Experimental report

16/02/2026

Proposal: 6-02-678 **Council:** 4/2025

Title: Origin of the Non-Dispersive Mode Governing the Structural Relaxationat the Mesoscale in Glass-Forming Molecular Liquids

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: deuterated diethylene glycol monomethyl ether
diethylene glycol monomethyl ether
D-Squalane (C30D62); H-Squalane (C30H62)
Deuterated Propylenecarbonate (C4D6O3)
Propylenecarbonate (C4H6O3)
D-Glycerol (C3D8O3); H-Glycerol (C3H8O3)

Instrument	Requested days	Allocated days	From	To
IN15	4	3	10/10/2025	13/10/2025
WASP	7	4	13/10/2025	17/10/2025

Abstract:

For a variety of molecular liquids with different intermolecular interactions we have recently found that both collective and self dynamics show a Q-independent process at the mesoscale. Thus, in contrast to the general belief, the self-atomic dynamics of molecular liquids at such large length scales cannot be described only by a diffusion process. To discern the origin of this non-dispersive relaxation mode, the precise determination of the temperature dependence of its characteristic time and its comparison with the diffusion coefficient is crucial. In addition, resolving the functional form of the scattering function associated to this process is needed. This is hampered by multiple scattering contributions. We propose a thorough investigation of collective and self-motions through combined NSE experiments on deuterated and protonated counterparts of four different glass-forming liquids, over a large temperature range approaching the glass-transition and accounting for multiple scattering contamination, to address these fundamental questions.

Both, IN15 and WASP experiments were performed with λ= 6Å. The samples investigated were squalane (SQ), diethylene glycol monomethylether (2EG), propylene carbonate (PC) and glycerol (GC).

IN15 experiments with better time resolution exclusively focused on the protonated systems. We chose the Q-values of 0.2 $Å^{-1}$ and 0.4 $Å^{-1}$ as representative for the mesoscale; 0.2 $Å^{-1}$ results shall be dominated by pure diffusion, while at 0.4 $Å^{-1}$ the amplitude of the expected fast process can be large enough to identify and characterize well this process. Figure 1 (a) shows a representative example of IN15 results for protonated SQ at 235K. Within the uncertainties, the 0.2 $Å^{-1}$ data decay exponentially according to simple diffusion (dashed line). This functional form provides a worse description of the data obtained at 0.4 $Å^{-1}$ than the model proposed in Ref. [1] (solid line), which assumes convolution of a fast process and diffusion:

$$I(Q,t) = C\left\{e^{-\frac{t}{\tau_d}}\left[A + (1-A)e^{-\frac{t}{\tau_o}}\right]\right\} \qquad (1)$$

Here, $\tau_d = D^{-1}Q^{-2}$ is the diffusion time and τ_o the time of the fast local process. We assumed a single exponential for this fast process in a first approximation. For some Ts and other samples, we also investigated other Q-values (0.1, 0.3 and 0.5 $Å^{-1}$). The results demonstrate the presence of the fast process in all the systems.

Figure 1(b) shows WASP results on the same protonated SQ sample at 300K. The quality of the data is extraordinary –the error bars are hardly distinguishable. Simple as well as anomalous diffusion can be discarded as the *only* relaxation mechanism at the mesoscale (see corresponding fits for 0.4 $Å^{-1}$ results in Figure 1(b)). The proposed model Eq. (1) (solid lines) accounts very well for the functional form of the incoherent scattering function at all the Q-values investigated by WASP.

