Experimental report

22/04/2025

Proposal: **6-02-662**

Council: 4/2024

Title: Unravelling local and collective dynamics associated with hydrogen bonding network in the liquid state of propanol-glycerol mixtures

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Anand kumar TIWARI**

Experimental team:

Local contacts: Markus APPEL
Bela FARAGO

Samples: 1-propanol-(20%) glycerol mixture
Deuterated 1-propanol (OD)-(50%) glycerol (D8) mixture
Deuterated 1-propanol (OD)-(20%) glycerol (D8) mixture
1-propanol-(50%) glycerol mixture

Instrument	Requested days	Allocated days	From	To
WASP	5	4	27/05/2024	31/05/2024
IN16B	3	0		

Abstract:

Mono-alcohols have been studied using a variety of methods for a very long time, and they have demonstrated a strong Debye and alpha relaxation. Here we aim to investigate the dynamics of the H-bond in propanol-glycerol mixtures. We deuterate the sample in order to study the dynamics of the carbon backbone vs. hydrogen bond network since neutrons have a contrast in the density of their scattering lengths for different elements. By creating two different types of samples, one with deuterated combination (propanol-glycerol), and the other entirely protonated, separation can be accomplished. The ultimate goal is to separate coherent and incoherent QENS signals from overall scattering to better comprehend observed relaxation processes. As recently Arbe et al. have measured coherent and incoherent dynamic structure factors of heavy water with sub-meV resolution. We wish to apply a similar tactic in the case of propanol and propanol-glycerol mixtures. In present case, we want to focus on slower dynamics up to several nanoseconds with IN16B and WASP, whereas polarization spectroscopy is possible for fast dynamics with contemporary spectrometers like LET.

Unravelling local and collective dynamics associated with hydrogen bonding network in the liquid state of propanol-glycerol mixtures

Anand Kumar Tiwari[1,2], Markus Appel[1], Bela Farago[1], Kristine Niss[2]

[1]Institut Max von Laue - Paul Langevin (ILL), France

[2]Department of Science and Environment (INM), Roskilde University, Denmark

Monohydroxy alcohols, such as 1-propanol, have been extensively studied due to their distinct relaxation dynamics, which are strongly influenced by hydrogen bonding. Dielectric spectroscopy and depolarized dynamic light scattering have revealed that these systems exhibit a pronounced Debye-type relaxation process, which is significantly slower than the structural α-relaxation. The Debye relaxation is commonly attributed to the cooperative dynamics of hydrogen-bonded supramolecular structures that form transiently in the liquid state, whereas the α-relaxation corresponds to the structural rearrangement of the molecular matrix. The clear separation between these two relaxation processes in monohydroxy alcohols provides a unique opportunity to investigate the role of hydrogen bonds in dynamic processes. In contrast, polyalcohols, such as glycerol, exhibit considerably more complex relaxation behavior due to the presence of multiple hydroxyl groups, which lead to an intricate hydrogen-bonding network. Dielectric spectroscopy studies have identified multiple relaxation processes in these systems; however, unlike monohydroxy alcohols, these processes are not as distinctly separated. Instead, the various relaxation modes in polyalcohols tend to overlap, making it challenging to isolate individual contributions. This merging of relaxation modes suggests a more interconnected hydrogen-bonding network, where different dynamic processes become intertwined.

In this study, we use spin-echo neutron spectroscopy to investigate how the dynamics of hydrogen bonds evolve with increasing hydrogen bond concentration and how they change with temperature in liquid alcohols above the glass transition. A central question driving this experiment is to determine the extent to which the dynamics of the hydrogen-bonding network are coupled to the primary structural relaxation of the liquid. Additionally, we aim to establish connections between the different dynamic contributions observed using various experimental techniques, including dielectric spectroscopy and neutron backscattering. By probing these interrelations, we seek to advance our understanding of the molecular mechanisms governing hydrogen-bond dynamics in alcohols and their impact on macroscopic relaxation behavior. This study was conducted under proposal number **6-02-662**, focused on temperature-dependent measurements on WASP for four different systems:

a) 1-propanol-(20%) glycerol mixture: [330, 300, 270, 250, 220, 200, 180, 150]K
b) 1-propanol (OD)-(20%) glycerol (D_8) mixture: [330, 250, 220, 200, 180, 150, 130, 10]K
c) 1-propanol-(50%) glycerol mixture: [330, 300, 270, 250, 220, 200, 180, 150]K
d) 1-propanol (OD)-(50%) glycerol (D_8) mixture: [330, 300, 270, 250, 220, 200, 180, 150]K

