On thermodynamic stability of heteropolymer mesophases formed under weak segregation regime

S.I. Kuchanov[1,a], M.A. Livshits[2], and V.E. Pichugin[1]

[1] Physics Department, Lomonosov Moscow State University, Vorobjevi Gory, 119992 Moscow, Russia
[2] Engelhardt Institute of Molecular Biology, RAS, Vavilova str. 32, 119991, Moscow, Russia

Abstract. Conditions of local and global thermodynamic stability of spatially-periodic mesophases formed in an incompressible melt of binary monodisperse copolymers with molecules of arbitrary chemical structure are theoretically scrutinized. For the first time a bifurcation analysis of the Landau free energy in the first harmonic approximation is carried out. Based upon this analysis, feasible scenarios of bifurcation and phase transitions between mesophases of different morphology are discussed. The description of thermodynamic behavior of some systems is presented to exemplify the implementation of the approach proposed.

PACS. 02.30.Oz Bifurcation theory – 64.10.+h General theory of equations of state and phase equilibria – 82.35.Jk Copolymers, phase transitions, structure

1 Introduction

The distinctive feature of heteropolymer liquids is the formation in such systems of thermodynamically equilibrium superstructures with nanoscale spatially periodic distributions of densities of different type monomeric units. The most experimentally studied here are melts of monodisperse diblock and triblock copolymers showing the rich phase behavior [1–3]. The existence of the classical mesophases such as Lamellar, Hexagonal and Body-Centered Cubic (BCC) has been revealed for the first time by Leibler [4] who invoked the Landau theory of phase transitions to describe an incompressible melt of monodisperse binary diblock copolymer. The region of this mean-field theory applicability is confined to the vicinity of the critical point where the value of the order parameter is small enough. Under such a weak segregation limit (WSL) regime macromolecules demonstrate the Gaussian conformation, and the composition profile of ordered mesophases is approximately sinusoidal.

In the wake of Leibler's pioneer work [4] a considerable number of papers have been published in which the WSL theory has been used for the construction of phase diagram of a variety of block copolymers differing in architecture and composition (see, for instance, [1–3,5–8] and references therein). In the framework of this theory each boundary separating the regions of the existence of any two mesophases in the phase diagram is traditionally determined from the condition of the equality of their free energy values. However, such a procedure is evidently correct only provided the mesophases of interest are thermo-

dynamically stable with respect to any small fluctuations of the densities of monomeric units.

When constructing phase diagrams of a polymer liquid in the framework of the Landau theory of phase transitions, it is common practice to focus the attention on the analysis of the minimal stability of the superstructures, i.e. the stability with respect to the perturbations by the plane waves of *identical* small amplitude, directed along the wave vectors constituting the harmonic set of the superstructure of interest. In this paper we will formulate more strong necessary conditions of the mesophases' local stability by considering perturbing plane waves whose amplitudes may *be different* and the wave vectors be aligned along the edges of a regular tetrahedron. This choice of the orientation of the wave vectors of perturbations is due to the fact that in the first harmonic approximation the most frequently examined superstructures (such as Lamellar, Hexagonal and BCC) can be constructed just on this set of wave vectors.

Apart from revealing the conditions of the loss of local thermodynamic stability by some spatially-periodic mesophase, it is of considerable significance to elucidate to which of mesophases the unstable system goes. In this paper we will address the cases when the loss of the local stability by one of the mesophases in hand happens with respect to the perturbations with wave vectors aligned along the edges of Face-Centered Cubic (FCC) lattice which is reciprocal with respect to the BCC lattice.

For the thermodynamics of polymer liquids, as distinct from low-molecular weight ones, metastable states are of prime significance. The reason is an extremely large viscosity of such liquids conducive to the fact that the life

a e-mail: kuchanov@orc.ru

time of the metastable mesophases can become comparable with the performance time of polymer materials. As a consequence, the solution of several theoretical problems acquires primary actuality. Among them are revealing the complete set of local minima of the free energy, establishing the boundaries of their local stability as well as finding the heights of the energetic barriers separating these minima.

The solution of two first problems implies finding all extremals of the amplitude expansion of the Landau free energy and choosing among them those, in which all eigenvalues of the matrix of its second derivatives are positive. To solve the third problem such a linear analysis of the stability of extremals should be supplemented with an additional nonlinear bifurcation analysis. As a result, the height of potential barrier between two local minima, which is equal to the value of the function of the Landau free energy in the transition state separating these two minima, can be found. In the present paper we restricted this analysis in the framework of the WSL theory to the fourth order terms of the Landau free energy expansion.

Earlier, approaching problems of such a kind, Qi and Wang [9,10] made use of the kinetic treatment. Its key idea consists in the investigation of kinetic pathways along which a system starting from some non-equilibrium state evolves at fixed temperature to the equilibrium. The initial spatial distribution of the order parameter is believed to have the symmetry of a certain mesophase. The evolution of a system to the equilibrium is described by the authors in terms of the time-dependent Ginzburg-Landau (TDGL) theory. They examined kinetic pathways between LAM, HEX and BCC mesophases of a diblock copolymer melt regarding the order parameter to be conservable as well as neglecting the angular dependence of the vertex functions of the Landau free energy expansion. Upon numerical simulations of TDGL equations by the cell-dynamics method, the authors [9,10] came to the following conclusion. A transient state in the above-mentioned pathway is present in case of metastability of the initial mesophase and absent when this is absolutely unstable. Along with the direct solution of TDGL partial differential equation, Qi and Wang [10] wrote down and computed the set of ordinary differential equations for the amplitudes of the first harmonics of the order parameter. However, they assumed some of these amplitudes to be interdependent, that imposes certain restrictions on the choice of pathways leading to the equilibrium devaluating to some extent the results achieved.

This drawback was rectified by Ohta and co-workers [11–13]. They exploring the kinetics of structural transitions in diblock copolymers refined the approach proposed by Qi and Wang [9,10] by regarding the amplitudes of all harmonics to be independent. Moreover, they did not confine the consideration to the first-harmonic approximation [11] having added the equations for the amplitudes of the second harmonics [12,13]. It should be stressed, that to construct the phase diagram of an incompressible melt of diblock copolymers, the authors of paper [11] calculated the lines of the loss not only of

global stability but also of local stability of LAM, HEX and BCC mesophases. The addition of the equations for the amplitudes of the second harmonics [12,13] enabled the authors to extend their analysis by covering the gyroid mesophase as well. Besides, a considerable number of stationary points of the amplitude expansion of TDGL equations were found [13], among which are points corresponding to metastable and transient states.

In paper [14] the kinetic equations have been written down for the amplitudes of the first harmonics of the order parameter whose spatial distribution corresponds to the Face-Centered Cubic (FCC) mesophase. The authors have numerically found and tested for stability the stationary points of these equations assuming that only two of four amplitudes considered are independent. This analysis brought the authors to the conclusion about the instability of FCC mesophase.

In all papers [9–14] the angular dependence of the vertex functions of the Landau free energy expansion was taken to be absent. This assumption is a fair approximation under the consideration of the thermodynamic behavior of a diblock copolymer melt in the framework of the WSL theory [15]. However, under an analogous examination of block copolymers with more complicated architecture such a dependence was found [16,17] to be highly essential. Its proper account [16,17] results in the appearance in phase diagrams of regions where Simple Cubic (SC) and FCC mesophases are stable, whereas the disregard of the angular dependence of the vertex functions leads to the conclusion about the absence of such stability regions [14].

The kinetics of phase transitions in melts of block copolymers is not of our concern in the present paper. Mathematically speaking, our approach reduces to the analysis of extreme points of a certain polynomial which is a phenomenological expression for the amplitude expansion of the Landau free energy of this melt. The number of phenomenological parameters representing coefficients of this expansion is controlled by the appearance of the set of fundamental reciprocal lattice vectors of the mesophase in hand. In particular, in case under examination, when vectors of this set form the tetrahedron the number of these coefficients equals four, whereas for the octahedron it is three. Numerical values of these parameters are governed by the architecture of block copolymers' macromolecules and can be found from a microscopic theory. When the angular dependence of the vertex functions is absent all phenomenological parameters discussed above turn out to be identical. In the present paper these parameters are assumed to be positive values. Nevertheless, as it will be shown bellow, important analytic results can be obtained even under such an assumption. Our analytic approach supplements numerical consideration [9–14] of the phase behavior of block copolymers.

It's worth emphasizing that all problems posed in this paper can be basically formulated in terms of the equivariant bifurcation theory [18,19], extensively used under the description of spatial patterns in active media. Once achieved this, the above-mentioned problems can be

solved on the basis of the formalism of this theory using a rigorous mathematical algorithm. Particularly, such an algorithm has been minutely developed [19] when considering patterns, whose wave vectors are taken from the set of wave vectors forming a tetrahedron. However, practical implementation of this algorithm presents a real challenge for a physicist since it implies a good command of rather sophisticated mathematics such as the theory of polynomial equivariants.

The paper is organized as follows. At first, the problem is stated and the complete set of all extremals of the Landau free energy is found. The third section is devoted to the analysis of local stability of the extremals obtained. The fourth section addresses the states corresponding to the saddles of the hypersurface of the Landau free energy that characterize the probability of the transition from a metastable state to stable one. In the fifth section the analysis is undertaken of the global stability of extremals. Further the algorithm of finding feasible scenarios of temperature-induced transitions between all locally stable states in polymer liquids with given chemical structure of macromolecules is exemplified by a number of model systems. The Conclusion section is followed by three Appendices comprising some mathematical expressions necessary for the derivation of principal theoretical results presented in the main body of the paper.

2 Extremals of the Landau free energy

The Landau theory of phase transitions [20] is built upon the expansion of non-equilibrium free energy functional $\Delta F_L[\widetilde{\Psi}(\mathbf{q})]$ in a power series of order parameter $\Psi(\mathbf{r})$. Under thermodynamic description of polymer liquids, it is customary to write down this functional in momentum representation, omitting the terms whose order is higher than four [1–8]. The corresponding expression in the case of an incompressible melt of binary heteropolymer whose molecules consist of units of A and B type reads

$$\Delta F[\widetilde{\Psi}(\mathbf{q})] \equiv \frac{\Delta F_L[\widetilde{\Psi}(\mathbf{q})]}{TM}$$
$$= \sum_{l=2}^{4} \frac{1}{l!} \sum_{\{\mathbf{q}_i\}} \widetilde{\Gamma}^{(l)}(\mathbf{q}_1, ..., \mathbf{q}_l) \delta_k(\mathbf{q}_1 + ... + \mathbf{q}_l) \prod_{i=1}^{l} \widetilde{\Psi}(\mathbf{q}_i)$$
$$(1)$$

here T and M stand, respectively, for the absolute temperature expressed in energetic units and overall number of monomeric units in macromolecules. Function $\widetilde{\Psi}(\mathbf{q})$ is the Fourier transform of the order parameter

$$\Psi(\mathbf{r}) \equiv \Psi_A(\mathbf{r}) = -\Psi_B(\mathbf{r}), \quad \text{where} \quad \Psi_\alpha(\mathbf{r}) \equiv [\rho_\alpha(\mathbf{r}) - \bar{\rho}_\alpha]/M$$
$$(2)$$

proportional to the difference in density of type $\alpha =$ A, B units at point $\mathbf{r}$ and its average value $\bar{\rho}_\alpha$ throughout the system. In disordered phase $\Psi(\mathbf{r}) \equiv 0$, whereas the value of the order parameter periodically changes in space when $\Psi(\mathbf{r})$ describes some mesophase.

