

Nonhydrodynamic molecular motions in a complex liquid: Temperature dependent dynamics in pentylcyanobiphenyl

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The isotropic phase of nematogenic substances above the nematic–isotropic phase transition temperature T_{ni} is characterized by short range orientational correlation of the molecules and the existence of pseudonematic domains. This microscopic structure has a strong influence on reorientational dynamics in the liquid. We present time resolved transient grating optical Kerr effect measurements of pentylcyanobiphenyl between 35 and 120 °C, which allow us to monitor dynamics on timescales from subpicoseconds to tens of nanoseconds. The well-known collective component characterizing the reorientational dynamics of the pseudonematic domains follows Landau–deGennes behavior up to 30–35 degrees above T_{ni} where the theoretical correlation length $\xi \approx$ three molecular lengths. Additionally fast relaxation channels (with time constants between 1 and 300 ps) are observed which are associated with local reorientational and intermolecular dynamics *within* the pseudonematic domains. The local dynamics are *temperature independent* in the range where the pseudonematic domains dominate the liquid structure, demonstrating a decoupling of the molecular motions from the bulk viscosity. Only at high temperatures, $T > 70$ °C, where the pseudonematic domains cease to exist, is a viscosity dependence observed. At these elevated temperatures, the slowest contribution to the fast molecular dynamics approximately follows hydrodynamic theory.

I. INTRODUCTION

The nematic–isotropic phase transition is weakly first order; the phase transition is associated with a very small volume change and latent heat.^{1,2} As in second order phase transitions, one finds that many properties of the isotropic liquid display critical behavior on cooling to temperatures close to the phase transition temperature T_{ni} . The microscopic origin of this behavior (often called pretransitional behavior in the liquid crystal literature) is the existence of short range orientational order among the molecules. DeGennes has applied Landau theory to the nematic–isotropic phase transition and shown that the temperature dependence of the coherence or correlation length $\xi(T)$, over which this local order persists, is given by $\xi(T) = \xi_0 [T^*/(T - T^*)]^{1/2}$. Here ξ_0 is a molecular length and T^* is a temperature slightly below T_{ni} .^{1,3} $T_{ni} - T^*$ is typically around 1–2°, and therefore right above the phase transition ξ is of the order of 10–20 molecular lengths, i.e., the pseudonematic domains have a diameter of 10–20 nm. The validity of the Landau–deGennes (LdG) theory close to the phase transition has been experimentally confirmed by the measurement of static parameters like magnetic⁴ and electric birefringence^{5,6} and scattered light intensity,^{4,7} as well as dynamic effects as observed in nuclear spin lattice relaxation,⁸ dynamic light scattering (DLS),^{4,7} and optical Kerr effect (OKE)^{6,9,10} experiments. Magnetic and electric birefringence measurements over a large temperature range¹¹ indicate deviations from the LdG behavior at 15–20° above the phase transition. However, it is still unknown

what effect the reduction in size of the pseudonematic domains with temperature increase has on the *dynamics* of molecular reorientation. The central goal of the experiments presented here is to monitor molecular dynamics in the pretransitional phase of a nematogenic substance over a large temperature range and to investigate the effect of the disappearance of the pseudonematic domains on rotational (and intermolecular) dynamics. This has been made possible by using subpicosecond time resolution, which represents an improvement of four orders of magnitude compared to the bulk of earlier experiments.^{6,9,10}

The isotropic phase of a liquid crystal is macroscopically a normal liquid. However, the existence of a high degree of local order, which persists for an extended time period, provides an opportunity to investigate the influence of local liquid structure on the dynamics of molecules. Hydrodynamic theory has been remarkably successful in describing the reorientation of molecules in relatively simple liquids. Here we report molecular reorientational dynamics which are nonhydrodynamic. Fast relaxation channels (with time constants between 1 and 300 ps) are observed which are associated with local reorientational dynamics *within* the pseudonematic domains. The local dynamics are *temperature independent* in the range where the pseudonematic domains dominate the liquid structure, demonstrating a decoupling of the molecular motions from the bulk viscosity. Only at high temperatures, $T > 70$ °C, where the pseudonematic domains cease to exist, is a viscosity dependence observed.

In the seventies the investigation of reorientational dy-

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namics in the isotropic phase of nematogenic substances focused on the slow collective motion arising from the fluctuations of the order parameter and described by the LdG theory.^{4,6,7,9,10,12} This motion characterizes the dynamics of the domains as a whole and can be associated with the relaxation time of these structures. However, early on Flytzanis and Shen¹³ argued that besides this slow component there should be fast rotational motions due to local molecular dynamics affecting a single or a few molecules within the pseudonematic domain. The existence of this fast contribution was indeed confirmed by a frequency domain¹⁴ and a time domain¹⁵ experiment. However, due to limited time resolution and/or temperature range, the effect could only be established. With the improved time resolution of the experiments presented here, a more detailed investigation over a large temperature range was possible.

In ordered and partially ordered structures like liquid crystals molecular motions are extremely complex,¹⁶ involving internal degrees of freedom, translation and rotation of the whole molecule as well as coupling between these types of motion. Molecular rotational dynamics can be investigated by a large number of spectroscopic techniques,¹⁷ e.g., Raman scattering, infrared line shape analysis, fluorescence depolarization, neutron scattering, nuclear magnetic resonance (NMR), electron spin resonance (ESR), DLS and OKE experiments. Each of these experiments monitors a certain observable and its time correlation function, thereby focusing on a different aspect of the molecular motion and being sensitive to a different type of coupling between rotational motion and translational and internal degrees of freedom. Only through the multitude of these experimental techniques can one obtain a detailed picture of the molecular dynamics and hope to achieve a satisfying description. NMR¹⁸ and ESR¹⁹ experiments have been especially popular in the investigation of liquid crystals. They measure single particle rotational dynamics and give access to single particle correlation times. They allow site-selective studies, i.e. the observation of the rotational dynamics of specific atoms in the mesogen and thereby an investigation of the coupling of whole molecule rotation with internal motions.^{20,21} A disadvantage of these methods is that one has to assume a certain form of the reorientational correlation function and the coupling of the spins to the molecular motion to interpret the spectral densities found in the experiments. Also, to simplify the experiment, it is often necessary to study a selected solute in the nematogenic solvent, and one cannot directly investigate the reorientation of the nematogenic molecules. Nevertheless, the magnetic resonance methods have revealed a large amount of detailed information about rotational motion in liquid crystal forming substances.^{18–25}

OKE and DLS experiments give a more direct model-free access to the correlation function or its Fourier transform. In contrast to NMR and ESR, the DLS and OKE techniques measure fluctuation and relaxation of the dielectric susceptibility in the sample and therefore give access to collective dynamics. In addition to rotational dynamics, the dielectric susceptibility is influenced by so-called interaction-induced or collision-induced (CI)

phenomena, i.e., intermolecular translational motions. For this reason, DLS and OKE data can contain CI contributions that allow one to gain information about intermolecular dynamics.

Whereas frequency domain DLS has been applied to the study of molecular rotational dynamics for some time,¹⁷ the complementary time resolved experiment has only recently become feasible.^{26–30} As rotational dynamics of small molecules take place on a picosecond and subpicosecond timescale, it took the advent of reliable subpicosecond laser systems to perform the appropriate time domain experiment on a regular basis. The data presented in this paper have been recorded with a transient grating (TG) method. A TG approach to study the OKE was first used by Eyring and Fayer.³¹

In a TG experiment two coherent time coincident laser excitation pulses overlap in the sample and generate an optical interference pattern. If the length τ_p of the pulses is short compared to the characteristic response times of the sample, the interference pattern sets up a spatially periodic response in the sample, which is described by the impulse response function $G(t)$ of the material. The probe pulse, which is variably delayed in time, is scattered off this grating. Neglecting absorption, the intensity of the scattered light is given by

$$I(t) \propto |\chi^{(3)}(t)|^2 \propto |\delta\epsilon(t)|^2 \propto |G^{\text{ee}}(t)|^2. \quad (1)$$

Here $\chi^{(3)}$ is the third-order nonlinear susceptibility, $\delta\epsilon$ is the peak-null difference of the dielectric constant in the optical grating, and G^{ee} is the impulse response function of the dielectric constant of the sample. On the other hand, the DLS frequency domain spectrum is given by

$$I(\omega) \propto (kT/\omega) \text{Im}[G^{\text{ee}}(\omega)], \quad (2)$$

with $G^{\text{ee}}(\omega)$ and $G^{\text{ee}}(t)$ being related by Fourier transform. Yan and Nelson in two recent papers³² have given a detailed account of the TG experiment and have compared it to the DLS technique. They have shown that in the limit of infinite time and frequency resolution, the TG and the DLS experiment contain the same information and monitor the same processes. They have analyzed a number of special cases and have demonstrated that, nevertheless, the time resolved or frequency resolved experiment can be advantageous to extract certain information from the data. We have recently studied the reorientational dynamics of biphenyl³⁰ and compared it to a DLS investigation of the same system.³³ In the case of several decay components, the TG-OKE approach readily permits the observation of the faster phenomena characterized by a higher signal/noise (S/N) ratio whereas the opposite is true for the DLS method, favoring the investigation of the slower phenomena.

