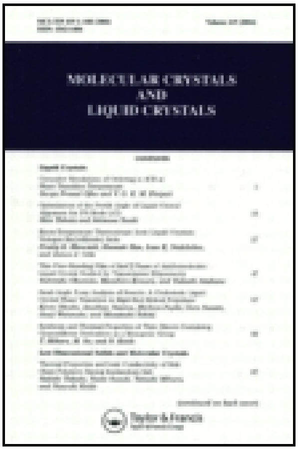

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Multicritical Behaviour of Smectic A Liquid Crystal With Conformational Degrees of Freedom

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MULTICRITICAL BEHAVIOUR OF SMECTIC A LIQUID CRYSTAL WITH CONFORMATIONAL DEGREES OF FREEDOM

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Abstract The statistical model of the smectic A system of semiflexible molecules (SmSSM) is formulated, and numerical analysis of phase behaviour of the model is fulfilled.

INTRODUCTION

The necessity of the account of intramolecular degrees of freedom for theoretical description of the smectic mesophase is caused by various experimental data concerning influence of structure and conformations of mesogeneous molecules on the thermostability of partially ordered state. Below, the version of McMillan model[1] of smectic A generalized for the case of conformationally labile molecules and the results of numerical calculations of its phase behaviour are shown.

MODEL AND FORMALISM

The Hamiltonian of SmSSM is given by

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

where N is a number of molecules, α is the McMillan[1] parameter describing the value of the translational interaction , $\theta_{i,i+k}$ are angles between long axes of the i-th particle and $\varkappa$ of its nearest neighbours,

$z_{\iota,\iota+k}$ is a difference of the positions of z-coordinates, d is a period of the layered structure along the axis OZ, P_2 is the Legandre polynomial. The values $V^{(\iota,\iota+k)}_{\mu\nu}$ determine the interparticle interaction depending on molecular conformational states (μ,ν).

The value $n_\mu(l_\iota)=1,0$ is an occupying operator of the μ-th conformational state by the ι-th particle. A certain set of molecular configurations $\{l_\iota\}$ with energies $E(l_\iota)$ corresponds to each of conformational states.

The expression (1) is written at the approximation of two conformational states where all the possible conformations of molecules are divided into two types[2]: "folded" and "unfolded" ones $(n_1 = 1-n_2)$.

The free energy of the system F is calculated by means of the variational principle[3]

$$F \le F_V = - T \ln \mathrm{Sp} \exp(-H_o/T) + \langle H - H_o \rangle \tag{2}$$

with approximated Hamiltonian

$$H_o = - \rho\sum_{\iota=1}^{N} P_2(\cos\theta_\iota) - \sigma\sum_{j=1}^{N}\cos(2\pi z_j/d)P_2(\cos\theta_j) + \\ - h\sum_{\iota=1}^{N} n_1(l_\iota) + \sum_{j=1}^{N} E(l_j), \tag{3}$$

where ρ,σ,h are variational parameters and T is the temperature expressed in energetic units. The system of equations describing equilibrium states of the mesophase and allowing to find temperature dependencies of parameters of orientational $(\langle P_2\rangle)$ and translational $(\langle\omega P_2\rangle)$ order and also of conformational disorder (x) determined by the condition $\nabla F=0$ is

$$\tilde{\rho} = \langle P_2\rangle[(1-\gamma)x - 1]^2,$$

$$\tilde{\sigma} = \alpha\ \langle\omega P_2\rangle[(1-\gamma)x - 1]^2, \qquad \omega=\cos(2\pi z/d), \tag{4}$$

$$\tilde{h} = - (1-\gamma)\{\langle P_2\rangle^2 + \alpha\ \langle\omega P_2\rangle^2\}*[(1-\gamma)x-1],$$

$$x = z_1/\{z_1+z_2\exp(\tilde{h}/\tau)\}, \qquad z_k = \sum_{(n_k(l_\iota)=1)}^{N} E(l_\iota), \qquad k=1,2$$

where $\tilde{\rho}, \tilde{\sigma}, \tilde{h}$, are sizeless variational parameters and τ is a sizeless temperature.
x is a parameter of conformational disorder characterizing a part of molecules in the "folded" conformation, γ is an effective molecular rigidity, $\lambda = \ln(z_1/z_2)$ is an effective molecular length[2].

