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Approach to a second-order nematic-isotropic phase transition in a lyotropic liquid crystal

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We report on the results of a magnetic birefringence study of the nematic-isotropic transition in the lyotropic liquid crystal cesium perfluoro-octanoate in water. The transition is weakly first order at T_K with mean-field divergences and a virtual second-order transition temperature that can be within 20 mK of T_K.

The nematic lyotropic phases are formed by orientational long-range ordering of the symmetry axes of nonspherical micelles. A relatively recently discovered liquid-crystal phase,[1] they have attracted the attention of a number of liquid-crystal physicists who seek to understand the statistical mechanics governing their behavior.[2-4] They are also materials interesting to those concerned with the statistical mechanics of surfactants, micelles, and microemulsions.[4]

The micelles may be either disklike (DM) or cylindrical (CM) in their approximate shape, and the uniaxial nematics are classified as type I or type II according to whether the diamagnetic susceptibility is greater along or transverse to the nematic symmetry axis. There are also biaxial micellar nematics.[3] Recently we reported studies of the nematic to isotropic (N-I) transition in a type-II DM material formed by decylammonium chloride in a aqueous solution of NH_4Cl. Pretransitional behavior in the isotopic phase showed[5,6] the classical mean-field divergences expected near a second-order transition at temperature T_c^* preempted by a first-order transition at T_K. The N-I transition is required by symmetry to be first order, at least in a mean-field approximation, and the temperature difference $T_K - T_c^*$ is one way of measuring how strongly first order it is. While $T_K - T_c^*$ is not a universal quantity for all N-I transitions, reported values for all thermotropic nematics as well as the decylammonium chloride lyotropic are of order $(T_K - T_c^*)/T_K \approx 3\times10^{-3}$. It is an interesting puzzle of the N-I transition that the pretransitional divergences are characterized by mean-field exponents but the mean-field value[7] for $(T_K - T_c^*)/T_K$ is 9.2×10^{-2}.

In this article we report measurements of the nematic order produced by a magnetic field applied to the isotropic phase of cesium perfluoro-octonate (CsPFO) micelles in water. This system has type-I DM and neat soap phases[8] without the necessity to add a third compound; also, a stable nematic phase exists over a rather wide range of molar concentration x of CsPFO. Our central result is that $T_K - T_c^*$ depends strongly upon x. We have found that $T_K - T_c^* \simeq 0.6$ K for $x = 0.045$, 0.17 K for $x = 0.034$, 0.035 K for $x = 0.026$, and approximately 0.015 K for $x = 0.020$. These values permit a much closer approach to T_c^* (to reduced temperature $T/T_c^* - 1 \simeq 5\times10^{-5}$) than N-I transitions previously studied. This holds the possibility of learning more about the nature of the N-I transition and the effect of fluctuations on it. We also analyze our data to determine the susceptibility exponent γ and the effect of higher-order terms in the free-energy expansion near T_K.

Samples of CsPFO were prepared by neutralizing perfluoro-octanoic acid with CsOH; the product was filtered through 0.5-μm Teflon (millipore) filter, dried, and recrystallized three times from ethanol at 0 °C. We analyze here the measurements for the sample with $x = 0.026$ with $T_K \simeq 33$ °C. Although $T_K - T_c^*$ is smaller for concentration $x = 0.020$, the lower $T_K \simeq 24$ °C rendered temperature control more difficult; this also prevented our exploration of smaller CsPFO concentrations until the sample oven is redesigned. Samples were placed in a stoppered glass cuvette with 2-mm optical pathlength that was enclosed in a cylindrical oven. The oven could be inserted in the bore of a Bitter magnet. The temperature control and birefringence apparatus were closely similar to that described previously,[9] although the sensitivity in Δn was improved to 10^{-8} and compensating voltage to the Pockels cell was controlled by a feedback loop. At each temperature the compensating voltage, proportional to Δn, was plotted as a function of H^2 on an x-y recorder. The field was typically swept from 0 to 105 kG in 2 min. The order-parameter susceptibility χ_s was obtained from the slope of Δn vs H^2 at $H = 0$. Several temperature scans were made and the data were fitted to $\chi_s = \chi_0(T - T_c^*)^{-\gamma}$ with χ_0, T_c^*, and γ as adjustable parameters. We obtained $\gamma = 1.01 \pm 0.04$ and found no departure from the $\gamma = 1$ power law even very close to T_K (Fig. 1). (This is clearly different from the case of thermotropics, which generally exhibit an anomalous increase in the Cotton-Mouton and Kerr coefficients for $T \lesssim T_K + 2$ K.[10]) We determined $T_K - T_c^* = 0.035 \pm 0.007$ K, where the first appearance of nematic phase at T_K was indicated by the appearance of a large and noisy birefringence signal. Because of the latter, we could not reliably determine the existence of hysteresis or the width of the coexistence region at the N-I transition.

