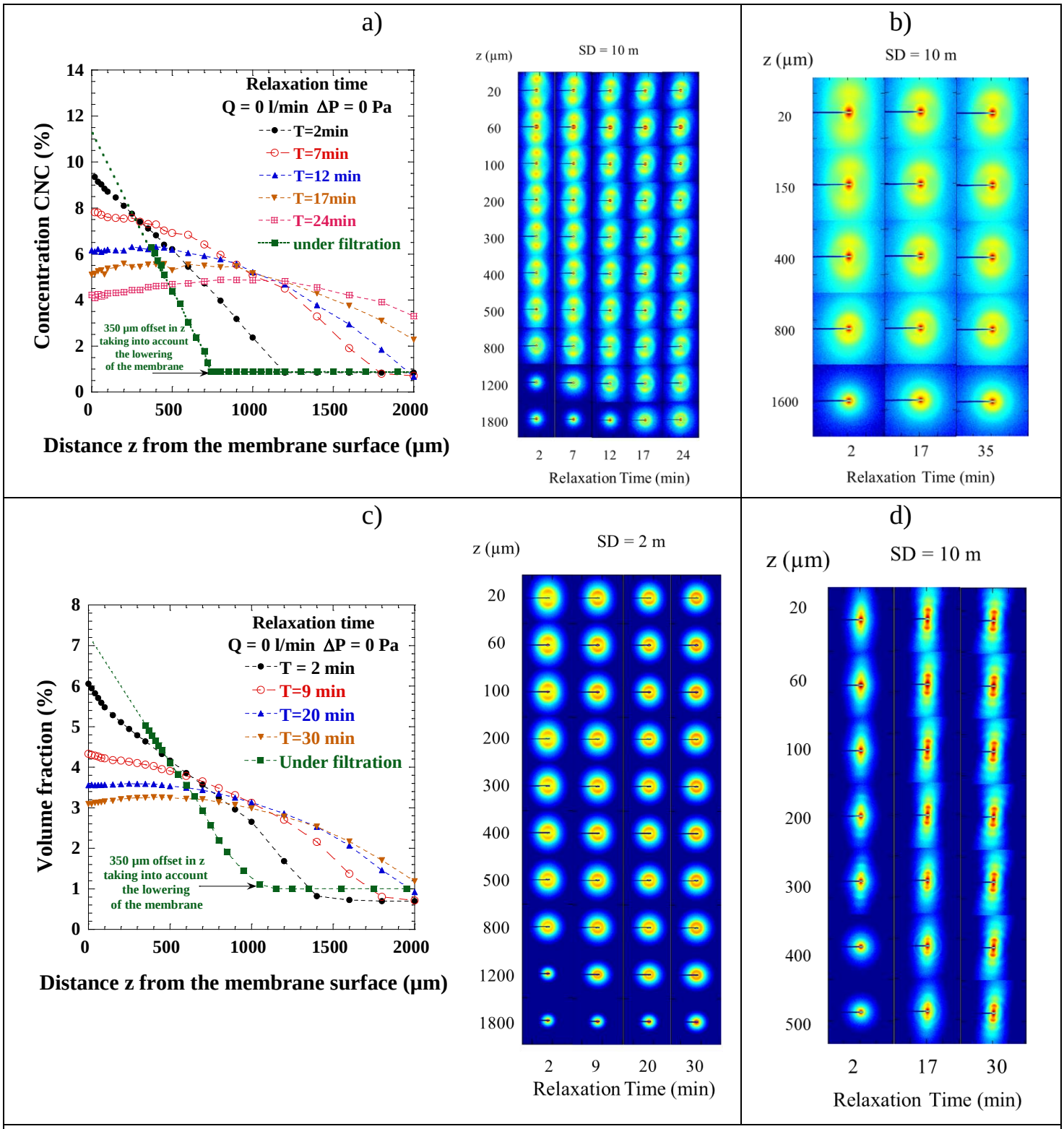

Fig. 2: concentration profiles and anisotropic organization (2D-SAXS patterns) deduced from *in-situ* SAXS during cross-flow ultrafiltration. Relaxation of oriented structure in the accumulated layers after cessation of filtration: a) cellulose nanocrystals, b) Wyoming T2 Montmorillonite c) Laponite d) Beidellite dispersions.