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Smectic A–nematic phase transition in a system of biaxial molecules

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The thermodynamics of the S_A –N phase transition has been studied within the framework of the McMillan model generalized to biaxial molecules. The influence of the biaxiality of the molecular pseudopotential has been shown to be weak for the transition temperature $T_{S_A N}$, noticeable for the tricritical point position T_{icp} on the line of S_A –N transitions and strong for the entropy of the transition $\Delta S_{S_A N}$. With the McMillan parameters α and δ being constant the entropy change $\Delta S_{S_A N}$ decreases with increasing biaxiality parameter λ . For sufficiently high values of δ and for α corresponding to a narrow nematic range increasing λ can result in changing the S_A –N transition from first to second order. The influence of λ on the change of the biaxiality $G = S_{xx} - S_{yy}$ of the molecular order parameter in the smectic phase is in agreement with available experimental data.

1. Introduction

A rich variety of well-known liquid-crystalline phases [1] is caused by the molecular shape anisotropy as well as by anisotropic steric, dispersion and other intermolecular interactions. The form of the phase diagram, the order of the phase transitions and their thermodynamic parameters, as well as the temperature dependence of the molecular order parameters are determined by the balance of intermolecular interactions of different types and depend essentially on the delicate structural features of molecules or the structural units formed by them.

One of these important features is the biaxiality of the molecular shape. Within the framework of the molecular statistical [2–8] and phenomenological [9–11] theories and computer simulation [12, 13] it has been found that the biaxiality is important for explaining the weakness of the first order nematic–isotropic transition for real mesomorphic compounds. In addition to this the molecular biaxiality influences noticeably the orientational order parameters and their temperature dependence [2–6], molecular dynamics and orientational correlation functions [14–16], the cholesteric pitch [17, 18], and the macroscopic anisotropic diamagnetic susceptibility in the nematic phase [6, 19]. All of this has stimulated the intensive development of the theory for pure [2–14] nematics as well as for nematic mixtures [20–23] formed from biaxial molecules on the one hand and its experimental validation by the different methods [20–31] on the other.

There is also a great number of papers concerned with the features of the smectic A–nematic transition [11, 32, 33]. However, theoretical investigations of the influence of a molecular biaxiality on this transition are absent. Moreover, there are experimental reasons for such studies. For example, the first order S_A –N transition influences the value and the temperature dependence of the order parameter $G = S_{xx} - S_{yy}$ for the

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solvent [29] and solute [20, 21, 27, 28, 30, 31] biaxial molecules of liquid crystals. The dependence $G(S = S_{zz})$ in the S_A phase changes in comparison with that in the N phase [20, 21, 27, 28, 30]. The change of the rotational diffusion coefficient D_{\parallel}^r at the S_A -N transition for molecules with small biaxiality has been found also by optical spectroscopy [34]. Finally, the change in energy of the anisotropic dispersion interactions of biaxial molecules at the S_A -N transition and corresponding shifts of polarized absorption bands of molecules have been observed [30]. All of this testifies to the fact that the molecular biaxiality has to be taken into account in order to describe the structural and thermodynamic properties of smectics.

The first attempt of such consideration [35] has been made within the framework of the McMillan model [36] generalized to biaxial molecules. This allowed the explanation of the experimental data [30] quantitatively and to elucidate the influence of smectic layering on the orientational, translational and mixed order parameters of solute molecules as well as on their positional-orientational correlations. However, the thermodynamics of the S_A -N transition has not been investigated in that case. The athermal system of biaxial hard particles (spheroplatelets) has been studied [37], where a rich phase diagram has been obtained in the density-particle biaxiality frame, composed of uniaxial and biaxial nematic and smectic phases. Moreover, it has been shown that translational ordering of particles narrows drastically the biaxial nematic range. Therefore, to a first approximation it should be reasonable to study the thermodynamic and structural-statistical consequences of a molecular biaxiality for the S_A -N transition between uniaxial phases within the model [35]. This problem is solved here.

The positional-orientational pseudopotential in a smectic A phase composed of biaxial molecules is considered briefly and the main assumptions are discussed in § 2. The equations determining the temperature $T_{S_A N}$ for the second order S_A -N transitions and for the tricritical point are obtained analytically. The results for the numerical analysis of the influence of the molecular biaxiality on $T_{S_A N}$ of the first and second order phase transitions, the tricritical point, the width of the nematic range, the change of the transitional entropy as well as on the dependence $G(S)$ in the S_A phase are presented in § 3. The joint influence of the biaxiality parameter λ [2] of the pseudopotential and the parameters α, δ introduced by McMillan [36] on the character of the S_A -N transition is examined. The results obtained are compared with the available experimental data. The main conclusions are summarized in § 4.

2. The positional-orientational pseudopotential and the thermal stability in a smectic A phase formed of biaxial molecules

We consider a uniaxial, apolar monolayer smectic A phase formed of molecules with C_{2v} , D_2 or D_{2h} symmetry. The molecular frame $(x_1 y_1 z_1)$ is determined by the symmetry elements and selected to diagonalize the Saupe ordering matrix

$$S_{ii} = \langle 3 \cos^2 \theta_i - 1 \rangle / 2, \quad (i = x_1 y_1 z_1). \quad (1)$$

Here θ_i is the angle made by the i th axis of the molecular frame with the director \mathbf{n} and the brackets $\langle \dots \rangle$ denote a statistical average. The axis z_1 corresponds to the maximum value of the principal components S_{ii} . For planar molecules with C_{2v} and D_{2h} symmetry the x_1 axis is in the plane of the molecule and the y_1 axis is perpendicular to this plane. The orientation of the director in the frame $(x_1 y_1 z_1)$ is determined by the polar angle $\theta = \theta_i$ and the azimuthal angle ψ made by the x_1 axis with the projection of \mathbf{n} to the plane $x_1 y_1$.

