

Pretransitional scaling close to a double critical point in a potassium laurate, 1-decanol, and heavy water lyotropic liquid crystal

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Light scattering measurements were done close to the double critical point of the isotropic boundary of the lyotropic liquid crystal potassium laurate, 1-decanol, and heavy water. From scaling analysis we find susceptibility and correlation length exponents that are clearly higher than the mean-field values usually found in other studies on this and similar systems. In order to recover mean-field analysis, we use a parabolic version of the Landau–de Gennes free energy in account of the convex nature of the phase diagram. We also observe pretransitional characteristic domain sizes greater than the correlation length. Furthermore, we show that the transition goes into a new two-phase coexistence region, between the convex tips of pure isotropic and discotic nematic boundaries.

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I. INTRODUCTION

Reentrant phase transitions in multicomponent liquid mixtures are poorly reported or understood as compared to binary liquid systems [1]. In 1980 Yu and Saupe [2] discovered the first biaxial nematic phase in a lyotropic liquid crystal, which displayed a series of reentrant phases. They obtained a partial phase diagram for the ternary system potassium laurate, 1-decanol, and heavy water (PLDW) at a fixed weight concentration of 6.24% of 1-decanol. Around 26% of potassium laurate they did obtain a rich sequence of transitions including many reentrant phases: reentrant isotropic \leftrightarrow reentrant discotic nematic \leftrightarrow reentrant biaxial nematic \leftrightarrow calamitic nematic \leftrightarrow biaxial nematic \leftrightarrow discotic nematic \leftrightarrow isotropic. Since then, the focus has been on this rich region of the phase diagram, from which much has been learnt about this system. Galerne *et al.* [3] showed by x-ray measurements that the anisotropy of the discotic micelles in the nematic phase decreased further towards the isotropic phases. This finding set a scenario to understand qualitatively the isotropic reentrant to nematic transition in terms of molecular theories as the Onsager mean-field theory [4]. While anisotropy has clearly become a temperature controlled key parameter modulating transitions, still the thermodynamics of anisotropy or shape variations remains to be elucidated. McClymer and co-workers [5,6] studied the pretransitional scaling at the isotropic to nematic transitions for PLDW. From light scattering experiments they obtained mean-field exponents for both the susceptibility ($\gamma=1.0$) and correlation length ($\beta=0.50$) at both low and high temperature transitions. In contrast, at the nematic side of the transitions, Boden *et al.* [7] have found discotic micelles to obey another class of universality [$\beta=0.34(2)$]. Parenthesis are used for last significant digit deviation. These results are also in con-

trast to the exponents found for binary liquids fully compatible with the three-dimensional Ising model ($\gamma=1.24, \beta=0.63$), as reported by Narayanan and Kumar [1]. In the present work we report on light scattering measurements close to the double critical point (DCP) of the isotropic boundary of PLDW lyotropic liquid crystal. From scaling analysis we find susceptibility and correlation length exponents that are clearly higher than the mean-field values usually found in other studies of this and similar systems. In order to recover mean-field analysis, we use a parabolic version of the Landau–de Gennes free energy in account of the convex nature of the phase diagram. We also observe a characteristic size greater than the correlation length. Furthermore, we show that the transition goes into a new two-phase coexistence region, between the convex tips of pure isotropic and discotic nematic boundaries.

II. SAMPLE PREPARATION AND SCATTERING SETUP

The lyotropic phase was prepared by mixing potassium laurate (purified by recrystallization), 1-decanol (>99%, Fluka), and D₂O (Sigma) in the weight proportions 23.8%, 6.36%, and 69.8%, respectively. The mixture was sealed in a Pyrex tube, homogenized by vigorous shaking combined with centrifugation and then left at rest for several weeks. The lyotropic mixture used here exhibits a discotic nematic phase in a large temperature range, from about 21 °C to an upper transition temperature above 30 °C. The upper temperature remained undetermined in this experiment. Next, the tube was placed in the index matching scattering cell, which is an oven in thermal contact with a circulating heat bath, controlled so that the long term thermal stability (for 1 h) is better than 0.1 °C. The sample temperature is monitored with help of a thermistor. The main components of the light scattering setup are as follows. A He:Ne 35-mW laser (Spectra Physics, model 127) beam traverses without focusing the