The presence of the Kronecker delta symbol δ_k in formula (1) means that the summation in each its term is over whole set of l wave vectors adding up to zero. Coefficients $\bar{\Gamma}^{(l)}(\mathbf{q}_1 + ... + \mathbf{q}_l)$ of expansion (1) referred to as "vertex functions" are governed by the chemical structure of macromolecules. Since a general algorithm of finding this dependence for any linear heteropolymers has been formulated [8,21], below we will take the vertex functions as known. Among them the second order one

$$\bar{\Gamma}^{(2)}(\mathbf{q}_1, \mathbf{q}_2) \delta_k(\mathbf{q}_1 + \mathbf{q}_2) \equiv \widetilde{\Gamma}_2(q) = H(q) - 2\chi,$$
$$\text{where} \quad q = |\mathbf{q}_1| = |\mathbf{q}_2| \quad (3)$$

holds a special position since unlike other vertex functions it is controlled along with the chemical structure of a heteropolymer also by temperature due to the dependence of the Flory parameter χ on T.

In the present paper we will concern ourselves with monodisperse heteropolymer comprised of identical macromolecules imposing no constraints on the pattern of arrangement of A and B monomeric units along copolymer chains. This, being responsible for the appearance of positive function $H(q)$, does not affect its asymptotic behavior at $q \to 0$ and $q \to \infty$ where function $H(q)$ diverges for the melt of any monodisperse heteropolymer. As a consequence this function is certain to have the minimum at some value $q = q^* > 0$.

The behavior of a heteropolymer liquid under temperature change is easy to follow for copolymers whose macromolecules are invariant with respect to the inversion of units A and B. The description of the thermodynamic behavior of such symmetric copolymers in terms of the Landau theory becomes substantially simplified because of vanishing of vertex function $\widetilde{\Gamma}^{(3)}$ at all values of its arguments. In this case the homogeneous state of a melt remains globally thermodynamically stable over whole temperature range as long as the Flory parameter χ remains less than its spinodal value $\chi_s = H(q^*)/2$. As temperature goes down, parameter χ rises to become at a certain moment larger than χ_s. At this moment unstable harmonics appear in the system the growth of the amplitude of which is saturated by terms in expansion (1) whose order is higher than the second one. Such a saturation results in the formation of a stable mesophase with spatially-periodic distribution of the densities $\rho_\alpha(\mathbf{r})$ of monomeric units.

In general case, when the symmetry of macromolecules with respect to the inversion of units A and B is absent, the phase behavior of a heteropolymer liquid qualitatively differs from that described in the foregoing. Since vertex function $\widetilde{\Gamma}^{(3)}$ for asymmetric copolymer is distinct from zero, the homogeneous state of a system looses global stability at value of parameter $\chi = \chi_b$ smaller than χ_s. Then, with lowering temperature, a system undergoes the first kind phase transition from local stable homogeneous state into mesophase with certain spatial symmetry. The latter is characterized by periodic function $\Psi(\mathbf{r})$ (2) which in the vicinity of the critical point can be approximated by a sum of n pairs of harmonics. Each kth of these pairs is
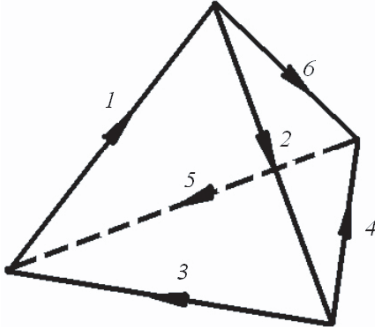
Fig. 1. The first harmonic set of wave vectors $\{\mathbf{q}_i\}$ $(i = 1, 2, \ldots, 6)$ of BCC mesophase. The figure at an edge of the tetrahedron denotes the number of corresponding wave vector.

specified by wave vectors $(\mathbf{q}_{k'} - \mathbf{q}_k)$ with length q^* as well as by amplitude a_k and phases $(\varphi_{k'} - \varphi_k)$ [22]

$$\Psi(\mathbf{r}) = \frac{2}{V} \sum_{k=1}^{n} a_k \cos(\mathbf{q}_k \mathbf{r} + \varphi_k), \qquad |\mathbf{q}_k| = q^* \qquad (4)$$

$$\widetilde{\Psi}(\mathbf{q}) = \sum_{k=1}^{n} a_k \left[e^{i\varphi_k} \delta(\mathbf{q} - \mathbf{q}_k) + e^{-i\varphi_k} \delta(\mathbf{q} + \mathbf{q}_k) \right]. \qquad (5)$$

For the sake of convenience of the notation of the subsequent formulas we omitted in these expressions factor $\sqrt{n}$, normally present in them.

In the present work we will be primarily concerned with the consideration of mesophases whose all wave vectors of the first harmonic sphere $\{\mathbf{q}_k\}$ can be aligned along the edges of the regular tetrahedron (see Fig. 1). Among such mesophases are Lamellar $(n = 1)$, Hexagonal $(n = 3)$, BCC $(n = 6)$ and some other. The sets of wave vectors of the first harmonic sphere of the first two mesophases are, evidently, subsets of the set of the third mesophase.

Substituting expression (5) into functional (1) yields the expression for the specific Landau free energy

$$F = \frac{\tau}{2} \sum_{i=1}^{6} a_i^2 - 2\alpha \left[a_1 a_2 a_3 \cos(123) + a_1 a_5 a_6 \cos(156) \right.$$

$$\left. + a_2 a_4 a_6 \cos(24\bar{6}) + a_3 a_4 a_5 \cos(3\bar{4}5) \right] + \frac{\gamma_0}{4} \sum_{i=1}^{6} a_i^4$$

$$+ \gamma_1 \left[a_1^2 \left(a_2^2 + a_3^2 + a_5^2 + a_6^2 \right) + a_2^2 \left(a_3^2 + a_4^2 + a_6^2 \right) \right.$$

$$\left. + a_3^2 \left(a_4^2 + a_5^2 \right) + a_4^2 \left(a_5^2 + a_6^2 \right) + a_5^2 a_6^2 \right]$$

$$+ \gamma_2 \left(a_1^2 a_4^2 + a_2^2 a_5^2 + a_3^2 a_6^2 \right) + 2\gamma_3 \left[a_1 a_3 a_4 a_6 \cos(13\bar{4}6) \right.$$

$$\left. + a_1 a_2 a_4 a_5 \cos(1245) + a_2 a_3 a_5 a_6 \cos(235\bar{6}) \right] \qquad (6)$$

considered as a function of amplitudes $\{a_k\}$ and phases $\{\varphi_k\}$ of six pairs of harmonics. Here every sequence of numbers representing arguments of cosine denotes the algebraic sum of phases of corresponding plane waves, whereas a bar over the number means that the corresponding phase enters into the sum with negative sign. So, $\cos(13\bar{4}6)$ is abridged notation of expression $\cos(\varphi_1 + \varphi_3 - \varphi_4 + \varphi_6)$.

Amplitude expansion of the free energy (6) is controlled by six dimensionless parameters τ, α и $\{\gamma_i\}(i = 0, 1, 2, 3)$, which are governed by the chemical structure of a copolymer macromolecule. These parameters are related in a simple manner to vertex functions $\widetilde{\Gamma}^{(l)}$ whose arguments are wave vectors $\{\mathbf{q}_k\}$ pertaining to the first harmonic sphere of BCC mesophase. The lengths of all these vectors adding up to zero are equal to q^*. This signals the existence of a single triple of such wave vectors aligned along the sides of an equilateral triangle as well as that of four different quadruples of the above-mentioned wave vectors. Their mutual orientation in the momentum space was proposed [4] to describe by a set of three angular variables h_1, h_2, h_3 whose sum is four. Recourse to the earlier formulated algorithm [21] permits finding function for $\Gamma(h_1, h_2, h_3)$ heteropolymer consisting of linear macromolecules of arbitrary chemical structure. The knowledge of this function, enables to calculate the values of parameters $\{\gamma_i\}$. Formulas for the calculation of these and the other two parameters, τ and α, look as follows

$$\tau = \widetilde{\Gamma}^{(2)}(\mathbf{q}_1, -\mathbf{q}_1) = 2(\chi_s - \chi)$$

$$\alpha = \widetilde{\Gamma}^{(3)}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3)$$

$$\gamma_0 = \widetilde{\Gamma}^{(4)}(\mathbf{q}_1, -\mathbf{q}_1, \mathbf{q}_1, -\mathbf{q}_1) = \Gamma(0, 0, 4)$$

$$\gamma_1 = \widetilde{\Gamma}^{(4)}(\mathbf{q}_1, -\mathbf{q}_1, \mathbf{q}_2, -\mathbf{q}_2) = \Gamma(0, 1, 3),$$

$$\gamma_2 = \widetilde{\Gamma}^{(4)}(\mathbf{q}_1, -\mathbf{q}_1, \mathbf{q}_4, -\mathbf{q}_4) = \Gamma(0, 2, 2)$$

$$\gamma_3 = \widetilde{\Gamma}^{(4)}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_4, \mathbf{q}_5) = \Gamma(1, 1, 2), \qquad (7)$$

where wave vector $\mathbf{q}_i$ is aligned along the ith edge of a tetrahedron depicted in Figure 1. Numerical factors entering in formula (6) in front of parameters α and $\{\gamma_i\}$ are, respectively, equal to $\kappa^{(3)}/3!$ and $\kappa_i^{(4)}/4!$ $(i = 0, 1, 2, 3)$ where $\kappa^{(3)}$ and $\kappa_i^{(4)}$ are combinatoric factors. They equal the number of the permutations of the arguments of vertex functions $\widetilde{\Gamma}^{(3)}$ and $\widetilde{\Gamma}^{(4)}$ retaining their values unaltered.

Below taking all coefficients $\{\gamma_i\}$ as being positive, we will not impose some additional constraints on their values. This is quite justified since no universal inequalities comprising these parameters are currently known in a microscopic theory.

Expression (6) may be given a simple geometric interpretation by turning to the tetrahedron in Figure 1. So, to each of four the third order terms a contour corresponds situated on one of this tetrahedron faces. Number of the amplitude in the product corresponds to that of wave vector in a contour. If a vector is aligned along the contour, the sign in front of the phase involved in the sum is positive, otherwise it is negative. An analogous rule is also valid for the fourth-order terms, each corresponding to particular contour of length four on the tetrahedron. Among such contours four their types $i = 0, 1, 2, 3$ should be distinguished. The zero-type contour represents the walk on a single tetrahedron edge passed twice in both directions. Each contour of type 1 and 2 is the walk on two edges, adjacent and non-adjacent, of a tetrahedron, respectively, passed once in both directions. At last, contours of type 3 are non-planar and are the walks aligned

Table 1. Complete set of all single-amplitude extremals of the Landau free energy.

