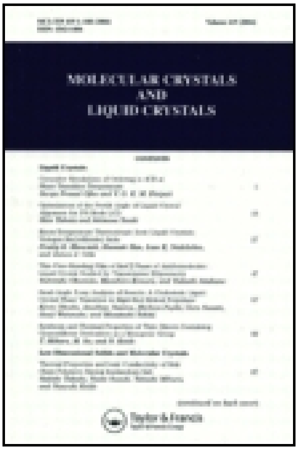

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Shear Stability, Partial Disorder and Phase Transitions in Smectic Liquid Crystals. Nonlinear Effects

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A layer system of uniaxial molecules is studied. Smectic (Sm) phases are considered as system states in which shear moduli (i.e., terms linear with respect to the wave vector $\vec{K}$ in frequencies of translational oscillations) are zero and, however, corresponding terms nonlinear with respect to $\vec{K}$ are nonzero. It is established that the nonlinear terms provide intermolecular translational correlations if corresponding shear moduli are zero. On the basis of this idea a correlation between translational order and elastic properties of known Sm phases is investigated and new "intermediate" Sm phases are predicted also. The free energy F is written as a function of shear moduli. Temperatures at which the jump-like zero conversion of the shear moduli occurs (i.e., temperatures of transitions into corresponding Sm phases) are calculated from the condition of minimum F. It is shown that this approach allows to predict a sequence of phase transitions at the layer crystal heating and, in particular, to formulate conditions of its smectogeneity.

Keywords: smectic liquid crystals, partial translational disorder, shear moduli, phase transitions, nonlinear effects

It is well known[1] that the account of nonlinear effects is of fundamental importance for understanding a structure of systems with a one- and two-dimensional periodicity. This idea had been used[2–4] in the investigation of translational ordering of the smectic A (SmA) and discotic columnar mesophase in liquid crystal physics. This idea is generalized in the present paper. We believe that terms nonlinear with respect to the wave vector $\vec{K}$ are to be always taken into account when corresponding terms linear with respect to $\vec{K}$ (shear moduli) are zero.

TRANSLATIONAL ORDER AND ELASTIC PROPERTIES

We write frequencies of translational oscillations ω_i of the layer crystal formed by uniaxial molecules in the form[5–7]

$$\rho\omega_1^2 = C_{11}K^2 + \mu_1 K_3^2 + \mu_1' K_3^4,$$

$$\rho\omega_2^2 = \mu_3 K^2 + \mu_3' K^4 + \mu_1 K_3^2 + \mu_1' K_3^4,$$

$$\rho\omega_3^2 = \mu_2 K^2 + \mu_2' K^4 + C_{33} K_3^2. \qquad (1)$$

Here ρ is a density; $K^2 = K_1^2 + K_2^2$; $\mu_1 = C_{1313}$; $\mu_2 = C_{3131}$; $\mu_3 = C_{66} = (C_{11} - C_{12})/2$ are shear moduli. They characterize a shear of layers parallel to each other, a layer bend, a shear within layers, respectively. $\mu_1 \neq \mu_2$ due to the orientational order existence[6,7] ($\mu_1 = \mu_2 = C_{44}$ in atomic crystals). The coefficients at nonlinear corrections μ_1', μ_2', μ_3' are obtained in connection with the account of the translational interaction with the second neighbours and the influence of orientational degrees of freedom on the translational ones. The OX_3 axis of the coordinates system is perpendicular to layers, the OX_1 axis is parallel to one of the vectors of fundamental translations within the layer.