Within 0.3 K of T_K, we observed departures from the linear dependence of Δn on H^2; this suggested that we could measure higher-order terms in an expansion of the free energy in a power series of the nematic order parameter. According to the scaling hypothesis, such an expansion can always be made, although the coefficients may not be analytic functions of reduced temperature. These higher-order

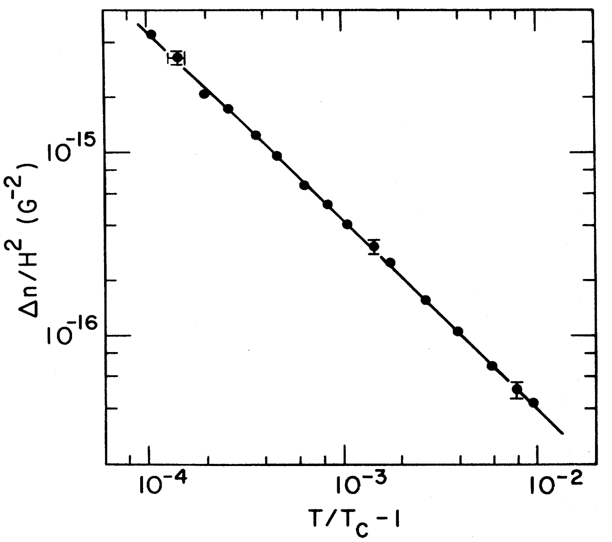

FIG. 1. Generalized susceptibility $\Delta n/H^2$ vs reduced temperature. The solid line gives critical exponent $\gamma = 1.01 \pm 0.04$.

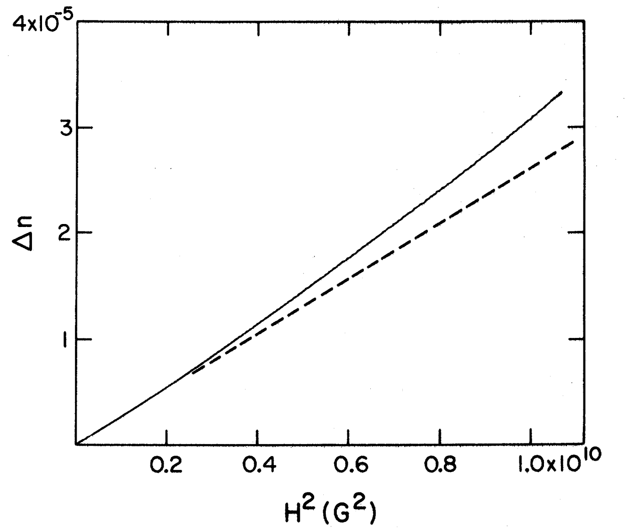

FIG. 2. Raw data showing Δn vs H^2 at $T - T_c^* = 57$ mK. The dashed line is the linear term $\partial\Delta n/\partial H^2|_{H=0}$.

terms are usually discussed in terms of a gap exponent Δ.[11] As $H^2 \rightarrow 0$, $\partial\Delta n/\partial H^2 \sim (T - T_c^*)^{-\gamma}$, and $\partial^2\Delta n/\partial(H^2)^2 \sim (T - T_c^*)^{-\gamma-\Delta}$. There has been some interest in measuring Δ in thermotropic materials[12,13] because of the intriguing suggestion of Keyes[14] that the pretransitional fluctuations, whose divergence is preempted by the first-order *N-I* transition, are governed by the presence of a nearby tricritical point rather than a classical critical point. This is a difficult idea to verify experimentally, since the first-order transition makes the critical isotherm T_c^* inaccessible and prevents a reliable direct determination of the critical exponents β and δ. Keyes proposed[12] that measuring Δ would suffice to determine the nature of the fluctuations. Unfortunately this suggestion was based on an error (the exponent ω of Ref. 12 should be 3 rather than 2), and a correct calculation shows $\Delta = 2$ for both critical and tricritical mean-field behavior in this first-order transition. Given the controversial situation with thermotropic materials,[12,13] we decided to measure Δ for our CsPFO sample with $T_K - T_c^* = 35$ mK.

