PHYSICAL REVIEW E VOLUME 48, NUMBER 4 OCTOBER 1993

Dynamics of order-parameter and director fluctuations in the nematic phase of a lyotropic liquid crystal

J. P. McClymer
Department of Physics and Astronomy, University of Maine, Orono, Maine 04469

P. H. Keyes
Department of Physics and Astronomy, Wayne State University, Detroit, Michigan 48202

(Received 21 January 1993)

We report measurements of the critical slowing down of order-parameter fluctuations in the nematic phase, obtained using photon-correlation spectroscopy. These critical fluctuations, as well as the noncritical director fluctuations, which are also measured, are compared to predictions from mean-field theory and good agreement is found.

PACS number(s): 64.70.Md, 61.30.−v

It is well known that the isotropic phase of a liquid displays a type of critical opalescence as it is cooled downward toward the transition to a nematic liquid-crystalline phase. The situation on the nematic side of the transition, however, is more complex and some aspects of the light scattering there are better known than others. First of all, there are *at all temperatures* the well-known transverse fluctuations in the *direction* of the ordering called the director fluctuations. In addition, however, mirroring the behavior above the transition, there is also a pretransitional increase in the light scattering as the transition is approached from below. This contribution, which we refer to as the *critical* part, is due to fluctuations in the *degree* of orientational ordering (sometimes called longitudinal fluctuations). The strong director fluctuations are responsible for the characteristic turbidity of the nematic phase which normally obscures detection of the critical pretransitional fluctuations.

In an earlier paper [1] we showed theoretically how these two contributions to the light scattering of a nematic liquid crystal could be separately resolved. Then, carrying out the experiment, we reported observing the critical order-parameter fluctuations in both nematic and isotropic phases as well as the director fluctuations in the nematic phase of a lyotropic liquid crystal using static light scattering. A comparison of the data to mean-field theory for the nematic- isotropic transition allowed a fit involving no free parameters that substantially agreed with the data.

We extend these measurements in this paper by reporting on the dynamics of both the order-parameter and director fluctuations obtained by means of photon-correlation spectroscopy. Once again, good agreement with the mean-field predictions is found and, in addition, enough independent observations have now been made to allow for a complete determination of all of the free-energy coefficients.

As discussed in Ref. [1], the light scattering from director fluctuations in the lyotropic nematic is much smaller than in thermotropic nematics allowing the critical order-parameter fluctuations to easily be separated from the noncritical director fluctuations through polarization selection rules. The result is that the scattered intensity is approximated by

$$I \propto \tfrac{9}{4}Q^2 \sum_{\alpha=x,y} (f_\alpha i_z + f_z i_\alpha)^2 (\delta n_\alpha)^2 + (\delta Q)^2 (\tfrac{3}{2} f_z i_z - \tfrac{1}{2}\hat{\mathbf{i}}\cdot\hat{\mathbf{f}})^2 , \tag{1}$$

where $\hat{\mathbf{i}}_\alpha$ and $\hat{\mathbf{f}}_\beta$ are unit vectors along the directions of polarization of the incident and scattered light, respectively. The director $\mathbf{n}$ is taken to be along the z direction and the fluctuations of the director and the magnitude of the order parameter Q are assumed to be uncorrelated.

The first term in the above equation is the well-known selection rule for observing director fluctuations [2] while the second term gives the polarization selection rules for observing order-parameter fluctuations. In order to separate out the individual contributions to the total scattering intensity, a scattering geometry in which the director lies in the scattering plane and at right angles to the path of the incident laser beam ($\lambda = 5145$ Å) is employed. A polarization rotator mounted on the front of the laser polarizes the incident beam either parallel to the director (designated H polarization, $i_z = 1$), or perpendicular (designated V polarization, $i_y = 1$). In both cases the scattered light passes through a V-mounted analyzer ($f_y = 1$) where it is picked up by a multimode optical fiber and transmitted to a photomultiplier tube.

