

Experimental report

02/05/2024

Proposal: DIR-269

Council: 10/2022

Title: COLLECTIVE DYNAMICS FROM MESOSCOPIC TO INTERMOLECULAR LENGTH SCALES IN SYSTEMS WITH DIFFERENT SPECIFIC INTERACTIONS

Research area: Physics

This proposal is a new proposal

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Samples: 2-ethyl-1-hexanol (2E1H)
deuterated 2-ethyl-1-hexanol (2E1H)
tributyl phosphate (TBP)
deuterated tributyl phosphate (TBP)

| Instrument | Requested days | Allocated days | From | To |
|------------|----------------|----------------|------------|------------|
| IN15 | 5 | 6 | 28/06/2023 | 04/07/2023 |
| WASP | 5 | 5 | 12/04/2023 | 17/04/2023 |

Abstract:

We want to fully characterize by neutron scattering the coherent scattering function of systems with different specific interactions from mesoscales to intermolecular length scales. A system with HBs leading to chain-like supramolecular aggregates and a highly polar liquid will be studied. We will scrutinize the relaxation of the emerging nano-structures, and check the universality of the Q-independent mode found in water and THF at mesoscales. The proposed experiments are really challenging. The huge Q-range we need to cover will be accessed by combining WASP and IN15. The combined analysis of results on fully deuterated and protonated samples will allow separating coherent and incoherent contributions in the Q-regions where the latter is not negligible in the deuterated ones. Direct comparison of the microscopic information obtained from the different correlators accessed by neutron scattering with that compiled from other spectroscopic methods (dielectric, mechanical) shall shed light on the puzzling situation currently present in the community when interpreting results from different macroscopic techniques.

COLLECTIVE AND SELF-DYNAMICS FROM MESOSCOPIC TO INTERMOLECULAR LENGTH SCALES IN SYSTEMS WITH DIFFERENT SPECIFIC INTERACTIONS

The NSE signal was measured by WASP and IN15 for protonated and fully deuterated tributylphosphate (TBP) and 2-ethyl-1-hexanol (2E1H). Cylindrical geometry was chosen for the samples. For the deuterated samples, the thickness between the walls of the container was 0.5mm, while for the protonated ones the thickness was 0.1mm.

In both instruments a wavelength of 6\AA was used, and, since the temperature range to be covered included low temperatures, the cryofurnace was used as sample environment, leading to a relatively high background in the particular case of the IN15 experiment. The resolution was measured on a TiZi sample. Empty cell contribution was subtracted from the samples' results.

On WASP, the Q -range $0.09 \leq Q \leq 1.56\text{\AA}^{-1}$ was accessed, and Fourier times $4.4\text{ ps} \leq t \leq 3.9\text{ ns}$. For all samples we explored the following temperatures: 140, 160, 180, 200, 215, 230, 250, 275 and 298K. In addition, 20K and 340K were measured for the 2E1H samples.

On the fully protonated samples, the scattered intensity is dominated by the incoherent contribution from the hydrogens. The NSE signal away from the partial structure factor peaks is also largely dominated by this contribution. Figure 1 shows the results on the protonated samples at 298K for different Q -values. Though they reflect a Q -dependence that indicates strong contributions from diffusion, their functional form cannot be described by a single exponential even at very low Q -values. This observation suggests additional contributions related with internal degrees of freedom.

