Universal Nature of the Nematic-to-Isotropic Transition in Solutions of Discotic Micelles

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The effective exponents characterizing the orientational order parameter at the nematic-to-isotropic transition in discotic micellar solutions obtained on dissolution of either cesium pentadecafluoro-octanoate or ammonium pentadecafluoro-octanoate in water have been measured and found to have the value 0.34 ± 0.02 over a wide range of concentrations. Thus, within experimental error, these exponents appear to be universal to a remarkably high degree. It is argued that, as for second-order phase transitions, these exponents characterize the fluctuations near the transition and can presumably be associated with some inaccessible fixed point of the renormalization-group flow.

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The nature of first-order phase transitions in the presence of a long correlation length is poorly understood, partly because of the relative lack of accurate experimental data on such transitions. Similarly, the theoretical interpretation is hampered because one cannot apply simple renormalization-group ideas to discontinuous transitions.

In this paper we observe that for sufficiently weak first-order phase transitions one can still define effective exponents characterizing the order parameter for the nematic-to-isotropic transition curves in two different discotic micellar liquid-crystal systems and that these exponents are universal to a remarkably high degree. We believe that, as for second-order phase transitions, these exponents characterize the fluctuations near the transitions and can presumably be associated with some inaccessible fixed point of the renormalization-group flow.

Experiments have been carried out on two separate solutions of discotic micelles. These were obtained by dissolution of cesium pentadecafluoro-octanoate[1,2] (CsPFO) or ammonium pentadecafluoro-octanoate[3] (APFO) in water. In both cases, on cooling the isotropic solution phase I, a transition takes place to a nematic phase N_D characterized by long-range correlations in the orientation of the symmetry axes of the micelles. At still lower temperatures, a transition occurs to a discotic lamellar phase L_D where the micelles are arranged on equidistant planes.[4,5] This sequence of transitions is quite analogous to the isotropic-liquid-to-nematic-to-smectic-A sequence observed for thermotropic calamitic liquid crystals. Yet, significant differences in behavior are expected in view of the exceptionally low packing fractions. In the CsPFO/^2H_2O system, this varies from 0.11 (and as low as 0.07 in monotropic phases) to 0.43 along the N_D^+-to-I transition line. Thus, this transition, though of necessity first order, is only very weakly so, and weakens as the concentration decreases. The latter is manifest in the behavior of $T_{IN} - T^*$, where T_{IN} is the temperature at which the nematic phase first separates and T^* is the extrapolated supercooling limit of the isotropic phase; this quantity has been found to decrease as the weight fraction w of CsPFO decreases[6,7] and to become as small as 16 mK at $w=0.30$.[8] Since the shape of the micelles is invariant with dilution along the transition line, though their diameter increases (Table I), this behavior is more likely to have its origin in the effect of dilution on the intermicellar interactions[9] than in a crossover from uniaxial to biaxial behavior.[6]

The weakness of the transition makes it possible to measure effective exponents. Magnetic birefringence measurements in the isotropic phase of a sample of CsPFO/H_2O with $w=0.447$ have yielded[6] the mean-field value for the effective susceptibility exponent: $\gamma = 1.01 \pm 0.04$. Optical birefringence measurements in the nematic phase have also been used to obtain values for β, the order-parameter exponent: $\beta = 0.57 \pm 0.06$ at $w=0.50$,[10] $\beta = 0.40 \pm 0.06$ at $w=0.40$,[10] and $\beta = 0.34 \pm 0.06$ at $w=0.398$.[11] These values appear to decrease on dilution, and it has been suggested[10,11] that this could be due to a crossover from classical mean-field behavior ($\beta = 0.5$) to tricritical behavior ($\beta = 0.25$). There is also the possibility of systematic errors arising from not being able to make measurements close to the transition at high concentrations and also from the use of optical birefringence to monitor orientational order. Such measurements will contain contributions from the reorientational motion of surfactant molecules within the micelle and these will vary with the size of the micelle which is itself a function of temperature.[5] This Letter reports new measurements of the concentration dependence of β along the N_D^+-I transition lines in both the CsPFO and APFO systems. The values of β are obtained from the absolute values of the nematic order parameter S calculated from electrical conductivity measurements.[12,13] This method is practicable because the conductivity is solely determined by the diffusivity of the Cs^+ and $NH_4{}^+$ ions around the micelles. The contribution from the micelles is negligible at these high concentrations as their diffusive motion is hindered by strong intermicellar interactions.

