Orientational Fluctuations of a Lyotropic Nematic Liquid Crystal Measured by Quasielastic Light Scattering

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The nematic-isotropic and the nematic-to-lamellar phase changes in the lyotropic liquid crystal formed by decylammonium chloride micelles in a water–ammonium chloride solution have been studied by light scattering. The former transition shows behavior identical to that observed in thermotropic liquid crystals. The nematic-lamellar transition appears closely similar to a thermotropic nematic-smectic-*A* change and the elastic constants diverge according to the analogy to superfluid helium and the three-dimensional *xy* model.

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Lyotropic mesophases are formed by surfactant molecules in a suitable solvent, which is often an aqueous electrolyte. They exhibit a variety of ordered phases depending on temperature and solvent concentration. Many of these phases seem analogous to phases that exist in thermotropic liquid crystals. Lamellar or neat soap phases, for example, are similar to thermotropic smectic-*A* and -*C* phases while the hexagonal or middle soap phases may be analogous to the columnar discotic phase. The first lyotropic phase to orient readily in a magnetic field was described by Lawson and Flautt[1]; Reeves and his colleagues recognized that these phases were lyotropic analogs to nematics and elucidated many of their properties.[2] Although a great deal is known about lyotropic liquid-crystalline order, the exact structure of many phases and the nature of transitions from one phase to another, as well as details of their similarities to, and differences from, thermotropic phases, are relatively unexplored. The nematic lyotropics are formed by the interaction of nonspherical micelles which are designated type I or type II according to whether the diamagnetic anisotropy is greater along or transverse to the nematic symmetry axis.[2] Either type-I or type-II nematics may, in principle, be formed by the orientational ordering of the symmetry axes of either disklike (DM) or rod-like (CM) micellar solutions. The DM nematic phase may also have a second-order transition to a neat soap or lamellar phase which appears closely similar to the thermotropic nematic–smectic-*A* transition. Prior studies[3] strongly suggest that lyotropic and thermotropic nematics have the same symmetry and that the neat soap phases that form from them are similar to thermotropic smectic-*A* phases. Since we believe that the properties of these ordered phases are determined by symmetry and spatial dimensionality, behavior of the lyotropic nematic phases and their analogs should be identical. In particular, breaking the orientational symmetry should result in lyotropic nematic Goldstone modes identical to thermotropic director modes and the behavior of the neat soap (smectic *A*) to nematic as well as the nematic to isotropic phase changes should be identical to those in thermotropic materials. These expectations can be tested by quasielastic light scattering and we report such measurements in this paper. We found the behavior of the lyotropic material we studied, decylammonium chloride micelles in aqueous solution of ammonium chloride, to be essentially identical to that of thermotropic materials.

Decylammonium chloride (DACl) was prepared by neutralizing *n*-decylamine, purchased from Aldrich Chemical Co., in cold diethyl ether with hydrochloric acid. The product was purified by recrystallization from a mixture of ethanol and petroleum ether (1:4) in an ice bath. Mixtures of DACl, NH_4Cl, and distilled deionized water were prepared in concentrations that exhibit lamellar, nematic, and isotropic phases at convenient temperatures. For example, combining 100 g DACl with 9.87 g NH_4Cl in 113.4 g H_2O gave a nematic-isotropic phase change at $T_K = 63$ °C and a lamellar-nematic transition at $T_c = 43$ °C. The samples were mixed by vigorous shaking and sonication.

For light scattering measurements commercial spectrophotometer cells, sealed with epoxy to avoid water evaporation and subsequent drift of the transition temperature, were used. The nematic-isotropic transition was studied in a

cell with 1-mm pathlength while nominal 0.1-mm-path cells were used for nematic-phase director-mode scattering. Surface interactions aligned the nematic director normal to the cell walls. The cells were enclosed in an oven whose temperature was measured by a Hewlett-Packard model 2804A quartz thermometer and controlled to ±1 mK. An argon-ion laser was used as a light source and a digital autocorrelator analyzed the scattered light.

Let us choose a coordinate system in which the director $\vec{n}$ lies along $\hat{z}$ and the scattering wave vector $\vec{q}$ lies in the x-z plane. We observed no scattering with both incident and scattered light polarization along $\hat{y}$; director-mode fluctuations were observed either with both polarization states in the x-z plane or with one along $\hat{y}$ and the other in the x-z plane. These are the same selection rules for scattering from thermotropic nematics. Because the scattered intensity was 10^4 weaker than from thermotropic nematics, laser power up to 100 mW was used. The sample absorbs little light and any sample heating with constant laser power would produce a constant temperature offset. Measurements were made within 25 mK of T_c and the results were reproducible.

