Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF. Once completed, the original report should be sent, together with 5 reduced (A4) copies, to the User Office.

In addition, please send a copy of your file as an e-mail attachment to reports@esrf.fr**,** using the number of your experiment to name your file. This will enable us to process your report for the ESRF Annual Report.

Reports accompanying requests for additional beam time

If your report is to support **a new proposal**, the orginal report form should be sent with the new proposal form, and a copy of your report should be attached to each copy of your proposal. The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.
- bear in mind that the report will be reduced to 71% of its original size. A type-face such as "Times", 14 points, with a 1.5 line spacing between lines for the text, produces a report which can be read easily.

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ESRF	**Experiment title:** Self-assembly of noble-metal clusters in Langmuir layers	**Experiment number**: 28-01-114
Beamline: 28	**Date of experiment**: from: 5 December 2001 to: 11 December 2001	**Date of report**: 26 Sept 2002
Shifts: 18	**Local contact(s)**: Dr. Simon Brown	*Received at ESRF:*

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Report:

A grazing incidence small angle X-ray scattering (GISAXS) study was carried out at the XMaS beamline in December 2001 by the University of Leicester in collaboration with the University of Liverpool. The samples consisted of gold nanoparticles (~2.0nm in diameter) in toluene. The aim of this beamtime was to initially assemble the particles on a water surface in a langmuir trough and subsequently transfer the arrangement to a solid substrate using either the Langmuir-Schaeffer or Langmuir-Blodgett techniques. Computer controlled barriers on the trough allow the packing densities of the clusters to be varied and the behaviour can be characterised by measuring isotherms (Figure 1) and Brewster angle microscopy (Figure 2).

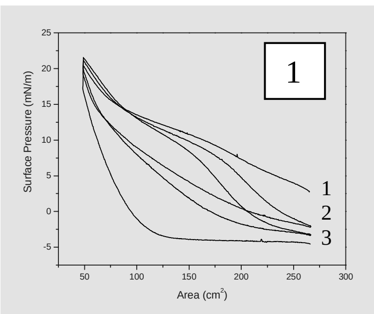
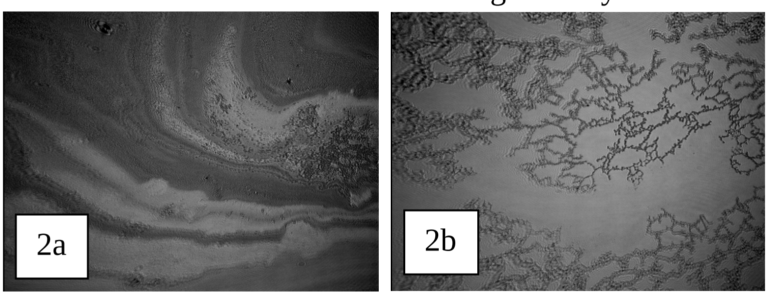


Figure 1 shows isotherms (surface pressure versus water area) for a solution of particles for three compression and expansion cycles (labelled). Several features are immediately apparent; the compression and expansion cycles follow different paths, indicating some hysteresis. Additionally, the paths are different depending on the number of previous cycles again indicating some non-reversible behaviour. There are other more subtle features in the curves, including a bump in the compression curves that always appears at a surface pressure of close to 7mN/m. This is typical of a phase change or collapse of the langmuir layer and we attribute it to a transition from a fully compressed layer to a disordered multilayer structure. Figure 2 indicates the domain structure present in the layer, at the micron scale. The structure in Figure 2a indicates that prior to compression, the particles all appear in bands in one layer, whilst after a full compression-expansion cycle they have aggregated into permanent fractal like branches (Figure 2b). We believe this to be the



origin of the hysteresis in the isotherm data. Having created the cluster layer, GISAXS measurments were recorded for films transferred to a Si(111) sample using the Langmuir-Blodgett technique (dipping through the layer). Initially these films were compared with those created using the evaporating solvent method, where a drop of solution is allowed to evaporate on a surface leaving behind ordered domains of particles. The langmuir deposition method will in theory produce more well ordered domains of particles, due to the increased mobility.

