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Reorientation dynamics of ferroelectric liquid-crystal molecules near the smectic-A –smectic-C^* transition

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A transient optical Kerr measurement is used to study molecular reorientation about the long molecular axis of chiral and nonchiral smectic-A liquid crystals. Two relaxation components were identified, associated with individual and collective molecular motions. In contradiction with a recent report [J. R. Lalanne *et al.*, Phys. Rev. Lett. **62**, 3046 (1989); Phys. Rev. A **44**, 6632 (1991)], no critical behavior of this reorientation was observed as the transition to the ferroelectric smectic-C^* phase was approached.

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Dynamic effects of molecular reorientation near the transition from the smectic-A (Sm-A) to the ferroelectric smectic-C^* (Sm-C^*) phase have been the subject of considerable recent interest [1–5]. The Sm-A–Sm-C^* transition, like the Sm-A–Sm-C transition in nonferroelectric liquid crystals (LC's), is known to be driven by the tilting of the long molelcular axis away from the smectic layer normal [3]. The tilt angle is the primary order parameter for this second-order phase transition, and tilt angle fluctuations in the Sm-A phase show the expected slowing-down behavior predicted by Landau theory [4]. Coupled to the tilt angle is a macroscopic transverse polarization, which results from a biased or hindered rotation of the chiral (polar) molecules about their long axes in the Sm-C^* phase [3]. This transverse polarization $\mathbf{P}_\perp$ can be regarded as a secondary order parameter for the Sm-A–Sm-C^* transition, and it too can exhibit pretransitional behavior. One would then ask whether the rotational dynamics about the molecular long axes might also shown some pretransitional characteristics. Recently, Lalanne *et al.* [1] reported a degenerate four-wave-mixing experiment with results suggesting the presence of a critical behavior in this molecular reorientation above the transition. Their experiment, however, only monitored the temperature dependence, but not the temporal behavior, of the signal. Thus they could not observe directly the expected critical slowing-down behavior, and their results are difficult to interpret. In more recent dielectric spectroscopic studies [5], no evidence of critical slowing down was found, but these experiments were limited to detection of rotational motions longer than 1 ns.

In this paper, we report an experiment using the transient optical Kerr effect (TOKE) technique to study the rotational dynamics in the 50 ps–1 ns range. Both the amplitude and time dependence of our signal were measured as functions of temperature. In both chiral and nonchiral Sm-A liquid crystals we observe two components in the relaxation of the molecular reorientation about the long molecular axis, which we associate separately with individual (fast) and collective (slow) molecular motions. Since for the chiral ferroelectric liquid crystals (FLC's) the characteristic times for these motions remain constant in approaching the Sm-A–Sm-C^* transition, we conclude that there is no detectable pretransitional slowing down in these rotations. This result can be understood if the couplings of the laser-induced molecular reorientation with the tilt angle and the transverse polarization $\mathbf{P}_\perp$ are weak. In addition, the fact that the molecular response for FLC's and nonchiral LC's exhibits the same general behavior implies that the correlated molecular reorientation observed is not related to the Sm-A–Sm-C^* transition.

We performed experiments on two different ferroelectric liquid crystals. Sample 1 was the mixture ZLI-3488 used by Lalanne *et al.* [1,6]. It was provided by Merck and has a phase sequence of

$$\text{isotropic} \xrightarrow[85\,^\circ\text{C}]{} \text{chiral nematic} \xrightarrow[66\,^\circ\text{C}]{} \text{Sm-}A \xrightarrow[61\,^\circ\text{C}]{} \text{Sm-}C^* \xrightarrow[<-30\,^\circ\text{C}]{} \text{crystal}$$

and a spontaneous polarization of $+9.7\ \text{nC/cm}^2$ at 20 °C. Sample 2 was a pure substance, 4-(2-methyloctanoyl)-4′-biphenyl 3-chloro-4-butyloxybenzoate [7], with a phase sequence of

$$\text{isotropic} \xrightarrow[104\,^\circ\text{C}]{} \text{Sm-}A \xrightarrow[63\,^\circ\text{C}]{} \text{Sm-}C^* \xrightarrow[8\,^\circ\text{C}]{} \text{crystal}$$

and a spontaneous polarization of $-229\ \text{nC/cm}^2$ at 53 °C. If there were a pretransitional slowing down of the molecular reorientation due to coupling with $P_\perp$, one would expect the effect to be more significant for a system with a higher spontaneous polarization. For purposes of comparsion we also studied the nonchiral liquid crystal 4′-n-octyl-4-cyanobiphenyl (8CB) and the standard Kerr liquid carbon disulfide (CS_2).

