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| | **Experiment title:**<br>Microscopic dynamics near the glass transition in supercooled liquids | **Experiment number**:<br>HD-385 |
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## Report:

The purpose of this experiment was to study the microscopic dynamics of a supercooled liquid near its glass transition temperature, $T_g$. Understanding why and how the dynamics slow down in the supercooled regime is one of the most important and challenging endeavours in condensed matter physics. X-ray Photon Correlation Spectroscopy (XPCS) covers the slow time-scales characteristic of relaxations close to the glass transition within the mesoscopic length-scale regime and can thus provide unique information about glass-formation. We were for the first time able to measure the coherent intermediate scattering function (ISF) at the molecular length scale in a molecular supercooled liquid, pentaphenyltrimethyltrisiloxane (DC705 $T_g$=224.0 K), see Fig. 1. This system has been investigated by several complementary techniques. which allows a cross-check of the results obtained.

The presence of 3 Si atoms in the molecule results in a sufficient scattering cross section for conducting XPCS at the peak in the structure factor at Q=0.743 Å-1 Fig.1a. The correlation functions (CF) were calculated from a series of 5000 CCD images with an acquisition time of 3-5 seconds each. Due to the weak scattering the CCD image contains only 10000-15000 single photon events. A special software event correlator was applied to extract the intensity autocorrelation function $g_2$. The dynamics were measured within the temperature range 230-110 K. This temperature range covers the supercooled and the glassy states of the liquid. A typical CF is shown in Fig.1b.

We find strong evidence in these experiments supporting that translational dynamics at molecular length scales can be detected by XPCS in a molecular glass former, in spite of a low scattering cross section, see

Fig. 1. Due to the low contrast of the initial measurements, however, we were not able to carefully map out the temperature dependence of the structural relaxation time, or to resolve the expected considerable stretching of the ISF (as observed in dielectric or mechanical spectroscopy). As the simplest approximation, we analysed the intensity autocorrelation function using a single exponential expression as $g_2 = 1 + A\exp(-2(t/\tau))$, where $A$ is the coherence factor. An example of a typical data set together with a fit can be found in Fig.1b for DC-705 at T=223 K. The determined relaxation time appears to follow the structural relaxation as measured independently using dielectric or mechanical spectroscopy [1] , see Fig. 1c. Due to a strong contribution from the quartz sample cells, however, we were not able to determine the wave-vector dependence of the observed dynamics. In addition, we found evidence also for a relaxation feature within the glass; we presently have no explanation for this observation, which in itself clearly requires continued investigations.

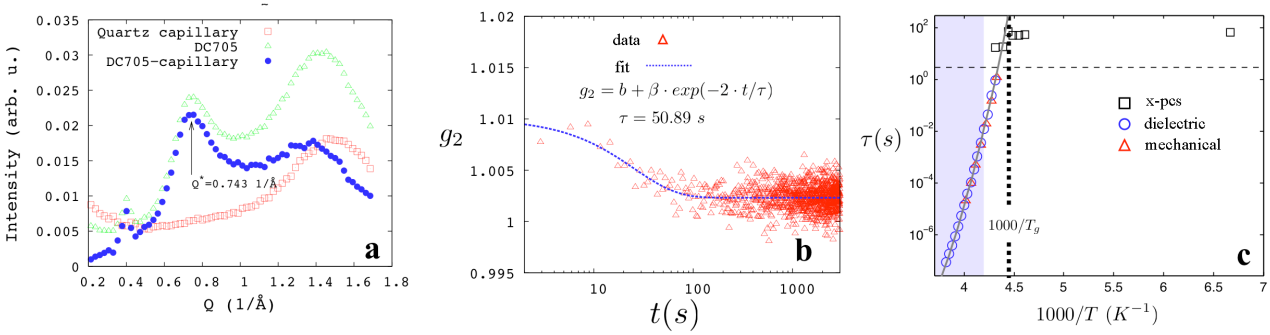


**Figure 1**: a) Scattered intensity vs wave vector for DC-705. Note the marked pre-peak in the structure factor and the strong contribution of the quartz sample cell around the main peak. b) The measured correlation function $g_2$ at 223 K together with a single exponential fit. c) The determined relaxation time, as measured by XPCS, dielectric spectroscopy and mechanical spectroscopy [3]. Within the shaded area performed measurements did not detect any relaxation within the experimental window suggesting that the relaxation is too fast to be observed, in accordance with an interpretation of the relaxation as the structural relaxation. The dashed line marks the shortest measurable time-scale using this XPCS set-up. Note also the intriguing evidence for a relaxation feature within the glassy state of DC-705.

To conclude, we have measured the translational dynamics at molecular length scales in the glass-former DC705 with XPCS. The technique proved to be sensitive to detect dynamics both in the supercooled and glassy states of the system. Due to the low contrast and large sample cell contributions we were not able to perform a careful mapping of the temperature and wave-vector dependence of the relaxation times. The statistics was not sufficient at this time to conclude regarding the stretching of the relaxation functions. We have no explanation at present for the observed relaxation within the glassy state. All these important topics require further investigation.

To resolve these questions, we need to increase the signal-to-noise ratio (SNR). This is needed not only to improve the quality of the CFs but also to be able to measure the wave-vector dependent dynamics. As is shown in Fig.1a there is a substantial background scattering coming from the quartz capillary. This diminishes the contrast of the CF and consequently the SNR. To eliminate this background contribution we plan to perform the experiment on a 'free' liquid. confined in a loop. DC705 has a low vapor pressure ($3 \cdot 10^{-10}$ torr at 25°C) and will thus not evaporate under vacuum in the experiment chamber. A further strategy for increasing the contrast is to use 2 CCD cameras that monitor the same $Q$ vector but are placed at different position in real space. The experiment should thus be further optimized with respect to the sample and detector set-up as well as the sample detector distance.