PHYSICAL REVIEW B VOLUME 57, NUMBER 6 1 FEBRUARY 1998-II

Liquid-to-glass transition in glycerol: A ^{1}H rotating-frame spin-lattice relaxation study

Luiz G. Mendes, M. Engelsberg, Inês C. L. de Souza, and Ricardo E. de Souza
Departamento de Física, Universidade Federal de Pernambuco, 50670-901, Recife, Pernambuco, Brazil

(Received 12 May 1997)

Rotating-frame ^{1}H spin-lattice relaxation measurements in glycerol with various isotopic substitutions are presented. The data cover the supercooled liquid-to-glass transformation region and, combined with earlier ^{2}H relaxation measurements, may reveal aspects of the crossover from ergodic-to-nonergodic behavior that appears to take place near the calorimetric anomaly at $T_g = 185$ K. The much faster rate of relaxation in the rotating frame and its dependence on the amplitude of the rotating field increase considerably the time window of available data and may help in the understanding of the glass transition. [S0163-1829(98)03006-9]

I. INTRODUCTION

Considerable interest in the transition from a supercooled liquid to a glass has been stimulated by the introduction in the last decade of the mode-coupling theory (MCT).[1–3] Within the framework of MCT the glass transition is viewed as a process involving two different regimes. With increasing temperature, fast but spatially localized motion of increasing amplitude (β process) soften the glass structure until, at some critical density, or temperature, the network breaks down leading to translational motion over long distances (α process). Thus the glass transition may be regarded as an ergodic-nonergodic transition where, at a critical value of a coupling parameter λ, related to the density, the particles become arrested in cages formed by neighboring particles and can therefore sample only a restricted phase space. In a simplified model of the glass transition[1] it was predicted that the correlation function for density fluctuations should decay with a time constant that diverges at the critical value λ_g of the coupling constant as $|1-\lambda/\lambda_g|^{-\mu}$ with $\mu = 1.765$.

From the experimental point of view, unambiguous confirmation of predictions of MCT has not yet been put forward. In many glass formers there is no way to meaningfully identify a liquid-to-glass transition since in the window of time scale available to the particular experimental probe, changes are often gradual. However, since many masking effects can conceivably take place, an active search of convincing confirmation of the predictions of MCT using appropriate experimental techniques is still underway.

Nuclear magnetic resonance (NMR) is especially suitable as a way to monitor the transition from ergodic-to-nonergodic behavior which is believed to characterize the glass transition. The changes that take place at the crossover from a regime of spatially localized motion to one involving long-range translational motion can be detected by various NMR techniques[4,8] provided the masking effect of spin diffusion can be avoided. This usually favors the choice of nuclei with a quadrupole moment such as ^{2}H, where spin diffusion is largely quenched, over spin-$\frac{1}{2}$ nuclei such as ^{1}H.

In this paper, we present results which suggest that ^{1}H spin-lattice relaxation (SLR) in glycerol, a widely studied glass former, can also be sensitive to the crossover from ergodic-to-nonergodic behavior when the relaxation of the magnetic moment occurs along a rotating magnetic field. In addition to higher sensitivity and a purely dipolar coupling, ^{1}H rotating-frame spin-lattice relaxation (RFSLR) permits us to extend the available time window of relaxation times by more than three orders of magnitude in relation to ^{2}H SLR along the static laboratory field.

In Sec. II of this paper the basic aspects of RFSLR in glycerol are reviewed and the experimental results are presented in Sec. III. In Sec. IV, the connection between our results and ^{2}H SLR data and their bearing upon the ergodic-nonergodic crossover are discussed.

II. SPIN-LATTICE RELAXATION IN THE ROTATING FRAME IN GLYCEROL

Glycerol is one of the most extensively studied glass-forming liquids. It exhibits a specific-heat anomaly at $T_g = 185$ K and is extremely difficult to crystallize. Besides NMR,[4–21] a variety of other techniques such as dielectric relaxation,[22] neutron-scattering,[23,24] light-scattering,[23,25] and dynamic specific-heat measurements[26] have been employed to probe the supercooled liquid-to-glass transition region. Although a vast amount of NMR data have been reported, only in a few cases[16,17] has RFSLR been employed as an experimental tool in spite of its sensitivity to slower motions, which are of interest in the glass transition region.

For SLR in the laboratory frame in a dipolar coupled system of spins of a single species, with gyromagnetic ratio γ, spin I, and Larmor frequency ω_0 the relaxation rate is given by[26]

$$1/T_1 = \tfrac{3}{2}\gamma^4\hbar^2 I(I+1)\sum_k \left[J_{ik}^{(1)}(\omega_0) + J_{ik}^{(2)}(2\omega_0)\right], \quad (1)$$

where $J_{ik}^{(1)}(\omega)$ and $J_{ik}^{(2)}(\omega)$ are spectral density functions corresponding to the dipolar interaction between pair spins with internuclear distance r_{ik}. The upper indices identify two of the three types of terms in the magnetic dipole-dipole interaction, namely, those which involve transitions where the magnetic quantum number m of the pair changes by $|\Delta m| = 1$ or $|\Delta m| = 2$, respectively.