CsPFO and APFO were prepared as described in Refs. 2 and 3, respectively, and conductivity measurements were made as described in Ref. 12. For the CsPFO sample with $w=0.247$ and the APFO sample with $w=0.490$, measurements were made at 10-mK intervals allowing 10 min for equilibrium to be attained at each temperature: For all other samples the temperature increment was 100 mK. Measurements in the nematic phase were recorded on heating and in the isotropic phase on cooling to avoid phase separation in the biphasic region.

For nonconducting, ellipsoidal micelles undergoing reorientational fluctuations with respect to the director of a uniaxial nematic phase the conductivity transforms as a second-rank tensor with a principal axes coincident with that of the moment-of-inertia tensor. Thus, the experiment measures the partially averaged component $\tilde{\kappa}_{zz}$ of the conductivity tensor κ along the direction of **E** which is taken to be along the z axis of the laboratory frame $L(x,y,z)$. This is given by

$$\tilde{\kappa}_{zz}(\phi)=\kappa_i+\tfrac{2}{3}P_2(\cos\phi)S(\kappa_{\parallel}-\kappa_{\perp})_M\ , \qquad (1)$$

where ϕ is the angle between the mesophase director and the direction of **E**. S corresponds to the ensemble average of the orientational fluctuations of the micellar axes $M(a,b,c)$ with respect to $L(x,y,z)$ over a time scale determined by the measurement period (1.67×10^{-5} s). κ_i is the trace of the conductivity tensor as measured in the isotropic phase ($S=0$) and in the liquid-crystalline phases when $\phi=54°44'$ [i.e., $P_2(\cos\phi)=0$]. $(\kappa_{\parallel})_M$ and $(\kappa_{\perp})_M$ are the conductivities measured parallel and perpendicular to the micellar symmetry axis in the frame $M(a,b,c)$ and may be interpreted as $\tilde{\kappa}_{zz}(0°)$ and $\tilde{\kappa}_{zz}(90°)$ in a perfectly ordered system ($S=1$). If for any S we define $\Delta\tilde{\kappa}=\Delta\tilde{\kappa}_{zz}(0°)-\Delta\tilde{\kappa}_{zz}(90°)$, Eq. (1) can be rewritten as

$$\Delta\tilde{\kappa}/\kappa_i=S(\kappa_{\parallel}-\kappa_{\perp})_M/(\tfrac{1}{3}\kappa_{\parallel}-\tfrac{2}{3}\kappa_{\perp})_M\ . \qquad (2)$$

This equation has been used to obtain values for S from the conductivity measurements (Fig. 1) using values for $(\kappa_{\parallel})_M$ and $(\kappa_{\perp})_M$ calculated from the Fricke equations[14] and micelle dimensions obtained from x-ray measurements.[15]

Values of S within 2 K of T_{NI} were fitted by the power law[16] $S-S^+=A(T^+-T)^{\beta}$, where S^+ is the order parameter at T^+, the superheating limit of the nematic phase. In practice, the logarithmic form of the equation was subjected to a least-mean-squares regression analysis, with S^+, T^+, and A as adjustable parameters. Range shrinking was applied to ascertain the asymptotic behavior of β and any possible range dependence. The actual range of the fit was critically dependent upon the proximity of T_{NI} to T^+. The lower the concentration of the sample, the smaller is T^+-T_{NI}, the closer the approach to T^+, and hence the greater the number of decades of reduced temperature accessible. This is illustrated by the plots of $S-S^+$ vs $(T^+-T)/T^+$ in Figs. 2 and 3 for CsPFO with $w=0.247$ and APFO with $w=0.490$, respectively: The lowest reduced temperature difference is 1.5×10^{-4} in the former as compared with 7×10^{-4} in the latter. These values are to be compared with 2.5×10^{-3}, the lowest accessible value reported[17] for a thermotropic nematic.

The results obtained in this manner are summarized in Tables I and II. We see that within the bounds of experimental error, β is invariant along the N_D^+-to-I transition line and has the same value of 0.34 ± 0.02 for both CsPFO and APFO. In contrast, the values of the order parameter at T_{NI} and T^+ decrease as w decreases.

