Fast relaxation mode in a thermotropic uniaxial nematic liquid crystal

Sanjay Tripathi, Hua Zhong, Rolfe G. Petschek,* and Charles Rosenblatt[†,‡]
Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106-7079
(Received 5 April 1995)

Results are reported from a light scattering measurement in the uniaxial nematic phase in the thermotropic liquid crystal octylcyanobiphenyl, a material which does not exhibit a biaxial phase. In addition to a slow Goldstone mode associated with twist fluctuations, a fast mode whose relaxation time is independent of both wave vector and temperature has been observed. The possible origins of this relaxation are discussed.

PACS number(s): 61.30.Eb

The study of nematic biaxiality has been arduous and often confusing. In 1980 Yu and Saupe discovered an unambiguous biaxial nematic phase in the ternary lyotropic liquid crystal composed of potassium laurate, water, and 1-decano [1]. Above the uniaxial-biaxial nematic phase transition temperature T_{ub}, Lacerda Santos, Galerne, and Durand [2] used quasielastic light scattering to observe biaxial nematic *fluctuations* in the uniaxial phase. They showed that the fluctuations may be described by a Landau–de Gennes mean-field model [3,4] with both amplitude and relaxation time diverging at T_{ub}. Despite demonstrations of biaxiality in a lyotropic system, the situation with thermotropic liquid crystals is considerably murkier. Over the years there has been an ongoing search for a thermotropic biaxial nematic phase. Although numerous claims of biaxiality have appeared in the literature, [5–13], nearly all reports of this phase have been called into question [14]. Theoretical analysis has also shown that it is challenging to design a compound with sufficiently large biaxiality to form a biaxial nematic phase [15–17]. In this light a measurement of the biaxial susceptibility in the thermotropic uniaxial nematic phase would serve as an excellent probe of the existence and location of an incipient thermotropic biaxial nematic phase. In this paper we report on results of a light scattering experiment in the uniaxial nematic phase of the thermotropic liquid crystal octylcyanobiphenyl (8CB). The results of the experiment, which was designed to probe biaxial fluctuations in a material that does not possess a biaxial nematic phase, are equivocal. Although the data exhibit a rapid relaxation independent of wave vector, which is characteristic of biaxial fluctuations well above T_{ub}, both the relaxation time and the amplitude of the relaxation are larger than expected from a Landau–de Gennes analysis. Other possible sources of the rapid relaxation are also examined, most notably higher-order director fluctuations.

The light scattering geometry, to be discussed below, requires homeotropic orientation of the director. To facilitate this alignment, two microscope slides were dipped into a 0.5% (by weight) mixture of hexadecyltrimethylammonium bromide in enthanol and allowed to dry. The residue was removed with a Kimwipe and the two slides were cemented together, separated by spacers of nominal thickness 25 μm. The cell was filled in the isotropic phase by capillary action with 8CB, which was obtained from E. Merck and used as received. The cell was then placed into an oven, which was temperature controlled to 10 mK, and cooled into the nematic phase. Excellent, defect-free homeotropic alignment was observed by means of polarized optical microscopy. Finally, the oven-cell assembly was mounted in our quasielastic light scattering apparatus, which is described in detail elsewhere [18].

The light scattering geometry is shown in Fig. 1, where the uniaxial director $\hat{n}$ was oriented along the $\hat{z}$ axis and the plane of the cell was situated in the $\hat{x}\hat{y}$ plane of the laboratory. Light from a 1-W Ar-ion laser was incident at an (internal) angle θ_i in the $\hat{y}\hat{z}$ scattering plane with ordinary polarization directed along the $\hat{x}$ axis. The depolarized scattering signal was detected at an (internal) angle θ_f, such that the scattering wave vector $\vec{q}=\vec{K}_f-\vec{K}_i$ was completely along the $\hat{y}$ axis, as shown in Fig. 1. This configuration, which corresponds to a "*VH*" depolarized scattering geometry in which $q_z=0$, probes several collective modes associated with the traceless, symmetric, second-rank nematic order parameter tensor $\overleftrightarrow{Q}$, viz.

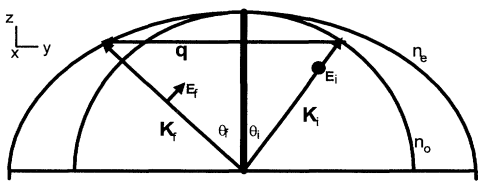

FIG. 1. Light scattering geometry. The nematic director $\hat{n}$ lies along the $\hat{z}$ axis. $\vec{K}_i$ and $\vec{K}_f$ correspond to incident (ordinary polarization) and scattered (extraordinary polarization) wave vectors of light and $\vec{q}$ the scattering wave vector. θ_i and θ_f are the *internal* incident and scattering angles for the wave vectors and n_e and n_0 the effective extraordinary and ordinary refractive indices.

