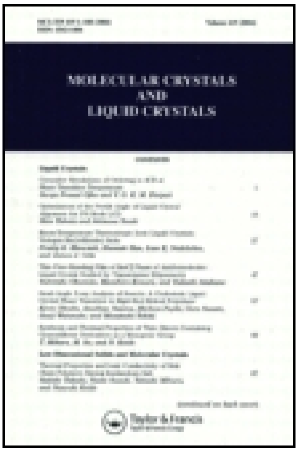

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Topological Types of Phase Diagrams of Smectic A Liquid Crystal in External Field: SBroaden Version of the Mean-Field Landau-De Gennes Model

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TOPOLOGICAL TYPES OF PHASE DIAGRAMS OF SMECTIC A LIQUID CRYSTAL IN EXTERNAL FIELD: BROADEN VERSION OF THE MEAN-FIELD LANDAU-DE GENNES MODEL

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Abstract. The influence of an external magnetic field on successive phase transitions, specifically of isostructural mode, taking place in smectic A liquid crystals with positive molecular anisotropy of magnetic susceptibility is studied on the basis of a broaden version of the mean-field Landau-de Gennes model. Topological classification of bifurcation sets (separatrices) and phase diagrams of the model are performed. It is shown that there are two critical values of the field: at the smaller value the isostructural phase transition of nematic-paranematic (N-pN) type cannot be realized and at the greater one the isostructural phase transition of smectic-smectic (Sm-Sm) type is absolutely suppressed. It is found a new kind of critical point in which the Sm-Sm critical end point, the triple Sm-Sm-N point and tricritical Sm-N point merge.

INTRODUCTION.

To date, a variety of liquid crystal substances has been discovered which exhibit complicated phase diagrams with multicritical points whose behavior can be explained in terms of coupled order parameters only. Among such systems are those that have layered orientationally ordered structure and demonstrate transformations without symmetry breaking, i.e. isostructural phase transitions, in the layered state. Isostructural phase transitions are observed in homological series of lecithines[1,2], alkyloxy-benzoic acids[3,4], paraffines[5], chlorides[6,7] and metallic chlorides[8,9] of alkylammonium compounds, binary mixtures of 11OPCBOB and 9OBCB[10] etc.

During the two most recent decades the problem of the influence of an external magnetic (or electric) field on liquid crystals has been intensively discussed (see, for example, References 11-25). Experimental studies have been mainly directed towards the verification of the theoretically predicted quadratic dependence of the isostructural nematic-paranematic (N-pN) phase transition versus the applied field value and a conclusion about the existence of the critical end point in the phase diagram in the "field-temperature" coordinates. From a theoretical point of view the latter two problems are completely solved at present, at least in terms of the approximation of rigid particles experiencing dispersional attraction, of the uniaxial type of their orientational ordering and of the quadrupole nature of the field applied[12,15,19,20] in the framework of the most popular Maier-Saupe[12] and Landau-de Gennes[15] models. Some other theoretical results derived on the basis of more complicated model[22-25] concerning the influence of the field on the orientationally ordered systems of molecules with internal degrees of freedom in nematic state are so far waiting for experimental verification. Besides, studies of the effects bound up with isostructural behavior of smectic A under the external field and in this connection the consideration of other attendant multicritical phenomena are put forward. Such a problem was solved earlier neither theoretically nor experimentally and for the first time is discussed in the present paper.

Nowadays there exist a number of models of smectic A liquid crystals that explain many experimental results (see, for example, References 26-38). The McMillan[31] and the Landau-de Gennes models remain the most universal ones. In original statement these models, however, do not take into account some factors that stipulate isostructural phase transitions and, therefore, do not allow to elucidate their mechanisms. In Reference 36 a new model of smectic A mesophase based on the microscopic McMillan approach was proposed by the present authors. It was shown that internal (conformational) rearrangements of liquid crystal molecules can give rise to transformation without global symmetry change both in smectic and nematic states of layered compounds. To solve the problem described above in the more common formulation we generalize in this paper the phenomenological Landau-de Gennes model of smectic A mesophase[26]. Below, the bifurcational analysis (see for details, for example, References 24,25,32,33,37,38) of a broaden version of the Landau-de Gennes model is carried out. All of the types of its separatrices are constructed and on this basis a topological classification of phase diagrams of smectic A liquid crystals with isostructural behavior in the external field is fulfilled.

