Experimental report

29/04/2022

Proposal:	**6-05-1043**	**Council:**	4/2021
Title:	Crossover of collective dynamics from intermediate to intramolecular length scales: the role of inter-molecular interactions		
Research area:	Physics		

This proposal is a new proposal

Main proposer:	**Arantxa (Maria Aranzazu) ARBE**
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Samples:	deuterated poly(ethylene oxide) deuterated tetrahydrofuran protonated poly(ethylene oxide)

Instrument	Requested days	Allocated days	From	To
WASP	4	4	04/06/2021	08/06/2021

Abstract:

We want to investigate the behavior of collective dynamics at the mesoscale and the crossover toward intermolecular length scales in systems with different kinds of predominant inter-molecular interactions, e. g., van der Waals vs H-bonds, or under the constraints of intramolecular connectivity (polymers). Mainly due to the contamination of the low-Q signal by incoherent scattering, this is a challenging problem, even using fully deuterated samples. By means of PLET (the ToF instrument at ISIS with Polarization Analysis capabilities) we have isolated the collective dynamics of heavy water, and, more recently, of deuterated tetrahydrofuran and deuterated poly(ethylene oxide). For a complete characterization of the collective and self-motions in a wide length scales and temperature range, we want to combine those results with WASP experiments. WASP offers a huge Q-range (in particular, extending towards the mesoscale) and an exceptional resolution. These two state-of-the-art and complementary instruments shall shed light on this intriguing and still `white area¿ on the relaxation map of glass-forming systems.

Our aim was to investigate the behavior of collective dynamics at the mesoscale and the crossover toward intermolecular length scales in systems with different kinds of predominant inter-molecular interactions, e. g., van der Waals vs H-bonds, or under the constraints of intramolecular connectivity (polymers). Mainly due to the contamination of the low-Q signal by incoherent scattering, this is a challenging problem, even using fully deuterated samples. By means of PLET (the ToF instrument at ISIS with Polarization Analysis capabilities) we have isolated the collective dynamics of heavy water, and, more recently, of deuterated tetrahydrofuran (dTHF) and deuterated poly(ethylene oxide) (dPEO). For a complete characterization of the collective and self-motions in a wide length scales and temperature range, we want to combine those results with WASP experiments. WASP offers a huge Q-range (in particular, extending towards the mesoscale) and an exceptional resolution. These two state-of-the-art and complementary instruments shall shed light on this intriguing and still 'white area' on the relaxation map of glass-forming systems.

With these ideas in mind, we performed WASP experiments on THF and PEO. In both cases we studied fully deuterated and fully hydrogenated samples. WASP measurements on the latter allow to very accurately determine the diffusive component of the dynamics. For THF, we investigated 175K and for PEO, 350K. We started with THF, employing an incident wavelength of 4Å. The data were affected by Aluminum Bragg peaks; therefore we switched to 5Å and repeated the measurements with this wavelength for the case of dTHF. This wavelength was also used to investigate PEO, for which we complemented the experiment using in addition 7Å.

Figure 1 shows some representative results obtained on THF. Since NSE measures a combination of coherent and incoherent signals (normalized $I_{coh}(Q,t)-I_{inc}(Q,t)/3$ function), negative values are obtained for dTHF in the low Q-region (see Fig. 1(a)). There, the coherent contribution is very weak; in addition, the incoherent contribution, which is dominated by diffusion, has a very long characteristic time ($\tau \propto Q^{-2}$). The results on hTHF are dominated by the incoherent scattering, though some coherent contribution can also be noticed in the neighborhood of the structure factor peak (note some negative values of the signal around $1.5A^{-1}$). As can be seen in Fig. 1(b), the results on hTHF –which show a two-step decay in the NSE window-- can be well described in terms of the model previously proposed for water [1,2]. This model assumes a vibrational and a relaxational contribution, the latter resulting from the convolution of diffusion and a Q-independent mode (called Q^o-mode). From the fit of the model to WASP-hTHF results we obtained the values of the diffusion coefficient, the amplitude of the vibrational contribution (1-C), the relative amplitude of the diffusive part to the relaxational contribution (A) (A and C shown in Fig. 2) and the characteristic time of the Q-independent mode (7ps).

The model also was applied to the dTHF results obtained on both, WASP and PLET instruments. Considering as input the incoherent contribution as deduced from hTHF analysis, the description of the NSE results is very good, as can be seen in Fig. 1(a). In Fig. 3(a) and (b) the values of the coherent characteristic times and relative amplitudes, respectively, are shown. We have represented in red the parameters corresponding to diffusion, in green to the Q-independent mode affected by diffusion and in blue to the vibrational contribution. Empty symbols correspond to WASP analysis, filled symbols to PLET analysis. They agree very well, taking into account the worse Q-resolution of the NSE data. This agreement provides support to the model applied.

The analysis of the PEO results is on going.

We also measured methanol at 200K –for which PLET data also exist-- and made some exploratory experiments on polybutadiene, for which MD-simulations are available.