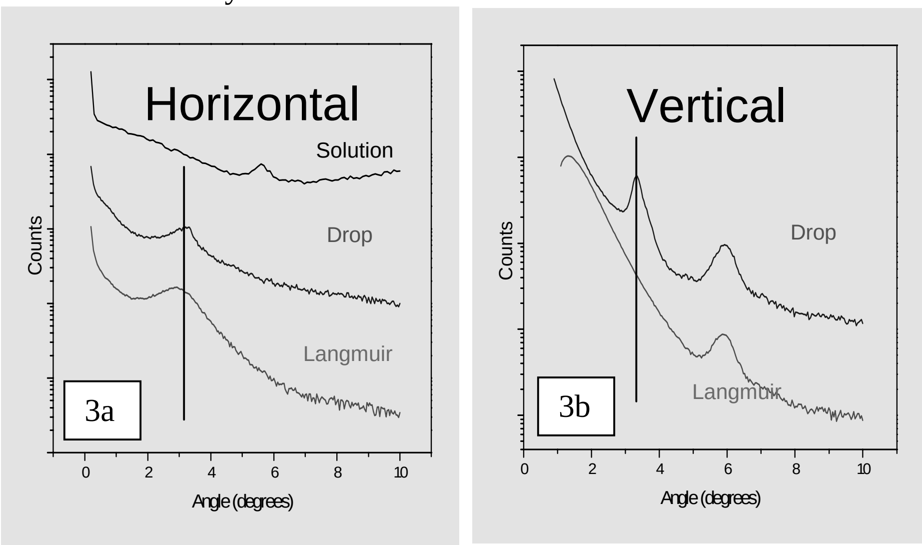
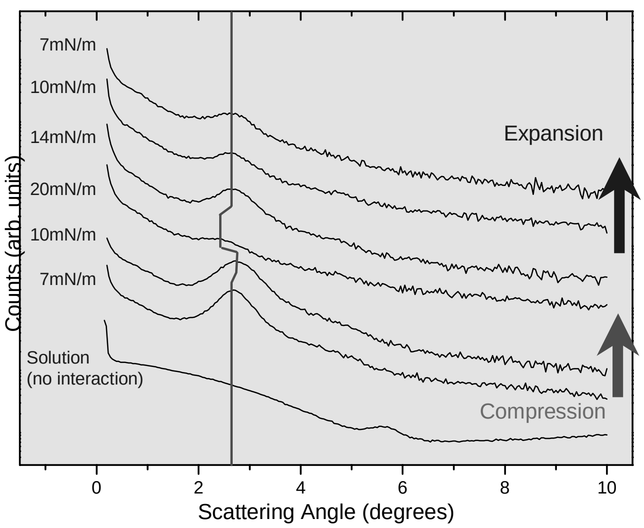


Figure 3 shows the GISAXS scattering in both the in-plane (Fig 3a) and out-of-plane (Fig 3b) directions. Some differences are visible, in particular the in-plane peak appears broader in the langmuir deposition method, whilst it is absent in the vertical scattering. These results are consistent with the transfer of a single layer to the sample, where there is no stacking normal to the surface and therefore no scattering. The broad in-plane peak may be due to the layer being non-close packed. The drop method shows peaks in both directions indicating that a three-dimensional structure occurs even for small volumes of solution. The langmuir-blodgett deposition therefore appears successful and able to transfer individual layers of particles.



The measurements were then extended to investigate whether a compressed layer could be transferred to the sample and remain in its compressed state. Figure 4 shows the GISAXS signal in the in-plane direction as function of the surface pressure. During the compression cycle, the peak is seen to shift slightly to higher scattering angle, indicating that the layer is indeed reamining compressed. However, as the layer is compressed past the monolayer collapse point, the peak shifts to lower angle and has a lower intensity. This is expected if the clusters collapse into multiple layers where the particles relax in the in-plane direction and the scattering is spread in all directions due to the 3d structure of the layers. As the barriers are expanded the peak returns, although it never achieves the same intensity as the original scattering. This behaviour is due to the hysteresis effects caused by the irreversible agglomeration of the particles into the fractal like structure shown in Figure 2b.

These results show that the langmuir-blodgett deposition method is suitable to transfer ordered arrangements of particles to a solid substrate. It is possible to transfer the particles one layer at a time and the scattering indicates a steady buildup of the layers (data not shown). It is also possible to transfer compressed arrangements of particles to the sample in tact up to the langmuir layer collapse point. The scattering after the monolayer has collapsed indicates that the particles have formed a 3d disordered network.

Future measurements will focus on the role of the ligand in the cluster assembly process, by performing similar measeuments to those shown in this report as a function of ligand chain length. It is predicted that this will not only change the interparticle separation, but will also have an effect on the long range order of the assembled structures.