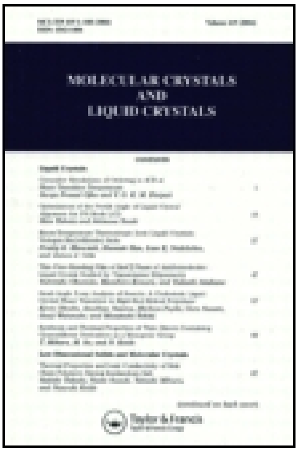

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Orientational Dynamics in the Isotropic Phase of a Nematic Mixture: Subpicosecond Time Resolved Optical Kerr Effect Experiments on ZLI-1167 Liquid Crystal

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ORIENTATIONAL DYNAMICS IN THE ISOTROPIC PHASE OF A NEMATIC MIXTURE: SUBPICOSECOND TIME RESOLVED OPTICAL KERR EFFECT EXPERIMENTS ON ZLI-1167 LIQUID CRYSTAL.

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Abstract We have investigated the orientational dynamics of the ternary mixture of propyl, pentyl and heptyl cyano-cyclohexyls (ZLI-1167) in the isotropic phase over a wide temperature range (372-453 K) by means of transient optical Kerr effect spectroscopy. The orientational dynamics of ZLI-1167 isotropic phase shows a complex relaxation pattern where several dynamical processes take place. We substantially observed three time scales of relaxation: fast (from hundreds of fsec to few psec), intermediate (from tens to hundreds of psec) and slow (from hundreds of psec to few nsec). The slow orientational relaxation shows a temperature dependence characterized by strong pre-transitional effects. The critical slowing down of these relaxation times can be correctly interpreted by Landau-de Gennes theory. The fast and intermediate decay times show a different temperature dependence without any observable pre-transitional effects. We suggest an interpretation of the experimental results in term of averaged single molecule dynamics and collective dynamics.

INTRODUCTION

The study of structure and dynamics of liquid phases is may be one of the most challenging research of the condensed matter physics. Recently, thank to new time resolved spectroscopic analysis, the reorientational dynamics of molecular liquids have shown a new variety of relaxation processes[1,2]. Especially the liquid phases of mesophase forming material, such as liquid crystals or plastic crystals, display complex pattern of decay. In these "complex" fluids the dynamical processes range over a large spread of time scales: from the slow collective fluctuations to the very fast local and conformational motions[3,4]. Therefore it is very important for a better understanding to perform the experiments following the dynamics on the largest possible time window.

From this point of view time resolved laser spectroscopy, like for example Optical Kerr Effect (O.K.E.) or Transient Grating[5,6,7], are unique tools of analysis. The possibility of measuring molecular dynamics directly in the time domain improves substantially the ability of detecting complex time decays and allows to monitor a large time window.

Previous experimental works performed on pure materials (isotropic phase of nematic liquid crystals: MBBA and 5CB[3] and liquid phase of plastic forming materials: *p*-Terphenyl[4]) have shown some new remarkable and recurrent characteristics. The reorientational dynamics display a complex relaxation where, at least, a couple of decay times are present: a slow relaxation time and an intermediate one. In all the materials the temperature dependence of the slow dynamics shows a critical slowing down in good agreement with the Landau-de Gennes theory of phase transitions, instead the intermediate relaxation times are characterized by a different temperature dependence unaffected by the phase transition.

In this paper we report on the orientational dynamics on isotropic phase of a mixture nematic liquid crystal investigated by means of time resolved optical Kerr effect. The signal decay has been detected over several decades in time and amplitude. The experimental results show that the reorientational dynamics of ZLI-1167 is, in many aspects, very close to the previous measured dynamics of MBBA, 5CB and *p*-Terphenyl. In other words, we found that a liquid mixture of elongated molecules, like ZLI-1167, behaves likewise a pure liquid phase of similar shaped molecules.