*Electronic address: rpetsche@mrg.cwru.edu
†Also at Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106-7079.
‡Electronic address: cxr@po.cwru.edu

$$\overleftrightarrow{Q}(\vec{r})=\begin{bmatrix} -\frac{Q}{3}+Qn_xn_x+Q'_{xx} & Qn_xn_y+Q'_{xy} & Qn_x \\ Qn_xn_y+Q'_{xy} & -\frac{Q}{3}+Qn_yn_y-Q'_{xx} & Qn_y \\ Qn_x & Qn_y & 2\frac{Q}{3}-Qn_xn_x-Qn_yn_y \end{bmatrix}, \quad (1)$$

where Q'_{xx} and Q'_{xy} correspond to biaxial terms, Q is the scalar magnitude of the order parameter, and n_i $(i=x,y)$ corresponds to deviations $\delta\hat{n}$ of the nematic direction from the $\hat{z}$-axis. One mode probed by our experiment involves twist distortions for which the director fluctuation $\delta\hat{n}=n_x$ and $\vec{q}=q_y\hat{y}$. The other component of the signal involves fluctuations of the off-diagonal elements of $\overleftrightarrow{Q}$, again for which the wave vector $\vec{q}=q_y\hat{y}$. This off-diagonal component involves two collective modes, viz., a biaxial mode (Q'_{xy}) and a mode involving higher-order director fluctuations (Qn_xn_y). In a temporal intensity-intensity light scattering autocorrelation measurement all three modes are expected to appear and may be experimentally separated if they have very different relaxation times. To facilitate such a measurement, a portion of the incident beam was added to the scattered signal just before the detector. In this way a clean heterodyne measurement was made. When we account for polarization selection rulers, the total *observed* correlation function $G^{\rm obs}(q_y,\tau)$ was simply the sum of terms proportional to the observed off-diagonal correlation function

$$G^{\rm obs}_{xy}(q_y,\tau)=\cos^2\theta_f G_{xy}(q_y,\tau)$$
$$=\cos^2\theta_f\langle Q_{xy}(q_y,\tau)Q_{xy}(-q_y,0)\rangle$$

[where $Q_{xy}(\vec{q})=Qn_{xy}(\vec{q})+Q'_{xy}(\vec{q})$ and $n_{xy}(\vec{q})$ is the Fourier transform of $n_x(\vec{r})n_y(\vec{r})$, viz., $n_{xy}(\vec{q})=\Omega^{-1}\sum_{\vec{q}_1}n_x(\vec{q}_1)n_y(\vec{q}-\vec{q}_1)$], the observed twist mode correlation function

$$G^{\rm obs}_t(q,\tau)=\sin^2\theta_f G_t(q_y,\tau)$$
$$=\sin^2\theta_f Q^2\langle n_x(q_y,\tau)n_x(-q_y,0)\rangle\ ,$$

and a τ-independent local oscillator term.

In order to determine the scattering wave vector $\vec{q}$, refractive index measurements of the liquid crystal 8CB were made with an Abbe refractometer as a function of temperature at optical wavelength $\lambda=5145$ Å; results are shown in Fig. 2.

Time autocorrelation measurements were first performed at a fixed temperature $T=37.1$ °C (approximately 2.8 °C below the nematic-isotropic phase transition temperature $T_{NI}=39.9$ °C) as a function of the wave vector q_y. The *external* angle of incidence $\theta_i^{\rm ext}$ was varied between 5° and 32°, corresponding to q_y between 2.2×10^4 and 1.35×10^5 cm^{-1}, as calculated from the refractive index data in Fig. 2. Exploiting the multi-τ capabilities of our digital autocorrelator, the first 32 channels and subsequent 64 channels were set for different acquisition times, thereby allowing us to simultaneously observe decay processes on widely different time scales. Data were collected at each wave vector $\vec{q}=q_y\hat{y}$ and were least-squares fitted to the sum of two exponentials plus an offset. A typical experimental run is shown in Fig. 3, where the time base increases discontinuously at channel 33. To aid the reader and avoid the apparent temporal discontinuity and resulting cusp in $G^{\rm obs}(q_y,\tau)$, Fig. 4 displays the same data plotted against the logarithm of time. In Fig. 5 we plot the slow relaxation time τ_t vs q_y obtained from the double exponential least-squares fit, which we associate with twist elastic fluctuations. Additionally, Fig. 5 shows a least-squares fit of τ_t to the function $\tau_t=\bar{\eta}/K_{22}q_y^2$, where K_{22} is the twist elastic constant and $\bar{\eta}$ is an appropriate viscosity coefficient. The fit clearly demonstrates that the slow mode corresponds to twist elastic fluctuations. In Fig. 6 we plot the fast relaxation time $\tau_{\rm fast}$ vs q_y, which we associate with off diagonal fluctuations in $\overleftrightarrow{Q}$. In addition to relaxation times, we also have extracted the relative magnitudes of $G^{\rm obs}_{xy}(q_y,0)$ and $G^{\rm obs}_t(q_y,0)$. As $G^{\rm obs}_t(q_y,0)\propto q_y^{-2}$, we plot in Fig. 7 the quantity

$$R_1\equiv\frac{G^{\rm obs}_{xy}(q_y,0)\tan^2\theta_f}{G^{\rm obs}_t(q_y,0)}=\frac{G_{xy}(q_y,0)}{G_t(q_y,0)}$$