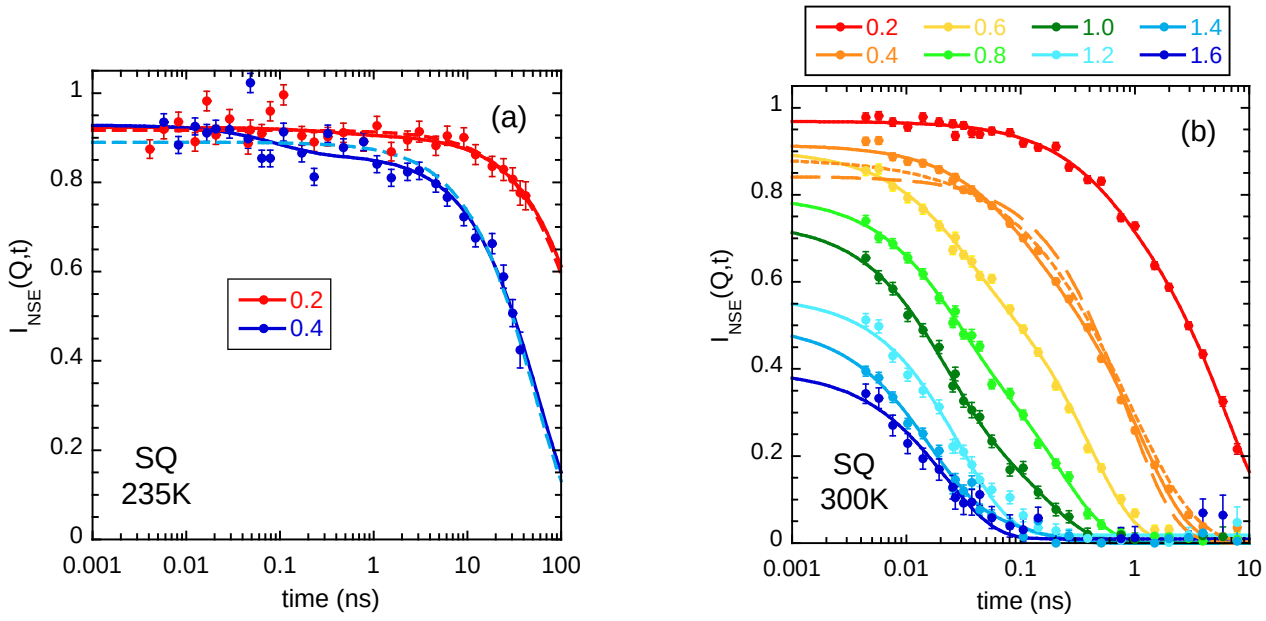


Figure 1: IN15 (a) and WASP (b) results on protonated SQ at the Q-values indicated (in $Å^{-1}$). Solid lines are fits of the model proposed in Ref. [1]; dashed lines are single exponential fits and the dotted line in (b) is a stretched exponential fit. Note that for the 0.2 $Å^{-1}$ results the model reduces to a single exponential (A≈1).

The normalized coherent dynamic structure factor $S(Q,t)/S(Q)$ was addressed with WASP. For deuterated samples, the coherent contribution dominates in the neighborhood of the structure factor peak, while in the mesoscale region coherent and incoherent scattering are nearly equally contributing (see the case of deuterated SQ in the inset of Fig. 2(a)). This complicates the interpretation of the NSE signal, which is the combination:

$$I_{NSE}(Q,t) = \frac{I_{coh}(Q)\frac{S(Q,t)}{S(Q)} - \frac{1}{3}I_{inc}F_S(Q,t)}{I_{coh}(Q) - \frac{1}{3}I_{inc}} \quad (2)$$

Here $F_s(Q,t)$ is the incoherent scattering function that is fully reflected by the experimental NSE results on the protonated counterpart. Thus, $S(Q,t)/S(Q)$ can be obtained from the NSE results on the deuterated and protonated samples as:

$$\frac{S(Q,t)}{S(Q)} = \left(1 - \frac{1}{3}\frac{I_{inc}}{I_{coh}(Q)}\right) I_{NSE}^{d-sample}(Q,t) + \frac{1}{3}\frac{I_{inc}}{I_{coh}(Q)} I_{NSE}^{h-sample}(Q,t) \quad (3)$$

The results obtained after this correction on the example of SQ at 300K are displayed in Figure 2(a). They show a predominant first fast decay with characteristic time τ_o(coh)≈20ps. Thus, we corroborate in SQ the same general phenomenology observed for other liquids (alcohols and low-molecular weight systems [1]). We also observe in the corrected data a long-time tail with the same characteristic time as the diffusive contribution. This tail, present in the $S(Q,t)/S(Q)$ of the previously investigated molecular liquids as well, is not expected to exist in the mesoscale [1,2]. In Ref. [1] we attributed this remaining incoherent-like contribution to multiple scattering (MS) effects of incoherent origin (twice spin-flip events that contribute to non-spin flip and are thereby apparently coherent-like). Unfortunately, proving that MS is the source of the unexpected long-time tail of the corrected NSE results –one of the major goals of this experiment-- was not possible due to a leak in the cryofurnace; DDT has been granted to confirm this hypothesis in an experiment (DIR-416) to be performed in May 2026. Due to the leak, we also gave up extending the study to lower Ts for the case of deuterated glycerol.

