Correlation of Primary and Secondary Relaxations in a Supercooled Liquid

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The widespread assumption that primary and secondary relaxations in glass-forming materials are independent processes is scrutinized using spin-lattice relaxation weighted stimulated-echo spectroscopy. This nuclear magnetic resonance (NMR) technique is simultaneously sensitive to the dynamics on well-separated time scales. For the deeply supercooled liquid sorbitol, which exhibits a strong secondary relaxation, the *primary* relaxation (that is observable using NMR) can be modified by suppressing the contributions of those subensembles which are characterized by relatively slow *secondary* relaxations. This is clear evidence for a correlation between primary and secondary relaxation times. In the disordered crystal orthocarborane high-frequency processes are absent and consequently no such modifications could be achieved.

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In soft condensed matter various motional processes take place on time scales which at a given temperature can differ by many orders of magnitude. A prominent example is the complex dynamics associated with the different tiers in disordered materials such as proteins typically involving changes within the protein backbone, regional reorganizations, as well as local conformational changes [1]. Even with the advent of modern broadband spectroscopic methods, which cover ten and more decades in frequency or time [2], the mutual relationship between various dynamical processes has to be inferred *indirectly*. This is particularly true for the multitude of primary (also called α), secondary (or β), etc., relaxations in amorphous materials. Just above their glass transition the time scales of the α- and of the β-process are typically separated by more than 5 decades [3]. The analysis of data from dielectric and other spectroscopies is practically always based on the implicit assumption that the α- and β-relaxations are additive in the frequency or time domains (see, e.g., Ref. [2]) or multiplicative in the latter [4]. Both options imply that the time scales of the two processes are independent of one another. It is this often tacitly made assumption which we will directly test in the present Letter.

An indication of a possible connection between these processes was reported for polystyrene [5]. However, an unambiguous demonstration of a mutual dependence of these relaxations has so far only been achieved for a few amorphous polymers which, very atypically for glass formers, show an *anisotropic* α-process [6]. Theoretical approaches explicitly dealing with a statistical dependence or independence of these processes for glass formers are rare [7]. Only one approach [8] assumes a correlation of α- and β-relaxations. A correlation among the latter means that the faster contributions of one process are to be related with the faster contributions of the other, and that also the slower contributions are mutually associated. If one associates the low-energy minima in the energy landscape of glasses with their β-relaxations, then a near absence of such a correlation is indirectly implied by recent simulations of the low-temperature properties of a Lennard-Jones system [9].

Here we demonstrate a deuteron NMR method that is simultaneously sensitive to both dynamical processes which differ by several orders of magnitude in time scale. In addition, the technique allows us to directly investigate *how* the primary and secondary relaxations are interrelated with one another. For a supercooled liquid with a strong β-process [10] we find a correlation. Thus, the above mentioned decompositions of the α- and β-processes are not generally valid.

The heterogeneous nature of the α- as well as that of the β-relaxations has been firmly established [11]. Therefore it is physically well justified to associate different *distributions* of correlation times, $G_\alpha(\tau_\alpha)$ and $G_\beta(\tau_\beta)$, with the two processes. Here $G_\alpha(\tau_\alpha)$ refers to the relatively slow, overall isotropic, large-amplitude molecular motions of the α-process, while $G_\beta(\tau_\beta)$ accounts for the relatively fast, locally anisotropic, small-amplitude secondary dynamics.

In some experiments sensitive to the correlation function $\Phi_\alpha(t) = \langle \phi_\alpha(t) \rangle = \int \phi(t, \tau_\alpha) G_\alpha(\tau_\alpha) d\tau_\alpha$, associated with the α-process, it was successfully demonstrated how to modify the corresponding distribution by filtering out subensembles [12], here designated as $\phi(t, \tau_\alpha)$. Such modifications are the hallmark for what is called dynamic heterogeneity and establish the concept of dynamic low-, band-, or high-pass filters for isolating dynamically distinguishable subensembles out of the α-process. Distinguishable subensembles within the α-relaxation could be detected using experiments [11] and simulations [13]. The idea of the present experiment is to implement a filter which is sensitive not to the α- but to the β-relaxation and nevertheless to detect possible changes on the scale of the α-process.