As demonstrated recently by Etchepare *et al.*^{34,35} and Deeg and Fayer,³⁶ a polarization selective TG setup allows identification and discrimination of physical processes which are characterized by different symmetries of the third-order nonlinear susceptibility tensor $\chi^{(3)}$. For example, it is possible to separate the electronic and nuclear OKE, and suppress thermal and acoustic wave effects.^{31,36}

In the measurements presented in this paper, we have used several experimental configurations which suppress the unwanted contributions to the TG signal and monitor only the nuclear OKE, the signal of interest.

The nuclear OKE is caused by the interaction of the excitation pulses with the polarizability of the sample, and the torque the pulses exert on the induced molecular dipoles. One can distinguish between single molecule polarizability, which governs the response of individual molecules in the medium, and higher order polarizabilities, which determine the response of molecule pairs and oligomers³⁷ (corresponding to the CI phenomena mentioned earlier).

As discussed in the papers of Nelson's and Kenney-Wallace's groups,²⁶⁻²⁹ the short time response ($\tau < 1$ ps) of the sample is dominated by molecular librations. (Librations, which involve rotations, are coupled to translations. The motion which is referred to as a libration is almost certainly a mixed mode.) The interaction with the single molecule polarizability kicks the molecules out of their equilibrium orientations within their solvent cages. The molecules start to librate within the solvent cages and the initially induced anisotropy decays due to dephasing of the coherently excited librations and damping (thermalization). At room temperature the molecules are librating even under equilibrium conditions; therefore strictly speaking one should say that the optical pulse only induces a deviation from the equilibrium distribution of phase factors and populations of the librators. Based on a molecular dynamics approach, Ladanyi and Geiger³⁸ have recently calculated the OKE response of a CS₂ sample and compared it to the available experimental data.²⁶⁻²⁸ In their analysis, the signal on the ultrafast timescale is dominated by higher order polarizabilities, i.e. intermolecular motions, and not single molecule librational motion. A reliable interpretation of the ultrafast timescale dynamics is still to come.

There exist a number of models with different degrees of refinement for molecular reorientation in liquids.³⁹ However, the vast majority of the experiments can be described by a modified Stokes-Einstein-Debye (SED) equation of the form^{37,40}

$$\tau_r = V_{\text{eff}} \eta / kT + \tau_0. \quad (3)$$

Here τ_r is the rotational relaxation time, η and T are the shear viscosity and the temperature of the sample, k is the Boltzmann constant and τ_0 is an experimentally determined time. V_{eff} is the effective molecular volume.^{41,42} That is, the complex multiparticle interactions in the molecular liquid can be reduced to the volume of the rotating molecule and the macroscopic parameters η and T using hydrodynamic continuum theory. As mentioned earlier, an OKE or DLS experiment measures a collective orientational function, i.e. the relaxation time τ_c observed is (under certain, rather general, circumstances⁴⁰) given by

$$\tau_c = g_2 \tau_r, \quad (4)$$

with g_2 a static orientational correlation parameter for the molecules under investigation. In a TG-OKE study of bi-

phenyl (the parent molecule of pentyl cyanobiphenyl),³⁰ two orientational decay components were found. In both cases a relationship of the form in Eq. (3) was observed.

II. EXPERIMENTAL PROCEDURES

The laser system used has been described in detail elsewhere.⁴³ The 70 ps output pulses of a cw mode-locked Nd:YAG laser at a repetition rate of 83 MHz are sent through an optical pulse compressor and frequency doubled. The resulting 2.5 ps pulses at 532 nm are used to synchronously pump a linear astigmatically compensated three mirror dye laser which is tuned by a single plate birefringent filter. The dye pulses are amplified by pumping a three stage amplifier with frequency doubled pulses from a cavity-dumped, Q-switched and mode-locked Nd:YAG laser operating at 1 kHz repetition rate. For DCM typical pulsewidths are 200 fs with an average pulse energy of 10–20 μ J. To eliminate two-photon absorption in 5CB, which becomes significant at shorter wavelengths,³⁶ an excitation and probe wavelength of 665 nm was chosen.

For the TG-OKE experiments described here, the amplified pulse is split into three pulses to yield the two excitation pulses and the probe pulse. The two excitation pulses, focused to 120 μ m spot sizes, are crossed in the sample at an angle of 15° to produce an optical interference pattern. The optical interference pattern induces the OKE grating, which mimics the interference pattern spatially. This grating is monitored by the 90 μ m spot size probe pulse which is incident at the phase matching angle for Bragg diffraction (slightly noncollinear with the excitation beam to achieve spatial separation). The probe pulse can be variably delayed by an optical delay line which is controlled by a 1 μ m resolution stepper motor. This is used for the short timescale measurements. The stepper motor delay line is mounted on a long optical rail and can be moved along the optical rail with a computer controlled dc motor. The longest delay used in the experiment was 16 ns. Because the TG signal decays as the square of the sample response, this delay is equivalent to a 32 ns delay in a linear experiment.

The intensity as well as the polarization of all three beams can be independently controlled by sets of half-wave plates and linear polarizers. A fourth linear polarizer is set in the signal path and permits any polarization of the diffracted beam to be monitored. Typical single pulse energies used in the experiments were in the range 200 nJ–1 μ J. One of the excitation beams or the probe beam is chopped and the signal, which is picked up by a photodiode or a photomultiplier, is fed into a lock-in amplifier. The output of the lock-in amplifier is connected to a computer, which allows signal averaging by controlling multiple scans of either optical delay line.

5CB from BDH was filtered through a pore size of 0.2 μ m to remove dust particles. *n*-Heptane (Baker, for UV-spectrophotometry) was also filtered. The liquids were placed in a 1 mm spectrophotometric cuvette, which was inserted into a variable temperature cell. The cell temperature could be regulated and controlled within ± 0.2 °C.

The viscosities of the 5CB/*n*-heptane solutions were measured with a Cannon–Ubbelohde semimicro type viscometer. The density over the investigated temperature ranges was calculated using the isobaric expansion formula. Literature values were used for the viscosity of neat 5CB.⁴⁷ The concentration of the 5CB/*n*-heptane solution investigated was 0.66 mol/ℓ. The nematic–isotropic phase transition temperature of 5CB $T_{ni} = 35.2$ °C.⁶

n-Heptane has a small electronic polarization anisotropy of its own. However, TG-OKE experiments on a pure *n*-heptane sample showed that the contribution to the signal due to *n*-heptane molecules is negligible in the 5CB/*n*-heptane samples.

III. RESULTS AND DISCUSSION

Typical TG-OKE results of a neat 5CB sample in the isotropic liquid phase above the nematic–isotropic phase transition are shown in Fig. 1. Figures 1(a–c) show the TG-OKE signal of 5CB at $T = 41.7$ °C on three different timescales. The two traces in Fig. 1(a) have been recorded with two different polarization configurations of the TG setup. The nearly symmetric signal, labeled “electronic-only”, is due to the electronic OKE. As the response time of the electrons (10^{-15} s) is negligible compared to the laser pulsewidths used, this trace gives the instrument response. It demonstrates the time resolution of the experimental setup and defines the $\tau = 0$ position of the optical delay line. The second trace, labeled “nuclear-only”, exhibits the response of the nuclear OKE. The decays on the intermediate [Fig. 1(b)] and slow timescale [Fig. 1(c)] have been recorded with a crossed grating configuration,^{31,36} which suppresses any contributions from laser induced acoustic waves and heating.⁴⁴ As the electronic OKE contribution is negligible on this timescale, the whole signal is due to the nuclear OKE.³⁶ A closer look at the different timescales, involved in Figs. 1(a–c), demonstrates the large dynamic range of the processes monitored. The decay stretches over five orders of magnitude in time, and it is characterized by time constants of hundreds of fs to tens of ns. Figs. 1(a–c) reveal three distinct parts of the signal. There is the ultrafast timescale behavior ($\tau < 2$ ps), which exhibits a sharp rise, a maximum at $\tau \approx 200$ fs and then a decay on the several hundred fs timescale. This part of the signal is due to the dynamics of coherently excited molecular vibrations, as discussed for other liquids like CS₂^{26–28} and nitrobenzene,²⁹ and CI phenomena. Then one finds a smooth intermediate timescale decay for 2 ps $< \tau < 1$ ns, which is followed by a distinctly slower relaxation process for $\tau > 1$ ns.

This slow relaxation process on the ns timescale exhibits a strong temperature dependence. This is illustrated by Figs. 1(c) and 1(d). They show the signal on the ns timescale for two temperatures ($T = 41.7$ °C and $T = 69.4$ °C), but otherwise identical conditions. In strong contrast to this, the ultrafast and intermediate timescale behavior is essentially identical at $T = 41.7$ °C and $T = 69.4$ °C. We will first focus on the slow timescale decay and come back to the faster processes later.

