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Correlation of primary relaxations and high-frequency modes in supercooled liquids. II. Evidence from spin-lattice relaxation weighted stimulated-echo spectroscopy

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Using spin-lattice relaxation weighted stimulated-echo spectroscopy, we report evidence for a correlation of the primary and secondary relaxation times. The experiments are performed using deuteron nuclear magnetic resonance somewhat above the calorimetric glass-transition of ortho-terphenyl, D-sorbitol, and cresolphthalein-dimethylether. The data analysis is based on the procedure outlined in the accompanying theoretical paper [B. Geil, G. Diezemann, and R. Böhmer, Phys. Rev. E **74**, 041504 (2006)]. Direct experimental evidence for a modified spin-lattice relaxation is obtained from measurements on a methyl deuterated acetyl salicylic acid glass. The limitations of the present experimental method are discussed.

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I. INTRODUCTION

Near the calorimetric glass transition temperature the primary as well as the secondary relaxations in small-molecule glass formers are dynamically heterogeneous [1]. This means that the correlation function of the α relaxation, $\Phi_\alpha(t)$, can be written as the ensemble average of dynamically distinguishable subensembles, $\phi_\alpha(t)$, such that $\Phi_\alpha(t)=\langle\phi_\alpha(t)\rangle$ [2]. At first glance, this perspective may suggest that the relaxation spectra are generally composed of contributions that should be linearly superposed. In the same spirit, an additivity was often assumed for the overall correlation function $\Phi(t)$ of α and β relaxations, e.g., in analyses of dielectric experiments [3]. There, one usually decomposes $\Phi(t)$ into independent contributions, the α- *and* the β-relaxations, as $\Phi(t)=\Phi_\alpha(t)+\Phi_\beta(t)$ [4]. Such an independence arises if some molecules are involved in one process and other molecules in the other one. A long time ago, Williams and Watts [5] suggested that $\Phi(t)$ be written as a product. A factorization, i.e., $\Phi(t)=\Phi_\alpha(t)\times\Phi_\beta(t)$, implicitly assumes that each molecule is involved in both processes but that the time scale of the α and β relaxations are independent of each other. The additive as well as the multiplicative approaches become questionable if the time scales of the involved processes are *not* independent of one another.

Potential correlations between the α- and the β-relaxation processes, i.e., between τ_α and τ_β, can be studied directly by spin-lattice relaxation weighted stimulated-echo experiments with deuterons as the nuclear probe [6]. Experiments on supercooled sorbitol, carried out just above the calorimetric glass transition temperature T_g, showed that a correlation indeed exists. According to the considerations in the accompanying theoretical paper, Ref. [7] (hereafter designated as Paper I), such a correlation can be expressed by the conditional probability $P_{1|1}(\tau_\alpha|\tau_\beta)$ of finding a molecule that is characterized by a primary relaxation time τ_α under the condition that it has a secondary correlation time τ_β. The latter dominates the spin-lattice relaxation, i.e., the longitudinal magnetization recovery $M(t)$ measured subsequent to a radio-frequency perturbation. In the slow motion regime, in which we perform our experiments, secondary correlation time, τ_β, and the spin-lattice relaxation time, T_1, are proportional to each other. It is important to emphasize that each deuteron subensemble recovers exponentially [8] with a function $m_\beta(t)$ such that $M(t)=\langle m_\beta(t)\rangle$.

The implementation of the present nuclear magnetic resonance (NMR) technique involves three steps. First, the longitudinal magnetization is destroyed by a saturation sequence. Then, the magnetization is allowed to recover during a build-up time interval t_B. Close to T_g it will do so in a nonexponential fashion. The components associated with the slowest secondary relaxations, i.e., with the longest T_1 will recover last. Thus, if a complete buildup is not allowed for, these slowest components will appear with a reduced weight in the last step of the experiment. In other words, the slower components of the *secondary* relaxation will be (partially) suppressed. In the third step the dynamics of the selected subensembles is tested on the time scale of the *primary* relaxation. The signal measured in the present experiment can be written as

$$\Phi(t_\mathrm{B},t)=\langle\phi_\alpha(t)[1-m_\beta(t_\mathrm{B})]m_\beta(t)\rangle, \tag{1}$$

which does not involve the conditional probability $P_{1|1}(\tau_\alpha|\tau_\beta)$ directly, but rather the closely related quantity $P_{1|1}(\tau|T_1)$ which was designated $C(\tau|T_1)$ in Ref. [6]. Here the time constant τ, obtained by stimulated-echo experiments, is a measure of the primary, i.e., the slow correlation times, τ_α. On the other hand, let us reiterate that the spin-lattice relaxation time T_1 reflects the about five to six orders of magnitude faster secondary correlation times, τ_β, (see Paper I). Spin-lattice relaxation weighted stimulated-echoes are thus simultaneously sensitive to motions on primary *and* secondary time scales.

