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Microphase Separation in Ternary ABC Block Copolymers: Ordering Control in Molten Diblock AB Copolymers by Attaching a Short Strongly Interacting C Block

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ABSTRACT: Some specific features of the microphase separation in molten ternary ABC triblock copolymers (in particular, modifications of the molten AB diblock copolymers by attaching a short third block C strongly incompatible with both A and B blocks) are studied rigorously within the framework of the weak segragation approach. It is shown that via such a modification one can control both the stability as to the microphase separation transition (i.e., the corresponding spinodal temparatures) and the smoothness of such a transition. Two modes of such modifications for every composition are studied in detail: (i) those resulting in the minimal spinodal temperatures and (ii) those that result in the smooth order−disorder transition at this composition. The corresponding dependencies of the transition temperature and the periodicity of the occurring supercrystal structures are built and analyzed.

1. Introduction

One of the most appealing features of molten AB block copolymers is the possibility to control their morphology (and, therefore, mechanical and other properties) via changing the temperature as well as composition and/or architecture of the macromolecules forming these systems. The recently synthesized ternary ABC block copolymers provide even more opportunities to design new morphologies due to the larger number of independent enthalpic interaction parameters and composition variables.[1−5] In turn, the large number of *a priori* imaginable combinations in ABC triblock copolymers makes it necessary that theory and experiment have to be closely linked. By such a close feedback it may be avoided that the development of new materials is merely based on accident.

In particular, it might be of interest for some applications to know in advance how much we could change the temperature of the order−disorder transition in AB diblock copolymers and arising morphologies of the ordered phases by attaching to the AB macromolecules a third C block of a chemical nature different both from A and B species. To give the complete answer to the question means building phase diagrams indicating clear succession of the phase transitions occurring in a molten $A_nB_mC_l$ triblock copolymer for arbitrary values of the compositions $f_A = n/N$ and $f_C = l/N$ ($N = n + m + l$ is the total degree of polymerization) and interaction parameters χ_{AB}, χ_{BC}, and χ_{CA}.

Until now the theoretical treatment of the ternary ABC block copolymers was carried out only in the "strong segregation (narrow interface)" limit.[5−8] In this paper we start to study microphase separation in these systems within the framework of the "weak segregation" approach introduced by Leibler, de Gennes, and one of the authors.[9−11] As a first step in that direction we consider here a more special problem. Namely, we discuss how much one can control (i) the stability of the uniform (disordered) state of the molten AB diblock copolymer and (ii) the degree of smoothness in the order−disorder transition by attaching to the AB macromolecule a short (but strongly interacting) third block C. Thereby, for the sake of simplicity, we restrict ourselves to the famous Hildebrand approximation for the χ-parameters:

$$2\chi_{ij} = v\frac{(\delta_i - \delta_j)^2}{2T} = \frac{\Theta_{ij}}{T} \tag{1}$$

where the temperature T is measured in energetic units, v is the excluded volume of the repeating units A, B, and C (further, for the sake of brevity these units are referred to as monomers), δ_i is the conventional solubility parameter of the i-th component (for the sake of simplicity it is assumed that v is the same for all kinds of monomers and δ_i do not depend on temperature), and we determined three Flory temperatures Θ_{ij}.

The material is presented in the following manner. In the next section we discuss the most convenient parametrization enabling us to characterize the linear ternary ABC block copolymers under consideration. In section 3 the conditions of the disodered (uniform) state of ABC block copolymers' stability as to microphase separation (supercrystallization, domain structure formation) are discussed. We show here that attaching to an AB macromolecule a third (short but strongly incompatible) block C may result in both a decrease and increase of the ABC block copolymer stability depending on the positioning of this C block and the specific value of its incompatibility with the other two blocks. In section 4 we describe (on a somewhat intuitive level) what and for what importance are the critical points as applied to microphase separation of the ternary ABC block copolymers. In section 5 we present a quantitative procedure enabling us to determine the critical point's location and plot the critical lines for some special cases of the systems under consideration. The general discussion of the peculiarities of the ternary ABC block copolymers as compared to binary block copolymers is given in the Conclusion.

2. Parametrization

To visualize the stoichiometry of the linear block copolymers $A_nB_mC_l$, let us indicate it by a point in the plane of the side blocks' compositions (f_A, f_C). Evidently,

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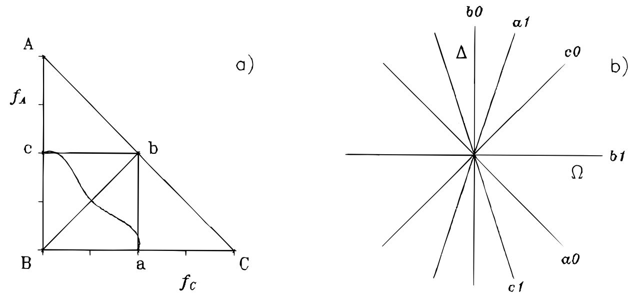

Figure 1. Visual parametrization of the linear ternary ABC triblock copolymers' characteristics. (a) The triangle of the compositions (the bowlike curve *ac* is the line of the critical points for asymmetric ABA triblock copolymer described in more detail in section 4; other lines are described in section 2). (b) The plane of the energetic parameters (Δ, Ω) and the nonselectivity lines described in text.

all these points lay inside of the right triangle *ABC* shown in Figure 1a. Thereby, the sides *AB*, *BC*, and *AC* represent the compositions of the corresponding diblock copolymers, the diagonal *Bb* corresponds to symmetrical copolymers $A_nB_mC_n$, and the lines *cb* and *ac* represent the linear ABC block copolymers in which the composition of the largest side block (f_A and f_C, respectively) is equal to 0.5. There are two reasons to make use of this right triangle of the compositions to describe the structure of the linear ABC block copolymers instead of the conventional regular one: (i) it is much easier to use the rectangular coordinates axes, and (ii) it reveals explicitly the intrinsic asymmetry of these systems (the last reason is not valid for the ternary ABC star copolymers).

