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Theory of Polydisperse Multiblock Copolymers

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ABSTRACT: We study the self-organization of a polydisperse A−B multiblock copolymer melt with repulsive interactions between the different monomers. In the framework of the one-loop (Hartree) approximation we consider the influence of the polydispersity parameter u, which is the ratio of the first two moments of the block length distribution $u = (\langle l^2 \rangle / \langle l \rangle^2) - 1$, on the condition for the order−disorder transition. At low polydispersity ($u < 0.3$) the system undergoes the ordinary block copolymer microphase separation transition. The value of the Flory parameter χ on the line of the order−disorder transition increases with increasing polydispersity of the system. The transition to macrophase separation at the classical Lifshitz point $u = 0.5$ is precluded by a fluctuation-induced instability of the homogeneous state with respect to finite-wavelength composition fluctuations. The characteristic length scale L of these critical fluctuations above the microphase separation transition and the period of the domain structure below changes weakly with temperature as $((T - T_c)/T_c)^{-1/6}$. In the case of an exponential block length distribution ($u \approx 1$), the period of the domain structure exhibits stronger temperature dependence $L \approx ((T - T_c)/T_c)^{-1/4}$ than that derived for this system near the Lifshitz point due to strong coupling between composition fluctuations. For values of the polydispersity parameter $u > 0.4$ the value of the Flory parameter on the line of the first-order order-disorder phase transition decreases with increasing polydispersity of the system.

1. Introduction

Numerous theoretical studies in past years have been devoted to the problem of copolymers. Copolymers are macromolecules consisting of two or more different monomer units or monomer blocks *randomly or regularly* distributed along the polymer chain. The interest was stimulated not only by the unique theoretical properties of these polymer systems but also by their broad technological applications.[1−3]

The simplest example of copolymers is diblock copolymers $A_n B_m$ that consist of two different A and B blocks with n and m monomers in the blocks, respectively, with repulsive interactions between A and B monomers. The homogeneous state of this system is unstable with respect to composition fluctuations with finite wavenumber q_0 that result in microphase separation transition below the critical temperature T_c.[4−9] This instability is due to a competition between two effects: a short-range monomer−monomer interaction that tends to reduce the number of unfavorable contacts between A and B monomers and a long-range entropic effect induced by the presence of chemical bonds linking A and B blocks together. As a result of this competition a periodic domain structure appears below the transition point. Similar behavior is demonstrated by other copolymers, such as triblock and trigraft,[10,11] star-like,[11,12] and multiblock[11,13] and multicomb copolymers.[11] Although the conditions of phase transitions between phases with different types of symmetry of domain structures change from system to system and depend on the chemical structure of macromolecules (how A and B blocks are connected into copolymer macromolecules) the topological structure of the phase diagram does not change.[4−13] There are regions on the phase diagram with one-dimensional lamellar, two-dimensional hexagonally closed-packed cylinders, three-dimensional body-centered cubic, and ordered-bicontinuous phases.

A very interesting question is how defects (frustrations) of the chemical structure change the phase behavior of copolymer systems. The answer to this question is very important, because copolymers are produced by a polymerization reaction[14] that is a random process and, as any random process results in a distribution of macromolecules according to their chemical structure.[14] The width of the distribution depends on polymerization reaction constants. It was shown by de Gennes[15] that the phase behavior of a copolymer system depends essentially on the correlation between location of monomers along the chain. He studied how the stability of A-B multiblock copolymer melt depends on the degree of chemical disorder. When all blocks have the same length, at low temperatures the homogeneous state of the system becomes unstable with respect to composition fluctuations with finite wavenumber q_0. When the distribution of the block lengths is introduced, the value of the critical wavenumber, q_0, shifts to the region of small q and remains at $q = 0$ for a strongly frustrated (random copolymer) system. The point in the parameter space describing the correlation in the monomer distribution along the chain, at which the value of the critical wavenumber q_0, is first equal to zero, is called the Lifshitz point. More realistic copolymer systems have been considered later in the refs,[16−22] but all of these systems demonstrate behavior similar to the simple de Gennes model.[15]

The instability of the homogeneous state of a system at zero wavenumber suggests that the system has to undergo a macrophase separation transition into pure A and pure B phases with decreasing temperature. However this is a mean field picture only. More sophisticated fluctuation analysis of phase transitions

in random copolymers[17,18,21,23,24] shows that the fluctuation corrections to the mean field lead to a microphase separation rather than a macrophase separation. The characteristic length scale of the critical fluctuations above the phase transition point and the period of the domain structure below it exhibit extreme temperature sensitivity. One should note that these scales at very low temperatures $T \ll T_c$ could be as small as a bond size if there is no correlation between different types of monomers along the copolymer chain.

Although there are many publications dealing with the problem of phase transitions in random copolymers,[16−22] there is still no quantitative phase diagram of these systems that could stimulate practical experiments to confirm theoretical predictions. The aim of this paper is to calculate a phase diagram of such systems and to give a quantitative answer on the question of how the phase behavior of two component copolymers depends on the degree of chemical disorder. With this purpose we develop a fluctuation theory of self-organization in $(A_l B_l)_n$ multiblock copolymer melt and calculate a phase diagram for this particular copolymer system in terms of the Flory parameter χ and polydispersity of the system.

The paper is organized as follows: Section 2 discusses a model and formulates the problem in terms of a Landau functional. In Section 3 we consider a system at low polydispersity and show that increasing the width of the block length distribution will result in stabilization of the homogeneous state of the system (decreasing the temperature of the order−disorder transition). In Section 4 we investigate the behavior of the system near the mean field Lifshitz point and demonstrate that fluctuation effects result in the renormalization of bare properties of the system and the development of critical fluctuations with temperature-dependent length scales. These critical fluctuations result in the formation of a domain structure at low temperatures. In Section 5 we apply the method of Section 4 to the case of multiblock copolymers with a higher degree of polydispersity. Section 6 discusses our results.

2. Model

Consider a melt containing M two-component multiblock copolymers with n blocks on each. We assume that these multiblock copolymers have been prepared during a two-step polymerization reaction. During the first step A and B monomers were polymerized into A_l and B_l blocks. Due to random nature of a polymerization process there exists a block length distribution given by the Schultz−Zimm formula: [25,26]

$$P(l) \approx l^{1/u-1} \exp\left(-\frac{l}{u\langle l \rangle}\right) \qquad (2.1)$$

where $\langle l \rangle$ is the average block length and u is the ratio of the second and first moments of the distribution (2.1).

$$u = \frac{\langle l^2 \rangle}{\langle l \rangle^2} - 1 \qquad (2.2)$$

The value u varies between 0 and 1. The value $u = 0$ corresponds to a monodisperse system with δ-like block length distribution, and at $u = 1$ the distribution (eq 2.1) has an exponential form.