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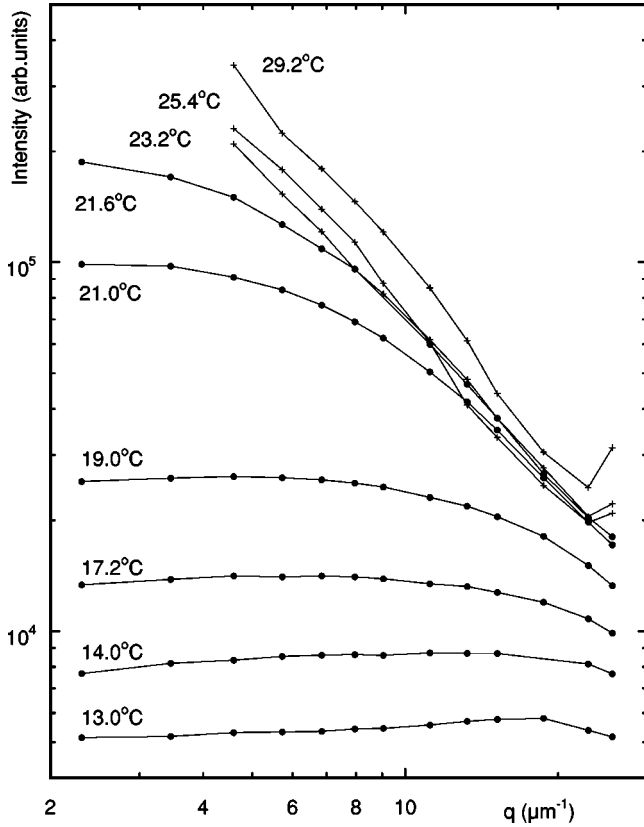


FIG. 1. Log-log plot of the PLDW depolarized scattering intensity versus wave number close to DCP. The curves correspond to temperatures of (13.0, 14.0, 17.2, 19.0, 21.0, 21.6, 23.2, 25.4, and 29.2 °C). A phase transition occurs at 22.0 °C. The lower phase (●) is reentrant isotropic while the upper phase (+) is nematic.

sample tube. The incident and scattered wave vectors make an internal angle corresponding to a wave number q and the scattering plane is kept horizontal. A motorized Brookhaven goniometer stage is used to sweep the wave-vector range of the measurements. A Glan prism is used to assure the incident polarization vector is perpendicular to the scattering plane within 0.5°, and another one is used to define the polarization of the scattered beam parallel to the scattering plane. In order to calculate q we use a (mean) refractive index of $n=1.38$, which was determined before for the PLDW system at nearby concentrations [10]. Next, the selected scattered light beam is collected through a pinhole of 0.2 mm opening diameter and focused on to the photocathode of a photomultiplier tube. The photopulses are then discriminated and counted for 30 min at each scattering angle to give intensity raw data.

III. DEPOLARIZED STATIC LIGHT SCATTERING

The anisotropic or traceless part of the dielectric tensor can be taken as the order parameter for the (weak) first-order nematic-isotropic transition [8,9]. At the same time, molecular or supramolecular anisotropy becomes a source for depolarization to light scattering. Depolarized light scattering is, thus, sensitive to molecular orientation or director fluctuations in liquid crystals. The Landau–de Gennes mean-field

