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Secondary super-structures in random copolymers

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Abstract. Secondary domain superstructures in correlated random block copolymers are considered theoretically using the concept of the second order parameter related to fluctuations of the local mean block length. It is shown that the size of secondary domains, Λ, is much larger than the primary domain size, L: $\Lambda \propto \epsilon^{-1}$, while $L \propto \epsilon^{-1/2}$, where ϵ is a small parameter defining the composition asymmetry. Different secondary morphologies are characterized. It is also shown that separation of the system in two macroscopic phases with different primary morphologies predicted earlier using the free energy expansion up to ψ^4 (ψ is the usual order parameter related to local composition) is an artifact of this widely accepted theoretical model.

PACS. 36.20.Ey Conformation (statistics and dynamics) – 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling – 61.41.+e Polymers, elastomers, and plastics

1 Introduction

It is well-known that block-copolymers can form periodic microdomain superstructures under appropriate conditions [1,2]. The driving force for the structure formation is an incompatibility of the blocks. Domain structures have been investigated theoretically both for diblock [3–11] and multi-block [12–35] copolymers. Although the earlier theoretical work was mainly focused on the regular copolymer systems with monodisperse blocks [3,4,12–16], more recently the effects associated with randomness of the copolymer primary chemical structure and block polydispersity attracted much attention [17–35].

The motivation of these studies is clear: on one hand all synthesized copolymers are at least partially chemically disordered, on the other hand important biological polymers like proteins are characterized by an essentially random monomer sequence [36,37]. It was shown, in particular, that thermal fluctuations tend to destroy microdomain structures in completely random copolymers [24,25,38], however the fluctuation effect is suppressed in correlated random copolymers [27] which are characterized by relatively long blocks of similar monomers. Hence correlated random copolymers can be adequately described by a mean-field approach (both in the strong and weak segregation regimes except a rather close vicinity of the critical point).

A number of interesting features of microphase separation in correlated random copolymers has been revealed theoretically near the critical point, *i.e.* in the weak segregation regime [27–29,34,35,39]. Classical lamellar, cylindrical and spherical morphologies were predicted in this regime together with rather wide windows of phase separation between different super-structures. The phase separation phenomenon is indeed inherent to polydisperse systems like diblock copolymers [9]. However recently we found [30,40] that in the case of multi-block copolymers with weakly polydisperse blocks the macroscopic phase separation is suppressed and secondary domain structures must be formed instead (*i.e.* droplets of minor phase do not grow up to a macroscopic size but remain finite and arrange in a secondary superlattice). Since correlated random copolymers can be considered as multi-block copolymers with extremely high block polydispersity, it is tempting to expect the secondary structures also in these systems.

The aim of the present paper is to verify this idea and to characterize the secondary super structures in correlated random copolymers.

In the next section the general equations for the free energy of the system are derived in terms of the primary order parameter ψ. Although the resultant free energy expansion has been obtained before [21,22,24,28,29], the way it is derived and discussed is useful for what follows. Primary superstructures and the corresponding phase diagram of the system with quenched chemical disorder obtained in references [28,35,39] are described at the end of the section. The second order parameter φ related to a coexistence of different primary structures and the resultant secondary superstructures are considered in Section 3. The main results are discussed in the last section.

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2 Primary microdomain structures

2.1 The primary order parameter

Let us consider a melt of long AB copolymers, *i.e.* linear polymer chains consisting of two types of monomers A and B. The number of monomers per chain, N, is assumed to be very large, $N \to \infty$. The system is also assumed to be incompressible:

$$\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) = 1$$

where $\phi_A(\mathbf{r}) = \rho_A(\mathbf{r})/\rho_0$ is the volume concentration of A monomers, and ϕ_B is ditto for B. Here $\rho_A(\mathbf{r})$ is the number concentration of A monomers, and $\rho_0 = \text{const}$ is the total monomer concentration.

The mean fraction of A monomers is $\bar{\phi}_A = 0.5 + \epsilon$, where the composition asymmetry parameter ϵ is assumed to be small; $\bar{\phi}_B = 0.5 - \epsilon$. The disordered state is characterized by homogeneous distribution of A and B monomers: $\phi_A(\mathbf{r}) = \bar{\phi}_A$. Therefore a structural order in the system can be described by the order parameter field $\psi(\mathbf{r}) = \phi_A(\mathbf{r}) - \bar{\phi}_A$.

2.2 Copolymer chemical structure

We assume block-copolymer structure with random block sizes. The average number of monomers per block, n, is large, $n \gg 1$. In other words, the probability p_{AB} of B monomer next to A is much smaller than p_{AA} and p_{BB}: $p_{AB} \simeq 1/n \ll p_{AA} \simeq p_{BB} \simeq 1$. Below we adopt the so-called correlated random model of copolymer chemical structure [27] assuming that its monomer sequence is characterized by the equilibrium statistics inherent to a one-dimensional lattice system of A and B units which repel each other: each AB contact (*i.e.* neighboring A and B monomers along polymer chain) increases the total energy by $Ek_{\mathrm{B}}T$, $E \gg 1$. Hence $p_{AB} \simeq \mathrm{e}^{-E}$, *i.e.* $n \simeq \mathrm{e}^{E} \gg 1$ (here we assume a nearly symmetric copolymer with nearly equal numbers of A and B monomers).

The copolymer chemical structure can be alternatively characterized by a sequence of spins $\{s_i\}$, where i is the monomer position along the chain, $s = 1/2$ for A monomer and $s = -1/2$ for B. The spin correlation function (for correlated random model with $\epsilon = 0$) is

$$\langle s_i s_j \rangle_c = \frac{1}{4}\mathrm{e}^{-2|i-j|/n}. \tag{1}$$

It is important to distinguish between two possible situations: (1) *annealed* disorder, when the monomer chemical sequence can change from time to time[1], so that each sequence can be realized with the appropriate *a priori* statistical weight determined by the parameter E. (2) *Quenched* disorder when the monomer sequence of each polymer chain is frozen. It is this case that we focus on below. In this latter case the averaging in equation (1) should be treated as ensemble – rather than time – averaging. This case is not deterministic: under the same preparation conditions chains with different chemical structures can be formed. Hence physical properties of a finite system must fluctuate from one copy to another. Fortunately here we are primarily interested in the free energy which has the property of self-averaging (see *e.g.* [41]): its relative fluctuations vanish in the thermodynamic limit (*i.e.* when total volume V of the system tends to infinity).

2.3 Free energy with annealed disorder

It is convenient to represent the free energy as a sum of two terms

$$F = F_{\mathrm{int}} + F_{\mathrm{conf}} \tag{2}$$

where F_{int} is the excess free energy of interactions between monomers, and F_{conf} is the conformational free energy related to the total number of conformations of all polymer chains compatible with given gross distributions of A and B monomers, $\phi_A(\mathbf{r})$ and $\phi_B(\mathbf{r})$[2]. The Flory-Huggins model [42] implies that

$$F_{\mathrm{int}} = k_{\mathrm{B}}T\rho_0\chi \int \phi_A(\mathbf{r})\phi_B(\mathbf{r})\mathrm{d}^3 r \tag{3}$$

where χ is the Flory interaction parameter. Note that $\chi > 0$ is a measure of an effective repulsion of A and B monomers. Note also that χ has nothing to do with the parameter E which characterizes the statistics of the monomer sequence; it is the conformational energy F_{conf} that depends on E.

Let us turn to the conformational term assuming annealed chemical structure and a large scale inhomogeneity associated with the order parameter field $\psi(\mathbf{r})$. Then the system can be coarse grained so that ψ and $\phi \equiv \phi_A$ were nearly constant in each grain which is assumed to be much larger than the monomer size. The microscopic state of the system is determined by the set of trajectories of all polymer chains and by their monomer sequences. With fixed polymer trajectories each grain $\tilde{V}$ comprises a number of copolymer fragments $\{N_\alpha;\ \alpha = 1, 2, ...\}$ which all are typically long, $N_\alpha \gg 1$, and

$$\sum_\alpha N_\alpha = \rho_0 \tilde{V}.$$

Each fragment is characterized by its own fraction p_α of A monomers,

$$\sum_\alpha p_\alpha N_\alpha = \rho_0 \tilde{V} \phi. \tag{4}$$

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[1] This is not unrealistic: for example one could think of monomer B as actually being A modified by a reversible bond with a small molecule C.

