

Nanosecond time scale dynamics of pseudo-nematic domains in the isotropic phase of liquid crystals

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The slow reorientational dynamics of isotropic methoxybenzylidene-butylaniline (MBBA) were measured, using a transient grating optical Kerr effect experiment, over a wide temperature range (49.4°–119.7°C). The range of validity of the Landau-de Gennes theory for hydrodynamic relaxation in ordered fluids is determined. The results are compared to previous experiments on pentylcyanobiphenyl (5CB). Both liquid crystals conform to the Landau-de Gennes theory until the pseudo-nematic domain correlation length falls below three molecular lengths.

1. Introduction

Landau-de Gennes (LdG) theory, as applied to nematic liquid crystals in their isotropic phase, gives the temperature dependence of the correlation length, $\xi(T) = \xi_0 [T^*/(T - T^*)]^{1/2}$. $\xi(T)$ describes the size of pseudo-nematic domains that exist in the isotropic phase near the phase transition. ξ_0 is the molecular length, and T^* is a temperature slightly below the nematic-isotropic phase transition temperature, T_{ni} . At T^* the domain size becomes infinite [1,2]. The LdG theory has been successfully used to describe phenomena in liquid crystals near the phase transition, including magnetic [3] and electric birefringence [4,5], scattered light intensity [3,6], dynamic light scattering [3,6], optical Kerr effect [5,7–10] and nuclear spin lattice relaxation [11,12]. Magnetic and electric birefringence experiments have been performed over a wide temperature range, and show a deviation from LdG theory 15°–20°C above the phase transition [13].

The reorientational dynamics of normal liquids can be described by Debye-Stokes-Einstein (DSE) hy-

drodynamic equation [14,15] $\tau = V_{eff}\eta/kT$, where V_{eff} is the effective volume of the molecule [16,17], η is the viscosity, and k is the Boltzmann constant. A modified Debye-Stokes-Einstein equation, according to LdG theory, is used to describe the orientational relaxation of pseudo-nematic domains, i.e. $\tau = V_{eff}\eta/k(T - T^*)^\gamma$. For liquid crystals γ has been shown to be ≈ 1 , indicating the validity of the application of mean field theory [1].

As the temperature is increased, one would expect the domain size to become small enough that the isotropic phase of a liquid crystal would no longer exhibit LdG behavior and would finally behave as a normal liquid. In this paper, experiments are presented that show the temperature where deviation from LdG theory begins to occur for MBBA. Prior measurements of MBBA orientational relaxation did not observe the deviation from LdG theory due to the limited temperature range studied [9,18]. Prior measurements over a broad temperature range on the liquid crystal 5CB by Deeg et al. [19] observed deviations from the LdG theory at temperatures well above T_{ni} . Both liquid crystals began to deviate from the predictions of LdG theory when the correlation length dropped to a value of $\approx 2.7\xi_0$.

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2. Experimental procedures

The MBBA was obtained from American Tokyo Kasei. The MBBA was used without further purification. The sample was filtered through a 0.2 μm Gelman Acrodisc CR filter that had been rinsed with 500 ml of ethanol using a peristaltic pump and dried in an oven at $\approx 120^\circ\text{C}$. The sample was filtered into a 1 mm path length Type 37 cell from Wilmad which had its seams glass blown to insure their integrity. The MBBA was degassed with several freeze (liquid nitrogen)–thaw cycles on a vacuum line. The glass cell was then sealed under vacuum. The sample was temperature controlled to within 0.1°C by placing the cell in a heated aluminum holder that was regulated using a temperature controller. The temperature was independently measured using a platinum resistance thermometer from Omega. The phase transition of the MBBA (determined by observing the clearing temperature) was $T_{\text{ni}} = 46.9^\circ\text{C}$. MBBA hydrolyzes at elevated temperatures. Water adds across the C=N linkage between the two rings in MBBA. This contamination leads to a drop in the clearing temperature. The measurements on MBBA reported in the literature have been on samples of greatly varying clearing temperature, indicating the great range of purities used. This experiment was initially attempted with MBBA from Aldrich. Aldrich sells MBBA (98%) as a resolving agent, not as a liquid crystal. The clearing temperature for the Aldrich MBBA was 42.5°C , indicating it was impure. The high clearing temperature of the samples used in these experiments is indicative of the high purity of the MBBA.