Sensitivity to fast relaxations can be achieved in the vicinity of the calorimetric glass transition temperature, T_g. Here the time dependent magnetization associated with spin-lattice relaxation in deuterated supercooled liquids is usually due to the β-relaxation [14]. The corresponding magnetization will be designated $M_\beta(t) = \langle m_\beta(t) \rangle = \int m(t, T_1) G_{T_1}(T_1) dT_1$ and is understood to be normalized such that it decays from 1 to 0. Theoretically, it is well established that each deuteron magnetization subensemble relaxes in an exponential fashion, $m(t, T_1) = \exp(-t/T_1)$ [15]. In deuteron NMR experiments, the mapping of the distribution of τ_β onto a distribution of T_1 typically leads to a nonexponential $M_\beta(t)$ that was often described phenomenologically by $\exp[-(t/T_1)^{1-\nu}]$ [14,16]. The finding of exponents $\nu > 0$ clearly demonstrated the existence of distributions of spin-lattice relaxation times $G_{T_1}(T_1)$ and consequently of secondary relaxation times $G_\beta(\tau_\beta)$ [17]. However, somewhat above T_g, exchange processes can render spin-lattice relaxation exponential ($\nu \to 0$), despite an underlying distribution $G_\beta(\tau_\beta)$.

To check for a possible correlation between primary and secondary relaxation times we use the following protocol: We first destroy the total nuclear magnetization within our samples by a saturation pulse sequence and then wait for a time t_B in which the magnetization can, at least partially, build up again. Subsequently, we perform a stimulated-echo experiment [14]. Via the latter we test the molecular dynamics on the time scale corresponding to that of the primary response, however, using as input only the subensembles contributing to the partial magnetization built up during t_B.

Obviously, during t_B the magnetization of each subensemble is allowed to build up according to $1 - m(t_B, T_1)$. Thus, if prior to detecting the slow dynamics one waits long enough, i.e., if one fulfills $t_B \gg \langle T_1 \rangle = \int M_\beta(t) dt$ for all subensembles, then the saturation will already be forgotten by the time the slow response is probed. Consequently, one will then record the α-relaxation function $\Phi_\alpha(t)$. However, for $t_B \ll \langle T_1 \rangle$ those subensembles with the shortest τ_β and thus with the shortest T_1 enter the detection part of the experiment with the largest amplitude, i.e., weighted by $1 - \exp(-t_B/T_1)$. Now the decisive point is that if subensembles with relatively *fast* β-relaxations also exhibit relatively *fast* α-relaxations then the subsequently detected two-time function $\Phi(t_B, t)$ will decay *faster* than $\Phi_\alpha(t)$. If, on the other hand, slower β- and faster α-relaxations are connected, which we call "negative correlation", this could lead to a decay *slower* than $\Phi_\alpha(t)$ [18]. If no correlation exists then no changes should show up; i.e., the time scale of $\Phi(t_B, t)$ then is independent of t_B. These expectations are confirmed by detailed numerical simulations, also if effects of dynamic exchange processes or spin diffusion are included which weaken the described trends somewhat but otherwise leave them unchanged [19].

In order to characterize the primary response of sorbitol-d_4 [10] we first recorded the spin-lattice relaxation and then the stimulated deuteron echo [14] as a function of the mixing time t for a long buildup time t_B; see Fig. 1(a). Taking into account spin-lattice relaxation, this two-time function can be written as $\Phi(t_B \to \infty, t) = \langle \cos[\omega_Q(0) t_p] \cos[\omega_Q(t) t_p] m_\beta(t) \rangle$. Here the time dependent quadrupolar frequencies ω_Q specify the molecular orientations with respect to an external magnetic field. For the experiments on sorbitol the evolution time t_p was set to 25 ms and B_0 was 14.1 T [20].

