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Temperature Evolution of a Smectic Liquid Crystal with Inner Degrees of Freedom

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A statistical model of the smectic A mesophase with inner degrees of freedom (MIDF-model) is formulated in which the interlayer interaction of molecules is described in the McMillan approximation and the intramolecular interaction account is fulfilled in the pseudo-spin approximation. In terms of the variational Feynman-Bogoljubov principal the MIDF-model free energy depending on three order parameters: orientational $\langle P_2 \rangle$, conformational $(1\text{-}x)$ and mixed translationally-orientational $\langle \omega P_2 \rangle$ ones and also on four control parameters: a sizeless temperature (t), effective length (ε), rigidity (γ) and characteristic size of central core (α) of molecules is calculated. By means of numerical methods the investigation of equilibrium equations is fulfilled which allows to separate qualitatively different versions of the smectic liquid crystal temperature evolution to which different versions of dependence $\langle P_2 \rangle$, x and $\langle \omega P_2 \rangle$ on t, of the state diagrams in coordinates "ε-γ" and of the phase diagrams in variables "t-γ" of the MIDF-model correspond. A fundamentally new result of the paper is an establishing of the conditions at which a conformational disorder increase causes successive isostructural phase transitions in stability ranges of the system's smectic and nematic states. Those are realized in accordance to one of following schemes: coSm (conformationally ordered smectic)—cdSm (conformationally disordered smectic)—N (nematic)—IL (isotropic liquid), coSm—cdSm—IL and Sm—coN (conformationally ordered nematic)—cdN (conformationally disordered nematic)—IL which are found experimentally in lipids, alkylammonium compounds, *p-n*-octyloxybenzoic acids.

Keywords: statistical model, smectic liquid crystal, order parameters, conformational disordering, isostructural phase transitions

1. INTRODUCTION

It is considered[1,2] that the main cause of polymorphic transformations in liquid crystals is bound up with the possibility of the realization of different variants of the space arrangement of molecules and their structural conformational rearrangements are assigned an accessory part. However, proceeding from general principles it can be accepted that, on contrary, in a number of cases the change of molecular packings stabilizing the orientationally ordered state is due to conformational changes of mesophase particles. The aim of the paper is a confirmation of such a point of view based on the theoretical investigation of the MIDF-model described below.

2. MIDF-MODEL

We take the MIDF-model Hamiltonian in the form[3-5]

$$H = -\frac{1}{2}\sum_{i=1}^{N}\sum_{k=1}^{\varkappa}\sum_{\sigma,\nu=1}^{2} V_{\sigma\nu}^{(i,i+k)}\{1 + \alpha\cos(2\pi z_{i,i+k}/d)\} \cdot P_2(\cos\theta_{i,i+k})n_\sigma(l_i)n_\nu(l_{i+k}) + \sum_{i=1}^{N} E(l_i), \quad (1)$$

where N is a number of particles, P_2 is the second Legendre polynominal; $\theta_{i,i+k}$ is an angle between long axes of the i and $i + k$ particles; values $n_\sigma(l_i)$ equal to 1 or 0 describe the presence or absence of the i particle in the σ-th conformational state, α is the McMillan parameter, $z_{i,j}$ is a difference between z-coordinates of the i and j particles, d is an interlayer spacing in the smectic. Formula (1) is written in the nearest neighbours ($\varkappa$ is their number) and two conformational states[4] approximations in which all the possible conformations $\{l_i\}$ of molecules with configurational energies $E(l_i)$ are conditionally divided into two subsets corresponding to "unfold" ($n_2 = 1$) and "fold" ($n_1 = 1$) conformations at the geometric anisotropy conservation. The latter allows to introduce an effective molecular rigidity parameter γ according to the relation $V_{22}:V_{12}:V_{11} = 1:\gamma:\gamma^2$ $(0 < \gamma < 1)$[6,7] where V_{22} is a parameter of the effective translational interaction of particles being in the "unfold" conformation.