Orientalional–translational ordering of the molecules is characterized by the order parameters of the lowest rank [3, 35, 36]

$$\left. \begin{aligned} S &= S_{z_1z_1} = \langle P_2(\cos \theta) \rangle \equiv \langle P_2 \rangle, \\ G &= S_{x_1x_1} - S_{y_1y_1} = 3 \langle \sin^2 \theta \cos 2\psi \rangle / 2 \equiv \langle D \rangle, \\ \tau &= \langle \cos \xi \rangle, \quad \sigma = \langle P_2 \cos \xi \rangle, \quad \kappa = \langle D \cos \xi \rangle, \end{aligned} \right\} \quad (2)$$

where $P_2(\cos \theta)$ is a second Legendre polynomial; $\xi = 2\pi z/d$, z is the translational coordinate of the centre of mass of a molecule along the axis $z \parallel \mathbf{n}$, and d is the smectic periodicity. Taking into account the order parameters in equation (2) within the framework of the McMillan model [36] generalized to biaxial molecules we obtain the molecular pseudopotential [35]

$$U(\theta, \psi, z) = -V_0[(S + \lambda_1 G)P_2 + \alpha(\sigma + \lambda_1 \kappa)P_2 \cos \xi + (\lambda_1 S + \lambda_2 G)D + \alpha(\lambda_1 \sigma + \lambda_2 \kappa)D \cos \xi + \alpha \delta \tau \cos \xi], \quad (3)$$

where the following definitions:

$$\left. \begin{aligned} V_0 &= u_{200} \exp[-a^2/r_0^2], & \alpha &= 2 \exp[-(\pi r_0/d)^2], \\ \lambda_1 &= \frac{2u_{220}}{(6)^{1/2}u_{200}} & \lambda_2 &= \frac{2u_{222}}{3u_{200}}. \end{aligned} \right\} \quad (4)$$

are used. Here $u_{2pq} = u_{2qp}$ are the expansion coefficients of the pairwise potential for the effective anisotropic intermolecular interactions, which according to the McMillan model [36] is supposed to be independent of the orientation of the intermolecular radius vector \mathbf{R}_{12} relative to the axes of the frame (x_1, y_1, z_1) ; a is the average intermolecular distance within a smectic layer; r_0 is the effective interaction radius which is approximately equal to the length of the molecular core [32, 33, 36]. The parameter V_0 characterizes the strength of the anisotropic part of the intermolecular interaction, while the parameter δ determines the relative contribution of its isotropic part and characterizes the translational ordering tendency of molecules independent of their orientational ordering.

It should be noted that as in the nematic phase [2, 3, 6] the pseudopotential for a smectic A phase in equation (3) contains, in general, three anisotropic parameters V_0 , λ_1 and λ_2 . Moreover, the relationship $u_{220}^2 = u_{200}u_{222}$ or $\lambda_2 = \lambda_1^2$ is not strictly valid even for anisotropic dispersion London–van der Waals interactions [6]. For a uniaxial nematic phase there is the mutually unambiguous correlation between the pseudopotential in equation (3) and that presented in [6]

$$\lambda_1 = \frac{1}{2}(\beta + \Delta), \quad \lambda_2 = \beta \Delta, \quad (5)$$

where

$$\beta = \frac{\gamma_{x_1x_1} - \gamma_{y_1y_1}}{3(\gamma_{z_1z_1} - \bar{\gamma})}, \quad \Delta = \frac{A_{x_1} - A_{y_1}}{3(A_{z_1} - \bar{A})}. \quad (6)$$

Here γ_{ii} are the components of the molecular polarizability tensor, which is diagonalized in the frame (x_1, y_1, z_1) ; $\bar{\gamma} = \text{Tr } \hat{\gamma}/3$; $A_i = \gamma_{ii}\omega_i$, where ω_i are the characteristic frequencies of three effective harmonic oscillators polarized along the axes (x_1, y_1, z_1) and determining the components γ_{ii} . For $\Delta = \beta + 2b$ we can obtain using equation (5) $\lambda_1 = \beta + b$, $\lambda_2 = \lambda_1^2 - b^2$. As for molecules mentioned previously the inequality $\gamma_{x_1x_1} > \gamma_{y_1y_1}$

corresponds experimentally to $\omega_x < \omega_y$, so we can suppose $\beta > |b|$ and taking into account $0 \leq \beta \leq 1$ the probable correlation $\lambda_2 \approx \lambda_1^2$ can be assumed to a first approximation.

The relationship $\lambda_2 = \lambda_1^2$ is not true for steric interactions of biaxial molecules [7] and this circumstance seems to be essential for the nematic phase near the S_A -N transition, where the ratio G/S reaches a maximum at $S = 0.4-0.5$ [2-6, 16, 24, 29]. However, for smectogenic molecules at high values of S the inequalities $S \gg G$ [16, 29] and $\sigma \gg \kappa$ are valid, so taking into account $\lambda_1 > \lambda_2$ we should expect $\lambda_1 S \gg \lambda_2 G$, $\lambda_1 \sigma \gg \lambda_2 \kappa$ and the difference $|\lambda_2 - \lambda_1^2|$ can be neglected. Then equation (3) reduces to the final form

$$\mathcal{U}(\theta, \psi, z) = -V_0[(S + \lambda_1 G)(P_2 + \lambda_1 D) + \alpha(\sigma + \lambda_1 \kappa)(P_2 + \lambda_1 D) \cos \xi + \alpha \delta \tau \cos \zeta]. \quad (7)$$

This potential can be formally obtained from McMillan's potential [36] for uniaxial molecules by substituting $P_2 + \lambda_1 D$, $S + \lambda_1 G$ and $\sigma + \lambda_1 \kappa$ for P_2 , S and σ , respectively.

The single particle distribution function has the form

$$f(\theta, \psi, z) = \exp[-\mathcal{U}(\theta, \psi, z)/kT]/Z, \quad (8)$$

and the order parameters S, \dots, τ in equation (7) are determined by the system of self-consistency equations

$$\left. \begin{aligned} S &= \frac{1}{Z} \int_{-1}^1 dx \int_0^{2\pi} d\psi P_2(x) \exp \left\{ \frac{V_0}{kT} (S + \lambda_1 G) [P_2(x) + \lambda_1 D(x, \psi)] \right\} I_0(q), \\ G &= \frac{1}{Z} \int_{-1}^1 dx \int_0^{2\pi} d\psi D(x, \psi) \exp \left\{ \frac{V_0}{kT} (S + \lambda_1 G) [P_2(x) + \lambda_1 D(x, \psi)] \right\} I_0(q), \\ \sigma &= \frac{1}{Z} \int_{-1}^1 dx \int_0^{2\pi} d\psi P_2(x) \exp \left\{ \frac{V_0}{kT} (S + \lambda_1 G) [P_2(x) + \lambda_1 D(x, \psi)] \right\} I_1(q), \\ \kappa &= \frac{1}{Z} \int_{-1}^1 dx \int_0^{2\pi} d\psi D(x, \psi) \exp \left\{ \frac{V_0}{kT} (S + \lambda_1 G) [P_2(x) + \lambda_1 D(x, \psi)] \right\} I_1(q), \\ \tau &= \frac{1}{Z} \int_{-1}^1 dx \int_0^{2\pi} d\psi \exp \left\{ \frac{V_0}{kT} (S + \lambda_1 G) [P_2(x) + \lambda_1 D(x, \psi)] \right\} I_1(q), \\ Z &= \int_{-1}^1 dx \int_0^{2\pi} d\psi \exp \left\{ \frac{V_0}{kT} (S + \lambda_1 G) [P_2(x) + \lambda_1 D(x, \psi)] \right\} I_0(q). \end{aligned} \right\} \quad (9)$$