In this experiment, wide-angle neutron spin-echo (NSE) measurements were performed using the high-intensity WASP spectrometer to investigate the microscopic dynamics of hydrogen-bonded liquids. The measurements were conducted with an incident neutron wavelength of $\lambda = 6$ Å, providing an optimal balance between resolution and intensity. Precise temperature control was maintained using an orange cryostat, ensuring a stable and well-defined thermal environment throughout the experiment. The sample geometry was carefully optimized for neutron scattering efficiency. Cylindrical sample cells were used, with a thickness of 0.2 mm for deuterated samples and 0.1 mm for protonated samples. This design helped optimize the scattering conditions while minimizing multiple scattering effects. The accessible momentum transfer range covered $0.12 \leq Q \leq 1.36$ Å^{-1}, enabling the study of dynamic processes over a broad range of length scales. The Fourier time window spanned from 4.4 ps to 7.8 ns, allowing both fast and slow relaxation processes to be captured. Each temperature point was measured for approximately 2.5 hours to ensure sufficient statistical accuracy. All neutron scattering data were carefully corrected for background contributions, including instrument noise and empty cell scattering. Data reduction and analysis were carried out using specialized software developed at ILL. No signs of crystallization were detected throughout the measurements, confirming that the sample remained in a stable liquid or supercooled state during the entire experimental run.