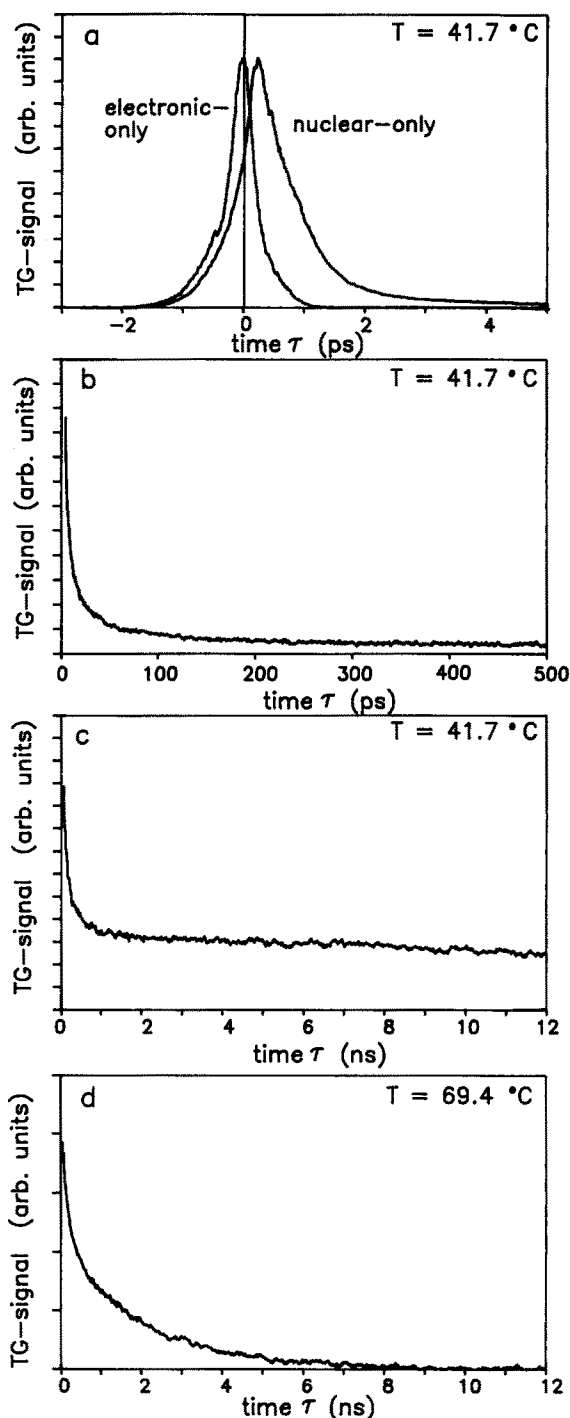


FIG. 1. Optical Kerr effect transient grating signals $S(t)$ for a neat pentacyanobiphenyl (5CB) sample. For Figs. (a–c) $T = 41.7$ °C, in Fig. d $T = 69.4$ °C. (a) Ultrafast timescale behavior. Signals 1 and 2 are recorded with the electronic-only and nuclear-only TG-OKE polarization configuration, respectively. (Ref. 36). (b) Intermediate time scale behavior of the signal, recorded with the crossed grating configuration. (c) and (d) Slow time scale behavior of the signal, recorded with the crossed grating configuration.

A. Slow timescale collective dynamics

Equation (1) shows that the intensity of the diffracted light is proportional to the square of the sample impulse response function $G(t)$. Therefore, before any further data manipulation, we have taken the square root of the recorded TG-OKE signals. This will be important for the

TABLE I. Collective reorientation rates and times for a neat pentylcyano-biphenyl sample. The lower temperature data $36.4\text{ }^\circ\text{C} < T < 41.7\text{ }^\circ\text{C}$ are from the analysis of results with an IR 100 ps experimental setup.

Temperature ($^\circ\text{C}$)	Relaxation time (ns)	Relaxation rate (10^9 s^{-1})
36.4	170	0.0060
37.4	122	0.0082
38.6	95	0.0106
39.6	71	0.0140
40.7	60.6	0.0165
41.7	49.7	0.0201
43.9	33.7	0.0297
46.3	24.9	0.0402
48.6	19.0	0.0527
51.7	13.7	0.0730
55.6	9.9	0.1007
59.0	7.8	0.1286
63.5	5.56	0.1798
69.4	3.96	0.2524
85	1.79	0.560
100	1.02	0.981
120	0.69	1.44

analysis of the faster timescale dynamics discussed below. A semilogarithmic plot then demonstrates that the slowest decay component [for $\tau > 1\text{ ns}$ in Fig. 1(c)] shows single exponential behavior characterized by a single decay constant. A compilation of the relaxation times found this way and their inverse, the relaxation rates, is given in Table I. Over the temperature range investigated, the relaxation time changes from 170 ns to 700 ps.

The temperature dependence of the relaxation time shows that the relaxation time diverges as one lowers the temperature towards the phase transition and the virtual transition temperature $T^* = 34.0\text{ }^\circ\text{C}$,⁶ as expected for an observable with critical behavior. This slow rotational relaxation process characterizes the collective reorientation time, i.e. the decay of the pseudonematic domains. The relaxation times τ_c of the slow decays for $36.4\text{ }^\circ\text{C} \leq T < 41.7\text{ }^\circ\text{C}$ have been verified with a different experimental setup. With the limited range of the optical delay line (ca. 32 ns), the extraction of a decay constant gets more and more difficult as the relaxation time increases. We could obtain a better S/N ratio for the ns timescale signal with a TG setup which used two color, 100 ps pulses (excitation $\lambda = 1064\text{ nm}$ and probe $\lambda = 532\text{ nm}$)⁴⁴ instead of the single color femtosecond pulses. Therefore the numbers in Table I for the lower temperatures originate from an analysis of the IR ps data.

A comparison with the LdG theory is possible if one plots the relaxation rates versus the temperature, as depicted in Fig. 2. The insert shows a magnified section of the low temperature rates. Close to the phase transition, the relaxation rate $k_c = 1/\tau_c \propto (T - T^*)$, as expected from earlier measurements.^{6,7,9,10} At higher temperatures, the temperature dependence of the viscosity is no longer negligible. If one takes this dependence explicitly into account, one expects

$$k_c = 1/\tau_c = b(T - T^*)/\eta = c(T - T^*)\exp(-E_a/kT). \quad (5)$$

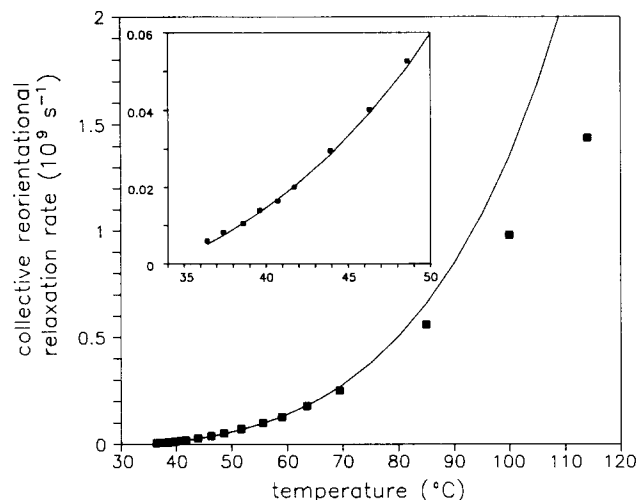


FIG. 2. Temperature dependence of the collective reorientational relaxation rate in a neat pentylcyanobiphenyl sample. The insert shows the magnified lower temperature data. The solid line (in both parts of the figure) is from a one parameter fit through the low temperature $36.4\text{ }^\circ\text{C} < T < 41.7\text{ }^\circ\text{C}$ data according to Eq. (5) with $E_a = 34.3\text{ kJ mol}^{-1}$ and $T^* = 34.0\text{ }^\circ\text{C}$.

In Eq. (5) one assumes the viscosity to follow an Arrhenius law with a single activation energy E_a . The isotropic phase of nematogenic substances is described by three viscosity coefficients η , μ and ν .¹ As demonstrated by several investigations,⁴⁵⁻⁴⁷ the activation energy for the coefficient ν , which influences the collective reorientation, is the same as for η , the static capillary viscosity. We have used the activation energy $E_a = 34.3\text{ kJ mol}^{-1}$ for the shear viscosity, as found by Martinoty *et al.*⁴⁷ Using a virtual phase transition temperature $T^* = 34.0\text{ }^\circ\text{C}$,⁶ we calculated the best fit of the form in Eq. (5) to the low temperature data $36.4\text{ }^\circ\text{C} \leq T < 41.7\text{ }^\circ\text{C}$, by optimizing only the constant c . The result is shown by the solid lines in Fig. 2.