Here $I_n(q)$ are modified Bessel functions and

$$q = \frac{\alpha V_0}{kT} \{(\sigma + \lambda_1 \kappa)[P_2(x) + \lambda_1 D(x, \psi)] + \delta \tau\}. \quad (10)$$

The smectic free energy per molecule F_A has the form

$$\frac{F_A}{RT} = \frac{V_0}{2kT} [(S + \lambda_1 G)^2 + \alpha(\sigma + \lambda_1 \kappa)^2 + \alpha \delta \tau^2] - \ln Z. \quad (11)$$

The system of equations (9) has three kinds of solutions: $S = \dots = \tau = 0$ corresponds to the isotropic phase; $S \neq 0$, $G \neq 0$ and $\sigma = \kappa = \tau = 0$ —nematic phase; $S \neq 0, \dots, \tau \neq 0$ —smectic A phase. For a given temperature only that phase exists, which corresponds to a minimum of the free energy in equation (11). The temperatures of the N-I, S_A -N and S_A -I phase transitions are determined by the equality of free energies of the

corresponding phases. For the first order S_A -N transition the entropy change $\Delta S_{S_{AN}}$ is given by

$$\frac{\Delta S_{S_{AN}}}{R} = \frac{V_0}{2kT_{S_{AN}}} [(S_A + \lambda_1 G_A)^2 - (S_N + \lambda_1 G_N)^2 + \alpha(\sigma + \lambda_1 \kappa)^2 + \alpha \delta \tau^2], \quad (12)$$

where the subscripts denote the mesophases.

In addition to three adjustable parameters V_0 , α and δ in McMillan's theory there is the supplementary parameter λ_1 in the model based on equation (7). For the first order S_A -N transitions these four parameters can be evaluated from independent measurements of T_{NI} , $T_{S_{AN}}$, $\Delta S_{S_{AN}}$ [36, 38, 39] and the correlation $G(S)$ in the nematic phase near $T_{S_{AN}}$ [16, 29, 40] or from the other set of experimental data. The signs of the parameters G and κ coincide with the sign of λ_1 , so that changing the sign of λ_1 does not influence the values of T_{NI} , $T_{S_{AN}}$ and $\Delta S_{S_{AN}}$.

To obtain the temperature $T_{S_{AN}}$ for second order phase transitions and the tricritical point T_{tcp} on the line of S_A -N transitions the computational procedure can be accelerated significantly and carried out more precisely by choosing one of the order parameters σ , τ or κ as the independent variable and analysing the derivatives of F_A with respect to this variable [41]. Taking the parameter σ as such a variable we can expand F_A around that of the nematic state F_N

$$F_A = F_N + \frac{1}{2} \left. \frac{d^2 F_A}{d\sigma^2} \right|_{\sigma=0} \sigma^2 + \frac{1}{4!} \left. \frac{d^4 F_A}{d\sigma^4} \right|_{\sigma=0} \sigma^4 + \dots \quad (13)$$

The equation for the second order transition line is

$$\left. \frac{d^2 F_A}{d\sigma^2} \right|_{\sigma=0} = 0, \quad (14)$$

while the tricritical point is determined by the system of two equations

$$\left. \frac{d^2 F_A}{d\sigma^2} \right|_{\sigma=0} = 0, \quad \left. \frac{d^4 F_A}{d\sigma^4} \right|_{\sigma=0} = 0. \quad (15)$$

These equations transfer to

$$F_{\tau\sigma}^2 - F_{\tau\tau} F_{\sigma\sigma} = 0, \quad (16 a)$$

$$3[F_{S\sigma\sigma} + 2F_{S\tau\sigma}\gamma + F_{S\tau\tau}\gamma^2]^2 - F_{SS}[F_{\tau\tau\tau}\gamma^4 + 4F_{\tau\tau\sigma}\gamma^3 + 6F_{\tau\sigma\sigma}\gamma^2 + 4F_{\tau\sigma\sigma}\gamma + F_{\sigma\sigma\sigma}] = 0, \quad (17 a)$$

where the definitions

$$\gamma = -F_{\tau\sigma}/F_{\tau\tau}, \quad F_{\alpha\beta} = F_{\beta\alpha} = (\partial^2 F_A / \partial \alpha \partial \beta)_{\sigma=0, \dots}$$

are used. Equations (16 a) and (17 a) coincide with the analogous ones for a smectic A with uniaxial molecules [41] and differ only by the expressions for partial derivatives presented in the Appendix. Then equations (16 a) and (17 a) can be written as

$$\left(\frac{2kT}{\alpha V_0} - \delta \right) \left(\frac{2kT}{\alpha V_0} - \langle (P_2 + \lambda_1 D)^2 \rangle_N \right) = (S_N + \lambda_1 G_N)^2 \delta, \quad (16 b)$$

$$\begin{aligned} & X^4 + 4(S_N + \lambda_1 G_N)X^3 + 2[4(S_N + \lambda_1 G_N)^2 - \langle (P_2 + \lambda_1 D)^2 \rangle_N]X^2 \\ & + 4[2(S_N + \lambda_1 G_N)\langle (P_2 + \lambda_1 D)^2 \rangle_N - \langle (P_2 + \lambda_1 D)^3 \rangle_N]X \\ & + 2\langle (P_2 + \lambda_1 D)^2 \rangle_N^2 - \langle (P_2 + \lambda_1 D)^4 \rangle_N \\ & = \frac{2\{(S_N + \lambda_1 G_N)\langle (P_2 + \lambda_1 D)^2 \rangle_N - \langle (P_2 + \lambda_1 D)^3 \rangle_N + 2[(S_N + \lambda_1 G_N)^2 - \langle (P_2 + \lambda_1 D)^2 \rangle_N]X\}^2}{(kT/V_0) - \langle (P_2 + \lambda_1 D)^2 \rangle_N + (S_N + \lambda_1 G_N)^2} \end{aligned} \quad (17 b)$$

where

$$X = \frac{\delta(S_N + \lambda_1 G_N)}{(2kT/\alpha V_0) - \delta}$$

These equations simplify significantly the analysis of the dependence of the second order transition temperature $T_{S_A N}$ and T_{icp} on the parameters α , δ and λ_1 , since in order to determine $T_{S_A N}$ and T_{icp} at fixed values of these parameters only two self-consistency equations (9) for S and G in the nematic phase have to be solved.

