ESRF	**Experiment title:** Towards the LTP: combining Interfacial Shear Rheology and XPCS measurements on a Langmuir monolayer	**Experiment number**: SC2962
Beamline: ID10A	**Date of experiment**: from: 27-10-2010 to: 02-11-2010	**Date of report**: 28-02-2011
Shifts: 18	**Local contact(s)**: Anders Madsen	*Received at ESRF:*

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Report:

This experiment investigated the feasability of a grazing incidence XPCS experiment performed on a sample constituted by a Langmuir monolayer at the air-water interface, in order to have access to its internal dynamics on a microscopic spatial scale, in analogy with similar experiments on atomic diffusion in crystals [1]. The experiment was performed employing a Langmuir trough installed on the sample goniometer of the ID10A beamline. The trough allowed us to change the temperature and surface pressure of the sample *in situ.*

In the first part of the experiment we studied stearic acid, known to form higly-ordered Langmuir monolayers with a strong GID peak [2]. The monolayer was formed on a 0.1mM Ba acetate acqueous solution. Our aim was to measure the dynamics of the stearic acid molecules via the increased scattering intensity granted by Ba ions.

The GID was correctly detected, but beam damage problems made XPCS experiments impossible on this sample, since the GID peak intensity was rapidly decreasing during the measurements.
Hence, we switched to a 0.1mM $CaCl_2$ pH 7.0 water subphase; the use of Ca ions with smaller atomic number Z strongly reduced the radiation damage. The GID peak of this sample is reported in the left panel of figure 1.

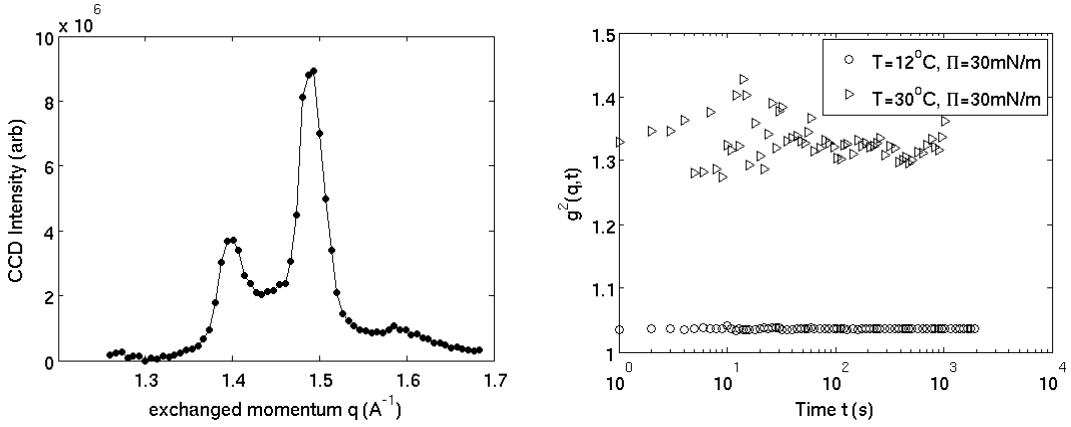

Figure 1 left *GID peak measured on a stearic acid film formed on a 0.1mM $CaCl_2$, pH 7.0 subphase.**right** for the same sample, correlation functions measured at q=1.5 A^{-1}, Π=30 mN/m, for different temperatures.*

To measure the microscopic dynamics on the molecular lenght scale, we correlated the intensity measured on the GID peak. Long exposure times (longer than 1sec) were used to reach a sufficiently high intensity.

Previous calculations suggested that the time scales of the dynamics of this sample are compatible with the temporal windows accessible in our experiment. Correlation functions were measured at several temperatures and surface pressures Π. Despite showing a sufficiently high contrast (3%-30%), the correlation functions do not decay even after several minutes, as shown in the right panel of figure 1. The high contrast measured suggests the relaxation times at the spatial scale corresponding to q=1.5 A^{-1} to be very slow for the sample under exam.

