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Dynamic Light Scattering Study of Biaxial Ordering in a Thermotropic Liquid Crystal

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Dynamic light scattering from orientational order fluctuations in a liquid crystalline tetrapode reveals successive, weakly first-order isotropic to uniaxial and uniaxial to biaxial nematic phase transitions. The order parameter relaxation rates exhibit temperature dependences consistent with Landau–de Gennes mean field theory. Combined with previous evidence of a second-order uniaxial-biaxial transition in a closely related tetrapode, the present study supports the existence of a nematic-nematic tricritical point in thermotropic liquid crystals.

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Yu and Saupe [1] discovered a biaxial nematic phase in lyotropic liquid crystals over 25 years ago. However, only in the past two years—and following several earlier approaches that generated ambiguous results [2–5]—has a positive experimental consensus emerged on biaxiality in low molecular weight (nonpolymeric) thermotropic nematics. Evidence has come from various researchers employing a panoply of techniques, including polarizing microscopy [6–8], infrared absorbance [6], x-ray scattering [7], and deuterium NMR [8,9], all focused on two relatively new classes of thermotropic compounds—bent-core nematics [7,10,11] and organosiloxane tetrapodes [12,13]. The tetrapodes feature four identical mesogenic groups laterally attached through siloxane chains to a Si or Ge core (Fig. 1) [6]. Hindrance of molecular rotations due to the mesogen-core linkages, or to interdigitation of mesogens connected to different cores, is expected to favor biaxial order [13].

Based on data published so far on both bent-core compounds and tetrapodes, the uniaxial to biaxial nematic ($N_u - N_b$) transition appears to be second order, in agreement with Landau theory in which the free energy is expanded in terms of invariants formed from the tensor order parameter for orientational order [14,15], and the coefficient of the fourth order invariant is positive, while the fifth order coefficient is small. However, under other conditions such as the fourth order coefficient being negative, the Landau theory predicts the interesting possibility of lines of second-order and first-order $N_u - N_b$ transitions joined at a tricritical point (TCP). A recent microscopic mean field theory [16,17] also predicts the same behavior. In fact, by scaling the reduced isotropic to nematic ($I - N_u$) transition temperatures of two closely related tetrapodes to a specific prediction of the mean field theory, Merkel *et al.* [6] argued that the $N_u - N_b$ transitions of these compounds should lie on either side of the TCP. Experimental reports to date have focused almost exclusively on the “second-order” compound.

In this Letter, we present a dynamic light scattering study of the fluctuations in orientational order in an organosiloxane tetrapode, differing only by a substitution of core atoms (Ge for Si) from the proposed “first-order” $N_u - N_b$ compound. We detect distinct relaxational modes associated with the uniaxial and biaxial order parameters, and find both $I - N_u$ and $N_u - N_b$ transitions to be weakly first order. The biaxial mode, in particular, slows down with temperature through the uniaxial phase, until the linear decrease in its relaxation rate is cut off by the transition to the biaxial phase at a temperature (T_{ub}) above the supercooling limit of the uniaxial phase. On the low temperature side ($T < T_{ub}$), the scattered intensity due to fluctuations of the optic axis associated with the biaxiality (biaxial director) increases linearly with decreasing T . The

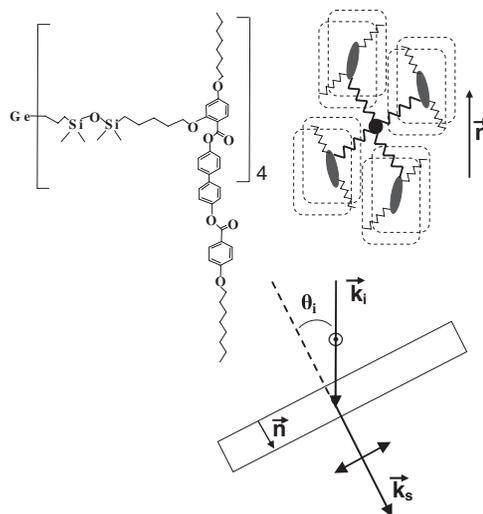


FIG. 1. Chemical structure of the tetrapode studied and “cartoon” of a molecule in the nematic phase. Dashed rectangles suggest a possible biaxial configuration. Lower right: scattering geometry for which uniaxial director (\vec{n}) fluctuations are dark and biaxial order parameter fluctuations revealed.

linear pretransitional temperature dependence of measured parameters associated with the biaxiality is explained by a Landau–de Gennes theory of the $I - N_u - N_b$ sequence of transitions. Combined with the previously published experimental data [6,9] on the “second-order” $N_u - N_b$ compound, our results point to the novel prospect of experimental investigation of a nematic-nematic TCP in tetrapode mixtures.

