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Kinetic-freezing dynamics of the supercooled liquid state in 2-cyclooctylamino-5-nitropyridine

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The nature of the supercooled liquid state, namely, either a kinetic freezing phenomenon or an equilibrium glass phase transition, has been studied in the organic material [2-N-(cyclooctylamino)-5-nitropyridine] (COANP) and the results were compared to a deuteron glass phase of $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$ (DRADP-44). In partially deuterated COANP the ^1H line-shape analysis shows a continuous broadening of the spectrum on cooling that is typical for a slowing-down molecular dynamics where the thermal motions gradually freeze out. The motions are characterized by a nonexponential decay of the autocorrelation function. Two types of motion are involved in the freezing scenario. On cooling the isotropic molecular reorientations with the Vogel-Fulcher-type dynamics freeze first. This is followed by the freezing of the Arrhenius-type intramolecular motions. The kinetic-slowing down dynamics is observed also in the gradual broadening of the deuteron spectrum. In the low-temperature part of the supercooled phase the frozen-in molecular orientations result in a strongly disordered amorphous structure where all molecular orientations are equally probable. The corresponding deuteron static NMR spectral shape in the supercooled phase equals that of a crystalline powder. The degrees of static and dynamic disorder have been observed spectroscopically separated by the two-dimensional (2D) NMR separation of static and dynamic line-shapes technique. It is found that the glass disorder in the high-temperature part of the supercooled state is purely dynamic, exhibiting no static component. This is different from the deuteron glass phase in DRADP-44 where a similar 2D separation experiment has shown that the static component of the disorder is present in both the fast and the slow motion regimes. The asymmetric static ^{87}Rb line shape demonstrates that the glass disorder in DRADP-44 is weak and represents small deviations from the crystalline order. The supercooled state in COANP appears as a pure kinetic-freezing phenomenon when observed on the frequency scale of the NMR line shape. [S0163-1829(98)05702-6]

I. INTRODUCTION

Strongly disordered materials like glasses and supercooled melts are characterized by the lack of orientational and translational long-range order. The theories of magnetic spin glasses,[1] electric dipolar (pseudospin) glasses,[2] and quadrupolar[3] glasses predict the existence of a thermodynamic glass phase below the glass transition temperature T_g, determined experimentally from the cusp in the dielectric susceptibility. At still lower temperatures the glassy system undergoes a new kind of an ergodic-nonergodic phase transition at a freezing temperature T_f. Below T_f molecular reorientational and translational time constants become macroscopically long and the system cannot visit the whole phase space in a finite time so that the ergodicity is broken. The observation of the ergodic-nonergodic phase transition is however difficult as experimentally one monitors the glass phase with a finite frequency observation window of a given experimental technique and observes at least a part of the physical observables (such as random atomic displacements) static on the experimental time scale. In the presence of macroscopic molecular reorientation times it is thus in principle difficult to discriminate between the real thermodynamic glass phase transition and a kinetic slowing-down phenomenon, where the molecular glassy structure is observed static only because of the finite time scale of the measurement.

The same problem arises in the context of dynamics of another type of glassy structures, namely, the supercooled liquids and melts. These structures are less understood than the spin and pseudospin glasses due to a much higher complexity of the glass disorder. In a two-state spin glass (e.g., a magnetic spin glass or a H-bonded proton glass) the spin variables orient randomly between two possible orientations only, which simplifies the problem considerably. In spin glasses with a higher value of the spin number and in quadrupolar glasses the number of possible orientations is larger than two but still relatively small. In supercooled liquids, on the other hand, the possible molecular orientations form a quasicontinuum (e.g., all orientations on a sphere are in principle possible) and the theoretical approach is more involved. It has been known for a long time that some organic as well as inorganic compounds form extremely stable supercooled liquid states (e.g., ordinary window glasses, melts of salol, and Glauber salt solutions), which could be kept in the supercooled liquid state for a practically infinite time.[4] Interesting organic compounds forming stable supercooled liquid states have been discovered recently. These are the nonlinear optical materials COANP (Ref. 5) [2-N-(cyclooctylamino)-5-nitropyridine] and MBANP (Ref. 6) [(S)-2-N-α-(methylbenzylamino)-5-nitropyridine]. Chemically pure melts of these compounds do not show crystallization upon cooling below the melting point at cooling rates that are typical for differential scanning calorimetry (DSC) experiments (1–20 K/min). Even further cooling to much lower

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temperatures does not lead to crystallization. A crucial question is whether this disordered state results from a kinetic slowing-down molecular dynamics so that the state is metastable but with a macroscopically long lifetime or it results from a phase transition to a nonergodic thermodynamic state corresponding to a structural glass as in the case of spin, dipolar, and quadrupolar glasses.

In our previous work[7] on the NMR spin-lattice (T_1) and spin-spin (T_2) relaxation in COANP, the autocorrelation function $g_\omega(t)$ of the fluctuations of the deuteron electric-field gradient (EFG) tensor elements has been determined. $g_\omega(t)$ was found to be polydispersive and could be well approximated by the Kohlrausch-Williams-Watts (KWW) function[8]

$$g_\omega(t)=\exp\{-(t/\tau_c)^\alpha\}, \tag{1}$$

where α is the ''stretched'' exponent $(0<\alpha<1)$. The average autocorrelation time τ_c was found to be non-Arrhenius and the empirical Vogel-Fulcher modification

$$\tau_c=\tau_0\ \exp[E_0/k_B(T-T_0)] \tag{2}$$

described well the temperature dependencies of T_1 and T_2 using the Vogel-Fulcher temperature $T_0=239\,\mathrm{K}$ and $\alpha=0.55$. The polydispersity and the non-Arrhenius character of the relaxation is in agreement with the dielectric and second-harmonic measurements[9] where similar values of T_0 and α were found. The polydispersive nature appeared already in the liquid phase of COANP, in contrast to the ordinary liquids where the relaxation is strictly monodispersive $(\alpha=1)$. This demonstrates that correlations between molecules may play a significant role in the formation of the supercooled liquid state.