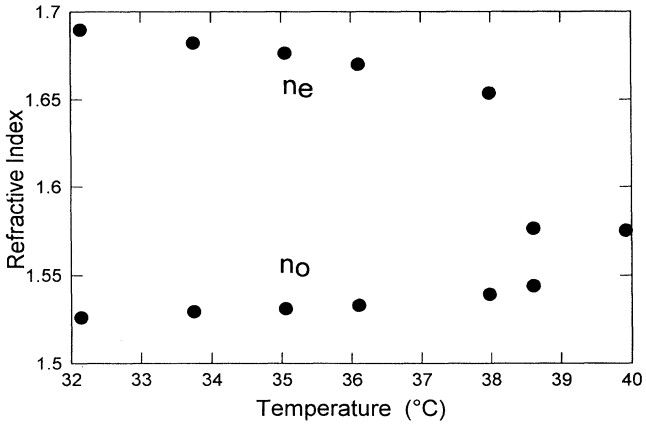

FIG. 2. Extraordinary (n_e) and ordinary (n_0) refractive indices vs temperature at $\lambda=5145$ Å. Note that the temperature scale for the Abbe refractometer is slightly different from the scattering apparatus. When calculating $\vec{q}$ the refractive indices are evaluated relative to the transition temperature T_{NI}.

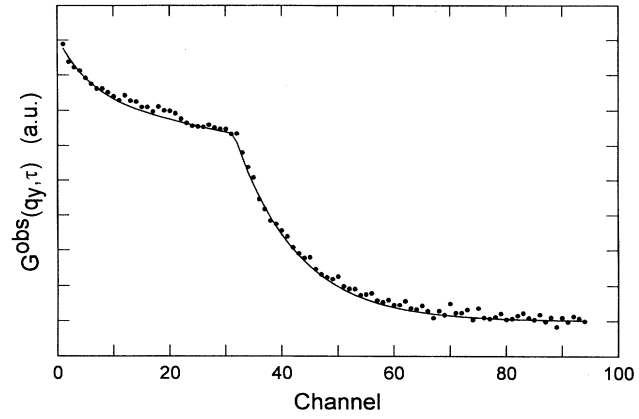

FIG. 3. Observed intensity-intensity correlation function $G^{\rm obs}$ obtained in the heterodyne mode. For this example, $T=37.46\,^{\circ}\mathrm{C}$ and $q_y=1.07\times10^5\ \mathrm{cm}^{-1}$. First 32 channels correspond to 1 μs/channel and the remaining channels correspond to 16 μs/channel. $\tau_{\rm fast}=5.7\pm1.5\ \mu$s and $\tau_t=175\pm20\ \mu$s.

at a fixed temperature $T=37.1\,^{\circ}\mathrm{C}$ and in Fig. 8 we plot

$$R_2\equiv\frac{G_{xy}^{\rm obs}(q_y,0)\tan^2\theta_f}{q_y^2G_t^{\rm obs}(q_y,0)}=\frac{G_{xy}(q_y,0)}{q_y^2G_t(q_y,0)}\ .$$

The quantity R_2 is expected to be independent of q_y if $G_{xy}(q_y,0)$ is largely due to wave-vector-independent biaxial fluctuations. The fact that R_2 exhibits a significant q_y dependence is perhaps the first indication that $G_{xy}^{\rm obs}(q_y,0)$ may have origins other than biaxiality. If, on the other hand, $G_{xy}(q_y,0)$ is dominated by the higher-order director fluctuation term, then $R_1\propto q_y$ (see below), which again does not seem to describe the data. We shall return to this later.

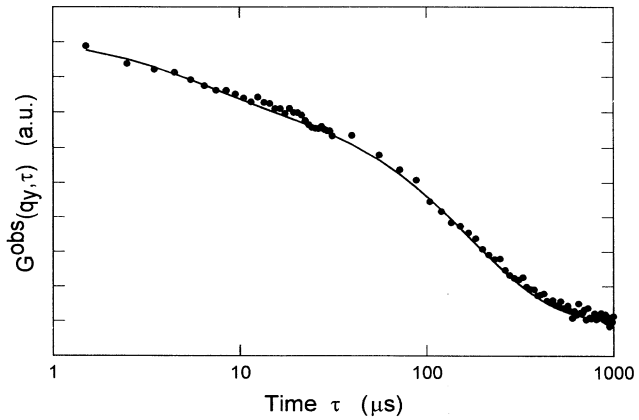

FIG. 4. Same as Fig. 4, except the time axis is continuous and logarithmic.