Now, in the adopted Hildebrand approximation (1) there are only two independent energetic parameters which we may choose:

$$\Delta = \delta_A - \delta_C \qquad \Omega = 2\delta_B - \delta_A - \delta_C$$

$$\delta_B - \delta_C = (\Omega + \Delta)/2 \qquad \delta_A - \delta_B = (\Delta - \Omega)/2 \qquad (2)$$

There are six straight lines in the plane (Δ, Ω) shown in Figure 1b that correspond to certain naturally distinguished degenerated states of the ternary $A_nB_mC_l$ block copolymers:

(b1) $\Omega = 0$ or $\chi_{AB} = \chi_{CB} \neq 0$, $\chi_{AC} \neq 0$ (blocks A and C are different, but block B is equally incompatible with both A and C blocks);

(c1) $\Omega = -3\Delta$ or $\chi_{AC} = \chi_{BC} \neq 0$, $\chi_{AB} \neq 0$ (blocks A and B are different, but block C is equally incompatible with both A and B blocks);

(a1) $\Omega = 3\Delta$ or $\chi_{AC} = \chi_{AB} \neq 0$, $\chi_{BC} \neq 0$ (blocks B and C are different, but block A is equally incompatible with both B and C blocks);

(b0) $\Delta = 0$ or $\delta_A = \delta_C$ (blocks A and C are indistinguishable; the system is equivalent to triblock copolymer $A_nB_mA_l$);

(c0) $\Delta = \Omega$ or $\delta_A = \delta_B$ (blocks A and B are indistinguishable; the system is equivalent to diblock copolymer $B_{n+m}C_l$);

(a0) $\Delta = -\Omega$ or $\delta_B = \delta_C$ (blocks B and C are indistinguishable; the system is equivalent to diblock copolymer A_nB_{m+l}).

All the lines are labeled by the letter corresponding to that block which is nonselective about the two others. Therewith the indices 0 and 1 imply that the nonselectivity is due respectively just to the interaction identity of the other blocks and to equal incompatibility with them.

Thus, to describe the relative strength of the different components incompatibilities, it is natural to introduce the selectivity parameter

$$x = \Omega/\Delta \qquad (3)$$

or the selectivity angle defined as the polar angle of the point (Δ, Ω):

$$\alpha = \mathrm{arctg}\,(x) \qquad (4)$$

Thereby, the square of the radius of the point (Δ, Ω)

$$R^2 = \Delta^2 + \Omega^2 = 2(\chi_{AB} + \chi_{BC}) \qquad (5)$$

characterizes the total incompatibility among the central block and both side ones.

3. Spinodal Surfaces for the Ternary ABC Block Copolymers and the Disordered State Stability Control

As shown in refs 9−11 the microphase separation in copolymer systems is due to the instability of its uniform state with respect to certain spatial fluctuations of the local monomer densities having a finite wavenumber q_* and the corresponding period $L = 2\pi/q_*$.

Indeed, let the system under consideration consist of *n* sorts of monomers and be characterized by certain nonuniform distribution of the *n* corresponding densities where $\rho_i(r) = \bar{\rho}_i + \Phi_i(r)$, where $\rho_i(r)$ is the local density of monomers of the i-th component (i.e., the number of the monomers per unit volume) and $\bar{\rho}_i = \int \rho_i(r)\, dV/V$ is the average value of the density over the volume *V* of the system. The free energy of the system in this nonuniform state can be expanded in powers of the density fluctuations $\Phi_i(r)$ as follows:

$$F(\{\rho_i(r)\},T) = F_0 + \sum_{k=2}^{k=\infty} \Delta F_k/k! \qquad (6)$$

$$\Delta F_2 = \sum_{i,j=1}^{i,j=n} \int \Gamma_{ij}(q)\, \varphi_i(\mathbf{q})\, \varphi_j(-\mathbf{q})\, d\mathbf{q}/(2\pi)^3 \qquad (7)$$

$$\Delta F_k = (2\pi)^3 \sum_{\{i_1...i_k\}} \int \delta\Big(\sum_{i=1}^{i=k} \mathbf{q}_i\Big) \gamma_{i_1...i_k}(\mathbf{q}_1...\mathbf{q}_k) \prod_{j=1}^{j=k} \varphi_{i_j}(\mathbf{q}_j) \frac{d\mathbf{q}_j}{(2\pi)^3} \qquad (8)$$

where $F_0 = F(\{\bar{\rho}_i\},T)$ is the free energy of the uniform state of the system, $\varphi_i(\mathbf{q}) = \int \Phi_i(r) \exp(iqr)\, dV$ are the Fourier transforms of the density fluctuations $\Phi_i(r)$, and the coefficients $\Gamma_{ij}(q)$ and $\gamma_{i_1...i_k}(\mathbf{q}_1...\mathbf{q}_k)$ of the expansion (6) depend, in general, on both structural and interactional characteristics of the system.

It follows from (6) and (7) that the uniform (disordered) state of the system is stable with respect to infinitesimal density fluctuations having wavenumber *q* only if all *n* eigenvalues of the matrix $\mathbf{\Gamma}(q)$ are positive. Otherwise the fluctuations increase to a certain finite level determined by the higher terms of the expansion (6) and an ordered state appears.[10] So, the condition of the uniform state stability takes the form

$$\Lambda(q) \geq 0 \qquad (9)$$

where $\Lambda(q)$ is the minimal (at a given value of *q*) eigenvalue of the matrix $\mathbf{\Gamma}(q)$. The condition (9) is valid until the curve $y = \Lambda(q)$ touches the *q*-axis at point q_*

and, under the next change of the system parameters, takes negative values in the interval $q_1 < q_* < q_2$. So, the surface confining the region where the uniform state of the system under consideration stays stable (at least metastable) is determined as follows:

$$\min \Lambda(q) = \Lambda(q_*) = 0 \tag{10}$$

This surface and eq 10 are usually referred to as the spinodal surface and equation. In particular, describing our system by the parameters T, f_A, f_B, f_C, χ_{AB}, χ_{BC}, χ_{CA}, and N, one writes its spinodal equation in the form

$$T = T_s(f_A,f_B,f_C,\chi_{AB},\chi_{BC},\chi_{CA},N) \tag{11}$$

where T_s is referred to as the spinodal temperature, the uniform state of the system usually being stable (at least metastable) at temperatures $T > T_s$ and absolutely unstable at $T < T_s$.

The explicit forms of this equation were presented first in refs 9 and 10 for certain molten AB block copolymers and in the most general form in refs 11and 12. For the ternary ABC block copolymers the right-hand side of eq 11 may be written as follows:

$$T_s(N,f_A,f_B,f_C,\chi_{AB},\chi_{BC},\chi_{CA}) = vNW(Q_*)$$

$$W(Q) = (\delta_C - \delta_B)^2\eta_A(Q^2) + (\delta_A - \delta_C)^2\eta_B(Q^2) + (\delta_A - \delta_B)^2\eta_C(Q^2) \tag{12}$$

where $Q = qR$, $R = \sqrt{Na^2/6}$ is the gyration radius of the whole chain, $\eta_i(Q^2)$ are certain explicit functions of Q and f_i presented in the Appendix, and the reduced wavenumber Q_* characterizing the most dangerous fluctuations is determined as the position of the absolute maximum of the function $W(Q)$ at fixed values of f_i and δ_i.

