Critical compositions in the microphase separation transition of random copolymers

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We study the microphase separation transition of random copolymers with two kinds of monomers with attraction between similar kinds. We perfom a mean field analysis for nonsymmetric compositions where the total amount of the one kind of monomer exceeds that of the other. We find a critical composition $f_{cr} \approx 0.173$. For compositions $f < f_{cr}$ or $f > 1 - f_{cr}$ we find a first order transition of the Landau type in the presence of a cubic term in the effective Hamiltonian. For $f_{cr} < f < 1 - f_{cr}$ our mean field analysis predicts an unusual continuous transition even in the presence of the cubic term. The effect of fluctuations is also discussed.

I. INTRODUCTION

Recent analytical studies of the microphase separation transition of random copolymers have generated many interesting results regarding the mean field and the fluctuation behavior of such systems [1–6].

The copolymer problem is quite rich in the case where there is a tendency for phase separation between the two components. Due to polymeric bonds a microphase separation appears instead of macroscopic segregation and this phenomenon is studied extensively in the past 15 years for the case of block copolymers with well-defined sequence architecture both theoretically and experimentally [7,8].

In the case of the random, or statistical, copolymers each monomer along the sequence can be randomly of one or the other kind and we refer to it as the *uncorrelated* random copolymer [1]. Instead, if there is a wide distribution of block lengths around a mean homopolymeric segment length l of each monomer kind we refer to it as the *correlated* random copolymer where the correlations between monomer kinds decay exponentially along the sequence with a correlation length l [2,9,10]. This is the model we will examine in the present work.

The effective Hamiltonian for the study of the microphase separation transition has been derived by using perturbation methods [2,1]. These studies estimated only terms that give the major contribution to the mean field free energy. This was done under the valid assumption that, near the transition point, the microdomain scales are much larger than the microscopic scale which in the case of *correlated* random copolymers corresponds to the coil size of the average homopolymeric segment.

Mean field theory for $f = 1/2$ predicted lamellar mesophases after a third order transition with a decreasing size of microdomains as temperature decreases. However, studies beyond mean field have recently shown [3,4] that the ordered mesophase is unstable in the framework of the Hamiltonians studied before. This was indicated with a variational method [4,5] and was verified as an exact result in [3].

Then, the need for the seemingly subdominant terms in the free energy became apparent and the effect of these terms in the polymer problem was indicated in a recent work [6] for the case of symmetric sequence composition $f = 1/2$, i.e., equal content of the two kinds of monomers. We found that there is a fluctuationally induced weak first order transition at a shifted temperature instead of the third order continuous one predicted by mean field. The size of the predicted domains depends on temperature and is larger than the coil size scaling as $l^{1/2}$ of the average homopolymeric block l. These results obtained by direct loop expansion were in agreement with the results of a variational approach on a similar generalized Hamiltonian model [5].

In the present work we complete this study for the case of nonsymmetric compositions. Here the effect of the subdominant terms is important even on the level of mean field and the effect of fluctuations is also discussed. A complete derivation of all the important terms is given in the Appendix. We also find and discuss a critical composition $f_{cr} \approx 0.173$ where the nature of the transition changes.

II. THE MODEL

In describing the random heteropolymer we will adopt the model used by Fredrickson *et al.* [2] describing the identity of each kind of monomer as a first order Markov stationary stochastic process. The probability matrix P_{KL} for a monomer of kind K to be followed by a monomer of kind L with $K = 1, 2$ and $L = 1, 2$ has a nontrivial eigenvalue λ which is one of the parameters of the system. Positive values of this eigenvalue correspond to homopolymeric blocks where negative eigenvalues correspond to alternating sequences. In this work we will only consider positive eigenvalues. The other parameter is the total composition f which corresponds to the total fraction of monomers of each kind. In fact, we express all of our results in terms of the correlation length of the stochastic process $l = -(\ln \lambda)^{-1}$.

The random variable θ_i takes values ± 1 corresponding to monomers i of one or the other kind and its average

value is $\langle\theta\rangle_{\mathrm{av}} = 2f - 1$. Then we introduce the variable

$$\sigma_i = \theta_i - \langle\theta\rangle_{\mathrm{av}}, \tag{2.1}$$

and the two body interaction term is taken in the form

$$H = \frac{1}{4}\chi\sum_{i,j}\sigma_i\sigma_j\delta(\mathbf{r}_i - \mathbf{r}_j). \tag{2.2}$$

The connectivity between monomers is introduced by the Gaussian elastic term

$$g(\mathbf{r}_{i+1} - \mathbf{r}_i) = \frac{1}{(2\pi a^2)^{3/2}}\exp\left[-\frac{(\mathbf{r}_{i+1} - \mathbf{r}_i)^2}{2a^2}\right], \tag{2.3}$$

where a corresponds to the length of the polymeric bond.

In this system, attraction between similar types of monomers occurs when the Flory parameter $\chi < 0$. This corresponds to an energetic preference for phase separation. In the absence of polymeric bonds, a complete phase separation is taking place. In the presence of polymeric bonds, though, we can only expect a microphase separation. This phase separation is described by the order parameter

$$m(\mathbf{R}) = \frac{1}{2}\sum_i\sigma_i\delta(\mathbf{r}_i - \mathbf{R}) \tag{2.4}$$

which corresponds to the difference between the densities of the two types of monomers.

