

Orientalional order and critical behavior of discoidal nematics

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Experimental data are presented on the degree of molecular orientational ordering, $S(T)$, for two thermotropic liquid crystals in the thermodynamically stable and metastable discoidal nematic phases, N_D , and in the discotic phase D_{hd} . The Landau-de Gennes theory is shown to be valid for describing $S(T)$ for the N_D phases of both types of liquid crystal. The N_D-I phase transition (I is the isotropic liquid) is simultaneously close to the isolated Landau critical point and to the tricritical point, as is the $N-I$ transition in ordinary calamite nematics. The difference in the local symmetry of the N and N_D phases shows up as a difference in the relationship between the direct correlation length ξ_0 of the spatial fluctuations in the order parameter S and the molecular dimensions. The relation between the susceptibilities $S^{(n)} = (\partial^n S / \partial h^n)_{T; h \rightarrow 0}$ of the nematic phase to the field h , thermodynamically conjugate to the modulus S with the temperature dependence $S(T)$ in zero field and its derivative with respect to temperature is found. The critical behavior of S , $S^{(1)}$, $S^{(2)}$, and the correlation length ξ in the nematic phase N_D are studied and an explanation is given for the controversial empirical values of the exponents for these quantities in thermotropic calamite and micellar discoidal nematics. It is shown that the N_d-D_{hd} phase transition is a strong first-order transition with a large jump ΔS and strong coupling between the orientational and translational ordering of the molecules. Here the low entropies $\Delta \Xi$ and enthalpy ΔH of the N_d-D_{hd} phase transition are caused by an increase in the conformational mobility (orientational melting) of the flexible chains of molecules in the D_{hd} phase. © 1996 American Institute of Physics. [S1063-7761(96)01911-7]

1. INTRODUCTION

Liquid crystals consisting of disc-shaped molecules are characterized by a large variety of structures and interesting physical properties, which have stimulated intense research on them.¹ A key to understanding their molecular nature and optimizing their properties may be provided by information on the parameters of the orientational and translational orderings of the molecules (of their fragments) in the limits of the isolated liquid crystal phases and on the changes in these properties during phase transitions. However, the mixed orientational-translational ordering parameters of the molecules in discotic liquid crystals^{1,2} have not yet been determined experimentally, and the most important parameter is the degree of orientational ordering of the molecules, S . Most work on the physical properties of discotic liquid crystals and their orientational ordering concern the discoidal columnar phases $D_{h,r,i}$ (intrinsically discoidal phases), while the discoidal nematic phases N_D have been studied very little. Only recently have the first experimental data been obtained on the magnitude of S and variation $S(T)$ in the N_D phase of liquid crystal mixtures³ and pure components,⁴ as well as on the features of the discoidal nematic-isotropic liquid (N_D-I) phase transition,⁴ on the magnitude of S in the recovered phase N_{DR} , and on the change $\Delta S(T_{ND})$ during the $N_{DR}-D_{hd}$ transition.⁵

Besides extending the above mentioned data, developing a theory of $I-N_D-D$ phase transitions and the phase diagram of discotics^{1,2,6-9} requires clarification of such basic questions as the applicability of the molecular-statistical and

phenomenological theories developed for ordinary calamite nematics N (consisting of rod-shaped molecules) to the description of $S(T)$ and the N_D-I transition; the general features of and differences between $N-I$ and N_D-I transitions; the change $\Delta S(T_{ND})$ during an N_D-D_{hd} transition; and, the relationship of the behavior of $S(T)$ and $I-N_D-D_h$ transitions to the conformational degrees of freedom of the molecules and their flexible end chains, whose presence is a necessary molecular property for the existence of discotic mesomorphism.¹

On the other hand, the dependence $S(T)$ determines the susceptibility χ of the nematic phase to changes in S under external influences¹⁰ and is important for practical applications of N_D nematics. It has recently been observed¹¹ that the birefringence $\Delta n \propto S \propto \chi_i$ of the isotropic phase of a discoid nematic in a shear flow is several orders of magnitude greater than for the calamite nematics. This suggests a need for a theoretical and experimental study of the nonlinear susceptibilities $S^{(n)} = (\partial^n S / \partial h^n)_{T; h \rightarrow 0}$ of N_D nematics to the field h , conjugate to the order parameter S , as well as a need to establish an interrelationship between $S^{(n)}$ and $S(T)$ analogously to the case of the linear susceptibility χ .¹⁰

The critical change in the parameters S , χ , and $S^{(2)}$ in the N_D phase is also of interest because of the difference in the local symmetry of the N and N_D phases.⁸ Whereas in the isotropic phase of a discoid nematic the reciprocal susceptibility varies as $\chi_i^{-1} \propto T-T^*$ with a difference^{12,13} $T_c-T^* \approx 1-2$ K (T_c is the temperature of the N_D-I transition and T^* is the temperature of maximum supercooling of

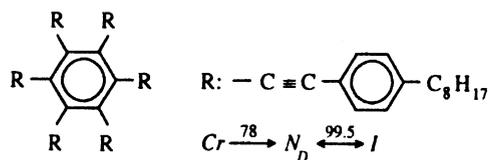


FIG. 1. Structural formula of the molecule and the temperatures ($^{\circ}\text{C}$) of the phase transitions of LC-1. (Cr denotes the crystalline phase).

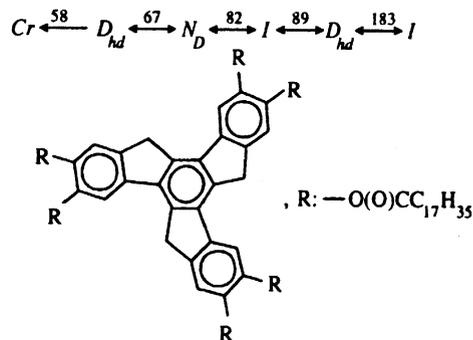


FIG. 2. Structural formula of the molecule and the temperatures ($^{\circ}\text{C}$) of the phase transitions of LC-2. (Cr denotes the crystalline phase).

the isotropic phase) that is of the same magnitude as for the calamite nematics, the change $\Delta H = 20\text{--}300$ J/mole in the enthalpy during the N_D - I transition^{11,14,15} is anomalously small compared to the N - I transition. Since we have $\Delta H = aS_c^2 T_c / 2$, where $S_c = S(T_c)$, the anomalously low value of ΔH may correspond to small S_c and strong fluctuations in the order parameter S , or to a small parameter a and a large bare correlation length $\xi_{0i} = \sqrt{L_1 / aT^*}$ in the fluctuations of S in the isotropic phase. Information on ΔH and S for the thermotropic N_D phases makes it possible to investigate the question¹⁶ of the relationship between ξ_0 and the molecular dimensions and to establish the interrelationship between the local symmetry of the nematic phase and ξ_0 . It is known¹⁷ that in lyotropic micellar N_D phases a is tens of times smaller, while ξ_0 is several times greater, than in the thermotropic N phases. Based on the same local symmetries⁸ of the N_D phases in thermotropic and lyotropic liquid crystals, we can expect an analogous relationship between the parameters a and ξ_0 in the thermotropic N and N_D phases. On the other hand, it is interesting to compare the critical behavior of the order parameter S in thermotropic N_D nematics with the available data for micellar N_D nematics.¹⁸⁻²⁰

This paper is devoted to a study of the orientational ordering of molecules and I - N_D - D_{hd} phase transitions in two thermotropic liquid crystals of different chemical classes and to investigating the questions raised above. In Sec. 2 the temperature dependence of the order parameter is presented and compared with the molecular-statistical theory and computer simulations. Section 3 includes a quantitative interpretation of $S(T)$ in the N_D phase in terms of the Landau-de Gennes theory and a comparison of N_D - I and N - I transitions. The response of a nematic to external influences and the interrelation of the susceptibilities $S^{(n)}$ with the function $S(T)$ are examined in Sec. 4. The critical behavior of S , χ , and $S^{(2)}$ for the samples studied here is discussed and this behavior is compared with published data for thermotropic calamite and discoid micellar nematics in Sec. 5. The main results of this work are summarized in the Conclusion.

2. ORIENTATIONAL ORDERING OF MOLECULES IN THE N_D AND D_h PHASES

Test samples. In order to account for the factors which influence the orientational ordering of the molecules in liquid crystals and are important for solving the problems stated above, the compounds LC-1²¹ and LC-2¹⁴ with the structural formulas and phase transition temperatures shown in Figs. 1 and 2 were selected.

Unlike the low temperature N_D phases³ in liquid crystal mixtures with nonideal phase diagrams, LC-1 and LC-2 are

pure components. Precision data on the refractive indices $n_{\parallel,\perp}$ ($\lambda = 589$ nm) are available for these materials for use below in determining the S , N_D , and D_h phases. Because of the nonpolarity of the molecules and the absence of low temperature D phases for LC-1, it is natural to propose that the associates and cybotactic groups which affect S and $S(T)$ in the N_D phase are absent.^{3,15} The nematic phase of LC-1 is strongly supercooled, which ensures a wide range of variation in $S(T)$ for comparison with theory. In LC-2, both the low temperature phases, I and N_D , are metastable^{14,22} and are of interest for comparing the difference $T_c - T^*$ with the observed interval of the N_D phase. Data on ΔH are available¹⁴ for all the transitions of LC-2 and, when data exist on $S_c = S(T_c)$, they can be used to estimate ξ_0 . The polar LC-2 molecules form dimers whose stability depends on the conformation of the molecules.²³ From the extent of the change $\Delta S(T_{ND})$ and the degree of influence of the fluctuations in the column ordering of the molecules on the behavior of S in the N_D phase near the transition temperature T_{ND} it is possible to ascertain the character of the N_D - D_{hd} transition in LC-2.

