

Ultrafast to Slow Orientational Dynamics of a Homeotropically Aligned Nematic Liquid Crystal†

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The orientational dynamics of a homeotropically aligned nematic liquid crystal, 4'-pentyl-4-biphenylcarbonitrile (5-CB), is studied over more than six decades of time (500 fs to 2 μ s) using optical heterodyne detected optical Kerr effect experiments. In contrast to the dynamics of nematogens in the isotropic phase, the data do not decay as a highly temperature-dependent exponential on the longest time scale, but rather, a temperature-independent power law spanning more than two decades of time, the final power law, is observed. On short time scales (\sim 3 ps to \sim 1 ns) another power law, the intermediate power law, is observed that is temperature dependent. The power law exponent of the correlation function associated with the intermediate power law displays a linear dependence on the change in the nematic order parameter with temperature. Between the intermediate power law and the final power law, there is a crossover region that displays an inflection point. The temperature-dependent orientational dynamics in the nematic phase are shown to be very different than those observed in the isotropic phase.

I. Introduction

In this paper we present a study of the dynamics of a homeotropically aligned nematic liquid crystal, 4'-pentyl-4-biphenylcarbonitrile (5-CB), over more than six decades of time (500 fs to 2 μ s) using optical heterodyne detected optical Kerr effect (OHD-OKE) experiments. The dynamics of nematogens in the isotropic phase of liquid crystals has been studied extensively both experimentally and theoretically for the past thirty years.^{1–13} Above but close to the $N-I$ phase transition temperature, T_{NI} , orientational relaxation dynamics in the isotropic phase are strongly influenced by the local nematic structure (pseudo-nematic domains).¹⁴ Within domains, the isotropic phase is nematically ordered over a distance scale characterized by the correlation length, ξ , that diverges as the isotropic-to-nematic phase transition is approached from above.¹⁴

Previous optical Kerr effect experiments, which measure the time derivative of the polarizability–polarizability correlation function (closely related to the orientational correlation function) revealed power law decays at short times and an exponential decay at long time.^{7,9,11,12} The long time scale relaxation is attributed to the randomization of the pseudo-nematic domains that is well described by Landau–de Gennes (LdG) theory.¹⁴ LdG theory predicts that the correlation length, ξ , is highly dependent on temperature T according to

$$\xi(T) = \xi_0 [T^*/(T - T^*)]^{1/2}, \quad T > T^* \quad (1)$$

where ξ_0 has a value on the order of a molecular dimension, and T^* is the mean-field second-order phase transition temperature, below which supercooling of the isotropic phase becomes impossible. T^* is typically 0.5–1.0 K lower than T_{NI} due to the weak first-order property of the phase transition. As the $N-I$ phase transition is approached from above, ξ grows, becoming infinite in the nematic phase. In the isotropic phase, on time

scales of many nanoseconds to hundreds of nanoseconds, depending on the temperature, the local order randomizes, giving rise to exponential decays in time domain optical Kerr effect experiments. The relaxation time τ_{LdG} of the exponential decay is given by

$$\tau_{LdG} = \frac{V_{\text{eff}}^* \eta(T)}{k_B (T - T^*)^\gamma} \quad (2)$$

where $\eta(T)$ is the viscosity, V_{eff}^* is the effective volume, k_B is the Boltzmann constant, and γ has been shown to be 1,⁷ indicating the validity of mean-field theory.¹⁴ τ_{LdG} increases dramatically with decreasing temperature and diverges as the temperature approaches T^* . LdG theory describing the long time orientational dynamic of nematogens in the isotropic phase has been confirmed many times experimentally using techniques such as the optical Kerr effect,^{1,2,7} depolarized light scattering,³ dynamical light scattering,¹⁵ magnetic¹⁶ and electric birefringence,¹⁷ and dielectric relaxation.^{4,5}

In contrast to the highly temperature-dependent long time scale dynamics, the short time scale (less than a few ns) power law decays have temperature-independent exponents and are not treated by LdG theory.^{8,11,12} Theoretical treatments based on single-particle dynamics^{18,19} or collective orientational relaxation of the nematogens^{11,20} yielded power law functions, but none of them predicted multiple power laws or the exponents correctly. In the pseudo-nematic domain picture, the short time scale dynamics is dominated by intradomain relaxation. On a distance scale short compared to ξ and on time scale fast compared to the LdG relaxation of the local domain structure, the nematogens are locally ordered and are undergoing orientational relaxation in an effectively nematic ordered environment.

