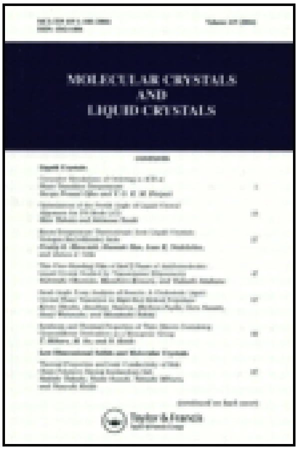

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Nematic-Nematic Phase Transition as a Consequence of Orientational-Translational Order Parameters Interaction

Vladimir A. Konoplev [a], Boris M. Borovik [a], Dmitry E. Isaychenko [a] & Vladimir K. Pershin [b]

[a] Ural State Technical University, Ekaterinburg, 620002, RUSSIA

[b] Ural State Economical University, Ekaterinburg, 620062, RUSSIA

Version of record first published: 24 Sep 2006

Mol. Cryst. Liq. Cryst., 1999, Vol. 330, pp. 581-592
Reprints available directly from the publisher
Photocopying permitted by license only

Nematic-Nematic Phase Transition as a Consequence of Orientational-Translational Order Parameters Interaction

VLADIMIR A. KONOPLEV[a], BORIS M. BOROVIK[a], DMITRY E. ISAYCHENKO[a] and VLADIMIR K. PERSHIN[b]

[a]*Ural State Technical University, Ekaterinburg 620002, RUSSIA and* [b]*Ural State Economical University, Ekaterinburg 620062, RUSSIA*

A model of smectic A liquid crystal with nonlinear competiting orientational and translational order parameters in the eight-dimensional control parameters space is developed. Topological analysis is performed which allows to construct all possible, at least two-dimensional, phase diagrams of the model under consideration. It is shown that orientational and translational interactions can be the only reason leading to the existence of two different nematic phases and isostructural phase transitions of the nematic-nematic type which were observed in some mesogeneous compounds.

Keywords: smectic A liquid crystal; phase diagrams; isostructural phase transitions

INTRODUCTION

To date, a variety of liquid crystal substances has been discovered which exhibit complicated phase diagrams and whose behaviour 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 (IPTs). The latter are observed in homologous series of lecithins[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.

There are many theoretical papers devoted to the description of IPTs of the nematic–nematic type[11–15]. As it is suggested in these papers, the mechanism responsible for IPTs is the competition of molecular conformational and orientational degrees of freedom. But let us emphasize once more that the majority of isostructural orientationally ordered states are observed in lamellar structures and therefore it is important to clarify the problem theoretically by way of models of smectic liquid crystals taking into account translational order. To date, there is no phenomenological model of smectic mesophase that allows to describe IPTs. In the present paper in terms of phenomenological approach it is shown that the reason of the existence of intermediate nematic states and, consequently, transformations without symmetry breaking is not necessarily the interaction of conformational and orientational ordering, but the one of translational and orientational order parameters. Such a conclusion is derived from topological analysis of a model of smectic liquid crystal whose thermodynamical potential represents the version of the modal catastrophe of the $W_{1,0}$ type[16].

FORMALISM

According to symmetry of the smectic A liquid crystal and the formulae of the $W_{1,0}$ catastrophe[16] the free energy potential of the system is taken in the form

$$F(Q,S) = \tau_1 Q^2/2 - \beta Q^3/3 + \gamma Q^4/4 - \delta Q^5/5 + \alpha Q^6/6 + \\ + \tau_2 S^2/2 + bS^4/4 - \chi Q S^2 + \eta Q^2 S^2/2, \qquad (1)$$

where β, γ, δ, α, χ, b and η are positive constants; parameters $\tau_k = a_k\left(T - T_c^k\right)$, $(a_k > 0,\ k = 1,2)$ characterize deviation of the mesophase temperature T from the lower stability boundary T_c^1 of the isotropic liquid (I) and the smectic A (A) – nematic (N) phase transition (PT) temperature T_c^2 in the case when orientational Q and translational S order parameters are non–interacting. The equations of state of the potential (1) can be written in the form