Orientational ordering and birefringence of the N_D phase

Let us consider a uniaxial, nonpolar, uniformly oriented nematic N_D with disc-shaped molecules whose symmetry axes $\mathbf{I} \parallel \mathbf{C}_n$ ($n \geq 3$) are normal to the molecular planes and oriented along the directrix \mathbf{n} . The orientational order parameter of the molecules, $S = \langle 3 \cos^2 \theta_{in} - 1 \rangle / 2$ is the modulus of the macroscopic order parameter of the N_D phase,¹⁶ $S_{ij} = S(n_i n_j - \delta_{ij} / 3)$, where the $n_{i,j}$ are the components of the directrix \mathbf{n} . While the global symmetry of the N and N_D phases is the same, we note that their local symmetries differ.⁸ If in the N phase the vector \mathbf{n} is perpendicular to the direction of the minimum intermolecular separation that coincides with the transverse dimension of the stretched molecules and ξ_{0i} ,¹³ then in the N_D phase the direction of \mathbf{n} coincides with the direction of the minimum intermolecular separation in the direction transverse to the flattened molecule. In addition, the molecules forming the N phase have a biaxial form and polarizability tensor γ , while the discoidal molecules are uniaxial and the molecular biaxiality does not contribute to the intermolecular interaction energy. For the same reason, the anisotropy of the dielectric tensor ϵ of the

N_D nematic is determined solely by the value of S .

We introduce the parameters

$$A = \frac{\gamma_a}{\gamma}, \quad Q = \frac{\varepsilon_a}{\varepsilon - 1},$$

where

$$\gamma_a = \gamma_{\parallel} - \gamma_{\perp}, \quad \gamma = \frac{\gamma_{\parallel} + 2\gamma_{\perp}}{3}, \quad \varepsilon_a = \varepsilon_{\perp} - \varepsilon_{\parallel},$$

$$\varepsilon = \frac{\varepsilon_{\parallel} + 2\varepsilon_{\perp}}{3}, \quad \varepsilon_k = n_k^2 \quad (k = \parallel, \perp),$$

n_k are the refractive indices of the N_D phase for the light waves polarized with $\mathbf{E} \parallel \mathbf{n}$ and $\mathbf{E} \perp \mathbf{n}$. Given the anisotropy of the local field of the light wave in a light crystal,²⁴ the parameter S has the form

$$SAS = Q \frac{1 + (\varepsilon - 1)(P - 1)/3f}{1 + \varepsilon_a(P - 1)(1 + 2Q/3)/9f} \equiv Q(1 + \sigma). \quad (1)$$

Here σ is a correction for the anisotropy of the local field, $P = \tau/\tau_k = \text{const}$,²⁵ $\tau = (L_{\parallel} - L_{\perp})/3$ is the anisotropy of the Lorentz tensor \mathbf{L} of the liquid crystal,²⁴ and

$$\tau_k = Q/9(1 - Q/3), \quad f = (\varepsilon - 2\varepsilon_a\tau + 2)/3. \quad (2)$$

Given the inequalities $2Q \ll 3$ and $\varepsilon_a \ll 9f$, to first order in ε_a the expression for σ reduces to

$$\sigma = (\varepsilon - 1)(1 - Q/3)(P - 1)/3f. \quad (3)$$

For $P > 1$ the increase in $Q > 0$ with increasing S in the N_D phase is accompanied by a weak reduction in σ as opposed to the growth in σ in the N phase with $Q < 0$. However, in both phases this change in σ is small, since usually $Q \ll 3$ and $(\varepsilon - 1)/f \approx \text{const}$.

The samples selected here differ substantially in the correction for the anisotropy in the local field. The LC-1 molecules have a strongly polarizable aromatic core and large $\Delta n = n_{\perp} - n_{\parallel}$. For the N phase of these liquid crystals, the components L_j ($\text{Tr } \mathbf{L} = 1$) derived from experimental data^{24,25} are in good agreement with calculations using the model of Ref. 25, according to which for the N_D phase when $S = 1$ the component $L_{\parallel}^{(0)}$ is determined by the ratio $m = a_{\parallel}/a_{\perp}$ of the semiaxes of the molecular spheroid and is given by

$$L_{\parallel}^{(0)} = \frac{1 + \eta^2}{\eta^3} (\eta - \arctan \eta), \quad \eta = \sqrt{m^2 - 1}. \quad (4)$$

The interval $1 \leq m < \infty$ corresponds to the interval $0 \leq \tau_0 = 1/3 - L_{\perp}^{(0)} < 1/3$, which is twice that for the calamite liquid crystals. In the N_D phase for $S < 1$, the dependence $\tau(T)$ is given by $\tau = \tau_k \tau_0 / \tau_{k0}$,²⁴ where $\tau_{k0} = \tau_k$ ($Q = Q_0$, $S = 1$).

For real discogenic molecules the spatially-branched location of their fragments and the substantially nonlocal character of the molecular polarizability must cause a reduction in τ .²⁴ Thus, for LC-1 the model (4) can be used only to obtain upper bound estimates for τ , σ , and the range of variation of $\sigma(T)$ in the confines of the N_D phase. We obtain the values

$$a_{\parallel} = d_{\parallel}/2 = 2.25 \text{ \AA}, \quad a_{\perp} = \sqrt{3M/4\pi\rho N_A} a_{\parallel} = 15.43 \text{ \AA},$$

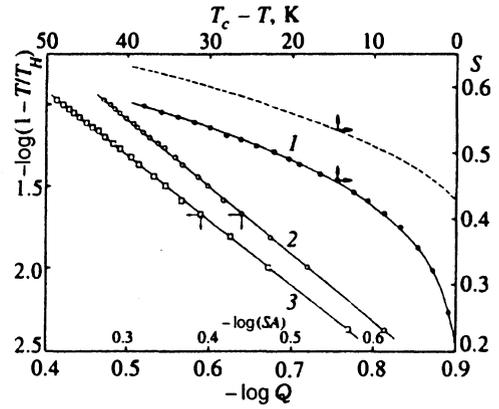


FIG. 3. Temperature variations in the orientational order parameter of the molecules, S (solid circles), the product SA (1) (hollow circles) and parameter Q (1) (squares) in the nematic N_D phase of LC-1. The smooth curves are calculated from the equation of state (11) (curve 1) and by interpolation (curves 2 and 3). The dashed curve is the theoretical $S_{MS}(T)$ curve according to the Mayer-Saupe theory.^{7,15}

where $d_{\parallel} = 4.5 \text{ \AA}$ is the average of the typical intermolecular distances along \mathbf{n} for disc-shaped molecules such as LC-1 in the uniaxial N_D and biaxial N_B phases according to x-ray scattering data,^{26,27} M is the molecular weight, N_A is the Avogadro number, and $\rho \approx 1 \text{ g/cm}^3$ is the density of the liquid crystal. Substituting $m = 6.86$ in Eq. (4) yields $\tau_0 = 0.235$ (Ref. 4).

As can be seen from Fig. 3, the $Q(T)$ curve for LC-1 can be described by Haller's formula²⁸

$$Q = Q_0(1 - T/T_H)^{\beta_H} \quad (5)$$

with the parameters $Q_0 = 0.687_{-0.010}^{+0.015}$, $T_H - T_c = 0.7 \pm 0.1 \text{ K}$, and $\beta_H = 0.255_{-0.001}^{+0.008}$. With a measurement accuracy for the refractive indices of $\eta_{\parallel, \perp} = \pm 1 \cdot 10^{-4}$ (Refs. 14 and 21), the accuracy in determining the parameters Q_0 , β_H , and $T_H - T_c$ depends mainly on the accuracy of determining T_c , which is limited by the presence of the two-phase region of the $N_D - I$ transition. Here and in the following we take $\delta(T_c) = \pm 0.1 \text{ K}$ when indicating the accuracy of all the parameters for both liquid crystals. The labels on the values denote the experimental error and correspond to $T_H - T_c = 0.7 + 0.1 \text{ K}$ for the superscripts and $T_H - T_c = 0.7 - 0.1 \text{ K}$ for the subscripts. For $A = \text{const}$ the ratio $Q(T)/Q_0$ gives $S(T)$ in the approximation of $\sigma = 0$. Substituting Q_0 in Eq. (2) gives $\tau_{k0} = 0.099$ and $P = \tau_0/\tau_{k0} = 2.374$. For $\tau = P\tau_k$ the parameter σ in Eq. (2) changes from 0.44 near T_c to 0.39 for $\Delta T = T_c - T = 40 \text{ K}$. The temperature dependences $AS(T)$ and $S(T)$ are shown in Fig. 3. $AS(T)$ in Eq. (1) well approximated by Eq. (5) with $AS_0 = 0.943_{-0.007}^{+0.016}$, $T_H - T_c = 0.7 \pm 0.1 \text{ K}$, and $\beta_H = 0.247_{-0.003}^{+0.007}$. For $S_0 = 1$ the anisotropy in the local field shows up as a large increase in $A = 0.943$ compared to the case $A_j = Q_0$, but has little effect on β_H and the relative values of $S(T)$ in the N_D phase owing to the small variation in the factor $1 + \sigma$ in Eq. (1). Over the entire range of the N_D phase, the difference satisfies $S(\sigma) - S(\sigma = 0) \approx \text{const} \approx 0.01$.