The experimental data follow the theoretical temperature dependence up to $T = 65\text{--}70\text{ }^\circ\text{C}$. Thus, the LdG theory describes the reorientational dynamics of the pseudonematic domains up to $30\text{--}35^\circ$ above the phase transition. The model of the pseudonematic domain with a correlation length $\xi(T) = \xi_0[T^*/(T - T^*)]^{1/2}$ is valid up to $\approx 70\text{ }^\circ\text{C}$, where the correlation length $\xi = \xi_0[307/(343 - 307)]^{1/2} \approx 3\xi_0$. This is on the order of three molecular lengths. At this temperature, the experimental rates indicate that pseudonematic domain structures of such small size are reducing their effect on the dynamics of the liquid. The T -dependence gets shallower, as expected for a transition from a LdG law described by Eq. (5) to the SED behavior given by Eq. (3). It is interesting to note that the temperature range over which the *dynamic* variable “collective reorientation time” follows the LdG law is larger than the range of $15\text{--}20^\circ$ found for static variables.¹¹ We do not know if this is a significant difference or within the error of the measurements and the theoretical fits.

B. Fast timescale molecular dynamics

To investigate the faster dynamics on the ps timescale, we have for each temperature subtracted the slow collective reorientational decay for that temperature from the

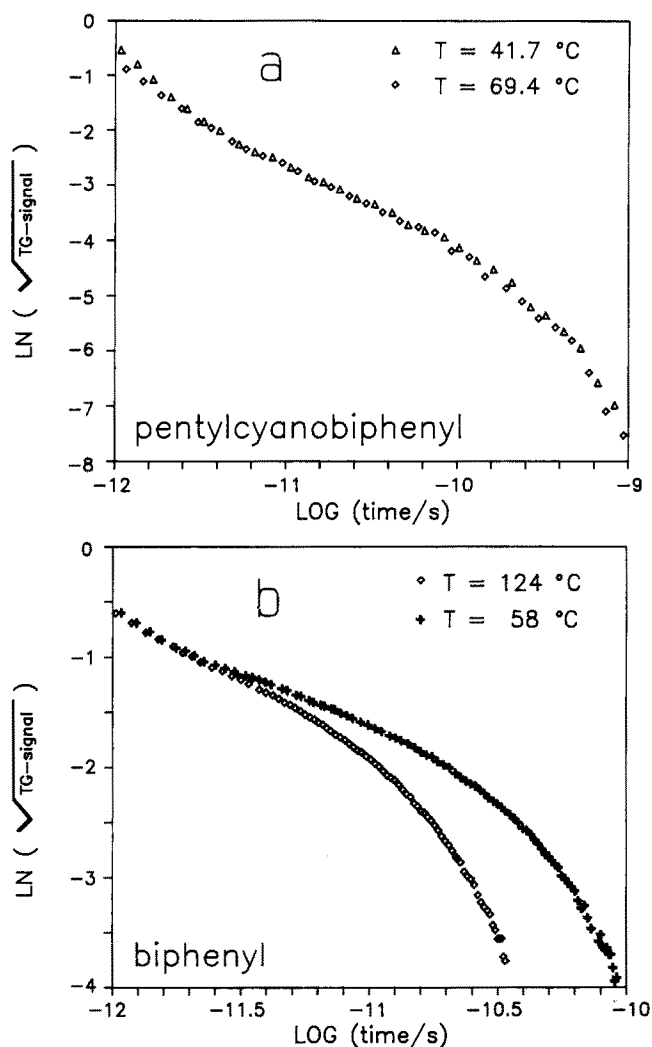


FIG. 3. (a) Intermediate time scale dynamics of neat 5CB at $T = 41.7^\circ\text{C}$ and $T = 69.4^\circ\text{C}$. Double logarithmic plot of $\sqrt{S(t)}$ after subtraction of the slow timescale collective reorientation exponential decays for each temperature. The bulk viscosities at these temperatures are 18.35 cP and 6.35 cP, respectively. The dynamics are temperature independent in spite of the large change in viscosity. (b) Reorientational dynamics of neat biphenyl at $T = 124^\circ\text{C}$ and $T = 58^\circ\text{C}$. Double logarithmic plot of $\sqrt{S(t)}$ with $S(t)$ being the TG-OKE signal. The bulk viscosities of biphenyl at these temperatures are 0.67 cP and 1.93 cP, respectively. Biphenyl is the parent molecule of 5CB but is a simple liquid. For the same magnitude change in viscosity experienced by the 5CB, the two biphenyl curves are very different. (Note that the biphenyl data cover a decade less time than the 5CB data.)

experimental response function; i.e., we have taken the square root of the TG signal and subtracted the slow collective reorientational component. Semilogarithmic plots of these fast and intermediate timescale response functions reveal a strongly nonexponential relaxation pattern with time constants between 1 ps and 300 ps. Only a double-logarithmic plot as shown in Fig. 3(a) provides a clear representation of these fast dynamics.

Figure 3(a) shows the response functions for two different temperatures, $T = 41.7^\circ\text{C}$ and $T = 69.4^\circ\text{C}$. The respective capillary viscosities of 5CB at these temperatures are 18.35 cP and 6.35 cP;⁴⁷ i.e., they differ by nearly a factor of three. It is very evident that the two data sets are

virtually indistinguishable (the small deviation at very early time is due to the effect of slight differences in laser pulsewidths for the two scans on the convoluted experimental response function). The fast dynamics are temperature independent over a range in which the characteristic time constant of the collective dynamics changes by over an order of magnitude.

To illustrate that this is a very uncommon behavior, we have depicted in Fig. 3(b) the diffusive reorientational relaxation dynamics of neat biphenyl, the parent molecule of 5CB.³⁰ The biphenyl data were taken at $T = 124^\circ\text{C}$ and $T = 58^\circ\text{C}$, where the viscosity of biphenyl is 0.67 cP and 1.93 cP, respectively. As in Fig. 3(a), the sample viscosity changes by a factor of three between the two plots in Fig. 3(b). In biphenyl, this change leads to a change of the reorientational decay constant by a factor of three and a large change of the sample response as depicted in Fig. 3(b). It should be noted that the 5CB decays cover one more decade of time and an additional factor of 50 in the dynamic range than the biphenyl data and the 5CB decays are still indistinguishable.

This comparison suggests that the peculiar relaxation behavior of 5CB is associated with the distinct local structure and orientational order in the nematogenic substance which is absent in biphenyl. To gain more information about these circumstances, we have investigated a solution of 5CB in *n*-heptane. The dilution of 5CB in the solvent reduces the influence of the specific intermolecular interactions in the nematogenic substance and suppresses the local orientational order of the molecules. Figure 4 shows typical TG-OKE signals of a 0.66 mol/l 5CB/*n*-heptane solution. The polarization selective TG setup permits the separation of electronic and nuclear contributions to the OKE on the ultrafast timescale [Fig. 4(a)]. The ultrafast dynamics are comparable to the 5CB sample and are caused by librational motions and CI effects. Diffusive reorientation takes place on a timescale of tens and hundreds of ps. A comparison with Figs. 1 reveals one pronounced difference: there is no slow reorientational decay component on the ns timescale as observed in the neat 5CB data. This confirms that no pseudonematic domains with orientational order exist in the 5CB/*n*-heptane solution.

The $\tau > 1$ ps diffusive reorientation reveals nonexponential dynamics. The decay cannot be fit with a biexponential as found for the OKE decay of biphenyl.³⁰ There are several possible explanations for this fact. First, the 5CB molecule cannot be described by a single molecular conformation. Due to different rotameric states around the various C-C bonds, there exists a number of possible *trans-gauche* configurations of the alkyl chain (there are exactly 27 different conformations for 5CB).⁴⁸ At room temperature one expects an equilibrium distribution, to which more or less all of these conformers contribute. Therefore this distribution contains conformers with the alkyl chain directed parallel as well as perpendicular to the length axis of the cyanobiphenyl skeleton. As these different conformers are characterized by different rotational diffusion tensors and reorientational relaxation times, one expects the TG-OKE decay to reflect this distribution of decay con-