The orientational relaxation dynamics of liquid crystals are complex and differ from those of conventional liquids. It is of particular interest to study the universal critical behavior on both

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sides of the phase transition. Although the molecular dynamics of the isotropic phase has been studied extensively on the ps to 100 ns scale, the studies on the nematic phase have been limited to time scales of μs or longer. Time-resolved spectroellipsometry,²¹ NMR,^{22–24} and FTIR²⁵ have been applied to study how the director reorients in response to the applied external electric and magnetic field on a time scale of ms or longer. A hydrodynamic theory, the Leslie–Ericksen theory,^{26,27} has been shown to describe such slow time scale exponential dynamics well. There have also been some light scattering experiments^{28,29} performed to detect the dynamics of the nematic phase, but they were either focused on nematic samples confined in nanoscopic pores in a porous host or applied in a time window longer than a μs . To our knowledge, there has been no work done on the dynamics of pure nematogen liquids macroscopically ordered in the nematic phase on time scales faster than a μs .

Twenty years ago, the transient grating optical Kerr effect technique was shown to be able to investigate the orientational dynamics of aligned liquid crystal films with time resolution of ~ 100 ps out to ~ 10 ns.³⁰ Because of limitations in the signal-to-noise ratios (S/N) and the relatively limited time window, no conclusive information on the dynamic behavior of the nematic phase was obtained. Recent improvements in experimental technique now make it possible to study the nematic phase quantitatively over a broad range of times. In this work we present quantitative time domain experimental data on the orientational dynamics of a homeotropically aligned nematic liquid crystal, 5-CB. The experiments cover a broad time range from 500 fs to 2 μs and a number of temperatures below the isotropic to nematic phase transition. Comparison is made to data taken in the identical manner in the isotropic phase. A striking difference between the nematic phase and the isotropic phase orientational relaxation occurs at long time. In the isotropic phase the long time decay is a single exponential with a decay constant that increases dramatically as the temperature is lowered toward the isotropic to nematic phase transition. In the nematic phase the long time decay is a temperature independent power law, the final power law. The final power law is distinct from the short time scale power laws observed in the isotropic phase, where there is an intermediate power law that is temperature independent. In the nematic phase, on short time scales (~ 3 ps to ~ 1 ns) an intermediate power law is observed. However, it is temperature dependent. The power law exponent of the correlation function associated with the nematic phase intermediate power law displays a linear dependence on the change in the nematic order parameter with temperature. Between the intermediate power law and the final power law, there is a crossover region that displays an inflection point. Except on the very shortest time scale, < 3 ps, the functional form and temperature dependence of the OHD-OKE data in the nematic phase are fundamentally different from those observed in the isotropic phase.

II. Experimental Procedures

Optical heterodyne detected optical Kerr effect spectroscopy^{13,31–33} was used to measure the orientational dynamics in the nematic phase of the liquid crystal, 5-CB. A pump pulse creates a time-dependent optical anisotropy that is monitored via a heterodyne detected probe pulse with a variable time delay. The OHD-OKE experiment measures the time derivative of the polarizability–polarizability (orientational) correlation function. The Fourier transform of the OHD-OKE signal is directly related to data obtained from depolarized light scattering,^{34–37} but the time domain OHD-OKE experiment can provide better S/N over

a broader range of times for experiments conducted on very fast to moderate time scales.

To observe the full range of the dynamics, at each temperature several sets of experiments were performed with different pulse lengths and delays. For times $t < 30$ ns, a mode-locked 5 kHz Ti:sapphire laser/regenerative amplifier system was used ($\lambda = 800$ nm) for both pump and probe. The pulse length was adjusted by adjusting the compressor from 75 fs to 10 ps as the time scale of the measurement increased to improve the signal-to-noise ratio. The shortest pulses were used for times 100 fs to a few tens of ps. For longer times, a few ps to 600 ps, the pulses were lengthened to 1 ps. The longer pulses produce more signal for the longer time portions of the data. For intermediate times, a 10 ps pulse was used with a long delay line to obtain data from 100 ps to 30 ns. Because the experiments are nonresonant optical Kerr effect measurements, a frequency chirp on the pulse does not influence the data. For even longer times, a CW diode laser was used as the probe, and a fast digitizer (1 ns per point) recorded the data. The scans taken over various time ranges overlapped substantially, permitting the data sets to be merged by adjusting only their relative amplitudes. Additional experimental details have been published elsewhere.^{11,38}

5-CB was purchased from Aldrich and used without further purification. To prepare the samples, 5-CB was placed between two ITO-coated glass windows treated with the surfactant DMOAP.³⁹ The director is normal to the sample cell windows. The sample had a thickness of 390 μm , as determined by a Teflon spacer. The homeotropic alignment was verified by the characteristic dark cross observed through a conoscopic microscope. A 5 kHz 23V (rms) sinusoidally oscillating electric field was applied across the two windows to prevent the molecules from losing alignment under laser irradiation. To examine the effect of external field on the molecular dynamics, three experiments were performed and compared: (1) the laser pulses were not synchronized with the electric field, thus the dynamics were probed under an averaged external field; (2) the laser was synchronized with external electric field and tuned by a timing delay box such that the external electric field was zero when the optical pulses reached the sample; and (3) the laser was synchronized such that the external electric field was maximum (~ 30 V) when the optical pulses reached the sample. The data taken under the three sets of conditions were identical, showing that the external electric field had no effect on the orientational dynamics over the time window probed by the experiments.

