	Experiment title: Probing the relation between the heterogeneous structure and relaxational dynamics around the glass transition in ionic liquids using X-ray photon correlation spectroscopy	**Experiment number**: SC-4131
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Report:

The aim of the experiment was to measure slow dynamics in ionic liquids close to the glass transition temperature. Ionic liquids display structural heterogeneities on nanometer length scales, hence present a more complex structure than atomic or molecular liquids, observed through a well pronounced peak at low Q in the static structure factor (S(Q)). In this experiment we attempted to study the slow structural relaxation behaviour on the length scales of structural heterogeneities in a series of ionic liquids where we systematically can tune the strength and the length scale of the mesoscopic structural features in S(Q). Doing this we aimed to explore to which extent nanometer structural features influence the Q-dependence of the relaxation times $\tau(Q)$ and the functional forms of the intermediate scattering functions (i.e. deviations from simple exponential decay) and also to quantify possible heterogeneous dynamics.

Results

The experiment was first configured in a WAXS setup at 8.1 keV providing high flux of coherent photons. However, after the beam optimization our preliminary measurements showed a decay of the intensity over time and a change in S(Q) during consecutive measurements (see Fig. 1) indicating that even at room temperature the samples were suffering from severe beam damage.

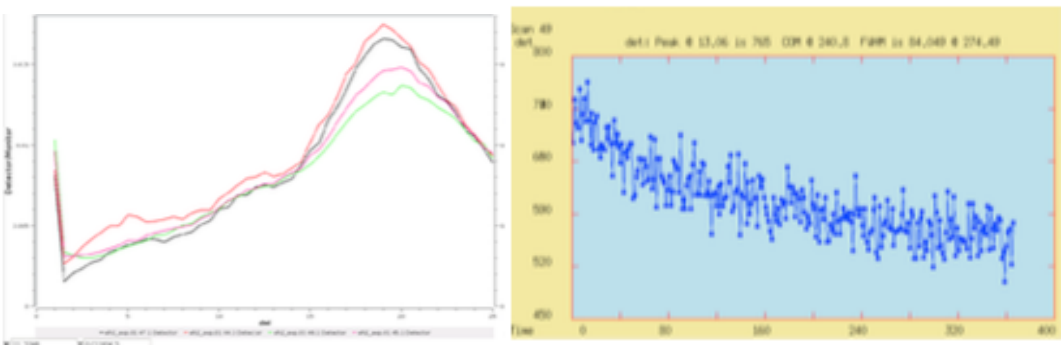

Figure 1. Left: S(Q) from consecutive scans: red (49 points 10 sec), pink (49 points 30 sec) and green (49 points 30 sec) respectively, and black the same S(Q) after letting the sample rest for one hour. Right: Time scan at a fixed angle (19°, Q≈1.3 $Å^{-1}$) showing the continuous decrease in intensity.

In an attempt to reduce beam damage the set-up was changed to allow experiments at 21 keV. One should note that XPCS-experiments at 21keV are not a standard technique at present and only few tests have been performed previously. We showed that it indeed was possible to do experiments at these conditions. As predicted we found that the sample was much less damaged at 21 keV and no beam damage could be detected around room temperature. However, upon cooling down and approaching the glassy state of the sample, where the interesting dynamics also is expected, the mobility of the ions decreases and hence beam damage was again (see Fig. 2). We could conclude that the liquid is stable for exposures of at least a couple of seconds at 21 keV. Thus, our results show that it is in principle possible to perform XPCS on these, as well as other, radiation sensitive materials, but not in a traditional scheme. Instead the results point to a general applicability of scheme where one uses very short consecutive exposures with a delay in between to obtain information on the dynamics. Such a scheme is very similar to what one envisages for XPCS at free-electron laser sources.