3. Results and discussion

To analyse the influence of the biaxiality parameter $\lambda = (3/2)^{1/2} \lambda_1$ [2, 3] on the thermodynamic parameters of the S_A -N transition it is reasonable to consider the ranges of the changes $\alpha = 0.2-1.2$ and $\delta = 0-1.2$, which contain typical values of these parameters obtained earlier from the quantitative interpretation of experimental data [36, 39, 42] and used for the theoretical studies of the McMillan model [38, 41]. At $\beta = \Delta$ in equation (5) the value $\lambda_0 = 1/(6)^{1/2}$ corresponds to the hypothetical situation of the continuous N-I phase transition that is not really observed. For pure nematics effective values of λ corresponding to the experimental dependences $G(S)$ are usually not more than 0.3. However, for some mesogens effective values of λ in the nematic phase near the S_A -N transition and in the S_A phase can reach values of 0.4-0.6 [15, 40] that are not non-physical due to the known growth of the effective value of λ with increasing S [15, 20-22, 29] and at the S_A -N transition [27-31]. In consequence, it is reasonable to study the influence of λ changing it within the complete range $0-1/(6)^{1/2}$.

Taking into account the pseudopotential biaxiality modifies the phase diagram of the McMillan model [36, 38, 41]. The comparison of these diagrams is presented in figure 1. For $\lambda = 0$ our data are the same as those obtained in [41]. With increasing λ T_{NI} is found to increase as well [2, 3, 6, 43]. The dependence $T_{S_A N}(\lambda)$ is weaker and more complex. For each value of δ and λ there is a critical value $\alpha_c(\delta, \lambda)$ such that the inequalities $T_{S_A N}(\delta, \lambda) \geq T_{S_A N}(\delta, 0)$ are valid for $\alpha \geq \alpha_c$. For each value of λ there is a limited range of changes $0 < \delta \leq \delta_1(\lambda)$, where $\alpha_{icp}(\delta, \lambda) \leq \alpha_c(\delta, \lambda)$. Here $\alpha_{icp}(\delta, \lambda)$ corresponds to the tricritical point. For example, for $\lambda = 0.3$ the equality $\alpha_{icp} = \alpha_c = 0.646$ is true at $\delta = \delta_1 = 0.098$. As we can see from figure 1 the values of α_c and the corresponding ones for t_c decrease quickly with the growth of δ and for values $\delta \approx 0.65$ used to interpret the experiments [36, 39, 42] the correlation $T_{S_A N}(\lambda) > T_{S_A N}(0)$ is valid both for second and for first order S_A -N transitions.

The dependences of α_{icp} and t_{icp} on λ for several values of δ are presented in the table. Figure 1 and the table show that for constant δ the parameters α_{icp} and t_{icp} grow with increasing λ and the stronger the higher δ . However, because $T_{NI}(\lambda)$ increases faster

The tricritical points for several values of the parameters δ and λ .

λ	$\delta = 0$		$\delta = 0.65$		$\delta = 1.2$	
	α_{icp}	t_{icp}	α_{icp}	t_{icp}	α_{icp}	t_{icp}
0	0.707	0.870	0.401	0.939	0.294	0.982
0.1	0.708	0.870	0.403	0.942	0.297	0.987
0.2	0.713	0.872	0.411	0.952	0.306	1.005
0.3	0.723	0.877	0.427	0.973	0.325	1.042
$1/(6)^{1/2}$	0.745	0.889	0.460	1.017	0.367	1.125

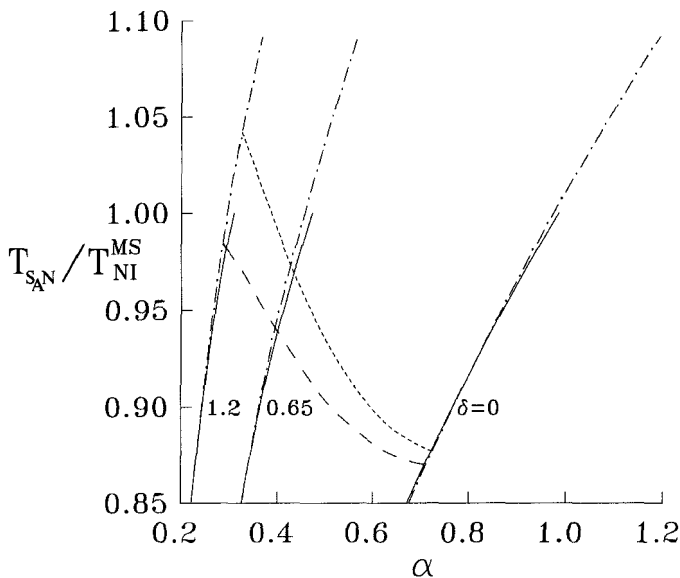


Figure 1. Phase diagram in the model based on equation (7) for several values of the parameters δ and λ in the (α, t) plane. Here $t = T_{S_{AN}}/T_{NI}^{MS}$, where the Maier-Saupe transition temperature $T_{NI}^{MS} = 0.2202 V_0/k$ corresponds to the value $\lambda = 0$. Dashed and dotted lines are the lines of tricritical points of the S_A -N transition for $\lambda = 0$ and $\lambda = 0.3$, respectively. Full and dot-and-dash lines correspond to the lines of the S_A -N transitions for $\lambda = 0$ and 0.3 , respectively.

with changing λ within the complete range $0-1/(6)^{1/2}$ the difference $T_{NI} - T_{S_{AN}}$ grows for all values of α and δ considered here. That is valid also for the difference $T_{NI} - T_{icp}$. In consequence, for small values of the difference $T_{NI} - T_{icp}$ observed in experiments [11, 32, 33] and corresponding high values of δ [36, 38, 41] taking into account the biaxiality parameter λ is supposed to be essential for the discussion of the molecular aspects of the tricritical nature of the S_A -N transition in real compounds in addition to general reasons of a small $T_{NI} - T_{icp}$ considered before [11, 32, 33, 44, 45].

