Microphase separation in two-length-scale multiblock copolymer melts
Smirnova, Yuliya Georgiyevna

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In this chapter we take into account fluctuation effects in the one-loop approximation for the multiblock copolymer melts investigated in the previous chapters. Near the order-disorder transition two regimes are revealed. In the ”multiblock” regime microphase separation occurs at the scale of the diblock - the repeat unit of the multiblock. Here fluctuation effects are large and scale as $1/N^{1/3}$ where $N$ is the length of the repeat unit. In the ”triblock” regime separation occurs at the scale of the whole macromolecule. Therefore fluctuation effects decrease upon increasing the architectural parameters $n$ and $m$ (e.g. the total polymer length $N_{tot} = (n + m)N$) as $1/N_{tot}^{1/3}$. Inside the region where both scales are important we investigate fluctuation effects on a semi-quantitative level.
4.1. Introduction

It is well established that block copolymer melts undergo order-disorder transitions (ODT) resulting in the formation of ordered morphologies with different symmetries [5, 23, 25, 66]. The periodicity of these structures is usually of the order of the gyration radius of the macromolecule and ranges from 10 to 100 nm. This transition is called microphase separation in contrast to the ordinary separation into two or more macroscopic phases.

The first physically consequent theory of microphase separation in block copolymer, formulated by Leibler [5], is the Landau-like mean-field theory according to which the ODT in the critical point (if any) is a second order phase transition. As has already mentioned by Leibler [5], this result is actually only an artifact of the mean-field approach. Fluctuation corrections to the mean-field zero approximation, first discussed by Brazovskii [67], transform this smooth second order phase transition into a more or less pronounced first order phase transition. Therewith the appearance of a genuine long range ordered periodic structure occurs at lower (as compared to the mean field prediction) temperatures, whereas the local composition profile near the ODT always looks like a more or less distorted periodic structure [68]. The Leibler analysis for diblock copolymers was generalized by Fredrickson and Helfand [28], who included these fluctuation corrections. Later it has been applied to melts of block copolymers with more complicated architectures as well [23, 25, 29, 30, 66].

Block copolymer melts belong to the Landau-Brazovskii (weak crystallization [31, 34]) universality class, which means that the spatially homogeneous phase becomes unstable at a non zero wave number, \( q^* \neq 0 \). Homopolymer blends on the other hand belong to the Ising or Landau-Ginzburg universality class with \( q^* = 0 \), and they are less affected by fluctuations [25, 68, 69]. It has also been shown [70, 71] that homopolymer/copolymer mixtures belong to the so-called Lifshitz universality class, since such systems are characterized by competing tendencies to phase separate into bulk or spatially ordered phases. The important feature of block copolymer melts is that the fluctuation corrections to mean field decrease with increasing number of chain segments \( N \).
Fredrickson and Helfand [28] mapped the coarse grained Hamiltonian for diblock copolymers onto the form analyzed by Brazovskii. Using perturbation theory, they include all relevant diagrams on the level of the Hartree approximation and obtained the free energy for the system. The main conclusions reached are as follows: 1) The second order phase transition at the critical point transforms, with due regard for the fluctuation corrections, into a first order transition to the lamellar phase. They also determined the regions in the phase diagram where disordered-lamellar and disordered-hexagonal transitions are possible. 2) The transition value of the reduced \( \chi N \) parameter increases with decreasing chain length \( N \), the shift being \( \Delta \chi N \propto N^{-1/3} \). Their analysis showed that the Hartree approximation is accurate for \( N > 10^4 \). This approach has, however, some limitations. In particular, they neglected the so-called angle dependence of the fourth order vertex function, which is justified for block copolymer systems similar to the simplest diblock case, but in other cases not. The angle dependence of the vertex functions has been included by Mayes and de la Cruz [72], and by Dobrynin and Erukhimovich [73, 74], who calculated phase diagrams for block copolymer melts with different architectures.

The influence of fluctuations on a specific class of polymer systems, so-called random copolymer melts, were investigated by many authors, [75–79] and the corresponding phase diagrams with fluctuation corrections have been calculated [53, 80]. In contrast to monodisperse melts, the fluctuations are much more important here. It has been shown that for the correlated random copolymers the fluctuation corrections decrease [77] as \( \Delta \chi N \propto N^{-1/4} \), which is more slowly than the \( N^{-1/3} \) for the monodisperse melts. Recently, the mean-field theory of random block copolymers was readdressed [81], which will lead to modifications in the existing fluctuation theory for this class of copolymers.

