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ESRF

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.

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

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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.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal 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:** Grazing incidence XPCS on supercooled ionic liquids close to the glass transition	**Experiment number**: HD-515
Beamline: ID10A	**Date of experiment**: from: 13/04/2011 to: 19/04/2011	**Date of report**: 31/8/2011
Shifts: 18	**Local contact(s)**: Dr Yuriy Chushkin	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Aim of the experiment

The aim of the present experiment is to investigate the low frequency dynamics in ionic liquids (ILs) using grazing incidence X-ray Photon Correlation Spectroscopy (GIXPCS), in the temperature regime in which the effect of viscosity is dominating, in order to provide information on how the strong damping of fluctuations due to an exponentially increasing structural relaxation time alters the capillary waves dynamics as measured by GIXPCS on approaching the glass transition temperature T_g. For the present investigation we choose the ionic liquid $PyR_{14}TFSI$ (N-methyl-N-butylpyrrolidinium bis[trifluoromethyl(sulfonyl)]imide). The glass transition temperature for this IL, as reported from calorimetry, is T_g=183 K.

Results

Dynamic surface height-height correlation functions $g^{(2)}(t)$ where measured with an avalanche photodide detector (APD) for different values of the axchanged momentum q_x parallel to the surface, and for different temperatures. High quality data could be obtained over a large temperature and exchange momentu range. A selection of the $g^{(2)}(t)$ is reported in Fig. 1.a for a fixed value of q_x. The data have been analyzed according to an exponential relaxation model

$$g^{(2)}(q_x,t)=b+C(q_x)[\mathrm{e}^{-t/\tau(q_x)}]^2 \quad (1)$$

The extracted relaxation rates $\Gamma(q_x,T)$ are reported, for all accessed temperatures and momenta, in Fig. 1.b. Moreover, a linear regression procedure over the lowest q_x points (see figure caption for more details) provides the angular coefficient D and intercept C of the $\Gamma(q_x,T)$ trend.

According to a Voigt-Kelvin model of viscoelasticity, the complex storage modulus is related to viscosity η and elasticity E: $G(\omega)=E-i\omega\eta$. Once put into a linearized Navier-Stokes equation, this form of $G(\omega)$ gives the following behavior for the relaxation rate:

$$\Gamma = \frac{q_x \gamma}{2\eta} + \frac{E}{\eta} \qquad (2)$$

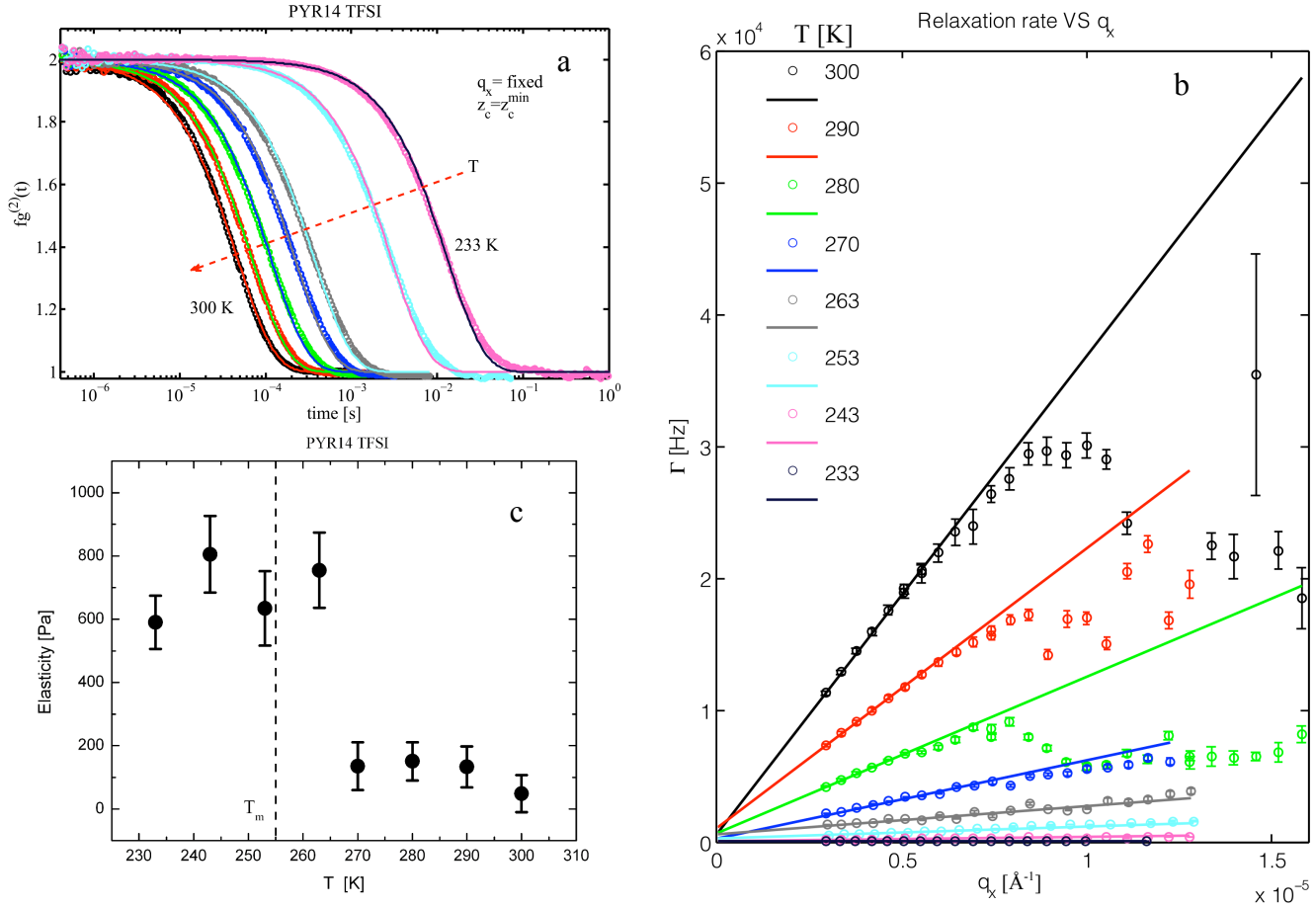

Figure 1: a. *Normalized intensity autocorrelation functions $g^{(2)}(q_x,t)$, obtained from GIXPCS on PYR_{14} TFSI for a fixed value of q_x, and for temperatures ranging from 233 K to 300 K. The data have been normalized to the intercept value. Lines are fit to Eq. (1).* **b.** *Relaxation rate $\Gamma(q_x)$ for the temperatures investigated. Lines are linear fits (on the first 9 q_x points) $\Gamma = Dq_x + C$.* **c.** *Elasticity for PYR_{14} TFSI as computed from Eq. (2). The melting point is indicated as a dashed line.*

where γ is the surface tension. In Fig. 1.c the elasticity extracted from the linear fits of the relaxation rate as a fucntion of temperature, according to Eq. (2), is reported. We find that on cooling elasticity sets in at a temperature T_E above T_m. Moreover, from Fig. 1.b we find that for $T>T_E$ a strong bending of the relaxation rate is observed at the highest accessed q_x values. Thus, the temperature T_E marks the onset of a new dynamical behavior. It has been proposed for molecular liquids that an elasticity $E \neq 0$ could be related to the occurrence of dynamical and structural heterogeneities, characterized by a slow relaxation rate, even several decades slower than the typical structural relaxation, which makes them appear as elastic clusters on the experimental time scales [1,2].

Moreover, the observed phenomenology, especially the onset of elasticity in PYR_{14}TFSI at a well defined temperature, may be related to the ionic nature of this system. In perspective, a focused GIXPCS investigation on selected ILs, in the neat liquid and supercooled regimes, would provide confirmation of the present results as well as a more thorough understanding of the underlying dynamical phenomena.

References

[1] E. W. Fischer *et al., J. Non-Cryst. Solids* **307-310**, 584 (2002).

[2] Y. Chushkin, C. Caronna and A. Madsen, *Europhys. Lett.* **83**, 36001 (2008).