The dependence of the transitional entropy $\Delta S_{S_{AN}}$ (cf. equation (12)) on reduced temperature $t = T_{S_{AN}}/T_{NI}^{MS}$ for several values of the parameters δ and λ is presented in figure 2. For $\lambda = 0$ these data coincide with those published before [41]. For fixed values of δ and t the growth of λ leads to a lowering of $\Delta S_{S_{AN}}$ and the stronger the higher t . For fixed λ lowering $\Delta S_{S_{AN}}$ strengthens quickly with the growth of δ . Thus, for small real values of the difference $T_{NI} - T_{icp}$ mentioned previously and corresponding high values of δ the growth of λ can result in the change of the transitional order from first to second for mesogens with a weak first order S_A -N phase transition. Figure 3 shows the rate of changing $\Delta S_{S_{AN}}(\lambda)$ for the same initial value $\Delta S_{S_{AN}}(0) = 0.173$ is within the range of experimental data for weak S_A -N transitions [11, 36-39] with a small change of the orientational order parameter S at $T_{S_{AN}}$. We see from figure 3 that for $\delta = 0$ the appearance of the tricritical point can be induced only with the value $\lambda = \lambda_0 = 1/(6)^{1/2}$, while for the adjustable parameters $\alpha = 0.3-0.4$ and $\delta = 0.65-1.2$ [36, 39] being typical for real mesogens the tricritical point arises at values $\lambda < 0.3$, which are characteristic of pure nematic liquid crystals [2, 3, 29]. Thus for real mesogens taking into account the

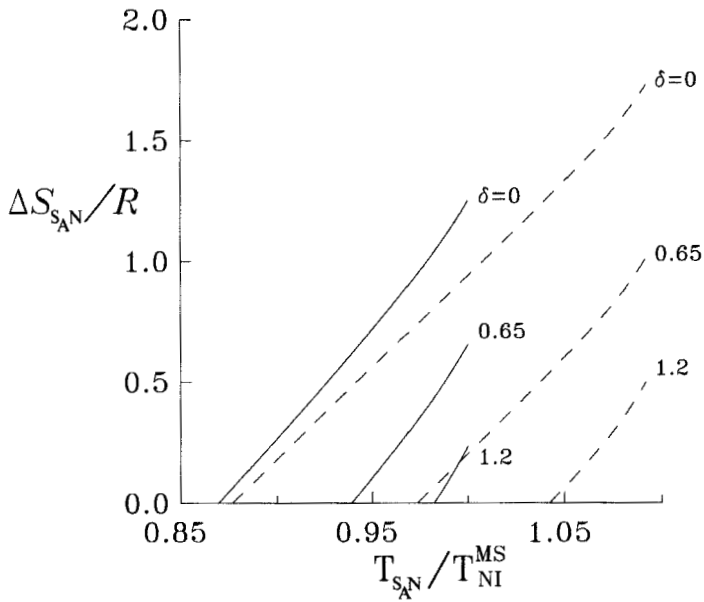


Figure 2. The entropy of the transition $\Delta S_{S_{AN}}/R$ versus reduced temperature $t = T_{S_{AN}}/T_{NI}^{MS}$ for several values of the parameters δ and λ . Full and dashed lines correspond to the values $\lambda = 0$ and $\lambda = 0.3$.

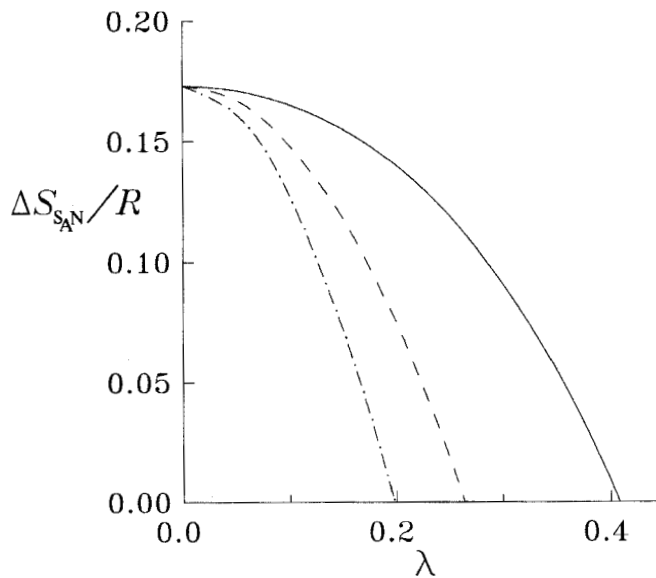


Figure 3. The dependence of the transitional entropy $\Delta S_{S_{AN}}$ on λ for $\delta = 0$, $\alpha = 0.745$ (full line); $\delta = 0.65$, $\alpha = 0.421$ (dashed line) and $\delta = 1.2$, $\alpha = 0.306$ (dot-and-dash line).

pseudopotential biaxiality is important in interpreting the thermodynamic parameters of the S_A-N transition and to determine the adjustable values of V_0 , α , δ from experimental data for T_{Nl} , $T_{S_A N}$ and $\Delta S_{S_A N}$ [36, 38, 39, 41].

Among the order parameters in equation (2) the magnitudes S , G and τ are of interest, because they can be measured experimentally. Within the framework of the McMillan model and that based on equation (7) the parameters σ and κ are given by the correlations $\sigma \approx S\tau$ and $\kappa \approx G\tau$ with a good precision [35, 46]. Moreover, $\Delta_{P\tau} \equiv (\sigma - S\tau) > 0$ but $\Delta_{D\tau} \equiv (\kappa - G\tau) < 0$ and the inequalities $\Delta_{P\tau} \ll \sigma$, $|\Delta_{D\tau}| \ll \kappa$ are valid. For $0.25 \leq S \leq 1$ and the maximum possible value $\lambda_{\max} = (3/2)^{1/2}$ the equality $\Delta_{D\tau} = -\Delta_{P\tau}$ holds, while for $\lambda < \lambda_{\max}$ we have $|\Delta_{D\tau}| < \Delta_{P\tau}$. Correspondingly to this $G > \kappa$ is valid within the complete range of the smectic phase and this inequality strengthens at $T \rightarrow T_{S_A N}$ for both first and second order transitions. However, for the first order transitions lowering τ is compensated for by the growth of G and $\kappa \approx \text{constant}$ is possible within the wide range of the smectic phase. At $T \rightarrow 0$ we observe $\kappa \rightarrow 0$ due to $G \rightarrow 0$.

To interpret the experimental data the influence of smectic layering on the change $\Delta G(T_{S_A N})$ as well as on the dependences $G(T)$ and $G(S)$ in the smectic phase at fixed value of λ is of interest. In figure 4 we can see the temperature dependence of the order parameters S , G and τ for $\lambda = 0.3$ and a fixed value of $t_{S_A N}$, that corresponds to the horizontal cross-section of the phase diagram presented in figure 1 with $t_{S_A N} = t_{\text{tcp}} (\delta = 0.65; \alpha = 0.427)$ (cf. the table). For the nematic phase the values of S and G in figure 4 coincide with those published before [2, 6]. The first order S_A-N transitions are followed by increasing S and lowering G having a discontinuous character. For second order transitions the change $\Delta G(T_{S_A N})$ is absent, in agreement with experiment [16]. However, the form of the dependence of the derivative dG/dT on temperature is found to change for both orders of transition. For experimentally observed values