The correlation functions for the stochastic process introduced above can be calculated with the tranfer matrix method [2] and are given by

$$\langle\sigma_i\sigma_j\rangle_{\mathrm{av}} = 4f(1 - f)e^{-|i-j|/l},$$

$$\langle\sigma_i\sigma_j\sigma_k\rangle_{\mathrm{av}} = 8f(1 - f)(1 - 2f)e^{-|i-j|/l}e^{-|j-k|/l},$$

$$\langle\sigma_i\sigma_j\sigma_k\sigma_\ell\rangle_{\mathrm{av}} = 16f(1 - f)e^{-|i-j|/l}e^{-|k-\ell|/l}$$
$$\times[f(1 - f) + (1 - 2f)^2e^{-|j-k|/l}]. \tag{2.5}$$

We consider one collapsed chain with infinite length and impose the incompressibiliy condition by taking the density equal to unity. This is equivalent to the case of a melt of long chains as explained before [2].

In our study we omit the effects of finite length which allow for a small region of macrophase separation as is studied in [2]. The corresponding region in the phase diagram is of order $1/N$. The appearance of this phase is not related to the effects of quenched disorder in the sequence and nothing new is expected in our study.

III. MEAN FIELD THEORY

In the Appendix we derive the effective Hamiltonian for the system providing also subdominant terms that were previously neglected. We show that these terms are important for describing the phase transitions even on the level of mean field for compositions $f \neq 1/2$. Recently we have shown [6] that these terms are also important for the fluctuational analysis and the stability of the previously predicted mesophases in composition $f = 1/2$.

The effective Hamiltonian obtained in the Appendix is

$$\mathcal{H} = \frac{1}{2}\sum_{\mathbf{k}\neq 0}(c^2\mathbf{k}^2 + \tau)m(\mathbf{k})m(-\mathbf{k}) - V^{-1/2}\mu\sum_{\mathbf{k}_1,\mathbf{k}_2\neq 0}m(\mathbf{k}_1)m(\mathbf{k}_2)m(-\mathbf{k}_1 - \mathbf{k}_2)$$

$$+V^{-1}\lambda_1\sum_{\mathbf{k}_1,\mathbf{k}_2\neq 0}\frac{m(\mathbf{k}_1)m(-\mathbf{k}_1)m(\mathbf{k}_2)m(-\mathbf{k}_2)}{\mathbf{k}_1^2 + \mathbf{k}_2^2} + V^{-1}\lambda_2\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3\neq 0}m(\mathbf{k}_1)m(\mathbf{k}_2)m(\mathbf{k}_3)m(-\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{k}_3), \tag{3.1}$$

with

$$c^2 = \frac{a^2}{2C_2}, \quad \tau = \frac{1}{2C_2l} + 2\chi, \quad \mu = \frac{C_3}{8lC_2^2},$$

$$\lambda_1 = \frac{1}{8a^2l^2C_2^2}, \quad \lambda_2 = \frac{1}{16lC_2^2}\left(1 + \frac{5C_3^2}{4C_2}\right), \tag{3.2}$$

where $C_2 = f(1 - f)$, $C_3 = 1 - 2f$, and the Fourier transform is taken in the form $m(\mathbf{k}) = (1/\sqrt{V})\int d\mathbf{R}\,m(\mathbf{R})e^{i\mathbf{k}\cdot\mathbf{R}}$.

The behavior of this Hamiltonian is symmetric around $f = 1/2$. Positive values of C_3 correspond to positive mean field values of the order parameter and vice versa. So from now on for simplicity we will only consider $f < 1/2$ and $C_3 > 0$.

The fourth order vertex labeled as λ_1 comes entirely from the polymeric effect and prohibits phase separation at macroscopic scales. The vertex labeled λ_2 is the regu-

lar stabilizing fourth order term in the usual ideal gas entropy in any binary system. Omission of this term corresponds to a Gaussian approximation, where the random variables σ_i follow a Gaussian probability distribution instead of a discrete model where the random variable takes the values ± 1 [3,6].

This effective Hamiltonian exibits very rich behavior and it is more instructive to start from the simplest case, the symmetric composition $f = 1/2$ where $C_3 = 0$ and the cubic term is absent.

From previous studies of the symmetric case [1] we know that the mean field solution can be taken in the form

$$m(\mathbf{k}) = m_0\sqrt{V/2}\Big[\Delta(\mathbf{k} - \mathbf{k}_0) + \Delta(\mathbf{k} + \mathbf{k}_0)\Big], \tag{3.3}$$

where Δ is Kronecker's delta. This solution corresponds to the lamellar phase. The mean field amplitude m_0 and the frequency k_0 can be determined by minimization of

Eq. (3.1) to be

$$m_0 = 0 \quad \text{for} \quad \tau > 0; \qquad m_0 = -\frac{\tau}{3\sqrt{\lambda_1}}, \qquad k_0^2 = -\frac{\tau}{3}$$

$$\text{for} \quad \tau < 0. \quad (3.4)$$

The contribution of λ_2 to the free energy is negligible because in the region of validity of the Landau expansion $\tau \ll 1/l$ and therefore $\lambda_1/k_0^2 \gg \lambda_2$. The transition predicted by mean field at $\tau = 0$ is third order.

