Time-resolved optical Kerr effect in a fragile glass-forming liquid, salol

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We report an optical Kerr effect experiment, performed on liquid and supercooled liquid salol, in order to test some predictions of the mode-coupling theory of the liquid-glass transition. We show that this experiment is sensitive mostly to the reorientational motion of the molecules and the corresponding correlation function exhibits, above the critical temperature T_C, a von Schweidler relaxation followed by an α relaxation regime. The critical temperature and the critical exponent derived from the analysis of the experiment are in good agreement with the same quantities previously determined, in the frequency domain, through a depolarized light-scattering experiment, by Li *et al.* [Phys. Rev. B **46**, 3343 (1992)]. [S1063-651X(98)04702-3]

I. INTRODUCTION

The liquid-glass transition of fragile molecular glass-forming liquids has been studied, during the past ten years, by a large variety of experimental techniques such as incoherent and coherent quasielastic neutron scattering (QENS) [1–3], polarized [4,5] and depolarized light scattering (DLS) [6–8], and dielectric measurements [9,10] as well as through molecular-dynamics (MD) computations [11]. Many of those experiments and/or computations have aimed at testing the scheme, proposed by the mode-coupling theory (MCT) [12(a)], of an unattained dynamical transition at some temperature T_C, always higher than the thermodynamical glass transition T_g. Indeed, in its ideal version, this theory predicts the freezing, at temperature T_C, of any density fluctuation whatever its wave vector, while other dynamical processes, not taken into account in the ideal MCT, always restore ergodicity below T_C. This theory makes in particular specific predictions for the dynamics of the density fluctuations above T_C. In the vicinity of that temperature, these fluctuations, after a short-time dynamics (in the picosecond range), enter a relaxation process, itself divided into two parts: an intermediate regime, or β relaxation process, followed by a long time, or α relaxation process. In the latter, the normalized space Fourier transform of the correlation function of the density fluctuations decays as

$$\phi_q(t) = f_c^q \exp\{-[t/\tau_\alpha(q)]^\beta\}. \quad (1)$$

A complete description of the β process, which follows a universal dynamics, can be found in [12(b)]. For our purpose, it is sufficient to recall that it may be characterized, at each temperature, by a β relaxation time τ_e, $\phi_q(t) - f_c^q$, following the two scaling laws

$$\phi_q(t) - f_c^q = (T - T_C)^{1/2} h_q(t/\tau_e)^{-a} \quad \text{for } t \ll \tau_e, \quad (2a)$$

$$\phi_q(t) - f_c^q = -(T - T_C)^{1/2} h_q(t/\tau_e)^b \quad \text{for } t \gg \tau_e, \quad (2b)$$

where h_q is a smooth function of the temperature and a and b are two correlated positive numbers, temperature and wave-vector independent. Moreover, τ_e, which is also wave-vector independent, is proportional to $(T - T_C)^{-1/2a}$ while τ_α diverges as $(T - T_C)^{-\gamma}$, with $\gamma = (1/2a + 1/2b)$. Finally, the coefficient β_q is bounded by the two inequalities $b < \beta_q < 1$.

These predictions have been largely substantiated by MD computations performed, for instance, on a mixture of two types of Lennard-Jones particles [11] and also by experiments made on some colloidal systems [13]. Nevertheless, those cases may be partly pathological. Experimentalists have thus tried to test those predictions on real glass-forming liquids; molecular liquids have appeared to be good candidates for such tests because MCT is a theory built up for atomic fluids, for which molecular fluids may be considered a possible approximation. However, one requires a very large dynamical range in order to check simultaneously the three different dynamical regimes, which strongly limits the possible experimental techniques. In particular, to check properly the consistency between the α and the β relaxation regimes in a neutron-scattering experiment, one needs to Fourier transform the β relaxation data, obtained in the frequency regime on a time-of-flight machine, in order to compare them with the α relaxation data obtained with a spin-echo machine. This has been done, e.g., on orthoterphenyl (OTP) by Petry *et al.* [3]. In order to avoid the technical uncertainties related to such a Fourier transform method, one has alternatively used the DLS technique that allows one to record, through a combination of various instruments, the entire dynamics in the frequency space, at least in some temperature range close to T_C.

Through this technique, one obtains the imaginary part of a susceptibility function, the DLS $\chi''(\omega)$. This function exhibits a two-peak structure: one at low frequency, related to the α relaxation process, and a second at high frequency created by the microscopic motion of the particles of the fluid, these two regions being separated by a minimum. The vicinity of this minimum should correspond to the β relaxation regime, for which $\chi''(\omega)$ can be approximated by

$$\chi''(\omega) = \chi_{\min} \frac{a(\omega\tau_e)^{-b} + b(\omega\tau_e)^a}{a+b}. \quad (3)$$

