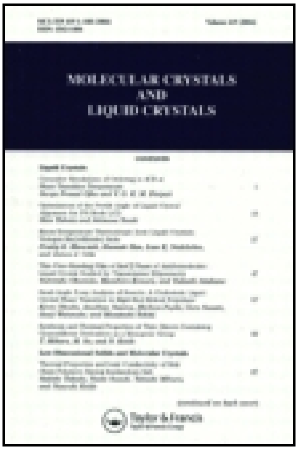

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Tricritical Points in Ferroelectric Liquid Crystals

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TRICRITICAL POINTS IN FERROELECTRIC LIQUID CRYSTALS

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Abstract A molecular theory is applied to the problem of the tricritical point existence in ferroelectric liquid crystals. Various cases of the tricritical points locations on the density - temperature phase diagrams are discussed.

INTRODUCTION

Recently there has been a considerable interest in the problem of the critical and multicritical points existence in phase diagrams of liquid crystalline systems[1-4]. Up to now, the most efficient approach to this question is the Landau free energy expansion method[1-4]. Generally, in the theory of the tricritical point (TCP) the Landau expansion up to sixth order terms in order parameters is considered[5]. Within this theory the TCP separates the first and second order parts of the phase transition line.

Our theory[6] allows to construct the Landau free energy terms of arbitrary order enabling one to analyse the higher order critical points. Here we have analysed the possibility of occurence of TCP in the density - temperature plane of systems with a simple model interaction potential yielding the variety of polar orderings of ferroelectric and antiferroelectric types[7,8]. The presented approach allows to find the explicit dependence of the Landau expansion coefficients on the number density n and temperature $T = 1/k_B\beta$.

BASIC THEORY

Following the formerly developed method [6,7] we determined the order parameters and Landau free energy for system of uniaxial polar molecules with the simple model interaction potential

$$U_2(1,2) = \sum_{\ell=0}^{2} W_\ell(|\underline{r}_1 - \underline{r}_2|)\, P_\ell(\cos\vartheta_{12}). \tag{1}$$

In the free energy calculations the contributions from higher order diagrams[8] are included.

The order parameters are selected from the expansion coefficients $\alpha_\ell^m(\underline{q})$ of the one-particle distribution function

$$\rho(\underline{r},\Omega) = n\, V^{-1/2} \sum_{\ell,m,\underline{q}} \alpha_\ell^m(\underline{q})\, Y_\ell^m(\vartheta,\varphi)\, e^{i\underline{qr}}, \tag{2}$$

n - number density, V - volume of the system.
From the complete set of order parameter determined by the interaction potential (1) we choose the particular three ones: $\alpha_o \equiv \alpha_o^o(Q_o)$ - translational, $\alpha_1 \equiv \alpha_1^o(Q_1)$ - polar, $\alpha_2 \equiv \alpha_2^o(Q_2)$ - orientational; which are suitable for the description of the polar and nonpolar smectic phases, with incommensurate Q_o, Q_1, Q_2.

The free energy can be written now as

$$F = F^{[2]} + F^{[4]} + F^{[6]}, \tag{3}$$

where

$$F^{[2]} = \sum_{\ell} \mathcal{A}_\ell\, |\alpha_\ell|^2, \tag{4}$$

$$F^{[4]} = \sum_{\ell} \mathcal{B}_\ell |\alpha_\ell|^4 + \sum_{\ell,k} \mathcal{B}_{\ell k}\, |\alpha_\ell|^2 |\alpha_k|^2, \tag{5}$$

$$F^{[6]} = \sum_{\ell} \mathcal{E}_{\ell}|\alpha_{\ell}|^{6} + \sum_{\ell,k} \mathcal{E}_{\ell k}|\alpha_{\ell}|^{4}|\alpha_{k}|^{2} + \sum_{\ell,k,m} \mathcal{E}_{\ell k m}|\alpha_{\ell}|^{2}|\alpha_{k}|^{2}|\alpha_{m}|^{2} \qquad (6)$$

$$(\ell,k,m = 0,1,2).$$

Coefficients $\mathcal{A},\mathcal{B},\mathcal{E}$ are given in terms of Fourier transforms $\tilde{W}_{\ell}(q)$ of the interaction potentials $W_{\ell}(r)$, Eq.(1); for example

$$\mathcal{A}_{\ell} \sim n(T - T^{*}_{\ell}) \qquad (7)$$

$$\mathcal{B}_{\ell} \sim n\left[a_{\ell} + n^{3}\beta^{4}(b_{\ell} - \beta^{2}d_{\ell}) + c_{\ell}n^{4}\beta^{5}\right], \qquad (8)$$

where

$$T^{*}_{\ell} = -n\tilde{W}_{\ell}(\underline{q}) - \sum_{k=2}^{5} n^{k}\beta^{k}D_{k}(\ell) + n^{3}\beta^{5}S(\ell) + n^{4}\beta^{9}P(\ell) + \ldots \qquad (9)$$

$D_{k}(\ell)$ are the contributions from the higher order ring diagrams, $S(\ell)$ and $P(\ell)$ are the contributions from the more than double connected diagrams, respectively ; $a_{\ell},b_{\ell},c_{\ell},d_{\ell}$ - constants given by the appropriate convolution integrals of the interaction functions $W_{\ell}(r)$ [4,8,9].