III. Results and Discussion

Figure 1 displays two data sets at temperatures on either side of the phase transition. The data are log plots, spanning the range of times from 500 fs to 2 μs , which is over six decades. 5-CB has $N-I$ phase transition temperature of 307–308 K. Figure 1a is the decay at 309 K just above the phase transition. Figure 1b is the decay at 306 K just below the phase transition. By reducing the temperature by only 3 K, but crossing through the phase transition, the relaxation dynamics changes fundamentally.

The isotropic phase data display the typical behavior found previously,¹² although these data are for the temperature point closest to the phase transition, go out to the longest time, and have the best S/N. It has been shown that the decay in the isotropic phase has the same functional form as data taken for supercooled liquids.^{10,13} Mode coupling theory (MCT)^{40,41} terminology, which describes the decays in supercooled liquids, has been applied to the liquid crystals and will be used here.^{10,13} In Figure 1a, starting at short time the curve begins with a steep

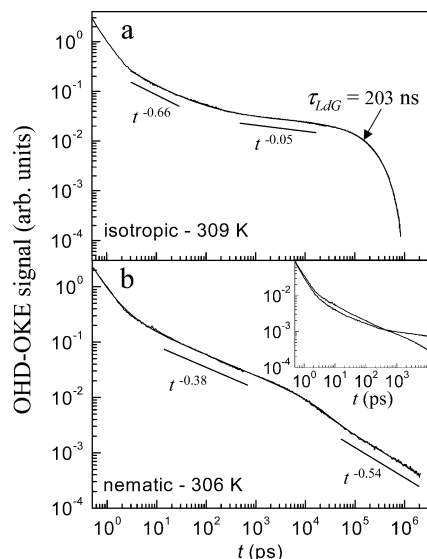


Figure 1. OHD-OKE 5-CB data displayed on a log plot. (a) Data in the isotropic phase taken at 309 K, just above the phase transition. The longest time component is an exponential decay described by the Landau–de Gennes theory with a decay constant of 203 ns. Prior to the exponential decay is a power law, $t^{-0.05}$. The lines below the data are aids to the eye. At shorter time ($> \sim 3$ ps) is another power law, $t^{-0.66}$, the intermediate power law. There is also a very short time decay that is very fast for $t < 3$ ps. There is also a fit to the data using eq 3, see text. (b) Data in the nematic phase taken at 306 K, just below the phase transition. The longest time component in the nematic phase is a power law, $t^{-0.54}$, the final power law. At shorter times is another power law, $t^{-0.38}$, the intermediate power law. Between the two power laws is a crossover region. At very short time is a very fast decay that is like that in the isotropic phase. There is also a fit to the data using eq 4, see text. (Inset) Data from Figure 1a and Figure 1b from 500 fs to 10 ns scaled to match at 500 fs. The curve at top at 50 ps and on the bottom at 5 ns is the nematic phase data.

decay, but the length of the decay is insufficient to determine its functional form. In MCT, this is predicted to be a power law called the fast β process.^{40,41} Following the short time decay is the “intermediate power law” that has recently been identified in five supercooled liquids^{33,42} and four nematogen liquids in the isotropic phase.¹³ The intermediate power law has recently been reproduced by an expanded MCT analysis.⁴³ It has been shown in the previous analysis of supercooled liquids and nematogens in the isotropic phase, that a global fit of the data is required to separate various contributions to the decay and to obtain an accurate description of each component.^{13,33,42} A decomposition into the various components from a global fit is necessary because the components overlap in the regions of transition from one to another.

The solid line through the data in Figure 1a is a global fit to the data using the function $F_1(t)$ (I for isotropic) that has been applied previously.³³

$$F_1(t) = [pt^{-z} + dt^{b-1}] \exp(-t/\tau) \quad (3)$$

where the first term with $z \leq 1$ corresponds to the intermediate power law. The line at short time below the data is an aid to the eye. It reflects the intermediate power law, $t^{-0.66}$. The line runs from ~ 3 ps to ~ 30 ps, but the intermediate power law extends much further. However, it merges with the next slowest component. It has been shown that the intermediate power law portion of the data can be observed for times to ~ 1 ns when the von Schweidler power law contribution and the exponential relaxation portion of the signal are removed.¹³ In the language of MCT, following the intermediate power law, the system

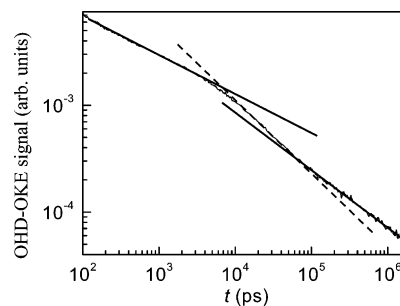


Figure 2. Expanded view of the crossover region of Figure 1b showing that there is an inflection point between the intermediate power law and the final power law.

