



# Short time dynamics in the isotropic phase of liquid crystals: the aspect ratio and the power law decay

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## Abstract

Optical heterodyne detected optical Kerr effect (OHD-OKE) experiments are used to study the orientational dynamics of the liquid crystal 4'-octyl-4-biphenylcarbonitrile (8CB) in the isotropic phase near the isotropic to nematic phase transition. The results are compared to those for three other liquid crystals. The 8CB data display a short time scale temperature independent power law decay and a long time scale exponential decay with a temperature dependence described by Landau–de Gennes theory. The power law exponent is  $-0.56$ . Combining this result with previous results for three other liquid crystals [J. Chem. Phys. 116 (2002) 6339; J. Chem. Phys. 116 (2002) 360], it is found that the power law exponent depends linearly on the aspect ratio of the liquid crystal.

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## 1. Introduction

The orientational relaxation dynamics of nematogens in the isotropic phase of liquid crystals is complex. Recent experiments have shown that the dynamics can be divided roughly into two time scales [1,2]. On a long time scale, the orientational relaxation is exponential and highly temperature dependent. The exponential relaxation is well described by the Landau–de Gennes theory [3]. In the isotropic phase, a liquid crystal sample is macroscopically isotropic but microscopically anisotropic. On a distance scale short compared to a correlation length,  $\xi$ , the local structure is like that of a nematic liquid crystal. As the temperature is

lowered toward the nematic–isotropic phase transition temperature,  $T_{\text{NI}}$ , the correlation length diverges. Below  $T_{\text{NI}}$ , the liquid crystal is macroscopically ordered. The long time scale exponential orientational relaxation is caused by the decay of the local nematic structure. The decay slows as the correlation length increases, diverging as  $T_{\text{NI}}$  is approached from above.

The local order can be thought of as pseudo-nematic domains, that is, regions that are nematically ordered on a distance scale  $< \xi$ . Landau–de Gennes (LdG) theory predicts that the domain randomization in the isotropic phase is described by an exponential decay function with the relaxation time  $\tau_{\text{LdG}}$ , which diverges at a transition temperature  $T^*$  as [3]

$$\tau_{\text{LdG}} \propto \frac{V_{\text{eff}}^* \eta(T)}{T - T^*}, \quad (1)$$

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where  $\eta(T)$  is the viscosity,  $T$  is the temperature, and  $V_{\text{eff}}^*$  is the nematogens effective volume.  $T^*$  is generally about one degree below  $T_{\text{NI}}$  for the weak first order isotropic to nematic transition [3]. (Properties scale as  $T^*$  is approached rather than  $T_{\text{NI}}$  because the phase transition has both first- and second-order character.) LdG theory has been confirmed experimentally using techniques such as optical Kerr effect [4–6], depolarized light scattering [7], dynamic light scattering [8], magnetic [9], and electric birefringence, [10] and dielectric relaxation [11,12]. The influence of the pseudo-nematic domains on the long time scale dynamics continues up to  $\sim 50$  K above the N–I phase transition temperature [6].

On a time scale short compared to  $\tau_{\text{LdG}}$ , the orientational dynamics occur for nematogens that have pseudo-nematic order. As will be shown below for 8CB, and has been observed previously [1,2,13–15], on the shortest time scale the observed decay of the signal is a power law,  $t^{-p}$ . While  $\tau_{\text{LdG}}$  is highly temperature dependent,  $p$  is temperature independent. The question arises, what determines the value of  $p$ ? It is known that the aspect ratio of a molecule determines whether a molecule is a nematogen [16]. MD simulations show that for aspect ratios below  $\sim 2.5$ , liquid crystalline behavior is not observed [16]. In previous studies of liquid crystal dynamics, there was some indication that the value of  $p$  depends on the aspect ratio of the nematogen. Here we will provide evidence that  $p$  does indeed depend on the aspect ratio and that the dependence is approximately linear.