The laser system for the transient grating optical Kerr effect experiment is a mode-locked and Q -switched Nd:YAG laser running at a repetition rate of 1 kHz. A single IR (1064 nm) pulse is selected out of the Q -switched pulse train with a LiNbO₃ Pockels Cell. A small portion (10%) of the 1064 nm IR single pulse is doubled in a CD*A crystal to produce 532 nm green pulses. The undoubled IR is split off from the green and is used as the grating excitation pulses. The green pulse is sent down a variable length optical delay line, providing up to 16 ns of delay. A polarization grating was used to eliminate acoustic wave generation in the sample [20]. The IR is split into two beams whose polarizations are set perpendicular

to each other. These pulses cross in space and time, setting up a grating where the polarization varies from circular to linear and back to circular along the grating wave vector direction [21]. The green probe beam is incident at the Bragg angle and diffracts off of the induced grating. The diffracted light is sent through a detector polarizer set perpendicular to the incident green beam and into a cooled photomultiplier tube. One of the IR excitation beams is chopped at half the laser frequency. The output of the photo tube is measured using a lock-in amplifier. The output of the lock-in is digitized and stored on computer. The delay line is also computer controlled, which permits averaging of multiple delay line scans.

3. Results and discussion

The orientational relaxation decay constants of MBBA were measured from $49.4^\circ\text{--}119.7^\circ\text{C}$. At very short times (femtosecond to several nanosecond) the decays are caused by librational relaxation and the dynamics of the internal structure of the pseudo-nematic domains [19]. Here we are interested in the long time behavior that is caused by the orientational relaxation of the domains themselves. It is this relaxation that is described by the LdG theory. Typical transient grating data is shown in fig. 1. As the transient grating experiment is a non-linear experiment, the signal is related to the square of the ori-

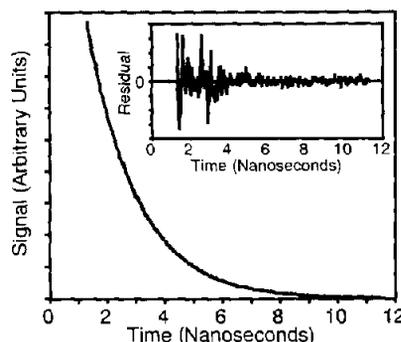


Fig. 1. Typical transient grating data set, taken at 85.6°C , with a single-exponential fit. The insert shows the residuals of the fit. The decay time is 3.45 ns. The data is fit for times (> 1.5 ns) long compared to the short time non-exponential behavior associated with librational relaxation and local structure relaxation [19].

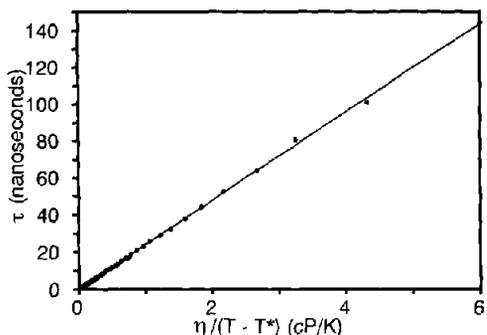


Fig. 2. Single parameter fit of τ versus $\eta/(T - T^*)$, showing the LdG modified hydrodynamic behavior near the phase transition. The fit shown is done on the temperature range $49.4^\circ - 70.0^\circ\text{C}$. $T^* = 46.9^\circ\text{C}$.

entational anisotropy [20,22,23]. Thus, the data was fit for times after the signal became a single exponential, to a squared exponential. The faster effects (< 2 ns) in MBBA will be the subject of a future paper [24].

