Experimental report

03/11/2022

Proposal: 9-10-1659 **Council:** 4/2020

Title: CONVECTION IN COLLOIDAL SUSPENSIONS BY NEUTRON TOMOGRAPHY

Research area: Physics

This proposal is a new proposal

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Samples: silica nanoparticules in H2O

Instrument	Requested days	Allocated days	From	To
D33	3	2	21/06/2021	23/06/2021
NEXT	6	3	03/03/2021	06/03/2021

Abstract:

We proposed here to:
(i) - study the processus of skin formation on the drying surface of colloidal suspensions in presence of convection
(ii) - characterize the intertwinned actions of convection on skin formation and structure, and of fluid structure on convection, by Neutron tomography and SANS.
The samples are silica nanoparticules (D=14nm and 8nm) in water as solvent; the water evaporation at the top surface will be controlled by closing the cell temporary or imposing a flux of dry N2; the bottom of the cell could also be kept at a hot temperature T=40-50°C with a circulating bath in order to enhance convection by the generation of active hot upwellings. The initial colloidal particle concentration, as well as the particle diameter will be varied.
We ask for 6 days at the test tomography station of the ILL and for 3 days on D33 to analyze the aggregation process of the nanoparticles that takes place in the convection cell.

Beamtime report - exp_9-10-1659

NEXT (3-6 March 2021) and D33 (21-23 June 2021)

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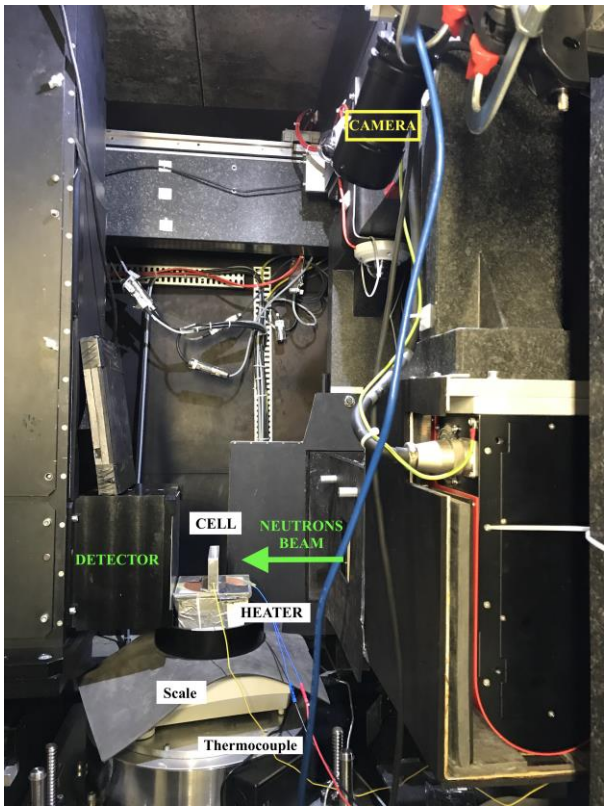
Local contact: Lukas Helfen (NEXT) and Olga Matsarkia (D33)

Samples: silica colloidal dispersions « Ludox » HS40 and TM50 in H_2O or D_2O

A) Neutron imagery on NEXT (3-6 march 2021):

After setting up the experimental environment (fig.1), we ran 3 drying experiments during one night each, where the fluid in the experimental cell is dried from above and heated from below at 45°C (initial Troom=24°C). Three different fluids were tested: Ludox HS40 coming directly from the bottle (Particle volume fraction ϕ_P ~ 22 %; particle radius r_P ~7.5 nm); Ludox TM50 dialyzed in D2O (ϕ_P ~ 26 %; r_P ~13 nm) ; concentrated Ludox HS40 (ϕ_P ~ 25.6 %). At the end of each run, a tomography was attempted. Then samples were taken in different locations on the cell for post-mortem analysis by SANS (D33-ILL), and TGA, DSC (thermogravimetric analysis, calorimetry at LLB).

a) b



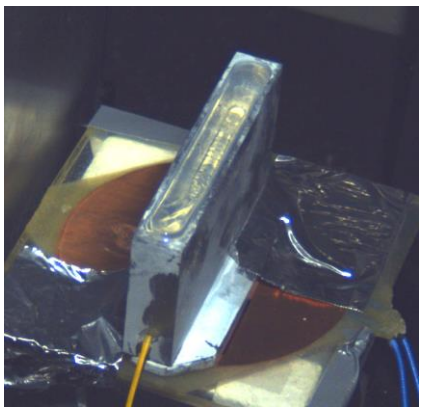


Fig.1: a) Experimental set up: On top of a scale (which allows to follow the evaporation through time), the cell is placed on a heater and some insulation. Heating and ambiant temperatures are monitored through time by thermocouples, as well as humidity. The cell is placed perpendicular to the neutrons beam, as close as possible to the neutron detector (here 7 cm). Top view of the cell is recorded with a classical camera. b) close up on the experimental Alu cell filled with Ludox as seen by the top camera.