During the second step of a polymerization reaction, A_l and B_l blocks were coupled into multiblock copolymer chains by the random copolymerization that is described

by the Markov growth process.[14,16,17] The random growth process is determined by the average copolymer composition f (the fraction of the A blocks in the system) and the 2×2 transfer matrix $p_{\alpha\beta}$. The elements $p_{\alpha\beta}$ give the conditional probability that the sort of the block $i + 1$ is type β if the sort of the block i is of type α. In combination with the conservation conditions of the probability, for the symmetric case $f = 0.5$ there is only one independent parameter $h = p_{aa} + p_{bb} - 1$ defining distribution of the blocks along polymer chain. At $h = -1$ we have alternating multiblock copolymers. Below we consider only the case of alternating block copolymers consisting of polydisperse blocks.

To describe a quenched disorder in the block distribution along the chain and their length distribution, a set of variables $\sigma_i(s,p)$ is introduced,[15−18,21,23,24] the indices i label the chain ($i = 1, ..., M$), the variable s indicates the block position along the polymer chain ($s = 1, ..., n$) and the index p gives the monomer position inside the block ($p = 1, ..., l_s$). The variables $\sigma_i(s,p)$ assume values of $+1$ and -1 for A_l and B_l blocks, respectively.

The configuration partition function of the melt of polydisperse multiblock copolymer melt at given distributions of blocks along the polymer chain and their polydispersity is

$$Z(\{\sigma_i(s,p)\}) = \int d\Gamma \, g(\Gamma) \, \delta(1 - \nu\rho(\mathbf{x})) \exp(-U(\Gamma)) \qquad (2.3)$$

where $\Gamma = (\mathbf{x}_1(1,1), \mathbf{x}_1(1,2), ..., \mathbf{x}_M(n,l_{n_M}))$ is the point of the configuration space of the system, $x_i(s,p)$ is the radius vector of the pth monomer of the sth block located on the ith chain. The function $g(\Gamma)$ describes connection of monomer units into polymer chains and is defined as

$$g(\Gamma) = \prod_{i,s,p} g(\mathbf{x}_i(s,p) - \mathbf{x}_i(s,p-1)) \qquad (2.4)$$

For the Gaussian model of the chain $g(\mathbf{x})$ has the form

$$g(\mathbf{x}) = (a\sqrt{2\pi})^{-3} \exp\left(-\frac{\mathbf{x}^2}{2a^2}\right) \qquad (2.5)$$

where a is bond size, assumed to be the same for all sort of bonds. Function $U(\Gamma)$ gives the energetic contribution due to pair interactions between monomers that is usually represented in the following form:[15−21]

$$U(\Gamma) = -\frac{\nu\chi}{4} \sum_{i,j} \sum_{s,k} \sum_{p,m} \sigma_i(s,p)\sigma_j(k,m) \, \delta(\mathbf{x}_i(s,p) - \mathbf{x}_j(k,m)) \qquad (2.6)$$

where ν is the excluded volume of monomer and χ is the Flory parameter characterizing the strength of the interactions. The delta function in the rhs of eq 2.3 takes into account the incompressibility condition of the copolymer melt and $\rho(\mathbf{x})$ is the local monomer density:

$$\rho(\mathbf{x}) = \sum_{i,s,p} \delta(\mathbf{x} - \mathbf{x}_i(s,p)) \qquad (2.7)$$

Introducing local composition fluctuation

$$\psi(\mathbf{x}) = \sum_{i,s,p} \sigma_i(s,p) \, \delta(\mathbf{x} - \mathbf{x}_i(s,p)) \qquad (2.8)$$

that is the order parameter for microphase separation transition, we can rewrite the partition function (eq 2.3) in terms of the functional integral

$$Z(\{\sigma_i(s,p)\}) = \int D\rho(\mathbf{x})\, D\psi(\mathbf{x})\, \delta(1 - \nu\rho(\mathbf{x})) \times$$
$$\exp\left(-F_s(\{\sigma_i(s,p)\}) + \frac{\nu\chi}{4}\int\psi(\mathbf{x})^2\, dV\right) \quad (2.9)$$

F_s is the free energy of the ideal polydisperse multiblock copolymer melt (i.e., noninteracting) with a given chemical structure of macromolecules (at fixed distribution of variables $\sigma_i(s,p)$):

$$F_s(\{\sigma_i(s,p)\}) = -\text{Ln}\langle(\delta(\rho(\mathbf{x}) - \sum_{i,s,p}\delta(\mathbf{x} - \mathbf{x}_i(s,p)))\,\delta(\psi(\mathbf{x}) - \sum_{i,s,p}\sigma_i(s,p)\,\delta(\mathbf{x} - \mathbf{x}_i(s,p)))))\rangle_0$$

$$(2.10)$$

The brackets $\langle\ \rangle_0$ denote an averaging over all conformations of macromolecules with weight $g(\Gamma)\, d(\Gamma)$. It is very important to note that the structural part of the free energy is a self-averaging value over all possible chemical structures of macromolecules, because every chain is an independent realization of the distribution of blocks along the chain and their polydispersity.[17] So, it could be rewritten

$$F_s(\{\sigma_i(s,p)\}) = \langle F_s(\rho(\mathbf{x}),\psi(\mathbf{x}))\rangle_{av} \quad (2.11)$$

where brackets $\langle\ \rangle_{av}$ denote the ensemble average over all possible chemical structures of the copolymer chains. Of course, we always can use a replica trick to average the logarithm of the partition function over all distributions of quenched disorder. However, both of these methods result in the same answer for the case of the symmetric in the replica space solution. In our calculation of the average characteristic of the multiblock copolymer system we use nonreplica trick based on the self-averaging of structural part of the free energy. Omitting the intermediate calculation that is technically similar to the one presented in ref[17] for random multiblock copolymers with fixed block length distribution, we give only the final answer for the partition function of the polydisperse two-component muliblock copolymer melt in terms of the functional integral:

$$Z = \int D\psi(\mathbf{q})\, \exp(-H(\psi(\mathbf{q}))) \quad (2.12)$$

where $\psi(\mathbf{q})$ is the Fourier transform of the order parameter $\psi(\mathbf{x})$ and $H(\psi(\mathbf{q}))$ is the effective Hamiltonian that expansion in the power series of the order parameter up to the fourth order term is

$$H(\psi(\mathbf{q})) = \frac{1}{2}\int\left(G_0^{-1}(\mathbf{q}) - \frac{1}{2}\nu\chi\right)\psi(\mathbf{q})\psi(-\mathbf{q})\frac{d^3\mathbf{q}}{(2\pi)^3} +$$
$$\frac{1}{24}\int\lambda(\{\mathbf{q}_i\})\,\delta(\sum_i\mathbf{q}_i)\prod_{i=1}^{4}\psi(\mathbf{q}_i)\frac{d^3\mathbf{q}_i}{(2\pi)^3} +$$
$$\frac{1}{8V}\int\kappa(\{\mathbf{q}_i\})\,\delta(\mathbf{q}_1 + \mathbf{q}_2)\,\delta(\mathbf{q}_3 + \mathbf{q}_4)\prod_{i=1}^{4}\psi(\mathbf{q}_i)\frac{d^3\mathbf{q}_i}{(2\pi)^3}$$