## 2. Experimental procedures

Optical heterodyne-detected optical Kerr effect (OHD-OKE) spectroscopy [17] was used to measure the liquid crystal orientational relaxation. 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 system's impulse response function, which is the time derivative of the polarizability–polarizability (orientational) correlation function. The methods for the analysis of OHD-OKE data have been de-

scribed in detail [18]. The Fourier transform of the OHD-OKE signal is directly related to data obtained from depolarized light scattering [19], but the time domain OHD-OKE experiment can provide better signal-to-noise ratios over a broader range of times for experiments conducted on very fast to moderate time scales.

To observe the full range of liquid 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 from 100 fs to 1 ps to improve S/N. 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, the pulse compression was bypassed, and a 100 ps pulse was used with a long delay line to obtain data from 100 ps to 30 ns. Because the experiments are non-resonant 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 for probing, and a fast digitizer (2 ns per point) recorded the data. The scans taken over various time ranges always overlapped substantially permitting the data sets to be merged by adjusting only their relative amplitudes. Additional experimental details have been published recently [2,20].

8CB was purchased from Aldrich and used without further purification except for filtration through a 0.2  $\mu\text{m}$  disc filter to reduce scattered light. The sample was sealed under vacuum in 1 cm glass cuvettes. The cuvettes were held in a constant flow cryostat where the temperature was controlled to  $\pm 0.1$  K.

## 3. Results and discussion

Fig. 1 displays OHD-OKE 8CB data on a log plot at 15 temperatures (316–358 K) in the isotropic phase. The data sets have been offset along the vertical axis for clarity of presentation. The

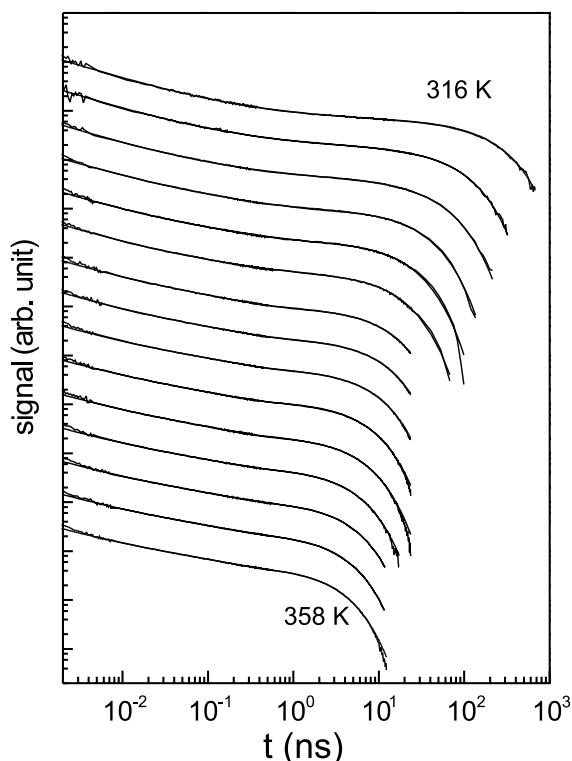


Fig. 1. Temperature dependent OHD-OKE 8CB data displayed on a log plot. The data sets have been offset along the vertical axis for clarity. The temperature for each curve (top to bottom) is 316, 319, 322, 325, 328, 331, 334, 337, 340, 343, 346, 349, 352, 355 and 358 K. Also shown are calculated curves for each set of data using Eq. (2). Because of the high quality of the data, in some portions of the curves it is difficult to distinguish the fit from the data.

temperatures are given in the figure caption. Also shown in Fig. 1 is a fit to each data set using the function discussed below. On the log plot, the decay is initially relatively gradual but becomes a steeper exponential decay at long time. At the lowest temperature, the displayed portion of the data spans the time range from 2 ps to 700 ns. The short time portion of the data decays as a power law, and the long time portion decays exponentially. Between these two regimes is a crossover time range that is akin to the Von Schweidler region observed in equivalent data taken on supercooled liquids [20,21].

