ESRF	**Experiment title:** Structure formation of colloidal solutions in confined geometry – a time resolved in-situ Grazing Incidence Small Angle X-ray Scattering investigation …	**Experiment number**: ME-777
Beamline:	**Date of experiment**: from: 5.4.2006 to: 11.4.2006	**Date of report**: 25.2.2007
Shifts: 15	**Local contact(s)**: M. Burghammer	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

S.V. Roth*, T. Autenrieth*, HASYLAB at DESY, Notkestr. 85, D-22603 Hamburg, Germany

C. Riekel*, M. Burghammer*, ESRF, 6 r Jules Horowitz, F-38043 Grenoble, France

P. Müller-Buschbaum*, L. Schulz*, R. Hengstler*, Physik-Department E13, Technische Universität München, James-Franck-Str. 1, D-85748 Garching, Germany

Report:

Nanostructuring using solution casting is one method of choice to install large-area two-dimensional (2D) thin films with specific morphology. This method is especially important and applicable in the field of colloidal particles, as colloidal particles are often suspended in aequous solutions. The nanostructuring, however, is a very complex process involving several mechanisms [1]. The solvent evaporates and increases the concentration of the colloidal particles. The increased evaporation near the contact line drives a convective flow within the drop that transports material towards the periphery [2]. Additionally, an increased solute concentration and a decreased temperature near the three-phase contact line may trigger solutal [3] and thermocapillary [4] Marangoni flows. However, also the interaction with the substrate [5] and transversal contact line instabilities [6] have to be taken into account. Finally, capillary forces come into play as soon as the solution film has a comparable thickness as the colloidal particles' diameter [7].

The in-situ experiment described here was conducted at the microfocus beamline ID13/ESRF. Initially proposed using the 5 µm-size beam, due to the ongoing development of ID13, we were actually able to exploit the extremely brilliant 300 nm-size beam (FWHM) produced by Fresnel zone plates at a wavelength of 0.0976 nm, enabling us to reduce the beam-size compared to previous experiments [1,8,9] up to a factor of ten! The experimental setup combined this nanobeam small-angle x-ray scattering (nanoSAXS) geometry for the first time with a grazing incidence setup, giving rise to an new class of experiments, namely nanobeam-grazing incidence small-angle x-ray scattering (nanobeam-GISAXS) experiments.

As samples, we chose commercial unconjugated colloidal gold solutions [Kisker Biotechnologie]. Gold nanoparticles have the advantage of strong scattering contrast to the solvent (water). A droplet of 25 µl volume was deposited on a blank, acidly cleaned Si-wafer surface using a high-precision, remotely controlled syringe pump available at ID13. The resulting droplet diameter on the surface was 3 mm. Due to the small

incident angle of 0.6°, the footprint on the sample surface was only 0.3x29 μm^2. Hence the surface curvature of the droplet can be neglected and the droplet surface with respect to the beam can be considered as locally flat, see fig. 1. The beam was positioned at the Si-surface to probe the approach of the three-phase contact line. As an example, we focus on a colloidal particle diameter of 2 nm. Fig. 2a)-c) shows the different stages of solvent evaporation. For the in-situ experiment, an acquisition time of 120 s and a time-between-frames of 130 s were chosen. Fig. 3 shows the corresponding results. The 2D nanoGISAXS signal at a sample-to-detector distance SDD=0.809 m is decomposed in two components. The so-called detector cut [1, 8,9] shown in Fig. 3a probes the intensity distribution as a function of scattering vector component q_z (vertical to the sample surface). From bottom to top the time after deposition increases. In Fig. 3b, the so-called out-of-plane cut is presented. It shows the intensitiy distribution of the scattering vector component q_y (parallel to the sample surface) and hence probes lateral length scales, e.g. most-prominent radii of clusters.

For t<tb=3250 s, no change in the nano-GISAXS spectra is observed. At time tb, the three phase contact line reaches the beam position and clear changes in the nano-GISAXS pattern occur. From fig 3b, we are able to extract a most-prominent length scale ξ using a Guinier-approximation as a function of time. The results are shown in fig. 4. ξ increases according to a power-law as function of time, $\xi(t) \sim t^{1/3}$, indicating that the structure formation is governed not only by diffusive process, which would lead to $t^{1/2}$. Additionally the detector scan in fig. 3a shows the decreasing solution film thickness, as indicated by the arrows.