$$\begin{cases} \tau_1 Q - \beta Q^2 + \gamma Q^3 - \delta Q^4 + \alpha Q^5 - (\chi - \eta Q)S^2 = 0, & (2) \\ S(\tau_2 - 2\chi Q + \eta Q^2 + bS^2) = 0, & (3) \end{cases}$$

and stability matrix is equal

$$\mathrm{Hes}(F) = \begin{bmatrix} \tau_1 - 2\beta Q + 3\gamma Q^2 + 5\alpha Q^4 & 2(\eta Q - \chi)S \\ 2(\eta Q - \chi)S & \tau_2 - 2\chi Q + \eta Q^2 + 3bS^2 \end{bmatrix}. \qquad (4)$$

There are three groups of possible solutions of the state equations (2), (3)

$$S = 0,\ Q = 0; \qquad (5)$$

$$S = 0,\ \alpha Q^4 - \delta Q^3 + \gamma Q^2 - \beta Q + \tau_1 = 0; \qquad (6)$$

$$\begin{cases} S^2 = (2\chi Q - \eta Q^2 - \tau_2)/b, & (7) \\ b\alpha Q^5 - b\delta Q^4 + (b\gamma - \eta^2)Q^3 + (3\chi\eta - b\beta^2)Q^2 + & (8) \\ \quad + (\tau_1 b - 2\chi^2 - \tau_2\eta)Q + \chi\tau_2 = 0 \end{cases}$$

which correspond to I (5), N (6) and A (7),(8) mesophase states.

The model separatrix can be represented as a combination of the three X_I, X_N, X_A subsets

$$X_I: \tau_1\tau_2 = 0, \quad (9)$$

$$X_N: \begin{cases} \tau_1 = \beta Q - \gamma Q^2 + \delta Q^3 - \alpha Q^4, & (10) \\ (\tau_1 - 2\beta Q + 3\gamma Q^2 - 4\delta Q^3 + 5\alpha Q^4)(\tau_2 - 2\chi Q + \eta Q^2) = 0, & (11) \end{cases}$$

$$X_A: \begin{cases} \tau_1 = \beta Q - \gamma Q^2 + \delta Q^3 - \alpha Q^4 + (\chi - \eta Q)S^2/Q, & (12) \\ \tau_2 = 2\chi Q - \eta Q^2 - bS^2, & (13) \\ b(\tau_1 - 2\beta Q + 3\gamma Q^2 - 4\delta Q^3 + 5\alpha Q^4 + \eta S^2) - 2(\chi - \eta Q)^2 = 0 & (14) \end{cases}$$

The analysis of Eqs. (2)–(14) allows to derive a number of critical values of the model parameters affecting significantly the topology of separatrix and, hence, phase diagrams of the system.

In addition, analysis shows that results of the present model coincide qualitatively with the ones obtained earlier in terms of the $X_{1,0}$ catastrophe potential[17] at the condition $\gamma \ge \gamma_S^*$, where

$$\gamma_S^* = 2\delta^2/(5\alpha) + \eta^2/b. \quad (15)$$

In situation, when $\gamma \le \gamma_N^*$, where

$$\gamma_N^* = 3\delta^2/(8\alpha), \quad (16)$$

these models are essentially distinguished for emergence of some novel topological features both in the X_A and X_N separatrices. Two additional critical values

$$\beta_N^m = \delta\left(3\gamma/2 - \gamma_N^{\bullet}\right) - \left(D'_N\right)^{1/2} \Big/ \left(72\alpha^2\right), \qquad (17)$$

$$\beta_N^M = \delta\left(3\gamma/2 - \gamma_N^{\bullet}\right) + \left(D'_N\right)^{1/2} \Big/ \left(72\alpha^2\right), \qquad (18)$$

where

$$D'_N = 3\left(\gamma_N^{\bullet} - \gamma\right)^3 \Big/ (8\alpha)^3$$

are important for the topological investigation under consideration.