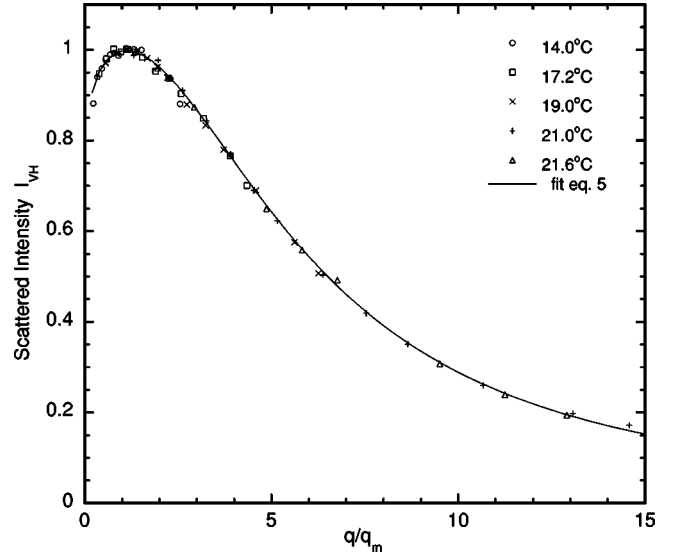


FIG. 2. Scaled linear plot of the intensities versus wave number for the reentrant isotropic phase (14.0, 17.2, 19.0, 21.0 and 21.6 °C). A master curve, of quasi-Ornstein-Zernike form, as given by Eq. (5) and fit to the data, is also represented.

theory is usually taken in order to describe critical phenomena. In the isotropic phase the mean order parameter vanishes, and it suffices to retain quadratic terms in the symmetric order parameter tensor $Q_{\alpha\beta}$, for the free energy expansion. Including the elastic deformation energy, one has in Fourier space at wave number q ,

$$F = F_0 + \frac{1}{2} A Q_{\alpha\beta} Q_{\beta\alpha} + \frac{1}{2} k q^2 Q_{\alpha\beta}^2, \quad (1)$$

where

$$A = A_0(T - T^*) = A_0 T^* x^\gamma \quad (2)$$

is the transition temperature phenomenological control parameter (A is positive in the isotropic phase, x is the reduced temperature and $\gamma=1$ in mean field), while k is a simplified (single) elasticity. From energy equipartition, the depolarized scattered intensity at q wave number is then predicted to have the Ornstein-Zernike form,

$$I_{VH} \sim \langle Q_{VH}^2 \rangle = \frac{k_B T}{A + k q^2} \sim \frac{T x^{-\gamma}}{1 + (\xi q)^2}, \quad (3)$$

with a correlation length

$$\xi = (k/A)^{1/2} = \xi_0 x^{-\beta}, \quad (4)$$

where $\beta = \gamma/2 = 0.5$ in mean field. The bare correlation length prefactor $\xi_0 = (k/A_0 T^*)^{1/2}$ is estimated as being of molecular size. From a series of static depolarized measurements at different temperature and scattering angles in the isotropic phase one should, thus, obtain γ and β scaling exponents as well as the extrapolation values for T^* and ξ_0 . We have measured depolarized (VH geometry) light scattering intensities from PLDW at the temperatures of

