	Experiment title: Slow dynamics of poly(propylene glycol) studied by XPCS	**Experiment number:** SI-1082
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Report:

We studied the under-cooled surfaces of poly(propylene glycol) close to the glass transition temperature $T_G \approx 195K$. The aim of the experiment was to investigate whether the surface glass transition differs form that of the bulk and the experimental technique was correlation spectroscopy with coherent X-rays (XPCS). The experiment was performed under grazing incidence conditions and the surface scattering was collected by a direct illumination CCD detector. From the CCD frames the temporal auto-correlation function of the scattered intensity could be calculated for various momentum transfers parallel to the surface ($q_{\parallel}$) as shown in Fig. 1. The correlation functions all show a simple exponential behavior as expected for quasi-elastic scattering from over-damped capillary waves. The damping constant Γ can be extracted by fitting the correlation functions to the simple exponential form $\propto \exp(-\Gamma\tau)$ and hence the dispersion relation Γ vs. $q_{\parallel}$ can be mapped out as a function of temperature (Fig. 2). For overdamped capillary waves the dispersion relation is $\Gamma \propto q_{\parallel}$ which here only seems to hold in the low-q limit (Fig. 2).

For a glassy surface it has been predicted by Jäckle and Kawasaki [1] that the dispersion is slowing down for larger $q_{\parallel}$ values and this is what is illustrated in Fig. 2. The solid line is a fit following Jäckle and Kawasaki who interpret the slowing down in terms of the length $l_0 = \gamma/G(\infty)$, the surface tension over the high-frequency shear modulus. To our knowledge it is the first time that such a length-scale dependent glass transition has been directly observed at the surface.

The length parameter l_0 can be mapped out versus temperature following the above outlined method. The result is shown in the inset to figure 2 and a sudden jump around 212K is observed. One may speculate that this is related to the famous T_C from mode-coupling theory (MCT) which predicts a critical density or temperature where the viscosity diverges [2]. T_C has previously been estimated in bulk PPG to about 238K [3] i.e. quite far from the 212K where we see a sudden change in l_0 at the surface.

To summarize, the experiment was very successful and our measurements suggest that the sample surface already is in the glassy phase about 20K above T_G. In addition this transition seems length scale dependent. This appears to be in conflict with recent X-ray reflectivity measurements of the time-averaged surface roughness [4] where we concluded that the PPG surface still behaves like an under-cooled liquid at 200K. Obviously more experimental work is needed to achieve a deeper understanding of these phenomena.
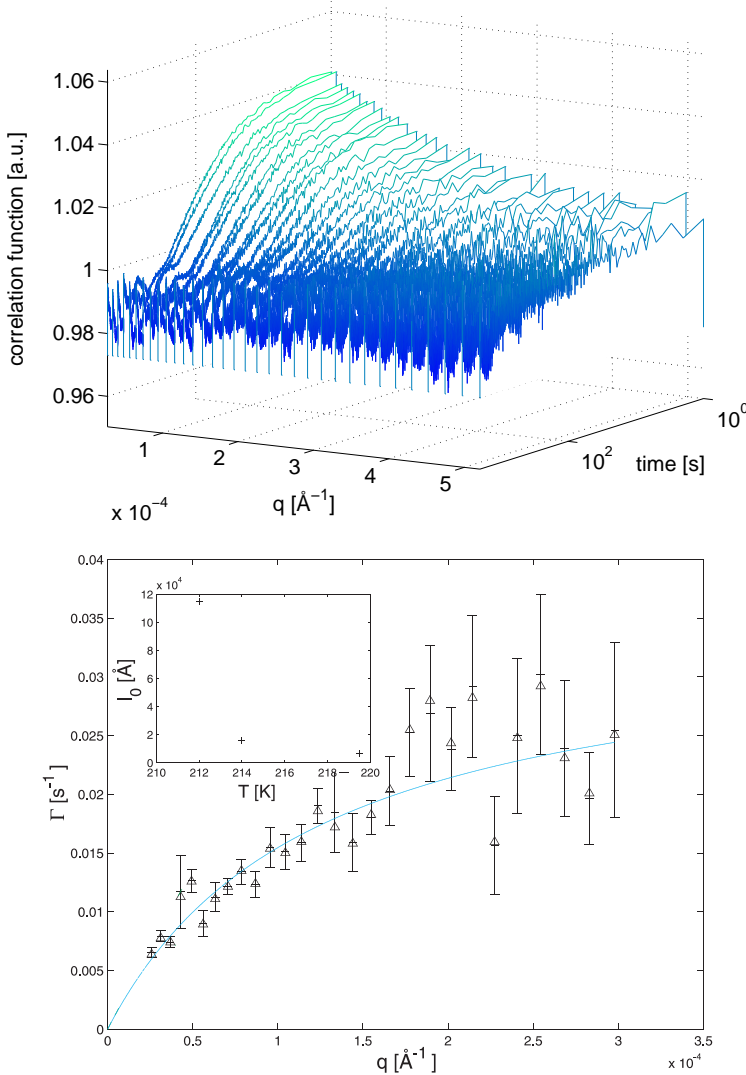

Figure 1. Correlation functions measured for PPG (molecular weight 4000) at T=214K. For each $q_\parallel$ the damping constant Γ may be found by fitting the correlation function to the form $\propto \exp(-\Gamma t)$.

Figure 2. Dispersion relation Γ vs. $q_\parallel$ for PPG-4000 at 214K. The solid line is a fit following Ref. [1]. The inset shows the evolution of l_0 versus temperature where a sudden increase is evident around 212K.

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