To summarize, for the first time we have employed nanobeam-GISAXS to follow in-situ the structure formation during solution casting quantitatively. A most prominent length scale emerges, which can be interpreted as a clustering of the 2 nm colloidal nanoparticles during evaporation of the solvent. The non-diffusive character of the power-law behaviour can be interpreted due to convective flows, which reduce the exponent.

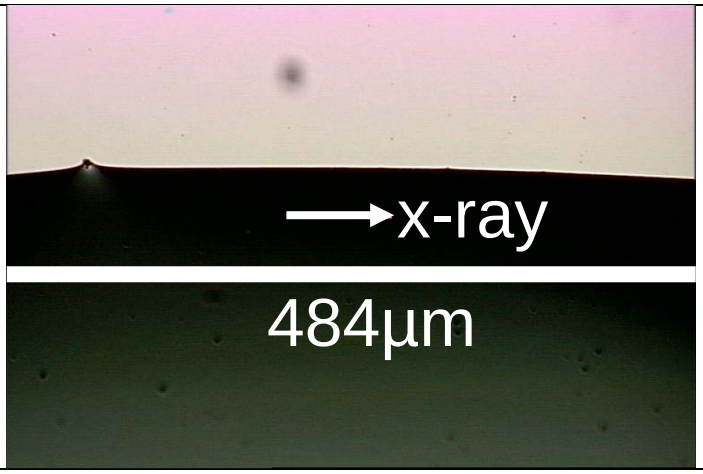

Fig. 1: Optical photograph of the deposited droplet. The scale bar denotes 484 µm. The beam direction is indicated by an arrow. Its length represents the footprint in beam direction.

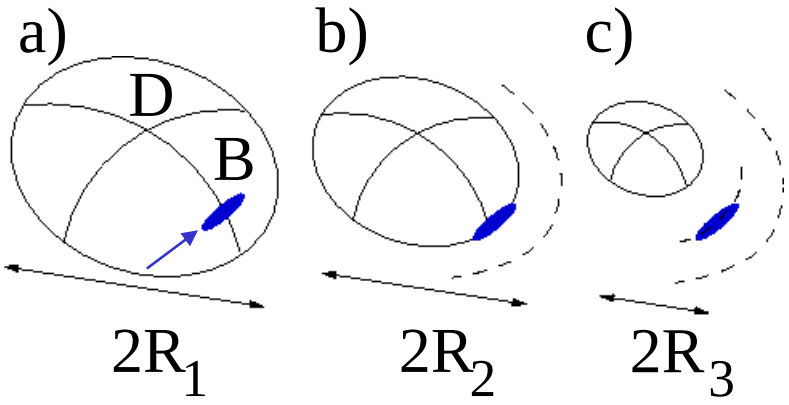

Fig. 2: The nanobeam ist positionend with 50 µm of the three-phase-boundary (TPB). a) TPB is far away. b) TPB reaches the beam. c) TPB has passed the beam. $R_1 > R_2 > R_3$ during solvent evaporation with R_j (j=1,2,3) being the droplet radius.