Since LC-2 is characterized by the absence of π -electron conjugation of the R fragments in the molecular

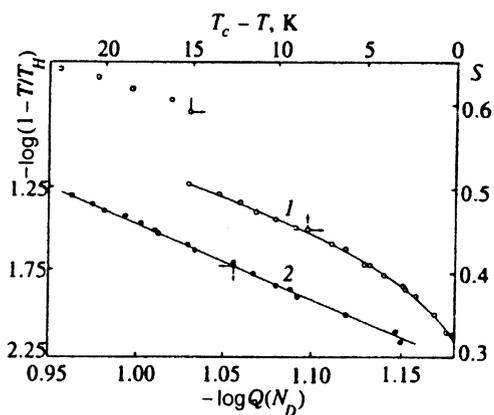


FIG. 4. Temperature variations in the parameters $S = Q/A_0(N_D)$ (hollow circles) and $Q(N_D)$ (solid circles) in the nematic N_D and discotic D_{hd} phases of LC-2. The N_D - D_{hd} phase transition takes place at a temperature $T_{ND} = T_c - 15.1$ K. The continuous curves have been calculated from the equation of state (11) (curve 1) and by interpolation (curve 2).

core, by weak birefringence, and by a more friable molecular structure than that of LC-1, it has a small anisotropy in the local field.²⁴ In fact, as can be seen from Fig. 4, in the N_D phase the change in $Q(T)$ is well approximated by Eq. (5) with parameters $Q_0 = 0.215^{+0.005}_{-0.0}$, $T_H - T_c = 2.5 \pm 0.1$ K, and $\beta_H = 0.228^{+0.006}_{-0.002}$. $\tau_{k0} = 0.026$ for LC-2 is a factor of four smaller than for LC-1. Since for fixed λ and S the parameter τ falls off more rapidly with decreasing ε_a than ε_a and τ_k because of the change in the chemical and electronic structure of the molecules,²⁴ we have $\sigma(\text{LC-2}) \ll \sigma(\text{LC-1})$ and the local field correction in Eq. (1) can be neglected for LC-2.

The contribution of the polarizability of the flexible C_8H_{17} end chains to the parameters ε_a and γ_a for the LC-1 molecules is negligibly small and the resulting S characterizes the orientational ordering of the molecular cores. For the LC-2 molecules, with a weakly polarizable core, the long flexible $C_{17}H_{35}$ chains could make a significant contribution to ε_a and γ_a when they undergo a rigid trans-conformation and are oriented radially in the plane of the core. However, the equilibrium conformation of the LC-2 molecule for the trans-state of the chains corresponds to their leaving the plane of the core,²³ while a lengthening of the chains in LC-2 molecules rapidly increases the free volume attributable to them in the N_D phase, which is accompanied by orientational disordering of their fragments and a drop in the contribution from the polarization anisotropy to A and Q . Thus, we can assume a slow variation for $A(T)$ within the relatively narrow interval of the N_D phase of LC-2.

The nematic phase and the N_D - I transition

Figures 3 and 4 show that for equal reduced temperatures $\Delta T = T_c - T$, S is higher for LC-2 than for LC-1. The probable reason for this is the presence of cybotactic clusters of the D_h phase in the nematic phase of LC-2 with a higher value of S . This kind of behavior of the local structure of the I and N_D phases is characteristic for liquid crystals consisting of polar molecules with low- or high-temperature D phases.^{15,23,26} The parameters $T_H - T_c = 1.8$ K, $\beta_H = 0.225$, and $A = Q_0 = 0.270$ in Eq. (5) and the values of S for the N_D phase in the liquid crystal mixture³ are close to those

obtained here for LC-2. Note the close values of $\beta_H = 0.23 - 0.25$ for the three samples discussed here with their different chemical structures and values of the parameter A , which characterizes the anisotropy in the dispersive intermolecular interactions. This suggests that steric intermolecular interactions play a controlling role in the orientational ordering of the N_D phases, as for the calamite nematics.

The value of $S(\Delta T)$ for the discoid nematics is close to that for the calamite nematics and is less than that predicted by the molecular-statistical theory,⁷ especially near T_c . The theory of Ref. 7 is a generalization of the MacMillan theory for $A(N - S_A)$ nematic-smectic transitions and yields the universal Mayer-Saupe dependence $S_{MS}(T)$ in the N and N_D phases. A molecular-dynamics model of a system of ellipsoidal particles^{29,30} predicts a sequence of $I - N_D - D_{hd}$ transitions with $S_c = 0.5 - 0.7$ and high values of $S = 0.7 - 0.95$ in the N_D phase. This differs substantially from experiment. The same sequence of transitions has been obtained by a Monte-Carlo method for an athermal system of disc-shaped particles (sliced spheres with diameter D and thickness L) for $L/D < 0.14$ [Ref. 9]. The $I - N_D$ phase transition in this kind of system is a weak first-order transition with $S_c = 0.3 - 0.4$. For a system of discs with $L = 0$ and an effective density $\rho = ND^3/V$ (Ref. 31), the $I - N_D$ transition point for $\rho = \rho_c$ corresponds to $S_c \approx 0.37$ and the $S(\rho)$ dependence in the N_D phase is well approximated by $S \propto (\rho - \rho_H)^{\beta_H}$ with $\beta_H = 0.23 \pm 0.03$. Here ρ_H is analogous to T_H in Eq. (5). The good agreement between β_H and the experimental value confirms the role, mentioned above, of steric intermolecular interactions in the ordering of the N_D phase, but a noticeable discrepancy in the values of S_c remains, especially with LC-1.

The quantity ξ_0 calculated using the same model of infinitely thin discs³¹ in the isotropic phase far from the $I - N_D$ transition was small compared to the diameter of a disc. It is interesting to compare this with experimental data for LC-2. Taking an upper-bound estimate $\Delta H = 200$ J/mole for this sample,¹⁴ $S_c = 0.322$ (Fig. 4), and $\rho \approx 0.8$ g/cm³ (Ref. 32), we obtain an upper-bound estimate of $a = 4.24 \cdot 10^{-3}$ J/cm³ K, which is a factor of 22 smaller than for MBBA¹⁰ with the same value of S_c and comparable to a typical value $a = 2.9 \cdot 10^{-3}$ J/cm³ K for the micellar nematic discoid phase of DACI.¹⁷ In the one-constant approximation the parameter L_1 in the formula $\xi_{0i} = \sqrt{L_1/aT^*}$ is related to the elastic deformation modulus of the nematic by the formula $K = 2s^2L_1$. Since the elastic moduli for thermotropic calamite and discoid nematics (in particular, for LC-2 and the members of its homological series) are similar,^{14,32} as are the values of S , for LC-2 the parameter ξ_{0i} must be at least $\sqrt{22} \approx 5$ times greater than the value $\xi_{0i} \approx 6$ Å for MBBA (Ref. 23), i.e., $\xi_{0i} \geq 30$ Å. This is comparable to the diameter $2a_i \approx 42$ Å of the LC-2 molecule modelled as a spheroid with $a_i = 2.25$ Å for $\rho \approx 0.8$ g/cm³ (Ref. 32). Thus, the anomalously low ΔH for the $N_D - I$ transition^{11,14,15} mentioned in the Introduction is related to the smallness of the parameter a , so that the thermotropic nematics form a bridge between the thermotropic calamite and micellar discoid nematics. Note that ξ_{0i} is comparable to the molecular size in a direction perpendicular to the directrix \mathbf{n} for the thermotropic N

and N_D phases, on one hand, and for the N_D phases in the thermotropic and lyotropic liquid crystals, on the other. This establishes a relationship between ξ_{0i} and the local symmetry of the nematic phase.

