Smectic fluctuations in the Ornstein-Zernike approximation

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It is shown that Ginzburg's criterion for the nematic-smectic-*A* (*NA*) transition contains a small parameter: the ratio of the molecular diameter to the molecular length. This permits studying smectic fluctuations in the Ornstein-Zernike approximation. The nature of the critical behavior in this case depends essentially on the width of the nematic zone.

The model describing phase transitions in liquid crystals (LC) contains two interacting order parameters: the nematic (N) and smectic (Sm) parameters.[1] The cross terms involving the order parameters in the Hamiltonian of this model have the form $\gamma_{\rm int}(N)(Sm)^2$ and $\lambda_{\rm int}(N)^2(Sm)^2$ where $\gamma_{\rm int} < 0$, $\gamma_{\rm int} > 0$. The smectic order parameter is defined on the sphere $|\mathbf{p}| = p_0$ (p_0 is the wave vector in the smectic lattice, in dimensionless values on the order of the ratio a/L, where a is the intermolecular distance, and L is the length of an LC molecule).

The interaction of order parameters leads to the appearance of "singular" points in the phase diagram: a re-entrant point (RP), a triple nematic–smectic-A–smectic-C point (NAC), and a tricritical point (TCP). A typical phase diagram obtained in the model is shown in Fig. 1. The quantity Δ_0 is the difference between the critical tem-

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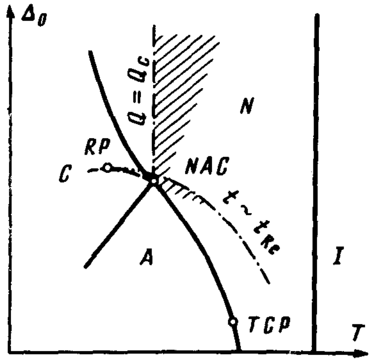

Fig. 1. A typical phase diagram of LC. The singular points on the NA line, which determine the behavior of different quantities for $Q \leqslant Q_c$ (A regime), are indicated. The shaded region shows the region of non-Lorentzian behavior.

peratures of the isotropic-nematic and isotropic-smectic transitions in the absence of their interaction. The phase diagrams are close to the real diagrams precisely in the Δ_0-T plane. The lines of NA and NC transitions are sections of parabolas which join without a break at the NAC point. The re-entrant point of the NA line (the apex of the NA parabola in the Δ_0, T plane) can occur both to the right and left of the NAC point (in the last case it is unattainable; see Fig. 1). We shall show that when the influence of singular points (even in cases when they are unattainable) on the behavior of real physical quantities is taken into account, the physical situation in LC is already clarified considerably within the framework of the self-consistent field.

In the nematic phase, within the framework of the model in Ref. 1, the correlation function of smectic fluctuations has the form

$$<|\psi_{\mathbf{p}}|^2> = \left[\Delta_A + \xi_0^2 (p - p_0)^2 + \frac{\lambda_{int} Q}{2} (Q_c - Q) \sin^2\theta + \frac{3\lambda_{int} Q^2}{8} \sin^4\theta \right]^{-1} . \quad (1)$$

Here $\psi_{\mathbf{p}}$ is the amplitude of the smectic wave, Δ_A is the inverse susceptibility of the smectic A, ξ_0 is the direct correlation length in the isotropic phase, θ is the angle between the wave vector $\mathbf{p}$ and the nematic director, Q is the amplitude of the nematic condensate, and $Q_c = -3\gamma_{\text{int}}/\lambda_{\text{int}}$.

A series of important physical consequences, which we will now discuss, follows directly from (1).

1. DOUBLING OF CRITICAL INDICES. DEPENDENCE OF THE DIRECT CORRELATION LENGTH ON THE WIDTH OF THE NEMATIC ZONE

The equation of the NA line has the form $\Delta_A = 0$. At RP, by definition $(\partial\Delta_A/\partial t)|_{NA} = 0$, and the expansion of Δ_A in terms of $t = (T - T_{NA})/T_{NA}$ begins with the term $\sim t^2$ (the index NA here and below indicates that the corresponding quantity is evaluated on the NA line). In the region

$$t \gg t_{Re} \equiv \frac{\partial \Delta_A}{\partial t}\Big|_{NA} \frac{\partial^2 \Delta_A}{\partial t^2}\Big|_{NA}^{-1}$$

the term in Δ_A, which is linear with respect to t, can be ignored, and the critical indices of the susceptibility and correlation length are doubled. The doubling of the γ and ν indices in the vicinity of RP was observed experimentally by Kortan *et al.*[2] The increase in the indices as the distance from the NA transition is increased was erroneously interpreted in Ref. 3 as a crossover from mean-field behavior to helium behavior. The nonlinear nature of Δ_A appears, in addition to the neighborhood of RP, also near the isotropic-nematic (IN) transition, which must be taken into account for substances with a narrow nematic band such as $8CB$.[4] It is evident that either the region $t \ll t_{Re}$ close to the transition or the nonlinearity of Δ_A must be taken into account in the index analysis. Otherwise, the indices γ and ν are effective: they are too high and depend on the width of the nematic zone.

