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## Dynamics of the nematic phase of a bent-core liquid crystal

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The dielectric fluctuations in the uniaxial nematic phase of a bent-core liquid crystal have been studied by dynamic light scattering. Polarization selection of the scattering cross-section reveals one mode due to ordinary director fluctuations and, in the lower part of the nematic phase, a second mode attributable to fluctuations of the biaxial order parameter. The director fluctuations are  $\sim 100$  times slower than observed in typical nematics based on straight-core molecules, suggesting that the bent core nematogenic units may be microscopic smectic domains (“cybotactic” clusters).

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In recent years, studies of the thermodynamic assembly of molecules with a bent core has produced a wealth of new liquid crystalline phenomena [1–4]—most notably, the discovery of achiral ferroelectricity in a smectic fluid [1]. The bowl-like shape of these molecules also gives rise to some interesting features for nematic phases, including the possibilities of spontaneous biaxiality and polar order [5,6]. To account for polar ordering of the short axis of the bow, one needs an independent vector order parameter  $\vec{P}$  in addition to the usual, second rank tensor orientational order parameter  $Q_{\alpha\beta}$ . Very recently, it has been pointed out [6] that a third rank tensor is also required to fully characterize the possibilities for orientational ordering of bent-core molecules. Among these possibilities are a number of potentially stable, distinct biaxial phases. Given this theoretical promise, experiments on the structure and properties of bent-core nematics are of great interest.

The present communication describes the results of a dynamic light scattering study of the nematic phase of an achiral bent-core molecule, whose chemical structure (abbreviated 12-CPOB) is shown in Fig. 1 [7] and whose phase sequence is  $I$ -(124.0 °C)- $N$ -(70.7 °C)-smectic- $C$ -(62.0 °C)-crystal. Here  $N$  refers to a nematic phase that, as far as we can presently ascertain [8], has uniaxial symmetry, and smectic  $C$  is a tilted smectic phase which shows no polarization. For *depolarized* scattering, we detect a single hydrodynamic director mode whose relaxation rate is two orders of magnitude lower than the range typically observed at similar temperatures in ordinary nematics composed of rodlike molecules. For *polarized* scattering and in the lower region of the nematic phase ( $T - T_{NS} \leq 14$  °C, where  $T_{NS}$  is the  $N$ -smectic- $C$  transition temperature), we observe an additional mode with a relaxation rate  $\sim 10$  times higher than that of the depolarized fluctuations. Based on an analysis of the dielectric scattering selection rules, we argue that the faster mode arises from fluctuations of the biaxial order parameter. The marked difference in viscoelastic ratio between the bent-core and conventional straight-core nematics leads

us to propose that the nematogenic units in the bent-core case may be “cybotactic” smectic clusters.

Our light scattering experiment was performed on homogeneously aligned, 25  $\mu\text{m}$  thick samples of 12-CPOB. As

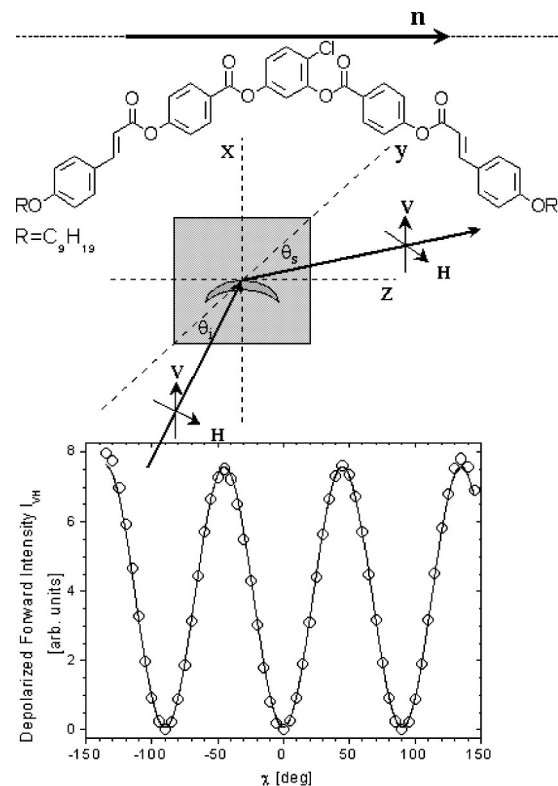


FIG. 1. Top: Molecular structure of 12-CPOB and corresponding optic axis (director)  $\vec{n}$  in the uniaxial nematic phase. Middle: Light scattering geometry. Bottom: Transmission of normally incident laser light through crossed polarizers as a function of the angle  $\chi$  between  $\vec{n}$  and the polarizer axis, taken in the middle of the nematic phase. The solid line is a fit to the  $\sin^2 2\chi$  dependence expected for a uniaxial phase.