The smallness of a corresponds to high values of the nematic susceptibility $\chi_i = 1/a(T - T^*)$ in the isotropic phase and χ in the N_D phase. This explains the above-mentioned high birefringence $\Delta n \propto \chi_i$ of the isotropic phase in a shear flow for a discoid nematic with anomalously low $\Delta H = 20 \pm 10$ J/mole.¹¹

The discotic phase and the $N_D - D_{hd}$ transition

The values of $S = Q(D_{hd})/Q_0(N_D)$ for the discotic phase of LC-2 shown in Fig. 4 show that the $N_D - D_{hd}$ transition is accompanied by a large change $\Delta S \approx 0.1$, as is the $D_{hd} - N_{DR}$ transition into the recovered nematic phase in other compounds of the same homological series.⁵ The value of S in the D_{hd} phase of LC-2 is noticeably lower than $S \approx 0.85 - 0.95$ for the D_{ho} phase with translational ordering of the molecules along the axes of the columns.^{1,33,34} This is evidence of strong coupling of the translational ordering of the molecules in a column with the orientational ordering of their I axes relative to the axis of a column coinciding with \mathbf{n} . In the N_D phase of LC-2 near T_{ND} there is no anomalous rise in S of the sort that is characteristic for first order $N - S_A$ transitions close to the tricritical point.^{13,35} An $N_D - D_{hd}$ transition is not accompanied by strong pretransition fluctuations of the local discotic ordering in the nematic phase. This explains the lack of fluctuation growth in the K_{11} modulus near T_{ND} in LC-2 [Ref. 14] and other homologs of this series³² that might be expected when the $N_D - D_{hd}$ transition is close to a second-order transition.^{2,8,36}

The large magnitude of $\Delta S(T_{ND})$ is in qualitative agreement with the data of Refs. 6, 7, and 9 and differs substantially from a molecular-dynamics simulation^{29,30} which predicts a jump $\Delta S \approx 0.01$ for $S(T_{ND}) = 0.9 - 0.95$. For the $N_D - D_{h(o,d)}$ transition the order parameter S is noncritical and the change $\Delta S(T_{ND})$ is caused by its interaction with the critical order parameter for this transition, the multicomponent vector ψ which fixes the two-dimensional lattice.^{1,2,8} The lower order invariant which takes this interaction into account in the thermodynamic potential of the D_h phase has the form $\Delta\Phi(S_{ij}, \psi) = -\lambda_I S |\psi|^2$ (Refs. 8 and 12), where $\lambda_I = \text{const} > 0$. Thus, in the D_h phase

$$S = S_N + \lambda_I \chi |\psi|^2, \quad (6)$$

and the large magnitude of ΔS when $T_c - T_{ND}$ is large is evidence of a large value of λ_I .⁵ This provides a qualitative distinction between the $N_D - D_{h(o,d)}$ transition and the first-order $N - S_A$ transitions, for which the analogous coupling constant λ_I of the nematic and one-dimensional smectic orderings of the molecules is small¹³ and ΔS is large only in the neighborhood of an $N - I$ transition for low S_N , a strong dependence $S_N(T)$, and large susceptibilities χ .¹⁰ Substituting S from (6) in the expression⁸ for $\Delta\Phi(S_{ij}, \psi)$ shows that the coupling of S and ψ leads to a shift in T_{ND} , to renormalization of the expansion coefficient for the invariant $\propto |\psi|^4$ in the one-parameter potential $\Phi(P, T, |\psi|)$, and to a change in the equilibrium value and temperature dependence

of $|\psi|$, but does not affect the order of the $N_D - D_h$ transition. It is clear from Fig. 4 that in the D_{hd} phase, the $S(T)$ dependence is an extension of the dependence $S_N(T)$ shifted upward by a constant amount $\Delta S(T_{ND})$. With Eq. (6) this is evidence of a weak change in $|\psi(T)|$, of a value of $|\psi(T_{ND})|$ close to saturation, and of a strong first order $N_D - D_{hd}$ transition.

On the other hand, calorimetric data¹⁴ indicate that $\Delta H(T_{ND})$ is small and that the $N_D - D_{hd}$ transition is close to second order. The apparent contradiction in the structural data is eliminated if we note that $\Delta H(T_{ND}) = a_D |\psi(T_{ND})|^2 T_{ND}/2$ and the smallness of ΔH may be caused by a smallness of the parameter a_D in a way similar to the smallness of $\Delta H(T_c)$ for an $N_D - I$ transition. The change in the entropy of the liquid crystal during an $N_D - D_{hd}$ transition is equal to

$$\Delta\Xi(T_{ND}) = \Xi_N - \Xi_D = a_D |\psi(T_{ND})|^2/2.$$

The microscopic reason for the smallness of $\Delta\Xi$ and a_D is the following: the $N_D - D_h$ transition is characterized by layering of the nematic phase with segregation of the molecular aromatic cores and aliphatic chains. Because of a major limitation in the freedom of the orientational fluctuations of the molecular axes I relative to the column axis, here the increase $\Delta S(T_{ND})$ for the cores causes a reduction in the entropy Ξ_D along with the reduction owing to the discotic ordering of the molecules. However, because of the friability that is intrinsic to discogenic molecules, the columnar ordering of the molecules greatly increases the free volume at their free ends compared to the nematic phase. This reduces the steric limitation on the spectrum of possible conformational states of the chains and explains their high conformational mobility and the orientationally molten state in the discotic phases,^{1,33,34} including for the homologs of the LC-2 series.^{26,37} We note the analogy between the orientational melting of peripheral fragments of the molecular chains in $N - S_A$ transitions³⁵ and $N_D - D_{h(o,d)}$ transitions. Since the D_h phases are formed by molecules with rather long chains¹ and a large set of possible conformational states in the absence of steric limitations, the conformational disordering of the chains in an $N_D - D_{hd}$ transition enhances the entropy Ξ_D and reduces the entropy jump $\Delta\Xi(T_{ND})$, thereby leading to small $\Delta H(T_{ND})$.

Thus, unlike the structural phase transitions in systems of rigid particles, where the fact that ΔH and $\Delta\Xi$ are small is related to a small jump in the ordering parameter, in the case of first-order phase transitions in liquid crystals, their closeness to second-order transitions in the thermodynamic sense (small ΔH and $\Delta\Xi$) does not always correspond to weak structural changes—a small jump in the corresponding critical order parameter and in the noncritical order parameters which interact with it.³⁸

The high value of the parameter λ in Eq. (6) is also related to the presence of peripheral chains of molecules. In fact, the tendency to layering of the N_D phase is enhanced as the chains become longer, and this is accompanied by a narrowing of the region where the N_D phase exists.¹ The latter corresponds to a growth in λ_I (Ref. 8) or in the ratio d/d_0 of the column diameter d to the diameter d_0 of the molecular core. For sufficiently long chains,¹ large interaction constants

λ_1 (Ref. 8) or parameters $\alpha = 2 \exp[-(2\pi d_0/\sqrt{2}d)^2] > 0.64$ (Ref. 7), the D_h phase develops directly from the isotropic liquid, as happens for LC-2.

The nature of the recovered polymorphism of the discotics can be related to the above-mentioned dependence of the conformational state of the peripheral molecular chains on the temperature and phase state. It can be shown by analogy with earlier papers^{35,39} that the opposite effect of the nematic and columnar orderings of the molecules on the orientational order (conformational state) of the molecular chains R leads to a reduction in the interaction constant λ_1 and to the appearance of an additional invariant $\Delta\Phi(S, \psi) = \lambda_2 S^2 |\psi|^2$, where $\lambda_2 > 0$, in the thermodynamic potential of the D_h phase. For an appropriate ratio of λ_1 and λ_2 this ensures the possibility of a $D_h - N_{DR}$ transition into the recovered nematic phase with a drop in temperature by analogy with the $S_A - N_R$ transition.¹³

3. S(T) AND THE LANDAU-DE GENNES THEORY

In the N phase the increase in the conformational mobility of the chains and the reduction in the anisotropy of the molecular form on approaching T_c take place in conjunction with a reduction in S .^{13,39} This shows up in the temperature dependence $S(T)$ and in the character of the $N_D(N) - I$ transition or in the functional dependence of $\Delta\Phi(T, S)$, the density of the thermodynamic potential of the N_D phase. Thus, in the framework of the Landau-de Gennes theory for a uniformly oriented nematic N_D we write $\Delta\Phi(T, S)$ in the form

$$\Delta\Phi(T, S) = \frac{1}{2} a(T - T^*)S^2 + \frac{1}{3} BS^3 + \frac{1}{4} CS^4 + \frac{1}{6} DS^6. \quad (7)$$

which makes it possible to account for the possible closeness of an $N_D - I$ transition to an isolated Landau critical point ($B=0$) and a tricritical point ($C=0$). When a term αS^3 is present, the term αS^5 is unimportant.¹³ We now switch to the variable $y = S/S_1$ and introduce the parameter

$$R = (4y_c^3 - 9y_c + 4)/(4 - 3y_c), \quad (8)$$

where $S_1 = S(T_1)$, T_1 is the maximum temperature for stability of the N_D phase, and $y_c = y(T_c)$. The coefficients in the expansion (7) can be written in the form

$$a/D = S_1^4 R / (T_1 - T^*), \quad B/D = 2S_1^3 (1 - R), \\ C/D = S_1^2 (R - 3), \quad (9)$$

from which it is clear that the parameter R determines the relative magnitude and sign of the coefficients B and C and the character of the $N_D - I$ transition. Values of $S > 0$ correspond to $B < 0$ and $R > 1$. The reciprocal susceptibility of the N_D phase equals

$$\chi^{-1} = \Phi''(y) = 2DS_1^4(y-1)[2y(y+1)+R-1], \quad (10)$$

and the conditions $\chi(y_c) > 0$ and $D \geq 0$ imply the restrictions $y_c \leq 4/3$ and $1/R \geq 0$. Given Eq. (9), the equation of state takes the form

$$(y-1)^2[(y+1)^2+R-1] = Rt/t^*, \quad (11)$$

where $t = 1 - T/T_1$ and $t^* = 1 - T^*/T_1$.

