Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 22 Sep 2006.

To cite this article: Vladimir Konoplev & Vladimir Pershin (1990): Elementary Catastrophes in Microscopic Models of Nematic Mesophase, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 192:1, 167-171

To link to this article: http://dx.doi.org/10.1080/00268949008035625

Mol. Cryst. Liq. Cryst. 1990, Vol. 192, pp. 167–171
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Printed in the United States of America

ELEMENTARY CATASTROPHES IN MICROSCOPIC MODELS OF NEMATIC MESOPHASE

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Abstract By means of the applied theory of catastrophes the stability of orientationally ordered state of the nematic liquid crystal (NLC) in the Maier-Saupe and Kimura-Nakano models is investigated on the basis of the variational Feynman principle .

MAIER-SAUPE MODEL

In the model[2] the system of elongated rigid particles is described by the potential of free energy

$$\Phi(\alpha;\tau) = -\tau \ln J_0(\alpha) + \tau\alpha(2\langle P_2\rangle+1)/3 - \langle P_2\rangle^2/2, \quad (1)$$

where τ is a sizeless temperature. In (1) the orientational order parameter, $\langle P_2\rangle$, is associated with a certain state variable, α, by the equalities

$$\langle P_2\rangle = (3J_1(\alpha)J_0^{-1}(\alpha) - 1)/2,$$

$$J_m(\alpha) = \int_0^1 u^{2m}\exp(\alpha u^2)du, \quad m = 0,1. \quad (2)$$

Critical points of the potential (1) are found from the condition

$$\alpha\langle P_2\rangle' - \langle P_2\rangle = 0, \quad (\langle P_2\rangle' \equiv d\langle P_2\rangle/d\alpha),$$

and the bifurcational multitude is determined by the system

$$\alpha\langle P_2\rangle' - \langle P_2\rangle = 0, \quad \tau - 3\langle P_2\rangle'/2 = 0. \quad (3)$$

A numerical analysis shows that the system (3) has two solutions:

$$\alpha^{*} = 0.0, \quad \tau^{*} = 0.2000;$$
$$\alpha^{**} = 2.2, \quad \tau^{**} = 0.2228.$$

Thus, there are two points which totality form a separatrix of the model in the one-dimensional space of the control parameters[1] (on the τ-axis). From the physical point of view the temperature τ^{**} is an upper stability border of NLC and τ^{*} determines a lower stability border of the isotropic liquid phase of the molecular system. The analytical calculations (here not shown) show that in the vicinity of points (α^{**},τ^{**}) and (α^{*},τ^{*}) such smooth (different) reversible non-linear substitutions of the variables $\hat{x}(\alpha,\tau),\tau=\tau(c)$ exist that potentials of family (1) behave, respectively, in following manner

$$\Phi(\alpha;\tau) = \hat{x}^3 + c\hat{x}, \tag{4}$$

$$\Phi(\alpha;\tau) = \hat{x}^3 + c\hat{x}^2. \tag{5}$$

Hence, two catastrophes of type "folding" disposed on the temperature scale are met in the model[2]. The deduction of the equations (4), (5) is a new result; the first one corresponds to the typical and the second one to the non-typical version of the theory of catastrophes[1]. The analysis shows that the potential (5) possesses an additional extremum in comparison with the potential (4) which is a consequence of the existence of the trivial solution of equations (3). Such a feature of the theory must be characteristic of any microscopic model of the nematic liqiud crystal generalizing the Maier-Saupe approach[2].

The last conclusion is, in particular, illustrated below on the example of the Kimura-Nakano model of NLC.