N°	Extremal	Abbr.	$(a_1 a_2 \ldots a_6)$	Expression for amplitude A	Phases
0	Disorder	D	(000000)	$-$	$-$
1	Lamellar	L	$(A00000)$	$\sqrt{-\tau/4\beta_L},\quad 4\beta_L = \gamma_0$	$t_1 = 0,\quad t_2 = -t_3$
2	Rhombic	R	$(AA0000)$	$\sqrt{-\tau/2\beta_R},\quad 2\beta_R = \gamma_0 + 2\gamma_1$	$\cos t_{123} = 0$
3	Square	S	$(A00A00)$	$\sqrt{-\tau/2\beta_S},\quad 2\beta_S = \gamma_0 + 2\gamma_2$	$t_i = 0,\quad i = 1, 2, 3$
4	Hexagonal	H	$(AAA000)$	$3\left\|\alpha\left(1 \pm \sqrt{1 - \tau/\tau_H^*}\right)\right\|/4\beta_H,$ $\tau_H^* \equiv 3\alpha^2/4\beta_H,$ $4\beta_H \equiv 3\left(\gamma_0 + 4\gamma_1\right)$	$\cos t_{123} = 1$
5	Rhombo-hedric	Rh	$(000AAA)$	$\sqrt{-3\tau/4\beta_{Rh}},\quad \beta_{Rh} = \beta_H$	$t_i = \pi/2, i = 1, 2, 3$
6	Deformed FCC2	F2	$(AA0AA0)$	$\sqrt{-\tau/\beta_{F2}},$ $\beta_{F2} = \gamma_0 + 4\gamma_1 + 2\gamma_2 - 2\gamma_3$	$t_1 = t_3 = 0,$ $t_2 = \pi$
7	Deformed FCC3	F3	$(AA0AA0)$	$\sqrt{-\tau/\beta_{F3}},$ $\beta_{F3} = \gamma_0 + 4\gamma_1 + 2\gamma_2 + 2\gamma_3$	$t_1 = t_3 = \pi/2,$ $t_2 = -\pi/2$
8	BCC	B	$(AAAAAA)$	$3\left\|\alpha\left(1 \pm \sqrt{1 - \tau/\tau_B^*}\right)\right\|/\beta_B,$ $\tau_B^* \equiv 6\alpha^2/\beta_B,$ $2\beta_B \equiv 3\left(\gamma_0 + 8\gamma_1 + 2\gamma_2 + 4\gamma_3\right)$	$t_i = 0,\quad i = 1, 2, 3$
9	BCC2	B2	$(AAAAAA)$	$\sqrt{-3\tau/2\beta_{B2}},$ $2\beta_{B2} \equiv 3\left(\gamma_0 + 8\gamma_1 + 2\gamma_2 - 4\gamma_3\right)$	$t_i = \pi/2, i = 1, 2, 3$

along four mutually non-collinear edges of the tetrahedron.

As is evident from formula (6), phase factors are present only in terms describing contours of length three as well as those contours of length four whose type is 3. It is easy to show that all arguments of cosines can be expressed through linear combinations of three independent quantities

$$t_1 \equiv \varphi_1 + \varphi_5 + \varphi_6,$$
$$t_2 \equiv \varphi_2 + \varphi_4 - \varphi_6,$$
$$t_3 \equiv \varphi_3 - \varphi_4 - \varphi_5 \tag{8}$$

because the following relationships are the case

$$\cos(123) = \cos(t_1 + t_2 + t_3) \equiv \cos t_{123},$$
$$\cos(12\bar{4}5) = \cos(t_1 + t_2) \equiv \cos t_{12},$$
$$\cos(13\bar{4}6) = \cos(t_1 + t_3) \equiv \cos t_{13},$$
$$\cos(23\bar{5}\bar{6}) = \cos(t_2 + t_3) \equiv \cos t_{23}. \tag{9}$$

In order to get the full set of metastable states of the equilibrium system under examination, it is necessary to find all local minima of the Landau free energy (6). This implies finding the extremals of function (6) with respect to six amplitudes $a_1, ..., a_6$ and three phase variables t_1, t_2, t_3 as well as subsequent revealing among all such extremals those which are locally-stable. The system of nine equations for obtaining, finding the above-mentioned extremals is written down in Appendix A. Below we will exclusively deal with the extremals whose all non-vanishing amplitudes $\{a_k\}$ are identical. The complete set of such single-amplitude extremals is presented in Table 1. Extremals differing in configuration $(a_1 a_2 ... a_6)$ have been ascribed the names according to their spatial symmetry in such a manner as to ensure the coincidence of these names with those earlier used for corresponding mesophases.

Inspection of Table 1 invites some additional comments of general character. The region of the existence of every extremal represents a half-line bounded on the right by point $\tau = \tau^*$. For all extremals tabulated here, but for 4 and 8, value $\tau^* = 0$. At this point high codimension bifurcation happens resulting in the appearance of seven pairs of new extremals. Amplitudes of every such a pair of extremals are the same, whereas all phase variables (8) differ by π. At points $\tau_H^* > 0$ and $\tau_B^* > 0$ "rigid" secondary bifurcation occurs leading to the emergence of two branches of extremals. One of them (to which minus sign in front of the radical in formula for the amplitude in Tab. 1 corresponds) is necessarily unstable.

To our knowledge, in all theoretical works where the thermodynamic behavior of heteropolymer melts of particular structures was considered in the framework of WSL, inequality $\tau_H^* < \tau_B^*$ holds. However, as it follows from Table 1, a reverse inequality will be true, provided $4\beta_H < \beta_B$. Hence, temperature decrease can lead to the situation when the hexagonal extremal appears before the BCC one.

Naturally, all extremals presented in Table 1 can be obtained in a trivial way, i.e., by minimization of the Landau free energy written down in a traditional manner

$$F = (n\tau/2)A^2 - \alpha_n A^3 + \beta_n A^4, \tag{10}$$

where the values of coefficients α_n, β_n differ for distinct mesophases. Some of them (up to the factor $1/\sqrt{n^3}$ for α_n and $1/n^2$ for β_n) have been reported earlier. Mesophases corresponding to Lamellar, Rhombic, Square, Hexagonal, Rhombohedric and BCC extremals have been theoretically studied by Leibler [4]. Later BCC2 mesophase has been also considered [22]. However, as far as we are concerned, Deformed FCC2 and Deformed FCC3 extremals included in Table 1 have not been addressed so far. Showing the same configuration $(AA0AA0)$, they yet differ in values of phase variables (8). Assigning the above-mentioned names to these mesophases, we proceeded from the fact that the nonplanar contour which comprises

four wave vectors $\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_4, \mathbf{q}_5$ on the tetrahedron edges (Fig. 1) corresponding to non-zero amplitudes in the mentioned configuration, can be obtained by corresponding deformation of the contour built up of four non-collinear vectors of the first harmonic set of FCC mesophase.

Expression (10) is derived immediately from expression (6), provided values of all non-vanishing amplitudes in the latter are put identical and equal to A. Essentially, dealing with expression (10), the only question possible to answer concerns exclusively the *trivial* local stability of extremals with respect to the variations of only one variable which is amplitude A. As for the *non-trivial* local stability with respect to arbitrary variations of six amplitudes and three phase variables, this issue under such a consideration remains open. To investigate this *non-trivial* stability, one should find regions of positive definiteness of the ninth order Hess matrix of the Landau free energy (6) on extremals from Table 1. This problem is equivalent to that of finding the region where all nine its eigenvalues are positive.

3 Analysis of the local stability

Expressions for the Hess matrix of function (4) and its eigenvalues $\{\lambda_i\}$ are given in Appendix B for each extremal presented in Table 1. Essentially, the Hess matrix $\mathbf{H}$ on every extremal under examination is block diagonal

$$\mathbf{H} = \begin{pmatrix} \mathbf{H}^a & 0 \\ 0 & \mathbf{H}^t \end{pmatrix}, \quad \begin{array}{l} \mathbf{H}^a_{ij} \equiv \partial^2 F/\partial a_i \partial a_j \quad (i,j=1,...,6) \\ \mathbf{H}^t_{ij} \equiv \partial^2 F/\partial t_i \partial t_j \quad (i,j=1,2,3) \end{array}, \tag{10}$$

where $\mathbf{H}^t$ is null matrix on all extremals shown in Table 1 with the exception of B and B2 extremals.

Noteworthy, two extremals from those demonstrated it Table 1, R and F3, do not correspond to the local minima of the free energy at any values of parameters $\{\gamma_i\}$. This is because the spectrum of matrix $\mathbf{H}$ (10) necessarily comprises on these extremals a pair of eigenvalues differing by sign. The first of the above-mentioned extremals is trivially stable, that enabled Leibler [4] to consider it as corresponding to the metastable state.

All eigenvalues of the Hess matrix (10) can be divided into two groups. The first group incorporates eigenvalues for which the conditions of the alteration of their sign do not depend on being exclusively controlled by the relationships between parameters $\{\gamma_i\}$. All the other eigenvalues $\{\lambda_i\}$ belong to the second group.

Full set of signs of all eigenvalues pertaining to the first group prescribes qualitative appearance of the bifurcation diagram, whereas bifurcation values of parameter τ are obtained from the analysis of the second group eigenvalues. As it follows from formulas presented in Appendix B, the condition of the sign alteration by the first group eigenvalues coincides with the condition of vanishing of the certain linear combination of four parameters $\{\gamma_i\}$. Therefore, the set of signs of all these $\{\lambda_i\}$ is actually governed by values of only three parameters. As such parameters the following $b_i \equiv \gamma_i/\gamma_0 \ (i=1,2,3)$ may be chosen. They may be envisaged as components of vector b in the three-dimensional

parametric space. This space can be separated into regions in each of which the appearance of bifurcation diagram is identical. Surfaces separating these regions are governed by the condition of vanishing of some of the eigenvalues belonging to the first group. In the case under examination the number of such surfaces is too large for corresponding partitioning of the three-dimensional parametric space to be presented graphically. However, bellow an algorithm will be formulated which enables the construction of the phase diagram for every particular point b of this space.

Inspecting formulas of Appendix B it is easy to notice that the bifurcation values of parameter τ are proportional to the square of parameter α where proportionality coefficient $k(b) \equiv \tau/\alpha^2$ depends on point b of the parametric space. Interestingly, the above-mentioned dependence of this coefficient on α takes place even for extremals 1, 3, 5, 6, 9 in Table 1 for which the expression of the Landau free energy (6) is independent of parameter α. This is because of the effect of this parameter on the intensity of the perturbations whose wave vectors together with those of the first harmonic sets of the above-mentioned extremals form contours of length three. Just such perturbations are responsible for the stability loss with respect to H or B mesophases by the mesophases which these extremals correspond to.
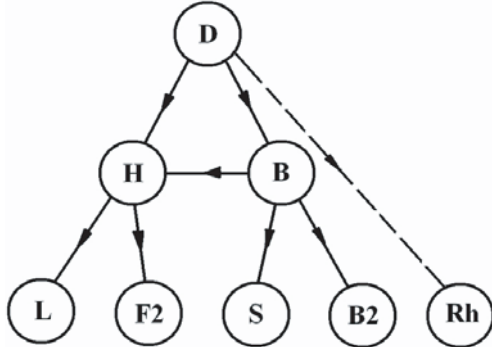
Of particular importance is the specific feature of the phase behavior of a heteropolymer liquid which our treatment enabled to reveal. So, under the traditional approach the secondary bifurcation corresponding to the formation of either H or B mesophase necessarily results in the appearance of one stable and one unstable branches. In the framework of the analysis of the trivial stability, such a situation is the only feasible for the above-mentioned secondary bifurcation. However, the consideration of the non-trivial stability casts doubt on this conclusion. For example, when $\tau_H^* < \tau_B^*$, the secondary bifurcation at point $\tau = \tau_H^*$ leads to the appearance of a pair of unstable branches of H-extremal. On the first of them there is one negative eigenvalue, while on the second branch their number is two. As for the secondary bifurcation at point $\tau = \tau_B^*$, here the numbers of negative eigenvalues on the first and the second branches of B-extremal are equal to zero and unity, respectively. For heteropolymer liquids in which reverse inequality $\tau_H^* > \tau_B^*$ holds the above reasoning remains in force, provided B- and H-extremals are transposed.