The equations (4) possess solutions of three types corresponding to smectic A (SmA) ($\langle P_2 \rangle \neq 0$, $\langle \omega P_2 \rangle \neq 0$), nematic (N) ($\langle P_2 \rangle \neq 0$, $\langle \omega P_2 \rangle = 0$), and isotropic liquid (IL) ($\langle P_2 \rangle = 0$, $\langle \omega P_2 \rangle = 0$) phases and transforms into the equations similar to the McMillan model[1] in the limit of conformationally rigid particles.

RESULTS AND DISCUSSION

Numerical calculations has shown that the increase of the effective molecular flexibility ($\gamma \to 1$) of mesophase particles leads to the increase of the dependence of translational and orientational order on the degree of conformational disorder in the system. As a consequence three qualitatively different types of the temperature evolution of SmSSM are realised, which can be identified with the behaviour of systems of conformationally flexible, semiflexible and relatively rigid molecules (Figure 1,a-d).

Conformational disordering is continuously rised in the system of relatively rigid particles at temperatures considerably lower then the temperature of the transition from smectic into nematic state or isotropic liquid (Figure 1,a). On the contrary, simultaneous stepwise translational and orientational disordering at the point of smectic-nematic transition is typical for the system of flexible molecules (Figure 1,b).

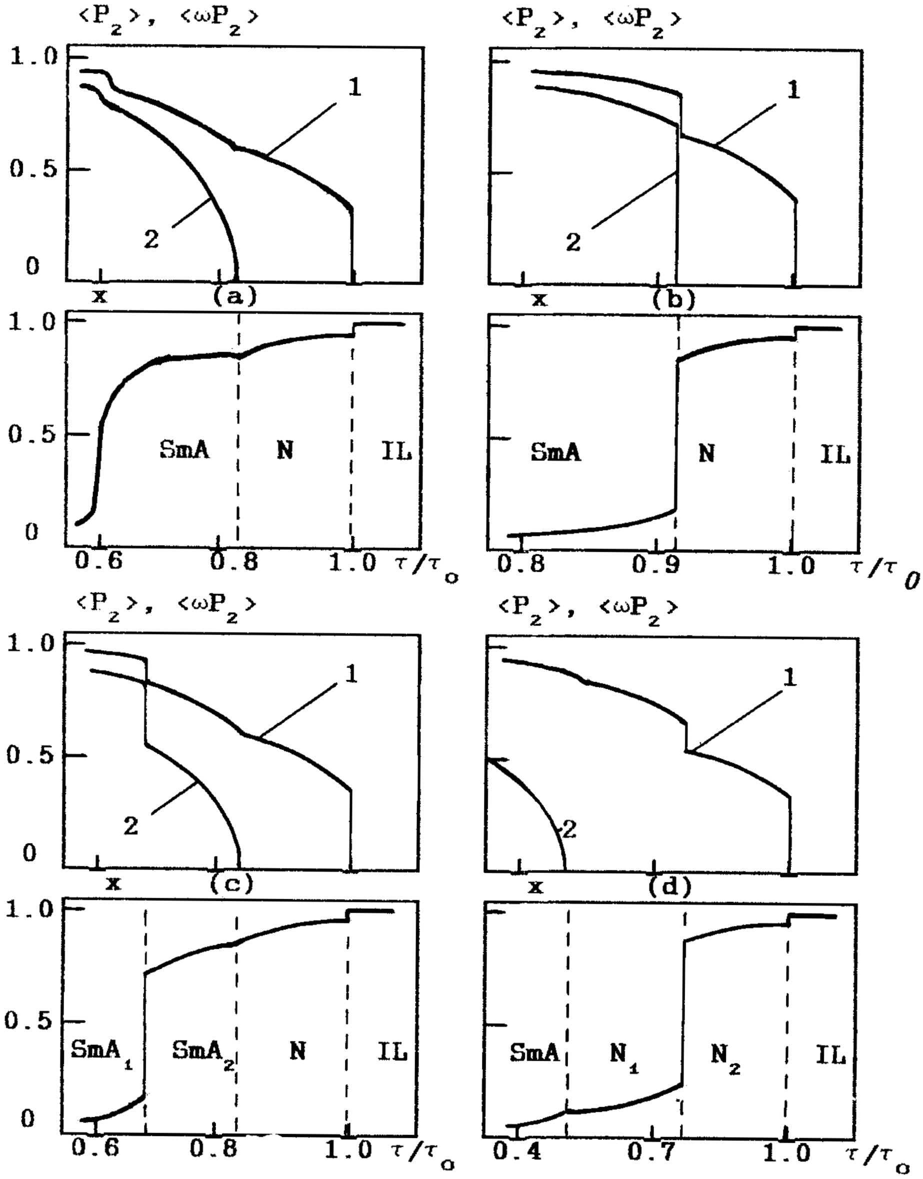

FIGURE 1 Temperature dependences of order parameters $\langle P_2 \rangle$ (curve 1), $\langle \omega P_2 \rangle$ (curve 2) and x at the various values of model parameters (λ=6.0): (a)-α=0.6, γ=0.67; (b)-α=0.6, γ=0.57; (c)-α=0.6, γ=0.62; (d)-α=0.35, γ=0.57; τ_0 is a temperature of the N-IL transition.

Isostructural first order phase transitions of the type SmA_1-SmA_2 is realised at $\alpha>0.4$ (Figure 1,c) and N_1-N_2 at $\alpha<0.4$ (Figure 1,d) in the intermediate case of semiflexible molecules where the effect of conformational rearrangements of particles is not so high as to induce complete orientational disordering in the system.