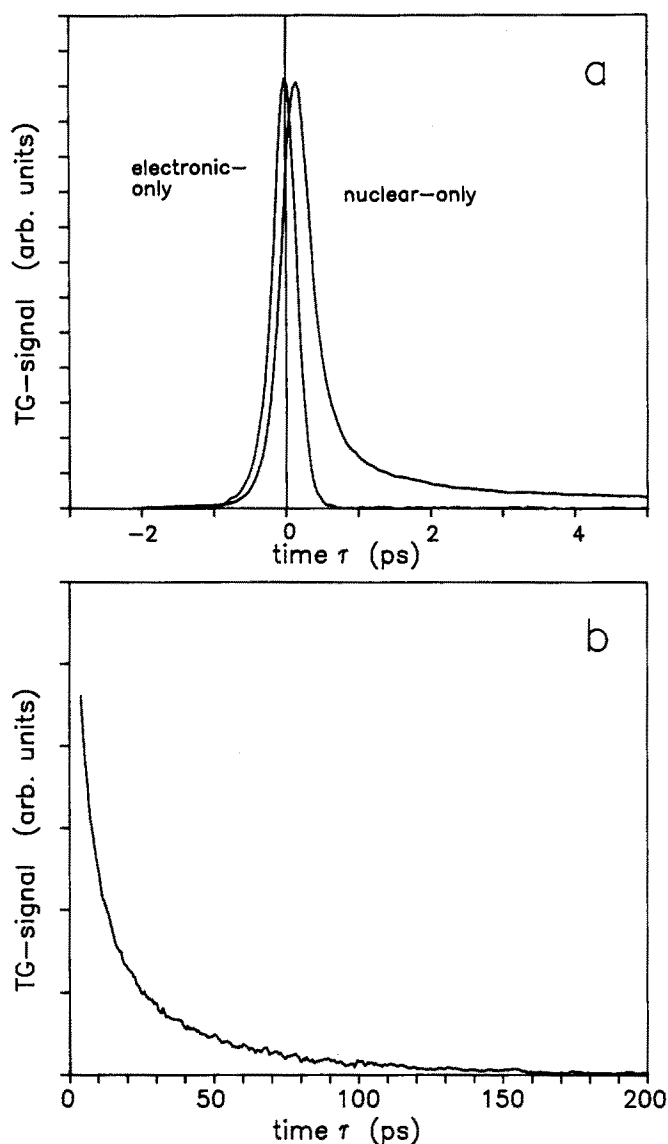


FIG. 4. Optical Kerr effect transient grating signals $S(t)$ for a 0.66 mol/l pentylcyanobiphenyl/*n*-heptane sample at $T = 35^\circ\text{C}$. (a) Ultrafast time scale behavior. The signals are recorded with the electronic-only and nuclear-only TG-OKE polarization configuration, respectively (Ref. 36). (b) Intermediate/slow time scale behavior of the signal, recorded with the crossed grating configuration.

stants. Second, one expects that for some of these conformers (notably those with the alkyl chains sticking out to the side) the principal axis system for the polarizability tensor and the rotational diffusion tensor do not coincide. Under these circumstances the reorientational correlation function (even for a single conformer) is given by a sum of five exponentials.¹⁷ Third, even if one could reduce the rotational dynamics of 5CB to two degrees of freedom of a single conformer (i.e., tumbling and spinning), the intramolecular torsional motion of the two phenyl rings might contribute a third exponential to the TG-OKE decay function.^{30,49}

To analyze the TG-OKE signals of the 5CB/*n*-heptane solution, we have applied an exponential decomposition procedure. That is, after plotting the square root of the TG-OKE signal $\sqrt{S(t)}$ in a semilogarithmic form, we have

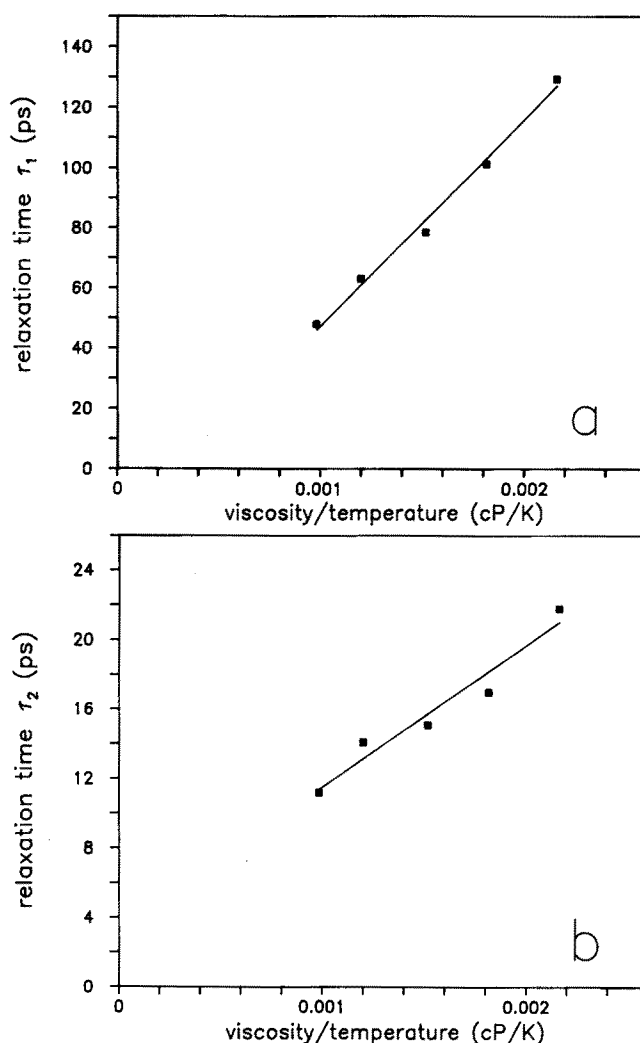


FIG. 5. (a) η/T dependence of relaxation time τ_1 of the slowest decay component of a 0.66 mol/l pentylcyanobiphenyl/*n*-heptane sample. The straight line is a linear fit through the data. (b) η/T dependence of relaxation time τ_2 of the second slowest decay component. The straight line is a linear fit through the data. The straight lines indicate hydrodynamic behavior in the solutions, in contrast to the neat 5CB.

applied a linear fit to the slowest part of the data and extracted a decay constant τ_1 . Then we have subtracted the slow exponential $A \exp[-t/\tau_1]$ calculated in this manner from $\sqrt{S(t)}$. One can extract a second time constant τ_2 from a linear fit to the slowest part of these difference data.

The decay times τ_1 and τ_2 obtained this way over a range of temperatures are plotted in Fig. 5 versus η/T , the ratio of viscosity and absolute temperature. The linear fits, as indicated by the straight lines, demonstrate that the relaxation times τ_1 and τ_2 follow a linear relationship with η/T as expected for a SED type hydrodynamic behavior. The fits through the data of the form in Eq. (3) $\tau_r = \tau_0 + a \eta/T$ yield $\tau_1 = (-21 \pm 8) \text{ s} + (68.5 \pm 3.6) 10^{-9} (\eta/T) \text{ s K/cP}$ and $\tau_2 = (3.3 \pm 1.9) \text{ s} + (8.2 \pm 0.8) 10^{-9} (\eta/T) \text{ s K/cP}$.

The TG-OKE data discussed above clearly demonstrate that rotational dynamics of 5CB in a *n*-heptane solution where there is no or only very small orientational

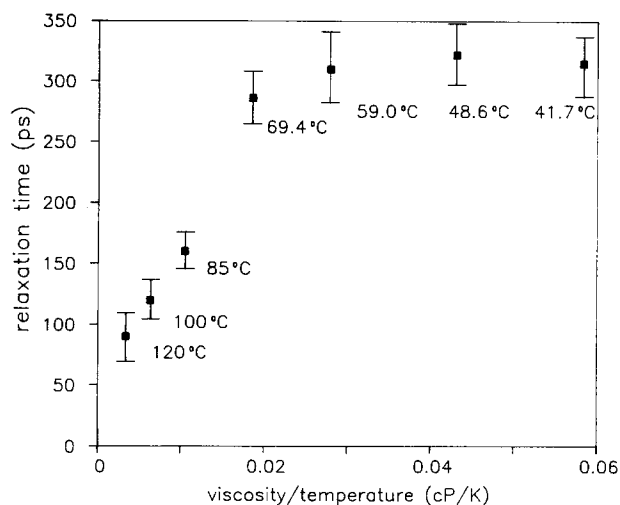


FIG. 6. η/T dependence of the relaxation time of the slowest contribution to the intermediate time scale dynamics $\sqrt{S(t)}$ of 5CB. Below 70 °C the data are temperature independent within experimental error.

order of the 5CB molecules, are consistent with the SED model. This confirms the statement made above that the unusual temperature independence of the intermediate timescale dynamics in neat 5CB is associated with the existence of pseudonematic domains and a distinct local orientational order.

Below 70 °C the data on neat 5CB are temperature independent as displayed in Fig. 3(a). The time constant for the slowest contribution to the intermediate timescale dynamics, however, changes at the elevated temperatures, $T > 70$ °C. Semilogarithmic plots of the intermediate timescale dynamics (the square root of the TG-OKE signal after subtraction of the collective reorientation component) for $\tau > 50$ ps at the various temperatures were made. While the data sets are identical within the experimental error between the phase transition temperature and 70 °C, the data sets for the higher temperatures show a clear acceleration of the dynamics on the 100 ps timescale. The TG-OKE decay for $\tau < 50$ ps, even at $T = 120$ °C, is indistinguishable from the low temperature data.

One can extract a number characterizing this temperature induced change by fitting the slow tail of the intermediate timescale dynamics with a single exponential. The temperature dependence of the decay constants obtained this way is plotted versus η/T in Fig. 6. This graph illustrates the negligible change for $T < 70$ °C (zero change within experimental error) as well as the decreasing relaxation time at higher temperatures. Especially noteworthy in Fig. 6 is the fact that the four high temperature points 69.4 °C $< T < 120$ °C considered alone suggest a linear dependence of the relaxation time on η/T as typically found for rotational dynamics in simple molecular liquids.