Now it is convenient to rewrite the spinodal equation (12) in terms of a reduced temperature $\tau = T/(N\theta_{AC})$. As following from the definitions (2) and (3), the reduced spinodal equation takes the form

$$\tau = \tilde{T}_s = \max \tilde{W}(Q) = \tilde{W}(Q_*)$$

$$\tilde{W}(Q) = \Phi_0(Q) + x\Phi_1(Q) + x^2\Phi_2(Q)$$

$$\Phi_0(Q) = \eta_B(Q^2) + \Phi_2(Q)$$

$$\Phi_1(Q) = \frac{\eta_A(Q^2) - \eta_C(Q^2)}{2}$$

$$\Phi_2(Q) = \frac{\eta_A(Q^2) + \eta_C(Q^2)}{4} \tag{13}$$

One can see from eq 13 that both the reduced spinodal temperature $\tilde{T}_s$ and critical wavenumber Q_* depend on three compositions $\{f_i\}$ (two of which are independent) and the selectivity parameter x. It provides much more opportunity to control $\tilde{T}_s$ and Q_* than for molten diblock copolymers A_nB_m, where these quantities depend on the composition $f_A = n/(n + m)$ only. Even though we have at our disposal the exact expressions for $\tilde{W}(Q)$, the results of these calculations are still to be visualized, which is a difficult task due to the large number of relevant variables.

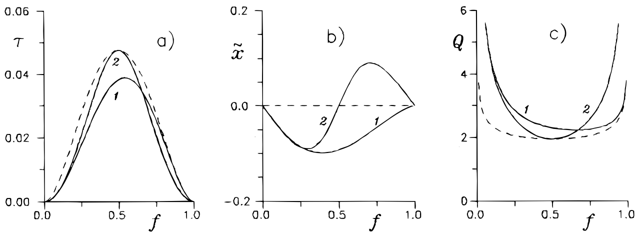

Figure 2. Disordered state stability control. The solid lines show the dependencies of the reduced temperatures $\tau = T/(N\Theta)$ (a), the selectivity parameters $\tilde{x}$ (b), and the critical wavenumbers $Q = q_*a(N/6)^{1/2}$ (c) for the most stable modifications of an A_nB_m diblock copolymer corresponding to eq 17 of the composition $f = f_B = m/(n + m)$. Curves 2 and 1 correspond respectively to modifications by the middle and side (the modifying strongly nonselective C block being attached to the B end of AB macromolecule) blocks. The dashed curves show the corresponding dependencies for the nonmodified ("pure") molten A_nB_m diblock copolymer.

To begin with, let us consider the limit when the shortest block may be considered as the pointlike one but cannot be neglected because of its strong incompatibility with the other two blocks. There are two possibilities: (i) the pointlike block is the middle block B and we are interested in the limiting behavior when approaching the side AC of the composition triangle:

$$f_B \rightarrow 0 \qquad |x_B| \rightarrow \infty \qquad \frac{x_Bf_B}{2} = \tilde{x} \rightarrow \text{const} \tag{14}$$

and (ii) the pointlike block is the side block C(A) and we are interested in the limiting behavior when approaching the sides AB (BC) of the composition triangle

$$f_C \rightarrow 0 \qquad |x_C| \rightarrow \infty \qquad \frac{x_Cf_C}{2} = \tilde{x} = \text{const} \tag{15}$$

the selectivity parameters in the limits B and C, respectively, being defined as follows:

$$x_B = \frac{2\delta_B - \delta_A - \delta_C}{\delta_A - \delta_C} \tag{3a}$$

$$x_C = \frac{2\delta_C - \delta_A - \delta_B}{\delta_A - \delta_B} \tag{3b}$$

In these limits eq 13 takes the form

$$\tilde{T}_s(f_A,\tilde{x}) = \max \bar{W}(Q) = \bar{W}(Q^*(f_A,\tilde{x}),f_A,\tilde{x}) \tag{16}$$

with $\bar{W}(Q) = \lim \tilde{W}(Q) = \varphi_0(Q^2,f_A) + \tilde{x}\varphi_1(Q^2,f_A) + \tilde{x}^2\varphi_2(Q^2,f_A)$. The explicit expressions for φ_i corresponding to both of these limits are presented in the Appendix.

Thus, now the quantities $\tilde{T}_s$ and Q^* depend on the composition f_A *and* the reduced selectivity $\tilde{x}$. (Note that setting $\tilde{x} = 0$ results in values of $\tilde{T}_s$ and Q^* corresponding to the original "pure" molten diblock copolymer.) Putting it in other words, attaching a short (pointlike) but strongly incompatible block C to a diblock copolymer may result in a considerable change of both the spinodal temperature and periodicity of the arising domain structure in the corresponding melt. To evaluate the possibility of stabilizing the uniform (disordered) state of molten diblock copolymers in such a manner, we calculated the quantity

$$T_s^m(f_A) = \min \tilde{T}_s(f_A,\tilde{x}) \tag{17}$$

where the minimum is sought with respect to all possible values of $\tilde{x}$.

As shown in Figure 2a, the reduction of the spinodal temperature (i.e., increasing the region of the disordered state stability) of the molten AB diblock copolymer due to its proper modification may be quite significant. As is seen from merging the left parts of the curves 1 and 2 in Figure 2a, modifying the highly asymmetric AB diblock copolymer via inserting the pointlike strongly interacting block C between two finite blocks or attaching it to the end of the shorter block results in almost the same reduction in the spinodal temperature. This similarity is also revealed in the behavior of the reduced selectivity parameter $\tilde{x}$ (Figure 2b) and critical wavenumber Q (Figure 2c) and has quite transparent physical meaning: if the pointlike block C is adjacent to the shortest of two finite blocks A and C, it is only their interaction and connectivity that determine the instability of the uniform (disordered) state as to microphase separation, the longest block playing the role of a diluent only. Therewith, both of these modifications are much more efficient than that via attaching the pointlike block C to the end of the longer block (cf. the left and right parts of curve 1 in Figure 2a).