In regard to the extremals 1, 3, 5, 6, 9 in Table 1, which emerge as a result of the primary bifurcation at point $\tau = 0$, their amplitudes are described on the bifurcation diagram by trivial formula $A = \kappa\sqrt{-\tau}$ where the dependence of coefficient κ on parameters $\{\gamma_i\}$ can be found in Table 1. It is readily shown that among these five extremals from two to four ones certainly are saddle extremals at all negative values of parameter $\tau < 0$. Given relationships between parameters $\{\gamma_i\}$, it is easy using Table 2 to determine the extremals which necessarily will be saddles.

It is clear from this table that in order to perform an analysis of the global stability of a particular polymer

Table 2. Extremals from those 1, 3, 5, 6, 9 in Table 1 which are certain to be saddles.

$\gamma_0 - 2\gamma_2 > 0$		$\gamma_0 + 2\gamma_2 + 2\gamma_3 > 4\gamma_1$	L, S, Rh
		$\gamma_0 + 2\gamma_2 + 2\gamma_3 < 4\gamma_1$	L, Rh, F2, B2
$\gamma_0 - 2\gamma_2 < 0$	$\gamma_0 - 2\gamma_1 > 0$	$2\gamma_2 - \gamma_0 > 4\gamma_4$	L, S, F2, B2
		$2\gamma_2 - \gamma_0 < 4\gamma_4$	L, S, Rh
	$\gamma_0 - 2\gamma_1 < 0$	$2\gamma_2 - \gamma_0 > 4\gamma_4$	S, Rh, B2
		$2\gamma_2 - \gamma_0 < 4\gamma_4$	S, Rh

Fig. 2. Orgraph of the extremals presented in Table 1.

system with fixed set of values of parameters $\{\gamma_i\}$, indispensable for the construction of its complete phase diagram, it will suffice to consider apart from H- and B-extremals not more than three locally stable extremals.

At every fixed value of parameter τ there is a specific set i of local minima of the free energy characterized by their number and types. As τ changes this set transforms at point $\tau = \tau_{ij}$ to other set j. Particular sequence of such bifurcation points τ_{ij} and sets a system goes through during the evolution of parameter τ will be referred to as *bifurcation scenario*. A challenging theoretical problem is to elucidate how the bifurcation scenario of a heteropolymer liquid depends on the chemical structure of its macromolecules.

This scenario may be conveniently interpreted in terms of re-coloring of the vertices of some orgraph depicted in Figure 2. To each vertex of this orgraph an extremal corresponds among those presented in Table 1, except for 2 and 7. This couple of extremals is ruled out from further consideration, since they are saddles of the hypersurface of the Landau free energy (6) at all values of parameters $\{\gamma_i\}$. The admissible directions of the instability growth which arises as bifurcation parameter τ decreases are associated with arcs of the orgraph shown in Figure 2 [23]. We will put its particular set of vertices colored black in correspondence to the appropriate set i of local minima of the Landau free energy. Hence, a bifurcation scenario is unambiguously characterized at each given set of parameters $\{\gamma_i\}$ both by the succession of colorings of an orgraph vertices and by bifurcation values of coefficients $k_{ij} \equiv \tau_{ij}/\alpha^2$.

4 Transient states

It is clear that the path linking some minimum on the hypersurface of the Landau free energy with a neighboring

minimum is certain to necessarily go through a saddle point on this hypersurface. The extremal corresponding to this point bellow will be referred to as the transient state. A knowledge of the value of the free energy at this saddle point is critically important for estimating the lifetime of the metastable state corresponding to the neighboring minimum where the value of the free energy is larger.

Table 3 provides exact analytical expressions we managed to derive for the extremals of function (6) that correspond to the transient states between all locally stable extremals among those presented in Table 1 [24]. Deriving these expressions, we proceeded from the following considerations. In the simplest case the stability loss happens as the result of vanishing of eigenvalue λ_i (whose multiplicity is one) of the Hess matrix (10) which eigenvector $x^{(i)}$ corresponds to. This vector indicates the direction of the instability growth in the nine-dimensional space of amplitudes and phase variables. The collinearity of a pair of some eigenvectors of the Hess matrix on different extremals is the necessary condition for the possibility of the transition between mesophases associated with these extremals. If at the point of the stability loss the eigenvalue with multiplicity $r > 1$ turns into zero, the null-space of the eigenvectors will have dimensionality $r > 1$ which coincides with the number of linearly independent eigenvectors corresponding to this eigenvalue. Any direction in this null-space is "dangerous" from the point of view of the instability development. Knowing coinciding eigenvector of the instability of two mesophases, one can make a conjecture about possible configuration of the transient state dividing them.

However, more intricate situations exist when some mesophases are characterized by an instability vector to which a collinear one is impossible to choose up from the set of instability vectors of all the other mesophases given in Table 1. Such a situation takes place for H- mesophase when eigenvalue $\lambda_{4,5}$ vanishes (see Appendix B). In this case the configuration $(AABCC0)$ of the transient state from H- into F2-mesophase was found to be specified by three, A, B and C, independent values of the amplitude. Therefore, the transient state represents a superposition of five pairs of plane waves. The first four of them (two with amplitude A, one with amplitude B and one with amplitude C) have zero values of the phase variables. The remaining pair of plane waves has amplitude C and values of phase variables π. Dependencies of amplitudes A, B and C on τ exhibit the following peculiarities. Firstly, at $\tau = \tau_{HF2}$ equalities $A = B = A_H$, $C = 0$ are true, while at $\tau = \tau_{F2H}$ we have $B = 0$, $A = C = A_{F2}$. Here A_H, A_{F2} stand for the values of the amplitudes of plane waves on H-extremal at point $\tau = \tau_{HF2}$ and on F2-extremal at point $\tau = \tau_{F2H}$, respectively. Secondly, in the vicinity of point $\tau = \tau_{HF2}$ amplitudes A and B decrease linearly $(A_H - A) \sim (\tau - \tau_{HF2})$ and $(A_H - B) \sim (\tau - \tau_{HF2})$, respectively, whereas the amplitude C grows as $C \sim \sqrt{\tau - \tau_{HF2}}$. An analogue of these relationships in the neighborhood of point $\tau = \tau_{F2H}$ are $(A_{F2} - A) \sim (\tau_{F2H} - \tau)$, $(A_{F2} - C) \sim (\tau_{F2H} - \tau)$ and $B \sim \sqrt{\tau_{F2H} - \tau}$. Inspection of Table 3 discloses that in

Table 3. Characterization of the transitions between mesophases caused by the loss of their local stability.

Type I-J	Expression for $k_{IJ} \equiv \tau_{IJ}/\alpha^2$	Instability eigenvector	Trans. state configuration	Expression for amplitudes
D-B	$k_{DB} = 0,$ $k_{BD} = \frac{6}{\beta_B},$	(1 1 1 1 1 1) ($\bar1\,\bar1\,\bar1\,\bar1\,\bar1\,\bar1$)	$(BBBBBB)$	$B = \frac{3\left|\alpha\left(1-\sqrt{1-\tau/\tau_B^*}\right)\right|}{\beta_B}$
D-H	$k_{DH} = 0,$ $k_{HD} = \frac{3}{4\beta_H},$	(1 1 1 0 0 0) ($\bar1\,\bar1\,\bar1\,0\,0\,0$)	$(BBB000)$	$B = \frac{3\left|\alpha\left(1-\sqrt{1-\tau/\tau_H^*}\right)\right|}{4\beta_H}$
B-H	$k_{BH} = -\frac{4(8\beta_H-\beta_B)}{(\beta_B-4\beta_H)^2},$ $k_{HB} = -\frac{4(6\beta_H-\beta_B)}{(\beta_B-4\beta_H)^2},$ $(8\beta_H > \beta_B > 4\beta_H)$	$(0\,0\,0\,\bar1\,\bar1\,\bar1)$ $(0\,0\,0\,1\,1\,1)$	$(AAABBB)$	$A = \frac{3|\alpha|}{\beta_B-4\beta_H}$ $B = \sqrt{\frac{3(\tau-\tau_{HB})}{2\beta_B}}$
H-L	$k_{HL} = -\frac{8(\gamma_0+\gamma_1)}{(2\gamma_1-\gamma_0)^2},$ $k_{LH} = -\frac{4\gamma_0}{(2\gamma_1-\gamma_0)^2},$ $(2\gamma_1 - \gamma_0 > 0)$	$(0\,\bar1\,\bar1\,0\,0\,0)$ $(0\,1\,1\,0\,0\,0)$	$(ABB000)$	$A = \frac{2|\alpha|\gamma_0}{(2\gamma_1-\gamma_0)^2}$ $B = \sqrt{\frac{\tau_{LH}-\tau}{\gamma_0+2\gamma_1}}$
H-F2	$k_{HF2} = -\frac{8(\beta_{F2}+4\gamma_1)}{(\beta')^2},$ $k_{F2H} = -\frac{8\beta_{F2}}{(8\gamma_1-\beta_{F2})\beta'},$ $\beta' \equiv \gamma_0 - 2(\gamma_2+\gamma_3),$ $(\beta' > 0)$	$(0\,0\,0\,1\,\bar1\,0)$ $(0\,0\,1\,0\,0\,0)$	$(AABCC0)$	$A^2 = g(\tau) + h(\tau),\ C^2 = g(\tau) - h(\tau)$ $g(\tau) \equiv -\frac{\tau+2\gamma_1 B^2}{\beta_{F2}},\ h(\tau) \equiv \frac{2|\alpha|B}{\beta'}$ $B = \sqrt{\frac{(\tau_{F2H}-\tau)(8\gamma_1-\beta_{F2})}{(16\gamma_1^2-\gamma_0\beta_{F2})}}$
B-S	$k_{BS} = -\frac{24(\gamma_0+2\gamma_1+2\gamma_2+\gamma_3)}{(4\gamma_1-\gamma_0-2\gamma_2+2\gamma_3)^2},$ $k_{SB} = -\frac{16(\gamma_0+2\gamma_2)}{(4\gamma_1-\gamma_0-2\gamma_2+2\gamma_3)^2},$ $(4\gamma_1 - \gamma_0 - 2\gamma_2 - 2\gamma_3 > 0)$	$(0\,\bar1\,\bar1\,0\,\bar1\,\bar1)$ $(0\,1\,1\,0\,1\,1)$	$(ABBABB)$	$A = \frac{4|\alpha|}{4\gamma_1-\gamma_0-2\gamma_2+2\gamma_3}$ $B = \sqrt{\frac{\tau-\tau_{SB}}{\gamma_0+4\gamma_1+2\gamma_2+2\gamma_3}}$
B-B2	$k_{BB2} = -\frac{\gamma_0+8\gamma_1+2\gamma_2}{\gamma_3^2},$ $k_{B2B} = 0,$			

the vicinity of bifurcation points τ_{HF2} and τ_{F2H} the evolution of the transient state H-F2 considered in the first order in small parameter ε (proportional to the square root of the deviation of parameter τ from its bifurcation value) occurs along the direction specified by the instability vector. To provide an adequate description of the transition into final state whose instability vector is noncollinear to the analogous vector of the initial state, when performing a bifurcation analysis in the neighborhood of point $\varepsilon = 0$, one should, generally speaking, take into account the terms next to the principal term of the power expansion in this small parameter. However, for the transition between H- and F2-mesophase in hand there is no need for such an account, because we managed to derive exact analytical expressions for the dependencies of amplitudes A, B and C on parameter τ which are valid at arbitrary ε.