undergoes complete structural relaxation, which begins with another power law, the von Schweidler power law. The von Schweidler power law is followed by the final α -relaxation, which is exponential.^{33,40,41} The second term in eq 3 with b in the exponent is the crossover von Schweidler power law. For the nematogen 5-CB in the isotropic phase, the von Schweidler power law is $t^{-0.05}$, indicated by the line beneath it in Figure 1a from 300 ps to 30 ns. On the log plot, an exponential appears as the knee and then a steep descent at long time. The exponential part of the decay (last term in eq 3) spans about 5 factors of e on the plot, and can be followed for much longer time. The exponential portion of the decay for nematogens in the isotropic phase is described by LdG theory (see eqs 1 and 2). The fit to the data using eq 3 follows the data so well that it is barely discernible on the plot. The data were fit for times longer than 3 ps. The values obtained here for z and b are consistent with the previously published work on 5-CB.^{10,13}

The most obvious difference between the nematic phase data (Figure 1b) and the isotropic phase data is the long time behavior. In fact, the data are different on all but the very shortest time scale. In the isotropic phase, the decay at long time is exponential. In the nematic phase, the decay is a power law, $t^{-0.54}$. The data are shown to $2 \mu\text{s}$. Data were collected to $20 \mu\text{s}$ and there is no evidence of a change in functional form. As far as it is possible to tell, the final decay in the nematic phase is a power law. We will call this the final power law. In the isotropic phase, prior to the exponential decay is the very shallow, $t^{-0.05}$ von Schweidler power law, and at even shorter times, the $t^{-0.66}$ intermediate power law. These power laws are temperature independent. In the nematic phase, the von Schweidler power law does not exist. At shorter times, there is a single power law, $t^{-0.38}$, which we will also call the intermediate power law. At the shortest times we can observe, ~ 300 fs to a few ps, is the very fast decay, which is similar to that observed in the isotropic phase. Times less than 300 fs are obscured by the electronic response of the system, which is so strong that even with short pulses it overwhelms all other contributions to the signal. A fit to the data is also shown in Figure 1b as the solid line through the data that is barely discernible because of its near perfect agreement. The fitting function is discussed below. The inset in Figure 1b shows the data from Figure 1a and the main portion of Figure 1b from 500 fs to 10 ns. The curves have been scaled to match at 500 fs. The curve that is on top at 50 ps and on the bottom at 5 ns is the nematic phase curve of Figure 1b. The inset shows clearly the differences in the shapes of the curves on the short to moderate time scales.

Figure 2 displays a blow up of the transition region between the intermediate power law and the final power law. The transition from the intermediate power law to the final power law is not a simple progressive change in slope on the log plot. The two solid lines in Figure 2 show the slopes of the

intermediate and final power laws. The dashed line shows that the slope in a portion of the transition region is actually steeper than that of the final power law. The dashed line is an aid to the eye, and it is not intended to suggest that the portion of the data on which it falls is functionally another power law. The point is that the transition region has a mild “S” shape; that is, there is an inflection point. The data progress from the intermediate power law to a decay that is steeper than the final power law, before becoming again less steep as the final power law. The data in the transition region are steeper than the final power law for approximately one decade in time.

To examine the functional form of the decay curve in the nematic phase and to investigate its temperature dependence, the data were fit to an empirical function. The final power law can be fit independently without using the fitting function. The intermediate power law can be fit independently over a limited time window because it is sandwiched between the short time decay and the transition region (Figure 2). The fitting function makes it possible to more accurately determine whether the single intermediate power law is all that occurs between the short time decay and the transition region and whether it is temperature dependent. The fitting function, $F_N(t)$ (N for nematic) is

$$F_N(t) = [at^{-s} + pt^{-z}] \exp(-t/\tau) + gt^{-f}(1 - \exp(-t/\tau)) \quad (4)$$

The very short time behavior is modeled as a power law, t^{-s} . The intermediate power law is represented by the same term as in eq 3, t^{-z} . The final power law is t^{-f} . The crossover from the intermediate power law to the final power law is modeled as a decaying exponential that damps the intermediate power law and an exponential that grows to unity that turns on the final power law. The two exponential terms have the same time constant, τ , and they do not have adjustable amplitude factors. The line through the data shows the quality of the fit that is achieved over the entire time range. As shown on Figure 1b, the intermediate power law exponent $z = 0.38$ and the final power law exponent $f = 0.54$. The short time dynamics, modeled as a power law, gives the exponent $s = 1.65$.

In the exponential terms used to model the crossover region between the intermediate and final power laws, $\tau = 18.8$ ns for the fit shown in Figure 1b. The exponential model reproduces that data very accurately. It yields the mild S shaped form of the data in the transition region, as discussed in connection with Figure 2, and it is useful for obtaining a global fit. However, it is unclear what, if any, physical meaning should be attached to the decaying and growing exponential model of the transition region.