RESULTS AND DISCUSSION

Stability areas together with separatrices of different states of the model in (τ_2,τ_1) coordinates are presented in Figure 1 for the cases as follows: $\beta>\beta_N^M$ (Figures 1 a, b), $\beta_N^m<\beta<\beta_N^M$ (Figures 1c, d), $\beta=\beta_N^m$ (Figures 1 e, f). The parameter values are chosen as $\alpha=1/4$, $\delta=4/3$, $b=1$, $\chi=4/3$, $\eta=0$, $\gamma=2.2$ and provide the condition $\gamma \le \gamma_N^{\bullet}$. It is seen from Figures 1 c–f that there are two different nematic states N and N′ which exist together at the condition $\beta_N^m\le\beta<\beta_N^M$ only. By reason of overlapping of stability areas of these phases at the condition $\beta_N^m<\beta<\beta_N^M$ there is the IPT between them. In the limit $\beta=\beta_N^m$, when the minimum and the right maximum of the X_N curve degenerate into an inflection point (see Figures 1 e, f), the overlapping area of the N and N′ phases vanishes and, hence, the N–N′ IPT becomes of the second order.

Typical phase diagram in (τ_2,τ_1) coordinates are presented in Figures 2, 3 depending on the β parameter value. The curves of first and second order PTs are drawn by solid and dashed lines

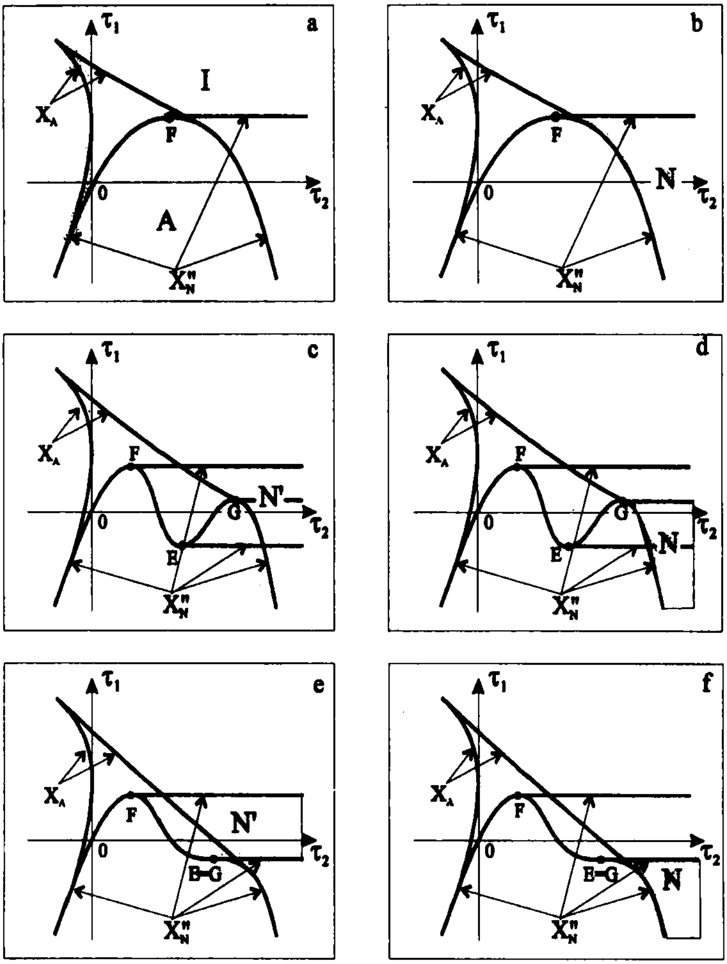

FIGURE 1 Stability areas of smectic A (A), isotropic liquid (I) (a), nematic N and N' states (b-f) in (τ_2,τ_1) coordinates at various β parameter values

respectively. Thin lines are the X_A and X_N separatrices curves. Solid lines correspond to the condition Q>0, points — to the alternative case. As it is seen from Figure 2 a, the line of the A–N PTs possesses virtual tricritical point (TCP_V). This line is convex upwards and finishes in the triple point TP_1 where three phases (A, N and I) coexist simultaneously. Moreover, the other smectic phase A′ exists in the cross–hatched part of the phase diagram. Therefore, there is the line of the A–A′ IPTs which begins in the A–A′–I TP_2 and finishes in corresponding critical end point (CEP). Details of this part of the phase diagram will be discussed elsewhere.

