Fluctuation theory of phase transitions with the formation of translational order in nematics

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The weak-crystallization phase transition in an anisotropic system is considered for the example of a nematic liquid crystal. The phase diagram of the system with respect to the magnitude and sign of the coupling of the orientational order with the crystal lattice is constructed in the framework of the Landau theory. The effect of fluctuations on the diagram is studied.

1. In recent years interest in the problem of describing weak crystallization in the framework of the Landau theory has arisen again (see, e.g., Ref. 1). This interest has been simulated primarily by the discovery of phase transitions of this kind (weak first-order phase transitions) in liquid crystals.[2] However, complete or partial solidification of liquid crystals occurs, as a rule, from an orientationally anisotropic phase, and therefore the results of the theory of weak crystallization[1] are not strictly applicable to this case. The first attempt to take anisotropy into account in the theory of weak crystallization was made by Gorodetskiĭ and Podnek.[3] However, in Ref. 3 the authors took the anisotropy into account as a specified external weak field. In addition, the entire analysis of Ref. 3 neglects fluctuations, and, for weak phase transitions, the latter turn out to be very important. In the present paper we use the example of a nematic liquid crystal to consider the crystallization of an orientationally anisotropic liquid. In the next section the model used will be described. In Sec. 3 it is investigated in the framework of the Landau theory. The role of fluctuations is discussed in Sec. 4, and the limitations of the model and the possibilities for its development are considered in Sec. 5.

2. The Landau free energy of a crystallizing orientationally anisotropic system in the general case can be written in the following form:

$$\Phi=\Phi_\rho+\Phi_N+\Phi_{int}, \tag{1}$$

where Φ_ρ is the energy associated with the crystalline modulation of the density ρ, Φ_N is the energy associated with the orientational anisotropy, and Φ_{int} is the interaction energy.

The contributions Φ_ρ and Φ_N are both well known[1,4]:

$$\Phi_\rho=\tau\sum|\rho_{\mathbf{k}}|^2+\mu\sum\rho_{\mathbf{k}_1}\rho_{\mathbf{k}_2}\rho_{\mathbf{k}_3}+\sum\lambda(\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4)\rho_{\mathbf{k}_1}\rho_{\mathbf{k}_2}\rho_{\mathbf{k}_3}\rho_{\mathbf{k}_4}, \tag{2}$$

$$\Phi_N=\tau_{IN}Q_{\alpha\beta}^2/2-bQ_{\alpha\beta}^3/3+cQ_{\alpha\beta}^4/4. \tag{3}$$

Here $Q_{\alpha\beta}$ is the nematic order parameter, $\rho_{\mathbf{k}}$ is a Fourier component of the density, τ is the temperature measured from the "bare" or fiduciary point of absolute instability of the isotropic liquid for crystalline ordering, τ_{IN} is the same for orientational ordering, and μ, λ, b, and c are coefficients of the Landau expansion. In each term in (2) the vectors have a given length k_0 and are such that their sum is equal to zero.

Using symmetry considerations, to lowest order we can choose the interaction energy in the following form:

$$\Phi_{int}=\tilde{W}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}Q_{\alpha\beta}(\mathbf{k}_1)\left[k_2^\alpha k_3^\beta-\frac{1}{3}\delta_{\alpha\beta}(\mathbf{k}_2\mathbf{k}_3)\right]\rho_{\mathbf{k}_2}\rho_{\mathbf{k}_3}, \tag{4}$$

where, as above $\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3=0$. In (4) we have omitted terms containing higher powers of the orientational order parameter, which do not qualitatively change the results of the analysis (see also below). The most important terms in (4) are those in which $\mathbf{k}_1=0$ and $|\mathbf{k}_2|=|\mathbf{k}_3|=k_0$. Taking this into account, we have

$$\Phi_{int}=2WQ_{\alpha\beta}(0)\sum_{\mathbf{v}}v_\alpha v_\beta a_{\mathbf{v}}^2, \tag{5}$$

where

$$W=-\tilde{W}k_0^2,\quad \mathbf{v}=\mathbf{k}/k_0,\quad a_{\mathbf{v}}=|\rho_{\mathbf{k}}|.$$

The orientational order parameter (a traceless symmetric second-rank tensor $Q_{\alpha\beta}$) can be parametrized by means of a set of three mutually orthogonal vectors $\mathbf{n}$, $\mathbf{m}$, and $[\mathbf{nm}]$ ($\equiv\mathbf{n}\times\mathbf{m}$) and two scalar parameters x and y:

$$Q_{\alpha\beta}=\tfrac{3}{2}x(n_\alpha n_\beta-\tfrac{1}{3}\delta_{\alpha\beta})-\tfrac{1}{2}y(m_\alpha m_\beta-[\mathbf{nm}]_\alpha[\mathbf{nm}]_\beta). \tag{6}$$

The parameter y characterizes the degree of biaxiality; with $y=0$ we obtain the usual uniaxial nematic order ($\mathbf{n}$ is the director).

