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Sudipta Gupta

JCNS-SNS Oak Ridge National laboratory, sudiptag@lsu.edu

Eugene Mamontov

Oak Ridge National laboratory, mamontove@ornl.gov

Niina Jalarvo

Oak Ridge National Laboratory

Laura Stingaciu

JCNS-SNS, Oak Ridge National laboratory

Michael Ohl

JCNS-SNS, Oak Ridge National laboratory

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Characteristic length scales of the secondary relaxations in glass-forming glycerol

S. Gupta^{1,a}, E. Mamontov², N. Jalarvo^{1,2}, L. Stingaciu¹, and M. Ohl¹

¹ JCNS-SNS, Biology and Soft-matter Division, Neutron Sciences Directorate, Oak Ridge National Laboratory (ORNL), PO BOX 2008 MS6473, Bethel Valley Road, TN-37831 Oak Ridge, USA

² Chemical and Engineering Materials Division, Neutron Sciences Directorate, Oak Ridge National Laboratory (ORNL), PO BOX 2008 MS6473, Oak Ridge TN 37831-6473, USA

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Abstract. We investigate the secondary relaxations and their link to the main structural relaxation in glass-forming liquids using glycerol as a model system. We analyze the incoherent neutron scattering signal dependence on the scattering momentum transfer, Q , in order to obtain the characteristic length scale for different secondary relaxations. Such a capability of neutron scattering makes it somewhat unique and highly complementary to the traditional techniques of glass physics, such as light scattering and broadband dielectric spectroscopy, which provide information on the time scale, but not the length scales, of relaxation processes. The choice of suitable neutron scattering techniques depends on the time scale of the relaxation of interest. We use neutron backscattering to identify the characteristic length scale of 0.7 Å for the faster secondary relaxation described in the framework of the mode-coupling theory (MCT). Neutron spin-echo is employed to probe the slower secondary relaxation of the excess wing type at a low temperature ($\sim 1.13T_g$). The characteristic length scale for this excess wing dynamics is approximately 4.7 Å. Besides the Q -dependence, the direct coupling of neutron scattering signal to density fluctuation makes this technique indispensable for measuring the length scale of the microscopic relaxation dynamics.

1 Introduction

The ever-increasing importance of molecular glass formers is evident in many applications, from biological processing [1] to organic light-emitting diodes (OLEDs) [2]. They also form the basis of the soft colloidal glass formers where material properties are tuned by varying the concentration [3, 4]. However, understanding the underlying secondary relaxation in glasses remains one of the greatest challenges in condensed matter physics, especially as far as the characteristic length scales are concerned. The effect of glassy dynamics is reflected in the imaginary part of susceptibility χ'' as the dominant peak (the structural α relaxation) followed by a shoulder or second smaller peak. The microscopic origin of these secondary dynamic processes illuminated by the shoulder or small peak remains in debate. Broadband dielectric spectroscopy (DS) is the most widely used technique for investigation of molecular dynamics in glass [5–8]. In this case, the aforementioned effects are observed experimentally by measuring the dielectric loss permeability ε'' . In this regard, the collective dynamics of supercooled liquids occur at a characteristic interaction length identified by the static structure

factor peak [9, 10], where the structural α relaxation is predominant. On the other hand, the hidden secondary processes emerge only in the supercooled state (near T_g) and are difficult to access by MD simulation. At T_g the α relaxation is 14 orders of magnitude slower than the microscopic motion, and the main peak is almost not measurable with conventional techniques. As such, low temperatures ($T > T_g$) are preferred to isolate the secondary process from the overwhelming α mode at high temperatures ($T \gg T_g$). The three well-established secondary processes are the excess wing (EW) a.k.a. slow β process [5–8, 11–14], the Johari-Goldstein (JG) β relaxation [6, 8, 15–17], and the fast β relaxation [6, 8, 13, 15–24]. They generally appear at frequencies between 10^8 Hz and 10^{12} Hz, and were usually identified by DS [5, 6, 13, 17, 25]. Materials in which a pronounced and well-separated JG secondary β relaxation peak is detected are called type B glass formers. Whereas, systems that exhibit a simple power law at high frequencies are called type A glass formers [16, 26]. It has been predicted that for type A systems like glycerol, translational [27, 28] and rotational [29] motions of mobile particles inside a slow matrix coexist [30]. In molecular dynamics (MD) simulation [31] where the crossover from type A to B dynamics was studied by the mean square displacement (MSD), the density correlation

^a e-mail: s.gupta@fz-juelich.de

function analysis corroborates such predictions. The excess wing (EW) phenomena are usually found at relatively low frequencies ($\nu \geq 10^8$ Hz) in χ'' spectra from neutron and light scattering. As a result of the dominating α -relaxation signal both in loss ε'' and χ'' , which has much stronger temperature dependence, these fast dynamics merge with the α -relaxation peak at higher temperature ($T \gg T_g$) and cannot be detected at the relatively high frequencies covered by almost every neutron scattering experiment. Detection of the so-called excess wing by neutron scattering (NS) experiments [14, 32, 33] became possible very recently through a combination of state-of-the-art neutron spin echo (NSE) and backscattering (BS) spectroscopy techniques. However, the nature of the correlation between the excess wing (EW) and the secondary fast β process is not well understood. In this regard, compared to ionic and metallic glass formers, molecular glasses are easily prepared model systems for studying the evolution of the density correlation function and hence χ'' by NS on different observation length scales. A proper quantitative analysis of such systems is important for understanding the microscopic origin and nature of the secondary relaxation processes, aiming to provide a better understanding of the unsolved problems of glasses.

