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Dynamical heterogeneity in α - and β -relaxations of glass forming liquids as seen by deuteron NMR

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Abstract. ^2H NMR experiments in deuterated supercooled liquids are discussed in relation with α - and β -relaxation heterogeneity with particular emphasis on the latter. The results are exemplified using data from deuterated *ortho*-terphenyl, propylene carbonate and toluene where partial deuteration provides additional information on intramolecular motion.

1. Introduction

The complex behaviour of supercooled liquids close to the caloric glass transition temperature, T_g , is usually analysed in terms of different processes attributed to different time domains. The slow α -process responsible for solidification at T_g has been found to show various aspects of spatial and dynamical heterogeneity that are intensively studied and the main results have been described in recent reviews [1, 2]. The situation is less transparent in the faster time domain at times smaller than about three decades, say, below the mean α -relaxation time τ_α . In some glass forming liquids (termed ‘type A’ by Rössler *et al* [3–5], e.g. glycerol) the frequency spectrum of the α -relaxation exhibits a pronounced high frequency wing. In others (termed ‘type B’ [3–5], e.g. toluene) a characteristic β -relaxation peak is seen in the range of (and in addition to [3, 4]) the high frequency wing of the α -relaxation. Furthermore, it was recently discovered by Richert and coworkers [6–8] that a peak at ~ 1 kHz can appear in type A glass formers (*o*-terphenyl [6, 7], salol [8]) if the samples are quenched into the amorphous solid state. This peak vanishes on annealing at $\sim T_g - 10$ K. The situation is further complicated by the different temperature dependences of the α - and β -processes and an apparent merging into a single process at $T \gtrsim 1.2T_g$ [9]. We should also mention the secondary relaxations caused by internal side group motions [10] that can easily be confused with the Johari–Goldstein β -process [11] occurring even in glass formers made of effectively rigid molecules. Finally, there are ‘fast’ β -processes in the sub-nanosecond domain which can be described by mode coupling theory [12] provided one properly accounts for high frequency relaxations related with the phonon spectrum [13]. Heterogeneity of the β -relaxation has already been discussed by Johari and Goldstein [14–16] who assumed that the β -peak (Johari–Goldstein process [11]) is caused by cooperative small amplitude motions of molecules within ‘islands of mobility’ that are present in the solid glass. This view has been challenged by experiments which show that *all* molecules of the sample participate in the β -process [17–19]. Nevertheless, there is clear evidence from ^2H -NMR experiments that β -relaxation is spatially heterogeneous and that

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the heterogeneity persists on a time-scale much longer than the mean β -relaxation time, τ_β [4, 5, 17, 19–27]. The purpose of this paper is to present the essence of these results in a form that is amenable to readers who are not experts in NMR spectroscopy. Our goal is to provide some further insight into the problem of what happens to the heterogeneity of the α -relaxation [1, 2] as one proceeds into the high frequency regime where the various β -relaxations occur. A review that provides more details on the interpretation of NMR results is in progress [28].

In the following we concentrate on the time regime $t < 10^{-3} \tau_\alpha$, since the heterogeneity of the primary relaxation has recently been reviewed [1, 2]. After some general remarks on how ^2H -NMR is affected by the heterogeneity of α - and β -relaxations we discuss three typical examples of type A and type B glass formers.

2. Heterogeneity of α - and β -relaxations as seen by ^2H -NMR

2.1. Structural heterogeneity

There is ample evidence from various experimental observations that the structure of amorphous solids is heterogeneous with respect to molecular packings and density. This is most pronounced in polymer glasses since the amorphous packing of macromolecular chains implies additional constraints resulting in increased density fluctuations. We refer to the reviews in [29] and [30] where further literature on ^2H -NMR and optical hole burning results can be found. In ^2H -NMR, the heterogeneity is probed by very broad distributions of rotational correlation times of deuterated probe molecules, e.g. benzene (C_6D_6). Here, the fast in-plane rotation in loosely packed sites can be observed down to ~ 20 K in polymer glasses [29] whereas this rotation is frozen at much higher temperature for probe molecules in densely packed sites. By evaluating the ^2H -NMR line shape or the non-exponential recovery of longitudinal spin magnetization one arrives at distributions of rotational barriers modelling the activation energy landscape of the amorphous solid [20, 29].

