



	Experiment title: In-situ nanoparticle self-assembly by controlled nanowetting	Experiment number: SI1599
Beamline: ID10B	Date of experiment: from: 18/06/2008 to: 24/06/2008	Date of report: 23/02/2010
Shifts: 18	Local contact(s): Alexei Vorobiev	<i>Received at ESRF:</i>

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Report:

The old wetting chamber that we had planned to use in the original proposal was irreversibly damaged during the second half of year 2007. A new improved wetting chamber was designed and realized after this event. This new chamber reached its first assembly/test stage in June 2008. It became clear that most of the assigned SI1599 beamtime would be necessarily dedicated to the commissioning of the new sample environment rather than to the scientific investigation of nanoparticle self-assembly. After discussion with the local contact Dr Alexei Vorobiev and with the beamline responsible Dr Oleg Konovalov we decided to use the beamtime for more scientific, rather than technical, purposes. Consequently, we studied in-situ nanoparticle self-assembly at the water surface rather than at the sapphire surface as originally planned. We did not use at all the new wetting chamber. We used instead the Langmuir trough available at the ID10B beamline to study in-situ self-assembly of binary mixtures of 2nm and 6nm gold nanoparticles at the water surface at various surface pressures and at varying mixture ratios.

We found in particular the coexistence of a monolayer phase of large particles with a multilayer phase of small particles at relatively high surface pressures. This phase coexistence is stable only in conditions of large excess of small particles. If the fraction of large particles in the mixture is increased, the phase coexistence apparently becomes unstable and the surface diffraction signal from the small particles fades away and disappears on a time scale of approximately one hour after the deposition of the nanoparticles on the water surface. In the following, we present a small subset of the rather large amount of data that we were able to acquire from several different samples. These results prompted a significant data analysis/simulation activity in collaboration with Dr Jean Daillant. These modeling/simulation efforts are currently being completed in order to become integral part of the PhD thesis of the ID15 student Davide Calzolari.

In the meantime, we commissioned and intensely used at the ID15A/HEMD instrument our new x-ray chamber allowing in-situ nanoparticle deposition studies. We are now (winter 2009/2010) in a position to resume our originally planned experiments at ID10B, with in addition a much clearer understanding of the aspects that can be most efficiently studied at standard x-ray energies at ID10B and at high x-ray energies at

ID15A. This motivated us to submit a new proposal for the use of ID10B in combination with our new nanoparticle-deposition chamber.

Regarding our SI1599 measurements, we used chloroform solutions of decane-thiol-stabilized gold nanocrystals of average size 2nm (stock solution concentration $C_S=35\mu\text{M}$) and 6nm ($C_L=3.5\mu\text{M}$) having low polydispersity ($<10\%$). We performed initially two control experiments in which we spread at the water surface sub-monolayer amounts of pure small and pure large particles. In subsequent experiments we studied 5 mixtures of the two original solutions containing small:large (S:L) ratios (by number) of S:L=99:1; 97:3; 95:5; 80:20; 50:50. In each experiment we studied several surface pressures in the range 0~20 mN/m. The initial concentration was tailored so as to start from a sub-monolayer condition and end, at the maximum compression allowed by the Langmuir trough, at a bilayer/multilayer condition. At each pressure we measured full 2D grazing-incidence diffraction (GID) maps, grazing incidence off-specular diffuse profiles (GIXOS) and occasionally high-statistics q_z scans at a fixed q_{\parallel} value (ROD scans). All these measurements were done with the vertically mounted 1D position-sensitive detector.

Figure 1 presents typical GID maps and GIXOS profiles for the pure small particles at various pressures. The particles are already well correlated in the initial sub-monolayer (a), the order becomes shorter range in the complete monolayer (b), and at high pressure (c) there is clearly a multilayer structure as also suggested by GIXOS profiles (d). Figure 2 suggests that adding just 1% of large particles gives a structure in which the small particle multilayer coexists with a monolayer-like phase of large particles. Figure 3 suggests that this phase coexistence becomes unstable as soon as the fraction of large particles is increased to 3%. Modeling and simulation work is ongoing in order to rationalize this intriguing finding.

