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Microphase separation in correlated random copolymers: Mean-field theory and fluctuation corrections

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The behavior of a random *AB* multiblock copolymer melt with a Markovian sequence of monomers has been studied in the region where the spatially homogeneous state loses its stability. We use a generalization of the weak crystallization theory to the case of a polydisperse system. In the framework of both mean-field and Brazovskiĭ approximations phase diagrams of such a system are constructed. It is shown that the major difference of these diagrams from the monodisperse ones is the presence of regions where two phases with different symmetry of the superlattice (lamellar, hexagonal, and bcc) coexist with each other in the finite temperature range. We show that the account of fluctuations alters the phase diagram near the critical point in comparison with the mean-field picture. In particular, in addition to ''windows'' of direct transitions from disordered to lamellar and hexagonal phases, three phase lines appear, where one of the two coexisting phases changes its symmetry. We demonstrate also that the period of the superstructures varies continuously with the temperature variation. [S1063-651X(98)10206-4]

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I. INTRODUCTION

Interest in copolymer systems is stimulated by their numerous technological applications [1]. The majority of theoretical and experimental studies have been devoted to the consideration of model copolymer materials with well-defined architectures, such as diblock and triblock copolymers. Considerable attention has been also given to regular (alternating) multiblock copolymers. One of the most interesting physical phenomena is the formation of microdomain structures (microphase separation transition). The homogeneous state of a heteropolymer is unstable with respect to composition fluctuations with a finite wave vector q_0 below the critical temperature if different types of monomers ''do not like each other.'' Since such monomers are connected in a single macromolecule, they cannot go apart into different macrophases and can only segregate on microscopic scales. In the case of a relatively narrow distribution of block length the system forms regular superstructure with the period about a block size. The phase diagram of such copolymers includes regions with one-dimensional lamellar, two-dimensional hexagonally close-packed cylinders (hex), and three-dimensional body-centered-cubic (bcc) phase [2].

The formation of copolymers with a regular architecture is rather a state of the art. They are usually synthesized by a polymerization reaction which produces a wide distribution of macromolecules according to their chemical structure. The randomness of the synthesis process results in copolymers with ill-defined architecture. The phase diagram of a copolymer depends essentially on correlations in the monomer sequence along the chain. The effect of chemical disorder on the stability of the homogeneous phase was considered in Ref. [3]. It was shown that the value of the critical wave vector q_0 decreases with the disorder and turns to 0 for a random copolymer system. A similar behavior was found later for more realistic copolymer systems [4,5].

Consideration of the ordered phases of the random multiblock copolymers shows that the period of the superstructure can exceed the average spatial size of one block because of the local redistribution of the chain fragments with an excess of monomers of a given type [6–8]. The mean-field phase diagram of multiblock copolymer systems is constructed in Ref. [9]. Unfortunately, the possibility of the coexistence of microphases with different symmetries of the superlattice has not been taken into consideration in this work. Such two-phase regions for random correlated copolymers were later found in Ref. [10].

The mean-field picture of the microphase transitions breaks down near critical points. The presence of large-amplitude composition fluctuations in the pretransitional disordered phase of the model of a regular diblock copolymer was demonstrated in Ref. [11]. These fluctuations are manifested in small-angle neutron scattering (SANS) experiments as a peak in the structure factor, the position of which, q_0, only weakly varies with the temperature. An important question is how such fluctuation effects affect the mean-field picture. There is a very wide spectrum of conjectures about the fluctuation picture of random uncorrelated copolymers. It is supposed [12,13] that thermal fluctuations should prevent the formation of any superstructure (see also Ref. [14]), or a glasslike state should be established because of the quenched randomness in the sequence of monomers along the chain [15,16]. The weakly first-order transition to the microstructure in random correlated copolymers was found in Refs.

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[17,18]. The behavior of such copolymers near the Lifshitz point, at which q_0 is first equal to zero, was studied in Refs. [19,20].

The effect of fluctuations on the phase diagram of symmetric correlated Markovian copolymers was studied in Ref. [21]. Here we construct the phase diagram of general nonsymmetric Markovian correlated multiblock copolymers and find the temperature and composition dependences of all possible microphases in the weak segregation regime. The main results of this work were announced in Ref. [22].

In Sec. II we develop the mean-field theory for nonsymmetric Markovian copolymers. In Sec. III we take into consideration fluctuation corrections to the mean-field theory within the framework of the Brazovskiĭ approximation. Our main predictions are summarized in Sec. IV.

II. MEAN-FIELD THEORY

A. Free energy

We consider a melt of heteropolymer chains with Markovian statistics of monomers A and B for which probability (transition matrix) ν_{ij} that a monomer of type $j=A,B$ will follow a monomer of type i along the chain does not depend on monomers farther removed along the chain. Average densities $\overline{\rho_i}$ of monomers of the given type i and the average block length N of chains can be expressed in terms of elements of the transition matrix ν [23]:

$$\overline{\rho_A}=f\rho,\quad \overline{\rho_B}=(1-f)\rho,\quad f=\frac{\nu_{BA}}{\nu_{AB}+\nu_{BA}},$$

$$N=\frac{1}{\nu_{AB}+\nu_{BA}}. \tag{1}$$

Here f is the fraction of monomers A and ρ is the total monomer density. We assume that the block length N is small with respect to the average length of the chain; i.e., each chain contains a large number of blocks. Using the incompressibility condition $\rho_A(\mathbf{x})+\rho_B(\mathbf{x})=\rho$, it is convenient to introduce the dimensionless order parameter

$$\psi(\mathbf{x})=\Delta\rho_A(\mathbf{x})/\rho,\quad \rho=\overline{\rho_A}+\overline{\rho_B}, \tag{2}$$

which characterizes the deviations $\Delta\rho_A(\mathbf{x})=-\Delta\rho_B(\mathbf{x})$ of the density of monomers of the given type from their average value. Near the critical point $f=1/2$, the free energy of the system can be expanded in powers of Fourier components

$$\psi_{\mathbf{q}}=\int d\mathbf{x}\;\psi(\mathbf{x})\exp(i\mathbf{q}\cdot\mathbf{x}) \tag{3}$$

of this order parameter (2):

$$\begin{aligned}\frac{\mathcal{F}[\psi]}{\rho T}=&\frac{1}{2}\int\frac{d^3\mathbf{q}}{(2\pi)^3}\,(\chi_c-\chi+a^2q^2)\,\psi_{\mathbf{q}}\psi_{-\mathbf{q}}\\&-\frac{\lambda}{6}\int\delta\left(\sum_{i=1}^{3}\mathbf{q}_i\right)\prod_{i=1}^{3}\psi_{\mathbf{q}_i}\frac{d^3\mathbf{q}_i}{(2\pi)^3}\\&+\frac{g}{24}\int\delta\left(\sum_{i=1}^{4}\mathbf{q}_i\right)\prod_{i=1}^{4}\psi_{\mathbf{q}_i}\frac{d^3\mathbf{q}_i}{(2\pi)^3}\\&+\frac{k}{4V}\int\frac{d^3\mathbf{q}}{(2\pi)^3}\int\frac{d^3\mathbf{q}'}{(2\pi)^3}\,\frac{\psi_{\mathbf{q}}\psi_{-\mathbf{q}}\psi_{\mathbf{q}'}\psi_{-\mathbf{q}'}}{a^2[q^2+(q')^2]}.\end{aligned} \tag{4}$$

Here V is the volume of the system and the temperature T enters into the free energy through the dimensionless interaction parameter χ. Note that the loss of stability of the spatially homogeneous state [positive definiteness of the quadratic ψ term in the free energy (4)] takes place at $\chi=\chi_c$ for zero wave vector. In the case of polydisperse polymeric systems this fact does not imply [6,23] the emergence of a new spatially homogeneous phase (macrophase separation) as in the case of monodisperse systems.