At first, the novel nematic state occurs in PD at the condition $\beta=\beta_{TP}<\beta_N^M$ which corresponds to the equality of minima of the potential (1) for three phases: $F_N=F_{N'}=F_I$ in the situation when the right maximum of the separatrix X_N is higher than the left one (see Figure 2b). Note that in this case the N–I line is in fact the N–N′–I line of triple points, and the TP_1 is actually the quadruple A–N–N′–I point. Decrease of the β parameter results in its splitting into two triple points TP_1 and TP_3. Here the A–N line is the second order one and the A–N′ line is the first order one (see Figure 2 c).
The situation becomes fundamentally different at the condition $\beta=\beta_{TCP}>\beta_N^m$ which corresponds to coincidence of the A–N–N′ TP with TCP (see Figure 3 a). Further decrease of the β orientational parameter ($\beta<\beta_{TCP}$) leads to the appearance of the real TCP on the A–N boundary (see Figure 3 b). Hereinafter, at $\beta=\beta_N^m<\beta_{TCP}$ the

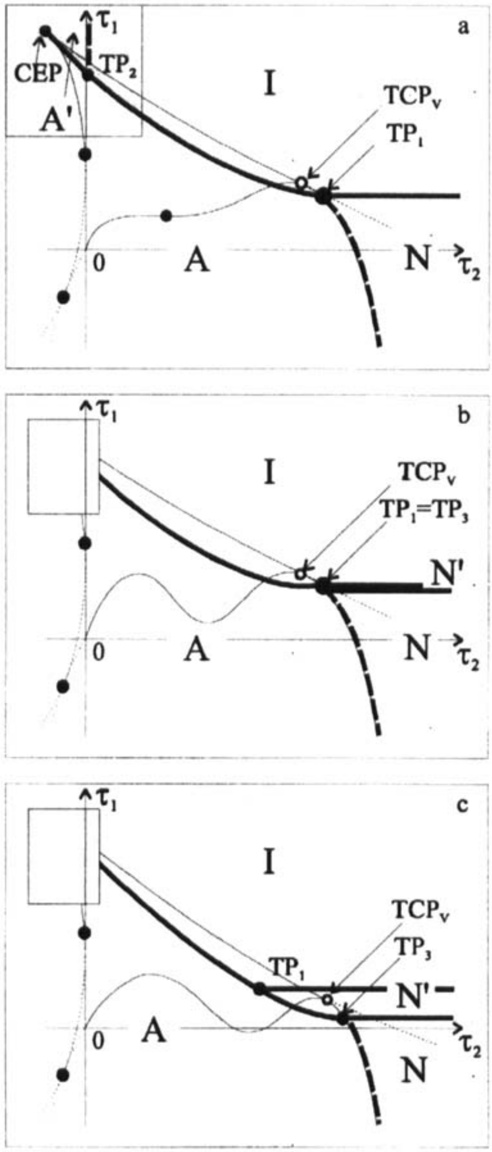

FIGURE 2 Phase diagrams of smectic A in (τ_2,τ_1) coordinates at various β parameter values: $\beta=\beta_N^M$ (a), $\beta_N^M > \beta = \beta_{TP}$ (b), $\beta_{TP} > \beta > \beta_N^m$ (c)