We have applied the same least-mean-squares regression analysis to the corresponding values of $\Delta\tilde{\kappa}/\kappa_i$ and find that the values of T^+ and β obtained are identical

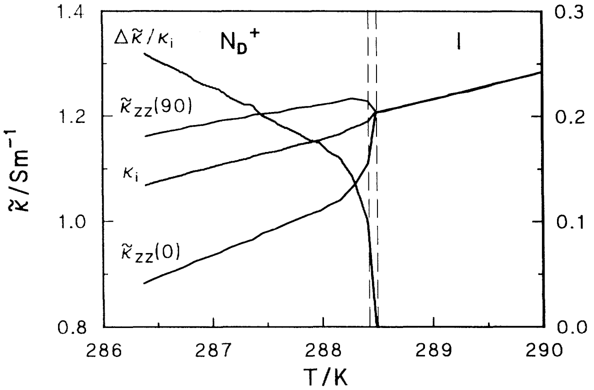

FIG. 1. The electrical conductivity $\tilde{\kappa}_{zz}(\phi)$ as a function of temperature measured at 30 kHz for CsPFO/^{2}H$_2$O with $w=0.247$ ($T_{NI}=288.42$ K and $T_{IN}=288.50$ K). $\tilde{\kappa}_{zz}(0°)$ and $\tilde{\kappa}_{zz}(90°)$ are the conductivities measured parallel and perpendicular to the nematic director, respectively, while in the nematic and lamellar phases, κ_i corresponds to $\tilde{\kappa}_{zz}(54°44')$. The relative conductivity anisotropy is $\Delta\tilde{\kappa}/\kappa_i=[\tilde{\kappa}_{zz}(0°)-\tilde{\kappa}_{zz}(90°)]/\kappa_i$.

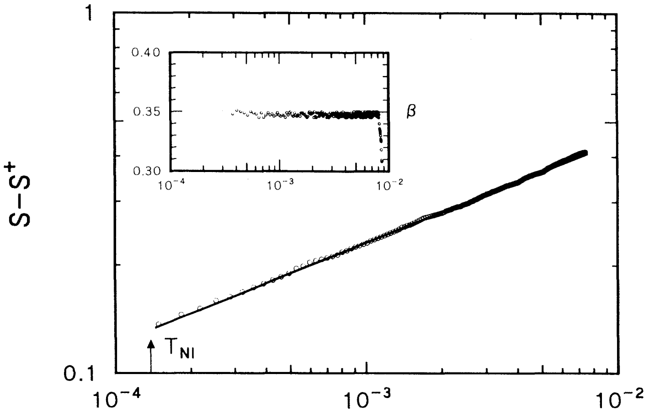

FIG. 2. Log-log plot of $S-S^+$ vs $(T^+-T)/T^+$ for CsPFO/^{2}H$_2$O with $w=0.247$. Solid line represents the best fit by the power law $S-S^+=A(T-T^+)^{\beta}$, with $\beta=0.347$, $T^+=288.46$ K, and $S^+=0.06$. Inset: The effect of range shrinking on the value of β.

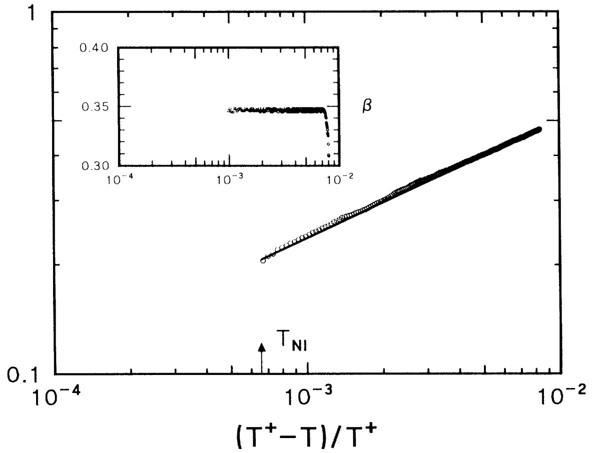

FIG. 3. Log-log plot of $S-S^+$ vs $(T^+-T)/T^+$ for APFO/^2H_2O with $w=0.490$: $\beta=0.346$, $T^+=309.85$ K, and $S^+=0.08$.

to within experimental error. Thus, the data in Tables I and II are not dependent upon the model[5,18] used in the interpretation of the conductivity measurements. This also accounts for the agreement with the value of β obtained[11] directly from optical birefringence measurements for a sample of CsPFO with $w=0.398$.