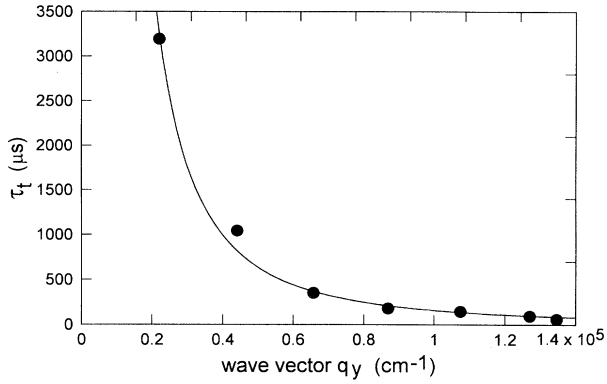

FIG. 5. τ_t vs q_y at 37.1 °C. The solid line represents a fit of the data to the function $\tau_t=\eta/Kq_y^2$.

In addition to the wave-vector-dependent measurements, $G^{\rm obs}(q_y,\tau)$ was measured as a function of temperature at a fixed external angle of incidence $\theta_i^{\rm ext}=25\,^{\circ}$. For each temperature in the nematic phase the relevant scattering angle and wave vector q_y were calculated from the refractive index data in Fig. 2, such that $q_y=1.07\times10^5\ \mathrm{cm}^{-1}$ near $T_{NI}\sim39.9\,^{\circ}$ and $q_y=1.085\times10^5\ \mathrm{cm}^{-1}$ near the nematic–smectic-A phase transition temperature $T_{NA}\sim3.7\,^{\circ}\mathrm{C}$. Figure 9 shows τ_t vs temperature. Although there appears to be a very weak trend of increasing relaxation time with temperature on approaching T_{NI}, the error bars are quite large and do not facilitate a simple interpretation of the temperature dependence of either K_{22} or $\bar{\eta}$. Figure 10 shows $\tau_{\rm fast}$ vs T. Again, $\tau_{\rm fast}\ll\tau_t$ and $\tau_{\rm fast}$ is apparently independent of temperature.

As an additional check of possible biaxiality, we also performed light scattering measurements in the smectic-A phase. Although the amplitudes of the bend, twist, and splay fluctuations do not vanish in the smectic-A phase, they are significantly reduced. This is because they must couple to layer compression and director tilt

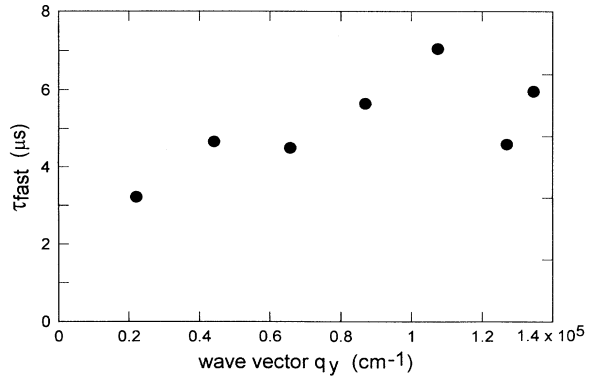

FIG. 6. $\tau_{\rm fast}$ vs q_y at 37.1 °C.

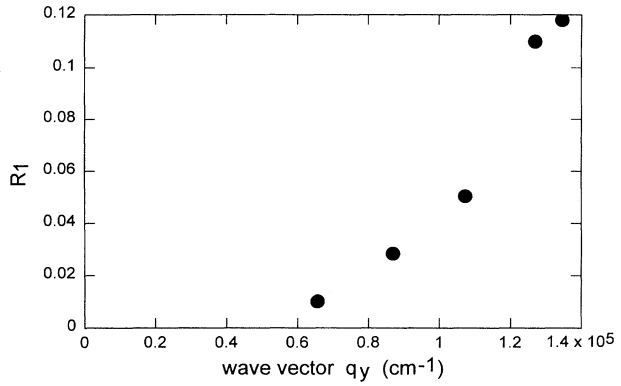

FIG. 7. The quantity $R_1 \equiv G_{xy}^{\rm obs}(q_y,0)\tan^2\theta_f / G_t^{\rm obs}(q_y,0)$ vs q_y at $T=37.1\,^{\circ}$C. Note that we have not shown the data points for the two smallest wave vectors because of excessive uncertainty in the fitted amplitudes.