Smectic phases SmA_1 and SmA_2 (and also nematic ones N_1 and N_2) have the same global symmetry but differ over the values of order parameters (with major difference over the conformational disordering value) (Figure 1,c,d). These phenomena were not seen in the detailed modern theories[4-6], but were obtained experimentally for anhydrous amphiphilic systems of n-alkylammonium chlorid type[7,8], n-alkanes[9], p-n-octyloxybenzoic acid[10] and some others.

It is established also that at α=const there are lines of triple points of types SmA_1 - SmA_2 - IL ($\alpha>0.98$), SmA_1 - SmA_2 - N ($0.4<\alpha<0.98$) or N_1 - N_2 - IL ($\alpha<0.4$), and lines of critical points at which isostructural phase transitions become a second order ones in the model parameters space (α,γ,λ).

At $\alpha<0.98$ the McMillan model[1] demonstrates a sequence of phase transitions SmA - N - IL. In the case of SmSSM a similar sequence of phase events is observed for relatively rigid particles (Figure 1,b). However, the molecular flexibility increase leads to suppression of the nematic phase, analogously to one observed in homological series of smectics. At $\alpha<0.7$ the phase transition SmA - N is always a second order one in the McMillan model[1] and for case of SmSSM this phase transformation can be both a second and first order one for semiflexible molecules depending on the level of conformational disordering of the system (Figure 1,c).

Besides, the triple points line at which two smectic and one nematic phase coexist simultaneously is at the same time the tricritical points line for the nematic - smectic transition. The phenomenon of similar type is found in a mixture of cyano compounds where the tricritical point being near (or coinciding) the triple point of coexistence of nematic, smectic C and smectic A phases is revealed by the scanning calorimetry method in the line of phase transitions nematic-smectic C[11].

CONCLUSION

At the generalization of the results it can be said that conformational ordering influences considerably the macroscopic behaviour of a smectic mesophase and determines often not only a type but also an occurence of phase transitions in the molecular system.

It, very likely, can play an essential role in the whole number of phenomena observed in smectics such as the induced, bounded, reentrant mesomorphism, and multicritical phenomena.

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