With the addition of the cubic term for nonsymmetric compositions $f \neq 1/2$ an interesting and peculiar behavior appears. In the mean field we need to minimize the free energy with respect to both m_0 and k_0. Minimization with respect to k_0 gives

$$k_0^2 = \frac{\lambda_1^{1/2} m_0}{c}. \quad (3.5)$$

By substitution of this into the free energy we see that the polymeric fourth order vertex λ_1 gives a contribution, effectively, to the cubic term. We can consider that the order parameter is [7]

$$m(\mathbf{k}) = \left(\frac{V}{2n}\right)^{1/2} m_0 \sum_{i=1}^{n} [\Delta(\mathbf{k} - \mathbf{k}_i) + \Delta(\mathbf{k} + \mathbf{k}_i)], \quad (3.6)$$

where different sets of $\mathbf{k}_i$ correspond to different reciprocal lattice vectors and n is the number of the reciprocal lattice vectors for the selected lattice. Then the mean field free energy can be writen as

$$F = \frac{1}{2}\tau m_0^2 + (\lambda_1^{1/2} c - \mu A_n) m_0^3 + \lambda_2 B_n m_0^4, \quad (3.7)$$

where A_n, B_n are the combinatoric symmetry coefficients that depend on the selected lattice.

For temperatures near transition the free energy is minimized for the largest value of the symmetry coefficient A_n. The face-centered cubic (fcc) reciprocal lattice has $n = 6$ components and corresponds to a body-centered cubic (bcc) lattice in real space. This lattice has a larger combinatoric coefficient $A_6 = 2/\sqrt{3}$ than the two-dimensional triangular (honeycomb) lattice with $A_3 = \sqrt{2/3}$. Therefore, the bcc lattice corresponds to lower free energy as in the case of block copolymers [7].

It is easy to see with the help of Eq. (3.2) that as the composition deviates from $f = 1/2$, at some critical composition f_{cr}, the coefficient of the total effective cubic term becomes negative. The value of the critical composition for the bcc lattice is $f_{cr} \approx 0.173$. In the absence of the so far subdominant term λ_2 the Hamiltonian would have been unstable. Therefore, we see that this term is important even in the mean field for nonsymmetric compositions.

With all this in mind we can now distinguish between the following regimes.

(i) For $f > f_{cr}$ the total effective cubic term in the free energy is positive and the transition is third order at $\tau = 0$ with

$$m_0 = \frac{1}{8\lambda_2}\left[-3(\lambda_1^{1/2} c - \mu A_6)\right.$$

$$\left. +\sqrt{9(\lambda_1^{1/2} c - \mu A_6)^2 - 16\tau\lambda_2 B_6}\right], \quad (3.8)$$

at $\tau < 0$. Away from the critical composition we can ignore the λ_2 contribution and find that the transition amplitude is given by

$$m_0 = \frac{-\tau}{3(\lambda_1^{1/2} c - \mu A_6)}. \quad (3.9)$$

For systems near the critical composition $m_0 \sim (-\tau/\lambda_2)^{1/2}$.

(ii) For $f < f_{cr}$ the overall third order coefficient is negative (corresponding to the positive value of m_0) and λ_2 can no longer be neglected. Then we have a first order transition of the Landau type at

$$\tau = \frac{(\mu A_6 - \lambda_1^{1/2} c)^2}{2\lambda_2 B_6} > 0, \quad (3.10)$$

and a jump in the transition amplitude

$$m_0 = \frac{(\mu A_6 - \lambda_1^{1/2} c)}{2\lambda_2 B_6}. \quad (3.11)$$

We see that this jump at the transition point is finite and independent of the length of the average homopolymeric block length l. The Landau mean field predictions for this first order transition are valid for $m_0 \ll 1$, i.e., for small deviations from the critical composition.

The bcc mesophase is the one that appears directly after the disordered phase in both regimes although by different transitions. The transition orders are only mean field predictions and are modified by the fluctuational analysis as it will be explained in the next section. The above predictions are qualitatively summarized to the phase diagram of Fig. 1. We see that the difference in the transition temperature is small but it is important to remember that the solid line represents a first order mean field transition.
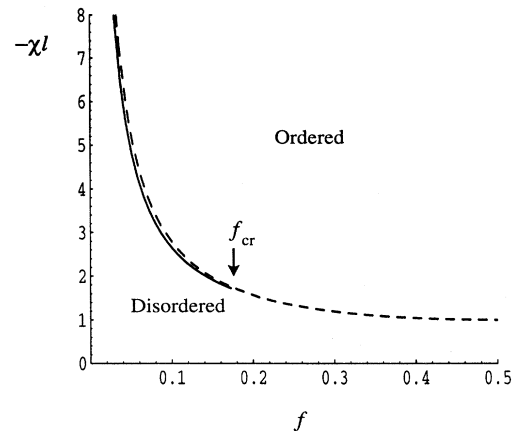

FIG. 1. The phase diagram for the transition between the disordered phase and an ordered bcc mesophase predicted by mean field. The dependence of χl as a function of composition is given. There is a critical composition at $f_{cr} \approx 0.173$. For $f < f_{cr}$ there is a first order transition of the Landau type represented by the solid line. For $f > f_{cr}$ there is a continuous third order transition represented by the dashed line. The transition temperature shift in the region $f < f_{cr}$ is seen as the difference between the solid and dashed line.

IV. EFFECT OF FLUCTUATIONS

We have recently examined [6] the effect of fluctuations in the Hamiltonian with the general form of Eq. (3.1) for the symmetric composition $f = 1/2$ where $\mu = 0$.