The first three terms in expression (4) have the form of the usual Landau expansion of the free energy, where the coefficient λ of the cubic term vanishes in the critical point $f=1/2$. The last ''nonlocal'' term ($\sim k$) describes polydispersity effects because of the finite width of the block length distribution. This term gives the entropy cost due to the local variation of the block length distribution to create the density inhomogeneity $\Delta\rho_A(x)$ with characteristic spatial scale of the order the reciprocal wave vector q^{-1}. Since the formation of such an inhomogeneity involves only blocks with characteristic size q^{-1}, in effect it ''sucks in'' chains with such blocks from the surrounding space. This phenomenon depletes the block length distribution outside of this inhomogeneity and, as the consequence, leads to the effective infinite-range interaction of two (or more) inhomogeneities.

The parameters λ, g, and k of the Landau free-energy expansion (4) are determined from microscopic theory [7,23]:

$$\lambda=\frac{3}{4N}\frac{1-2f}{f^2(1-f)^2},\quad g=\frac{3}{8N}\frac{5-16f(1-f)}{f^3(1-f)^3},$$

$$k=\frac{1}{4N^2}\frac{1}{f^3(1-f)^3}. \tag{5}$$

In the case of the symmetric copolymer, $f=1/2$, the coefficient λ of the cubic term vanishes and the coefficient g of the quadratic term remains positive for arbitrary f. The parameter $a=b(\chi_cN)^{1/2}$ can be expressed in terms of the monomer size b and the critical value $\chi_c=1/[2Nf(1-f)]$ of the interaction parameter χ.

B. Phase diagram

The equilibrium value of the order parameter $\psi(\mathbf{x})$ in the microphase-separated system is determined from the condition of the minimization of the free energy (4). We begin our analysis by considering single-phase states of the polymer.

Near the critical point the order parameter can be taken [2] as the superposition of n plane waves with wave vectors $\mathbf{q}_k$ which have equal magnitudes $|\mathbf{q}_k|=q$ and are chosen to describe lamellar $(n=1)$, hexagonal $(n=3)$, and body-centered-cubic (bcc, $n=6$) phases:

$$\psi_{\mathbf{q}}|_n=\frac{A_n}{\sqrt{n}}\sum_{k=1}^{n}[e^{i\varphi_k}\delta(\mathbf{q}-\mathbf{q}_k)+e^{-i\varphi_k}\delta(\mathbf{q}+\mathbf{q}_k)]. \tag{6}$$

Constant phases φ_k can be taken to zero for all the above long-range-ordered structures. Beside these structures, the disordered random structure has been considered in Refs. [6,5,8]. For this structure the wave vectors $\mathbf{q}_k$ are selected uniformly on the sphere $|\mathbf{q}_k|=q$, the φ_k are random phases, and the positive integer n will later be taken to infinity. Substituting expression (6) in Eq. (4) we represent the free energy of the phase with a given number n of plane waves,

$$\frac{\mathcal{F}_n}{T\rho V}=F_n(q,A_n)+\frac{k}{2}\frac{A_n^4}{a^2q^2}, \tag{7}$$

by the sum of the local contribution

$$F_n(q,A_n)\equiv(\chi_c-\chi+a^2q^2)A_n^2-\lambda\alpha_nA_n^3/6+g\beta_nA_n^4/24 \tag{8}$$

and the nonlocal contribution $\sim k$. The coefficients α_n and β_n depend on the type of structure:

Structure	lamellar	hexagonal	bcc	random
n	1	3	6	∞
α_n	0	$4/\sqrt{3}$	$8/\sqrt{6}$	0
β_n	6	10	15	12

(9)

For ordered structures these coefficients had been calculated in Ref. [2]. The value of β_∞ for the random wave structure can be determined from the following estimation:

$$\beta_n=6(2n-1)/n+\beta_{\text{osc}}\{\varphi_k\}, \tag{10}$$

where β_{osc} is the contribution of configurations of four vectors $\mathbf{q}_k$ $(\Sigma_{k=1}^{4}\mathbf{q}_k=\mathbf{0})$, the directions $\pm\mathbf{q}_k/|\mathbf{q}_k|$ of which are all different each from other. This contribution is a strongly oscillating function of randomly distributed phases φ_k with zero average. In the limit $n\rightarrow\infty$ we can substitute this average for the function $\beta_{\text{osc}}\{\varphi_k\}$ and find $\beta_\infty=12$.

Minimizing the resulting free energy (7) with respect to the amplitude A_n and the wave vector q we get

$$A_n=\frac{3}{g\beta_n}\left\{\lambda\alpha_n/2-3(2k)^{1/2}+\left[[\lambda\alpha_n/2-3(2k)^{1/2}]^2+\frac{4}{3}g\beta_n(\chi-\chi_c)\right]^{1/2}\right\},\quad a^2q^2=(k/2)^{1/2}|A_n|. \tag{11}$$

Consequently, in the single-phase region both the amplitude and the wave vector of the superstructure increase monotonically with the interaction parameter χ. For sufficiently large values χ the period of structure becomes of the order of the block length and the single-harmonic approximation (6) becomes inadequate for the description of such structures. Consideration of this strong segregation regime is beyond the scope of this work.

Several phases with different symmetries of the superlattice can coexist one with the other. In contrast to monodisperse systems, where each of the coexisting phases can be considered separately, in polydisperse systems one has to take into account the exchange of chains between these phases. Consider a two-phase state with volume fractions ϕ and $1-\phi$ occupied by phases n and m, respectively. Substituting the order parameter (6) with the numbers n and m of plane waves in each of these phases into Eq. (4), we find the free energy of the two-phase state:

$$\frac{\mathcal{F}_{nm}}{TV}=\phi F_n(q_n,A_n)+(1-\phi)F_m(q_m,A_m)+k\left[\frac{\phi^2A_n^4}{2a^2q_n^2}+\frac{2\phi(1-\phi)A_n^2A_m^2}{a^2(q_n^2+q_m^2)}+\frac{(1-\phi)^2A_m^4}{2a^2q_m^2}\right]. \tag{12}$$

The first two terms of Eq. (12) give local contributions (8) of each phase to the free energy and are proportional to the volumes $V_n=\phi V$ and $V_n=(1-\phi)V$ of these phases. The last term $(\sim k)$ describes the effects of the redistribution of chains with different block lengths between the two coexisting phases. The minimization of the free energy (12) with respect to parameters of the phases is performed in Appendix A, where we show that both coexisting phases have identical wave vectors $q\equiv q_n=q_m$ and their amplitudes A_n and A_m do not depend on χ and ϕ. The dependences of the wave vector q and the volume fraction ϕ of the phase n on the interaction parameter χ (temperature) are defined by the equations

$$3a^2q^2=\chi-\chi_c+\lambda\alpha_nA_n/4-g\beta_nA_n^2/12, \tag{13}$$

$$\phi=(2a^4q^4/k-A_m^2)/(A_n^2-A_m^2). \tag{14}$$

Inspection of Eq. (14) shows that ϕ varies from 0 to 1 as the interaction parameter varies in the finite temperature interval. This behavior is different from that of monodisperse diblock copolymer melts where there is only one temperature at which the transition between microphases with different symmetries takes place [2].

