Experimental report

11/05/2022

Proposal: **9-10-1657** **Council:** 4/2020

Title: L3 Sponge phase - effects of confinement and shear

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: D2O
NaCl
hexanol
Cetylpyridinium chloride

Instrument	Requested days	Allocated days	From	To
D17	0	1	21/06/2021	22/06/2021
FIGARO User-supplied	3	0		
D22	1	1	18/06/2021	19/06/2021

Abstract:

The sponge, or L3, phase consists of interconnected networks of water and solvent channels forming between bilayers. While locally these phases may be considered as bilayers but the correlations, which distinguish the lamellar L phase rapidly, disappear into the bulk solution. Typically the bulk sponge has low viscosity and are isotropic, and Lalpha, is a anisotropic viscous lamellar. Sufficient shear has been shown to produce a bulk phase transition from L3 to the lamellar L in a Couette geometry rheometer with SANS. Here we would aim to simplify the study of the structure of the sponge phase and its relationship to shear in which very thin layers of the sponge phase are sheared under confinement between two parallel surfaces.

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Background

The original aim of the 9-10-1657 experiment was to study the Lα transition of mechanical confined L3 layers under interfacial shear by means of a new sample environment for structural studies of confined and sheared thin soft films (https://github.com/juanfran2018/Ofelia-Confinement-Shear-Cell). For this, we got 1 day in D22 and 1 day in D17.

Deviations from the experimental plan: Because of COVID travel restrictions, the member of the team with the knowledge to prepare sponge phases could not join the experiment. We decided after discussing with the local contact, to continue testing instead the new sample environment using model samples, with the long-term goal of optimizing the setup so that we could address the original aims in future experiments. Specifically, at D22 we investigated silica nanoparticles deposited in a Langmuir through on Si blocks. We previously investigated a similar sample in D22 with a similar setup, but where only mechanical confinement in the direction normal to the surface could be applied (Experimental Report 8-05-437). By repeating this experiment, this time using the new sample environment and applying shear, we aimed to i) test the new instrument in a vertical configuration for GISANS geometry in general and that of D22 in particular and ii) investigate the possibility to investigate shear-induced structural changes by means of GISANS. At D17 we investigated polylysine-heparin multilayers. We recently successfully investigated this sample under mechanical confinement and shear in Figaro (Experimental Report 9-10-141). By repeating the same experiment in D17, we aimed to investigate the suitability of D17 for studies with the new instrument.

Results and Discussion

D22 - Silica nanoparticles layer: Silica nanoparticles deposited by Langmuir deposition organize in a monolayer with hexagonal structure. D22, as a GISANS instrument, can characterize the in-plane structure of this interface illuminating the sample at low angles that are close to the critical edge, by observing the scattering away from the specular direction. In our experiments, D22 was configured with a sample slit aperture of 0.4 x 14 mm and a sample to detector distance of 17.6 m. Specifically, the following series of experiments was performed: 1) Reflectivity measurement in confinement (P = 1 bar, static), 2) GISANS measurement in confinement (P = 2 bar, static), 3) Reflectivity measurement in confinement (P = 2 bar, static), 4) GISANS measurement in confinement (P = 2 bar, unidirectional movement at 17 µm/min), 5) Reflectivity measurement in confinement (P = 2 bar, unidirectional movement at 17 µm/min). 6) GISANS measurement in confinement (P = 2 bar, unidirectional movement at 112 µm/min), 7) Reflectivity measurement in confinement (P = 2 bar, unidirectional movement at 112 µm/min). Data was reduced using GRASP and plotted using XSact software.

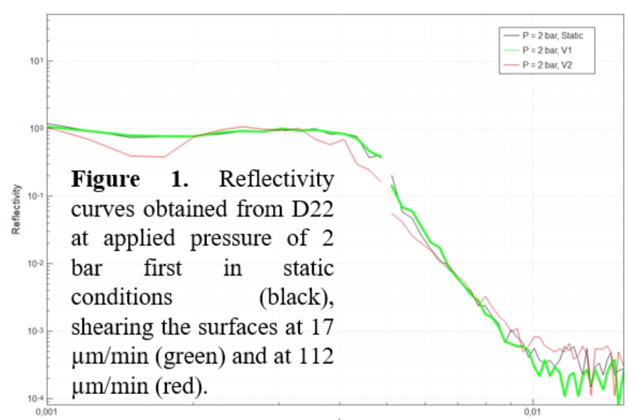

Figure 1. Reflectivity curves obtained from D22 at applied pressure of 2 bar first in static conditions (black), shearing the surfaces at 17 µm/min (green) and at 112 µm/min (red).