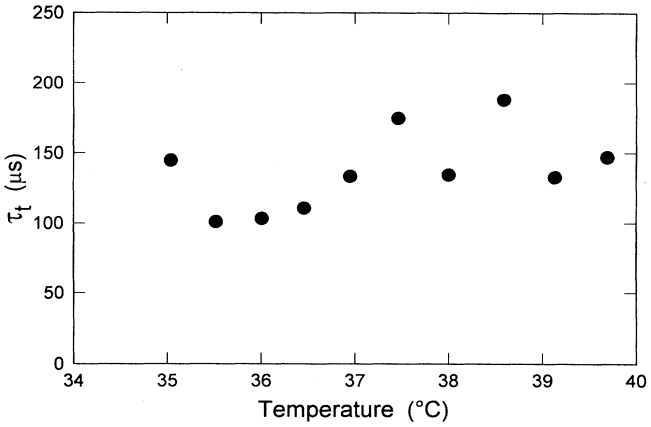

FIG. 9. τ_t vs temperature at a fixed *external* angle of incidence of 25°.

with respect to the layer normal, both of which tend to be very rigid [19]. In consequence, $G_t(q_y,\tau)$ should become quite small in the smectic-A phase. On the other hand, one does not expect a large change in either amplitude or relaxation time of biaxial fluctuations. A correlation measurement was therefore made in the smectic-A phase at $T_{NA}-T\sim 3\,^{\circ}$C. The signal was found to be considerably nosier than in the nematic phase and a data collection time of 4 h was required to ascertain the existence of a rapid decay. The amplitude $G_{xy}^{\rm obs}(q_y,0)$ of the observed fast decay was reduced to approximately 40% of its value in the nematic phase, in addition to its considerably larger noise. Likewise, the relaxation time was approximately 3^{+2}_{-1} μs, faster than in the nematic phase. Additionally we note that the slow twist decay disappeared completely into the noise. In the smectic-A phase the amplitude of the mode involving a combination of twist and tilt with respect to the layer normal is expected to be quite small, as is its relaxation time τ_t. If τ_t were to become sufficiently small so that it is comparable to $\tau_{\rm fast}$, the amplitude of this mode would need to be reduced by a factor of order 30. In consequence, it would be much smaller in amplitude than the fast mode (cf. Fig. 3 for the nematic phase) and the observed fast mode would correspond largely to biaxial fluctuations.

In an attempt to understand these results we have first considered fluctuations that would be expected if we assume that 8CB can be described by a simple Landau–de Gennes theory in terms of a single tensor order parameter, e.g., the expectation value of the long axis of 8CB. This seems reasonable given the rather simple structure of the molecule. Although 8CB does not have a uniaxial-biaxial phase transition, it is plausible that the biaxial fluctuations may play an important role in the scattered signal. Consider the order parameter tensor $\overleftrightarrow{Q}(\vec{r})$in Eq. (1). The Landau free energy includes both

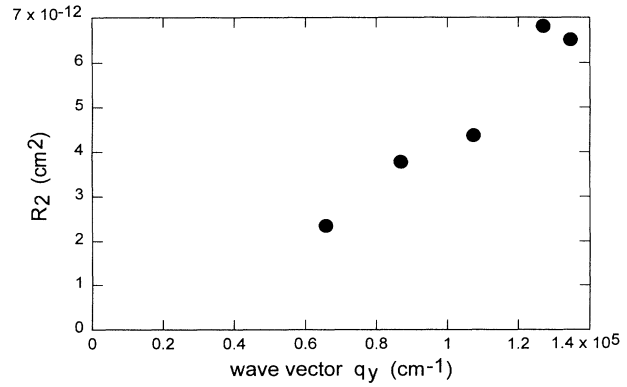

FIG. 8. The quantity $R_2 \equiv G_{xy}^{\rm obs}(q_y,0)\tan^2\theta_f / q_y^2 G_t^{\rm obs}(q_y,0)$ vs q_y at $T=37.1\,^{\circ}$C.

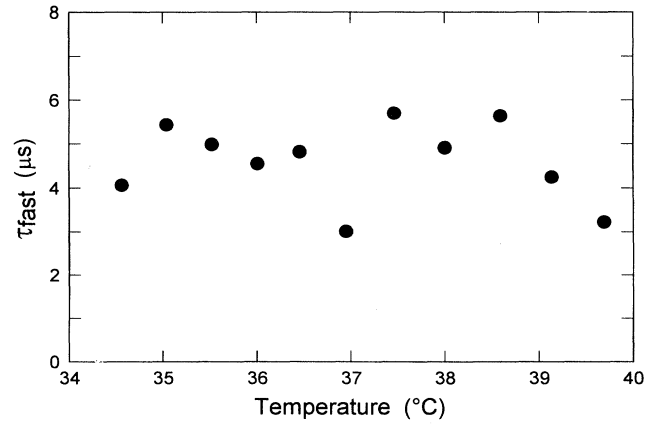

FIG. 10. $\tau_{\rm fast}$ vs temperature at a fixed *external* angle of incidence of 25°.