It is useful to write the experimentally determined quantity generally as [19]

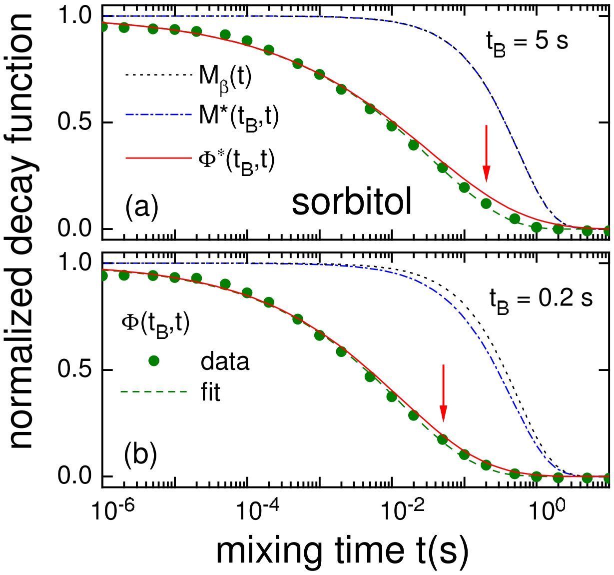

FIG. 1 (color online). Spin-lattice relaxation weighted stimulated-echo data, $\Phi(t_B, t)$, of sorbitol as measured at 268.4 K for a long buildup time $t_B = 5$ s [frame (a)] and for a short $t_B = 0.2$ s [frame (b)] are represented by the symbols. They were fitted using stretched exponentials (dashed lines) and are seen to decay much faster than the conventionally measured and the modified magnetizations. The latter ones, designated $M_\beta(t)$ and $M^*(t_B, t)$, are represented here by the dotted and by the dash-dotted lines, respectively. $M_\beta(t)$ and $M^*(t_B, t)$ coincide for the long buildup time and could be described by $\exp[-(t/0.55\text{ s})^{0.9}]$. The weighted subensemble correlation functions $\Phi^*(t_B, t)$ are shown as solid lines. They were obtained from $M^*(t_B, t)$ and a fit to $\Phi(t_B, t)$ using Eq. (2). The $\Phi^*(t_B, t)$ functions can be described by stretched exponentials with $\langle \tau^*(t_B = 5\text{ s}) \rangle = 0.20$ s and $\langle \tau^*(t_B = 0.2\text{ s}) \rangle = 0.055$ s (as marked by the arrows), as well as $\beta = 0.35$. Data and fits are normalized to unity for $t \to 0$. The initial amplitudes $\Phi(t_B, t \to 0)$ scale according to $1 - M_\beta(t_B)$, as confirmed experimentally (not shown).

$$\begin{aligned}\Phi(t_B, t) &= \langle \phi_\alpha(t)[1 - m_\beta(t_B)]m_\beta(t)\rangle \\ &= \iint d\tau_\alpha dT_1 \phi(t, \tau_\alpha) C(\tau_\alpha|T_1)[1 - m(t_B, T_1)] \\ &\quad \times m(t, T_1) G_{T_1}(T_1). \qquad (1)\end{aligned}$$

Here we introduced the correlation matrix, $C(\tau_\alpha|T_1)$, as the probability of finding a subensemble characterized by a value τ_α under the condition that it is also characterized by a value T_1. For sorbitol $\Phi(t_B \to \infty, t)$ was previously measured, but only at temperatures for which the spin-lattice relaxation is exponential [10]. Under those circumstances the primary response function $\Phi_\alpha(t)$ can be obtained easily since then the occurrence of a specific τ_α does *not* depend on T_1, i.e., $C(t_\alpha|T_1) = G_\alpha(\tau_\alpha)$. Consequently, the quantity $\Phi(t_B \to \infty, t) = \langle \phi_\alpha(t)[1 - m_\beta(t_B \to \infty)]m_\beta(t)\rangle = \langle \phi_\alpha(t) m_\beta(t)\rangle$ appearing in Eq. (1) can be written as the product $\langle \phi_\alpha(t)\rangle\langle m_\beta(t)\rangle = \Phi_a(t) M_\beta(t)$.