In the following, experiments are reported on supercooled D-sorbitol, which from dielectric [9–13] and from NMR [14,15] measurements is known to exhibit a pronounced peak-type β process. Furthermore, the spatial and the dynamic heterogeneity of the primary [16] as well as of the secondary [17,18] relaxations have been tested for this glass

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former. As an intermediate case, exhibiting a relatively weak dielectric β-process [19–21], ortho-terphenyl was chosen. The heterogeneity of the primary [22–24] and secondary [25] relaxations of this supercooled liquid was investigated particularly intensively. Furthermore, spin-lattice relaxation weighted stimulated-echo experiments were carried out on cresolphthalein-dimethylether, a glass former showing a wing-type secondary process [26]. Previously, we studied ortho-carborane [6], a disordered crystal devoid of a β-relaxation peak or even a dielectric high-frequency wing [27].

The outline of this article is as follows: After giving the experimental details in Sec. II, direct experimental evidence of a modified spin-lattice relaxation is provided for a glass former that shows a pronounced nonexponential magnetization recovery. Then, in Sec. III the experimental findings on several substances are presented and analyzed. These results are subsequently discussed in Sec. IV and summarized in Sec. V.

II. EXPERIMENTAL DETAILS

In the present work we investigate several glass-forming liquids that were previously characterized by deuteron NMR. Fully deuterated ortho-terphenyl-d$_{14}$ (OTP) is studied at an external magnetic field of 6.2 T [28], methyl deuterated acetyl salicylic acid (ASA-d$_3$) at 7 T [29], cresolphthalein-dimethylether-d$_2$ (CDE) deuterated at the phenyl rings in one of the ortho positions to the methoxy groups at 8.4 T [26], and D-sorbitol-d$_4$ (SOR) deuterated at the terminal carbon atoms at 14.1 T [14]. In all cases the samples are identical to those used in the cited previous works.

The 90° pulses typically were 2–3 μs long. For the saturation of the magnetization a suitably adapted train of five to seven pulses was used. The phase-cycling [30] in the experiments was such that the cos-cos part of the stimulated-echo function was measured. Neglecting spin-relaxation effects this function can be written as

$$F_2(t_p,t) = \langle \cos[\omega_Q(0)t_p]\cos[\omega_Q(t)t_p]\rangle, \tag{2}$$

with t and t_p designating the mixing time and the evolution time, respectively. The quadrupolar precession frequency $\omega_Q = \frac{1}{2}\delta_Q\,(3\cos^2\theta - 1)$ depends on the anisotropy parameter $\delta_Q = (3/4)(e^2qQ/\hbar)$ and on the polar angle θ that is enclosed by the C-D bond and the static external magnetic field. The magnitude of δ_Q is about $2\pi \times 125$ kHz; experimental values can be found in the references given above. The evolution times were chosen to be 20–25 μs.

The temperature stability was ±0.1 K during each run and was monitored for possible variations directly by measuring the magnetization recovery curves before and after each stimulated-echo experiment. The uncertainty in the *absolute* temperatures is estimated to be about 2 K. The relatively long measuring times required for the present work imply that all measurements were carried out on well-annealed samples.