KIMURA-NAKANO MODEL

In the model[3] the nematic phase of the system of flexible molecules is described by a potential of free energy

$$\Psi(\alpha,x;\gamma,z^*,\tau) = -\tau \ln J_0(\alpha) + \tau\alpha(2\langle P_2\rangle+1)/3+$$
$$+\tau \ln(1-x) + \tau xR(x;z^*) - \langle P_2\rangle^2 Q^2(x;\gamma)/2, \quad (6)$$

the state equations following from (6) have the form

$$2\alpha\tau = 3\langle P_2\rangle Q^2(x;\gamma),$$
$$\tau R(x;z^*) = (1-\gamma)\langle P_2\rangle^2 Q(x;\gamma). \quad (7)$$

In expressions (6),(7) the following designations (besides the ones introduced in (2)) are used

$$x=\left\{1+(z^*)^{-1}\exp\left[-\langle P_2\rangle^2 Q(x;\gamma)(1-\gamma)/\tau\right]\right\},$$
$$Q(x;\gamma)=(1-\gamma)x-1, \quad R(x;z^*)=\ln[x/(1-x)z^*].$$

The values $x,\gamma,\ln z^*$ mean the parameter of conformational disordering (reflecting a part of molecules in the "folded" conformation),the effective rigidity and length of particles, respectively. From the point of view of the theory of catastrophes[1] the expression (6) describe the family of potential functions with two state variables (α,x) and three control parameters (γ,z^*,τ). Critical points of the potential (6) are determined by the solutions of the equations (7) and the bifurcational multitude of the model[3] is found from the combined solution of the equation

$$\left[2\tau/3-\langle P_2\rangle' Q^2(x;\gamma)\right]\left[\tau/x(1-x)-(1-\gamma)^2\langle P_2\rangle^2\right] =$$
$$= 4\langle P_2\rangle'\langle P_2\rangle^2 Q^2(x;\gamma)(1-\gamma)^2 \quad (8)$$

and the system (7). Numerical calculations show that the thrice-degeneralized critical point is determined by the following approximated equations

$$\alpha_0 \simeq 5.8, \quad x_0 \simeq 0.77;$$
$$\gamma_0 \simeq 0.56, \quad \ln z_0^* \simeq 3.02, \quad \tau_0 \simeq 0.079.$$

The applied theory of catastrophes[1] allows us to state that the potential (6) in the vicinity of the five-dimensional point $(\alpha_0, x_0, \gamma_0, z_0, \tau_0)$ can be represented in the form

$$\Psi = \text{const} + \lambda_2 \hat{x}_2^2 + \hat{x}_1^5 + c_1 \hat{x}_1^3 + c_2 \hat{x}_1^2 + c_3 \hat{x}_1, \qquad (9)$$

where $\hat{x}_1, \hat{x}_2$ are the functions of the variables (α, x) and the parameters (γ, z^*, τ), and the coefficients $\lambda_2 > 0$, c_i, $i=1,2,3$ depend on the parameters only. The formula (9) corresponds to the catastrophe "swallow tail" over the variable $\hat{x}_1$. The latter means that in this case the physical instability of molecular system is bound both with orientational and conformational disordering. However, the numerical evaluations show that the contribution into the instability of the first of them is prevailing.

Besides, the trivial solution

$$\alpha^* = 0, \quad x^* = z^*/(1+z^*), \qquad (10)$$

existing at any permissible values of the parameters γ, τ. satisfies the system of equations (7),(8) describing the multitude of degeneralized critical points of the model.[3] By means of smooth substitution of variables the potential (6) in the vicinity of the point (10) can be reduced to the form

$$\Psi = \text{const} + \lambda_2 \hat{x}_2^2 - \hat{x}_1^3 + c\hat{x}_1 \qquad (11)$$

which corresponds to the catastrophe "folding" over the variable $\hat{x}_1$ with the pertubation of the non-standard type (see the formula (1)). The formula (11) shows that the conclusions of the previous section concerning the phase transformation nematic-isotropic liquid remain valid, however, the lower stability border of the isotropic liquid is in this case the function of the effective rigidity and length of molecules according to the formula

$$\tau^* = Q^2(x^*, \gamma).$$

Numerical calculations (here not shown) allow one to draw also the following conclusion: the fact that in the certain range of molecular parameters of the model[3] the sequence of two phase transitions can realize (the first one associated with conformational disordering of molecules and occuring in the stability interval of the orientationally ordered state (isostructural transformation) and the second one being the ordinary first order transition mesophase-isotropic liquid) is the physical consequence of the catastrophes of type "folding"(9), and "swallow tail"(11).

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