The resulting phase diagram of the system (Fig. 1) displays different types of phases: 0, isotropic; 1, lamellar; 3, hexagonal; and 6, bcc. We found no regions of the existence of the random wave structure which has a larger energy than that for regular wave structures. In the case of a symmetric copolymer, $f=1/2$, the lamellar phase appears by the third-order transition [the free energy of the ordered phase $F\sim(\chi_c-\chi)^3$]. The amplitude A_1 changes continuously from zero in the isotropic phase to a finite value in the lamellar microphase. Note the presence of two-phase ''windows'' on the phase diagram of the unsymmetrical copolymer, $f\neq1/2$, where different phases coexist each with other. For the first time the presence of such two-phase regions in polydisperse heteropolymers was predicted in Ref. [24]. Note also the broad domain of coexistence of the isotropic and bcc phases and relatively narrowness of the domain of coexistence of all other phases. More detailed information on the properties of

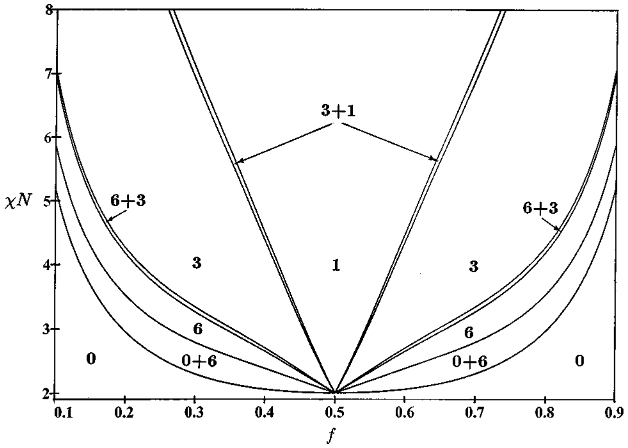

FIG. 1. Mean-field phase diagram of the melt of Markovian polyblock copolymers in variables $(\chi N - f)$, where χ is the interaction parameter, N is the average number of monomers per block, and f is the monomer fraction. The numbers alongside the curves indicate the different types of phases: 0, isotropic; 1, lamellar; 3, hexagonal; and 6, bcc.

the coexisting phases can be obtained from an investigation of the temperature dependence of their parameters—wave vector q and amplitudes A_i of superstructures. The dependence of the wave vector on the parameter χ in the case $f = 0.3$ is shown in Fig. 2 in variables $(q^2b^2N - \chi N)$. Vertical lines indicate the values of χ for the beginning and the end [$\phi = 0$ and $\phi = 1$, respectively—see Eq. (14)] of the corresponding transitions between various phases. Note that q increases continuously, with the rise of χ becoming of the order of the Gaussian block length for large χ. The dependences of amplitudes A_i for all phases on χ in the case $f = 0.3$ are shown in Fig. 3. In the single-phase regions amplitudes increase monotonically with χ and in the two-phase regions they are independent of χ and take two values A_n and A_m, corresponding to the two coexisting phases n and m. The volume fractions occupied by each phase are drawn in Fig. 4 as functions of the interaction parameter χ.

The influence of a variation of the monomer densities of coexisting phases on the phase diagram of *diblock* $(n_{bl} = 2)$ copolymers has been studied in Ref. [27] in the mean-field approach. We show in Appendix B that the variation of the average monomer density in each coexisting phase can be neglected in the case of polyblock copolymers with average molecular length $L \gg N$.

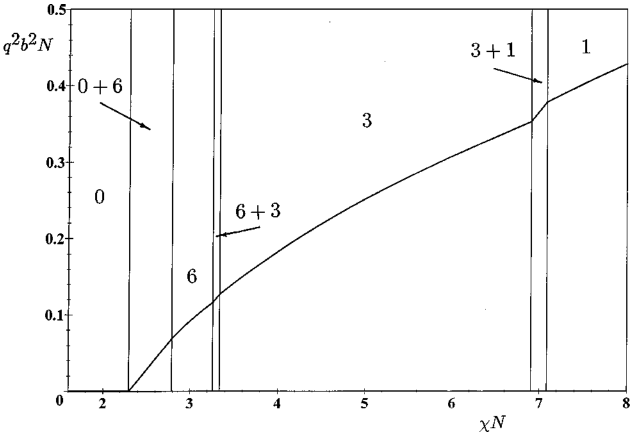

FIG. 2. Mean-field dependence of the wave vector q of periodic superlattice on the interaction parameter χ (temperature) for $f = 0.3$. The same designations as in Fig. 1.

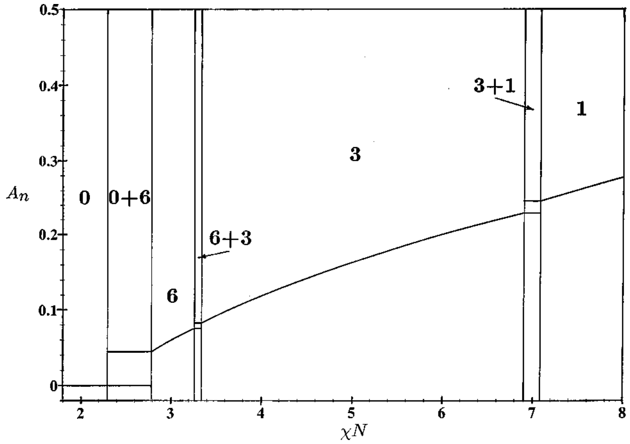

FIG. 3. Mean-field dependence of amplitudes A_n of superlattice on the interaction parameter χ for $f = 0.3$. The same designation as in Fig. 1.

III. FLUCTUATION THEORY

A. Brazovskiĭ approximation

We now discuss how the above mean-field picture of phase transitions is affected by fluctuations of the order parameter $\psi(\mathbf{r})$. In order to recast the functional (4) to the standard Brazovskiĭ form [25], we use the Hubbard-Stratonovich transformation which "splits" the quadratic nonlocal item at the expense of the introduction of "chemical potentials" μ_l of blocks with l monomers:

$$\frac{F[\mu,\psi]}{T\rho} = -V\int_0^\infty dl\,\frac{\mu_l^2}{4k} + \frac{1}{2}\int \frac{d^3\mathbf{q}}{(2\pi)^3}\,(\chi_c - \chi + \tau_q + a^2q^2)\,\psi_{\mathbf{q}}\psi_{-\mathbf{q}} - \frac{\lambda}{6}\int \delta\left(\sum_{i=1}^{3}\mathbf{q}_i\right)\prod_{i=1}^{3}\psi_{\mathbf{q}_i}\,\frac{d^3\mathbf{q}_i}{(2\pi)^3} + \frac{g}{24}\int \delta\left(\sum_{i=1}^{4}\mathbf{q}_i\right)\prod_{i=1}^{4}\psi_{\mathbf{q}_i}\,\frac{d^3\mathbf{q}_i}{(2\pi)^3},$$

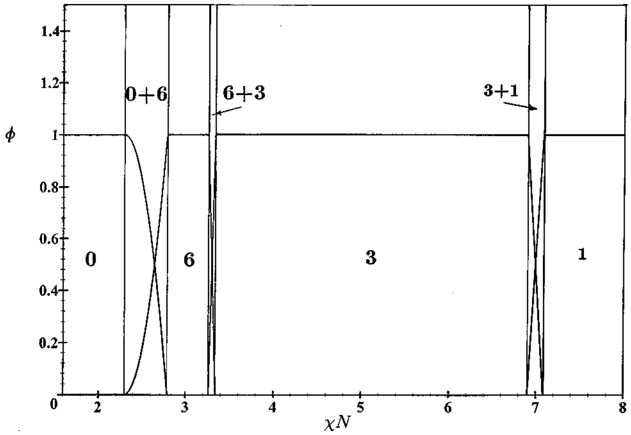

FIG. 4. Volume fractions ϕ occupied by each of the phases at $f = 0.3$. The same designations as in Fig. 1.

$$\tau_q \equiv \int_0^\infty dl\, \mu_l \exp(-a^2q^2l). \tag{15}$$

The fields μ_l do not fluctuate in the thermodynamic limit and can be found from the condition of minimization of the free energy (15).