Further, as seen from Figure 2b, the value of the reduced selectivity parameter $\tilde{x}$ corresponding to the optimal (as to the disordered state stabilization) modification via attaching the pointlike strongly interacting block to any side block of the AB diblock copolymer is always negative. It means that such a block always should be more incompatible with the adjacent middle block. If the AB diblock copolymer is modified via inserting the pointlike strongly interacting block between two finite blocks, then, as demonstrated by a change of the selectivity parameter x sign with reversal from $f_A < 0.5$ to $f_A > 0.5$, the modifying block should be more incompatible with the smaller block.

At last, it is seen from Figure 2c that the critical wavenumber of the optimal modification for the highly asymmetric ABC copolymer with adjacent short block B and the pointlike one C is much larger than that of the pure AB diblock copolymer, or, putting it in other words, the periodicity of the supercrystal lattice arising after the uniform state becomes unstable is much smaller for the most stable modification than for the original diblock copolymer. It gives one more confirmation of the fact that such a modification results in changing from AB microphase separation to BC microphase separation, the arising superstructure being immersed in the A matrix.

4. Critical Points' Surfaces for the Ternary ABC Block Copolymers: General Description and Implication

The spinodal surface S determined by eq 13 confines those regions of the system parameters space where the uniform state is getting absolutely unstable. Inside these regions, heterogeneities of the system are described conventionally in terms of the vector order parameter $\Phi_i(r) = \rho_i(r) - \bar{\rho}_i$ defined above.

This order parameter is equal to zero, throughout the entire volume of the system, in the high-temperature uniform (disordered, liquid) phase and has the symmetry of a Bravais lattice:

$$\Phi_i(r) = \sum C_i(\mathbf{q}) \exp iqr + \mathrm{cc} \tag{18}$$

where the sum is carried out over all vectors of the corresponding reciprocal lattice, when the temperature decreases. The equilibrium order–disorder transition (ODT) occurs on a surface $\mathcal{T}$ where the free energy of an ordered phase becomes less than that of the disordered one. This phase transition surface never crosses the spinodal surface but may be tangent to the latter. In the points of tangency of the surfaces S and $\mathcal{T}$ (critical points) the ODT is a second-order phase transition characterized by a continuous increasing of the order parameter amplitudes $C_i(\mathbf{q})$ (starting from zero) whereas in other points of the surface $\mathcal{T}$ the ODT is the first-order phase transition, the jump of the amplitudes $C_i(\mathbf{q})$ being increased with an increase of the distance between the surfaces S and $\mathcal{T}$. Thus, in the vicinity of the set of critical points (we will refer to that set as C), the amplitudes of heterogeneities arising in the ordered states are small and, therefore, the system remains weakly segregated.

To locate the set of the critical points C is important due to the following reasons: (i) the dynamics of the second-order phase transition in viscous media like polymers is much faster than that of the first-order one (even though a critical slowing down takes place, there is no retardation due to waiting until droplets are formed), so that one can expect that the system will be able to obey the conditions of the thermodynamic equilibrium only in the vicinity of the set C; (ii) the symmetry formed here may be "frozen" under the following decrease of the temperature; (iii) these symmetries may be described quantitatively within the weak segregation approach.

As follows from the presented considerations, when considering properties of the weakly segregated systems in the vicinity of the critical set C only the first nonvanishing (and necessary to stabilize an ordered state) terms of the expression (6) for the free energy must be taken into account. Thereby, the points that belong to the set C itself are to satisfy both the spinodal equation (10) and the condition that the cubic term in the expansion (6) vanishes:

$$\Delta F_3 = 0 \tag{19}$$

As shown first by Leibler,[10] the ODT goes continuously (in the mean field approximation) in symmetric diblock copolymers, i.e., for the special composition $f_A = n/(n + m) = 0.5$. In general, for molten incompressible AB block copolymers the conditions $\varphi_C(q) = 0$ and $\varphi_A(\mathbf{q}) = -\varphi_B(\mathbf{q})$ hold and eq 19 takes the form

$$\alpha(q_*) = \sum_{i,j,k=A,B} \gamma_{ijk}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3) c_i c_j c_k = 0 \tag{20}$$

Here, $c_A = 1$ and $c_B = -1$, the vectors $\mathbf{q}_1$, $\mathbf{q}_2$, and $\mathbf{q}_3$ are equal to q_* in magnitude and make a regular triangle and the quantities γ_{ijk} satisfy the following relationship valid under the assumption that the energetic addendum to the total free energy of the system does not contribute to ΔF_3:

$$\gamma_{ikj}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3) = \sum_{l,m,n} g_{lmn}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)\, g_{li}^{-1}(q_1)\, g_{mj}^{-1}(q_2)\, g_{nk}^{-1}(q_3) \tag{21}$$

where the matrices $g_{ij}(q)$ and $g_{ijk}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)$ are so-called higher correlators defined and calculated explicitly for a number of architectures in refs 10, 13, and 14.

Critical Points for the Asymmetric Triblock Copolymer $A_lB_mA_n$. In particular, asymmetric triblock $A_lB_mA_n$ molten copolymers were studied in refs 13 and 14. The architecture of the system is described by both the composition of the middle block $f_B = m/N$ and the asymmetry parameter $s = (n - l)/(n + l)$. The

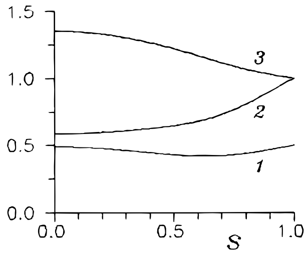

Figure 3. Critical composition $f_B(s)$ (curve 1), reduced critical temperature $\tau(s)/\tau(1)$ (curve 2), and wavenumber $q_*(s)/q_*(1)$ (curve 3) as functions of the asymmetry parameter $s = (n - l)/(n + l)$ for molten binary triblock copolymers $A_nB_mA_l$.

presence of an additional degree of freedom related to the parameter s results in the fact that the value f_{cr} of the composition corresponding to the continuous ODT becomes a function of the asymmetry parameter s shown in Figure 3. (The bowlike line *ac* shown inside of the composition triangle in Figure 1a is just the same line presented in the coordinates (f_A, f_C).) Therewith, the temperature T and the critical wavenumber value q_* also are certain functions of the parameter s. These functions (more exactly, their ratios α to the values of the corresponding quantity for diblock melts of the same composition) also are shown in Figure 3. As is seen from this picture, when increasing the asymmetry parameter s from 0 till 1 (moving from the symmetric triblock ABA to diblock AB) the critical wavenumber decreases and the transition temperature increases.