[2] Note that equation (2) is an approximation itself; it is valid if $\rho_0 b^3 \gg 1$, where b is the statistical segment: in this case short-scale fluctuations are negligible.

The free energy defined by the total statistical weight of all possible sequences compatible with the above condition is

$$F_{\mathrm{seq}} = \min_{\{p_\alpha\}} \sum_{\alpha} F_1\left(N_\alpha, p_\alpha\right) \tag{5}$$

where $F_1(N,p) = -k_{\mathrm{B}}T \ln Z_1(N,p)$ and Z_1 is the statistical weight accounting for all sequences of Np A-monomers and $N(1-p)$ B-monomers. In the limit $N \gg n$ this "sequence" free energy is proportional to the number of monomers: $F_1(N,p) = Nf_1(p)$. The density function $f_1(p)$ is calculated in Appendix A: $f_1 = -k_{\mathrm{B}}T\frac{2}{n}\sqrt{p(1-p)}$, where $n = \mathrm{e}^E$. Minimizing F_{seq}, equation (5), over $\{p_\alpha\}$ under the condition (4) we get $p_\alpha = \phi$, and the free energy of the grain $F_{\mathrm{seq}} = \rho_0\tilde{V}f_1(\phi)$. Note that F_{seq} does not depend on spatial trajectories of copolymer chains provided the incompressibility condition is fulfilled (*i.e.* the total monomer concentration is constant $= \rho_0$). Hence conformational statistics of copolymer chains are nearly not affected by the imposed (large-scale) order parameter field, *i.e.* the free energy contribution related to the total number of copolymer trajectories is a constant which can be omitted. Thus, the total conformational/sequence free energy is $F_{\mathrm{conf}} = \sum F_{\mathrm{seq}}$ with summation over all grains, *i.e.*

$$F_{\mathrm{conf}} = -\frac{2}{n}k_{\mathrm{B}}T\rho_0 \int \sqrt{\phi(1-\phi)}\mathrm{d}^3r \tag{6}$$

Thus the total free energy F is thus defined by equations (2, 3, 6). It is qualitatively very similar to the standard Flory-Huggins free energy of a blend of two homopolymers (A and B): one have to replace $\phi\ln\phi + (1-\phi)\ln(1-\phi)$ in the Flory-Huggins model by $-2\sqrt{\phi(1-\phi)}$ and also replace the homopolymer length by the average block length n. The phase behavior of the annealed copolymer system is also similar to the blend case: the system is homogeneous if $\chi n < 2$; it separates into two macroscopic phases if $\chi n > X(\epsilon)$, where $X(\epsilon)$ is just a numerical factor depending on the composition asymmetry ϵ. The critical point corresponds to $\chi n = 2$, $\epsilon = 0$ (*i.e.* $\phi = 0.5$). The fact that phase separation is macroscopic validates the initial assumption of large-scale inhomogeneity of the order parameter field.

2.4 Nonlocal free energy

Let us return to the case of quenched chemical disorder. Then the free energy corresponding to a given $\psi(\mathbf{r})$ is different from that with annealed disorder:

$$F = F_{\mathrm{anneal}} + F_{\mathrm{nloc}}. \tag{7}$$

The second term in the r.h.s. of equation (7) is the nonlocal free energy which is *defined* as the difference between the "quenched" (F) and "annealed" (F_{anneal}) free energies.

Why the difference? The most general reason for it is related to the fact that in the case of annealed disorder the sequence distribution can be affected by the field $\psi(\mathbf{r})$ while in the quenched case this distribution is fixed. However there is an important regime when the "quenched" and "annealed" free energies do coincide: this is the case when the whole system is infinite and the order parameter ψ vanishes outside a finite region (which can be large itself). In fact, let us consider a copolymer chain with prescribed both trajectory and monomer sequence inside the region where $\psi \neq 0$. In the case of annealed disorder its statistical weight is proportional to the *a priori* probability $\mathcal{P}_0(s)$ of the prescribed sequence s. In the case of quenched disorder its statistical weight is proportional to $\mathrm{e}^{\mu(s)/(k_{\mathrm{B}}T)}$, where $\mu(s)$ is the chemical potential of chains with the prescribed sequence. Obviously, probability (concentration) of such chains outside is directly proportional to the same factor: $\mathcal{P}(s) = \mathrm{const}\,\mathrm{e}^{\mu(s)/(k_{\mathrm{B}}T)}$. On the other hand $\mathcal{P}(s)$ must be equal to the average fraction of chains with the sequence s in the whole system, $\mathcal{P}_0(s)$, since any distortion in a finite region can not possibly affect any intensive parameter (like sequence distribution) of an infinite system. Hence the same chain statistical weight for the cases of annealed and quenched chemical disorder, *i.e.* the same total free energy (apart from a constant contribution).

Thus the nonlocal free energy is zero if $\psi(\mathbf{r}) = 0$ outside a finite region, *i.e.* it can not be represented as an integral over the free energy density (in contrast to F_{anneal}): it would be identically zero otherwise. Hence F_{nloc} is indeed a nonlocal characteristic.

There is no general way to calculate F_{nloc}. Yet it was calculated analytically [18,20–22] for the case of weak enough inhomogeneity, *i.e.* for small ψ. Below I formulate the result is a slightly more general way:

Let us attribute a generic random (quenched) spin variable s to each monomer, and define the order parameter as $\psi(\mathbf{r}) = \sum s_i\delta(\mathbf{r}-\mathbf{r}_i)$, assuming that the average spin is zero, $\langle s\rangle = 0$. Correlations between the spins along the polymer chain are assumed to be finite (short) range. Next we define $s(i)$ as coarse grained s_i assuming that the scale of coarsening is larger than the spin correlation length (here i is the monomer position along the polymer chain). Then the distribution of $s(i)$ must be nearly Gaussian: $\mathcal{P}\left[s(i)\right] = \mathrm{const}\,\exp\left(-\int f_{\mathrm{s}}(s(i))\mathrm{d}s\right)$, where $f_{\mathrm{s}}(s) = \frac{1}{2}\kappa s^2$. Thus κ is the only essential parameter that characterizes the quenched spin sequence disorder on large scales. Note that the same parameter determines the quadratic term of the local (annealed) conformational free energy expansion[3]:

$$F_{\mathrm{conf}} = \frac{1}{2}k_{\mathrm{B}}T\rho_0 \int \kappa\psi^2\mathrm{d}^3r + \mathcal{O}(\psi^3). \tag{8}$$

Unsurprisingly κ is the only sequence parameter that enters the non-local free energy:

$$F_{\mathrm{nloc}}\left[\psi(\mathbf{r})\right] \simeq \frac{\kappa^2}{2V}k_{\mathrm{B}}T\frac{\rho_0}{a^2}\int_{q,q'}\frac{\left|\psi_{\mathbf{q}}\right|^2\left|\psi_{\mathbf{q}'}\right|^2}{q^2+q'^2} \tag{9}$$

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[3] The order parameter $\psi(\mathbf{r})$ is assumed to be smooth enough, *i.e.* coarse-grained.

where V is the total volume of the system, $a^2 = b^2/6$, b, the chain statistical segment, $\psi_{\mathbf{q}} = \int \psi(\mathbf{r}) \mathrm{e}^{-\mathrm{i}\mathbf{qr}} \mathrm{d}^3 r$, and $\int_q \equiv \frac{1}{(2\pi)^3} \int \mathrm{d}^3 q$. The non-local free energy, equation (9), was originally derived for a genuine random copolymer in reference [18] and later further generalized for correlated sequences [20–22]. Equation (9) is valid if $\kappa\psi^2\lambda^2/a^2 \ll 1$ where ψ is the typical real-space amplitude, and λ is the typical spatial scale associated with the order parameter (see Refs. [30,40] for more detail).

