Experimental report

16/09/2024

Proposal: **6-02-658** **Council:** 4/2024

Title: Dynamics in systems with supramolecular structures of different topologies

Research area: Physics

This proposal is a continuation of 6-02-637

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Samples:
n-butanol
tert-butanol
n-butanol (deuterated hydroxyl group)
n-butanol (deuterated except hydroxyl group)
tert-butanol (deuterated except hydroxyl group)
tert-butanol (deuterated hydroxyl group)
n-butanol deuterated
tart-butanol (deuterated)

Instrument	Requested days	Allocated days	From	To
WASP	6	5	15/05/2024	20/05/2024
IN16B Si 111 BATS	3	2	04/06/2024	06/06/2024

Abstract:

In many liquids and glass-forming systems the presence of specific interactions, as e.g. hydrogen bonds (HBs), can lead to supramolecular organization with emergence of clusters. This is the case of many mono-alcohols (MAs), where HBs form `chain-like¿ and other kinds of supramolecular structures. To unravel the distinct processes contributing to the diverse observables (usually dielectric and mechanical spectroscopies are employed) and address the impact of aggregates morphology on the molecular dynamics demands for a concerted effort, where neutron scattering with selective deuteration plays a central role. With the present experiments we want to characterize the motions of the hydroxyl hydrogens involved in the HBs, and the motions of the rest of the hydrogens in the molecule, in two isomeric MAs (n-Butanol and tert-Butanol) giving rise to aggregates of very different morphology (chain versus ring-like).

EXPERIMENTAL REPORT

DYNAMICS IN SYSTEMS WITH SUPRAMOLECULAR STRUCTURES OF DIFFERENT TOPOLOGIES

PROPOSAL NUMBER: **6-02-658**

Specific interactions, as e.g. hydrogen bonds (HBs), can lead to supramolecular organisation with emergence of clusters, or even percolating networks. An example are many mono-alcohols (MAs), where HBs form ‘chain-like’ and other kinds of supramolecular structures.

n-Butanol (nB), considered as a ‘canonical’ MA forming chain-like supramolecular aggregates, has been used to prove the ‘transient chain’ model (Fig. 1(a)). An interesting question arising is how the relaxation of the aggregates and the HB dynamics behave in systems where the formed supramolecular aggregates have morphologies different from chain-like. This is the case of tert-butanol (tB), an isomer of n-butanol (see Fig. 1(b)).

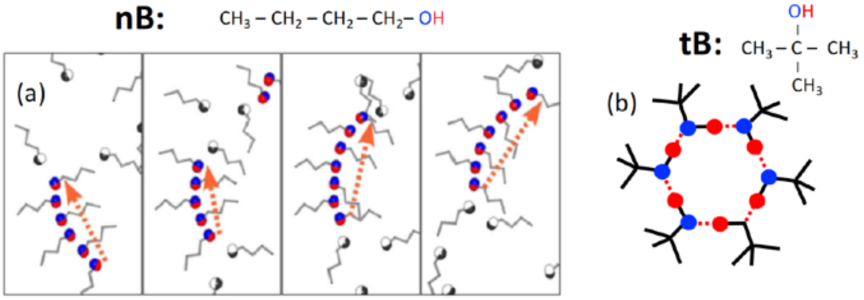

Fig. 1: (a) Schematic illustration of the transient chain model to visualize how molecules attach to the chain and detach from it. Mutually bonded OH groups are colored. The dotted arrows highlight the end-to-end vector of the self-restructuring, transient chain. For tB, the hexamer ring cluster is shown in (b).

In fact, it has been suggested that the morphology of the supramolecular aggregates can have an impact on the relationship between viscosity enhancement, size of the aggregates and dielectric strength of the Debye relaxation.

The purpose of the experiment was to characterize the motions of the hydroxyl hydrogens involved in the HBs, and the motions of the rest of the hydrogens in the molecule, in two isomeric MAs (nB and tB) giving rise to aggregates of very different morphology (chain versus ring-like).