Fig. 1 reveals, a single nematic domain [9] was studied; rotation of the sample (angle  $\chi$ ) between crossed polarizers yields the expected behavior of the transmitted intensity,  $I_T = I_0 \sin^2 2\chi$ , for normally incident laser light and for a well-defined optical axis (or director)  $\vec{n}$ . The minimum in  $I_T$  occurs when the cell rubbing direction lies along the polarizer (or analyzer) axis ( $\chi=0,90^\circ$ ) and corresponds to uniform extinction over the optical texture. Since the long molecular axis in thermotropics is known to align along the polyimide rub direction, we conclude that  $\vec{n}$  corresponds to the direction connecting the ends of the bow, as indicated in Fig. 1. Time correlation functions of the scattered intensity of 488 nm light were collected with  $\vec{n} \equiv \hat{z}$  in the scattering plane ( $y-z$ ) and for scattering vectors  $\vec{q}$  in the range  $1.7$  to  $14 \mu\text{m}^{-1}$ . Both the incident ( $i$ ) and scattered ( $s$ ) polarizations could be varied over the four combinations  $(i,s) = (V,H), (V,V), (H,V), (H,H)$ . As indicated in Fig. 1, the labels  $V$  ( $H$ ) refer to vertical (horizontal) to the scattering plane. The incident laser power was kept to a minimum in order to avoid damaging the light sensitive cinnamate linkage in 12-CPOB.

We now review the optical scattering selection rules expected for a uniaxial nematic and include the effect of biaxial fluctuations in the  $x-y$  plane perpendicular to  $\vec{n}$  [10,11]. The uniaxial orientational order parameter is given by the traceless symmetric second rank tensor  $Q_{\alpha\beta}^u = S(n_\alpha n_\beta - \delta_{\alpha\beta}/3)$ , where  $\vec{n} = \hat{z} + \delta n_x \hat{x} + \delta n_y \hat{y}$ ,  $\delta_{\alpha\beta}$  is the Kronecker  $\delta$  function, and the label  $\delta$  otherwise implies a fluctuating quantity. For the biaxial fluctuations, we need to consider only two additional elements [12,13],  $Q_{xx}^b = -Q_{yy}^b \equiv Q_b$  and  $Q_{xy}^b = Q_{yx}^b \equiv Q_b'$ . The relevant quantity for light scattering is the polarization-selected combination  $(i,s)$  of the fluctuating components of the dielectric tensor,  $\delta\epsilon_{is}(\vec{q},t) \equiv i_\alpha \delta\epsilon_{\alpha\beta}(\vec{q},t) s_\beta$ , where  $\delta\epsilon_{\alpha\beta} = \Delta\epsilon_u \delta Q_{\alpha\beta}^u + \Delta\epsilon_b \delta Q_{\alpha\beta}^b$ ,  $\vec{q}$  is the scattering vector,  $\Delta\epsilon_u = \epsilon_3 - (\epsilon_1 + \epsilon_2)/2$ ,  $\Delta\epsilon_b = |\epsilon_2 - \epsilon_1|/2$ , and  $\epsilon_3$  is the largest eigenvalue of  $\epsilon_{\alpha\beta}$ . One then obtains  $\delta\epsilon_{VV} = \Delta\epsilon_b \delta Q_b$ ,  $\delta\epsilon_{V(H)H(V)} = \Delta\epsilon_u \delta n_x \cos \theta_{s(i)} + \Delta\epsilon_b \delta Q_b' \sin \theta_{s(i)}$ , and  $\delta\epsilon_{HH} = \Delta\epsilon_u \delta n_y \sin(\theta_s - \theta_i) - \Delta\epsilon_b \delta Q_b \sin \theta_i \sin \theta_s$ . Here  $\theta_{i(s)}$  are the incident (scattering) angles inside the sample.