$$(2.13)$$

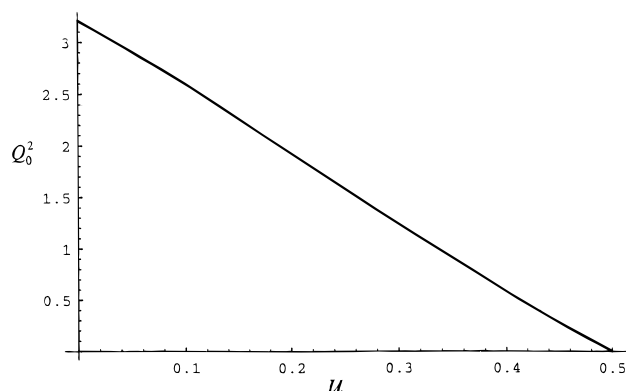where $G_0(\mathbf{q})$ is the structural correlation function which

Figure 1. Dependence of the wave vector Q_0^2 characterizing the period of the domain structure on the polydispersity parameter u.

in the limit of the large number of blocks on the chain $n \gg 1$ is

$$G_0(Q) = \frac{2\rho\langle l\rangle}{Q^4}\left(Q^2 - 1 + f(Q) - \frac{(1 - f(Q))^2}{1 + f(Q)}\right) \quad (2.14)$$

$Q = \mathbf{q}a(\langle l\rangle/6)^{1/2}$ is the wavenumber normalized on the Gaussian size of the block, $\rho = Mn\langle l\rangle/V$ is the average monomer density in the system and

$$f(Q) = (1 + uQ^2)^{-1/u} \quad (2.15)$$

(Here and below we are interested in the case $n \gg 1$). Functions $\lambda(\{\mathbf{q}_i\})$, $\kappa(\{\mathbf{q}_i\})$ depend on the chemical structure of the macromolecules. Vertex $\kappa(\{\mathbf{q}_i\})$ is equal to zero for monodisperse multiblock copolymers. One should note that the vertex $\kappa(\{\mathbf{q}_i\})$ is in fact an infinite range. In the real space this is a function of distances $|\mathbf{x}_1 - \mathbf{x}_2|$ and $|\mathbf{x}_3 - \mathbf{x}_4|$ but not the distance $|\mathbf{x}_1 - \mathbf{x}_3|$. We will give the asymptotic expressions for these vertex functions in the following chapters.

The spinodal of the homogeneous state of the polydisperse multiblock copolymer melt is defined from the condition

$$\min_{\mathbf{q}}\Gamma_2(\mathbf{q}) = \min_{\mathbf{q}}\left(G_0^{-1}(\mathbf{q}) - \frac{\nu\chi}{2}\right) = 0 \quad (2.16)$$

The minimum of eq 2.16 is sought on the half-interval $0 \le q$. If the minimum of eq 2.16 occurs at finite wavenumbers q_0, then in the region $\Gamma_2(q_0) < 0$ the domain structure with period $L = 2\pi/q_0$ forms in the system. In Figure 1 we plot the dependence of the critical wavenumber minimizing eq 2.16 as a function of the polydispersity parameter u. At small u the minimum is at finite wavenumber that is of the order of Gaussian block size. The position of the minimum shifts into the region of small q when the polydispersity parameter u tends to 0.5. Point $u = 0.5$ is the classical Lifshitz point for this class of copolymer systems. At higher polydispersity $u > 0.5$ the homogeneous state is always unstable with respect to macrophase separation in the Gaussian model on fluctuations approximation. However, we show below that in this region the fluctuation corrections due to interactions between the fluctuations of the order parameter through fourth-order terms in the Landau expansion (eqs 2.12 and 2.13) result in strong renormalization of the bare characteristics of the system, and we again recover the instability at finite length scales. It is useful to approximate the structural correlation function (eq 2.14) by the function having the

simple analytical form

$$G_0^{-1}(Q) \approx \frac{1}{\rho\langle l\rangle}\left(\frac{2}{3}Q^2 + \frac{1}{Q^2/6 + u}\right) \qquad (2.17)$$

This function gives the position of the minimum with accuracy of the order of 7% in the region of small $u < 0.1$ and very good approximation at $u > 0.3$. The function in eq 2.17 has the minimum at Q equal to

$$Q_0^2 = 3(1 - 2u) \qquad (2.18)$$

Substituting this solution for Q_0 into eq 2.16 we can find the spinodal of the homogeneous state of the system

$$\chi\langle l\rangle = \begin{cases} 8(1 - u), & u < 0.5 \\ 2/u, & u \geq 0.5 \end{cases} \qquad (2.19)$$

In the case of the monodisperse system ($u = 0$) the expression 2.19 reproduces the results of ref 27. Near the critical point Q_0 the function in (eq 2.17) can be expanded in the Taylor series on the powers of $|Q| - Q_0$:

$$G_0^{-1}(Q) \approx \frac{1}{\rho\langle l\rangle}\left(4(1 - u) + \frac{8}{3}(1 - 2u)(|Q| - Q_0)^2\right) \quad (2.20)$$

However, near the Lifshitz point this approximation fails, because higher order terms in the Taylor series become important. In the interval of the parameters $|u - 0.5| < 0.05$ the correlation function has the form

$$G_0^{-1}(Q) \approx \frac{1}{\rho\langle l\rangle}\left(2 + 4\varepsilon + \frac{2}{9}Q^4 - \frac{8}{3}\varepsilon Q^2\right) \qquad (2.21)$$

where $\varepsilon = 0.5 - u$. The classical Lifshitz point is the point in the space of the parameters of the system where coefficient at Q^2 changes its sign. Finally, we summarize the possible forms of the correlation function (eq 2.14):

$$G_0^{-1}(Q) \approx \frac{1}{\rho\langle l\rangle}$$

$$\begin{cases} 4(1 - u) + \frac{8}{3}(1 - 2u)(|Q| - Q_0)^2, & u < 0.4 \\ 2 + 4\varepsilon + \frac{2}{9}Q^4 - \frac{8}{3}\varepsilon Q^2, & |u - 0.5| < 0.05 \\ \frac{2}{3}Q^2 + \frac{1}{u}, & u > 0.6 \end{cases}$$

$$\qquad (2.22)$$

In the following sections we consider different regimes of the multiblock copolymer melt, classifying it in accordance with the form of the correlation function 2.22.

3. Weakly Polydispersed System

At small polydispersity u the homogeneous state of the system is unstable with respect to fluctuations with finite wavenumber Q_0 which result in the formation of a domain structure with period $L \approx a\langle l\rangle^{1/2}/Q_0$ at low temperatures. The condition of the first-order phase transition between homogeneous state and ordered state could be found in the framework of the Brazovskii approximation[28] discussed in the papers.[8,10–12,19] Here we give a generalization of Brazovskii's approach[28] to the effective Hamiltonian (eq 2.13).