According to mode-coupling theory (MCT), the fast β process is related to the center-of-mass dynamics in the transient cage formed by the neighboring molecules, whereas the low frequency α peak is the relaxation mode by which particles escape from their cages [18, 19]. On the other hand, the universal explanation of the generic nature and microscopic origin of the excess wing and whether it can be related to the fast β process, remains a mystery. Based on the predictions of Johari and Goldstein islands of mobility, dynamic heterogeneities, can create EW-like [15] response. Again, JG relaxation is related to the motions within a multiple-well energy landscape at a length scale smaller than the α relaxation [34, 35]. Therefore, a quantitative estimation of the relevant length scale is significant. In this respect, the dependence of the corresponding fast dynamic relaxation over a wide range of momentum transfer (Q) accessible by neutron scattering is important. Other explanations of excess wing and JG relaxation were based on the dynamically correlated domain model [36], the coupling model [37], and/or within extensions of the mode-coupling theory [38]. It is also not clear if the EW that appears as a peak or submerged shoulder in Type A glass formers or the well separated JG relaxation peak [16, 39–41] in Type B glass formers are separate relaxation processes [8, 16, 42, 43].

Both dielectric measurements and, to some extent, light-scattering experiments [44, 45] on dipolar molecular glass formers probe the excess wing and fast β processes, giving access to orientational motions. On the other hand, neutron scattering directly couples to density fluctuations, and the results of the neutron scattering measurements are consistent with fast β process described by MCT ($T > T_c$) [18, 19, 23] thus highlighting the microscopic origin of this secondary fast process. It should be noted that a relaxation process accessed by different spectroscopic methods may vary in amplitude compared

to the α process. This effect is apparent when the excess wing and JG relaxation are investigated by different experimental probes like DS and light scattering. The detected excess wing appears to be stronger when probed by scattering methods compared to the DS spectra [8, 46, 47]. Likewise, differences in the amplitudes of dynamic processes in glass formers were also observed for Boson peak and the fast β process [5] by different experimental probes such as neutron scattering, light scattering, and DS. In fact for dipolar hard spheres, MCT based calculation of the non-ergodicity parameter predicts that the relaxation strength of the α peak from NS can be much smaller than that obtained from DS [48, 49]. The present work aims to achieve a better understanding of secondary relaxations in glass at different length scales. This should enable us to determine the extent of the underlying local constraints.

Recent results show the effect on the NS spectra of the excess wing in an aqueous solution of LiCl [32, 33] and in a mixture of glycerol and LiCl [14] at low temperatures. Hence, in our present work, we utilize NS experimental techniques at low temperature to conduct a detailed investigation of the underlying fast dynamics and their connection to the characteristic length scales. In this paper we show incoherent neutron scattering results from neutron spin echo (NSE) and incoherent quasi-elastic neutron scattering (QENS) results obtained by backscattering (BS) spectroscopy. From the NSE measurements we obtain data for long Fourier time scales of the order of 100 ns, which corresponds to a lower frequency limit of about 10^7 Hz. The results from neutron backscattering (BS) experiments cover a relaxation time range of the order of 10^{-11} – 10^{-9} s. Employing both NSE and BS, we studied in detail the Q -dependence of the fast dynamics in pure glycerol. For this reason we choose a low temperature ($215\text{ K} \sim 1.13T_g$) [50] around which EW and α relaxation mode is well separated, [14] thereby making the system an ideal candidate for for such investigation [25]. In the current paper we report the results of this study.

2 Experimental details

For the incoherent NSE, backscattering and dielectric spectroscopy, glycerol- H_8 ($\text{C}_3\text{H}_8\text{O}_3$) of $\geq 99.5\%$ purity from Sigma-Aldrich was bought. To ensure the absence of water in hygroscopic glycerol, the sample was treated inside a glovebox in an inert (helium) atmosphere, with water vapor content less than 0.1 ppm. There the glycerol was transferred from a sealed bottle (Sigma Aldrich) to the aluminum sample containers directly without further processing. The sample container was then sealed using indium wire and the leakage was measured using a helium detector (the leakage rate was less than 10^{-9}).