FORMALISM

The free energy potential of smectic A mesophase in the external field H is taken in the form

$$F(Q,S) = \tau_1 Q^2/2 - \beta Q^3/3 + \gamma Q^4/4 + \tau_2 S^2/2 + bS^4/4 - \chi Q S^2 - \mu Q \qquad (1)$$

where state parameters Q, S are respectively orientational and translational order parameters; positive values β, γ, b and χ are material constants; the value $\mu \sim \chi_a H^2 (\chi_a > 0)$ describes the dimensionless contribution bound up with the action of the external magnetic field. Parameters

$$\tau_i = a_i (t - t_{c_i}), \qquad (a_i > 0, i=1,2) \qquad (2)$$

characterize a deviation of the system temperature t from temperatures t_{c_1}, t_{c_2} of corresponding mean-field phase transitions bound up with the order parameters Q, S respectively in the case when the latters are non interacting. It is important to keep in mind that the parameter χ characterizes the strength of coupling (interaction) of the order parameters Q and S. The expression (1), at account of Eqs. (2), corresponds, from a mathematical point of view, to the particular case of the $X_{1,0}$ type catastrophe[39] and from a physical one - to the broaden version of the Landau-de Gennes model with two coupled order parameters and seven coefficients $\tau_1, \tau_2, \beta, \gamma, b, \chi, \mu$ - control parameters of the model. Analysis performed for such a multiparametric potential at not fixed control parameters values but in the general form (i.e. in the seventh-dimensional control space $\{\tau_1, \tau_2, \beta, \gamma, b, \chi, \mu\}$) encounters sufficient calculational difficulties. Overcoming the latters, one may suppose, can lead to description of new effects. Below we simplify the problem considering only the case

$$\chi^2 > b\beta^2/(9\gamma) \tag{3}$$

of strong translational and orientational coupling.

Analysis shows that the inequality (3) is responsible for existence of a stable tricritical Sm-N point on phase boundary between the Sm and N states without magnetic field action (at $\mu=0$).

The expression (1) allows to determine the equations of state

$$\gamma Q^3 - \beta Q^2 + \tau_1 Q - \mu = 0, \tag{4}$$

$$\beta S^3 + \tau_2 S - 2\chi QS = 0 \tag{5}$$

and the stability matrix

$$\frac{1}{2}\left[\frac{\partial^2 F}{\partial Q^i \partial S^j}\right] = \begin{bmatrix} \tau_1 - 2\beta Q + 3\gamma Q^2 & -2\chi S \\ -2\chi S & \tau_2 + 3bS^2 - 2\chi Q \end{bmatrix} \tag{6}$$

of the molecular system. As it is known from catastrophe theory[39,40], the zero value of the stability matrix (6) determinant

$$\det\left[\frac{\partial^2 F}{\partial Q^i \partial S^j}\right] = 0 \tag{7}$$

defines, at account of the solutions of the system of Eqs. (4),(5), bifurcation sets (or separatrices) dividing the control space $\{\tau_1,\tau_2,\beta,\gamma,b,\chi,\mu\}$ into open areas with topologically different structure of the thermodynamic potential (1). On the basis of expressions (4)-(7) we write below the equations of state of different phases of the model and their separatrices for two cases $\mu=0$ and $\mu\neq 0$ separately.