Because the fluctuations with a finite wavenumber Q_0 give significant contribution near the phase transition point, we will approximate fourth-order vertex functions $\lambda(\{\mathbf{q}_i\})$ and $\kappa(\{\mathbf{q}_i\})$ by their values at $|\mathbf{q}_i| = 6^{1/2}Q_0/a\langle l\rangle^{1/2}$. In this approximation we have

$$\lambda \approx 32\rho\langle l\rangle^3\frac{(G_0^{-1}(Q_0))^4}{Q_0^6} \qquad (3.1)$$

$$\kappa \approx 4u\rho\langle l\rangle^3\frac{(G_0^{-1}(Q_0))^4}{Q_0^4} \qquad (3.2)$$

To reduce the effective Hamiltonian (eq 2.13) to the form of Brazovskii's Hamiltonian, it is useful to introduce the dimensionless variables:

$$\tau = \frac{3}{8(1 - 2u)}(4(1 - u) - \rho\nu\chi\langle l\rangle/2)$$

$$\psi^2(Q) = \frac{16(6)^{1/2}}{\rho a^3\langle l\rangle^{5/2}}(1 - 2u)\psi^2(\mathbf{q}) \qquad (3.4)$$

$$\lambda = \frac{256(6)^{1/2}}{\rho a^3\langle l\rangle^{1/2}}\frac{(1 - u)^4}{(1 - 2u)^5}, \qquad \kappa = u\frac{96(6)^{1/2}}{\rho a^3\langle l\rangle^{1/2}}\frac{(1 - u)^4}{(1 - 2u)^4}$$

One should note that for incompressible melt the volume fraction $\rho\nu$ is equal to unity.

In these new variables the effective Hamiltonian (eq 2.13) reads

$$H(\psi(Q)) = \frac{1}{2}\int((|Q| - Q_0)^2 + \tau)\psi(Q)\psi(-Q)\frac{d^3Q}{(2\pi)^3} +$$

$$\frac{\lambda}{24}\int\delta(\sum_i Q_i)\prod_{i=1}^{4}\psi(Q_i)\frac{d^3Q_i}{(2\pi)^3} + \frac{\kappa}{8V}\int\delta(Q_1 + Q_2)\,\delta(Q_3 +$$

$$Q_4)\prod_{i=1}^{4}\psi(Q_i)\frac{d^3Q_i}{(2\pi)^3} \quad (3.5)$$

To calculate the free energy of the system in both homogeneous and ordered phases, we will use the Feynman variational principle[29] which corresponds to the one-loop Brazovskii's approximation for effective Hamiltonian (eq 3.5). The variational free energy is

$$F = \langle H(\psi(Q)) - H_0(\delta\psi(Q))\rangle_{H_0} - \frac{1}{2}Tr(\text{Ln}(G(Q))) \quad (3.6)$$

where

$$H_0(\delta\psi(Q)) = \frac{1}{2}\int G^{-1}(Q)\,\delta\psi(Q)\,\delta\psi(-Q)\frac{d^3Q}{(2\pi)^3} \qquad (3.7)$$

The brackets $\langle\ \rangle_{H_0}$ denote an averaging with the Gaussian Hamiltonian (eq 3.7), and $G(Q)$ is the renormalized Green's function, and $\delta\psi(Q)$ is the composition fluctuation with respect to average value $\langle\psi(Q)\rangle$, and is equal to zero in the homogeneous state. There is a nonzero average value of the order parameter $\langle\psi(Q)\rangle$ in the ordered phase that describes the average composition fluctuations between domains. For the lamellar type of the domain structure that corresponds to the minimum of the free energy in the case of symmetric

copolymers[6,8,10–12] the average value of the order parameter has the following form:

$$\langle \psi(Q) \rangle = A(\delta(|Q| - Q_0) + \delta(|Q| + Q_0)) \quad (3.8)$$

where A is the amplitude of the order parameter. The order parameter $\psi(Q)$ in the ordered phase has to be written as the sum of two terms $\langle \psi(Q) \rangle + \delta\psi(Q)$.

However, to calculate the variational free energy, we have to know the form of the trial function $G(Q)$. Here we assume that the fluctuations result only in renormalization of the effective temperature and do not change the position of the minimum of the renormalized correlation function.[8,10–12,28] In this approximation the renormalized correlation function $G(Q)$ is

$$G^{-1}(Q) = (|Q| - Q_0)^2 + r \quad (3.9)$$

where r is the variational parameter.

Substituting the trial functions (eqs 3.8 and 3.9) into variational free energy eq 3.6, we arrive at the following expression for free energy:

$$F = \frac{V6^{3/2}}{a^3\langle l \rangle^{3/2}}\left\{\frac{1}{2}\alpha r^{1/2} + \frac{1}{2}\alpha\tau r^{-1/2} + \frac{1}{8}(\lambda + \kappa)\alpha A^2 r^{-1/2} + \right.$$
$$\left. \tau A^2 + \frac{1}{2}\kappa A^4 + \frac{1}{4}\lambda A^4\right\} \quad (3.10)$$

where we have introduced the parameter $\alpha = Q_0^2/2\pi$. Parameters A and r are roots of extremal equations

$$\partial F/\partial r = \partial F/\partial A = 0 \quad (3.11)$$

that for the disordered phase have the form

$$\tau = r - \frac{\lambda + \kappa}{2}\alpha r^{-1/2} \quad (3.12)$$

For the ordered one it could be reduced to

$$\tau = -\frac{\lambda + 2\kappa}{\lambda}r - \frac{\lambda + \kappa}{2}\alpha r^{-1/2} \quad (3.13.a)$$

$$A^2 = \frac{2r}{\lambda} \quad (3.13.b)$$

It is important to note that only vertex λ contributes to the value of amplitude A and the vertex κ is important for renormalization of the effective temperature r. Numerical comparisons of the free energies of the system in homogeneous and ordered phases show that the first-order phase transition occurs at

$$\frac{\chi\langle l \rangle}{4} \approx 2(1 - u) + 67.92\left(\frac{\nu}{a^3}\right)^{2/3}\langle l \rangle^{-1/3}\left(1 + \frac{7}{6}u\right) \quad (3.14)$$

One can see that the phase transition shifts into the region of higher χ with increasing polydispersity u. The fluctuations corrections for the symmetric multiblock copolymers are very important due to the large prefactor in front of the second term in the rhs of eq 3.14. In the case $u = 0$ the formula in eq 3.14 reproduces the result of ref 11.

Throughout this section we have neglected the contributions of the higher order diagrams on the power of vertices κ and λ in the variational free energy given by eqs 3.6 and 3.10. This approximation is correct if these contributions are small in comparison with those that

we considered in the framework of the variational approach (eq 3.6).