To describe the nature of the dynamics observed in the nematic phase, it is first necessary to discuss our qualitative understanding of the dynamics in the isotropic phase.⁸ In the isotropic phase, the liquid is macroscopically isotropic, but microscopically it has nematic-like alignment locally. The data shown in Figure 1a can be divided into two time regimes; that is, the LdG relaxation time scale and times fast compared to the LdG relaxation time, τ_{LdG} (eq 2). These domains can be discussed in terms of a local director and a local order parameter.⁸ In the isotropic phase, the macroscopic liquid has an order parameter, $S = 0$; that is, macroscopically there is no orientational order. However, on a distance scale short compared to ξ (eq 1), and on a time scale short compared to τ_{LdG} , there is pseudo-nematic order, which can be characterized by a local order parameter, S_L , relative to a local director. When the pump pulse E -field is applied, the nematogens experience a torque that produces a slight alignment with the field. When the field

is removed, the macroscopic system is left with $S \neq 0$. Field free evolution will reestablish $S = 0$.

To understand the origin of the dynamical time scales, it is necessary to consider the problem microscopically. There are two contributions to the relaxation, intradomain relaxation and domain randomization (LdG relaxation). The E -field induces a small net alignment of the individual nematogens. The nematogen alignments change the local order parameter, S_L . Unlike S , which is a macroscopic parameter, S_L is nonzero prior to the application of the optical field. S_L defines the local nematic structure relative to the local director associated with a given pseudo-nematic domain. Initially, $S_L = S_L^0$. Immediately following the application of the field, $S_L > S_L^0$. (S_L can also be $< S_L^0$, depending on the direction of the local director relative to the field direction.) The small alignment of the nematogens with the field changes S_L , and it also rotates the direction of the local director. Fast intradomain relaxation occurs, restoring the local order parameter to S_L^0 . This fast intradomain relaxation is responsible for the intermediate power law. Relaxation of the perturbed local order back to S_L^0 occurs on fast time scales but leaves the ensemble of domain local directors still slightly aligned with the direction defined by the E -field. This long-lived anisotropy can only decay by randomization of the domains and is responsible for the long time decay described by LdG theory.

The nature of the experiment performed on the nematically aligned sample is fundamentally different. The sample is macroscopically aligned and has an order parameter S prior to the application of the laser E -field. The director is perpendicular to the sample cell window. Call this direction the z direction and the plane of the window the x - y plane. The laser pump beam propagates along z and has its E -field in the x - y plane. Take the E -field direction to be the x direction. The torque exerted by the laser E -field on the nematogens will pull them away from the z axis, the director. This will change the order parameter. An anisotropy will develop in the x - y plane. The probe E -field, which is also in the x - y plane, will detect the anisotropy and its decay with time. The decay observed in Figure 1b returns the perturbed nematic system to its original configuration. In the isotropic phase, the system is initially macroscopically isotropic and it decays (exponentially) to being macroscopically isotropic at long time. In the nematic phase, the system is initially anisotropic with a well-defined order parameter S , and it decays back to its initial nematic ordering with order parameter S . The final decay is a power law.

Decays in the nematic phase were measured at five temperatures, from just below the isotropic to nematic phase transition to 8 K below it. The decay curves at each temperature are shown in Figure 3 along with the corresponding global fits using eq 4. The final power law decay is observed at all the temperatures. Figure 4 displays the final power law exponent, f , as a function of temperature. Within experimental error f is constant with temperature. In contrast to the final power law, the intermediate power law exponent, z , shows significant temperature dependence, as displayed in Figure 5a. The exponent changes from 0.38 to slightly over 0.47 as the temperature is decreased 8 K. The OHD-OKE observable is the derivative of the correlation function, $C(t)$. Considering only the intermediate power law, the integral of t^{-z} gives a power law for $C(t)$ of $-z + 1$. This term in the correlation function will be preceded by a negative sign because $C(t)$ is a decaying function of time. As the temperature is decreased, the order parameter increases. For 5-CB, the order parameter as a function of temperature is known.⁴⁴ Figure 5b shows a plot of the $C(t)$ exponent, $-z + 1$,

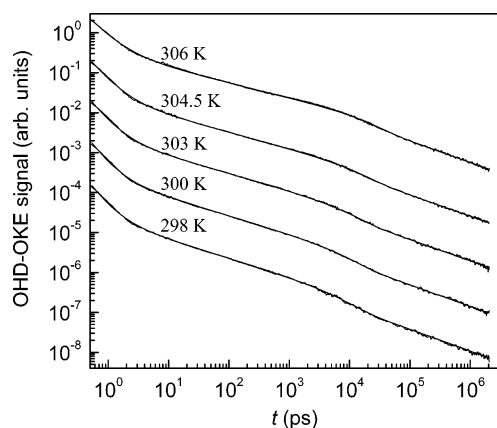


Figure 3. Temperature-dependent nematic phase data displayed on a log plot with fits using eq 4. The data sets have been offset along the vertical axis for clarity. The final power law is temperature independent (see Figure 4), but the intermediate power law is temperature dependent (see Figure 5).