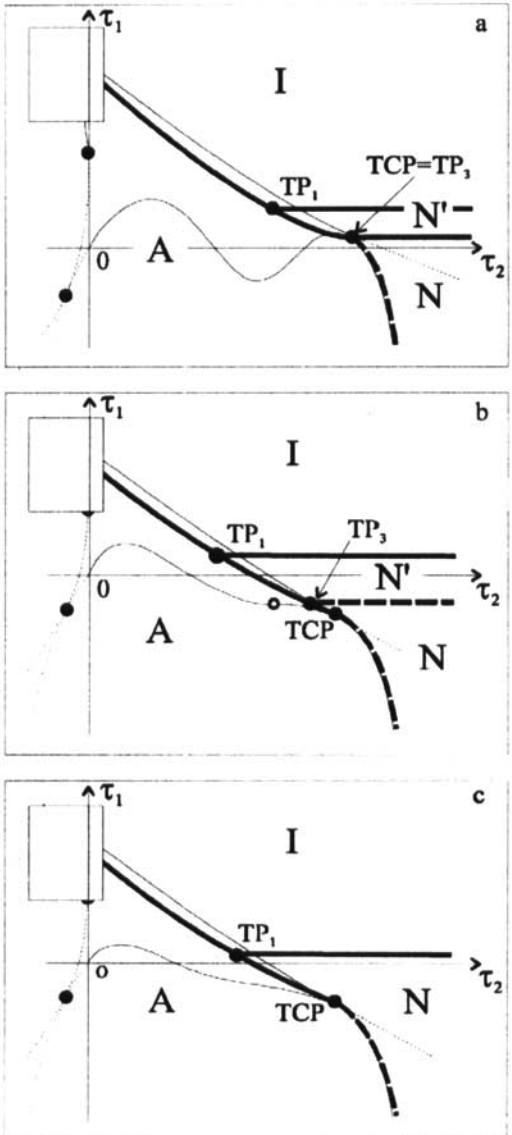

FIGURE 3 Phase diagrams of smectic A in (τ_2,τ_1) coordinates at various β parameter values: $\beta=\beta_{TCP}>\beta_N^m$ (a), $\beta=\beta_N^m$ (b), $\beta<\beta_N^m$ (c)

overlapping area of the N and N′ phases vanishes and the N–N′ IPT becomes the second order one (see Figure 3 b). At the condition $\beta<\beta_N^m$ only the N state appears in the phase diagram (see Figure 3 c).

In Figure 4, as a case in point, temperature dependences of orientational and translational order parameters are presented which correspond to three characteristic variants of thermodynamic pathes. According to the Landau theory the latter may be introduced in parametric form

$$\tau_1 = A\tau + B, \quad \tau_2 = \tau, \tag{19}$$

and are depicted in the insertions to Figure 4 as oriented straight lines. In (19) A>0 and B are control parameters of thermodynamic path. In Figure 4 the dimensionless temperature of the system τ is normalized to the temperature τ_0 of the PT to isotropic liquid state. It is seen that there can be PTs in the A–N–N′ sequence both of the first and the second order. Note that the most typical situation should correspond to the case when the N–N′ PT is of the first order.

CONCLUSION

In the present paper the different, as opposed to conventially discussed, mechanism is proposed for the nematic–nematic isostructural phase transition originated from competition of and translational order parameters, but not being a consequence of the influence of internal degrees of freedom on smectic ordering.