Obviously the non-local free energy prevents macroscopic phase separation: the r.h.s. of equation (9) diverges as $q \to 0$, *i.e.* for an infinite-scale inhomogeneity. Hence one should expect large but finite domains (*i.e.* microphase separation) instead. The local conformational free energy, F_{conf}, should be then generalized in order to account for a finite scale inhomogeneity: the free energy density must depend on both local composition ϕ and on its gradient $\nabla\phi$. The latter dependence is given by the standard Lifshitz-de Gennes [42,43] square gradient term. So we get $F_{\text{conf}} = \int f_{\text{conf}} \mathrm{d}^3 r$, where

$$f_{\text{conf}} = k_{\mathrm{B}} T \rho_0 \left\{ -\frac{2}{n} \sqrt{\phi(1-\phi)} + \frac{a^2}{4} \frac{(\nabla\phi)^2}{\phi(1-\phi)} \right\} . \qquad (10)$$

Here the first term in curly brackets corresponds to the limit of vanishingly small gradient $\nabla\phi$ considered in the previous section and in Appendix A[4]. In the case of a weak composition inhomogeneity, $\phi(\mathbf{r}) = \bar{\phi} + \psi(\mathbf{r})$, where $\bar{\phi} = 0.5 + \epsilon$ and $\psi \ll 1$, the conformation free energy can be expanded as

$$F_{\text{conf}} = -2 k_{\mathrm{B}} T \frac{\rho_0}{n} \sqrt{\bar{\phi}(1-\bar{\phi})} + \frac{1}{2} \int_q \gamma_2(q) \left|\psi_{\mathbf{q}}\right|^2 + \mathcal{O}(\psi^3) \qquad (11)$$

where

$$\gamma_2(q) = k_{\mathrm{B}} T \rho_0 \left(\frac{4}{n} + 2a^2 q^2 \right) + \mathcal{O}(\epsilon^2). \qquad (12)$$

The linear term is missing since $\int \psi(\mathbf{r}) \mathrm{d}^3 r \equiv 0$.

Comparing equations (8, 6) we get $\kappa = \left[4 + \mathcal{O}(\epsilon^2)\right]/n$. Now using equation (7) with $F_{\text{anneal}} = F_{\text{int}} + F_{\text{conf}}$ defined by equations (3, 10) and F_{nloc} defined by equation (9) with $\kappa \simeq 4/n$ we get the total free energy

$$F \simeq \int \left\{ \chi n \phi(1-\phi) - 2\sqrt{\phi(1-\phi)} + \frac{1}{4} \frac{(\nabla\phi)^2}{\phi(1-\phi)} \right\} \mathrm{d}^3 r + \frac{8}{V} \int_{q,q'} \frac{\left|\psi_{\mathbf{q}}\right|^2 \left|\psi_{\mathbf{q}'}\right|^2}{q^2 + q'^2}$$

where $R_n \equiv n^{1/2} a$ and $(k_{\mathrm{B}} T/n)\rho_0$ are set to be unities for simplicity, and $\phi = \phi(\mathbf{r}) = 0.5 + \epsilon + \psi(\mathbf{r})$. The first term in the r.h.s. can be expanded as a series of ψ; the result is:

$$F = \int_q \left(q^2 - 2\tau\right) \left|\psi_{\mathbf{q}}\right|^2 + \frac{8}{V} \int_{q,q'} \frac{\left|\psi_{\mathbf{q}}\right|^2 \left|\psi_{\mathbf{q}'}\right|^2}{q^2 + q'^2} + \int f_{34}(\psi) \mathrm{d}^3 r \qquad (13)$$

where

$$f_{34}(\psi) = \frac{\gamma_3}{3!}\psi^3 + \frac{\gamma_4}{4!}\psi^4. \qquad (14)$$

$\tau = \chi/\chi_{\mathrm{s}} - 1$ is the relative distance to the spinodal $\chi_{\mathrm{s}} = 2/n + \mathcal{O}(\epsilon^2)$, $\gamma_3 \simeq 48\epsilon$, $\gamma_4 \simeq 48$. The free energy expression, equation (13), has been obtained in references [21–23,28]. It is valid near the critical point, *i.e.* for $\epsilon \ll 1$, $\tau \ll 1$.

2.5 Phase diagram

Microdomain structures corresponding to the free energy minimum have been analyzed in references [28,39]. The mean-field results valid in the vicinity of the critical point (*i.e.* for $\tau \ll 1$, $n^{-1/4} \ll \epsilon \ll 1$) are briefly described below.

The system is disordered ($\psi \equiv 0$) if $\tau < 0$, *i.e.* $\chi < \chi_{\mathrm{s}}$. In the region $\tau > 0$ the free energy is dominated by the first two terms in the r.h.s. of equation (13). Minimization of their sum defines the mean-square order parameter

$$C \equiv \frac{1}{V} \int \psi^2 \mathrm{d}^3 r = (\tau/3)^2 \qquad (15)$$

and the dominant wave-vector $q^* = \sqrt{2\tau/3}$; the Fourier components $\psi_{\mathbf{q}}$ with $|\mathbf{q}| \neq q^*$ can be neglected. The microdomain symmetry (morphology) is determined by the subdominant 3rd term in the r.h.s. of equation (13). The following superstructures have been found (see phase diagram in Fig. 1a): 1-dimensional lamellar in the region $\tau/\epsilon > 10.16$, 2-dimensional hexagonal (cylindrical) for $3.405 < \tau/\epsilon < 9.479$, and 3-dimensional body centered cubic (bcc) for $1.847 < \tau/\epsilon < 3.111$. The gaps between these regions correspond to phase separation between "pure" microdomain structures: disordered and bcc for $0 < \tau/\epsilon < 1.847$; bcc and cylindrical for $3.111 < \tau/\epsilon < 3.405$; cylindrical and lamellar for $9.479 < \tau/\epsilon < 10.164$. The fractions of the total volume occupied by two superstructures, p_1, p_2, are defined by the following lever rule:

$$C_1 p_1 + C_2 p_2 = C$$

where $C_i = \left\langle\psi^2\right\rangle_i$, $i = 1, 2$, is the mean-square order parameter averaged over the corresponding phase (both C_1 and C_2 do not depend either on p or on τ within the separation region). Taking into account that according to equation (15)

$$C_i = \frac{\tau_i^2}{9}, \ i = 1, 2$$

where τ_1 and τ_2 correspond to the boundaries of the phase separation window (*i.e.* for disordered/bcc phase separation $\tau_1 = 0$, $\tau_2 = 1.847\epsilon$), and defining $p \equiv p_2$ we rewrite

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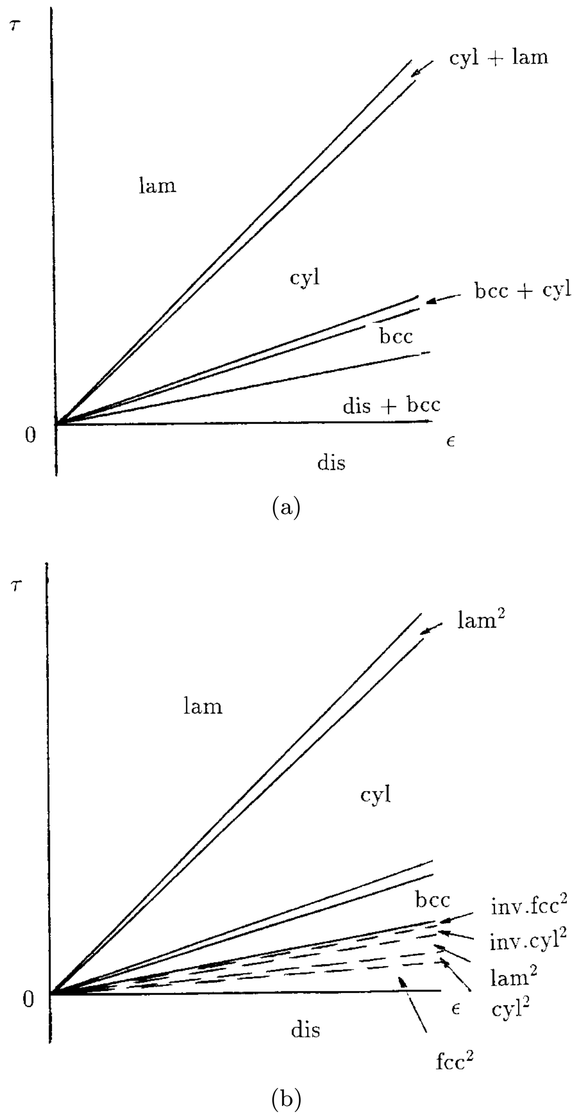
[4] Of course the reference to "the standard gradient term" can not be regarded as a derivation which is left as an exercise for the reader.