Case 1: $\mu=0$

It can be found from Eqs.(4),(5) that, at $\mu=0$, their possible solutions fall into three groups

$$Q = S = 0, \tag{8}$$

$$S=0,\ \gamma Q^2 - \beta Q + \tau_1 = 0, \tag{9}$$

$$\begin{cases} b\gamma Q^3 - b\beta Q^2 + (b\tau_1 - 2\chi^2)Q + \chi\tau_2 = 0, \\ S^2 = -(\tau_2 - 2\chi b)/b, \end{cases} \tag{10}$$

the first (8) of which corresponds to isotropic liquid (IL), the second (9) one - to the N phase and the third (10) one - to the Sm phase. It follows from Eqs. (6)-(10) that separatrices X_{IL}, X_N, X_{Sm} of the IL, N and Sm states can be written as

$$X_{IL}:\quad \tau_1\tau_2 = 0, \tag{11}$$

$$X_N:\ \begin{cases} \tau_1 = \beta^2/(4\gamma), & (12) \\ \tau_1 = -\gamma\,\tau_2^2/4\chi^2 + \tau_2\,\beta/(2\chi), & (13) \end{cases}$$

$$X_{Sm}:\ \begin{cases} \tau_1 = -3\gamma Q^2 + 2\beta Q + 2\chi^2/b, \\ \tau_2 = Q^2(2b\gamma Q - b\beta)/\chi, \end{cases} \tag{14}$$

respectively. Analysis shows (see below) that Eqs. (10), (14) describe two different smectic states.

Case 2: $\mu \neq 0$

As it can easily be seen, the solution (8) can not be realized at $\mu \neq 0$. Instead, in weak fields there are two orientationally ordered and translationally disordered states - N and pN - which are described by the Equation

$$\gamma Q^3 - \beta Q^2 + \tau_1 Q - \mu = 0 . \qquad (15)$$

Orientationally and translationally ordered states are described as

$$\begin{cases} b\gamma Q^3 - b\beta Q^2 + (b\tau_1 - 2\chi^2)Q + (\chi\tau_2 - \mu) = 0, \\ S^2 = -(\tau_2 - 2\chi b)/b. \end{cases} \qquad (16)$$

It follows from Eqs. (6),(7),(15) ,and (16) that separatrices $X_{N(pN)}, X_{Sm}$ of the N(pN) and Sm states can be written as

$$X_{N(pN)}: \quad 4\gamma\tau_1^3 - \beta^2\tau_1^2 - 18\beta\gamma\mu\tau_1 + 4\mu\beta^3 + 27\mu^2\gamma^2 = 0, \qquad (17)$$

$$\begin{cases} \tau_1 = -\gamma Q^2 + \beta Q + \mu/Q, \\ \tau_2 = 2\chi Q, \end{cases} \qquad (18)$$

$$X_{Sm} \quad \begin{cases} \tau_1 = -3\gamma Q^2 + 2\beta Q + 2\chi^2/b, \\ \tau_2 = (2\gamma Q^3 - \beta Q^2 + \mu)b/\chi, \end{cases} \qquad (19)$$

respectively.

RESULTS AND DISCUSSION

We now try to determine explicit forms of bifurcation sets, stability areas of different phases and corresponding phase diagrams in the $\{\tau_1, \tau_2\}$ coordinates plane considering the rest of the control parameters to be arbitrary (at account of the inequality (3)) but fixed ones in every concrete calculation. Then, Eq. (11) determines curves coinciding with coordinates axes, Eqs. (12),(13) determine a straight line parallel to the τ_2 axis and a parabola, respectively. Eqs. (14) define the Sm A phase separatrix in parametric representation with the parameter Q taking as a parameter of the curve in the $\{\tau_1,\tau_2\}$ coordinates (the same, as well, is true for formulae (18),(19)). The latter is an algebraic curve with a turning point. Results concerning bifurcation sets of the model under consideration, at $\mu=0$, are presented in Figure 1a.

Analogously, at $\mu\neq0$, cubic Eq. (17) depending on the sign of its discriminant

$$D = \mu(\mu - \mu^*)/(16\gamma^2), \tag{20}$$

determines three, two or one straight lines parallel to the τ_2 axis (see dashed lines in Figures 1b-d). Eq. (20) includes the first critical value

$$\mu^* = \beta^3/(27\gamma^2) \tag{21}$$

of the field.