The normal modes of the fluctuating variables that contribute to light scattering may be calculated through a Landau-de Gennes expansion of the free energy density  $f$  describing fluctuations of biaxial order in the uniaxial  $N$  phase [11]. In the case of bent-core molecules, we must supplement the standard expansion in  $Q_{\alpha\beta}^b$  and  $\vec{n}$  with terms accounting for the polar and third rank tensor order parameters [5,6]. Neglecting the more exotic effects of the latter, and since we observed that the nematic phase of 12-CPOB is uniaxial [8] and nonpolar (see bottom panel of Fig. 2), we may express  $f$  purely as an expansion in the fluctuations  $\delta Q_{\alpha\beta}^b$ ,  $\delta \vec{P}$ , and gradients of  $\vec{n}$ . Then, because bilinear coupling of  $\vec{n}$  and  $\vec{P}$  is forbidden if the system is achiral [5] and the remaining coupling term  $P_\alpha P_\beta Q_{\alpha\beta}^b$  does not contribute to the part of  $f$  that is quadratic (i.e., lowest order) in the fluctuations,  $f$  may be readily diagonalized to yield a pair of

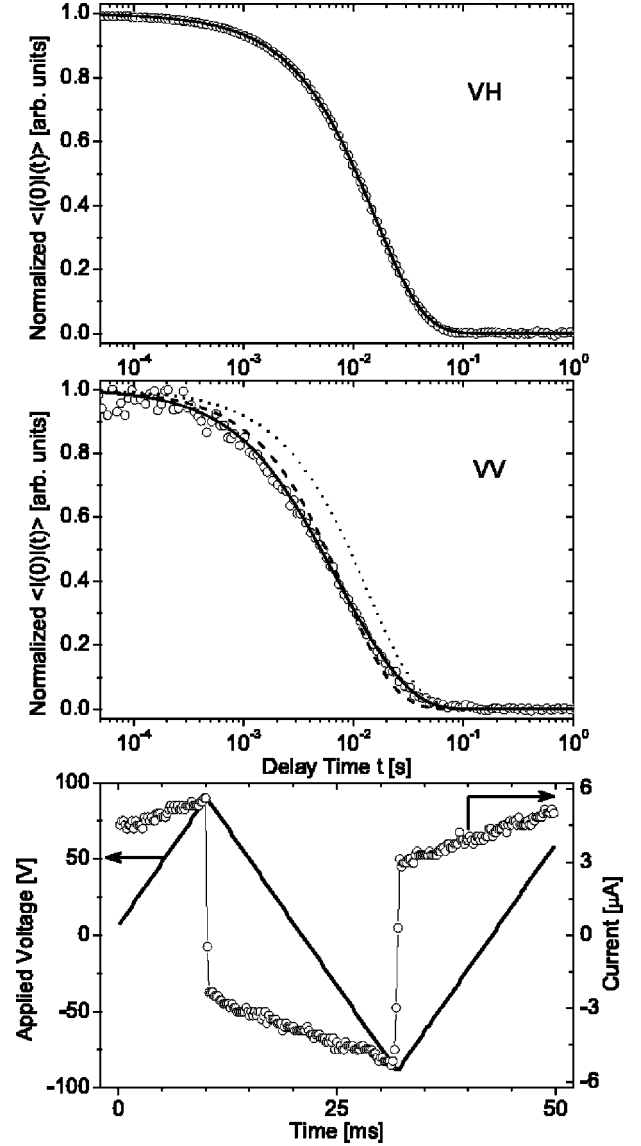


FIG. 2. Top and middle: Intensity-intensity cross correlation functions  $\langle I(0)I(t) \rangle$  recorded in the nematic phase of 12-CPOB at  $T = 77.91^\circ\text{C}$ , with  $q = q_z = 9.1 \mu\text{m}^{-1}$ , and  $\vec{n} = \hat{z}$  in the scattering plane. Data were obtained for  $10^{-8} \leq t \leq 10^3 \text{ s}^{-1}$ , but only the interesting range is shown. Results for depolarized ( $VH$ ) director scattering (top) include fits to a single exponential decay. Those for polarized ( $VV$ ) scattering (bottom) are shown with fits to a double exponential decay (solid line) and to a single decay with the relaxation rate varied freely and fixed to the value of the director mode (dashed and dotted lines). The normalized  $\chi$  squared for the single mode  $VV$  fits is at least three times that for the double mode fit over the range shown. Bottom: Electric current across the sample cell due to an applied triangular voltage, measured at  $72.00^\circ\text{C}$  just above  $T_{NS}$ . Except for the capacitive contribution when the voltage changes sign, the current is purely Ohmic. The noise on the data places an upper bound of  $0.1 \text{ nC/cm}^2$  on the polarization.

doubly degenerate opticlike normal modes ( $\delta Q_b, \delta Q_b'$ ) and ( $\delta P_x, \delta P_y$ ), and a doubly degenerate acousticlike mode ( $\delta n_x, \delta n_y$ ). Below we will focus on  $\delta Q_{\alpha\beta}^b$  and  $\delta \vec{n}$ , as these correspond to the fluctuations coupling to light.