The Hamiltonian contains two fourth order vertices with different structure. The vertex λ_1 has only two free momentum integrations and it it shown [3,4] that due to this degeneracy the one-loop Dyson expansion is exact. Then it is seen [11] that the inverse propagator has a minimum at nonzero momenta and it can be taken in the form

$$G^{-1}(\mathbf{k}) = (k - k_0)^2 + r. \qquad (4.1)$$

Immediately, as in any system with finite wavelength mesophases, the effect of fluctuations has to be taken into account as predicted first by Brazovskii [12].

In his seminal work Brazovskii showed that in systems where the inverse propagator has an absolute minimum at $\mathbf{k}_* \neq 0$ a continuous transition of the Landau type is impossible. In particular, he showed on the level of the Hartree approximation, that fluctuations stabilize the disordered phase and prevent the renormalized mass from becoming zero or negative. However, for a Hamilitonian with the usual ideal gas (Ising) fourth order vertex, he showed that, in the range where the Hartree approximation is valid, a first order phase transition is possible, because the ordered phase can become first locally stable and eventually globaly stable.

For the heteropolymeric system we took into account the interplay between the two kinds of vertices. The vertex with the Ising structure λ_2 is known to have negligible contribution to the free energy on the level of mean field. However, if this vertex is omitted from the fluctuational analysis the predicted mesophases are completely unstable [3,4].

We then showed that including this vertex the mesophases are stable and the transition is possible. This is done with the following strategy. As we mentioned earlier, the one-loop Dyson equation is exact for vertex λ_1. We calculated the Ginsburg criteria for vertex λ_2 and found that the fluctuation effects of this vertex can be neglected in the ordered phase for

$$-\tau \gg \frac{1}{l^{5/4}}. \qquad (4.2)$$

By taking the exact one-loop contribution of vertex λ_1 to the Dyson equation we showed that there is a fluctuationally induced first order transition to an ordered mesophase at $-\tau \sim 1/l^{5/4}$.

In the presence of the cubic term in the full Hamiltonian we have to calculate the Ginsbourg criterion for the three point vertex. The most divergent diagram is given in Fig. 2. However, the mean field picture is very different in the two regimes around the critical composition $f = f_{cr}$ and the two cases must be considered separately.

A. The region $f < f_{cr}$

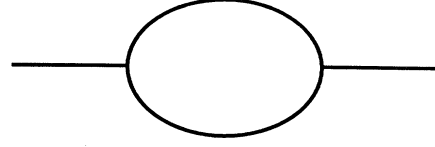In the region $f < f_{cr}$ we have a first order transition of the Landau type on the level of mean field. The transi-

FIG. 2. Feynman diagram for the one-loop contribution of the cubic vertex to the Dyson equation.

tion temperature is $\tau \sim \mu_{eff}^2/\lambda_2$, the transition amplitude $m_0 \sim \mu_{eff}/\lambda_2$, and $k_0^2 \sim \mu_{eff}$ where $\mu_{eff} = \mu A_6 - \lambda_1^{1/2}c$ is the smallness parameter in our study. We see immediately that the Landau expansion is valid for $\mu_{eff} \ll 1/l$.

The contribution of the diagram of Fig. 2 to the Dyson equation in the disordered phase is

$$\mu^2 \int \frac{d^3\mathbf{k}}{(\mathbf{k}^2 + \tau)(|\mathbf{k} - \mathbf{k}_0|^2 + \tau)} \sim \frac{\mu^2}{\tau^{1/2}}. \qquad (4.3)$$

This can be neglected from the Dyson equation for

$$\frac{\mu^2}{\tau^{1/2}} \ll \tau \quad \text{or} \quad \tau \gg \frac{1}{l^{4/3}}. \qquad (4.4)$$

By taking into account that $\tau \sim \mu_{eff}^2/\lambda_2$ this is equivalent to

$$\mu_{eff} \gg \frac{1}{l^{7/6}}. \qquad (4.5)$$

In the ordered phase the mean field mass is given by [6]

$$r = c^2 k_0^2 + \tau + \frac{2\lambda_1 m_0^2}{k_0^2} + 12\lambda_2 B_6 m_0^2$$

$$= \frac{\mu_{eff}}{2\lambda_2}(7\mu A_6 - 4\lambda_1^{1/2}c) \sim \mu_{eff}. \qquad (4.6)$$

The contribution of the diagram given in Fig. 2 is estimated by

$$\mu^2 \int \frac{d^d\mathbf{k}}{[(k - k_0)^2 + r][(|\mathbf{k} - \mathbf{k}_1| - k_0)^2 + r]} \sim \frac{\mu^2 k_0}{r}. \qquad (4.7)$$

This can be neglected from the Dyson equation when $\mu^2 k_0/r \ll r$. By taking $\mu \sim 1/l$, $k_0 \sim \mu_{eff}^{1/2}$, and $r \sim \mu_{eff}$ we obtain

$$\mu_{eff} \gg \frac{1}{l^{4/3}}. \qquad (4.8)$$

Between these two criteria the one for the disordered phase is stronger, so the final conclusion is that the mean field description is accurate in the region

$$\frac{1}{l^{7/6}} \ll \mu_{\text{eff}} \ll \frac{1}{l}. \qquad (4.9)$$

The lower limit is related to the fact that fluctuations become very important near the tricritical point $\mu_{\text{eff}} = 0$.