The quasi-elastic neutron scattering experiments were performed at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL) using the BS spectrometer BASIS [51] and the Spin Echo spectrometer SNS-NSE [52]. The energy resolution at BASIS (full-width at half maximum FWHM, Q -averaged value) was $3.5\text{ }\mu\text{eV}$ and the dynamic range selected for analysis was

$\pm 120 \mu\text{eV}$. The sample was loaded into an annular aluminum cylindrical sample holder with an outer diameter of 29.0 mm and an inner diameter of 28.9 mm, resulting in a sample thickness of approximately 0.05 mm. This sample thickness was chosen to keep the transmission of the incoming neutron beam $\geq 95\%$, in order to minimize multiple scattering. The low temperature (20 K) sample measurement was used as the resolution function for the experiment. The data reduction was performed with the standard MANTID software package [53] of the BASIS instrument. At the NSE experiment an incoming wavelength band from 5 to 8 Å with 42 time channels for the time-of-flight data acquisition was chosen. This allowed us to access a dynamic range of $2 \text{ ps} \leq t \leq 100 \text{ ns}$. The Q -range was $0.2\text{--}0.3 \text{ Å}^{-1}$. For the measured incoherent NSE data, corrections were performed using the resolution data from a TiZr sample and the background from the empty cell. We used flat aluminum sample containers maintaining a sample thickness of 0.1 mm, sealed with indium wires. The data reduction was performed with the standard ECHODET software package of the SNS-NSE instrument [54–56].

3 Results and discussion

We studied the microscopic length scale dependencies of fast dynamics in a type A molecular glass former, glycerol, with incoherent Neutron scattering. We systematically followed the steps summarized below.

- We started with the comparison between the well-documented α -relaxation time τ_α from DS [5, 6, 39] and the self-diffusion coefficient D_{self} of the glycerol molecule to obtain the specific τ_α at $\sim 215 \text{ K}$, where excess wing is dominant [5, 6, 25].
- To achieve this, we calculated D_{self} using the hydrodynamic radius of the glycerol molecule. We extracted the effective self-diffusion coefficient for α -relaxation (D_α) by comparing the scaled $1/D_{\text{self}}$ with dielectric loss spectra at 215 K (fig. 1).
- Once obtained, the parameter D_α can be scaled with the scattering momentum transfer, Q , to yield the corresponding τ_α for glycerol from the $\tau_\alpha = 1/(D_\alpha Q^{2.2})$ scaling [57]. This allows us to explain the NSE data in the time-space (fig. 2) by using a two-step KWW function (eq. (2)), one for the slow α -relaxation mode (τ_α , β_α) and the other for the relatively faster, shallow EW mode (τ_{EW} , β_{EW}), in order to obtain an estimation of their relative strengths. The corresponding stretched exponents are kept fixed as follows: for the α mode: $\beta_\alpha = 0.7$ [14, 58]; EW mode: $\beta_{\text{EW}} = 0.4$ from the observed EW power-law fall-off in dielectric data [5, 6]. The only fitting parameters are the relative strength factor, $p(Q)$, and EW relaxation time, τ_{EW} . The latter parameter is verified to be in a close proximity to the dielectric EW relaxation time (fig. 1). We have verified that the NSE signal decay as a function of Fourier time is incompatible with the presence of the α relaxation alone.

Fig. 1. A comparative Arrhenius representation for molecular glass former glycerol is illustrated. The α -relaxation times (black) and the red lines are of the excess wing relaxation determined from dielectric spectroscopy [5, 6, 39]. The open squares represent the inverse of the self-diffusion ($1/D_{\text{self}}$) coefficient as calculated based on the size and viscosity data taken from the literature [59, 60]. The star represents the value of equivalent effective diffusion coefficient for the α -relaxation D_α as explained in the text. The inset shows a hypothesized schematic diagram of the microscopic relaxation dynamics of glasses adopted from ref. [33], where the temperatures and relaxation times are approximate.

- Next, to explain the backscattering data in fig. 3 in the energy-space we used single Fourier-transformed (FT)-KWW (eq. (4)) for the underlying fast mode (τ_{fast} , β_{fast}). To estimate its relative strength with respect to the slow dynamic process we used the mixing ratio $p(Q)$. The fitted parameters are the $p(Q)$, τ_{fast} and β_{fast} for different Q 's (fig. 5).
- Finally, the obtained Q -dependence of the relative strength parameter, $p(Q)$, from NSE and BS is used to extract the characteristic relative length scales of the slow and fast secondary relaxation processes, respectively. (fig. 4).
- Figure 5 was used to examine the Q -dependence of the relaxation times obtained for various processes.
- To determine the true nature of the fast relaxation mode (τ_{fast}), a comparative study between dielectric loss ϵ'' and loss susceptibility χ'' from BS data was performed in the frequency space (fig. 6).