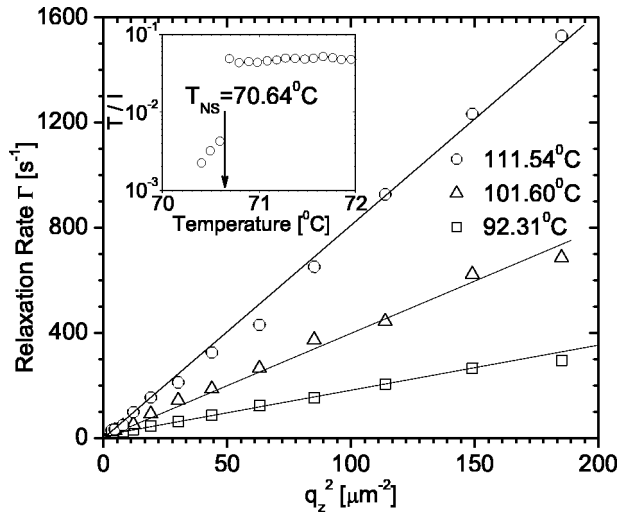


FIG. 3. Dispersion of the director mode measured for  $VH$  scattering. Solid lines are fits to the expected hydrodynamic  $q^2$  dependence. Inset: Behavior of  $T/I$  ( $I$  = scattered intensity) near the transition to the smectic phase for  $VH$  scattering.

In the uniaxial phase, well away from a transition to a biaxial phase and for small  $q$ , one expects that the mean square amplitude of the biaxial order parameter fluctuations should be much smaller (and the relaxation rate significantly higher) than that of the director fluctuations—i.e.,  $\langle |\delta Q_{\alpha\beta}^b|^2 \rangle \ll \langle |\delta \vec{n}|^2 \rangle$ . This combined with the expectation that  $\Delta \epsilon_b^2 \ll \Delta \epsilon_u^2$  [14] means that the contribution to the scattering cross-section  $\sigma \sim \langle |\delta \epsilon_{is}|^2 \rangle$  due to the biaxial fluctuations is likely to be much less than that for the director fluctuations. Consequently, the foregoing analysis of  $\delta \epsilon_{is}$  leads us to conclude that the  $VH$ ,  $HV$ , and  $HH$  scattering should

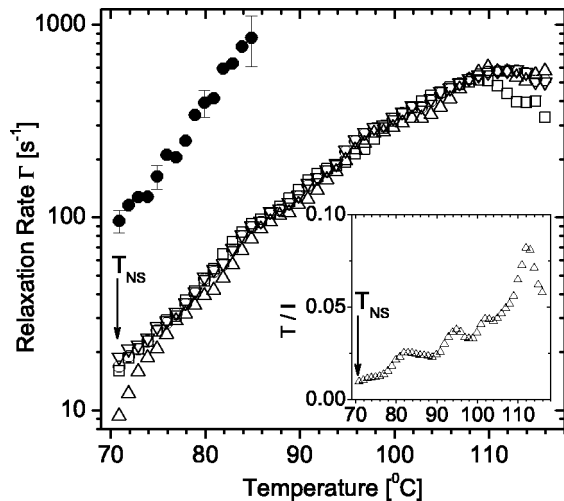


FIG. 4. Temperature dependence of the relaxation rates  $\Gamma$  of the fluctuation modes detected in the nematic phase of 12-CPOB for  $q_z = 9.1 \mu\text{m}^{-1}$ . Open triangles, inverted triangles, squares, and circles correspond to  $\Gamma$  for the director modes measured for  $VH$ ,  $HV$ ,  $HH$ , and  $VV$  scattering, respectively. Filled circles correspond to the mode assigned to biaxial order parameter fluctuations and detected for  $VV$  scattering.

be dominated by the director modes, whereas faster modes due to biaxial fluctuations should appear in the  $VV$  scattering.

This is essentially what we observe in the nematic phase of 12-CPOB. Let us first consider the depolarized and  $HH$  spectra. Throughout the nematic phase, as shown in Fig. 2 for the  $VH$  case, the correlation data are well described by a single overdamped mode; similar results were obtained for  $HV$  and  $HH$  scattering. Figure 3 reveals that this mode is acousticlike, with  $\Gamma \sim q^2$ , as expected for acousticlike director fluctuations. (In our  $VH$  experiment,  $q^2 \approx q_z^2$  and  $q_y^2 \ll q_z^2$  with  $\hat{y}$  being the direction for normal incidence.) Figure 4 shows that the relaxation rates of the director fluctuations observed for the three scattering processes (with  $\vec{n}$  in the scattering plane and fixed  $q$ ) are approximately the same over the major part of the nematic range. We additionally find that  $\Gamma$  is changed only by a factor of 2 when the sample is rotated so that  $\vec{n}$  is normal to the scattering plane. The striking fact, however, is that the relaxation rate of the director modes in the bent-core material is roughly two orders of magnitude lower than the corresponding rate observed in typical straight-core nematics—e.g.,  $\sim 10^1 - 10^2 \text{ s}^{-1}$  versus  $\sim 10^3 - 10^4 \text{ s}^{-1}$ —at optical wave vectors and similar temperatures.

