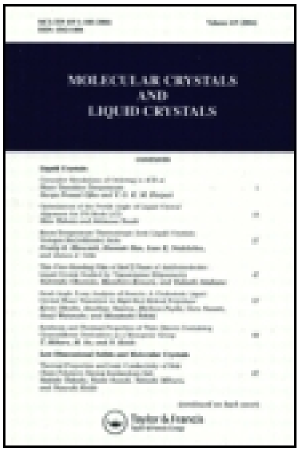

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Novel Bifurcation Set Cross-Section Method for Topological Analysis of Phase Diagrams

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NOVEL BIFURCATION SET CROSS–SECTION METHOD FOR TOPOLOGICAL ANALYSIS OF PHASE DIAGRAMS

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Abstract Bifurcation set cross–section method is proposed which allows to construct all the possible, at least, two–dimensional phase diagrams of models described by multiparametric thermodynamic potentials. The method is applied to investigation of the de Gennes model of smectic A mesophase in external field. Among other results, the most important one is that all the critical (end critical, tri–critical etc.) points of phase diagrams are peculiar points of the corresponding bifurcation sets.

INTRODUCTION

Nowadays, it is generally accepted in physics of liquid crystals that the type of temperature evolution of a system is mainly effected by various competing order parameters. Therefore, development of methods of investigation of multiparametric thermodynamic potentials is significant. Model thermodynamic potentials with one order parameter are usually studied by a rather simple calculation techniques which frequently leads to specific physics results. Therefore, the procedure of reduction of multiparametric potentials to uniparametric (concerning the number of order parameters only) ones is conventional and is used broadly in theoretical research work (see, for example[1]). But, in catastrophe theory language[2], such a way of solving of stability problems implies that with the help of not rigorously approved manipulations thermodynamic potentials (or, in mathematics definition, catastrophes) with several "essential" order parameters are reduced to catastrophe with one order parameter which contradicts to the classification Thome theorem[2]. Besides, by going from multi– to uniparametric potential ("physics" method for dissolving of stability problems) one part of important information can be retained (in view of the existence of the hierarchy of catastrophes in which the "lower" catastrophes are included as sub–sets into the "upper" ones), but the other part is lost. Thus, at a rigorous approach there must be evolved such methods of investigation of multiparametric potentials and systems with competing couplings which are based on catastrophe theory and bifurcation analysis ideology. Such an approach is undertaken lower by the way of example of thermodynamic potential of a broaden version of the de Gennes model of smectic A (Sm) in external magnetic (or electric) field.

FORMALISM

The free energy potential of Sm mesophase is taken in the form

$$F = \tau_1 Q^2/2 - \beta Q^3/3 + \gamma Q^4/4 + \tau_2 S^2/2 + bS^4/4 - \chi QS^2 - \mu Q, \qquad (1)$$

where β, γ, b, χ are positive material constants; the value $\mu=\chi_a H^2/3$ ($\chi_a>0$) describes the dimensionless contribution bound up with the action of the external field H. Parameters $\tau_k=a_k(T-T_c^k)$, ($a_k>0$, k=1, 2) characterize deviation of the system temperature T from temperatures T_c^1, T_c^2 of corresponding mean–field phase transitions bound up with the orientational Q and translational S order parameters in the case when the latters are non–interacting. The equations of state of the potential (1) have the form

$$\gamma Q^3 - \beta Q^2 + \tau_1 Q - \mu - \chi S^2 = 0, \qquad (2)$$

$$S(\tau_2 - 2\chi Q + bS^2) = 0 \qquad (3)$$

describing three types of solutions S=0, Q=0 (isotropic liquid (IL)), S=0, Q≠0 (nematic (N)), S≠0, Q≠0 (Sm) at μ=0 and two types of solutions S=0, Q≠0 (N or paranematic (pN)), S≠0, Q≠0 (Sm) at μ≠0.