With formulas presented in Tables 1 and 3, it is easy to find the height of potential barrier ΔF^* that is equal to the difference of the free energy values in transient state and in higher minimum. Essentially, the lifetime of the metastable state corresponding to such a minimum depends exponentially on value ΔF^*.

5 Global stability

Since at fixed value of parameter τ several local minima of the Landau free energy often exist, the problem is normally encountered how to select the deepest (i.e., global) among them. The solution of this problem is of utmost

importance because just to this minimum the thermodynamically stable mesophase corresponds. The values of the free energy in mesophases L, S, Rh, F2 and B2 are determined according to formula (6) and Table 1 by expression

$$F_J = -\nu_J\tau^2/4\beta_J \qquad (J = \text{L}, \text{S}, \text{Rh}, \text{F2}, \text{B2}) \qquad (11)$$

here ν_J represents the number of non-vanishing amplitudes in configuration $(a_1 a_2 \dots a_6)$ of mesophase J. The values of the free energy in mesophases H and B can be calculated from formula

$$F_J = \frac{\nu_J(\tau_J^*)^2}{12\beta_J}G(y_J), \quad y_J = \tau/\tau_J^* \quad (J = \text{H}, \text{B}) \qquad (12)$$

where function $G(y)$ is defined by the following expression

$$G(y) \equiv 8(y-1)\left(1+\sqrt{1-y}\right) + (4-3y)y. \qquad (13)$$

Noteworthy, the thermodynamic transitions between all mesophases are the first order. Such a transition from mesophase I into mesophase J occurs at $\tau = \tau_{IJ}^+$ when the values of free energies of both mesophases become equal. The transition from disordered state to some of mesophases is, generally speaking, the first order as well. A special case is a heteropolymer liquid whose molecules are invariant with respect to the inversion of A and B units. In melt of such a symmetric heteropolymer the above-discussed transition being the second order happens always on spinodal $\tau = 0$.

Unlike the bifurcation scenario considered in the previous section, the scenario characterizing the sequence of

phase transitions induced by the temperature change is described by a particular succession of thermodynamically stable mesophases and values of coefficient $k_{IJ}^{+} \equiv \tau_{IJ}^{+}/\alpha^2$ at which phase transitions between them take place. To every such a scenario the specific walk corresponds on the orgraph depicted in Figure 2. As our analysis revealed, on the orgraph there is the only vertex, corresponding to extremal F2, into which none of these walks can enter. Therefore, never can the region of existence of mesophase F2 appear in the phase diagram. Its construction in the case under examination consists in indicating the points on straight line τ where phase transitions happen between globally stable states.

As already emphasized in the preceding section, the lifetime of metastable state I in the vicinity of the point of phase transition $\tau = \tau_{IJ}^{+}$ depends exponentially on the difference ΔF_L^* of free energy values in transient state IJ and the state I. This difference is, obviously, proportional to the number of monomeric units in the critical nucleus. The proportionality coefficient in this dependence equals $\Delta F_{IJ} \equiv F_{IJ} - F_I$ where values of F_I are defined by formulas (11), (12), whereas F_{IJ} is the value of the specific free energy in the transient state IJ obtainable from formula (6) and Table 3. Since the probability for a system to be found in metastable state exponentially decreases as it moves away from point $\tau = \tau_{IJ}^{+}$, in order to estimate the lifetime of such a state it is enough to determine value of ΔF_{IJ} only at point $\tau = \tau_{IJ}^{+}$ where, by definition, $F_J = F_I$.

In the system in hand all possible phase transitions, in accordance with the appearance of the orgraph pictured in Figure 2, are divided into three types, each being described by the individual equation for finding the locus of the transition point. To the first type D $\rightarrow$ B and D $\rightarrow$ H transitions belong, to the second one B $\rightarrow$ H transition does, while all the remaining possible transitions are ascribed to type three.

Equation which permits calculating the point $\tau = \tau_{DJ}^{+}$ of the first type equilibrium transition reads

$$G(y) = 0, \quad \text{where } y = \tau_{DJ}^{+}/\tau_J^*, \qquad (14)$$

here $G(y)$ is defined by formula (13), whereas $J = $ H and $J = $ B in the case of D $\rightarrow$ B and D $\rightarrow$ H transitions, respectively. It can be readily shown that this equation has unique solution $y = 8/9$. This means that as parameter τ decreases, the homogeneous state looses its global stability at value $y = 8/9$ on the binodal where the first order phase transition occurs either into H ($\tau_H^* > \tau_B^*$), or into B ($\tau_H^* < \tau_B^*$) mesophase.

The only representative of the second type phase transitions is B $\rightarrow$ H one which proceeds at point $\tau = \tau_{BH}^{+}$ whose value is found from the solution $y(x)$ of the following equation

$$2G(y) = x^3 G(y/x), \quad \text{where } y \equiv \tau_{BH}^{+}/\tau_H^*, \ x \equiv 4\beta_H/\beta_B. \qquad (15)$$

Such a solution exists only in the interval $1 \leqslant x < 2$. It decreases monotonically with the growth of x from $y(1) \cong 0.80$ to $-\infty$ at $x \rightarrow 2$ vanishing at $x \cong 1.25$ (see Fig. 3a). Physical interpretation of these results is
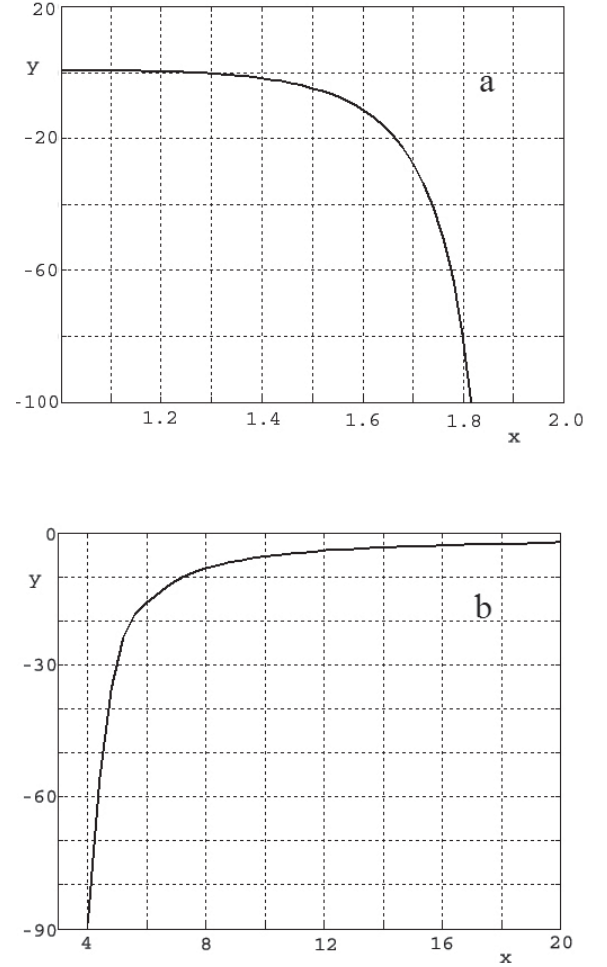

Fig. 3. Curves a and b representing solutions $y(x)$ of equations (15) and (16), respectively.

fairly transparent. So, within the region $x < 1$ D $\rightarrow$ H transition necessarily happens, upon which the H $\rightarrow$ B transition, as shown in Figure 2, is impossible any longer. At $x > 1$ as τ increases D $\rightarrow$ B transition takes place first of all. Then B $\rightarrow$ H transition either occurs, provided condition $1 \leqslant x < 2$ (i.e., $\gamma_0 < 2\gamma_2 + 4\gamma_3 < 3\gamma_0 + 8\gamma_1$) holds, or does not occur, if $x > 2$. Interestingly, the last phase transition may happen both before the spinodal $\tau = 0$ ($1 \leqslant x < 1.25$) and after it ($1.25 < x < 2$).

To the third type H $\rightarrow$ L, B $\rightarrow$ S and B $\rightarrow$ B2 phase transitions belong. The value of parameter $\tau = \tau_{JK}^{+}$ at point of each of these $J \rightarrow K$ transitions can be calculated from the solution of equation

$$G(y') = -zy'^2, \quad \text{where } y' \equiv \tau_{JK}^{+}/\tau_J^* \qquad (16)$$

at value $z = z_{JK} \equiv 3(\nu_K \beta_J/\nu_J \beta_K)$. In the last of expressions (16) index $J = $ H, B, while index $K = $ L, S, B2. It is easy to show that only negative solutions $y'(z)$ have a physical meaning, because any mesophase K exists exclusively at $\tau < 0$. Such a negative solution $y'(z)$ exists only in the region $z > 3$ being there unique. In this region it grows monotonically from $-\infty$ at $z = 3$, approaching zero at $z \rightarrow \infty$ (see Fig. 3b). In order for the solution

of equation (16) to correspond to the value of the phase transition point $\tau = \tau_{JK}^+$, the extremal K has to be locally stable at this point. For the above three transitions belonging to the third type this necessary condition turns out to be sufficient as well. To make sure that this is so, let us examine individually each of these transitions.

Evidently, the fulfillment of inequality $z_{HL} > 3$ ($\gamma_0 - 2\gamma_1 < 0$) is the necessary condition of the existence of H → L transition, inasmuch as equation (16) has physically meaningful solution only within the region $z > 3$. On the other hand, this condition is sufficient as well, because at point $\tau = \tau_{HL}^+$ the fulfillment of inequality $z_{HL} > 3$ coincides, as it is clear from Table 2, with the condition of the local stability of extremal L. The above reasoning concerning H → L transition can be fully extended to B → S transition, the condition of the existence of which will be the fulfillment of inequality $z_{BS} > 3$ ($\gamma_0 - 4\gamma_1 + 2\gamma_2 + 2\gamma_3 < 0$). As for B → B2 transition, it conceptually differs from both transitions considered in the foregoing. The fact is that inequality $z_{BB2} > 3$ indispensable for the existence of this transition is true at any set of parameters $\{\gamma_j\}$. However, this condition will be sufficient one only in the case of the fulfillment of inequality $\gamma_0 - 4\gamma_1 + 2\gamma_2 + 2\gamma_3 > 0$. Which, according to Table 2, specifies the region of the local stability of the B2-extremal. If reverse inequality (equivalent to inequality $z_{BS} > 3$) holds, B → B2 transition does not happen. However, in this case B → S phase transition is realized, since just inequality $z_{BS} > 3$ specifies the region of the extremal S local stability.