2.2. Dynamical heterogeneity

The term ‘dynamical (or motional) heterogeneity’ was introduced in discussions of early ^2H -NMR probe experiments [20, 31] but is now mainly used in connection with experiments where a dynamically distinguishable subensemble can be selected in a supercooled liquid (close to T_g) and its return to the full equilibrium ensemble can be subsequently monitored [1, 2, 32]. In these experiments (e.g. reduced 4D-NMR [33] or nonresonant dielectric hole burning [34]), the heterogeneity of the α -relaxation is probed and one finds [35] that the return to equilibrium occurs on the time-scale of τ_α ; in other words, there seems to be only one relevant α -relaxation time-scale which is probed differently by different experiments [32].

The situation appears rather different in the short-time domain, $t < 10^{-3} \tau_\alpha$. Here, the results from ^2H -NMR can be summarized as follows. In all deuterated liquid and polymer glass formers investigated so far the recovery of longitudinal spin magnetization $M(t)$ after irradiation of appropriate saturation RF pulses, see e.g. [21], becomes nonexponential at $T \lesssim 1.1T_g$. This behaviour can be described by [22, 23]

$$\Phi(t) = [M_0 - M(t)]/M_0 = \int_0^\infty V(T_1) \exp(-t/T_1) dT_1 = \exp[-(t/T_1)^{\beta_1}]. \quad (1)$$

$M_0 = M(\infty)$ is the equilibrium magnetization and $V(T_1)$ represents a distribution of spin-lattice relaxation times, T_1 , approximated by a stretched exponential with stretching parameter β_1 . Below, we have plotted the average $\langle T_1 \rangle = \beta_1^{-1} \Gamma(\beta_1^{-1}) T_1$ where Γ is the gamma function [21]. It is important to realize that equation (1) is not only a mathematical expansion of

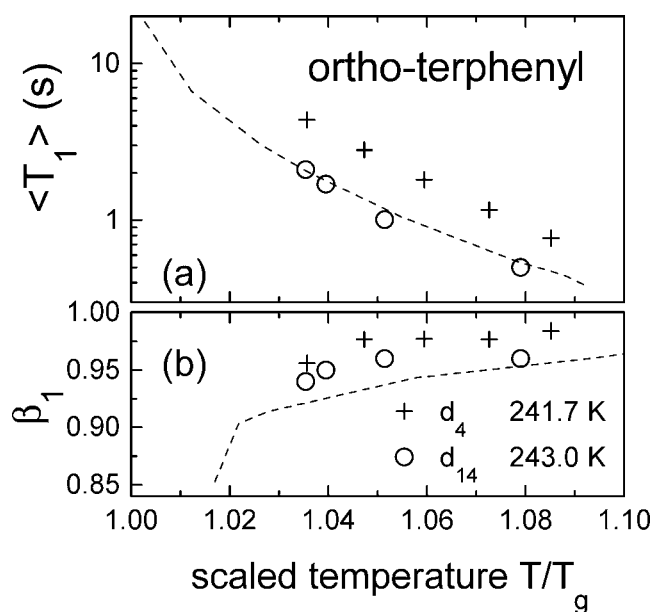


Figure 1. (a) Mean ^2H spin-lattice relaxation times $\langle T_1 \rangle$ and (b) stretching parameters β_1 determined for *ortho*-terphenyl (OTP) from stretched exponential fits to magnetization curves $\Phi(t)$ (see equation (1)) at 40 MHz. The results are plotted versus the temperature, T , normalized by T_g . +: ring deuterated OTP-d₄. O: fully deuterated OTP-d₁₄. Data from [21] determined in OTP-d₁₄ at 55 MHz are shown as dashed lines.

