Experimental report

25/01/2024

Proposal: **6-02-637** **Council:** 4/2023

Title: Dynamics in systems with supramolecular structures of different topologies

Research area: Physics

This proposal is a new proposal

Main proposer: **Maria Aranzazu ARBE MENDEZ**

Experimental team: Maria Dolores RUIZ MARTIN
Silvia ARRESE IGOR
Juan COLMENERO
Maria Aranzazu ARBE MENDEZ

Local contacts: Markus APPEL
Bela FARAGO

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

Instrument	Requested days	Allocated days	From	To
IN16B Si 111 BATS	4	2	28/06/2023	30/06/2023
IN5	2	1	25/09/2023	27/09/2023
WASP	6	0		

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: 6-02-637

The presence in many liquids and glass-forming systems of specific interactions, as e.g. hydrogen bonds (HBs), can lead to supramolecular organization with emergence of clusters, or even percolating networks. An example is the case of many mono-alcohols (MAs), where HBs form ‘chain-like’ and other kinds of supramolecular structures. A particularity of this kind of materials is the presence of a feature in the dielectric spectra, slower than the α-relaxation, called Debye process, which has been associated to the relaxation of the aforementioned “chain-like” aggregates. However, this process has later been found in HB systems with other aggregation behaviour, and even in absence of HBs. Furthermore, an additional rheological contribution in some MAs with characteristic time between the α-relaxation and the Debye process, which is believed to reflect the HB-exchange dynamics in the chain-like aggregates, has been identified. The presence of this component in the dielectric spectra is unclear.

n-butanol and tert-butanol are isomers that form different supramolecular aggregates. The former is considered as a “canonical” MA whose aggregation behaviour is known to be chain-like, whereas the latter form ring-like clusters. We have performed time-of-flight (TOF) and backscattering (BS) experiments with the aim of studying the microscopic origin of the complex macroscopically observed behaviour of MAs. With these experiments we wanted to characterize the motions of the hydroxyl hydrogens involved in the hydrogen bonds, and the motions of the rest of the hydrogens in the molecule, in these two isomeric alcohols. To follow the self-dynamics of the hydroxyl hydrogens, we measured the quasielastic spectra of samples with protonated hydroxyl groups and the rest of the molecule deuterated (DnB-OH and DtB-OH), while the opposite labelling (HnB-OD and HtB-OD) was required to investigate the dynamics of the hydrogens in the rest of the molecule, mainly driven by the α-relaxation. We also aimed at measuring the H-motions of the whole molecule on a fully protonated sample, allowing us to check the consistency of the data analysis and interpretation.

Two neutron scattering experiments were performed, one on IN5 and another on IN16B with the BATS configuration, in order to fully describe the expected scattering functions $S(Q,\omega)$. The experiment on IN5 was performed with an incident wave length set to $\lambda = 6$ Å ($E_i = 2.27$ meV) which yielded an energy resolution of ~ 45μeV (FWHM). We could measure the 6 samples as proposed, the fully hydrogenated and the partially deuterated isomers, n- and tert-butanol, together with the resolution using a vanadium standard and the empty container, to subtract the background from the measured intensity.

We had 4 days on BATS, where we could unfortunately measure only 3 samples: one partially deuterated tert-butanol (DtB-OH) and two partially deuterated n-butanols (DnB-OH and HnB-OD). We could not measure the fully hydrogenated samples due to lack of time, which has prevented us to rigorously analyse the IN5 data.

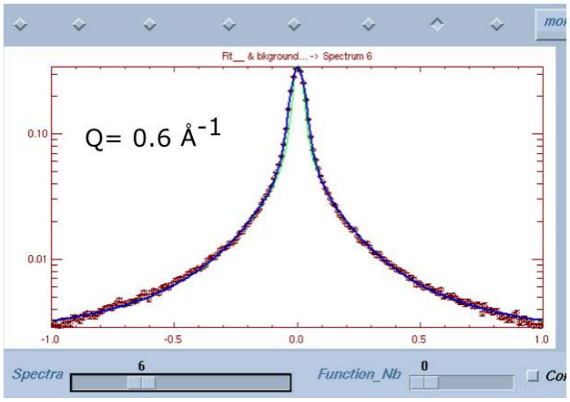
The IN5 experimental spectra were analysed in terms of a convolution model given by:

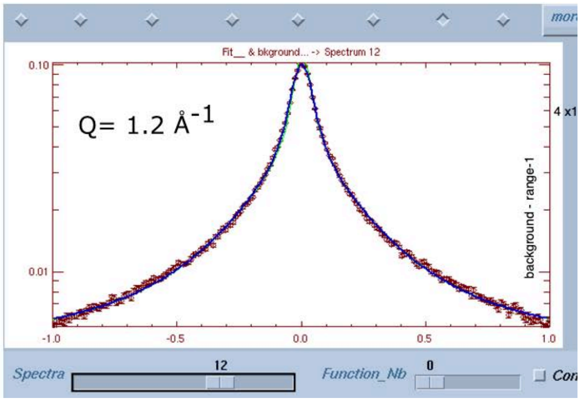
$S(Q,\omega) = [S^{T}(Q,\omega) \otimes S^{L}(Q,\omega) \otimes S^{V}(Q,\omega)] \otimes R(Q,\omega)$, where S^T, S^L and S^v stands for the long-range translational diffusion, a localised contribution and vibrational processes, respectively. As one can see in the formula below, the translational contribution can be described by a Lorentzian (P5'= HWHM), convoluted with the localised contribution $S^L(Q,\omega) = A_0(Q)\delta(\omega) + (1 - A_0(Q))\frac{1}{\pi}\mathcal{L}(Q,\omega)$, giving rise to a second Lorenztian, whose HWHM is the sum of those two individual processes.

$$Y = P_1' \cdot e^{-P_3' Q^2/3} \cdot \left[P_4' \cdot \frac{1}{\pi} \cdot \frac{P_5'}{(\omega - P_2')^2 + P_5'^2} + (1 - P_4') \cdot \frac{1}{\pi} \cdot \frac{P_5' + P_6'}{(\omega - P_2')^2 + (P_5' + P_6')^2} \right] + P_1 \cdot P_4 \cdot \frac{P_3 \cdot P_2^2}{(\omega^2 - P_2^2)^2 + (\omega + P_3^2)}$$

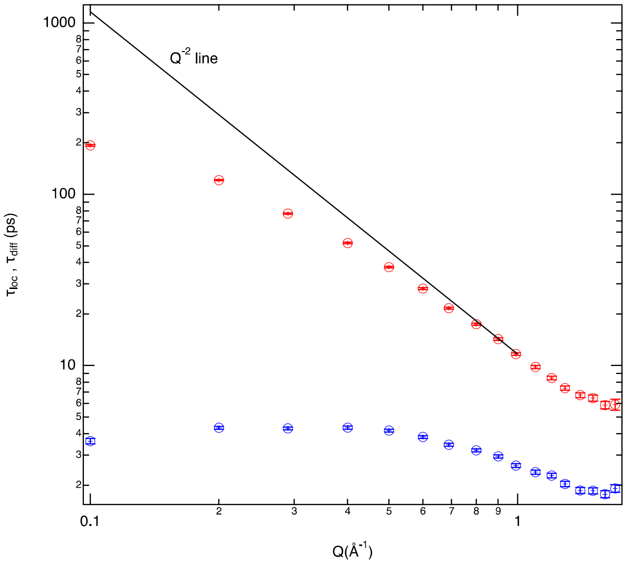
At first, we tried to fit the experimental data in the quasielastic region taking into account only these two processes but the model failed and we probed the necessity of including a vibrational contribution in terms of a damped harmonic oscillator, being P2 and P3 in the equation above the frequency and width of the resonance, respectively.

The overall agreement between the calculated and observed spectra is fairly good for the studied Q-range (see figure below), but by inspecting the wave vector dependence of the parameters describing the translational component, we observe that the resolution of the spectrometer is not sufficient, especially at low Q values.





The expected Q^{-2} dependence of the characteristic time is not fulfilled at low Q values: one can see a much faster process than the one expected which can only be an instrument artifact due to limited resolution. Note that the measured linewidths for $Q < 0.4$ Å^{-1} are smaller than 5 μeV, which is approximately 10% of the instrument resolution.


Q^{-2} line
τ_{loc} , τ_{diff} (ps)
1000
8
7
6
5
4
3
2
100
8
7
6
5
4
3
2
10
8
7
6
5
4
3
2
0.1
2
3
4
5
6
7
8
9
1
Q(Å^{-1})