We first examine single-phase states of the system. The thermodynamic average of the order parameter $\langle \psi(\mathbf{r}) \rangle$ vanishes in the isotropic phase and can be taken as the superposition of plane waves (6) in each microphase-separated phase. It is shown in Appendix B that we can neglect the zero Fourier component of the order parameter in this superposition and the fluctuating order parameter ψ can be written down in the form

$$\psi_{\mathbf{q}} = \frac{A_n}{\sqrt{n}} \sum_{k=1}^{n} [e^{i\varphi_k}\delta(\mathbf{q}-\mathbf{q}_k) + e^{-i\varphi_k}\delta(\mathbf{q}+\mathbf{q}_k)] + \delta\psi_{\mathbf{q}},$$

$$|\mathbf{q}_k| = q_0. \tag{16}$$

The function $\delta\psi_{\mathbf{q}}$ ($\langle \delta\psi_{\mathbf{q}} \rangle = 0$) describes fluctuations of the order parameter around its average value. Substituting Eq. (16) into Eq. (15) and integrating over $\delta\psi_{\mathbf{q}}$ using the one-loop approximation, we get the following expression for the free energy:

$$\frac{\mathcal{F}}{T\rho V} = -\int_0^\infty dl\, \frac{\mu_l^2}{4k} + F[\mu, A_n, G],$$

$$\begin{aligned} F[\mu, A_n, G] \equiv{}& \frac{1}{2} \int \frac{d^3q}{(2\pi)^3} (\chi_c - \chi + \tau_q + a^2q^2) \\ & \times [2(2\pi)^3 \delta(\mathbf{q}-\mathbf{q}_n) A_n^2 + a^3 G_q] - \lambda \alpha_n A_n^3/6 \\ & + \frac{g}{24} \left(\beta_n A_n^4 + 12 A_n^2 \int \frac{d^3(qa)}{(2\pi)^3} G_q \right. \\ & \left. + 3 \left[\int \frac{d^3(qa)}{(2\pi)^3} G_q \right]^2 \right) \\ & - \frac{1}{2} \int \frac{d^3(qa)}{(2\pi)^3} \ln G_q, \end{aligned} \tag{17}$$

where G_q is the correlation function of fluctuations, $\langle \delta\psi_{\mathbf{q}} \delta\psi_{\mathbf{q}'} \rangle = a^3 G_q \delta(\mathbf{q}+\mathbf{q}')$.

To describe the transition from the microphase n to the other one m, we write down the free energy of the two coexisting phases:

$$\begin{aligned} \frac{\mathcal{F}_{nm}}{T\rho V} ={}& -\int_0^\infty dl\, \frac{\mu_l^2}{4k} + \phi F[\mu, A_n, G_n] \\ & + (1-\phi) F[\mu, A_m, G_m]. \end{aligned} \tag{18}$$

Here ϕ and $1-\phi$ are volume fractions of phases n and m, respectively, and the free-energy functional F is defined by expression (17). If one of the coexisting phases (n) is isotropic, one has to substitute $A_{n=0} = q_{n=0} = 0$. Minimization of the free energy (18) with respect to parameters of both phases is performed in Appendix C. Before proceeding to the solution of Eqs. (C8) which define the dependence of parameters of the two-phase state on χ (see Appendix C), we will find the region of applicability of the mean-field approach. We first consider the transition from the isotropic phase with $A_{n=0} = 0$ to the microphase m with $A_m \neq 0$ and $1-\phi \ll 1$. It is easy to check that Eqs. (C8) turn to the mean-field equations (Appendix A) for

$$(1-\phi) A_m^2 \gg a^2 q_0^2 r_n^{-1/2}. \tag{19}$$

Substituting the mean-field estimation $A_m \sim \lambda/g$ for the amplitude of the microphase in the two-phase region we get $q_0^4 a^4 \sim (1-\phi) k A_m^2$, $r_n \sim \lambda^2/g$, and the inequality (19) can be recast in the form

$$(1-2f)^4 N (1-\phi) \gg 1. \tag{20}$$

For $N \gg 1$ the mean-field approximation remains valid for those values of f which lay far enough from the critical point value $f_c = 1/2$. A similar estimation can be carried out for the transitions from one microphase, $A_n \neq 0$, to another one, $A_m \neq 0$. Now we have $q_0^4 a^4 \sim k A_n^2$ and the condition of applicability of the mean-field approach, $A_n^2 \gg a^2 q_0^2 r_n^{-1/2}$, can be written as

$$(1-2f)^4 N \gg 1. \tag{21}$$

Inspection of inequalities (20) and (21) shows that the region of applicability of the mean field for the transition between two microphases is wider than that for the transition from the isotropic phase to a microphase. In each of these cases the fluctuations are only important in the interval $1/2 - f_G < f < 1/2 + f_G$. The value $f_G \sim N^{-1/4}$ plays the role of the Ginzburg parameter and it is small for large values of N.

B. Two-phase state of symmetric copolymers

In the case of the symmetric copolymer, $f = 1/2$, the account of fluctuations of the order parameter changes the mean-field picture of the third-order phase transition. First of all (see Appendix D for details) the continuous transition is replaced by the sequence of first-order transitions and the single-phase state of the system can exist only in the cases $\chi < \chi^{(0)}$ and $\chi > \chi^{(1)}$, where the parameters $\chi^{(0)}$ and $\chi^{(1)}$ are defined by

$$\chi^{(0)} N = 2 + 2.78 N^{-1/4} + 2.35 N^{-1/2},$$

$$\chi^{(1)} N = 2 + 3.58 N^{-1/4} + 2.74 N^{-1/2}. \tag{22}$$

The case $\chi < \chi^{(0)}$ corresponds to the isotropic phase, and $\chi > \chi^{(1)}$ to the lamellar one. In the intermediate region $\chi^{(0)} < \chi < \chi^{(1)}$ these phases coexist with each other. We find that the energy of the lamellar phase is always smaller than the energy of the hexagonal phase, and equations of the two-phase state, Eqs. (C8), have no solution for the bcc and for the random wave structure. In the transition point $\chi = \chi^{(0)}$, from the isotropic phase to the two-phase state the amplitude A_1 jumps from zero up to the value

$$A_1^{(0)} = 0.35 (k/g)^{1/4} = 0.32 N^{-1/4}. \tag{23}$$

In the coexistence region $\chi^{(0)} < \chi < \chi^{(1)}$ the amplitude A_1 increases monotonically with χ up to the value

$$A_1^{(1)}=0.38(k/g)^{1/4}=0.35N^{-1/4}. \qquad (24)$$

In contrast to the mean-field picture of the phase transition from the isotropic to the lamellar phase, which takes place for zero wave vector $q_0=0$, fluctuations lead to the appearance of the microphase with finite period $D=2\pi/q_0$. In the corresponding transition points $\chi^{(0)}$ and $\chi^{(1)}$, the wave vectors are (see Appendix D)

$$bq_0^{(0)}=0.25(k^3/g)^{1/8}=0.48N^{-5/8},$$

$$bq_0^{(1)}=0.29(k^3/g)^{1/8}=0.55N^{-5/8}. \qquad (25)$$

Note that the period of the appearing microstructure $D\approx bN^{5/8}$ exceeds the average Gaussian size of the block, which is a consequence of the polydispersity of the system under consideration. This result was first predicted in Ref. [17]. Remember that in the theory of monodisperse copolymers [2,26] the period does not depend on the Flory parameter χ and near the transition point $D\approx bN^{1/2}$. In our polydisperse system the wave vector q_0 of the density fluctuations in the isotropic phase does not vanish and strongly depends on the temperature. In approaching the transition point to the microphase the spatial scale of the fluctuation $R\sim 1/q_0$ in the isotropic phase decreases (it is ''tuned up'' to the period of microphase) and it becomes of the order of the period of the superstructure in the very transition point. The arising droplet of the ordered phase in the isotropic phase (the so-called crystallite island in the polymer liquids) is in equilibrium; i.e., it exists in the finite temperature interval $\chi^{(0)}<\chi<\chi^{(1)}$ and occupies a macroscopic fraction ϕ of the system. The volume of this droplet grows with χ until the crystal phase occupies the whole volume of the system.