Equation (1) predicts that the *HV* scattering geometry detects director fluctuations only while the *VV* geometry responds to order-parameter fluctuations only. These predictions are borne out by our earlier static light-scattering study in which the *VV* scattering data show a pretransitional increase and the *HV* data exhibit no such behavior [1].

The nematic director is aligned along the z direction using two large permanent magnets. The magnets generate a field of about 2 G which produces uniform alignment in a day or two. The samples are previously aligned in a larger field and transferred to the scattering cell. As the magnets obscure the 90° scattering direction (along

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the director), a multimode fiber is bent between the magnet and sample holder to collect the scattered light. The temperature-controlled aluminum sample holder is slightly bigger than the 1-cm^2 cross-section cuvette it contains. The analog output of the photomultiplier tube is fed to a correlator connected to a microcomputer.

The liquid crystal studied, the same sample used in the previous static measurements, consists of a mixture of 26.80% potassium laurate, 6.24% decanol, and 66.94% deuterium oxide by weight. This particular concentration exhibits a rather simple phase behavior [3]: from below room temperature to about 48 °C the sample is in the N_c phase, which consists of rodlike micelles that align parallel to a magnetic field.

The experiment started with a well-aligned nematic heated up through the nematic-isotropic transition and into the isotropic phase. The correlation functions in both phases are well described by single exponentials.

The decay data are analyzed, as were the static data, within the framework of the Landau–de Gennes mean-field theory [2]. The free-energy expansion in terms of the tensor order parameter is given as

$$F=F_0+\tfrac{1}{3}AQ_{\alpha\beta}Q_{\beta\alpha}-\tfrac{4}{9}BQ_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha}+\tfrac{1}{9}C(Q_{\alpha\beta}Q_{\beta\alpha})^2 +\tfrac{1}{2}L_1Q_{\alpha\beta,\gamma}Q_{\beta\alpha,\gamma}+\tfrac{1}{2}L_2Q_{\alpha\beta,\beta}Q_{\alpha\gamma,\gamma}\ , \tag{2}$$

with $A=a(T-T^*)$, and B and C taken to be constants. In this analysis we will set L_2 to zero, which is equivalent to assuming equal elastic constants.

The order-parameter fluctuation relaxation rate in the isotropic phase is predicted to be

$$\Gamma=\frac{a(T-T^*)}{\nu}\ , \tag{3}$$

where ν is the dynamic viscosity coefficient [2].

The theoretical expression for the relaxation in the nematic phase is more complicated owing to the more complex behavior of the susceptibility in the nematic phase [1]. Using the susceptibility χ found in our earlier experiment [1] and the equation $1/\Gamma=\chi\nu$, which relates the static and dynamic behaviors [2,4], we find

$$\Gamma^{-1}\propto\nu\left[\frac{k_BT}{2BQ-4A+3L_1q^2}+\frac{k_BT}{2BQ+L_1q^2}\right]\ , \tag{4}$$

where the scattering wave number is $q=(4\pi/\lambda)\sin(\theta/2)$, and Q, the magnitude of the order parameter in the nematic phase, is given by

$$Q=\frac{B}{2C}(1+\sqrt{1-4AC/B^2})\ , \tag{5}$$

as follows from the minimization of Eq. (2).

Figure 1 shows the temperature dependence of the inverse decay times for *VV* scattering in both the nematic and isotropic phase. The order-parameter fluctuations within the nematic phase could only be followed over a restricted temperature range before the decay rates exceeded the limits of the correlator. Within the isotropic phase the decay rates for this lyotropic nematic are much smaller than those reported for the isotropic phase of the thermotropic N-(4′methoxybenzlidine)-4-(n-butyl)aniline (MBBA) [5] but are comparable to the decay times found in the isotropic phases of the chiral materials cholesteryl oleyl carbonate (COC) [6] and cholesteryl 2-(2-ethoxyethoxy)ethyl carbonate (CEEEC) [7].