Such experiments have been performed on a variety of fragile glass-forming liquids, including an ionic salt mixture 0.4 Ca(NO$_3$)$_2$, 0.6 KNO$_3$ [6] and some molecular liquids such as salol [7], OTP [8], or metatoluidine [14]. The analysis of these experiments has yielded values for a, b, and T_C, consistent with MCT: This means that the correct relationship between a and b is fulfilled and that, with the help of these three quantities, it is possible to describe simultaneously $\chi''(\omega)$ in the vicinity of its minimum [Eq. (3)], the thermal behavior of the value of this minimum $\chi_{\min}$, as well as $\tau_e(T)$ and $\tau_\alpha(T)$. Unfortunately, there is a basic problem with the DLS technique, namely, the difficulty of making precise the light-scattering mechanisms responsible for these spectra. Indeed, in molecular liquids composed of optically anisotropic molecules, two different mechanisms may give rise to such spectra. One is the rotation of the molecules, which induces a local change of the susceptibility tensor of the liquid. A second one is the dipole-induced-dipole (DID) mechanism, which originates from the fact that each molecule is polarized not only by the electric field, at frequency ω, of the laser with which the experiment is performed, but also by the dipoles created on all other molecules by the same laser electric field. In the absence of a molecular polarizability anisotropy, only the second mechanism exists and the spectrum reflects only the motion of the center of mass; vice versa, when the isotropic part of the polarisability tensor is small with respect to its anisotropic part, one detects only the molecular orientation motions. But when both effects are comparable in magnitude, the situation is complex and it is *a priori* difficult to disentangle the two types of effects and to distinguish between the types of motions. Numerical comparisons between the integrated intensities produced by the two individual effects have shown that as soon as the polarizability anisotropy is not negligible, its integrated intensity is much larger than the one produced by the DID effect related to the center of mass motion and to the isotropic part of the polarizability tensor; the measurements of these integrated intensities in some molecular liquids have shown that their values are in fact close to what would be predicted by the rotational effect alone [15]. Also, a measurement performed on a glass-forming liquid, salol, diluted in CCl$_4$ showed [15(a)] that the extra susceptibility induced by the diluted salol molecules exhibited the same two-peak structure as seen in pure salol. It was then tentatively deduced from that experiment that the total DLS spectrum originated from the molecular reorientation process. Because the MCT of a monomolecular liquid [16] shows that both the correlation functions for the center of mass and for the reorientation motion should exhibit, in the vicinity of T_C, the same three different dynamical regimes, with the same a and b coefficients, the DLS experiments may be considered as good tests of MCT, provided one assumes that the spectrum totally originates from the rotational motion.

Such a point of view may be criticized because, e.g., in salol and in metatoluidine, the largest contribution to the integrated intensity comes from the low-frequency part of the spectrum. It is thus *a priori* possible that the α peak would originate from the reorientation motion, while the high-frequency part could predominantly arise from the center of mass motion; a recent comparison between the DLS and the QENS spectra of OTP [17] suggests that this may be the case in that liquid. Because the microscopic peak of the

susceptibility is affected very little by the freezing mechanism, while the frequency of the maximum of the α relaxation process strongly decreases with temperature, a minimum in the DLS $\chi''(\omega)$ could take place *even if the MCT prediction of such a minimum would be incorrect*. Indeed, even if the center-of-mass motion exhibited no, or a negligible, α relaxation process, while the orientational motion susceptibility function had no high-frequency maximum, a minimum in the susceptibility spectra would still appear as the sole consequence of an increasing separation between the two peaks upon cooling.

Within such a model, it is worthwhile to the shape of the susceptibility curve below its minimum: There is general agreement for the description of the α relaxation processes as a stretched exponential or Kolhrausch-Williams-Watt (KWW) function [Eq. (1)]. A first-order development of the exponential shows that the corresponding susceptibility should then decrease as $\omega^{-\beta}$. Such a prediction contrasts with all the DLS experiments on fragile molecular liquids analyzed so far; these experiments have shown that the spectra display, in the vicinity of the minimum, the form predicted by Eq. (3), which is the sum of a high-frequency process in ω^a and a low frequency part in ω^{-b}. As $b < \beta$, this slower decay of the high-frequency tail of the α relaxation process with respect to the $\omega^{-\beta}$ prediction is a nontrivial result; therefore, it is important to show that such a decay is an intrinsic property of a one-correlation function and *not an artifact* introduced by the addition, to the α relaxation process, of the low-frequency tail of a high-frequency spectrum generated by a different scattering process. The present paper describes an optical Kerr effect experiment performed on salol ($T_m = 315$ K, $T_g = 218$ K, and $T_C = 260 \pm 5$ K), which shows that the value of b deduced from the analysis of the vicinity of the minimum of its DLS $\chi''(\omega)$ is an intrinsic property of some dynamical correlation function of this molecular liquid. The artifact described above is thus not the major origin of this minimum.

The present paper is organized as follows. Section II presents a qualitative discussion of the mechanisms involved in an optical Kerr effect (OKE) experiment and shows that such an experiment provides information mostly related to the molecular orientation motion. Section III describes this OKE experiment, recalls the relationship between the OKE signal and the orientational correlation function, makes precise the experimental setup, and presents the raw data collected. In Sec. IV, after recalling the previous experimental results obtained on salol that are relevant for the present paper, we perform a numerical analysis of our data, the results of which are discussed in detail in Sec. V. Section VI summarizes our findings.

II. OKE IN MOLECULAR LIQUIDS: A QUALITATIVE DISCUSSION

As stated in Sec. I, the analysis of a DLS experiment performed on a molecular liquid consisting of optically anisotropic molecules is a complicated problem because both the center-of-mass motion and the orientational motion contribute to the signal. The word ''contribute'' is in fact not precise enough because this ''contribution'' acts at two different levels. One is the dynamical level: Both types of motion correspond to the dynamical degrees of freedom in equi-

librium with the thermal bath. In the classical limit, they have a thermal mean energy equal to $k_B T$. The second level is the light-scattering one: Both types of motion generate a change in the total susceptibility of the liquid.