For calculation of the system's free energy F we use the variational principle[8] $F \leqslant F_V = -kT\ln Tr[\exp(-H_0/kT)] + \langle H - H_0\rangle$ where k is the Boltzman's constant, T is the temperature, brackets $\langle \ldots \rangle$ indicate a thermodynamical averaging with the Hamiltonian

$$H_0 = H_0^{or} + H_0^{con},$$

$$H_0^{or} = -p_1\sum_{i=1}^{N} P_2(\cos\theta_i) - p_2\sum_{j=1}^{N}\cos(\omega z_j)\,P_2(\cos\theta_j),$$

$$H_0^{con} = -p_3\sum_{i=1}^{N} n_1(l_i) + \sum_{j=1}^{N} E(l_j), \quad (2)$$

where p_i $(i = 1, 2, 3)$ are variational parameters. Using (2) we find statistical sum $Z_N = [Z_{or}Z_{con}]^N$ of the MIDF-model

$$Z_{con} = Z_2'[\exp(\varepsilon) + \exp(-p_3/kT)], \qquad Z_{or} = \int_0^1 du\int_0^d dz D(u, z),$$

$$Z_k' = \sum_{l_i(n_1(l_i)=k-1)}^{N}\exp[-E(l_i)/kT], \qquad (k = 1, 2), \qquad \varepsilon = \ln(Z_1'/Z_2'),$$

$$D(u, z) = \exp[(p_1' + p_2'\cos\omega z)P_2(u)/t]/d,\ u = \cos\vartheta_i, \qquad \omega = 2\pi/d,$$

$$p_i' = p_i/(\varkappa V_{22}),\ (i = 1, 2, 3),\ t = kT/(\varkappa V_{22}) \quad (3)$$

and also order parameters

$$\langle P_2\rangle = (Z_{or})^{-1}\int_0^1 du\, P_2(u)\int_0^d dz\, D(u, z),$$

$$\langle \omega P_2\rangle = (Z_{or})^{-1}\int_0^1 du\, P_2(u)\int_0^d dz\, \cos(\omega z) D(u, z) \tag{4}$$

and conformational disorder parameter

$$x = \langle n_1(l_i)\rangle = \exp(\varepsilon)/[\exp(\varepsilon) + \exp(-p_3'/t)], \tag{5}$$

characterizing a share of molecules in the "fold" conformation.

The statistical sum of Z_N at the account of (3) allows to determine the sizeless variational free energy for one particle

$$F_V/(\varkappa N V_{22}) = p_i'\langle P_2\rangle + p_2'\langle \omega P_2\rangle - p_3' x - [\langle P_2\rangle^2 + \alpha\langle \omega P_2\rangle^2]Q^2(x, \gamma)/2 - t\ln(Z_{or}Z_{con}) \tag{6}$$

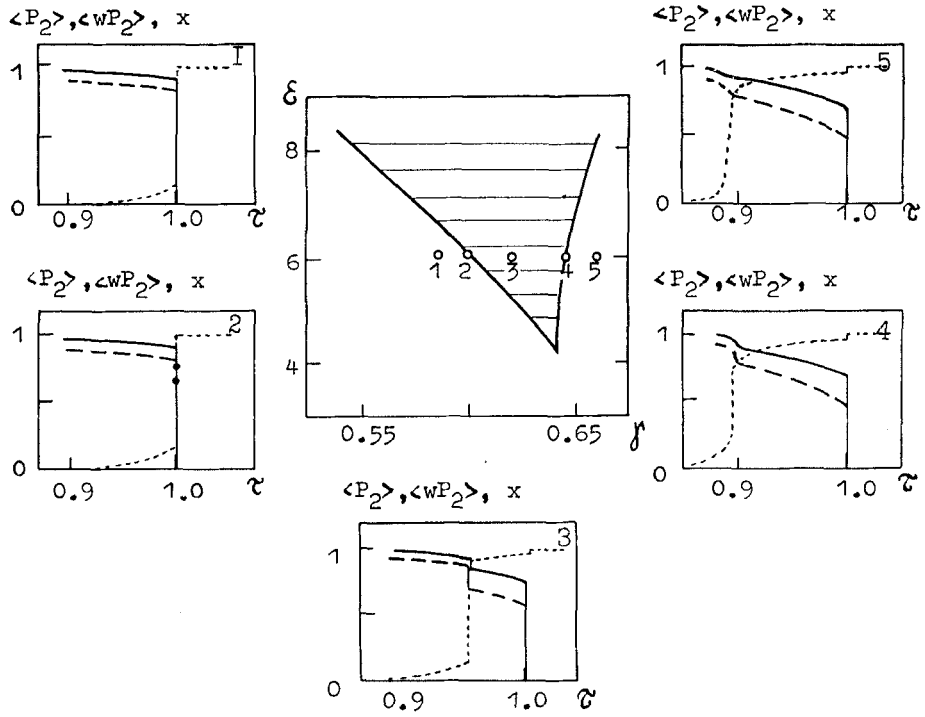

FIGURE 1 MIDF-model states diagram in variables "ε-γ" (in the center) at $\alpha = 1.1$; horizontal hatching indicates a range of parameters for which an isostructural coSm-cdSm transformation is realized. Plots 1–5: temperature dependences of the orientational order $\langle P_2\rangle$ (solid lines), mixed translational-orientational order $\langle \omega P_2\rangle$ (dashed lines) and conformational disorder x (dotted lines) parameters for the characteristic set of points 1–5 of the diagram. $\tau = t/t_{or}$, t_{or}—phase transition temperature into orientationally disordered state.