III. RESULTS AND ANALYSES

A. Experimental evidence for modified spin-lattice relaxation

With the T_1-weighted stimulated-echo experiment, one measures a signal that is given by Eq. (1). If α and β relaxation are correlated, it is in general not possible to *strictly* factor out the various terms in Eq. (1). However, as shown experimentally in Ref. [6] and numerically in Paper I, the factorization given by

$$\Phi(t_B,t) = \Phi^*(t_B,t)M^*(t_B,t), \tag{3}$$

provides a good approximation. The factors appearing here are the subensemble correlation function $\Phi^*(t_B,t)$ and the modified spin-lattice relaxation $M^*(t_B,t)$. Phenomenologically the former can often be written as a stretched exponential. In normalized form $[\Phi^*(t_B,t\to 0)=1]$ one has

$$\Phi^*(t_B,t) = Z(t_B) + [1 - Z(t_B)]\exp\{-[t/\tau^*(t_B)]^{\beta(t_B)}\}. \tag{4}$$

Here the final state amplitude Z, the subensemble correlation time τ^*, and the associated stretching parameter β all can depend on the build-up time t_B. Note that these parameters also are a function of the evolution time. However, since the experiments are conducted at constant values of t_p, this dependence is not written out here. Guided by the uncorrelated scenario for which the factorization of Eq. (3) is exact (see Paper I), we define also for the correlated cases that

$$M^*(t_B,t) = M(t) - M(t_B + t). \tag{5}$$

In the limit $t_B \to \infty$ this expression reduces to $M(t)$. For an arbitrary t_B, $M^*(t_B,t)$ is exponential only if $M(t)$ is exponential. In preliminary runs we tried to measure $M^*(t_B,t)$ directly for those substances for which the T_1-weighted stimulated-echo experiment was carried out. However, $M^*(t_B,t)$ could not reliably be determined experimentally, presumably because close to T_g the time scales defined by T_1 and by τ_α are very similar in these systems.

In order to obtain direct experimental evidence for $M^*(t_B,t)$ a substance is required which allows one to generate a finite stimulated-echo amplitude and which additionally exhibit a nonexponential $M(t)$. These requirements are typically fulfilled for glasses that contain molecules with "fast" methyl groups that freeze in at very low temperatures [31]. In this work we use acetyl salicylic acid selectively deuterated at the methyl group (ASA-d$_3$) [29], for which the tunneling motion of the CD$_3$ has been thoroughly studied in the crystalline phase [32]. Also in the glass, the methyl group motion keeps the spin-lattice relaxation short (for $T > 30$ K) so that spin-diffusion can be neglected which otherwise often renders the spin-lattice relaxation exponential [29]. A pronounced nonexponentiality of the magnetization recovery was observed for ASA-d$_3$ in a large temperature range [29]. Furthermore, deep in the glassy phase there is no primary relaxation dynamics taking place in the experimental time window from ms to s and thus $\Phi^*(t_B,t)$ is constant.

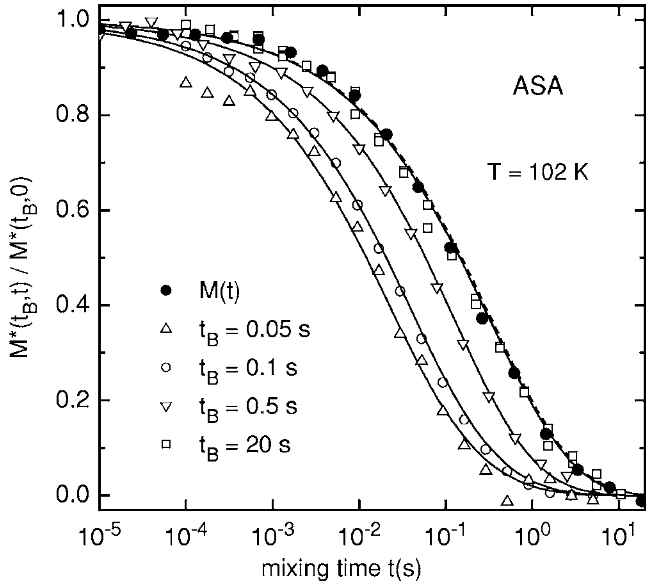

FIG. 1. Normalized echo signals $M^*(t_B,t)/M^*(t_B,0)$ of ASA-d$_3$ as measured for several build-up times t_B. For the longest t_B the echo signals agree with $M(t)$ as determined using the saturation recovery technique. The dashed line is a fit using Eq. (6) with T_1=0.34 s and ν=0.55. The solid lines were calculated from $M(t)$ using Eq. (5).