Figure 1 shows an Arrhenius representation for molecular glass former, glycerol, based on dielectric relaxation times τ_ϵ [5, 6, 39]. The α -relaxation times (τ_α) and the excess-wing relaxation (τ_{EW}) or slow β relaxations are represented by the solid lines. As shown in the legends, they are determined using the dielectric loss spectra ϵ'' . The open symbols are the inverse of vertically scaled self-diffusion coefficients ($1/D_{\text{self}}$) and are calculated using the size and viscosity data from the literature considering the hydrodynamic radius of glycerol molecule to be

Fig. 2. Normalized dynamic structure factor $S(Q,t)/S(Q,0)$ at $Q = 0.236 \text{ \AA}^{-1}$, $0.259 \text{ \AA}^{-1}$ and $0.3 \text{ \AA}^{-1}$ for pure glycerol measured at 215 K which is indicated in the legend. The solid lines are fits using eq. (2) with fixed parameters from the dielectric α -relaxation, as described in the text. The dotted lines are calculated for single KWW representing corresponding α relaxation modes τ_α for better illustration. Inset shows magnified initial decay.

1.6 Å [59, 60]. The inset shows a hypothesized schematic diagram of the microscopic relaxation dynamics of glasses adopted from ref. [33], wherein the temperatures and relaxation times are approximate. A comparison between vertically shifted $1/D_{\text{self}}$ and τ_ϵ from dielectric spectroscopy Arrhenius plot univocally illustrates the fact that they are the same structural α relaxation phenomena. Our point of interest is the low temperature response at $215 \pm 2 \text{ K}$ (along the vertical dashed line). At this temperature, the well-pronounced effect of excess wing process is observed in glycerol [5, 6, 14, 25]. Based on the corresponding self-diffusion coefficient (marked by a star), one can define the so-called effective diffusion coefficient for the structural α -relaxation (D_α). For pure glycerol we obtain $D_\alpha = 3.255 \times 10^{-7} \text{ \AA}^2 \text{ ns}^{-1}$ at 215 K. This value of D_α is used in the further course of this work to scale the α -relaxation times following $\tau_\alpha = 1/(D_\alpha Q^{2.2})$ [57], with the observations made in a neutron scattering experiment at different momentum transfer Q . At this particular temperature (215 K) one expects the presence of both EW and fast β relaxations in the system (inset of fig. 1), both coupled to the center-of-mass relaxations without involving intra-molecular relaxations [33]. The main goal of this paper is the detailed investigation and verification of these relaxation modes in order to determine their characteristic length scales.

The Q dependence of the effective self-diffusion coefficient (D_α) from fig. 1 is used to directly couple the structural α relaxation mode with density correlators measured by neutron scattering. For this, we perform incoherent neutron spin echo (NSE) measurements on pure glycerol- H_8 , measured at 215 K, for a $Q = 0.2\text{--}0.3 \text{ \AA}^{-1}$, as shown in fig. 2. NSE spectroscopy measures the normal-

ized dynamic structure factor or the intermediate scattering function $S(Q,t)/S(Q,0)$ as a function of Fourier time at a given momentum transfer Q . However, because of the 1/3rd probability of spin-flip for spin incoherent scattering at the NSE instrument, we measure the normalized total signal as the sum of coherent and incoherent scattering [54–56], *i.e.*

$$I_{\text{NSE}}(Q, t) = \frac{\sigma_{\text{coh}} S_{\text{coh}}(Q, t) - \frac{1}{3} \sigma_{\text{inc}} S_{\text{inc}}(Q, t)}{\sigma_{\text{coh}} S_{\text{coh}}(Q, 0) - \frac{1}{3} \sigma_{\text{inc}} S_{\text{inc}}(Q, 0)}. \quad (1)$$

Here σ_{coh} and σ_{inc} are the coherent and incoherent scattering cross-sections, respectively. $S_{\text{coh}}(Q, t)$ and $S_{\text{inc}}(Q, t)$ correspond to coherent and incoherent intermediate scattering functions, respectively. The solid lines in fig. 2, illustrate the incoherent data modeling by a two-step relaxation function, that combines two [14, 33] Kohlrausch-Williams-Watts (KWW) functions [61, 62], namely

$$\Phi(t) = A \left[p(Q) \exp \left\{ - \left(\frac{t}{\tau_\alpha} \right)^{\beta_\alpha} \right\} + (1 - p(Q)) \exp \left\{ - \left(\frac{t}{\tau_{\text{EW}}} \right)^{\beta_{\text{EW}}} \right\} \right]. \quad (2)$$