Terms nonlinear with respect to $\vec{K}$ in relations (1) correspond to terms proportional to $u_{i\alpha\alpha}^2(\vec{x})$ in the elastic energy ($u_i(\vec{x})$ is an i-component of the translational displacement from the equilibrium position $\vec{x}$, $u_{i\alpha} = \partial u_i/\partial x_\alpha$; $u_{i\alpha\alpha} = \partial^2 u_i/\partial x_{\alpha\alpha}^2$; $i \neq \alpha$). For example, the elastic energy of the shear of layers parallel to each other has the form

$$F_{in} = \frac{\mu_1}{2}(u_{13}^2 + u_{23}^2) + \frac{\mu_1'}{2}(u_{133}^2 + u_{233}^2). \tag{2}$$

It can be shown that[5-7]

$$\xi(\vec{x}) = \frac{32T}{\pi^3\rho l^2 l_3}\int(\omega_1^{-2} + \omega_2^{-2})\mathrm{Sin}^2(\vec{K}\vec{x}/2)d^3\theta, \tag{3}$$

$$\xi_3(\vec{x}) = \frac{32T}{\pi^3\rho l^2 l_3}\int \omega_3^{-2}\mathrm{Sin}^2(\vec{K}\vec{x}/2)d^3\theta, \tag{4}$$

where $\xi_i(\vec{x}) = \langle[u_i(0) - u_i(\vec{x})]^2\rangle$; $\langle\ldots\rangle$ indicates an averaging; $\xi(\vec{x}) = \xi_1(\vec{x}) + \xi_2(\vec{x})$, T is a temperature; l is a lattice spacing, l_3 is a layer spacing; $\theta_1 = K_1 l/2$, $\theta_2 = K_2 l/2$, $\theta_3 = K_3 l_3/2$, $0 \leq \theta_i \leq \pi/2$.

We describe translational correlations and ordering in the system by means of functions (see Table I)

$$\mathrm{Or}(x) = \exp[-2\pi^2\xi(x)/l^2],$$

$$\mathrm{Or}(x_3) = \exp[-2\pi^2\xi_3(x_3)/l_3^2],$$

$$C_1(x_3) = \exp[-2\pi^2\xi(x_3)/l_3^2],$$

$$C_2(x) = \exp[-2\pi^2\xi_3(x)/l^2], \tag{5}$$

where $x = \sqrt{x_1^2 + x_2^2}$.

The integration in relations (3) and (4) in the approximation $x \gg 1$, $x_3 \gg l_3$ is in detail described in References 5 and 6. The results are shown in Table I. The coefficients $a_1 - a_{12}$ obtained as a result of the integration in relations (3) and (4)

TABLE I

N	$P(t_1t_2t_3)$ phase	μ_1	μ_2	μ_3	Or(x)-order and correlations within the layer	Or(x_3)-order perpendicular to layers	$C_1(x_3)$-interlayer correlations	$C_2(x)$-layer bend correlations
1	P(111) crystal	$\neq 0$	$\neq 0$	$\neq 0$	$\sim\exp(a_1/x)$ long range	$\sim\exp(a_2/x_3)$ long range	$\sim\exp(a_3/x_3)$	$\sim\exp(a_4/x)$
2	P(011) SmB	$= 0$	$\neq 0$	$\neq 0$	$\sim\exp(\sqrt{a_5/x})$ long range	$\sim\exp(a_2/x_3)$ long range	$\sim\exp(a_6/x_3)$	$\sim\exp(a_4/x)$
3	P(110) SmF	$\neq 0$	$\neq 0$	$= 0$	$\sim x^{-a_7}$ quasi-long range	$\sim\exp(a_2/x_3)$ long range	$\sim x_3^{-a_8}$	$\sim\exp(a_4/x)$
4	P(010) new	$= 0$	$\neq 0$	$= 0$	$\sim\exp(-a_9x)$ short range	$\sim\exp(a_2/x_3)$ long range	$\sim\exp(-a_{10}x_3)$	$\sim\exp(a_4/x)$
5	P(101) new	$\neq 0$	$= 0$	$\neq 0$	$\sim\exp(a_1/x)$ long range	$\sim x_3^{-a_{11}}$ quasi-long range	$\sim\exp(a_3/x_3)$	$\sim x^{-a_{12}}$
6	P(001) new	$= 0$	$= 0$	$\neq 0$	$\sim\exp(\sqrt{a_5/x})$ long range	$\sim x_3^{-a_{11}}$ quasi-long range	$\sim\exp(a_6/x_3)$	$\sim x^{-a_{12}}$
7	P(100) new	$\neq 0$	$= 0$	$= 0$	$\sim x^{-a_7}$ quasi-long range	$\sim x_3^{-a_{11}}$ quasi-long range	$\sim x_3^{-a_8}$	$\sim x^{-a_{12}}$
8	P(000) SmA	$= 0$	$= 0$	$= 0$	$\sim\exp(-a_9x)$ short range	$\sim x_3^{-a_{11}}$ quasi-long range	$\sim\exp(-a_{10}x_3)$	$\sim x^{-a_{12}}$