In our OKE experiment, we send a ''subpicosecond'' polarized light beam (the pump), which very rapidly generates a macroscopic optical anisotropy in the liquid; the decay of this birefringence is later monitored through the change of polarization of a second polarized laser beam (the probe), which propagates in the liquid in the same direction as the pump. The basic point we want to make in this section is that, in our experiment, the pump will efficaciously perturb the orientational equilibrium of the liquid, while the position of the center of mass will be affected very little by the initial pumping field. Furthermore, we will point out that the dynamical coupling of translational and orientational dynamics will have no important effect on the measured signal.

It has been argued that an experiment performed in the time domain with a pulse of infinitely short duration gives exactly the same information as an experiment performed in the frequency domain, the two response functions being connected by a Fourier transform [18,19]. Vice versa, for a pulse of finite duration, there is a frequency filtering effect on the excitation and probing mechanism [20]. This effect is particularly important to define which molecular dynamics dominates the time domain response function: Typically, there is a strong enhancement of the low-frequency dynamics compared to the high-frequency one. A precise definition of the excited and probed dynamics is very complex when several molecular degrees of freedom are dynamically coupled. This is why we must make use here of a rather intuitive picture of our OKE experiment on salol.

Let us first look at the effect of the initial pump pulse, considering that the pulse duration does not provide any resonance with the high-frequency dynamics. Its electric field has two effects on the molecules, considered here as rigid objects. On the one hand, through the anisotropic part of the molecules' polarizability tensor, this field develops, on each molecule, a dipole that is not parallel to the field and thus creates a torque that tends to align its polarizability tensor with the field. On the other hand, the presence of a gradient in the field produces a force on the molecule, through its coupling with its own dipole, which tends to translate the molecule. We already mentioned, in the Introduction, that the low-frequency part of the spectrum is due to the reorientation dynamics of the molecules. Filtering this part of the spectrum by the pulse shape means that we enhance the torque effect (rotation of the molecules) with respect to the gradient effect that generates the motion of the center of mass.

The center-of-mass motion could also have another origin: The laser field has a Gaussian transverse profile and we must consider a possible effect of the field gradient on the OKE signal. This gradient originates from the radial distribution of the field in the pump beam. The inhomogeneity of the electric field creates an inhomogeneous electrostriction, which could result in a force on each center of mass; because the pump beam is rather broad, the electrostriction gradient is weak and so is this secondary effect. (We note also that this effect has a radial symmetry. As the probe beam propagates parallel to the axis of symmetry of this inhomogeneity,

it does not experience any anisotropy associated with this effect.)

In summary, when the molecule has an anisotropic polarizability, it is a very good approximation to consider that it is only the electrical torque that gives rise to the initial optical orientational anisotropy of the liquid and that this torque, as well as the pump beam, does not generate an appreciable effect on the position of the center of mass.

Let us now discuss whether a slow hydrodynamics mode could be induced indirectly by an orientational-translational coupling, taking place during the relaxation processes, and contribute to the decay measured by the OKE experiment. The orientational anisotropy induced by the pump beam is characterized by a very small $\mathbf{q}$ vector (not bigger than the inverse of the laser beam spot size [18]) and for such values of $\mathbf{q}$ the relaxation of hydrodynamic modes is extremely slow and out from the measured time window. Also, one cannot invoke a recombination effect of $\mathbf{q} \sim \mathbf{0}$ orientational modes into $\mathbf{q} \neq \mathbf{0}$ hydrodynamics modes, which is quite unlikely. In fact, the decay of the induced anisotropy takes place partly through the deexcitation of localized librations and partly through a direct thermalization process. None of these effects is able to create, by recombination, a macroscopic effect more pronounced in one direction of $\mathbf{q}$ than in any other: The decay of the OKE signal is thus the same as the decay of a normal orientation fluctuation in the liquid at equilibrium, but, in first approximation, it is not mixed with contributions from the center-of-mass dynamics, contrary to the case of the DLS signal.

Let us finally remark that the preceding argument does not precisely determine the value of the polarizability tensor. In the presence of a DID interaction, the bare polarizability tensor is renormalized and a precise definition of this renormalization effect, as well as a numerical calculation of the effect in the case of the CS_2 molecule, can be found, for instance, in [21]. The technique used in that paper is valid for the case of axially symmetric molecules; another method has to be used for less symmetrical cases [22]. The only aspect that is worth pointing out here is that the main quantity that enters into the renormalization procedure is the product of the isotropic part of the bare polarizability tensor by the fluid density. Because the density does not change with the orientational order created by the pump, the effective polarizability tensor does not change during the OKE experiment and the renormalization effect will not have to be taken into account in the analysis of such an experiment.

III. OKE EXPERIMENTS

A. Time-resolved OKE experiment

As already mentioned, in a transient OKE experiment, an excitation pulse produces a transient anisotropy in the sample, which is monitored by the change of polarization of a probe pulse. The intensity of the new polarization component of the probe pulse can be written as [18,23]

$$S(\tau) \propto \int_{-\infty}^{+\infty} I_p(t-\tau) \left[\int_{-\infty}^{t} R(t-t') I_e(t') dt' \right]^2 dt, \quad (4)$$

where τ is the delay between the pump and probe pulses, $R(t)$ is the response function of the system, and I_p and I_e are

the average intensities of the probe and pump fields, respectively. When the duration of the pulses is short compared to the characteristic response time, which is the case in our experiment for times larger than approximately 1 ps, the pulses being approximately 200 fs long, the convolution in Eq. (4) can be forgotten, yielding

$$S(t) \propto |R(t)|^2. \qquad (5)$$

Ignoring the electronic contribution that responds adiabatically to the exciting field, as long as the system has an ergodic dynamics, which is always the case for $T > T_C$, $R(t)$ can be directly connected with the time-dependent correlation function of the linear susceptibility of the molecular liquid through

$$R(t - t_0) = - \frac{\theta(t - t_0)}{k_B T} \frac{\partial}{\partial t} \langle \chi_{ij}(-\mathbf{q}, t_0) \chi_{ij}(\mathbf{q}, t) \rangle. \qquad (6)$$

