ESRF	Dynamics of colloid thin films at the nanometer scale using surface XPCS	**Experiment number:** SC1412
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Report:

We recently demonstrated the feasibility of investigating the surface dynamics at the nanometer scale using x-ray photon correlation spectroscopy (XPCS) in the grazing incidence geometry. In order to enhance the scattering signal from the surface at a large parallel wavevector transfer ($q_{\parallel}$), the thin polymer film surface is decorated with gold clusters presenting strong interference maxima due to the mean particle-particle distance. Therefore, the XPCS signal is amplified and the intensity auto-correlation function, which contains the dynamic information, can be measured. Both surface diffusion of the nano-particles and capillary waves motion at the polymer surface are thereby observed for length scales of about 10 nm (see report SC1179). The viscosities deduced separately from the two motions lead surprisingly to values much higher than the bulk ones. The aim of the present experiment is to confirm such a large surface viscosity and to measure the dispersion curve via the $q_{\parallel}$ dependance investigation of the dynamics.

Three polystyrene thin films (100 nm thick) are investigated with molecular weights of 34.4, 220 and 592 kg/mol, respectively and with rather large gold coverages in order to enhance the surface scattering. The sample surface is illuminated with a coherent beam, produced by a 12 or 20 μm pinhole placed at about 1.3 m upstream, impinging on the surface with an angle of incidence of about 0.15°. The sample is placed horizontally in a furnace equipped with kapton windows, previously developed at Dortmund University. The full small angle scattering signal (GISAXS) is measured by a direct illumination CCD as a function of time for temperatures increasing from 290 K up to 450 K. The use of the CCD allows us to

- increase the statistics by measuring the $\pm q_{\|}$ regions simultaneously and by integrating the signal over the perpendicular directions where no dependance is expected,
- measure simultaneously all $q_{\|}$ values from 0.1 to 1 nm^{-1} and thereby investigate the dispersion relation,
- follow the aging of the polymer film under radiation and avoid the loss of the auto-correlation function for large accumulation time.

Due to the readout time of the CCD, only the slower dynamics (*i. e.* the cluster diffusion) can be probed. The picture 1 shows half of the coherent GISAXS patterns measured on the 34.4 kg/mol (resp. 220 kg/mol) sample taken at 290 K (a,c) and at 450 K (b,d), resulting from an accumulation of 400 frames of 10 s each. The oscillations along the exit angle (α_f) direction correspond to interference fringes of the polymer film. The high temperature measurements look more fuzzy than the low temperature ones. Although no statistical analysis of the measurements is performed yet, the grainy aspect of the picture (a) is attributed to static speckles while the fuzzy aspect of the high temperature measurements is attributed to dynamic speckles faster than the total accumulation time. Further analysis are now performed in order to calculate the $q_{\|}$ and time dependant autocorrelation function.

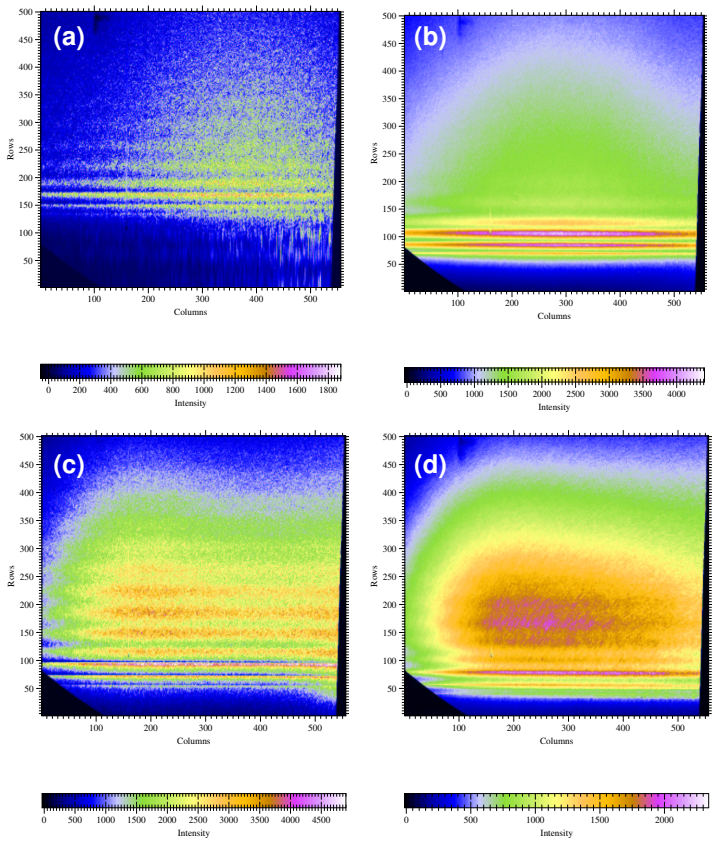

Figure 1: Coherent GISAXS patterns measured on polystyrene thin films with molecular weights of 34.4 kg/mol (top) and 220 kg/mol (bottom) taken at 290 K (a,c) and 450 K (b,d). The CCD area recovers the 1 ± 0.5 nm^{-1} reciprocal space region.