TRANSIENT O.K.E. EXPERIMENT

In a transient OKE experiment an off-resonance laser pulse (pump pulse) produces an optical anisotropy in the sample. This transient excitation causes a polarization change in a second off-resonance laser pulse (probe pulse) crossing the sample. Controlling the time delay between pump and probe pulse it is possible to monitor the relaxation of the induced transient anisotropy. The intensity of the probe beam detected though a crossed polarizer can be written as[4,5,6] :

$$S(\tau) \propto \int_{-\infty}^{+\infty} I_p(t-\tau)\left[\int_{-\infty}^{t} R_{ijij}(t-t')I_e(t')dt'\right]^2 dt \qquad (1)$$

where τ is the time delay between 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. The response function consists of two contributions[5]:

$$R(t) = R^{e}_{ijij}(t) + R^{n}_{ijij}(t) \tag{2}$$

where R^e represents the adiabatic electronic contribution (responding within 10^{-15} sec) and R^n is a contribution due to the nuclear motions. The nuclear response function is defined according to the following equations[5] :

$$R^{n}_{ijij}(t) = -\frac{\theta(t)}{kT}\frac{\partial}{\partial t}C(t) \quad ; \quad C(t) = \left\langle \chi_{ij}(0)\chi_{ij}(t) \right\rangle \tag{3}$$

In the above expressions χ_{ij} is the linear susceptibility of a macroscopic, but small, volume of the sample, $\theta(t)$ is the Heavy-side step function and <..> is the equilibrium ensemble average. Equation (3) shows that the nuclear response is determined by the time correlation function of the linear susceptibility, C(t). When, as in the present case, the duration of the pulses is short compared to the characteristic response time, the convolution in eq.(1) can be approximated as:

$$S(t) \propto \left| R^{n}_{ijij}(t) \right|^2 \tag{4}$$

Thus, by measuring the intensity of the transmitted probe as a function of the delay time, the nuclear relaxation time can be obtained directly from the experiment.

BACKGROUND THEORIES

As we pointed out, the transient OKE experiment measures the spontaneous relaxation of the optically induced anisotropy; the physical process responsible for OKE can be described in the frame of linear response theory. Equations (3) state the link between spontaneous relaxation and the equilibrium molecular dynamics. In order to extract from the experimental results information on the molecular dynamics, a microscopic interpretation of the correlation function is required. Therefore, we express the macroscopic susceptibility in term of molecular polarizability by expanding of χ_{ij} in series of isolated molecule polarizabilities and pair interaction terms[2,8]. According to this expansion, two principal contributions have to be taken in account in the correlation function[8] :

$$C(t) = C^{OR}(t) + C^{CI}(t) \tag{5}$$

The C^{CI} term includes the pure Collision Induced effects, while C^{OR} describes the pure orientational dynamics. The C^{OR} term can be directly related to the isolated molecule polarizability[8], α_{ij}:

$$C^{OR}(t) \propto \left\langle \sum_m \alpha_{ij}^m(0) \sum_n \alpha_{ij}^n(t) \right\rangle \tag{6}$$

where the sums run over the molecules in the sample volume. Molecular dynamics simulation and experimental results show that the C^{CI} term relaxes on very fast time scales (few psec or less). Vice versa the relaxation of the C^{OR} contribution is strongly dependent on the nature of the liquid, encompassing time scales from few psec to hundreds of psec. According to the previous equations it is possible to connect the OKE signal directly to the dynamics of microscopic parameters. To give a complete description of the experimental data, we should consider a theoretical evaluation of the time dependent correlation functions C^{CI} and C^{OR}. Unfortunately these kind of calculations have been proved to be very difficult even for simple liquids and to be almost impossible for structured liquids. However we can evaluate the C^{OR} contribution using some basic theoretical models and relate them to the experiments introducing a time scale separation.

It has been shown from experiments that a time scale separation is present in the molecular dynamics of many molecular liquids[1]. Substantially three time scales: from hundreds of fsec to few psec (fast), from tens to hundreds of psec (intermediate) and from hundreds of psec to few nsec (slow). Although this is an oversimplified picture that cannot be expected to be extendible to any kind of molecular liquids, it appears to apply surprisingly well to a series of liquids characterize by elongated shape of the constituent molecules, and by rather strong anisotropic intermolecular interactions.