Eq. (17) describes a disconnected curve, consisting of two parts, being a consequence of bifurcation of the parabola curve (13) at $\mu\neq0$. These two parts of the curve (17) have three ($D<0$) or one ($D>0$) extreme points in totality (or one maximum and one inflection point at $D=0$; see Figure 1c) depending on the sign of the discriminant (20) (compare Figures 1b-e). Eqs. (19) define, as above, the separatrix of the Sm phase at $\mu\neq0$. Its turning point (TP) has the following coordinates

$$\tau_2^{TP} = (\mu - \mu^*)b/\chi, \tag{22}$$

$$\tau_1^{TP} = 2\chi^2/b + \beta^2/(3\gamma). \tag{23}$$

The coordinate $\tau_1{}^{TP}$ satisfies requirements of Eq. (17) at the second critical value

$$\mu^{**} = \mu^* + 2\beta\chi^2/(3b\gamma) \tag{24}$$

of the field (see Figure 1e).

There is one else important circumstance requiring to note. At $\mu=0$, the Sm phase separatrix (14) has a point of tangency with the straight line $\tau_2=0$ (the IL phase separatrix) and, if the condition

$$2b\gamma Q^2 - b\beta Q - 2\chi^2 = 0 \tag{25}$$

s fulfilled, it has two points of tangency with the parabola (13)(Figure 1a). At $\mu \neq 0$, if the condition

$$2b\gamma Q^3 - b\beta Q^2 - 2\chi^2 Q + b\mu = 0$$

is satisfied, the separatrix X_{Sm} has three (Figures 1b-d) or one (Figure 1e) points of tangency depending on the sign of a discriminant of cubic Eq. (26). Analysis shows that the former takes place at $0 < \mu < \mu^{**}$ and the latter - at $\mu = \mu^{**}$. Ultimately, Figures 1a-f reflect a topological classification of possible types of separatrices of the model under consideration.

Stability areas of different phases are determined by existence of solutions of Eqs. (15),(16) at $\mu > 0$, if the stability relations

$$\frac{\partial^2 F}{\partial Q^2} > 0, \quad \det\left[\frac{\partial^2 F}{\partial Q^i \partial S^j}\right] > 0 \tag{26}$$

are fulfilled on these solutions. Investigation of Eqs. (8)-(10) and (15),(16) in conjunction with the inequalities (26), with due regard for the bifurcational analysis fulfilled above, gives an opportunity to formulate eventual result in the form of topological classification of stability areas of the IL, N and Sm states showed in Figures 2a,c,e at $\mu=0$, and of the pN, N and Sm states showed in Figures 2b,d,f at $0 < \mu < \mu^*$. Note that the cases $\mu^* < \mu < \mu^{**}$ and $\mu > \mu^{**}$ can easily be reproduced by comparison of Figures 1d-f and 2b,d,f.

Now, in view of previous conclusions, it is easy to derive fundamentally different topological types of phase diagrams of the Sm liquid crystal. They are presented in Figure 3. As it is seen from Figure 3a, the main feature of the broaden version of the Landau-de Gennes model is that, at $\mu=0$, there is always two smectic phases - weak (Sm_1) and strong (Sm_2) modulated ones (see Eqs. (10)) - divided by the first order phase transition line terminated in the turning TP point of the smectic separatrix. As it is seen from Figure 3, another important features of the phase dia-