The liquid-crystal samples were homeotropically aligned between fused quartz plates treated with the surfactant N,N-dimethyl-N-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP). They were cooled from the isotropic (I) phase into the Sm-A phase in the presence of a 1.7-T magentic field to ensure a uniform alignment. The FLC cells were temperature controlled to within ±15 mK. The Sm-A–Sm-C^* transition temperature T_{AC} could be identified by a sudden increase in light scattering. The CS_2 and 8CB samples were measured at room temperature (23 °C). All cells were 130 μm thick.

A schematic of the experimental setup is shown in Fig. 1. An s-polarized pump pulse induces molecular reorientation about the surface normal and hence a birefringence in the homeotropically aligned Sm-A liquid crystal [1,8]. As the molecules relax back to their original orientation distribution, the birefringence decays. A linearly polarized probe laser pulse propagating along the optical axis of the sample is used to monitor the birefringence. The probe pulse can be delayed to measure the time dependence of the birefringence. Thus both the magnitude and the time dependence of the molecular reorientation can be deduced.

We used an actively mode-locked neodymium-doped yttrium lithium fluoride (Nd:YLF) laser yielding 55-ps (full width at half maximum), 1.053-μm optical pulses at 100-MHz repetition rate. The output was split into a pump beam and a probe beam. The 5.5-W pump beam was amplitude modulated and focused to a beam waist of 80 μm in the sample. The intensity of the pump field in the sample was 10 MW/cm^2. The probe beam was frequency doubled to yield a 10-mW green beam, which was focused to a beam waist of 20 μm and overlapped with the pump beam in the sample. To increase the sensitivity we used a polarization heterodyne-detecton technique [9], wherein the polarization was rotated by a small angle α ($<1°$) away from crossing with the analyzer, and a quarter-wave plate with its slow or fast axis along the analyzer direction was inserted. Assuming that the birefringence induced in the sample is small, one finds the signal S as

$$S(t_D)=\int_{-T/2}^{T/2} dt\,|E_{\text{probe}}(t-t_D)|^2 \sin(2\alpha) \times(2\pi L/\lambda)\Delta n(t)\ , \qquad (1)$$

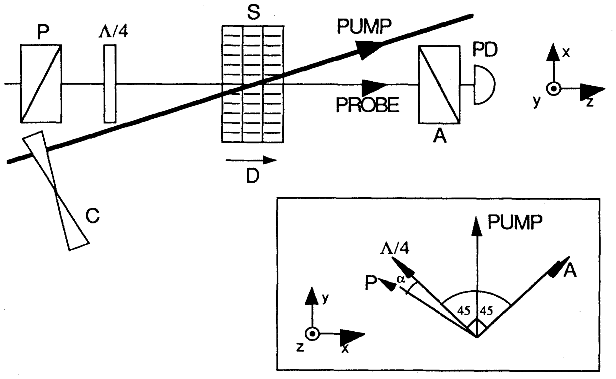

FIG. 1. Simplified schematic of the experimental setup: (P) polarizer, (Λ/4) quarter-wave plate, (S) sample, (D) liquid crystal director, (A) analyzer, (PD) photodetector, (C) chopper. The inset shows the polarization configuration: (P) polarizer direction, (Λ/4) quarter-wave plate fast or slow axis, (PUMP) the pump beam polarization, (A) the analyzer direction, (α) polarizer misalignment angle (exaggerated for clarity).

where $E_{\text{probe}}(t)$ is the probe field, t_D the delay between the probe and pump pulses, L the thickness of the sample, λ the probe wavelength, $\Delta n(t)$ the induced birefringence, and T is the data collection time much longer than the pulse width. In terms of a response function $G(t)$, the induced birefringence is given by

$$\Delta n(t)=\int_{-\infty}^{t} dt' G(t-t')|E_{\text{pump}}(t')|^2\ , \qquad (2)$$

where $E_{\text{pump}}(t)$ is the pump field [9].