Using Eqs. (1)–(3), we can find the stability matrix

$$\mathrm{STAB} = \begin{bmatrix} \tau_1 - 2\beta Q + 3\gamma Q^2 & -2\chi S \\ -2\chi S & \tau_2 + 3bS^2 - 2\chi Q \end{bmatrix}, \qquad (4)$$

which accept the following form

$$\mathrm{STAB}|_{\mathrm{IL}} = \begin{bmatrix} \tau_1 & 0 \\ 0 & \tau_2 \end{bmatrix}, \qquad (5)$$

$$\mathrm{STAB}|_{\mathrm{N(pN)}} = \begin{bmatrix} -2\tau_1 + \beta Q + 3\mu/Q & 0 \\ 0 & \tau_2 - 2\chi Q \end{bmatrix}, \qquad (6)$$

$$\mathrm{STAB}|_{\mathrm{Sm}} = \begin{bmatrix} \tau_1 - 2\beta Q + 3\gamma Q^2 & -2\chi S \\ -2\chi S & 2bS^2 \end{bmatrix} \tag{7}$$

at the IL, N (pN) and Sm solutions

$$\mathrm{IL}:\ S = 0,\ Q = 0, \tag{8}$$

$$\mathrm{N, pN}:\ S = 0,\ \gamma Q^3 - \beta Q^2 + \tau_1 Q - \mu = 0, \tag{9}$$

$$\mathrm{Sm}: \begin{cases} b\gamma Q^3 - b\beta Q^2 + (b\tau_1 - 2\chi^2)Q + (\chi\tau_2 - b\mu) = 0, \\ S^2 = (2\chi Q - \tau_2)/b, \end{cases} \tag{10}$$

respectively. In accordance with (5)–(7), stability matrix hessians can be represented at these solutions as

$$\mathrm{Hess}|_{\mathrm{IL}} = \tau_1\tau_2, \tag{11}$$

$$\mathrm{Hess}|_{\mathrm{N(pN)}} = (-2\tau_1 + \beta Q + 3\mu/Q)(\tau_2 - 2\chi Q), \tag{12}$$

$$\mathrm{Hess}|_{\mathrm{Sm}} = 2S^2\left[(\tau_1 - 2\beta Q + 3\gamma Q^2)b - 2\chi^2\right]. \tag{13}$$

As it is known from catastrophe theory[2], the zero value of hessians at these solutions defines bifurcation sets (or separatrices) $X_N = X_N' \cup X_N''$ and $X_{Sm} = X_N \cup X_{Sm}'$ of correspondent phases

$$X_N' : \begin{cases} \tau_1 = \beta Q - \gamma Q^2 + \mu/Q, \\ \tau_1 = 2\beta Q - 3\gamma Q^2; \end{cases} \tag{14}$$

$$X_N'' : \begin{cases} \tau_1 = \beta Q - \gamma Q^2 + \mu/Q, \\ \tau_2 = 2\chi Q^2; \end{cases} \tag{15}$$

$$X_{Sm}' : \begin{cases} \tau_1 = 2\beta Q - 3\gamma Q^2 + 2\chi^2/b, \\ \tau_2 = b(2\gamma Q^3 - \beta Q^2 + \mu)/\chi. \end{cases} \tag{16}$$

Note that Formulae (14)–(16) are parametric representations of curves in (τ_2, τ_1) coordinates where the Q order parameter plays a part of a parameter of the curves.

The X_N' bifurcation set corresponds to one, two or three parallel straight lines depending on a sign of the discriminant

$$D = \mu(\mu - \mu_1^*)/(16\gamma^2), \tag{17}$$

where

$$\mu_1^* = \beta^3/(27\gamma^2), \tag{18}$$

of the cubic equitation

$$2\gamma Q^3 - \beta Q^2 + \mu = 0 \tag{19}$$

which is the consequence of the system (14). These straight lines pass through extreme points of the X_N'' curve which can also possess one, two or three extremumes (the last case is shown in Figure 1a). It is seen from Eq. (17) that in (τ_2, τ_1) plane the X_{Sm}' separatrix is the curve with a turning point whose coordinates are

$$(\tau_1^D, \tau_2^D) = (2\chi^2/b + \beta^2/(3\gamma), b(\mu - \mu_1^*)/\chi), \; Q^D = \beta/(3\gamma). \tag{20}$$

It is followed from Eqs. (15), (16) that the X_N'' and X_{Sm}' separatrices have common points of tangency in which the Q parameter takes the values complying the following equation

$$2b\gamma Q^3 - b\beta Q^2 - 2\chi^2 Q + b\mu = 0. \tag{21}$$

Depending on a sign of the discriminant

$$D = \mu^2/16 - \beta\mu\chi^2/(24b\gamma) - \beta^3\mu/(432\gamma^2) - \beta^2\chi^4/(432b^2\gamma^2) - \chi^6/(27b^3\gamma^3) \tag{22}$$

of Eq. (21), there can be realized three (D<0), two (D=0) or one (D>0) such points of tangency.