In Fig. 1 we show a measurement of $M(t)$ using a saturation recovery experiment performed at T=102 K. The data are scaled such that they appear as a decay from 1 to 0. They could be fitted well using an empirical stretched exponential function

$$M(t) = \exp[-(t/T_1)^{1-\nu}]. \tag{6}$$

with a time constant T_1=0.34 s and a stretching parameter ν=0.55. The average relaxation time

$$\langle T_1 \rangle = \int_0^\infty M(t)dt = \frac{T_1}{1-\nu}\Gamma\left(\frac{1}{1-\nu}\right) \tag{7}$$

gives $\langle T_1 \rangle$=0.84 s. Measurements using the T_1-weighted stimulated-echo experiment were performed for several build-up times t_B and, since $\Phi^*(t_B,t)$ is constant, are represented as $M^*(t_B,t)/M^*(t_B,0)$ in Fig. 1 as well. The solid lines in this figure were calculated from Eq. (5) with no adjustable parameters. The good agreement with the data clearly demonstrates the importance of the modified spin-lattice relaxation $M^*(t_B,t)$. Its effective, average decay time, $\langle T_1^*(t_B) \rangle$, depends strongly on t_B. It can be calculated from

$$\langle T_1^*(t_B) \rangle = \int_0^\infty \frac{M(t)-M(t+t_B)}{M(0)-M(t_B)}dt = \frac{1}{1-M(t_B)}\int_0^{t_B} M(t)dt. \tag{8}$$

This equation is completely analogous to the linear-response expression derived in the context of pulsed dielectric spectroscopy [33]. This analogy is not surprising since the magnetization behavior that we encounter in the present context can be understood as reflecting the linear pulse response to the nonzero external magnetic field that is effectively "switched on" for the time interval t_B following the saturation period. At the end of the latter, the magnetization is zero, i.e., it looks as if no magnetic field was present prior to t_B=0. Also for $t > t_B$, the magnetization tends to vanish due to the applied phase cycling. This situation resembles the one implemented in the one-pulse experiments described in Ref. [33].

Although Eq. (8) can be evaluated for any functional form of $M(t)$ it is instructive to assume that it is given by Eq. (6) which provides a good fit to our data. Using the incomplete gamma function $P(a,x)$ [34] the effective decay time of $M^*(t_B,t)$ according to Eq. (8) becomes

$$\langle T_1^*(t_B) \rangle = \langle T_1 \rangle \frac{P[(1-\nu)^{-1},(t_B/T_1)^{1-\nu}]}{1-\exp[-(t_B/T_1)^{1-\nu}]}. \tag{9}$$

For finite t_B this shows that $\langle T_1^*(t_B) \rangle$ is always shorter than $\langle T_1 \rangle$.

In stimulated-echo signals, measured subsequent to an incomplete magnetization recovery, a shortening of the effective spin-lattice relaxation should *generally* be detectable for substances with partially narrowed absorption spectra *and* a nonexponential $M(t)$. In fact such effects have previously been observed, albeit in an uncontrolled way, for glassy propylene carbonate deuterated at the methyl group [35].

B. Raw data and correction for modified spin-lattice relaxation

In this section we present our experimental data and analyze them in a way which is suitable for comparison with the theoretical framework developed in Paper I. Stimulated-echo decays $\Phi(t_B,t)$ measured for SOR and OTP using various build-up times t_B are shown in Fig. 2. The data were normalized to unity for $t \to 0$. For both substances the effective decay times of $\Phi^*(t_B,t)$ become shorter for shorter t_B. The t_B dependence of the initial amplitudes is compatible with the buildup of magnetization as determined from independent saturation recovery experiments, see Fig. 3 for OTP as an example. The magnetization $M_{sat}(t_B)$ follows to an excellent approximation the form

$$M_{sat}(t_B) = M_0\{1-\exp[-(t_B/T_1)^{1-\nu}]\}, \tag{10}$$

with M_0 denoting the equilibrium magnetization.