and equations $\Delta F_V(p_i) = 0$ of state

$$p_1' = \langle P_2\rangle Q(x, \gamma)^2,\ p_2' = \alpha\langle \omega P_2\rangle Q(x, \gamma)^2,$$

$$p_3' = -(1 - \gamma)[\langle P_2\rangle^2 + \alpha\langle \omega P_2\rangle^2]Q(x, \gamma),\ Q(\gamma, x) = (1 - \gamma)x - 1. \quad (7)$$

The latter equations together with (4) and (5) form a system of equations closed with respect to values x, $\langle P_2\rangle$ (ωP_2) allowing to investigate a temperature evolution of the MIDF-model.

RESULTS AND DISCUSSION

Figures 1–3 show state diagrams of the MIDF-model in the "γ-ε" plane for parameter α values 1.1, 0.85, 0.6, respectively. Temperature dependences of the parameters $\langle P_2\rangle$, $\langle \omega P_2\rangle$ and x calculated according to Equations 4–7 for character-

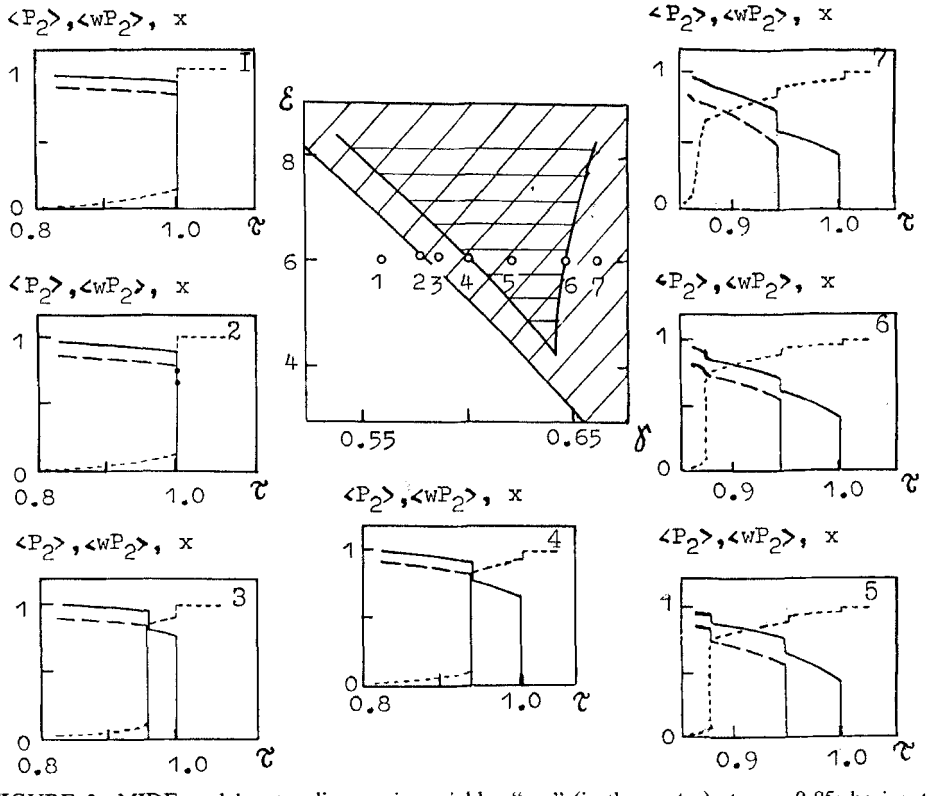

FIGURE 2 MIDF-model states diagram in variables "ε-γ" (in the center) at α = 0.85; horizontal hatching indicates a range of parameters for which an isostructural coSM-cdSm transformation is realized. Oblique hatching indicates a range of parameters for which a phase transition into the nematic state is realized. Plots 1–7: temperature dependences of the parameters $\langle P_2\rangle$ (solid lines), $\langle \omega P_2\rangle$ (dashed lines) and x (dotted lines) for the characteristic set of points 1–7 of the diagram.