The mean-field picture of the phase transition is reproduced if one takes the limit $N\rightarrow\infty$, $\chi N=\text{const}$. The region of the coexistence of different phases disappears in this limit and the transition to the lamellar phase takes place on the spinodal $\chi_c N=2$ [Eq. (22)]. Such a transition becomes continuous, since the amplitude of the ordered phase, Eqs. (23) and (24), vanishes in the transition point.

Note that the renormalized susceptibility $1/r$ diverges in the random microphase [see first equation of Eqs. (C8) with $\alpha_\infty=0$ and $\beta_\infty=12$, Eq. (9)]. This means that the composition fluctuations prevent the formation of such a random wave structure.

C. Phase diagram

To construct a complete phase diagram, where both transitions from the isotropic phase to microphases and transitions between different microphases are taken into account, we should not restrict our attention to only Eq. (C8) of two-phase states. It is shown in Appendix E that there are also lines on the phase diagram where one of the two coexisting phases changes its symmetry.

The phase diagram of the random copolymer with an average number of monomers in the block $N=100$ is shown in Fig. 5. In contrast to the mean-field phase diagram, Fig. 1, where for $f\neq 1/2$ the isotropic phase can undergo only the transition to bcc structure, direct ''windows'' of transitions from the isotropic to the lamellar and also to the hexagonal phases appear on the fluctuation phase diagram. Such a picture of transitions resembles that for monodisperse copolymers [26], where similar ''windows'' of direct transitions to lamellar and hexagonal phases exist. However, the region of stability of the two-phase states always takes precedence for the appearance of each of the crystal phases for random copolymers. Note that the coexisting *isotropic and lamellar* and *isotropic and hexagonal* phases are absent in the mean-field phase diagram. For rather long blocks $N\geqslant 10^4$ the size of these two-phase regions $\Delta\chi N\sim N^{-1/4}$, $\Delta f\sim N^{-1/4}$ becomes smaller than the size $\Delta\chi N\sim 1$, $\Delta f\sim 1$ of the other coexisting phases and in the limit $N\rightarrow\infty$ the two-phase regions shrink to the point ($f=1/2$, $\chi N=2$) on the phase diagram.

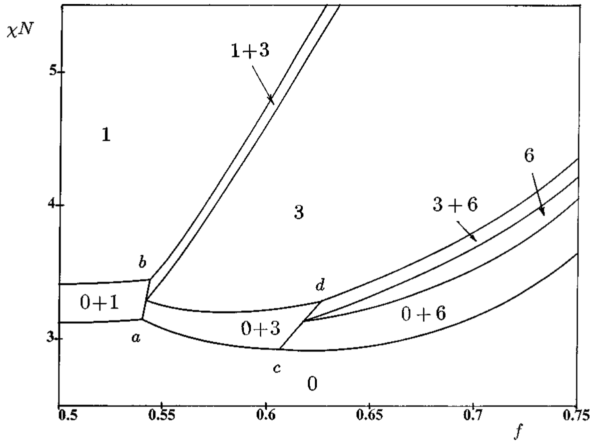

FIG. 5. Fluctuation phase diagram of the melt of Markovian polyblock copolymers with an average number of block monomers $N=100$; (ab) and (cd) are the three phase lines, and other designations are the same as in Fig. 1.

One of the tree phase lines, ab, is defined by the equation (see Appendix E)

$$\chi N=\chi_e N+297N(\lambda^6/g^5)^{1/2}+6.4N\lambda^2/g. \qquad (26)$$

When crossing this line the transition can be observed either from the hexagonal to lamellar phase at the presence of the isotropic phase, or from the hexagonal to isotropic phase at the presence of the lamellar phase (see Fig. 6), depending on the composition f on this line. The values of the monomer fraction f for each of the coexisting phases on the tree phase line are defined by the equation

$$2.6+\phi_1+0.47\phi_3=7267\lambda^4/g^3k. \qquad (27)$$

Here ϕ_1 and ϕ_3 are volume fractions of the lamellar and the hexagonal phases (the volume fraction of the isotropic phase is $\phi_0=1-\phi_1-\phi_3$). This line begins at the point $\phi_1=\phi_3=0$, where there is only an isotropic phase, and ends at the point $\phi_1=1$. For intermediate values of f, Eq. (27) defines the value of the jump of the volume fraction of those phases which change their symmetry; see Fig. 6. Similar equations are found for the second three-phase line cd.

The fluctuation region increases with the decrease of the block length N and, therefore, regions of coexistence of isotropic and lamellar as well as of isotropic and hexagonal phases become larger.

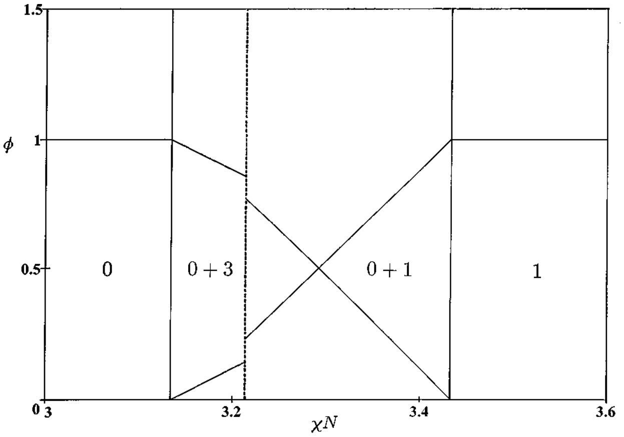

FIG. 6. Temperature dependence of the volume fraction ϕ of phases for the case $N=100$ and $f=0.542$ [corresponding to the crossing of the three-phase line (ab) on the phase diagram, Fig. 5].

IV. DISCUSSION

We have shown that the account of the possibility of the coexistence of phases with different symmetry of the superlattice significantly changes the phase diagram of the system with respect to studies [9] where this effect had not been taken into consideration. We have shown in the self-consistent field approximation that as the temperature is varied, the melt of polyblock copolymers undergoes a succession of first-order transitions into microphase-separated states with a wave vector of finite amplitude, which varies continuously from zero to the characteristic block length $aN^{1/2}$; see Fig. 2. Note that a similar conclusion in Refs. [6,23] has been made on the assumption of a third-order phase transition from the isotropic state to the microstructure. This microphase state actually corresponds to metastable conditions and the corresponding transition describes spinodal decomposition of the isotropic state. It is readily shown that the free energy of two-phase states lies below the free energy of the above single-phase state. Consequently, a thermodynamic transition with the formation of a microphase-separated phase takes place through the formation of an equilibrium droplet of a new phase in the old one. The volume of this droplet grows with the increase of the interaction parameter χ until the new phase occupies the entire volume of the system; see Fig. 4. We therefore have a finite temperature interval in which both phases coexist.

We have shown that in the mean-field approximation the random wave structure has a higher energy than the regular wave structures. Based on such a mean-field picture we can expect that this structure can be observed at least as a metastable state. However, our study (see Sec. III C) shows that thermodynamic fluctuations prevent the formation of this random microstructure.