A number of theoretical predictions for the value of the critical exponent have been put forward. The Landau-de Gennes model has been extensively explored.[16] Taking the free-energy expansion up to the fourth power of the order parameter gives $\beta=0.5$, the mean-field value. Considering the sixth-order term leads to the tricritical value of 0.25. Agreement with the latter value has been shown for thermotropic systems,[17] but neither prediction conforms with the values measured for the micellar nematics. A large sixth-order term could lead to an intermediate value as a result of crossover from a tricritical to a mean-field exponent on approaching T^+.[19] However, given the constancy of the effective exponent along the curve of nematic-to-isotropic phase transitions, and the fact that the transitions have weakened[20] very considerably from the first to the last entry in Table I, this explanation[11] now seems less likely. Alternative explanations based on the idea that the effective exponents are characteristic of some other fixed point of the renormalization-group flow seem more attractive. Thus, in the nematic phase near the transition to the isotropic phase one conceives of a correlation volume of dimension ξ^3 (ξ is the bulk correlation length of the phase) where the critical fluctuations producing domains of isotropic phase are characteristic of a certain universality class. As the transition is approached the correlation length increases and the order parameter appears to change as if governed by a critical exponent. Since the transition is weak, we recognize that the free-energy difference of the two phases is small so the correlation length will be large at the first-order phase transition. One would expect the effective exponent to be that characteristic of the appropriate fixed point. One candidate that is compelling on physical grounds is the three-dimensional five-component vector model Landau point.[21,22] While an accurate value of the order-parameter exponent is not yet available, we may estimate[11] a value of 0.39 by extrapolation of the resummed $O(\varepsilon^5)$ series that have been calculated[23] for $N=1$ to $N=3$. However, our near-universal values of β [$=0.346(2)$ for APFO and 0.347(2) for CsPFO] are more consistent with the $O(\varepsilon)$ value for $N=5$ of 0.342.[21] Given the near constancy of the measured values, the agreement may not be fortuitous and the order parameter near this weak first-order transition may be dominated by the $O(\varepsilon)$ term of the scaling function. It should be noted, however, that such critical behavior would not seem to be consistent with the magnetic birefringence measurements[6] in the isotropic phase, which yield a mean-field result for the effective susceptibility exponent, an observation which seems to imply that, at least in the isotropic phase, fluc-

TABLE I. Parameters obtained for CsPFO/^2H_2O.

w_A	ϕ_A [a]	$T_{IN}-T_{NI}$ (K) [b] ± 0.01	T^+-T_{NI} (K) ± 0.01	$S(T_{NI})$ ± 0.05	S^+ ± 0.05	β ± 0.02	$a/b(T_{NI})$ [c] ± 0.03
0.558	0.355	0.60	0.20	0.35	0.15	0.34	0.37
0.507	0.311	0.34	0.08	0.29	0.10	0.35	0.32
0.457	0.270	0.23	0.11	0.29	0.08	0.37	0.30
0.411	0.235	0.16	0.10	0.23	0.09	0.35	0.28
0.356	0.196	0.13	0.06	0.21	0.07	0.34	0.27
0.312	0.167	0.10	0.05	0.21	0.07	0.32	0.27
0.247	0.133	0.08	0.04	0.20	0.06	0.347 [d]	0.26
0.200	0.096	0.06	0.03	0.16	0.02	0.34	0.25

[a] At T_{NI}.

[b] Obtained by NMR measurements (Ref. 5).

[c] The axial ratios a/b have been calculated assuming the micelle to be an oblate ellipsoid with minor axis $a=2.2$ nm.

[d] Measurement performed at 10-mK intervals. The error in β is therefore reduced, ±0.002.

TABLE II. Parameters obtained for APFO/^2H_2O.

w_A	ϕ_A [a]	$T_{IN}-T_{NI}$ (K) [b] ± 0.01	T^+-T_{NI} (K) ± 0.01	$S(T_{NI})$ ± 0.05	S^+ ± 0.05	β ± 0.02	$a/b(T_{NI})$ [c] ± 0.03
0.490	0.361	0.62	0.18	0.28	0.08	0.346 [d]	0.38
0.450	0.326	0.48	0.19	0.28	0.06	0.34	0.36
0.398	0.281	0.32	0.17	0.18	0.06	0.35	0.32

[a-d] See Table I.

tuations do not become very strong. However, since the transition is ultimately first order, one should not necessarily expect the effective exponents to be the same on both sides of the transition.

The essential conclusion of the present experimental study is that the variation of the order parameter on approaching the nematic-to-isotropic transition is universal, within experimental error, over a wide concentration interval. These and future detailed measurements may provide the basis for a full understanding of weak first-order phase transitions which are strongly affected by fluctuations.

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