(a)

(b)

Fig. 1. Mean-field phase diagram of a correlated random copolymer (a) as obtained in reference [39]; (b) including secondary structures.

the "lever rule" as

$$\tau_1^2(1-p)+\tau_2^2 p=\tau^2.$$

This equation shows, in particular, that volume fraction of bcc phase in the disordered/bcc biphasic window is proportional to τ^2 [39].

3 Secondary microphase separation

Let us focus on the biphasic windows considered in the previous section where the minimum of the free energy, equation (13), is attained with two *macroscopic* phases $V_1 = p_1 V$ and $V_2 = p_2 V$ characterized by different microdomain morphologies.

Below I present a general argument showing that the predicted *macroscopic* phase separation can not be true. First note the basic reason for the phase coexistence: with two coexisting phases the free energy $F(C_1, C_2, V_1, V_2)$ as defined by equation (13) is formally *lower* than the sum of free energies of subsystems V_1 and V_2 considered separately: $\Delta F = F_{12}(C_1, C_2, V_1, V_2) - F_1(C_1, V_1) - F_2(C_2, V_2) < 0$. Obviously the local (annealed) free energy terms do not contribute to ΔF: it is the nonlocal term only (the second term in the r.h.s. of Eq. (13)) that is important. Noting that $F_{\mathrm{nloc}}(C_1, C_2, V_1, V_2) = F_{\mathrm{nloc}}(C_1 p_1 + C_2 p_2, V_1 + V_2)$ with $F_{\mathrm{nloc}}(C, V) = (4/q^{*2})VC^2 = (6/\tau)VC^2$ we get

$$\Delta F=-\frac{6}{\tau}Vp_1p_2\left(C_2-C_1\right)^2. \qquad (16)$$

So, when two subsystems, V_1 and V_2, come into contact, the total free energy decreases by ΔF. This sounds like miracle: note that the free energy change is proportional to the volume V rather than to the area of the interface which is not considered here. The only reason for a free energy change is a possibility of a redistribution of copolymer molecules between the two phases: some copolymer sequences may selectively prefer one of the phases. However in the limit of very long copolymer molecules, $N \to \infty$, the relative fluctuation of any parameter which characterizes the sequence must be of order $1/\sqrt{N}$. Therefore, while a redistribution is certainly possible, its effect on the average free energy density must vanish in the limit $N \to \infty$, *i.e.* $\Delta F/V$ must tend to zero, *i.e.* no driving force for phase separation.

Thus we arrive at a contradiction: a general argument ensures that $\Delta F/V = 0$ while the free energy expression derived above implies a finite $\Delta F/V$. The formal way out is simple: the nonlocal free energy has been approximated by the main 4th-order term of its ψ expansion. This is not enough to consider the separation problem: higher-order terms (in fact, up to the 8th order, see below) are also important. This notion is not very useful as such, as a derivation of higher order nonlocal terms seems to be a very hard problem. Below we consider another way to solve the problem.

3.1 The second order parameter

To summarize the above discussion: there is a tendency for a phase separation between different microdomain structures, however a macroscopic separation is not allowed. Hence a possibility of a secondary superstructure, *i.e.* alternating finite domains characterized by different primary morphologies.

The driving force for the separation between primary structures is related to the fractionation effect, *i.e.* a possibility of redistribution of different copolymer sequences which might result in a decrease of the total free energy. The free energy (see Eq. (13)) is sensitive to the sequence redistribution because it affects the parameters like τ, γ_3 and γ_4. Obviously the most important effect is related to τ since the free energy contributions corresponding to $\gamma_{3,4}$ are subdominant anyway. In other words, dominant contribution to the free energy variation due to sequence redistribution comes from the variation of the first quadratic term which can be written as

$$\begin{aligned} F_2 &= \frac{1}{2}\int_q \left[\gamma_2(q) - 2\chi\right] |\psi_{\mathbf{q}}|^2 \\ &\simeq \frac{1}{2}\int_q \left[\gamma_2(q^*) - 2\chi\right] |\psi_{\mathbf{q}}|^2 \\ &= \frac{1}{2}\int \left[\gamma_2(q^*) - 2\chi\right] \psi^2 \mathrm{d}^3 r. \end{aligned}$$

The last two equations are valid since $\int \psi^2 \mathrm{d}^3 r = \int_q |\psi_{\mathbf{q}}|^2$ and the last integral is strongly dominated by the region $q \simeq q^*$. Here $\gamma_2(q)$ is defined in equation (12). Hence the free energy variation with a fixed first order parameter field $\psi(\mathbf{r})$ is

$$F_1^{\varphi} \simeq \delta F_2 \simeq \frac{k_{\mathrm{B}} T \rho_0}{n} \int \varphi(\mathbf{r}) C(\mathbf{r}) \mathrm{d}^3 r \tag{17}$$

where $C(\mathbf{r}) = \left\langle \psi^2(\mathbf{r}) \right\rangle_{\mathrm{local}}$ is the mean-square order parameter locally averaged (coarsened) over a scale larger than the primary domain size $\sim 1/q^*$, and

$$\varphi(\mathbf{r}) \equiv \frac{n}{2 k_{\mathrm{B}} T \rho_0} \delta\gamma_2(\mathbf{r}, q^*) \tag{18}$$

is the second order parameter. Here $\delta\gamma_2(\mathbf{r}, q^*) = \langle \gamma_2(q^*) \rangle_{\mathrm{local}} - \bar{\gamma}_2(q^*)$ is the difference between the locally averaged value of γ_2 and its mean value $\bar{\gamma}_2(q^*)$ averaged globally over the whole system. Note that by this definition

$$\int \varphi(\mathbf{r}) \mathrm{d}^3 r = 0. \tag{19}$$

Let us calculate the free energy corresponding to a small second order parameter $\varphi(\mathbf{r})$ assuming first that $\psi \equiv 0$. The second order parameter φ is directly related to the sequence distribution. In fact, it is well-known [3] that γ_2 is related to the monomer correlation functions of noninteracting copolymer chains. In the case $\epsilon = 0$ this relation is fairly simple: $\gamma_2(q) = k_{\mathrm{B}} T \rho_0 / S(q)$, where the structure factor

$$S(q) = \frac{1}{N} \sum_{i,j=1}^{N} s_i s_j g(i-j). \tag{20}$$

and $g(n) = \mathrm{e}^{-a^2 q^2 n}$ is the Gaussian propagator of a chain fragment of n monomers. The sequence-averaged structure factor is

$$\bar{S}(q) = \sum_j \langle s_i s_j \rangle g(i-j).$$

Using equation (1) we get $\bar{S}(q) = n/(4 + 2nq^2a^2)$, *i.e.* $\bar{\gamma}_2(q) = k_{\mathrm{B}} T \rho_0 \left(4 + 2na^2q^2\right)/n$ in agreement with equation (12). Let S be the structure factor (the wave-number q is omitted for brevity) averaged inside a finite volume $\tilde{V}$ (the size of this volume is assumed to be larger than $1/q^*$); S is defined by equation (20) with N replaced by the number of monomers in the volume, $\tilde{N} = \rho_0 \tilde{V}$. Let us calculate the mean-square thermal fluctuation of S:

$$\begin{aligned} \delta S^2 &\equiv \left\langle \left(S - \bar{S}\right)^2 \right\rangle \\ &= \frac{1}{\tilde{N}^2} \sum_{iji'j'} g(i-j) g(i'-j') \\ &\quad \times \left\{ \langle s_i s_j s_{i'} s_{j'} \rangle - \langle s_i s_j \rangle \langle s_{i'} s_{j'} \rangle \right\} \cdot \end{aligned}$$

