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# Fluctuation effects on microphase separation in random copolymers

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**Abstract.** We study random copolymers consisting of two kinds of monomers, with attraction between similar kinds. The mean-field analysis of this system indicates a continuous phase transition into a phase with periodic microdomain structure. It is shown that the inverse of the renormalized propagator has a minimum at non-zero wavenumbers. Consequently, there is an anomalously large contribution of fluctuations that make the disordered phase locally stable at every finite temperature. However, below a certain temperature, the ordered phase is shown to be locally stable and a weak first-order transition is possible, similar to the weak crystallization theory developed by Brazovskii.

## 1. Introduction

Copolymers with attraction between similar kinds of monomers have received a lot of attention in the previous decade [1–4]. Their most important applications arise from the remarkable changes in their mechanical properties when they undergo a microphase separation transition. Regular block copolymers, with well defined architectures along the sequence, constitute the most important class of such materials. The study of these systems shows that they can undergo a temperature-induced microphase separation transition into a variety of phases with a periodic domain structure and different crystalline symmetries. The scale of the domains is proportional to the coil size of a block defined by the sequence architecture and, therefore, does not depend on temperature.

A different class of copolymeric materials are the random—or statistical—copolymers where each monomer along the sequence can be, randomly, of one kind or the other [5, 6] or there is a large distribution of block lengths [7–9]. The important feature of these systems is the quenched disorder along the sequence. The theoretical study on the level of the mean field [6] showed that they also undergo a temperature-induced phase separation transition. It was shown that, near the transition point, the domain size depends very strongly on temperature. The transition from the disordered to the ordered phase has been predicted to be third order.

In all these cases, the finite scale of domains is a natural consequence of the polymeric effect that prevents macrophase separation, as would happen in a gas of disconnected *A* and *B* species with attraction between similar kinds. As a result of this finite scale, the inverse of the renormalized propagator has a minimum at finite momenta and the effect of fluctuations is anomalously large.

In the case of regular block copolymers [1, 10], where the phase separation scale does not depend on temperature, the inverse propagator of the effective Hamiltonian in the Fourier representation has a minimum at  $k_* \neq 0$ . The mean-field theory for this Hamiltonian

[1] predicts a continuous second-order transition. Then, the Hamiltonian of the regular block copolymer can be mapped onto the Hamiltonian for the Brazovskii theory of weak crystallization [11–13].

In his seminal work [11], Brazovskii showed that in systems where the inverse propagator has an absolute minimum at  $k_* \neq 0$ , 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. For Hamiltonians of this kind, however, he showed that, in the range where the Hartree approximation is valid, a phase transition is possible because the ordered phase becomes first locally stable and eventually globally stable, so a first-order transition occurs.

The analogy between the Brazovskii theory and regular block copolymers was pointed out by Fredrickson and Helfand [14], who calculated the corrections to the phase diagram of Leibler. In a later study, Dobrynin and Erukhimovich [15] proposed a variational method to modify the Brazovskii theory in order to take into account the explicit momentum dependence of the fourth-order vertex, reproducing the results of [14].

Interesting predictions of the fluctuation effects based on the Brazovskii theory were also made by taking into account higher harmonics of the phase separation order parameter, regarding the behaviour of some exotic structures observed with hexagonal cylinders arranged in lamellar layers [16].

The explicit analogy between the Brazovskii theory and the theory of regular block copolymers is due to the fact that the phase separation scale in the latter does not depend on temperature and is fixed by the well defined architecture of the sequence. In random copolymers, the strong temperature dependence of the phase separation scale creates qualitative differences in the fluctuation treatment of the problem, as will be seen in the present work.

A first effort to describe the microphase separation transition in random copolymers beyond the mean field was made in [17]. It was shown that, although the inverse of the bare propagator has a minimum at zero momentum, the renormalized propagator has a minimum at a finite momentum. In that case, it is known from Brazovskii theory that fluctuations make the disordered phase locally stable.

In all the previous mean-field studies [6–8] of random copolymers, certain terms of the Hamiltonian were ignored because they were shown to have a very weak effect within the limits of the mean field. The consecutive fluctuation studies [15] also ignored these terms. For this Hamiltonian, it was shown recently [18, 19] that the one-loop calculation is exact and higher-loop diagrams do not contribute to the Dyson equation in the thermodynamic limit. It was also found that, in the framework of the examined Hamiltonian, fluctuations destroy the stability of the ordered phase and the microphase separation transition disappears.