With that objective in mind, we performed quasielastic neutron scattering experiments on IN16B (BATS option) and on IN5 (see experimental report 6-02-637), using samples with different isotopic substitutions, i.e. nB and tB with a protonated hydroxyl group and the rest of the molecule deuterated (DnB-OH and DtB-OH) with the aim of characterising the motions of the hydroxyl hydrogens involved in the HBs, and the opposite labelling (HnB-OD and HtB-OD) in order to investigate the dynamics of the hydrogens of the rest of the molecule, mainly driven by the α-relaxation. For completeness, we also planned to measure the fully protonated sample, allowing to check the consistency of the data analysis and interpretation.

The first experiment was performed on IN16B, and we could use the allocated time to measure only 3 samples (DtB-OH, DnB-OH and HnB-OD), together with the vanadium, empty can and empty cryo-furnace necessary to correct the raw data and obtain the dynamic structure factors, $S(Q,\omega)$. The BATS configuration of the instrument was employed, which provided us with a wide energy transfer range $\hbar\omega$= (-147, 187) μeV and a resolution of 1.5 μeV, as measured at the elastic peak position of a vanadium standard, of dimensions matching those of the sample.

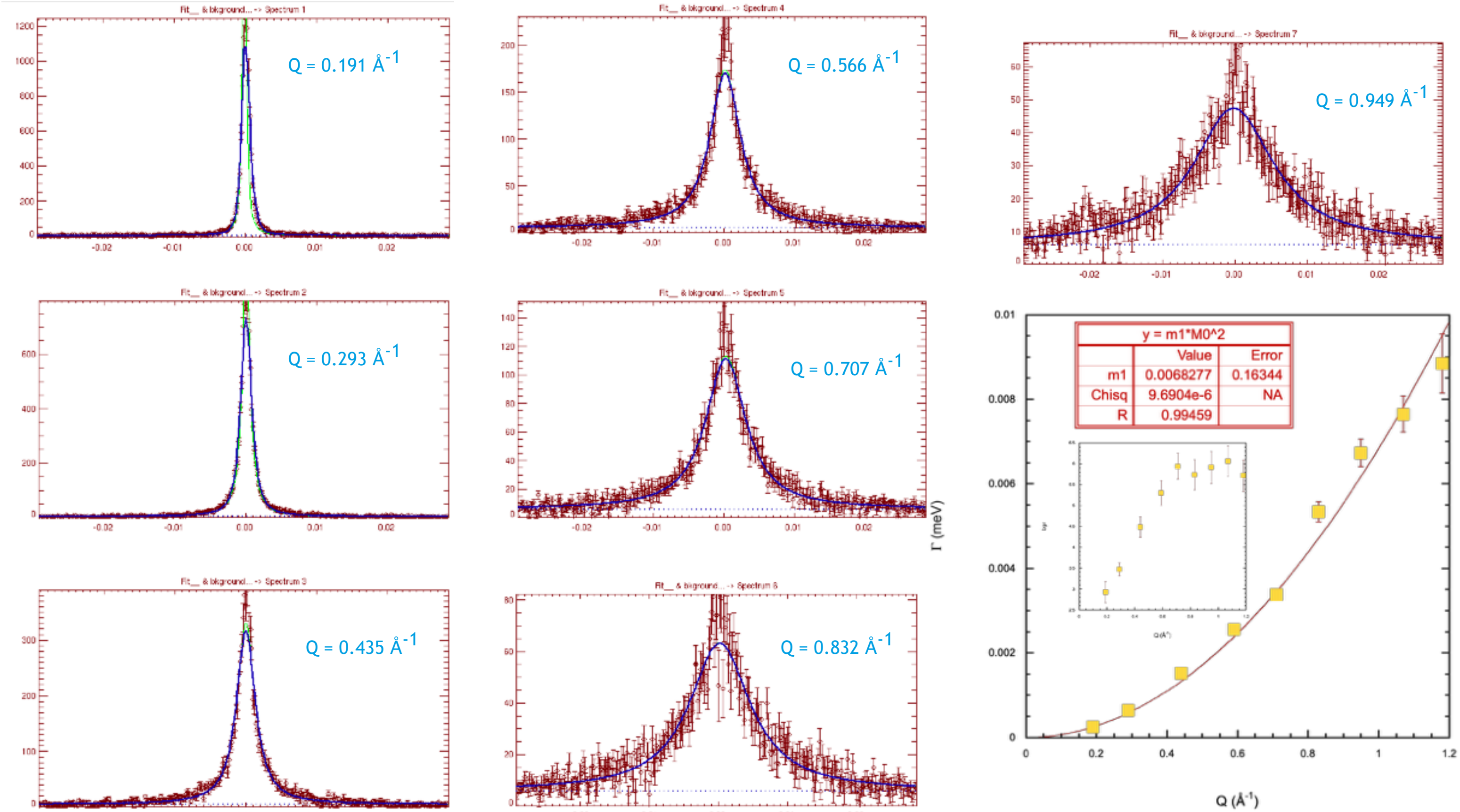

Fig. 2: Experimental corrected intensities for the fully hydrogenated n-butanol sample measured at 250 K. The solid line represents the fit to a single Lorentzian function convoluted with the experimental resolution. The wave vector value Q of each spectra is also displayed. On the right-hand side the linewidth dependence of the Loretzian function used to model the experimental data at first, as a function of Q, is depicted. Also, the wave vector dependence of the background term can be found on the inset of the mentioned plot.

Unfortunately, due to lack of time we could not measure the fully deuterated and hydrogenated samples of both isomers, and the tert-butanol with only the hydroxyl group deuterated (HtB-OD). For that reason we submitted a continuation proposal, whose outcome was favorable. A measuring time of 2 days was granted. However, the BATS option was not available. We performed therefore an experiment on IN16B using the high flux configuration and a Si(111) monochromator, selecting the wavelength of the incoming neutrons to λ = 6.271 Å. The energy transfer and energy resolution was ± 31 μeV and 0.8 μeV, respectively. This energy