Carbon disulfide was used as a calibration. Data from CS_2 are shown in Fig. 2. Since the orientational relaxation time for CS_2 (~2 ps) [9] is much shorter than our laser pulse width, $S(t_D)$ is essentially a cross-correlation trace of the pump and probe pulses. Data taken from 8CB are also shown in Fig. 2. There is a unresolved fast component of the relaxation process with a characteristic time shorter than our 55-ps pulses. Recent experiments performed with 5-ps pulses show that this fast component has a characteristic time less than 5 ps [10]. In addition, there is clearly a slow component of smaller magnitude, with a time constant of 1±0.5 ns. We can qualitatively understand the result by considering a group of molecules moving in a cage [9,11]. The fast component corresponds to individual molecular motion within the cage; the slow one to the collective reorientation of the whole cage. We note that the measured time constant of the correlated motion is in fair agreement with the values measured in the dielectric spectroscopy experiments [5].

Representative data taken using the FLC mixture (sample 1) at two temperatures are shown in Fig. 3(a). There are again both fast and slow components of the relaxation. The slow component has a characteristic time of 3.0±1.5 ns. We found no change in our signal over the entire temperature scan from 3.3 °C to 0.1 °C above T_{AC}. Data taken using the single-component FLC (sample 2) is shown in Fig. 3(b). Again we can resolve two components. The slow component has a relaxation time of 0.7±0.3 ns. The results at two temperatures 1.2 °C and 0.1 °C above T_{AC} also show no critical divergence or slowing down. The signal at zero delay from 8CB and the FLC samples are approximately three times larger than the signal from CS_2.

The absence of critical slowing down at the Sm-

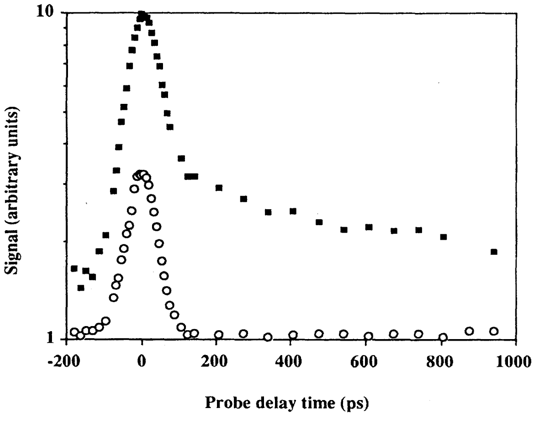

FIG. 2. TOKE signal vs probe delay time. (○) CS2; (■) 8CB.

A-Sm-C^* transition can be explained in terms of a Landau–de Gennes (LdG) theory. We are interested in the pretransitional behavior, under the influence of a pulse of optical radiation, of the order parameter associated with the biaxiality of our sample. Since the LdG theory describes collective rather than individual molecular behavior, the order parameter is associated with the slow component of the response observed in our experiment.

To describe the Sm-A-Sm-C^* transition, we must include in the calculation the usual order parameters θ and P, representing the tilt angle of the director away from the smectic layer normal and the transverse polarization, respectively. Since we are particularly interested in the biaxial ordering induced by the laser field, we must also include a biaxial order parameter B defined as the biaxial part of the general orientation order parameter $\mathbf{Q}$ [12]

$$\mathbf{Q}=\begin{bmatrix} S+B & 0 & 0 \\ 0 & S-B & 0 \\ 0 & 0 & -2S \end{bmatrix} . \tag{3}$$

Here the scalar S describing uniaxial nematic ordering may be considered constant, since this degree of freedom is frozen out in the Sm-A phase. We can write the free energy F of the FLC in its Sm-A phase as a power series in θ, P, and B, including terms only to the third order:

$$F=a(T-T_c)\theta^2+b\theta^4+cP^2+dB^2+e\theta P+f\theta^2B +gP^2B+h\theta PB-\chi E^2B , \tag{4}$$

where a, b, c, d, e, f, g, h, and χ are weakly temperature-dependent constants depending on the material. Although for simplicity we have not expressed F in terms of θ, $\mathbf{P}$, and $\mathbf{Q}$, Eq. (4) is actually equivalent to the free-energy expression used by Lalanne *et al.* [1] and by Blinc [3]. Since θ is the primary order parameter driving the transition, the coefficient of the θ^2 term must contain a T-T_c temperature dependence [13]. The Sm-C^* phase is invariant under a 180° rotation about the layer normal. This operation causes θ and P to change sign, but leaves B unchanged. Consequently, all terms in F containing θ^nP^m with $n+m$ being odd, including the linear coupling terms θB and PB, must vanish. Thus to first order, the biaxial order B is not coupled to θ or P. We have included the θ^4 term in F for stability. Finally, the χE^2B term describes the coupling of the biaxiality to the incoming linearly polarized optical field E.