In the present work, we examine the complete effective Hamiltonian for random copolymers with strong short-range correlations of monomer kinds along the sequence, *i.e.* with a wide distribution of block lengths. We show that the previously omitted terms play an important role in restoring the phase transition. This result is in agreement with the results obtained by an investigation of a qualitatively similar Hamiltonian with a variational approach [20, 21].

Due to the presence of these extra terms, the ordered phase becomes stable at some temperature and the system can undergo a weak first-order transition to a phase with periodic microdomain structure. The period of the domains and the amplitude of the separation below the transition temperature are the same as those predicted by the mean field.

### 2. The model and the mean-field theory

The random two-letter copolymer is described by a microscopic Hamiltonian that takes into account the self-interactions between monomers as

$$\mathcal{H} = \frac{1}{2} \sum_{i \neq j} B_{ij} U(\mathbf{r}_i - \mathbf{r}_j) \tag{2.1}$$

where the conformation of the polymer is described by the coordinates of its monomers  $\{\mathbf{r}_i\}$  and  $U(\mathbf{r})$  is a short-range potential. The binary interaction virial coefficient is given by [22]

$$B_{ij} = \chi \sigma_i \sigma_j + c_1 (\sigma_i + \sigma_j) + c_2. \tag{2.2}$$

The sequence of monomers is described by a quenched set of random values  $\{\sigma_i\}$  with equal probabilities for the two types of monomer;  $\sigma_i = 1$  if monomer  $i$  is of type  $A$  and  $\sigma_i = -1$  if it is of type  $B$ . When the interactions between similar monomers are equal ( $B_{AA} = B_{BB}$ ), then  $c_1 = 0$ . The composite Flory parameter  $\chi = (B_{AA} + B_{BB})/2 - B_{AB}$  will be negative in the case of interest, where similar monomers attract each other. The constant  $c_2$  corresponds to an overall attraction in the two-body term. This overall attraction, in combination with a three-body repulsion term which is not explicitly introduced in the Hamiltonian, are known to lead the polymer to a compact state with constant density [23]. This well studied effect is purely homopolymeric and will not be considered in the present study where only heteropolymeric effects are taken into account.

In this model, we consider that a monomer of one kind is followed, with high probability, by a monomer of the same kind. Correspondingly, the correlations between kinds of monomers decay as

$$\langle \sigma_i \sigma_j \rangle \sim e^{-|i-j|/l} \tag{2.3}$$

where  $l \gg 1$  represents the average block length with monomers of one kind.

The polymeric effect is explicitly introduced through the elastic term [23] that constrains the position of consecutive monomers at an average distance of unity:

$$g(\mathbf{r}_{i+1} - \mathbf{r}_i) = \frac{1}{(2\pi)^{3/2}} \exp \left[ -\frac{(\mathbf{r}_{i+1} - \mathbf{r}_i)^2}{2} \right]. \tag{2.4}$$

In this system, attraction between similar types of monomers generates an energetic preference for phase separation. In the absence of polymeric bonds, a complete phase separation takes place. In the presence of polymeric bonds, we can only expect a microphase separation. This phase separation is described by the order parameter [5]

$$m(\mathbf{R}) = \sum_i \sigma_i \delta(\mathbf{r}_i - \mathbf{R}) \tag{2.5}$$

which corresponds to the difference  $\rho_A - \rho_B$  between the densities of the two types of monomers. In the present study, we refer to the case where there is an equal amount of  $A$  and  $B$  types, which is usually referred to as composition  $f = \frac{1}{2}$ .

The effective Hamiltonian is of the form [6, 7]

$$\begin{aligned} \mathcal{H} = & \frac{1}{2} \sum_{\mathbf{k} \neq 0} (\mathbf{k}^2 + \tau) m(\mathbf{k}) m(-\mathbf{k}) + V^{-1} \lambda_1 \sum_{\mathbf{k}_1, \mathbf{k}_2 \neq 0} \frac{m(\mathbf{k}_1) m(-\mathbf{k}_1) m(\mathbf{k}_2) m(-\mathbf{k}_2)}{\mathbf{k}_1^2 + \mathbf{k}_2^2} \\ & + V^{-1} \lambda_2 \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3} m(\mathbf{k}_1) m(\mathbf{k}_2) m(\mathbf{k}_3) m(-\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{k}_3) \end{aligned} \tag{2.6}$$

where  $V$  is the volume of the system and the Fourier transform is defined as  $m(\mathbf{k}) = (1/\sqrt{V}) \int d\mathbf{R} m(\mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}}$ .