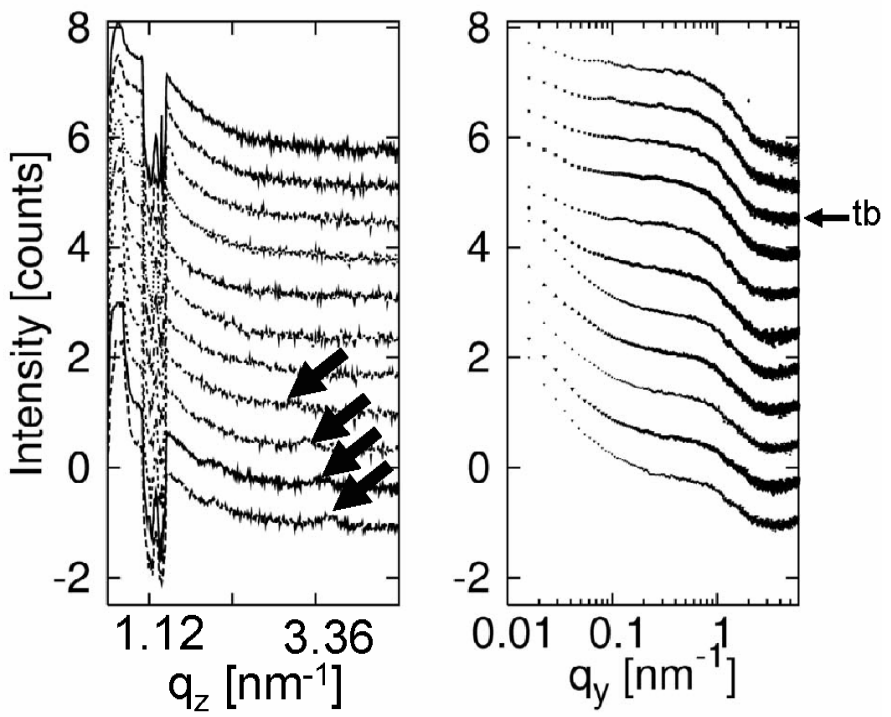

Fig. 3: Detector cut (left) and out-of-plane cut at the critical angle of Si (right). From top to bottom, the evaporation time increases (tb=3250 s denotes corresponds to the situation in fig. 2b). The time interval between subsequent measurement is Δt=130 s. The curves are shifted for clarity. In the detector cut the arrows denote the thickness of the drying colloidal solution. In the out-of-plane cut, clear structural changes occur for t>tb for q_y<0.7 nm^{-1}.

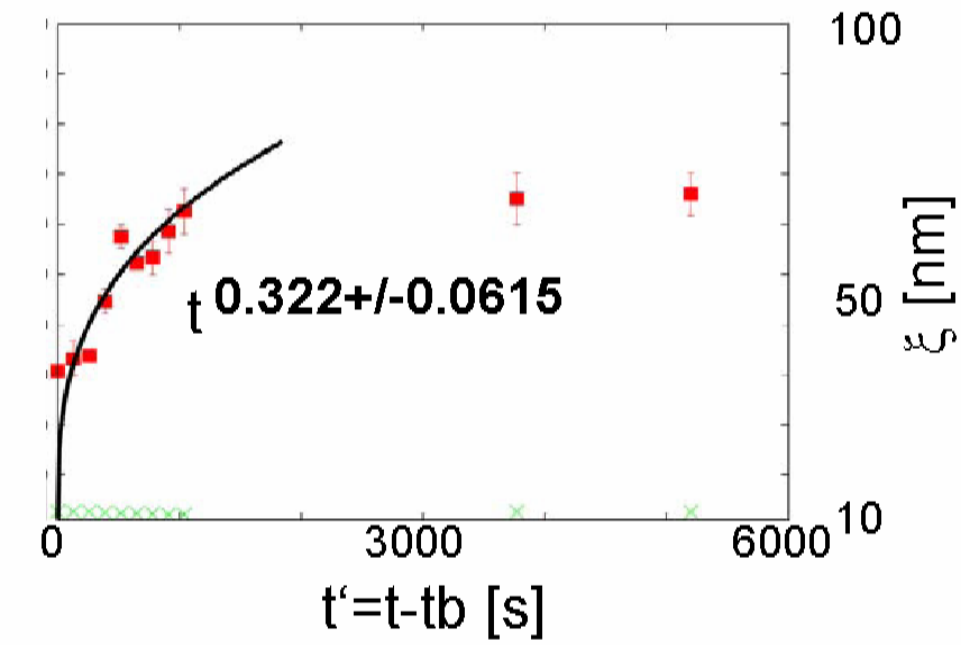

Fig. 4: Quantitative analysis of the increase q_y<0.7 nm^{-1}. The time evolution of the structural changes follows a nearly a $t^{1/3}$-power-law, indicating a non-diffusive mechanism of cluster growth.

[1] Müller-Buschbaum P. et al., Europhysics Lett. **73** (2006) 35
[2] Gonuguntla M. and Sharma A., Langmuir, **20** (2004) 3456
[3] Nguyen V. X. and Stebe K. J., Phys. Rev. Lett. **88** (2002) 164501
[4] Haw M. D. et al., Langmuir, **18** (2002) 1626
[5] Warner M. R. E. et al., Colloid Interface Sci. **267** (2003) 92
[6] Deegan R. D., Phys. Rev. E **61** (2000) 475
[7] Denkov N.D. et al., Nature **361** (1993) 26
[8] Roth S.V. et al., Appl. Phys. Lett. **88** (2006) 021910
[9] Roth S.V. et al., Appl. Phys. Lett. **82** (2003) 1935