Effect of smectic fluctuations on pretransitional phenomena in the isotropic phase of a nematic liquid crystal

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A new model that gives a unified description of the formation of nematic and smectic phases of liquid crystals is proposed. Including in this model the influence of smectic fluctuations on the transition from the isotropic liquid to the nematic phase has permitted explaining for the first time the anomalies in the thermodynamic quantities in the isotropic phase of liquid crystals with a narrow nematic region.

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1. In studying phase transitions in liquid crystals, it is necessary to take into account their effect on each other. This is due to two circumstances: 1) many liquid-crystalline transitions are second-order transitions or first-order transitions that are nearly second-order, transitions (i.e., they are accompanied by quite strongly developed fluctuations; 2) the region of existence of mesophases, as a rule, is quite narrow and transitions from one liquid-crystalline modification to another turn out to be close to each other and strongly interacting (see Refs. 1 and 2).

The purpose of this paper is to construct a model that gives a unified description of transitions to the nematic and smectic phases and thereby includes their influence on each other.

In contrast to all known models, we shall assume that the smectic phase, just as the nematic phase, is described by a tensorial order parameter S_{ij}. S_{ij} is a symmetrical traceless tensor of rank 2, whose uniaxial mode has a minimum at some $k = k_0 \sim L^{-1}$, where L^{-1} in dimensionless units is a quantity of the order of the length-to-width ratio of the molecule. This model can be obtained in the phenomenological theory from the usual Landau–de Gennes Hamiltonian for a nematic[1] (with some additional conditions on the constants of the nematic), if terms of sufficiently high order in the gradient expansion are included and the short wavelength part of the nematic order parameter Q_{ij} is separated (which plays the role of S_{ij}).

2. The Hamiltonian of such a system has the form

$$H = H_N + H_{Sm} + H_{int}, \tag{1}$$

where

$$H_N = \frac{1}{2} R_{ij}^{kl} Q_{ij} Q_{kl} + \frac{\gamma_N}{3!} Q_{ij} Q_{jk} Q_{ki} + \frac{\lambda_N}{4!} Q_{ij} Q_{jk} Q_{kl} Q_{li} ,$$

$$H_{Sm} = \frac{1}{2}\Delta_{ij}^{kl} S_{ij} S_{kl} + \frac{\gamma_{Sm}}{3!} S_{ij} S_{jk} S_{ki} + \frac{\lambda_{Sm}}{4!} S_{ij} S_{jk} S_{kl} S_{li},$$

$$H_{int} = \frac{\gamma_{int}}{2} Q_{ij} Q_{jk} S_{ki} + \frac{\lambda_{int}}{4!} (4Q_{ij} Q_{jk} S_{kl} S_{ei} + 2Q_{ij} S_{jk} Q_{kl} S_{ei}).$$

Here H_N and H_{Sm} are the free Hamiltonians which describe the transitions to the nematic and smectic phases, respectively; $H_{\rm int}$ is the Hamiltonian which describes the interaction of the nematic (Q_{ij}) and smectic (S_{ij}) order parameters; R_{ij}^{kl} and Δ_{ij}^{kl} are the tensors of the inverse susceptibility of the nematic and smectic order parameters. In the single-correlation-length approximation, the tensor R_{ij}^{kl} is diagonal,

$$R_{ij}^{kl} = \alpha_N (\tau + r_0^2 q^2) I_{ij}^{kl}, \tag{2}$$

where

$$I_{ij}^{kl} = \frac{\delta_{ik}\delta_{ji} + \delta_{il}\delta_{jk}}{2} - \frac{\delta_{ij}\delta_{kl}}{3}$$

plays the role of the unit tensor; $\tau = (T - T^*)/T^*$ is the dimensionless deviation of the temperature from the critical value (T^*), obtained by extrapolation from a region far from the bleaching temperature (T_{NI}), and r_0 is the direct correlation radius of nematic fluctuations, measured in units of the average distance between molecules. Because of the interaction with the nematic, the cubic invariant, which couples the uniaxial smectic modes, vanishes in the nematic region.