Regarding the behavior of the vertex λ_1, we can neglect the fluctuation one-loop correction in the ordered phase for $\lambda_1/r^{1/2} \ll r$ or equivalently $\mu_{\text{eff}} \gg 1/l^{4/3}$. For the disordered phase this is true for $\lambda_1/\tau^{1/2} \ll \tau$ which corresponds to $\mu_{\text{eff}} \gg 1/l^{7/6}$. We conclude than that in the region of Eq. (4.9) the fluctuation effects of vertex λ_1 is negligible. The contribution of λ_2 to the Dyson equation is weaker than that of λ_1 and can also be neglected [6].

B. The region $f > f_{\text{cr}}$

In the region $f > f_{\text{cr}}$ we have a continuous transition predicted by mean field where the stabilizing term in the free energy is a positive effective cubic term. However, the stabilization with respect to fluctuations is due to the vertex λ_2 as in the symmetric case studied in [6]. This situation is quite different from the traditional Landau first order transition in the presence of a cubic term. The mass in the ordered phase on the mean field level is $r \sim (-\tau)^2 l$ as in the symmetric case [6] and $m_0 \sim -\tau l$.

The diagram of Fig. 2 for the disordered phase is scaling as $\mu^2/\tau^{1/2}$ and can be neglected from the Dyson equation for

$$\frac{\mu^2}{\tau^{1/2}} \ll \tau \quad \text{or} \quad \tau \gg \frac{1}{l^{4/3}}. \qquad (4.10)$$

In the ordered phase we can neglect this diagram for

$$\frac{\mu^2 k_0}{r} \ll r \quad \text{or} \quad -\tau \gg \frac{1}{l^{8/7}}. \qquad (4.11)$$

The Landau expansion breaks down for $-\tau \sim 1/l$, so that the mean field estimates for the ordered phase are accurate in the region

$$\frac{1}{l^{8/7}} \ll -\tau \ll \frac{1}{l}. \qquad (4.12)$$

In this region the one-loop contribution of the vertices λ_1 and λ_2 can also be neglected as shown in [6].

It is hard to predict at this point what happens with the order of the transition and the exact transition temperature when the diagram of Fig. 2 starts contributing to the Dyson equation because this contribution has a negative sign and starts destabilizing both the ordered and the disordered phase. Although a region of temperatures exists where the one-loop correction coming from the vertex μ is much larger then the equivalent two-loop contribution, a more careful study is required due to the destabilization of both the ordered and disordered phase mentioned above. This question will be addressed in a different work. In conclusion, we cannot describe the transition for $f > f_{\text{cr}}$, but we have proven its existence.

V. DISCUSSION

We have discussed the mean field theory and the region of its validity for the effective Hamiltonian of a random heteropolymer of two kinds of monomers that exibit an energetic tendency for phase separation. We introduce a correlation length l along the sequence corresponding to an average homopolymeric block length, where the model assumes a random distribution of these blocks. In the present work we have investigated the complete Hamiltonian including nonsymmetric compositions, i.e., cases where the total amount of one kind of monomer is larger than the total amount of the other kind, where the cubic term appears in the effective Landau Hamiltonian.

The appearance of cubic terms in the effective Hamiltonian induces some unusual changes in the behavior of the system even on the level of mean field. In the usual Landau Hamiltonian with a cubic term and an ideal gas (Ising) fourth order vertex, the presence of a cubic term results in a first order transition observed on the level of mean field, at positive temperature τ. In the effective Hamiltonian derived in the Appendix and analyzed in the present work we found two composition regions where the system exibits different behavior.

In the region $f < f_{\text{cr}}$, mean field theory predicts a first order transition of the Landau type from the disordered phase to a bcc mesophase. This transition is analogous to the corresponding microphase separation in diblock or periodic multiblock copolymers [7]. By examining the effect of fluctuations we defined the composition region in which mean field adequately describes the transition.

In the region $f > f_{\text{cr}}$ the transition is predicted by mean field to be a third order continuous transition. The situation at $f = 1/2$ has been investigated before [6] and a complete fluctuational analysis has shown that fluctuations induce a weak first order transition of the Brazovskii type. There are, however, certain qualitative differences between the heteropolymeric system examined in [6] and the Brazovskii Hamiltonian. The most important of these differences is the temperature dependence of the microdomain size in the heteropolymeric case. For $f_{\text{cr}} < f < 1/2$, the presence of the cubic term does not provide, in mean field, a first order transition as it happens in the Landau or in the Brazovskii system. The fluctuation effects of the three-point function are, therefore, very serious and shold be taken into account in a different work.

The nonsymmetric case was previously studied in [2]. There, although it was mentioned that the subdominant terms were necessary to determine the nature of the transition, the authors suggested that the cubic term in the Landau Hamiltonian was very small and the difference in the free energy of the various symmetries would be unable to demonstrate a preference for a particular long-range mesophase. Consequently it was speculated that this degeneracy may allow for a phase with structures without long-range order which is called *disordered microphase*. Our calculation here shows that the cubic term is of order $1/l$ as opposed to $1/l^3$ predicted in [2] and the free energy of the bcc (body centered cubic) phase is lower.

In the present work we investigated a model of *corre-*

lated sequences where the correlations decay exponential. If we consider a model where we have homopolymeric blocks of fixed length M that are randomly connected to each other we can repeat the calculation of the effective Hamiltonian. In that case we will find that the coefficients in the free energy are $\mu \sim 1/M$, $\lambda_1 \sim 1/M^2$, and $\lambda_2 \sim 1/M$ so that M plays the same role as the average homopolymeric segment l in the model examined in the present work. The same qualitative conclusions will then hold, but the numerical values of the coefficients will vary and the value of the critical composition will be different.