Finally, in analogy with Ref. 1 we shall consider the simplest case of an interaction λ that is independent of the momenta (more precisely, of the angles between them). Allowance for this dependence introduces further, arbitrary (in general) parameters into the theory, and the problem becomes too cumbersome.

3. Even the highly simplified model to be analyzed still contains many unknown parameters. It is convenient to eliminate some of them by changing to dimensionless variables. We shall assume that the free energy Φ_ρ in measured in units of μ^4/λ^3, the Fourier components of the density are measured in units of μ/λ, the temperature τ has the dimensions of μ^2/λ, and the fundamental period of the modulation has the dimensions of $\mu^{3/2}/\lambda^2$. The coefficients τ_{IN}, b, c, and W appearing in Φ_N and Φ_{int} will also be measured in units of μ^4/λ^3. The construction of the phase diagram in the framework of the Landau theory reduces to the minimization of the total free energy (1). Taking into account the explicit expressions (2), (3), (5), and (6), we have

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$$\Phi=2\tau A+12\lambda A^2-6\lambda\sum_{\nu}a_\nu^4+\mu\sum\rho_1\rho_2\rho_3+\lambda\sum\rho_1\rho_2\rho_3\rho_4$$

$$+\alpha(x)+y^2\beta(x)+y^4\gamma+W\sum_{\nu}\{3x(\mathbf{n}\nu)^2-x+y([\mathbf{nm}]\nu)^2$$

$$-y(\mathbf{m}\nu)^2\}a_\nu^2. \qquad (7)$$

Here, following Ref. 1, in the crystal part of the energy we have distinguished the sums over nontrivial closed triangles and quadrilaterals. In addition, in (7) we have introduced the notation

$$A=\sum_{\nu}a_\nu^2, \qquad (8)$$

$$\alpha(x)=3\tau_{IN}x^2/4+bx^3/4+9cx^4/16,$$

$$\beta(x)=\tau_{IN}/4-bx/4+3cx^2/8, \quad \gamma=c/16. \qquad (9)$$

The situation depends in an essential way on the relative magnitudes of the bare temperatures of the crystalline ordering and orientational ordering. If these temperatures are not too close (for more detail, see below), there exist two possibilities: As the temperature is lowered, starting from the isotropic liquid, either Landau crystallization occurs first and then a nematic order parameters develops, or these transitions occur in the reverse order.

In the first scheme the Landau crystallization occurs in an isotropic system, and we can make direct use of all the results of Ref. 1. As in Ref. 1, in the absence of fluctuations there are three absolutely stable phases—a bcc lattice, a planar triangular lattice of liquid filaments (Δ), and a one-dimensional density wave (S). The energies of these phases and the crystallization temperatures are

$$\Phi_{bcc}=2\tau A-8|\mu|A(A/6)^{1/2}+15\lambda A^2, \quad \tau_{bcc}={}^4/_{45}\mu^2/\lambda,$$
$$\Phi_\Delta=2\tau A-4|\mu|A(A/3)^{1/2}+10\lambda A^2, \quad \tau_\Delta={}^1/_{15}\mu^2/\lambda,$$
$$\Phi_S=2\tau A+6\lambda A^2, \quad \tau_S=0. \qquad (10)$$

For an orientational transition superposed on this crystalline order the parameter A plays the role of an external field. Because of the condition $\mathrm{Tr}Q_{\alpha\beta}=0$ the interaction energy for the bcc lattice is equal to zero. But the triangular and one-dimensional phases do interact with the nematic order. Here, depending on the relative magnitudes of the parameters of the model, different sequences of phases are possible. We note only certain possibilities, which are of interest from the experimental point of view. For $Wx<0$ the "external field" makes the nematic order parameter biaxial. A one-dimensional crystal structure with biaxial orientational order corresponds to a smectic-C. In this case, as the temperature is lowered the following sequence of phases, which is actually observed in liquid crystals,[5] is possible: smectic-A (i.e., a one-dimensional crystal with uniaxial orientational order)—bcc (the so-called smectic-D)—smectic-C. We note also that, depending on the amplitude of the field A, these phase transitions can be either first-order or second-order.