It is evident from the results discussed above that any plausible model for the characteristics of the local molecular dynamics of neat 5CB in the pretransitional region has to take into consideration the pseudonematic domain structure in the liquid. In contrast to a simple liquid, re-

orientational relaxation of 5CB takes place within an anisotropic potential of the local domain structure which persists for times characterized by the collective reorientation time τ_c . The time scales of local reorientational relaxation and complete structure randomization are widely separated. The liquid is made up of an ensemble of pseudonematic domains, each domain being characterized by a director. In equilibrium these directors have a uniform distribution of angles, ensuring the isotropic properties of the macroscopic liquid. For the molecules within each domain one finds an orientational distribution around the director which can be characterized by a (local) order parameter S . In the following discussion we will present a qualitative model which is useful in understanding the observed experimental features. It associates the local reorientational relaxation with the dynamics of the order parameter S and the complete structure randomization with the dynamics of the domain director distribution.

As discussed in the introduction, the electric field of the optical pulses exerts a torque on the polarizable molecules. The molecules try to align with the electric field. Because of the short duration of the optical pulse, the molecules experience a sudden impulse and begin to coherently librate (librations excited or phase relationships modified) within the potential well defined by their individual solvent cages. These coherent librations thermalize rapidly on the ultrafast timescale $\tau < 1-2$ ps.

After the librations have thermalized, the molecules find themselves in a nonequilibrium orientational distribution. One can imagine the deviation from the equilibrium distribution to be made up of two contributions: (i) a modified spread of molecular orientations around the director within any given domain and (ii) a preferential alignment of the directors more parallel to the previously applied electric field. We want to illustrate this idea with the help of Fig. 7 which shows (in an exaggerated manner) the evolution of the molecular orientations in a pseudonematic domain upon application of a short optical pulse with a given direction of the electric field relative to the direction of the domains director. The left column of Figs. 7(a, d and g) shows the equilibrium orientational distribution within a pseudonematic domain with the domain director pointing upwards for an order parameter $S_0 = 0.5$ (these figures were generated using a Monte Carlo method). If the applied electric field is parallel to the director [Figs. 7(a-c)], the optical pulse orients the molecules towards the director and creates an orientational distribution within the pseudonematic domain which is described by an order parameter $S > S_0$ [Fig. 7(b)]. If the applied electric field is perpendicular to the director [Figs. 7(d-f)], the optical pulse orients the molecules away from the director and the new orientational distribution is characterized by $S < S_0$ [Fig. 7(e)]. The change of S within the pseudonematic domains depends on the angle between director and applied field. For an angle between 0° and 90° one obtains a distribution intermediate between the extreme cases described above. This is illustrated in Figs. 7(g-i), where the angle between electric field and director is 25°. The optical pulse induces an increase of the local order parameter S

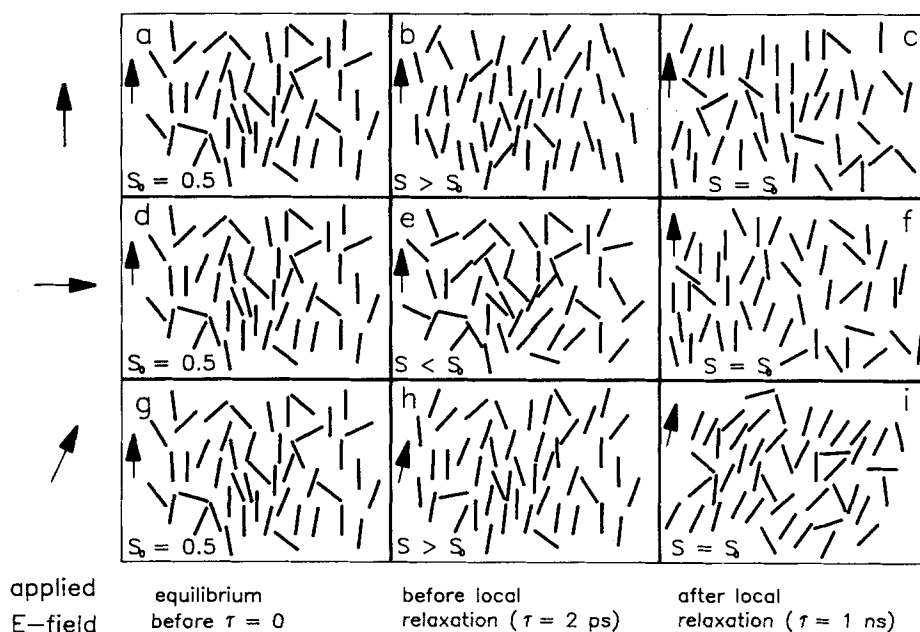


FIG. 7. Illustration of the evolution of the molecular alignment in the pseudonematic domain of a nematogenic substance after perturbation by a short optical pulse. In all cases the original domain director is pointing upwards. S_0 is the order parameter before the sample interacts with the optical pulse. The left column (a, d, and g) shows the equilibrium orientational distribution with $S_0 = 0.5$. (These panels were generated using a Monte Carlo method.) (a)–(c) The applied electric field is parallel to the domain director. (d)–(f) The applied electric field is perpendicular to the domain director. (g)–(i) The applied electric field is at an acute angle to the domain director. Depending on the relative orientation of the E -field and the director, a domain can have a transient increase or decrease in S . If the director is not parallel or perpendicular to the E -field, the director will be rotated and remain rotated following local relaxation (see panel i).

but the increase is smaller than for the situation in Figs. 7(a–c). These perturbations of the relative molecular orientations within the pseudonematic domains, which can be characterized by the order parameter S , are the ones which relax through local molecular rotational (and probably translational, as discussed later) motions. These local relaxations, which do not affect the domain directors, determine the TG-OKE signal at intermediate times.

So far we have talked only about the change in the spread of the molecular orientations with respect to the director. The second effect mentioned earlier is a realignment of the director of the pseudonematic domain with respect to the electric field. This comes about by the net reorientation of all molecules in the direction of the electric field. This net reorientation is zero for the case of the electric field and the director parallel as sketched in Figs. 7(a–c). After the local relaxation mechanisms have established a new equilibrium within the domain, characterized by the original order parameter S_0 [Fig. 7(c)], the director of the domain points in the original direction. This domain does not contribute to the optical anisotropy of the sample at $\tau = 1$ ns. It can be shown that the same is true for the case of perpendicular electric field and domain director sketched in Figs. 7(d–f). However, for any case in between the extremes, as the one depicted in Figs. 7(g–i), the optical perturbation induces a net reorientation of all molecules within the domain on top of the change of the relative molecular orientations, expressed by the order parameter S . Therefore, after local molecular configurational equilibrium has been reestablished within the domains (the domains' order parameters have returned to S_0), there is an anisotropy left in the sample due to the accumulated effect of the domains with their director preferentially aligned parallel to the electric field [Fig. 7(h)]. This anisotropy can only decay through complete structural randomization and loss of correlation in the pseudonematic domains on a multianosecond timescale.

The experiments demonstrated that local relaxation (the reestablishment of the S_0 order parameters in the

pseudonematic domains) is independent of temperature and bulk viscosity over large ranges. In the model presented above, this is due to the fact that the rotation of the molecules takes place in and its dynamics are determined by the strongly structured local environment of the pseudonematic domain. As long as the structure of this environment and the potential surface with which the rotating molecule interacts are essentially fixed on the timescale of the local dynamics, the reorientational relaxation is independent of the bulk viscosity. At temperatures $T > 70$ °C, the correlation length ξ is smaller than three molecular lengths, and the domain no longer serves as a "screening" environment for the molecular rotations. Therefore reorientations are again coupled to the bulk viscosity, and the rates of the rotational motions increase with rising temperature.

The model also offers an explanation for the strongly nonexponential character of the local reorientational relaxation. In the sample there are domains with directors pointing in all directions relative to the polarization of the applied electric field. As discussed in connection with Fig. 7, following the optical pulse there will be a broad distribution of modified order parameters. Some will be greater than S_0 and some will be less than S_0 . It seems plausible that there will be a distribution of relaxation rates associated with this distribution of perturbed order parameters. The circumstances leading to a nonexponential reorientational relaxation of 5CB in the n -heptane solution, i.e. the different rotational motions (tumbling, spinning) and the distribution of molecular conformers, will also influence the decay characteristics in neat 5CB. With this background, one can speculate that the slowest part of the intermediate timescale dynamics, which shows a temperature dependence at the higher temperatures measured, is associated with a tumbling motion and that this tumbling motion is more sensitive to the shrinking domain size than the faster spinning motion.