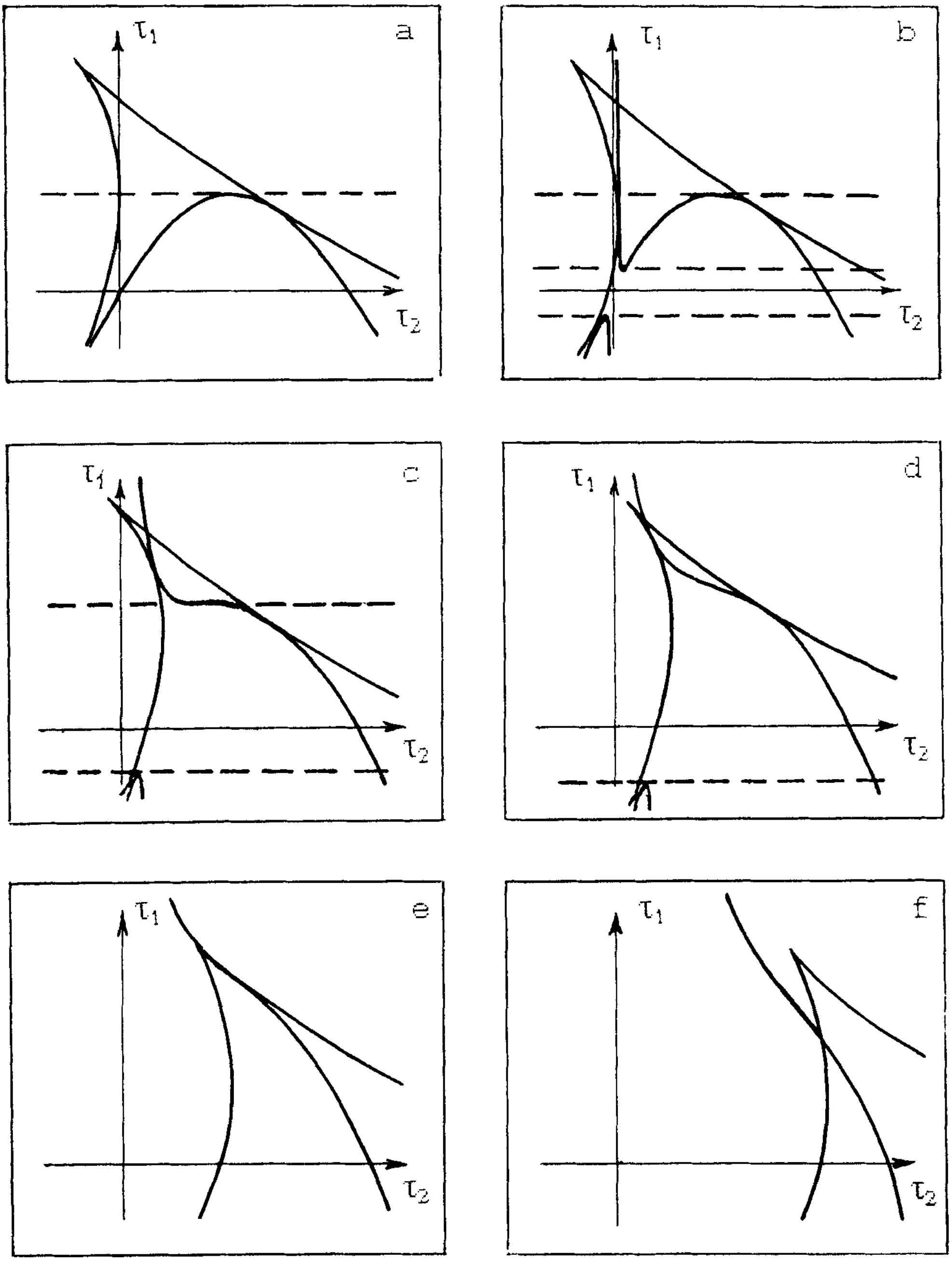

FIGURE 1 Topological types of separatrices of the model versus magnetic field : $\mu=0$ (a), $0<\mu<\mu^{*}$ (b), $\mu=\mu^{*}$ (c), $\mu^{*}<\mu<\mu^{**}$ (d), $\mu=\mu^{**}$ (e), $\mu>\mu^{**}$ (f).