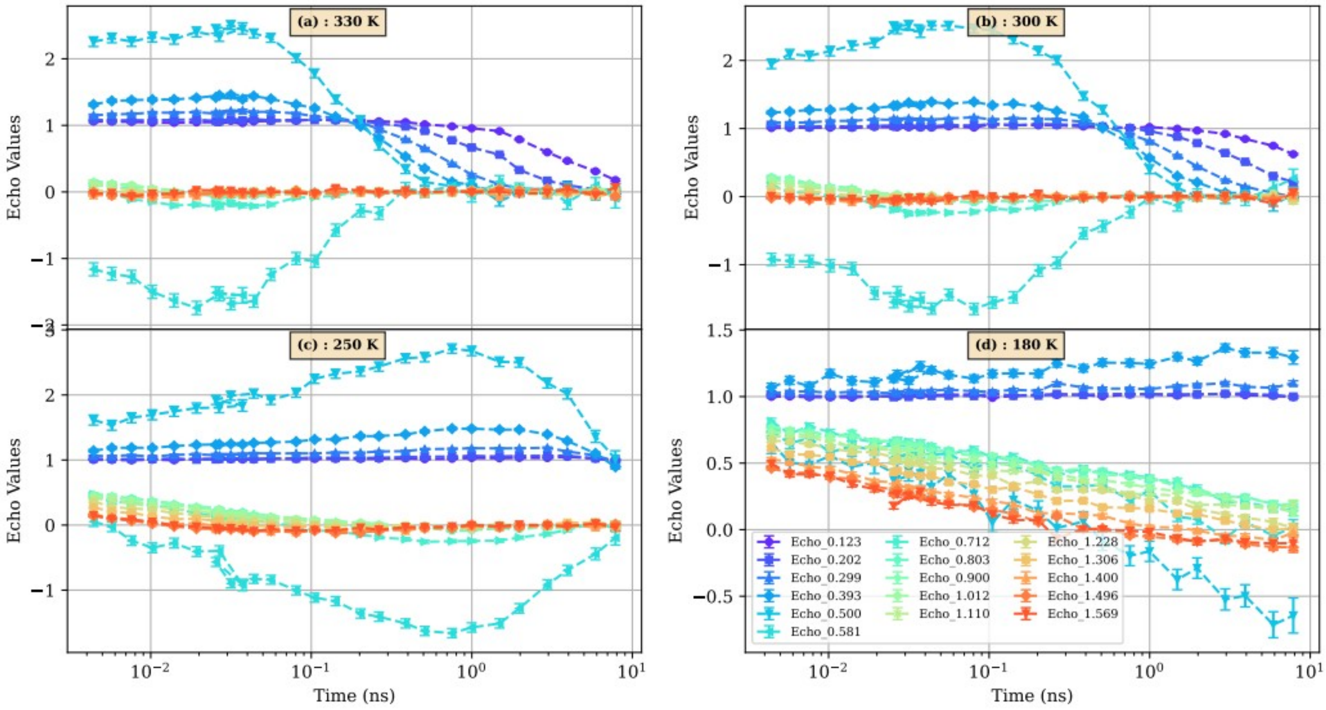
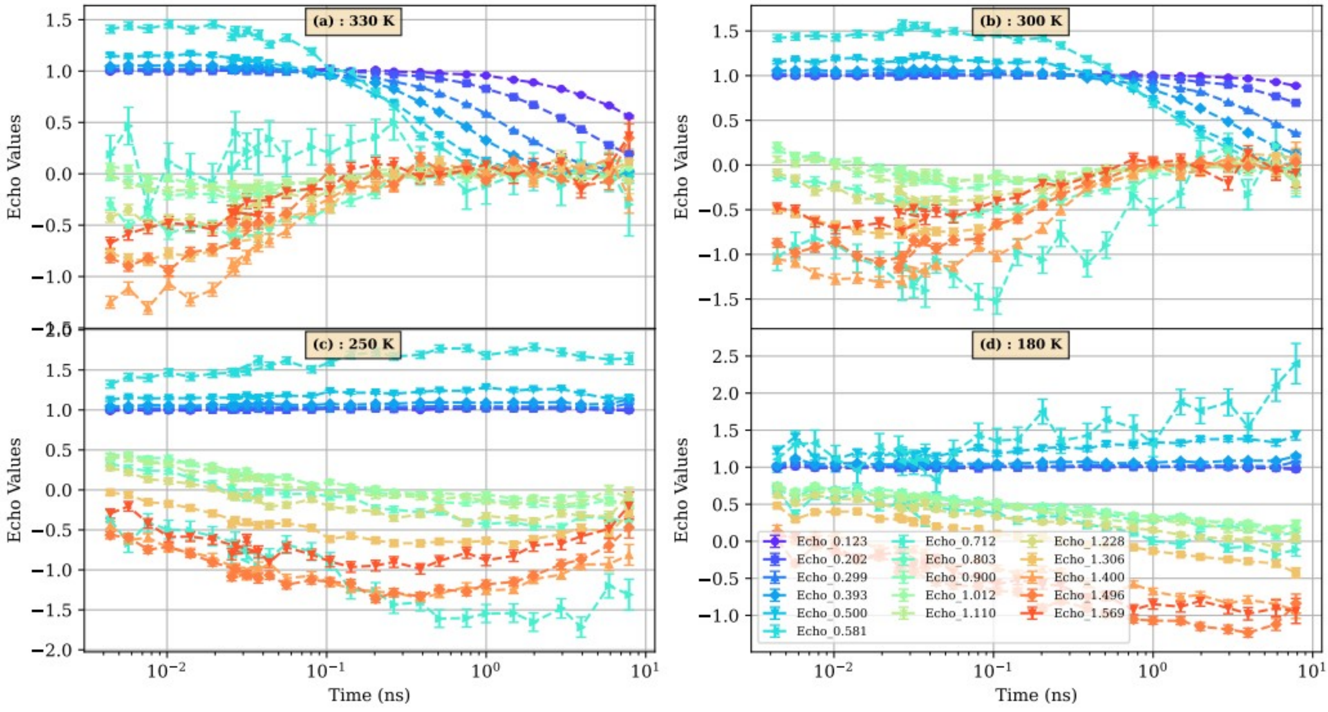


Figure 1: *NSE spectrum for Deuterated 1-propanol(OD)-(20%) glycerol(D_8) mixture at temperatures [330,300,250,180]K with λ=6 Å neutrons.*