The coefficient  $\lambda_1$  of the first vertex is inversely proportional to the square of the average block length  $l$ , i.e.  $\lambda_1 \sim 1/l^2$ . This vertex corresponds to the loss of entropy due to polymeric bonds that connect different blocks with each other. We can see immediately that, due to this term, long wavelength modes become unfavourable. On the other hand, very short wavelength modes are unfavourable due to the surface tension contribution in the second-order term.

The  $\lambda_2$  vertex has the usual form of the vertex in the Ising model effective Hamiltonian. This term is due to the discrete values  $\pm 1$  of the sequence  $\{\sigma_i\}$ . In an annealed system, as for example in a binary alloy where the quenched polymeric bonds are absent, this is the entropic fourth-order term that provides stability of the ordered phase with macroscopic phase separation into two domains. In the case of random copolymers, the coefficient of this vertex is  $\lambda_2 \sim 1/l$ , i.e. it is of order unity per typical block in units of  $k_B T$ . The momentum dependence of this term can be neglected for scales larger than the coil size of the average block, which is of order  $l^{1/2}$ . This is the term omitted from all previous mean-field studies. It is seen immediately that this term becomes comparable with the other vertex  $\lambda_1/k^2$  only at scales  $k \sim 1/l^{1/2}$  and, therefore, it was argued that it can be omitted for larger domain scales predicted by the mean field. Then, it was shown [6] that the mean-field solution can be taken in the form

$$m(\mathbf{k}) = m_0 \sqrt{V/2} (\Delta(\mathbf{k} - \mathbf{k}_0) + \Delta(\mathbf{k} + \mathbf{k}_0)) \quad (2.7)$$

where  $\Delta$  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 (2.6) to be

$$\begin{aligned} m_0 &= 0 & \text{for} & \quad \tau > 0 \\ m_0 &= -\frac{\tau}{3\sqrt{\lambda_1}} & k_0^2 &= -\frac{\tau}{3} & \text{for} & \quad \tau < 0 \end{aligned} \quad (2.8)$$

where the effect from  $\lambda_2$  is negligible because  $k_0$  is very small near the transition.

Thus, the mean-field theory predicts a continuous phase transition at  $\tau = 0$ . This transition is found to be third order. The effective Hamiltonian which contains only the heteropolymeric vertex is equivalent to a Gaussian sequence model, i.e. a quenched sequence of Gaussian variables  $\{\sigma_i\}$  instead of discrete variables  $\pm 1$ . This approximation does not change the mean-field results but is crucial for the fluctuation analysis that will be performed in the following sections. We will show in section 4 that this is the only term that provides the stability of the order phase. We will refer to the effective Hamiltonian without the  $\lambda_2$  vertex as the Gaussian sequence approximation.

### 3. The Gaussian sequence approximation

In this section, we will consider the effective Hamiltonian in the Gaussian sequence approximation, describing the microphase separation transition in random copolymers, as

$$\mathcal{H} = \frac{1}{2} \sum_{\mathbf{k} \neq 0} (k^2 + \tau) m(\mathbf{k}) m(-\mathbf{k}) + V^{-1} \lambda_1 \sum_{\mathbf{k}_1, \mathbf{k}_2 \neq 0} \frac{m(\mathbf{k}_1) m(-\mathbf{k}_1) m(\mathbf{k}_2) m(-\mathbf{k}_2)}{k_1^2 + k_2^2}. \quad (3.1)$$

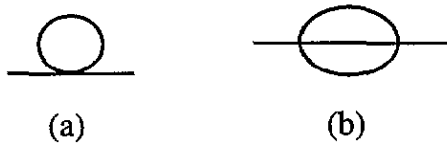


Figure 1. One-loop and two-loop Feynman diagram contribution to the self-energy.