The decay times for the lower temperatures are plotted versus $\eta/(T - T^*)$ in fig. 2. The viscosity of MBBA has been reported by Martinoty et al. [25]. T^* was determined using the approximation, $(T_{ni} - T^*)/T_{ni} \approx 2 \times 10^{-3}$, from formula by de Gennes [1] followed by a slight variation in the fit. T^* was found to be 319.6 K. At high enough temperature, the data must deviate from the LdG theory. Therefore, it is important to fit the data to the LdG theory only over a low temperature range in which the theory is clearly applicable. The slope of the line plotted in fig. 2 was fit for $49.4^\circ \rightarrow 60.0^\circ\text{C}$, $49.4^\circ \rightarrow 70.0^\circ\text{C}$, and $49.4^\circ \rightarrow 80.3^\circ\text{C}$. All these ranges of fits give the same slope to within 1%. These fits provide an accurate determination of the LdG curve.

All of the data (full temperature range) and the LdG curve obtained from fig. 2 are plotted as rate versus temperature in fig. 3. It can be clearly seen that the fit deviates by $\approx 90^\circ\text{C}$. At this temperature the correlation length is somewhat less than $3\xi_0$. The data are also plotted as $\ln(t/\eta)$ versus $\ln(T - T^*)$ in fig. 4. At the lower temperatures, the data are clearly fit by a straight line that corresponds to $\gamma = 1$. The deviations at higher temperatures cannot be accounted for by a change in γ . An accurate value of γ was obtained from the fit ($< 70^\circ\text{C}$) in fig. 2. The value of γ is 1.01 ± 0.01 . Light scattering and optical

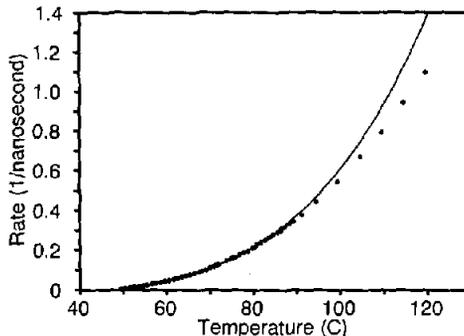


Fig. 3. Plot of the rate versus temperature showing the deviation from LdG theory at $\approx 90^\circ\text{C}$. The fit is from the values in fig. 1. The fit was done on the data from $49.4^\circ - 70.0^\circ\text{C}$ where LdG theory applies.

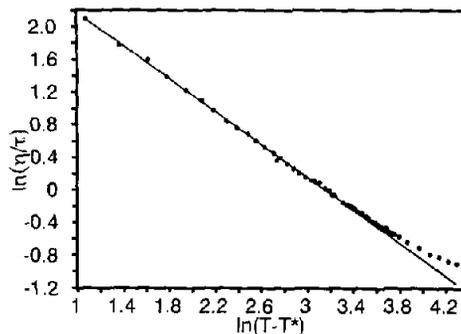


Fig. 4. Plot of $\ln(\tau/\eta)$ versus $\ln(T - T^*)$. This plot shows that $\gamma = 1.01 \pm 0.01$, confirming the applicability of a mean field theory.

Kerr effect experiments previously done on MBBA only covered a small temperature range [9,18]. These studies also gave a value of $\gamma = 1$. Because of the large temperature range covered here, this is probably the most accurate determination of the exponent γ and supports the applicability of mean field theory over a broad range of temperatures.

Deeg et al. also used transient grating experiments to examine the behavior of the liquid crystal 5CB (pentylcyanobiphenyl). The 5CB data were fit to the LdG theory and were shown to deviate when the correlation length became somewhat less than $3\xi_0$. The range of applicability of the LdG theory was virtually identical for 5CB and MBBA.