Before concluding this discussion it is interesting to mention a different aspect of heteropolymers concerning the effects of quenched disorder in these systems [13,14]. Early studies showed that frustration differentiates the free energies of the low-energy conformations and creates a strong thermodynamic preference for a few of them [16]. In particular it was shown that the energy spectrum of random heteropolymers is accurately described by the random energy model [15] and there is a phase transition into the so-called *frozen state* where the number of dominant conformations is of order unity and the conformation is frozen to microscopic scale [16,17].

The temperature for this transition is higher for more heterogeneous systems. However, we were able to show [14] that, even in copolymers where the chain consists of only two kinds of monomers, the frustration induced by polymeric bonds is strong enough to allow a similar freezing transition when the chain is stiff.

In the *correlated* model we examined here, the heteropolymeric chains, which consists of significantly long homopolymeric segments, can be considered as flexible and according to our previous work [14] the freezing transition mentioned above can be suppressed. Therefore, a regime is defined where the microphase separation transition study is meaningful and independent of the freezing transition.

In this work we have estimated the region in which mean field theory is correct and showed that there exists an ordered phase with bcc structure immediately below the disordered phase. The transition order and transition temperature changes due to fluctuations for the case $f > f_{cr}$ are now much more difficult to handle since they are influencing a continuous transition as opposed to the traditional first order one. The contribution of the three-point vertex to the Dyson equation for both the ordered

and disordered phase reduces the total mass and destabilizes both the ordered and disordered phase, so that the Brazovskii analysis no longer applies. This is an open question to be addressed in the future.

The dynamics of this system is another open problem with many unresolved questions [18,19], that has not received as much attention as the thermodynamics and should be addressed in future studies.

APPENDIX A: DERIVATION OF THE LANDAU FREE ENERGY

In this Appendix we calculate the Landau effective Hamiltonian for the random copolymer model with short-range sequence correlations defined in Sec. II. We follow the cumulant method introduced in [2] avoiding the use of replicas [1,9,10] since the order parameter that describes the microphase separation transition is a one-replica order parameter and the use of cumulants gives equivalent results in the study of the microphase separation transition. Here we recover the subdominant terms that were neglected in [2]. These terms, as explained in the text, are essential for our analysis.

The partition function is

$$Z = \left\langle \delta \left(\sum_i \delta(\mathbf{r}_i - \mathbf{R}) - 1 \right) \right.$$
$$\left. \times \exp \left[-\frac{1}{4} \sum_{i,j} \frac{\chi}{T} \sigma_i \sigma_j \delta(\mathbf{r}_i - \mathbf{r}_j) \right] \right\rangle_{\text{th}} , \qquad (A1)$$

The average $\langle \ \rangle_{\text{th}}$ denotes the thermal average over all conformations, taking into account that successive monomers are connected by polymeric bonds according to the elastic term introduced in Eq. (2.3). The density is fixed to unity by the δ-function constraint. The interaction potential is taken approximately as a δ function. A gradient term related to the surface tension can be added as a correction to this approximation.

The order parameter of the system related to the difference between the densities of the two kinds of monomers is given in Eq. (2.4). In order to express the free energy in terms of the order parameter we rewrite the partition function

$$Z = \int \mathcal{D}m(\mathbf{R}) e^{-\chi \int d\mathbf{R} m^2(\mathbf{R})} \left\langle \delta \left(\sum_i \delta(\mathbf{r}_i - \mathbf{R}) - 1 \right) \delta \left(\frac{1}{2} \sum_i \sigma_i \delta(\mathbf{r}_i - \mathbf{R}) - m(\mathbf{R}) \right) \right\rangle_{\text{th}}$$
$$= \int \mathcal{D}m(\mathbf{R}) e^{-\chi \int d\mathbf{R} m^2(\mathbf{R})} \int \mathcal{D}\tilde{J}_\phi(\mathbf{R}) \mathcal{D}\tilde{J}_m(\mathbf{R}) \exp \left\{ i \int d\mathbf{R}(\tilde{J}_\phi + \tilde{J}_m m) + G[\tilde{J}_\phi, \tilde{J}_m] \right\} \qquad (A2)$$

with

$$G[\tilde{J}_\phi, \tilde{J}_m] = \ln \left\langle \exp \left\{ -i \int d\mathbf{R} \left[\tilde{J}_\phi \sum_i \delta(\mathbf{r}_i - \mathbf{R}) \right. \right. \right.$$
$$\left. \left. \left. + \tilde{J}_m \frac{1}{2} \sum_i \sigma_i \delta(\mathbf{r}_i - \mathbf{R}) \right] \right\} \right\rangle_{\text{th}} . \qquad (A3)$$

Addition of constants to the free energy are not important and we can introduce new variables

$$J_\phi(\mathbf{R}) = \tilde{J}_\phi(\mathbf{R}) - V^{-1} \int d\mathbf{R} \tilde{J}_\phi(\mathbf{R}),$$
$$J_m(\mathbf{R}) = \tilde{J}_m(\mathbf{R}) - V^{-1} \int d\mathbf{R} \tilde{J}_m(\mathbf{R}). \qquad (A4)$$