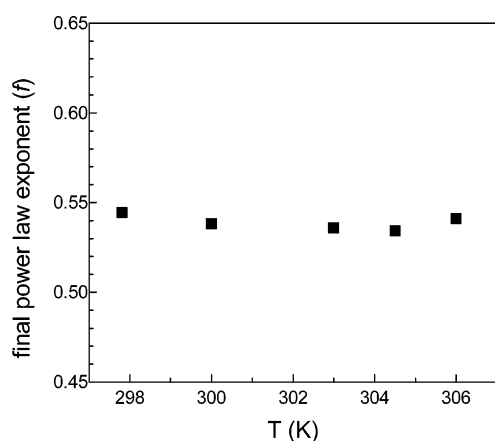


Figure 4. The final power law (t^{-f}) exponent f vs temperature obtained from the fits in Figure 3. Within experimental error, the exponent is temperature independent.

for the intermediate power law as a function of the 5-CB order parameter, S . As the order parameter increases, the exponent decreases. Over the range of data measured within experimental uncertainty, the trend is linear. As the temperature is lowered, the order parameter increases, and the relaxation of the intermediate part of the correlation function becomes slower.

There has been some theoretical work on the short time dynamics of nematogens in the isotropic phase that shows it is possible for the correlation function to decay as a power law.^{11,18} One of the calculations predicts a correlation function decay of $t^{-0.5}$, which would produce an OHD-OKE decay of $t^{-1.5}$, which is similar to the value that is observed for the shortest time scale power law in both the isotropic phase and the nematic phase. To date there is no theory that accurately reproduces the dynamics in the isotropic phase nor is there a theory for the nematic phase dynamics. It is therefore worthwhile to make a few comments that describe some possibilities, although they may be considered in the realm of speculation.

In going from the isotropic phase to the nematic phase, the correlation length of the pseudonematic domains diverges and the Landau–de Gennes exponential relaxation time, τ_{LdG} , becomes infinite. Although not considered in LdG theory, in MCT the von Schweidler power law is the onset of complete structural relaxation that progresses into the final α -relaxation (exponential decay).⁴⁵ Therefore, it is reasonable to assume that both the von Schweidler power law and the exponential decay

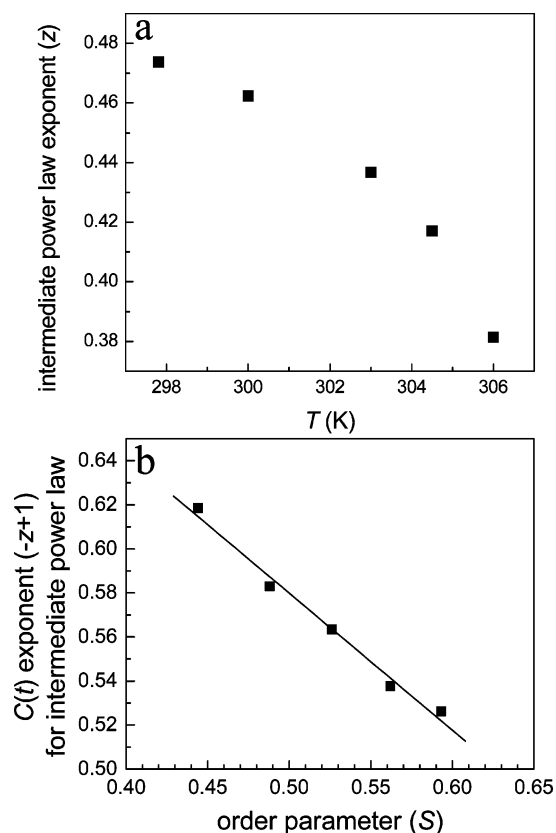


Figure 5. (a) Final power law (t^{-z}) exponent z vs temperature obtained from the fits in Figure 3. The exponent is temperature dependent. (b) The corresponding correlation function ($C(t)$) exponent, $-z+1$, vs the 5-CB nematic phase temperature dependent order parameter, S . The exponent and the order parameter appear to be linearly correlated.

will not occur in the nematic phase. If everything else remained the same as in the isotropic phase, then the very short time decay and the intermediate power law would be the dynamics observed in the nematic phase. The intermediate power law in the isotropic phase is temperature independent within experimental error. Clearly the simple extension of the nature of the dynamics from the isotropic phase to the nematic phase is not a correct picture of the nematic phase dynamics. The von Schweidler power law and the exponential decay are absent in the nematic phase and the very short time dynamics is approximately the same. However, the intermediate power law has a substantially different exponent, z , and it is temperature dependent (Figure 5). At longer times, there is the crossover region that has an inflection point, followed by the final power law decay. While the final exponential decay in the isotropic phase is highly temperature dependent, the final power law is temperature independent (Figure 4).

