Experimental report

24/10/2025

Proposal: **LTP-9-11** **Council:** 10/2022

Title: A new in situ centrifugation set-up for the separation of fluids by SANS and Diffraction

Research area:

This proposal is a new proposal

Main proposer: **Christiane ALBA SIMIONESCO**

Experimental team: Sylvain PREVOST
Firoz MALAYIL KALATHIL
Marie PLAZANET
Christiane ALBA SIMIONESCO
Frederic LEGENDRE

Local contacts: Sylvain PREVOST
Lionel PORCAR

Samples: silica nanoparticles (D=16nm)
water ethanol octanol
D20/H20 + SiO2 nanoparticles

Instrument	Requested days	Allocated days	From	To
D22	12	4	01/09/2023	04/09/2023
			06/03/2024	07/03/2024
D16	4			

Abstract:

We propose to develop a new generation of sample environment never used so far at any neutron scattering center nor synchrotron while commonly used in soft matter laboratory : it is based on centrifugation principle, where the new key control parameter is the degree of acceleration expressed as multiples of gravity. A density gradient will be generated in the sample, which gradually will induce phase transformations and nanophase separation. The new set-up is a vertical centrifugal machine, with 8 hellma cells (thickness of 1 mm, or 2mm) inserted in a rotating disk; we plan to impose 1000 to 6000g on various samples at room temperature. Such experiments in the context of low energy and eco compatible solvents have been never used by neutron scattering (nor X-Rays) for the analysis of phase transitions. All SANS diffractometers are equivalently possible. This proposal in a simpler form was submitted last year and was asked by the ILL to become a Long Term Proposal because of its very innovative approach. We ask for 4 days per year on a SANS instrument and 4 days on D16.

In Situ Centrifugation for Neutron Scattering (LPT-9-11, 1 day sept 23, 1 day march 24, 9-10-1817)

In situ centrifugation introduces a controllable gravitational field directly during neutron scattering experiments, making it a new thermodynamic control parameter, on par with temperature, pressure, or magnetic fields. By applying high gravitational accelerations (up to several thousand *g*), it enables real-time observation of structure and phase evolution in soft matter systems (colloidal suspensions, aggregates, micelles, liquid crystals, etc.).

For that purpose, we have developed a new generation of sample environment never used so far at any neutron scattering center nor synchrotron while commonly used in soft matter and life sciences laboratories based on a vertical centrifugation principle, using soft centrifugation, meaning between 2 000 g and 6 000 g (g=9.81 m/s2 on Earth). The photos of Fig.1 represent (a) the full set-up installed on D22, (b) the disk with 8 cells, (c) the aperture for neutron beam, and position of the cell for scans along the height of the cell (every 1, 0.5 or 0.2mm, total h=30mm). The disk radius is 12cm, inserted in the carter (at room T, no thermalization yet), converting the rpm to a relative centrifugal force, (ex= 1000rpm leads to 134g; 5000rpm leads to 3251g). The upper limit of speed for the current disk was evaluated via Finite element calculation: strength, eigenfrequencies – deformation (Calculation with SolidWorks SIMULATION 2022) at 8000rpm (i.e. 8500g).

The first experiments (LPT-9-11, sept 23, march 24), as proof of concept, were conducted on the SANS diffractometer D22 at 6A° and 17.6m, testing several rotational speeds and ambient temperature. The samples were colloidal suspensions of silica nanoparticles (known as Ludox TM50, R=13.8nm). The samples previously dialyzed in H2O (with and without small additional amount of NaOH) at various volume fractions (also characterized by TGA, density, pH etc.…). All spectra were measured for 60s.

1- Samples TM50 first characterized at equilibrium in a standard sample changer with quartz cell 1mm thickness
2- Centrifugation test of Water for calibration with the 8 Hellma cells, static then at 500rpm and 2000rpm (few problems of leak and unfortunately several cells were broken and we had to repeat the experiments; the second test was ok up to 3000rpm for bulk water.
3- TM50 samples at various initials volumes fractions and various rpm (from 50 to 5000): the first test with sample was not successful (leak and cell broken at 5000rpm), T hall=28°C, T carter=35°C. This set of data is still currently analyzed.

The second set of experiments, after an upgrade version of the cell closure and positioning on the disk, were performed on 3 samples:

- at a fixed 3000rpm (~1200g) in safety conditions. The aim was to follow the establishment of a density (viscosity) gradient in the cell with time.
- Three samples always based on the same silica nanoparticles (base TM50) have been measured with the same initial volution fractions in NP (~2.9%) but with different np interactions, gel formation ability and polydispersity. The 3 samples at equilibrium before

the experiment are shown in Fig.2: dialyzed TM50 + H2O, TM50 + Glycerol and H2O, TM50 +HS40 2 different sizes of NP, R_{TM50}=13.8nm and R_{HS40}= 7.22nm.

- Several results are shown in figures below in the case of TM50+H2O, after 6h30 at 3000rpm and 25°C. It illustrates and confirms the interest of in situ centrifugation, these processes would not been seen by standard experiments.