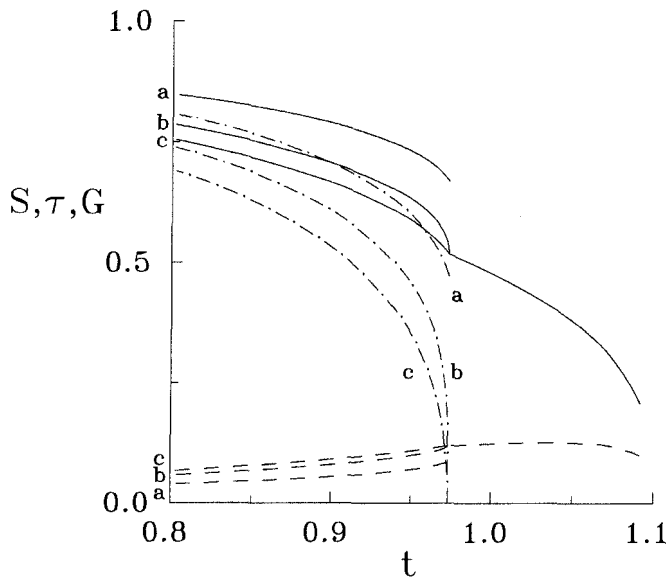


Figure 4. Temperature dependence of the order parameters S (full lines), G (dashed lines) and τ (dot-and-dash lines) in the model based on equation (7) at fixed values $\lambda = 0.3$ and $t_{S_A N} = 0.973$ for (a) $\delta = 0$; (b) $\delta = 0.65$ and (c) $\delta = 1.2$.

$S_N(T_{S_A N}) > 0.4$ the derivative dG/dT increases with increasing temperature in the smectic phase and decreases at $T > T_{S_A N}$ in the nematic. It is also in agreement with available data for pure liquid crystals [16, 29] and shows that, in general, the change $\Delta G(T_{S_A N})$ and the dependence $G(T)$ in smectics are determined by the change of the order parameter S at $T = T_{S_A N}$ and by the dependence $S(T)$ in the smectic phase.

The presence of mixed orientational–translational terms in equation (7) results in changing the dependence $G_A(S_A)$ in the smectic phase in comparison with that in the nematic. This investigation has shown the inequality $G_A(S_A) < G_N(S_N = S_A)$ to be valid for fixed values of λ , $T_{S_A N}$ and $S_N(T_{S_A N})$ at $T \leq T_{S_A N}$, which strengthens for stronger first order S_A – N transitions. Here values of S_N and G_N corresponds to equation (7) at $\alpha = \delta = 0$. Moreover, for fixed values of S the inequality $|G_A - G_N| \ll G_N$ holds and the difference between G_A and G_N disappears at $S \rightarrow 1$. It means that smectic layering results in lowering the effective parameter λ_{eff} determined by the correlation between G_A and S_A for equation (7) when $\alpha = \delta = 0$. Changing λ_{eff} at the S_A – N transition depends on two contributions. The former being characteristic of the nematic phase [15, 20–22, 29] is determined by the dependence $\lambda_{\text{eff}}(S)$ [21] and is concerned with the change of S at the S_A – N transition. The latter is determined by smectic layering and, according to available data for solute molecules, can be both positive [21, 28, 30, 31] and negative [27]. The last circumstance corresponds qualitatively to the consequences of the model based on equation (7). The compensation of contributions of nematic and smectic molecular ordering to the effective value λ_{eff} can result in λ_{eff} being constant or decreasing on lowering the temperature in the smectic phase in the presence of the growth of λ_{eff} in the nematic phase; this has been observed in [27].

It should be noted as well that, in principle, the character of the S_A – N phase transition, the dependence $G_A(S_A)$ and the value of λ_{eff} can be affected by the dependence of the pair potential on the orientation of the intermolecular radius vector \mathbf{R}_{12} relative to the coordinate axes of molecules 1 and 2. This dependence, that is the so-called non-separability of the interaction, is not considered in the McMillan model and that based on equation (7). For uniaxial molecules taking into account the non-separability to a first approximation results in additional terms proportional to $\sigma \cos \xi$ and $\tau P_2 \cos \xi$ in the pseudopotential [47–52]. They correspond to the term $2\alpha\gamma\sigma\tau$ in the expression for the free energy of the smectic A [51], which reduces to $2\alpha\gamma S\tau^2$ when $\sigma \approx S\tau$ and is equivalent to the anisotropic term $S|\psi|^2$ within the framework of the phenomenological de Gennes theory [11, 32]. The possibility of the formal transfer from the McMillan model [36] to equation (7) mentioned previously as well as the results of [51] allow us to conclude that the formal consideration of the non-separability has to result in the additional term $\alpha\gamma[\sigma + \lambda_1\kappa + \tau(P_2 + \lambda_1 D)] \cos \xi$ in equation (7) with one new adjustable parameter γ . However, as experimental data about the thermodynamic and structural characteristics of the S_A – N transition for real mesogens are not enough at the present stage of investigations, it is reasonable to study the models containing as small a number of adjustable parameters as possible. For all this the elucidation of the relative contributions of each of them stays to be actual. In consequence, it should be noted that the simplified model based on equation (7) describes satisfactorily the orientational–translational statistics of molecules and allows us to give the reasonable interpretation of the optic spectral properties of pure and solute smectics A [35].

As we have mentioned, the influence of the biaxiality parameter λ on the thermodynamic properties of the S_A – N transition grows with increasing δ . The parameter δ strengthens the layering tendency independent of orientational ordering

and has to increase as the alkyl chain is lengthened at fixed length r_0 of the molecular aromatic core. It also leads to increasing α . If the dominant contribution to the total energy of the anisotropic intermolecular interactions is made up of anisotropic dispersion forces, the parameter λ_1 in equation (5) would depend, in general, on the anisotropy of the polarizability (cf. equation (6)) of the molecular aromatic core, since lengthening the terminal chains does not affect the parameters β and Δ in equation (6) noticeably. Thus we may expect λ to change weakly within a homologous series and to be independent of the parameters α and δ . However, anisotropic steric interactions do make a significant contribution to the effective value of λ . Lengthening the terminal chains causes the ratio $\langle P_4 \rangle / \langle P_2 \rangle$ for aromatic cores to be lowered and the deviation of the axis of the preferred orientation of the cores from the nematic director or from the normal to a smectic layer [49, 53, 54]. Moreover, this deviation strengthens on moving away from T_{NI} . The tilt of flat molecules hampers their rotational mobility relative to the longitudinal axes, which is equivalent to increasing G and the effective value of λ . Thus the simultaneous growth of the parameters δ and λ should be expected when lengthening the terminal chains. The same is valid for biaxial aromatic solute molecules localized within the field of a smectic layer occupied by aromatic cores of the mesogenic molecules. It is in agreement with increasing the effective parameter λ_{eff} at the S_A -N transition [21, 28, 30] and within the limits of homologous series with the growth of the terminal chain [31] usually observed for solute molecules. In consequence, the maximum manifestation of a molecular biaxiality should be expected for the highest members of a homologous series with narrow ranges of the nematic phase.