The expression in curly brackets is small unless i is close to i' and j to j' or i close to j' and i' to j. Hence

$$\begin{aligned} \delta S^2 &\simeq \frac{2}{\tilde{N}^2} \sum_{ii'jj'} g(i-j) g(i'-j') \langle s_i s_{i'} \rangle \langle s_j s_{j'} \rangle \\ &\simeq \frac{1}{8\tilde{N}} \frac{n^2}{q^2 a^2} \cdot \end{aligned} \tag{21}$$

Let us consider the averaged within the volume $\tilde{V}$ order parameter $\tilde{\varphi} = (1/\tilde{V}) \int \varphi(\mathbf{r}) \mathrm{d}^3 r$. Obviously $\tilde{\varphi} = (n/2k_{\mathrm{B}} T \rho_0) \langle \delta\gamma_2 \rangle_{\tilde{V}} = -(n/2)(\delta S/\bar{S}^2)$, so that its mean square thermal fluctuation is

$$\left\langle \tilde{\varphi}^2 \right\rangle = n^2 \frac{\delta S^2}{4\bar{S}^4} = \frac{8}{\tilde{V} \rho_0 q^{*2} a^2} \cdot \tag{22}$$

Note that $\left\langle \tilde{\varphi}^2 \right\rangle \propto 1/\tilde{V}$ since $\varphi(\mathbf{r})$ is random (uncorrelated) on scales larger than $1/q^*$. Hence its large-scale fluctuations are Gaussian, *i.e.* the free energy penalty of a thermal fluctuation $\varphi(\mathbf{r})$ can be written as a quadratic form:

$$F_2^{\varphi} = \frac{1}{2} k_{\mathrm{B}} T \rho_0 \kappa_{\varphi} \int \varphi^2 \mathrm{d}^3 r \tag{23}$$

with

$$\kappa_{\varphi} = \frac{q^{*2} a^2}{8} \cdot \tag{24}$$

Next we apply the approach outlined in Section 2.4: the order parameter φ is essentially determined by the copolymer chemical sequence which is quenched. Hence the nonlocal free energy (see Eq. (9)):

$$F_{\mathrm{nloc}}^{\varphi} = \frac{\kappa_{\varphi}^2}{2V} k_{\mathrm{B}} T \frac{\rho_0}{a^2} \int_{q,q'} \frac{|\varphi_{\mathbf{q}}|^2 |\varphi_{\mathbf{q}'}|^2}{q^2 + q'^2} \cdot \tag{25}$$

3.2 Free energy of a secondary structure

We are now in a position to write out the general free energy expression in terms of ψ and φ. Let us first consider a clarifying example: the system which is separated into two regions V_1 and V_2 with different primary morphologies and mean-square amplitudes C_1 and C_2. By setting $\varphi(\mathbf{r}) \equiv 0$ in the whole volume we suppress the most important channel of sequence redistribution between the two phases.

Hence the total free energy in this case is equal to the sum of the free energies of each phase:

$$F\left[\psi,\varphi\equiv 0\right]=F_1(C_1,V_1)+F_2(C_2,V_2). \qquad (26)$$

The φ-dependence of the free energy was considered in the previous section; it is defined by the sum $F_1^{\varphi}+F_2^{\varphi}+F_{\rm nloc}^{\varphi}$, see equations (17, 23, 25):

$$F\left[\psi,\varphi\right]=F\left[\psi,0\right]+F_1^{\varphi}+F_2^{\varphi}+F_{\rm nloc}^{\varphi}.$$

Assuming that $\varphi=\varphi_1$ in one phase and $\varphi=\varphi_2$ in the second phase we get $F_1^{\varphi}=\varphi_1 C_1 V_1+\varphi_2 C_2 V_2$ and $F_2^{\varphi}=(\tau/24)\left(\varphi_1^2 V_1+\varphi_2^2 V_2\right)$, where we take into account that $R_n^2\equiv na^2=1$ and $(k_{\rm B}T/n)\rho_0=1$. Let us neglect the non-local term $F_{\rm nloc}^{\varphi}$ at this stage. Minimizing $F_1^{\varphi}+F_2^{\varphi}$ over φ_1, φ_2 under the condition $\varphi_1 V_1+\varphi_2 V_2=0$ (see Eq. (19)) we get $F=F_1(C_1,V_1)+F_2(C_2,V_2)+\Delta F$,

$$\Delta F=\min\left(F_1^{\varphi}+F_2^{\varphi}\right)=-\frac{6}{\tau}\left(C_2-C_1\right)^2 V_1 V_2/V.$$

Note an agreement with equation (16) which shows that the second order parameter φ is defined properly. The agreement also confirms that the physical meaning of the coupling term ΔF discussed above is correct.

The above argument can be easily generalized in order to account for any number of secondary domains (V_1, V_2, ...), and in fact for an arbitrary secondary structure provided that the size Λ of the secondary domains is much larger than L.

Thus it is obvious that the only term missing in the free energy, equation (13), is the non-local free energy $F_{\rm nloc}^{\varphi}$ related to the second order parameter φ which in general case is determined by minimization of $F_1^{\varphi}+F_2^{\varphi}$ defined by equations (17, 23) under the condition 19[5]:

$$F=\int_q\left(q^2-2\tau\right)\left|\psi_{\mathbf q}\right|^2+\frac{8}{V}\int_{q,q'}\frac{\left|\psi_{\mathbf q}\right|^2\left|\psi_{\mathbf q'}\right|^2}{q^2+q'^2}+\int f_{34}(\psi){\rm d}^3r+F_{\rm nloc}^{\varphi}$$

where

$$F_{\rm nloc}^{\varphi}=\frac{1}{2V}\left(\frac{\tau}{12}\right)^2\int_{q,q'}\frac{\left|\varphi_{\mathbf q}\right|^2\left|\varphi_{\mathbf q'}\right|^2}{q^2+q'^2} \qquad (27)$$

and

$$\varphi(\mathbf r)=\frac{12}{\tau}\left[\bar C-C(\mathbf r)\right],\ \bar C\equiv\frac{1}{V}\int C(\mathbf r){\rm d}^3r. \qquad (28)$$

Note that the new non-local term $F_{\rm nloc}^{\varphi}$ is essentially proportional to ψ^8 since $\varphi\propto\psi^2$.

The non-local term, $F_{\rm nloc}^{\varphi}$, does not allow for a macroscopic phase separation: secondary domains are formed instead. Then the total free energy can be written as

$$F=F_{\rm bulk}+F_{\rm intf}+F_{\rm nloc}^{\varphi} \qquad (29)$$

where $F_{\rm bulk}$ is the free energy formally corresponding to the macroscopically separated system, *i.e.* $F_{\rm bulk}$ is obtained by minimization of the r.h.s. of equation (13), and $F_{\rm intf}$ incorporate the effect of interfaces between secondary domains:

$$F_{\rm intf}=\int\sigma{\rm d}A_{\rm intf}.$$

Here σ is the interfacial tension which is integrated over the interfacial area. Equation (29) implicitly implies no coupling between the interfacial and the non-local term. This assumption is valid if the interfacial thickness ξ is much smaller than the secondary domain size Λ which defines the typical distance between the interfaces; the validity of this condition is discussed in the last section.

We now focus on the last two terms in equation (29) which determine the secondary structure.

3.3 Interfacial free energy

In the limit $\Lambda\gg\xi$ we can neglect the effect of the secondary non-local free energy $F_{\rm nloc}^{\varphi}$ on the interfacial energy, *i.e.* calculate the tension σ assuming coexistence of two macroscopic phases with different morphologies and using equation (13).