To analyze the light scattered from the nematic phase we recall the results for thermotropic nematics.[4] Our scattering geometry was chosen to observe director mode two[4] which causes dielectric-constant fluctuations

$$\langle \delta\epsilon_{yz}^*(\vec{q},0)\,\delta\epsilon_{yz}(\vec{q},\tau)\rangle = \epsilon_a^2\langle n_y^*(\vec{q},0)\,n_y(\vec{q},\tau)\rangle = kT\epsilon_a^2[K_2q_x^2+K_3q_z^2]^{-1}\exp(-\Gamma_2\tau). \quad (1)$$

In (1) $\epsilon_a = \epsilon_{zz} - \epsilon_{xx}$, and K_2 and K_3 are the twist and bend[4] elastic constants. Typically $\epsilon_a \simeq 0.65$ in thermotropics; it is $\simeq 0.0065$ in DACl.[3] From the time decay of the autocorrelation function we measure

$$\Gamma_2(\vec{q}) = [K_2q_x^2+K_3q_z^2]/\eta_2(\vec{q}), \quad (2)$$

where

$$\eta_2(\vec{q}) = \gamma_1 - (\gamma_1 - \eta_b + \eta_c)^2(q_z/2)^2(\eta_a q_x^2 + \eta_c q_z^2)^{-1}$$

and γ_1 is the director twist viscosity. The fluid viscosities for various orientations of $\vec{n}$ and velocity $\vec{v}$ are η_a (with $\vec{n}\perp\vec{v}$, $\vec{n}\perp\nabla v$), η_b (with $\vec{n}\parallel\vec{v}$, $\vec{n}\perp\nabla v$), and η_c (with $\vec{n}\perp\vec{v}$, $\vec{n}\parallel\nabla v$).

Smectic short-range order can be characterized by correlation lengths $\xi_\parallel = \xi_\parallel{}^0 t^{-\nu_\parallel}$ and $\xi_\perp = \xi_\perp{}^0 t^{-\nu_\perp}$ along and transverse to $\vec{n}$, respectively, where $t = (T/T_c - 1)$. This causes a divergence in the bend and twist elastic constants but has no effect on K_1.[5] Dynamical scaling arguments for isotropic critical behavior, $\nu_\parallel = \nu_\perp$, predict[6,7] that a divergent contribution $\bar{\gamma} \sim \xi^{1/2}$ should be added to γ_1 and η_b as a result of the smectic fluctuations. The behavior of the elastic constants has been calculated by Jähnig and Brochard[7]; using their results, we find that the elastic terms in the square brackets of (1) and (2) should have added to them the fluctuation contributions

$$(kTq_0^2/4\pi\xi_\parallel)[(X+X^{-1})\tan^{-1}X - 1], \quad (3)$$

where $X = (\frac{1}{2})[(q_x\xi_\perp)^2 + (q_z\xi_\parallel)^2]^{1/2}$ and q_0 is the wave vector of the smectic density wave. In the hydrodynamic limit $X \to 0$, (3) becomes

$$(kTq_0^2/24\pi)[(\xi_\perp^2/\xi_\parallel)q_x^2 + \xi_\parallel q_z^2]. \quad (4)$$

The divergence of K_3 and a pretransitional increase of γ_1 in the DACl system have been observed by Haven, Armitage, and Saupe[3]; they were unable to determine the critical exponents. Our experiments were carried out at scattering angles corresponding to $q = 2.18\times10^4$ cm^{-1} with $(q_x/q_z)^2 = 10.3$ and to $q = 3.68\times10^4$ cm^{-1} with $(q_x/q_z)^2 = 1.9$. The intensity was obtained from the zero intercept of the autocorrelation function, although the total photomultiplier current gave essentially identical results if a small temperature-independent background was subtracted. The reciprocal of the intensity was well fitted by a single power law $t^{-\nu}$ over the entire temperature range in which we made measurements. Using T_c as an adjustable parameter we found the exponents $\nu = 0.64\pm0.05$ for $(q_x/q_z)^2 = 10.3$ and 0.68 ± 0.05 for $(q_x/q_z)^2 = 1.9$. The data and fits are shown in Fig. 1. These results suggest that, different from the thermotropics,[8] the exponents $\nu_\parallel$ and $\nu_\perp$ are equal within our measurement sensitivity. The reliability of this conclusion depends on the unknown ratio $\xi_\perp/\xi_\parallel$, and direct x-ray measurements would be desirable. We measured $q_0 = 1.6\times10^7$ cm^{-1} by x-ray scattering; a simple calculation assuming $\xi_\parallel{}^0 q_0 \simeq 1.0$ and $\xi_\perp{}^0 q_0 \simeq 0.3$, which are values typical of thermotropics,[8] shows that we should have observed nonhydrodynamic behavior and Eq. (4) should adequately describe our data. Another interesting result is that the intensity followed the power law as high as 11 °C above T_c, indicating that the smectic fluctuation terms still dominate in (1). For thermotropic materials, the