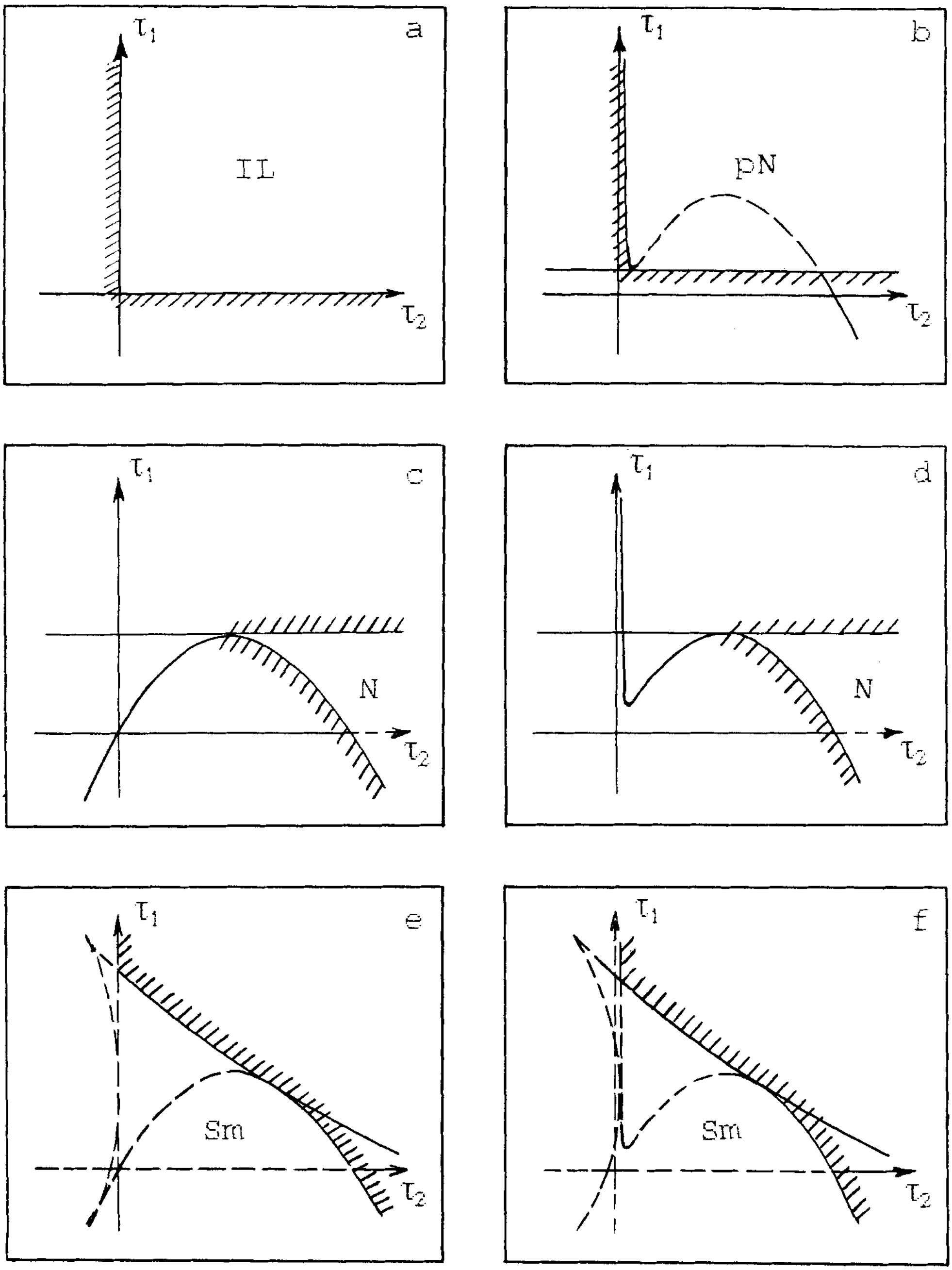

FIGURE 2 Stability areas of the IL (a), N (c), Sm (e) states at $\mu=0$ and the pN (b), N (d), Sm (f) states at $0 < \mu < \mu^*$.