When going to the $A_lB_mC_n$ triblock copolymer, we get more degrees of freedom and new possibilities to control the sharpness or smoothness of the transition from the spatially homogeneous state to the supercrystal one by adjusting proper triple of components and synthesizing the triblock copolymer macromolecules having the necessary composition. So, the analysis of the whole variety of all possible critical points seems to be a good starting point for detailed study of the crystalline morphologies arising in molten ABC triblock copolymers.

5. Critical Points' Surfaces for the Ternary ABC Block Copolymers: Strict Definition and Some Examples

To generalize the critical point condition (20), let us make use of the standard spectral resolution of the matrix $\mathbf{\Gamma}(q)$:

$$\Gamma_{ij}(q) = \sum_{s=1}^{s=n} \lambda_s(q)\, E_i^{(s)}(q)\, E_j^{(s)}(q) \qquad (22)$$

where λ_s and $E_i^{(s)}$ are respectively the sth eigenvalue and eigenvector of the symmetric matrix $\mathbf{\Gamma}$. Substituting (22) into quadratic contribution (7) to the free energy (6), one can rewrite it in terms of new order parameters $\Phi_s(\mathbf{q}) = \sum_{i=l}^{i=n} \mathrm{E}_i^{(s)}(\mathbf{q})\ \varphi_i(\mathbf{q})$. Now, it is convenient to single out the order parameter corresponding to the minimal eigenvalue $\Lambda(q)$. In what follows it will be referred to as the strongly fluctuating field and designated $\Psi(\mathbf{q})$, unlike all other order parameters referred to as the weakly fluctuating fields and designated $\Phi_s(\mathbf{q})$:

$$\Delta F_2 = \int (\Lambda(q)|\Psi(\mathbf{q})|^2 + \sum_{s=2}^{s=n} \lambda_s(q)|\Phi_s(\mathbf{q})|^2)\ \mathrm{d}\mathbf{q}/(2\pi)^3$$

Near the spinodal $\Lambda(q_*) = 0$ both the strongly and weakly fluctuating fields within the weak segregation approach are approximated as

$$\Psi(r) = \sum C \exp(i\mathbf{q}_i r + \theta_i) + \mathrm{cc}$$

$$\Phi_i^{(s)}(r) = \sum A^{(s)} \exp(i\mathbf{q}_i r + \vartheta_i^{(s)}) + \mathrm{cc}$$

where, unlike (18), the sum is carried out only over those vectors $\mathbf{q}_i$ of the corresponding reciprocal lattice that belong to the first coordination sphere of the lattice. Thereby, the cubic contribution into the free energy takes the form

$$\Delta F_3/V = \alpha C^3 + \alpha_s C^2 A^{(s)} + \alpha_{sr} C A^{(s)} A^{(r)} + \alpha_{srp} A^{(s)} A^{(r)} A^{(p)} \quad (23)$$

But the the weakly fluctuating fields A may differ from zero only due to their coupling to the strongly fluctuating one C and, therefore, A are at least of the second order of smallness as compared to C.[12,16] Thus, we come to the conclusion that it is sufficient to require that only the cubic contribution of the strongly fluctuating fluctuations corresponding to the eigenvalue $\Lambda(q_*) = 0$ vanishes on the set C, which is equivalent to the following condition:

$$\Gamma(q_*) = \sum_{i,j,k} \gamma_{ijk}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) E_i E_j E_k = 0 \qquad (24)$$

where E_i is the eigenvector of the matrix $\mathbf{\Gamma}(q)$ corresponding to the eigenvalue $\Lambda(q_*) = 0$ and the vectors $\mathbf{q}_1$, $\mathbf{q}_2$, and $\mathbf{q}_3$ are equal to q_* in magnitude and make a regular triangle.

Using some methods of the regular perturbations theory by Lifshitz, as shown in ref 12, one gets the following expression for this eigenvector:

$$E_i = N g_{ij} F_j \qquad F_j = \sum_{k \neq j} (\delta_k - \delta_j) g_k = d_j + (x/2) f_j$$

$$\mathbf{f} = (g_B, -(g_A + g_C), g_B)$$

$$\mathbf{d} = \left(-\left(g_C + \frac{g_B}{2}\right), \frac{g_A - g_C}{2}, g_A + \frac{g_B}{2}\right) \quad (25)$$

where $g_i = \sum_{j=1}^{j=3} g_{ij}$, the functions g_{ij} are defined in (A.2) of the Appendix, N is the normalization constant, and the definition (3) of the selectivity parameter x is invoked. Substituting the eigenvector (25) into (24), one can write the equation for the set C of the critical points in the following form:

$$\omega_0(Q^*, f_A, f_C) + 3\frac{x}{2}\omega_1(Q^*, f_A, f_C) + 3\left(\frac{x}{2}\right)^2 \omega_2(Q^*, f_A, f_C) + \left(\frac{x}{2}\right)^3 \omega_3(Q^*, f_A, f_C) = 0$$

$$\omega_0 = \sum_{i,j,k} g_{ijk}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) d_i d_j d_k$$

$$\omega_1 = \sum_{i,j,k<\mathrm{bu}} g_{ijk}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) d_i d_j f_k$$

$$\omega_2 = \sum_{i,j,k} g_{ijk}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) d_i f_j f_k$$

$$\omega_3 = \sum_{i,j,k} g_{ijk}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) f_i f_j f_k \quad (26)$$

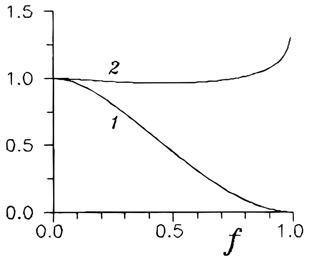

Figure 4. Reduced critical temperature $T(f)/T(0)$ (curve 1) and wavenumber $q_*(f)/q_*(0)$ (curve 2) as functions of the central block composition f for symmetric ternary triblock copolymers $A_nB_mC_n$ (the nonselectivity case b1).

where $Q^*(x,f_A,f_C)$ is the critical reduced wavenumber satisfying the spinodal equation (12) and, to define the functions ω, the relationship (21) was used. The explicit expressions for the functions g_{ijk} may be derived readily from the corresponding results for ABA triblock copolymers given in refs 13 and 14, and we will not present them here.