Reflectivity measurements in between GISANS experiments (Fig. 1) probed that the sample was always aligned (no realignment needed during the experiment as reflected beam was always in the same position).

GISANS measurements were able to spot the difference between static and dynamic measurements, as the shear applied by the confinement cell was enough to modify the surface of the sample. A representative 2D GISANS image from our experiment is shown in Fig. 2a. Qualitatively, all images were similar. However, they differed in intensity values. This is better observed in Figs. 2b and 2c, which show intensity averages of strip of pixels from the GISANS images for all performed experiments. This data is representative from nanoparticle's hexagonal arrangement (where the diameter could also be obtained, in this case, 210±5 nm in good agreement with the expected value). Of relevance from the data in Figs. 2b and 2c is that the intensity of the peaks decreased as the shear speed increase. The process was not completely gradual, as only after applying shear at the higher speed for 2 hours the maximum difference could be spotted. Overall, we were able to identify by means of GISANS, shear-induced structural modifications of the sample. This was seen macroscopically after removing the sample from the beamline as shown in Fig. 3a. AFM images of regions of the sample that were in contact with the Melinex during the whole experiment (Fig. 3b) and from sheared regions that moved away from the Melinex contacted area (Fig. 3c) indicate that moving away from the sheared area resulted in the removal of some nanoparticles.

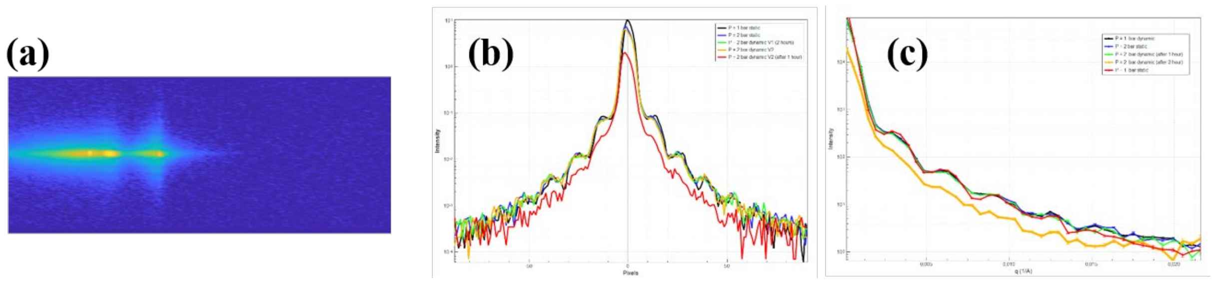

Figure 2. a) 2D GISANS image obtained by data reduction using GRASP. Similar images were obtained for different shear speeds. Changes in the surface could not be spotted directly without further processing the data. **b)** and **c)** Intensity averages of strip of pixels from the GISANS images for all performed experiments vs pixels and scattering vector respectively. The main observation was that increasing the shear speed decreased the intensity of the peaks.

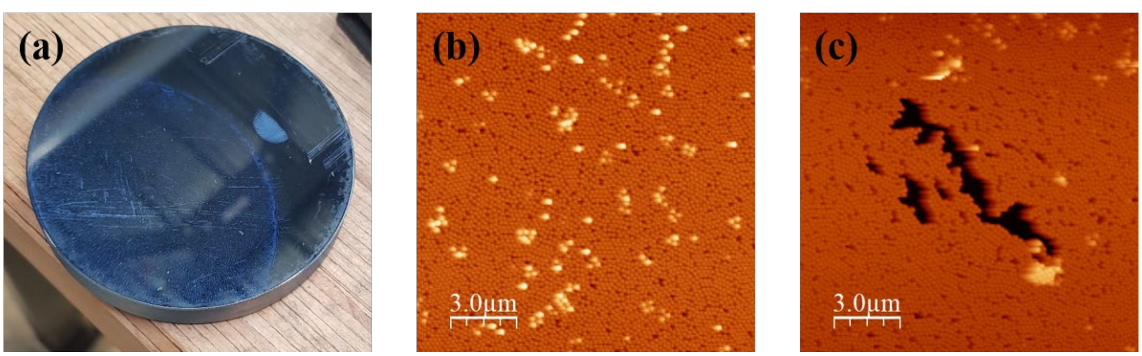

Figure 3. a) Silicon block with the silica nanoparticles on top, after being sheared. The brighter blue region corresponds to that in contact with Melinex during the whole experiment. The darker blue region corresponds to a sheared region that moved away from the area in contact with the Melinex during the experiment. **b)** and **c)** AFM images of the bright and dark blue region of the block in (a).

D17 - Polylysine-heparin multilayers

Because of time consuming characteristic of the proposed experiments, we were not able in the allocated 1 day to acquire data that would allow to obtain firm conclusions.