Here, $p(Q)$ is the relative strength factor of the α process; $p(Q) = 1$ leads to a single step arising from the α relaxation as shown by the dashed lines. The average relaxation time is defined by $\langle \tau \rangle = (\tau_{\text{KWW}} / \beta_{\text{KWW}}) \Gamma(1/\beta_{\text{KWW}})$ [57, 63], where Γ denotes the Gamma function. At first glance, it may seem difficult to distinguish between the one or two component interpretations of the data presented in fig. 2. Further examination from DS reveals that the α relaxation is clearly slower ($\sim 10^7 \text{ ns}$) than any other process, so the obvious decay of the $S(Q,t)/S(Q,0)$ must be due to additional faster process. For the Q -dependence of α relaxation time, τ_α , we used $Q^{-2.2}$ scaling for glycerol following Wuttke *et al.* [57]. Thereby, we used the effective self-diffusion coefficient scaling (from fig. 1) as $\tau_\alpha = 1/(D_\alpha Q^{2.2})$ to fix the corresponding τ_α constant over the fits (dashed line in fig. 2). The stretching parameter of the α relaxation was set to $\beta_\alpha = 0.7$ following our previous NSE studies at higher temperatures [14] and Wuttke *et al.* [58] for glycerol. In fact fig. 2 and its inset clearly shows that the single KWW fits for α relaxation failed to represent the observed decay. Hence a two step KWW (eq. (2)) is necessary. The amplitude A in eq. (2) represents the Debye-Waller (DW) factor [64]. It yields a value between 0.92 to 0.97 (< 1). This highlights the presence of faster process like the fast β and vibrational dynamics. The width parameter for the excess wing (EW) process was kept constant at $\beta_{\text{EW}} = 0.4$, following the EW power-law fall-off in dielectric and NSE measurements [14, 25]. The free parameters used in the fits are $p(Q)$ and the EW relaxation time. The average Fourier-time obtained from the NSE data is $\langle \tau_{\text{EW}} \rangle = 526 \pm 182 \text{ ns}$ over a Q -range of $0.2\text{--}0.3 \text{ \AA}^{-1}$, which lies in close vicinity of the dielectric relaxation time, τ_ϵ , from DS (cf. fig. 1) [5, 6, 25]. Here $p(Q)$ is the elastic incoherent structure factor (EISF) for the β -slow relaxation

Fig. 3. BS data for pure glycerol at low temperature of 215 K, measured at $Q = 0.35 \text{ \AA}^{-1}$ (a) and $0.75 \text{ \AA}^{-1}$ (b). The shaded regions represent the resolution. The solid lines represent the fit using eqs. (3) and (4) as described in the text. Here the elastic resolution measured at 20 K is convoluted with the model.

motions in the transient confinement. Its significance lies in the Q -dependence, which yields the characteristic size of the dynamic entities associated with the secondary relaxations. Equation (2) depicts the single-particle dynamics and is valid for hydrogenated samples that scatter neutrons predominantly incoherently. It is to be noted that over the Q -range accessible by NSE, very slight, if any, Q -dependence of the $\langle \tau_{EW} \rangle$ was observed. This supports the assumption that excess-wing is a result of localized motions rather than diffusive (which would be $\sim Q^{-2}$ dependent) motions. At higher Q 's the dynamic coherent contribution $S_{coh}(Q, t)$ from the α relaxation increases on approaching the structure factor peak ($Q_0 \sim 1.44 \text{ \AA}^{-1}$) [58], whereas the dynamic incoherent contributions $S_{inc}(Q, t)$ would remain unchanged in eq. (1). Since the coherent α relaxation contribution, $S_{coh}(Q, t)$, which is in the order of a 10^{-4} s (cf. fig. 1), starts to dominate we begin observing a flat elastic signal for the slow dynamics within the NSE time window. Therefore, in order to access the faster dynamics and their length scales, we perform neutron backscattering (BS) experiments.

As a representative example, fig. 3 illustrates our quasi-elastic neutron scattering (QENS) data from BASIS backscattering spectroscopy at fixed temperature, $T = 215 \text{ K}$ for $Q = 0.35$ and $0.75 \text{ \AA}^{-1}$, normalized to unity. Similar measurements are done over a Q -range of 0.35 to $1.15 \text{ \AA}^{-1}$. Here we perform an incoherent QENS study on pure glycerol- H_8 . The BS data were acquired at the edge

of the instrument resolution but with long measurement times to obtain the best measurement statistics. All obtained BS results were fitted for each Q value using the following expression:

$$I(Q, E) = \left[p(Q)\delta(E) + (1 - p(Q)) S(Q, E) \right] \otimes R(Q, E) + B(Q, E) \quad (3)$$

Here $\delta(E)$ is the delta function centered at zero energy transfer. $p(Q)$ represents the fraction of the elastic scattering or the elastic incoherent structure factor (EISF). It is the relative strength factor of the slow EW dynamics which are not accessible by BS. The corresponding α relaxation is too slow (10^7 ns) to have any effect on the BS data. $B(Q, E)$ is the elastic linear background term arising from various contributions [66]. $S(Q, E)$ is the dynamic structure factor in the frequency space. $R(Q, E)$ is the resolution function, and $\otimes$ denotes the convolution. For the BASIS spectrometer the elastic resolution was measured from low temperature (20 K) sample. We used a single Fourier transformed (FT) KWW function [61, 62] in the time space to describe the dynamic structure factor in frequency or energy space as

$$S(Q, E) = \int_0^\infty dt e^{i \frac{E}{\hbar} t} \exp \left\{ - \left(\frac{t}{\tau_{fast}} \right)^{\beta_{fast}} \right\}. \quad (4)$$