Experiments and computer simulations proved to be in a good agreement with many predictions of the fluctuation theory (see ref.[68] and references therein). Nevertheless, in contrast to the theory, the critical wave number \( q^* \neq 0 \) was shown to be temperature dependent near the phase transition. Moreover it scales with \( N \) in a manner that is not in accordance with the theory (theory predicts \( q^* \propto N^{-1/2} \)). Barrat and Fredrickson [82] proposed a
procedure to allow for this so-called $q^*$ renormalization. Still some problems with relating theoretical and experimental data remain.

In this chapter we study the fluctuation corrections for a new class of AB-block copolymer melts characterized by so-called two-length-scale behavior [17–19, 21, 22, 45, 83, 84]. We consider monodisperse melts of binary (AB) multiblock copolymers, with the architecture shown in Figure 2.1. Each molecule consists of a multiblock middle part containing $n$ repeat symmetric AB diblocks of size $N$, and two homopolymer blocks (tails) A and B that are attached to both ends of the multiblock. Parameter $m$ characterizes the relative length of the tails with respect to that of the diblock unit, while parameter $f$ characterizes the asymmetry ratio of the end blocks. Hence, the total degree of polymerization reads, $N_{\text{tot}} = nN + Nmf + Nm(1 - f) = N(n + m)$. The Flory-Huggins $\chi$ parameter characterizes short-range interactions (incompatibility) between different types of monomers (A and B). The system has two different length scales, one related to the size of the diblock $N$ and another to the total size of the macromolecule. In the previous chapters we analyzed the phase behavior of these systems in the mean-field approach and plotted phase diagrams in the weak segregation regime [84]. For the symmetric systems ($f = 0.5$) non-conventional one-length-scale cubic phases, such as face centered cubic FCC (space group $Fm\bar{3}m$), simple cubic SC (space group $Pm\bar{3}m$), and single gyroid SG (space group $I4_132$) were predicted to be stable instead of the lamellar LAM structure. Depending on the values of the architectural parameters ($n$ and $m$), in the weak segregation the system undergoes microphase separation either on short, $D \propto N^{1/2}$ (multiblock-like), or long length scale, $D \propto N_{\text{tot}}^{1/2}$ (triblock with nonselective middle block). There is a region in the $(n, m)$ plane where both length scales are important [21, 22]. Experimentally, one can synthesize only molecules with finite length and fluctuations near the ODT will play a significant role for not extremely large $N$. Here we study the influence of the order parameter fluctuations on the phase behavior of two-length-scale multiblock copolymer melts described by the general formula $A_{fmN-b-(B_{N/2-b-A_{N/2}})n-b-B_{(1-f)mN}}$. 


4.2. Theory

To describe microphase separation it is common to introduce the order parameter (or composition profile) $\Psi_i(r) = \phi_i(r) - f_i$, which is the deviation of the volume fraction $\phi_i(r)$ of monomers of the $i$-th sort ($i = A, B$) at point $r$ from its average value $f_i$. We assume the melt to be incompressible. Hence, $\Psi_A(r) = -\Psi_B(r)$ and in what follows the simplified notation $\Psi_A(r) \equiv \Psi(r)$ is used. The ordered state is characterized by a nonzero expectation value of the order parameter, $\langle \Psi(r) \rangle \neq 0$.

In order to calculate a phase diagram it is necessary to evaluate the partition function of the system. The partition function can be written as the integral over all possible composition profiles:

$$Z = \int \exp(-F(\Psi(r)))\delta\Psi(r)$$ (4.1)

We consider the system in the vicinity of ODT, therefore the order parameter is sufficiently small and the free energy functional $F(\Psi(r))$ may be expanded in powers of $\Psi(r)$. The fourth order Landau expansion of the free energy reads:

$$\frac{F}{V k_B T} = F_0 + \sum_{n=2}^{n=4} \frac{1}{n!(2\pi)^3n} \int \gamma_n(q_1, \ldots, q_n)\delta(q_1 + \cdots + q_n) \prod_{i=1}^{i=n} \Psi(q_i) \, dq_i$$ (4.2)

Because of translational invariance, $F_1$ is omitted from the expansion. $F_0$ is the free energy of the disordered state. In Fourier space the order parameter $\Psi(q) = \int \Psi(r) \exp(iqr) \, dr$ is the amplitude of the harmonic concentration wave with wave vector $q$ and finite period $D = 2\pi/|q|$. The coefficients of the expansion $\gamma_n$ are called vertex functions and are related to the $n$th order Gaussian single-chain correlation functions $g_{\alpha_1 \ldots \alpha_n}(r_1 \ldots r_n)$. Vertex functions for the simplest case of diblock copolymers have been presented in the classical paper by Leibler.[5] For our system the expressions for the vertex functions are rather cumbersome and some details of the calculation can be found in the appendix A to chapter 2.