The NMR relaxation measurements provide an insight into the dynamics of the supercooled state but a conclusive microscopic picture cannot be made on that basis. The question remains which types of molecular motions play the dominant role in the formation and dynamics of the supercooled state. The motions considered are the translational and rotational diffusion of COANP molecules as rigid objects and the intramolecular motions of CH_2 groups of the octyl ring. It is not clear whether the diffusional motions are isotropic in space so that the slowing-down dynamics could result in an amorphouslike structure with all the frozen-in molecular orientations equally probable or the diffusion is anisotropic, so that a part of the crystalline order could still exist in the frozen-in supercooled state. To elucidate this question we performed a study of proton and deuteron one-dimensional (1D) and two-dimensional (2D) NMR line shapes in the selectively deuterated COANP (D-COANP). The proton line shape is determined predominantly by the secular part of the nuclear magnetic dipole-dipole interaction, whereas the deuteron line shape is determined by the electric quadrupole interaction. These two interactions are both traceless and are averaged to zero by a fast isotropic molecular motion in space, producing a complete motional narrowing of the NMR spectrum in the fast motion limit. If, on the other hand, the motion is anisotropic, only a part of the rigid lattice spectrum is motionally averaged. The question whether all frozen-in molecular orientations are equally probable or some of them are preferred, so that a certain degree of order still exists in the static limit is addressed by studying the shape of the static NMR spectrum. A complete lack of order (strong disorder) results in a static shape which equals that of a crystalline powder, whereas in case that the disorder represents small random deviations from a crystalline order (weak disorder) an asymmetric inhomogeneous line shape results. Another important question in the context of dynamics of the supercooled phase is whether the glass disorder is static or dynamic or both of them coexist on the experimental time scale. The degrees of static and dynamic orientational disorder have been determined by the 2D NMR separation of static and dynamic parts of the electric quadrupolar interaction of deuterons.

The 1D and 2D NMR results presented in this paper show that the supercooled liquid state in D-COANP is a pure kinetic slowing-down phenomenon. The resulting NMR line shape shows no static inhomogeneous broadening in the high-temperature part of the supercooled phase whereas in the low-T part the shape equals that of a crystalline powder. This demonstrates that all frozen-in molecular orientations are equally probable and the disorder is strong. The 2D experiment in the supercooled liquid phase of D-COANP is contrasted to the similar experiment in a proton glass $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$ (DRADP-44). There the asymmetric shape of the inhomogeneous NMR spectrum demonstrates that the disorder is weak. Random atomic displacements exhibit static components already at room temperature that is far above the nominal glass temperature $T_g\approx 90\,\mathrm{K}$, and the static disorder increases on cooling. By comparing the D-COANP and DRADP-44 results we show that the disorder in the proton glass phase is weak so that on a small scale (few unit cells) the structure looks ordered as in a crystal whereas the supercooled state exhibits a strong amorphouslike disorder with a complete lack of a crystalline order.

II. NMR LINE SHAPE IN THE GLASSY STATE

A. Static line shape

A general disordered state—here referred to as the glassy state—is characterized by the absence of a long-range order so that the surroundings of the molecules and the molecular geometry (i.e., bond angles and bond distances) vary from place to place. As a result, the NMR resonance frequency of a given type of nuclei also becomes space-dependent. We thus have in disordered systems an inhomogeneous frequency distribution $f(\omega)$ of resonance lines for each physically nonequivalent site in the sample instead of a few discrete homogeneous resonance lines of the physically inequivalent sites in the unit cell as in translationally invariant single crystals. For quadrupolar nuclei the disorder of the lattice is manifested in the fact that the EFG tensor varies randomly over the lattice sites so that the electric quadrupole interaction is smeared. The EFG tensor variation comes both from the differences in eigenvalues and orientations of the principal axes. In most cases however the dominant effect of the disorder is the rotation of the EFG tensor, whereas the eigenvalue changes are only minor so that the glass disorder is predominantly of the orientational character.

The static NMR spectrum exhibits different shapes in the cases of weak and strong disorder. Assuming an isotropic glass where the disorder can be described by a single scalar quantity $u(\mathbf{r})$ distributed by a distribution function $g(u)$ symmetric around $u=0$, one obtains in the weak disorder case an asymmetric static line shape.[10] In the strong disorder case, on the other hand, $u(\mathbf{r})$ can assume all possible values with equal probability so that the static line shape equals that of a crystalline powder.

B. Dynamic effects on the NMR line shape in the supercooled liquid state

In the supercooled liquid the NMR line shape is generally expected to be motionally averaged because of fast stochastic rotational and translational molecular motions. Fast isotropic motion averages to zero any traceless tensorial interaction like the secular part of the magnetic dipole-dipole interaction or the electric quadrupole interaction and produces a complete narrowing of the rigid lattice spectrum. An anisotropic motion produces on the other hand only partial narrowing of the rigid spectrum, reflecting the fact that not all of the tensor elements are averaged to zero. A study of the motionally narrowed spectrum provides a way to distinguish between the isotropic liquidlike motion and the motion in restricted geometries.

The line shape $I(\omega)$ is given by the Fourier transform of the free induction decay function $\widetilde{G}(t)$

$$I(\omega)=\int \widetilde{G}(t)e^{-i\omega t}dt. \tag{3}$$

Here

$$\widetilde{G}(t)=e^{i\omega_0 t}G(t)=e^{i\omega_0 t}\left\langle \exp\left[i\int_0^t \omega(t')dt'\right]\right\rangle, \tag{4}$$

with the brackets $\langle\ \rangle$ representing an average over the distribution of frequencies between which the resonance frequency randomly jumps. Following Abragam,[11] $G(t)$ can be expressed as

$$G(t)=\exp\{-\omega_p^2 Z(t)\}, \tag{5}$$

with

$$Z(t)=\int_0^t (t-\tau)g_\omega(\tau)d\tau. \tag{6}$$

Here ω_p^2 is the second moment of the resonance line for a rigid lattice and $g_\omega(\tau)$ is the reduced autocorrelation function for the frequency $\omega(t)$ of the fluctuating random fields

$$g_\omega(\tau)=\frac{\langle\omega(t)\omega(t-\tau)\rangle}{\omega_p^2}. \tag{7}$$

Since $\omega_p^2=\langle\omega^2\rangle$, we have $g_\omega(\tau=0)=1$.

In organic melts and polymer glasses[12] it has been many times observed that the loss of correlation expressed by $g_\omega(\tau)$ is strongly nonmonoexponential. The autocorrelation function can be in many cases approximated by the KWW stretched-exponential function of Eq. (1). In that case it is possible to obtain an analytic solution for $Z(t)$ (see Appendix)

$$Z(t)=\frac{\tau_c t}{\alpha}\,\gamma\left[\frac{1}{\alpha},\left(\frac{t}{\tau_c}\right)^{\alpha}\right]-\frac{\tau_c^2}{\alpha}\,\gamma\left[\frac{2}{\alpha},\left(\frac{t}{\tau_c}\right)^{\alpha}\right]. \tag{8}$$

Here γ represents the incomplete γ function that depends on the value of the stretched exponent α.