With the E -field applied along x in the plane (x - y) perpendicular to the director along z , the induced anisotropy can be viewed as having two contributions. The z contribution will be associated with a change in the order parameter, S . The y contribution does not involve a change in order parameter. Clearly, the z motions of a nematogen and motions perpendicular to z are strongly coupled. Nonetheless, the temperature dependence of the intermediate power law exponent and the fact that it correlates with the temperature dependent order parameter suggest that this relaxation involves substantially a restoration of the order parameter. The change in the thermal energy $k_B T$, where k_B is the Boltzmann constant, with T changing only 8 K, is too small in its self to account for the temperature dependence. Measurements of bulk viscosities in the nematic phase of 5-CB

show substantial changes in rotational viscosity and moderate change in shear viscosity with temperature. These measurements occur on very slow time scales, and it is unclear what relationship such measurements have to the fast and moderate time scale relaxations reported here in which the intermediate power law exponent is temperature dependent but the final power law exponent is not.⁴⁶ A change in the order parameter may not influence the relaxation of the y contribution to the anisotropy as much as it does the z contribution, suggesting that the final power law involves predominantly relaxation perpendicular to the director. The pump pulse E -field along x , destroys the cylindrical symmetry about the director z , as well as changing the order parameter. The relaxation associated with the intermediate power law may restore the order parameter locally without restoring the cylindrical symmetry. Therefore, there would still be an anisotropy, which relaxes as the final power law decay. Even in this picture, it is unclear why the final relaxation of the anisotropy is a power law rather than exponential.

IV. Concluding Remarks

In this paper we have presented the first detailed experiments examining the orientational dynamics of a nematogen in its nematic phase. The experiments were conducted on a broad range of times from very fast (500 fs) to slow (2 μ s) as a function of temperature. The temperature-dependent experiments began just below the isotropic to nematic phase transition. The experimental results were compared to experiments conducted in the identical manner on nematogens in the isotropic phase.

Currently it is safe to say that there is no detailed theoretical understanding of the dynamics observed in the nematic phase, nor is there theoretical understanding of the short time scale dynamics of nematogens in the isotropic phase. The long time scale dynamics in the isotropic phase are described well by the Landau–de Gennes theory that explains the longest time scale temperature dependent exponential relaxation. There have been comparisons between experiments on the dynamics of nematogens in the isotropic phase and supercooled liquids. It has been found that the nature of the dynamics is very similar and many features of mode coupling theory apply to both.^{10,13,43} In the language of mode-coupling theory, the final structural relaxation (the LdG exponential decay in this case) is preceded by a power law, the von Schweidler power law. It was anticipated that these features would be absent in the nematic phase because the randomization of the isotropic phase pseudo-nematic domains, which are associated with the LdG decay (see eqs 1 and 2), would be absent and that the fast dynamics observed in the isotropic phase would occur in the nematic phase. While it is true that the von Schweidler power law and the exponential relaxation of the isotropic phase do not occur in the nematic phase, the nematic phase dynamics are fundamentally different from the short time isotropic phase dynamics.

The main features of the nematic phase dynamics are the temperature dependent intermediate power law with the exponent that correlates with the order parameter, the crossover region that has an inflection point, and the final power law that is temperature independent. Experiments are currently under way to examine other liquid crystals in the nematic phase. The experimental results presented here combined with the experiments presented previously on nematogens in the isotropic phase^{6,8–13} are providing the necessary data to obtain a detailed understanding of liquid crystal dynamics.