In order to explain the analysis of $\Phi(t_B,t)$, the data for OTP are replotted in Fig. 4 for three build-up times roughly covering the range $0.015 \leq t_B/T_1 \leq 7.5$. The dotted lines represent $M(t)$ as obtained from the saturation recovery experiments. The dash-dotted lines represent $M^*(t_B,t)$ as calculated thereof using Eq. (5). For the longest t_B the curves for $M(t)$ and $M^*(t_B,t)$ are very hard to distinguish and even for the shorter t_B the differences are minor. The experimental $\Phi(t_B,t)$ were fitted using the product $\Phi^*(t_B,t)M^*(t_B,t)$ from Eq. (4), yielding $\tau^*(t_B)$ and $\beta(t_B)$. The stretched exponential fit to $\Phi(t_B,t)$, shown as dashed line in Fig. 4, and the function $\Phi^*(t_B,t)$ calculated from $\Phi(t_B,t)/M^*(t_B,t)$ (solid line) are seen to overlap practically completely. In other words, due to the fact that the overall decay time of $\Phi(t_B,t)$ is much

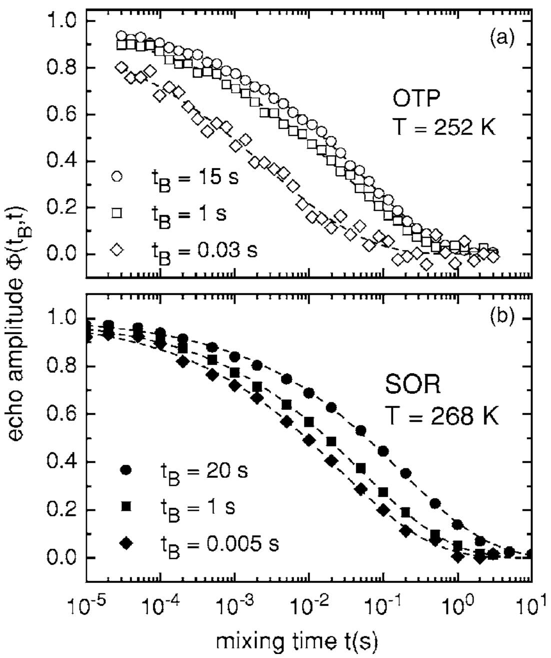

FIG. 2. Stimulated-echo decays as measured (a) for SOR and (b) for OTP using several build-up times. The lines were calculated using stretched exponential functions but here serve as guides to the eye, only.

faster than that of $M^*(t_B,t)$ and of $M(t)$, the modification of the spin-lattice relaxation function *here* is almost negligible. The t_B dependence of $\tau^*(t_B)$ and of $\beta(t_B)$ for this and other substances will be discussed further below. Similar data for SOR at $T=268$ K were previously analyzed in Ref. [6] and are not reproduced here.

Now we will demonstrate that the modification of T_1 is not always negligible and discuss some limitations of the method. Figure 5 contains results from an experiment carried out for SOR at a somewhat lower temperature at two build-up times. Here, for $t_B=5$ ms the modified spin-lattice relaxation is only slightly longer than $\Phi(t_B,t)$, and the overall decay of the latter function is dominated by $M^*(t_B,t)$. The time scale $\tau^*(t_B)$ of the modified response, $\Phi^*(t_B,t)$, tentatively evaluated thereof, is somewhat longer than that of $M(t)$. This precludes a reliable determination of $\tau^*(t_B)$. The requirement that $\tau^*(t_B)<T_1^*(t_B)$ in general rules out to extend the present technique to very short build-up times which otherwise would be useful since for sufficiently short t_B dynamical exchange processes become inoperative [36,37]. Hence, since such exchange processes cannot be neglected they have to be included into the theoretical analysis of the experiment, as we have done in Paper I.

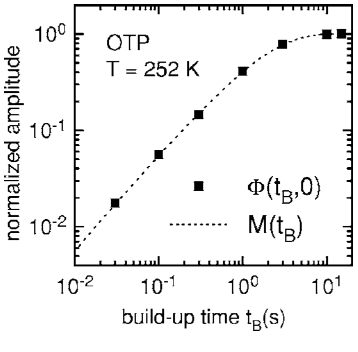

FIG. 3. The fit to the longitudinal magnetization buildup of OTP (dotted line) is compared to the initial amplitude of $\Phi(t_B,0)$ (symbols). Excellent agreement is obtained. The dotted line represents Eq. (10) with $T_1=2.02$ s and $\nu=0.05$.