Experimental data for sorbitol, recorded at a short t_B are given in Fig. 1(b) and indicate that $\Phi(t_B, t)$ decays faster than it does for longer t_B. These results demonstrate that a suppression of the slow parts of the secondary response renders the *observable* primary one faster. In other words, we find strong evidence for a correlation of the α- and β-relaxations.

For a more detailed discussion let us note that the correlation function given in Eq. (1) can be evaluated theoretically only if the relationship between $\phi_\alpha(t)$ and $m_\beta(t_B)$ is known. Since in the experiment we usually deal with averaged quantities, we introduce the spin-lattice- or β-relaxation weighted subensemble function $\Phi^*(t_B, t)$, which we wish to measure, and the modified spin-relaxation function $M^*(t_B, t) = \langle [1 - \exp(-t_B/T_1)] \times \exp(-t/T_1)\rangle$. Using these quantities we operationally factorize Eq. (1), i.e., the experimentally measured function $\Phi(t_B, t)$ as

$$\Phi(t_B, t) = \Phi^*(t_B, t) M^*(t_B, t). \qquad (2)$$

Via $M^*(t_B, t) = M_\beta(t) - M_\beta(t_B + t)$ the modified magnetization can be obtained from the independently measured magnetization $M_\beta(t)$. Then, from Eq. (2) the subensemble function can be determined as $\Phi^*(t_B, t) = \Phi(t_B, t)/M^*(t_B, t)$. The approximation inherent in Eq. (2) was carefully tested using computer simulations [19].

From Fig. 1(b) it is seen that $M^*(t_B, t)$ (dash-dotted line) decays slightly faster than $M_\beta(t)$ (dotted line). This demonstrates that the filter removes slow components from the T_1 distribution. Furthermore, the experimentally determined function $\Phi(t_B, t)$ (symbols) and $\Phi^*(t_B, t)$ (solid line) as obtained from Eq. (2) almost coincide. Thus the approximation expressed by Eq. (2) is seen to be very good. The decay time $\langle \tau^*(t_B)\rangle = \int \Phi^*(t_B, t) dt$ $(\approx \langle \tau(t_B)\rangle = \int \Phi(t_B, t) dt)$ of the β-relaxation weighted subensemble function was evaluated by fitting it with a stretched exponential function, $\Phi^*(t_B, t) \propto \exp\{-[t/\tau^*(t_B)]^\beta\}$. Results obtained for a number of buildup times are summarized in Fig. 2. It is evident that $\langle \tau^*(t_B)\rangle$ steadily increases with increasing t_B. This important result can be explained only by a correlation of α- and β-relaxation times in supercooled sorbitol [21].