The Ge-core tetrapode used in our study (Fig. 1) has the following transition sequence (observed on cooling): I -(133.4)- N_u -(132.9)- N_b -(62.3 °C)-smectic- C , essentially the same as observed in the Si-core analogue. Optical conoscopy on the latter clearly indicates biaxiality in the lower temperature nematic phase [6]. For light scattering, our sample was contained in a 10 μm gap between parallel glass substrates, whose inner surfaces were specially treated to induce high quality alignment of the uniaxial director \vec{n} normal to the substrates. (The direction of \vec{n} corresponds to the average long axis of the mesogens in Fig. 1.) This facilitates a depolarized scattering geometry that isolates fluctuations in the magnitude of the biaxial order parameter (P) in the N_u phase, where ordinarily \vec{n} director scattering would be overwhelming. In fact, for the geometry used (Fig. 1), the cross section due to \vec{n} scattering is calculated to vanish [18]. However, owing to slight mosaicity in \vec{n} or optical misalignment, \vec{n} fluctuations cannot be expected to be completely “dark” in the actual experiment, but should be reduced in intensity sufficiently to reveal faster, much more weakly scattering fluctuations in P . The quantities measured in our experiment are the average scattered intensity \bar{I} and the time correlation function $\langle I(0)I(\tau) \rangle$. To determine the dispersion of the fluctuation modes detected, the scattering vector $\vec{q} = \vec{k}_s - \vec{k}_i$ was varied in the dark uniaxial geometry by varying \vec{k}_i (i.e., varying incident angle θ_i), while keeping $\vec{k}_s \parallel \vec{n}$ (scattering angle $\theta_s = 0^\circ$). For temperature (T) scans, θ_i was fixed at 10° (again with $\theta_s = 0^\circ$).

Figure 2 shows experimental correlation functions (wiggly gray lines) recorded in the I , N_u , and N_b phases. In the I phase (upper panel of the figure), the smooth black lines are fits to a single exponential decay that corresponds to fluctuations in the magnitude of the uniaxial order parameter (S). These slow down on approach to the $I - N_u$ transition (T_{IN}), as is typically observed in thermotropics [14,19]. However, the relaxation rate is in the 10^4 – 10^5 s^{-1} range, one to two orders of magnitude lower than for classic, calamitic (rodlike) thermotropics. In the uniaxial phase (lower panel of Fig. 2), the correlation data contain two relaxational modes—a fast relaxation ($\Gamma \sim 10^3$ – 10^4 s^{-1}) and a much slower process ($\Gamma \sim 10$ s^{-1}). As will be confirmed below, the fast mode can be assigned to biaxial order parameter (P) fluctuations, whereas the slow process arises from the anticipated “leakage” of the intrinsically strong uniaxial director scattering. The correlation functions in the N_u phase are well fitted with a double exponential decay (smooth black lines in the figure), with a

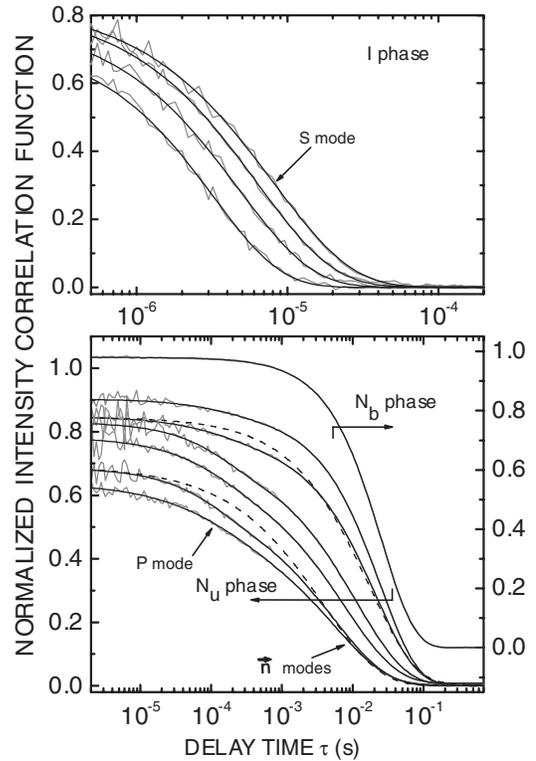


FIG. 2. Representative data (wiggly gray lines) for intensity correlation functions taken with $q = 17300 \text{ cm}^{-1}$ in the isotropic (top panel, 135.20, 134.60, 134.10, 133.70 °C, left to right) and nematic phases (bottom panel, 133.15, 133.06, 132.99, 132.96, 132.94, 132.92, 132.80 °C, left to right) of the tetrapode in Fig. 1. Smooth solid and dashed black lines: fits to exponential decays as described in the text.