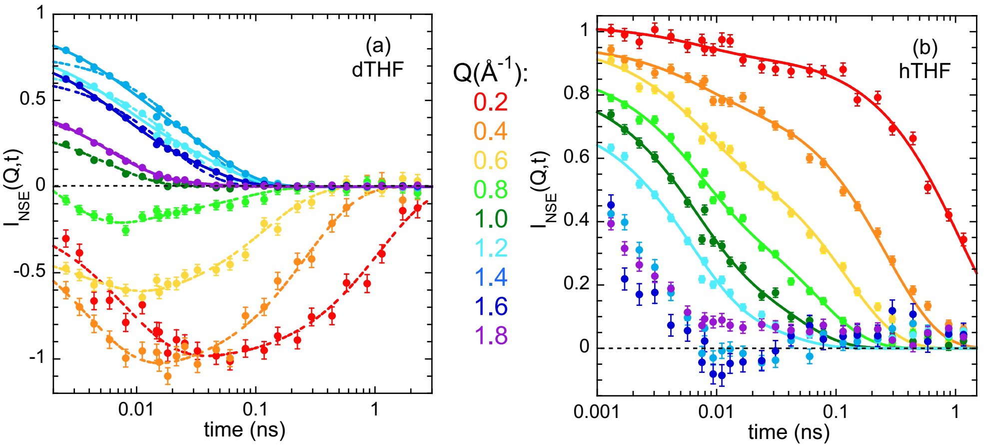

Figure 1: NSE results on dTHF (a) and hTHF (b) at 175K and the Q-values indicated. Solid lines are fits with the proposed model. Dotted lines in (a) are fits with an exponential function for the coherent contribution; for the Q<0.9A-1 data an incoherent contribution has been also considered, fixing it as that from the hTHF sample.

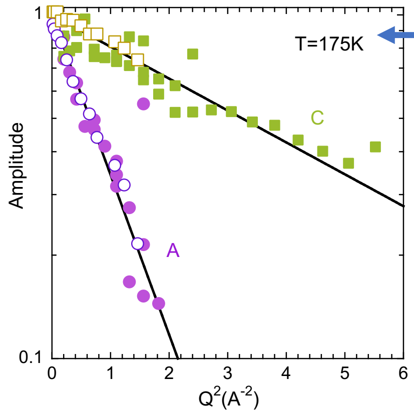

Figure 2: Amplitude of the diffusive part of the diffusive process (A) (circles) and amplitude parameter C (squares), for hTHF at 175K. Empty symbols correspond to PLET and solid symbols to WASP.

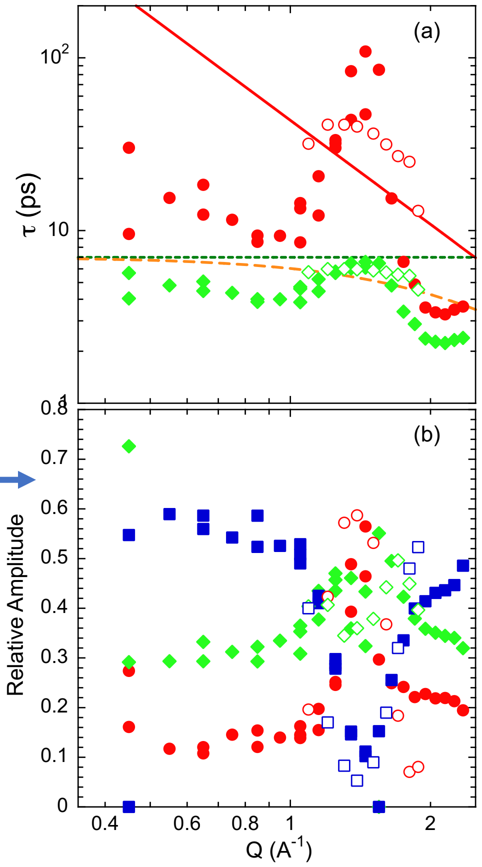

Figure 3: Collective characteristic times (a) and relative amplitude (b) obtained for dTHF at 175K (solid symbols: PLET; empty symbols: WASP) for the diffusive process (red), effective Q^{o}-mode (green) and vibrational contribution (blue). In (a), solid red line corresponds to $D^{-1}Q^{-2}$, where D is the diffusion coefficient deduced from hTHF WASP results; green line to the characteristic time of the Q^{o}-mode and dashed red line to the effective Q^{o}-mode for self-motions.

References:

[1] "Coherent Structural Relaxation of Water from Meso- to Inter-molecular Scales Measured Using Neutron Spectroscopy with Polarization Analysis" A. Arbe, G. J. Nilsen, J. R. Stewart, F. Alvarez, V. García-Sakai and J. Colmenero, Physical Review Research **2**, 022015 (2020)

[2] "Dielectric Susceptibility of Liquid Water: Microscopic Insights from Coherent and Incoherent Neutron Scattering", A. Arbe, P. Malo de Molina, F. Alvarez, B. Frick and J. Colmenero, Physical Review Letters **117**, 185501 (2016)