ESRF	**Experiment title:** Dynamics and ageing of 2D colloidal gels at the air/water interface	**Experiment number**: SC3288
Beamline: ID10A	**Date of experiment**: from: 19-10-2011 to: 25-10-2011	**Date of report**: 01-03-2012
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Experiment SC3288 was planned to complete and expand the previous experiment SC2962, in which we were able to measure the 2D fast and slow dynamics of Langmuir films composed by gold nanoparticles (GNPs, 7nm diameter) at the air water interface. The SC2962 experiment made use of GISAXS geometry; the relevant relaxation times of the dynamics were accessed by calculating the second and fourth order correlation functions [Ors12] of the scattered intensity.
The experimental setup is composed by a single barrier Langmuir trough, fixed to an anti-vibration table placed onto the ID10A goniometer. A Plexiglas cap was used to keep a controlled helium atmosphere in the beam path, thus reducing scattering from air.
After the formation of the Langmuir monolayer, it was measured by a grazing beam impinging on the air/water interface with a angle $\alpha = 0.1°$ (GISAXS geometry). The beam size was $10\mu m \times 10\mu m$. The scattered signal is then detected around the reflected beam, using the Medipix detector.

First sample: Gold nanoparticles, 80nm diameter
We planned to extend our previous investigations on gold nanoparticles (experiment SC2962); in particular, we varied the size of the nanoparticles and we studied possible out-of-equilibrium effects, by measuring the slow and fast dynamics of 2D gels formed at the interface.
We used 80nm diameter GNPs, coated by dodecanethiol polymeric chains. A compact film was formed, after spreading, through several compression/expansion cycles performed at low surface pressure (3-5 mN/m).

The investigation of the slow dynamics retrieved results compatible with what was previously observed on 7nm GPNs films: the second order correlation functions decays as Kohlrausch-William-Watts compressed exponentials $g^{(2)}(q,t) = A + \beta \exp\left[-2\left(\frac{t}{\tau}\right)^{\gamma}\right]$ with compression exponent $\gamma = 1.5(1)$. The relaxation time , reported in the right panel of figure 1, is of the order of 10s-100s, and it scales as $\tau \propto q_p^{-n}$, where $q_{\|}$ is the component of the exchanged momentum parallel to the interface, with n=0.8(1) in nice agreement with our previous results [Ors12]. Next we addressed the out-of-equilibrium dynamics, by measuring correlation functions after sudden expansion/compression of the Langmuir film. Relaxation times as a function of q, and their fits, are shown as continuous lines in figure 1 (left panel). Interestingly, the q-dependence of the relaxation time is not affected by external perturbation: however, the magnitude of the relaxation time is

modified irreversibly, as a consequence of the modifications induced in the gel network formed by the gold nanoparticles.

Next, we addressed the issue of characterizing faster dynamics, if present. This investigation was, however, unfruitful. One possible reason is that the measurements performed with short exposure times (1-10 msec) are deeply affected by spurious contributions to the scattering, that result in oscillating, q-independent correlation functions (figure 1, left panel). Despite extended investigations, it was not possible to identify the source of such oscillations, that do not originate nor from capillary waves (the oscillation frequency is q-independent, besides being too low for the q-range involved), nor from external sources such as rotative pumps, the antivibration table, the helium flux or the trough's thermostatic equipment. These q-independent oscillations precluded any calculation of any higher-order correlation functions, and therefore we could not investigate the dynamical heterogeneities that are likely to affect the system.