4. Conclusion

The results presented here show that the biaxiality of the molecular pseudopotential influences the thermodynamic properties of the S_A -N transition. Moreover, the joint manifestation of the parameters α , δ and λ has to be taken into account. By analogy with the N-I transition the molecular biaxiality lowers the entropy of the transition $\Delta S_{S_A N}$. Thus for sufficiently high values of δ and narrow ranges of the nematic phase the change of the S_A -N transition order from first to second can take place for small values of λ corresponding to experiments. Unlike T_{NI} the growth of λ can be followed both by increasing and by decreasing $T_{S_A N}$ depending on the values of the parameters α and δ . However, for all values of α and δ corresponding to experiments the growth of λ results in broadening the temperature range of the nematic phase. The change $\Delta G(T_{S_A N})$ and the dependence $G(T)$ in the smectic phase are determined by the change of the order parameter S at $T_{S_A N}$ and by the dependence $S(T)$. The character of the dependence of the derivative dG/dT on temperature changes qualitatively both for first and second order S_A -N transitions. These features of the dependence $G(T)$ correspond to the available experimental data. Qualitative considerations, which are in agreement with known experiments, show that the maximum manifestation of the pseudopotential biaxiality should be expected for mesogens having sufficiently long end chains and narrow nematic ranges.

Appendix

$$F_{SS} = \left(\frac{V_0}{kT} \right)^2 \left[\frac{kT}{V_0} + (S_N + \lambda_1 G_N)^2 - \langle (P_2 + \lambda_1 D)^2 \rangle_N \right], \quad (\text{A } 1)$$

$$F_{\sigma\sigma} = \frac{\alpha V_0}{kT} - \frac{1}{2} \left(\frac{\alpha V_0}{kT} \right)^2 \langle (P_2 + \lambda_1 D)^2 \rangle_N, \quad (\text{A } 2)$$

$$F_{\tau\tau} = \frac{\delta\alpha V_0}{kT} - \frac{1}{2} \left(\frac{\delta\alpha V_0}{kT} \right)^2, \quad (\text{A } 3)$$

$$F_{\tau\sigma} = -\frac{1}{2} \left(\frac{\alpha V_0}{kT} \right)^2 \delta(S_N + \lambda_1 G_N), \quad (\text{A } 4)$$

$$F_{S\sigma\sigma} = \frac{\alpha^2}{2} \left(\frac{V_0}{kT} \right)^3 [(S_N + \lambda_1 G_N) \langle (P_2 + \lambda_1 D)^2 \rangle_N - \langle (P_2 + \lambda_1 D)^3 \rangle_N], \quad (\text{A } 5)$$

$$F_{S\tau\tau} = \frac{\delta\alpha^2}{2} \left(\frac{V_0}{kT} \right)^3 [(S_N + \lambda_1 G_N)^2 - \langle (P_2 + \lambda_1 D)^2 \rangle_N], \quad (\text{A } 6)$$

$$F_{S\tau\tau} = 0, \quad (\text{A } 7)$$

$$F_{\tau\tau\tau} = \frac{3}{8} \left(\frac{\delta\alpha V_0}{kT} \right)^4, \quad (\text{A } 8)$$

$$F_{\tau\tau\sigma} = \frac{3}{8} \left(\frac{\alpha V_0}{kT} \right)^4 \delta^3(S_N + \lambda_1 G_N), \quad (\text{A } 9)$$

$$F_{\tau\tau\sigma\sigma} = \frac{1}{8} \left(\frac{\alpha V_0}{kT} \right)^4 \delta^2[4(S_N + \lambda_1 G_N)^2 - \langle (P_2 + \lambda_1 D)^2 \rangle_N], \quad (\text{A } 10)$$

$$F_{\tau\sigma\sigma\sigma} = \frac{3}{8} \left(\frac{\alpha V_0}{kT} \right)^4 \delta[2(S_N + \lambda_1 G_N) \langle (P_2 + \lambda_1 D)^2 \rangle_N - \langle (P_2 + \lambda_1 D)^3 \rangle_N], \quad (\text{A } 11)$$

$$F_{\sigma\sigma\sigma\sigma} = \frac{3}{8} \left(\frac{\alpha V_0}{kT} \right)^4 [2 \langle (P_2 + \lambda_1 D)^2 \rangle_N^2 - \langle (P_2 + \lambda_1 D)^4 \rangle_N]. \quad (\text{A } 12)$$

Here the subscript N denotes the following statistical average

$$\langle B(\theta, \psi) \rangle_N = \frac{\int \int B(\theta, \psi) \exp [(V_0/kT)(S_N + \lambda_1 G_N)(P_2 + \lambda_1 D)] d \cos \theta d\psi}{\int \int \exp [(V_0/kT)(S_N + \lambda_1 G_N)(P_2 + \lambda_1 D)] d \cos \theta d\psi}. \quad (\text{A } 13)$$

The right hand parts of equations (A 1)–(A 12) differ from analogous ones in [41] by substituting of $(P_2 + \lambda_1 D)$ and $(S + \lambda_1 G)$ for P_2 and S .

References

- [1] DEMUS, D., 1989, *Liq. Crystals*, **5**, 75.
- [2] LUCKHURST, G. R., ZANNONI, C., NORDIO, P. L., and SEGRE, U., 1975, *Molec. Phys.*, **30**, 1345.
- [3] LUCKHURST, G. R., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press), Chap. 4.
- [4] GELBART, W. M., and BARBOY, B., 1979, *Molec. Crystals liq. Crystals*, **55**, 209.