Recently, a model function was introduced to describe the broad time range of the decay of the

liquid crystal data ( $\sim 2$  ps through the exponential decay) [1,2]

$$f(t) = e^{-t/\tau_{\text{LdG}}} \left[ a + e^{-t/\gamma} \left( b + \left( \frac{t}{t_\delta} \right)^{-p} \right) \right]. \quad (2)$$

$\tau_{\text{LdG}}$  is the decay constant of the LdG single exponential decay with an amplitude of  $a$ . All other terms apply to the intradomain relaxation. The exponential term contained inside the square brackets with a decay constant of  $\gamma$  is an intermediate time scale exponential decay that is only important in the crossover regime between the short time power law and the long time LdG exponential. The power law term with an exponent of  $-p$  is scaled by the constant  $t_\delta$  to give a unitless quantity.  $t_\delta$  determines the amplitude of the power law decay. The time dependent terms inside the square brackets describe the intradomain non-LdG dynamics. The intradomain decay leaves a residual anisotropy of amplitude  $a$ , which then decays via the domain randomization with time constant  $\tau_{\text{LdG}}$ .

The fits to the data shown in Fig. 1 are obtained using Eq. (2). The function given in Eq. (2) works at all temperatures, and it describes the 8CB data extremely well. The fitting function also provides equally good fits to data taken previously on three other liquid crystals [1,2]. While there are a large number of parameters in Eq. (2), they can be determined quite accurately because most of them are relatively independent of the others. The long time portion of the data is a single exponential, which makes it possible to determine  $\tau_{\text{LdG}}$  and a independent of the other parameters. The short time behavior is dominated by the power law, which makes it possible to determine  $p$  and  $t_\delta$ . The intermediate time scale exponential is the most difficult to determine accurately because it is sandwiched between the short time scale power law and the long time scale LdG exponential decay, and it has small amplitude. The data cannot be fit well without the intermediate term.

Fig. 2 displays the results of the fits for the long time LdG portion of the data. The line through the data was calculated using Eq. (1). The values of the viscosity were obtained from the literature [22]. The agreement with the predictions of LdG theory is very good. According to LdG theory

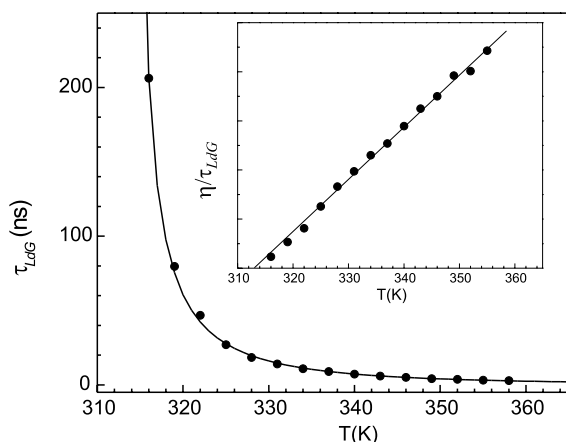


Fig. 2. The temperature dependent LdG relaxation times,  $\tau_{LdG}$ , for the long time exponential part of the data plotted vs. temperature. The solid line through the points is the LdG theoretical curve. The inset shows the linear relation predicted by LdG theory.

$$\frac{\eta(T)}{\tau_{LdG}} \propto T - T^* \quad (3)$$

A plot of  $\eta/\tau_{LdG}$  should be linear with an intercept of  $T^*$ . The inset in Fig. 2 shows this type of plot. We obtain the transition temperature,  $T^* = 313 \pm 1$ , which is close to NI transition temperature 313.5 K [22].