On the other hand, for spin-lattice relaxation along a strong resonant-rotating magnetic field of amplitude B_1 large compared to the local dipolar field and assuming that the correlation time τ_0 satisfies the condition $\omega_0\tau_0 \gg 1$, the RFSLR rate is given by[27]

$$1/T_{1r}=\tfrac{3}{2}\gamma^4\hbar^2 I(I+1)\sum_k \tfrac{1}{4}J_{ik}^{(0)}(2\omega_1). \tag{2}$$

Here $J_{ik}^{(0)}(\omega)$ denotes the spectral density function corresponding to the $\Delta m=0$ term in the dipole-dipole coupling and $\omega_1=\gamma B_1$.

The validity of Eq. (2) is not limited to liquids and strongly narrowed solids. As shown by Look and Lowe,[28] it is also applicable to the study of much slower motions provided that, in a time that is much shorter than the spin-lattice decay time, a spin temperature in the rotating frame is established. Under this condition, the decay of the magnetization in the rotating frame should be monoexponential with a relaxation rate given by Eq. (2).

The spectral density functions for the dipolar terms can be evaluated if one assumes a definite model for the motion. For a simple rotationally diffusive motion with exponentially decaying correlation functions[27] and assuming a continuous distribution of correlation times $g(\tau)$, one obtains[10]

$$\langle 1/T_1\rangle \approx \tfrac{2}{5}\gamma^4\hbar^2 I(I+1)\langle 1/r_{ik}^6\rangle \int g(\tau)[\tau/(1+\omega_0^2\tau^2) + 4\tau/(1+4\omega_0^2\tau^2)]d\tau. \tag{3}$$

Implicit is the assumption that the motion of internuclear vectors whose contributions to $1/r_{ik}^6$ are dominating, is correlated. Under these circumstances one may factor out the average value $\langle 1/r_{ik}^6\rangle$, as shown in Eq. (3).

If the same set of assumptions leading to Eq. (3) are applied to Eq. (2), the following expression for the RFSLR rate is obtained:

$$\langle 1/T_{1r}\rangle \approx \tfrac{3}{5}\gamma^4\hbar^2 I(I+1)\langle 1/r_{ik}^6\rangle \int g(\tau)[\tau/(1+4\omega_1^2\tau^2)]d\tau. \tag{4}$$

Provided that the evolution of the nuclear magnetization towards equilibrium is exponential, the relaxation functions $\Phi_l(t)=\exp(-t\langle 1/T_1\rangle)$ and $\Phi_r(t)=\exp(-t\langle 1/T_{1r}\rangle)$ are completely determined by Eqs. (3) and (4), respectively. However, this condition may not hold. With a distribution of correlation times, and consequently of T_1 (T_{1r}) values, one can have regions containing many molecules with a well-defined correlation time that maintains their identity for a certain time. The decay of the relaxation function may become nonexponential depending upon the lifetime of these regions.

The above scenario is adequately described by the Zimmermann-Brittin model.[29] Denoting by Γ_k the lifetime of the kth region characterized by a relaxation time T_{1k} (T_{1rk}), if the slow exchange condition $\Gamma_k \gg T_{1k}$ (T_{1rk}) is satisfied for all these regions, the relaxation function $\Phi(t)$ decays nonexponentially and, in the continuous distribution limit, $\Phi_r(t)$ is given by

$$\Phi_r(t)=\int \exp(-t/T_{1r})G(T_{1r})dT_{1r}, \tag{5}$$

where $G(T_{1r})$ denotes the distribution of relaxation times. On the other hand, in the fast exchange regime where $\Gamma_k \ll T_{1rk}$, the relaxation function assumes the exponential form $\Phi_r(t)=\exp(-t\langle 1/T_{1r}\rangle)$ with $\langle 1/T_{1r}\rangle$ given by Eq. (4).

In many cases involving glassy systems[4] and in systems with spatially localized motion,[30] the relaxation function has been found to be described by a stretched exponential $\Phi_r(t)=\exp[-(t/t_{se})^\beta]$ with $0<\beta<1$ over a considerable range of time. Provided that the experimental relaxation function $\Phi_r(t)$ can be fitted by a stretched exponential, the average value $\langle T_{1r}\rangle$ is determined by t_{se} and β. Given that the integral of Eq. (5) over all values of time yields $\langle T_{1r}\rangle$, one can perform this integral analytically yielding[8]

$$\langle T_{1r}\rangle = t_{se}\Gamma(1/\beta)/\beta, \tag{6}$$

where $\Gamma(x)$ is the gamma function. Thus, for an exponential decay ($\beta=1$), $1/t_{se}=1/\langle T_{1r}\rangle=\langle 1/T_{1r}\rangle$.

Although the relaxation function $\Phi_r(t)$ of Eq. (5) should be completely determined by $g(\tau)$ of Eqs. (3) and (4) in the slow exchange regime, this is only true in the absence of spin diffusion.[31] If spin diffusion cannot be neglected and is capable of transporting magnetization between neighboring spins faster than they can relax directly to the lattice, thus establishing a uniform spin temperature, an exponential decay of $\Phi_r(t)$ would prevail,[32] even in the presence of a distribution of correlation times $g(\tau)$. Since the spin-diffusion constant is temperature independent whereas spin-lattice relaxation is strongly temperature dependent, the regime of negligible spin diffusion may only prevail in a limited range of temperature.

