Experimental report

19/08/2022

Proposal: **6-03-455** **Council:** 4/2020

Title: Fast and slow dynamics of ionic liquids and the effect of nano-scale structures

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Kira ELIASEN**

Experimental team: David NOIRAT

Local contacts: Markus APPEL

Samples: 1-ethyl-3-methylimadazolium tricyanomethanide
1-butylpyridinium tetrafluoroborate
1-methyl-3-propylimidazolium tetrafluoroborate

Instrument	Requested days	Allocated days	From	To
IN16B	2	2	14/06/2021	16/06/2021

Abstract:

The objective is to study the fast and slow dynamics in a series of ionic liquids (IL) by measuring the mean square displacement through elastic incoherent scattering. This is in order to test the relation between slow and fast dynamics by the so-called Shoving model and to see how the nano-scale structures formed by the cations in the IL affect this. The Shoving model is an elastic model that aims to connect fast and slow dynamics in liquids and to explain the non-Arrhenius slow down of the structural relaxation time when the liquid is cooled. Fast dynamics can be probed by neutrons on a short time scale, making it possible to test the Shoving model on IN16b. It has been tested before on simple, molecular liquids, showing a clear connection between fast and slow dynamics as predicted by the Shoving model. The question posed here is therefore: Is this also the case for complex IL with varying sizes of nano-scale structures? If yes, this could point towards universal behavior of supercooled liquids.
Three IL will be studied with different cation chain lengths thus varying the size and fraction of the nano-scale structures.

Experimental report

for proposal number 6-03-455, IN16B, date: 14-15th of June 2021

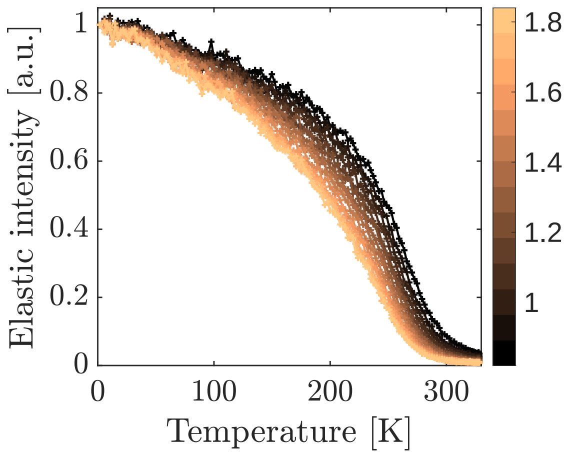
Background One of the today's major challenges in condensed matter physics is to develop a theory that encompasses the drastic viscous slow-down of supercooled liquids and the transition into the glassy state. This glass transition, which happens at T_g, is not a well defined phase transition, but rather a continuous transition from a liquid state to an amorphous solid-like state, where the molecules are "frozen" in place due to an extremely slow structural relaxation, the α-relaxation [1][2]. One of the questions of these supercooled, viscous liquids is that the temperature dependence of the α-relaxation time, τ_α, is not governed by an Arrhenius behavior, as one would expect if the dynamics of the system are dominated by overcoming potential energy barriers through thermodynamic fluctuations [3]. One model that aims to explain this non-Arrhenius behavior is the so-called Shoving model [4]. It is an elastic model that connects the slow and fast dynamics; slow dynamics from τ_α that can be explained by large potential energy barriers that the molecules must overcome in order to rearrange and fast dynamics from the fact that the transition from one energy state to another in itself is fast. The properties of these fast dynamics can be probed and determined by neutrons on a short time-scale which makes it possible to test the Shoving model at IN16b.

Aim of the experiment The aim of the experiment is to measure the mean square displacement (MSD) in a series of Ionic Liquids (IL) with Fixed Window Scans (FWS) in order to test the relation between slow and fast dynamics, to test the so-called Shoving model and how the fragility in the ionic liquids affect this. Both elastic and inelastic FWS will be measured.

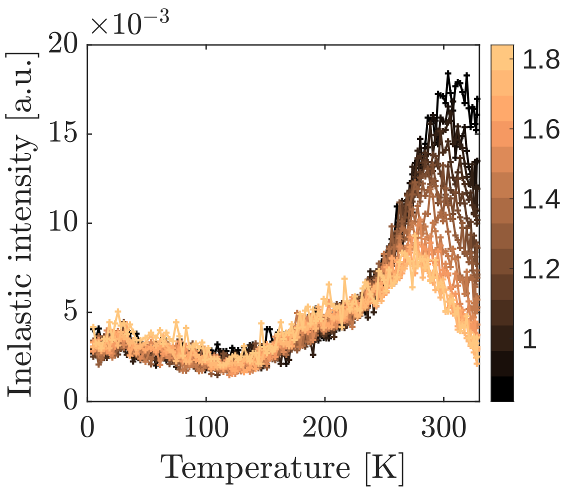
Results Three samples where measured; 1-propyl-3-methylimidazolium tetrafluoroborate (Pmim-BF4), 1-butylpyridinium tetrafluoroborate (Bpyr-BF4) and 1-ethyl-3-methylimidazolium tricyanomethanide (Emim-TCM) which range in fragility from 78 to 158. All three samples showed good promise in the preliminary calorimetry measurements, with no visible crystallization. However, two of the samples crystallized in this experiment leaving only liquid results from Pmim-BF4. The sample was measured from 2 K to 320 K with continuous heating and with the elastic and inelastic scans being performed alternately. Inelastic scans where performed at energy transferes of both $\Delta E = 3\mu$eV and $\Delta E = 6\mu$eV. Figure 1a shows the elastic intensity at all Q-values except for the first four. Data have been normalized to the lowest measured temperature where the scattering is purely elastic since all dynamics are frozen in.

Figure 1b and figure 1c show the inelastic FWS at $\Delta E = 3\mu$eV and $\Delta E = 6\mu$eV respectively. Both dataset have also been normalized to the elastic intensity at the lowest measured temperature.

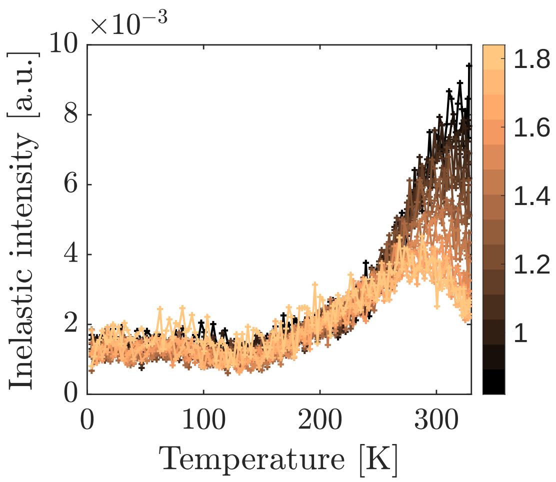
References **[1]** C. A. Angell, Science, **267**, 5206 (1995). **[2]** P. G. Debenedetti *et al.*, Nature, **410**, 6825 (2001). **[3]** J. C. Dyre, Rev. Mod. Phys., **78** (2001). **[4]** J. C. Dyre *et al.*, Phys. Rev. B, **5** (1996).



(a)



(b)



(c)

Figure 1: Results for the elastic (a) and inelastic FWS at $\Delta E = 3\mu$eV (b) and $\Delta E = 6\mu$eV (c) for each Q-value (0.8-1.8 Å^{-1}).