In the slow motion limit $[(t/\tau_c)^{\alpha}\ll 1]$ we get $Z(t)\approx t^2/2$, yielding a Gaussian line shape with the α-independent standard deviation ω_p,

$$G(t)\approx\exp\{-\tfrac{1}{2}\omega_p^2 t^2\}. \tag{9}$$

In the fast motion limit $[(t/\tau_c)^{\alpha}\gg 1]$ we get, on the other hand, $Z(t)\approx\tau_c t\Gamma(1/\alpha+1)$, where Γ is the complete γ function. This yields a Lorentzian line shape

$$G(t)\approx\exp\left\{-\omega_p^2\tau_c\Gamma\left(\frac{1}{\alpha}+1\right)t\right\}, \tag{10}$$

the width of which depends on the value of the stretched exponent α. Since in the fast motion limit $\tau_c\to 0$, the asymptotic Lorentzian line shape is infinitely narrow. Equation (5) can be adapted to yield a nonzero residual linewidth in this limit by splitting the second moment into two parts; $\omega_p^2=\omega_p'^2+\omega_p''^2$. Here only the $\omega_p'^2$ term is destroyed by the motion, whereas the $\omega_p''^2$ term represents the residual linewidth, originating from the interactions which are not averaged to zero by the motion. Experimentally this residual width is often determined by the external magnet inhomogeneity. Equation (5) can be now rewritten as

$$G(t)=\exp\{-\tfrac{1}{2}\omega_p''^2 t^2\}\exp\{-\omega_p'^2 Z(t)\}. \tag{11}$$

III. SEPARATION OF STATIC AND DYNAMIC DISORDER IN GLASSES BY 2D NMR

The question whether the glass disorder is static or dynamic on the time scale of the experiment can be resolved in an elegant way by the 2D NMR separation of inhomogeneous and homogeneous line-shapes technique.[13] The basic idea of separation of static and dynamic disorders lies in the fact that the nuclear spin precession in static local random electric and magnetic fields can be refocussed in a spin-echo experiment whereas the refocussing is not possible in dynamic randomly fluctuating fields. A general consequence of the glass disorder is a smearing of the tensorial interactions like the nuclear electric quadrupole interaction. Such an inhomogeneous interaction broadens the NMR absorption spectrum. In case that the glass disorder is static on the frequency scale of the experiment, the broadening is static inhomogeneous and directly reflects the static frequency distribution function $f(\omega)$. The free precession of spins in the static fields can be refocused into a spin echo by an appropriate rf pulse sequence. At the echo maximum the accumulated free precession angle over a well-defined time interval in the pulse sequence (the time between the first rf pulse in the two-pulse sequence and the echo top) is zero for all precessing spins. This time interval is labeled as t_1 and corresponds to the evolution period of the 2D experiment. The pulse sequence that refocuses the inhomogeneous electric quadrupole interaction for spin $I=1$ is the solid echo sequence $90_x-t_1/2-90_y-t_1/2-t_2$ whereas second-order quadrupole effects (e.g., central transition $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ of noninteger spins $I>1$) can be best refocused by the sequence $90_x - t_1/2 - 180_{x,y} - t_1/2 - t_2$. Since the precession under the static part of the quadrupole interaction is refocused in t_1, the effect of static disorder is not observed in the evolution period. The precession in randomly time-fluctuating fields can however not be refocused and is thus not eliminated in t_1. In the detection period (t_2) one acquires one half of the echo and the echo decay shape is determined by the full inhomogeneous interaction including static and dynamic parts of the quadrupole Hamiltonian.

The 2D NMR line shape shows in the ω_1 domain (conjugated to the t_1 time domain) the homogeneous line shape $L(\omega_1)$, determined by the dynamic part of the quadrupole interaction (here we neglect the effect of a much weaker magnetic dipolar interaction). The line shape in ω_2 domain is determined by the full (static plus dynamic) nuclear spin Hamiltonian. It represents the inhomogeneous spectrum $F(\omega_2)$ that is a convolution of the static frequency distribution function $f(\omega)$ and the dynamic (homogeneous) line shape $L(\omega)$

$$F(\omega_2)=\int f(\omega')L(\omega_2-\omega')d\omega'. \qquad (12)$$

In a 2D separation experiment the line shapes $L(\omega_1)$ and $F(\omega_2)$ appear in two orthogonal frequency domains and their deconvolution yields the pure static frequency distribution function $f(\omega)$. The static and dynamic disorder can be thus separated in a clear way. A high degree of static disorder manifests in the fact that the $F(\omega_2)$ line is much broader than $L(\omega_1)$ whereas the lack of static disorder results in equal shapes and widths of these two lines. Further mathematical details on this 2D NMR separation technique can be found in Ref. 13.

IV. EXPERIMENTAL OBSERVATION OF THE GLASS DISORDER IN SUPERCOOLED LIQUIDS AND STRUCTURAL GLASSES

The nature of the glass disorder has been studied experimentally in the supercooled liquid phase of D-COANP by proton and deuteron 1D line shape NMR and deuteron 2D separation of inhomogeneous and homogeneous line shapes NMR. The results are contrasted to the ^{87}Rb NMR in a proton glass $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$ (DRADP-44) where identical 2D separation experiment has been performed.

A. ^1H NMR line shape in the supercooled phase of D-COANP

D-COANP with the formula $C_{13}H_{18}DN_3O_2$ has been selectively deuterated in one of the nineteen hydrogen sites on the molecule, particularly at the site that makes a hydrogen bond N(2)-H-O(2) between two neighboring molecules when in the crystalline state.[5] Both NMR measurements of protons and deuterons have been performed on the same sample. To avoid the effects of crystallization during the experiment when the supercooled melt was left at room temperature for a long time, we heated the sample above the melting temperature $T_m \approx 72$ °C prior to any measurement. The crystallization did not occur during the measurements as could be verified visually—the supercooled melt is yellow transparent, whereas the crystallized substance is nontransparent.