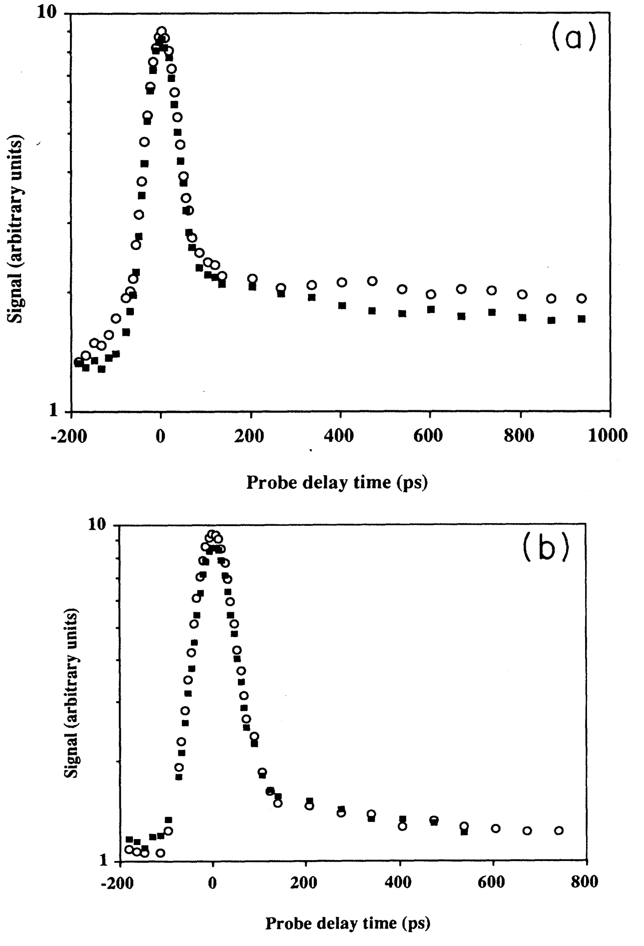

FIG. 3. TOKE signal vs probe delay time. (a) Merck ZLI-3488. (○) $\Delta T=T-T_{AC}=3.3\,^\circ\mathrm{C}$; (■) $\Delta T=0.1\,^\circ\mathrm{C}$. (b) Sample 2. (○) $\Delta T=1.2\,^\circ\mathrm{C}$; (■) $\Delta T=0.1\,^\circ\mathrm{C}$.

We are interested in the critical behavior of the biaxial order parameter B as the temperature is reduced toward the Sm-A-Sm-C^* transition. We first consider the amplitude of the steady-state response to E. This is obtained by minimization of F with

$$\frac{\partial F}{\partial \theta}=0 , \quad \frac{\partial F}{\partial P}=0 , \quad \frac{\partial F}{\partial B}=0 . \tag{5}$$

Since all the order parameters θ, P, and B are expected to be small in the Sm-A phase, we will neglect, in the first-order approximation, all the higher-order terms in F. We then find

$$B=\frac{\chi E^2}{2d} , \quad \theta=P=0 . \tag{6}$$

This shows explicitly that the induced biaxial order should remain essentially constant as the Sm-A-Sm-C^* transition is approached. This prediction describes our experimental observations very well, showing that the couplings between B and θ,P are negligible.

Since critical slowing down is always correlated with critical divergence, absence of critical divergence in B indicates that no critical slowing down of the biaxial response should be observed. This can be seen explicitly from the Landau-Khalatnikov equations describing the dynamic response of the order parameters [14]

$$\frac{\partial B}{\partial t}=-\gamma\frac{\partial F}{\partial B} , \tag{7}$$

with similar equations for θ and P, where γ is the effective rotational viscosity of the medium. Neglecting the higher-order terms in F leads to

$$\frac{\partial B}{\partial t}=-2\gamma dB , \tag{8}$$

with the field off. The solution is an exponential decay with a time constant $1/2\gamma d$, which is nearly independent of temperature. This again agrees with our experimental results, exhibiting no critical slowing down of B at the Sm-A–Sm-C^* transition.