The second part of the experiment was focused on Langmuir monolayers of gold nanoparticles (radius: 7nm). A solution of thiolated gold nanoparticles in ethanol, previously charachterized by P-Area isotherms, Dynamic Light Scattering, SEM imaging and ellipsometry, was spread at the air/water interface. A succession of compression-expansion cycles of the Langmuir trough barrier was performed to increase the uniformity of the film [3]. In analogy with the previous part of the experiment, we performed grazing incidence reflectometry. GID peaks, indicating an ordered arrangement of the nanoparticles, were not observed on this sample.
In analogy with our previous XPCS experiments from solid surfaces [4,5], we focused our investigation on the smal angle scattering around the reflected beam.
We observed correlation functions $g^{(2)}$, reported in the left panel of figure 2, that are compatible with a "compressed exponential" form, $g^{(2)}(\tau)=A+\beta exp[-2(t/\tau)^{p}]$, with compression exponent $\gamma \approx 1.5$, commonly observed in many arrested gels, glasses and polymers.
The relaxation time τ is roughly inversely proportional to the component of the exchanged momentum q parallel to the surface, as shown in the right panel of figure 2.
This dependence over $q_{//}$ instead that over |q| indicates that this experiment is probing a 2D motion of the nanoparticles, confined at the air/water interface. At the same time, the $\tau \approx q^{-1}$ dependence is commonly associated in literature with arrested dynamics.

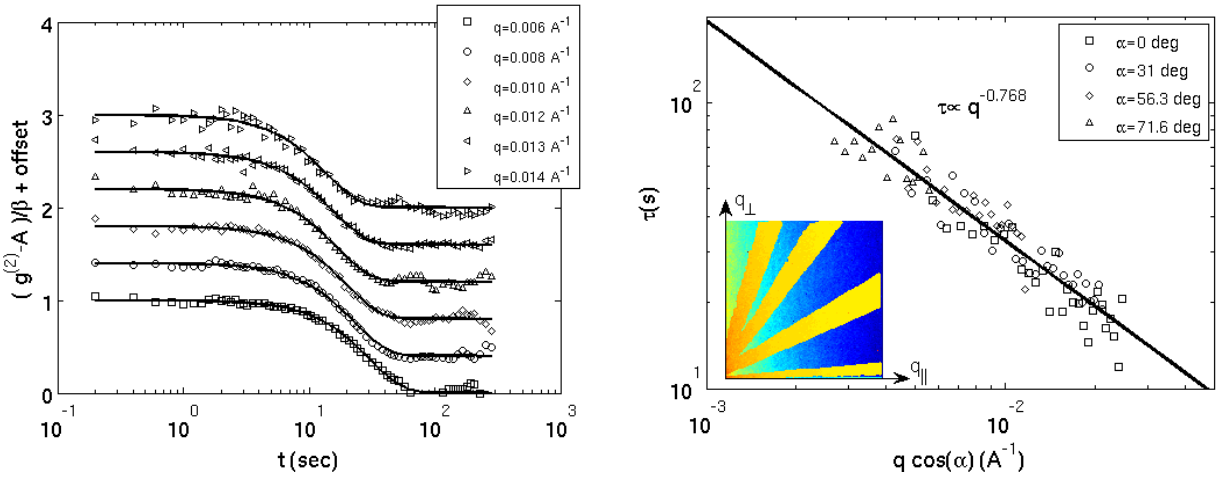

Figure 2; left *correlation functions measured at Π=30mN/m and T=18°C at several values of q around the reflected beam. Continuous lines are fit with compressed exponentials.* ***right*** $q_{//}$ *dependence of the relaxation time* τ.

These measurements on gold nanoparticles evidence the feasability of XPCS measurements at the air/water interface that open the way to investigations of the 2D dynamics of the sample. Such a promising result encourages futher developments, such as investigating the dependence of the 2D dynamics of the colloidal particles as a function of particles dimensions, type of interaction (e.g. repulsive or attractive), subphase.

Bibliography

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