In this expression $\chi = \varepsilon_0(\varepsilon - 1)$ is the macroscopic linear susceptibility, k_B is the Boltzmann constant, T is the temperature, and $\theta(t)$ is the Heaviside step function. Note that, in an OKE experiment, the excited anisotropy is characterized by a zero wave vector, so that we must consider $\mathbf{q} \sim \mathbf{0}$.

Let us stress again that, in a molecular liquid, for times longer than the relaxation times of internal degree of freedom of the molecule, the macroscopic linear susceptibility may be considered as the sum of rigid molecular polarizability tensors (second-rank tensors): The correlation function entering Eq. (6) will be sensitive mainly to the collective orientational dynamics probed through these second-rank tensors. As MCT proposes an analytic form for this correlation function for both the α and the β relaxation regimes, the form of $R(t)$ is also known; it will thus be possible to compare the results of an OKE experiment to those predictions independently in those two regimes.

B. Experimental setup

The experimental apparatus has been presented in detail in a previous paper [24]. The 100-ps output pulses of a cw mode-locked Nd:YAG laser (where YAG denotes yttrium aluminum garnet), with a repetition rate of 82 MHz, are first fiber compressed into approximately 5-ps duration pulses and then duplicated and used to synchronously pump a dye laser (rhodamine 590). The 350-fs dye laser pulses are again fiber compressed to about 100 fs. An amplification system, made of three dye cells and pumped by a Q-switched Nd:YAG laser (30 Hz), is used to reach an energy of approximately 100 μJ per pulse. The amplified pulses are finally beam split: half of the energy is sent directly to the experiment as the pump signal and the other half is targeted on a water cell to produce a continuum spectrum. A narrow frequency band is selected from this continuum and amplified, which will form the probe signal, used in conjunction with a delay line. The specifications of the system are 150 fs, 600 nm, and 5 μJ (energy on the sample) for the pump pulse and 200 fs, 580 nm, and 1 μJ for the probe pulse.

The salol (phenyl-salicylate) was purchased from Merck (purity greater than 99%) and purified by vacuum distillation using a Vigreux tube. The purified salol produced a very stable supercooled liquid phase that could be kept as such for
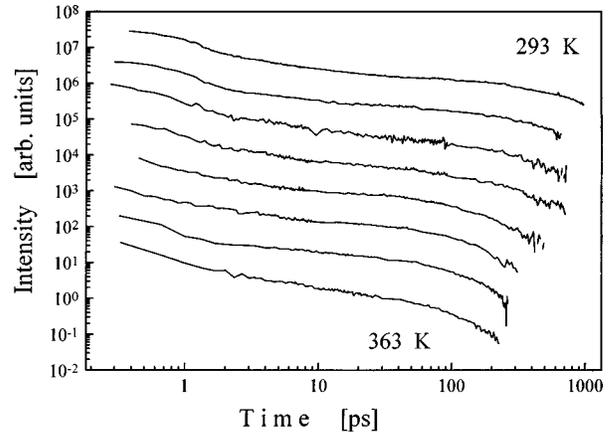

FIG. 1. OKE signal of salol. The temperatures are, from top to bottom, 293, 303, 313, 323, 333, 343, 353, and 363 K. The different curves have been vertically shifted by a factor 10 to allow for a clear view of them.

several months at room temperature. The sample was kept in a quartz cell of very good optical quality and the temperature was controlled by a cryostat system having an accuracy of ± 0.1 K.

C. Data collection and handling

Due to the large dynamical range and the broad time window needed to follow the relaxation processes taking place in a supercooled liquid, the OKE signal was recorded separately for different time scales: 0–10 ps, 0–100 ps, and 0–1 ns. For each time range, we performed repeated scans of the optical delay line in order to obtain a good signal-to-noise ratio. The alignment of the optical delay line was tested scrupulously before each scan. Then we carefully joined the decay curves corresponding to different time windows, matching their overlapping range; as can be seen in Fig. 1, where we show the square root of the measured OKE signal for all temperatures, this signal decays for more than three decades in time. The data were collected from 363 K down to 293 K, the lowest temperature at which we were able to get a reasonable signal; in the rest of this paper we shall always represent and call ''signal'' the square root of $S(t)$, i.e., the absolute value of $R(t)$. All the curves of Fig. 1 turned out to be practically identical from approximately 1 ps to a few picoseconds. Conversely, the long-time part of this signal is very sensitive to the temperature: The lower the temperature, the slower the corresponding decay; it is only the second part of these curves that will be analyzed in Sec. IV.