The exponent β_{fast} determines the stretching of the exponential function, whereas τ_{fast} represents the relaxation time of the fast dynamics with $\omega = E/\hbar$, the angular frequency. It is to be noted that combination of eq. (3) and eq. (4) is based on the same formalism as used in eq. (2) but a constant $p(Q)$ represents the spectral weight of the slow α relaxation in eq. (2) and of the EW in eq. (3). The FT-KWW is computed by C based library by Wuttke *et al.* [67], following in house C++ code for Levenberg-Marquardt fitting. It is represented in fig. 3 by the solid line that is convoluted with the experimental resolution. The corresponding fast dynamic illustrated by the shaded area is also convoluted with the resolution data and weighted by $(1 - p(Q))$, to be consistent with eq. (4). For the fast dynamics over a Q range 0.25 to $1.05 \text{ \AA}^{-1}$, the extracted values of the stretched exponent, β_{fast} , vary between 0.3 and 0.4. The corresponding mean relaxation time $\langle \tau_{fast} \rangle = 0.026 \pm 0.008 \text{ ns}$. It is by a factor $\sim 2 \times 10^4$ less than $\langle \tau_{EW} \rangle$ and by a factor $\sim 4 \times 10^8$ less than τ_α . In fig. 4 the relative strength parameter, $p(Q)$, is plotted as a function of momentum transfer, Q . The solid lines are *diffusion in a sphere* model fits, $p(Q) = [3j_1(QR)/(QR)]^2$ [65], where j_1 is the first order spherical Bessel function. The “diffusion in a sphere” model, originally developed to describe diffusion in pores with impenetrable boundaries, in materials such as silica, is applicable in the same manner to diffusion in transient confinement. From the standpoint of the fast secondary relaxation process, the diffusing particle experiences a confinement caused by the neighboring particles, until the time the cage of the neighboring particles relaxes through

Fig. 4. The Q dependence of $p(Q)$ from eq. (2) (NSE) and eq. (4) (BS) fitted by diffusion in a sphere model (solid lines) [65], yielding $4.7 \text{ \AA}$ and $0.65 \text{ \AA}$ for EW and fast mode, respectively. Here $p(Q)$ from BS data represents the relative strength of slow EW with respect to fast relaxation. $p(Q)$ from NSE data represents relative strength of slow α -relaxation with respect to EW.

the slower, main structural relaxation process. Determination of dimensions of such transient confinement for various secondary relaxation processes is the main goal of the present work. In fig. 4, the downward triangles from BS data (eq. (4)) represent the spectral weight of the EW process with respect to the EW and fast dynamics considered together. This yields a transient confinement length of $R = 0.65 \pm 0.02 \text{ \AA}$. The corresponding value for near-ambient water was $0.73 \text{ \AA}$ [68]. The upward triangles from NSE data (eq. (2)) represent the spectral weight of the slow α relaxation with respect to the α and EW process considered together. This yields a radius of transient confinement $R = 4.7 \pm 0.2 \text{ \AA}$. These two different length scales are important. A radius of $4.7 \text{ \AA}$ signifies a transient confinement “cage” in which the EW process takes place, but the corresponding fast event occurred within a confinement radius of $0.65 \text{ \AA}$ [32, 33] — a factor of 7 smaller. It should be noted that the value for the $p(Q)$ and, ultimately, the spatial extent of the EW relaxation can be somewhat dependent on the choice of the β_{EW} parameter. However, we have verified that changing β_{EW} from 0.4 to 0.3, the lowest value compatible with the dielectric data at higher frequency, results in a change of the parameter R from 4.7 to $4.2 \text{ \AA}$. That is, the spatial extent of the EW relaxation much exceeds (by almost an order of magnitude) the spatial extent of the fast secondary relaxation, irrespective of the details of the fit procedure. These results suggest the localized nature of the center-of-mass motions associated with both fast and slow secondary relaxations, although with an order of magnitude difference in the localization scale.

In fig. 5 we illustrate the Q -dependence of all the different mean relaxation times, $\langle\tau\rangle$, over a Q range, $0.2\text{--}1.15 \text{ \AA}^{-1}$, obtained from BS and NSE spectroscopy in a log-log representation. The solid line depicts the

Fig. 5. The Q -dependence of the different mean relaxation times $\langle\tau\rangle$ over a Q range $0.2\text{--}1.15 \text{ \AA}^{-1}$ obtained from BS and NSE spectroscopy in a log-log representation. The solid line illustrates the power-law scaling of the α relaxation time depicting $\tau_\alpha \sim Q^{-2}$ dependence [57], with the open circles the τ_α used to extract $\langle\tau_{EW}\rangle$ from NSE. The open upward triangles represent the corresponding EW relaxation $\langle\tau_{EW}\rangle$ as obtained from the fits shown in fig. 2 (NSE) with α relaxation together with EW. The open squares denote the value of fast-relaxation $\langle\tau_{fast}\rangle$ as obtained from BS data as obtained from the fits following fig. 4(b) with EW together with the fast mode. The shaded area illustrates the variation of the corresponding mean relaxation time.