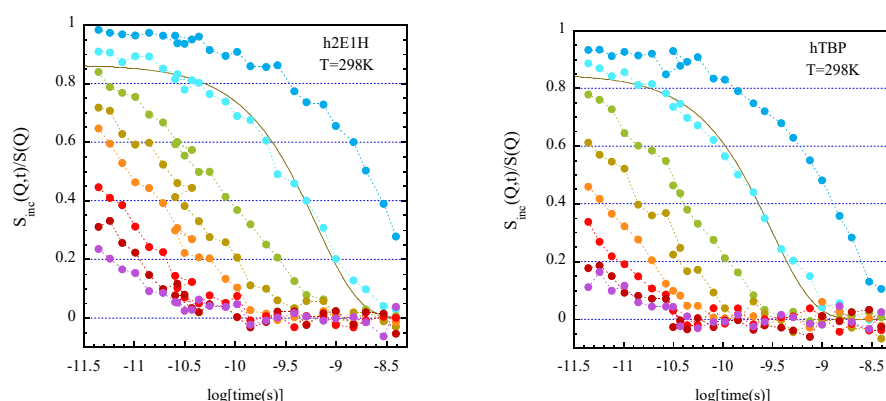


Figure 1: WASP results on the protonated samples at 298K and Q -values between 0.1 and 1.5\AA^{-1} (shown every 0.2\AA^{-1}). For 0.3\AA^{-1} , the brown lines show fits with single exponentials.

We expect to extract information about coherent scattering from the NSE results on the deuterated samples, where the incoherent contribution of hydrogens is strongly suppressed. Figure 2 shows the ratio between coherent and incoherent contributions to the scattering in the deuterated samples. In both samples, this ratio is very large close to the main structure factor peak (at around 1.3\AA^{-1}), but at low Q -values is small and close (or, at low temperatures, even lower) than 1. This implies that the dynamic measurements are difficult in this Q -regime: the intensity of the NSE signal is low, and it contains non-negligible contributions from incoherent scattering. We also see the emergence of a prepeak in the case of 2E1H at $Q \approx 0.5\text{\AA}^{-1}$, indicative for the presence of supramolecular aggregates in this sample. There, the conditions for the NSE measurements are more favourable than at lower Q -values, but isolating the coherent signal is still a delicate question.

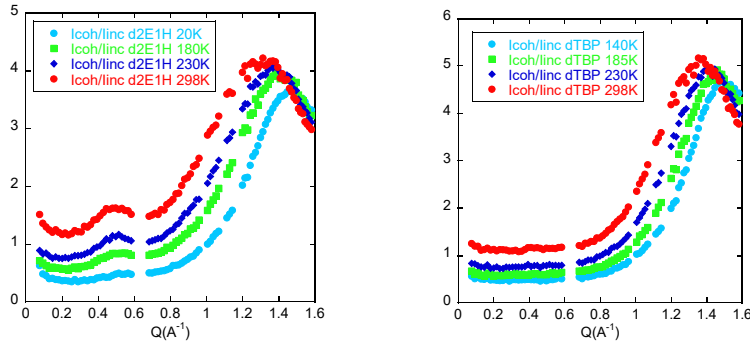


Figure 2: ratio between coherent and incoherent differential scattering cross sections determined by WASP on the fully deuterated samples: 2E1H sample (left) and TBP (right) at the different temperatures indicated

The strong influence of incoherent contributions to the NSE signal at low Q -values is evidenced in Figure 3 (left panel) for the case of deuterated TBP. The results become negative at long times, indicating the presence of a slow contribution which characteristic time is strongly Q -dependent (dominated by diffusion).

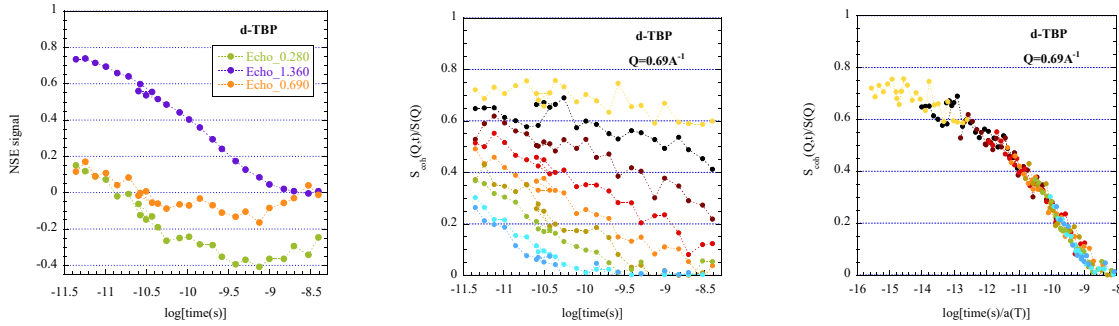


Figure 3: Left: WASP signal obtained on deuterated TBP at 230K and three Q -values, close to the structure factor peak and at lower Q -values, where $S(Q)$ is approximately flat (0.28 and 0.69 \AA^{-1} , see Figure 2). Middle: Normalized coherent scattering function obtained for this sample at $Q = 0.69 \text{ \AA}^{-1}$, applying the correction from incoherent scattering as measured on the protonated counterpart (see the text). Different colours correspond to different temperatures investigated in the range from 140K to 298K. Right: Master curve obtained from these results, by applying suitable shift factors to the time scale.