The direct correlation radius $t \ll t_{Re}$, measured in the region $\tilde{\xi}_0 = \xi_0 |\partial \Delta_A / \partial t|_{NA}^{-0.5}$, depends on the width of the nematic zone, since

$$\frac{\partial \Delta_A}{\partial t}\Big|_{NA} = \frac{\partial \Delta_A}{\partial Q}\Big|_{NA} \frac{\partial Q}{\partial t}\Big|_{NA} \sim \frac{Q_{RP} - Q_{NA}}{Q_{NA} - Q^*_{IN}}, \tag{2}$$

where Q_{RP} and Q^*_{IN} are the values of the nematic order parameter at RP at the boundary of absolute instability of the nematic phase. In the case $|Q_{RP} - Q_{NA}| \gg Q_{NA} - Q^*_{IN}$ (narrow nematic zone) $\tilde{\xi}_0$ is anomalously small. In the case $|Q_{RP} - Q_{NA}| \ll Q_{NA} - Q^*_{NI}$, $\tilde{\xi}_0$ increases and diverges at RP. Kortan *et al.*[2] observed the change in $\tilde{\xi}_0$ from 4 Å in the case of a narrow nematic zone to 40 Å near RP.

2. SMECTIC FLUCTUATIONS OF THE *A* AND *C* TYPE. *A–C* CROSSOVER

The correlation function (1) with $Q \leqslant Q_c$ describes the pretransitional fluctuation regime of the A type: the average slope angle of the smectic fluctuations that appear is 0. At $Q \geqslant Q_c$ a nonzero average slope angle θ_0 of cybotactic clusters, determined by the equation

$$\sin^2 \theta_0 = \frac{2}{3} \frac{Q - Q_c}{Q}$$

separates out. The region $Q \geqslant Q_c$ is the region of the pretransitional regime of the C type.

The line $Q = Q_c$ which emanates from the triple NAC point, is the line of the crossover from the fluctuational regime of the A type to the C type regime (see Fig. 1). Being the line of constant Q, the line of the $A–C$ crossover must be parallel to the line of the IN transitions. An $A–C$ crossover was observed experimentally by Safinya *et al.*[5]. These authors do not call attention anywhere to the parallelism of the crossover line that they observed and the line of IN transitions, but this is clear from the figure shown in Ref. 5.

3. CHANGE IN THE RATIO OF DIRECT CORRELATION LENGTHS OF LONGITUDINAL AND TRANSVERSE FLUCTUATIONS

In the region $\Delta_A \ll \lambda_{\text{int}} (Q_c - Q)^2$, adjacent to the NA line, the peak of the intensity of the transverse scattering of x rays ($|\mathbf{p}| = p_0, p_\perp = p_0 \sin \theta$ has a Lorentzian shape.

The quantity

$$\xi_{0\perp}^2 = \frac{\lambda_{int} Q}{2} (Q_c - Q) p_0^{-2} \qquad (3)$$

plays the role of the square of the direct transverse correlation length. It follows from (3) that the ratio of the longitudinal and transverse correlation lengths depends considerably on the temperature. This temperature dependence can be observed experimentally as a difference between the indices $\nu_\parallel$ and $\nu_\perp$. We will not discuss the question of the "anisotropic scaling," because the experimental situation here is unclear.[6]

The ratio of the correlation lengths in the vicinity of the NA transition depends on the width of the nematic zone. In the NA transition, close to the NAC point, the correlation lengths are strongly anisotropic: $\xi_\parallel \gg \xi_\perp$; in Ref. 7 $\xi_\parallel \approx 30\xi_\perp$.