bulk and elastic terms, viz., $F=F_{\text{bulk}}+F_{\text{elastic}}$, where

$$F_{\text{bulk}}=\int d\vec{r}[\,AQ_{\alpha\beta}Q_{\beta\alpha}+BQ_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha}+C(Q_{\alpha\beta}Q_{\beta\alpha})^2] \tag{2}$$

(repeated indices are assumed) and

$$F_{\text{elastic}}=\int d\vec{r}\frac{1}{2}\{\bar{K}\nabla_\alpha n_\beta\nabla_\alpha n_\beta+L\nabla_\alpha Q'_{\alpha\beta}\nabla_\gamma Q'_{\gamma\beta} +LQ(\nabla_\alpha n_\beta\nabla_\alpha n_\gamma)Q'_{\beta\gamma}\}\ , \tag{3}$$

where the first two terms account for the elastic energy associated with director fluctuations and biaxial fluctuations (in the one elastic constant approximation $\bar{K}\sim LQ^2$) and the last term describes the coupling between the two types of fluctuations. It is known that the cholesteric phase enhances the biaxiality [20–22]; although small, it has been measured experimentally [23]. Theoretically it has been shown that the biaxial fluctuations induced by the twist in a cholesteric are reasonably well described by using the twist-biaxial coupling term as a source and using the susceptibility for biaxial fluctuations derived from this free energy. We therefore intend to keep the last term in the free energy to include possible twist or bend fluctuation-induced biaxial fluctuations.

For convenience, we express $\hat{n}(\vec{r})$ and $Q'(\vec{r})$ in terms of their Fourier transforms. Substituting the Fourier transformed order parameter [Eq. (1)] into Eqs. (2) and (3), the total free energy can be written as $F=F_0+F_{2,Q'}+F_{2,n}+F_{\text{coupl}}$, where $F_{2,Q'}$ and $F_{2,n}$ are the free energies of second order in $Q'(\vec{q})$ [i.e., $Q'_{xx}(\vec{q})$ or $Q'_{xy}(\vec{q})$] and $\hat{n}_i(\vec{q})$, and F_{coupl} includes the coupling terms:

$$F_0=\Omega(\tfrac{2}{3}AQ^2+\tfrac{2}{9}BQ^3+\tfrac{4}{9}CQ^4)\ , \tag{4}$$

$$F_{2,Q'}=2\Omega^{-1}\sum_{\vec{q}}\{(A-BQ+\tfrac{4}{3}CQ^2+\tfrac{1}{4}Lq^2) \times[|Q'_{xx}(\vec{q})|^2+|Q'_{xy}(\vec{q})|^2]\}\ , \tag{5}$$

$$F_{2,n}=\tfrac{1}{2}\Omega^{-1}\bar{K}\sum_{\vec{q}}q^2[n_x(\vec{q})|^2+|n_y(\vec{q})|^2]\ , \tag{6}$$

and

$$F_{\text{coupl}}=-\frac{LQ}{2\Omega^2}\sum_{\vec{q},\vec{q}_1}q^2n_x(\vec{q}_1)n_y(\vec{q}-\vec{q}_1)Q'_{xy}(-\vec{q})+\cdots\ , \tag{7}$$

where we have used the one elastic constant approximation and Ω is the bulk volume. More complicated expressions for the elastic energy do not alter the following discussion in any significant way. Finally, note that these equations apply to the general wave vector $\vec{q}$; later we shall examine our result for $\vec{q}=q_y\hat{y}$.

From Eq. (4) we find that at equilibrium $A(T)=-BQ(T)/2-4C[Q(T)]^2/3$. Within the Gaussian approximation, and by using Eq. (5) and the partition theorem, it is straightforward to obtain

$$\langle|Q'_{xx}(\vec{q})|^2\rangle_0=\langle|Q'_{xy}(\vec{q})|^2\rangle_0=\frac{\Omega k_BT}{-3BQ(T)+Lq^2}\ . \tag{8}$$

Note that the scalar order parameter Q is temperature dependent. In the above equation $\langle\ \rangle_0$ represents the thermal average within the Gaussian approximation and k_B is Boltzmann's constant. The relaxation of the biaxial mode can be described by

$$\langle Q'(\vec{q},\tau)Q'(-\vec{q},0)\rangle_0=\langle|Q'(\vec{q})|^2\rangle_0\exp(-\tau/\tau_b)\ , \tag{9}$$

where the relaxation time τ_b is

$$\tau_b=\eta_b/[-3BQ(T)+Lq^2] \tag{10}$$

and η_b is the viscosity associated with the biaxial fluctuation mode. Also, using Eq. (6), we find for the twist fluctuations

$$\langle|n_i(\vec{q})|^2\rangle_0=\frac{\Omega k_BT}{\bar{K}q^2} \tag{11}$$

and

$$\langle|n_i(\vec{q},\tau)n_i(\vec{q},0)|\rangle_0=\langle|n_i(\vec{q})|^2\rangle\exp(-\bar{K}q^2\tau/\bar{\eta})\ , \tag{12}$$

where i corresponds to either x or y. For $\vec{q}=q_y$, $\tau_t=\bar{\eta}/\bar{K}q^2$.