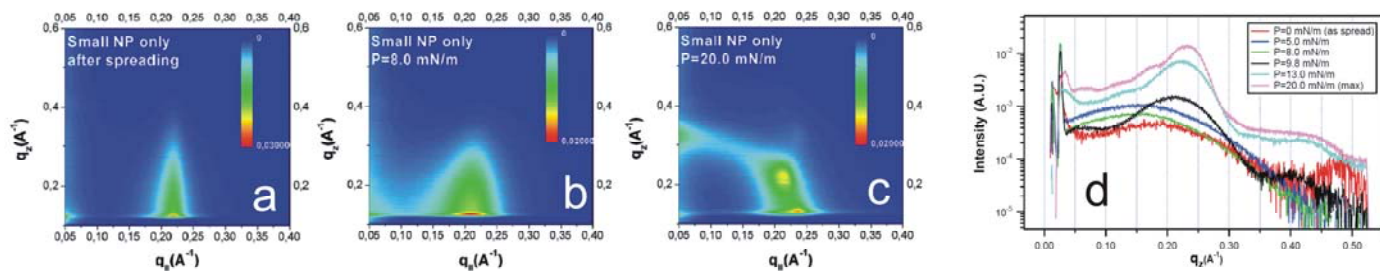


Figure 1 Sample containing only small (2nm) particles. (a)-(c) GID and (d) GIXOS at various pressures.

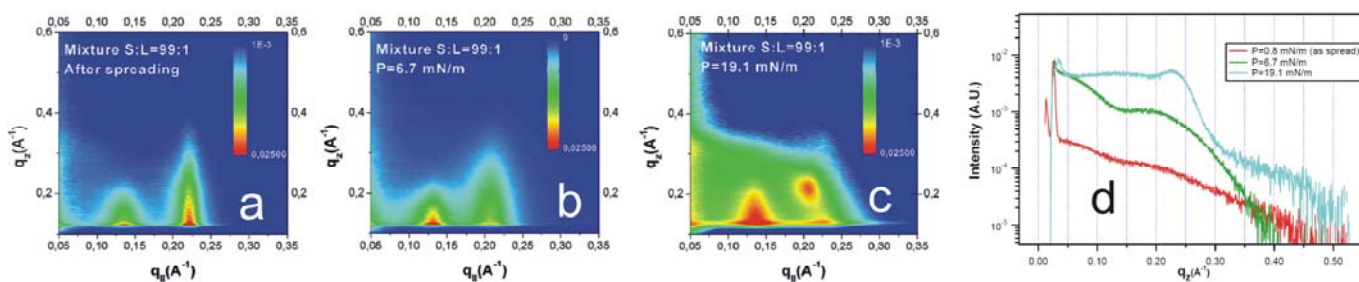


Figure 2 Mixture containing 1% (by number) of large (6nm) particles. (a)-(c) GID and (d) GIXOS at various pressures.

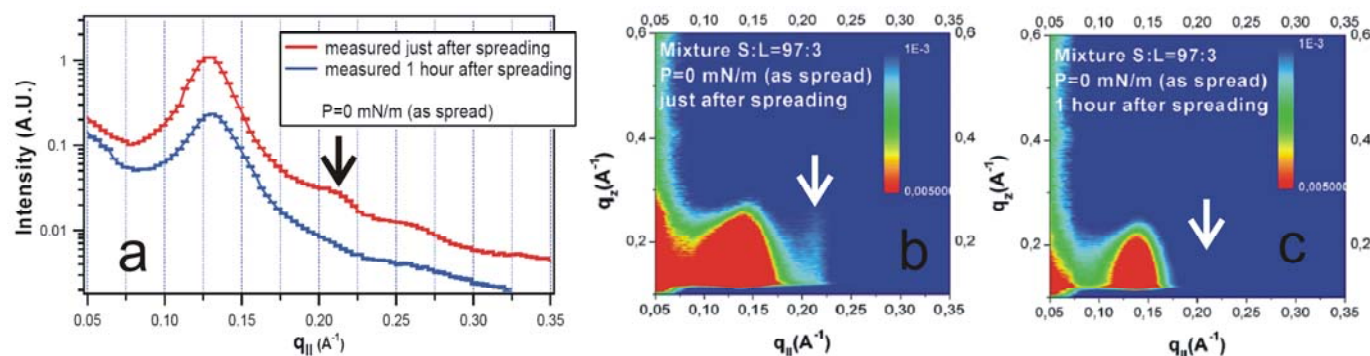


Figure 3 Mixture containing 3% of large particles. The faint GID peak from the smalls disappears rapidly.