power-law scaling of α relaxation time representing $\tau_\alpha = 1/(D_\alpha Q^{2.2})$ dependence [57]. The open circles are the calculated values of τ_α used to extract $\langle\tau_{EW}\rangle$ from NSE. The open upward triangles represent the EW relaxation, $\langle\tau_{EW}\rangle$, as obtained from NSE. The extracted values of $\langle\tau_{EW}\rangle$ vary between 694 and 332 ns, which is represented by the shaded area. The fast relaxation time, $\langle\tau_{fast}\rangle$, obtained from the BS data is represented by the open squares. Here the shaded area illustrates the variation of mean relaxation time $\langle\tau_{fast}\rangle$ between 0.015 and 0.05 ns. The dashed line represents the average values of the corresponding relaxation times.

To determine the nature of the fast dynamic with relaxation time $\langle\tau_{fast}\rangle$ we have compared the BS results to the well-established broadband dielectric measurements [6]. Therefore, to make a comparison with the dielectric loss permittivity, ε'' , we calculated the corresponding loss susceptibility, χ'' , from neutron BS intermediate scattering function $S(Q, \omega)$ in the energy or frequency space $\nu = \omega/2\pi = E/\hbar$. The loss susceptibility is derived from neutron scattering anti-Stokes spectra by

$$\chi''(Q, \omega) = (S(Q, \omega))/(n(\omega, T)), \quad (5)$$

where $(n(\omega, T))$ is the Bose factor at an absolute temperature T [23, 65]. The corresponding dielectric loss ε'' at 213 K from DS [5, 6, 39] and loss χ'' at $215 \pm 2 \text{ K}$ from the BS data are shown in fig. 6(a) and (b), respectively, in a log-log representation. The vertical dashed lines in fig. 6(a) illustrate the position of relaxation times in the frequency space which was obtained from the average Fourier time,

Fig. 6. (a) Broadband dielectric loss data of pure glycerol for low temperature (213 K), from ref. [6]. The lines are guides to the eye. The vertical dashed lines show the position of the average Fourier times $\langle\tau\rangle = 1/(2\pi\nu)$ in frequency space for EW and fast mode as obtained from NSE and BS spectroscopy. The corresponding stretched exponents reflect the power law dependencies. (b) Loss χ'' covering a Q range 0.2–1.05 Å⁻¹ as described in the legend, calculated from the BS data. The shaded area illustrates the BS dynamic range.

$\langle\tau_{EW}\rangle$, from NSE and, $\langle\tau_{fast}\rangle$, from BS data. The corresponding average value of the stretched exponent β_{EW} and β_{fast} represents a power-law fall-off in the frequency space. As shown in fig. 6(b), the BS data covers a dynamic frequency range of 2×10^9 – 3×10^{10} Hz, since the data for $\nu < 2 \times 10^9$ Hz is masked by the instrument resolution (shaded area). Here we report the calculated loss χ'' , covering a Q range 0.35 to 1.05 Å⁻¹ as described in the legend. Interestingly, the position of the fast relaxation mode ($\langle\tau_{fast}\rangle = 1/(2\pi\nu_{fast})$) in fig. 6(a), lies on a broad shallow minima of the loss ε'' , which manifests a distinguished shoulder-like response in the loss χ'' spectra in fig. 6(b). For different Q 's, the positions of the shoulder, the nature of the minima around 10^{10} Hz and the shallow peak around 2×10^{10} Hz remain unchanged. It unequivocally confirms the Q -independent nature of the underlying fast dynamics, which clearly bears the signature of a localized fast β process. It should be noted that the shallow peak around 2×10^{10} Hz could not be the so-called Boson peak, as this only occurs at THz region for glycerol [25]. The fast β process, as described in the framework of idealized MCT [18, 19, 23, 25] is valid only above a critical cross over temperature, $T > T_c$ (or $T > 1.2T_g$). In the framework

of extended MCT, [5, 18, 19, 49] T_c represents a crossover temperature from the dominating cage effect in the liquid phase to the activated hopping processes at lower temperatures. For pure glycerol, $T_c = 262$ K [25, 50] from DS and 225 K from NS [23] has been reported. However, in our case for pure glycerol at temperature around 215 K ($\sim 1.13T_g$, glass transition at $T_g \sim 190$ K [50]), the system is below the crossover temperature ($T < T_c$), where a strong deviation from idealized MCT scaling has been previously observed for pure glycerol [23, 25, 50]. Here, the particle dynamics are considered to be almost frozen in an effective free-energy landscape, and the shallow minimum could be the effect of thermally activated hopping mechanism [26, 69]. Also the limited frequency window of QENS BS data prevents us from investigating the hopping effects as proposed by extended MCT [49] for propylene carbonate.