4. NON-LORENTZIAN NATURE OF X-RAY SCATTERING

In the region $\Delta_A \gg \lambda_{\rm int}(Q_c - Q)^2$, the term $\sim \sin^4\theta$ dominates in (1), while the shape of the peak of the intensity of transverse scattering of x rays is not Lorentzian (see Fig. 1). As the NAC point is approached, $(Q_c - Q)^2 \sim t^2$ and the non-Lorentzian shape of the peak is observed only in the region $t \ll t_{Re}$ (where $\Delta_A \sim t$). This region narrows to zero width if the NAC point coincides with RP. Such a situation occurs at the NAC point of the binary mixture $7S5$–$8S5$[8,9] (see also other NAC points[10]). The proximity of this point to RP explains the suppression at this point of fluctuation anomalies of the heat capacity,[8] as well as the result obtained in Ref. 7, in which the shape of the peak of the intensity of transverse scattering of x rays was, as the NAC point was approached, everywhere almost ideally Lorentzian.

5. FLUCTUATION PART OF THE HEAT CAPACITY. GINZBURG'S CRITERION

The entropy of smectic fluctuations, which is simply related to (1), is expressed in terms of a first-order elliptic integral. The fluctuation part of the heat capacity is not described in this case by a single critical index and assumes a square-root behavior in terms of the susceptibility only in the asymptotic region $\Delta_A \ll \{\lambda_{\rm int}(Q_c - Q)^2, \xi_{0\perp}^2 p_0^2\}$

$$\delta C_p = \frac{1}{16\pi \xi_0 \xi_{0\perp}^2} \left(\frac{\partial \Delta_A}{\partial t}\right)^2 \Delta_A^{-0.5} . \qquad (4)$$

An anomaly appears in the heat capacity in the region $t \ll t_{Re}$ (in the region $t \gg t_{Re}$, $\delta C_p \sim t$). Its amplitude depends on the width of the nematic zone: it decreases as RP is approached[11] and increases as the NAC point is approached. Comparing the anomaly with the mean-field jump of the heat capacity in the NA transition

$$\Delta C_p = \frac{1}{2\lambda_{eff}} \left(\frac{\partial \Delta_A}{\partial t}\right)^2_{NA}$$

($\lambda_{\rm eff}$ is the quartic constant of the smectic, renormalized by the nematic, whose vanishing determines the TCP[12]), we obtain the condition for applicability of the Ornstein-Zernike approximation,

$$t \gg Gi = \frac{\lambda_{eff}^2}{64\pi^2 \xi_0^2 \xi_{0\perp}^4 \left| \frac{\partial \Delta_A}{\partial t} \right|_{NA}} \tag{5}$$

Setting $\xi_0 p_0 \sim 1$, to within unimportant factors, we can write criterion (5) in the form

$$t \gg Gi = \frac{(\Delta Q)_{TCP}^2 (\Delta Q)_{IN}}{(\Delta Q)_{NAC}^2 (\Delta Q)_{RP}} \left(\frac{a}{L}\right)^6, \tag{6}$$

where $(\Delta Q)_i$ is the difference between Q_{NA} and the value of Q at the corresponding "singular" point of the phase diagram. The existence of the small parameter $a/L \sim 1/5$ leads to the fact that the results obtained here are, in general, applicable over a broad temperature range.

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[1]M. A. Anisimov, E. E. Gorodetskiĭ, and V. É. Podnek, Pis'ma Zh. Eksp. Teor. Fiz. **37**, 352 (1983) [JETP Lett. **37**, 414 (1983)]; E. E. Gorodetskiĭ and V. É. Podnek, Kristallografiya (to be published).

[2]A. R. Kortan, N. V. Kanel, *et al.*, Phys. Rev. Lett. **47**, 1206 (1981).

[3]J. Als-Nielsen, *et al.*, Phys. Rev. Lett. **39**, 352 (1977).

[4]J. D. Litster, *et al.*, J. Phys. (Paris) **40**, C3-339 (1979).

[5]C. R. Safinya, *et al.*, Phys. Rev. Lett. **50**, 53 (1983).

[6]J. Als-Nielsen, *et al.*, Phys. Rev. Lett. **41**, 1626 (1978).

[7]C. R. Safinya, *et al.*, Phys. Rev. Lett. **47**, 668 (1981).

[8]R. De Hoff, *et al.*, Phys. Rev. Lett. **47**, 664 (1981).

[9]D. Brisbin, *et al.*, Phys. Rev. Lett. **43**, 1171 (1979).

[10]D. Brisbin, *et al.*, Phys. Rev. Lett. **50**, 178 (1983).

[11]K. J. Lushington, *et al.*, Phys. Rev. B **22**, 2569 (1980).

[12]P. de Gennes, The Physics of Liquid Crystals, Oxford University Press, Oxford, 1974.

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