It is seen from Eqs. (21), (22) that, besides μ_1^*, two more critical values of the field

$$\mu_2^* = \mu_1^* + 2\chi^2\beta/(3b\gamma), \tag{23}$$

$$\mu_3^* = \left\{\mu_2^* + \left[\beta^2/(9\gamma) + 4\chi^2/(3b\gamma)\right]^{3/2}\right\}/2. \tag{24}$$

take place in the model. At $\mu=\mu_2^*$ the turning point of the X_{Sm}' separatrix is at the same time the point of tangency of the X_N'' and X_{Sm}' separatrices (the value Q^D from Eq. (20) satisfies Eq. (21)), and at $\mu=\mu_3^*$ there is degeneration according to the number of points of tangency of the X_N'' and X_{Sm}' separatrices (it corresponds to the case when D=0 in Eq. (17)). Thus, the values μ_i^* (i=1, 2, 3) from Eqs. (18), (23), (24) are critical ones at which the separatrix topology changes essentially. It can be shown that these geometric peculiarities are at the same time the physics ones. At $\mu=\mu_1^*$ the N–pN phase transitions is suppressed by the field. At $\mu=\mu_2^*$ a new TCP and at $\mu=\mu_3^*$ the double TCP arises on the phase boundary.

Below we consider only the approximations of weak fields ($\mu<\mu_1^*$) and weak translational and orientational coupling ($\chi^2 < b\beta^2/(9\gamma)$). The opposite case was discussed in Reference[3].

Results of separatrices (14)–(16) calculations at $\mu = \mu_1^*/2$ are presented in Figure 1a. Stability areas of N, pN and Sm phases obtained by bifurcation set cross–section method (BSCSM) are also shown in this Figure. Figure 1b gives the illustration of application of the BSCSM for analysis of stability conditions of the Sm state only. Analogous analysis can be carried out for N and pN phases as well.

In BSCSM analysis the main part belongs to: 1) Eqs. (14)–(16) of separatrices and corresponding graphs of bifurcation sets (Figure 1a); 2) Eq. (10) dissolving over the τ_2 parameter

$$\tau_2 = -\left(b\gamma Q^3 - b\beta Q^2 + (b\tau_1 - 2\chi^2)Q - b\mu\right)/\chi; \tag{25}$$

3) Equation $\tau_2=2\chi Q$, at which $S^2(Q)=0$ in formula (10). One can choose the cross–section τ_1=const (for example, A–B–C in Figure 1a) of the $X_N \cup X_{Sm}$ separatrix in the (τ_2, τ_1) Cartesian plane. For this cross–section we plot graphs of functions (25) and $\tau_2=2\chi Q$ in (Q, τ_2) coordinates. In Figure 1b these graphs are shown for the A–B–C cross–section. Let us denote extreme values of the Q parameter of the curve (25) by Q_1^0, Q_2^0.

In formula (10) inequality $S^2(Q) > 0$ is fulfilled in that part of the (Q, τ_2) plane where the condition $\tau_2-2\chi Q<0$ is valid (see section lining on the straight line $\tau_2=2\chi Q$ in Figure 1b). Every fixed point (for example, R) of the cross–section in Figure 1a corresponds to the entire straight line (for example, R–R line) parallel to τ_2 axis in Figure 1b. Crossover points of this line and the curve (25) conforms with minimum (if inequalities $Q<Q_1^0$ or $Q>Q_2^0$ are valid, i.e. $Hess|_{Sm}>0$) or saddle (otherwise, i.e. $Hess|_{Sm}<0$) points of the potential (1). Thus, it can be seen that thermodynamic potential in smectic state has