We turn now to our measurements of $\partial^2\Delta n/\partial(H^2)^2$; clearly temperature control[13] is very important since a small temperature change while H is swept, especially near T_c^*, would give a false effect. The long-term stability of our oven was 10 mK; short-term stability was much better and was determined primarily by the magnetoresistance of thermistors used for temperature control and measurement. The oven characteristics were carefully measured. Magnetoresistance caused a reduction in the set point temperature of the controller proportional to H^2 and equal to 10 mK with $H = 100$ kG.[15] The brass oven wall responded to a change in the set point temperature with a time constant of 20 sec, and the sample itself followed the oven wall temperature with a time constant of 120 sec. Thus, to measure the nonlinear change of Δn with H^2, we swept the field to 105 kG in 30 sec; one readily calculates the sample temperature change to be less than 0.5 mK during the sweep. A typical trace is shown in Fig. 2.

Δn can be expanded in a power series in H^2 and H^4, where the ratio of the quartic contribution to the quadratic contribution is given by[12]

$$f = \frac{\frac{1}{2}H^2\partial^2\Delta n/\partial(H^2)^2|_{H=0}}{\partial\Delta n/\partial H^2|_{H=0}} \sim (T - T_c^*)^{-\Delta}\ .$$

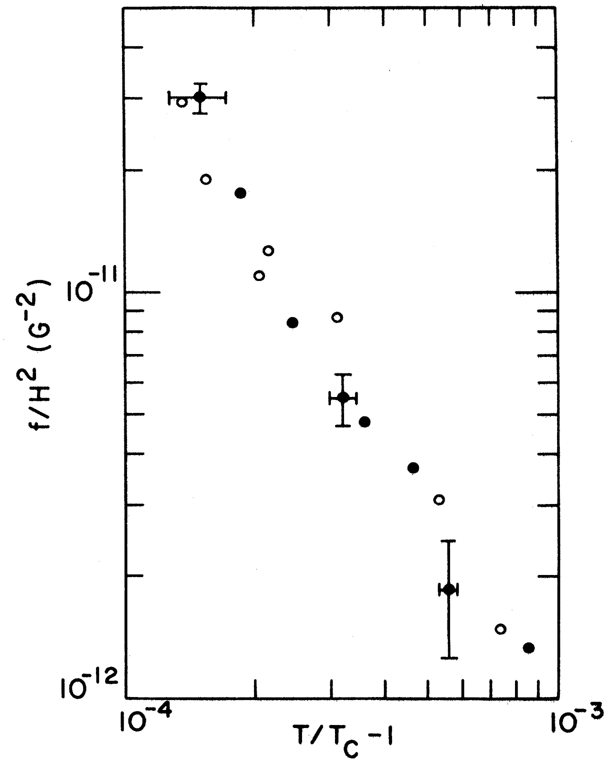

FIG. 3. Ratio of the H^4 coefficient to the H^2 coefficient in the magnetic birefringence for two separate experimental runs. The data give a gap exponent $\Delta = 1.75 \pm 0.25$. Temperature error bars result from uncertainty in T_c^*.

Thus f represents the deviation from linearity in Δn vs H^2 and

$$\Delta n = \left.\frac{\partial \Delta n}{\partial H^2}\right|_{H=0} H^2(1+f+\cdots)\ .$$

The data were fitted to this quartic form and f/H^2 versus reduced temperature is shown in Fig. 3. There are large uncertainties, including a possible error in T_c^* of 6 mK, which gives us the value $\Delta = 1.75 \pm 0.25$. Within error bars our results are consistent with the mean-field value $\Delta = 2$ and larger than Δ reported by Keyes and Shane,[12] who may have been plagued by temperature problems. Nevertheless, we cannot say for certain whether the difference between our experimental and the Landau theoretical value for Δ is due to experimental uncertainty or is perhaps real.

We do not yet understand the reason for $T_K - T_c^*$ becoming so small as the water content of the system is increased. A possibility is that the system is crossing over from uniaxial to biaxial behavior;[16] however, that is difficult to reconcile with our observations that the coefficient of the power-law divergence of the magnetic birefringence is essentially the same for all mixtures we studied. One could also make a number of Landau models which involve coupling to some other order parameter, such as higher-order spherical harmonics in the orientational distribution function. Any such model with the coupling dependent upon water concentration could explain the observed behavior, but is not particularly helpful in the absence of more experimental information on the water CsPFO system. To summarize, we have shown that the N-I transition in this system can be first order with a $T_K - T_c^*$ less than 20 mK while the generalized susceptibility shows a classical mean-field divergence. The lowest-order nonlinear correction to this susceptibility also shows a divergence consistent with mean-field predictions. The CsPFO-water system is an interesting one with further study.

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