Various distribution functions have been employed to fit relaxation data in glycerol. For ^{1}H spin-lattice relaxation in the temperature range $253<T<343$ K and Larmor frequency in the range $0.45<\omega_0/2\pi<117$ MHz, it was shown by Noack and Preissing[10] that reasonable agreement could be obtained with the function

$$g(\tau)=\tfrac{3}{2}[B_{3/2}(\sqrt{\tau_0/\tau})]^2/\tau, \tag{7}$$

where $B_{3/2}(x)$ is the Bessel function of order $\tfrac{3}{2}$ and τ_0 is the temperature-dependent characteristic correlation time of the distribution.

The origin of the function $g(\tau)$ in Eq. (7) can be found in Torrey's theory[11] of relaxation by translational diffusion. For a purely rotational motion a Debye-like spectral density function is expected under the assumption of rotational diffusion.[27] However, when the time dependence of the dipole-dipole interaction caused by translational motion is also taken into account via a diffusion equation, the spectral density function becomes an integral of the Debye-like spectrum[11] where $g(\tau)$ acts as a distribution function.

III. EXPERIMENTAL RESULTS

^{1}H RFSLR measurements in glycerol were performed at a frequency of 90 MHz in a Bruker CXP-100 spectrometer. The samples were dried by heating for several hours in a dry nitrogen atmosphere at a temperature of 90 °C and then sealed in a 9 mm-diam tube in a vacuum. Three different samples were employed: glycerol-d_0 (fully protonated), glycerol-d_5 (deuterated at the nonhydroxyl protons), and

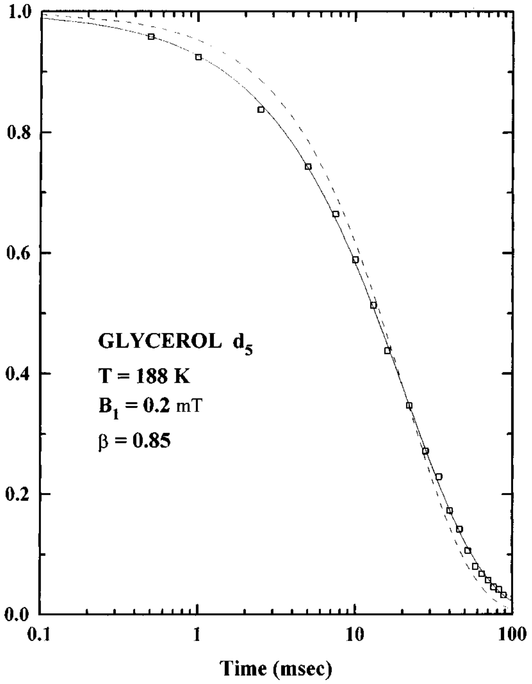

FIG. 1. Decay of the ^{1}H magnetization in a rotating field of amplitude $B_1 = 0.2$ mT for glycerol-d_5 at $T = 188$ K (□). The solid line is a stretched exponential fitting function $\Phi_r(t) = \exp[-(t/t_{se})^\beta]$ with $\beta = 0.85$ and $t_{se} = 20.6$ msec. The dashed line represents an exponential decay obtained from $\Phi_r(t)$ by setting $\beta = 1$.

glycerol-$^{13}C_3$ (99% ^{13}C trisubstituted, fully protonated) (Isotec Inc.).

Pulsed rotating magnetic fields of up to $B_1 = 0.4$ mT with maximum width of 300 msec were produced in a coil 10 mm in diameter and 34 mm in height. The validity of the condition $B_1^2 \gg B_{loc}^2$ where B_{loc} denotes the local dipolar field, was monitored by the ratio of the spin-locked magnetization to the thermal equilibrium magnetization in the temperature region of long values $\langle T_{1r} \rangle$. This ratio should be only slightly smaller than one when this condition is fulfilled.[33] It was found that in glycerol-d_5, with a smaller dipolar local field than glycerol-d_0, the condition was satisfied for $B_1 = 0.2$ mT as well as for $B_1 = 0.4$ mT. For glycerol-d_0 a rotating field of amplitude $B_1 = 0.4$ mT was employed in all measurements.

The decay of the magnetization in the rotating frame could be followed for approximately two decades in amplitude and for times longer than approximately 100 μsec it decayed monotonically. A gas flow cryostat system was employed to control the temperature in the glass transformation region to within ± 0.5 K with an estimated absolute reproducibility of ± 1 K.

Our ^{1}H RFSLR data suggest that in the vicinity of the calorimetric glass transition temperature $T_g = 185$ K nonexponential decays prevail for glycerol-d_5. Figure 1 shows a decay of the magnetization in the rotating frame for glycerol-d_5 at $T = 188$ K and $B_1 = 0.2$ mT. A stretched exponential relaxation function $\Phi_r(t) = \exp[-(t/t_{se})^\beta]$ with $\beta = 0.85$ and $t_{se} = 20.6$ msec appears to fit the data over a considerable range and yields, from Eq. (6), $\langle T_{1r} \rangle = 22.45$ msec. For comparison the exponential function resulting from setting $\beta = 1$ in $\Phi_r(t)$ is also shown.