The equilibrium interfacial thickness ξ is much larger than the primary period $2\pi/q^*$ (see below). Hence the Fourier spectrum of the order parameter, $\left|\psi_{\mathbf q}\right|^2$, must be concentrated in the region $|\mathbf q|\simeq q^*$. The interfacial energy in this case is obtained in Appendix B, equation (B.4):

$$F_{\rm intf}=2\int_q\left|\psi_{\mathbf q}\right|^2\left(|\mathbf q|-q^*\right)^2+\int\tilde f(\psi(\mathbf r)){\rm d}^3r \qquad (30)$$

where

$$\tilde f(\psi)=f_{34}(\psi)-\alpha\psi^2-\beta$$

the function $f_{34}(\psi)$ is defined in equation (14), and the parameters α and β are determined by the conditions $\left\langle\tilde f(\psi)\right\rangle_1=0$, $\left\langle\tilde f(\psi)\right\rangle_2=0$, where $\langle\ldots\rangle_{1,2}$ means averaging in the bulk of phases 1, 2.

Each morphology and the two-phase structure as a whole is characterized by a set of basic wave-vectors $\{\mathbf Q_i\}$, $|\mathbf Q_i|=q^*=\sqrt{2\tau/3}$, *i.e.* the Fourier spectrum $\psi_{\mathbf q}$ must be concentrated near these base vectors: $\psi_{\mathbf q}=\sum_i A_i(\mathbf q-\mathbf Q_i)$, where each function $A_i(\mathbf q)\equiv\int A_i(\mathbf r){\rm e}^{-{\rm i}\mathbf{qr}}{\rm d}^3r$ is localized in the region $|\mathbf q|\lesssim 1/\xi\ll q^*$. Hence the corresponding real-space functions $A_i(\mathbf r)$ are smooth: their characteristic scale ξ is much larger than the primary domain size $\sim 1/q^*$.

It is useful to write out the free energy in terms of these smooth amplitudes $A_i(\mathbf r)$ instead of the first order parameter ψ. Assuming that interfacial plane is perpendicular to z-axis and using equation (30) we get the following energy per unit area:

$$\mathcal F=\int{\rm d}z\left\{\tilde f(\mathbf A)+2\sum_i\cos^2\theta_i\left|\frac{{\rm d}A_i}{{\rm d}z}\right|^2\right\} \qquad (31)$$

---

[5] The non-local term $F_{\rm nloc}^{\varphi}$ can be neglected during the minimization since it is much smaller than F_2^{φ} for any near-equilibrium structure as can be checked using the results obtained below.

where $\mathbf{A} = \{A_i(z)\}$, θ_i is the angle between the basic vector $\mathbf{Q}_i$ and the z-axis, and $\tilde{f}(\mathbf{A})$ is a 4th-order polynomial which can be easily found by averaging out "fast" components (varying with wave-numbers $q \sim q^*$) of $\tilde{f}(\psi)$. The functional $\mathcal{F}$, equation (31), is formally identical to the one describing interfacial structure in a regular block-copolymer system in the weak segregation regime [40]. The interfacial tension σ can be obtained by minimization of $\mathcal{F}$ over $\mathbf{A}(z)$ with appropriate boundary conditions at $z = \pm\infty$ where the corresponding pure morphologies should be revealed. This minimization problem has been considered in reference [40] for the interface between disordered and bcc morphologies. It was shown that the tension nearly does not depend on the interfacial plane orientation, *i.e.* the orientation-averaged tension σ_{av} could be used to a good approximation,

$$\sigma_{\text{av}} = \frac{2^9}{45^3}\sqrt{20}\frac{\gamma_3^3}{\gamma_4^{2.5}} \simeq 0.174\epsilon^3. \tag{32}$$

The interfacial (half) thickness is [40]

$$\xi = \frac{2}{\sqrt{3}}\frac{3}{4}\sqrt{60}\frac{\gamma_4^{0.5}}{\gamma_3} \simeq 0.97/\epsilon. \tag{33}$$

Hence the interface is indeed much thicker than the primary domain size $1/q^* \sim 1/\sqrt{\epsilon}$.

3.4 Secondary superstructures

As discussed above the secondary domain structure corresponds to the minimum of nonlocal plus interfacial free energies

$$F_{\text{ex}} = F_{\text{intf}} + F_{\text{nloc}}^{\varphi} \tag{34}$$

where $F_{\text{nloc}}^{\varphi}$ is defined by equation (27).

Let us focus on the biphasic window of coexistence of disordered and bcc primary morphologies. The interfacial free energy here is

$$F_{\text{intf}} \simeq \sigma_{\text{av}} A_{\text{intf}} \tag{35}$$

where the tension σ_{av} is defined in equation (32), and A_{intf} is the total interfacial area. Within the approximation of narrow secondary interfaces adopted here the second order parameter φ must be nearly constant inside each secondary domain:

$$\varphi(\mathbf{r}) = \frac{12}{\tau}\left(\bar{C} - C(\mathbf{r})\right) = \frac{12h}{\tau}\tilde{\varphi}(\mathbf{r}) \tag{36}$$

where $\tilde{\varphi}(\mathbf{r}) = p$ in a disordered domain, $\tilde{\varphi}(\mathbf{r}) = p - 1$ in a bcc domain, $h = C_2 - C_1 = (1/9)\left(\tau_2^2 - \tau_1^2\right)$, and $\tau_1 = 0$, $\tau_2 = 1.847\epsilon$ are the boundaries of the disordered/bcc separation region (see Sect. 2.5). Using equation (36) we finally write the nonlocal term as

$$F_{\text{nloc}}^{\varphi} = \frac{K^2}{2V}\int_{q,q'} \frac{|\tilde{\varphi}_{\mathbf{q}}|^2\,|\tilde{\varphi}_{\mathbf{q}'}|^2}{q^2 + q'^2} \tag{37}$$

where $K = (12/\tau)h^2 \simeq 1.73(\epsilon^4/\tau)$.

The free energy F_{ex} defined by equations (34–37) is formally identical to the one obtained for weakly polydisperse block-copolymers [40]. Hence similar secondary structures which are briefly described below (see Fig. 1b).

In the region $0 < \tau < 0.77\epsilon$ (this region corresponds to the range $0 < p < 0.174$ for the volume fraction of primary bcc morphology) spherical secondary domains arranged in face-centered-cubic (fcc) superlattice are formed. Each sphere is characterized by bcc primary morphology, and the matrix is disordered. The radius of secondary spheres is

$$R \simeq \frac{1.9}{\epsilon} \tag{38}$$

if $\tau \ll \epsilon$.

Cylindrical secondary morphology (bcc cylinders arranged in 2-dimensional hexagonal lattice) is stable in the region $0.77\epsilon < \tau < 1.05\epsilon$. Lamellar secondary structure is formed in the region $1.05\epsilon < \tau < 1.52\epsilon$, and the regions $1.52\epsilon < \tau < 1.68\epsilon$, $1.68\epsilon < \tau < 1.85\epsilon = \tau_2$ correspond to the inverse cylindrical and spherical secondary morphologies respectively. In the vicinity (but below) τ_2 the radius of inverse (*i.e.* disordered) secondary spheres is

$$R \simeq \frac{1.50}{\epsilon}\left(1 - \frac{\tau}{\tau_2}\right)^{-1/3} \tag{39}$$

i.e. the domain size is increasing as τ tends to τ_2.