small amount of stretching on the slow decay allowed to account for two closely spaced \vec{n} modes (corresponding to nearly pure splay and twist fluctuations of \vec{n}). The average stretching exponent is 0.80 (with uncertainty ± 0.04). To demonstrate the presence of distinct fast and slow relaxation processes, we also present examples of single mode fits to the N_u phase data in Fig. 2, which are shown as dashed lines; these fits are clearly inadequate. At lower temperatures, the scattering dramatically intensifies due to the onset of the N_b phase and the contribution of biaxial director (\vec{m}) fluctuations, which are not dark since \vec{m} is perpendicular to \vec{n} , lies in the substrate plane, and consequently $\vec{m} \perp \vec{k}_s$. The corresponding correlation data are described well by an almost pure single exponential fit (average stretching exponent = $0.99 \approx 1$).

In order to confirm the identity of the fast and slow modes observed in the N_u phase, we performed a q scan in the dark geometry at 133.0 °C. Figure 3 displays the results. The main figure shows the slow mode to be hydrodynamic ($\Gamma \sim q^2$), as expected for director fluctuations. Here $q^2 \approx q_x^2$ as the component q_z along the average director \vec{n} was always very small. The value of Γ essentially represents an average relaxation of splay and twist distortions in \vec{n} . The slope of the linear fit to the data in Fig. 3 gives an orientational elasticity to viscosity ratio of

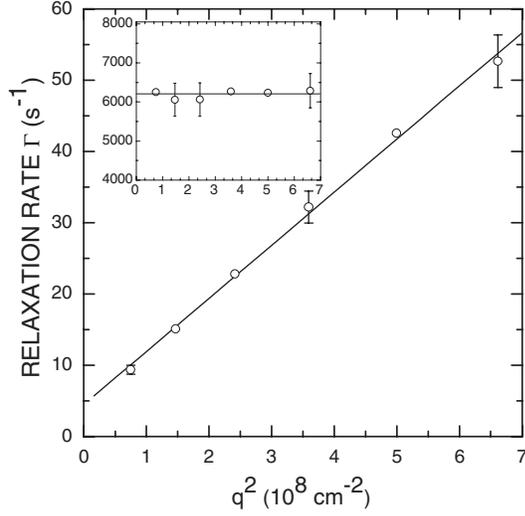


FIG. 3. Dispersion of the fluctuation modes observed at 133.0 °C in the uniaxial nematic phase. Main figure: hydrodynamic uniaxial director (\vec{n}) modes (detected as “leakage” for the scattering geometry pictured in Fig. 1). Inset: nonhydrodynamic biaxial order parameter (P) mode (axes’ labels are same as main figure).

$7.9 \times 10^{-8} \text{ s}^{-1} \text{ cm}^2$ in the tetrapode, roughly 100 times lower than in conventional calamitic nematics. The low value of this ratio suggests large orientational viscosities, which could result from the siloxane linkages of the mesogens to the core and/or the interdigitation of the mesogenic groups attached to neighboring cores. The data in the inset to Fig. 3 clearly demonstrate that the fast mode is nonhydrodynamic (Γ essentially independent of q), as anticipated for the dynamics of an orientational order parameter in the standard phenomenological description [14, 18, 19]. In as much as this mode is observed throughout the N_u phase (and is quite distinct from the ~ 10 times faster S order parameter fluctuations detected in the I phase), we can assign it to fluctuations in the biaxial order parameter P [18].