IV. ANALYSIS OF THE OPTICAL MEASUREMENT

A. Previous dynamical results on salol

Let us summarize here the results, obtained during the past five years or so, on the dynamics of supercooled salol in the vicinity of its critical temperature T_C that are pertinent to the MCT analysis we shall perform in Sec. IV B. Experiments were performed by Li *et al.* [7] by the DLS technique and analyzed within the framework of the ideal version of MCT briefly summarized in the Introduction. It yielded a value of the b coefficient $b = 0.64$ (whence $a = 0.33$) as well

as $T_C = 255 \pm 5$ K. These authors also deduced from their measurements a value for the stretching coefficient $\beta = 0.86$ approximately constant above T_C as well as values of $\tau_\alpha(T)$ for temperatures ranging from 383 K down to 273 K. They found that this version of MCT could fit their experiments from the vicinity of T_C up to 313 K for the region of the minimum of $\chi''(\omega)$ and could be extended to 383 K for $\tau_\alpha(T)$. The line shape of the Brillouin spectrum produced by the longitudinal phonons was analyzed later on within the same framework [4]: It confirmed the approximate location of T_C ($T_C = 275 \pm 10$ K), but it was found that the maximum linewidth of the phonon took place at a temperature at which the maximum of the DLS $\chi''(\omega)$ was at a much lower frequency than the Brillouin peak. A detailed comparison between the values of $\tau_\alpha(T)$ obtained in the DLS [hereafter called $\tau_{VH}(T)$] and in the Brillouin scattering [$\tau_{VV}(T)$] experiments showed that, in the whole region of accuracy of the two experiments, $\tau_{VH}(T)$ exceeded $\tau_{VV}(T)$ by a factor larger than 10 [25]. Another analysis of the same longitudinal phonon dynamics was performed by Yang and Nelson [5] via a reportedly impulsive stimulated thermal scattering technique, through which the decay of the phonons was analyzed in the time regime. This experiment confirmed the value of T_C obtained earlier, reported a decrease of the coefficient β below T_C, but displayed an α relaxation process characterized by $\tau_{VH}(T)$ and not by $\tau_{VV}(T)$ at the temperature at which the two experiments could be compared.

The existence of a minimum in the susceptibility spectra was demonstrated not only in the DLS experiment but also by a QENS experiment performed on a hydrogenated sample (incoherent scattering) between 343 and 241 K [26]. This technique tests only the self-correlation function of the positions of the center of mass: The experiment yielded, for each temperature, a position of the susceptibility minimum independent of the scattered wave vector and this position coincided with the value obtained in the DLS experiment close to T_C, but, for $T - T_C > 10$ K, its value increased less rapidly than in the DLS experiment. Also, the low-frequency cutoff of the experiment did not allow for a detailed analysis of the shape of $\chi''(\omega)$ far below the value of its minimum; the value of the coefficient b then could not be obtained from the QENS experiment and the need for a measurement of this coefficient independent from the early measurement of [7] was one of the motivations of this work.

B. Fitting procedure

Equations (5) and (6), in conjunction with Eqs. (1) and (2), are the necessary ingredients for the comparison of our OKE data with the predictions of MCT. Equations (1), (2a), and (2b) give the form of the correlation function for three different regimes: the α relaxation regime at very long times, with a KWW decay [Eq. (1)], characterized by $\tau_\alpha(T)$ and β; the two asymptotic parts of the β regime, i.e., the so-called critical region for $t \ll \tau_e$ [Eq. 2(a)]; and the von Schweidler (VS) regime for $\tau_e \ll t \ll \tau_\alpha$ [Eq. (2b)], both characterized by a power law with exponents a and b, respectively.

To compare the data of Fig. 1 with the MCT predictions, we must use the time derivatives of Eqs. (2) and (1): In the β regime we had to fit our data with
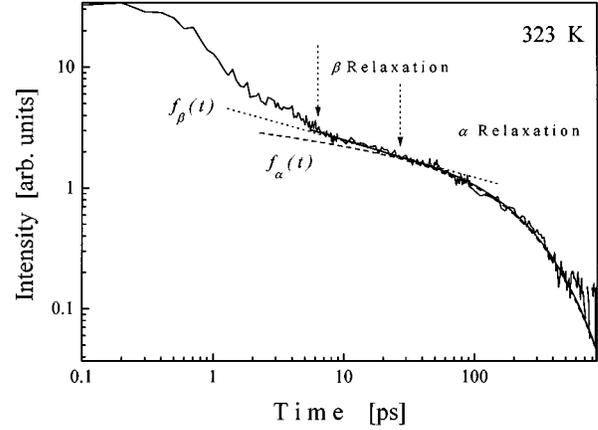

FIG. 2. OKE signal at 323 K and its two fitting functions: derivative of a KWW function $f_\alpha(t) \sim (\beta/t)(t/\tau_\alpha)^\beta \exp[-(t/\tau_\alpha)^\beta]$ (dashed line) for $t > 25$ ps and derivative of a VS function $f_\beta(t) \sim Bt^{-1+b}$ (dotted line) for 6 ps $< t < 25$ ps. The fits parameters are given in Table I and the vertical arrows indicate the two limits of the VS regime.

$$f_\beta(t) \approx A t^{(-1-a)}, \quad t \ll \tau_e \quad (7a)$$

$$f_\beta(t) \approx B t^{(-1+b)}, \quad t \gg \tau_e, \quad (7b)$$

while, in the α regime, we tested the fitting function

$$f_\alpha(t) \sim (\beta/t)(t/\tau_\alpha)^\beta \exp[-(t/\tau_\alpha)^\beta]. \quad (8)$$

Making a comparison between such articulated relaxation predictions and the experimental data was not an easy task, so we had to reduce somewhat the number of free parameters; in order to test the quantities we were mostly interested in, we only fixed the β factor to the literature value of Li et al. [7]. We then fitted the long-time part of our data to $f_\alpha(t)$ [Eq. (8)] using τ_α as a fit parameter: At each temperature, the time window was chosen to optimize the quality of fit and the best value of $\tau_\alpha(T)$ was obtained through a standard nonlinear least square fitting.