To describe the SQ results at the mesoscale, Eq. (1) was not good enough and stretching for the fast component had to be assumed, parametrized by a Kohlrausch-Williams-Watts function:

$$I(Q,t) = C\left\{e^{-\frac{t}{\tau_d}}\left[A + (1-A)e^{-\left(\frac{t}{\tau_o}\right)^{\beta}}\right]\right\} \quad (4)$$

The β-value was found to be close to 0.5 at the highest Ts investigated (300, 330K) and decrease with decreasing T. Actually the incoherent scattering function measured on the protonated sample is also slightly better described if a stretched functional form is used for the fast contribution. In this case, however, since the amplitude of this contribution is very small at the mesoscale, it is not possible to unambiguously determine the value of the stretching parameter. We note that for the other systems reported until now, in the high-temperature range where the fast characteristic time is of the order of few ps (methanol, THF, tributylphosphate, propylene carbonate and glycerol) [1], no significant stretching of the scattering functions has been found.

The characteristic times obtained using Eq. (4) with β ≈0.5 from both incoherent and coherent scattering for SQ at the highest temperature investigated, 330K, are displayed in Figure 2(b). In stark contrast with the other low-molecular weight samples investigated where τ_o^{inc} is Q-independent and rather similar to time τ_o^{coh}) in the mesoscale region, the fast incoherent characteristic time for SQ shows a marked Q-dependence ($\tau_o^{inc} \approx Q^{-3}$). This finding, together with the stretching observed even at the highest temperatures investigated above commented, suggests that connectivity in SQ –which can be considered as an oligomer, half way between a low-molecular weight glass-forming system and a polymer—plays a crucial role in its fast contribution to the dynamics.

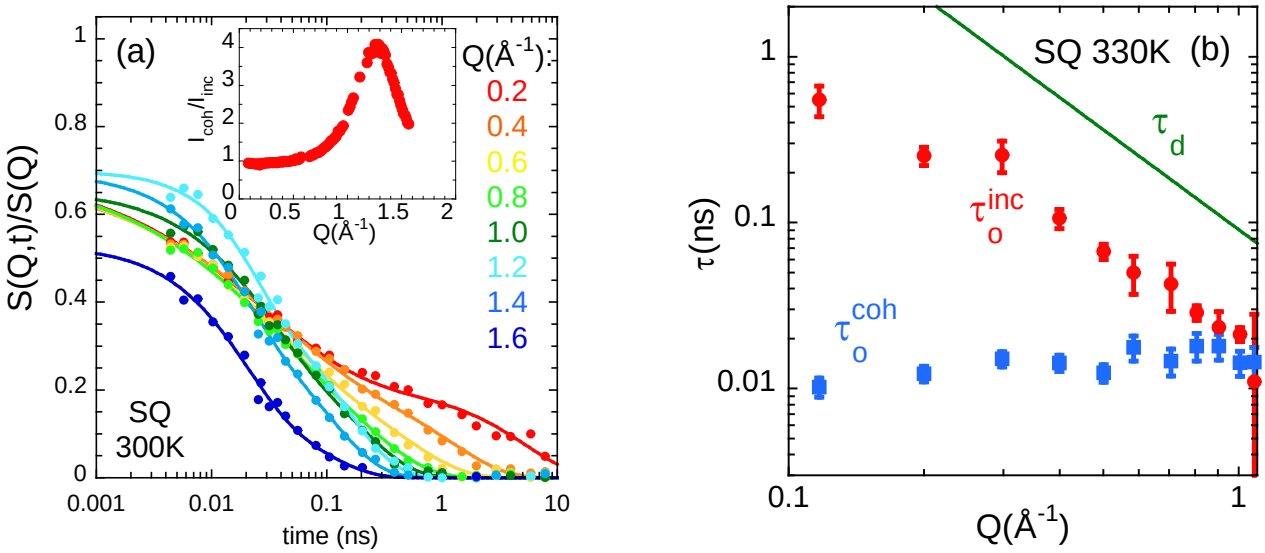


Figure 2: (a) Coherent dynamic structure factor obtained for SQ at 300K. Lines are fits of Eq. (4) with β=0.5 for Q≤0.8 Å^{-1}. (b) Characteristic times obtained for SQ at 330K from incoherent (diffusion time $\tau_d = D^{-1}Q^{-2}$ and incoherent fast time τ_o^{inc}) and coherent scattering (τ_o^{inc}) in the mesoscale region.

We note that one of the proposed deuterated samples, (diethyleneglycol monomethylether) had some contamination leading to low-Q unexpected scattering and was discarded.

REFERENCES: [1] Arbe et al., PRL 134 (2025) 098001; [2] Alvarez et al, J. Chem. Phys. 155 (2021) 244509.