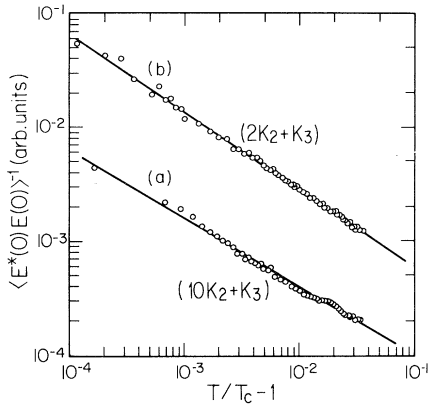

FIG. 1. Inverse of the intensity of light scattered by director-mode–two fluctuations above the nematic to lamellar phase change. Curve (*a*): $(q_x/q_z)^2 = 10.3$, $T_c = 302.79$ K; the solid line has slope 0.64. Curve (*b*): $(q_x/q_z)^2 = 1.9$, $T_c = 306.33$ K; the line has slope 0.68.

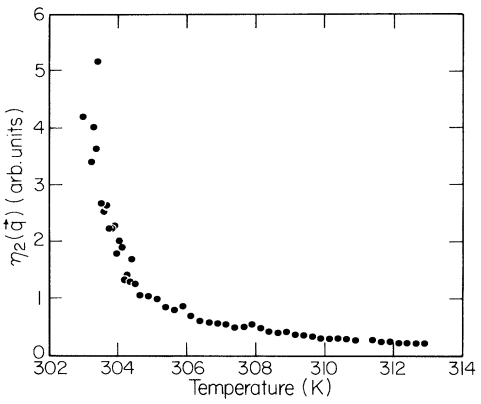

FIG. 2. The viscosity $\eta_2(q)$, Eq. (4), determined for $(q_x/q_z)^2 = 10.3$. The data are scaled to give $\eta_2 = 5$ P at 308 K.

intrinsic nematic constants K_3 and K_2 typically cause deviations from power-law behavior for $T > T_c + 3$ °C.[9]

From the autocorrelation function decay time divided by the intensity we obtain the temperature dependence of the viscosity $\eta_2(\vec{q})$; when $(q_x/q_z)^2 = 10.3$ this is dominated by γ_1. The quantity γ_1/χ_a is reported in Ref. 3 and may be combined with recent measurements[10] of $\chi_a \simeq 2\times10^{-9}$ cgs units to estimate $\gamma_1 \simeq 5$ P and $\partial \ln\gamma_1/\partial(1/T) \simeq 28$ kcal/mole at $T_c + 5$ °C. Our data show $\partial \ln\eta_2/\partial(1/T) \simeq 30$ kcal/mole at $T_c + 5$ °C, which is satisfactory agreement given the experimental uncertainties. Accordingly, in plotting η_2 in Fig. 2, we have scaled the data to give $\eta_2 = 5$ P at $T_c + 5$ °C. Figure 2 shows a divergence of η_2, but the scattered intensity is very small near T_c and the data are too noisy to enable us to determine a critical exponent.

We now discuss the nematic-isotropic transition. In the isotropic phase, light is scattered by fluctuations in short-range nematic order and is typically 10^3 less intense than director-mode scattering. A detailed discussion of nematic short-range order, based upon a model of de Gennes,[4] was given by Stinson, Litster, and Clark.[11] The scattered light is proportional to the susceptibility for the nematic order parameter, and we show its reciprocal in Fig. 3. As in thermotropics, the susceptibility diverges as $(T - T^*)^{-1}$ but a first-order transition intervenes at $T_K = T^* + 0.8$ °C. For a sample with $T_K = 31.46$ °C there was a two-phase coexistence for 0.3 °C below T_K but no observable hysteresis. The time dependence of the correlations was too rapid to measure with our correlator's 100-nsec resolution. Analogous pretransitional behavior has recently been reported[12] in the isotropic phase near a concentration-driven transition of rodlike virus particles.

In summary, we find a thermally driven nematic-isotropic transition in a system of disk micelles which is quite similar to that of thermotropic nematics formed by rodlike molecules. The disk-micelle system of DACl has a lamellar or neat soap phase which is also quite like a thermotropic smectic-*A* and shows the same effect of smectic short-range order on the nematic director modes. We are continuing to study other properties at the nematic-isotropic transition and to use high-resolution x-ray scattering to

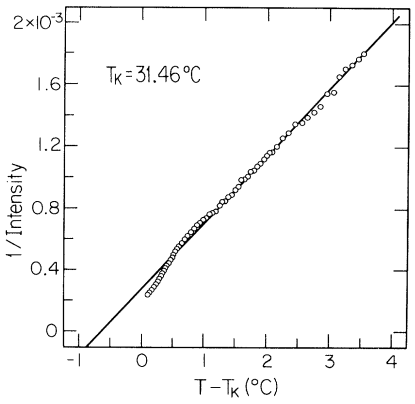

FIG. 3. Reciprocal of the intensity of depolarized light scattered by fluctuations in nematic short-range order in the isotropic phase of a DACl micellar lyotropic nematic.

study the lamellar phase.

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