Experimental report

21/10/2021

Proposal: 1-10-41 **Council:** 10/2018

Title: A new sample environment for structural studies of confined and sheared thin soft films

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Poly(ethylene oxide)
Polystyrene

Instrument	Requested days	Allocated days	From	To
FIGARO User-supplied	5	3	14/06/2021	17/06/2021
D17	5	0		
D22	1	0		

Abstract:

The study of soft matter films under mechanical confinement was originally made possible by the emergence of the Surface Force Apparatus and the Atomic Force Microscope. These techniques provide accurate interaction forces at different separations. However, they do not provide structural information. Going beyond measurements of forces and measuring near-surface structures has been a challenge for a number of decades. In this regard, Neutron Reflectometry (NR) offers unparalleled possibilities for extracting structural information of mechanically confined thin films. Recently, a team partly formed by the applicants developed a sample environment for NR studies of mechanically confined thin soft films that has been a breakthrough in confined soft matter investigations. However, there is significant room for improvement. Specifically, the possibility to study shear-induced structural rearrangements would be of great value in lubrication science along with a number of other fields. We have addressed this challenge and designed a new NR confinement cell allowing shearing of two opposing surfaces. Here, we apply for beam time to test the first prototype of this novel sample environment.

A new sample environment for structural studies of confined and sheared thin soft films: Experimental Report 9-10-41

Background

The main aim of the 9-10-41 experiment was to test the performance of the newly developed sample environment for structural studies of thin soft matter films under mechanical confinement and shear (https://github.com/juanfran2018/Ofelia-Confinement-Shear-Cell). Specifically, the proposal included three different goals:

i) to reproduce (in the absence of shear) the results obtained with the already available confinement cell where only mechanical pressure in the direction normal to the surface can be applied.[1,2]

ii) to investigate the mechanical stability of the new cell when applying shear.

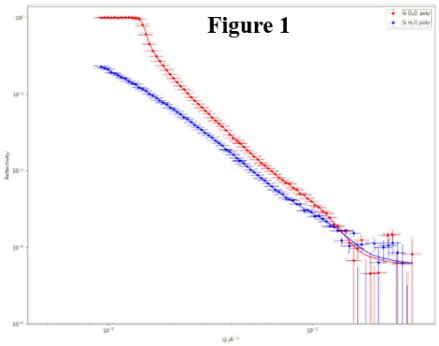
iii) to test the capacity of the new cell to investigate shear-induced structural changes of mechanically confined thin soft matter films.

Deviations from the proposal: Initially, we proposed to use polymer brushes as a model sample for the above mentioned studies. However, the colleague that had the knowledge for preparing the polymer brushes became pregnant before the beam time. As a backup plan, we decided to work with polyelectrolyte layers and polystyrene layers instead. These were samples we had previous experience with e.g.,,[3] and their use would adjust to the aims of the experiment detailed above. Specifically, the previously available cell had been used for investigating polyelectrolytes multilayers.[1] In the case of PS layers, no structural changes were expected in the range of pressures that can be applied with the new cell (<10 bar), so the use of this sample was considered suitable for stability studies.

Materials

Polylysine-heparin multilayers: Multilayers (5 polylysine/heparin double layers) were prepared in MES hydrate buffer (50 mM, pH adjusted to 5.5).

Polystyrene layers: Deuterated PS layers were achieved by spin coating 5 mL of a 10 g/L dPS-toluene solution on the Si blocks while rotating it at 2000 rpm.



Results and Discussion

Polylysine-heparin multilayers at solid-liquid interface: data in PBS and deuterated PBS along with fits to a Si/SiO_2/Multilayer/Background model is shown in Fig. 1. The fits indicated a thickness for the multilayer of 50.9±1.0 Å and a hydration of 87.6±0.3%.

Mechanically confined polylysine-heparin multilayers: NR data obtained while mechanically confining the multilayers at both 2 and 5 bar is presented in Figure 2. A clear critical angle was observed at $Q \sim 0.0049$ $Å^{-1}$ for both investigated pressures. The location of this critical angle is what is expected for a Si/Melinex (the membrane used to mechanically confine the samples) interface. Fits to a Si/SiO_2/Multilayer/Melinex model are also shown in the Figure. These fits indicate that mechanically confining the multilayers at 2 bar decreased their thickness from ~51 Å to ~28 Å, and their hydration from 87.6% down to 4%. Our fits also indicate that the multilayers were not further modified when increasing the pressure to 5 bar, providing similar values for the thickness and hydration of the multilayer.

Mechanically confined and sheared polylysine-heparin multilayers: NR data on the polylysine-heparin multilayers compressed at 5 bar was subsequently acquired while shearing the sample at speed of 33.3 µm/min. Afterwards, the sample was again characterized in the absence of shear (Fig. 2b). All three datasets in the figure also show the fit to a Si/SiO_2/Multilayer/Melinex model. Actually, all 3 fits are identical i.e., same parameters are those provided in Table 4 could fit the 3 different NR data sets from Fig. 3. This indicates that the multilayer was not modified under the applied shear.