The first experiment was run into a quartz cell 100 mm long, 50 mm tall and 10 mm thick (inner dimensions, Hellma type). Preliminary trials in a thicker cell (20 mm) showed that neutrons absorption there was too strong for our aqueous dispersions and that we were completely lacking contrast within the cell. However, the experiment within the 10 mm thick cell showed that the dynamics was very strongly constrained by the lateral walls. The two subsequent experiments were therefore done in a 13 mm thick-cell in aluminum Teflon-coated surface (fig 1b). As expected, the best contrast was obtained for the TM50 dialyzed in D_2O (fig.2).

This experiment was successful in developing a skin more concentrated in nanoparticles (and of a visco-elasto-plastic rheology as its buckling is showing) on the surface and producing its spontaneous subduction, whereby the skin breaks and sinks back in the bulk of the cell (fig.2a). However, we encounter two problems in the quantitative analysis of the experiment:

(i) we could not relate the occurrence of subduction with a signature in the evaporation rate. The mass records showed regular oscillations (increase and decrease) with a periodicity ~15 mins, as if something was pushing against the scale regularly. This was due to the air conditioning of the room which was moving periodically the thermocouple attached to the heater. As a result, the evaporation rate could be calculated with a moving average of an hour, but any shorter event (such as a subduction) was masked by the air conditioning oscillations.

(ii) The calibration of the TM50 could not be done in the appropriate conditions. Calibrations as a function of the fluid thickness were done using two geometries: first, in March, a cylindrical pyramid was placed against the detector (fig.3a) and the transmission was measured on the different steps which correspond to different fluid thickness (fig.3b). This calibration was run for all the fluids we used, but was not satisfactory for two reasons: the cylindrical shape is introducing a significant uncertainty about the fluid thickness, and the calibration was not done at the same position as the experimental convection cell, which modifies the contribution of neutron diffraction. Indeed, the averaged transmission measured at the beginning of each experiment could differ by 5 to 10% to the calibration value obtained for the same fluid thickness with the pyramid. So a second set of calibrations were done by Lukas Helfen using a triangular-shape cell (l=20, L=11.8, h=45mm) positioned at 7 cm from the detector. As can be seen in fig.3b, this second calibration results differ significantly from the first one. But unfortunately, there was no time to run the same calibration for the TM50 dialysed in D_2O.

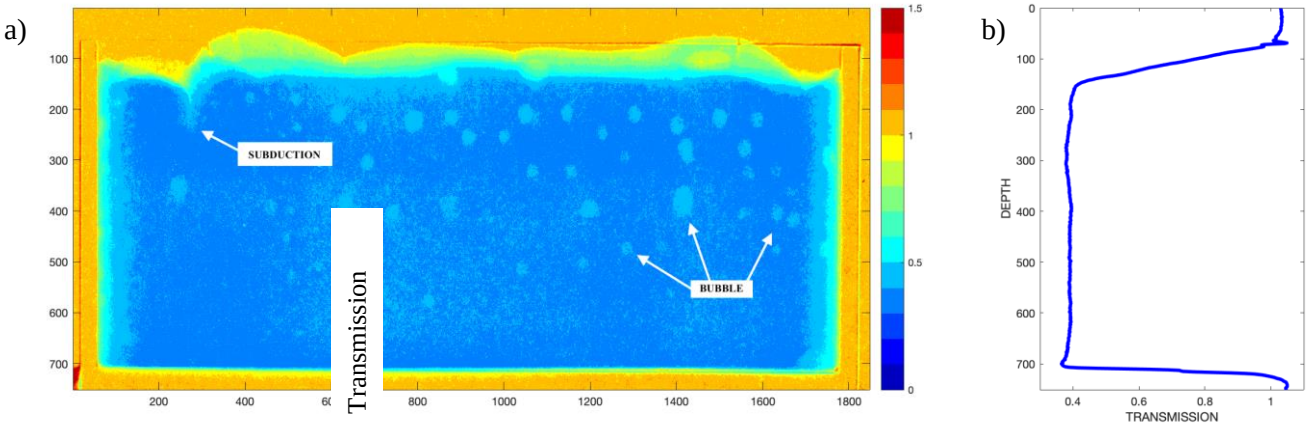


Fig.2: Neutron transmission for the experiment with TM50 dialysed in D_2O. a) snapshot at time t=360 min. The top interface is showing folds and a subduction on the left. Air bubbles caused by the heating are also visible. b) Depth profile of the transmission average along the cell.