This is the Hamiltonian that has been used in all previous mean-field studies. Shortly after the derivation of this Hamiltonian, it was observed [17] that a renormalization of the Green function on the one-loop level changes its form qualitatively. The one-loop Dyson equation for the Green function is

$$G^{-1}(k) = (k^2 + \tau) + V^{-1} \sum_{k_1} \frac{4\lambda_1}{k_1^2 + k^2} G(k_1). \tag{3.2}$$

By substituting even the bare Green function into the integral of (3.2) for  $\tau > 0$ , the renormalized Green function in three dimensions is

$$G^{-1}(k) = k^2 + \tau + \frac{2\lambda_1/\pi}{\tau^{1/2} + k} \tag{3.3}$$

with  $k = |k|$ . We see immediately that there is a minimum of  $G^{-1}(k)$  at some  $k_* \neq 0$ . It was, therefore, proposed that the form of the renormalized Green function can be described by the form used in the weak crystallization theory [11]

$$G^{-1}(k) = C(k - k_*)^2 + r. \tag{3.4}$$

This approximation is good for  $r \ll k_*^2$ . By substitution of (3.4) into (3.2), it is found that

$$r = \tau + \frac{3\lambda_1}{2\pi(Cr)^{1/2}} \quad k_*^2 = \frac{\lambda_1}{2\pi(Cr)^{1/2}} \quad C = 2. \tag{3.5}$$

According to the first relation in (3.5), the renormalized mass  $r$  cannot become zero except for  $\tau = -\infty$ , which corresponds to  $T = 0$ . Therefore, the disordered phase never loses stability, as in Brazovskii theory. This result is quite general and is due to the fact that the integral corresponding to the one loop correction

$$\int \frac{d^3 k_1}{(k^2 + k_1^2)[(k_1 - k_*)^2 + r]} \tag{3.6}$$

is divergent as  $r \rightarrow 0$ . On the basis of this evidence, it was assumed that this system will have a first-order transition of Brazovskii type. A more careful study, however, was performed in [18, 19] and is presented briefly in the rest of this section.

Consider the diagrams that contribute to a perturbation expansion. The contribution of the one-loop diagram shown in figure 1(a) to the Dyson equation is of order

$$V^{-1}\lambda_1 \sum_{k_1} \frac{G(k_1)}{k_1^2 + k^2} = V^{-1}\lambda_1 \frac{V}{(2\pi)^3} \int d^3 k_1 \frac{G(k_1)}{k_1^2 + k^2} \sim 1. \tag{3.7}$$

The two-loop diagram shown in figure 1(b) is of order

$$\lambda_1^2 V^{-2} G(k) \frac{V}{(2\pi)^3} \int d^3 k_1 \frac{G^2(k_1)}{(k_1^2 + k^2)^2} \sim V^{-1} \quad (3.8)$$

and should be neglected in the thermodynamic limit. We can easily see that all higher-loop diagrams do not contribute for the same reasons.

From the above remarks, we conclude that the one-loop Dyson equation given in (3.2) is exact and the lack of continuous transition for the effective Hamiltonian (3.1) is a general result that does not depend on the smallness of the parameter  $\lambda_1$ .

On the premises discussed above, we calculate here the stability of the ordered phase. If we assume that the symmetry is broken as described by (2.7), we need to write down the free-energy functional  $\mathcal{H}\{m_0, k_0; \psi\}$ . The order parameter is

$$m(k) = \begin{cases} m_0 \sqrt{V/2} & \text{for } k = \pm k_0 \\ \psi(k) & \text{for } k \neq \pm k_0. \end{cases} \quad (3.9)$$

Fluctuations of the mode  $k = k_0$  are of order 1 and are ignored, compared to the mean field  $m(k) \sim \sqrt{V}$ . Fluctuations of other modes are denoted by  $\psi$ . Then, the free-energy functional becomes

$$\begin{aligned} \mathcal{H}'\{m_0, k_0; \psi\} = & \mathcal{H}\{m_0, k_0\} + \frac{1}{2} \sum_{k \neq k_0} \left( k^2 + \tau + \frac{4\lambda_1 m_0^2}{k_0^2 + k^2} \right) \psi(k) \psi(-k) \\ & + \lambda_1 V^{-1} \sum_{k_1, k_2 \neq k_0} \frac{\psi(k_1) \psi(-k_1) \psi(k_2) \psi(-k_2)}{k_1^2 + k_2^2} \end{aligned} \quad (3.10)$$

where  $\mathcal{H}\{m_0, k_0\}$  is the value of Hamiltonian (3.1) if we substitute the mean-field solution in the form given by (2.7).