After having found the α regime parameter, we moved to the β regime, i.e., we tried to fit the data corresponding to times shorter than the KWW regime. We first tried this fit using Eqs. (7), neither of which is a good approximation of the derivative of the exact β correlator for $t \approx \tau_e$, but which properly describe the two asymptotic regimes. Our reason for not making use of the full $T > T_C$ β correlator for this fit is that we rapidly realized that the critical decay [Eq. (7a)] corresponded to times shorter than or of the order of 2–3 ps. Since in this time region our signal is partly polluted by parasitic effects, we decided not to take into account this time domain, i.e., not to try to measure separately the coefficient a, but rather to concentrate on the VS part [Eq. (7b)], which gave access to the coefficient b. The range of fitting of our data was thus limited, at long times, by the beginning of the KWW regime and, at short times, by the time below which a good fit to Eq. (7b) could not be obtained.

For each temperature, a value of the coefficient b was then obtained. Figure 2 shows, as an example, an OKE signal decay for an intermediate temperature 323 K: At this temperature, the range of fitting of the VS function extends from

TABLE I. Values of the fitting parameter β and results of the fitting procedure: α relaxation time τ_α, VS coefficient b, and the range of time (Range) and measured duration (Δt) of this process. The relaxation times measured by DLS in [7] are shown for comparison in the fourth column. An asterisk denotes an interpolated time.

	α regime			β regime		
T (K)	β[a]	τ_α (ps)	τ_{VH} (ps)[a]	b	Range (ps)	Δt (ps)
293	0.88	628	522	0.6	6–50	44
303	0.86	429	370	0.68	6–45	39
313	0.86	286	233	0.57	6–35	29
323	0.86	200	179	0.66	6–25	19
333	0.83	127	128	0.71	6–20	14
343	0.84	104	81*	0.67	5–18	13
353	0.84	86	63*	0.64	5–15	10
363	0.83	65	62	0.43	4–12	8

[a]From Ref. [7].

6 ps up to 25 ps and for the KWW part from 25 ps to about 600 ps. The best fit was obtained for $b=0.66\pm0.06$ and $\tau_\alpha=200\pm20$ ps, taking $\beta=0.86$.

Within the accuracy of our signal, our fits show that, in general, there is a small intermediate region where the late β regime and the early α regime appear to overlap slightly. Vice versa, at the lowest temperature used (293 K) there exists a short intermediate region where neither the VS nor the KWW function is able to fit the data perfectly. In Table I we report the results of our fits for all the temperature analyzed, including the time range (Range) and time length (Δt) during which the VS function fits the relaxation properly. Our data support a substantial temperature independence of the stretching factor β.

V. DISCUSSION OF RESULTS

The analysis performed in Sec. IV B has shown that the signal obtained in our OKE experiment could be analyzed as the successive appearance of three different regimes: a) a ''short-time'' portion, ending approximately at 2 or 3 ps, where the signal was difficult to analyze within the MCT scheme and to which we shall return at the end of this section; b) an ''intermediate-time'' regime, extending, roughly speaking, from 5 ps to a value ranging, depending on temperature, from 12 to 50 ps, where the signal could be fitted by Eq. (7b); and c) a ''long-time'' decay, which started approximately at the end of the previous period, where the signal could be fitted with the help of Eq. (8).

Both Eqs. (7b) and (8) are the results expected from MCT [12(a)]. To proceed further with the comparison between that theory and our results, we must now analyze them more carefully and discuss them in the light of the experimental results recalled in Sec. IV A.

A. The von Schweidler part

The first objective of the present paper was to obtain a value of the coefficient b, only measured, up to now in [7], in the context of the ideal version of MCT. Table I shows that if we discard the measurement performed at the highest temperature ($T=363$ K), where the fitting domain for the VS process becomes short enough to lead to large numerical

uncertainties, the values obtained for the coefficient b are fairly constant, as expected from MCT: They give a mean value $b=0.64$ with deviations appearing as statistical errors with respect to this mean value. Our value is remarkably equal to its determination, made in [7], in the frequency domain, up to 313 K; it thus confirms, at the same time, that the β relaxation regime could be seen in the DLS experiment and the value of the coefficient that was deduced from it.