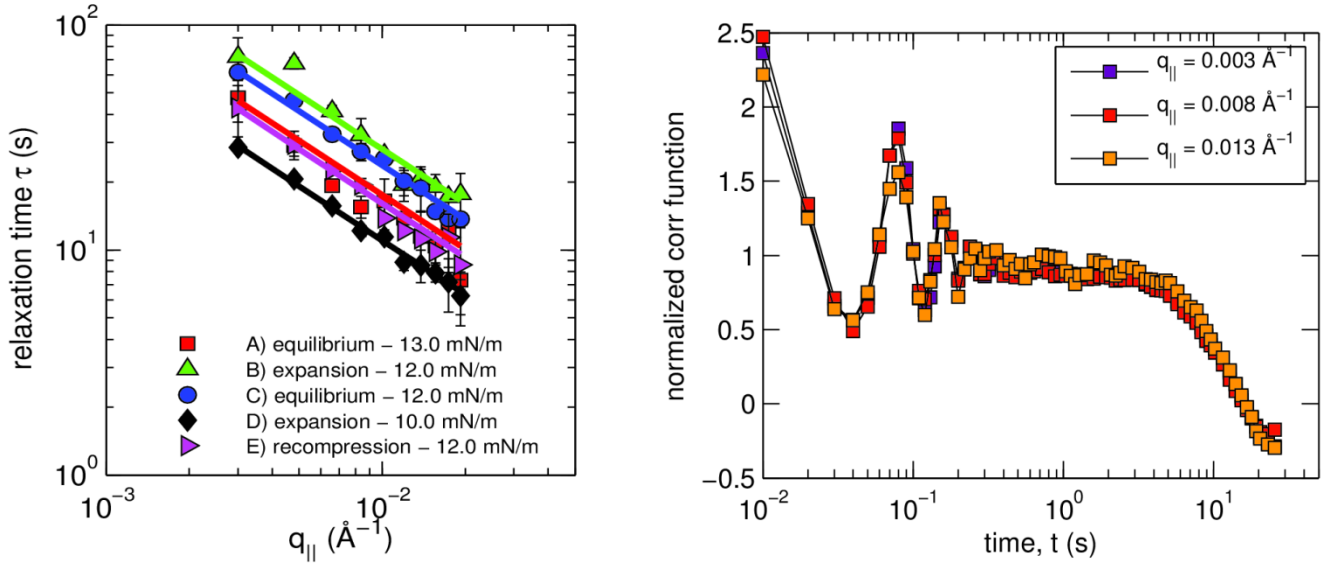

Figure 1, Left: *slow dynamics of a 2D GNP gel, driven out-of-equilibrium by uniaxial compression / expansion of the Langmuir film. Lines are fits described in the text.* ***Right:*** *spurious q-independent, fast oscillations are found in fast measurements.*

Second sample: Iron oxide (Fe_3O_4) nanoparticles – SDS mixed films.
As an exploratory measurement, we also investigated films made of magnetic Fe_3O_4 nanoparticles with 7nm diameter. An aqueous solution of nanoparticles is spread on an aqueous subphase containing a small concentration of the surfactant SDS (sodium dodecyl sulfate, 10 μM). Previous experiments have demonstrated that in these conditions a stable film is formed at the air/water interface. This film is remarkably compact and homogeneous even at very low surface concentrations (1-3 mN/m).
A measurement of the slow dynamics of the system, performed with a detector exposure time of 0.1sec, is started as soon as the desired surface pressure is reached.

The measurements indicate that the sample is characterized by a slow arrested dynamics, roughly compatible with the slow dynamics observed in GNP films despite some significant differences. The second order correlation functions decay as compressed exponentials: the compression exponent gamma is q-independent, The relaxation times scale with the parallel component of the exchanged momentum, which is the signature of 2-D confined dynamics, as opposed to the more usual 3D dynamics [Dur09].
Again, the presence of q-independent fast oscillating patterns in the correlation functions measured with low exposure times of the detector did not allow a more refined characterization of the dynamical heterogeneities of the system.

[Ors12] D. Orsi, L. Cristofolini, G. Baldi, and A. Madsen, Physical Review Letters **108**, 105701 (2012).
[Dur09] A. Duri, T. Autenrieth, L. M. Stadler, O. Leupold, Y. Chushkin, G. Grübel, and C. Gutt, Physical Review Letters **102**, 145701 (2009).