The classical field values  $m_0, k_0$  are found from the equation of state given by the thermodynamic relations

$$\left\langle \frac{\partial \mathcal{H}'\{m_0, k_0; \psi\}}{\partial m_0} \right\rangle = 0 \quad \text{and} \quad \left\langle \frac{\partial \mathcal{H}'\{m_0, k_0; \psi\}}{\partial k_0} \right\rangle = 0. \quad (3.11)$$

The first equation reads

$$(k_0^2 + \tau)m_0 + \frac{2\lambda}{k_0^2} m_0^3 + 4\lambda m_0 V^{-1} \sum_{k \neq k_0} \frac{\langle \psi(k) \psi(-k) \rangle}{k_0^2 + k^2} = 0 \quad (3.12)$$

where  $\langle \psi(k) \psi(-k) \rangle = G(k)$ . The Dyson equation for the ordered phase for  $k \neq k_0$  is

$$G^{-1}(k) = k^2 + \tau + \frac{4\lambda m_0^2}{k_0^2 + k^2} + 4\lambda V^{-1} \sum_{k_1 \neq k_0} \frac{G(k_1)}{k_1^2 + k^2}. \quad (3.13)$$

This equation is exact since higher-loop diagrams are subdominant in  $V$  due to the peculiar symmetry of our vertex.

Then, by comparison of equations (3.12) and (3.13), we see that  $G(k)$  depends only on the modulus  $k$  and

$$G^{-1}(k_0)m_0 = 0. \quad (3.14)$$

The minimum value of  $G^{-1}(k)$  is positive since, if  $G^{-1} = 0$ , the integral of (3.6) diverges. Then  $G^{-1}(k_0) > 0$  and, therefore, according to equation (3.14),  $m_0 = 0$ . We see that we cannot have a stable solution with  $m_0 \neq 0$  and  $k_0 \neq 0$  for Hamiltonian (3.1).

### 4. The complete Hamiltonian

#### 4.1. The Ginsburg criteria

In the previous section, we saw that, although on the level of the mean field the results should not be affected by the omission of the second vertex  $\lambda_2$ , the fluctuation analysis using only the heteropolymeric vertex  $\lambda_1$  results in the absence of any kind of microphase separation transition. This result is expectable even from mean-field estimates if we notice the following. The inverse propagator for the ordered phase calculated on the level of the mean field in the absence of  $\lambda_2$  is

$$G^{-1}(k) = k^2 + \tau + \frac{4\lambda_1 m_0^2}{k_0^2 + k^2}. \tag{4.1}$$

By substitution of the mean-field values (2.8), we see that the inverse propagator has a minimum at  $k_0$ . Then, the bare mass in the ordered phase is given by

$$r = \tau + k_0^2 + \frac{2\lambda_1 m_0^2}{k_0^2}. \tag{4.2}$$

By substitution of the mean-field values (2.8) for  $m_0$  and  $k_0$ , this gives  $r = 0$ . The consideration of the complete Hamiltonian (2.6) is then necessary. If  $\lambda_2$  is included, we see that the bare mass becomes positive and the ordered phase is stable independently of the relative smallness of  $\lambda_2$  compared to  $\lambda_1/k_0^2$ . It is straightforward to show that the mass for the ordered phase on the level of the mean field is

$$r = 8\lambda_2 m_0^2 \quad \text{or} \quad r \sim \tau^2 l. \tag{4.3}$$

We now shift our attention to the effect of fluctuations. The point at which fluctuations become important can be estimated by comparing the contribution of the diagram of figure 2(a) to the  $\Gamma^{(4)}$  function with the bare-vertex value. The vertex  $\lambda_1/k_0^2$  gives a larger contribution than the equivalent of  $\lambda_2$  at a given temperature and, therefore, the Ginsburg criterion for the validity of the mean field should be calculated by the diagram of figure 2(a) for the  $\lambda_1$  vertex.

