Experimental report

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Proposal: **6-02-558** **Council:** 10/2014

Title: Dynamics of an ionic liquid confined in nanoporous carbon substrates

Research area: Physics

This proposal is a new proposal

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Samples: nanoporous carbon filled with ionic liquid 1-N-butylpyridinium bis- ((trifluoromethyl)sulfonyl)imide

Instrument	Requested days	Allocated days	From	To
IN16B	5	5	08/05/2015	13/05/2015

Abstract:

Nanoporous carbon powders with different pore diameters in the range from a few nanometers down to subnanometre sizes and filled with a room-temperature ionic liquid shall be analyzed with neutron backscattering to investigate the cation dynamics at different temperatures in this system of strong confinement. These proposed measurements are intended to complement our QENS study on the same system which will take place on the FOCUS beamline at PSI in December.

Experimental Report

Proposal 6-02-558

Dynamics of an ionic liquid confined in nanoporous carbon substrates

The molecular dynamics of the ionic liquid 1-N-butylpyridinium bis- ((trifluoromethyl)sulfonyl)imide ([BuPy][Tf2N]) confined in carbide-derived nanoporous carbon (CDC) samples of different pore sizes, as well as the bulk ionic liquid (IL) as a reference, have been investigated using elastic and inelastic fixed window scans at the neutron backscattering spectrometer IN16b. Furthermore quasi-elastic spectra have been acquired at selected temperatures.

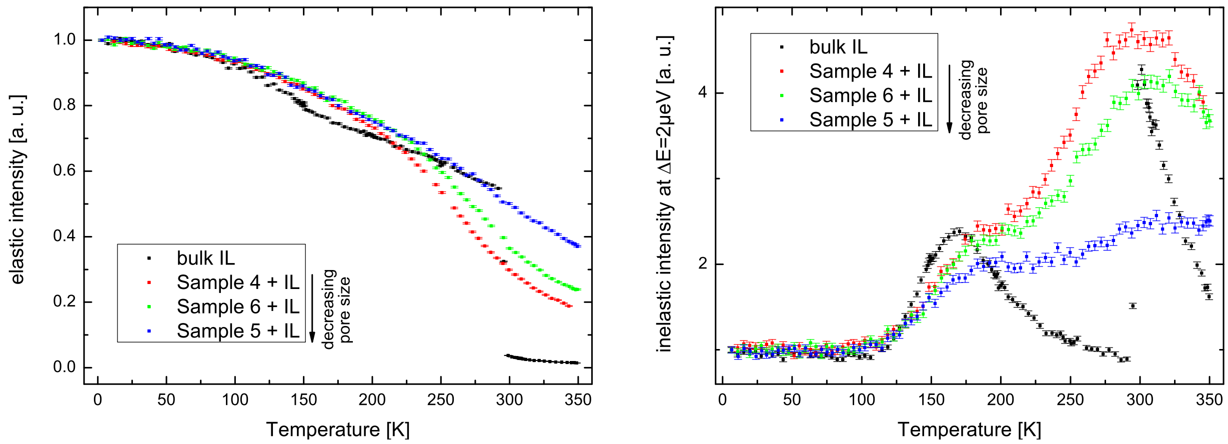

Figure 1: Elastic (*left*) and inelastic (*right*) fixed window scans of the bulk ionic liquid and several nanoporous carbon samples filled with the same ionic liquid in a temperature range from 2 K to 350 K.

The fixed window scans (FWS) have been done while continuously heating the respective sample from 2 K to 350 K. Thereby the elastic (EFWS) and inelastic fixed window scans (IFWS) have been performed alternately.

Figure 1 (*left*) shows the integrated intensity over the whole measured Q-range as a function of temperature for the bulk IL, as well as for the confined IL in CDC samples of three different pore sizes. All curves are normalized to the intensity at the lowest measured temperature where all dynamics are frozen in and the scattering is therefore purely elastic. This removes the effect of different amounts of IL in the different samples on the measured intensity and thus renders the curves directly comparable. While the melting of the IL is clearly visible for the bulk IL as a sudden drop in the elastic intensity at 296 K, i. e. a first order phase transition, this is not the case for the nanoconfined IL in CDC (Sample 4 - 6). In contrary the phase transition of the IL in the nanoporous carbon is continuously, while there is a clear pore size dependent effect: The decrease in elastic intensity is the steeper, the larger the pores are.

Similarly this pore size dependency of the IL phase transition can be observed in the IFWS. Figure 1 (*right*) depicts the intensity of inelastically scattered neutrons with an energy transfer of $\Delta E = 2\,\mu\text{eV}$. The curves are again scaled concerning the elastic intensity at low temperature. For the bulk IL two characteristic regimes are observable: Starting already at around 100 K there is an increase in the inelastic intensity in the 2 µeV channel and a second sudden intensity increase at around 296 K. While the latter is the consequence of the melting of the IL, like the sudden drop in the EFWS (see Fig. 1 (*left*)), the first rather continuous and less pronounced increase in intensity is originated by the activation of methyl group rotations [1], which leads also to a change of slope of the related EFWS (Fig. 1 (*left*)) in the corresponding temperature range. Also in the confined case the activation of methyl group rotations is visible in the IFWS at $\Delta E = 2\,\mu\text{eV}$, however the maximum of intensity in that energy channel is shifted to higher temperatures. Furthermore the signal overlaps with the solid-liquid phase transition of the IL which is now continuously distributed over a large temperature range.

Additional to the fixed window scans quasi-elastic spectra have been measured at certain temperatures, selected with the help of the fixed window scans. Figure 2 shows an example QENS-spectra of Sample 4 for $Q = 1.06\,\text{Å}$ at 310 K and 2 K. The latter is used as instrumental resolution in the further analysis.

As expected the diffusion of the ionic liquid confined in the nanoporous carbon is very slow compared to the bulk IL with a large amount of molecules being immobile.

The quasi-elastic spectra will be further analysed.

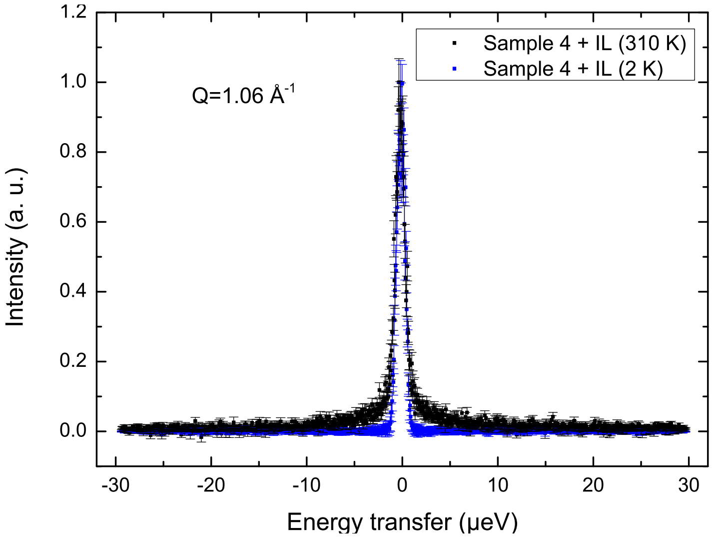

Figure 2: Example QENS-spectrum for $Q = 1.06\,\text{Å}$ for Sample 4 filled with the IL at 310 K (*black curve*) and 2 K (*blue curve*), respectively.

References

[1] Burankova, Tatsiana: *Dynamics and Structure of Ionic Liquids by Means of Neutron Scattering*, Universität des Saarlandes, Phd Thesis, 2014