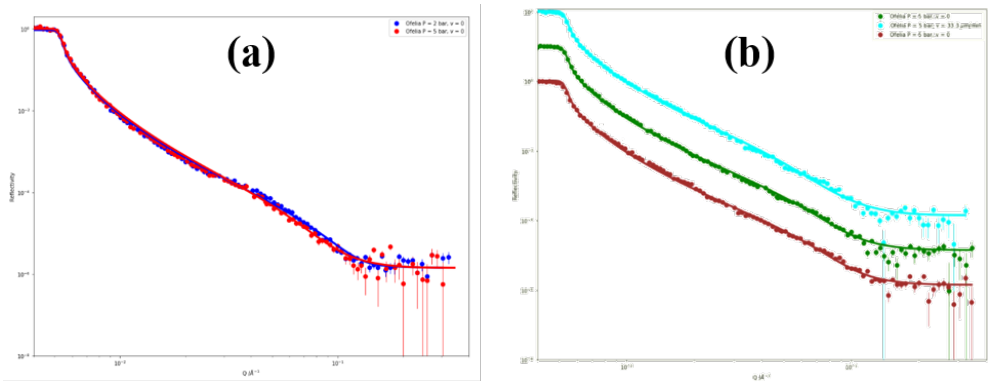


Figure 2. a) NR data obtained while mechanically confining the multilayers in dPBS at both 2 and 5 bar (static). **b)** NR data obtained for the multilayers compressed at 5 bar in static conditions (green), in dynamic conditions (33.3 µm/min, green) and under static conditions again (red).

Polystyrene layers: The dPS film was first characterize at the air-solid interface and then compressed by Melinex in the new cell at 1 and 4 bar. Then, the film was sheared at 33.3 µm/min, and characterized again in static conditions at 4 bar. Experimental data is shown in Figures 3a and 3b. NR data from the films at the Si/air interface were fitted to a Si/SiO_2/dPS/air model. For the static confinement data they were fitted to a Si/SiO_2/dPS/Melinex model. These fits indicated that the thickness of the non-confined film (303.50±0.05Å) was barely affected by the investigated confinement pressures. However, data obtained under mechanical confinement (4 bar) and shear could not be fitted to a Si/SiO2/dPS/Melinex model any longer. In this case, we needed to use a mixed reflectivity model. For one of the reflectivities we obtained similar parameters as those from the static measurements, whereas for the other reflectivity we needed to use a different SLD for the background. Whereas we do not have a solid explanation for this effect, the fact is that after removing the dPS coated Si block from the cell, we could see by eye that the dPS film was damaged. This indicates that the change in the data obtained under dynamic conditions was a result of the shear-induced damage of the dPS film.

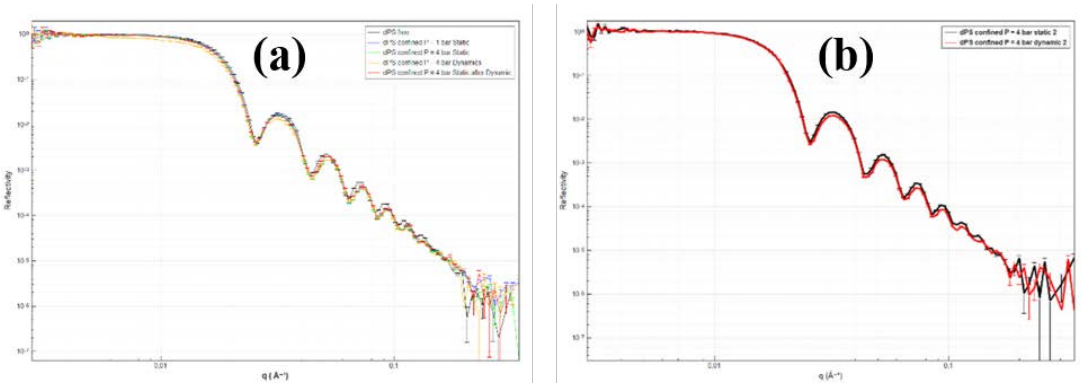


Figure 3. a) NR data obtained for the dPS layer at a solid – air interface, mechanically compressed at 1 and 4 bar (static conditions), mechanically compressed at 4 bar and sheared at 33.3 µm/min, and finally at 4 bar (static conditions). **b)** Comparison between the NR data obtained for the dPS film compressed at 4 bar in the absence and presence of shear (33.3 µm/min).

References: [1] S. B. Abbott et al., Macromolecules, 2014, 47, 3263-3273. **[2]** S. B. Abbott et al. Macromolecules, 2015, 48, 2224-2234. **[3]** A. Barrantes et al., J. Colloid Interface Sci., 2012, 388, 191-200.