We now consider the second transition scheme. In its bare form the nematic order parameter is uniaxial.[6] Let $Wx>0$. It is obvious that the triangular phase is formed in the plane perpendicular to the director $\mathbf{n}$. Then $a_1=a_2=a_3=(A/3)^{1/2}$, and

$$\Phi_{int}=-WxA. \qquad (11)$$

Consequently, the interaction leads simply to a shift of the transition temperature. The one-dimensional phase is also formed in the plane perpendicular to the director. The energy Φ_{int} is given by the same formula (11), but the interaction does not reduce merely to a shift $\tau\to\tau-Wx/2$ in the transition temperature. In fact, crystallization into the S phase for $Wx>0$ necessarily induces the appearance of the biaxial nematic order parameter y. The energy of the one-dimensional phase has the form

$$\Phi_S=by^2+2\tau A+6\lambda A^2-WxA+WyA\cos 2\varphi, \qquad (12)$$

where φ is the angle between $\mathbf{m}$ and ν. It is obvious that (12) has an extremum at

$$|y|=|WA/2b| \qquad (13)$$

and, at this extremum,

$$\Phi_S=\Phi_0-WxA-(WA)^2/2b. \qquad (14)$$

As already noted, such a one-dimensional phase corresponds to a smectic-C. We shall denote it by SC, in contrast to the uniaxial one-dimensional phase (smectic-A), which, as before, we denote by S. The triangular phase does not interact with the biaxial order parameter, and therefore is not modified.

Now let $Wx<0$. For the one-dimensional phase the situation is trivial. It is formed along the director, and the interaction reduces simply to a shift $\tau\to\tau+Wx$ in the transition temperature. The situation in the triangular phase, however, is more complicated. The director lies in the plane of crystallization. Two possibilities correspond to an energy minimum (we denote the corresponding structures by Δ_0 and Δ_1). In the first structure $\nu_1\|\mathbf{n}$ and $a_1>a_2=a_3$, while in the second structure $\nu_1\perp\mathbf{n}$ and $a_1<a_2=a_3$.

It is easy to calculate the energy of the two phases. We set $a_2=a_3=a$ ($A=2a^2+a_1^2$). The structure-dependent part of the energy (7) has the form

$$f=-6\lambda\sum_{\nu}a_\nu^4-12|\mu|a_1a^2+3Wx\{a_1^2\cos^2\varphi$$
$$+a^2[\cos^2(\varphi+2\pi/3)+\cos^2(\varphi-2\pi/3)]\}-W\times A.^{1)} \qquad (15)$$

The amplitudes of the Fourier harmonics of the density are determined by the system of equations obtained by minimizing (15) with respect to the amplitude a_1 and minimizing the total energy (7) with respect to the order parameter A. Unfortunately, the solution of the corresponding algebraic system is so complicated as to be useless, and further investigation can be carried out only numerically. A typical phase diagram is given in Fig. 1. An important feature of the diagram in Fig. 1, characteristic specifically of anisotropic systems, is the possibility of the re-entrant appearance of the one-dimensional (smectic) phase. We note also that, in contrast to the isotropic case, in the lower part of the Δ_0–S transition curve a tricritical point A can appear, at which the first order phase transition is replaced by a continuous transition.

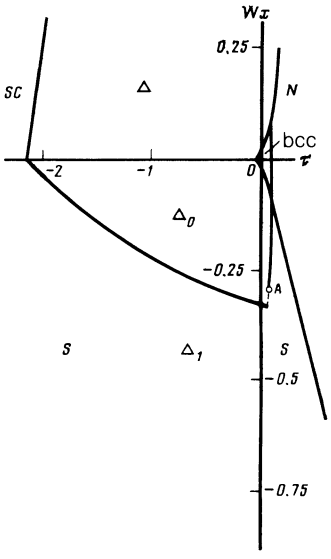

FIG. 1.

