EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal: *https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Unveiling nanoscale fluctuation dynamics during liquid-liquid transitions	**Experiment number**: SC-5359
Beamline: ID10	**Date of experiment**: from: 28.09.2022 to: 03.10.2022	**Date of report**:
Shifts: 15	**Local contact(s)**: Yuriy Chushkin, Federico Zontone	*Received at ESRF:* *21.12.2022*

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Report:

The hypothesis of the existence of two liquid states of water, the so-called high- and low-density liquid (HDL, LDL), has gotten increased support from experimental evidence and simulations in recent years. From these emerges a water phase diagram indicating a liquid-liquid transition (LLT) with a coexistence line that ends in a liquid-liquid critical point (LLCP) at slightly elevated pressures in the deeply supercooled regime, which is largely experimentally inaccessible due to rapid crystallization into ice. A different approach, where a second component is mixed with water, particularly cryoprotectants such as glycerol, can be utilized to suppress the crystallization and thereby allow further experimental insight into the anomalous behaviour of supercooled liquid water. Previous observations propose that the addition of the second component can act similarly to increasing pressure in pure water and indicate an LLT at supercooled temperatures in these mixtures as well, related to the transition between HDL and LDL.

In this experiment, we aimed at measuring the structural dynamics of the proposed LLT in supercooled binary aqueous solutions by means of X-ray photon correlation spectroscopy (XPCS) at the ID10 beamline. The use of XPCS, specifically by calculating the two-time intensity correlation functions (TTC), allows to follow the temporal evolution of structural dynamics during such a transition. Moreover, we combine XPCS in the small-angle scattering (SAXS) regime with wide-angle scattering (WAXS), which allows us to measure liquid dynamic fluctuations on the nanoscale while simultaneously monitoring changes in the short-range, inter-atomic liquid structure, including eventual crystallization upon supercooling.

We adopted an experimental scheme in which the sample solution, consisting of glycerol-water mixtures with concentrations 5-23 mol% glycerol, was quenched to a supercooled temperature in the range T=170-200 K, followed by simultaneous SAXS/XPCS and WAXS measurements (a total of 100 s each with 0.01 s exposure time) in a series of 10-20 fresh sample spots. In addition, corresponding glycerol-water solutions with 100-nm sized silica nanoparticle tracers were measured for reference of the nanoscopic viscosity. The experiment was performed at a photon energy of 8.67 keV with the Eiger 500k detector at a sample-detector distance of 6.72 m

for measuring SAXS/XPCS in the q-range 0.005-0.2 nm^{-1}, and the Pilatus 1M detector at close distance (~0.1 m) providing WAXS images in the q-range 12-25 nm^{-1}. The sample solution was contained in 1.5-mm thick (quartz or borosilicate) glass capillaries inside a liquid-nitrogen cooled cryostat (ID10 equipment). Vacuum grease was used between the capillaries and the sample holder to ensure good thermal contact.

To quench the sample solutions to cryogenic temperatures, the liquid-nitrogen flow was maximized (>10 L/min) to yield a cooling rate around 20 K/min, then slowed down to 3-4 L/min at about 20 K above the target temperature to avoid over-shooting. A drawback in this experimental setup was the lack of remote control of the liquid nitrogen flow rate from outside the hutch, as well as limited precision in setting the flow rate, as it had to be done manually and by eye-measure. The former delayed the earliest start of measurements upon quenching, and thus limited the possibility to capture an early liquid-liquid transition in the solution prior to rapid crystallization, particularly at low glycerol concentrations.

Fig. 1 presents preliminary results from a 16.5 mol% glycerol-water solution about 2-3 min after being quenched to T=180 K. Here, it is evident that the combination of SAXS/XPCS and WAXS is key to provide a whole picture of the measured dynamic process. Fig. 1A shows the WAXS intensity as a function of time indicating a transition in the inter-atomic liquid local structure, from a broad liquid peak with maximum at 17.3 nm^{-1} to the growth of a pronounced peak at 17.1 nm^{-1} with a shoulder at 16.3 nm^{-1}. While the new peak positions are similar to those of hexagonal ice, the broad peak width preliminary suggests that it is still a liquid state. At the same time, Fig. 1B shows a strong enhancement of the SAXS intensity as well as a changing lineshape, with growth of a curvature in the q-range 0.01-0.1 nm^{-1}, possibly indicating formation of nanoscale structures in the liquid. We can further observe a temporal evolution of the structural dynamics, as presented in Fig. 1C for q=0.013 nm^{-1}, by extracting the intensity autocorrelation (g_2) functions from the anti-diagonals of the TTC (inset, C). The correlation signal intensity appears to increase with time, by a decaying baseline of the TTC while the contrast β of the correlation functions increases. After about 80 s, the dynamics suddenly start to slow down, coincidently with the maximum and turnover of the SAXS intensity in the small-q regime (q<0.01 nm^{-1}, inset B).