For fixed structural parameters $(n, m, f)$ the function $\gamma_2$ determines the spinodal surface, which bounds the region in the space $(\chi, n, m, f)$, where the
disordered state of the system becomes unstable with respect to the growth of the concentration fluctuations of a certain critical wave length $D = 2\pi/q^*$ [5, 26, 27]

$$\min \gamma_2(q) = \gamma_2(q^*) = 0$$ (4.3)

In mean-field the integral in (4.1) is evaluated by the saddle point approximation, implying that only the contribution from the density profile, $\Psi_{mf}(r)$, which minimizes the Landau free energy functional is accounted for and contributions from all other profiles are neglected. Thus the mean field free energy is given by:

$$F_{mf} = \min F_L\{\Psi(r)\} = F_L(\Psi_{mf}(r))$$ (4.4)

This approximation is exact in the limit $N \to \infty$. For finite chain length, however, the contributions from the profiles close to the mean-field one are important as well. The influence of the fluctuations can be treated within the Hartree approximation [28]. In the one-loop Hartree approximation only the pair density-density correlation function, $G(r_1, r_2) = \langle \Psi(r_1)\Psi(r_2)\rangle - \langle \Psi(r_1)\rangle\langle \Psi(r_2)\rangle$, has to be renormalized. Only profiles with wave numbers $|q|$ close to the critical one $q^*$ are taken into account.

An efficient variation method to calculate fluctuation corrections for binary block copolymer melts with arbitrary architecture was developed in ref. [74]. The free energy functional has two contributions:

$$F = F_L\{\Psi(r_1)\} + F_{fl}\{\Psi(r_1), G(r_1, r_2)\}$$ (4.5)

where $F_{fl}$ is the free energy due to the fluctuations [53]. One can write this part in Fourier space using the Brazovskii-Frederickson-Helfand approximation including the angle dependence of the vertex functions [74]

$$\frac{F_{fl}}{Vk_BT} = \frac{1}{2(2\pi)^3} \int \gamma_2(q_1)(G(q_1) - g(q_1))dq_1 - \frac{1}{2(2\pi)^3} \int \ln(G(q_1))dq_1$$

$$+ \frac{1}{8(2\pi)^6} \int \gamma_4(q_1, -q_1, q_2, -q_2)G(q_1)G(q_2)dq_1dq_2$$ (4.6)

$$+ \frac{1}{4(2\pi)^9} \int \gamma_4(q_1, q_2, -q_3, -q_3)\Psi(q_1)\Psi(q_2)G(q_3)dq_1dq_2dq_3$$
where \( g(q) \) is the "bare correlation function", e.g the inverse of the second order correlation function, \( g(q) = \gamma_2^{-1}(q) \), which was calculated for the systems of interest in chapter 2. We assume that \( G(r_1, r_2) \) depends only on the distance between two points, therefore the Fourier transform of the correlation function satisfies \( G(q_1, q_2) = (2\pi)^3 \delta(q_1 + q_2)G(q_1) \).

The free energy functional (4.5) should be minimized with respect to both functions, density profile and renormalized correlation function. To perform this minimization proper trial functions are used. The trial function for the order parameter which acquires the symmetry of a crystal lattice with period \( D = 2\pi/q^* \) is the following:

\[
\Psi(r) = \sum_{q_i} A(q_i) \exp i(q_i r + \varphi(q_i)) \quad (4.7)
\]

where \( q_i \) is the set of vectors, that belong to the reciprocal lattice corresponding to the ordered structure of interest. The phases \( \varphi(q_i) \) are defined by the symmetry group of the lattice. In the weak segregation regime one adopts usually the first harmonics approximation, which corresponds to taking into account in the series (4.7) only the \( 2k \) vectors of length \( q^* \) belonging to the first coordination sphere. Due to symmetry all amplitudes of the first harmonic are the same, and according to convention they are normalized via the relationship \( A(q_i) \equiv A/\sqrt{k} \).

Since \( \gamma_2(q) \) attains its minimum at some \( q^* \neq 0 \), the usual choice of the trial function for \( G(q) \) is [67]

\[
G^{-1}(q) = c(|q| - q^*)^2 + r, \quad (4.8)
\]

where \( c = \gamma''(q^*)/2 \) and \( \sqrt{c/r} \) is the correlation radius. To obtain the expression for the free energy, the vertex functions and the order parameter have to be rescaled according to ref.[74] (see also [54]). The calculation of the second fluctuation integral can be found in ref.[74]