It is very important to note that the contributions of higher order diagrams on the power of vertex κ vanish in the thermodynamic limit.[23,24,31] For example, the second-order diagram in the expansion of the free energy is

$$I_2(\kappa) \approx \frac{\kappa^2}{V^2}(V\int G^2(\mathbf{r}) \, d\mathbf{r})^2 \approx V^0 \quad (3.15)$$

where

$$G(\mathbf{r}) = \frac{Q_0}{2\pi\sqrt{r}}\frac{\sin(Q_0\mathbf{r})}{\mathbf{r}}\exp(-\mathbf{r}\sqrt{r})$$

is the real space representation of the renormalized Green's function (eq 3.9). In a general case the diagram has factor V in front of it when the number of loops is equal to the number of vertices plus one. However, there exists only one such diagram that has already been taken into account in the variational free energy (eq 3.6). It is interesting to note that the effective Hamiltonian (eq 2.13) can be considered as a continual generalization of the n-component model.[30]

Let us compare the contribution of the second-order diagram on the power of vertex λ with that of the first-order diagram. The contribution from the second-order diagram is[12]

$$I_2(\lambda) = \frac{\lambda^2}{48}\int G^4(\mathbf{r}) \, d\mathbf{r} = \frac{\lambda^2}{48}\frac{Q_0^5}{(4\pi)^2 r^2} \quad (3.16)$$

This diagram can be neglected if the following ratio is less than unity:

$$\left(\frac{\lambda^2}{48}\frac{Q_0^5}{(4\pi)^2 r^2}\bigg/\frac{\lambda}{8}\frac{Q_0^2}{(2\pi)^2 r}\right) = \frac{\lambda Q_0}{24r} \approx \frac{\lambda^{1/3}}{3\pi^{1/3}Q_0^{1/3}} \leq 1 \quad (3.17)$$

Or we could rewrite for the parameter

$$\frac{\nu}{a^3\langle l \rangle^{1/2}} \leq 0.23 \quad (3.18)$$

Our theory correctly describes the phase transition for those multiblock copolymers for which the last inequality holds.

4. Behavior of the System near the Classical Lifshitz Point

The position of the peak of the correlation function (eq 2.17) shifts into the region of small wavenumbers near the classical Lifshitz point $u \approx 0.5$. In this limit $(Q \ll 1)$ the fourth-order vertex functions in the effective Hamiltonian (eq 2.13) have the asymptotic forms:

$$\lambda \approx \frac{8}{\rho^3\langle l \rangle}\frac{(1 + u + 0.75u^2)}{u^3} \approx \frac{108}{\rho^3\langle l \rangle} \quad (4.1)$$

$$\kappa \approx \frac{1}{\rho^3\langle l \rangle u^4}\frac{4u^2}{Q_1^2 + Q_2^2} \approx \frac{1}{\rho^3\langle l \rangle}\frac{16}{Q_1^2 + Q_2^2} \quad (4.2)$$

As in the previous chapter it is useful to introduce dimensionless parameters

$$\tau = \frac{9}{2}\left(\frac{1}{u} - \frac{\rho v \chi \langle l \rangle}{2}\right)$$

$$\psi^2(Q) = \frac{4}{3}\frac{6^{1/2}}{\rho a^3 \langle l \rangle^{5/2}}\psi^2(\mathbf{q}) \tag{4.3}$$

$$\lambda = \frac{13122(6)^{1/2}}{\rho a^3 \langle l \rangle^{1/2}}, \qquad \kappa = \frac{1944(6)^{1/2}}{\rho a^3 \langle l \rangle^{1/2}}$$

Now we can rewrite the effective Hamiltonian (eq 2.13) near the Lifshitz point:[32]

$$H(\psi(Q)) = \frac{1}{2}\int (Q^4 - \varepsilon Q^2 + \tau)\psi(Q)\psi(-Q)\frac{d^3Q}{(2\pi)^3} +$$

$$\frac{\lambda}{24}\int \delta(\sum_i Q_i)\prod_{i=1}^{4}\psi(Q_i)\frac{d^3Q_i}{(2\pi)^3} +$$

$$\frac{\kappa}{8V}\int \frac{\delta(Q_1 + Q_2)\,\delta(Q_3 + Q_4)}{Q_1^2 + Q_2^2}\prod_{i=1}^{4}\psi(Q_i)\frac{d^3Q_i}{(2\pi)^3} \tag{4.4}$$

where the parameter $\varepsilon = 12(0.5 - u)$ was introduced.

The bare propagator in eq 4.4 has a minimum at finite wavenumbers at positive ε, that is $Q_0^2 = \varepsilon/2$ which shifts to small Q as the value of ε tends to zero. At the Lifshitz point $\varepsilon = 0$ the bare propagator has fourth-power dependence on the wavenumber Q. The Dyson's equation for the renormalized correlation function $G(Q)$ in the one-loop approximation for the homogeneous state is

$$G^{-1}(Q) = Q^4 + \tau + \frac{\lambda}{2}\int G(Q_1)\frac{d^3Q_1}{(2\pi)^3} +$$

$$\frac{\kappa}{2}\int \frac{G(Q_1)}{Q_1^2 + Q^2}\frac{d^3Q_1}{(2\pi)^3} \tag{4.5}$$

Substituting in the rhs of eq 4.5 $G^{-1}(Q) = Q^4 + \tau$, one can see that due to the interaction between composition fluctuations through the long-range fourth-order vertex κ the position of the minimum of the renormalized Green function $G(Q)$ shifts in the region of finite Q. This is the reason why it is natural to look for a solution of the integral equation (4.5) on the class of trial functions of the following form:

$$G^{-1}(Q) = C(Q^2 - Q_*^2)^2 + r \tag{4.6}$$

where parameters C, r, and Q_* have to be found self-consistently. Substituting this trial function (eq 4.6) into the rhs of eq 4.5 we arrive at

$$G^{-1}(Q) = Q^4 + \tau + \frac{\lambda Q_*}{8\pi\sqrt{Cr}} + \frac{\kappa Q_*}{8\pi\sqrt{Cr}}\frac{1}{Q^2 + Q_*^2} \tag{4.7}$$
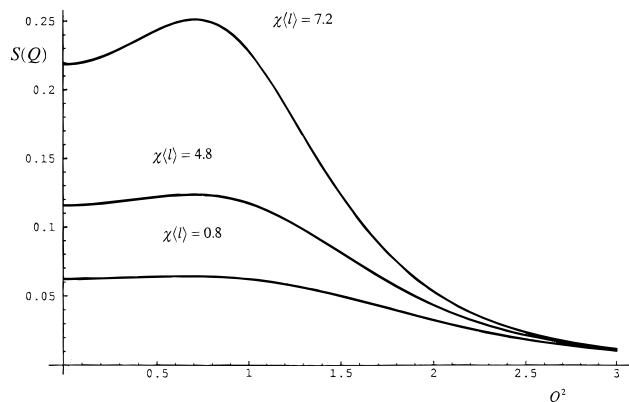

Figure 2. Dependence of the renormalized Green function given by eq 4.7 on the wavenumber Q at different values of the Flory parameter χ.