The fast dynamics include many different processes. In a fast time scale we can consider the molecular liquid characterized by a determinate structure and then the dynamics driven by the forces appropriate to this spatial configuration. Together we have to consider intramolecular degrees of freedom that give origin to the vibrational and conformational dynamics. In this respect the fast dynamics is a many-body problem. So in the fast time scale, according to previous microscopic interpretation, we can not neglect the collision induced effects (C^{CI}).

In a longer time scale the collision, vibrational and conformational effects are substantially averaged, thus the dynamics is described by the molecular motion induced by the averaged intermolecular interactions. Therefore in the intermediate and slow time scales we can neglect the C^{CI} contribution and the OKE signal have to be addressed to pure reorientational processes (C^{OR}). The complete theoretical evaluation of orientational part of the correlation function is again a very complex and in many respects open problem[10]. However we believe that two simple theoretical models are able to give the principal feature of the intermediate and slow orientational dynamics.

The first model is the Brownian rotational diffusion model, in the form of Debye-Stoke-Einstein hydrodynamics theory[2] (D-S-E). This theory reduces the collective dynamics to the motion of one average molecule rotating (freely or hindered by a local effective potential) under the effect of random collisions. Considering the rod-like molecules in a true symmetric top hypothesis, the D-S-E model computes the single molecule correlation function according to the following equations:

$$C^{OR}(t) \propto \left\langle \alpha_{ij}(0)\alpha_{ij}(t) \right\rangle \propto \beta^2 \exp(-t/\tau)\,; \qquad \tau = \frac{V_{eff}}{kT}\eta(T) \tag{7}$$

where β is the anisotropic part of molecular polarizability, η is shear viscosity of the liquid and V_{eff} is the renormalized molecular volume. The relaxation times predict by D-S-E theory have shown to be in good agreement with many experimental results[2].

The second theory we consider is the Landau-de Gennes model[4,9] (L-dG). This phenomenological theory applies to molecular liquid close to a first order phase transition (order-disorder type). It is based on the expansion of the molecular liquid free energy in powers of the order parameter connected with the change of symmetry induced by the phase transition. For an isotropic-nematic transition the order parameter defines the degree of local orientational order present in the liquid phase. The order parameter is a macroscopic quantity and can be directly connected with the linear susceptibility of the sample. According to the L-dG theory the orientational correlation function can be defined in the following way:

$$C^{OR}(t) \propto \left\langle Q_{ij}(0)Q_{ij}(t) \right\rangle \propto \exp(-t/\tau) \quad ; \qquad \tau \propto \frac{\eta(T)}{(T - T^*)} \tag{8}$$

where Q_{ij} is the order parameter and T^* is the virtual temperature of transition. The L-dG prediction has been successfully used to explain the pre-transitional effect present in the slow dynamics of isotropic phase of pure nematic liquid crystal materials[3].

These two models (D-S-E and L-dG) are based on opposite approach to the molecular dynamics. D-S-E theory is a typical stochastic theory based on single averaged molecule dynamics. Vice versa L-dG model uses a macroscopic frame without any microscopic prediction. A matching of these to aspects is still in discussion. Nevertheless the previous theories find a fair agreement with the experimental results even when the intermediate and slow dynamics are present in the same relaxation pattern.

EXPERIMENTS

Viscosity Measurement

The shear viscosity of ZLI-1167 liquid crystal was not known from literature. Since it is very important to know the temperature dependence of shear viscosity to compare dynamics experimental data with the theoretical predictions, we have undertaken direct measurement of ZLI shear viscosity. The shear viscosity has been measured, using the Oswald method, in the temperature range from 373 to 408 K. In Fig.1 we report the Ln(experimental viscosity data) Vs (1/T). The Arrhenius behavior of ZLI viscosity is proved by linear dependence in the plot.