$\Phi(t)$ in terms of exponentials, $\exp(-t/T_1)$, but rather a manifestation of spatial heterogeneity. This is because each T_1 describes spin-lattice relaxation of a subensemble of ^2H spins in environments characterized by the same rotational correlation function [36]. It has been shown [37] that spin-lattice relaxation must be exponential in homogeneous classical systems which provides unambiguous evidence that the heterogeneity is responsible for the non-exponential ^2H relaxation observed at $T \lesssim 1.1T_g$ [38]. It is not surprising that the mean spin-lattice relaxation time $\langle T_1 \rangle$ is considerably shorter for type B than for type A glass formers [21–26] since the Johari–Goldstein β -process contributes to spin-lattice relaxation in the former case. Some degree of heterogeneity can be obtained from the Kohlrausch parameter β_1 of equation (1) which decreases with increasing width of $V(T_1)$. However, a quantitative interpretation of $V(T_1)$ is difficult since the long time behaviour of $\Phi(t)$ is influenced by ^2H spin diffusion [24] resulting in an apparent distribution $V(T_1)$ that is affected by spin exchange narrowing. At higher temperatures $V(T_1)$ is narrowed by motional exchange due to the faster α -relaxation which yields exponential spin-lattice relaxation (see equation (1)) for $T > 1.1T_g$.

2.3. Examples

2.3.1. *Ortho*-terphenyl. The heterogeneity of the α -relaxation has been studied in deuterated *ortho*-terphenyl (OTP-d₁₄) by ‘reduced 4D-NMR’ of the ^2H spins at 253.7 K ($\sim T_g + 10$ K) [39, 40]. An important conclusion was that the lifetime of the dynamical heterogeneity probed over times of about 10^{-3} –1 s is of the order of the rotational correlation time at this temperature.

The situation is rather different for the much faster rotational fluctuations probed by the ^2H spin-lattice relaxation times, T_1 , shown in figure 1. Here, the relevant correlation times estimated from dielectric relaxation [6, 7] and frequency dependent ^2H - T_1 [21] experiments

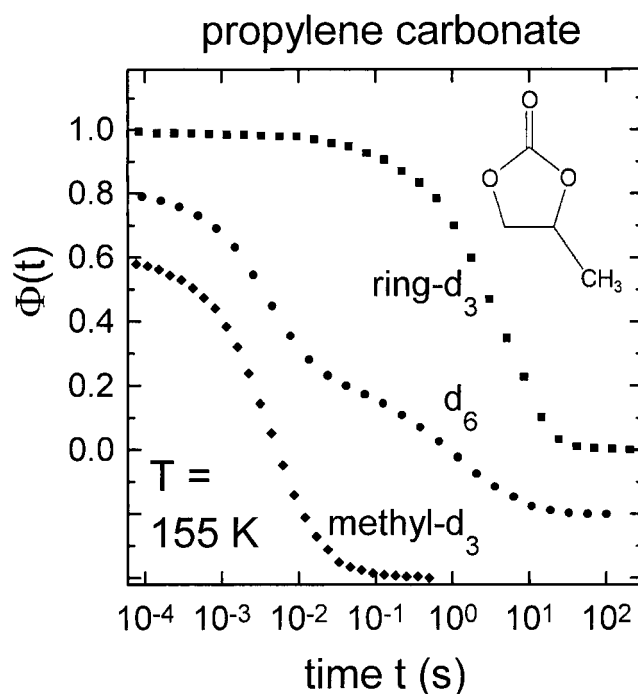


Figure 2. Magnetization curves $\Phi(t)$ (see equation (1)) determined at 155 K in the propylene carbonates, PC-ring-d₃ (upper curve), PC-d₆ (middle curve) and PC-methyl-d₃ (lower curve) recorded at 40 MHz. A vertical shift between the curves by 0.2 has been introduced for clarity.