Note that from the standpoint of the general theory of phase transitions a melt of Markovian copolymers is the system with the frozen-in or ''quenched'' randomness. It is well known that in the case of solids having a random distribution of interactions that is fixed in three-dimensional space, such systems exhibit a localization or nonergodic glass type of behavior. A fundamental distinction of polymer systems is the fact that only a one-dimensional sequence of monomers along the chain is random, whereas the chain can assume arbitrary spatial conformations and it can be located in any region of the space occupied by the system. The presence of such translational invariance leads to the possibility of the formation of regular three-dimensional structure in polymers with a random sequence of monomers along the chain. We shall not discuss here the effect of the usual thermodynamic fluctuations, which lead to the breakdown of long-range crystal ordering on large scales, similar to liquid crystal systems [28].

Finally, we should comment on the accuracy of the approximations used. Expression (4) for the free energy is written in the ''infinitely long chain'' approximation, when the characteristic wave vector $q \gg 1/(bL^{1/2})$, where L is the average number of monomers in the molecule. For finite L the curve in Fig. 2 will not begin with $q=0$ but with finite $q_{\rm min} \approx 1/(bL^{1/2})$. In our situation of a large number of blocks, $n_{\rm bl}=L/N$ per one chain, we can disregard this finite-size effect. The finiteness of the chain lengths can also be essential for the study of the effects of macrophase separation. We can estimate the variation of densities in coexisting macrophases as $\Delta\rho_A \approx (\rho/L)(Nn_{\rm bl}^{1/2}) = \rho/n_{\rm bl}^{1/2}$, where ρ/L is the chain concentration and $Nn_{\rm bl}^{1/2}$ is the dispersion of the number of monomers of a given type. For small $n_{\rm bl}$ and a large interaction parameter χ the macrophase separation becomes favorable; in the opposite limit of large $n_{\rm bl} \gg 1$ the variation of the density of two (or more) coexisting phases can be disregarded.

In deriving the free-energy expression (4) we have also disregarded the dependence of λ and g on the wave vectors. This approximation is admissible because in the region of validity of the Landau expansion (4) typical values of the wave vector of the superstructure are small in comparison with the reciprocal Gaussian block length. When developing the fluctuation theory in the Brazovskiĭ approximation (Sec. III A) we expected that the correlation function G_{nq}, Eq. (C6), has a sharp maximum $(cq_0^2 \gg r_n)$ in the point $q=q_0$. It is shown in Appendix D that this approximation is valid only for rather large values of $N \gg 1$ since we have $r_n/cq_0^2 \sim 1/N^{1/4}$.

Our general expression (4) used for the free-energy functional is not bound to any specific choice of model of Markovian copolymers, for which the parameters of the Ginzburg-Landau functional are given by expressions (5). Consequently, the main results of the present study remain valid for a multiblock copolymer of arbitrary structure.

We now discuss the possibility of experimental verification of our theory. The most interesting observation is the existence of two-phase regions and three-phase lines on the phase diagram of a random multiblock copolymer. The symmetry of one of the coexisting phases changes when crossing the lines ab and cd in Fig. 5. The volume fractions of the phases undergo jumps on these lines. For a copolymer with $N=100$ the width of the region, where such an effect can be observed (line cd), is about $\Delta f \approx 0.02$. The next type of experiments which can confirm the predictions of our fluctuation theory are neutron scattering experiments on the isotropic phase near the transition point. The intensity of density fluctuations, G_{0q}, reaches its maximum in the point of the first-order transition. For a symmetric copolymer it is estimated in Appendix D:

$$(G_{0q_0})_{\max}=1/r_0=83.8N^{3/2}. \tag{28}$$

This dependence can be checked using copolymers with different average lengths of blocks.

ACKNOWLEDGMENTS

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APPENDIX A: MINIMIZATION OF THE MEAN-FIELD FREE ENERGY

We minimize the free energy (12) with respect to the parameters of both coexisting phases n and m. In the event of a transition from the isotropic phase with $n=0$ we have $q_0=0$, $A_0=0$, and the value of the wave vector in the new microphase m is given by the expression

$$q_m^4=k(1-\phi)A_m^2/(2a^4). \tag{A1}$$

The amplitude A_m and the dependence of the volume fraction ϕ of the isotropic phase on χ are given by

$$A_m=2\frac{\lambda\alpha_m}{g\beta_m}, \quad \chi=\chi_c+3\sqrt{2k(1-\phi)}\,\frac{\lambda\alpha_m}{g\beta_m}-\frac{\lambda^2\alpha_m^2}{6g\beta_m}. \tag{A2}$$

The beginning and end of the phase transitions from the isotropic phase to the microstructure correspond to the values $\phi=1$ and $\phi=0$, respectively. It is easy to show that the bcc microphase is favorable at such a transition.

We now turn to consider the case of a transition between two microphases $n\neq 0$ and $m\neq 0$. Minimization of the free energy with respect to wave vectors q_n and q_m gives

$$\frac{k\phi A_n^2}{2a^4q_n^4}+\frac{2k(1-\phi)A_m^2}{a^4(q_n^2+q_m^2)^2}=1,$$

$$\frac{k(1-\phi)A_m^2}{2a^4q_m^4}+\frac{2k\phi A_n^2}{a^4(q_n^2+q_m^2)^2}=1. \tag{A3}$$

A solution of these equations is readily found:

$$q^4\equiv q_n^4=q_m^4=k[\phi A_n^2+(1-\phi)A_m^2]/(2a^4). \tag{A4}$$

Note that Eq. (A1) can be regarded as a special case of Eq. (A4) since $A_0=0$ in the isotropic phase. Keeping in mind the equality of the wave vectors in the coexisting phases with $n\neq 0$ and $m\neq 0$ along with Eq. (A4), the conditions for the minimum of the free energy (4) with respect to A_i, $i=n,m$ assume the form

$$2(\chi-\chi_c+3a^2q^2)-\lambda\alpha_iA_i/2+g\beta_iA_i^2/6=0 \tag{A5}$$

and the minimization of the free energy with respect to ϕ gives the equation

$$\begin{aligned}(\chi-\chi_c+3a^2q^2)A_n^2-\lambda\alpha_nA_n^3/6+g\beta_nA_n^4/24\\ =(\chi-\chi_c+3a^2q^2)A_m^2-\lambda\alpha_mA_m^3/6+g\beta_mA_m^4/24.\end{aligned} \tag{A6}$$

Substituting the combination $\chi-\chi_c+3a^2q^2$ from the two equations (A5) into the right and left hand sides of Eq. (A6), we find equations for amplitudes A_n and A_m:

$$-3\lambda\alpha_nA_n+g\beta_nA_n^2=-3\lambda\alpha_mA_m+g\beta_mA_m^2,$$

$$-2\lambda\alpha_nA_n^3+g\beta_nA_n^4=-2\lambda\alpha_mA_m^3+g\beta_mA_m^4. \tag{A7}$$

The most important consequence of these equations is the fact that neither of the amplitudes depends on ϕ and χ. We arrive at the conclusion that the amplitudes of the two coexisting phases do not vary with the temperature. Equations (A7) can be solved if one introduces the new variables $A_n=xA_m$:

$$A_m=3\frac{\lambda}{g}\frac{\alpha_nx-\alpha_m}{\beta_nx^2-\beta_m}, \tag{A8}$$

$$2(\alpha_nx^3-\alpha_m)(\beta_nx^2-\beta_m)=3(\alpha_nx-\alpha_m)(\beta_nx^4-\beta_m). \tag{A9}$$

In the case of a transition from the lamellar to the hexagonal phase, $\alpha_1=0$, and the solution of Eqs. (A8) and (A9) can be found analytically:

$$A_1=\frac{\lambda\alpha_3}{g\beta_3}\left[\frac{15}{2}(7+3\sqrt{6})\right]^{1/2}\simeq 10.37\frac{\lambda\alpha_3}{g\beta_3},$$

$$A_3=\frac{\lambda\alpha_3}{g\beta_3}\left(6+\frac{3}{2}\sqrt{6}\right)^{1/2}\simeq 9.67\frac{\lambda\alpha_3}{g\beta_3}. \tag{A10}$$

The amplitudes A_3 and A_6 for the transition from the hexagonal to the cubic phase can be found by solving Eqs. (A8) and (A9) numerically:

$$A_3\simeq 3.48\lambda\alpha_3/(g\beta_3), \quad A_6\simeq 3.17\lambda\alpha_3/(g\beta_3). \tag{A11}$$

Solving the second equation of Eq. (A5) with respect to q we find the temperature dependence of the wave vector of the superstructure: see expression (13) in Sec. III. Expression (14), which together with Eq. (13) describes the dependence of the volume fraction ϕ on χ, is determined by solving Eq. (A4) with respect to ϕ.