Inclusion of the nonlinear coupling terms in our theoretical treatment could impart to B a critical behavior, as suggested by Lalanne *et al.* [1]. Whether such a critical behavior is in fact observable in a real system depends on the relative magnitude of the linear and nonlinear coupling terms in the free energy. If the nonlinear coupling terms are weak, the resulting critical behavior in B could be very difficult to observe. On the other hand, if the nonlinear coupling is very large, the LdG theory is inapplicable and the system may enter a regime of strong nonlinear dynamics. To decide which possibility holds, we must turn to experiments. Since a lack of critical behavior in the biaxial response was observed in dielectric spectroscopy experiments [5], as well as in our optical experiment, we conclude that the nonlinear coupling terms between B and θ, P in the free energy must be negligible. In a separate case, we note that since the order parameters θ and P are linearly coupled, one does expect a critical divergence in the amplitude and time response of the polarization P under the application of a dc electric field.

In summary, our measurements of the temperature dependence of the ampltiude and time response of molecular reorientation of FLC's about their long axes show that there is no critical slowing down of this motion in the Sm-A phase near the Sm-A–Sm-C^* transition. This finding is in accord with a LdG theory neglecting nonlinear coupling between biaxiality and other order parameters. We have also found that the slow reorientation response is independent of the chiral nature of the LC since nonchiral LC's exhibit the same behavior. This slow relaxation component arising from the collective reorientational motion is presumably a precursor to a biaxially ordered phase, which is preempted by the energetically favored Sm-C phase.

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[1] J. R. Lalanne, J. Buchert, C. Destrade, H. T. Nguyen, and J. P. Marcerou, Phys. Rev. Lett. **62**, 3046 (1989); J. R. Lalanne, C. Destrade, H. T. Nguyen, and J. P. Marcerou, Phys. Rev. A **44**, 6632 (1991).

[2] H. R. Brand and H. Pleiner, Phys. Rev. Lett. **64**, 1309 (1990).

[3] R. Blinc, Phys. Status Solidi **70**, K29 (1975); Ferroelectrics **14**, 603 (1976).

[4] S. U. Vallerien, F. Kremer, H. Kapitza, R. Zentel, and W. Frank, Phys. Lett. A **138**, 219 (1989).

[5] F. Kremer, S. Y. Vallerien, H. Kapitza, R. Zentel, and E. W. Fischer, Phys. Rev. A **42**, 3667 (1990); S. U. Vallerien, F. Kremer, T. Geelhaar, and A. E. Wachtler, *ibid.* **42**, 2482 (1990).

[6] In the paper of Lalanne *et al.* [1] the sample number was misprinted as ZLI 13049. We thank J. R. Lalanne for clarifying this error.

[7] A. Yoshizawa, A. Yokoyama, and I. Nishiyama, Liq. Cryst. **11**, 235 (1992).

[8] Because the beam was linearly polarized perpendicular to the LC director there was no reorientation of the long axes of the molecules. This was confirmed by the fact that no dc component of induced birefringence was observed, knowing that such a reorientation would have a response time (>1 μs) much greater than the time between pump pulses (10 ns).

[9] D. McMorrow, W. T. Lotshaw, and G. A. Kenney-Wallance, IEEE J. Quantum Electron. **QE-24**, 443 (1988), and references therein.

[10] E. Freysz, T. Moses, X. W. Zhuang, and Y. R. Shen (unpublished).

[11] C. Flytzanis and Y. R. Shen, Phys. Rev. Lett. **33**, 14 (1974).

[12] E. B. Priestley, P. J. Wojtowicz, and P. Sheng, *Introduction to Liquid Crystals* (Plenum, New York, 1975).

[13] The temperature T_c is related to the Sm-A–Sm-C^* transition temperature T_{AC} by $T_c = T_{AC} + e^2/4ac$. In most FLC's, $e^2/4ac < 1$ K. See Ref. [3] for further details.

[14] E. M. Lifshitz and L. P. Pitaevskii, *Physical Kinetics Landau and Lifshitz Course of Theoretical Physics Vol. 10* (Pergamon, New York, 1981)