Using the above-achieved results and Figure 2, it is possible to prove that in the framework of the treatment employed in the present paper only six scenarios of phase transitions are possible:

1. D → H: $x < 1$, $z_{HL} < 3$.
2. D → H → L: $x < 1$, $z_{HL} > 3$.
3. D → B → H: $1 < x < 2$, $xy(x) > y'(z_{BS})$, $z_{BS} > 3$, $z_{HL} < 3$,
   or $1 < x < 2$, $xy(x) > y'(z_{BB2})$, $z_{BS} < 3$, $z_{HL} < 3$.
4. D → B → H → L: $1 < x < 2$, $xy(x) > y'(z_{BS})$, $z_{BS} > 3$, $z_{HL} > 3$,
   or $1 < x < 2$, $xy(x) > y'(z_{BB2})$, $z_{BS} < 3$, $z_{HL} > 3$.
5. D → B → S: $1 < x < 2$, $xy(x) < y'(z_{BS})$, $z_{BS} > 3$,
   or $x > 2$, $z_{BS} > 3$.
6. D → B → B2: $1 < x < 2$, $xy(x) < y'(z_{BS})$, $z_{BS} < 3$,
   or $x > 2$, $z_{BS} < 3$.

Here $y(x)$ and $y'(z_{JK})$ are solutions of equations (15) and (16), respectively.

6 Examples of scenarios of bifurcation and phase transitions

In theoretical papers devoted to the investigation of microphase separation in an incompressible melt of binary monodisperse heteropolymers, the only scenario of phase transitions, D → B → H → L, is normally found in the framework of the first harmonic approximation of WSL
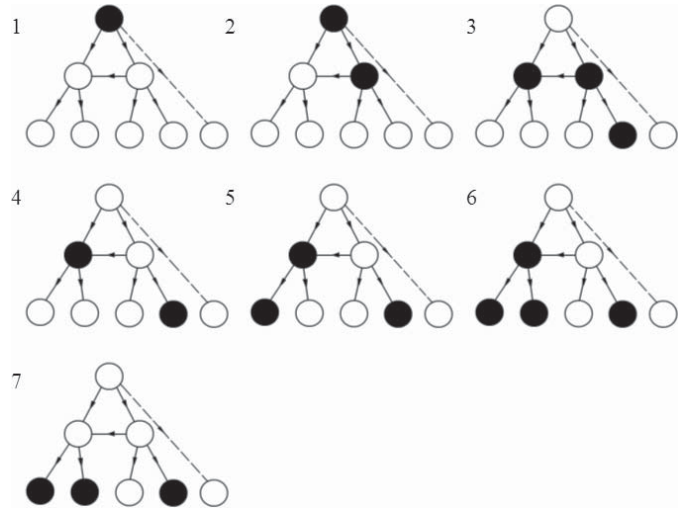

Fig. 4. Succession of the colorings of the orgraph depicted in Figure 2 which characterizes the bifurcation scenario inherent to a system with the set of parameters I (17).
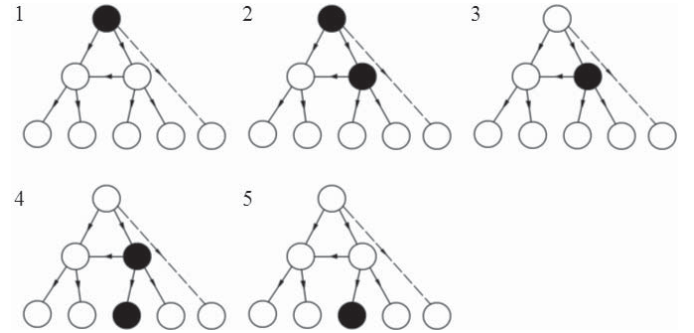

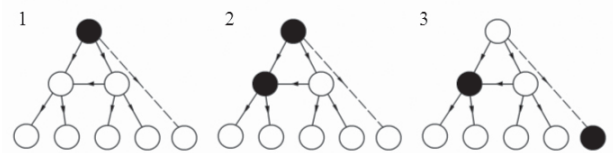**Fig. 5.** The same as in Figure 4 but with the set of parameters II (17).

Fig. 6. The same as in Figure 4 but with the set of parameters III (17).

approach. However, even in this approximation other scenarios are conceivable whose examples are provided below.

The application of our original approach is exemplified by consideration of three model system characterized by the following sets of parameters $\{\gamma_i\}$

$$
\begin{array}{ll}
\text{I.} & \gamma_0 = \gamma_1 = \gamma_2 = \gamma_3 = 1 \\
\text{II.} & \gamma_0 = \gamma_3 = 1, \quad \gamma_1 = \gamma_2 = 0.3 \\
\text{III.} & \gamma_0 = \gamma_2 = 1, \quad \gamma_1 = 0.3, \quad \gamma_3 = 0.1.
\end{array}
\tag{17}
$$

Bifurcation scenario of systems (17) is given in Figures 4–6 complemented by Table 4. These figures present the sequence of colorings of the vertices of the orgraph shown in Figure 2. In the second row of Table 4 the sequence is

Table 4. Bifurcation values of parameter $k_{IJ} \equiv \tau_{IJ}/\alpha^2$ which correspond for systems (17) to alteration of colorings of the orgraph, depicted in Figure 2.

System	I						II				III	
Bifurcation	1-2	2-3	3-4	4-5	5-6	6-7	1-2	2-3	3-4	4-5	1-2	2-3
k_{IJ}	k_{BD}	k_{HB}	k_{BH}	k_{LH}	k_{F2H}	k_{HL}	k_{BD}	k_{DB}	k_{SB}	k_{BS}	k_{HD}	k_{DH}
	0,28	0	$-0,8$	-4	-13	-16	0,4	0	-10	-40	0,4	0
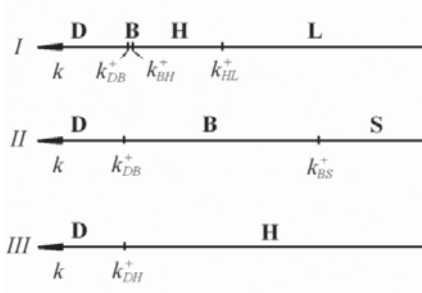
Fig. 7. Phase diagrams of three systems with values of parameters (17). Points on the straight line represent boundaries of the regions of the thermodynamic stability of mesophases whose names are indicated above.

Table 5. Values of parameter $k_{IJ}^+ \equiv \tau_{IJ}^+/\alpha^2$ and $\Delta F_{IJ}^+/\alpha^4$ at points of the phase transitions presented in Figure 7.

System	I			II		III
k_{IJ}^+	k_{DB}^+	k_{BH}^+	k_{HL}^+	k_{DB}^+	k_{BS}^+	k_{DH}^+
	0.24	-0.16	-6	0.4	-11	0.4
$\Delta F_{IJ}^+/\alpha^4$	1.4×10^{-3}	5.1×10^{-3}	7.2×10^{-1}	1.1×10^{-2}	9.6	9.0×10^{-3}

presented of the alteration of this orgraph colorings associated with appropriate bifurcation transitions. In the third row of this table bifurcation parameters $k_{IJ} \equiv \tau_{IJ}/\alpha^2$ are specified corresponding to these transitions whose numerical values are given in the fourth row.

The scenario of the phase transitions in systems (17) is illustrated by Figure 7 and Table 5. The second row of this table incorporates parameters $k_{IJ}^+ \equiv \tau_{IJ}^+/\alpha^2$ the numerical values of which are presented in the third row. And, finally, in the last row there are specified differences divided by α^4 of the specific free energy ΔF_{IJ}^* of transient and initial states at point of $I \rightarrow J$ phase transition.

Since to any scenario of phase transitions some walk on the above-mentioned orgraph unambiguously corresponds, no system under consideration in point can undergo more than three phase transitions over the whole range of temperature change. The reason is the absence in this orgraph of walks whose length exceeds three. The only walk of length three is that corresponding to the traditional sequence of phase transitions, $D \rightarrow B \rightarrow H \rightarrow L$, which is realized, in particular, in system I (17). Phase diagrams of other systems can have either two or one point of phase transitions, as it is the case in systems II and III (17), respectively.

7 Conclusion

The original approach put forward in this paper qualitatively differs from that traditionally used in the WSL approach to describe the phase transitions in heteropolymer liquids. A distinctive feature of our approach consists in invoking the mathematical apparatus of the bifurcation analysis. This makes possible to include into consideration the metastable states, that is of utmost importance in the investigation of the thermodynamic behavior of polymer systems. The values of temperature at which these states loose their local stability separate the regions where the phase transition proceeds by the spinodal decomposition mechanism and by the nucleation mechanism. Under the traditional approach the problem of determining the boundaries of these regions is not normally attacked.

One more advantage of our treatment is the possibility to calculate the height of the thermodynamic barrier which controls the probability of the transition from a metastable state and stable one. This permits evaluating the characteristic scale of the lifetime of the first of them.

Although in the main body of the paper we restricted the consideration to mesophases whose wave vectors, involved in their first harmonic sets, are aligned along the edges of the regular tetrahedron, the approach introduced can be easily extended to figures other than tetrahedron. So, if a cube is such a figure, the full set of single-amplitude extremals of the Landau free energy will comprise along with L and S extremals also Cubic (C) extremal (see Appendix C). Essentially, S-extremal always turns out to be unstable with respect to arbitrary perturbations whose wave vectors are aligned along the cube edges. This means that the S-mesophase involved in the orgraph depicted in Figure 2 does not exist in reality.

In order to perform a correct bifurcation and phase analysis on the set composed of all extremals of orgraph (Fig. 2) complemented by C-extremal, it is necessary to consider a set of nine wave vectors of identical length. This set consists of six vectors aligned along the edges of the regular tetrahedron presented in Figure 1 and three vectors which are perpendicular, respectively, to pairs of vectors 1 and 4, 2 and 5, 3 and 6 of this tetrahedron. In such a problem the Landau free energy in the first harmonic approximation will depend on nine independent amplitudes $\{a_i\}$ and on phenomenological coefficients $\{\gamma_i\}$ whose number is larger than four. Finding of

single-amplitude extremals of the Landau free energy and the analysis of their thermodynamical stability in such a model constitutes a far more complicated problem as compared with that addressed in the present paper.

The approach put forward in the present work is confronted by serious mathematical difficulties under the extension of the set of candidate mesophases, specifically when the mesophase having gyroid spatial symmetry of the distribution of densities of monomeric units is added. These difficulties are due to a large number of independent amplitudes of the order parameter of the gyroid symmetry. In this case it is advisable to supplement our approach with different numerical methods of the solution of sets of nonlinear algebraic equations. An example of such a consideration of the gyroid mesophase was provided [13] in particular case when the vertex functions are independent of angles.