The spectrum of the uniaxial mode, which describes smectic ordering, has the characteristic form of Brazovskiĭ's spectrum[3,4]:

$$\Delta(p) = \alpha_{Sm}\left[\Delta + \xi_{0\parallel}^2 \frac{(p^2 - p_0^2)^2}{4p_0^2}\right], \tag{3}$$

where $\Delta = (T - T_c^{(NA)})/T_c^{(NA)}$, $T_c^{(NA)} = (T_c^{(NI)} - \Delta T)$ is the critical temperature of the N-A transition, $T_c^{(NI)}$ is the critical temperature of the I-N transition, ΔT is approximately equal to the observed width of the nematic zone and $\xi_{0\parallel}$ is the direct correlation radius for the uniaxial smectic mode. Below we assume that $\xi_{0\parallel}^2 p_0^2 \gg \Delta_0 (\Delta_0 = \Delta T/T_c^{(NA)})$, which is satisfied for most liquid crystals with a smectic phase.

In Landau's theory, Hamiltonian (1) describes the following transitions: isotropic liquid-nematic (I-N transition: $Q \neq 0$; $S = 0$) and isotropic liquid-smectic (I-Sm transition: $Q \neq 0$; $S \neq 0$). The angle between the principal axes of the nematic and smectic order parameters is determined by $H_{\rm int}$. It turns out that if the appearance of a smectic condensate occurs for $Q < Q_c \sim \gamma_{\rm int}/\lambda_{\rm int}$, then this angle vanishes (smectic A), and in the opposite case, the angle does not vanish (smectic C). Correspondingly, additional transitions appear in the proposed model: nematic–smectic-A (N-A), nematic–smectic-C (N-C), smectic-A–smectic-C (A-C). All transitions from the isotropic liquid to the ordered phases turn out to be first-order transitions. A tricritical point appears on the

N-A transitions line, and re-entrant behavior is possible. The behavior of thermodynamic quantities is determined by the form of the phase diagrams. Thus, for example, when the nematic region expands, the magnitude of the anomaly is the heat capacity in the *N-A* transition decreases, disappearing completely as the re-entrant point is approached, in accordance with the experimental results (6).[1)]

3. Let us examine more closely the influence of the smectic fluctuations on an *I-N* transition using the proposed model. The phase volume, which is related to fluctuations of the uniaxial smectic mode, is anomalously large. As a result, in the first approximation it is sufficient to include only fluctuations of this type. In the self-consistent-field theory, this leads to the fact that the critical temperature corresponding to the *I-N* transition is displaced and itself becomes a function of the temperature of the system. The singularities of all thermodynamic quantities near this transition are now determined by the quantity $\tilde{\tau} = (T - T_c^{(NI)})/T_c^{(NI)}$.

In the single-loop approximation (as in Refs. 3 and 4) the contribution of other terms is small), the equation for the inverse susceptibility near an *I-N* transition has the form

$$\tilde{\tau} = \tau + \frac{a}{4\pi(\Delta_0 + \tilde{\tau})^{1/2}} - \frac{b}{8\pi(\Delta_0 + \tilde{\tau})^{3/2}}, \qquad (4)$$

where

$$a = \frac{2}{9}\,\frac{\lambda_{int}\, p_0^2}{\alpha_N\, \alpha_{Sm}\, \xi_{0\parallel}}, \qquad b = \frac{1}{30}\,\frac{\gamma_{int}^2\, p_0^2}{\alpha_N\, \alpha_{Sm}^2\, \xi_{0\parallel}}.$$

The quantity $\tilde{\tau}$, defined by Eq. (4) and directly related to the intensity of light scatter-