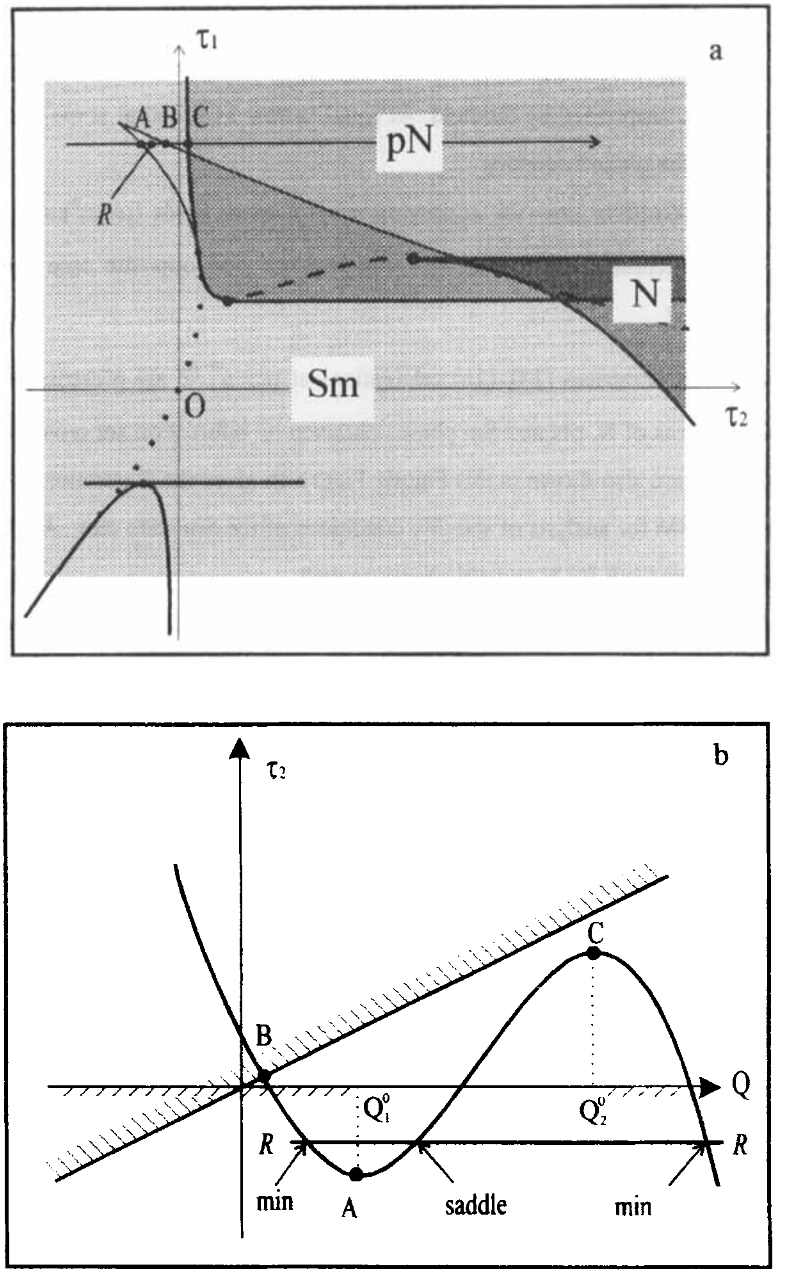

FIGURE 1 Separatrices in (τ_2,τ_1) coordinates (a) and stability diagram (b) of the de Gennes model of smectic A.

one minimum at the conditions $\tau_2<\tau_2(A)$ or $\tau_2(B)<\tau_2<\tau_2(C)$, two minima and one saddle point at the conditions $\tau_2(A)<\tau_2<\tau_2(B)$, and none critical points at $\tau_2>\tau_2(C)$ in A–B–C cross–section. There are bifurcations of "smectic" solutions in the A, B, C points in Figures 1a and 1b.

The main result of the BSCSM analysis is elucidation of the topological structure of thermodynamic potential (the Morse types of its stability) in the solutions of the system (2), (3) in that parts of (τ_2, τ_1) plane which corresponding cross–section passes through. The further analysis is the same as previous one but it concerns other cross–sections (see Figure 2).