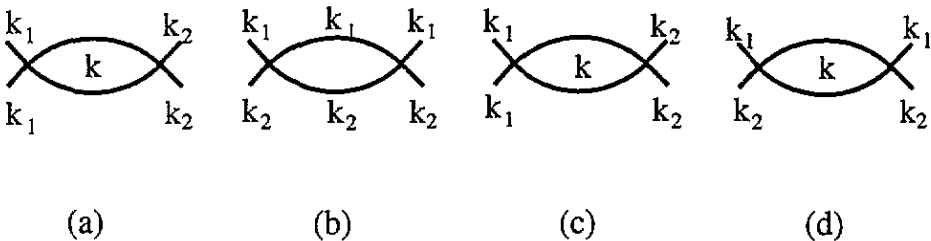


Figure 2. (a)–(b) One-loop diagram contribution to the four-point function  $\Gamma_1^{(4)}$  for vertex  $\lambda_1$ . (c)–(d) One-loop diagram contribution to the four-point function  $\Gamma_2^{(4)}$  for vertex  $\lambda_2$ .



We first consider the disordered phase. In this case, the Ginsburg criterion is given by

$$\lambda_1^2 \int \frac{k^2 dk}{(k^2 + k_1^2)(k^2 + k_2^2)(k^2 + \tau)^2} \ll \frac{\lambda_1}{k_1^2 + k_2^2}. \quad (4.4)$$

This is satisfied for any  $k_1, k_2$  if

$$\tau \gg \frac{1}{l^{4/3}}. \quad (4.5)$$

For the ordered phase, the Ginsburg criterion is equivalent to  $\lambda_1/r^{3/2} \ll 1$  which, owing to equation (4.3), becomes

$$-\tau \gg \frac{1}{l^{7/6}}. \quad (4.6)$$

On the other hand, we can see that the mean-field value for  $m_0$  becomes of order one at  $\tau \sim 1/l$  and the Landau expansion breaks down. Therefore, the region where the mean field is valid for the ordered phase is

$$\frac{1}{l^{7/6}} \ll -\tau \ll \frac{1}{l}. \quad (4.7)$$

Since the mean field is correct in this region, we can conclude that *there is* a phase transition between the disordered phase with  $m_0 = 0$  and the ordered phase with  $m_0 \neq 0$ .

Analogously, fluctuation corrections arising from the  $\lambda_2$  vertex can be neglected for  $\lambda_2 k_0^2/r^{3/2} \ll 1$ . This gives the Ginsburg criterion for this vertex in the ordered phase

$$-\tau \gg \frac{1}{l^{5/4}} \quad (4.8)$$

which is smaller than the Ginsburg value of  $-\tau$  for  $\lambda_1$ , as anticipated above.

#### 4.2. The effect of fluctuations

According to the derived criteria, there is a region of temperatures

$$\frac{1}{l^{5/4}} \ll -\tau \lesssim \frac{1}{l^{7/6}} \quad (4.9)$$

where the Dyson equation in the ordered phase should be described by

$$G^{-1}(k) = k^2 + \tau + \frac{4\lambda_1 m_0^2}{k_0^2 + k^2} + 12\lambda_2 m_0^2 + 4\lambda_1 V^{-1} \sum_{k_1 \neq k_0} \frac{G(k_1)}{k_1^2 + k^2} \quad (4.10)$$

because the one-loop contribution of the vertex  $\lambda_1$  is exact according to the analysis given in section 3. The equation obtained from the variation of the free-energy expression with respect to the amplitude  $m_0$  is

$$(k_0^2 + \tau)m_0 + \frac{2\lambda_1}{k_0^2} m_0^3 + 4\lambda_2 m_0^3 + 4\lambda_1 m_0 V^{-1} \sum_{k \neq k_0} \frac{G(k)}{k_0^2 + k^2} = 0. \quad (4.11)$$

By comparison of equations (4.10) and (4.11), we see that there is a solution for the field amplitude

$$m_0^2 = \frac{G^{-1}(k_0)}{8\lambda_2}. \tag{4.12}$$

From the minimization of the free energy with respect to the parameter  $k_0^2$ , we obtain

$$\frac{m_0^2}{2} \left[ 1 - \frac{\lambda_1 m_0^2}{k_0^4} - 4\lambda_1 V^{-1} \sum_{k \neq k_0} \frac{G(k)}{(k_0^2 + k^2)^2} \right] = 0. \tag{4.13}$$

This equation coincides with the equation for the minimum  $k_*$  of the inverse propagator by differentiation of the Dyson equation (4.10) for the ordered phase and  $k_*$  coincides with  $k_0$ . By taking  $G^{-1}(k) = (k - k_0)^2 + r$  and using Brazovskii's estimate for the integrals, it follows from equation (4.10) that

$$r = k_0^2 + \tau + \frac{2\lambda_1}{k_0^2} m_0^2 + \frac{3\lambda_1}{2\pi r^{1/2}}. \tag{4.14}$$