Now let us consider some examples to elucidate the ABC block copolymers peculiarities in the critical points' location more transparently.

Symmetric Triblock Copolymer $A_nB_mC_n$. In this case the selectivity parameter is defined by (3a), $f_A = f_C = (1 - f_B)/2$ and the function ω_0 appearing in eq 26 is identically equal to zero due to the symmetry of the system. Thus, the condition (26) holds and one can expect a continuous transition from the disordered phase to an ordered one (most probably, lamellar phase) for any composition f_B of the symmetric ABC triblock copolymer if only $x = x_B = 0$ which corresponds to the nonselectivity case b1. This degeneracy is similar to the case of symmetric diblock copolymer A_nB_n. The corresponding values of the critical transition temperature and wavenumber (normalized as to their values for diblock copolymer AC) are plotted in Figure 4 as functions of the composition f_B of the central block. The critical temperature decreases with a decrease of the more incompatible side blocks concentration, which is quite natural. The more surprising feature of this case is the rather weak concentration dependence of the critical wavenumber q_* and the periodicity $L = 2\pi/q_*$.

On the other hand, as shown in refs 13 and 14 and Figure 3, the critical behavior also occurs in the nonselectivity case b0, i.e., in the limit $A_nB_mC_n \rightarrow A_nB_mA_n$ in which case the critical composition of the central block is

$$f_c = 1 - 2n/(m + 2n) = 0.49 \qquad (27)$$

Now let us switch on a small distinction among A and C components, i.e., small (as compared to χ_{AB}) Flory parameter χ_{AC}. More exactly, let us consider the situation when the side blocks are much more incompatible to the central block than to each other, which is described by the condition

$$|x_B| \gg 1 \qquad (28)$$

Then the following natural question arises: how much could we change the critical temperature and the critical wavenumber by changing the composition and small parameter $1/x_B$? (Hereafter, we will refer to the latter situation as case B.) The answer is given in Figure 5.

There is no critical point satisfying the condition (28) for $f_B > f_c$. In the point $f_B = f_c$ corresponding to the critical composition for symmetric ABA triblock copolymer ($\chi_{AC} = 0$) both the critical temperature reduced by χ_{AC} and parameter x go to infinity. However, there is no genuine divergency since the actual critical temperature is proportional to χ_{AB}. Remarkably, for any $f_B < f_c$ there exists a finite value of the selectivity parameter x_B for which the ODT occurs (in the mean-field approximation) continuously. More precisely, due to the specific symmetry of the system there exist two equal in magnitude values of x_B with opposite signs. The temperature and critical wavenumber corresponding to such a continuous transition (normalized as to their values for symmetric $A_{f_A}B_{f_B}A_{f_A}$ triblock copolymer with $\chi_{AB}^{\text{eff}} = (\Omega/2)^2 = ((\chi_{AB} + \chi_{BC})/2 - \chi_{AC}/4)$ are plotted as functions of f_B in Figure 5a whereas the dependences of the absolute value of the selectivity parameter x_B and critical temperature normalized as to its value for symmetric AC diblock copolymer with the same degree of polymerization are shown in Figure 5b. As is seen from these pictures, the selectivity parameter x_B goes through a minimum as the size of the central block decreases. The case is that first (near $f_B = f_c$), when f_B is decreased, we increase the compatibility of the system under consideration so that, to make it undergo the order–disorder transition, we need to increase the incompatibility of the side blocks. However, it follows from the straightforward calculation that for $f_B < 0.251$ the further increase of A–C incompatibility will result in the first-order transition only. So, to return to the continuous ODT, one should properly increase (AC)–B incompatibility, i.e., increase x_B again, as shown in Figure 5b. Therewith, the reduced critical temperature (normalized as to its values for diblock copolymer AC) decreases as shown in Figure 5b.

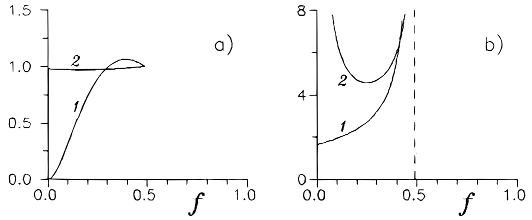

Figure 5. Dependences of the critical parameters of the symmetric ternary triblock copolymers $A_nB_mC_n$ of the central block composition f: (*a*) reduced critical temperature $\tau = T(f)/T(f_c)$ (curve 1) and wavenumber $\tilde{q} = q_*(f)/q_*(f_c)$ (curve 2) normalized as to their values for the symmetric ABA triblock copolymer; (b) reduced critical temperature $\tau = T(f)/T_{AB}$ normalized as to its value for the symmetric AC diblock copolymer (curve 1) and the selectivity parameter x (curve 2).

The most surprising feature of case B as compared to case b1 is that when the central block fraction is decreased to zero, we do not return again to the AC diblock situation. Putting it in other words, inserting into the AC diblock an infinitely small central block B infinitely incompatible with both side blocks (these side blocks having a finite incompatibility $\chi_{AC} \neq 0$) will result in a continuous microphase separation of the system under consideration at the temperature about 5/3 as much as the critical temperature for AC diblock system. This result obtained by the straightforward calculations seems to be rather paradoxical and is of interest far from purely theoretical. As a matter of fact, this result opens the possibility to control the ODT smoothness in a molten diblock copolymer via attaching to it a finite small central block strongly incompatible with the much larger side blocks. Another specific feature of the case B is that for $x_B > x_{\max} \approx 4.575$ there exist two compositions at which the transition from the disordered (homogeneous) phase to an ordered (supercrystal) one

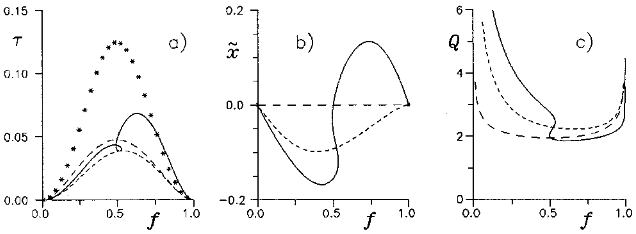

Figure 6. ODT smoothness control for the case of the side pointlike strongly incompatible modifying block. Solid lines show the dependences of the critical reduced temperature $\tau = T/(N\Theta_{AB})$ (a), selectivity parameter $\tilde{x}$ (b), and wavenumber $Q = q_*a\,(N/6)^{1/2}$ (c) of the modified A_nB_m diblock copolymer of composition $f = f_B = m/(n + m)$, the modifying short but strongly nonselective C block being attached to the B end of AB macromolecule. To facilitate comparison with the results of section 2, the curves describing the behavior of the nonmodified ("pure") molten A_nB_m diblock copolymer (dashed) and its most stable modification corresponding to eq 17 (dotted) as well as the "broken blocks system" (asterisks) are also presented.