When the isotropic phase correlation length falls below 3 molecular lengths, the nematic liquid crystals start making a transition from an ordered liquid to a simple liquid. It is remarkable that the orien-

tational dynamics follow the LdG theory to less than $3\xi_0$. This demonstrates the profound effect that local ordering in a liquid can have on liquid state dynamics [19]. Static variables only display LdG behavior for correlation lengths greater than $4.5\xi_0$ – $5.5\xi_0$ (10° to 15° above T_c) [13]. The transition to a simple liquid will occur over a broad temperature range. If a sufficiently high temperature could be reached, the orientational relaxation would display the normal DSE behavior of a simple liquid. For temperatures at which $\xi < 3\xi_0$ but below the onset temperature for DSE behavior, the liquids will display dynamics that do not follow the LdG theory but are, none-the-less, strongly influenced by the details of the local liquid structure. In this range of temperatures, thermal fluctuations are not sufficient to totally overcome intermolecular interactions that affect orientational dynamics. Conventional liquids having strong anisotropic intermolecular interactions that result in significant local structures can also display orientational dynamics that significantly deviate from the expectations of hydrodynamic theory [26].

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References

[1] P.G. de Gennes, *The physics of liquid crystals* (Clarendon Press, Oxford, 1974).

- [2] P.G. de Gennes, *Phys. Letters A* 30 (1969) 454.
[3] T.W. Stinson III and J.D. Litster, *Phys. Rev. Letters* 25 (1970) 503.
[4] J.C. Filippini and J. Poggi, *J. Phys. Lett. (Paris)* 35 (1974) L-99.
[5] H.J. Coles, *Mol. Cryst. Liquid Cryst.* 49 (1978) 67.
[6] J.D. Litster and T.W. Stinson III, *J. Appl. Phys.* 41 (1970) 996.
[7] G.K.L. Wong and Y.R. Shen, *Phys. Rev. Letters* 30 (1973) 895.
[8] G.K.L. Wong and Y.R. Shen, *Phys. Rev. Letters* 32 (1974) 527.
[9] G.K.L. Wong and Y.R. Shen, *Phys. Rev. A* 10 (1974) 1277.
[10] E.G. Hanson, Y.R. Shen and G.K.L. Wong, *Phys. Rev. A* 14 (1976) 1281.
[11] B. Cabane and G. Clarke, *Phys. Rev. Letters* 25 (1970) 91.
[12] S. Gosh, E. Tettamanti and E. Indovina, *Phys. Rev. Letters* 29 (1973) 638.
[13] J.C. Filippini and Y. Poggi, *J. Phys. Lett. (Paris)* 37 (1976) L-17.
[14] D. Kivelson and P.A. Madden, *Ann. Rev. Phys. Chem.* 31 (1980) 523.
[15] D. Kivelson, in: *Rotational dynamics of small and macromolecules*, eds. T. Dorfmueller and R. Pecora (Springer, Berlin, 1987) p. 1.
[16] F. Perrin, *J. Phys. Radium* 5 (1934) 497.
[17] C. Hu and R. Zwanzig, *J. Chem. Phys.* 60 (1974) 4354.
[18] J. Prost and J.R. Lalanne, *Phys. Rev. A* 8 (1973) 2090.
[19] F.W. Deeg, S.R. Greenfield, J.J. Stankus, V.J. Newell and M.D. Fayer, *J. Chem. Phys.* 93 (1990) 3503.
[20] G. Eyring and M.D. Fayer, *J. Chem. Phys.* 81 (1984) 4314.
[21] A. von Jena and H.E. Lessing, *Opt. Quantum Electron.* 11 (1979) 419.
[22] Y. Yan and K.A. Nelson, *J. Chem. Phys.* 87 (1987) 6240.
[23] Y. Yan and K.A. Nelson, *J. Chem. Phys.* 87 (1987) 6257.
[24] J.J. Stankus, R. Torre, S.R. Greenfield, A. Sengupta and M.D. Fayer, in preparation.
[25] P. Martinoty, S. Candau and F. Debeauvais, *Phys. Rev. Letters* 27 (1971) 1123.
[26] S.R. Greenfield, A. Sengupta, J.J. Stankus and M.D. Fayer, *Chem. Phys. Letters* 193 (1992) 49.