We now investigate the feasibility of describing the experimental $S(T)$ curve in the N_D phase of LC-1,2 by Eq. (11). Differentiating both sides of Eq. (11) with respect to t and then multiplying by t and using Eq. (11), we obtain

$$\beta_1^{\text{eff}} = \frac{d \ln y}{d \ln t} = \frac{(y-1)[(y+1)^2+R-1]}{2y[2y(y+1)+R-1]}. \quad (12)$$

Dividing Eq. (11) by Eq. (10) and using the first of Eqs. (9) yields

$$\chi = \beta_1^{\text{eff}} / a(T_1 - T). \quad (13)$$

On approximating the experimental $S(T)$ curve by Eq. (5) with Q replaced by S , we have

$$-\frac{d \ln S}{dT} = \frac{\beta_H}{T_H - T} = \frac{\beta_1^{\text{eff}}(T)}{T_1 - T}. \quad (14)$$

When $T_1 - T \gg T_H - T_1$ holds the equation $\beta_1^{\text{eff}} \approx \beta_H$ is satisfied and establishes the relationship of the experimental values of β_H to the character of the $N(N_D) - I$ transitions. For $T_c - T_p \gg T_H - T_c$, where T_p is a reference point, $\beta_1^{\text{eff}}(T_p)$ depends on the number and form of the terms in Eq. (7), but the form of the series (7) that describes the experimental $S(T)$ curve within the interval $T_c - T_p$ for a given sample can be judged from the experimental value of $\beta_H \approx \beta_1^{\text{eff}}(T_p)$ for a specific compound. The inequality $T_c - T_p \gg T_H - T_c$ is clearly satisfied at $S_p = S(T_p) = 2S_c$ for all the known mesogenic compounds which form N and N_D phases. The specific form of the series (7) with a range of variation $0 \leq 1/R < 1$ corresponds to the interval $5/24 < \beta_1^{\text{eff}}(2S_c) \leq 5/16$, which includes the experimental β_H for LC-1, 2. A description of the $S(T) \leq 2S_c$ curve for nematics with $\beta_H \approx \beta_1^{\text{eff}}(2S_c) \leq 0.2$ requires that higher order terms be included in the expansion (7). The reduction in the range of variation of $S(T) \leq 2S_c$ when the inequality $T_c - T_p \gg T_H - T_c$ is satisfied makes it possible to use Eq. (7) for describing $S(T)$ in nematics when $\beta_h < 0.2$, since the function $\beta_1^{\text{eff}}(S_p)$ falls off as S_p decreases for fixed R .

Setting $\beta_H = \beta_1^{\text{eff}}(T_p)$ in Eq. (12), using $y = py_c$ and $p = S_p/S_c$, together with $R(y_c)$ from Eq. (8), we obtain the following equation:

$$y_c^4 p [2 + (2 - 3p^2)(1 - 4\beta_H)] + y_c^3 [p^2(4p - 3)(1 - 4\beta_H) - 4] + y_c^2 p(4p - 3)(1 - 4\beta_H) + y_c(9 - 4p) - 4 = 0, \quad (15)$$

whose solution yields y_c , R , and the coefficients in Eq. (9).

The nematic phase of LC-1

For $\beta_1^{\text{eff}}(T_c - 38.2 \text{ K}) = \beta_H = 0.247^{+0.007}_{-0.003}$ and $S_c = 0.212^{+0.002}_{-0.004}$, the physical root of Eq. (15) is $y_c = 1.284^{+0.010}_{-0.007}$, which corresponds to $S_1 = 0.165^{+0.003}_{-0.002}$, $R = 6.159^{+2.492}_{-1.208}$, and the following parameters:

$$aT_c/D = 1.094^{+0.022}_{-0.012}, \quad B/D = -0.046^{+0.019}_{-0.012}, \\ C/D = 0.086^{+0.062}_{-0.034}. \quad (16)$$

Substituting R in Eq. (11) for the extremal points $T = T_c - 38.2 \text{ K}$ and $T = T_c$ yields $T_c - T^* = 1.344^{+0.389}_{-0.311} \text{ K}$ and $T_1 - T_c = 0.211^{+0.046}_{-0.040} \text{ K}$, which are typical for thermodynamically stable N and N_D nematics.^{12,13} Note that the

$S_{MS}(T)$ curves in Fig. 3 correspond to a difference $T_c - T^* = 34$ K. For intermediate values $0 < \Delta T < 38.2$ K, Eq. (11) yields good agreement between the calculated $S(T)$ and the experimental curve, as well as with the approximation (5) for $S(T)$ given the anisotropy of the local field and $\beta_H = 0.247$. The greatest difference in the values of $S(T)$ given by Eqs. (11) and (5) occurs for $T_c - T = 1 - 2$ K and is ≈ 0.004 , which corresponds to the accuracy with which S is determined. For $T = 0$, we obtain $S_0 = 1.013_{+0.001}^{-0.005}$ from Eq. (11), in agreement with the expected value, $S_0 = 1$, if we note that the relative interval for extraction to $T = 0$ is equal to $(T_c - 38 \text{ K})/38 \text{ K} = 8.8 \gg 1$.

When the correction for the local field is not included in Eq. (1) and we take $\beta_1^{\text{eff}}(T_c - 38.2 \text{ K}) = \beta_H = 0.255_{-0.001}^{+0.008}$ and $S_c = 0.212_{-0.007}^{-0.003}$, the physical root of Eq. (15) is $y_c = 1.293_{-0.002}^{+0.009}$, which corresponds to $S_1 = 0.156_{-0.005}^{-0.003}$, $R = 8.345_{-0.568}^{+3.470}$, and the following parameters:

$$\begin{aligned} aT_c/D &= 1.110_{-0.040}^{+0.056}, & B/D &= -0.056_{-0.019}^{+0.021}, \\ C/D &= 0.130_{-0.022}^{+0.076}, \end{aligned} \quad (17)$$

$T_c - T^* = 1.443_{-0.324}^{+0.371}$ K and $T_1 - T_c = 0.216_{-0.047}^{+0.040}$ K. For $T = 0$, Eq. (11) gives $S_0 = 1.009_{+0.015}^{-0.003}$. A comparison of these data with those given above shows that the magnitude of σ and the dependence $\sigma(T)$ in Eq. (1) have slight effect on the parameters which characterize the behavior of the $N_D - I$ transition. The values of y_c , R , $T_1 - T_c$, and $T_c - T^*$ do not depend on the absolute magnitude of S , but depend strongly on β_H and $T_H - T_c$. The values of S_1 and the parameters of Eq. (9) depend on the absolute magnitude of S .

The coefficients (16) of the potential (7) are small compared to the case of calamite nematics (roughly a factor of four smaller than for MBBA¹³) and the $N_D - I$ transition in LC-1 is simultaneously close to an isolated Landau critical point and to a tricritical point. The reason why B is small is not yet clear, since the biaxiality of the polarizability tensor γ (molecular form), which leads to a reduction in B and makes the $I - N$ transition close to a second order transition in the calamite liquid crystals,^{13,40} is absent in this case. One of the reasons why C is small, as for the calamite nematics, may be the interrelated variations in S and the conformational mobility of the molecular fragments.^{13,39}

The nematic phase of LC-2

For $\beta_1^{\text{eff}}(T_c - 15 \text{ K}) = \beta_H = 0.228_{-0.002}^{+0.006}$ and $S_c = 0.322_{-0.005}^{-0.006}$, Eq. (15) has the physical root $y_c = 1.311_{-0.003}^{+0.005}$, which corresponds to the parameters $S_1 = 0.246_{-0.001}^{+0.006}$, $R = 18.119_{-2.603}^{+6.352}$, $T_c - T^* = 9.036_{-0.608}^{+0.530}$ K, $T_1 - T_c = 1.232_{-0.072}^{+0.047}$ K, and the following coefficients for the series (7):

$$\begin{aligned} aT_c/D &= 2.295_{-0.155}^{+0.364}, & B/D &= -0.510_{-0.073}^{+0.139}, \\ C/D &= 0.915_{-0.152}^{+0.322}. \end{aligned} \quad (18)$$

As can be seen from Fig. 4, over the entire range of the mesophase the values of $S(T)$ given by Eq. (11) are in good agreement with experiment. For $T = 0$, Eq. (11) gives $S_0 = 1.132_{-0.005}^{+0.012}$ for a relative extrapolation interval of $(T_c - 15 \text{ K})/15 \text{ K} \approx 23$. The resulting value of $T_c - T^*$,

which is comparable to the region over which the N_D phase of LC-2 exists, correlates well with the metastable character of this phase in this compound^{14,22} and reveals the absence of any interrelation between the value of $\beta_H \approx 0.23$, which is close to 0.25, and the closeness of the $N_D - I$ transition to a tricritical point.³¹ In fact, for $\beta_H = 0.25$, Eq. (25) takes the form $y_c p = 2R(y_c)/[R(y_c) - 3]$, and y_c and $R(y_c)$ depend on the width of the interval $S_c \leq S \leq S_p$ and the value of p . When we go from Eq. (16) to Eq. (18) the relative values of B/D and C/D increased by a factor of 11, while aT_c/D only increased by a factor of two for similar values of T_c for both liquid crystals. This indicates the existence of common causes for the changes in and smallness of the coefficients B and C in thermodynamically stable N and N_D phases.