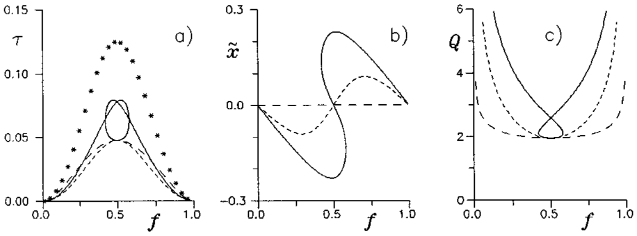

Figure 7. Same dependences as in Figure 6 for the case when the modifying C block is located between the A and B blocks of an A_nB_m macromolecule. All designations are the same as in Figure 6.

proceeds continuously, the larger fraction of the central block corresponding to the higher critical point temperature. At last, it is worthwhile to notice that the critical wavenumber along this critical line is only very slightly different from that for symmetric critical ABA triblock.

Order−Disorder Transition Smoothness Control. The peculiar limiting critical behavior of the symmetric ABC copolymer for $f_B \to 0$ is far from being an exception. To illustrate it, let us consider the limiting cases (14) and (15) defined above. In these cases the equation for the critical points set C may be written in the following parametric form:

$$\tilde{T} = \Phi_0(Q) + \tilde{x}\Phi_1(Q) + \tilde{x}^2\Phi_2(Q) \tag{29}$$

$$\tilde{\omega}_0(Q^*,f_A) + \tilde{x}\tilde{\omega}_1(Q^*,f_A) + \tilde{x}^2\tilde{\omega}_2(Q^*,f_A) + \tilde{x}^3\tilde{\omega}_3(Q^*,f_A) = 0 \tag{30}$$

where $\tilde{x}$ is defined in (14) and (15), respectively, for the middle and side pointlike strongly interacting blocks and $\tilde{\omega}_i$ are the corresponding limits of the functions ω_i appearing in (23). For the sake of brevity we will not present here the explicit expressions for these functions (they will be given elsewhere). Substituting into eq 30 for $Q^*(f_A,\tilde{x})$ the value satisfying the condition (16), one can solve the equation numerically and get the function $\tilde{x}(f_A)$ determining the value of the reduced selectivity which provides the critical behavior (i.e., the continuous order−disorder transition) for a given composition as well as the quantities $Q^*_c(f_A)$ and $\tilde{T}_c(f_A)$.

The results of the calculations are presented in Figures 6 and 7 for the limits (15) and (14), respectively. One can see that there is at least one critical point for every value of the composition $f = n/(n + m)$. Besides, the functions $Q^*_c(f_A)$, $\tilde{T}_c(f_A)$, and $\tilde{x}_c(f_A)$ prove to be three-valued in certain composition intervals, which means that modifying the same diblock copolymer by different pointlike strongly interacting blocks C may result in the continuous transition from the disordered state to three different supercrystal phases. Even though most of the critical points correspond to the higher temperatures as compared to the spinodal (dashed) line for the pure AB diblock copolymer (here we obtain a smooth transition at the cost of the disordered phase stability), there are some intervals of composition where the critical lines are located at lower temperatures than the latter. It means that the corresponding modifying will result in both the more stable disordered phase and continuous microphase separation.

As seen from Figures 6 and 7, the critical modification may be carried out typically via attaching a pointlike block C more incompatible with the *smaller* block. Thereby, if the smaller block is adjacent to the modifying one, then the critical points' temperatures are lower and the critical wavenumbers higher than those of the spinodal. On the contary, if the smaller block is remote, then the critical points' temperatures are higher and the critical wavenumbers lower than those of the spinodal. It is instructive now to compare the highest critical points' temperatures with the spinodal temperature of the blend of homopolymer chains A_n and B_m, the numbers of the chains being equal. (This system may be referred to as the "broken blocks' system" (BBS) since it may be thought of as that obtained from the molten A_nB_m copolymer under consideration by breaking the chemical bonds between blocks A and B.) The temperature is determined as

$$T_{BBS}/\Theta_{AB} = ((f_AN_A)^{-1} + (f_BN_B)^{-1})^{-1} = N(f^{-2} + (1 - f)^{-2})^{-1} \tag{31}$$

and shown in Figures 6 and 7 by the asterisks. One can see that the critical modification of the *asymmetric* AB diblock copolymer via attaching the third pointlike block C to the *larger* block may result in a rather considerable increase of the continuous order−disorder transition, above the corresponding T_{BBS}.

On the other hand, the *symmetric* AB diblock copolymer should be critically modified via attaching the pointlike block C *among* two finite blocks. Thereby, the corresponding ODT transition temperature also increases as compared to the AB diblock copolymer spinodal temperature but always stays below T_{BBS} (see Figure 7).

It may appear that the limiting situations (14) and (15), infinitely short and infinitely incompatible blocks C, are too theoretical. But it is not the case. Actually, these situations imply only that the size of the block C is less (much less, in the limit) than the period of the supercrystal structure occurring due to the instability of the uniform state of the system under consideration with respect to the critical density waves formation. Indeed, neither ODT temperature nor critical wavenumber curves shown in Figures 6 and 7 contain any singularity. Even the values of selectivity parameter $\tilde{x}$, which seems to be a singular quantity, may be viewed as the usual products of the small (but finite) value of the composition of the short block C and the large (but finite) value of ratio Ω/Δ. In this case the multivalence of the function $\tilde{x}(f)$ means simply the presence of several critical points at different compositions of the block C.