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References and Notes

- Hanson, E. G.; Shen, Y. R.; Wong, G. K. L. *Phys. Rev. A* **1976**, *14*, 1281.
- Wong, G. K. L.; Shen, Y. R. *Phys. Rev. Lett.* **1973**, *30*, 895.
- Gierke, T. D.; Flygare, W. H. *J. Chem. Phys.* **1974**, *61*, 2231.
- de Jeu, W. H. *Liquid Crystals, In Solid State Physics*; Liebert, L., Ed.; Academic Press: New York, 1978; p 109.
- Kresse, H. *In Advances in Liquid Crystals*; Brown, G. H., Ed.; Academic Press: New York, 1983; Vol. 6, p 109.
- Deeg, F. W.; Greenfield, S. R.; Stankus, J. J.; Newell, V. J.; Fayer, M. D. *J. Chem. Phys.* **1990**, *93*, 3503.
- Stankus, J. J.; Torre, R.; Marshall, C. D.; Greenfield, S. R.; Sengupta, A.; Tokmakoff, A.; Fayer, M. D. *Chem. Phys. Lett.* **1992**, *194*, 213.
- Stankus, J. J.; Torre, R.; Fayer, M. D. *J. Phys. Chem.* **1993**, *97*, 9478.
- Cang, H.; Li, J.; Fayer, M. D. *Chem. Phys. Lett.* **2002**, *366*, 82.
- Cang, H.; Li, J.; Novikov, V. N.; Fayer, M. D. *J. Chem. Phys.* **2003**, *119*, 10421.
- Gottke, S. D.; Brace, D. D.; Cang, H.; Bagchi, B.; Fayer, M. D. *J. Chem. Phys.* **2002**, *116*, 360.
- Gottke, S. D.; Cang, H.; Bagchi, B.; Fayer, M. D. *J. Chem. Phys.* **2002**, *116*, 6339.
- Cang, H.; Li, J.; Novikov, V. N.; Fayer, M. D. *J. Chem. Phys.* **2003**, *118*, 9303.
- de Gennes, P. G. *The Physics of Liquid Crystals*; Clarendon: Oxford, 1974.
- Stinson, T. W., III; Litster, J. D. *Phys. Rev. Lett.* **1970**, *25*, 503.
- Litster, J. D.; Stinson, T. W., III *J. Appl. Phys.* **1970**, *41*, 996.
- Poggi, Y.; Fillippini, J. C. *Phys. Rev. Lett.* **1977**, *39*, 150.
- Sengupta, A.; Fayer, M. D. *J. Chem. Phys.* **1995**, *102*, 4193.
- Ravichandran, S.; Perera, A.; Moreau, M.; Bagchi, B. *J. Chem. Phys.* **1998**, *109*, 7349.
- Jose, P. P.; Bagchi, B. *J. Chem. Phys.* **2004**, *120*, 11256.
- Tadokoro, T.; Toriumi, H.; Okutani, S.; Kimura, M.; Akahane, T. *Jpn. J. Appl. Phys., Part 1* **2003**, *42*, 4552.
- Luckhurst, G. R.; Miyamoto, T.; Sugimura, A.; Timimi, B. A.; Zimmermann, H. *J. Chem. Phys.* **2004**, *121*, 1928.
- Luckhurst, G. R.; Miyamoto, T.; Sugimura, A.; Timimi, B. A. *J. Chem. Phys.* **2002**, *116*, 5099.
- Wise, R. A.; Olah, A.; Doane, J. W. *J. Phys. Colloque* **1975**, *36*, 117.
- Sugisawa, H.; Toriumi, H.; Watanabe, H. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1992**, *214*, 11.
- Leslie, F. M. *Quart. J. Mech. Appl. Math.* **1966**, *19*, 357.
- Ericksen, J. L. *Arch. Ration. Mech. Anal.* **1960**, *4*, 231.
- Mertelj, A.; Copic, M. *Phys. Rev. E* **1997**, *55*, 504.
- Tripathi, S.; Zhong, H.; Petschek, R. G.; Rosenblatt, C. *Phys. Rev. E* **1995**, *52*, 5004.
- Eyring, G.; Fayer, M. D. *J. Chem. Phys.* **1984**, *81*, 4314.
- McMorrow, D.; Lotshaw, W. T.; Kenney-Wallace, G. A. *IEEE J. Quantum Elec.* **1988**, *24*, 443.
- Hinze, G.; Brace, D.; Gottke, S. D.; Fayer, M. D. *Phys. Rev. Lett.* **2000**, *84*, 2437.
- Cang, H.; Novikov, V. N.; Fayer, M. D. *J. Chem. Phys.* **2003**, *118*, 2800.
- Kai, Y.; Kinoshita, S.; Yamaguchi, M.; Yagi, T. *J. Mol. Liq.* **1995**, *65–6*, 413.
- Yan, Y. X.; Nelson, K. A. *J. Chem. Phys.* **1987**, *87*, 6240.
- Yan, Y. X.; Nelson, K. A. *J. Chem. Phys.* **1987**, *87*, 6257.
- Deeg, F. W.; Stankus, J. J.; Greenfield, S. R.; Newell, V. J.; Fayer, M. D. *J. Chem. Phys.* **1989**, *90*, 6893.
- Gottke, S. D.; Brace, D. D.; Hinze, G.; Fayer, M. D. *J. Phys. Chem. B* **2001**, *105*, 238.
- Kahn, F. J. *Appl. Phys. Lett.* **1973**, *22*, 386.
- Götze, W. *Liquids, Freezing and Glass Transition*; Elsevier Science Publishers: Amsterdam, 1989.
- Hinze, G.; Brace, D. D.; Gottke, S. D.; Fayer, M. D. *J. Chem. Phys.* **2000**, *113*, 3723.
- Cang, H.; Novikov, V. N.; Fayer, M. D. *Phys. Rev. Lett.* **2003**, *90*, 197401(4).
- Götze, W.; Sperll, M. *Phys. Rev. Lett.* **2004**, *92*, 105701.
- Collings, P. J.; Hird, M. *Introduction to Liquid Crystals: Chemistry and Physics*; Taylor & Francis: Bristol, PA, 1997.
- Götze, W.; Sjögren, L. *Rep. Prog. Phys.* **1992**, *55*, 241.
- Bock, F. J.; Knepp, H.; Schneider, F. *Liquid Crystals* **1986**, *1*, 239.