Thus, the Landau-de Gennes theory describes $S(T)$ quantitatively over the entire interval of the N_D phase and provides a justification for the empirical approximation of Haller (5) for the liquid crystals discussed here, as for the calamite nematics.⁴¹ Neglecting the weak anisotropy of the correlation lengths $\xi_{n,i}$ along and transverse to the directrix, when the gradient term $L_1(\nabla S)^2/2$ is included in Eq. (7) it is possible to obtain⁴² an expression for the correlation lengths $\xi = \sqrt{L_1 \chi}$ of the equilibrium fluctuations in the modulus of S . In the nematic phase, given Eq. (13), we have $\xi_0 = \sqrt{L_1 \beta_1^{\text{eff}}(T=0)/aT_1}$ and $\xi_0 = \xi_{0i} \sqrt{\beta_1^{\text{eff}}(T=0)}$. For similar L_1 and β_1^{eff} in the thermotropic N and N_D phases, the anomalously low values of a for the discoid nematics correspond to large ξ_0 . The root mean square long-wavelength fluctuation $\langle (\delta S)^2 \rangle_V$ in a given volume V of a sample is given in the gaussian approximation by⁴²

$$\langle (\delta S)^2 \rangle_V = k_B T \chi / V. \quad (19)$$

Let us approximate the functions $S(t)$ and $\chi(t)$ by the expressions

$$S = S_0 t^{\beta_1}, \quad \chi = \chi_0 t^{-\gamma'} \quad (20)$$

with temperature dependent exponents β_1 and γ' . According to Eq. (19), in the correlation volume of the sample, $V_\xi = 4\pi\xi^3/3$, we have

$$\kappa = \frac{\langle (\delta S)^2 \rangle_V}{S^2} = \frac{3k_B T t^\varepsilon}{4\pi S_0^2 L_1 \xi_0}, \quad (21)$$

with $\varepsilon = (\gamma' - 4\beta_1)/2$. For LC-1,2, over the entire interval of the N_D phase, we have $t^\varepsilon \approx 1$ and, because ξ_0 is large, the Levanyuk-Ginzburg criterion⁴² $\kappa \ll 1$ is satisfied, which justifies the use of the Landau-de Gennes theory in the nematic phase. This fact greatly simplifies the problem of obtaining quantitative information on the susceptibilities $S^{(n)}$ of the nematic phase.

4. NONLINEAR RESPONSE OF NEMATICS TO FIELD INTERACTIONS

A large group of interactions can be correlated with a tensor field h_{ij} that is thermodynamically conjugate to the order parameter S_{ij} , where the components h_{ij} are determined by the physical nature of the perturbation ($h_{ij} \propto E_i E_j$, $\nabla_i E_j$, $\nabla_i T \nabla_j T$, etc.). We shall consider fields h_{ij} which lead produce a change in S for a uniform orientation \mathbf{n} .

We write the thermodynamic potential density of the nematic in the form

$$\Delta\Phi(S, T, h) = \Delta\Phi(S, T) - hS. \quad (22)$$

where it is understood in both parts that Φ depends on the pressure. The equation of state

$$\partial\Phi(S, T)/\partial S = h, \quad (23)$$

for $h \neq 0$ and $h = 0$ has the solutions $S(T, h)$ and $S_e(T) = S(T, h = 0)$, respectively. Expanding the left hand side of Eq. (23) as a series in $\delta = S - S_e$ in the neighborhood of S_e for fixed T , we obtain

$$h = \sum_{n=1}^{\infty} \frac{1}{n!} \Phi^{(n+1)}(S_e) \delta^n = \sum_{n=1}^{\infty} \alpha_n \delta^n, \quad (24)$$

where $\Phi^{(n)}(S_e) = [\partial^n \Phi(S, T)/\partial S^n]_{S=S_e}$. Inversion of the series (24) gives

$$\delta = \sum_{m=1}^{\infty} \beta_m h^m, \quad (25)$$

where the coefficients β_m are expressed in terms of the coefficients α_n by solving the system of sequential equations obtained by equating to zero all the coefficients for all powers of δ ($p = 1, 2, 3, \dots$) in the equation

$$\delta - \sum_{p=1}^{\infty} \delta^p \sum_{m=1}^p \beta_m \sum_{\{m_k\}} C_m(m_1, \dots, m_p) \prod_k \alpha_k^{m_k} = 0.$$

Here the polynomial coefficient is

$$C_m(m_1, \dots, m_p) = m! \left[\prod_{k=1}^p (m_k!) \right]^{-1}$$

and the summation is taken over all possible sets $\{m_k\}$ of nonnegative integers $m_k = 0, 1, 2, \dots$ satisfying the conditions

$$\sum_k m_k = m, \quad \sum_k k m_k = p.$$

For the following discussion we introduce the first of these coefficients:

$$\begin{aligned} \beta_1 &= \alpha_1^{-1}, & \beta_2 &= -\alpha_1^{-3} \alpha_2, & \beta_3 &= \alpha_1^{-5} (2\alpha_2^2 \\ & & & & & - \alpha_1 \alpha_3), & \beta_4 &= \alpha_1^{-7} (5\alpha_1 \alpha_2 \alpha_3 - \alpha_1^2 \alpha_4 - 5\alpha_2^3). \end{aligned} \quad (26)$$

Comparing Eq. (25) with the expansion

$$\delta = \sum_{m=1}^{\infty} \frac{1}{m!} S^{(m)} h^m \quad (27)$$

yields the desired relationship

$$S^{(m)} = m! \beta_m. \quad (28)$$

In order to make the physical nature of the interaction specific or to compare the $S^{(m)}$ for different samples with a certain type of interaction, we must replace h in Eq. (22) by Kh , where the parameter K is defined by the nature of the interaction and the physical properties of the sample. Then we have $S_k^{(m)} = K^m S^{(m)}$, which is an indication of high nonlinear susceptibilities for samples with large K . Furthermore,

it is evident from Eqs. (26) and (28) that choosing a nematic with a large $\chi = 1/\alpha_1$ ensures high susceptibilities $S^{(m)}$ for all types of field h conjugate to the modulus S . Thus, discoid nematics with small a in Eq. (13) and large χ are promising materials for technical applications.

The Landau-de Gennes potential $\Delta\Phi(S, T)$

Let us consider a potential with the specific form

$$\Delta\Phi(S, T) = \sum_{n=2}^N \frac{a_n}{n} S^n \quad (29)$$

in Eq. (22) with $a_2 = a(T - T^*)$ and the remaining coefficients a_n independent of temperature. Here $a_n(n-1)! = [\partial^n \Phi(S, T)/\partial S^n]_{S=0} \equiv \Phi^{(n)}(0)$. For an isotropic phase with $S_e = 0$, the coefficients of the series (24) and (29) are related by $\alpha_n = a_{n+1}$ and in Eq. (28) $S^{(2)} \propto (T - T^*)^{-3}$, while the higher-order susceptibilities are not power-law functions of $(T - T^*)$. As can be seen from Eq. (26) the presence of odd powers of the order parameter in the potential (29) ensures that the even susceptibilities $S^{(m)}$ are nonzero in the isotropic phase.

For $h = 0$ the equation of state (23) with the potential (29) has the form

$$a(T - T^*) = - \sum_{n=3}^N a_n S^{n-2}. \quad (30)$$

Furthermore, Eq. (29) implies that

$$\Phi^{(2)}(S, T) = a(T - T^*) + \sum_n (n-1) a_n S^{n-2}. \quad (31)$$

Substituting Eq. (30) in Eq. (31) gives

$$\Phi^{(2)}(S_e) = \sum_n (n-2) a_n S_e^{n-2}, \quad (32)$$

where the equilibrium value of $S_e(T)$ is the solution of Eq. (30) and minimizes the potential (29) in the nematic phase. Differentiating both sides of Eq. (30) with respect to T , multiplying then by S , and comparing with Eq. (32) for $S = S_e(T)$, we obtain an expression

$$\Phi^{(2)}(S_e) \equiv \chi^{-1} = \left[\frac{1}{aT_1} \frac{d(\ln S_e)}{dt} \right]^{-1}, \quad (33)$$

which is independent of the number and form of the terms of the series (30) for $a_n = \text{const}$. Given Eq. (32), the expression for the derivative

$$\Phi^{(3)}(S_e) = \sum_n (n-2)^2 a_n S_e^{n-3} + \sum_n (n-2) a_n S_e^{n-3}$$

can be written in the form

$$\Phi^{(3)}(S_e) = \frac{d\Phi^{(2)}(S_e)}{dS_e} + \frac{\Phi^{(2)}(S_e)}{S_e},$$

from which, using Eq. (33), we obtain

$$\Phi^{(3)}(S_e) = - \frac{1}{aT_1 \chi^3} \frac{d(\chi/S_e)}{dt}. \quad (34)$$

Using Eq. (33) yields a recurrence relation for the higher-order derivatives in Eq. (24),

$$\Phi^{(n+1)}(S_e) = \frac{1}{aT_1 S_e \chi} \frac{d\Phi^{(n)}(S_e)}{dt} \quad (n \geq 3). \quad (35)$$

which, along with Eqs. (33) and (34), can be used to express α_n , β_m , and $S^{(m)}$ in terms of the function $S_e(T)$ and its temperature derivatives. For the calamite^{10,41,43} and discoid thermotropic nematics (Ref. 4 and the present paper), the experimental $S(T)$ curve is described by the equation of state (30) when the appropriate number and type of expansion terms are included for each specific sample. Thus, the experimental $S(T)$ curve can be used in Eqs. (24), (26), (28), and (33)–(35) to determine the nonlinear susceptibilities $S^{(m)}$ similarly to χ .¹⁰ This makes it possible to avoid separating the contributions from different orders of h in $\delta(h)$,^{19,43,44} shifts in $T_c(h)$ in strong fields, and other difficulties involved in the direct experimental determination of the $S^{(m)}$, which is important for studies of the critical behavior of the $S^{(m)}$ in the neighborhood of an $N(N_D) - I$ transition.