For the depolarized light scattering geometry shown in Fig. 1 the observed correlation function is given by

$$\begin{aligned}G^{\text{obs}}(q_y,\tau)&=\cos^2\theta_f\langle|Q'_{xy}(\vec{q}_y,\tau)Q'_{xy}(-\vec{q}_y,0)|\rangle+Q^2\cos^2\theta_f\langle|n_{xy}(q_y,\tau)n_{xy}(-q_y,0)|\rangle+Q^2\sin^2\theta_f\langle|n_x(q_y,\tau)n_x(-q_y,0)|\rangle\\&=\cos^2\theta_f[G_b(q_y,\tau)+G_h(q_y,\tau)]+\sin^2\theta_fG_i(q_y,\tau)\\&=\cos^2\theta_fG_{xy}(q_y,\tau)+\sin^2\theta_fG_t(q_y,\tau)\ ,\end{aligned} \tag{13}$$

where $n_{xy}(\vec{q})$ is the Fourier transform of $n_x(\vec{r})n_y(\vec{r})$

$$n_{xy}(\vec{q})=\Omega^{-1}\sum_{\vec{q}_1}n_x(\vec{q}_1)n_y(\vec{q}-\vec{q}_1)\ . \tag{14}$$

We have also defined the labels G_b, G_h, and G_t to be the correlation functions due to biaxial fluctuations, higher-order director fluctuations, and twist fluctuations, respectively.

The higher-order director fluctuation term $|n_{xy}(\vec{q})|^2$ comes from combined bend, twist, and splay effects. Using Eqs. (11) and (12), after some algebra we find

$$\langle |n_{xy}(\vec{q})|^2\rangle_0=\Omega^{-2}\sum_{\vec{q}}\langle |n_x(\vec{q}_1)|^2\rangle\langle |n_y(\vec{q}-\vec{q}_1)|^2\rangle$$
$$=\frac{\Omega k_B^2 T^2}{8\bar{K}^2 q} \tag{15}$$

and

$$\langle n_{xy}(\vec{q},\tau)n_{xy}(-\vec{q},0)\rangle_0$$
$$=\frac{\Omega k_B^2 T^2}{(2\pi)^2\bar{K}^2 q}\int_0^{2\tau_t} d\tau' g(\tau')\exp(-\tau/\tau') , \tag{16}$$

where

$$g(\tau')=\frac{1}{\tau'}\ln\left[\frac{\sqrt{\bar{K}q^2\tau'/\bar{\eta}}+\sqrt{2-\bar{K}q^2\tau'/\bar{\eta}}}{\sqrt{\bar{K}q^2\tau'/\bar{\eta}}-\sqrt{2-\bar{K}q^2\tau'/\bar{\eta}}}\right] . \tag{17}$$

Notice that the integral $I\equiv\int_0^{2\tau_t} d\tau' g(\tau')\exp(-\tau/\tau')$ is dimensionless. To account for the coupling term that appears in Eq. (7) of the free energy, we need to go beyond the Gaussian approximation. The standard Dyson equation can be written as

$$\langle |Q'_{xy}(\vec{q})|^2\rangle^{-1}=\langle |Q'_{xy}(\vec{q})|^2\rangle_0^{-1}-\Sigma(\vec{q}) , \tag{18}$$