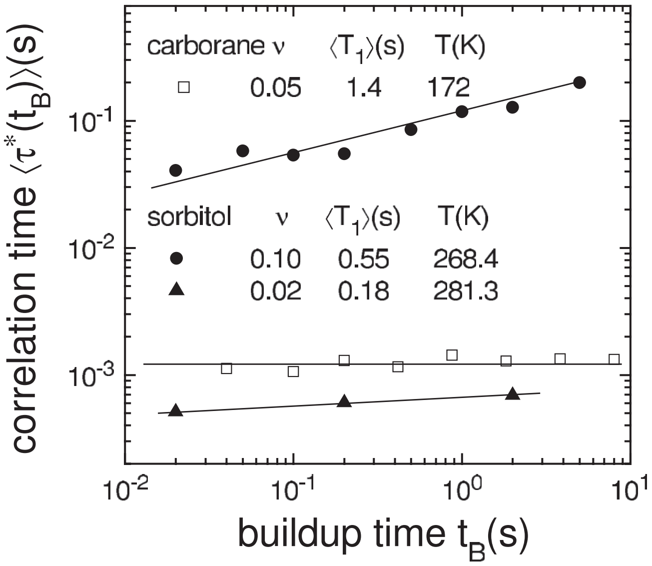

FIG. 2. The time constants $\langle \tau^*(t_B)\rangle$ of the spin-lattice relaxation weighted echo decays are plotted as a function of the buildup time. Additionally the figure displays the parameters ν and $\langle T_1\rangle$ characterizing the magnetization behavior. For sorbitol a pronounced increase of $\langle \tau^*(t_B)\rangle$ with increasing buildup time t_B shows up at $T = 268.4$ K. However, only a minor variation arising from a slight nonexponentiality ($\nu = 0.02$) is seen at $T = 281.3$ K. Although for orthocarborane the nonexponentiality of the spin-lattice relaxation is significantly larger ($\nu = 0.05$), here $\langle \tau^*(t_B)\rangle$ remains constant within experimental error. The results for orthocarborane were obtained at $B_0 = 6.2$ T. Lines are drawn to guide the eye.

As mentioned above, spin-lattice relaxation becomes exponential at temperatures which are somewhat larger than that discussed so far. Exponential relaxation implies that all subensembles are characterized by the *same* spin-lattice relaxation time. Then, $M_\beta(t)$ can no longer be exploited to distinguish subensembles in the present experiment. This expectation is confirmed by the results obtained for sorbitol at a temperature at which $M_\beta(t)$ is very close to exponential. Here only a minor variation with t_B is observed for $\langle \tau^*(t_B)\rangle$, cf. Fig. 2. The exponential limit, at still somewhat higher temperatures, is hard to reach in practice, because the stimulated-echo decay then becomes too short to be recorded reliably.

In the present context the disordered crystal orthocarborane presents an interesting test case. From NMR experiments the process associated with the freezing of the orientational degrees of freedom was shown to be dynamically heterogeneous [22]. Judged from dielectric measurements [23] no β-relaxation or any other processes, sometimes called excess contributions, are present up to the microwave range. Yet, somewhat above its freezing temperature, nonexponential spin-lattice relaxation could be detected [24]. The present experiments on orthocarborane, summarized in Fig. 2, reveal that here, within experimental error, $\langle \tau^*(t_B) \rangle$ is independent of t_B. This finding is compatible with the view that in the absence of an observable β-process it is not possible to modify the slow relaxation.

The observation that in supercooled liquids the α- and the β-relaxations are correlated calls into question the commonly used additive or multiplicative decompositions of the time correlation functions or susceptibility spectra of glass-forming materials close to T_g [2]. Only if the time scales of these relaxations are vastly separated from one another can such decompositions become equivalent and constitute well justifiable approximations.

The correlation evidenced by the present investigation suggests, but does not strictly imply, that the two processes are coupled. Here we mean a coupling in the sense that an externally induced change in either the slow *or* the fast dynamics of a subensemble will simultaneously modify both its slow *and* its fast response. Given that such a coupling can be unambiguously established, this would imply that the β-process is cooperative—*if* this holds true for the α-process, as is commonly envisioned. A clear-cut answer to this question has to await future investigations.

To summarize, we have demonstrated that the primary and secondary relaxations of the highly viscous glass former sorbitol are correlated. This finding is in contrast to the widely used assumption that these processes are statistically independent in deeply supercooled liquids. The magnetic resonance technique employed in the present work should be useful also for materials such as (bio-) macromolecules or ion conductors for which excitations on well-separated time scales are simultaneously present.

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