5. CRITICAL BEHAVIOR OF DISCOID NEMATICS

The critical behavior of nematics in the neighborhood of an $N(N_D) - I$ transition is characterized by temperature dependence in the exponents β_1 and γ' in Eq. (20) and in the indices β and Δ' defined by the equations

$$S = S_1 + (S_0 - S_1)t^\beta, \quad f \equiv S^{(2)}/\chi = f_0 t^{-\Delta'}. \quad (36)$$

For the correlation length $\xi = \xi_0 t^{-\nu'}$ we have $\nu' = \gamma'/2$. The isobaric specific heat of the nematic phase $\Delta C_p = -aTS(\partial S/\partial T)_p$ can be written using Eq. (33) in the form $\Delta C_p = a^2 TS^2 \chi = a^2 S_0^2 \chi_0 T t^{-\alpha'}$, with $\alpha' = \gamma' - 2\beta_1$ and $\chi_0 = \beta_1^{\text{eff}}(T=0)/aT_1$. Equations (26) and (28) imply

$$f = -\chi^2 \Phi^{(3)}(S_e) = -\chi_0^2 \Phi^{(3)}(S_0) t^{-\Delta'}. \quad (37)$$

The proper exponents in Eqs. (20) and (36) are given by

$$\beta_1 = \frac{\ln(y/y_0)}{\ln t}, \quad \beta = \frac{\ln[(y-1)/(y_0-1)]}{\ln t},$$

$$\gamma' = -\frac{\ln(\chi/\chi_0)}{\ln t}, \quad \Delta' = 2\gamma' - \frac{\ln[\Phi^{(3)}(y)/\Phi^{(3)}(y_0)]}{\ln t}. \quad (38)$$

They cannot be determined directly from experimental data if S_0 , χ_0 , f_0 , and $T - T_c$ are not known in advance. However, these exponents can be calculated when the equation of state which describes the experimental $S(T)$ curve is known for a specific sample. Thus, the equation of state (11) implies that

$$t = \frac{(y-1)^2[(y+1)^2 + R - 1]}{(y_0-1)^2[(y_0+1) + R - 1]}, \quad (39)$$

while the expression for $\Phi^{(3)}(y)$ has the form

$$\Phi^{(3)}(y) = 2DS_1^3[10y^3 + 3y(R-3) + 2(1-R)]. \quad (40)$$

Substituting these formulas in Eq. (38) yields an expression for the exponents as functions of $y = Sy_c/S_c$ and R .

For $t \rightarrow 1$ and $y \rightarrow y_0$ the asymptotic behavior of the exponents (38) is given by the formulas $\beta_1 = \beta_1^{\text{eff}}$ (12), $\beta = \beta_{\text{eff}}$, $\gamma = \gamma_{\text{eff}}$, and $\Delta' = \Delta'_{\text{eff}}$, where

$$\beta_{\text{eff}} = \frac{d \ln(y-1)}{d \ln t} = \frac{y}{y-1} \beta_1^{\text{eff}}(y), \quad (41)$$

$$\gamma'_{\text{eff}} = -\frac{d \ln \chi}{d \ln t} = 1 - y \frac{d\beta_1^{\text{eff}}}{dy}, \quad (42)$$

and

$$\Delta'_{\text{eff}} = -\frac{d \ln f}{d \ln t} = 2\gamma'_{\text{eff}} - y\beta_1^{\text{eff}} \frac{\Phi^{(4)}(y)}{\Phi^{(3)}(y)}. \quad (43)$$

Here in deriving Eq. (42) we have used Eq. (13). For a known value of $T_1 - T_c$ the exponents β_1^{eff} , γ'_{eff} , and Δ'_{eff} (the effective exponents) can be determined at each temperature point of the mesophase from the experimental $S(t)$, $\chi(t)$, and $f(t)$ curves. Substituting Eq. (34) in Eq. (37) yields the expression

$$f = \frac{\gamma'_{\text{eff}} + \beta_1^{\text{eff}}}{aS(T - T_1)}, \quad (44)$$

from which, together with Eq. (42), we obtain

$$\Delta'_{\text{eff}} = 1 + \beta_1^{\text{eff}} + \frac{S^2 \beta_1^{\text{eff}}}{\gamma'_{\text{eff}} + \beta_1^{\text{eff}}} \frac{d^2 \beta_1^{\text{eff}}}{dS^2}. \quad (45)$$

Equations (42), (44), and (45) are independent of the number and form of the terms in Eq. (30) with $a_n = \text{const}$, while Eqs. (41) and (43) are independent of the form of $\Delta \Phi(S, T)$. Using Eqs. (12), (40), (42), and (43), for the potential (11) we obtain⁴

$$\gamma'_{\text{eff}} = 1 - \frac{1}{2y} + \frac{(y^3 - 1)(4y + R - 1) + y^2(y - 1)(R + 3)}{2y[2y(y + 1) + R - 1]^2}, \quad (46)$$

and

$$\Delta'_{\text{eff}} = 2\gamma'_{\text{eff}} - \frac{3y\beta_1^{\text{eff}}(10y^2 + R - 3)}{10y^3 + 3y(R - 3) + 2(1 - R)}. \quad (47)$$

For $D = 0$ in Eq. (7), $1/R = 0$, small S_1 , and $y \gg 1$, the exponents approach their asymptotic values $\beta_1^{\text{eff}} = \beta_{\text{eff}} = \nu'_{\text{eff}} = 0.5$, $\gamma'_{\text{eff}} = 1$, $\alpha'_{\text{eff}} = 0$, and $\Delta'_{\text{eff}} = 1.5$ for second-order phase transitions.⁴² For $D \neq 0$, $y \gg 1$, and $y^2 \gg R - 1$, the exponents approach the tricritical values⁴² $\beta_1^{\text{eff}} = \beta_{\text{eff}} = 0.25$, $\nu'_{\text{eff}} = \alpha'_{\text{eff}} = 0.5$, $\gamma'_{\text{eff}} = 1$, and $\Delta'_{\text{eff}} = 1.25$.

For $t \rightarrow 0$ and $y \rightarrow 1$ the asymptotic behavior of the exponents β and γ' also obeys Eqs. (41) and (42) and for $t = 0$ we have $\beta_1 = 0$, $\beta_{\text{eff}} = \gamma'_{\text{eff}} = \alpha'_{\text{eff}} = 0.5$, $\nu'_{\text{eff}} = 0.25$, and $\Delta' = 2\gamma'_{\text{eff}} = 1$. Unlike Δ' (38), the effective exponent Δ'_{eff} (47) varies nonmonotonically as $y \rightarrow 1$ and has a minimum within the interval $1 < y < y_c$. Since β_1 , γ' , and Δ' increase with rising t , the inequalities $\beta_1^{\text{eff}} < \beta_1$, $\gamma'_{\text{eff}} < \gamma'$, and $\Delta'_{\text{eff}} < \Delta'$ are satisfied over the entire mesophase interval, but $\beta_{\text{eff}} > \beta$ holds.

The experimentally determined exponents m_a (the apparent exponents), which correspond to the linear portions of the logarithmic dependences $\ln M(t) = m_a(\Delta t) \ln t$ within a limited temperature interval Δt ,¹³ differ from the true or effective values of these exponents and depend on the location and width of the interval Δt . On the other hand, the values of the exponents $m_a(\Delta t)$ obtained by linearizing¹³ the functions