4. We now discuss the role of fluctuations. As is usual in the theory of weak crystallization (see, e.g., Ref. 1), we are concerned with fluctuations associated with the large phase volume (a sphere of radius k_0) over which they are built up. The condition for the validity of a model limited to terms of fourth order in the expansion of the free energy is given by the following inequalities:

$$k_0 \gg \lambda \gg k_0^4. \tag{16}$$

An analysis of such fluctuations in an isotropic system was first carried out by Brazovskiĭ,[7] who showed that the entire modification of the Landau theory reduces to self-consistent allowance for just one fluctuation diagram, depicted in Fig. 2, in which the solid line denotes the Green's function (correlator) $\langle\rho\rho\rangle$ and the small circle denotes the interaction vertex λ.

In anisotropic systems the situation can be altered substantially in comparison with that in Refs. 7 and 1. As can be seen from (7), the energy necessary to excite fluctuations with $k = k_0$ depends on the angular coordinates. In addition, the possibility is not ruled out that in certain regions of the sphere (at the poles or equator) this energy vanishes completely. In this case, the self-consistent description in Refs. 7 and 1 breaks down and the main fluctuation contribution will come from precisely these parts of the sphere. In the present paper we confine ourselves to the case when the coupling of the orientational and translational degrees of freedom is not too strong, when the fluctuations, like those in isotropic systems, are built up over the whole sphere of radius k_0.

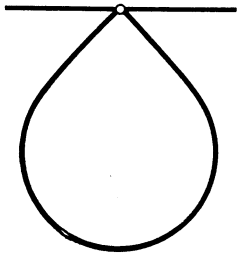

FIG. 2.

We shall consider for simplicity a uniaxial nematic order parameter. In this case, from (7) it is easy to obtain the following forms for the bare Green's functions in the nematic and crystalline phases:

$$g_N^{-1}(k) = \tau + WxP_2(t) + (k-k_0)^2, \tag{17}$$

$$g_C^{-1}(k) = \tau + 12\lambda A + WxP_2(t) + (k-k_0)^2. \tag{18}$$

Here $P_2(t)$ is a Legendre polynomial in $t = \cos\theta$, where θ is the angle between $\mathbf{n}$ and $\boldsymbol{\nu}$. Self-consistent allowance for the self-energy contribution depicted in Fig. 2 results in replacing τ with the inverse square of the correlation length $\varkappa$, which in our case depends on the angle θ. In the nematic phase we have

$$\varkappa_N(t) = \tau + WxP_2(t) + \alpha\lambda \int_0^1 dt\, \varkappa_N^{-1/2}(t), \tag{19}$$

where $\alpha = k_0^2/48\pi$. Obviously, $\varkappa_N(t)$ has the form

$$\varkappa_N(t) = r_N + 3Wxt^2/2, \tag{20}$$

where r_N satisfies the equation

$$r_N - \tau + \frac{1}{2}Wx = \alpha\lambda \int_0^1 dt \left(r_N + \frac{3}{2}Wxt^2\right)^{-1/2}. \tag{21}$$

Expressions for the correlation length in the crystalline phases are obtained analogously. For example, in the one-dimensional phase,

$$\varkappa_S(t) = \tau + 12\lambda A_S + WxP_2(t) + \alpha\lambda \int_0^1 dt\, \varkappa_S^{-1/2}(t). \tag{22}$$

From (19)–(22) we obtain the explicit form of the equations for r_N and r_S. For $Wx < 0$ we have (23), (24), while if $Wx > 0$ we have (25), (26):

$$r_N - \tau + Wx/2 = \alpha\lambda (2/3|Wx|)^{1/2} \arcsin(3|Wx|/2r_N)^{1/2}, \tag{23}$$

$$-r_S - \tau - 5Wx/2 = \alpha\lambda (2/3|Wx|)^{1/2} \arcsin(3|Wx|/2r_S)^{1/2}, \tag{24}$$

$$r_N - \tau + Wx/2 = \alpha\lambda (2/3Wx)^{1/2} \ln\{[(3Wx/2)^{1/2} + (r_N + 3Wx/2)^{1/2}] r_N^{-1/2}\} \tag{25}$$

$$-r_S - \tau + Wx/2 = \alpha\lambda (2/3Wx)^{1/2} \ln\{[(3Wx/2)^{1/2} + (r_S + 3Wx/2)^{1/2}] r_S^{-1/2}\}. \tag{26}$$