The dynamic contribution of incoherent scattering $I_{inc}(Q, t)$ to the NSE signal

$$\text{NSE} = \frac{I_{coh}(Q, t) - I_{inc}(Q, t)/3}{I_{coh}(Q, t \approx 0) - I_{inc}(Q, \approx 0)/3}$$

of the deuterated samples can in principle be corrected (i) taking into account that its relative weight can be obtained from the above presented polarization analysis results on the differential cross sections (Figure 2) and enters multiplied by $-1/3$ and (ii) assuming that it can be approximated by the NSE signal measured on the protonated counterpart [$I_{inc}^{deut}(Q, t) \approx I_{inc}^{hydro}(Q, t)$]. These corrections have been made, and Figure 3 (panel in the middle) shows the such obtained results for the dynamic structure factor of TBP at a Q -value of 0.69 \AA^{-1} . They do not show any hint of negative contributions anymore, supporting the procedure followed for the correction. From these results, the master curve shown in Figure 3 (right panel) has been obtained. The same corrections have been performed on the deuterated 2E1H results. The obtained coherent dynamic structure factor is shown in Figure 4 for three

representative Q-values: 0.21 \AA^{-1} (at the mesoscale), 0.49 \AA^{-1} (at the prepeak) and at 1.36 \AA^{-1} (at the main peak).

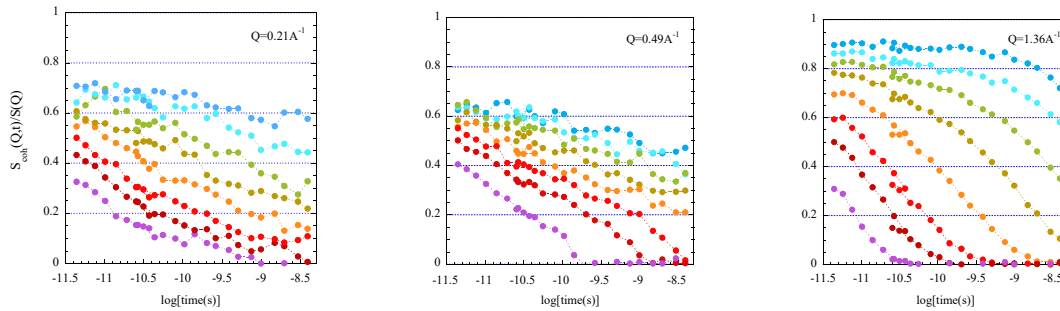


Figure 4: Normalized coherent scattering function obtained for the deuterated 2E1H sample at different temperatures investigated (from 180K to 340K) and the three values indicated. The data corresponding to 0.21 and 0.49 \AA^{-1} have been obtained by applying the correction from incoherent scattering as measured on the protonated counterpart (see the text).

These results show a significantly slower dynamics at the prepeak with respect to the main structure factor peak, as well as a more stretched functional form. This latter feature is also patent in the data corresponding to the mesoscopic scale.

We also made exploratory measurements by WASP on another polar system (propylene carbonate) and on the polyalcohol glycerol.

On IN15, the efforts were concentrated on the fully deuterated samples, in order to extend the information obtained on WASP toward lower Q-values with high resolution. Extremely careful measurements of the background were performed, which, as previously mentioned, was rather important in this case due to contributions arising from the use of the cryofurnace. We recall that this kind of measurements are really challenging, due to the very low intensity of the signal from deuterated samples in this Q-region, and its mixing with the incoherent contributions. We explored the values of Q: $0.1, 0.2, 0.4, 0.5$ and 0.6 \AA^{-1} . Unfortunately, due to the large error bars, the IN15 results did not add much information to that obtained on WASP on the same samples at the same conditions.