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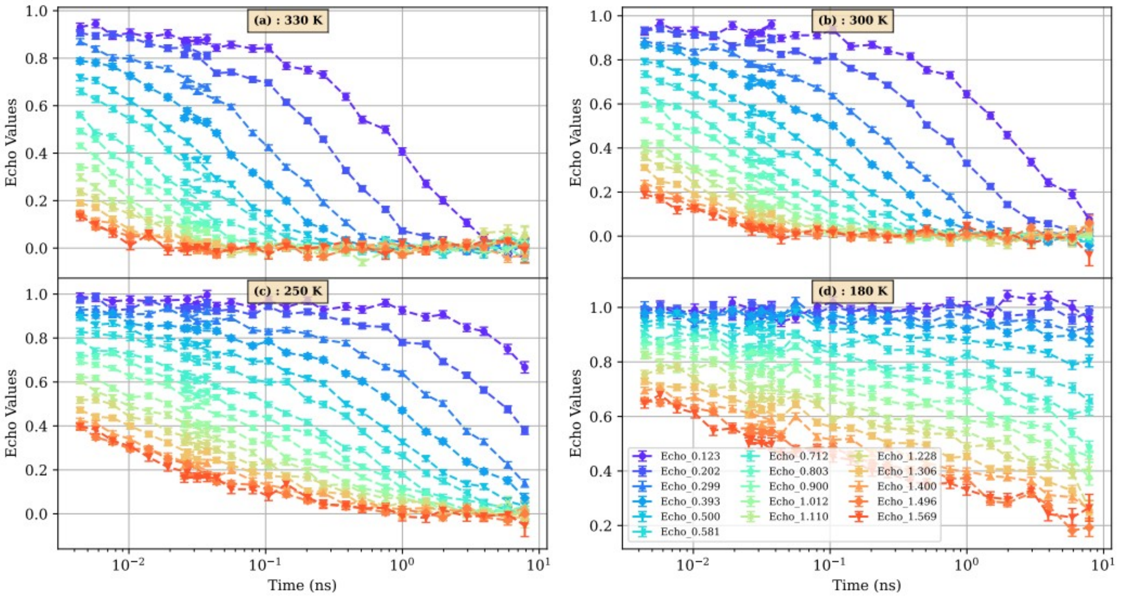

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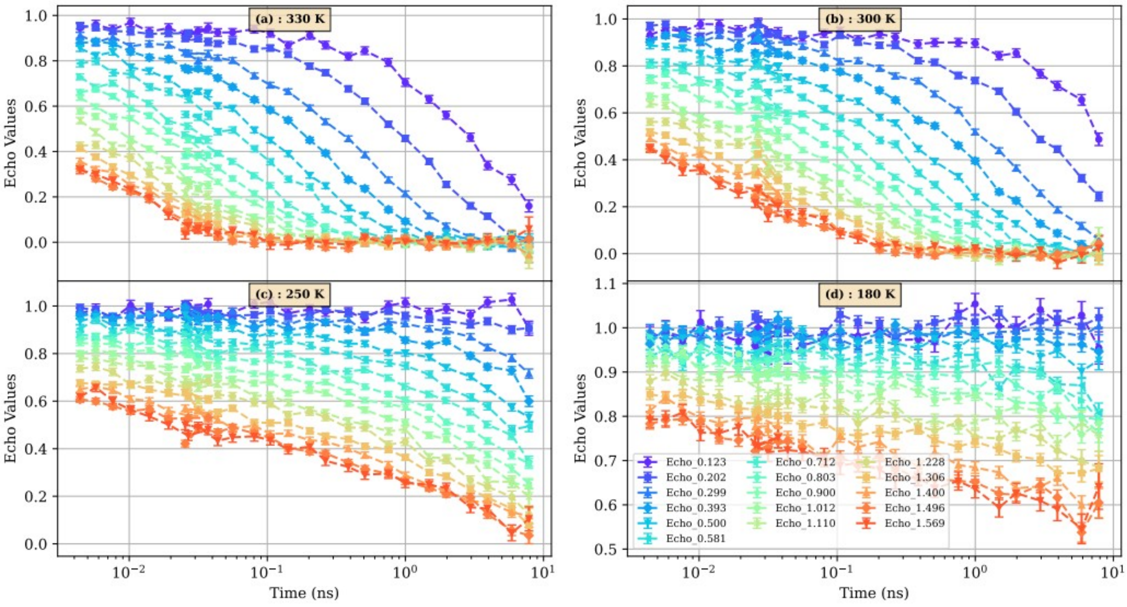

Figure 2: *NSE spectrum for 1-propanol–(50%) glycerol mixture at [330,300,250,180]K with λ=6 Å neutrons.*

A Q-dependent global fit will be performed to analyze the data, incorporating all Q-dependent NSE spectra across the entire temperature range. The planned approach involves using a simple exponential function for the slower process and a stretched exponential function for the faster process. In this model, the faster process is expected to correspond to structural relaxation, while the slower process is attributed to the formation of supramolecular structures through hydrogen bonding. The stretching factor, β, will quantify deviations from a purely exponential decay, where β = 1 represents simple exponential behavior. Mathematically, the neutron spin-echo data will be fitted using the following model:

$$I(Q,t) = A_{\kappa}(Q) * \exp\left(-\frac{t}{\tau_{\kappa}(Q)}\right)^{\beta} + A_{\mathcal{L}}(Q) * \exp\left(-\frac{t}{\tau_{\mathcal{L}}(Q)}\right) + B(Q)$$