When fluctuations are taken into account the expressions for the energies of the phases are changed. In analogy with Ref. 1, we have

$$\Phi_S = F(A) - 6\lambda A^2, \quad \Phi_\Delta = F(A) - 4\cdot 3^{-1/2}|\mu| A^{1/2} - 2\lambda A^2, \tag{27}$$

where

$$F(A)\equiv F(\varkappa)=\left[\frac{\varkappa^2}{12\lambda}+\frac{\alpha\varkappa^{1/2}}{6}-\frac{\alpha}{6}\left(\frac{3|Wx|}{2}\right)^{1/2}\right.$$
$$\left.\cdot\operatorname{arctg}\left(\frac{2\varkappa}{3|Wx|}\right)^{1/2}\right]\Bigg|_{\varkappa_N}^{\varkappa},\quad Wx<0,$$

$$F(A)\equiv F(\varkappa)=\left[\frac{\varkappa^2}{12\lambda}+\frac{\alpha}{6}\left(\varkappa+\frac{3Wx}{2}\right)^{1/2}\right]\Bigg|_{\varkappa_N}^{\varkappa},\ Wx>0. \tag{28}$$

The connection between A and $\varkappa$ is established by the relations

$$A_S=\varkappa_S/6\lambda, \tag{29}$$

$$A_\Delta^{1/2}=(3\mu^2/16\lambda^2+\varkappa_\Delta/2\lambda)^{1/2}-3^{1/2}|\mu|/4\lambda. \tag{30}$$

Of the two possible solutions (30) we must choose the larger. In an anisotropic system, the energy expression (27), (28) contain the values of the functions $\varkappa_N,\varkappa_S$, and $\varkappa_\Delta$ that give the minimum energy. For $Wx>0$ this corresponds to $t=0$ and $\varkappa_N=r_N,\varkappa_S=r_S$, while for $Wx<0$ it corresponds to $t=1$, i.e., $\varkappa_N=r_N+3Wx/2$, $\varkappa_S=r_S+3Wx/2$.

For $Wx>0$ the procedure described is easily extended to the triangular phase. We have the system of equations (30), (31):

$$\varkappa_\Delta(t)=\tau+12\lambda A_\Delta+WxP_2(t)+\alpha\lambda\int_0^1 dt\,\varkappa_\Delta^{-1/2}(t). \tag{31}$$

Solving the system (30), (31) gives

$$\varkappa_\Delta(t)=r_\Delta+3Wxt^2/2, \tag{32}$$

$$r_\Delta=\tau+12\lambda A_\Delta-\frac{Wx}{2}+\alpha\lambda\left(\frac{2}{3Wx}\right)^{1/2}$$
$$\times\ln\left\{\left[\left(\frac{3Wx}{2}\right)^{1/2}+\left(\frac{3Wx}{2}+r_\Delta\right)^{1/2}\right]r_\Delta^{-1/2}\right\}. \tag{33}$$

The extremal value of $\varkappa_\Delta(t)$ is attained, of course, at $t=0$.

The phase diagram of the system with allowance for fluctuations and for $Wx=1/4$ is depicted in Fig. 3 in the variables τ and $\alpha=k_0^2/4\pi$. It can be seen that enhancement of the fluctuations (i.e., growth of the parameter k_0) rapidly destroys the intermediate triangular phase and lowers the crystallization temperature. We note that this result agrees with the conclusions of Ref. 1. For $W=0$ our equations go over directly into the equations of Ref. 1.

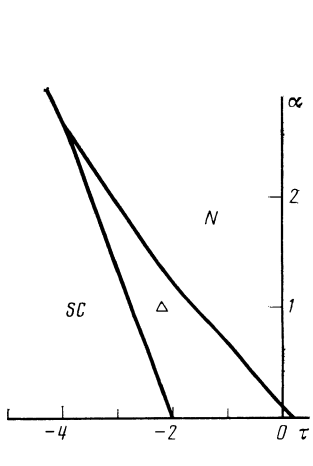

FIG. 3.

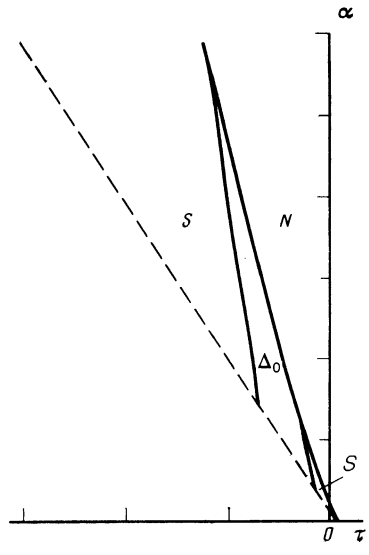

FIG. 4.