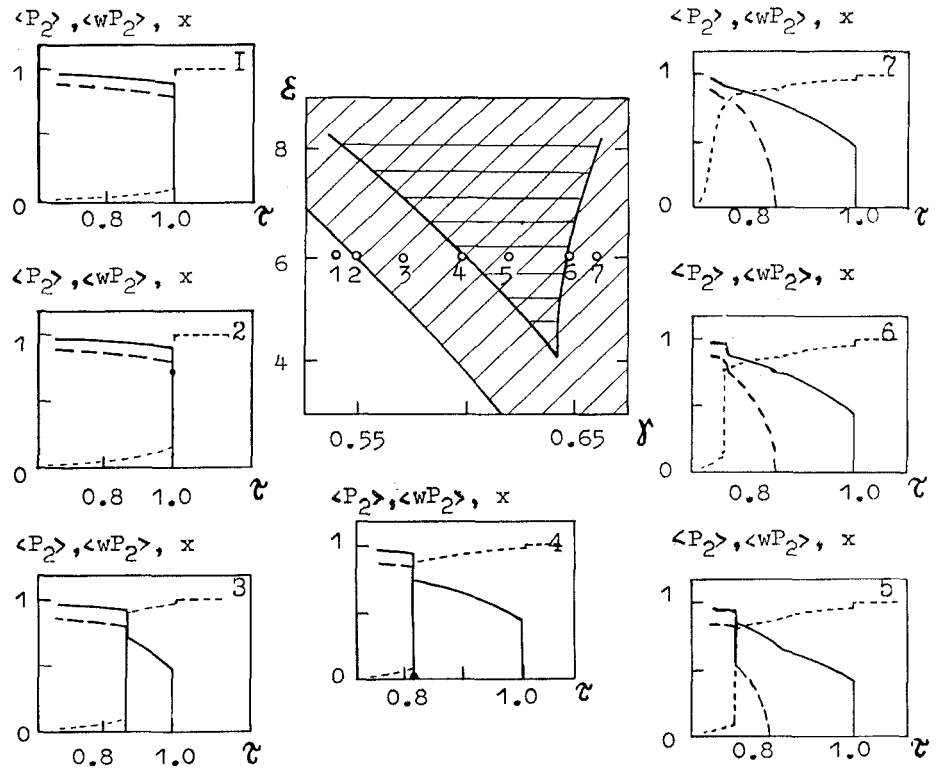

FIGURE 3 MIDF-model states diagram in variables "ε-γ" (in the center) at $\alpha = 0.6$; hatching indicates ranges similar to ones shown in Figure 2. Plots 1–7: temperature dependences of the parameters $\langle P_2 \rangle$ (solid lines), $\langle \omega P_2 \rangle$ (dashed lines) and x (dotted lines) for the characteristic set of points 1–7 of the diagram.

istic sets of diagrams points are shown in plots of these figures. It follows from Figure 1 that at $\alpha = 1.1$ the Sm-IL phase transition occurs for low and high parameter γ values (plots 1, 2, 4, 5) and moreover large order parameters jumps take place for flexible particles in comparison to rigid ones.

Phase transitions coSm-cdSm-IL are observed for intermediate values of γ (Figure 1, plot 3). Note that smectic phases coSm and cdSm are isostructural ones and differ by order parameters values only. It follows from Figure 2 that at $\alpha = 0.85$, besides of cases described above (plots 1, 2) the first order Sm-N transition is observed (plots 3, 4, 6, 7) and a sequence of transformations coSm-cdSm-N-IL is realized also (plot 5). The difference between Figure 3 and Figures 1 and 2 is that the second order Sm-N phase transition (plots 4, 6, 7) and also isostructural transformations in the sequence coSm-cdSm-N-IL, where the cdSm-N is a second order transition, are possible at $\gamma = 0.6$ (plot 5). Figure 4 shows MIDF-model diagrams in variables "γ-t" for different α values. Phase diagrams in Figure 4a–c correspond to state diagrams in Figures 1–3. Figure 4d describes how a topology of MIDF-model phase diagrams is changed at the decrease of the McMillan parameter from the values less than 0.6. It follows from Figure 4d that a sequence of transitions Sm-coN-cdN-IL is realized at $\alpha \to 0$ and moreover the Sm-coN is a second order