APPENDIX B: ESTIMATION OF CHANGE OF THE AVERAGE DENSITY IN COEXISTING PHASES

We now demonstrate that the variation of the average density in coexisting phases can be ignored for polymer molecules containing a large number of blocks, $n_{\mathrm{bl}}=L/N\gg 1$. To describe such a variation of the density on macroscopic scales it is necessary to include the zeroth harmonic in the expansion of the order parameter (6) in each phase:

$$\psi_{\mathbf{q}}|_n=\Delta_n\delta(\mathbf{q})+\frac{A_n}{\sqrt{n}}\sum_{k=1}^{n}[\delta(\mathbf{q}-\mathbf{q}_k)+\delta(\mathbf{q}+\mathbf{q}_k)]. \tag{B1}$$

The amplitudes Δ_n and Δ_m determine the variation of the average density in each of the coexisting phases n and m and they are related by the condition of invariance of the total number of molecules,

$$\phi\Delta_n+(1-\phi)\Delta_m=0, \tag{B2}$$

which allows one to parametrize these amplitudes with a single parameter Δ:

$$\Delta_n=(1-\phi)\Delta, \quad \Delta_m=-\phi\Delta. \tag{B3}$$

Here ϕ and $1-\phi$ are the volume fractions occupied by phases n and m, respectively. The account of the finiteness of the length of the polymer chain ‘‘removes’’ the singularity of the nonlocal term in the free energy (4) for zero wave vector $\mathbf{q}=0$ (see Sec. II and Ref. [7]). Consequently, substituting the order parameter for each of the coexisting phases in the form (B1) and (B3) into the functional (4), we get the expression for the free energy of the two-phase system:

$$\mathcal{F}_{nm}/TV=F_{nm}+\delta F(\Delta), \quad F_{nm}\equiv\mathcal{F}_{nm}/TV|_{L\to\infty},$$

$$\delta F(\Delta)=-\lambda\phi(1-\phi)(A_n^2-A_m^2)\Delta+\frac{k}{4}\,\frac{\phi^2(1-\phi)^2\Delta^4}{a^2q_{\min}^2}+\cdots, \tag{B4}$$

where the free energy F_{nm} in the limit $L\to\infty$ is calculated in Eq. (12), $q_{\min}^2=1/(b^2L)$, and the expansion of δF is written in the principal approximation with respect to Δ and L. Minimizing δF with respect to Δ and using expression (A4) for q (Appendix A), we obtain the estimates

$$F_{nm}\sim k^{1/2}[\phi A_n^2+(1-\phi)A_m^2]^{3/2},$$

$$\delta F\sim(Lk)^{-1/3}\lambda^{4/3}[\phi(1-\phi)]^{2/3}|A_n^2-A_m^2|^{4/3}. \tag{B5}$$

The variation of the average density in the coexisting phases can be ignored if the following inequality holds:

$$F_{nm}\gg\delta F. \tag{B6}$$

For a transition from the isotropic phase to the microphase we have to set $A_n=0$, $A_m\approx\lambda/g$, and $1-\phi\ll 1$. Inequality (B6) therefore takes the form

$$1-\phi\gg(N/L)^{2/5}|1-2f|^{6/5}. \tag{B7}$$

In the limit of infinitely long molecules inequality (B7) is always satisfied, and the variation of the average density in this limit can be ignored. In the transition from one microphase (n) to another one (m), inequality (B6) takes the form

$$1-\phi\ll(L/N)^{1/2}|1-2f|^{-3/2}, \tag{B8}$$

and is always satisfied for sufficiently long molecules (with $L\gg N$).

APPENDIX C: EQUATIONS OF THE TWO-PHASE STATE

Minimizing the fluctuation free energy of the two-phase state (18) with respect to wave vectors q_i, amplitudes A_i, ϕ, and functions μ_l and G_{iq} of the microphases $i=n,m$ we get

$$q\equiv q_n=q_m, \quad \int_0^\infty dl\; l\mu_l\exp(-a^2q^2l)=1, \tag{C1}$$

$$\chi_c-\chi+\tau_q+a^2q^2-\frac{\lambda\alpha_i}{4}A_i+\frac{g\beta_i}{12}A_i^2+\frac{g}{2}\int\frac{d^3(q'a)}{(2\pi)^3}G_{iq'}=0, \tag{C2}$$

$$F[\mu,A_n,G_n]=F[\mu,A_m,G_m], \tag{C3}$$

$$\begin{aligned}\mu_l/k={}&2[\phi A_n^2+(1-\phi)A_m^2]\exp(-a^2q^2l)\\&+\int\frac{d^3(q'a)}{(2\pi)^3}[\phi G_{nq'}+(1-\phi)G_{mq'}]\\&\times\exp[-a^2(q')^2l],\end{aligned} \tag{C4}$$

$$G_{iq}^{-1}=\chi_c-\chi+\tau_q+a^2q^2+gA_i^2+\frac{g}{2}\int\frac{d^3(q'a)}{(2\pi)^3}G_{iq'}. \tag{C5}$$

Inspection of Eq. (C5) shows that the functions G_{iq}^{-1} can be taken in the Brazovskiĭ form [25]

$$G_{iq}^{-1}=r_i+c(q-q_0)^2, \tag{C6}$$

where the parameters r_i, q_0, and c are defined by

$$r_i=G_{iq}^{-1}|_{q=q_0}, \quad \left.\frac{\partial G_{iq}^{-1}}{\partial q}\right|_{q=q_0}=0, \quad c=\frac{1}{2}\left.\frac{\partial^2G_{iq}^{-1}}{\partial q^2}\right|_{q=q_0}. \tag{C7}$$

The above statement (C6) is valid only if the function G_{iq} has a sharp maximum at the point $q=q_0$, when the condition $cq_0^2\gg r_i$ is satisfied. Substituting correlation functions in the form (C6) into Eqs. (C1)–(C5) and taking into account Eqs. (C7), we arrive at the following algebraic equations:

$$r_i=\lambda\alpha_iA_i/4+g(1-\beta_i/12)A_i^2, \quad i=n,m,$$

$$r_n-r_m=g(A_n^2-A_m^2)+g\sigma a^2q_0^2(r_n^{-1/2}-r_m^{-1/2})/2,$$

$$\chi-\chi_c=3a^2q_0^2-\lambda\alpha_nA_n/4+g\beta_nA_n^2/12+g\sigma a^2q_0^2r_n^{-1/2}/2,$$

$$\begin{aligned}4a^4q_0^4/k={}&\phi(2A_n^2+\sigma a^2q_0^2r_n^{-1/2})\\&+(1-\phi)(2A_m^2+\sigma a^2q_0^2r_m^{-1/2}),\end{aligned}$$

$$\begin{aligned}&(r_n^2-r_m^2)/g+\sigma a^2q_0^2(r_n^{1/2}-r_m^{1/2})\\&\quad=\lambda(\alpha_nA_n^3-\alpha_mA_m^3)/3+g[(1-\beta_n/12)A_n^4\\&\qquad-(1-\beta_m/12)A_m^4],\end{aligned} \tag{C8}$$

where the numerical coefficient $\sigma=1/2\pi\sqrt{2}$ and all integrals of the functions G_{iq} and G_{mq} are calculated in the principal approximation in the small parameter r_i/cq_0^2.