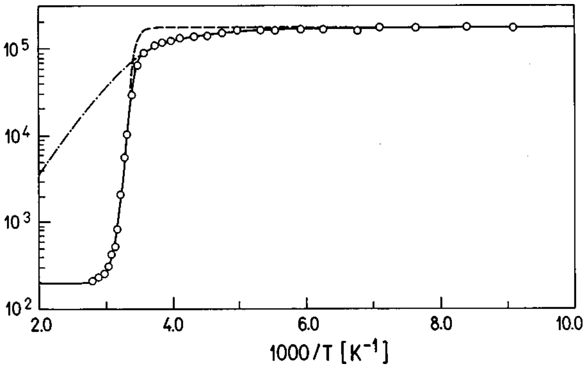

FIG. 1. Temperature dependence of the proton NMR linewidth [$\nu_0(^1H) = 86.1$ MHz] in the interval -170 °C$<T<82$ °C in D-COANP showing a motional transition from the fast to the slow motion limit. The fit (solid line) represents the Fourier transform of Eq. (11). The rigid lattice spectrum width is destroyed by two types of motion—the reorientational motion of molecules as rigid objects (dashed line) and the intramolecular motion (dash-dotted line).

^1H line shapes were measured at the Larmor frequency $\nu_L(^1H) = 86.1$ MHz from the paraphase through T_m down to -170 °C. The line shape was Gaussianlike in the whole temperature region with a strongly T-dependent width (Fig. 1). In the paraphase the line is narrow with the half width at half height (HWHH) of $\Delta\omega_{1/2} = 2\pi \times 27$ Hz. We verified that this residual width was determined by the inhomogeneity of our magnet. Below T_m the line starts to broaden continuously and reaches a plateau below -20 °C with the HWHH of $2\pi \times 26$ kHz so that the total change in width is a factor of 10^3. The static line shows a broad featureless Gaussian shape resulting from a dipolar interaction of eighteen coupled protons on a given molecule as well as from the intermolecular ^1H dipolar interactions. No anomaly is observed at the DSC-reported small anomaly in the specific heat at -10 °C. At this temperature, which is referred to as the glass temperature T_g, the reorientational part of the dielectric relaxation becomes infinitely long.[9] The behavior of the linewidth displayed in Fig. 1 is typical for a slowing-down dynamics of molecular motions. Two temperature regions can be identified. The rapid increase of the linewidth in the first region between T_m and about 15 °C is followed by a much slower increase in the second region between 15 °C and about -120 °C. Below that temperature the width remains constant and the spectrum is considered to be static on the NMR line shape scale. In the high-T region the narrow width above T_m changes rapidly on cooling and reaches the HWHH value of $2\pi \times 9$ kHz at 15 °C. This value is about one third of the low-T saturated value. The change for two orders of magnitude occurs on a temperature interval of $\Delta T \approx 40$ °C. Such temperature dependence of the linewidth can be induced by a motion which, when fast enough, averages the interproton dipolar interaction to zero. This interaction depends on the angular factor $1 - 3\cos^2\theta$ with θ being the angle between the internuclear vector and the external magnetic field. Only spatially isotropic motions can average the angular factor to zero. This linewidth transition indicates that the dynamics of the supercooled phase in the high-T interval is determined by the isotropic rotational diffusion of D-COANP molecules as rigid bodies. In the low-T region below 15 °C the linewidth change is much slower and the temperature dependence indicates that the associated motion is not capable of averaging the width to zero. This motion is thus anisotropic in space. On the other hand, this motion persists to considerably lower temperatures and can be associated with particles of smaller mass than in the high-T region. The dynamics in the low-T region is determined by the intramolecular motion of protons on octyl and phenyl rings of individual molecules. Due to confined geometry these motions are spatially anisotropic and can only reduce the linewidth but not destroy it to zero. The isotropic liquidlike tumbling of molecules as rigid bodies is however frozen-out in the low-T region.

The temperature dependence of the proton linewidth of Fig. 1 has been reproduced by Eq. (11). The fit of the HWHH has been made by assuming two types of motion with different temperature dependencies of their respective autocorrelation times. The isotropic liquidlike motion has been described by the Vogel-Fulcher form [Eq. (2)] of τ_c whereas the intramolecular motions were assumed to be of the Arrhenius type. The total autocorrelation time was taken in the form

$$\frac{1}{\tau_c}=\frac{1}{\tau_{\mathrm{VF}}}+\frac{1}{\tau_{\mathrm{Ar}}}=\frac{1}{\tau_0\ \exp[E_0/k_B(T-T_0)]}+\frac{1}{\tau_\infty\ \exp[E_a/k_BT]}. \tag{13}$$

This formula is a rather crude approximation as it treats the two types of motion as independent. Unfortunately, a satisfying theory that would describe the NMR relaxation of different but not independent motions still does not exist. The Vogel-Fulcher rate τ_{VF}^{-1} is nonzero for temperatures above the Vogel-Fulcher temperature T_0 whereas for $T<T_0$ this rate is taken to be zero, reflecting the fact that the associated motion is completely frozen out. Following the NMR relaxation results,[7] the autocorrelation function $g_\omega(\tau)$ was taken in the KWW stretched exponential form of Eq. (1). The linewidth at half height has been computed from the Fourier transform of the free-induction decay $G(t)$. The solid line in Fig. 1 represents the fit with both the reorientational and the intramolecular motions taken into account. The contribution of the isotropic reorientational diffusion to the total width is shown as a dashed line whereas the intramolecular contribution is represented by the dash-dot line. The following parameter values were obtained from the fit. The low- and high-T saturated values are determined by $\omega_p'=2\pi\times 23.0$ kHz and $\omega_p''=2\pi\times 27.2$ Hz. Here ω_p' is the second moment that is destroyed by the motion and ω_p'' is determined by the magnet inhomogeneity. The Vogel-Fulcher parameters describing the reorientational diffusion were obtained as $E_0=73.4$ meV, $\tau_0=4.41\times 10^{-13}$ s, and $T_0=239$ K. The Arrhenius parameters of the intramolecular motion were determined as $E_a=195.8$ meV and $\tau_\infty=1.42\times 10^{-9}$ s and the stretched exponent value $\alpha=0.55$ was used. Here the T_0 and α values were taken from the relaxation data[7] and since the fit was excellent with these values, they were not varied further in the fit procedure.

The above results allow to make the following conclusions about the dynamics of the supercooled phase in COANP. Two different types of motion are involved in the freezing scenario. On cooling below T_m the dynamics of the supercooled phase is first determined by the liquidlike tumbling of molecules as rigid bodies. As the temperature is decreased, the thermal energy needed to induce reorientations becomes insufficient and that motion gradually freezes out. After this motion is frozen-out the dynamics of the supercooled state is governed by the intramolecular motions. On further cooling these motions however also gradually freeze out so that the supercooled state is observed as completely frozen static on the NMR experimental scale below -100 °C. The polydispersive nature of the autocorrelation function ($\alpha<1$) demonstrates that the correlations between molecules may play an important role in the formation of the supercooled liquid state. The ^1H NMR line shape study observes the dynamics of the supercooled state in COANP as a kinetic slowing-down process where the thermally induced motions gradually freeze out and form a frozen-in glassy state at low temperatures. No trace of a kind of a structural phase transition at either the melting temperature T_m or the glassy temperature T_g has been observed on cooling. Here it should be mentioned that the DSC-determined T_g coincides rather accurately with the temperature at which the ^1H line shape starts to be observed as static.