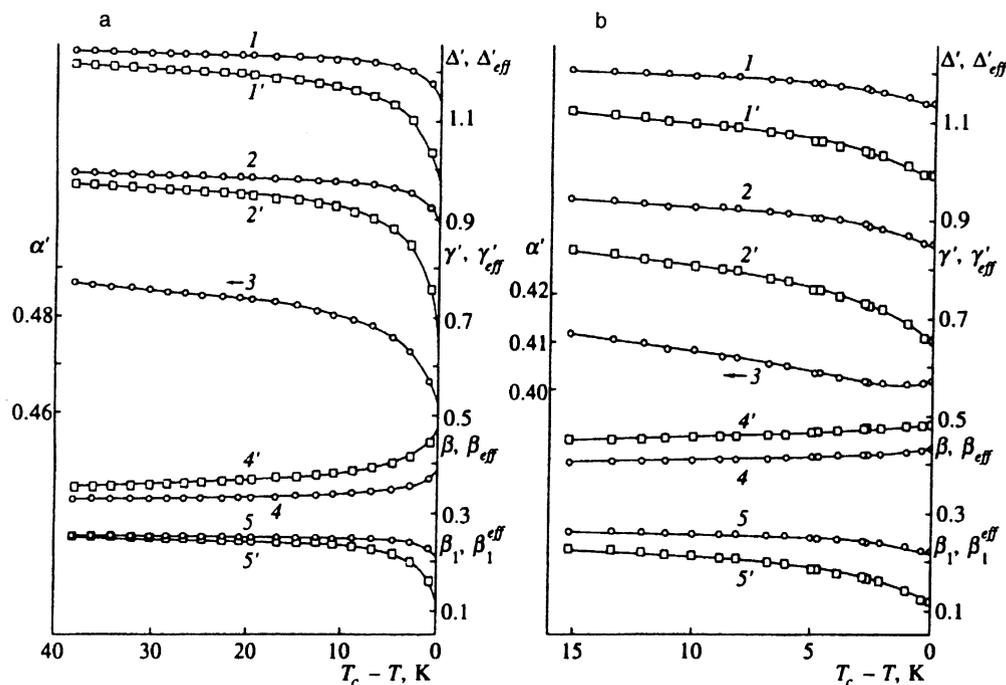


FIG. 5. Temperature variations in the true (circles and curves 1-5) and effective (squares and curves 1'-5') exponents Δ' (1,1'), γ' (2,2'), α' (3'), β (4,4'), and β_1 (5,5') in the nematic N_D phase of LC-1 (a) and LC-2 (b). The points are calculated using Eqs. 38-40 and (12), (41), (46), and (47) with $R=6.159$ (a) and $R=18.119$ (b) and the experimental values of $\gamma=y_c S/S_c$. The continuous curves are calculated with the values of y which satisfy the equation of state (11).

In $M(t)=m_a(\Delta t)\ln t$ within an interval $\Delta t=t_p-t_c$ while varying T_1-T_c (Ref. 13) also depend on Δt and are not associated to the character of the $N(N_D)-I$ transition, while the fit values of T_1 do not correspond to the actual values. Thus, it is natural that the exponents $m_a(\Delta t)$ found in this way for the nematic phases are often not included among any of the theoretical schemes.¹³

For example, using Eq. (36) with the fit parameters^{18-20,45-47} S_1 , S_0-S_1 , T_1 , and β makes it possible to approximate the experimental $S(T)$ curve over a narrow interval $\Delta T=T_c-T$ only at the cost of very low^{19,20} or nonphysical negative values of S_1 .^{18,45} The latter corresponds to $\beta=\text{const}\approx 0.25$. Positive parameters S_1 for the thermotropic calamite and micellar discoid nematics usually correspond to values $\beta=(0.34-0.40)\pm 0.06$ whose nature is still controversial.^{18-20,48}

Figure 5 shows the temperature of the true and effective exponents calculated using Eqs. 38-40 and (12), (41), (46), and (47) for LC-1,2 using the parameters given in Sec. 3. For both liquid crystals the systematic error in the calculated exponents corresponding to an uncertainty $\delta(T_H-T_c)=\pm 0.1$ K is $\delta(\alpha')=+0.01$ over the entire range of the N_D phase and is less than the size of the squares in Fig. 5 for the other exponents. For both samples the exponents (38) very little over the limits of the mesophase. Including the local field anisotropy for LC-1 has a negligibly small effect on the values of the exponents. For LC-1 with small S_1 and large y far from T_c the asymptotic values of the exponents (38) are in good agreement with the effective values (41)-(43). The other asymptotic region of small t , where we have $\beta\approx\beta_{eff}$ and $\gamma'\approx\gamma'_{eff}$, is not accessible to experiment.

The weak dependence $\gamma'(\Delta T)$ shows that on going to the scale of reduced temperatures T_H-T , with $T_H>T_1$, one can, within a limited temperature interval below T_c , approximate the experimental $\chi(T)$ and $\xi(T)$ curves by

expressions of the form $\chi(T)\propto(T_H-T)^{-\gamma'}$ and $\xi(T)\propto(T_H-T)^{-\nu'}$ with constant $\gamma'\approx 1$ and $\nu'\approx 0.5$. This procedure is analogous to the approximation (5) and explains data^{48,49} for the thermodynamically stable calamite nematics with a narrow interval T_1-T^* , while the empirically established interval $(T_H-T_c)/(T_c-T^*)=0.5-0.6$ which applies for a wide range of materials⁴⁹ (in the notation of Ref. 49, $T_H=T^+$) includes the value 0.526 for the LC-1 studied here.

For both liquid crystals the inequality $\Delta'_{eff}(T_c)<1$ indicates that Δ'_{eff} varies nonmonotonically within the interval $T_c<T<T_1$. We note the reduction in $\alpha'(\Delta T)$ on approaching T_c and the nonmonotonic variation in $\alpha'(T)$. For LC-2 and LC-1, respectively, $\alpha'(T)$ has a smooth minimum at $T_c-T=1.5$ K and a sharp maximum within the narrow interval $T_c<T<T_1$, since $\alpha'(T_1)=0.5$.

The $\beta(\Delta T)$ curve is of general interest. This dependence is very weak for both liquid crystals and the change $\beta(\Delta T)$ over the entire range of the N_D phase is less than the error in determining the fit parameter $\beta=\text{const}$.¹⁸⁻²⁰ For LC-1, with a narrow interval T_1-T^* and small R , we have $\beta\approx 0.35\pm 0.03$, which corresponds to the fit values of β for micellar discoid^{19,20} and thermotropic calamite nematics.⁴⁸ For LC-2, with a large R , the value of $\beta\approx 0.42\pm 0.02$ is essentially the same as the fit value $\beta\approx 0.40\pm 0.06$ for a micellar discoid nematic.¹⁸ Thus, the values $\beta=(0.34-0.40)\pm 0.06$ for the isotropic N_D phases, which are associated with highly developed fluctuations in the order parameter S in the neighborhood of the N_D-I transition,^{19,20} have obtained a natural explanation in terms of the Landau-de Gennes theory. This also makes it possible to eliminate the contradiction between the proposed fluctuational nature of the N_D-I transition in micellar nematics^{19,20} and the experimental value of $\gamma=1$ in the isotropic phase.¹⁷

6. CONCLUSION

The above discussion shows that S in the N_D phase is close to the values for the calamite thermotropic nematics and differs greatly from the values predicted by the molecular-statistical theory or computer simulation, especially near the temperature T_c of the N_D-I transition. The Landau-de Gennes theory provides a quantitative description of $S(T)$ over the entire range of existence of both the thermodynamically stable and metastable reversible N_D phases. This justifies the well known empirical approximation procedure of Haller for $S(T)$.

The applicability of the Landau-de Gennes theory in the N_D phase means that the nonlinear susceptibilities $S^{(n)}$ of the nematic phase to fields which are thermodynamically conjugate to the order parameter S can be expressed in terms of the experimentally determined $S(T)$ curve in zero field and its temperature derivatives. This opens up the possibility of choosing nematics with large $S^{(n)}$ for technical applications.

As for the N phases, the N_D-I transition in a thermodynamically stable nematic is simultaneously close to an isolated Landau critical point and to the tricritical point. The question of why the coefficients B (and C) are small remains open, since the molecules of the discoid nematics do not have the biaxial molecular form (or polarizability) which is usually associated with a weak first-order $N-I$ transition. The distinct feature of the N_D-I transitions is the anomalous smallness of the coefficient a compared to S^2 . This makes for a small change in the transition enthalpy ΔH and large direct correlation lengths ξ_0 (ξ_{0i}) for the equilibrium fluctuations S in the nematic (isotropic) phase. An estimate of ξ_0 (ξ_{0i}) is substantially greater than the minimum intermolecular distance (the radius of the maximum intermolecular interaction), so that the Lavanyuk-Ginzburg criterion for validity of the Landau-de Gennes theory is satisfied over the entire range of the nematic phase. The relationship of ξ_{0i} to the molecular dimensions in the N and N_D phases reflects the difference in the local symmetries of these phases.

The N_D-D_{hd} phase transition is a strong first-order transition with a large jump ΔS and no pretransition fluctuational growth in S for $T \geq T_{ND}$. For the D phase there is a strong coupling of the orientational ordering of the molecular cores with their one-dimensional translational ordering within the columns and the two-dimensional translational ordering of the columns themselves. Here orientational melting of the molecular chains during the N_D-D_{hd} transition causes a reduction in the entropy $\Delta \Xi$ (enthalpy ΔH) of the transition and in the coefficient a_D in front of $|\psi|^2$ in the Landau-de Gennes potential for the D phase. All these features of the N_D-D_{hd} transition are related to the very nature of discogenic molecules, for which the presence of peripheral chains is a necessary condition for the development of discotic mesomorphism.

The values of the true and effective exponents for S , $S-S_1$, χ , ξ , and $f=S^{(2)}/\chi$ obtained above from the equation of state for the N_D phase explain the known empirical fitting values of these exponents for the calamite thermotropic and discoid micellar nematics. This is evidence of similar critical behavior in all types of nematics with the same macroscopic symmetry, despite differences in their local symme-

try, the nature of the ordering structural elements (molecules, micelles), and the character of the interactions among them.

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