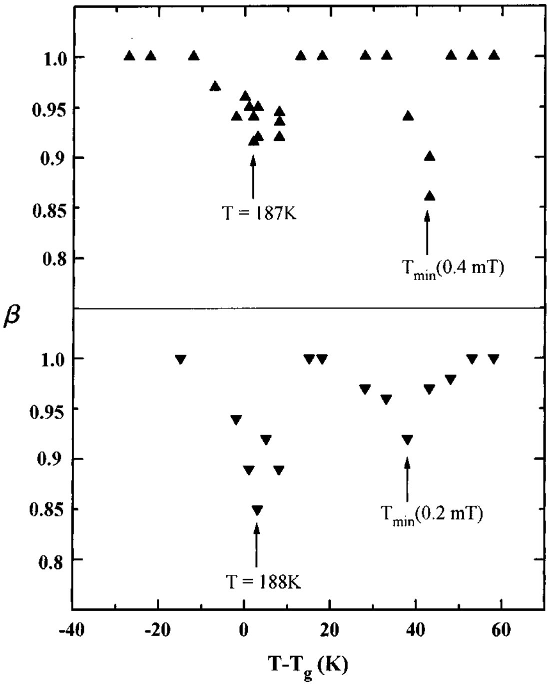

FIG. 2. Measured stretching exponents β in glycerol-d_5 as a function of temperature differences with respect to $T_g = 185$ K (Top) for a rotating magnetic field of amplitude $B_1 = 0.4$ mT. (Bottom) for $B_1 = 0.2$ mT.

Figure 2 shows the measured stretching exponent β in glycerol-d_5 as a function of temperature in the glass transformation region for two different values of B_1. For values of the stretching exponent in the range $0.98 < \beta < 1$ the decays appeared exponential within the available signal-to-noise ratio and could not be discriminated. Whenever the decays appeared as exponential, within the available accuracy, the value $\beta = 1$ was adopted in Fig. 2.

An apparent nonexponential decay of the magnetization in the rotating frame could be caused by effects unrelated to spin-lattice relaxation. This could occur in our data near the minima of $\langle T_{1r} \rangle$ where the time required for the establishment of a spin temperature in the rotating frame is no longer negligible compared with spin-lattice relaxation times. Residual overall nonexponentiality, which could have been caused in earlier data[7] by artifacts in the data acquisition, has been eliminated.

In addition to a drop in β that peaks close to $T = 187$ K, slightly above T_g, nonexponential decays are also apparent in Fig. 2 near a temperature $T_{min}(B_1)$ at which $\langle T_{1r} \rangle$ is a minimum for the particular value of B_1. This second peak is quite narrow for $B_1 = 0.4$ mT, and was not studied in an earlier report.[7] It is seen to somewhat shift towards lower temperatures and also broaden considerably with decreasing B_1.

Figure 3 shows ^{1}H measured values of $\langle T_{1r} \rangle$ in glycerol-d_0, glycerol-d_5, and glycerol-$^{13}C_3$ for $B_1 = 0.4$ mT. The data for glycerol-d_0 are shown with their actual values, whereas the data for glycerol-d_5 were multiplied by the normalization factor 0.35 and the data for glycerol-$^{13}C_3$ by 0.74 in order to facilitate a comparison with glycerol-d_0.

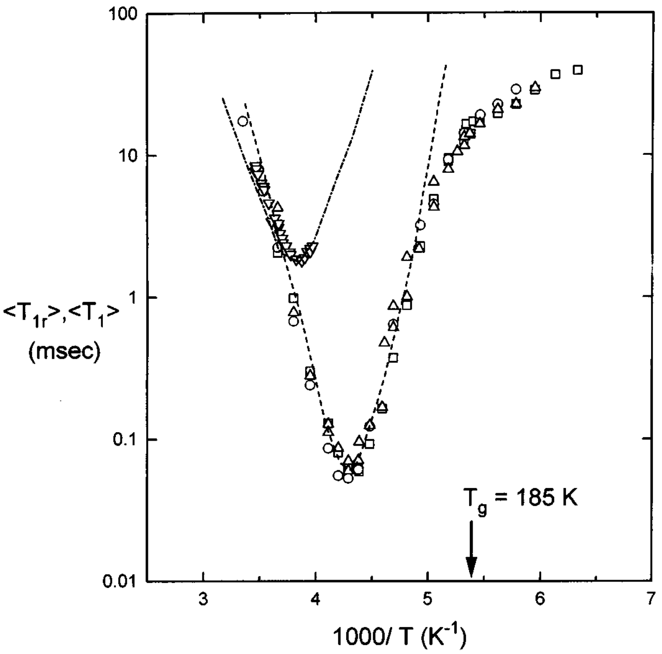

FIG. 3. Temperature dependence of ^{1}H $\langle T_{1r}\rangle$ values in glycerol-d_0 (△), in glycerol-d_5 (scaled) (□), and in glycerol-$^{13}C_3$ (scaled) (○) measured in a rotating field of amplitude $B_1=0.4$ mT. Also shown are ^{1}H $\langle T_1\rangle$ values in glycerol-d_0 measured at a Larmor frequency of 2 MHz (▽) (from Ref. 10). The dashed line is a theoretical fit of $\langle T_{1r}\rangle$ whereas the dot-dashed line is a theoretical fit of $\langle T_1\rangle$ using the same parameters.