B. 1D deuteron NMR line shape in the supercooled phase of D-COANP

In the proton NMR all the intramolecular and intermolecular ^1H interactions result in a broad featureless spectrum that is narrowed by the motion. A microscopic picture of the dynamics of the supercooled phase is thus not very site-specific. This deficiency is removed in the deuteron NMR. In D-COANP only one of the protons, namely, the one that forms a bond with the secondary amine N(2), is replaced by a deuteron. In the crystalline phase this deuteron forms an N-D...O bridge to the O(2) of the nitro group of an adjacent molecule. These bridges establish a connected network of COANP molecules and are thus located at the most sensitive sites with regard to the orientational disorder of the structure. Unlike the multiparticle ^1H magnetic dipole interaction, the deuteron electric quadrupole interaction is a single-particle interaction and the nuclear electric quadrupole moment interacts with the EFG of the surrounding ions and electrons. This EFG depends on the arrangement of the nearby ions so that the information obtained from the deuterons is much more site-specific than that from the protons. The glassy disorder results primarily in a distribution of the EFG tensor orientations. Since EFG is a traceless tensor, it is averaged to zero by a fast isotropic rotation whereas the averaging is incomplete in the case of an anisotropic motion. A study of the temperature-dependent deuteron spectrum thus provides another insight into the dynamics of the supercooled state.

In Fig. 2 the 1D deuteron spectra obtained at $\nu_L(^2H)=41.44$ MHz are displayed as a function of temperature. In the liquid phase above T_m the line shape is a narrow Lorentzian with the FWHH of about 1 kHz. This is a motionally averaged quadrupole-perturbed Zeeman spectrum, where the EFG is averaged to zero by the fast isotropic reorientations of the COANP molecules. Crossing T_m the motionally narrowed line starts to broaden and diminishes in intensity. The

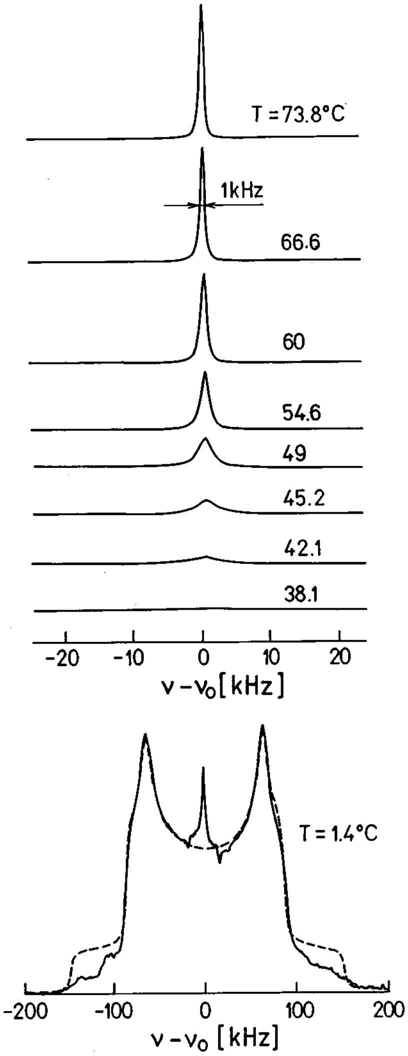

FIG. 2. Temperature dependence of the deuteron NMR spectrum of D-COANP in the supercooled state $[\nu_0(^2H) = 41.44\,\mathrm{MHz}]$. The line starts to broaden at the melting temperature $T_m = 72\ °\mathrm{C}$ and gradually disappears. Below room temperature a static deuteron spectrum is observed. The peak in the center of this spectrum is an artifact originating from the ringing of the resonance coil. The dashed line is a fit with an isotropic distribution of the EFG orientations (powder line shape). The fit parameters are $e^2qQ/h = 200$ kHz and $\eta = 0.15$.

line completely disappears at $T \approx 38\ °\mathrm{C}$. There is no trace of a static quadrupole spectrum in this part of the supercooled phase, showing that there is no static EFG tensor component present and the glass disorder is purely dynamic. Just below 38 °C the deuteron spectrum cannot be recorded but it reappears again below the room temperature, where a typical $I = 1$ powder pattern for the asymmetry parameter $\eta \approx 0.15$ is observed with the width of more than 200 kHz. The gradual disappearance of the narrow line and the reappearance of a broad powder spectrum is typical for a motional slowing-down process and is in complete agreement with the ^1H line-shape data. Like protons, the deuterons also see the dynamics of the supercooled phase as a pure kinetic-freezing process. The fact that the line shape in the slow motion limit equals that of a powder specimen shows that all the EFG orientations are equally probable as in a crystalline powder sample. COANP was however still in the supercooled phase as verified optically. The powder line shape demonstrates that the glass disorder in the low-temperature part of the supercooled liquid phase is strong and static on the deuteron NMR line-shape frequency scale and the supercooled phase cannot be discriminated from a crystalline powder by NMR.

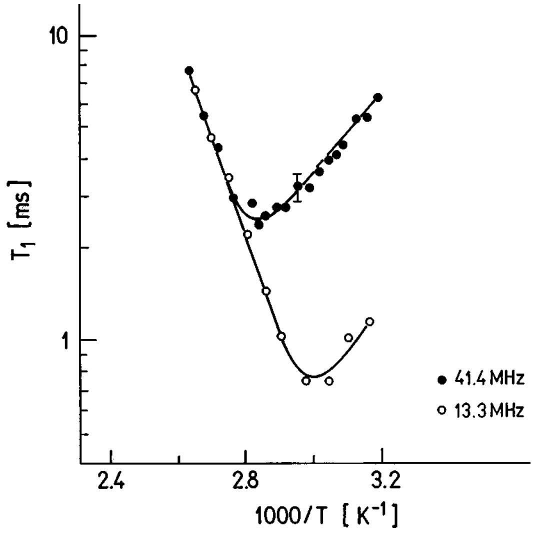

FIG. 3. Temperature dependence of the deuteron NMR spin-lattice relaxation time T_1 in D-COANP at two Larmor frequencies 41.4 and 13.3 MHz. Solid lines are guides for the eye.