Let us consider now the biphasic window with cylindrical and lamellar primary morphologies. Again the secondary structures here are similar to those predicted to weakly polydisperse multiblock-copolymers [40]. The lowest interfacial tension corresponds to the situation when both primary lamellae and cylinders are parallel to the interface, *i.e.* z-axis (normal to the interface) is perpendicular to all basic wave-vectors of primary structures. In this case $|\mathbf{q}| - q^*$ in equation (30) is of order of $(\Delta q_\perp)^2/q^*$, where $\Delta q_\perp \sim 1/\xi_\perp$ is the characteristic wave-vector defined by the interfacial thickness $\xi_\perp$. Hence $(\mathrm{d}/\mathrm{d}z)$ in equation (31) should be replaced by $(1/q^*)(\mathrm{d}^2/\mathrm{d}z^2)$. Then we get upon minimization

$$\xi_\perp \sim \epsilon^{-0.75}, \quad \sigma_\perp \sim \epsilon^{3.25}.$$

The orientation conditions mentioned above strongly favor a lamellar secondary morphology. The typical period of this lamellar structure is

$$\Lambda \sim \left(\frac{\sigma_\perp}{K^2}\right)^{1/3} \sim \epsilon^{-11/12}.$$

4 Discussion and conclusions

Microdomain structures in melts of random multi-block copolymers with quenched monomer sequence are considered in this paper. The correlated random model [27] of copolymer chemical structure is analyzed near the critical point corresponding to symmetric copolymer composition, $\epsilon = 0$, and $\chi n = 2$, where n is the mean number of monomers per block. A mean-field approach used here is valid not too close to the critical point, *i.e.* when the relative distance to this point, τ, is larger than $n^{-1/4}$ [24,34,35].

As the main result I showed that a macroscopic phase separation between different microdomain morphologies predicted earlier [28,35,39] is suppressed in the limit of very long chains: the macro-separation is an artifact of the ψ^4 model adopted in the previous studies. It is shown that a secondary superstructure is formed instead with finite (rather than macroscopic) domains arranged periodically. Each secondary domain is characterized by one of the two competing primary morphologies. The characteristic size of these secondary domains in the window of competition between disordered state and bcc (spherical) primary morphology scales as $\Lambda \sim (1/\epsilon)R_n$, where $R_n = an^{1/2}$ is the Gaussian block size and $\epsilon \ll 1$ is the composition asymmetry, *i.e.* Λ is much larger than the primary domain size $L \sim R_n/\epsilon^{1/2}$.

The predicted domain structures (as shown in the phase diagram of Fig. 1) are valid if the composition asymmetry parameter ϵ is larger than $n^{-1/4}$ since the characteristic τ is of order of ϵ. Yet the secondary structures are also expected in the region $\epsilon \lesssim n^{-1/4}$, where the effect of composition fluctuations was proved to be important [24,34,35]. The secondary domain size in this regime should be nearly independent of ϵ; it scales as $\Lambda \sim R_n n^{1/4}$. Calculation of the phase diagram (incorporating both primary and secondary structures) in the fluctuation zone should be a subject of a separate study which was not attempted here.

The secondary morphologies are analyzed in the narrow interface approximation, *i.e.* assuming that the thickness ξ of an interface between secondary domains is smaller than the domain size Λ. Five regions of different secondary superstructures are predicted in the disordered/bcc window, $0 < \tau < 1.847\epsilon$ (see Sect. 3.4). In particular an fcc structure of secondary spherical (bcc) domains is predicted for $0 < \tau < 0.77\epsilon$. The radius of secondary spheres, $R \simeq 1.9R_n/\epsilon$, as defined by equation (38), is about twice the predicted interfacial thickness $\xi \simeq 0.97R_n/\epsilon$ (Eq. (33)). Hence the narrow interface approximation is not strictly valid in this region. Yet one can hope that this approximation is appropriate at least qualitatively, *i.e.* that the predicted type of the secondary structure is correct. The predicted boundary of the fcc superstructure ($\tau = 0.77\epsilon$) is surely approximate. A further (perhaps numerical) work would be required in order to elucidate this issue: it would be necessary to minimize the excess free energy, F_{ex} (Eq. (34)), allowing a generic structure, *i.e.* neither thin nor plain secondary interfaces.

Other secondary morphologies (cylindrical, lamellar, and inverse) are predicted for larger τ's. As τ increases, the relative thickness of the interfaces decreases, so that the narrow interface approximation becomes more and more accurate. This approximation becomes asymptotically exact as τ tends to $\tau_2 \simeq 1.847\epsilon$ (the upper boundary of the inverse spherical secondary morphology): here $\xi/R \simeq 0.65\,(1-\tau/\tau_2)^{1/3}$ tends to zero (see Eqs. (33, 39)).

A lamellar secondary structure is predicted almost in the whole window where cylindrical and lamellar primary morphologies are competing, *i.e.* for $9.479\epsilon \lesssim \tau \lesssim 10.164\epsilon$. Here the thickness of secondary interfaces is $\xi_\perp \sim R_n/\epsilon^{0.75}$ and the thickness of secondary lamellae is $\Lambda \sim R_n/\epsilon^{11/12}$. Hence $\Lambda \gg \xi_\perp \gg L$, if $\epsilon \ll 1$, *i.e.* the narrow interface approximation is valid in this regime.

The theoretical approach developed in this paper involves the second order parameter φ which is proportional to the local fluctuation of the critical χ-parameter (in other words, of the effective block size) due to the randomness of the primary copolymer sequence. The nonlocal free energy associated with this order parameter, F_{nloc}, is calculated in the main φ^4 order, see equation (27). This φ^4 approximation is not valid if φ is large enough so that the probability P of fluctuation φ for a relevant chain fragment of $\tilde{N}$ monomers is small. Note that equation (23) implies that the probability $P \sim \exp\left[-(1/2)\kappa_\varphi \varphi^2 \tilde{N}\right]$, where κ_φ is defined in equation (24). The relevant $\tilde{N}$ is determined by the secondary domain size R: $\tilde{N} \sim R^2/a^2$, and the typical φ is defined by equation (36): $\varphi \sim h/\tau \sim \epsilon^2/\tau$. Thus the basic equation (27) is valid if $\kappa_\varphi \varphi^2 \tilde{N} \ll 1$, *i.e.*

$$R^2\tau\left(\epsilon^2/\tau\right)^2 \ll 1. \tag{40}$$

Hence the most dangerous regime corresponds to small τ, *i.e.* to the region of spherical (fcc) secondary superstructure. Using equation (38) we get the condition $\tau \gg \epsilon^2$, which is not strongly restrictive since typically $\tau \sim \epsilon$ in the region of interest. The region of inverse fcc structure is also dangerous since R is large there. Using equations (39, 40) we get another condition $1 - \tau/\tau_2 \gg \epsilon^{3/2}$ limiting the region of validity of the theory.

The last comment concerning mean copolymer composition inside the secondary domains, *i.e.* the mean values of the first order parameter ψ_1 and ψ_2, where 1 and 2 denote domains with one and the other primary structures. These values nearly does not depend either on the secondary structure or on the domain size. Hence ψ_1, ψ_2 can be obtained by minimization of the free energy, equation (13), *i.e.* neglecting both second non-local free energy $F^{\varphi}_{\text{nloc}}$ and the interfacial energy. It is sufficient to expand the free energy, equation (13), in powers of $\psi_{1,2}$ up to the quadratic order (note that allowing for $\psi_{1,2}$ is equivalent to consideration of Fourier components $\psi_{\mathbf{q}}$ with wave-vectors $q \sim 1/\Lambda$ much smaller than q^*). The result is

$$\psi_1 \simeq \frac{3}{4\tau}Hp, \quad \psi_2 = -\frac{3}{4\tau}H(1-p)$$

where $H = H_2 - H_1$, $H_i = \left\langle(\partial/\partial\psi)f_{34}(\psi(\mathbf{r}))\right\rangle_i$ where $\langle\cdot\rangle_i$ means averaging over domains of type $i = 1, 2$. For example $H_1 = 0$, $H_2 \simeq 6.95\epsilon^3$ for the disordered/bcc separation window. Hence in this case

$$\psi_1 \simeq 1.53\epsilon\tau, \quad \psi_2 \simeq -1.53\epsilon\tau\left(\frac{\tau_2^2}{\tau^2} - 1\right) \tag{41}$$

where we take into account that $p = \tau^2/\tau_2^2$ in this window. Therefore more ordered bcc secondary domains consist of copolymer fragments with more symmetric composition. The effect is small however: the composition change due to segregation, $|\psi_2| \sim \epsilon\tau \sim \epsilon^2$, is much smaller than the priming composition asymmetry ϵ. The composition difference between the two phases was considered before [39,35]. Equation (41) disagree both with the results of reference [39] where a weaker effect, $\psi_{1,2} \sim \epsilon^3$, was predicted, and with the conclusion of reference [35] that $\psi_{1,2} = 0$.