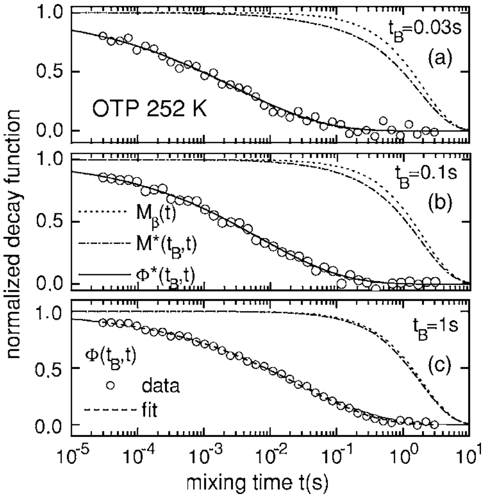

FIG. 4. The stimulated-echo data $\Phi^*(t_B,t)$ of OTP [cf. Fig. 2(a)] are shown as circles for three different build-up times t_B. The spin-lattice relaxation measurements are plotted here as decaying functions $M(t)$ (dotted lines). The modified spin-lattice relaxation function $M^*(t_B,t)$ is calculated from $M(t)$ according to Eq. (5) (dash-dotted lines). From the fits to the experimentally determined $\Phi(t_B,t)$ functions using Eq. (4) shown as dashed lines, the subensemble correlation functions $\Phi^*(t_B,t)\approx\Phi(t_B,t)/M^*(t_B,t)$ were estimated (solid lines). They decay much faster than $M^*(t_B,t)$.

At somewhat lower temperatures, no definitive conclusion can be drawn, at least on the long-time end of the t_B window. In Fig. 5(a) this is demonstrated using data obtained for sorbitol at $t_B=20$ s. Despite the fact that $M^*(t_B,t)$ and $M(t)$ are

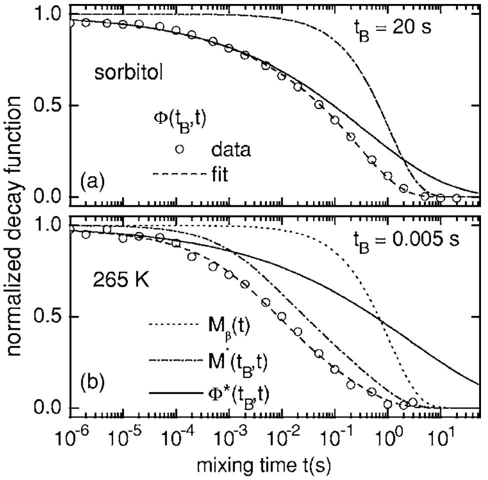

FIG. 5. Same as Fig. 4 but for SOR at 265 K. It should be noted that $\Phi^*(t_B,t)$ does *not* decay much faster than $M^*(t_B,t)$ or $M(t)$, thus precluding a reliable determination of $\tau^*(t_B)$. The dashed line is a fit to $M(t)$ using Eq. (6) with $T_1=1.08$ s and $\nu=0.22$.

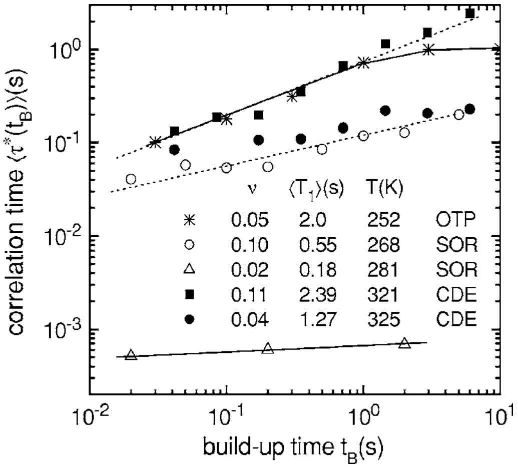

FIG. 6. For SOR at 268 K, for CDE, and for OTP the subensemble correlation times $\langle\tau^*(t_\mathrm{B})\rangle$ increase monotonously with increasing build-up time t_B. This provides clear evidence for a correlation of α- and β-relaxation times. For SOR at 281 K only a minor variation of $\langle\tau^*(t_\mathrm{B})\rangle$ is seen which is due to the near exponentiality of $M(t)$ at this temperature. The parameters ν and $\langle T_1\rangle$ characterizing the magnetization recoveries are shown as inset. The lines are drawn to guide the eye. The dotted lines represent power laws, $\tau^*\propto t_\mathrm{B}^s$, with exponents s of 0.6 and 0.28, respectively, and are drawn to guide the eye, only.

almost the same, the time scale $\tau^*(t_\mathrm{B})$, again evaluated on a trial basis, and T_1 do not differ much. Taken together, these limitations lead to a relatively narrow temperature range in which a possible correlation of primary and secondary relaxations can be studied.