Substituting equation (4.12) into (4.14), we obtain

$$-(\tau + k_0^2) = \left( \frac{\lambda_1}{4k_0^2\lambda_2} - 1 \right) r + \frac{3\lambda_1}{2\pi r^{1/2}}. \tag{4.15}$$

Since we are considering scales much larger than the coil size of the average block, we always have  $\lambda_1/(k_0^2\lambda_2) \gg 1$  and the Dyson equation for the ordered phase has the form

$$-(\tau + k_0^2) = \frac{\lambda_1}{4k_0^2\lambda_2} r + \frac{3\lambda_1}{2\pi r^{1/2}}. \tag{4.16}$$

We notice that the second term on the right-hand side of (4.16) is small compared to  $-\tau$  for  $-\tau \gg 1/l^{5/4}$ . The same condition is also valid in order to neglect the contribution of the last term in (4.13). Consequently, the mean-field results for  $r$ ,  $m_0$  and  $k_0$  will hold true in the region (4.9).

As we approach  $-\tau \sim 1/l^{5/4}$ , the three terms of (4.16) become of the same order. It is easy to show that for  $-\tau > \tau_c$  and, correspondingly, for  $r > r_c$ , this equation has real solutions for  $r$  where

$$r_c \sim \frac{1}{l^{3/2}} \quad \text{and} \quad \tau_c \sim \frac{1}{l^{5/4}} \tag{4.17}$$

and the solution with  $r$  growing as  $-\tau$  corresponds to the minimum of the thermodynamic potential. Correspondingly, for  $-\tau < \tau_c$ , equation (4.16) does not have a solution. This means that in that region the ordered phase is locally unstable.

We can easily see from the first equation in (3.5) that the disordered phase does not lose local stability at  $-\tau \sim 1/l^{5/4}$ . Then there must be a first-order phase transition, as in the Brazovskii theory of weak crystallization. It can be shown rigorously with Brazovskii's method [11] that, at the temperature of the order predicted by (4.17), the ordered phase becomes globally stable. The jump in the amplitude, according to (4.12), is given by

$$m_0 \sim \frac{1}{l^{1/4}} \quad \text{and} \quad k_0^2 \sim \frac{1}{l^{5/4}}. \tag{4.18}$$

We note that the order of the transition temperature coincides with the Ginsburg temperature for vertex  $\lambda_2$  predicted by equation (4.8). However, one-loop corrections to the Dyson equation due to this vertex need not be considered because the divergent contribution of the  $\lambda_1$  vertex is much larger. It is also easy to show that at  $-\tau \sim 1/l^{5/4}$ , the higher-loop terms for  $\lambda_2$  do not contribute.

As explained in section 3, the one-loop correction for vertex  $\lambda_1$  is not an approximation but the exact contribution of this vertex to the self-energy. We must also mention that, for the renormalization of the four-point function  $\Gamma_1^{(4)}$  for this vertex, only the channel of figure 2(a) contributes to the geometric progression for the ladder diagrams since the channel of figure 2(b) must be neglected according to the arguments of section 3. In contrast, for vertex  $\lambda_2$ , Brazovskii showed that there are two channels contributing to the renormalization of  $\Gamma_2^{(4)}$ , as shown in figures 2(c) and (d), and the geometric progression for the renormalized four-point function has a special form given by

$$\Gamma_2^{(4)} = \frac{1 - \lambda_2 \Pi}{1 + \lambda_2 \Pi} \quad (4.19)$$

where  $\Pi \sim k_0^2/r^{3/2}$ . It is seen that when  $\lambda_2 k_0^2/r^{3/2} > 1$ ,  $\Gamma_2^{(4)}$  changes sign, which does not happen for the four-point function  $\Gamma_1^{(4)}$ . This change of sign can be interpreted as a hint for the existence of an inflection in the thermodynamic potential which should exist at the temperature where the ordered phase becomes locally stable and below.

## 5. Discussion

We have investigated the effect of thermal fluctuations on the microphase separation transition in a melt of random copolymers. We have considered a quenched sequence consisting of an equal amount of monomers of two kinds in the thermodynamic limit. The model assumes that neighbouring monomers are, with high probability, of the same kind with average block length  $l \gg 1$  and a wide distribution of block lengths. Our analysis indicates that there is a weak first-order phase transition between a disordered and an ordered phase with periodic microdomain structure instead of a continuous third-order phase transition predicted by the mean field.