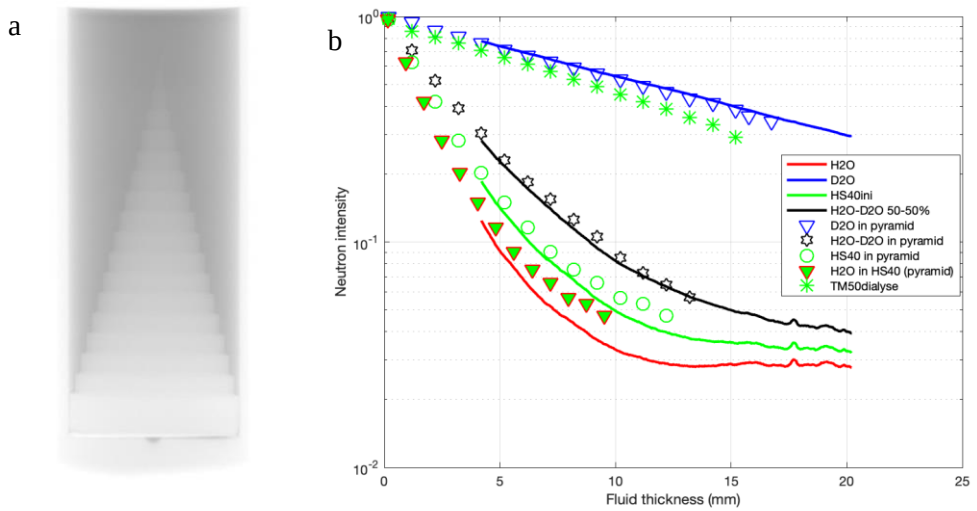


Fig.3: Calibration of the neutron transmission intensity as a function of the fluid thickness. a) snapshot of the calibration pyramid in D_2O (inner diameter=16.76mm). b) calibration measurements with the triangular cell at 7cm from the detector, i.e. at

B) <u>SANS measurements on D33 (21-23 June 2021)</u>:

The SANS measurements were done on the samples taken post-mortem from the NEXT experiments, and from convection experiments run in bigger tanks in FAST laboratory. Both liquids, pastes (gels) and solids were analyzed in Hellma cells (0.1 or 0.2mm) and in sandwich cells when solids. In addition, nanoparticles (NP) radius and polydispersity were measured for low concentration samples of HS40 and TM50 and compared to previous experiments. For large NP concentrations, the spectra allow to estimate NP volume fraction, inter-NP distance, and aggregation. Fig.4 shows the results for the samples taken in the first NEXT convection experiment with HS40 (H_2O). The increasing nanoparticle concentration and aggregation of the samples as we go from the initial liquid to the final solid crusts are clearly seen on the SANS spectra (fig.4a). Estimates of the particle volume fraction for each sample can be derived by different methods and compared to the mass fraction measured by TGA (fig.4b).

Additional SANS experiments were also done over time (and scanned at 11positions in height, every 1mm) to follow *in situ* the development of a gelled surface layer as a Ludox sample initially liquid is dried from above or put into contact with salted water. Analysis of the data is still in progress.

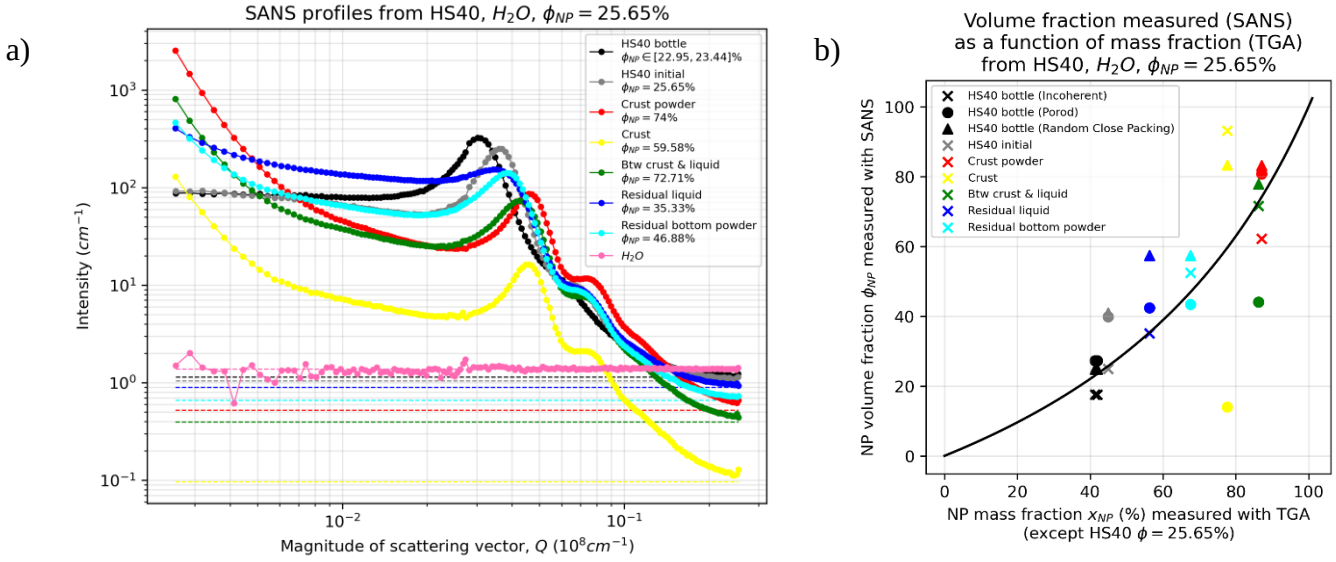


Fig.4: SANS results for HS40. a) Spectra. b) various determinations of the NP volume fraction.