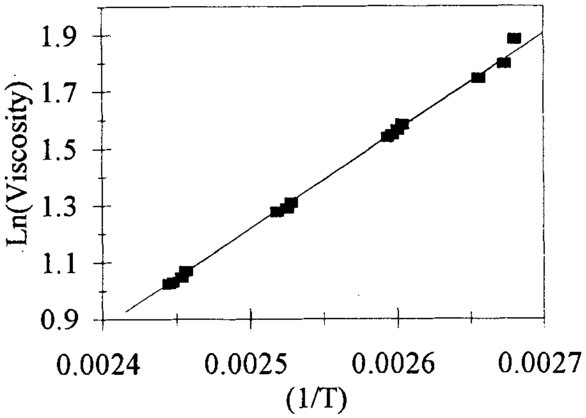


FIGURE.1 Temperature dependence of ZLI-1167 shear viscosity.

Therefore we fitted the data according the Arrhenius equation $[\eta(T) = \eta_0 \exp(E_a/kT)]$ getting the following results: $\eta_0 = (6 \pm 1) \cdot 10^{-4}$ [cP] and $E_a/k = (3400 \pm 50)$ [K].

OKE experiment details

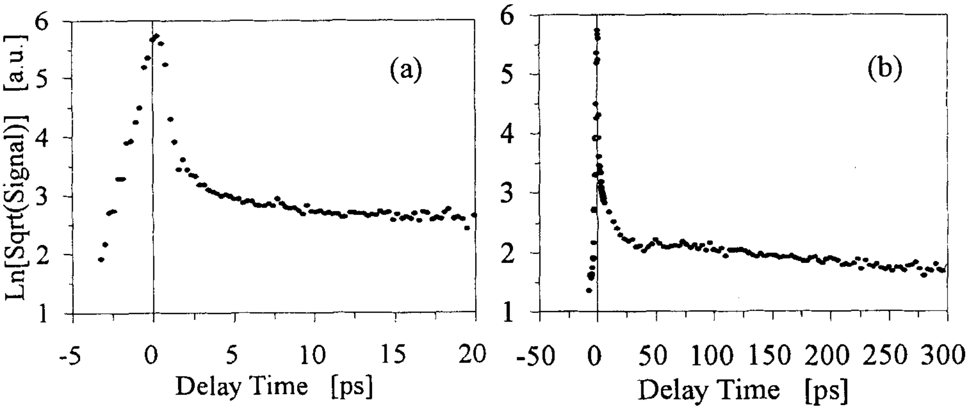
The experimental apparatus has been presented in detail in a previous paper[11]. The 70 psec output pulses of a CW mode locked Nd:YAG laser at a repetition rate of 82 Mhz is fiber-compressed to about 5 psec pulse duration, duplicated and used to synchronously pump a dye laser (Rhodamine 590). The 350 fsec dye laser pulses is fiber-compressed to about 100 fsec. 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 about 250 μJ per pulse.

The amplified pulse is beam-split: 50% of the energy is sent directly to the experiment (*pump pulse*: 100 fsec, 125 μJ, 600 nm), 50% is used to produce continuum in a water cell. From the continuum is selected the appropriate frequency and amplified, in this way we produce an other pulse used like probe (*probe pulse*: 150 fsec, 50 μJ, 580 nm).

ZLI-1167 is a ternary mixture of propyl, pentyl and heptyl cyano-cyclohexyls (i.e. trans, trans-4'-alkyl bicyclohexyl-4-carbonitriles), we purchased from Merck and we used without further purification. ZLI display a nematic-isotropic phase transition at critical temperature of T_C= 356 K. The sample has been sealed under vacuum in a quartz cell and kept in a heating system temperature controlled within 0.5 °C.