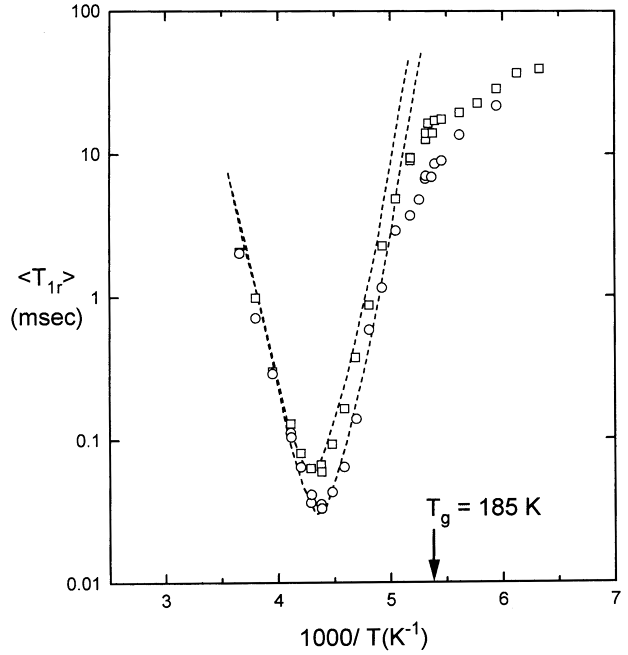

FIG. 4. Temperature dependence of ^{1}H $\langle T_{1r}\rangle$ values in glycerol-d_5 measured in rotating fields of amplitude $B_1=0.4$ mT (□) and $B_1=0.2$ mT (○). The dashed lines are theoretical fits.

From Fig. 3 one concludes that the time window of relaxation data, which spans approximately three decades, is now centered in a region that is more than three decades shorter than ^{2}H $\langle T_1\rangle$ values in the glass transition region. This expansion of the overall time window may be helpful in the characterization of the ergodic-nonergodic crossover. As in ^{2}H SLR, the data also exhibit the onset of a different regime below T_g with a much less pronounced temperature dependence. The combination of ^{2}H SLR data and ^{1}H RFSLR data confirms that this mechanism is inherent to the glass and not due to relaxation by phonons, in the ^{2}H case, or by paramagnetic impurities.

Although some slight systematic differences between the three different samples are apparent from Fig. 3, some conclusion can be drawn from the closeness of the data. As proposed earlier for a higher temperature range,[16] Fig. 3 also suggests that the motion of methylene proton-proton pairs, of proton-carbon pairs, and of hydroxyl-proton pairs must be correlated to some degree, since these are the dominating dipolar interactions in each case. Figure 3 also shows, for comparison, the temperature dependence of $\langle T_1\rangle$ for glycerol-d_0, near its minimum, at a Larmor frequency $\omega_0/2\pi=2$ MHz (from Ref. 10).

Figure 4 shows the temperature dependence of $\langle T_{1r}\rangle$ for glycerol-d_5 for $B_1=0.4$ and 0.2 mT. It appears that the B_1 dependence becomes somewhat less pronounced as one approaches T_g from the high-temperature side but that a considerable B_1-dependent relaxation still prevails below T_g.

Finally, Fig. 5 shows the stretching parameter β as a function of temperature in glycerol-d_0 at $B_1=0.4$ mT. For this value of B_1, $\langle T_{1r}\rangle$ values for glycerol-d_0 on the low-temperature sides of the minimum are almost identical to those of glycerol-d_5 at $B_1=0.2$ mT, the decrease in B_1 being compensated by the smaller dipolar local field in glycerol-d_5. This facilitates the discussion of the difference between Fig. 5 and Fig. 2 (bottom). It is apparent from Fig. 5 that the drop in β near T_g is absent but not the drop at $T_{\min}$ (B_1).

IV. DISCUSSION

The data presented in Sec. III reflect three different aspects of the molecular dynamics in glycerol that may be considered as a model hydrogen-bonded glass former. For $T>T_g$ one has to distinguish the following: first, the slowing down of molecular reorientation and bond breaking as the temperature is decreased and approaches T_g. As mentioned

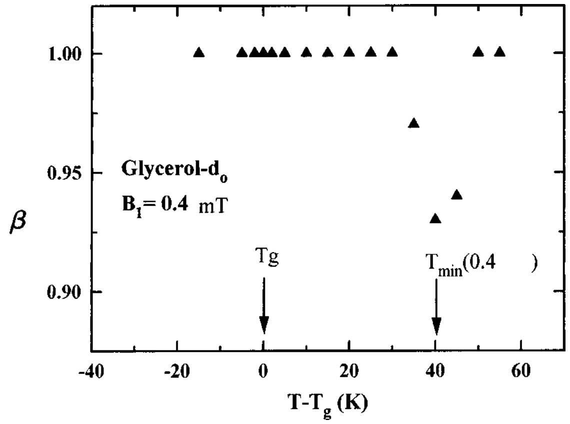

FIG. 5. Measured stretching exponent β as a function of temperature difference with respect to $T_g=185$ K in glycerol-d_0 for $B_1=0.4$ mT.

earlier in connection with Fig. 3, hydrogen bond making and breaking and molecular reorientation appear to be correlated to some degree. The relaxation can be described reasonably well by the temperature dependence of an average structural correlation time τ_0. Second, the increase in the lifetime of regions containing molecules with definite values of the structural correlation time τ and the crossover to nonergodic behavior in the vicinity of T_g.