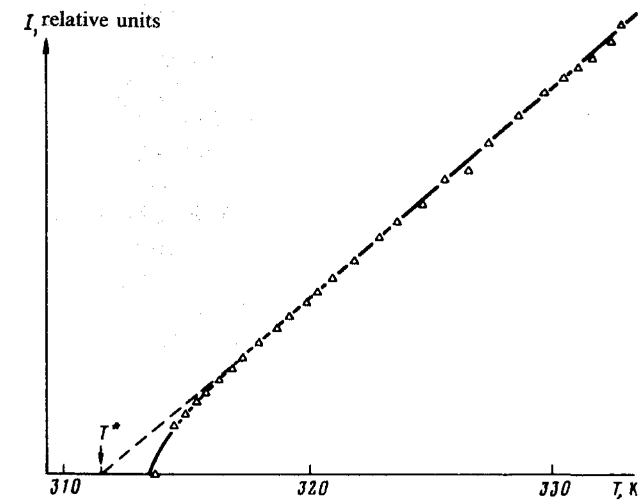

FIG. 1. Temperature dependence of the inverse intensity of light scattering near an *I-N* transition in 8 CB △ are the experimental results.[5] The solid line shows the calculation using Eq. (4) with the following values of the constants: $\triangle T = 7°$ and $a = 0.01$, $b = 0.001$.

ing near the I-N transition ($J \sim \tilde{\tau}^{-1}$), reproduces the "bend," observed experimentally, on the curve of the temperature dependence of the inverse susceptibility (Fig. 1).

4. Smectic fluctuations also renormalize the direct correlation length of smectic fluctuations:

$$\tilde{r}_0^2 = r_0^2 \left[1 + \frac{3b}{32\pi r_0^2 (\Delta_0 + \tilde{\tau})^{5/2}} \right] . \tag{5}$$

The growth $\tilde{r}_0^2$ (which amounts to 40% for 8CB with the values chosen for the constants) must widen the region of applicability of the self-consistent-field theory. We note that inclusion of smectic fluctuations leads to renormalization of the constants γ_N and λ_N in H_N, decreasing, in particular, λ_N, and thereby also extending the region of applicability of the self-consistent-field theory.

5. The fluctuation part of the heat capacity of the I-N transition in the Ornstein-Zernike approximation has the form

$$C_p = \frac{gR}{16\pi \tilde{r}_0^3} \left(\frac{\partial \tilde{\tau}}{\partial \tau} \right)^2 \tilde{\tau}^{-1/2} . \tag{6}$$

Here all quantities are assumed to be renormalized by smectic fluctuations. In the single-correlation-length approximation, $g = 5$. R is the universal gas constant.

The experimental results obtained by Thoen *et al.*[6] and the theoretical curve,

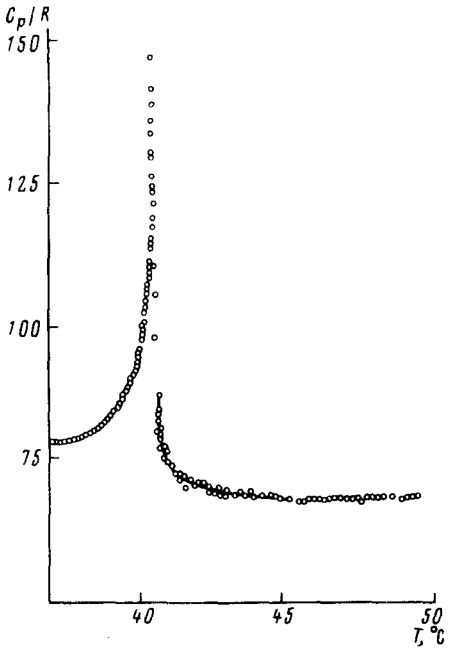

FIG. 2. Heat capacity of 8 CB near an I-N transition.[6] The solid line shows the calculation using Eq. (6).

constructed using Eq. (6) with the same values of the constants Δ_0, a, and b as in Fig. 1, are shown in Fig. 2. The only adjustable parameter was the quantity r_0. In the section from the bleaching point T_{NI} to $T - T_{NI} \approx 5°$, there is nearly complete agreement between theory and experiment, approximated in Ref. 6 by a crossover function. It turned out that $r_0 \approx 1.16$ and $T_{NI} - T_c^{(NI)} \approx 0.2°$ (in Ref. 6 $T_{NI} - T_c^{(NI)} \approx 0.07$).

Equation (6) apparently describes the general behavior of the heat capacity near the I-N transition, independent of whether or not a smectic phase exists in the liquid crystal. If, as the experiment on MBBA,[7] BMOAB,[2)] and others shows, the susceptibility has a "bend" near I-N, then the temperature dependence of the heat capacity will be renormalized according to Eq. (6).

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[1)] A more detailed analysis of the thermodynamic consequences of the proposed model will be published separately.
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