Being a type A glass former, glycerol exhibits EW rather than a well-separated pronounced secondary peaks as observed in type B glass formers [16, 42, 43]. The EW is just the high-frequency flank of the underlying β process overwhelmed by the dominating α relaxation, which could bear the same microscopic origin [25, 39, 50]. However, it is well known that in dielectric spectroscopy the relative amplitude is weaker than that of the susceptibilities determined by neutron and light scattering methods [13, 25, 50]. This excess amplitude might be one of the reasons as to why we see a shallow shoulder for the loss χ'' , in fig. 6(b) for the $\langle\tau_{fast}\rangle$ mode, when the corresponding dielectric loss ε'' , shows a broad minimum in fig. 6(a). On the other hand, it has been reported recently that in benzophenone [70, 71] the fast β process could lead to a symmetrically broadened shoulder, well approximated by a Cole-Cole (CC) like behavior [70], at the high-frequency flank of the α relaxation peak. At high temperatures in benzophenone the fast β process becomes completely submerged under the dominating α peak. In this regard, one cannot completely ignore similar behavior for the occurrence of a shallow shoulder in fig. 6(b) from neutron scattering. It might be related to the different coupling of the tensorial properties in these experimental probes [45, 48]. Dielectric experiments probe the reorientational motions of the glycerol molecules, whereas neutron scattering has access to the density fluctuations and translational degrees of freedom of the particles. The simplified MCT deals with a single correlator. However, more advanced MCT models [26, 49] with a second correlator for the reorientational dynamics can be fruitful to determine the difference between dielectric and neutron scattering data.

4 Summary and conclusions

In the present work, we studied the microscopic length scale dependence of secondary relaxations in a type A molecular glass former, glycerol, using incoherent quasi-elastic neutron scattering methods. QENS experiments routinely yield single-particle diffusion jump length, but in this work we measure very different quantities. The explanation of the meaning of transient confinement radii is

more intuitive for the case of the fast relaxation dynamics, which is commonly understood as motion in the transient cage of the neighboring particles, which eventually dissipates through the main structural relaxation process. In the presence of the transient caging effect, the time evolution of the mean-squared displacement (MSD) exhibits a transition from the caged to the long-range diffusive regime, at particular values of time and displacement. It is this MSD transition value between the different regimes that determines the characteristic length scale of the faster “in cage” relaxation. By applying the same formalism to the EW, or slow secondary relaxations, we infer that the experimentally determined Q -dependence of such relaxations originates from the underlying characteristic length manifesting in the mean-squared displacement time dependence. The different regimes in the MSD time dependence may manifest themselves in the multi-component decay of the intermediate scattering function (in NSE experiments) of the superposition of scattering components centered at zero energy transfer (in BS experiments). This approach using NSE allowed us to assess the underlying excess wing process as $\langle\tau_{EW}\rangle$ as was corroborated by the dielectric spectroscopy results at low temperature (215 K). The corresponding Q -dependence of the relative strength factor yields the confinement length of 4.7 Å for the EW process with respect to the slow α process. Additional experimental findings from BS spectroscopy strongly point to contributions from a faster process $\langle\tau_{fast}\rangle$. The corresponding Q -dependence of the relative strength factor yields the confinement length of the associated cage of 0.65 Å for the fast process with respect to the EW process. This is ~ 7 times smaller than the spatial extent determined for the excess wing. Compared to broadband dielectric data for dielectric loss, ϵ'' , the corresponding loss χ'' for the fast process shows the signature of fast β relaxation at $T < T_c$. The average relaxation time of the fast dynamics $\langle\tau_{fast}\rangle$ shows Q -independent behavior over a Q range from 0.2 to 1.05 Å⁻¹. Therefore, the excess-wing relaxation and fast β process not only reflect merely reorientational dynamics, as evident from dielectric investigations, but, also are detectable by incoherent neutron scattering, which couples directly to density fluctuations. Our results clearly highlight the length scale dependencies of the secondary dynamic processes in glycerol, which points towards similar localized microscopic origins of the different types of secondary relaxations. Furthermore, they yield the confinement length scales of the excess wing and fast β relaxation. Qualitatively, the results reported here are of general nature, and their applicability is not limited specifically to glycerol. The spatial extent of the fast secondary relaxation process has been reported for several liquid systems, including some temperature dependence results, using the same approach as we apply in this work. On the other hand, to date the EW or slow secondary relaxations have been analyzed in this manner only for aqueous systems and glycerol, including the present work and some previous work by the same authors. However, we believe that such analysis is applicable to liquid systems in general, provided that crystallization at low tem-

peratures can be avoided, and the secondary relaxations exhibit sufficient relative spectral strength. In general the relationship between the microscopic dynamics and localized translational and reorientational motions is crucial for understanding the unsolved mysteries of glassy dynamics.

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