Finally, for $T<T_g$, a different relaxation process becomes dominant. Although the mechanism does not seem to involve the fast motion predicted by MCT in the β regime, it appears to be intrinsic to the glassy state.

The first aspect mentioned above has been studied by several other techniques besides NMR, for example, by dielectric relaxation, which provides a very wide range of data. It is possible, in the case of glycerol, to correlate earlier measurements of ^{1}H SLR times $\langle T_1\rangle$, our RFSLR times $\langle T_{1r}\rangle$ of Sec. III, and dielectric relaxation data in a self-consistent manner.

Figure 3 shows the agreement between experimental data and calculated values of $\langle T_1\rangle$ and $\langle T_{1r}\rangle$ in glycerol-d_0 obtained from Eqs. (3) and (4), respectively, using the distribution function $g(\tau)$ of Eq. (7) and a value $[\langle 1/r_{ik}^6\rangle]^{1/6} = 1.98$ Å for both SLR and RFSLR. Given the simplifying assumptions about the model for the motion that lead to Eqs. (3) and (4), this value exhibits a known discrepancy,[12] with the value 1.71 Å calculated from proton-proton distances in glycerol.

The temperature dependence of the characteristic correlation time τ_0 was obtained directly from the inverse peak frequency of the imaginary part of the dielectric susceptibility of glycerol. The consistency of this procedure is checked in Fig. 6 where the measured inverse peak frequency of the imaginary part of the dielectric susceptibility of glycerol[22] is plotted together with values of τ_0 obtained from the position of minima of $\langle T_1\rangle$ and $\langle T_{1r}\rangle$ for various values of ω_0 (from Ref. 10) and B_1, respectively.

The good agreement between RFSLR and SLR data obtained through Eqs. (3) and (4), without any additional adjustable parameters, confirms that the same physical process, closely related to the one involved in dielectric relaxation for $T>T_g$, is responsible for both types of NMR relaxation mechanisms.

Figure 4 shows a fit of the experimental values of $\langle T_{1r}\rangle$ in glycerol-d_5 for two different values of B_1 calculated using Eqs. (4) and (7). The only change in relation to the fit of Fig. 3 was a value of $\langle 1/r_{ik}^6\rangle$ 2.86 times smaller than in glycerol-d_0. A smaller value of $\langle 1/r_{ik}^6\rangle$ is needed in this case because the distances in the dominating dipole-dipole interaction term involve protons that participate in hydrogen bonds. The value of the shortest proton-proton distance in glycerol-d_5 is not unambiguously determined by neutron diffraction studies but is expected to be larger than the 1.78 Å proton-proton distance in a methylene group, which dominates the dipolar interaction in glycerol-d_0. Recent *ab initio* molecular-orbital calculations of structure and vibrational spectra[35] suggest that intermolecular and intramolecular hydrogen bonding takes place in glycerol and that six-membered and twelve-membered O-H rings may be formed, with O-H distances of 1.87 and ~1.77 Å, respectively. Assuming a covalent O-H distance of 1.04 Å (Ref. 34) and, in the case of the inner six-membered ring,[35] right angles between the covalent O-H bond and the O-H hydrogen bond, one arrives at a proton-proton intermolecular distance of 2.14 Å. Thus, in a nearest-neighbor approximation, a ratio $(2.14/1.78)^6=3.0$ is obtained.

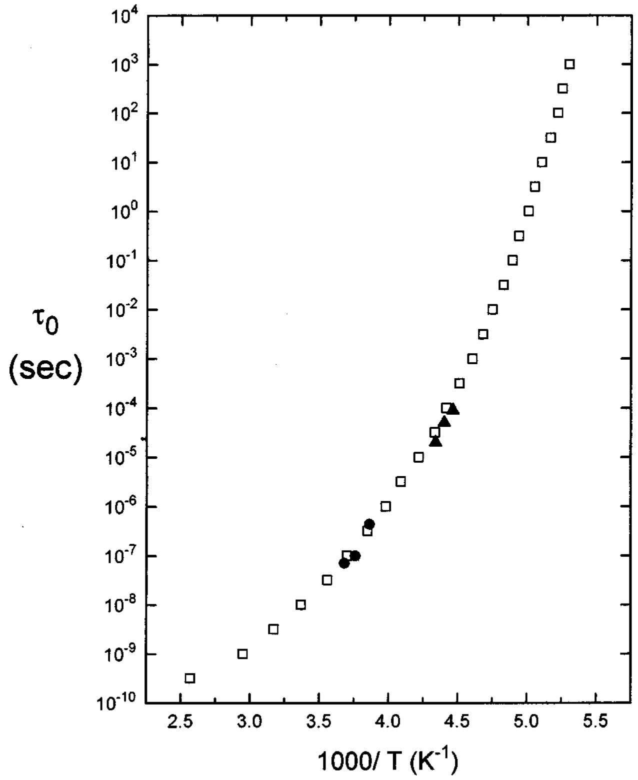

FIG. 6. Temperature dependence of the inverse peak frequency of the imaginary part of the dielectric susceptibility in glycerol (□) (from Ref. 22). Also shown are characteristic correlation times τ_0 calculated from values of $\omega_1 = B_1\gamma$ (with $B_1 = 0.1$, 0.2, and 0.4 mT) at the measured minima of $\langle T_{1r}\rangle$ for the given temperature (▲). Calculated values of τ_0 obtained from minima of $\langle T_1\rangle$ for various values of ω_0 (from Ref. 10) are also included (●).