B. The α relaxation process

Let us now analyze the values of τ_α as a function of temperature. As in the case of the coefficient b, our values are very close to $\tau_{VH}(T)$ obtained in [7] by the DLS technique; this is shown in the fourth column of Table I, where we have reported the interpolation of $\tau_{VH}(T)$ at the temperatures of our experiment. The analysis in [7] of the viscosity data [27,28] yielded a value of $T_C=263$ K, which is almost the mean value between the DLS value and the longitudinal phonon damping value [4]. We have represented, in Fig. 3, our values for $\tau_\alpha(T)$ and have compared them with the MCT prediction $\tau_\alpha(T)=\tau_0(T-T_C)^{-\gamma}$, taking $T_C=260$ K and $\gamma=2.31$, in accordance with the value found for b. The fit is quite good, giving $\tau_0\sim2.3\times10^6$ psec/K$^{-\gamma}$.
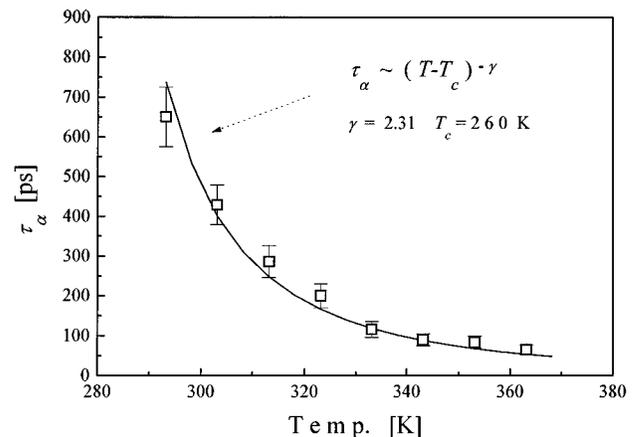
FIG. 3. τ_α ($\square$) vs temperature. The continuous line is a fit according to the MCT scaling law $\tau_\alpha=\tau_0(T-T_c)^{-\gamma}$.

There exists a previous OKE experiment on salol, performed by Ho and Alfano [29] twenty years ago at a time where MCT had not yet been formulated and the stretched character of the α decay had not been fully recognized. Ho and Alfano thus analyzed their data with a simple exponential decay and could describe only the longest part of their signal. Due to the small value of $1-\beta$, the simple exponential law was a rather good approximation to the α decay and their values of the α relaxation time are in fact very similar to ours, in the temperature range we explored.

Another aspect of our results is the consistent assessment of the dynamical mechanism responsible for the DLS spectrum below the minimum of its susceptibility. Due to the filtering effect, our OKE experiment is mostly sensitive to the collective rotational dynamics of the salol molecules and, as it should, our $\tau_\alpha(T)$, measured in the long-time limit, are identical to the $\tau_{VH}(T)$ measured, in the DLS experiment, in the low-frequency domain. However, because we have mostly excited the rotational dynamics, it was not obvious that, in the intermediate-time regime, we should obtain a t^b law with the same b as measured from the susceptibility minimum. The fact that we detected this regime implies that the latter is the long-time part of the β relaxation related to the reorientation dynamics. One can thus wonder whether there is any contribution of the DID mechanism related to the motion of the center of mass well below that minimum. This motion could have contributed to the DLS signal in two different ways.

One way is that the von Schweidler part of $\chi''(\omega)$ was simply the low-frequency part of this DID contribution, which could in principle have an exponent different from that of the rotational dynamics. This possibility is ruled out by the present experiment: The same VS signal (i.e., the same power law with the same nontrivial exponent) is detected in the OKE experiment, which has practically no contribution from the motion of the center of mass.

The second way is that the center of mass has essentially the same dynamics as the orientational motion so that the two types of motion cannot be distinguished. Though this is not impossible, we must stress that the analysis of the Brillouin scattering experiment [25] shows that, in the $\mathbf{q}\to 0$ limit, the relaxation time of the density fluctuations $\tau_{VV}(T)$ is at least ten times shorter than that of the orientation fluctuations $\tau_{VH}(T)$ in the same limit. It is unlikely that the increase of the relaxation times of the density fluctuations with $\mathbf{q}$ is so large that the signal corresponding to all $\mathbf{q}$ would have approximately the same dynamics as the reorientation one.

Let us conclude this subsection by noting that the identification of $\tau_\alpha(T)$ with a reorientation time makes it difficult to interpret some of the results of Yang and Nelson [5]: As already mentioned, their relaxation times appear to be the low-temperature continuation of $\tau_{VH}(T)$ and they are much longer than the times $\tau_{VV}(T)$ detected in the direct Brillouin scattering experiment [4,25]. A possible explanation is that those authors were only able to detect the end part of the longitudinal phonons relaxation process, which may be sensitive to the molecular reorientation motion through the orientation-translation coupling [22,30]. Another possibility is that the temperature ranges where the two experiments have the best sensitivity do not overlap and that the low-
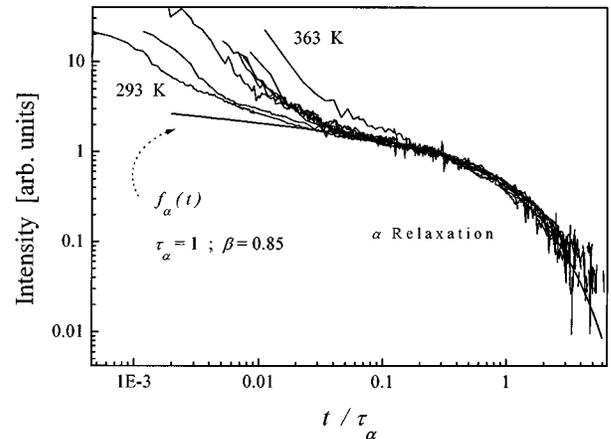

FIG. 4. Rescaled signals vs t/τ_α. The lower the temperature, the sooner the time temperature superposition principle is fulfilled.

temperature values of $\tau_{VV}(T)$ of [5] may be continued by the high-temperature values of [4,25]. More work has to be done to clarify this point.