As pointed out in the introduction, the OKE experiment yields collective correlation information. It measures

the dynamics of the single molecule polarizability, as determined by the rotation of the molecule, as well as of higher order polarizabilities, e. g., intermolecular translational motions (also called CI processes).^{37,40} One can separate the CI effects into an isotropic and an anisotropic contribution.^{50,51} The isotropic CI contribution has the same $\chi^{(3)}$ symmetry as the electronic OKE. From the polarization dependence of the TG-OKE signal, one can conclude that the isotropic CI contribution to the signal is negligible (smaller than 10^{-6}) for $\tau > 2$ ps [see Fig. 1(a)]. As the TG signal is proportional to the square of the correlation function, one can conclude that the isotropic CI contribution is less than one part in a thousand of the total OKE. On the other hand, the anisotropic CI effect has the same $\chi^{(3)}$ symmetry as the single molecule reorientational contribution to the nuclear OKE. Therefore these two effects cannot be separated experimentally.

Originally, the experimental light scattering literature used a separation of CI effects and reorientational motions timescales argument to interpret spectra in terms of single molecule rotational dynamics. As shown by Frenkel and McTague^{50,51} in a molecular dynamics study of some diatomic fluids, this argument is not generally valid. For these molecular fluids, the CI correlation decays on the same subpicosecond timescale as the rotational correlation. An extension of calculations of this kind to much larger molecules has turned out to be difficult. For example, the point-polarizability approximation which is adequate to describe the behavior of the small molecules, seems to fail for nematogens.⁵² Therefore, one can only invoke some general considerations to discuss the influence of CI effects on the intermediate timescale OKE signal. The local molecular dynamics of 5CB are characterized by time constants between 1 and 300 ps. To associate these dynamics with classic CI effects (translations only) would indicate intermolecular correlations between the molecules on the several 100 ps timescale. This seems very unlikely. Also, the approximate η/T dependence of the slowest contribution to the intermediate timescale decay (Fig. 6) at high temperature supports an interpretation in terms of rotational dynamics. One should also note that the anisotropic CI contributions must be at least 1000 times greater than the isotropic contributions for them to make up a significant part of the TG signal. These qualitative considerations suggest that CI effects are not of great significance on the intermediate timescale (2 ps to 1 ns) dynamics of 5CB.

While purely translational effects may not be important, the rotational and translational degrees of freedom of a 5CB molecule within the pseudonematic domain are almost certainly intimately coupled. The rodlike molecule within its anisotropic solvent cage cannot reorient without translating. Therefore the orientational order of the molecules in the pseudonematic domain is partly transferred to positional order. It is this coupled rototranslational motion of the whole 5CB molecule which is observed in the TG-OKE experiment. These motions are dominated by the characteristics of the persistent local domain structure and are decoupled from the bulk viscosity.

Some NMR experiments in the isotropic phase of a

nematogen have found a certain amount of decoupling of the rotational dynamics from the bulk viscosity. The experiments yield a distinctly smaller activation energy for the rotational relaxation time than for the bulk viscosity.²² However, temperature independent dynamics over an extended temperature range as reported here, to our knowledge, has never been observed. Recent site-selective nuclear spin-lattice relaxation measurements on 5CB in the nematic and isotropic phases^{20,53} have found results which differ from the NMR measurements mentioned above. Applying a model which takes into account internal rotations about the C-C bonds in the alkyl chain and rotations around the biphenyl axis, the studies find apparent activation energies between 22 and 32 kJ mol⁻¹ for the various rotational degrees of freedom in the isotropic phase. These activation energies are of the same order of magnitude as the activation energy for the capillary viscosity (34.3 kJ mol⁻¹). These NMR studies have focused on the internal degrees of rotational freedom and demonstrated their influence on the full molecular dynamics of 5CB. The alkyl chain of 5CB contributes very little to the electronic polarizability which is dominated by the properties of the biphenyl core. Therefore the TG-OKE experiment is only sensitive to the internal rotational dynamics of the alkyl chain observed in the NMR technique to the extent that differing conformations influence the overall dynamics of the molecule. If the NMR determined activation energies are dominated by rotational dynamics of the alkyl chain, the NMR and OKE experiments can find very different temperature dependences.

C. Magnitudes of the optical anisotropies

We have described the influence of the pseudonematic domain structure on the *time* dependence of reorientational motion. The domain structure also has an influence on the *magnitudes* of the optical anisotropies associated with the various reorientational relaxation mechanisms. This is illustrated in Fig. 8, which shows the ratio of the signal amplitude due to the collective reorientational optical anisotropy (extrapolated to $\tau = 0$) and the maximum signal amplitude, which is dominated by the librational anisotropy, versus temperature. In the model mentioned earlier^{30,49} the librally excited molecules, upon interaction with the optical pulse, are no longer in their equilibrium orientation. When the coherent librational motion is damped (thermalized), the molecules are "trapped" in a nonequilibrium orientation because of the evolution of the local structure which has occurred during the period of the coherent librational excitation. An optical anisotropy is generated in the sample which can only decay through incoherent reorientational motions. The amplitude of the trapped anisotropy depends on the characteristic timescales for librational damping and local structural evolution. In a crystal librational excitation and subsequent damping does not lead to an anisotropy because the lattice structure is fixed and the molecule returns to its original orientation. In a liquid, if the local structure surrounding the librating molecules changes little on the time scale of damping, the molecule will return to essentially its initial

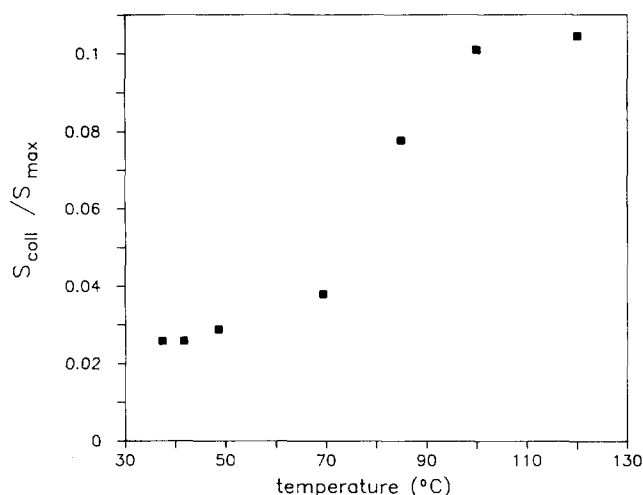


FIG. 8. Temperature dependence of the ratio of the TG-OKE signal amplitude due to the collective reorientational anisotropy S_{coll} and the maximum TG-OKE signal amplitude S_{max} . This ratio represents the ratio of the librational and long time collective orientational optical anisotropies. S_{coll} has been obtained from an extrapolation of the fit parameters for the slow timescale (ns) single exponential decay to $\tau = 0$. Below 70 °C the data is temperature independent within experimental error.

orientation, and residual anisotropy will be small. In contrast if the local structure changes substantially on the damping time scale, the molecules will damp (thermalize) to an orientation which has a significant deviation from its original orientation toward the direction of the applied optical field.

Assuming a very small change of the librational relaxation rate with temperature, as indicated by our data and suggested by other studies,²⁷ the temperature dependence of the trapped orientational anisotropy should be determined by the temperature dependence of the local structural evolution. The faster the surrounding molecules reorient around the librating molecules the greater the residual anisotropy. A rather good measure for the collective reorientational anisotropy (actually related to the square of it) is depicted in Fig. 8. It is clear that this ratio of the signal amplitudes changes very little for $T < 70$ °C. In this temperature range the fast decay channels due to local molecular relaxation, discussed throughout this paper, are dominated by the internal structure of the pseudonematic domains. Below 70 °C the local structural evolution enabling the buildup of the orientational anisotropy is also dominated by the domain structure and is temperature independent. At $T > 70$ °C the domains are becoming very small and their structure is no longer dominating the local dynamics. No longer confined by the strong ordering potential, local structural randomization occurs faster, thereby trapping a higher reorientational anisotropy.

As demonstrated by Fig. 8, the change of the generated anisotropy in the range around $T = 70$ °C is quite dramatic. At the highest temperature investigated the increase of the anisotropy is much more moderate. The steplike change in the data suggests a discontinuous change in dynamics around 70 °C which is not as evident in the characteristic time constants for the TG-OKE decay. 70 °C is

the temperature at which the intermediate timescale dynamics begin to display a temperature dependence (Fig. 6). At the highest temperature the distinction between intradomain and collective dynamics may no longer be justified and the observable in Fig. 8 has to be adjusted. Nevertheless the optical anisotropy amplitude information in Fig. 8 reinforces the picture described earlier: local reorientational dynamics of 5CB (intermediate timescale dynamics) are dominated by the structure of the pseudonematic domains. The local structure and therefore the dynamics are unchanged over a broad range of temperature in the pretransitional region. Only at elevated temperatures, where the domains are becoming vanishingly small, do the local dynamics couple to the bulk viscosity and become temperature dependent.