window is less favorable than that provided by the BATS configuration, especially for the high temperature measurements, where the motions of the molecules become too fast and the signal becomes flat above Q ~ 0.9 Å^{-1} already at 300 K. Since the tert-butanol isomer crystallises just below RT, only scans at slightly above this temperature could be done for H-tB, D-tB and H-tB-OD. The initially aimed higher temperature (T = 340 K) could not be measured with this instrument configuration. We could explore an extended T range for the n-butanol isomer. The investigated temperatures for each sample are summarised in table 1.

Sample	T (K)
H-tB	300
D-tB	300
H-tB-OD	300, 310
H-nB	2, 170, 190, 215, 250
D-nB	2, 170, 190, 215, 250

Aluminium hollow cylinders were used as sample containers and were filled under an argon atmosphere inside a glove bag. The volume (thickness) of the samples were calculated taking into account the scattering cross section of the individual components, σ_{scatt}, the density, ρ, and the molecular mass M, in order to have ~ 90% transmission of the incoming neutrons and avoid multiple scattering effects. With deuterated samples we used a sample thickness of 0.5 mm, being this value reduced to 0.05 mm when the hydrogenated samples were in the beam.

Some corrected experimental spectra can be seen in Fig. 2 for the fully hydrogenated n-butanol sample, collected at 250 K. As a first analysis step these spectra were modelled in terms of a single Lorentzian function convoluted with the Gaussian resolution. It can be seen, the experimental intensity is not fully described by this simple model. We have therefore added an additional component, a localised term, which is convoluted with the translational mode, resulting in the following expression:

$$S(Q,\omega) = \left[S^T(Q,\omega) \otimes S^L(Q,\omega) \otimes S^V(Q,\omega)\right] \otimes \mathfrak{R}(Q,\omega)$$

where S^T, S^L and S^V stand for the long-range translational diffusion, a localised contribution and vibrational processes, respectively, and $\mathfrak{R}(Q,\omega)$is the instrument resolution function.

The translational contribution can be described by a Lorentzian. The convolution of this component with the localised term, described with the following expression:

$$S^L(Q,\omega) = A_0(Q)\delta(\omega) + (1 - A_0(Q))\frac{1}{\pi}\mathscr{L}(Q,\omega)$$

gives rise to a second Lorenztian, whose half-width at half maximum (HWHM) is the sum of those two individual linewidths.