RESULTS

The OKE signal covers several decades in time and amplitude and so signal has been recorded separately for different time windows (0-20 psec, 0-300 psec and 0-3 nsec) and then accurately reconstructed. A typical OKE signal is shown in Fig.2. From Fig.2(a) is evident the electronic instantaneous response, that represents essentially the instrument response, and the fast part of nuclear response. Figures 2(b-c) show the intermediate and slow time scale relaxation. In our experiment the signal to noise ratio is not good enough to ensure a unique functional form of signal decay, however the slow part of the relaxation is unambiguously fitted by an exponential decay. Vice versa the intermediate and the fast relaxation display a more complex shape that could agree with several functional forms. Anyway we found that a second exponential fit reasonably well the intermediate part of decay.



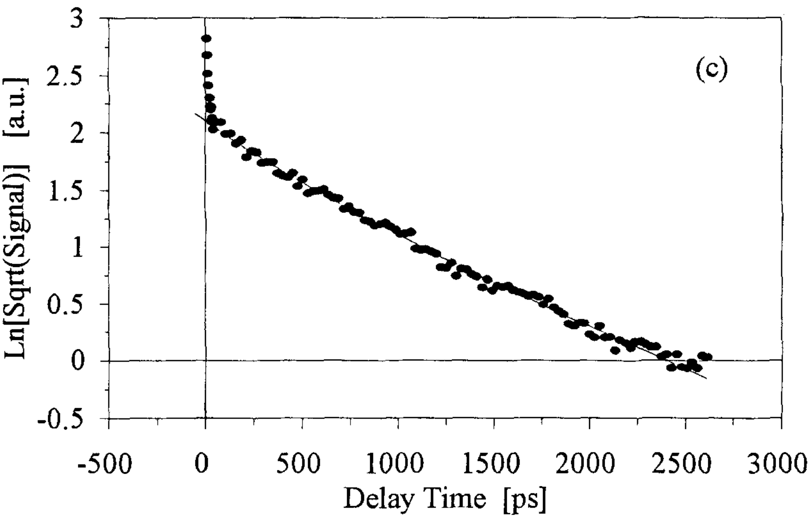


FIGURE 2 (a-c)
Decay of Transient OKE signal on ZLI for a temperature of 400 K. The fitting gives relaxation times of 500±70 psec and 1400±170 psec.

In Figure 2(c) we report the biexponentials fitting. The OKE signal has been measured for many sample temperatures from 372 K to 453 K. From the data fitting we extracted the relaxation times for each temperature and so determine the temperature dependence of all the dynamics present in the decay.

Slow dynamics

Figure 3 shows the temperature dependence of the slow relaxation time. The slow dynamics display clearly a critical slowing down effect in the relaxation times approaching the isotropic-nematic phase transition. The agreement between the temperature dependence of experimental data and the reorientational time defined by the L-dG theory, see equation (8), suggests unambiguously that the slow dynamics has to be addressed to the local orientational order parameter. From the fitting, continuous line in figure 3, we find T*= 354±0.5 K. The difference between real and virtual phase transition temperature, T_c-T*, is about 2 K in good agreement with other experimental values[9].

Intermediate dynamics

The measurement of the intermediate relaxation times (second exponential decay in the fitting) has been much less straightforward than the slow one. The visibility of this decay is strongly dependent by the relative intensity of the slow and intermediate decay and by the signal to noise ratio. To maximize the fitting sensitivity we apply a decomposition procedure: the slow decay has been fitted with a single exponential and subtracted to the data, the residual decay has been fitted with an other exponential. Approaching the phase-transition the relative weight of the slow decay increase and the signal to noise ratio decrease making the measurement of the intermediate relaxation time more difficult.