C. A possible measurement of the β relaxation time

An interesting aspect of the numerical analysis of our data performed in Sec. IV is the crossover between the β relaxation regime and the α relaxation decay. Equation (2b) states that $\phi_q(t)$ would tend to $-\infty$ for $t\to\infty$ if a crossover to Eq. (1) would not take place. This means that in the crossover region $\phi_q(t)$ will decrease less rapidly than predicted by Eq. (2b) and so will its derivative. One thus expects that the crossover region will be characterized by a rapid decrease of the absolute value of the slope of the curve of our signal versus temperature, this is what can be seen in the particular example of Fig. 2.

If $\phi_q(t)$ is plotted as $\phi_q(\hat{t})$, with $\hat{t}=t/\tau_\alpha$, as β does not depend on temperature, the time-temperature superposition principle (TTSP) holds for $1\leqslant\hat{t}$ but should not be valid for $\hat{t}\ll 1$. It has been already noticed (see, e.g., [11]) that the value of $\hat{t}_0=t_0/\tau_\alpha$ below which the TTSP does not hold decreases with $T-T_C$ because the ratio τ_e/τ_α goes to zero in this limit. This result should also be valid for an OKE experiment where one measures the derivative of $\phi_q(t)$; Fig. 4 shows that this is indeed the case as the lower the temperature, the sooner the signal joins the TTSP curve.

A check of the value of the coefficient a and of the approximate β relaxation time thermal evolution has been made as an extension of the previous remark. We already mentioned that the rapid decrease of our signal below 2–3 ps, visible in Fig. 2, is slightly temperature dependent. This decay may be due to some tail of the fast dynamical process, which here is the libration motion induced by the pump and obscures the existence of the critical decay. To check the value of the coefficient a, we have explored another route. Equation (2b) should be valid from a value of t/τ_e representing, in the β relaxation master function, the beginning of the VS regime, up to a time τ_c where the crossover phenomenon begins to take place; τ_c could also be proportional to τ_e. With such an hypothesis, Δt, in Table I, which is the total time during which the VS process is visible, should also be proportional to τ_e and should behave as $(T-T_C)^{-1/2a}$. We
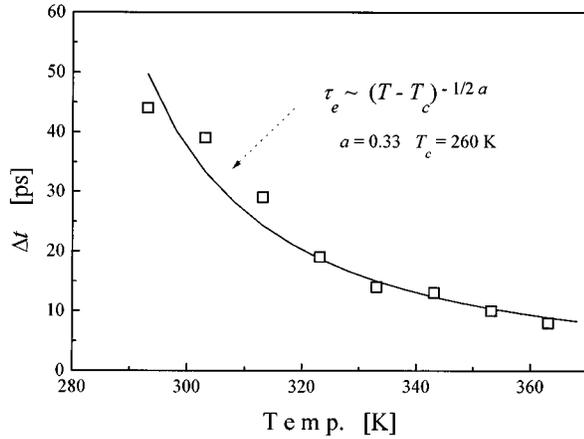
FIG. 5. Temperature dependence of the fitting ranges Δt of the VS function $f_\beta(t) \sim Bt^{-1+b}$ ($\square$) vs temperature. The continuous line is a fit according to the MCT scaling law $\tau_e = \tau_0(T - T_c)^{-1/2a}$, predicted for the β relaxation process.

checked the validity of that hypothesis, using the value of $a = 0.33$ corresponding to $b = 0.64$ and the same value of $T_C = 260$ K. Figure 5 shows that the proposed relationship is approximately valid in the temperature range explored, which confirms the value of a indirectly deduced from the VS process.

VI. SUMMARY AND FINAL REMARKS

The discussion in Sec. V has shown that our results are consistent with a certain predictions of MCT that are valid for any correlation function. They contain the following characteristics: an intermediate-time regime (β relaxation), which is the fastest regime we can safely analyze, behaving as t^{-b}; a long-time limit, behaving as a stretched exponential with a relaxation time $\tau_\alpha(T)$ and a stretching exponent fulfilling the inequality $b < \beta < 1$; and the merging of the asymptotic β process into the α process taking place at a crossover time τ_c increasing less rapidly than $\tau_\alpha(T)$. We have also found that the total time during which the VS approximation is valid, which we can identify with τ_c, is

proportional to the relaxation time of the β relaxation process.

As argued in Sec. II, there is only one correlation function detected in our OKE experiment, namely, the orientational correlation function corresponding to a second-rank tensor in an isotropic medium. The value of the b coefficient we measured was, as predicted by MCT, fairly independent of temperature. Also, the temperature behavior of $\tau_\alpha(T)$ was fulfilled, using for the coefficient γ the value inferred from the coefficient b and a critical temperature $T_C \sim 260$ K.

Comparing our results with those obtained by Li *et al.* [7] in a DLS experiment, we could identify our $\tau_\alpha(T)$ with the relaxation time $\tau_{VH}(T)$ of their α relaxation process, giving a consistent proof that, at low frequency, their experiment detected only the same orientational relaxation process as the OKE experiment.

Finally, the value of the coefficient b we obtained coincides with the value proposed in [7]. This provides an *a posteriori* basis and support for the existence of a minimum in the susceptibility data and for its temperature evolution, explained by the MCT mechanism and not by the competition between a low-frequency rotational α spectrum and a higher-frequency DID, center-of-mass-induced, spectrum. This does not mean that the high-frequency peak could not have mainly its origin in the motion of the centers of mass, detected by the DID mechanism. It simply implies that the contribution of the reorientation process to the DLS susceptibility spectrum, below its minimum, is large enough to impose the position of the minimum, even if the motion of the center of mass does not follow the MCT predictions in a temperature domain as large as the orientational motion.

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