Expanding the rhs of eq 4.7 in the power series of $Q^2 - Q_*^2$, we can define parameters C, r, Q_* as follows:

$$r = \tau + 5\frac{\kappa^{4/5}}{s^{4/5}r^{2/5}} + 8\frac{\lambda\kappa^{1/5}}{s^{6/5}r^{3/5}} \tag{4.8.a}$$

$$Q_*^5 = \frac{\kappa}{sr^{1/2}} \tag{4.8.b}$$

$$C = 2 \tag{4.8.c}$$

where parameter $s = 64\sqrt{2}\pi$ was introduced. From eq 4.8.a one can conclude that the homogeneous state exists, at least as a metastable one, for the whole interval of effective temperatures $-\infty \le \tau \le \infty$. Let us analyze the behavior of the system in the homogeneous state. At high temperatures $\tau > (\kappa/s)^{4/7}$ fluctuations are not important and the renormalized correlation function has a peak at small Q. With decreasing temperature $\tau < (\kappa/s)^{4/7}$ interactions between fluctuations of the order parameter will shift the position of the peak toward the region of finite wavenumbers. First, it will manifest itself as a shoulder at small Q, but at low enough temperatures this shoulder will transform into a peak. This can be seen in Figure 2 where the renormalized Green function given by the rhs of eq 4.7 is sketched at different temperatures. It follows from eq 4.8.a and 4.8.b.) that the characteristic length scale of the critical fluctuations L is proportional to $|\tau|^{-1/4}$ at an effective temperature higher than $\tau > -\kappa^2/\lambda^2$ and to $(\lambda/\kappa)^{1/6}|\tau|^{-1/6}$ at low temperatures.

The absence of the instability does not preclude the existence of a first-order phase transition into a domain structure with a period of the order of length scale L of critical fluctuations. In order to answer this question, whether such transition may occur, we have to calculate the free energy of such an ordered phase.

There is the average value of the order parameter in the form given by eq 3.8 in the ordered phase. Substituting the trial functions (eqs 3.8 and 4.6) into the variational free energy equation 3.6 we obtain the variational free energy for the polydisperse multiblock copolymers near the Lifshitz point:

$$F = \frac{V(6)^{3/2}}{a^3\langle l\rangle^{3/2}}\left\{\frac{1}{2}\alpha r^{1/2} + \frac{1}{2}\alpha(Q_*^4 + \tau)r^{-1/2} + \right.$$

$$\frac{1}{8}\left(\lambda + \frac{\kappa}{2Q_*^2}\right)\alpha^2 r^{-1} + \frac{1}{2}\left(\lambda + \frac{\kappa}{2Q_*^2}\right)\alpha A^2 r^{-1/2} +$$

$$\left.(Q_*^4 + \tau)A^2 + \frac{\kappa}{4Q_*^2}A^4 + \frac{1}{4}\lambda A^4\right\} \quad (4.9)$$

where parameter α is $Q_*^2/2\pi(C)^{1/2}$. The parameters of the renormalized Green's function in the ordered phase is defined from Dyson's equation:

$$G^{-1}(Q) = Q^4 + \tau + \frac{\lambda Q_*}{8\pi\sqrt{Cr}} + \frac{\kappa Q_*}{8\pi\sqrt{Cr}}\frac{1}{Q^2 + Q_*^2} +$$

$$\lambda A^2 + \frac{\kappa A^2}{Q^2 + Q_*^2} \quad (4.10)$$

The equilibrium amplitude of the order parameter is

$$A^2 = 2r/\lambda \quad (4.11)$$

Again, expanding the rhs of eq 4.10 on the powers of $Q^2 - Q_*^2$ we find the parameters of the renormalized Green' function (eq 4.6) in the ordered phase:

$$-\tau = r + 5\frac{\kappa Q_*}{sr^{1/2}} + 8\frac{\lambda Q_*}{sr^{1/2}} + \frac{5}{4}\frac{\kappa r}{\lambda Q_*^2} \quad (4.12.a)$$

$$Q_*^6 - \frac{\kappa Q_*}{sr^{1/2}} - \frac{1}{4}\frac{\kappa}{\lambda}r = 0 \quad (4.12.b)$$

$$C = 2 \quad (4.12.c)$$

In the region of the parameters at which $(\lambda Q_*^2/\kappa) \ll 1$ only the second and the last terms of eq 4.12.a are important. In the opposite limit the first and the third terms control the behavior of the system. In this approximation the solution for the ordered phase appears below the critical temperature:

$$\tau_{\text{crit}} \approx -6.2\frac{\kappa^{3/4}}{s^{1/2}\lambda^{1/4}}, \quad \text{for} \quad \lambda Q_*^2/\kappa < 1 \quad (4.13.a)$$

$$\tau_{\text{crit}} \approx -7.1\frac{\lambda^{5/8}\kappa^{1/8}}{s^{3/4}}, \quad \text{for} \quad \lambda Q_*^2/\kappa > 1 \quad (4.13.b)$$

However, at that point the length scales of critical fluctuations are equal to

$$Q_* \approx \frac{\kappa^{3/16}}{s^{1/8}\lambda^{1/16}} \quad (4.14)$$

In order to estimate a temperature of the first-order phase transition, we have to compare the free energies of the system in the homogeneous and ordered phases. It follows from eqs 4.13.a and 4.13.b that the period $L \approx 2\pi/Q_*$ of domain structure near the phase transition point changes with temperature as $|\tau|^{-1/4}$ for

$$\lambda^{7/8}/\kappa^{5/8}s^{1/4} \approx 10\left(\frac{\nu}{a^3\sqrt{\langle l\rangle}}\right)^{1/4} < 1$$

and as $|\tau|^{-1/6}$ in opposite limit. However, the first regime is unphysical for multiblock copolymers for which the

parameter $\nu/a^3(\langle l\rangle)^{1/2}$ can hardly be smaller than 0.01. Therefore the period L of the domain structure near the phase transition point is proportional to $|\tau|^{-1/6}$, for polydisperse multiblock copolymers.