C. Subensemble correlation times

Figure 6 summarizes the subensemble correlation times, $\langle\tau^*(t_\mathrm{B})\rangle$, for several substances and temperatures. This plot includes only data for which $\langle\tau^*(t_B)\rangle$ could be evaluated reliably. In addition to a similar plot in Ref. [6], also data for OTP and CDE are shown. A significant monotonous increase of $\langle\tau^*(t_\mathrm{B})\rangle$ with t_B is seen for OTP, for SOR, at least at the higher temperature, and for CDE. This is clear evidence for the existence of a correlation of the α relaxation with the β relaxation in these substances. In ortho-carborane-d$_2$ crystals which exhibit a dynamically heterogeneous primary relaxation, but no β relaxation [38], $\langle\tau^*(t_B)\rangle$ is independent of t_B, despite the fact that the spin-lattice relaxation proceeds in a nonexponential manner ($\nu=0.05$) [6]. An almost constant $\langle\tau^*(t_\mathrm{B})\rangle$ is also obtained for SOR at 281 K. Here it is due to an almost exponential $M(t)$ ($\nu=0.02\pm0.02$). In addition to what has been discussed in the previous section, the necessity of an nonexponential $M(t)$ also sets an additional upper threshold to the temperature range in which the experiment can reasonably be applied.

Now let us turn to a discussion of the random and systematic errors implied in the extraction of the parameters shown in Fig. 6. These were initially obtained by treating $\beta=\beta(t_\mathrm{B})$ as a free parameter in the fits. However, since no definitive trends as a function of t_B were obtained, β was subsequently kept constant. We found $\beta=0.37\pm0.02$ for OTP, $\beta=0.35\pm0.03$ for SOR at 268 K and 0.60 ± 0.03 for SOR at 281 K, as well as 0.28 ± 0.02 for CDE. Also the random errors from the saturation recovery experiments need to be taken into account. From repeated measurements of $M(t)$ the typical relative error in $\Delta T_1/T_1$ is about 3% and that in $\Delta\nu/\nu$ is about 1.5%. From these random errors one can estimate those in $\langle\tau^*(t_\mathrm{B})\rangle$. They turn out to be no larger than the size of the symbols in Fig. 6.

Systematic errors are more difficult to deal with. In principle the correction of the modified spin-lattice relaxation is independent of the shape of $M(t)$. However, the values of $M(t_\mathrm{B}+t)$ [and also of $M(t)$] which are necessary for an evaluation of $M^*(t_\mathrm{B},t)$ were interpolated from fits using a stretched exponential functions. Despite the fact that the latter provides an excellent parametrization, some systematic deviations cannot be ruled out. By far the largest error in the evaluation of $\langle\tau^*(t_\mathrm{B})\rangle$ presumably is the one arising from the approximate factorization of $\Phi(t_\mathrm{B},t)$ into $\Phi^*(t_\mathrm{B},t)M^*(t_\mathrm{B},t)$, Eq. (3). As pointed out in Paper I, the subensemble function $\Phi^*(t_\mathrm{B},t)$ cannot be determined independently from experimental data, alone. However, the experimental procedures could be mimicked in the corresponding numerical simulations (see Paper I).

Systematic errors would also arise either if the β relaxation would cause a significant decay of the stimulated echo, or if the α relaxation would make a significant contribution to the spin-lattice relaxation. The latter scenario was already discussed in Paper I and can be ruled out in the temperature range in which the present experiment operates. In order to discuss the former scenario, we start from the following consideration: The spectrum of β-relaxation times is relatively broad. Therefore one could argue that some of these processes contribute to the decay of the stimulated echo on the time scale of milliseconds or longer [39]. Thus the experiment would filter the same quantity one wishes to detect. Under such conditions, the experiment would only confirm the heterogeneity of the high-frequency excitations. However, this supposition is irrelevant for two reasons. On the one hand, the β process is characterized by small-amplitude molecular motions. Therefore, the spin-lattice relaxation times associated with it would be much longer than that of the equally slow α relaxation. Since spin-lattice relaxation is by far dominated by the fast processes, any β relaxation, on the scale of milliseconds or longer, plays no role for the weighting process taking place during t_B. On the other hand, even if they would affect the spin-lattice relaxation significantly, β relaxations anyway can account only for a small fraction of the decay of the stimulated echo function [40]. Hence their impact on the integral $\langle\tau^*(t_\mathrm{B})\rangle=\int\Phi^*(t)dt$ should be minor, in contrast to the observed enormous change in $\Phi^*(t)$ and hence in $\langle\tau^*(t_\mathrm{B})\rangle$ (cf. Fig. 6).