We explored the critical behavior of order parameter fluctuations by carrying out temperature scans through the $I - N_u$ and $N_u - N_b$ transitions for $\theta_i = 10^\circ$ and $\theta_s = 0^\circ$. The most significant results, presented in Fig. 4, can be discussed in terms of a Landau–de Gennes expansion of the orientational free energy. Recent experiments on tetrapodes [6, 9], as well as theoretical investigations [16, 17] based on microscopic mean field theory of the phase diagram in the vicinity of the $I - N_u - N_b$ triple point, clearly show the importance of including terms up to sixth order in the order parameters S and P . Expanding out the usual form [14] for F (which is given in terms of two invariants of the full tensor order parameter), one has

$$F = \alpha(S) + \beta(S)P^2 + \gamma(S)P^4 + \delta(S)P^6,$$

$$\text{where } \alpha(S) = \frac{3a}{4}S^2 + \frac{b}{4}S^3 + \frac{9c}{16}S^4 + \frac{9d}{40}S^5 + \left(\frac{9e'}{16} + \frac{3e}{32}\right)S^6, \\ \beta(S) = \frac{a}{4} - \frac{b}{4}S + \frac{3c}{8}S^2 - \frac{3d}{20}S^3 + \left(\frac{9e'}{16} - \frac{3e}{16}\right)S^4, \quad \gamma(S) =$$

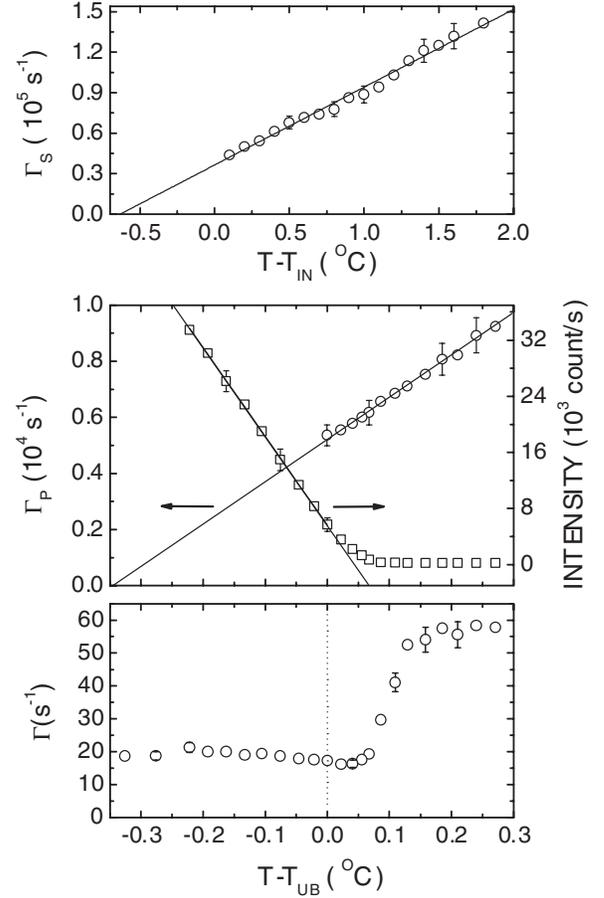


FIG. 4. Temperature dependence of the relaxation rate (Γ) of the uniaxial order parameter (S) mode in the isotropic phase (top panel), of Γ for biaxial order parameter (P) fluctuations (\circ) in the uniaxial phase and the total scattered intensity (\square) in the biaxial phase (middle panel), and of Γ for the director modes in the uniaxial and biaxial phases (bottom panel). $\theta_i = 10^\circ$, $\theta_s = 0^\circ$ in all cases.

$\frac{c}{16} - \frac{3d}{40}S + \left(\frac{3e'}{16} + \frac{3e}{32}\right)S^2$, and $\delta(S) = \frac{e'}{48}$. Except for $a = a_0(T - T^*)$, all expansion coefficients are assumed to be independent of T . In the isotropic phase, where $S = \delta S$ and $P = \delta P$ (purely fluctuating quantities), one has up to second order, $\delta F = (a/4)(3\delta S^2 + \delta P^2)$. Assuming $(\Delta\epsilon_u)^2 \gg (\Delta\epsilon_b)^2$ for the maximum dielectric anisotropies associated with uniaxial and biaxial orientational order, the single mode δS should dominate the scattering in the I phase (in agreement with the single decay observed in Fig. 2, top panel). The standard Landau-Khalatnikov dynamics for δS predict a relaxation rate $\Gamma_S = 3a_0(T - T^*)/2\eta_S$, where η_S is a phenomenological viscosity associated with δS . The linear fit to the data in Fig. 4 (top panel) confirms this prediction and gives $a_0/\eta_S = 3.9 \times 10^4 \text{ s}^{-1} \text{ }^\circ\text{C}^{-1}$ and $T^* = T_{IN} - 0.63 \text{ }^\circ\text{C}$. Thus the $I - N_u$ transition is weakly first order, as is characteristic of most thermotropic liquid crystals [15].