The case $Wx<0$ is more complicated for the calculation of the energy of the triangular phase, since even in the Landau theory, as we have seen in the preceding section, the relation between A and $\varkappa$ can be found only numerically. The phase diagram for $Wx=-1/4$ is given in Fig. 4. The dashed line denotes the boundary of the region of applicability of the model (see Sec. 5). For small α it evidently corresponds to a line of transitions to the smectic-A phase.

5. We now give a more rigorous discussion of the conditions of applicability of the model. As already stated, the main assumption is that the fluctuations are built up over the entire sphere. For $Wx<0$ and $r_N\lesssim 3|Wx|/2$ our model loses its meaning. This instability appears for any $Wx<0$ at temperatures below

$$T_c=-Wx-\pi\alpha(6|Wx|)^{-1/2}$$

(only for $Wx\to 0$ does the absolute-instability temperature satisfy $T_c\to-\infty$). Fluctuations stabilize the nematic phase, and for large α the crystallization to the one-dimensional phase by the Brazovskiĭ mechanism occurs before the model loses its applicability (see Fig. 4).

We note that it would seem that an analogous singularity appears in the one-dimensional phase [see Eqs. (23) and (24)]. However, this instability is unimportant for our analysis, since the transitions being studied occur at $\tau<0$ and the instability occurs at $\tau>0$.

Up to now we have been concerned only with the self-interaction of these crystallization fluctuations in an anisotropic system. However, these fluctuations also change the coefficients in the nematic part (3) of the energy. This renormalization is described, in particular by the diagrams of Fig. 5 (the wavy line symbolizes the Green function $\langle Q_{\alpha\beta}Q_{\delta\gamma}\rangle$ of the orientational fluctuations). The diagram of Fig. 5a renormalizes τ_{IN}. In order that this renormalization be unimportant, it is necessary that the nematic and crystalline tran-

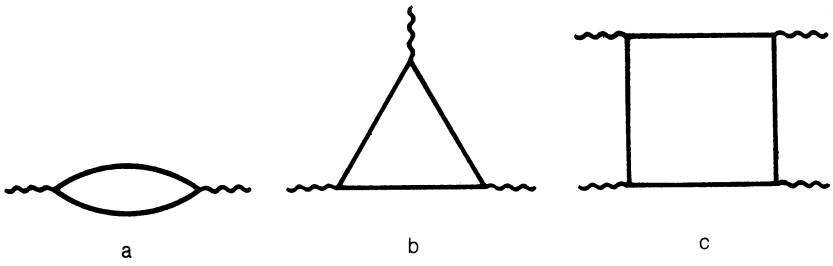

FIG. 5.

sitions be sufficiently separated. A simple estimate of the diagram of Fig. 5a gives the condition

$$(Wx)^2\alpha\tau^{-3/2}\ll\tau_{IN}-\tau.$$

In an analogous manner the diagram of Fig. 5b renormalizes the coefficient b in (3), and the diagram of Fig. 5c renormalizes the coefficient c. The restrictions arising from this have the form

$$(Wx)^3\alpha\tau^{-3/2}\ll b,\quad (Wx)^4\alpha\tau^{-7/2}\ll c.$$

Weak crystallization occurs at $\alpha\sim\tau^{3/2}$. Thus in effect, these inequalities reduce to the conditions

$$(Wx)^2\ll\tau_{IN}-\tau,\quad (Wx)^3\ll b\alpha^{2/3},\quad (Wx)^4\ll c\alpha^{4/3}.$$

Therefore, with increase of the amplitude α of the fluctuations the diagrams of Figs. 5b and 5c become less important.

A detailed comparison of the above scheme with experiment is difficult at the present time, since quite a few unknown parameters appear in it. Nevertheless, in the framework of this approach it is easy to give a qualitative description of all the observed sequences of phase transitions in lyotropic and thermotropic liquid crystals.

There are grounds to assume (see the discussion at the end of Ref. 1) that the general conclusions of the model do not depend on its simplifying assumptions. For example, fluctuations always stabilize the nematic phase. As the amplitude of the fluctuations increases, the regions of stability of the "intermediate" phases on the phase diagram disappear.

In conclusion, the authors express their gratitude to I. E. Dzyaloshinskiĭ for formulating the problem and for useful discussions.

[1)]The authors originally omitted the term $-W\times A$ from Eq. (15). Figures 1 and 4 have been modified to incorporate this correction.

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