are given in Reference 6.We do not rewrite these coefficients here since they are rather cumbersome. We note that their value is bound up with that of corresponding correlation radii. For example, $(a_9)^{-1}$ is a correlation radius in the smectic A layer.

Let us analyse the results obtained. At first we consider the influence of nonlinear effects. It is seen from relation (2) that if $\mu_1 = 0$ and $\mu_1' \neq 0$ then the system is unstable with respect to linear deformations $(u_{133}^2 + u_{233}^2 = 0)$. However, the nonlinear $(u_{133}^2 + u_{233}^2 \neq 0)$ ones lead to the elastic energy increase, i.e., they provide restoring forces. These forces stabilize the system since the nonlinear terms improve essentially a convergence of the integrals (3) and (4) at $|\vec{x}| \to \infty$. For example, if we assume $\mu_1' = 0$ in the state P(011) then we get that the layers are completely non-correlated ($C_1(x_3) = 0$ at any x_3). If nonlinear effects $\mu_1' \neq 0$ are taken into account then we have that the layers are correlated in the state P(011) as it takes place in the crystal ($C_1(x_3) \neq 0$ at $x_3 \to \infty$). On the basis of the above-stated we conclude that nonlinear terms provide intermolecular translational correlations in phases where corresponding shear moduli are zero.

Let us consider a system shear stability. We analyze the stability with respect to shear of layers parallel to each other in detail. The experimentally measured dynamical interlayer shear modulus μ_1^{eff} depends on μ_1, μ_1' and $C_1(x_3)$. It is evident that $\mu_1^{\text{eff}} = \mu_1$ in the state P(111). It will be easily understood that $\mu_1^{\text{eff}} = 0$ in the static case in the state P(011). However, it follows[5–8] from relations (1) and (2) that due to the nonlinear effects the dynamical shear modulus μ_1^{eff} is nonzero

$$\mu_1^{\text{eff}} = \mu_1' K_3^2 = (\rho\mu_1')^{1/2}\omega_{\text{ap}}. \tag{6}$$

Here ω_{ap} is an applied strain frequency. The layers are not correlated for high distances ($C_1(x_3) \to 0$ at $x_3 \to \infty$) in the state P(110). An exact quantitative investigation of the frequency dependence μ_1^{eff} in this state is, apparently, very complex. To describe this dependence qualitatively we introduce the correlation radius $x_3^{\perp}$. $x_3^{\perp}$ is a distance at which $C_1(x_3)$ gets e times lower. Substituting $K_3 = 2\pi/x_3^{\perp}$ into Equation (1) we get a corresponding frequency $\omega_0 = 2\pi\sqrt{\mu_1}/\sqrt{\rho}\ x_3^{\perp}$. It is clear from the consideration shown that if the passing wave length L_3 is far higher than $x_3^{\perp}$ (i.e., the frequency is low enough $\omega_{\text{ap}} << \omega_0$) then $\mu_1^{\text{eff}} = 0$. $\mu_1^{\text{eff}} = \mu_1$ if $\omega_{\text{ap}} >> \omega_0$.

