	Structure of monolayers of gold nanoparticles at the water surface	<b>number:</b> SC1309
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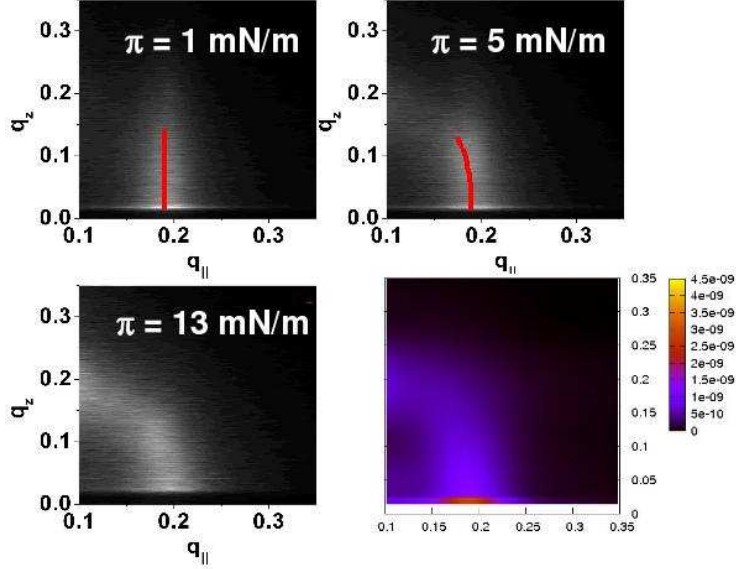
# Report:

Chemically synthesized nanoparticles with a metal core surrounded by a dielectric ligand shell have received a lot of interest in recent years because of their unique electrical, magnetic and optical properties. Perhaps best method for formation of monolayer film on substrate is to transfer the Langmuir monolayer of nanoparticles from the air-water interface to the substrate following Langmuir-Blodgett (LB) deposition technique, but this requires a good understanding of the monolayer structure and defects on the water surface. The aim of this experiment was to characterize such films on the water surface by surface diffraction and diffuse scattering.

Dodecanethiol encapsulated gold nanoparticles of 2 nm average diameter were prepared by reducing aqueous solution of hydrogen tetrachloroaurate ( $\text{HAuCl}_4$ ) with sodium borohydride ( $\text{NaBH}_4$ ) in presence of Tetra n-octyl ammonium bromide (TOABr) and dodecanethiol [1]. Approximately 1 ml of the toluene solution of the gold nano-particles (2 nm diameter) were spread on the water from a Millipore MilliQ system (resistivity  $> 18\text{MW-cm}$ ). The compression isotherms reveal a reversible region up to  $\approx 13\text{MN/m}$  above which irreversibility occurs.

A 8.06 keV x-ray beam in the 16 bunch mode was used. The grazing angle of incidence  $\theta_{in}$  was fixed to 1.9 mrad below the critical angle for total external reflection in order to enhance surface reflectivity. The scattered beam was collected using a vertically mounted 150mm long position sensitive detector (PSD). This setup was used for performing both the low  $q_{||}$  diffuse scattering and the large  $q_{||}$  grazing incidence diffraction.

The low  $q_{\parallel}$  region of  $(q_{\parallel}, q_x)$  intensity maps (below  $0.15 \text{ \AA}^{-1}$ ) was analysed using our standard diffuse scattering analysis procedure [2], including a capillary wave height-height correlation function to describe long-range correlations and a self-affine correlation function in order to describe a possible additional disorder in the gold nanoparticle organization resulting in a rougher film morphology. The higher  $q_{\parallel}$  region was analysed using the form factor of the gold nanoparticles plus a quasi two-dimensional structure factor describing the particle-particle correlations in the film with possible deviations in the vertical. We carefully checked that consistent absolute intensities were obtained in both cases, as well as the consistency of the parameters describing the film as a continuum in the low  $q_{\parallel}$  regime (since it is necessary to use here an effective refractive index) and the high  $q_{\parallel}$  where we are sensitive to the discrete nature of the nanoparticles. Good fits could be obtained this way over the entire  $q_{\parallel}$  range (Fig. 1).



*Fig. 1: top left: experimental data at 1mN/m; top right: experimental data at 5 mN/m; bottom left: experimental data at 13 mN/m; bottom right: calculated image for 13 mN/m.*

The main results obtained from this analysis<sup>1</sup> are the following:

- At very low pressure, the nanoparticles are organized in a 2-dimensional film.
- As pressure is increased in the reversibility region below 13 mN/m, the particles start to deviate from  $z=0$  upon compression, and the Bragg rod significantly bends.
- Above 13 mN/m, there is a significant growth of a second layer, whose structure and morphology can be obtained by fitting the low  $q_{\parallel}$  intensity.
- A flat film can be restored upon annealing at high pressure and 40°C. This will enable the formation of more condensed films of organic capped nanoparticles which are important for various applications.

## References

- [1] S. Pal, N. S. John, P. J. Thomas, G. U. Kulkarni, and M. K. Sanyal, J. Phys. Chem. B **108**, 10770 (2004).  
[2] S. Mora, J. Daillant, K. Mecke, D. Luzet, A. Braslau, M. Alba, and B. Struth, Phys. Rev. Lett. **90**, 216101 (2003)