IV. CONCLUDING REMARKS

We have investigated the rotational and intermolecular dynamics of the nematogenic substance 5CB in its isotropic phase using the transient grating optical Kerr effect technique. The large dynamic range (one hundred fs to tens of ns) and extended temperature range (up to 85° above the phase transition) of the experiments reveal a complex relaxation pattern and demonstrate an intimate relationship between rotational dynamics and the pseudonematic domain structure in the liquid. There is a hierarchy of three different levels of rotational motion. On the ultrafast timescale, $\tau < 1-2$ ps, the dynamics are dominated by intermolecular librational/translational dephasing and damping (thermalization) as in simple molecular liquids. On the ps to hundreds of ps timescale there is local reorientational relaxation within the pseudonematic domains. The anisotropic potential within the domains is stable on this timescale and is responsible for the unusual relaxation characteristics, particularly the temperature independent local dynamics. These fast mechanisms can only relax the disturbance of the local nematic structure within the domain, the deviation from the local order parameter induced by the optical pulse. The alignment of the domain directors, i.e., the net rotation by the optical pulse of all molecules within the domain by a small angle decays on a much slower ns timescale.

While these experiments were performed on the isotropic phase of a liquid crystal which has well-defined nematic domains, the results may have important implications for conventional liquids. Liquids formed from complex molecules can have local structures which persist for some time. On a time scale long compared to the local structural relaxation time, the liquid will conform to hydrodynamic theory. However, on a short timescale on which the local structures persist, the results presented here suggest that nonhydrodynamic reorientational dynamics may be observed.

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- ¹ P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).
- ² *Introduction to Liquid Crystals*, edited by E. B. Priestley, P. J. Wojtowicz, and P. Sheng (Plenum, New York, 1979).
- ³ P. G. de Gennes, *Phys. Lett. A* **30**, 454 (1969); *Mol. Cryst. Liq. Cryst.* **12**, 193 (1971).
- ⁴ T. W. Stinson, III and J. D. Litster, *Phys. Rev. Lett.* **25**, 503 (1970).
- ⁵ J. C. Filippini and Y. Poggi, *J. Phys. Lett. (Paris)* **35**, L-99 (1974).
- ⁶ H. J. Coles, *Mol. Cryst. Liq. Cryst. (Lett.)* **49**, 67 (1978).
- ⁷ J. D. Litster and T. W. Stinson, III, *J. Appl. Phys.* **41**, 996 (1970).
- ⁸ B. Cabane and G. Clarke, *Phys. Rev. Lett.* **25**, 91 (1970); S. Gosh, E. Tettamanti, and E. Indovina, *Phys. Rev. Lett.* **29**, 638 (1973).
- ⁹ G. K. L. Wong and Y. R. Shen, *Phys. Rev. Lett.* **30**, 895 (1973); *Phys. Rev. Lett.* **32**, 527 (1974); *Phys. Rev. A* **10**, 1277 (1974).
- ¹⁰ E. G. Hanson, Y. R. Shen and G. K. L. Wong, *Phys. Rev. A* **14**, 1281 (1976).
- ¹¹ J. C. Filippini and Y. Poggi, *J. Phys. Lett. (Paris)* **37**, L-17 (1976).
- ¹² T. D. Gierke and W. H. Flygare, *J. Chem. Phys.* **61**, 2231 (1974); G. R. Alms, T. D. Gierke and W. H. Flygare, *J. Chem. Phys.* **61**, 4083 (1974).
- ¹³ C. Flytzanis and Y. R. Shen, *Phys. Rev. Lett.* **33**, 14 (1974).
- ¹⁴ N. M. Amer, Y. S. Lin and Y. R. Shen, *Solid State Commun.* **16**, 1157 (1975).
- ¹⁵ J. R. Lalanne, B. Martin, B. Pouligny and S. Kielich, *Optics Commun.* **19**, 440 (1976).
- ¹⁶ G. R. Luckhurst and G. W. Gray, *Molecular Physics of Liquid Crystals* (Academic Press, London, 1979).
- ¹⁷ B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976), Ch. 7.
- ¹⁸ *NMR in Liquid Crystals*, edited by J. W. Emsley and C. A. Veracini (Reidel, Dordrecht, 1985).
- ¹⁹ J. H. Freed, in *Rotational Dynamics of Small and Macromolecules*, edited by Th. Dorfmueller and R. Pecora (Springer, Berlin, 1987), p. 89.
- ²⁰ P. A. Beckmann, J. W. Emsley, G. R. Luckhurst and D. L. Turner, *Mol. Phys.* **59**, 97 (1986).
- ²¹ R. Y. Dong and G. M. Richards, *J. Chem. Phys.* **91**, 7276 (1989).
- ²² R. Poupko, R. L. Vold and R. R. Vold, *J. Phys. Chem.* **84**, 3444 (1980).
- ²³ L. S. Selwyn, R. L. Vold and R. R. Vold, *Mol. Phys.* **55**, 287 (1985).
- ²⁴ C. F. Polnaszek and J. H. Freed, *J. Phys. Chem.* **79**, 2287 (1975).
- ²⁵ T. M. Barbara, R. R. Vold, R. L. Vold and M. E. Neubert, *J. Chem. Phys.* **82**, 1612 (1985).
- ²⁶ S. Ruhman, B. Kohler, A. G. Joly and K. A. Nelson, *Chem. Phys. Lett.* **141**, 16 (1987).
- ²⁷ S. Ruhman, L. R. Williams, A. G. Joly and K. A. Nelson, *IEEE J. Quant. Electron.* **24**, 470 (1988).
- ²⁸ C. Kalpouzos, W. T. Lotshaw, D. McMorrow and G. A. Kenney-Wallace, *J. Phys. Chem.* **91**, 2028 (1987).
- ²⁹ W. T. Lotshaw, D. McMorrow, C. Kalpouzos and G. A. Kenney-Wallace, *Chem. Phys. Lett.* **136**, 323 (1987).
- ³⁰ F. W. Deeg, J. J. Stankus, S. R. Greenfield, V. J. Newell and M. D. Fayer, *J. Chem. Phys.* **90**, 6893 (1989).
- ³¹ G. Eyring and M. D. Fayer, *J. Chem. Phys.* **81**, 4314 (1984).
- ³² Y. X. Yan and K. A. Nelson, *J. Chem. Phys.* **87**, 6240, 6257 (1987).
- ³³ Th. Dorfmueller, in *Rotational Dynamics of Small and Macromolecules*, edited by Th. Dorfmueller and R. Pecora (Springer, Berlin, 1987), p. 65.
- ³⁴ J. Etchepare, G. Grillon, J. P. Chambaret, G. Harmoniaux and A. Orszag, *Opt. Commun.* **63**, 329 (1987).
- ³⁵ J. Etchepare, G. Grillon and J. Arabat, *Appl. Phys. B* **49**, 425 (1989).
- ³⁶ F. W. Deeg and M. D. Fayer, *J. Chem. Phys.* **91**, 2269 (1989).
- ³⁷ D. Kivelson and P. A. Madden, *Annu. Rev. Phys. Chem.* **31**, 523 (1980).
- ³⁸ L. C. Geiger and B. M. Ladanyi, *Chem. Phys. Lett.* **159**, 413 (1989).
- ³⁹ S. K. Deb, *Chem. Phys.* **120**, 225 (1988).
- ⁴⁰ D. Kivelson, in *Rotational Dynamics of Small and Macromolecules*, edited by Th. Dorfmueller and R. Pecora (Springer, Berlin, 1987) p. 1.
- ⁴¹ F. Perrin, *J. Phys. Radium* **5**, 497 (1934).
- ⁴² C. Hu and R. Zwanzig, *J. Chem. Phys.* **60**, 4354 (1974).
- ⁴³ V. J. Newell, F. W. Deeg, S. R. Greenfield and M. D. Fayer, *J. Opt. Soc. Am. B* **6**, 257 (1989).
- ⁴⁴ M. D. Fayer, *IEEE J. Quantum Electron.* **QE22**, 1437 (1986).
- ⁴⁵ T. W. Stinson, J. D. Litster and N. A. Clark, *J. Phys. (Paris)* **33**, C1-69 (1972).
- ⁴⁶ P. Martinoty, S. Candau and F. Debeauvais, *Phys. Rev. Lett.* **27**, 1123 (1971).
- ⁴⁷ P. Martinoty, F. Kiry, S. Nagai, S. Candau and F. Debeauvais, *J. Phys. (Paris)* **38**, 159 (1977).
- ⁴⁸ J. W. Emsley, G. R. Luckhurst and C. P. Stockley, *Proc. R. Soc. Lond. A* **381**, 117 (1982).
- ⁴⁹ F. W. Deeg and M. D. Fayer, *J. Chem. Phys.* (to be published).
- ⁵⁰ D. Frenkel and J. P. McTague, *J. Chem. Phys.* **72**, 2801 (1980).
- ⁵¹ D. Frenkel, in *Intermolecular Spectroscopy and Dynamical Properties of Dense Systems*, edited by J. van Kranendonk (North-Holland, Amsterdam, 1980), p. 156.
- ⁵² D. Frenkel (private communication).
- ⁵³ J. S. Lewis, E. Tomchuk, H. M. Hutton and E. Bock, *J. Chem. Phys.* **78**, 632 (1983).