Examples of phase diagram topological types

The preceding information is enough for calculations of all the possible types of phase diagrams at various modal parameter values. In Figure 3 it is shown three examples of (τ_2, τ_1) phase diagrams versus the μ parameter. Characteristic features of phase diagrams consist in occurrence of: 1) the line of isostructural phase transitions terminated in the end critical point (CP); 2) two triple Sm_1–Sm_2–pN and Sm_1–N–pN points; 3) the first order Sm_1–pN and the second order Sm_2–pN phase transitions. As opposed to the case of strong orientational and translational coupling discussed earlier in Reference[3], the originality of the one under consideration is that tri–critical point (TCP) is observed on the Sm_1–N phase boundary in relatively strong fields only (Figure 3c) and it is absent in opposite case (Figure 3a). It is seen from Figure 3b that the intermediate situation occurs when the Sm_1–N TCP and the Sm_1–N–pN triple point (TP) coincide at some value of the field. Thus, the de Gennes model gives the solution of the problem of possibility of the occurrence of the Sm–N–IL TP and Sm–N TCP conjunction discussed experimentally in Reference[4]. From comparison of Figures 3a–c it follows that this effect can take place actually (with substitution of IL by pN phase) and the field is the factor regulating the position of TCP on phase boundary. The appearance of TCP in the field was predicted earlier theoretically[5] and was realized experimentally[6] as well. It is shown above not only that the field can induce the tricritical Sm–N behavior of a system but also why it takes place. The matter is that the point of tangency of the X_N'' and X_{Sm}