The numerical analysis of the variational free energy eq 4.9 for ordered and homogeneous states shows that the first-order phase transition occurs at

$$\frac{\chi\langle l\rangle}{4} \approx \frac{1}{2u} + 3.5\frac{(1 + u + 0.75u^2)^{5/8}}{u^{17/8}}\left(\frac{\nu}{a^3\sqrt{\langle l\rangle}}\right)^{3/4} \quad (4.15)$$

The description of the first-order phase transition presented above is correct near the Lifshitz point where the contribution of the quadratic term εQ^2 in the bare propagator could be neglected in comparison with term Q^4. It takes place near the point of the first-order phase transition for $|\varepsilon| \le (\kappa^{3/8}/\lambda^{1/8}s^{1/4})$ or for range of the distribution parameter:

$$|u - 0.5| < 0.13\left(\frac{\nu}{a^3\sqrt{\langle l\rangle}}\right)^{1/4} \quad (4.16)$$

5. Strongly Polydispersed System

In the region of the parameter $u \approx 1$ the block length distribution has the exponential form and the bare propagator is

$$\Gamma_2(Q) = \frac{1}{\rho\langle l\rangle}\left(\frac{2}{3}Q^2 + \frac{1}{u}\right) - \frac{\nu\chi}{2} \quad (5.1)$$

The minimum of the function (eq 5.1) occurs at $Q = 0$, and therefore we can again use the long range asymptotic for vertex functions:

$$\lambda \approx \frac{8}{\rho^3\langle l\rangle}\frac{(1 + u + 0.75u^2)}{u^3} \quad (5.2)$$

$$\kappa \approx \frac{1}{\rho^3\langle l\rangle u^4}\frac{4u^2}{Q_1^2 + Q_2^2} \quad (5.3)$$

To reduce the effective Hamiltonian (eq 2.13) into the dimensionless form, we introduce new variables:

$$\tau = \frac{3}{2}\left(\frac{1}{u} - \frac{\rho\nu\chi\langle l\rangle}{2}\right)$$

$$\psi^2(Q) = 4\frac{6^{1/2}}{\rho a^3\langle l\rangle^{5/2}}\psi^2(\mathbf{q}) \quad (5.4)$$

$$\lambda = \frac{108(6)^{1/2}}{\rho a^3\langle l\rangle^{1/2}}\frac{1 + u + 0.75u^2}{u^3}, \quad \kappa = \frac{54(6)^{1/2}}{\rho a^3\langle l\rangle^{1/2}}u^{-2}$$

In these variables the effective Hamiltonian describing the system near the phase transition point is

$$H(\psi(Q)) = \frac{1}{2}\int (Q^2 + \tau)\psi(Q)\psi(-Q)\frac{d^3Q}{(2\pi)^3} +$$

$$\frac{\lambda}{24}\int\delta(\sum_i Q_i)\prod_{i=1}^{4}\psi(Q_i)\frac{d^3Q_i}{(2\pi)^3} +$$

$$\frac{\kappa}{8V}\int\frac{\delta(Q_1 + Q_2)\,\delta(Q_3 + Q_4)}{Q_1^2 + Q_3^2}\prod_{i=1}^{4}\psi(Q_i)\frac{d^3Q_i}{(2\pi)^3} \quad (5.5)$$

One can see that there is a long-range fourth-order term that results in strong renormalization of the correlation function as in the case of the system near the Lifshitz point. Technically the procedure of calculating the renormalized correlation function is similar to the one discussed above in Section 4 with one difference. Now the bare propagator has quadratic dependence on the momentum Q. Omitting the intermediate calculations that can be found in refs 23, 24, and 31, we will give here only final answers. Substituting the trial functions for average value of the order parameter (eq 3.8) and renormalized Green's function (eq 4.6) into variational free energy (eq 3.6) we arrive at

$$F = \frac{V6^{3/2}}{a^3\langle l\rangle^{3/2}}\Big\{\frac{1}{2}\alpha r^{1/2} + \frac{1}{2}\alpha(Q_*^2 + \tau)r^{-1/2} + $$
$$\frac{1}{8}\Big(\lambda + \frac{\kappa}{2Q_*^2}\Big)\alpha^2 r^{-1} + \frac{1}{2}\Big(\lambda + \frac{\kappa}{2Q_*^2}\Big)\alpha A^2 r^{-1/2} + $$
$$(Q_*^2 + \tau)A^2 + \frac{\kappa}{4Q_*^2}A^4 + \frac{1}{4}\lambda A^4\Big\} \quad (5.6)$$

where parameter α is $Q_*^2/2\pi(C)^{1/2}$. The parameters C, Q_*, r, and A are determined from the following equations for the homogeneous state:

$$r = \tau + 3\frac{\kappa}{sr^{1/2}} + 4\frac{\kappa\lambda}{s^2 r} \quad (5.7.a)$$

$$Q_*^2 = \frac{\kappa}{sr^{1/2}} \quad (5.7.b)$$

and for the ordered one,

$$-\tau = r + 3\frac{\kappa}{sr^{1/2}} + 4\frac{\lambda Q_*^2}{sr^{1/2}} + \frac{3}{2}\frac{\kappa r}{\lambda}\frac{1}{Q_*^2} \quad (5.8.a)$$

$$Q_*^4 - \frac{\kappa}{sr^{1/2}}Q_*^2 - \frac{\kappa}{2\lambda}r = 0 \quad (5.8.b)$$

$$A^2 = \frac{2r}{\lambda} \quad (5.8.c)$$

with parameter $C = 2$ for both cases and $s = 16\sqrt{2\pi}$.

Introducing the new variable $z = sr/(\kappa\lambda)^{1/2}$ and substituting the solution of eq 5.8.b into eq 5.8.a, the analysis of the ordered phase can be reduced to the analysis of the single equation

$$-\tau = \frac{\sqrt{\kappa\lambda}}{s}\Big(z + \frac{2}{z}(1 + \sqrt{1 + 2z^2}) + $$
$$3\frac{\kappa^{1/4}s^{1/2}}{\lambda^{3/4}}\Big(z^{-1/2} + \frac{z^{3/2}}{1 + \sqrt{1 + 2z^2}}\Big)\Big) \quad (5.9)$$

There are two regimes of the system under consideration. If the parameter $\kappa^{1/4}s^{1/2}/\lambda^{3/4}$ is less than unity, the last bracket in the rhs of eq 5.9 is unimportant and the first two terms control behavior of the system near the phase transition point. For example, for $\nu/a^3(\langle l\rangle)^{1/2} = 0.1$ and $u = 1$ this parameter is equal to 0.65 and the solution of eq 5.9 appears below the critical temperature $\tau_{\text{crit}} \approx -2.58$ that is spinodal of the ordered phase. At

this value of the parameter

$$\kappa^{1/4}s^{1/2}/\lambda^{3/4} \approx 0.2\Big(\frac{\nu}{a^3\sqrt{\langle l\rangle}}\Big)^{-1/2}$$

the period of the domain structure L changes with the effective temperature as $|\tau|^{-1/4}$. In order to reproduce power dependence for the period of the domain structure $L \approx |\tau|{-1/2}$ expected for random copolymers[17,18,21,23,24,31] the parameter $\kappa^{1/4}s^{1/2}/\lambda^{3/4}$ has to be larger than 10 or parameter $\nu/a^3(\langle l\rangle)^{1/2}$ smaller than 10^{-4}.