Then we average the free energy with respect to disorder and get

$$\langle G[J_\phi, J_m]\rangle_{\mathrm{av}} = \left[\frac{1}{2}\langle\langle\epsilon_\phi^2\rangle_{\mathrm{th}}\rangle_{\mathrm{av}} + \frac{1}{2}\langle\langle\epsilon_m^2\rangle_{\mathrm{th}}\rangle_{\mathrm{av}} \right.$$
$$+ \frac{1}{3!}\langle\langle\epsilon_m^3\rangle_{\mathrm{th}}\rangle_{\mathrm{av}} + \frac{1}{2}\langle\langle\epsilon_\phi\epsilon_m^2\rangle_{\mathrm{th}}\rangle_{\mathrm{av}}$$
$$\left. + \frac{1}{4!}(\langle\langle\epsilon_m^4\rangle_{\mathrm{th}}\rangle_{\mathrm{av}} - 3\langle\langle\epsilon_m^2\rangle_{\mathrm{th}}^2\rangle_{\mathrm{av}})\right],$$

$$(A5)$$

with

$$\epsilon_\phi = -i\int d\mathbf{R}J_\phi(\mathbf{R})\sum_i \delta(\mathbf{r}_i - \mathbf{R}),$$

$$(A6)$$

$$\epsilon_m = -(i/2)\int d\mathbf{R}J_m(\mathbf{R})\sum_i \sigma_i\delta(\mathbf{r}_i - \mathbf{R}).$$

We introduce the Fourier transform

$$J(\mathbf{k}) = \frac{1}{\sqrt{V}}\int d\mathbf{R}J(\mathbf{R})e^{i\mathbf{k}\cdot\mathbf{R}},$$

$$(A7)$$

and we calculate the thermal conformational averages and the disorder averages. By using the correlators given in Eqs. (2.5) we obtain

$$\frac{1}{2}\langle\langle\epsilon_\phi^2\rangle_{\mathrm{th}}\rangle_{\mathrm{av}} = -N\sum_{\mathbf{k}\neq 0}\frac{J_\phi(\mathbf{k})J_\phi(-\mathbf{k})}{a^2\mathbf{k}^2},$$

$$(A8)$$

$$\frac{1}{2}\langle\langle\epsilon_m^2\rangle_{\mathrm{th}}\rangle_{\mathrm{av}} = -C_2 N\sum_{\mathbf{k}\neq 0}\frac{J_m(\mathbf{k})J_m(-\mathbf{k})}{(a^2\mathbf{k}^2 + 1/l)},$$

$$(A9)$$

where $C_2 = f(1 - f)$.

$$\frac{1}{3!}\langle\langle\epsilon_m^3\rangle_{\mathrm{th}}\rangle_{\mathrm{av}} = \frac{iC_2 C_3 N}{\sqrt{V}}\sum_{\mathbf{k}_1 \mathbf{k}_2 \neq 0}$$
$$\times\frac{J_m(\mathbf{k}_1)J_m(\mathbf{k}_2)J_m(-\mathbf{k}_1 - \mathbf{k}_2)}{(a^2\mathbf{k}_1^2 + 1/l)(a^2\mathbf{k}_2^2 + 1/l)},\quad (A10)$$

where $C_3 = (1 - 2f)$.

$$\frac{1}{2}\langle\langle\epsilon_\phi\epsilon_m^2\rangle_{\mathrm{th}}\rangle_{\mathrm{av}} = \frac{iC_2 N}{\sqrt{V}}\sum_{\mathbf{k}_1 \mathbf{k}_2 \neq 0}\frac{J_\phi(\mathbf{k}_1)J_m(\mathbf{k}_2)J_m(-\mathbf{k}_1 - \mathbf{k}_2)}{(a^2|\mathbf{k}_1 + \mathbf{k}_2|^2 + 1/l)}\left(\frac{2}{a^2\mathbf{k}_1^2} + \frac{1}{(a^2\mathbf{k}_1^2 + 1/l)}\right),\qquad (A11)$$

$$\frac{1}{4!}\langle\langle\epsilon_m^4\rangle_{\mathrm{th}}\rangle_{\mathrm{av}} = \frac{N}{V}\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3 \neq 0}J_m(\mathbf{k}_1)J_m(\mathbf{k}_2)J_m(\mathbf{k}_3)J_m(-\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{k}_3)$$
$$\times\left[\frac{C_2^2}{(a^2\mathbf{k}_1^2 + 1/l)(a^2|\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3|^2 + 1/l)a^2|\mathbf{k}_1 + \mathbf{k}_2|^2}\right.$$
$$\left. + \frac{C_2 C_3^2}{(a^2\mathbf{k}_1^2 + 1/l)(a^2|\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3|^2 + 1/l)(a^2|\mathbf{k}_1 + \mathbf{k}_2|^2 + 1/l)}\right]$$
$$+ \frac{N^2 C_2^2}{V}\sum_{\mathbf{k}_1,\mathbf{k}_2 \neq 0}\frac{J_m(\mathbf{k}_1)J_m(-\mathbf{k}_1)J_m(\mathbf{k}_2)J_m(-\mathbf{k}_2)}{(a^2\mathbf{k}_1^2 + 1/l)(a^2\mathbf{k}_2^2 + 1/l)},\qquad (A12)$$

$$\frac{3}{4!}\langle\langle\epsilon_m^2\rangle_{\mathrm{th}}^2\rangle_{\mathrm{av}} = \frac{C_2^2 N}{V}\sum_{\mathbf{k}_1,\mathbf{k}_2 \neq 0}J_m(\mathbf{k}_1)J_m(-\mathbf{k}_1)J_m(\mathbf{k}_2)J_m(-\mathbf{k}_2)$$
$$\times\left[\frac{N}{(a^2\mathbf{k}_1^2 + 1/l)(a^2\mathbf{k}_2^2 + 1/l)} + \frac{1}{(a^2\mathbf{k}_1^2 + 1/l)^2 a^2(\mathbf{k}_1^2 + \mathbf{k}_2^2)} + \frac{1}{(a^2\mathbf{k}_1^2 + 1/l)(a^2\mathbf{k}_2^2 + 1/l)a^2(\mathbf{k}_1^2 + \mathbf{k}_2^2)}\right].$$
$$(A13)$$