The intermediate time scale exponential decay constant,  $\gamma$ , is temperature independent within experimental error and has a value of  $60 \pm 15$  ns. Variations in this value do not have a significant influence on either the values of  $\tau_{LdG}$  or the power law exponents discussed below. At higher temperatures,  $\tau_{LdG}$  is approximately the same magnitude or shorter than the intermediate time constant  $\gamma$ , and it becomes very difficult to distinguish the two time constants. The difficulty is compounded by the fact that the amplitude,  $a$ , associated with the LdG term in Eq. (2) is generally five to six times larger than  $b$ , the amplitude associated with the intermediate exponential. In Eq. (2), multiplying through by the outer exponential,  $\exp(-t/\tau_{LdG})$ , causes the inner exponential to have the decay constant,

$$K = \frac{1}{\tau_{LdG}} + \frac{1}{\gamma}.$$

At the higher temperatures, effectively  $K = 1/\tau_{LdG}$ .

The most important feature of the data is the short time scale power law decay. Fig. 3 displays the power law portion of the data at 316 K with the contributions from the exponential terms removed. The power law spans almost four decades in time, from  $\sim 2$  ps to  $\sim 10$  ns and  $\sim 2$  decades of signal decay. The inset in Fig. 3 shows the power law exponent as a function of temperature from just above  $T_{NI}$  to well above the phase transition temperature. Within experimental error, the power law exponent is temperature independent and has a value of  $-0.56 \pm 0.01$ .

Previous experiments on liquid crystal samples 4'-(phenyloxy)-4-biphenylcarbonitrile (5-OCB), 4'-phenyl-4-biphenylcarbonitrile (5-CB) and 1-isothiocyabato-(4-propylcyclohexyl)benzene (3-CH-BT) display essentially identical behavior [1,2]. For all four liquid crystals, the long time behavior is described well by the LdG theory. On the shorter time scale, all four exhibit temperature independent power law decays with a crossover region at intermediate time that can be modeled as an exponential. Eq. (2) fits data from all four liquid crystals very well. The long time exponential decay

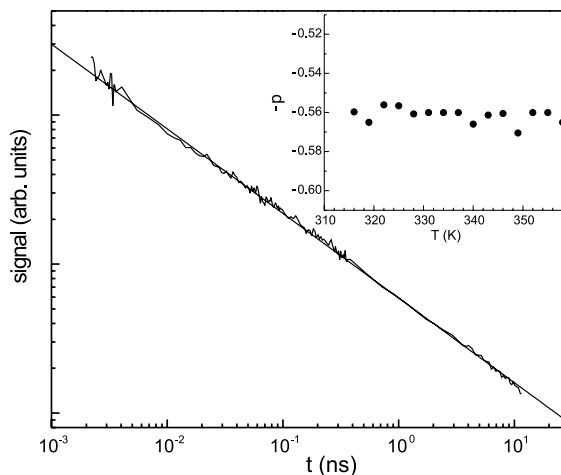


Fig. 3. A log plot of the short time portion of the 316 K data with longer time scale exponential contributions removed. A straight line on a log plot shows that the decay is a power law. The power law decay spans almost four decades in time and over two decades in signal. The inset shows the power law exponent,  $-p$ , vs. temperature. Within experimental error,  $p$  is temperature independent and has a value of  $0.56 \pm 0.01$ .

is produced by the randomization of the pseudo-nematic domains. The short time scale dynamics are the collective orientational relaxation of the nematogens in an environment that is locally nematic. The lack of temperature dependence suggests that the local pseudo-nematic structure is virtually temperature independent. The size of the domains grow (increasing correlation length) as the temperature is decreased toward the phase transition, but the data demonstrate that the dynamics at relatively short time are temperature independent (see inset in Fig. 3).