As follows from Eq. (8) the fourth order coefficient $\mathcal{B}_{1}$ can change sign with the density and temperature change which leads to the TCP occurrence on the phase transition line between polar and non-polar phases.

PHASE DIAGRAMS

We consider the phase diagrams on the temperature - density plane. Location of TCP on the phase transition line between polar and nonpolar smectic phases is determined by the solutions of equations: $\mathcal{A}_{1}(n,T) = 0$ and $\mathcal{B}_{1}(n,T) = 0$.

That leads to the following basic cases: (1) no TCP; (2) one TCP separating 1st and 2nd phase transition lines (Fig.1a,b); (3) two TCP (Fig.1c); (4) one isolated TCP on the second order phase transition line (Fig.1d).

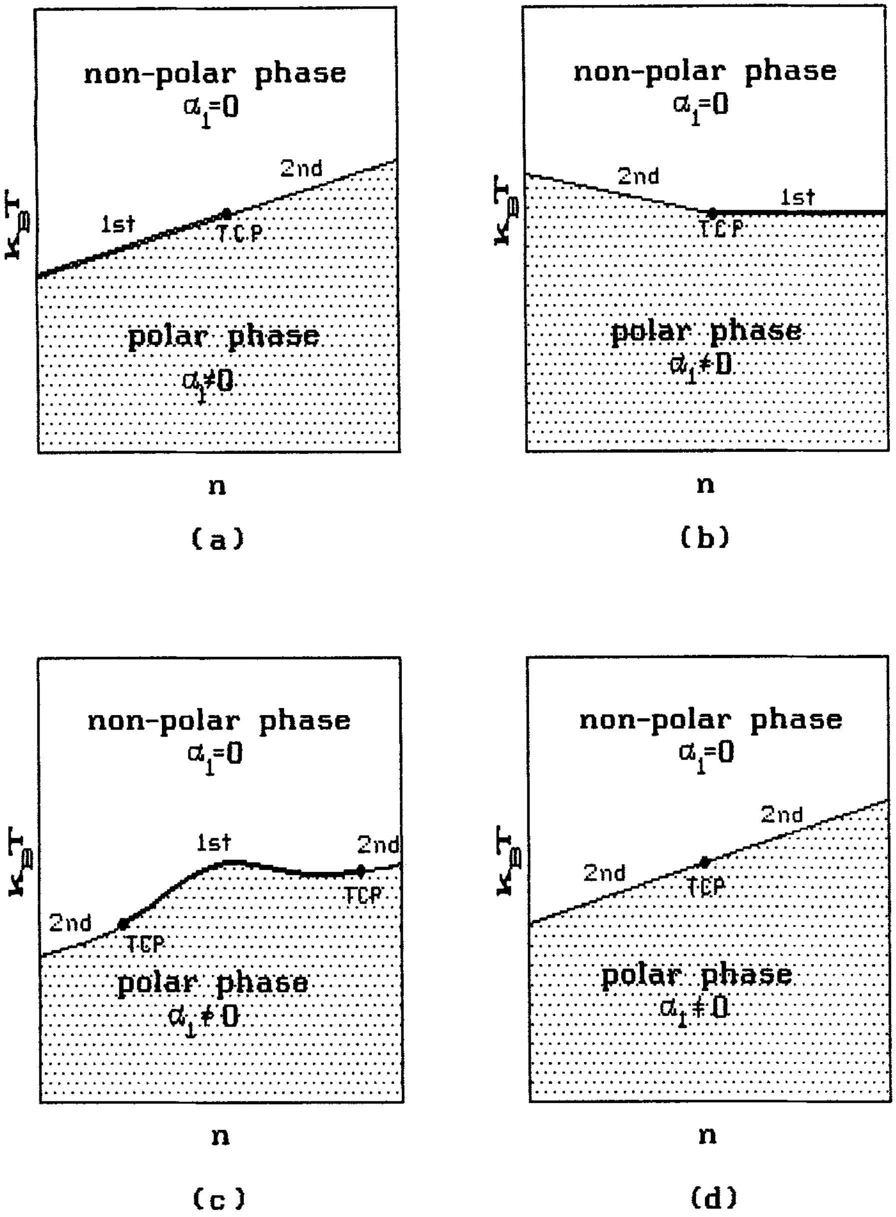

FIGURE 1 Possible cases of the tricritical point location on the phase transition lines between polar and non-polar phases.

CONCLUSIONS

We have pointed at three interesting possibilities of occurrence of TCP at phase transition line between polar and nonpolar smectics.

We hope that this rather simple model incorporates essential features of the phase diagram which can be found for the case of more realistic interaction potential.

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