$C_1(x_3) \to 0$ at $x_3 \to \infty$ in the state P(000). This means, according to the discussion fulfilled that $\mu_1^{\text{eff}} = 0$ if $\omega_{\text{ap}} << \omega_0'$; $\mu_1^{\text{eff}} = (\rho\mu_1')^{1/2}\ \omega_{\text{ap}}$ if $\omega_{\text{ap}} >> \omega_0'$ in the state P(000).

By analogy with this μ_2^{eff} and μ_3^{eff} can be analyzed. Besides, μ_2^{eff} depends on μ_2, μ_2' and $C_2(x)$; μ_3^{eff}depends on μ_3, μ_3' and Or(x).

Possible types of translational order in the system are described in Table I. It should be emphasized that μ_1, μ_2 and μ_3 do not coincide with the experimentally measured shear moduli μ_1^{eff}, μ_2^{eff} and μ_3^{eff} (μ_1, μ_2 and μ_3 can be called the local static shear moduli). In accordance with the analysis shown above the parameters μ_1, μ_2, μ_3, μ_1', μ_2', μ_3' can be experimentally obtained by means of the study of the frequency dependence μ_1^{eff}, μ_2^{eff}, μ_3^{eff}.

Translational order and shear stability are those features which allow to identify the states considered with smectic (Sm) phases (see Table I). For example, P(011) is a model for SmB. According to this model, SmB possesses crystalline translational order. At the same time, according to relation (6), the interlayer shear modulus μ_1^{eff} decreases with the applied strain ω_{ap} decrease and tends to zero in the static ($\omega_{\mathrm{ap}} \rightarrow 0$) case. This corresponds to experimental results.[9,10]

Thus, we believe that nonlinear effects provide intermolecular translational correlations in smectic phases and shear rigidity of these phases at sufficiently high frequencies of applied strain.

PHASE TRANSITIONS

The experimental result[11] that the entropy jump ΔS_{CB} at the crystal–SmB phase transition is, as a rule, several times higher than a summary jump ΔS_{BI} at the SmB–isotropic liquid one is of fundamental importance for understanding the melting nature and phase transitions in the layer system. The fact is that the first transition is not accompanied by disordering. The second one is characterized by complete translational and orientational disordering. We believe that this result contradicts to the ideas that the entropy jump is determined by the ordering change.

We believe that the entropy jump is (after all) determined by the intermolecular interaction change. This change is bound up with and can be characterized by the change of the shear moduli μ_i.

In connection with the above-stated we shall fulfill the phase transition investigation in accordance to the approach.[8] We write the free energy in the form of the shear moduli μ_i function[8]

$$F = \sum_{i=1}^{3} F_i = F(\mu_1, \mu_2, \mu_3; T) =$$

$$\sum_{i=1}^{3} \left\{ -\alpha_i \mu_i + \frac{1}{2} \sum_{j=1}^{3} \beta_{ij} \mu_i \mu_j + T \ln \left[\left(\sqrt{\mu_i} + \sqrt{\mu_i + \mu_i'} \right) \Big/ \sqrt{\mu_i'} \right] \right\}. \quad (7)$$

Here α_i and β_{ij} are phenomenological coefficients. They do not depend on the temperature; $\alpha_i > 0$, $\beta_{ij} < 0$ at $i \neq j$, $\beta_{ii} > 0$.

We suppose that the shear moduli μ_i value can be found from the condition of the free energy (7) minimum. In particular, temperatures at which the shear moduli μ_i turn into zero can be found from this condition, too. In accordance to results of the first part of the paper, phase transitions between the states considered (see Table I) occur at these temperatures. For example, the temperature T_c of the crystal–smectic B phase transition can be found from the relation $F(\mu_1, \mu_2, \mu_3; T_c) = F(0, \mu_2, \mu_3; T_c)$. It can be said for comparison that the shear moduli play the role in the present paper which is similar to that of order parameters in the Landau theory of phase transitions.[1]

It can be shown that F can have a minimum in all eight phases considered (see Table I). We write a condition of the minimum $\partial F/\partial\mu_i = 0$ at $\mu_i \neq 0$ in the form

$$\beta_{ii}\mu_i = \alpha_i - \beta_{ij}\mu_j - \beta_{ik}\mu_k - T/2\sqrt{\mu_i(\mu_i + \mu_i')}, \tag{8}$$

where $i \neq j \neq k \neq i$.