Figure 4 furthermore suggests that the B_1 dependence of $\langle T_{1r}\rangle$ in glycerol-d_5 can also be explained by the same distribution function $g(\tau)$ of Eq. (7) as long as the temperature is higher than approximately 210 K. For temperatures in the range $185 < T < 210$ K it appears that this distribution function is no longer adequate.

The second aspect of the molecular dynamics depends not on the reorientation of single molecules but on the lifetime of regions containing many molecules where molecular reorientation takes place at a given rate. The data of Fig. 2, combined with earlier ^{2}H SLR measurements,[8] could be used to monitor the lifetime of these regions of localized motion over a wide time window.

The condition $\beta<1$ for glycerol-d_5 is seen in Fig. 2 to prevail near T_g indicating that the spin diffusion times are long compared with direct relaxation times at this temperature. However, since the spin-diffusion constant is expected to be temperature independent while the relaxation rate is still decreasing below T_g, a crossover to a regime where spin diffusion predominates over direct relaxation is expected to be reached for $T<T_g$. When this takes place, the

condition $\beta \sim 1$ should prevail as seen in Fig. 2 for $T < 170$ K. Thus, in the case of glycerol-d_5 for $T > T_g$, direct relaxation times in the rotating frame are expected to be short compared to spin-diffusion times.

From the arguments leading to Eq. (5) one is led to conclude that when the condition $\beta < 1$ prevails in this negligible spin-diffusion region, one must have $\langle \Gamma \rangle > \langle T_{1r} \rangle$. Here $\langle \Gamma \rangle$ should be interpreted as a characteristic lifetime of regions with values of the structural correlation τ in the vicinity of $1/\omega_1$. Since near T_g, the average correlation time τ_0 can be seen from Fig. 6 to be much larger than $1/\omega_1$, $\langle T_{1r} \rangle$ should be dominated by the wing of the distribution function $g(\tau)$ at $\tau = 1/\omega_1 \approx 9$ μsec (for $B_1 = 0.4$ mT), where the relaxation process is most efficient. The ^{1}H RFSLR data of Fig. 2 (top) suggest that as the temperature is decreased from $T_g + 30$ K, where the condition $\langle \Gamma \rangle < \langle T_{1r} \rangle$ is expected to hold, a temperature is reached when this condition is no longer satisfied. Hence, for $T = 187 \pm 1$ K, one should have $\langle \Gamma \rangle \approx \langle T_{1r} \rangle \approx 20$ msec.

The striking similarity between the data of Fig. 2 near T_g and ^{2}H SLR data deserves some comment. One is led to believe that the above arguments can be applied also to the nonergodic behavior of ^{2}H SLR.[8] In this case one would infer $\langle \Gamma' \rangle \approx 30$ sec for $T = 185 \pm 0.5$ K, where $\langle \Gamma' \rangle$ represents the lifetime of regions with structural correlation times, which in this case would be of order $1/\omega_0 \sim 0.003$ μsec. This conclusion raises some questions concerning the physical origin of the fluctuations that lead to a lifetime for these regions near T_g, a subject that has generated considerable debate. Although the origin of these fluctuations is not completely understood at present,[5] it is believed that the temperature dependence may be more closely related to the temperature dependence of $g(\tau)$ than to that of τ_0. ^{1}H RFSLR, combined with ^{2}H SLR as a function of frequency, in the vicinity of T_g, could in principle answer important questions concerning the nature of these fluctuations.

One is tempted to apply some of the above arguments also to the nonexponential behavior in β near $T_{\min}(0.4\,\mathrm{mT}) = 228\,K$ and $T_{\min}(0.2\,\mathrm{mT}) = 224$ K but such a procedure would be questionable. The nonexponentiality near $T_{\min}$ could be caused by other reasons. Assuming $B_1 > B_{\mathrm{loc}}$ the time required for the establishment of a spin temperature in the rotating frame is of the order of $1/\gamma B_{\mathrm{loc}}$, which for glycerol-$d_0$, for example, is approximately 25 μsec. On the other hand, the decay caused by spin-lattice effects has a time constant of only 90 μsec for $B_1 = 0.4$ mT at the minimum. Hence, the nonexponential decay could be caused by Zeeman-dipolar cross relaxation in the rotating frame.[33]

Below T_g the values of the stretching exponent for glycerol-d_5 approach the value $\beta = 1$ more rapidly than for ^{2}H SLR. This indicates that the crossover to the region where spin diffusion is significant occurs at a lower temperature in the case of ^{2}H SLR. A possible explanation may be that, in the case of ^{1}H RFSLR, the more difficult to fulfill condition for negligible spin diffusion may be violated when $\langle T_{1r} \rangle$ increases by just a factor of approximately 2 compared to its value at T_g.