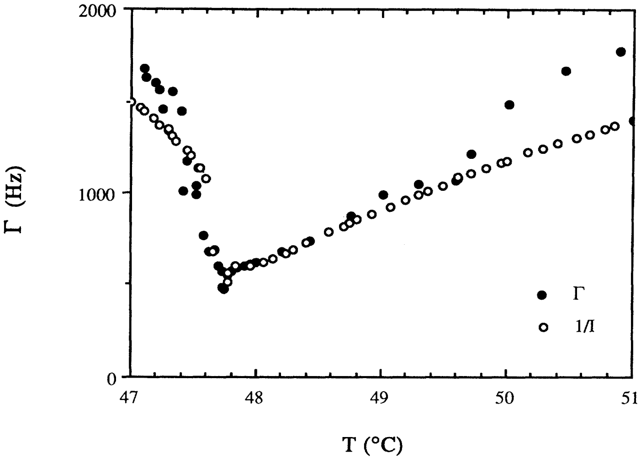

FIG. 1. The decay rate Γ of the critical order-parameter fluctuations in both the nematic and isotropic phases, where the transition between these two phases is $T_c=47.74$ °C. Also shown is the inverse of the scattered light intensity, taken from Ref. [1], with the arbitrary units being scaled to allow comparison with Γ.

Also shown in Fig. 1 are the previously obtained light-scattering data whose (arbitrary) units have been scaled so as to make these data coincide with the decay rate data in the immediate vicinity of the transition temperature T_c. As Eqs. (3) and (4) indicate, the relaxation rate data are expected to follow the same temperature dependence as the inverse intensity data only if the viscosity coefficient ν has a negligible temperature dependence. Earlier measurements using a falling ball viscometer on samples of similar compositions [8] showed marked temperature variations of the shear viscosity η. The observed differences between the static and dynamic light-scattering data are approximately consistent with these variations assuming that η and ν have similar temperature dependences.

Relations for the Landau–de Gennes phenomenological coefficients can be obtained using the above results and those of our earlier experiments. Equation (2) can be used to predict a value for a, the coefficient of the quadratic term in the Landau–de Gennes free-energy density. The value of (T_c-T^*) for this sample was found to be 0.40 K from the earlier static light-scattering measurements [1]. From our previous work [8] we find the shear viscosity η at the nematic-isotropic transition to be about 250 centipoise. If this value of the viscosity is used to estimate ν, then we obtain $a\approx340$ J m^{-3} K^{-1} in the isotropic phase. This value is more than two orders of magnitude smaller than that found for MBBA [9] (6.3×10^4 J m^{-3} K^{-1}). It is, however, nearly identical to the value of 300 J m^{-3} K^{-1} found by magnetically induced birefringence approaching an N_c phase in the same lyotropic system but at a different composition [10], indicating that the substitution of η for ν is a reasonable approximation.

For this same sample the bare correlation length ξ_0 was earlier found to be 22 Å from angular measurements of the scattered intensity [11]. From the relation $\xi_0=(L_1/aT^*)^{1/2}$ we estimate L_1, the coefficient of the gradient term in Eq. (2), to be 5.3×10^{-13} N.

The mean-field description also predicts a relation between the coefficients of $AC/B^2=\frac{2}{9}$ at $T=T_c$. From this relationship and the value of a, the value of B^2/C is found to be 610 J m^{-3}, some two-and-one-half orders of magnitude smaller than the equivalent ratio in the isotropic phase of MBBA [9]. A value for the ratio B/C can be obtained through the analysis of the noncritical director fluctuations, as we will now discuss, and thus independent values for B and C, as well as some other parameters, can then be determined.

Figure 2 shows the relaxation rate of director fluctuations, obtained using the HV geometry, as the N-I transition is approached. The relaxation rate is given by $\Gamma=Kq^2/\nu$, where K is a Frank elastic constant and q is the scattering wave number [2]. The temperature dependence of Γ is principally due to the decrease of the elastic constant K as the clearing temperature is approached.