For the case of  $VV$  scattering, a single mode fit is no longer adequate to describe the low temperature correlation data (Fig. 2). Since the sample conditions are exactly the same as for the other scattering processes, we conclude that a mode distinct from the director fluctuations contributes in the  $VV$  case. According to our analysis above, we do expect an independent mode to appear in this case—namely, biaxial order parameter fluctuations—but a strict interpretation of the polarization selection rules predicts *only* this mode. To justify an analysis with *two* modes, which are required for an accurate fit to the data (solid line in Fig. 2), we propose that if the biaxial scattering is intrinsically much weaker than the uniaxial (director) scattering (as remarked above), a small leakage of the latter into the  $VV$  channel could have a significant impact. The leakage could be due to imperfect alignment of the polarizers with respect to each other or to the average director, and (or) due to a slight mosaicity in the director alignment in the cell. Based on this effect, we fit the  $VV$  data to a double exponential decay, with  $\Gamma$  for the slower mode fixed to the amplitude-weighted average of the values obtained for the director mode in the  $VH$  and  $HV$  scattering geometries. For temperatures below about  $85^\circ\text{C}$ , the result is a reasonably well-determined value of  $\Gamma$  for the faster mode, which according to the selection rules must be attributed to biaxial fluctuations.

The relaxation rates are plotted in Fig. 4 as a function of temperature for all four polarization combinations. The values for both the uniaxial and biaxial modes decrease continuously with temperature over the ranges that they are observable. We also find that the relative amplitude of the biaxial mode in  $VV$  scattering increases from  $\sim 10\%$  at  $85^\circ\text{C}$  to  $\sim 50\%$  at about  $1^\circ\text{C}$  above the transition to the smectic- $C$  phase. In the insets to Figs. 3 and 4, we plot the temperature dependence of the inverse scattered intensity  $T/I$  measured

in a scattering geometry corresponding to nearly pure elastic bend fluctuations. As indicated by the inset to Fig. 3,  $T/I$  exhibits no anomalous pretransitional behavior in the immediate vicinity of the  $N$ -smectic- $C$  transition, but instead shows a gradual decrease—with a superposed oscillatory behavior—over the full nematic range (Fig. 4). These features differ from the available results on straight-core thermotropics [15], where nematic bend fluctuations generally harden—and  $T/I$  increases—at the  $N$ -smectic- $C$  transition according to  $T/I \sim K_3 \sim (T - T^*)^{-\nu_3}$  [16]. (Here  $T^*$  is an apparent critical temperature, since the  $N$ -smectic- $C$  transition is typically weakly first order, and  $\nu_3 \approx 1$  [15].)

To explain the temperature dependence of  $T/I$  and the relaxation rates  $\Gamma$  observed in the present study, let us then consider the possibility that the nematogenic units in our bent-core system consist of microscopic smectic- $C$  domains—i.e., a nematic based on the so-called smectic “cybotactic” clusters [17]. Relative to straight cores, close packing of orientationally ordered bent-core molecules would tend to favor smectic layering on short length scales. The surface area of the clusters would be significantly greater than for a single molecule, leading to larger rotational viscosities and correspondingly slower orientational fluctua-

tions. A continuous increase in mean cluster size plus an activated viscosity would account for the increase in  $T/I$  and decrease in  $\Gamma$  with decreasing  $T$ . On the other hand, the observed oscillations in  $T/I$  may indicate a degree of metastability in cluster size (shape) that could, through form birefringence of the clusters, cause variations in  $(\Delta\epsilon)^2$  to be superposed on a smooth change in  $T/I$  with decreasing  $T$ . In fact, we find that on different scans the oscillations are not generally reproducible at the same temperatures.

To conclude, we have performed a dynamic light scattering study of a bent-core nematic phase. By exploiting the polarization selection rules of the scattering, we detected separate modes attributable to uniaxial (director) fluctuations and, in the lower part of the nematic phase, to fluctuations of the biaxial order parameter. The viscosity to elasticity ratio for the director mode is anomalously large compared to typical straight-core nematics. Combined with other features of the scattering, this result could indicate that the nematogens in the bent core system are cybotactic groups (i.e., microscopic smectic domains).

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