	Experiment title: Collective dynamics and structural heterogeneity in ionic liquids	**Experiment number**: HD 598
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Report:

The aim of the experiment was to investigate the collective dynamics in the mesoscopic region of prototype ionic liquids which show structural nanoscale heterogeneity (in both glassy and undercooled state), as assessed by Small Angle X-ray Scattering esperiments [1] and Molecular Dynamics simulations [2]. The obtained data are preliminary measurements as a reduced allocation time has been assigned to check the feasibility of the experiment at low momentum transfer (Q).

Inelastic X-ray Scattering (IXS) data from 1-octyl-3-methylimidazolium chloride ([C8MIM]Cl) were collected in the momentum transfer (Q) range [1-15] nm^{-1} with a Q-step of about 0.4 nm^{-1}. The experiment was performed at 23.725 KeV, using the silicon (12,12,12) reflection providing an overall energy resolution of about 1.4 meV (FWHM) wich was determined from a plexiglass slab at T=10 K. The Q-resolution was set to 0.18 nm^{-1} for the first Q points (i.e. 1.0 nm^{-1}, 1.4 nm^{-1}, 1.8 nm^{-1}) and fixed to 0.37 nm^{-1} for the remaining Q's. The energy spectra were collected in the -30 to 30 meV energy (E) range. The sample cell was an Al tube of 5 mm lenght capped with two oriented monocrystal diamond windows (0.5-mm thick). The [C8MIM]Cl sample was loaded in the sample cell in an Ar-filled glove box to avoid water contamination. A cryostat was used to cool the sample to T=176.4 K, down to the glassy state (T_g = 214 K). The background contribution from the sample environment was measured in the same experimental configuration as the sample and subtracted from the data after normalization for the [C8MIM]Cl X-ray absorption coefficient.

Fig. 1 shows a series of IXS spectra for selected Q-values. High quality data were obtained for all measured wavevectors. At least one well-resolved inelastic feature, related to a longitudinal acoustic (LA) collective mode, is detectable in all the spectra, except for Q = 2.6 nm^{-1}, 3.0 nm^{-1} and 3.3 nm^{-1}, falling near the low-wavevector diffraction peak of the static strcture factor S(Q) (Q_{IRO} = 2.8 nm^{-1}) which is related to nanoscale segregation of the cations alkyl chains. In this latter case the inelastic contribution is indeed hidden by a very strong elastic signal. The experimental data I(Q,E) have been analyzed by modeling the dynamic strcture factor S(Q,E) with a sum of a delta function for the elastic component and a damped harmonic oscillator (DHO) function for the inelastic component. As shown in Fig. 1 the model describes the measured spectra at low-Q very well, whereas some discrepancies can be observed in the high-Q spectra. The Q-dependence of the characteristic energy, Ω, and broadening, Γ, of the LA mode are reported in Fig.2, togheter with the measured S(Q). Two main results can be inferred by an inspection of the collected data: (i) a kink in the Q-dispersion of Ω is observed for Q around 4 nm^{-1} (i.e. $Q > Q_{IRO}$); (ii) at the same Q the Q-dependence of Γ turns from a Q^4 into a Q^2 behavior. These findings can be associated to the heterogeneous structure of the ionic liquid at the nanometric scale, originating from a segregation of the alkyl chains (leading to non-polar domains) coexisting with polar domains generated by the imidazolium ring togheter with the anions. In particular, depending on the details of the microstructure, such as the

concentration of domains of a given phase, the kink in the LA wave dispersion can convert into a splitting [3-5]. Considering the poor agreement between data and best fit curve for $Q > 4$ nm^{-1} (see Fig.1 and Fig.3), we added to the previously described model function a DHO function to take into account the possible appearance of an extra LA mode (see Fig. 3).
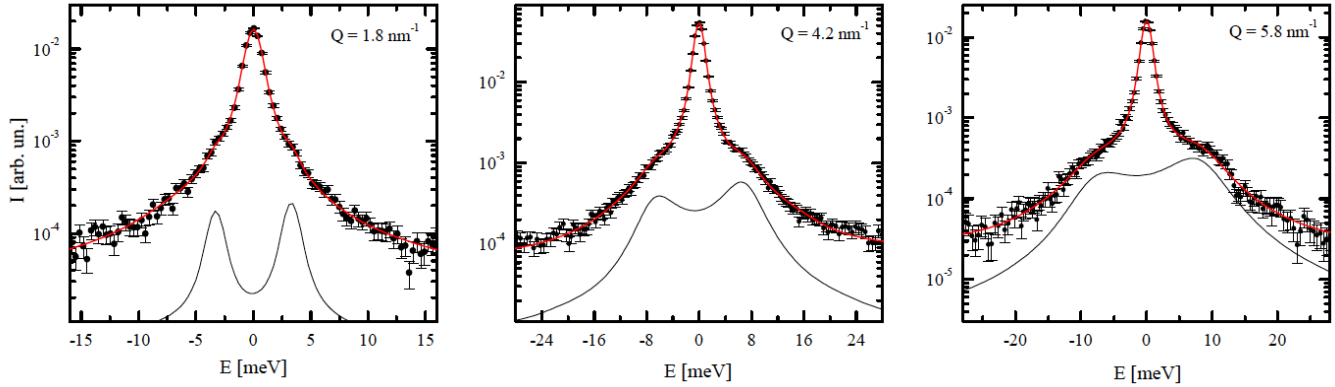