In the calculation of the quartic terms we have eliminated terms that contribute to the final free energy in the form

$$\frac{1}{l}\sum_{\mathbf{k}_1,\mathbf{k}_2 \neq 0}J_m(\mathbf{k}_1)J_m(-\mathbf{k}_1)J_m(\mathbf{k}_2)J_m(-\mathbf{k}_2)$$

$$(A14)$$

because these terms are not important for $k_0^2 \ll 1/l$.

By taking the mean field equation $\delta G/\delta J_\phi = 0$ we obtain

$$J_\phi(\mathbf{k}_1) = \frac{iC_2}{\sqrt{V}} \sum_{\mathbf{k}_2 \neq 0} \frac{J_m(\mathbf{k}_2) J_m(-\mathbf{k}_1 - \mathbf{k}_2)}{(a^2|\mathbf{k}_1 + \mathbf{k}_2|^2 + 1/l)} \left[1 + \frac{a^2 \mathbf{k}_1^2}{2(a^2 \mathbf{k}_1^2 + 1/l)} \right], \quad \text{for } \mathbf{k}_1 \neq 0. \tag{A15}$$

By substitution of this into the total equation for $G[J_\phi, J_m]$ we have complete cancelation of the fifth term of Eq. (A5). Then by taking the mean field equation for the total free energy $\delta F/\delta J_m = 0$ we obtain

$$J_m(\mathbf{k}) = \frac{im(\mathbf{k})}{2C_2}(a^2 \mathbf{k}^2 + 1/l) - \frac{3iC_3}{8lC_2^2\sqrt{V}} \sum_{\mathbf{k}_2 \neq 0} m(\mathbf{k}_2) m(\mathbf{k} - \mathbf{k}_2)$$

$$+ \frac{i}{2l^2 C_2^2 V} \sum_{\mathbf{k}_2 \neq 0} \frac{m(\mathbf{k}) m(\mathbf{k}_2) m(-\mathbf{k}_2)}{a^2(\mathbf{k}_1^2 + \mathbf{k}_2^2)} + \frac{i}{4lC_2^2 V} \left(1 - \frac{C_3^2}{C_2} \right) \sum_{\mathbf{k}_2, \mathbf{k}_3 \neq 0} m(\mathbf{k}_2) m(\mathbf{k}_3) m(-\mathbf{k} - \mathbf{k}_2 - \mathbf{k}_3). \tag{A16}$$

In the calculation of Eq. (A16) we have taken $(a^2 \mathbf{k}^2 + 1/l) \sim 1/l$ in the terms that contribute to the Hamiltonian in higher than quadratic order. This assumption corresponds to the case where the scales of phase separation of interest are much larger than the coil size of a block of sequence length l, i.e., microscopic scales. This assumption is finally verified by the predicted scale. We keep the $\mathbf{k}^2$ term to the quadratic order because the term $1/l$ is absorbed into the parameter τ that shows deviation from the mean field transition temperature and the remaining $\mathbf{k}^2$ term generates a surface tensionlike effect due to polymeric bonds so that this term does not depend on the arbitrary scale of the interaction potential. It is interesting to note that this polymeric term does not appear in uncorrelated sequences [1].

In the above calculations the sums over indices along the sequence were taken as integrals. This approximation is good for correlated sequences with $l \gg 1$ considered here but the sums should be considered in the calculation of the uncorrelated case otherwise important terms are missed.

By substitution of Eq. (A16) and collecting all terms in the free energy we take

$$\mathcal{H} = \frac{1}{2} \sum_{\mathbf{k} \neq 0} (c^2 \mathbf{k}^2 + \tau) m(\mathbf{k}) m(-\mathbf{k}) - V^{-1/2} \mu \sum_{\mathbf{k}_1, \mathbf{k}_2 \neq 0} m(\mathbf{k}_1) m(\mathbf{k}_2) m(-\mathbf{k}_1 - \mathbf{k}_2)$$

$$+ V^{-1} \lambda_1 \sum_{\mathbf{k}_1, \mathbf{k}_2 \neq 0} \frac{m(\mathbf{k}_1) m(-\mathbf{k}_1) m(\mathbf{k}_2) m(-\mathbf{k}_2)}{\mathbf{k}_1^2 + \mathbf{k}_2^2} + V^{-1} \lambda_2 \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3} m(\mathbf{k}_1) m(\mathbf{k}_2) m(\mathbf{k}_3) m(-\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{k}_3) \tag{A17}$$

with

$$c^2 = \frac{a^2}{2C_2}, \quad \tau = \frac{1}{2C_2 l} + 2\chi, \quad \mu = \frac{C_3}{8lC_2^2},$$

$$\lambda_1 = \frac{1}{8a^2 l^2 C_2^2}, \quad \lambda_2 = \frac{1}{16lC_2^2} \left(1 + \frac{5C_3^2}{4C_2} \right) \tag{A18}$$

with $C_2 = f(1 - f)$ and $C_3 = 1 - 2f$.

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