While all four liquid crystals exhibit power law decays of the signal at short time, the values of the exponents differ from one liquid crystal to another. The aspect ratio of a molecule is important in determining whether a molecule will form liquid crystals. MD simulations show that for an aspect ratio of  $< 2.5$ , liquid crystal phases will not occur [16]. Does the aspect ratio influence the nature of the dynamics of liquid crystals? Table 1 lists the aspect ratios and the power law exponents for the four liquid crystals that have been studied. The data are shown in Fig. 4. While there are only four points, the data clearly demonstrate that there is a strong dependence of the power law exponent on the aspect ratio. The line in Fig. 4 is the best linear fit to the data. For the power law  $t^{-p}$ ,  $p = mA + b$  where  $A$  is the aspect ratio. The line through the data gives  $m = -0.16 \pm 0.02$  and  $b = 1.25 \pm 0.09$ , that is, the power law exponent,  $p$ , is given by

$$p = -0.16A + 1.26. \quad (4)$$

If  $A$  is taken to be 2.5, the smallest aspect ratio for a liquid crystal, Eq. (4) gives  $p = \sim 0.9$ , which is still a reasonable value. The linear relationship in Eq. (4) cannot hold for very large values of  $A$  because  $p$  should always be a positive number.

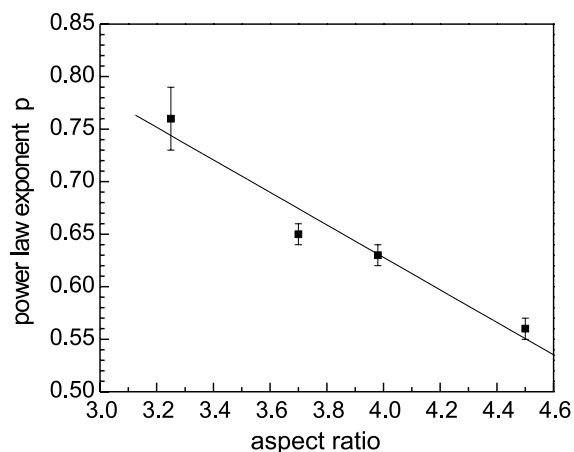


Fig. 4. The power law exponent  $p$  vs. the aspect ratios  $A$  of four liquid crystals (see Table 1). The exponent shows a pronounced dependence on  $A$  that is well approximated as linear. The line through the data is a linear fit.

The short time dynamics of the isotropic phase of liquid crystals arise from the collective motions of the nematogens in the pseudo-nematic domains [1,2,15]. On a distance scale short compared to the correlation length  $\zeta$ , there is a local director and a local order parameter. The dynamics that are observed on a time scale short compared to  $\tau_{\text{LDG}}$  are fluctuations of the local pseudo-nematic structure. The OKE perturbs the local nematic structure, and the power law decay reflects the relaxation of the perturbed structure. The results show that as the aspect ratio increases, the relaxation of the local pseudo-nematic structure slows through a change in the functional form of the decay, that is, a decrease in the power law exponent.

The OHD-OKE experiment measures the time derivative of the polarizability–polarizability correlation function, which is directly related to the orientational relaxation dynamics of the system

Table 1  
Aspect ratios and power law exponents for liquid crystals

	Length (nm)	Width (nm)	Aspect ratio	Power law exponent, $-p$
8CB	2.05	0.45	4.56	$0.56 \pm 0.01$
5OCB(1)	1.79	0.45	3.98	$0.63 \pm 0.01$
5CB(1)	1.67	0.45	3.71	$0.65 \pm 0.01$
3CHBT(2)	1.53	0.47	3.26	$0.76 \pm 0.03$

[23–26]. The model function for the decay given in Eq. (2) describes the data well. By integrating Eq. (2) and normalizing the function at  $t = 0$ , an empirical correlation function is obtained [1,2]. Using mode coupling theory, a preliminary theoretical development of the short time collective orientational dynamics of the pseudo-nematic domains has been presented [2]. Comparison to the experimental results is made possible by taking the time derivative of the theoretical correlation function. The theoretical treatment was able to qualitatively reproduce the nature of the short time behavior. However, important physical details, particularly the nematogen aspect ratio are not part of the development. The dependence of the power law exponent on the aspect ratio gives insight into the nature of liquid crystal dynamics, and the relationship in Eq. (4) provides an important benchmark for future theoretical treatments of the dynamics.

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