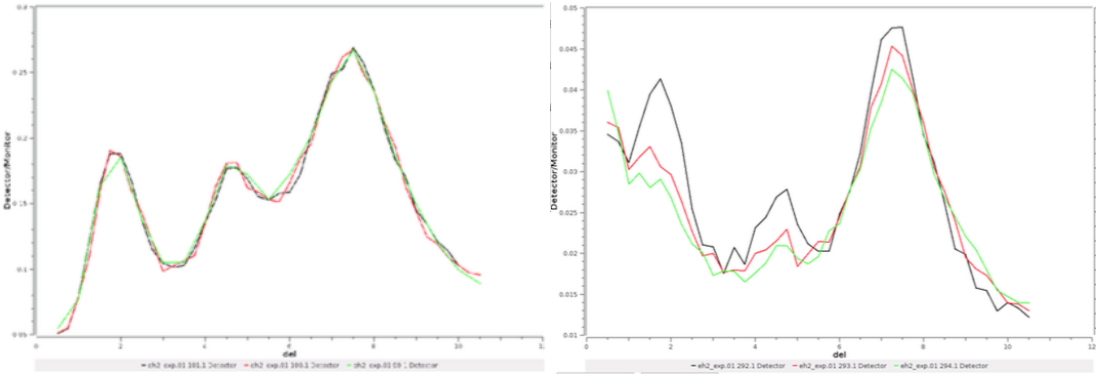

Figure 2. Consecutive measurements of S(Q) at room temperature (left) and 200K (right) respectively.

In a final attempt to obtain information on the dynamics we introduced colloids (1% volume fraction) in our samples in order to increase the scattered intensity and hence reduce the exposure time. The experiment is then performed in SAXS mode. This allowed us to extract some correlation functions at few different Q-values, see figure 3. The data shows an increase of τ with decreasing temperature which implied a slowing down of particle dynamic as expected and is connected to the free diffusion of particles in the solvent. To quantify the dynamics the data was fit with a KWW function $\frac{1}{\beta}\left(g_2(q,t)-1\right)=\exp\left(-2\left[\frac{t}{\tau}\right]^{\gamma}\right)$

where the exponent was found to be γ = 1.5 – 2, which has also been seen in other glass forming liquids at similar Q-values. Surprisingly, at temperature around T_g (between 170K ≤T≤190K), the relaxation time was more or less constant. Due to limit of beam time and low contrast at higher momentum transfers, we could not get information for a large Q-range for the dynamic of the colloidal systems in IL.

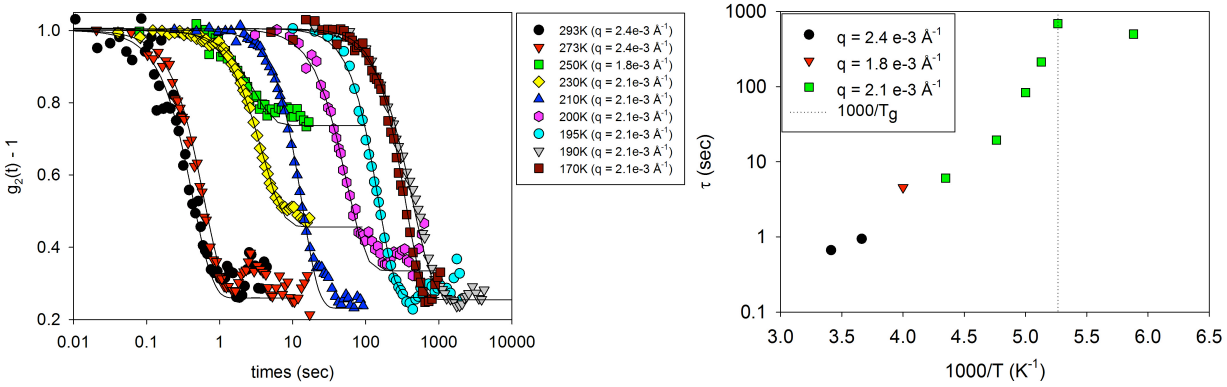

Figure 3. Left: Normalized intensity autocorrelation functions $g_{(2)}(q,t)$, obtained from colloids - $PYR_{14}TFSI$ for different values of Q and temperatures as indicated in the figure. Lines are KWW fits to the data. Right: extracted relaxation times for the temperatures investigated.