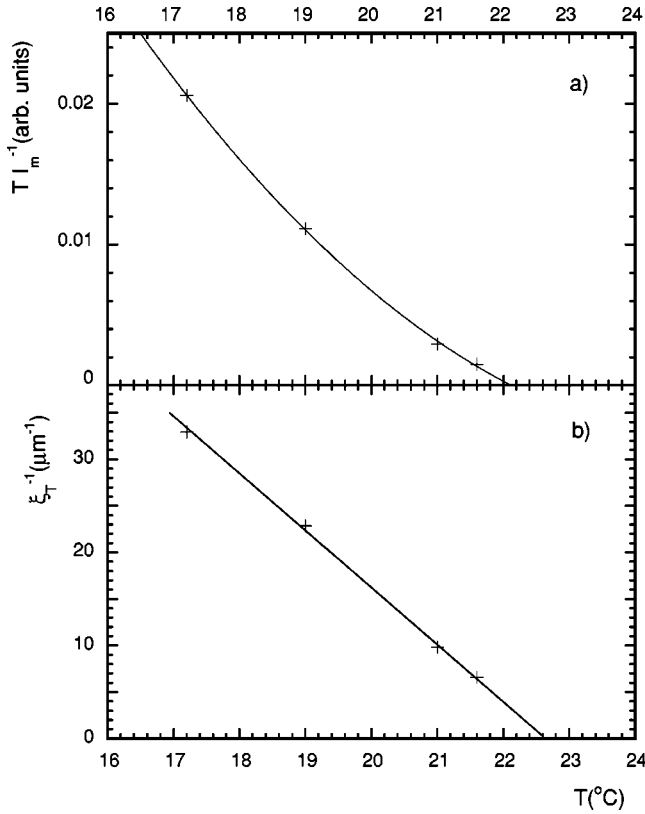


FIG. 3. (a) Temperature over intensity (inverse susceptibility) versus temperature. A parabolic fit, in the form of Eq. (7), giving $T^- = 22.2(2)^\circ\text{C}$ and $T^+ = 29(3)^\circ\text{C}$ is also displayed. (b) Inverse correlation length versus temperature. A linear fit to the data gives $T^* = 22.6(1)^\circ\text{C}$ and a bare correlation length of $\xi_0 = 5.6(1) \text{ \AA}$.

13.0, 14.0, 17.2, 19.0, 21.0, 21.6, 23.2, 25.4, and 29.2°C and scattering angles of $10^\circ, 15^\circ, 20^\circ, 25^\circ, 30^\circ, 40^\circ, 50^\circ, 60^\circ, 90^\circ$, and 120° . After scattering volume $\sim \sin(\theta)$ corrections, the intensities increase over 2 orders of magnitude with temperature and at low scattering angles as depicted in Fig. 1. Even above the phase transition at $T_c = 22.2^\circ\text{C}$, intensities still increase, although at a lower pace. Besides, in this situation, extrapolation to the hydrodynamic limit (small q) becomes infeasible.

IV. RESULTS

The measurements at different temperatures in the isotropic phase can be made to collapse into a single master curve by multiplying each scale by suitable factors as shown in Fig. 2. Contrary to the monotonic Ornstein-Zernike behavior [Eq. (3)], the intensity displays a maximum at finite wave number q_m . The abscissa of Fig. 2 is correspondingly normalized as q/q_m , while the ordinate as $I/I(q_m)$. The maximum in intensity characterizes a domain fluctuation length (characteristic size) $L_m = 2\pi q_m^{-1}$. We note that the following empirical modification of the Ornstein-Zernike correlation fits the data throughout,

$$I_{VH} \sim \frac{(\xi q)^{0.08}}{1 + (\xi q)^2}, \quad (5)$$

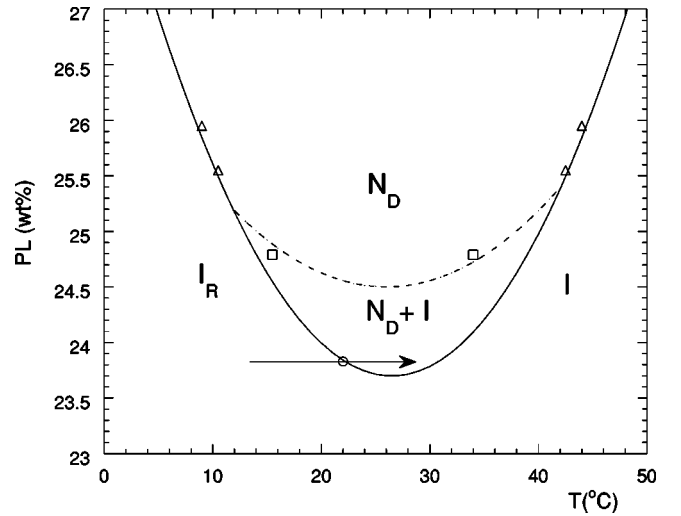


FIG. 4. Approximate phase diagram for PLDW at 6.24% of 1-decanol. I indicates isotropic and N_D indicates nematic discotic phases. Symbols are (Δ) data from Yu and Saupe [2], (\diamond) data from Galerie *et al.* [3], (\circ) this work. The arrow represents the transition region investigated. Above 26% of PL biaxial and calamitic phases appear (not represented). Around 24% of PL we observe a two-phase coexistence region, giving rise to a strong anisotropic scattering or an isotropic phase with pretransitional finite size domain fluctuations.