To determine a phase transition line from the homogeneous state to the ordered one the free energies in both phases have to be compared. The first-order phase transition occurs at

$$\frac{\chi\langle l\rangle}{4} = \frac{1}{2u} + 0.87\sqrt{\frac{1 + u + 0.75u^2}{u}}\frac{\nu}{a^3\sqrt{\langle l\rangle}} \times$$
$$\Big(6 + 1.8\Big(\frac{\nu}{a^3\sqrt{\langle l\rangle}}\Big)^{-1/2}\frac{u^{7/4}}{(1 + u + 0.75u^2)^{3/4}}\Big) \quad (5.10)$$

One should mention that the phase transition point shifts into the region of the higher χ with decreasing polydispersity of the system u.

To complete our analysis, we have to check the validity of the one-loop approximation and compare the second-order diagrams on the power of vertex λ with the one-loop one. It turns out that our approximation is correct when the following parameter is small:

$$\frac{\lambda Q_*}{24\pi r} \approx \Big(\frac{\nu}{a^3\sqrt{\langle l\rangle}}\Big)^{1/4} < 1 \quad (5.11)$$

6. Conclusion

We have presented the fluctuation theory of the self-organization of symmetric polydisperse multiblock copolymers. Our analysis of the phase behavior shows that with increasing polydispersity parameter u (for $u < 0.3$) composition fluctuations result in an increasing value of the Flory parameter χ of the first-order phase transition from a disordered (homogeneous) state to an ordered one. The period $L = 2\pi/q_0$ of the domain structure, appearing below the phase transition point, is proportional to the Gaussian size of the block $a(\langle l\rangle)^{1/2}$. In the Gaussian approximation the position of the peak of the correlation function shifts toward the small q region near the mean field Lifshitz point $u = 0.5$. In the classical picture of phase transition phenomena the Lifshitz point separates the parametric space of the system into two regions. In one region there exists a microphase separation transition. In another there is a macrophase separation. It turns out that, due to unique properties of polydisperse multiblock copolymers, the fluctuation corrections to the mean field approximation eliminate the classical Lifshitz point and the system always undergoes a microphase separation transition. The reason for that is the strong wavenumber dependence of the fourth-order vertexes of the effective Hamiltonian (eq 2.13). The characteristic length scale of the fluctuations destroying the homogeneous state near the phase transition point and the period L of the domain structure below the phase transition point decreases with the effective temperature as $|\tau|^{-1/6}$ about the classical Lifshitz point ($u = 0.5$). At high polydispersity, $u \approx 1$, the characteristic length scale of critical fluctuations has a stronger temperature
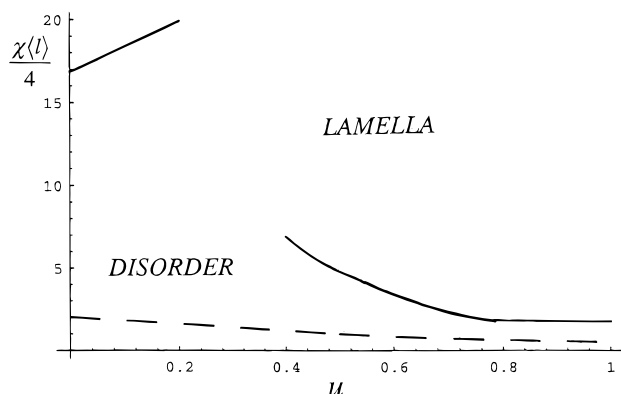
Figure 3. Phase diagram of the polydisperse multiblock copolymer melt on the plane $(u, \chi\langle l\rangle)$ at $v/a^3(\langle l\rangle)^{1/2} = 0.1$. The solid line is the line of the first-order phase transition. Spinodal of the homogeneous state (eq 2.19) is shown as the dotted line.

dependence of $|\tau|^{-1/4}$ than that for the system near the classical Lifshitz point. However, this exponent is smaller in comparison with the exponent 1/2 predicted for random copolymers considered in refs 16–18, 21, 23, 24, and 31. One should note that the value of the Flory parameter χ, of the order–disorder transition, decreases with increasing polydispersity of the system.

To illustrate all of our predictions discussed above, the dependence of the Flory parameter χ on the polydispersity parameter u is sketched out in Figure 3. The solid line is the line of the first-order phase transition from the homogeneous state to the ordered one with the lamellar symmetry of the domain structure. The dotted line shows the spinodal of the homogeneous state given by eq 2.19. One can see that the line of the order–disorder transition has nonmonotonic dependence on the polydispersity parameter u. It grows at low values of the parameter u, but it decreases at u larger than 0.4. We expect that the maximum on the curve occurs at polydispersity parameter $u \sim 0.33$ where asymptotics of the fourth-order vertexes in the Landau expansion (eq 2.13) of the free energy switches from short-wave to long-wave limit. The detailed calculation of the condition of the first-order phase transition is very complicated in this regime, and we hope to consider it in a future publication. On the contrary the spinodal line monotonically decreases with increasing polydispersity parameter u.

The last issue that we want to discuss is the possibility of the macrophase separation at higher polydispersity u. This selection mechanism of the copolymer chains can occur if only there is a very broad distribution of chains.[33] Let us estimate the width of the composition distribution. The average number of A monomers is defined by the following formula:

$$N_A = \sum_i l_i \qquad (6.1)$$

where the sum is carried out over all A blocks in the chain. Because the length of the blocks is independent of their position along the polymer chain, the sum in the rhs of eq 6.1 can be rewritten as

$$N_A = \frac{n}{2}\langle l\rangle \qquad (6.2)$$

The same calculation can be provided for N_A^2 which

leads to

$$N_A^2 = \sum_i \sum_j l_i l_j = \frac{n}{2}\left(\frac{n}{2} - 1\right)\langle l\rangle^2 + \frac{n}{2}\langle l^2\rangle \qquad (6.3)$$

The ratio of the second and first moments is evident from eqs 6.1–6.3:

$$\Delta N_A/N_A = \sqrt{2u/n} \qquad (6.4)$$

One can see that this ratio is small in the parameter $1/(n)^{1/2}$ and on the average all chains have the same composition, 1/2.

Let us comment on the case of polydisperse copolymers containing nonequal numbers of A and B monomers. In this case there exist a cubic term in the Hamiltonian (eq 2.13). As a result, there will be regions on a phase diagram with three- and two-dimensional domain structures.[4–12,34,35] However, the general predictions of this paper—the existence of the fluctuation-induced instability at a finite wavenumber—will not be affected by the cubic term in the effective Hamiltonian (eq 2.13).

Experimentally our predictions can be tested by SANS or SAXS experiments on the melt of two-component multiblock copolymers prepared by a two-step polymerization reaction with Schultz-Zimm distribution of block lengths. At the region of the polydispersity parameter $u > 0.4$ the development of fluctuations with finite wavenumber q_* will be manifested in these experiments by the appearance of the peak in the structural factor $S(\mathbf{q})$ whose position q_* will shift in the region of higher q with cooling of the system. One should note that the experimental scattering curves will qualitatively look as a set of curves on Figure 2 that represents the renormalized Green's functions at different temperatures for the polydispersity parameter $u = 0.5$.

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