When this approach is used, both the elastic and qualiselastic intensities are better reproduced. The application of this model to the rest of the measured samples is ongoing.

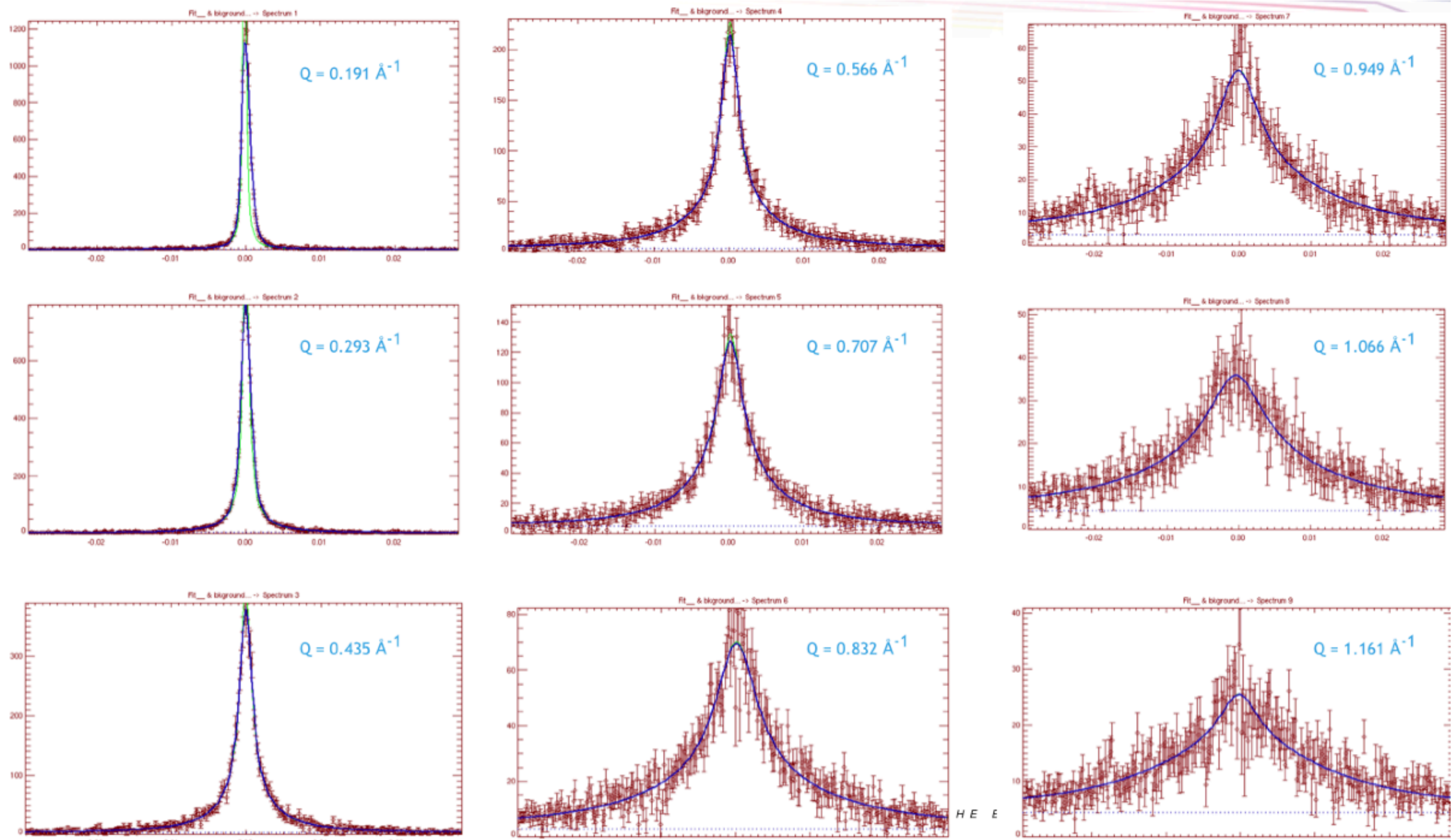

Fig. 3: Experimental corrected intensities for the fully hydrogenated n-butanol sample measured at 250 K and the fits using the convolution model described on the text.