It will be easily proved that transitions between the phases considered are accompanied by μ_i and entropy jumps. These transitions are the first order ones. The temperature $T_i[P(t_1t_2t_3), P(t_1't_2't_3')]$ of a transition from the phase $P(t_1t_2t_3)$ into the $P(t_1't_2't_3')$ one can be found from the condition $F_i = 0$ at $\mu_i \neq 0$ (see Table I). And besides, the shear modulus μ_i becomes zero.

$$T_i[P(t_1t_2t_3), P(t_1't_2't_3')]$$

$$= \alpha_i\mu_i/\{2\ln[(\sqrt{\mu_i} + \sqrt{\mu_i + \mu_i'})/\sqrt{\mu_i'}] - \sqrt{\mu_i/4(\mu_i + \mu_i')}\}. \tag{9}$$

Let us analyze the relations obtained. We consider in detail conditions at which the layer crystal heating leads to the SmB formation. It is evident that for this formation it is necessary that the temperature T_1[P(111), P(011)] at which μ_1 becomes zero would be less than those T_2[P(111), P(101)] and T_3[P(111), P(110)] at which μ_2 and μ_3 become zero, respectively

$$T_1[\mathrm{P}(111), \mathrm{P}(011)] < \min\{T_2[\mathrm{P}(111), \mathrm{P}(101)]; T_3[\mathrm{P}(111), \mathrm{P}(110)]\}. \tag{10}$$

At the same time the SmB phase formed at T_1[P(111), P(011)] can be thermodynamically unstable even if the condition (10) is fulfilled. The fact is that due to the availability of a coupling between shear moduli ($\beta_{ij} < 0$ at $i \neq j$) the μ_1 conversion into zero stipulates a stability decrease with respect to other degrees of freedom. In accordance to relation (8) the μ_1 zero conversion leads to the jump-like decrease of μ_2 and μ_3. According to relation (9), the transition temperatures decrease at which μ_2 and μ_3 become zero (for example, T_2[P(111), P(101)] > T_2[P(011), P(001)]) due to this. If even one of these temperatures is less than T_1[P(111), P(011)] then the SmB phase is thermodynamically unstable. The phase transition would continue with the conversion into zero of μ_2 or μ_3 in this case. Thus, the thermodynamical SmB stability condition has the form

$$T_1[\mathrm{P}(111), \mathrm{P}(011)] < \min\{T_2[\mathrm{P}(011), \mathrm{P}(001)]; T_3[\mathrm{P}(011), \mathrm{P}(010)]\}. \tag{11}$$

According to relation (9), this condition is expressed by parameters characterizing a crystalline phase. Therefore, relation (11) can be considered as a condition determining properties of the crystal necessary for its forming the SmB phase at heating. For example, it follows from relations (8), (9), and (11) that the crystal has to possess a significant anisotropy, i.e., the ratios μ_1/μ_2 and μ_1/μ_3 should be sufficiently low values.

Transitions between other phases considered can be investigated similarly. By means of the approach proposed a sequence of "translational" phase transitions can be predicted and critical temperatures can be calculated.

Thus, we propose an approach by means of which a sequence of "translational" phase transitions in a layer system is determined by the free energy dependence on shear moduli.

We note in the conclusion that the main ideas of the paper seem to be sufficiently general. We believe that nonlinear effects are to be taken into account in other systems, too where elastic moduli are zero. It is reasonable to investigate phase transitions accompanied by the zero conversion of shear moduli (for example, an ordinary melting) in connection with a consideration of the free energy dependence on the shear moduli.

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