ESRF	**Experiment title:** Study of the interaction of nanoparticles with lipidic layers	**Experiment number**: SC-3687
Beamline: ID10	**Date of experiment**: From: 10/04/2013 to: 16/04/2013	**Date of report**: 25/03/2014
Shifts: 18	**Local contact(s)**: Yuriy Chushkin	*Received at ESRF:*

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Report:

The experiment aimed at obtaining quantitative information on relaxation mechanisms and the time and space scales involved in the interaction of nanoparticles (NP) with lipidic layers. We employed XPCS in grazing incidence. The results are expected to help to understand the effect of NPs on lipid mechanical properties, and –in pesperctive- to highlight the basic mechanism of the known toxic effects of some NPs on pulmonary surfactant physiology in living organisms.

We used Langmuir monolayer of phospholipids (mainly DPPC) as models of pulmonary surfactant. These have been extensively studied in our laboratory [1,2].

Langmuir monolayers have were formed using the following procedure:

- In case of hydrophilic NPs, a chloroform solution of lipids (1mg/mL) was spread on a subphase containing the NPs in suspension; in case of hydrophobic NPs, those NPs have been co-spread with the lipid solution at the air/water interface; the subphase temperature was kept constant at 22°C.
- a waiting time of 1hour was used to allow chloroform evaporation and to let the interaction between NPs and lipids to reach equilibrium;
- the surface area was then reduced by moving the trough's barrier, to reach the desired pressure Π;
- isobaric XPCS experiments have been performed at selected values of Π.

The first 5 shifts have been used for beam preparation and the allignement of the Langmuir trough on the goniometer. The partly coherent beam (8keV, $10\mu m \times 10\mu m$) was directed at grazing incidence ($\alpha = 0.15°$) on the air/water interface. We measured the scattered signal in GI-SAXS geometry covering the scattering vector range q=0.01-0.05 nm^{-1}. Intensity fluctuations were recorded by the Medipix detector. Sequences of 5000 frames have been recorded, with exposure times 10-100msec. Each time the surface pressure was increased to the next desired value, we moved the Langmuir trough along the x axis by 100 microns, in order to perform the measurement on a portion of sample that had never been exposed before to X-rays.

In the following table, we report the details of the samples investigated, along with the number of shifts use for the characterization of each sample.

#	Monolayer components	Subphase	Π investigated	Shifts
1	DPPC	Silica NPs (30 nm) in water (1% wt)	6 mN/m - 60mN/m, 25 steps	3
2	DPPC	Silica NPs (120 nm) in water (1% wt)	6mN/m – 70mN/m, 25 steps	3
3	DPPC	Silica NPs (18 nm) in water (1% wt)	6mN/m – 70mN/m, 25 steps	3
4	DPPC+DOPC+Cholesterol (weight ratio 55:34:11)	Silica NPs (120 nm) in water (1% wt)	6mN/m – 70mN/m, 25 steps	2
5	DPPC	Fumed silica (DPPC:NPs 1:1, spread at air/water interface)	5mN/m – 55mN/m, 13 steps	1
6	DPPC	Carbon black (DPPC:NPs 1:1, spread at air/water interface)	5mN/m – 55mN/m, 13 steps	1

The correlation function (see below) have been fitted with the Kohraulsh-William-Watts exponential. The fitting procedure allowed us to extract the relaxation time of internal dynamics of the sample. All the investigated samples seem to follow the same general behavior. At low surface pressures (Π<15mN/m) the dynamic can not be accessed, because it is faster than the minimum usable exposure time (10msec), which is determined by the relatively low scattered intensity measured.

At larger surface pressure (Π>20mN/m) the relaxation time of the sample is of the order of hundreds of milliseconds: it suddenly increase to a value of a few seconds as soon as the surface pressure is increased above 30mN/m, reaching a constant value. An example of this behavior is reported in figure 1: the data corresponds to sample #1.

This phenomenology appears to be strongly related with the changes in the film's structure highlighted by previous laboratory characterization of similar samples, in particular mixed monolayers of DPPC and Silica Nanoparticles (30nm diameter) [1,2,3].

These measurements show that the domain structure of DPPC is strongly modified by the presence of the nanoparticles: the domains have circular shape and they persist along the whole Π – area isotherm. The domain size increases as Π is increased, reaching a stationary value at Π~ 30mN/m.

Further investigations, involving epifluorescence microscopy to track and characterize the diffusive motion of the domains in a direct way, are ongoing.

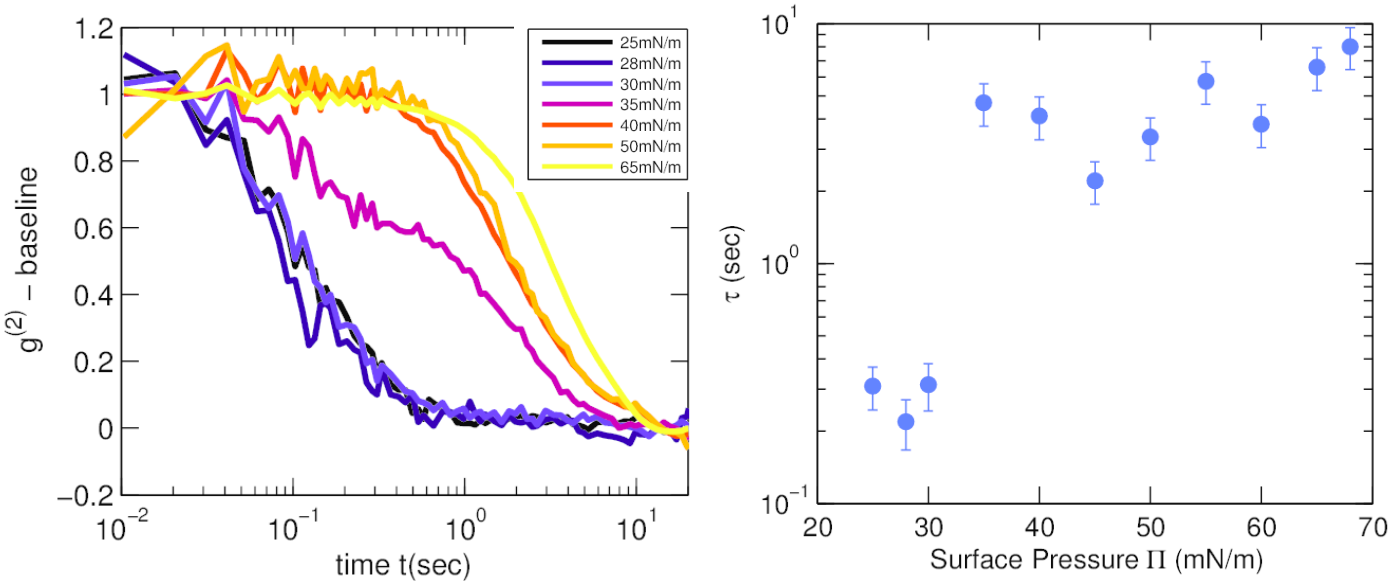

Figure 1: *the relaxation time of the systems increase abruptly as soon as a pressure threshold is crossed.* ***Left:*** *correlation functions measured for system #1 at different values of Π;* ***Right:*** *the relaxation time τ increases as Π is raised, reaching a stationary value at Π>35mN/m.*

[1] E. Guzmán, L. Liggieri, E. Santini, M. Ferrari, F. Ravera, Soft Matter 8:3938-48 (2012)

[2] E. Guzmán, D. Orsi, L. Cristofolini, L. Liggieri,F. Ravera, in preparation

[3] D. Orsi et al., in preparation