IV. DISCUSSION AND CONCLUSIONS

In an early experiment, Williams reported that upon the application of pressure to poly(methyl methacrylate) (PMMA) and for poly(ethyl methacrylate) (PEMA) the strength of its α relaxation increases at the expense of that of the β process [41]. These results provided evidence that the two processes are not independent in these substances. For PMMA [42] and for PEMA [43], the nature of this coupling was further investigated with ^{13}C-NMR. In the NMR studies the detection of a coupling between the time scales of the two processes became possible since the primary main chain motion and the motion of the carboxyl side group, executing the β process, are both highly anisotropic, a behavior that is rather peculiar. For other polymers, the molecular motion of the backbone is *isotropic* above the glass transition temperature. We should note that in supercooled polystyrene possible indications for a correlation of α and β processes were reported [44].

For supercooled liquids, more or less *indirect* indications for such a correlation have also been noted [45]. In this context we mention the observation that the strength of the β process in small-molecule glass formers depends on the thermal history [46] or, in other words, on the structural state that was frozen-in upon vitrification. This suggests that the slow primary degrees of freedom set the environment in which the faster β relaxations can take place [47]. In turn, this suggestion may be interpreted as an indication that the slow degrees of freedom dominate the behavior of the faster ones.

In Ref. [48], the opposite view has been taken that the short-time or high-frequency properties of supercooled liquids determine the primary process. In that context we mention that Ngai's coupling scheme even involves a positive correlation of the α- and β-relaxation times according to $\tau_\beta \propto (\tau_\alpha)^\beta$ [49]. Otherwise, a correlation of primary and secondary relaxation times was rarely directly addressed theoretically [50].

The present experiment only demonstrates the *existence* of possible correlations of the slow primary response with the high-frequency modes. It does not address the question whether the evolution of one process *triggers* that of the other. In order to investigate such a hierarchical scenario experimentally, one may imagine the modification of one process, e.g., using a nonlinear response technique, and subsequently monitor a possible change of the other process.

It should be mentioned that the nature of the secondary relaxation is still debated for OTP. On the one hand, on the basis of audio-frequency dielectric measurements, it has been reported that the β relaxation of this substance can be erased by a specific thermal treatment [20]. Corresponding measurements at radio frequencies are not available and from T_1 studies no such "erasure" effects have been reported so far. Also from our measurements we did not find any explicit time dependence of T_1 although under nonequilibrium conditions such dependences might well be observable [51]. On the other hand, it is known that also librational motions contribute to the spin-lattice relaxation of OTP, particularly at low temperatures, $T < T_g$ [52]. However, T_1 measurements on differently labeled species showed that in the temperature range relevant here, these contributions are relatively small [53].

The correlation data shown in Fig. 6 turns out to be relatively similar for the different glass formers with quite different β-relaxation strengths. This can be rationalized by noting that the β-relaxation strength determines the magnitude of the coupling constant K appearing in $T_1^{-1} = 4K/(5\omega_L^2\tau)$ [cf. Eq. (2) of Paper I]. Consequently, varying the relaxation strengths just rescales the x axis in plots such as Fig. 6 since in Eq. (10) the build-up time t_B is divided by T_1. A similar effect can be expected if one performs experiments at constant temperature for different external magnetic fields, i.e., Larmor frequencies.

To summarize, we presented data from T_1-weighted stimulated-echo experiments and described in detail the correction which is necessary due to the occurrence of a modified spin-lattice relaxation time. The latter was demonstrated using a methyl-deuterated glass. Taking these effects into account, we obtained evidence for a clear-cut correlation of primary and secondary relaxation times.

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