Appendix A

The set of nine equations for finding extremals of function (6) has the following appearance

$$
\begin{cases}
\partial F/\partial a_1 = \tau a_1 - 2\alpha\left(a_2 a_3 \cos t_{123} + a_5 a_6 \cos t_1\right) \\
\quad + \gamma_0 a_1^3 + 2\gamma_1 a_1\left(a_2^2 + a_3^2 + a_5^2 + a_6^2\right) \\
\quad + 2\gamma_2 a_1 a_4^2 + 2\gamma_3 a_4\left(a_2 a_5 \cos t_{12} + a_3 a_6 \cos t_{13}\right) = 0, \\
\partial F/\partial a_2 = \tau a_2 - 2\alpha\left(a_1 a_3 \cos t_{123} + a_4 a_6 \cos t_2\right) \\
\quad + \gamma_0 a_2^3 + 2\gamma_1 a_2\left(a_1^2 + a_3^2 + a_4^2 + a_6^2\right) \\
\quad + 2\gamma_2 a_2 a_5^2 + 2\gamma_3 a_5\left(a_1 a_4 \cos t_{12} + a_3 a_6 \cos t_{23}\right) = 0, \\
\partial F/\partial a_3 = \tau a_3 - 2\alpha\left(a_1 a_2 \cos t_{123} + a_4 a_5 \cos t_3\right) \\
\quad + \gamma_0 a_3^3 + 2\gamma_1 a_3\left(a_1^2 + a_2^2 + a_4^2 + a_5^2\right) \\
\quad + 2\gamma_2 a_3 a_6^2 + 2\gamma_3 a_6\left(a_1 a_4 \cos t_{13} + a_2 a_5 \cos t_{23}\right) = 0, \\
\partial F/\partial a_4 = \tau a_4 - 2\alpha\left(a_2 a_6 \cos t_2 + a_5 a_3 \cos t_3\right) \\
\quad + \gamma_0 a_4^3 + 2\gamma_1 a_4\left(a_2^2 + a_3^2 + a_5^2 + a_6^2\right) \\
\quad + 2\gamma_2 a_4 a_1^2 + 2\gamma_3 a_1\left(a_2 a_5 \cos t_{12} + a_3 a_6 \cos t_{13}\right) = 0, \\
\partial F/\partial a_5 = \tau a_5 - 2\alpha\left(a_1 a_6 \cos t_1 + a_4 a_3 \cos t_3\right) + \\
\quad \gamma_0 a_5^3 + 2\gamma_1 a_5\left(a_1^2 + a_3^2 + a_4^2 + a_6^2\right) \\
\quad + 2\gamma_2 a_5 a_2^2 + 2\gamma_3 a_2\left(a_1 a_4 \cos t_{12}\right. \\
\quad \left. + a_3 a_6 \cos t_{23}\right) = 0, \\
\partial F/\partial a_6 = \tau a_6 - 2\alpha\left(a_1 a_5 \cos t_1 + a_4 a_2 \cos t_2\right) \\
\quad + \gamma_0 a_6^3 + 2\gamma_1 a_6\left(a_1^2 + a_2^2 + a_4^2 + a_5^2\right) \\
\quad + 2\gamma_2 a_6 a_3^2 + 2\gamma_3 a_3\left(a_1 a_4 \cos t_{13} + a_2 a_5 \cos t_{23}\right) = 0, \\
\partial F/\partial t_1 = 2\alpha a_1\left(a_2 a_3 \sin t_{123} + a_5 a_6 \sin t_1\right) \\
\quad - 2\gamma_3 a_1 a_4\left(a_2 a_5 \sin t_{12} + a_3 a_6 \sin t_{13}\right) = 0, \\
\partial F/\partial t_2 = 2\alpha a_2\left(a_1 a_3 \sin t_{123} + a_4 a_6 \sin t_2\right) \\
\quad - 2\gamma_3 a_2 a_5\left(a_1 a_4 \sin t_{12} + a_3 a_6 \sin t_{23}\right) = 0, \\
\partial F/\partial t_3 = 2\alpha a_3\left(a_1 a_2 \sin t_{123} + a_4 a_5 \sin t_3\right) \\
\quad - 2\gamma_3 a_3 a_6\left(a_1 a_4 \sin t_{13} + a_2 a_5 \sin t_{23}\right) = 0,
\end{cases}
$$

$$(A.1)$$

where t_{ij}, t_{123} are defined by formulas (9).

The number of unknowns in set of equations (A.1) for each single-amplitude configuration $(a_1 a_2 \ldots a_6)$ is reduced to four which are the amplitude A and three phase variables t_1, t_2, t_3. Note, set (A.1) is consistent not for all single-amplitude configurations, but only for those presented in Table 1.

Appendix B

Bellow both blocks of the Hess matrix (10) are presented along with the complete spectrum of its eigenvalues on all extremals given in Table 1.

0. Disorder (D).

$$
\mathbf{H}^a = \begin{pmatrix}
S_0 & 0 & 0 & 0 & 0 & 0 \\
0 & S_0 & 0 & 0 & 0 & 0 \\
0 & 0 & S_0 & 0 & 0 & 0 \\
0 & 0 & 0 & S_0 & 0 & 0 \\
0 & 0 & 0 & 0 & S_0 & 0 \\
0 & 0 & 0 & 0 & 0 & S_0
\end{pmatrix}
\quad
\mathbf{H}^t = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\quad (B.1)
$$

$$S_0 \equiv \tau$$
$$\lambda_{1,\ldots,6} = S_0, \quad \lambda_{7,8,9} = 0$$

1. Lamellar (L).

$$
\mathbf{H}^a = \begin{pmatrix}
S_1 & 0 & 0 & 0 & 0 & 0 \\
0 & T_1 & V_1 & 0 & 0 & 0 \\
0 & V_1 & T_1 & 0 & 0 & 0 \\
0 & 0 & 0 & U_1 & 0 & 0 \\
0 & 0 & 0 & 0 & T_1 & V_1 \\
0 & 0 & 0 & 0 & V_1 & T_1
\end{pmatrix}
\quad
\mathbf{H}^t = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\quad (B.2)
$$

$S_1 \equiv 2\gamma_0 A^2$, $T_1 \equiv (2\gamma_1 - \gamma_0)A^2$, $U_1 \equiv (2\gamma_2 - \gamma_0)A^2$, $V_1 \equiv -2\alpha A$
$\lambda_1 = S_1$, $\lambda_{2,3} = T_1 + V_1$, $\lambda_{4,5} = T_1 - V_1$, $\lambda_6 = U_1$, $\lambda_{7,8,9} = 0$.

2. Rhombic (R).

$$
\mathbf{H}^a = \begin{pmatrix}
S_2 & V_2 & 0 & 0 & 0 & 0 \\
V_2 & S_2 & 0 & 0 & 0 & 0 \\
0 & 0 & T_2 & 0 & 0 & 0 \\
0 & 0 & 0 & U_2 & 0 & 0 \\
0 & 0 & 0 & 0 & U_2 & 0 \\
0 & 0 & 0 & 0 & 0 & T_2
\end{pmatrix}
\quad
\mathbf{H}^t = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\quad (B.3)
$$

$S_2 \equiv 2\gamma_0 A^2$, $T_2 \equiv (2\gamma_1 - \gamma_0)A^2$, $U_2 \equiv (2\gamma_2 - \gamma_0)A^2$, $V_2 \equiv 4\gamma_1 A^2$
$\lambda_1 = S_2 - V_2$, $\lambda_2 = S_2 + V_2$, $\lambda_{3,4} = T_2$, $\lambda_{5,6} = U_2$, $\lambda_{7,8,9} = 0$.

3. Square (S).

$$
\mathbf{H}^a = \begin{pmatrix}
S_3 & 0 & 0 & U_3 & 0 & 0 \\
0 & T_3 & V_3 & 0 & X_3 & V_3 \\
0 & V_3 & T_3 & 0 & V_3 & X_3 \\
U_3 & 0 & 0 & S_3 & 0 & 0 \\
0 & X_3 & V_3 & 0 & T_3 & V_3 \\
0 & V_3 & X_3 & 0 & V_3 & T_3
\end{pmatrix}
\quad
\mathbf{H}^t = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\quad (B.4)
$$

$S_3 \equiv 2\gamma_0 A^2$, $T_3 \equiv (4\gamma_1 - \gamma_0 - 2\gamma_2)A^2$, $U_3 \equiv 4\gamma_2 A^2$,
$V_3 \equiv -2\alpha A$, $X_3 \equiv 2\gamma_3 A^2$
$\lambda_1 = S_3 - U_3$, $\lambda_2 = S_3 + U_3$, $\lambda_{3,4} = T_3 - X_3$,
$\lambda_5 = T_3 + X_3 - 2V_3$, $\lambda_6 = T_3 + X_3 + 2V_3$, $\lambda_{7,8,9} = 0$.

4. Hexagonal (H).

$$
\mathbf{H}^a = \begin{pmatrix}
S_4 & U_4 & U_4 & 0 & 0 & 0 \\
U_4 & S_4 & U_4 & 0 & 0 & 0 \\
U_4 & U_4 & S_4 & 0 & 0 & 0 \\
0 & 0 & 0 & T_4 & V_4 & V_4 \\
0 & 0 & 0 & V_4 & T_4 & V_4 \\
0 & 0 & 0 & V_4 & V_4 & T_4
\end{pmatrix}
\quad
\mathbf{H}^t = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\quad (B.5)
$$

$S_4 \equiv 2\gamma_0 A^2 + 2\alpha A, T_4 \equiv (2\gamma_2 - \gamma_0) A^2 + 2\alpha A,$
$U_4 \equiv 4\gamma_1 A^2 - 2\alpha A, V_4 \equiv 2\gamma_3 A^2 - 2\alpha A$
$\lambda_{1,2} = S_4 - U_4, \lambda_3 = S_4 + 2U_4, \lambda_{4,5} = T_4 - V_4,$
$\lambda_6 = T_4 + 2V_4, \lambda_{7,8,9} = 0.$

5. Rhombohedric (Rh).

$$\mathbf{H}^a = \begin{pmatrix} T_5 & V_5 & V_5 & 0 & 0 & 0 \\ V_5 & T_5 & V_5 & 0 & 0 & 0 \\ V_5 & V_5 & T_5 & 0 & 0 & 0 \\ 0 & 0 & 0 & S_5 & U_5 & U_5 \\ 0 & 0 & 0 & U_5 & S_5 & U_5 \\ 0 & 0 & 0 & U_5 & U_5 & S_5 \end{pmatrix} \quad \mathbf{H}^t = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \text{(B.6)}$$

$S_5 \equiv 2\gamma_0 A^2, \; T_5 \equiv (2\gamma_2 - \gamma_0) A^2, \; U_5 \equiv 4\gamma_1 A^2, \; V_5 \equiv -2\gamma_3 A^2$
$\lambda_{1,2} = S_5 - U_5, \; \lambda_3 = S_5 + 2U_5, \; \lambda_{4,5} = T_5 - V_5,$
$\lambda_6 = T_5 + 2V_5, \; \lambda_{7,8,9} = 0.$

6. Deformed FCC2 (F2).

$$\mathbf{H}^a = \begin{pmatrix} S_6 & U_6 & V_6 & X_6 & U_6 & -V_6 \\ U_6 & S_6 & V_6 & U_6 & X_6 & V_6 \\ V_6 & V_6 & T_6 & -V_6 & -V_6 & 0 \\ X_6 & U_6 & -V_6 & S_6 & U_6 & V_6 \\ U_6 & X_6 & -V_6 & U_6 & S_6 & -V_6 \\ -V_6 & V_6 & 0 & V_6 & -V_6 & T_6 \end{pmatrix} \quad \mathbf{H}^t = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\text{(B.7)}$$