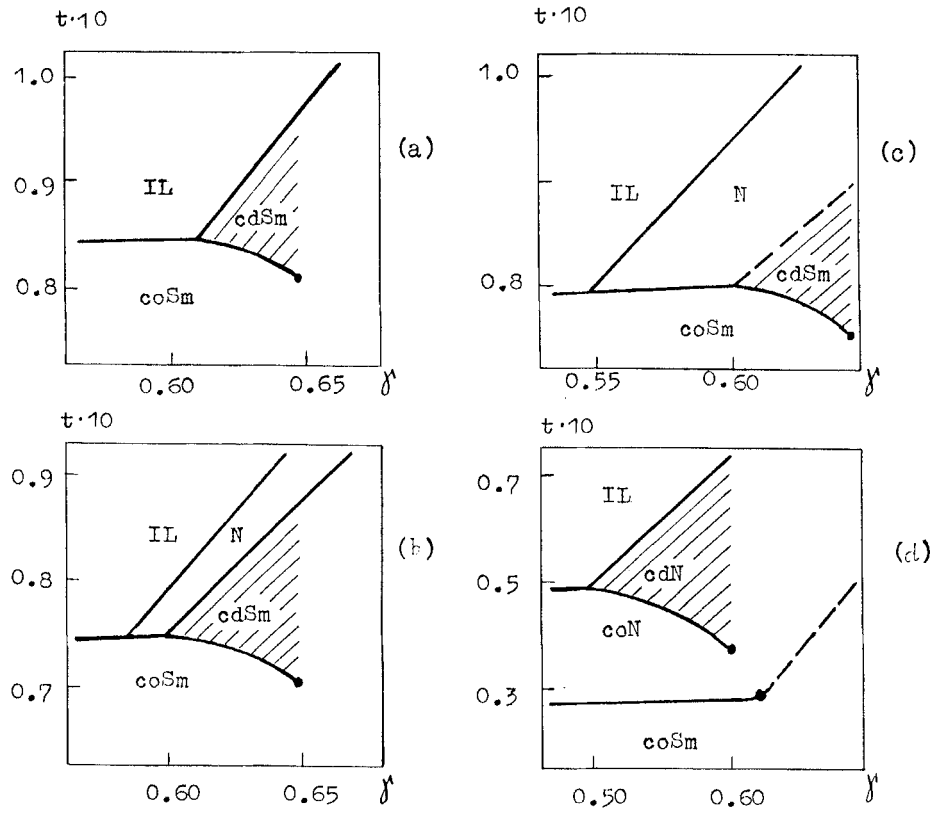

FIGURE 4 Phase diagrams of the MIDF-model in variables "γ-t" at the different values of the McMillan parameter α = 1.1 (a), 0.85 (b), 0.6 (c), 0.2 (d) (ε = 6). Solid lines correspond to first order phase transitions, dashed lines—to second order ones. Hatching indicates ranges of the existence of high temperature isostructural phases. Abbreviations: CoSm—conformationally ordered smectic, cdSm—conformationally disordered smectic, coN—conformationally ordered nematic, cdN—conformationally disordered nematic, N—nematic, IL-isotropic liquid.

transition and coN and cdN phases possess an identical global orientational symmetry and differ by the degree of orientational and conformational disorder development. It follows from Figure 4 that four types of triple, tricritical (Figure 4d) and two types of critical end points exist in the MIDF-model.

The MIDF-model includes all the results of the McMillan model[5] with certain modifications (see Figures 1–4). A fundamentally new conclusion is that the account of inner degrees of freedom of the molecules movement leads to occurrence of isostructural coSm, cdSM and coN, cdN phases. Such states are observed experimentally in a number of mesogenes in following sequences of transformations: Sm-N_1-N_2-IL in *p-n*-octyloxybenzoic acids,[9] Sm_1-Sm_2-N-IL in lipids and *n*-alkylammonium substances.[11,12] Let us also pay attention to the paper[13] in which a critical end point had been observed in the curve of the quasi-bilayer and bilayer smectics co-existence in the "temperature-concentration" plane in a mixture of cyanocompounds. This is qualitatively reproduced by the MIDF-model (see Figure 4(a–c)) in view of the fact that the change of the relative concentration of components is

followed by a corresponding change of the molecules flexibility. The latter allows to interpret in a new fashion the bilayer smectic—quasibilayer smectic transformation as an isostructural transition caused by conformational disordering of aromatic fragments of molecular dimers paired owing to opposite directions of cyanogroups' dipoles.

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