where, using Eqs. (7), (14), and (15),

$$\Sigma(\vec{q})\propto\frac{\Omega^{-1}L^2Q^2q^3}{8\bar{K}^2} . \tag{19}$$

To compare our model with the experimental results for 8CB, we set the parameters $A=6.3\times10^5(T-T^*)$, $B=-1.08\times10^7$, and $C=6.8\times10^6$ ergs cm^{-3} where T^* is the supercooling limit of the isotropic phase, and $\bar{K}=2.1\times10^{-7}$ dyn [24]. Using these parameters and considering a scattered wave with a wave number in the range 10^5 cm^{-1}, it is easy to see that $|B|$ is about 5000 times larger than $\bar{K}q^2$. Using Eq. (10) and the relationship $\tau_t=\bar{\eta}/\bar{K}q^2$ and assuming the viscosities η_b and $\bar{\eta}$ are about the same, we would expect τ_t/τ_b to be of order 5000. Additionally, Eqs. (8) and (11) suggest that the magnitude of the twist fluctuations is about 5000 times larger than that of the biaxial fluctuations. However, the *observed* ratio of $\tau_t/\tau_{\text{fast}}$ is only about 30 at this wave vector and the magnitude ratio (corrected for polarization rules) is about the same. As both of the observed ratios are considerably smaller than the model calculations, this analysis would seem to exclude the possibility that the fast mode observed in the experiment is from biaxial fluctuations. Also, using the same parameters, we can see that the contribution of the biaxial fluctuation induced by the twist or bend fluctuation $\langle |Q'_{xy}(\vec{q})|^2\rangle_0\Sigma(\vec{q})$ is of order 10^{-6}. This confirms that the biaxial fluctuations are not greatly enhanced over our predictions in the nematic phase. In other words, twist or bend fluctuation-induced biaxial fluctuations are negligible.

With the same material parameters and using Eqs. (11) and (15), we see that at $q_y=10^5$ cm^{-1} the amplitude ratio G_t/G_h is expected to be about 300, still much larger than the value obtained in the experiment. The correlation function $G_h(\vec{q},\tau)$ due to higher-order director fluctuations cannot be fitted with a single exponential relaxation. The Laplace form of the correlation function $G_h(\vec{q},\tau)$ [Eq. (16)] suggests, however, that this mode contributes significantly at short times τ. In Fig. 11 we plot the integral $I=\int_0^{2\tau_t} d\tau' g(\tau')\exp(-\tau/\tau')$. Although there is a slow component to the decay, its amplitude is small and does not add appreciably to G_t. Nevertheless, we point out that the initial decay is quite rapid and thus G_h may contribute to the measured fast relaxation, although it is unlikely to contribute sufficiently to account for the large, *observed* fast amplitude. It should also be noted that G_h may couple to other fast relaxations, although this coupling is likely to be small and would not appreciably change the results.

There are, of course, other potential order parameters in 8CB and the conclusion of the above analysis is that there must be such a mode with a relatively large susceptibility in order for the data reported herein to be explained. The smectic order parameter has a relaxation time that varies rapidly with temperature over the range of this experiment. As the observed fast relaxation time apparently does not vary rapidly with temperature (cf. Fig. 6), smectic fluctuations are not likely to account for the observed behavior. Nevertheless, other relaxations may exist, which may result in light scattering through a coupling to director fluctuations. A fluctuating tensor in the medium, which may arise, e.g., from significant correlations between pairs of cyanobiphenyl molecules [25–27], may be responsible for the observed behavior. The pair tends to have a rather biaxial shape and, potentially, the alignment of such pairs and a bond orientational order may result in unusually large biaxial fluctuations. This is consistent with the large fast decay that we have observed experimentally. Recent theoretical work by Ferrarini *et al.* [17] has indicated that in cyanobiphenyl dimers the conformational equilibrium can give rise to a large molecular biaxiality, yet not large enough to form a biaxial phase. Alternatively, one may also imagine confirmational fluctuations in the 8CB, such that some of the conformations may have significant biaxial character. Clearly, more work is needed to fully understand the ob-

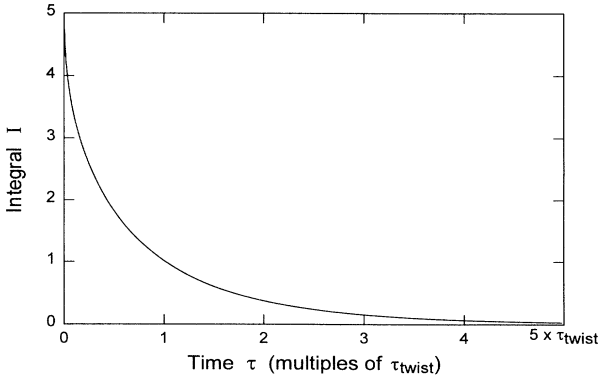

FIG. 11. The integral $I=\int_0^{2\tau} d\tau' g(\tau')\exp(-\tau/\tau')$ vs time τ, in units of the twist relaxation time $\tau_t=\bar{\eta}/\bar{K}q^2$.

served behavior.

In this paper we have reported on a light scattering experiment in the nematic phase in which we observed rapid relaxations in addition to the slower twist relaxation. A Landau–de Gennes model, which includes biaxial and higher-order director fluctuations, was developed in an attempt to explain the results. It was found that these fluctuations are unable to qualitatively account for the observed behavior. Other possible sources of the scattered signal were suggested.

We are grateful to Paul Keyes for useful conversations. This work was supported by the National Science Foundation Advanced Liquid Crystalline Optical Materials Science and Technology Center under Grant No. DMR-8920147.

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