Despite the limitations in the cooling protocol, we conclude that the experimental goals were successfully achieved. The above presented observations could be an indication of a nucleation and growth process associated with a liquid-liquid transition. Further careful analysis will however be required, to fully map the dynamic process and for other conditions measured, as well as to exclude any influence of ice nucleation. Nevertheless, we expect that these experimental data will eventually result in a scientific publication, with the beamline staff included as co-authors. We are highly appreciative of the excellent support given.

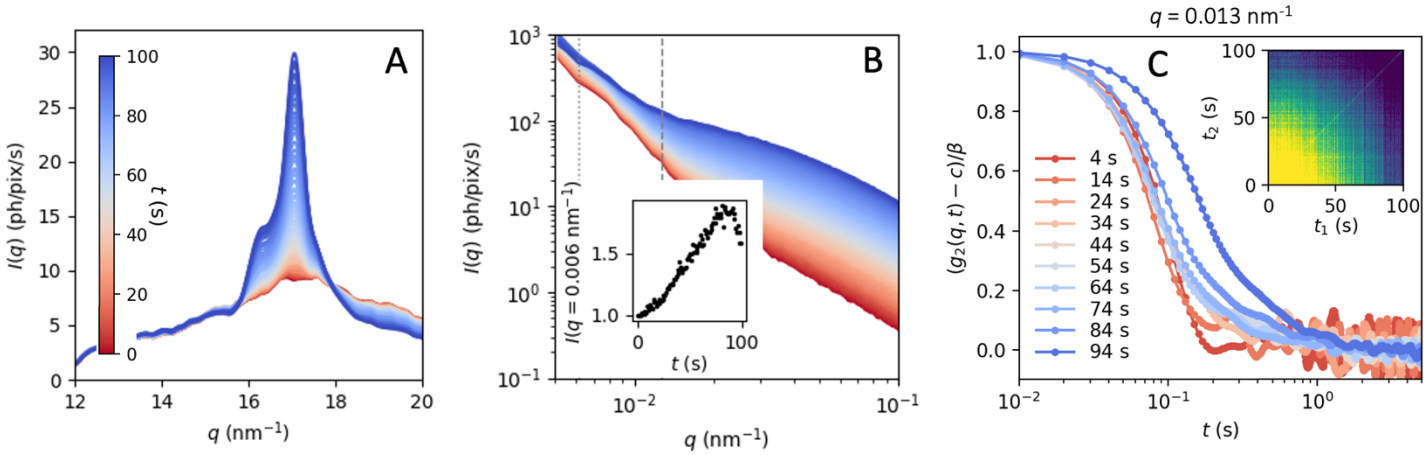

Fig. 1 The liquid structure and dynamics of 16.5 mol% glycerol-water solution after quenching to 180 K. Figure (a) and (b) show the temporal evolution of the wide-angle and small-angle scattering intensity (WAXS, SAXS), respectively, within a single spot about 2-3 min after reaching T=180 K. The WAXS notably shows the growth of a pronounced peak with maximum at 17.1 nm^{-1} and a shoulder at 16.3 nm^{-1}. At the same time, the SAXS intensity monotonically increases with the formation of a curved lineshape in the larger q-range 0.01-0.1 nm^{-1}, while exhibiting a maximum and turnover in the small-q region q<0.01 nm^{-1} after about 80 s (inset, a). (c) shows the corresponding intensity auto-correlation g_2 functions extracted from the anti-diagonals of the two-time intensity correlation function (TTC, inset) at q=0.013 nm^{-1}. A slowdown of the dynamics is observed after about 80 s. Note here that the g_2 functions are presented with subtracted baseline c and normalized by the contrast β.