while it gives the fixed size ratio

$$L_m(T)/\xi(T) \approx 35.4. \quad (6)$$

The scalings for the inverse correlation length and temperature divided by the scattering amplitude (inverse susceptibility) can be appreciated in Fig. 3. The divergences are clearly stronger than mean field, and the excess susceptibility can be associated with the reentrant nature of the transition as we approach a double critical point. The Landau-de Gennes free energy should be modified in order to take account of the two isotropic phases merging at the DCP. It suffices to take a parabolic prefactor in Eq. (1), instead of Eq. (2), as [10]

$$A = A_0(T - T^+)(T - T^-), \quad (7)$$

with an upper (lower) second-order transition temperature T^+ (T^-). At the DCP this form becomes quadratic while it retains its linear approximation away from it. A fit of Eq. (7) to the inverse susceptibility data is also shown in Fig. 3(a), giving $T^- = 22.2(2)^\circ\text{C}$ and $T^+ = 29(3)^\circ\text{C}$. It is quite remarkable that the upper transition can also be inferred (though with lesser precision) from measurements in the lower reentrant isotropic phase. As for the correlation length, insertion of Eq. (7) into Eq. (4) linearizes the inverse divergence at the DCP, and preserves the square root mean-field behavior away from it. The graph in Fig. 3(b) is already quite linear ($\beta = 1.0$), and fits well to $T^+ = T^- = 22.7(1)^\circ\text{C}$ and $\xi_0 = 5.6(1) \text{ \AA}$. It was not possible to infer the true upper critical temperature from this data.

V. ANALYSIS

Micellar sizes have been estimated to range from 26 to 85 Å [11]. The bare correlation length ξ_0 found is surprisingly small and rather of size order of individual decanol molecules. In contrast, McClymer and co-workers [5,6] have reported bare lengths of 22 and 28 Å, closer to micellar sizes in their measurements away from the DCP. As a matter of fact, the parabolic model is expected to hold only close to the transition, and a linear behavior will be restored away from it [1]. Thus, the prefactor ξ_0 should not be taken with the usual meaning (zero-temperature extrapolation). Instead, it becomes clear from Fig. 3(b) that restoring of the mean-field behavior will increase the zero-temperature correlation length. From the lowest temperature data, a mean-field extrapolation estimate gives $\xi_0 = 30(10)$ Å, much compatible with micellar sizes. On the other hand, the bare characteristic domain length $L_0 = 35.4\xi_0$ is already a large quantity, implying domain volumes composed of a few thousand correlated regions. There are no previous reports for a characteristic or domain length in PLDW and its presence here is a signature that the transition is going into a two-phase state. After the transition, the fluctuations (intensity) still increase, as can be seen from Fig. 1, while away from DCP scattered intensity in the nematic lyotropic phase significantly drops. We are led to the conclusion that next to the DCP there lays a previously unreported nematic-isotropic coexistence region. A PLDW phase diagram including these liquid crystalline phases is then schematized in Fig. 4.

VI. CONCLUSIONS

Reentrant behavior in the PLDW liquid crystal system displays a double critical point in the temperature-composition phase diagram. Close to the DCP, the isotropic to nematic phase transition loses its traditional mean-field behavior and becomes anomalous with growth exponents for the susceptibility and correlation length doubling. Landau-de Gennes mean-field analysis can be restored close to the DCP by using a parabolic term instead of a linear temperature dependence in the free energy development. Depolarized light scattering in the pretransitional regime clearly reveals the anomalous behavior close to the DCP. It also displays a characteristic length scale, associated with a domain coexistence region. From this analysis we propose the schematic closure of the nematic phase by a nematic-isotropic region.

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