The slowing-down dynamics of the supercooled phase is also evident from the deuteron spin-lattice relaxation measurements (Fig. 3). T_1 has been measured at two Larmor frequencies $\nu_L = 41.44$ and 13.3 MHz. A BPP-like minimum is observed in both cases. At 41.44 MHz the minimum occurs in the paraphase at $T = 79\ °\mathrm{C}$, whereas at 13.3 MHz it is shifted down into the supercooled phase where it occurs at $T = 60\ °\mathrm{C}$. At the minimum $(\omega_L \tau_c = 1)$ the internal motional frequencies equal the nuclear Larmor frequency $(\sim 10^7\ \mathrm{s}^{-1})$. The appearance of a minimum thus demonstrates the slowing-down molecular dynamics.

C. 2D deuteron NMR separation of static and dynamic disorder in D-COANP

The most direct observation of the static and dynamic parts of the glass disorder in the supercooled phase can be made by the 2D separation NMR technique. The separation of inhomogeneous and homogeneous deuteron spectra in D-COANP has been made in the temperature range $43\ °\mathrm{C} \leqslant T \leqslant 72\ °\mathrm{C}$, corresponding to the fast motion regime of the supercooled phase. The pulse sequence used was the solid echo sequence $90_x - t_1/2 - 90_y - t_1/2 - t_2$. The 2D spectra are shown in Fig. 4. The ω_2 domain shows the inhomogeneous line shape $F(\omega_2)$ [Eq. (12)], including the static and dynamic parts of the interaction. The ω_1 domain shows the homogeneous line shape $L(\omega_1)$ showing the dynamic part of the disorder only. In both frequency domains the magnetic dipole interaction also contributes to the line broadening, but this effect is negligible as compared to that of the electric quadrupole interaction. In Fig. 4 it is seen that the 2D spectrum at 72 °C (still in the liquid phase) is narrow and shows

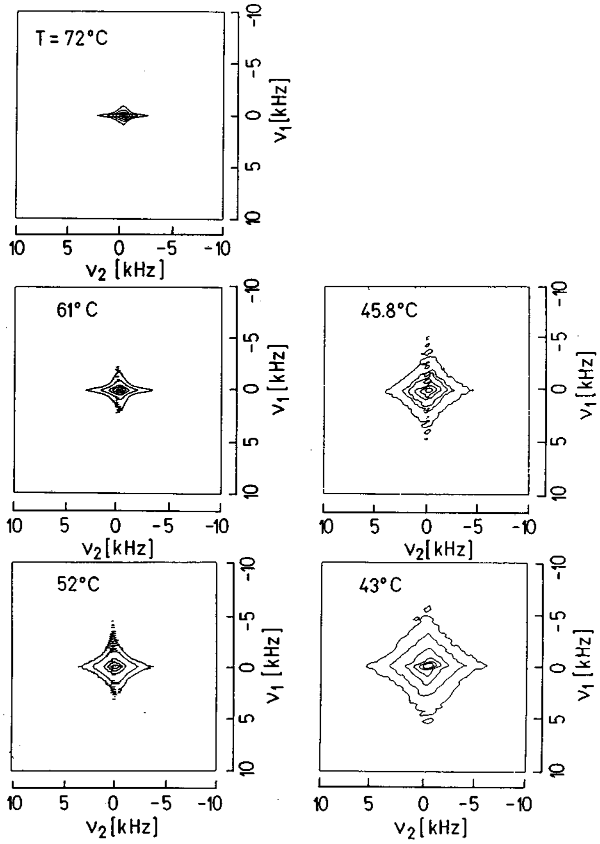

FIG. 4. 2D deuteron spectra of D-COANP with the separated inhomogeneous and homogeneous lines in two orthogonal frequency domains $[\nu_0(^2H) = 41.44$ MHz]. The inhomogeneous line, showing both static and dynamic parts of the electric quadrupole interaction, appears in the ω_2 domain. The homogeneous line is determined by the dynamic randomly fluctuating part of this interaction and appears in the ω_1 domain. In the supercooled phase both lines have equal widths and form squarelike contours (note that both frequency axes have equal magnitudes). This demonstrates that no static disorder is present in the investigated temperature range.

slightly broader line in the inhomogeneous domain. In the supercooled phase the spectra start to broaden and have equal widths in both frequency domains so that the 2D contour plots show a squarelike shape. The fact that the inhomogeneous and homogeneous line shapes have equal widths demonstrates that there is no static disorder present in the investigated part of the supercooled phase. In the presence of the static disorder the inhomogeneous line would be much broader than the homogeneous one. Both line shapes are homogeneously broadened only by the fluctuating EFG tensor elements originating from molecular motions that are fast enough to average the traceless static EFG tensor to zero. The glass disorder in this temperature interval of the supercooled phase is thus purely dynamic. In the following this result will be contrasted to an equivalent experiment in a proton glass DRADP-44.

D. ^{87}Rb 2D NMR separation of static and dynamic disorder in DRADP-44

A similar 2D separation NMR experiment has been performed also in the glass phase of the deuteron glass compound DRADP-44 on ^{87}Rb nuclei. The pulse sequence used to refocus the second-order quadrupole shifts of the central transition ($\frac{1}{2} \leftrightarrow -\frac{1}{2}$) in the evolution period was $90_x - t_1/2 - 180_y - t_1/2 - t_2$. A monocrystal sample was placed in the external magnetic field at an orientation $c \| H_0$. In Fig. 5 contour plots of the 2D spectra in the interval between room temperature and 33 K are shown. In Fig. 6(a) the 1D inhomogeneous lines (the crossections of the 2D spectra along ω_2 at the position $\omega_1 = 0$) are displayed, whereas in Fig. 6(b) the homogeneous lines (the crossections along ω_1 through the center of the line) are shown. It is observed that the inhomogeneous lines are much broader than the homogeneous ones in the whole investigated range (note the difference in the magnitude of ω_1 and ω_2 scales in the 2D spec-