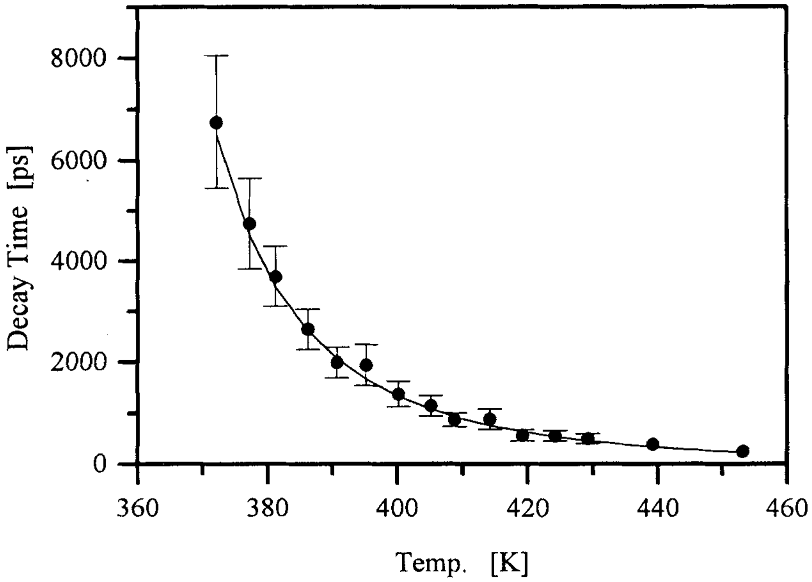


FIGURE 3 Temperature dependence of slow relaxation times (•) with the reorientational time defined by the L-dG theory (—).

Therefore, has been possible to fit reliably the second exponential decay up to 386 K. In Fig. 4 we report the intermediate relaxation times as function of the ratio $\eta(T)/T$. The linear function represents the prediction of D-S-E theory, see equations (7). From the linear fit we find an angular coefficient (according to D-S-E theory equal to V_{eff}/k) of (83 ±10) 10^3 [K·psec/cP] = 8.3 10^{-5} [K/Pa], that give an effective molecular volume of $V_{eff} = 1100 \pm 150$ Å^3. Considering the error affecting the intermediate relaxation data, we find a reasonable agreement between the experimental effective volume and the effective volume (averaged for the three different molecules present in the mixture) computed according the hydrodynamics theory with stick boundary condition[2]: $\langle V \rangle_{stick} \cong 1120$ Å^3 (being the axial ratio about 3.5 and the van der Waals volume about 400 Å^3). Within the experimental resolution, the intermediate dynamics is in substantial accord with the D-S-E theory. Therefore we can ascribe this dynamics to the diffusive reorientational motions of the long axis of molecules (tumbling). Because three distinct molecules are present in ZLI-1167 we observe the tumbling of averaged molecular long axis.

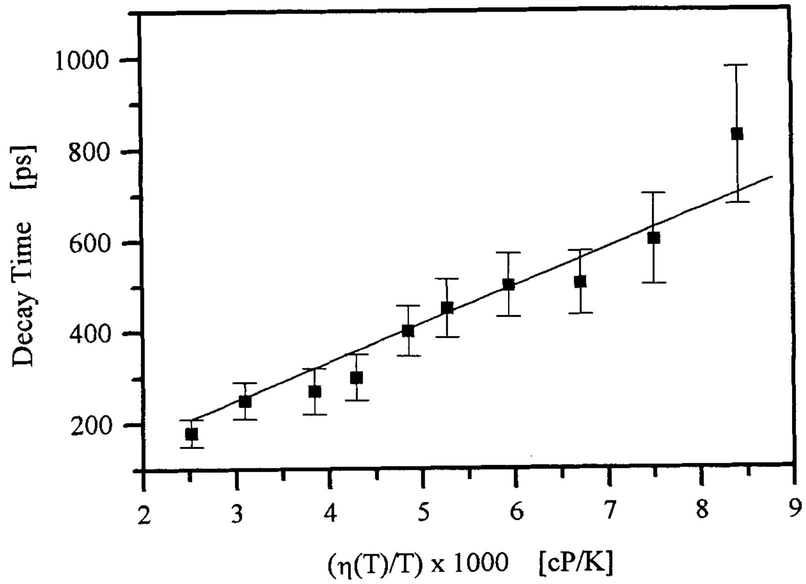


FIGURE 4 Temperature dependence of intermediate relaxation times (■) with the reorientational time defined by the D-S-E theory (—).