gram, at $\mu=0$, are as follows. Firstly, there are two triple Sm_1-Sm_2-IL and Sm_1-N-IL points. Secondly, the Sm_1-IL and N-IL phase transitions are first order ones and the Sm_2-IL phase transition is second order one (the corresponding lines of phases coexistence are described in figure 3 by the solid and double lines). Thirdly, one of two points of tangency of the Sm and N separatrices (point A in Figure 3a) corresponds to non-physical solutions range (where the bifurcation parameter Q is negative) and the other one (point TCP in Figure 3a) - to a tricritical point (TCP) on the Sm_1-N curve.
As it is seen from Figures 3a,b, there are small changes in the topology of phase diagram in weak fields comparative to the case $\mu=0$. The first essential moment at $\mu\neq0$, is that, at the condition $0<\mu<\mu^*$, there are two isostructural Sm_1-Sm_2 and pN-N phase transitions. The second one is that the field stabilizes the Sm_1-N tricritical point increasing the existence range of the first order Sm_1-N phase transition. The condition $\mu=\mu^*$ is the boundary one (see Figure 3c) and at $\mu>\mu^*$ the Wojtowicz-Shang effect[12] of the N-pN phase transition disappearance takes place (Figure 3d). There is a new kind of critical point in which the critical end Sm_1-Sm_2 point, the triple Sm_1-Sm_2-N point and the tricritical Sm-N point merge (Figure 3e). At $\mu>\mu^{**}$ there is the only second order Sm-N phase transition equilibrium curve in the (τ_1,τ_2) phase diagram (Figure 3f). Ultimately, Figures 3a-f reflect the topological classification of possible types of phase diagrams of the model under consideration.

CONCLUSION

The main result derived above is the prediction of the existence of the isostructural "weak - strong density wave"