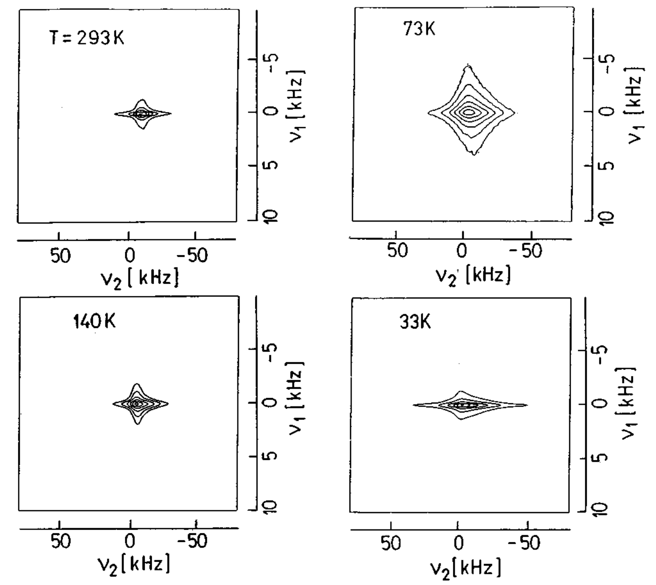

FIG. 5. ^{87}Rb 2D NMR spectra (central transition) of a proton glass DRADP-44 between 293 and 33 K with the separated inhomogeneous (ω_2) and homogeneous (ω_1) lines [orientation $c \| H_0, \nu_0(^{87}\text{Rb}) = 88.34$ MHz]. The large difference in linewidths (note the difference in the magnitudes of ω_1 and ω_2 scales) demonstrates that a static component of disorder exists.

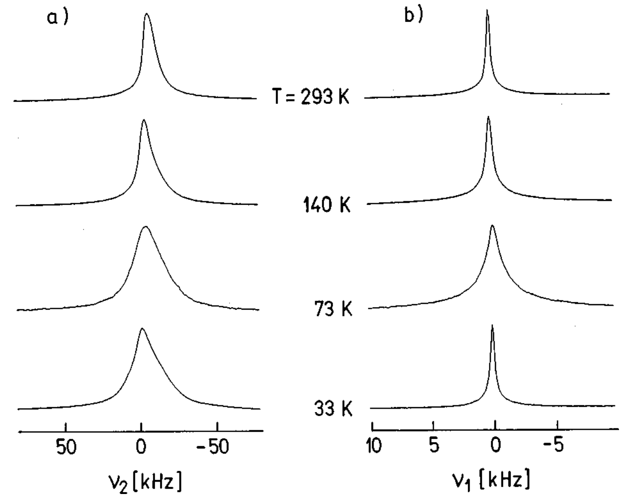

FIG. 6. Temperature dependence of the (a) inhomogeneous line and (b) the homogeneous line obtained from the spectra of Fig. 5.

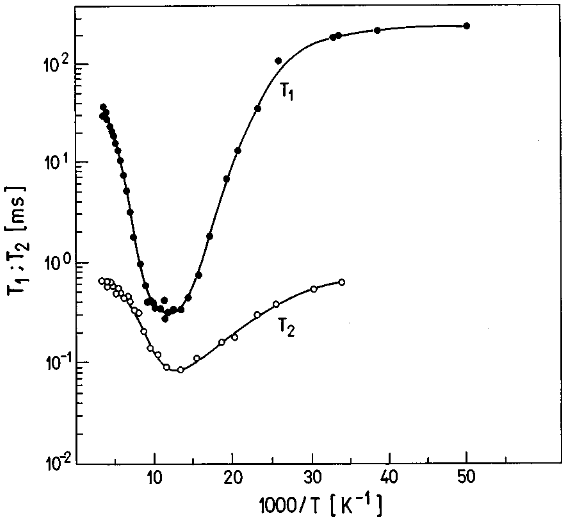

FIG. 7. Temperature dependence of the ^{87}Rb spin-lattice relaxation time T_1 and spin-spin relaxation time T_2 in DRADP-44 at $c \| H_0$ between room temperature and 20 K.

tra). The inhomogeneous line $F(\omega_2)$ shows a strongly asymmetric shape with a FWHH of 10 kHz at $T = 293$ K, whereas the homogeneous line $L(\omega_1)$ is a Lorentzian with a much smaller FWHH of 600 Hz. By lowering the temperature the inhomogeneous line continuously broadens and reaches the FWHH of 25 kHz at $T = 33$ K. The homogeneous line, however, exhibits a different behavior. Its width increases slowly from the room temperature value of 600 Hz down to the temperature of the minimum in the spin-lattice relaxation time T_1 at $T = 85$ K (Fig. 7) where a maximum FWHH of 1900 Hz is reached. Below that temperature the homogeneous line narrows again, reaching the value of 1000 Hz at 33 K. The maximum in the homogeneous line width has been confirmed also by the observed minimum in the temperature dependence of the spin-spin relaxation time T_2 [FWHH$=(\pi T_2)^{-1}$ for a Lorentzian line] using the Hahn-echo experiment (Fig. 7). Since the minima in T_1 and T_2 occur at the same temperature it seems a reasonable explanation that the homogeneous linewidth maximum is a consequence of a lifetime broadening.

Similar to the situation in the supercooled D-COANP, a broad BPP-like minimum in the ^{87}Rb spin-lattice relaxation time T_1 is observed also in DRADP-44, reflecting the gradual slowing-down dynamics of the internal molecular motions. The ^{87}Rb 2D line shape however shows a pronounced difference. There exists a large difference in widths of the inhomogeneous and homogeneous line shapes in the whole temperature range. The inhomogeneous-to-homogeneous linewidth ratio is found to be a factor of 16 already at room temperature, which is far above the glass temperature $T_g \approx 90$ K in this system. This ratio increases to 25 at 33 K. The inhomogeneous line shape is strongly asymmetric, which shows that the glass disorder is weak, representing only small deviations from the perfect crystalline order. The large difference in the inhomogeneous and homogeneous widths demonstrates that a large component of the glass disorder is static on the NMR line-shape scale. Since this effect is observed already in the fast motion limit (high above the T_1 minimum), this static component is present at all temperatures.

A comparison between the glass phases in the supercooled D-COANP and the proton glass DRADP-44 yields the following conclusions. In D-COANP the glass disorder in the fast motion limit is purely dynamic, whereas in the slow motion limit the degree of disorder is strong with all frozen-in molecular orientations being equally probable. In contrast, in the deuteron glass DRADP-44 a component of the static glass disorder exists at all temperatures and the degree of static disorder increases on going from the fast to the slow motion regime. The disorder is weak and can be described as a small deviation from the perfect crystalline order.