Appendix A: Free energy of a correlated random copolymer with annealed disorder

Let us consider a linear system (sequence) of N_A A-monomers and N_B B-monomers assuming that each AB contact increases the total energy by $k_{\rm B}TE$. The free energy of a long sequence ($N = N_A + N_B \gg n \equiv {\rm e}^E$) is proportional to the total number of units

$$F_1(N_A, N_B) = N f_1(p) \tag{A.1}$$

where $p = N_A/N$. The grand canonical partition function of the system is

$$Z(\mu_A,\mu_B) = \int {\rm d}N_A {\rm d}N_B {\rm e}^{\mu_A N_A + \mu_B N_B} {\rm e}^{-F_1(N_A,N_B)/(k_{\rm B}T)}.$$

Using equation (A.1) we rewrite Z as

$$Z(\mu_A,\mu_B) = \int {\rm d}N{\rm d}pN{\rm e}^{N[\mu_A p + \mu_B(1-p) - f_1(p)/(k_{\rm B}T)]}.$$

Obviously the function Z must show a singularity at the line defined by the condition

$$\min_p \left[\frac{f_1(p)}{k_{\rm B}T} - \mu_A p - \mu_B(1-p)\right] = 0. \tag{A.2}$$

The grand partition function can be alternatively represented as

$$Z(\mu_A,\mu_B) = \int {\rm e}^{-Em} \tilde{Z}(\mu_A,\mu_B,m){\rm d}m$$

where $\tilde{Z}(\mu_A,\mu_B,m)$ is the grand partition function of a system with m AB pairs:

$$\tilde{Z} = \prod_{i=1}^{m} \int {\rm e}^{-\mu_i n_i} {\rm d}n_i$$

where $\mu_i = \mu_A$ for odd i, and $\mu_i = \mu_B$ for even i. Hence (we assume even m) $\tilde{Z} = (1/\mu_A\mu_B)^{m/2}$, *i.e.* $Z(\mu_A,\mu_B)$ shows a singularity if

$$E + \frac{1}{2}\ln(\mu_A\mu_B) = 0. \tag{A.3}$$

Equation (A.2) must be true for any μ_A, μ_B satisfying equation (A.3). Considering small variations of μ_A and μ_B we get

$$p/(1-p) = \mu_B/\mu_A.$$

Hence $\mu_A = {\rm e}^{-E}\sqrt{p/(1-p)}$, $\mu_B = {\rm e}^{-E}\sqrt{(1-p)/p}$ and

$$f_1(p) = -2k_{\rm B}T{\rm e}^{-E}\sqrt{p(1-p)}.$$

Appendix B: Derivation of equation (30)

The free energy, equation (13), can be represented as

$$F = F_{12} + F_{34},$$

where $F_{34} = \int f_{34}(\psi){\rm d}^3r$. The gradient free energy (first term in the r.h.s. of Eq. (30)) comes from the first two dominant terms in the r.h.s. of equation (13):

$$\begin{aligned} F_{12} &= \int_q \left(q^2 - 2\tau\right)|\psi_{\mathbf{q}}|^2 + \frac{8}{V}\int_{q,q'} \frac{|\psi_{\mathbf{q}}|^2 |\psi_{\mathbf{q}'}|^2}{q^2 + q'^2} \\ &= CV\left\{-2\tau + \left\langle q^2\right\rangle_\rho + 8C\left\langle \frac{1}{q^2+q'^2}\right\rangle_{\rho\rho}\right\} \end{aligned} \tag{B.1}$$

where $C = \int_q |\psi_{\mathbf{q}}|^2$, $\langle\cdot\rangle_\rho$ means averaging with the spectrum distribution $\rho(\mathbf{q}) \equiv |\psi_{\mathbf{q}}|^2/(CV)$:

$$\left\langle q^2\right\rangle_\rho \equiv \int_q q^2\rho(\mathbf{q})$$

and $\langle\cdot\rangle_{\rho\rho}$ means double averaging over $\mathbf{q}$ and $\mathbf{q}'$. Equation (B.1) can be rewritten as

$$F_{12} = -2\tau CV + 2C^{3/2}V\langle x + 1/x\rangle_{\rho\rho}$$

where $x = x(q,q') = (q^2+q'^2)/2q^{*2}$ and $q^* = 2\sqrt{C}$. Obviously the free energy minimum

$$F_{12}^0 = -2\tau CV + 2C^{3/2}V$$

is attained for $x = 1$, *i.e.* if the spectrum is localized at $|\mathbf{q}| = q^*$. Such spectrum is characteristic for pure morphologies, but an interface would imply deviations from q^*. Assuming small deviations we write $x = 1 + \Delta + \Delta'$, where both $\Delta = 0.5\left(q^2/q^{*2} - 1\right) \simeq (|\mathbf{q}| - q^*)/q^*$, and $\Delta' \simeq (|\mathbf{q}'| - q^*)/q^*$ are small. Then $x + 1/x \simeq 2 + (\Delta + \Delta')^2$, so that

$$F_{12} = F_{12}^0 + F_{\rm grad},$$

where

$$F_{\rm grad} \simeq 4C^{3/2}V\left[\left\langle \Delta^2\right\rangle_\rho + \langle\Delta\rangle_\rho^2\right]. \tag{B.2}$$

The second term in square brackets is negligible, since both $\left\langle\Delta^2\right\rangle_\rho$ and $\langle\Delta\rangle_\rho$ are inverse proportional to the size L_z of the system (in the direction perpendicular to the interface)[6], hence $\left\langle\Delta^2\right\rangle_\rho / \langle\Delta\rangle_\rho^2 \propto 1/L_z$ vanishes in the macroscopic limit. So keeping only the first term and writing an integral for averaging we get

$$F_{\rm grad} \simeq 2\int_q |\psi_{\mathbf{q}}|^2 \left(|\mathbf{q}| - q^*\right)^2.$$

---

[6] One way to prove this statement is to represent $\left\langle\Delta^2\right\rangle_\rho$ in the form analogous to equation (31): then it becomes apparent that this quantity scales as $A_{\rm intf}/V$, where $A_{\rm intf}$ is the interfacial area; the same scaling for $\langle\Delta\rangle_\rho$ could be obtained using similar approach.

The total free energy $F = F_{12}^0 + F_{\mathrm{grad}} + F_{34}$ must be then minimized over ψ. Obviously

$$\min_\psi F = \min_C \left[F_{12}^0 + \alpha C V\right] + \min_\psi \left\{ \int \left[f_{34}(\psi) - \alpha\psi^2\right] \mathrm{d}^3 r + F_{\mathrm{grad}} \right\}$$

where α should be chosen self-consistently, so that C corresponding to the first minimum in the r.h.s. coincides with $(1/V)\int \psi^2 \mathrm{d}^3 r$ corresponding to the second minimum. The second minimum must correspond to a phase separation between two morphologies. Hence the effective energy densities, $f_{\mathrm{eff}} = f_{34}(\psi) - \alpha\psi^2$, must be equal in the bulk of two phases (otherwise one of the morphologies would be more favorable):

$$\langle f_{\mathrm{eff}} \rangle_1 = \langle f_{\mathrm{eff}} \rangle_2 \equiv \beta. \tag{B.3}$$

Hence

$$F = F_{\mathrm{bulk}} + F_{\mathrm{intf}}$$

where

$$F_{\mathrm{bulk}} = F_{12}^0 + \alpha C V + \beta V$$

is the bulk free energy which is proportional to the total volume V (note that parameters α and β are actually defined by Eq. (B.3) so that they depend only on ϵ), and

$$F_{\mathrm{intf}} = \int \left[f_{34}(\psi) - \alpha\psi^2 - \beta\right] \mathrm{d}^3 r + F_{\mathrm{grad}} \tag{B.4}$$

is the interfacial free energy.

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