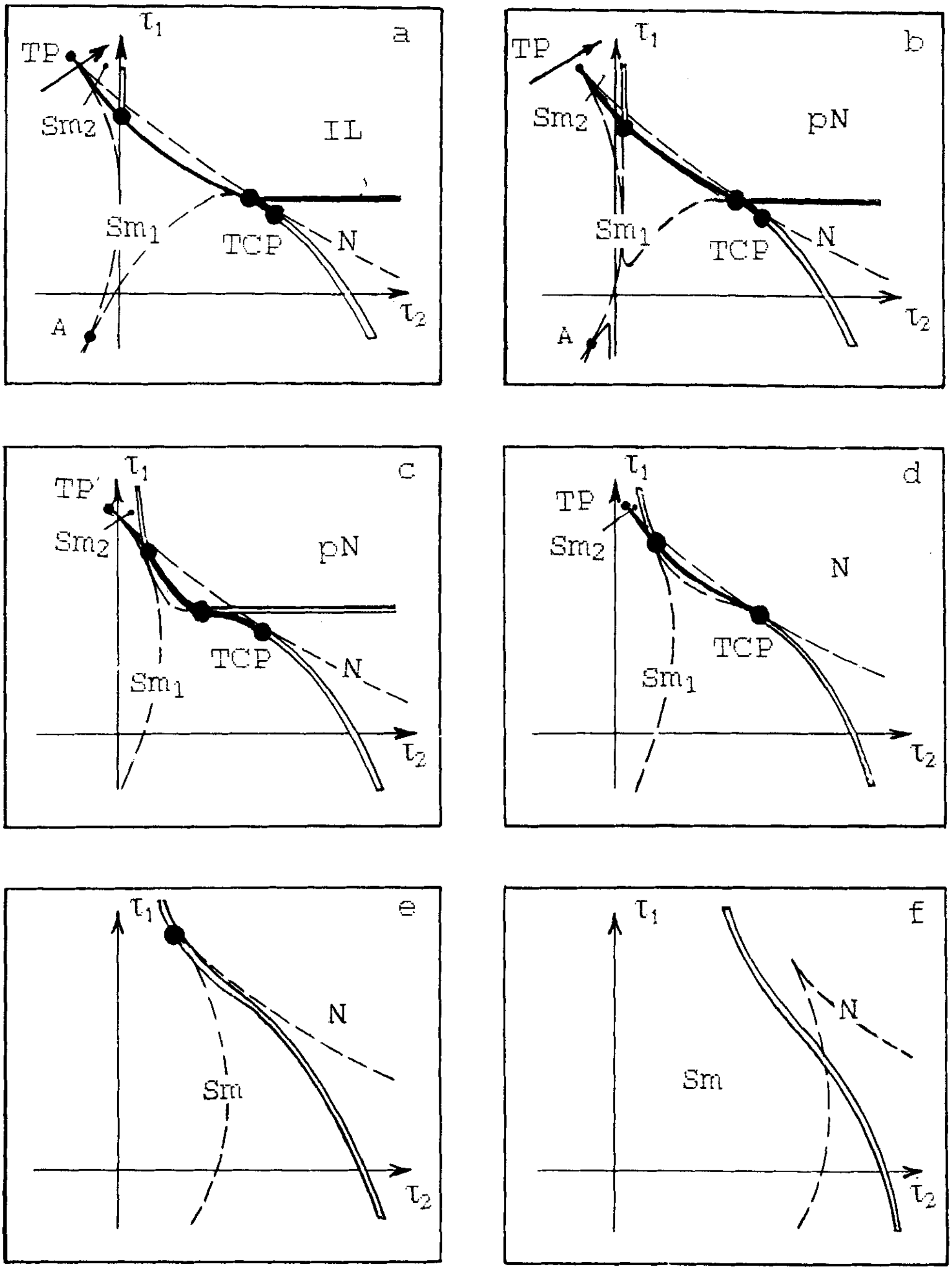

FIGURE 3 Topological types of phase diagrams versus magnetic field: $\mu=0$ (a), $0<\mu<\mu^*$ (b), $\mu=\mu^*$ (c), $\mu^*<\mu<\mu^{**}$ (d), $\mu=\mu^{**}$ (e), $\mu>\mu^{**}$ (f)

phase transition in smectic state and its suppression at the influence of external magnetic (or electric) field. The only reason for implementation of this isostructural transformation is the coupling between orientational and translational orderings of a system. Let us note that the suppression of the Sm_1-Sm_2 phase transition under field can proceed not only in strong fields ($\mu > \mu^*$) but also in any weakly ones ($\mu << \mu^*$). Actually, a thermodynamic evolution trajectory of a liquid crystal in the Landau-de Gennes model is, according to Eqs. (2), an oriented straight line directed from the third quadrant of the Cartesian plane to the first one (see vector in Figure 3a) and, if this trajectory is located close to the turning point of the smectic separatrix, then even a small increase of the field leads, at first, to continuous damping of the first order isostructural transition (when the evolution path passes through the end point of the Sm_1-Sm_2 equilibrium phase line; see Eq. (16)) with its full vanishing, as a result, at further rise of the field value (compare disposition of vectors with respect to the smectic separatrix in Figures 3a and 3b). It can be supposed that the same tendency can be realized for substances, placed in the field, with isostructural transformations such as bilayer-quasibilayer smectic etc. found experimentally (see, for example, Reference 29).

We would also like to emphasize the second interesting result. The broaden version of the Landau-de Gennes model demonstrates, at the condition of the fulfillment of the inequality (3), the existence of the tricritical Sm-N point in the absence of the field. We have shown that the field rise leads to stabilization of this TCP increasing the existence range of the first order Sm_1-N phase transition. The last result can be of practical importance for testing theoretical ideas about the behavior of mesomorphic structures in relatively weak ($\mu << \mu^*$) fields. In high fields ($\mu > \mu^*$) the opposite inclination takes place; at field increase an extent of the first order part of the Sm-N phase boundary decreases what is succeeded by coming together of the triple Sm_1-Sm_2-N and the tricritical $Sm_1 - N$ points. Eventually, when the terminal Sm_1-Sm_2, the triple Sm_1-Sm_2-N and the tricritical Sm_1-N points coincide a new kind of critical point arises.

Nowadays the last result is seemed to be of theoretical importance only since the condition of its realization is $\mu = \mu^{**} > \mu^{*}$. Meanwhile it is known[12,13] that the critical end point terminating the N-pN line of the most studied systems of quasi-rigid molecules is observed in the experimental resolution limit and, as was shown above, the mathematical condition at which the N-pN phase transition vanishes is $\mu = \mu^{*}$.

Let us finally note that in the present paper we have investigated the only case when the stable tricritical point locates on the Sm-N equilibrium boundary (see Eqs. (3)). Another case corresponding to a virtual tricritical Sm-N point that, from a mathematical point of view, is a consequence of validity of the inequality opposite to that in Eqs. (3) along with examination of topological types of phase diagrams of the broaden version of the Landau-de Gennes model in the "temperature-field" coordinates is the purpose of a future work.

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