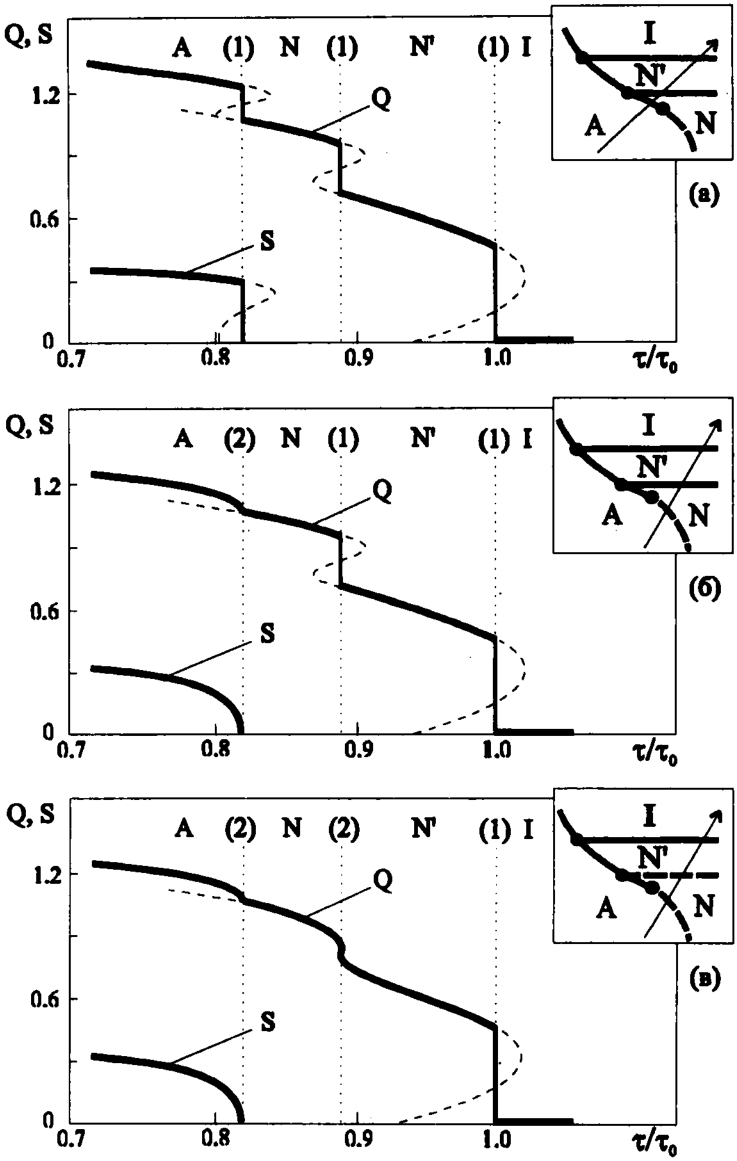

FIGURE 4 **Temperature dependences of order parameters for thermodynamic ways depicted as arrows in proper sertions**

Acknowledgments

This work was supported by RBRF Grant. Support received from the Organizing Committee of 16th ILCC, Kent, USA.

References

[1] K. Furuya, and T. Mitsui, *J. Phys. Soc. Jap.*, **46**, 611 (1979).
[2] H. Tanaka, and J. Freed, *J. Phys. Chem.*, **88**, 6633 (1984).
[3] P.D. Simova, and M. Petrov, *J. Phys. D.*, **14**, 1 (1981).
[4] Y.P. Kocherga, *Zhurn. Techn. Phys.*, **53**, 1649 (1983).
[5] B. Ewen, G. Strobl, and D. Richter, *Faraday Discuss. Chem. Soc.* , **69**, 19 (1980).
[6] V. Busico, A. Ferraro, and M. Vacatello, *Mol. Cryst. Liq. Cryst.*, **128**, 243 (1985).
[7] V. Busico et al, *J. Phys. Chem.*, **87**, 1631 (1983).
[8] I. Lelidis, and G. Durand, *Phys. Rev. E.*, **48**, 3822 (1993).
[9] P. Zuniga, and G. Chapius, *Mol. Cryst. Liq. Cryst.*, **128**, 349 (1985).
[10] R. Shashidhar et al, *Phys. Rev. Lett.*, **59**, 1209 (1987).
[11] J. Hanus, *Phys. Rev.* , **178**, 420 (1969).
[12] J. Firpo et al, *J. Chem. Phys.*, **74**, 2569 (1981).
[13] C. Rosenblatt, *Phys. Lett. A.*, **83**, 221 (1981).
[14] P. Palffy-Muhoray, and D. Dunmur, *Phys. Lett. A.*, **91**, 121 (1982).
[15] R. Hornreich, *Phys. Lett. A.*, **109**, 232 (1985).
[16] V.A. Vasil'ev, *Functoin. Analiz*, **11**, 1 (1977).
[17] Vl.K. Pershin, *Zurnal Phiz. Him.*, **69**, 65 (1995).