In the N_u phase, the order parameter $S = S_0(T)$ is obtained by minimizing F with $P = 0$. The component of F describing fluctuations in P up to second order is

$\delta F = \beta(S_0)\delta P^2$. Since the N_u phase is quite narrow, our data for Γ_P are taken fairly close to T^* (Fig. 4, middle panel), so that it is reasonable to expand S_0 as $S_0(T) \approx S^{*} + S'^*(T - T^*)$, where $S^* = S_0(T^*) > 0$ and $S'^* = (\partial S_0/\partial T)_{T^*} < 0$. Combining this with δF and the appropriate Landau-Khalatnikov equation for δP , we find $\Gamma_P = 2\beta(S_0)/\eta_P \approx 2[\beta^* + \beta'^*(T - T^*)]/\eta_P$, where $\beta^* = \beta(T^*)$, $\beta'^* = (\partial\beta/\partial T)_{T^*}$, and η_P is a phenomenological viscosity. Thus, Γ_P should be approximately linear in T through the narrow N_u phase. The data for Γ_P (open circles in the middle panel of Fig. 4) indeed show a linear decrease with T , corresponding to a mode that slows down at the $N_u - N_b$ transition. A straight line fit gives a slope of $1.5 \times 10^4 \text{ sec}^{-1} \text{ }^\circ\text{C}^{-1}$ and a zero intercept $\approx 0.35 \text{ }^\circ\text{C}$ below T_{ub} . In the framework of Landau theory, this behavior indicates a first-order $N_u - N_b$ transition: a second-order transition would require $\beta(S_0)|_{T=T_{ub}} = 0$ in the expression for F , yet $\Gamma_P \propto \beta(S_0)$ does not come close experimentally to vanishing at T_{ub} . Another effect of the $S - P$ coupling in F is that the extrapolated zero intercept for Γ_P need not occur at the same temperature (T^*) as that for Γ_S ; we estimate the difference to be $\sim 0.2 \text{ }^\circ\text{C}$ in the tetrapode studied.

Below T_{ub} , the scattering in the dark uniaxial geometry is dominated by fluctuations of the biaxial director \vec{m} . The intensity of this scattering should depend on the magnitude of P as $I_{\vec{m}} \propto (\Delta\epsilon_b)^2 \propto P_0^2$, where the equilibrium $P_0(T)$ is given by the solution to the system of equations $(\partial F/\partial S)_{S_0, P_0} = (\partial F/\partial P)_{S_0, P_0} = 0$. At a first-order transition, one may approximate the temperature dependence of P_0^2 by $P_0^2 \approx P_0^{2ub} + P_0^{2ub}(T_{ub} - T)$, where the superscript ub means evaluated at the transition temperature T_{ub} . Thus, to lowest order, $I_{\vec{m}}$ should scale linearly with T . Experimentally, we do not expect the measured intensity to vanish at any T , since the finite contribution from fluctuations δP takes over for $T > T_{ub}$. The data for \bar{I} in the biaxial phase (Fig. 4, middle panel) confirm these predictions; in particular, for T below but close to T_{ub} , \bar{I} increases linearly with decreasing T . Additionally, we find that the relaxation rate for director fluctuations (Fig. 4, bottom panel) decreases as $T \rightarrow T_{ub}$ from above, and remains approximately constant below T_{ub} , indicating a pretransitional increase in the viscosity for director motion yet comparable relaxation rates for director fluctuations in the N_u and N_b phases. Since splay, twist, and bend of \vec{n} are all allowed in the N_b phase, pretransitional effects of biaxial fluctuations on the uniaxial elastic constants are expected to be small. In our dark uniaxial geometry with $q \approx q_x, q_z \approx 0$, only a single director mode corresponding to splay-bend fluctuations of \vec{m} should dominate below T_{ub} ; this is confirmed by the essentially pure exponential relaxation observed and noted in the discussion of Fig. 2 above.

To summarize, our light scattering study strongly supports the existence of a biaxial nematic phase in liquid crystalline tetrapodes, and reveals weakly first-order isotropic-nematic and nematic-nematic transitions in the

material investigated. When combined with other recent experiments on a related tetrapode [6,9], our results suggest that a nematic-nematic tricritical point may be accessible through mixtures of existing compounds.

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