V. CONCLUSIONS

The nature of the supercooled liquid state has been studied in the organic material D-COANP and the results were compared to the deuteron glass state in DRADP-44. 1D NMR line-shape analysis allows for a discrimination between the cases of weak and strong glass disorder. 2D NMR separation technique allows for an independent spectroscopic observation of the static and dynamic components of the glass disorder on the frequency scale of the NMR line-shape experiment. ^1H line-shape analysis in the supercooled phase of D-COANP has shown on cooling a continuous transition from a narrow to a broad single line spectrum, typical for the slowing-down molecular dynamics where the thermal motions gradually freeze out on cooling. These motions are characterized by a distribution of correlation times and the corresponding autocorrelation function can be well described by a stretched exponential form. Two types of motion are involved in the freezing scenario. The dynamics of the supercooled liquid phase is first dominated by the isotropic reorientational diffusion of molecules as rigid bodies that follows the Vogel-Fulcher law. After this motion freezes out, the dynamics is determined by the Arrhenius-type intramolecular motions that slow down on further cooling and freeze out on the experimental time scale at still lower temperatures. The kinetic slowing-down molecular dynamics is observed also in the deuteron 1D spectrum, which on cooling shows a gradual transformation from a narrow Lorentzian shape to a broad spectrum, the shape of which equals that of a crystalline powder. This powder spectrum is characteristic for solid structures where all frozen-in molecular orientations are equally probable. Such a situation is realized in both the frozen supercooled state and in the crystalline powder so that these two cases cannot be discriminated on the basis of the static NMR line shape. The degree of glass disorder in the supercooled phase is thus strong and the frozen-in molecular orientations in the static limit result in an amorphous structure. The degrees of static and dynamic disorder have been observed spectroscopically separated in the high-T part of the supercooled phase by the 2D deuteron NMR separation of static (inhomogeneous) and dynamic (homogeneous) line shapes. It is observed that the static part of the electric quadrupole interaction is averaged out completely by the isotropic molecular motions in that temperature region so that the glass disorder has there no static component on the frequency scale of the deuteron line shape. This is different from the situation in the deuteron glass phase in DRADP-44 where a similar 2D separation experiment on ^{87}Rb nuclei has shown that the static component of the glass disorder is present in both the fast and the slow motion regimes. The static inhomogeneous ^{87}Rb 1D spectrum shows an asymmetric shape typical for the case of weak disorder where the glass deviations from the crystalline order are small.

The above results demonstrate that the frozen-in supercooled state in D-COANP is a pure kinetic phenomenon. No anomalies in any of the NMR observable physical parameters have been observed in the whole investigated temperature range. This indicates the absence of an equilibrium phase transition when the system is observed on the frequency scale of the NMR line shape. Since this scale lies in the kHz range, the measurements are in principle insensitive to dynamic processes with slower time constants. Orders of magnitude slower processes are evidently present in the supercooled phase of D-COANP as demonstrated by the spontaneous crystallization which starts after several hours or days when the supercooled melt is left at, e.g., room temperature. Such slow dynamical processes are however difficult to observe in a coherent way by the spectroscopic techniques.

ACKNOWLEDGMENTS

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APPENDIX

We derive here an analytical expression for the free-induction decay envelope $G(t)$ given by Eqs. (5) and (6) for the case that the autocorrelation function $g_\omega(\tau)$ has a stretched-exponential form of Eq. (1). The integral $Z(t)$ is written as

$$Z(t)=\int_0^t (t-\tau)\exp\{-(\tau/\tau_c)^\alpha\}d\tau. \tag{A1}$$

Using a new variable $y=(\tau/\tau_c)^\alpha$, this equation transforms into

$$Z(t)=\frac{\tau_c t}{\alpha}\int_0^{(t/\tau_c)^\alpha} e^{-y}y^{1/\alpha-1}dy-\frac{\tau_c^2}{\alpha}\int_0^{(t/\tau_c)^\alpha} e^{-y}y^{2/\alpha-1}dy. \tag{A2}$$

The integrals in the above equation represent the incomplete γ functions defined as

$$\gamma(a,x)=\int_0^x e^{-t}t^{a-1}dt, \tag{A3}$$

so that $Z(t)$ can be rewritten as

$$Z(t)=\frac{\tau_c t}{\alpha}\,\gamma\left[\frac{1}{\alpha},\left(\frac{t}{\tau_c}\right)^\alpha\right]-\frac{\tau_c^2}{\alpha}\,\gamma\left[\frac{2}{\alpha},\left(\frac{t}{\tau_c}\right)^\alpha\right]. \tag{A4}$$

$Z(t)$ is thus an analytical function of the parameters τ_c and α.

It is instructive to calculate the free-induction decay envelope $G(t)$ for the limiting cases of fast and slow molecular motions on the NMR line-shape frequency scale. In the slow motion limit $[(t/\tau_c)^\alpha \ll 1]$ the exponential factor in Eq. (A2) can be expanded into $e^{-y}\approx 1-y$. The integrals are then easy to perform yielding

$$Z(t)=\frac{t^2}{2}\left[1-\frac{2}{(2+\alpha)(1+\alpha)}\left(\frac{t}{\tau_c}\right)^\alpha\right]. \tag{A5}$$

The second term in the bracket can be neglected with respect to 1 so that $G(t)$ becomes

$$G(t)\approx\exp\{-\tfrac{1}{2}\omega_p^2t^2\}. \tag{A6}$$

The resulting line shape is Gaussian with the α-independent standard deviation ω_p.

In the fast motion limit $[(t/\tau_c)^\alpha \gg 1]$ we can extend the upper integration limit in Eq. (A2) to infinity. The integrals now become the complete γ functions

$$\Gamma(a)=\int_0^\infty e^{-t}t^{a-1}dt \tag{A7}$$

yielding

$$Z(t)=\frac{\tau_c^2}{\alpha}\left[\frac{t}{\tau_c}\Gamma\left(\frac{1}{\alpha}\right)-\Gamma\left(\frac{2}{\alpha}\right)\right]\approx\tau_c t\,\Gamma\left(\frac{1}{\alpha}+1\right). \tag{A8}$$

The free-induction decay is obtained in the form

$$G(t)=\exp\left\{-\omega_p^2\tau_c\Gamma\left(\frac{1}{\alpha}+1\right)t\right\}, \tag{A9}$$

which results in a Lorentzian line shape with the half width at half height $\Delta\omega_{1/2}=\omega_p^2\tau_c\Gamma(1/\alpha+1)$, depending on the value of the stretched exponent α. The case of a monoexponential relaxation $(\alpha=1)$ is recovered by using the equality $\Gamma(2)=1$.

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