- [5] REMLER, D. K., and HAYMET, D. J., 1986, *J. phys. Chem.*, **90**, 5426.
- [6] BERGERSEN, B., PALFFY-MUHORAY, P., and DUNMUR, D. A., 1988, *Liq. Crystals*, **3**, 347.
- [7] MULDER, B. M., 1989, *Phys. Rev. A*, **39**, 360.
- [8] TJIPTO-MARGO, B., and EVANS, G. T., 1991, *J. chem. Phys.*, **94**, 4546; 1991, *Molec. Phys.*, **74**, 85.
- [9] ALLENDER, D. W., and LEE, M. A., 1984, *Molec. Crystals liq. Crystals*, **110**, 331.
- [10] ALLENDER, D. W., LEE, M. A., and HAFIZ, N., 1985, *Molec. Crystals liq. Crystals*, **124**, 45.
- [11] ANISIMOV, M. A., 1991, *Critical Phenomena in Liquids and Liquid Crystals* (Gordon & Breach), p. 10.
- [12] LUCKHURST, G. R., and ROMANO, S., 1980, *Molec. Phys.*, **40**, 129.
- [13] ALLEN, M. P., 1990, *Liq. Crystals*, **8**, 499.
- [14] DOZOV, I., KIROV, N., and PETROFF, B., 1987, *Phys. Rev. A*, **36**, 2870.
- [15] ROSI, B., FONTANA, M. P., DOZOV, I., and KIROV, N., 1987, *Phys. Rev. A*, **36**, 2879.
- [16] KIROV, N., DOZOV, I., PETROV, M., FONTANA, M. P., and ROSI, B., 1987, *Molec. Crystals liq. Crystals*, **151**, 119.
- [17] VAN DER MEER, B. W., and VERTOGEN, G., 1976, *Physics Lett. A*, **59**, 279.
- [18] SAKHLEVNYKH, A. N., and SHLIOMIS, M. I., 1984, *Zh. éksp. teor. Fiz.*, **86**, 1309.
- [19] BUNNING, J. D., CRELLIN, D. A., and FABER, T. E., 1986, *Liq. Crystals*, **1**, 37.
- [20] EMSLEY, J. W., HASHIM, R., LUCKHURST, G. R., RUMBLES, G. N., and VILORIA, F. R., 1983, *Molec. Phys.*, **49**, 1321.
- [21] EMSLEY, J. W., HASHIM, R., LUCKHURST, G. R., and SHILSTONE, G. N., 1986, *Liq. Crystals*, **1**, 437.
- [22] EMSLEY, J. W., LUCKHURST, G. R., and SMITH, S. W., 1990, *Molec. Phys.*, **70**, 967.
- [23] PALFFY-MUHORAY, P., and HOATSON, G. L., 1991, *Phys. Rev. A*, **44**, 5052.
- [24] EMSLEY, J. W., LUCKHURST, G. R., and STOCKLEY, C. P., 1981, *Molec. Phys.*, **44**, 565.
- [25] AVERYANOV, E. M., GUNYAKOV, V. A., KORETS, A. YA., ZYRYANOV, V. YA., and SHABANOV, V. F., 1986, *J. appl. Spectrosc.*, **45**, 1117.
- [26] JEDE, F., STRATMANN, A. W., and SCHRADER, B., 1986, *Molec. Crystals liq. Crystals*, **140**, 287.
- [27] EMSLEY, J. W., LUCKHURST, G. R., SHILSTONE, G. N., and SAGE, I., 1987, *J. chem. Soc. Faraday Trans. 2*, **83**, 371.
- [28] CATALANO, D., FORTE, C., VERACINI, C. A., EMSLEY, J. W., and SHILSTONE, G. N., 1987, *Liq. Crystals*, **2**, 357.
- [29] WU, B.-G., ZIEMNICKA, B., and DOANE, J. W., 1988, *J. chem. Phys.*, **88**, 1373.
- [30] AVERYANOV, E. M., and GUNYAKOV, V. A., 1989, *Opt. Spectrosc.*, **66**, 72.
- [31] EMSLEY, J. W., LUCKHURST, G. R., and SACHDEV, H. S., 1989, *Liq. Crystals*, **5**, 953.
- [32] VERTOGEN, G., and DE JEU, W. H., 1988, *Thermotropic Liquid Crystals, Fundamentals* (Springer Series in Chemical Physics, Vol. 45) (Springer), p. 12.
- [33] DE JEU, W. H., 1991, *N.A.T.O. School on Phase Transitions in Liquid Crystals*, Erice, Italy, May.
- [34] FONTANA, M. P., ROSI, B., KIROV, N., and DOZOV, I., 1986, *Phys. Rev. A*, **33**, 4132.
- [35] AVERYANOV, E. M., and PRIMAK, A. N., 1991, *Liq. Crystals*, **10**, 555.
- [36] McMILLAN, W. L., 1971, *Phys. Rev. A*, **4**, 1238; 1972, *Ibid.*, **6**, 936.
- [37] TAYLOR, M. P., and HERZFELD, J., 1991, *Phys. Rev. A*, **44**, 3742.
- [38] HUMPHRIES, R. L., and LUCKHURST, G. R., 1978, *Molec. Phys.*, **35**, 1201.
- [39] CATALANO, D., FORTE, C., VERACINI, C. A., EMSLEY, J. W., and SHILSTONE, G. N., 1987, *Liq. Crystals*, **2**, 345.
- [40] AVENT, A. G., EMSLEY, J. W., and LUCKHURST, G. R., 1983, *Molec. Phys.*, **49**, 737.
- [41] KLOCZKOWSKI, A., and STECKI, J., 1985, *Molec. Phys.*, **55**, 1223.
- [42] DOANE, J. W., PARKER, R. S., CVIKL, B., JOHNSON, J. L., and FISHEL, D. L., 1972, *Phys. Rev. Lett.*, **28**, 1694.
- [43] AVERYANOV, E. M., 1987, *Liq. Crystals*, **2**, 497.
- [44] AVERYANOV, E. M., ADOMENAS, P. V., ZHUIKOV, V. A., and ZYRYANOV, V. YA., 1986, *Sov. Phys. JETP*, **64**, 325.
- [45] AVERYANOV, E. M., 1990, *Sov. Phys. JETP*, **70**, 479; 1991, *Molec. Crystals liq. Crystals*, **199**, 207.
- [46] KVINTSEL, G. F., LUCKHURST, G. R., and ZEWDIE, H. B., 1985, *Molec. Phys.*, **56**, 589.
- [47] SCHRODER, H., 1974, *Ber. Bunsenges. phys. Chem.*, **78**, No. 9, 855.
- [48] SENBETU, L., and WOO, C. W., 1978, *Phys. Rev. A*, **17**, 1529.
- [49] KUSMA, M. R., and ALLENDER, D. W., 1982, *Phys. Rev. A*, **25**, 2793.

- [50] LIPKIN, M. D., and OXTOPY, D. W., 1983, *J. chem. Phys.*, **79**, 1939.
- [51] KLOCZKOWSKI, A., and STECKI, J., 1985, *Molec. Phys.*, **55**, 689.
- [52] LONGA, L., and KONIOR, J., 1990, *Molec. Crystals liq. Crystals*, **192**, 191.
- [53] AVERYANOV, E. M., VAITKYAVICHYUS, A., KORETS, A. YA., SIRUTKAITIS, P., SOROKIN, A. V., and SHABANOV, V. F., 1979, *Sov. Phys. JETP*, **49**, 910.
- [54] AVERYANOV, E. M., ADOMENAS, P. V., ZHUIKOV, V. A., and ZYRYANOV, V. YA., 1982, *Sov. Phys. solid St.*, **24**, 15.