The effective Hamiltonian (2.6) for this system contains two fourth-order vertices with completely different forms. The vertex labelled  $\lambda_1$  is solely due to the polymeric effect and prohibits macroscopic phase separation. Vertex  $\lambda_2$  which has the usual Ising model form is due to the discrete values  $\pm 1$  for the sequence labels  $\{\sigma_i\}$ . In the mean field, the contribution of the vertex  $\lambda_2$  is negligible around the transition point and can be omitted. An exact analysis of fluctuations in the absence of vertex  $\lambda_2$  is possible and shows that the disordered phase is always locally stable. At the same time, the ordered phase is locally unstable and the phase transition is impossible. Then, the effect of vertex  $\lambda_2$  has to be taken into account.

For the complete Hamiltonian (2.6), we have shown that the mean-field predictions

$$m_0 \sim -\tau l \quad \text{and} \quad k_0^2 \sim -\tau \quad \text{for } \tau < 0 \quad (5.1)$$

are correct in the region

$$\frac{1}{l^{5/4}} \lesssim -\tau \ll \frac{1}{l}. \quad (5.2)$$

The weak first-order transition takes place at  $-\tau \sim 1/l^{5/4}$ , with a jump in the amplitude

$$\Delta m_0 \sim \frac{1}{l^{1/4}} \quad \text{and} \quad k_0 \sim \frac{1}{l^{5/8}}. \tag{5.3}$$

The longer the average block length  $l$ , the higher the temperature of transition and the smaller the jump in the phase separation amplitude at the point of the weak first-order transition.

In the case of regular block copolymers, the jump in the corresponding fluctuationally-induced first-order transition predicted in [14] is  $\Delta m_0 \sim 1/l_b^{1/6}$ , where  $l_b$  is the fixed block size of the sequence. We see that the jump predicted for random copolymers is smaller. The temperature of transition in regular block copolymers is predicted at  $-\tau \sim 1/l_b^{4/3}$ . We see that the corresponding shift for random copolymers is also smaller. We notice that in random copolymers the domain size near transition  $k_0^{-1} \sim l^{5/8}$  is much larger than the corresponding domain size in regular block copolymers  $k_b^{-1} \sim l_b^{1/2}$ . The amplitude of the transition at the ordered phase in regular block copolymers  $m_0 \sim (-\tau l_b)^{1/2}$  is larger than the predicted amplitude of the random copolymer microphase separation at the same temperature.

We also see that, when there are no correlations along the sequence, i.e.  $l \sim 1$ , the predicted transition occurs at a region where the Landau expansion fails. The physics of this system is also described by a freezing transition into a phase where a small number of conformations are thermodynamically dominant [24] and depend strongly on the flexibility of the chain [25].

It is also worth noticing that in the absence of vertex  $\lambda_2$ , vertex  $\lambda_1$  does not have any preference for the different Bravais lattices [17]. This degeneracy of the polymeric vertex  $\lambda_1$  is related to the instability of the ordered phase predicted on the basis of only this vertex. All the structure dependence comes from vertex  $\lambda_2$ . Therefore, the analysis of structures other than the lamellar is expected to be similar to that of Brazovskii. In the case of composition  $f = \frac{1}{2}$ , there is no cubic term that breaks the inversion symmetry. Although other structures are locally stable, the lamellar would retain global stability. For compositions  $f \neq \frac{1}{2}$ , other structures like BCC and hexagonal cylinders may become globally stable and transitions between them may be possible.

In all our calculations, the integral for the one-loop correction of figure 1(a) has been estimated [11] to be of order  $\lambda k_0^2/r^{1/2}$ . In fact, this estimate is correct at  $r \ll k_0^4$ . For  $k_0^4 \ll r \ll k_0^2$ , the estimate

$$\lambda \int \frac{k^2 dk}{(k - k_0)^2 + r} \sim \lambda D + \frac{\lambda k_0^2}{r^{1/2}} \tag{5.4}$$

completely describes the behaviour of the integral and its derivatives, where  $D$  is a numerical constant that depends on the cut-off, as in the Ising case. The  $\lambda D$  term simply shifts  $\tau$ .

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