are in the μs range; the amplitudes of angular fluctuations are estimated to be around 10° [21]. The difference between the T_1 values of OTP-d₄ (deuterated at the central phenylene ring) and those of fully deuterated OTP-d₁₄ demonstrates that part of the angular fluctuations is due to additional intramolecular motions of the two outer phenyl rings. These may also be responsible for the smaller width parameter β_1 (cf equation (1)) of OTP-d₁₄ (figure 1(b)). However, the contribution of the intramolecular motions is relatively small in comparison with motions of the molecule as a whole. As was mentioned above, the narrowing of the apparent T_1 distribution $V(T_1)$ expressed by the increase of β_1 is caused by the decreasing α -relaxation times with increasing temperature. This can be understood as an exchange process [22, 41] where, say, the longer T_1 value of a 'slow' domain becomes shorter as the domain becomes 'fast' due to fluctuations on the α -relaxation time-scale that also limit the lifetime of α -relaxation heterogeneity (see above). On lowering the temperature β_1 decreases and reaches a minimum value of ~ 0.8 at T_g . Here, the apparent width $V(T_1)$ is already reduced by spin diffusion which also causes the increase of β_1 at $T < T_g$ [21, 24]. Therefore, it is not possible to obtain more quantitative information on β -relaxation heterogeneity which probably is at the origin of the broad frequency spectrum observed in dielectric relaxation [6, 7, 42]. We should mention that by analysing the decay of ^2H single and double quantum coherences in OTP-d₁₄ it was possible to eliminate the influence of spin diffusion and obtain information on the dynamics in the regime of $\tau \sim 10 \mu\text{s}$ [43].

2.3.2. Propylene carbonate. ^2H spin-lattice relaxation has been studied in fully deuterated propylene carbonate (PC-d₆) as well as in ring deuterated (PC-ring-d₃) and methyl group

deuterated (PC-methyl- d_3) samples [44]. This allows us to separate intra- and intermolecular contributions to secondary relaxations. Propylene carbonate has been classified as type A glass former since no β -relaxation peak has been identified in dielectric relaxation experiments [4, 45]. Apparently, the methyl group rotation is not detected in these dielectric experiments though the corresponding correlation times are in the same range (10^{-3} – 10^{-9} s) where the correlation time distribution characterizing the β -relaxation peak is expected at $T < T_g$. In figure 2, we show the decay of magnetization functions $\Phi(t)$ (see equation (1)) for the three propylene carbonates investigated at 155 K somewhat below $T_g \approx 160$ K [44]. For PC-ring- d_3 , a fit of $\Phi(t)$ with equation (1) yields $\langle T_1 \rangle = 5.9$ s and $\beta_1 = 0.7$. This is in harmony with the data in OTP- d_{14} and the dielectric results [4, 45] if we bear in mind that the nonexponentiality is reduced by spin diffusion effects in $^2\text{H-NMR}$. The decay curves of PC- d_6 and PC-methyl- d_3 are characterized by the strong influence of CD_3 rotation which is several decades faster in comparison with the tumbling motion of the whole molecule. Since there is no complete time-scale separation as in toluene (see below) the analysis of $\Phi(t)$ is rather complex. An extensive discussion will be given in [44].

2.3.3. Toluene. In toluene, the fast methyl group rotation is well separated from the dynamics of the tumbling motion [46]. $^2\text{H-NMR}$ in ring deuterated p -toluene- d_1 and toluene- d_5 is therefore not influenced by CH_3 rotation. Some $^2\text{H-T}_1$ results relevant for β -relaxation heterogeneity at $T < T_g$ are shown in figure 3 [23, 24, 47]. The different T_1 values of p -toluene- d_1 and toluene- d_5 have been interpreted to indicate increased angular fluctuations around the long molecular axis that do not affect T_1 of p -toluene- d_1 [47]. However, subsequently most of the difference has been shown to be due to the influence of ^2H spin diffusion [24]. This is demonstrated by the increase of $\langle T_1 \rangle$ and the decrease of β_1 as toluene- d_5 is diluted with nondeuterated p -toluene- d_0 (see figure 3) [48]. In particular, the β_1 parameter of p -toluene- d_1 and diluted toluene- d_5 are of the same order. This indicates that any anisotropy of angular fluctuations that may exist at $T < T_g$ [48] has little influence upon heterogeneity [49].