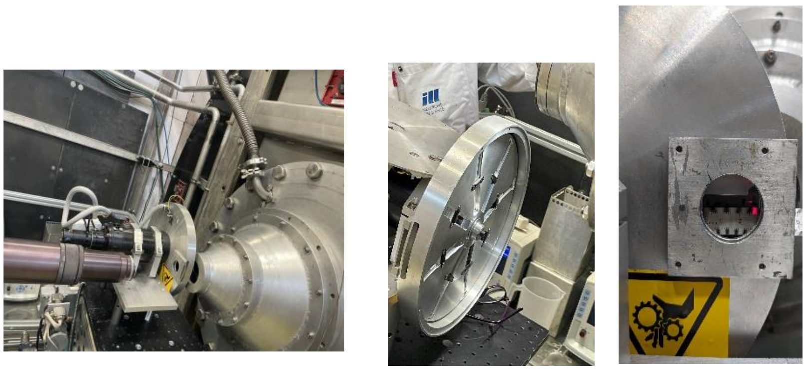


Fig.1 : vertical centrifugation set-up installed on D22 with rotating disk and the 8 Hellma cells.

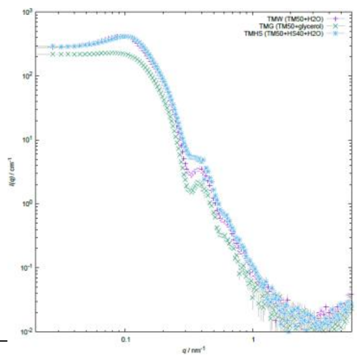
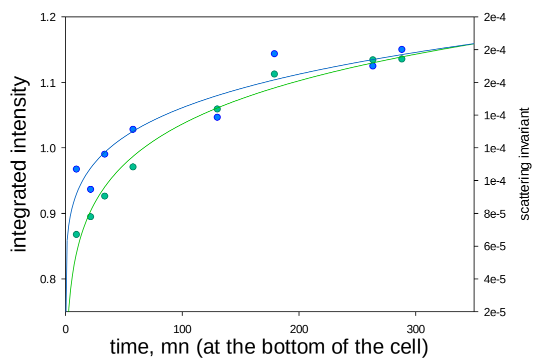


Fig.2 : initial samples at the same volume fraction of TM50, 3%: TM50+ H20, TM50+water+glycerol, TM50mixt with HS40.



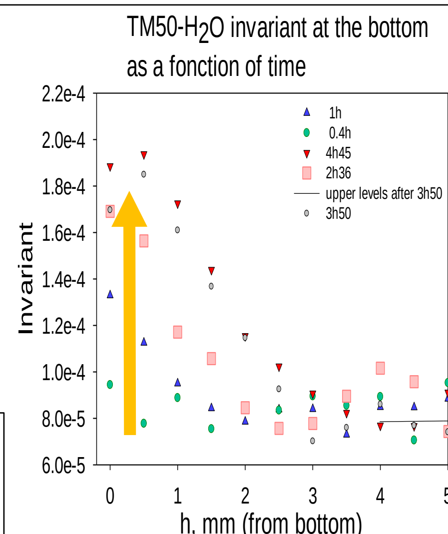


Fig.3, (left a): time dependence of the volume fraction of nanoparticles at the bottom of the cell, following a power law behavior**; (right b):** invariant of the SANS spectra over a height of 5mm (step 0.5mm) for

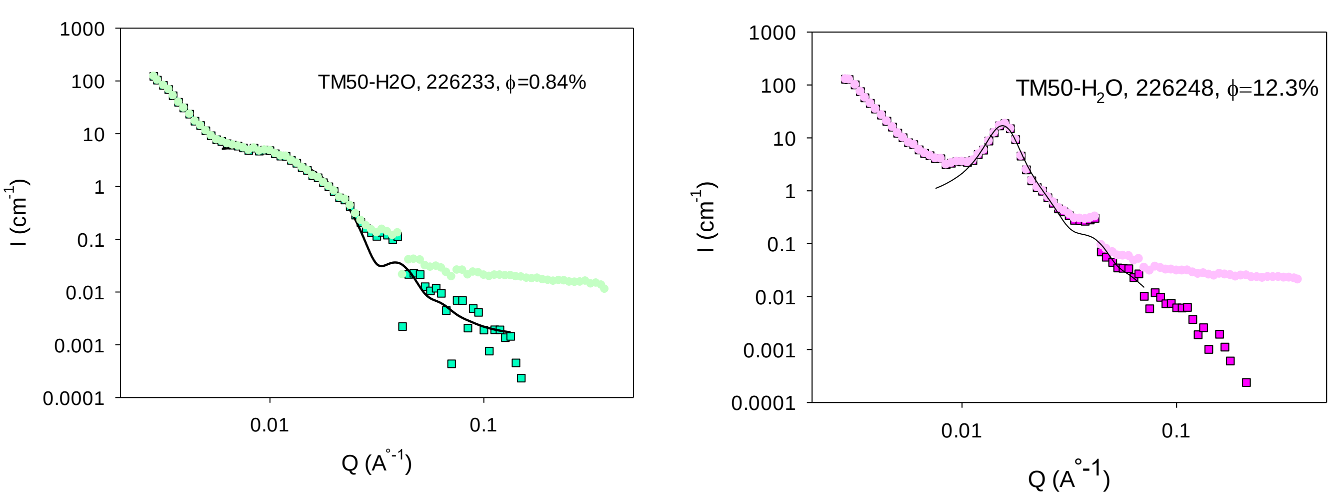


Fig.4 : from a initial homogeneous suspension at 2.9% , (left a) sample I(Q) at 3mm height with a volume fraction of 0.84% , (right b) same conditions at the bottom with a volume fraction of 12.3%.