$S_6 \equiv 2(\gamma_0 + \gamma_3) A^2, \; T_6 \equiv (4\gamma_1 - \gamma_0 - 2\gamma_2 + 2\gamma_3) A^2,$
$U_6 \equiv 2(2\gamma_1 - \gamma_3) A^2, X_6 \equiv 2(2\gamma_2 - \gamma_3) A^2, V_6 \equiv 2\alpha A$
$\lambda_1 = S_6 + X_6 - 2U_6, \lambda_2 = S_6 + X_6 + 2U_6,$
$\lambda_{3,4} = \left[(S_6 + T_6 - X_6) - \sqrt{(S_6 - T_6 - X_6)^2 + 16 V_6^2} \right]/2,$
$\lambda_{5,6} = \left[(S_6 + T_6 - X_6) + \sqrt{(S_6 - T_6 - X_6)^2 + 16 V_6^2} \right]/2,$
$\lambda_{7,8,9} = 0.$

7. Deformed FCC3 (F3).

$$\mathbf{H}^a = \begin{pmatrix} S_7 & U_7 & 0 & X_7 & U_7 & 0 \\ U_7 & S_7 & 0 & U_7 & X_7 & 0 \\ 0 & 0 & T_7 & 0 & 0 & V_7 \\ X_7 & U_7 & 0 & S_7 & U_7 & 0 \\ U_7 & X_7 & 0 & U_7 & S_7 & 0 \\ 0 & 0 & V_7 & 0 & 0 & T_7 \end{pmatrix} \quad \mathbf{H}^t = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \text{(B.8)}$$

$S_7 \equiv 2(\gamma_0 - \gamma_3) A^2, \; T_7 \equiv (4\gamma_1 - \gamma_0 - 2\gamma_2 - 2\gamma_3) A^2,$
$U_7 \equiv 2(2\gamma_1 + \gamma_3) A^2, X_7 \equiv 2(2\gamma_2 + \gamma_3) A^2, V_7 \equiv 4\gamma_3 A^2$
$\lambda_{1,2} = S_7 - X_7, \lambda_3 = S_7 + X_7 - 2U_7, \lambda_4 = S_7 + X_7 + 2U_7,$
$\lambda_5 = T_7 - V_7, \lambda_6 = T_7 + V_7, \lambda_{7,8,9} = 0.$

8. BCC (B).

$$\mathbf{H}^a = \begin{pmatrix} S_8 & T_8 & T_8 & U_8 & T_8 & T_8 \\ T_8 & S_8 & T_8 & T_8 & U_8 & T_8 \\ T_8 & T_8 & S_8 & T_8 & T_8 & U_8 \\ U_8 & T_8 & T_8 & S_8 & T_8 & T_8 \\ T_8 & U_8 & T_8 & T_8 & S_8 & T_8 \\ T_8 & T_8 & U_8 & T_8 & T_8 & S_8 \end{pmatrix} \quad \mathbf{H}^t = \begin{pmatrix} 2\Lambda_8 & \Lambda_8 & \Lambda_8 \\ \Lambda_8 & 2\Lambda_8 & \Lambda_8 \\ \Lambda_8 & \Lambda_8 & 2\Lambda_8 \end{pmatrix}$$

$$\text{(B.9)}$$

$S_8 \equiv 2(\gamma_0 - 2\gamma_3) A^2 + 4\alpha A, T_8 \equiv 2(2\gamma_1 + \gamma_3) A^2 - 2\alpha A$
$U_8 \equiv 4(\gamma_2 + \gamma_3) A^2, \Lambda_8 \equiv 2(\alpha - \gamma_3 A) A^3$
$\lambda_{1,2,3} = S_8 - U_8, \lambda_{4,5} = S_8 - 2T_8 + U_8,$
$\lambda_6 = S_8 + 4T_8 + U_8, \lambda_{7,8} = \Lambda_8, \lambda_9 = 4\Lambda_8.$

Table C1. Complete set of all single-amplitude extremals of the Landau free energy (C1) and the spectrum of the Hess matrix on these extremals.

N°	Extremal	Abbr.	$(a_1 a_2 a_3)$	Expression for amplitude A	Eigenvalues
0	Disorder	D	(000)	—	$\lambda_{1,2,3} = \tau$
1	Lamellar	L	(A00)	$\sqrt{-\tau/\beta_L},$ $\beta_L \equiv \gamma_0$	$\lambda_1 = 2\gamma_0 A^2,$ $\lambda_{2,3} = (2\gamma_2 - \gamma_0) A^2$
2	quare	S	(AA0)	$\sqrt{-\tau/\beta_S},$ $\beta_S \equiv \gamma_0 + 2\gamma_2$	$\lambda_1 = (\gamma_0 + 2\gamma_2) A^2,$ $\lambda_2 = (\gamma_0 - 2\gamma_2) A^2,$ $\lambda_3 = (2\gamma_2 - \gamma_0) A^2$
3	Cubic	C	(AAA)	$\sqrt{-\tau/\beta_C},$ $\beta_C \equiv \gamma_0 + 4\gamma_2$	$\lambda_1 = (\gamma_0 + 4\gamma_2) A^2,$ $\lambda_{2,3} = (\gamma_0 - 2\gamma_2) A^2$

9. BCC2 (B2).

$$\mathbf{H}^a = \begin{pmatrix} S_9 & T_9 & T_9 & U_9 & T_9 & T_9 \\ T_9 & S_9 & T_9 & T_9 & U_9 & T_9 \\ T_9 & T_9 & S_9 & T_9 & T_9 & U_9 \\ U_9 & T_9 & T_9 & S_9 & T_9 & T_9 \\ T_9 & U_9 & T_9 & T_9 & S_9 & T_9 \\ T_9 & T_9 & U_9 & T_9 & T_9 & S_9 \end{pmatrix} \quad \mathbf{H}^t = \begin{pmatrix} 2\Lambda_9 & \Lambda_9 & \Lambda_9 \\ \Lambda_9 & 2\Lambda_9 & \Lambda_9 \\ \Lambda_9 & \Lambda_9 & 2\Lambda_9 \end{pmatrix}$$

$$\text{(B.10)}$$

$S_9 \equiv 2(\gamma_0 + 2\gamma_3) A^2, T_9 \equiv 2(2\gamma_1 - \gamma_3) A^2,$
$U_9 \equiv 4(\gamma_2 - \gamma_3) A^2, \Lambda_9 \equiv 2\gamma_4 A^4$
$\lambda_{1,2,3} = S_9 - U_9, \lambda_{4,5} = S_9 - 2T_9 + U_9,$
$\lambda_6 = S_9 + 4T_9 + U_9, \lambda_{7,8} = \Lambda_9, \lambda_9 = 4\Lambda_9.$

Appendix C

Here we will examine mesophase whose wave vectors $\{\mathbf{q}_i\}$ of the first harmonic set are aligned along the edges of a cube. Because a cube, as distinct from a tetrahedron, has not contours of length three and length four contours distinct from the square, the function of the Landau free energy neither contain a cubic term nor depends on phases $\{\varphi_i\}$ of plane waves:

$$F = \frac{\tau}{2} \sum_{i=1}^{3} a_i^2 + \frac{\gamma_0}{4} \sum_{i=1}^{3} a_i^4 + \gamma_2 \left(a_1^2 a_2^2 + a_1^2 a_3^2 + a_2^2 a_3^2\right)$$

$$\text{(B.11)}$$

here $a_i \, (i = 1, 2, 3)$ are amplitudes of three pairs of harmonics with mutually perpendicular wave vectors, whereas the sense of the other coefficients is just the same as in formula (6).

Having performed the algebraic operations with the free energy (C1) analogous to those made in the foregoing with expansion (6), we obtained Table C1 presenting an information identical to that given in Table 1 and Appendix B.

In accordance with Table C1, the only state existing in the region $\tau > 0$ is disordered one. In this region it is locally stable, becoming unstable at $\tau = 0$ where two extremals, L and C, appear. One of them is the minimum, while the other is the saddle of the free energy (C1). Particularly, L-extremal will be locally stable or unstable, provided $2\gamma_2 - \gamma_0 > 0$ or $2\gamma_2 - \gamma_0 < 0$, respectively. Concerning S-extremal, it will not correspond at any set of

parameters γ_0, γ_2 to any mesophase. This is because one of eigenvalues, λ_2 or λ_3, is always negative as it follows from Table C1.

References

1. I.W. Hamley, *The Physics of Block Copolymers* (Oxford Univ. Press, Oxford, New York, 1998)
2. F.S. Bates, G.H. Fredrickson, Ann. Rev. Phys. Chem. **41**, 525 (1990)
3. H. Hasegawa, T. Hashimoto, in *Comprehensive Polymer Science, Second Suppl.,* edited by G. Allen (Pergamon Press, 1996) Chap. 14 p. 497
4. L. Leibler, Macromolecules **13**, 1602 (1980)
5. K. Binder, Adv. Polym. Sci. **112**, 181 (1994)
6. R. Holyst, T.A. Vilgis, Macromol. Theory Simul. **5**, 573 (1996)
7. G.H. Fredrickson, *The Equilibrium Theory of Inhomogeneous Polymers* (Clanderon Press, Oxford, 2006)
8. S.I. Kuchanov, S.V. Panyukov, in *Comprehensive Polymer Science, Second Suppl.*, edited by G. Allen (Pergamon Press, 1996) Chap. 13 p. 441
9. S. Qi, Z.-G. Wang, Phys. Rev. Lett. **76**, 1679 (1996)
10. S. Qi, Z.-G. Wang, Phys. Rev. E **55**, 1682 (1997)
11. M. Nonomura, T. Ohta, J. Phys.: Cond. Mat. **13**, 9089 (2001)
12. M. Nonomura, K. Yamada, T. Ohta, J. Phys. Cond. Mat. **15**, L423 (2003)
13. K. Yamada, M. Nonomura, T. Ohta, Macromol. **37**, 5762 (2004)
14. K. Yamada, M. Nonomura, A. Saeki, T.Ohta, J. Phys. Cond. Mat. **17**, 4877 (2005)
15. A.M. Mayes, M. Olvera de la Cruz, W.E. McMullen, Macromol. **26**, 4050 (1993)
16. Y. Smirnova, I. Erukhimovich, G. ten Brinke, Polym. Sci. A **47**, 430 (2005)
17. Y. Smirnova, G. ten Brinke, I. Erukhimovich, J. Chem. Phys. **124**, 054907 (2006)
18. B. Dionne, M. Golubitsky, ZAMP **43**, 36 (1992)
19. B. Dionne, ZAMP **44**, 673 (1993)
20. J.C. Toledano, P. Toledano, *The Landau Theory of Phase Transitions* (World Scientific, Singapore, 1987)
21. M.A. Aliev, S.I. Kuchanov, Eur. Phys. J. B **43**, 251 (2005)
22. I.Ya. Erukhimovich, A.V. Dobrynin, Macromol. Symp. **81**, 253 (1994)
23. Being interested in obtaining the bifurcation scenario realized at the increasing τ, one should consider instead of the orgraph portrayed in Figure 2 another one obtained from the former by the replacement of all arcs by those aligned in opposite direction
24. Phases of the transient states are not specified in Table 3 deliberately, since they coincide with the phases of the minima which are extreme points of the path on which this state is locate