6. Conclusion

Summarizing, the meaning of the presented results is 2-fold. From a practical point of view, we analyzed modifications of the molten AB diblock copolymer via attaching a short (in the limit, pointlike) but strongly incompatible block C to AB macromolecules as certain limiting cases of the general ternary ABC block copolymer behavior. Such modification was shown to be a quite efficient way to control both the spinodal and order−disorder transition temperatures as well as the corresponding critical wavenumbers. Thereby, the following peculiarities (as compared to the much more familiar AB block copolymer behavior) were found: (i) the possibility to undergo the ODT transition continuously even in the highly asymmetric (in respect of composition) system and (ii) the existence of several (at different compositions) critical points at fixed energetic parameters of the system. These peculiarities influence arising morphologies as well. For instance, one can expect that between two close critical points a lamellar-like phase (both simple lamellar and lamellar with cylinders or lamellar with spheres described, e.g., in ref 5) should exist. Moreover, one can show that these peculiarities are far from being characteristic of only the considered particular cases. In fact, the functions $x_c(f_A,f_C)$, $T_c(f_A,f_C)$, and $q_*(f_A,f_C)$ exist for any composition (f_A, f_C) and, in general, are multivalent so that the curves presented in Figures 4−7 are just the sections of the corresponding surfaces by the planes $f_A - f_C = 0$, $f_A + f_C = 1$, and $f_A = 0$ or $f_C = 0$.

From a theoretical point of view we demonstrated that the concept of symmetry in the ternary ABC block copolymers is more complicated and deep than in the conventional binary AB block copolymers. Indeed, it is just the symmetry or indistinguishability of the domains occurring below the ODT transition that causes continuousity of this transition. For an AB diblock copolymer the symmetry means nothing but the possibility to exchange all A and B monomers without changing the system behavior. Now, if we identify the continuous ODT transition and symmetry, then we are to conclude that in the ternary ABC block copolymers the symmetry means a transformation that involves both compositions and interactions (more precisely, selectivity parameters x) of A, B, and C monomers. A good idea of such a transform should provide an explicit building of the critical surface C determined by (26) and the phase diagrams in a vicinity of C within the whole triangle of compositions that will be presented elsewhere.

It is instructive to note also that the case when the short strongly interacting block C is located between the A and B blocks of the A_nB_m macromolecule was considered already within the framework of the simple Alexander−de Gennes approach in ref 8. Thereby, it was predicted that a decrease of the region, where the main blocks are demixed, could be observed with an increase of the incompatibility of the middle block. Thus, the results presented in this paper are in qualitative agreement with the results of ref 8.

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Appendix

The matrix $|\Gamma_{ij}(q)|$ of rank n that appears in (7) may be written as a sum of the following two matrices:[11,17,18]

$$\mathbf{\Gamma}(q) = (\mathbf{g}(q))^{-1} - \mathbf{c} \qquad \text{(A.1)}$$

The structural matrix $\mathbf{g}(\mathbf{q})$ describes effects of the chain connectivity and is determined in the most general form as follows:[11]

$$g_{ij}(\mathbf{q}) = \sum_S \nu_S \int \mathrm{d}r\, \langle \rho_i^S(r)\, \rho_j^S(0)\rangle_S \exp i\mathbf{q}r$$

where $\rho_i^S(r)$ is the local density of all residue of the i-th sort pertaining to a macromolecule characterized by a structure S, ν_S is the average number of such a macromolecule per unit volume and brackets $\langle\ \rangle_S$ imply averaging over the whole conformational set (assumed to be the Gaussian one) of the macromolecule S. For the case of the monodisperse molten ternary (linear) ABC block copolymers the components of the matrix $\mathbf{g}$ are easily calculated:[15]

$$g_{ii} = \nu N_i^{\,2} g_2(f_i z), \qquad i = A, B, C;$$
$$g_{AC} = g_{CA} = \nu N_A N_C \psi(zf_A)\, \psi(zf_C) \exp(-zf_B),$$

$$g_{iB} = g_{Bi} = \nu N_i N_B \psi(zf_B)\, \psi(zf_i),$$
$$i = A, C,\ z = Q^2 = q^2a^2N/6, \qquad \text{(A.2)}$$

$$g_2(x) = 2(\exp(-x) - 1 + x)/x^2,$$
$$\psi(x) = (1 - \exp(-x))/x$$

where a is the Kuhn length assumed to be the same for all three blocks.

The matrix $\mathbf{c}$ in A.1 is referred to as the matrix of direct correlation functions describing the interaction in the system of “broken” monomers. In the approximation (1) its components can be written as follows:[11,12]

$$c_{ij} = v\left(\frac{\delta_i\delta_j}{T} - \frac{1}{1-\phi}\right) \qquad \text{(A.3)}$$

where $\phi = v(\bar{\rho}_A + \bar{\rho}_B + \bar{\rho}_C) = v\nu N$ and $1 - \phi$ are the volume fractions of all monomers and holes, respectively, so that the limit

$$1 - \phi \rightarrow +0 \qquad \text{(A.4)}$$

corresponds to the incompressibility limit.

After straightforward calculations involving definitions (A.1) and (A.3) and some results of ref 12 as well as taking the limit (A.4), one can rewrite the spinodal equation as follows:

$$G(q)\left(\frac{v\Sigma_{\delta\delta}(q)}{T} - 1\right) - v\frac{\overset{2}{\underset{1\delta}{\Sigma}}(\mathrm{q})}{T} = 0 \qquad \text{with}$$

$$G(q) = \sum_{i,j=A,B,C} g_{ij}(q), \qquad \Sigma_{0\delta}(q) = \sum_{i,j=A,B,C} \delta_j g_{ij}(q),$$
$$\Sigma_{\delta\delta}(q) = \sum_{i,j=A,B,C} \delta_i\delta_j g_{ij}(q) \qquad \text{(A.5)}$$

Equation A.5 is readily transformed into eqs 11 and 12 with $\eta_i(q) = [\mathbf{g}^{-1}\,(q)]_i \det(\mathbf{g})/G(q)$, the vector $[\mathbf{a}]_i$ being defined for matrices of the rank 3 as follows: $[\mathbf{a}]_i = a_{ii} + a_{\alpha\beta} - a_{i\alpha} - a_{i\beta}$ where $\alpha \neq \beta \neq i$.

Finally, approaching the limits (14) and (15), we obtain the following explicit expressions for the functions φ_i appearing in eq 16:

$$\varphi_0 = (g_2(z,f)\, g_2(z,1-f) - (\psi(z,f)\, \psi(z,1-f))^2)/g_2(z,1)$$

$$\varphi_1/2 = \psi(z,1-f)[g_2(z,f) + \psi(z,f)\, \psi(z,1-f)] \exp(-sfz) - \psi(z,f)[g_2(z,1-f) + \psi(z,f)\, \psi(z,1-f)]$$

$$\varphi_2 = 1 - (\psi(z,f) + \psi(z,1-f) \exp(-sfz))^2/g_2(z,1)$$

where $s = 1$ for the side short block and $s = 0$ for the middle one.

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