In comparison with type A glass formers discussed above [21, 25] the type B glass former toluene is characterized by smaller T_1 values in a temperature range $T < T_g$ where the β -relaxation peak is most pronounced in dielectric experiments [4]. The rate average, $\langle T_1^{-1} \rangle^{-1}$ (full circles in figure 3), determined from the initial slope of $\Phi(t)$ which is not influenced by spin diffusion effects [50], has been analysed by a simple two site angular jump model assuming equal weights for the two sites and jump angles of about 10° [23]. This view of the Johari–Goldstein β -process is in harmony with an energy landscape model published recently by Diezemann *et al* [51]. A similar model (using a jump angle distribution related with an energy barrier distribution) was used to analyse ^2H solid echo spectra and stimulated echo amplitudes in toluene- d_5 at $T < T_g$ which provide more detailed information but confirm the dominance of small jump angles [19]. We also mention a ‘reduced 4D-NMR’ study of toluene- d_5 at 123 K where the lifetime of the heterogeneity of the α -relaxation was found to be of the same order as the rotational correlation time in harmony with the results in OTP- d_{14} [52].

3. Conclusions

The main conclusions on α - and β -relaxation heterogeneity can be summarized as follows.

At $T > T_g$, the dynamical heterogeneity of the α -relaxation can be probed by experiments [1, 2, 32–34, 39] that select a dynamically distinguishable subensemble that returns to the full equilibrium ensemble on a time-scale of the order of the α -relaxation time τ_α . In this sense, the system becomes ergodic on a time-scale $t \gg \tau_\alpha$.

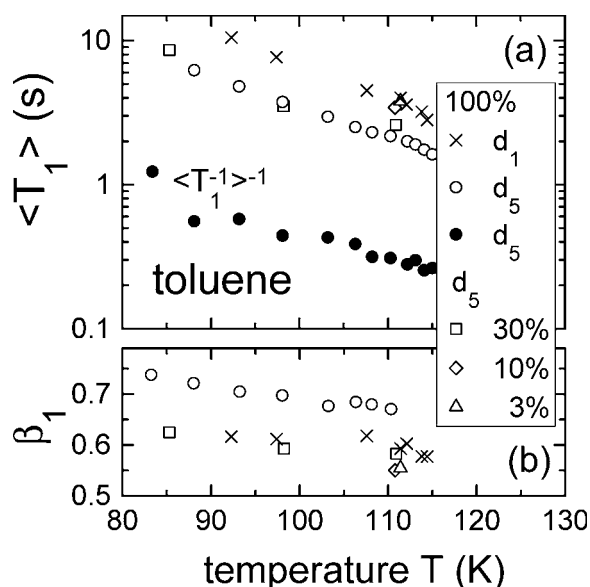


Figure 3. Mean ^2H spin-lattice relaxation times (T_1) and stretching parameters β_1 determined in p -toluene- d_1 (\times) and toluene- d_5 (\circ) at 55 MHz [47]. Also shown for toluene- d_5 are the averages $\langle T_1^{-1} \rangle^{-1}$ determined from the initial slope of $\Phi(t)$ [22] as well as $\langle T_1 \rangle$ and β_1 from solutions of toluene- d_5 in nondeuterated toluene- d_0 [24].

Heterogeneity of secondary relaxations on time-scales $t \ll \tau_\alpha$ has been demonstrated at $T < T_g$ by the nonexponentiality of ^2H spin-lattice relaxation. Though the degree of this nonexponentiality is reduced by spin diffusion [24] and no quantitative determination of spatial domains is possible, the existence of spatial heterogeneity follows unambiguously from the finite distribution of ^2H spin-lattice relaxation times, T_1 , as explained in section 2.2 below equation (1). Since all T_1 values within this distribution are much smaller than in the crystalline solid state [21] these experiments rule out the existence of distinguishable ‘islands of mobility’ [15] although spatial domains with different mobility due to secondary relaxations are confirmed. ^2H -NMR experiments in partially deuterated type A and type B glass formers exhibit no qualitative difference with respect to the heterogeneity of secondary relaxation the lifetime of which is of the order of the α -relaxation time τ_α .

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- $$G(t) = \int_0^\infty W(\tau_c) \exp(-t/\tau_c) d\tau_c \Leftrightarrow J(\omega) = \int_0^\infty W(\tau_c) [\tau_c / (1 + \omega^2\tau_c^2)] d\tau_c$$
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