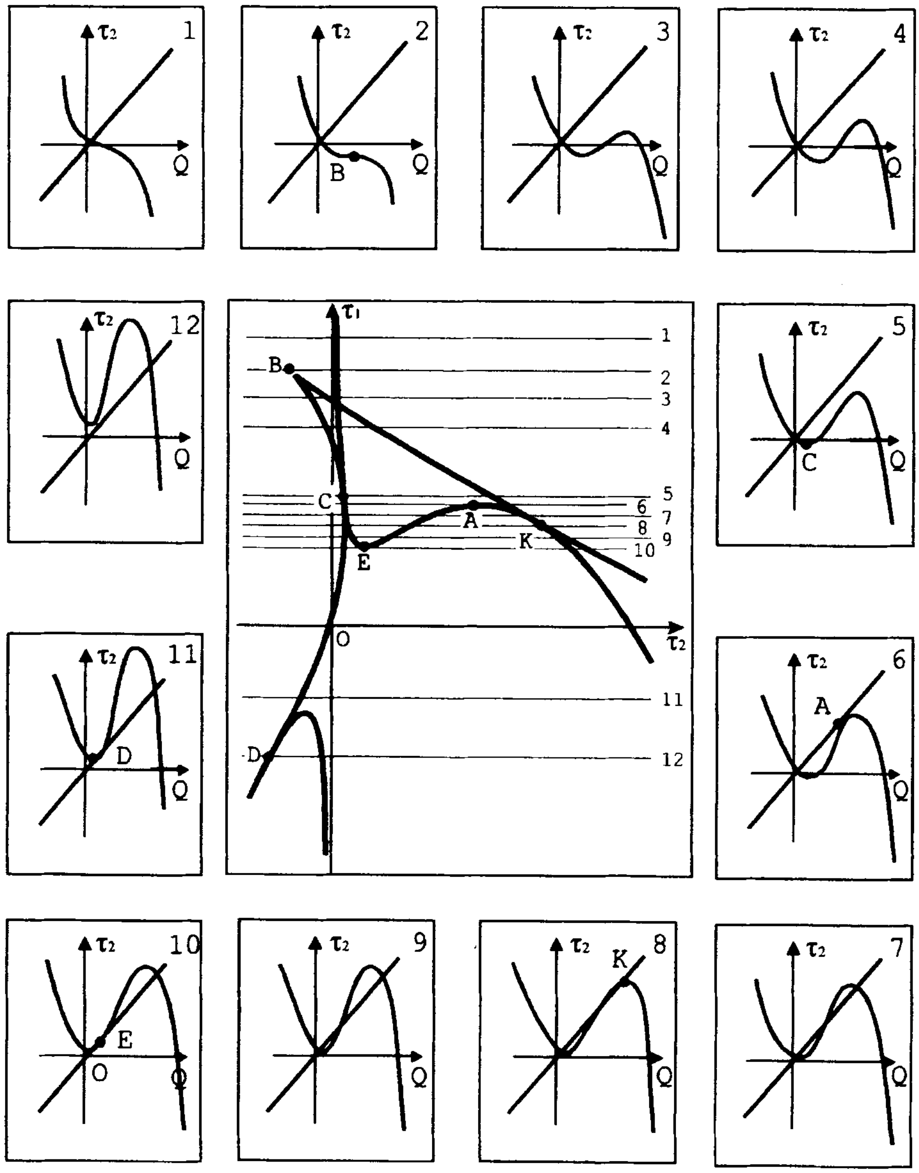

FIGURE 2 Stability analysis of smectic state by bifurcation set cross-section method.

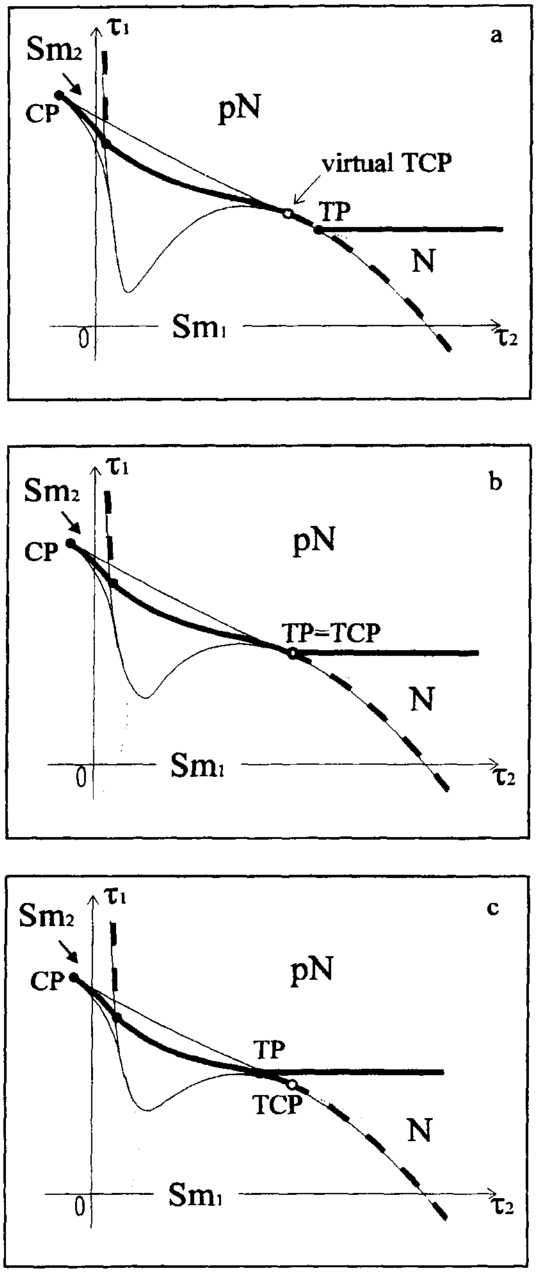

FIGURE 3 Topological types of phase diagrams of the de Gennes model for virtual (a) and actual (c) TCP and for the case of coincidence TP and TCP (b).

separatrices represents the virtual Sm–N TCP if the Sm–N–pN TP occurs below it (with respect to the τ_1 axis direction) on the X_N' separatrix (Figure 3a) and it is actual TCP otherwise (Figure 3c). The field turns the $X_N'' - X_{Sm}'$ point of tangency into genuine TCP as if it "pressurises" this point from the non–physics part of the separatrix in the Sm–N phase boundary.

CONCLUSION

The BSCSM as opposed to conventional calculation schemes is oriented to sophisticated topological treatment of thermodynamic potentials in corresponding control parameter spaces. We have discussed its application to the specific example of the de Gennes smectic A model. But it can be used in many others more complicated problems and allows to investigate all the possible types of model phase diagrams. In so doing, the most important result is that all the critical points of phase diagrams are at the same time peculiar points of corresponding bifurcation sets.

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