APPENDIX D: COEXISTENCE OF THE ISOTROPIC AND LAMELLAR PHASES

Analytical solution of Eqs. (C8) can be found in the case of coexisting isotropic and lamellar phases with $\alpha_1=0$. Introducing the new dimensionless variables p_n, a_n, and Q by the equations

$$r_n = p_n(kg)^{1/2}, \quad A_n = a_n(k/g)^{1/4}, \quad a^2 q_0^2 = Q(k^3/g)^{1/4}, \tag{D1}$$

we get the following equations:

$$\begin{gathered} p_1 = a_1^2/2, \\ p_1 - p_0 = a_1^2 + (\sigma Q/2)(p_1^{-1/2} - p_0^{-1/2}), \\ p_1^2 - p_0^2 + \sigma Q(p_1^{1/2} - p_0^{1/2}) = a_1^4/2, \\ 4Q^2 = \phi(2a_1^2 + \sigma Q p_1^{-1/2}) + (1-\phi)\sigma Q p_0^{-1/2}. \end{gathered} \tag{D2}$$

Note that they do not depend on the monomer fraction f. The temperature dependence of the volume fraction ϕ of the lamellar phase is defined by the equation

$$\chi - \chi_c = 3Q(k^3/g)^{1/4} + (gk)^{1/2}(a_1^2 + \sigma Q p_1^{-1/2})/2. \tag{D3}$$

Excluding a_1 from Eqs. (D2) and introducing the new variable $z = p_1/p_0$, we get the following dependence of the parameters of coexisting phases on the volume fraction ϕ:

$$\begin{gathered} p_0 = \frac{\sigma}{2}\,\frac{z^{1/2}-1}{z^2+1}\left[\frac{z^2+1}{z^{1/2}-1} + 2\phi(z-1)\right]^{1/2}, \\ Q = \frac{p_0^{3/2}}{\sigma}\,\frac{z^2+1}{z^{1/2}-1}, \quad a_1 = \sqrt{2zp_0}, \end{gathered} \tag{D4}$$

where $z \approx 5.27$ is the root of the equation $2\sqrt{z}(1+z) = 1 + z^2$.

The value of χ, corresponding to the appearance of the lamellar phase of the infinitesimally small (but macroscopic) volume, $\phi \to 0$, is determined from Eq. (D3) taking into account Eqs. (D4),

$$\chi^{(0)} = \chi_c + 0.77(k^3/g)^{1/4} + 0.12(gk)^{1/2}, \tag{D5}$$

and for the symmetric copolymer, $f = 1/2$, we get

$$\chi^{(0)}N = 2 + 2.78N^{-1/4} + 2.35N^{-1/2}. \tag{D6}$$

The lamellar phase is extended to the whole volume of the sample, $\phi \to 1$, at

$$\chi^{(1)} = \chi_c + 0.99(k^3/g)^{1/4} + 0.14(gk)^{1/2}. \tag{D7}$$

This condition for the symmetric copolymer looks like

$$\chi^{(1)}N = 2 + 3.58N^{-1/4} + 2.74N^{-1/2}. \tag{D8}$$

APPENDIX E: THREE-PHASE LINE (*ab*) ON THE PHASE DIAGRAM

To find the line on the phase diagram (Fig. 5), where one of the two coexisting phases changes its symmetry, we write down the free energy of the three-phase state:

$$\frac{\mathcal{F}_{123}}{T\rho V} = -\int_0^\infty dl\,\frac{\mu_l^2}{4k} + \phi_1 F[\mu, A_1, G_1] + \phi_3 F[\mu, A_3, G_3] + (1-\phi_1-\phi_3)F[\mu, 0, G_0]. \tag{E1}$$

Here ϕ_1 and ϕ_3 are the volume fractions of the lamellar and the hexagonal phases (the fraction of the isotropic phase is $\phi_0 = 1 - \phi_1 - \phi_3$), and the free energy F is defined in Eq. (17). The minimization of this free energy with respect to the amplitudes A_i, wave vectors q_i, volume fractions ϕ_i, and functions G_i of the coexisting phases and the chemical potentials μ_l is similar to that for the two-phase state. We find that the wave vectors for all the phases coincide and the functions G_i reach their maximum on the same wave vector. Taking these functions in the Brazovskiĭ form (C6) and introducing the variables (D1), we get the following equations:

$$\begin{gathered} p_1 = a_1^2/2, \quad p_3 = \omega\alpha_3 a_3/4 + a_3^2/6, \\ p_1 - p_0 = a_1^2 + (\sigma Q/2)(p_1^{-1/2} - p_0^{-1/2}), \\ p_3 - p_0 = a_3^2 + (\sigma Q/2)(p_3^{-1/2} - p_0^{-1/2}), \\ p_1^2 - p_0^2 + \sigma Q(p_1^{1/2} - p_0^{1/2}) = a_1^4/2, \\ p_3^2 - p_0^2 + \sigma Q(p_3^{1/2} - p_0^{1/2}) = \omega\alpha_3 a_3^3/3 + a_3^4/6, \\ 4Q^2 = \phi_1(2a_1^2 + \sigma Q p_1^{-1/2}) + \phi_3(2a_3^2 + \sigma Q p_3^{-1/2}) \\ + (1-\phi_1-\phi_3)\sigma Q p_0^{-1/2}. \end{gathered} \tag{E2}$$

Here the only factor $\omega = \lambda/(g^3 k)^{1/4}$ depends on the monomer fraction f, $\alpha_3 = 4/\sqrt{3}$, and the dependence of the interaction parameter χ on f looks like

$$\chi - \chi_c = 3Q(k^3/g)^{1/4} + (gk)^{1/2}(a_1^2 + \sigma Q p_1^{-1/2})/2. \tag{E3}$$

It is convenient to introduce the new variables $z = p_1/p_0$ and $w = p_3/p_0$. Then from Eqs. (E2) and (E3) we can find the parameters of all the phases and the transition temperature as the functions of the monomer fraction f,

$$\begin{gathered} p_0 = \frac{\omega^2\alpha_3^2[w - 1 + u(1 - w^{-1/2})/2]}{16(w - [w - 1 + u(1 - w^{-1/2})/2]/6)^2}, \\ Q = p_0^{3/2}u/\sigma, \quad u = (z^2+1)/(z^{1/2}-1), \\ a_3^2 = p_0[w - 1 + u(1 - w^{-1/2})/2], \\ \chi - \chi_c = 3\left(\frac{k^3}{g}\right)^{1/4}\frac{p_0^{3/2}u}{\sigma} + (gk)^{1/2}p_0\,\frac{z^{3/2}+1}{z^{1/2}-1}, \end{gathered} \tag{E4}$$

and also the jump of the volume fraction:

$$p_0 = \frac{\sigma}{2u}\,[u + 2\phi_1(z-1) + 2\phi_3(w-1)]^{1/2}. \tag{E5}$$

The variables z and w are defined by the equations

$$\begin{gathered} 2\sqrt{z}(1+z) = 1 + z^2, \\ [u(1 - w^{-1/2})/2 - 11w - 1]^2 = 18[7w^2 + 1 - u(w^{1/2} - 1)], \end{gathered} \tag{E6}$$

the numerical solution of which gives $z \approx 5.27$, $w \approx 2.99$.

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