Fast dynamics

Subtracting the intermediate and slow relaxation exponential decay from the experimental data a residual fast decay is present. The signal to noise ratio of this residual relaxation is pretty low and does not allow a confident fitting. The magnitude of relaxation times is ranging from about 9 psec at 400 K to about 3 psec at 439 K. Many different relaxation processes can contribute in this fast time scale. First of all the spinning reorientational dynamics (reorientation around the long axis) has to be consider because the symmetry of ZLI molecules is not exactly symmetric top. Simultaneously, other degree of molecular freedom must be contemplate and they could be coupled with spinning motion. Between them: conformational rearrangement, vibrational and librational dynamics. Often in the dynamics of molecular liquids a further time scale separation applies among the fast motions. An ultrafast time scale (≤1 psec) where the molecular vibration and librations are the principal channel of anisotropy relaxation, and a slower time scale (few psec) where the conformational motions and spinning reorientation are the main processes. The ultrafast motions are strongly coupled to the "local cage" and should be analyze in a many-body frame work. Therefore, according to the microscopic picture previously outlined, the C^{CI} term in eq. (5) cannot be neglected any more. Vice versa, the slower dynamics is normally characterized by a diffusive nature. However, in the case of ZLI this time separation, corresponding to two fast relaxation regimes, can be misleading: in fact, as a consequence of the articulated molecular structure, several different conformational dynamics, each one characterized by its own time constant, are expected to affect the relaxation. In conclusion, there is very little hope to safely identify the relaxation times present in the fast time scale.

GENERAL DISCUSSION

Considering the accord between the experimental results and the basic theoretical models of reorientation we can outline a picture of the molecular dynamics.

On the ultrafast time scale the dynamics is strongly determined by the instantaneous liquid phase structure. As we saw in the previous paragraphs, a microscopic interpretation based on isolated molecule polarizzability or on an averaged single molecule approach does not apply in this time scale. The fast relaxation of the induced anisotropy has contributions from several motions of different character: typically non diffusive dynamics, like vibrations and librations, and essentially diffusive processes like conformational and spinning motions. The introduction of a further time scale separation, that would be required in order to make the identification of the individual processes possible, appears arbitrary in view of the complex and articulated molecular structure.

The fast dynamics does not randomize completely the anisotropic molecular orientations and so other relaxations take place on longer time scale. In the intermediate and slow time scale the fast motions can be treated in an averaged way, thus limiting the possible relaxation processes to the reorientation of the long molecular axis. The agreement of the temperature dependence of the intermediate relaxation times with the D-S-E theory suggests a diffusive single molecule interpretation. In other words the residual orientational anisotropy relaxes by diffusive tumbling motion.

Finally, the slow relaxation observed in our experiments, shows that a residual anisotropy is left, which is not canceled by the above mentioned mechanism. The L-dG theory ascribes the slow dynamics to the motion of the order parameter (local orientational order). This short range order is due to the set up of orientational pseudo-domains in the liquid phase whose correlation length increase approaching the phase transition[9]. The agreement between L-dG theory and slow decay data suggests the collective nature of this dynamics but does not give clear indication if it has to be directly connected to the intermolecular correlation or to the cooperative effects on the single molecule dynamics. In a single molecule picture this features can be explained considering the long molecular axis moving in a local potential (restricted angular range of rotation) and an anisotropic orientational distribution of local potentials. The local potential is a local mean field effect (in this respect is different from the local cage) defined by the short-range orientational order. The slow dynamics, according to this picture, is the randomization of the local potential distribution and the randomization time of the local potential distribution corresponds to the decay time of the order parameter correlation function defined by L-dG theory.

This picture of molecular dynamics can apply not only to the present experimental results but also to the other complex fluids' data[3,4]. In our opinion, far from being a complete interpretation, this description captures some essential aspects of the dynamics in complex liquids.

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