In the context of mean-field theory, to a first approximation, the Frank constants have the same temperature dependence as the square of the order parameter [2,12]: $K=2L_1Q^2$. Putting this all together, including Eq. (5), we obtain

$$\Gamma=\left[\frac{B}{C}\right]^2\frac{L_1q^2}{2\nu}\left(1+\sqrt{1-4AC/B^2}\right)^2 . \tag{6}$$

The temperature scale is set by the factor AC/B^2, which is zero at T^* and $\frac{2}{9}$ at T_c, as previously mentioned. Of the other parameters, L_1, ν, and q^2 have already been determined [13], and so only the ratio B/C needs to be adjusted to produce a fit to the data. The solid line in Fig. 2 is the best fit, obtained for a value of $B/C=0.70$. Using the value for B^2/C deduced in the preceding paragraph, we find values of $B=870$ J m^{-3} and $C=1240$ J m^{-3}, both of which are nearly three orders of magnitude smaller than the corresponding values for MBBA [9].

It is perhaps worth recalling from Ref. [1] that, in contrast to the above behavior for the decay rate, the intensity of the director fluctuations showed no appreciable temperature dependence. This result is due to a cancellation of two competing effects: the scattering power is proportional to the square of the order parameter, whereas the fluctuations of the order parameter responsible for the scattering are inversely proportional to the elastic constant $K=2LQ^2$. It is only this latter effect that is important in setting the decay rate, and so the Γ data for director fluctuations are quite temperature dependent.

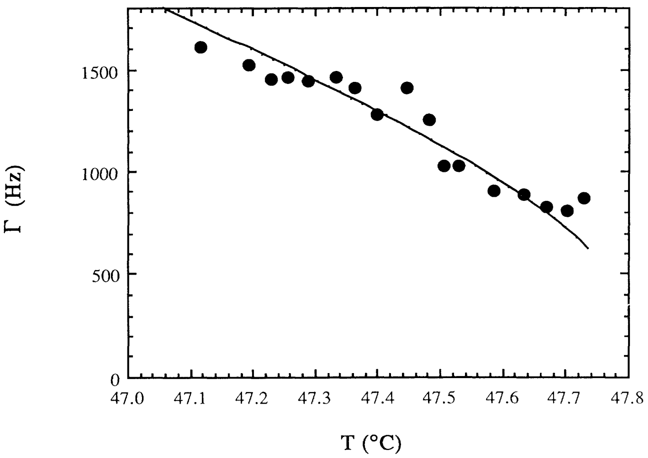

FIG. 2. The decay rate Γ of the director fluctuations in the nematic phase. The solid line is the prediction of Eq. (6) where the value of B/C has been adjusted to obtain the best fit.

Lastly, the relaxation data along with the viscosity measurements allow the average elastic constant to be estimated. It is about 5×10^{-13} N at 0.5° below T_c and decreases by about another factor of 2 as the transition to the isotropic phase is approached. These values are about a factor of 10 smaller than the average of the elastic constants for MBBA [14].

In summary, except for the bare correlation length, which is larger, we find that all of the parameters for this lyotropic nematic liquid crystal have much smaller values than do the corresponding parameters for a thermotropic material, such as MBBA. The larger bare correlation length is expected since a micelle is bigger than a single molecule of a typical thermotropic system. The smaller values for the other parameters could also probably have been anticipated in view of the "softness" of a micellar rod compared to the more rigid molecule of a thermotropic liquid crystal. The cubic and quartic coefficients B and C are especially small for this lyotropic system, consistent with the previous observation [3] that there is a nearby Landau point in the phase diagram, where B becomes zero and the transition becomes continuous. Indeed, in Ref. [10] data for an N_c sample very close to the Landau point yield values for the B coefficient (defined as in our expressions) of 200–700 J/m^3, all smaller than our value of 870 J/m^3. The average value of 1.8×10^4 J/m^3 found for the C coefficient in this same system is, however, inexplicably larger than our value of 1240 J/m^3, although both are much smaller than what is found in thermotropic systems.

This work was supported in part by the National Science Foundation under Grant No. DMR-8909815.

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