The data of Fig. 5 support this interpretation. In glycerol-d_0 the measured values of $\langle T_{1r} \rangle$ at $B_1 = 0.4$ mT are almost identical to those of glycerol-d_5 at $B_1 = 0.2$ mT but the spin-diffusion constant is expected to be larger in glycerol-d_0 because of the shorter H-H distances. From Fig. 5 it appears that the nonergodic behavior near T_g is absent in the case of glycerol-d_0. This may be explained by the larger spin-diffusion constant, in the case of glycerol-d_0, which would shift the crossover to the spin-diffusion-dominated regime to a temperature higher than T_g, making unobservable the drop in β near T_g.

V. CONCLUSIONS

We conclude that ^{1}H RFSLR in selectively deuterated glycerol may be a sensitive tool to study the crossover from ergodic-to-nonergodic behavior that is believed to be a signature of the glass transition. For temperatures $T > 210$ K, RFSLR rates and their B_1 dependence are shown to be consistent with laboratory frame SLR data using the same distribution function and to accurately scale with dielectric relaxation data. The shift in the time window for RFSLR times by more than three decades compared with ^{2}H SLR, may reveal features of the glass transition.

ACKNOWLEDGMENTS

We wish to thank CNPq and FINEP (Brazilian agencies) for support.

---

[1] E. Leutheuser, Phys. Rev. A **29**, 2765 (1984).

[2] U. Bengtzelius, W. Götze, and A. Sjölander, J. Phys. C **17**, 5915 (1984).

[3] W. Götze in *Liquid Freezing and the Glass Transition*, edited by D. Levesque, J. P. Hansen, and J. Zinn-Justin (Elsevier, Amsterdam, 1991).

[4] F. Fujara, W. Petry, R. M. Diehl, W. Schnauss, and H. Sillescu, Europhys. Lett. **14**, 563 (1991).

[5] K. Schmidt-Rohr and H. W. Spiess, Phys. Rev. Lett. **66**, 3020 (1991).

[6] J. Leisen, K. Schmidt-Rohr, and H. W. Spiess, Physica A **201**, 79 (1993).

[7] Inês C. L. de Souza, Luiz G. Mendes, M. Engelsberg, and Ricardo E. de Souza, Chem. Phys. Lett. **264**, 584 (1997).

[8] W. Schnauss, F. Fujara, and H. Sillescu, J. Chem. Phys. **97**, 1378 (1992).

[9] K. Luszczynski, J. A. Kail, and J. G. Powles, Proc. Phys. Soc. London **75**, 243 (1960).

[10] F. Noack and G. Preissing, Z. Naturforsch. A **143**, 24A (1969).

[11] H. C. Torrey, Phys. Rev. **92**, 962 (1953).

[12] J. P. Kintzinger and M. D. Zeidler, Ber. Bunsenges. Phys. Chem. **77**, 98 (1973).

[13] P. W. Drake and R. Meister, J. Chem. Phys. **54**, 3046 (1971).

[14] L. J. Burnett and J. F. Harmon, J. Chem. Phys. **57**, 1293 (1972).

[15] L. J. Burnett and S. B. Roeder, J. Chem. Phys. **60**, 2420 (1974).

[16] M. Wolfe and J. Jonas, J. Chem. Phys. **71**, 3252 (1979).

[17] P. Bendel, J. Magn. Reson. **42**, 364 (1981).

[18] P. L. Kuhns and M. S. Conradi, J. Chem. Phys. **77**, 1771 (1982).

[19] E. Koivula, M. Punkkinen, W. H. Tanttila, and E. E. Ylinen, Phys. Rev. B **32**, 4556 (1985).

[20] W. Schnauss, F. Fujara, K. Hartmann, and H. Sillescu, Chem. Phys. Lett. **166**, 381 (1990).

[21] R. M. Diehl, F. Fujara, and H. Sillescu, Europhys. Lett. **13**, 257 (1990).

[22] P. K. Dixon, L. Wu, S. R. Nael, B. D. Williams, and J. P. Carini, Phys. Rev. Lett. **65**, 1108 (1990).

[23] J. Wuttke, J. Hernandez, G. Li, G. Goddens, H. Z. Cummins, F. Fujara, W. Petry, and H. Sillescu, Phys. Rev. Lett. **72**, 3052 (1994).

[24] S. Kojima, J. Mol. Struct. **294**, 193 (1993).

[25] T. Franosch, W. Götze, M. R. Mayr, and A. P. Singh, Phys. Rev. E **55**, 3183 (1997).

[26] N. O. Birge, Phys. Rev. B **34**, 1631 (1986).

[27] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, Oxford, 1961), Chap. VIII.

[28] D. C. Look and I. J. Lowe, J. Chem. Phys. **44**, 2995 (1966).

[29] J. R. Zimmermann and W. E. Brittin, J. Chem. Phys. **61**, 1328 (1957).

[30] M. Engelsberg, R. E. de Souza, and Hsu Chang, Phys. Rev. B **54**, 15 978 (1996).

[31] A. Abragan (Ref. 27), Chap. IX.

[32] C. P. Slichter, *Principles of Magnetic Resonance* (Springer, Berlin, 1980), Chap. 5.

[33] P. Mansfield and D. Ware, Phys. Rev. **168**, 318 (1968).

[34] D. C. Champeney and R. N. Joarder, Mol. Phys. **58**, 337 (1986).

[35] Takashi Uchino and Toshinobu Yoko, Science **273**, 480 (1996).