Fig. 1 IXS spectra of [C8MIM]Cl glass at T= 176.4 K and for selected Q-values (black circles) togheter with the best fitting curve of the model accounting of one only inelastic excitation (full red line). The inelastic component of the fitting model (DHO function) is also reported (full black line).
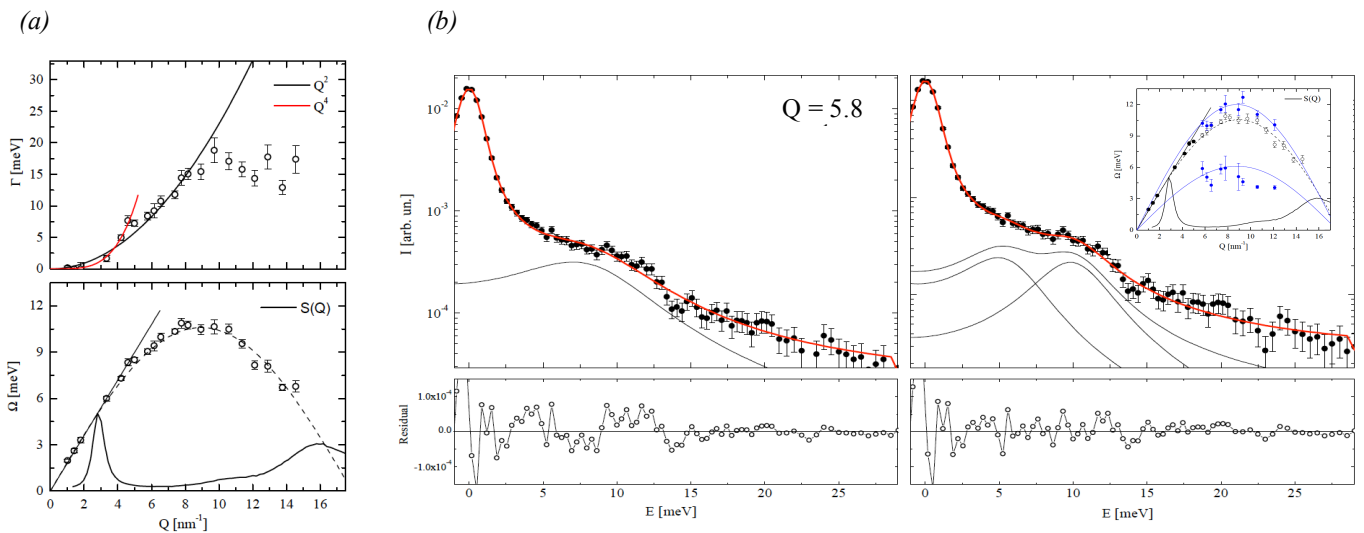

Fig. 2a (*Lower panel*) Q-dependence of the characteristic energy (Ω) of the inelastic excitation derived by the present IXS data accounting for one only inelastic component of the model fit function (open black circles). A kink in the dispersion is observed for Q around 4 nm^{-1}. The full black line is a linear interpolation of the low-Q points. The dashed black line describes the crystal-like bending of the acoustic dispersion curve on approaching the main diffraction peak. The measured S(Q) is reported for comparison. The first diffraction peak at $Q_{IRO} = 2.8$ nm^{-1} is observed. The main diffraction peak is around 16 nm^{-1}. (*Upper panel*) Q dependence of the broodening (Γ) of the inelastic excitation (open black circles).The full red and black line represent respetively Q^4 and Q^2 law fitting of the low and high Q trend of the experimental data.

Fig. 2b Portion of a representative high-wavevector IXS spectrum for a fixed Q. Experimental data (black circles), best fit curve (full red line) and inelastic contribution (full black line) for a model fit function including one only excitation (one DHO function) (*left panel*) and two excitations (sum of two DHO functions) (*right panel*). In the bottom panels the fit residuals (open black circles) are reported for both model functions. (*Inset*) Q-dispersion of the characteristic energies (Ω) of the low-Q single excitation (full black circle), the high-Q single excitation (reported also in Fig. 2) (open black circle) and of the two high-Q excitations (full blue circles).

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