The final expression for the free energy is obtained by substituting (4.7) and (4.8) into (4.2) and (4.6),

\[
\frac{F}{Vk_BT} = \tau A^2 + \alpha A^3 + \beta A^4 + \frac{s\tau}{2\sqrt{r}} + \frac{s\sqrt{r}}{2} + \frac{s^2\xi}{8r} + \frac{s\xi A^2}{2\sqrt{r}} \quad (4.9)
\]
The following designations are introduced:

$$\tau = \gamma_2(Q^*), \quad Q^* = \frac{(q^* a)^2 N}{6} \quad (4.10)$$

$$\alpha_k = \frac{\gamma_3}{k^{3/2}} \sum_3 \cos \Omega_j^{(3)} \quad (4.11)$$

$$\beta_k = \frac{\lambda_0(0)}{4k} + \frac{\sum \lambda_0(h) + \sum_4 \lambda(h_1, h_2, h_3) \cos \Omega_j^{(4)}}{k^2} \quad (4.12)$$

$$\xi = \frac{1}{4} \int_0^4 \gamma_4(0, h, 4 - h) dh \quad (4.13)$$

$$s = \frac{3 \sqrt{3 \Omega^*}}{\pi \sqrt{\gamma''(Q^*)}} \frac{v}{a^3 N^{1/2}} \quad (4.14)$$

It is worthwhile to notice that we do not perform the Barrat-Fredrickson\cite{82} $q^*$-renormalization here. However, we take into account the angle dependence of the fourth vertex function i.e. the $h$-dependence of the quantities $\lambda(h_1, h_2, h_3)$, which results also in difference of the quantities $\xi$ and $4\beta_{LAM}$ assumed to be identical in ref. [28] (see appendix).

As a result of renormalization, the dependence of the free energy (4.9) on the total polymer length $N$ is only via parameter $s$. In eqs. (4.10)–(4.12) we used the Leibler designations and parameters [5]

$$h_1 = \left[(q_1 + q_2)/q^*\right]^2, \quad h_2 = \left[(q_1 + q_3)/q^*\right]^2, \quad h_3 = \left[(q_1 + q_4)/q^*\right]^2 \quad (4.15)$$

$$\gamma_3 = \gamma_3(q_1, q_2, q_3) \quad (4.16)$$

$$\lambda_0(h) = \lambda(0, h, 4 - h), \quad \lambda(h_1, h_2, h_3) = \gamma_4(q_1, q_2, q_3, q_4) \quad (4.17)$$

with $|q_i| = q^*$ and $\sum q_i = 0$. The phases $\Omega_j^{(n)}$ are the algebraic sums of the phases $\varphi(q_i)$ for the triplets and non-coplanar quartets of the vectors involved in the definition of corresponding $\gamma_3$ and $\lambda$, the symbol $\sum_n$ designates summation over all sets of such $n$ vectors. The first summation in (4.12) is over all pairs of non-collinear vectors $q_i$ and $q_j$. 
4.3. Results and discussion

The free energy (4.9) is a function of the order parameter amplitude $A$, architecture parameters of the polymer $(n, m, f)$, total degree of polymerization $N$, Flory-Huggins $\chi$-parameter, and microscopic parameters such as the monomer volume $v$ and statistical (Kuhn) segment length $a$. The dependence of the free energy on the microscopic parameters comes as the ratio, $v/a^3$, which is the stiffness parameter. For completely flexible chains $v/a^3 = 1$. Usually, for polymer chains $v/a^3 \leq 0.5$ [85]. Finally, we minimize the free energy (4.9) with respect to the amplitude $A$ (the resulting amplitude is required to be small enough to ensure validity of the WST) and parameter $r$:

$$\frac{\partial F}{\partial A} = 0, \quad (4.18)$$

$$\frac{\partial F}{\partial r} = 0 \quad (4.19)$$

Then we compare the free energy values for different lattices to determine the most stable phase. For those phases, whose stability are studied in this chapter, the explicit expressions for the coefficients $\alpha$ and $\beta$ are listed in chapter 2.

4.3. Results and discussion

It is convenient to chose the length of the middle diblock unit $N$ as a parameter on which all length scales are normalized. Therefore, we use this parameter (instead of the total number of monomers $N_{tot}$) in the expression for the free energy (4.9). In what follows the stiffness parameter is fixed at $v/a^3 = 0.1$.

First we consider symmetric systems $(f = 0.5)$. The mean-field theory predicts a second order transition to the lamellar (LAM), simple cubic (SC), face centered cubic (FCC) or single gyroid (SG) phase, depending on the architectural parameters $n$ and $m$ (see Figure 2.4 of chapter 2). For the symmetric systems $\alpha = 0$, and the ODT occurs at the spinodal into the phase with minimal $\beta$. It is easy to see (4.9)–(4.13) that fluctuations only shift the phase transition lines to somewhat higher $\chi$ values and do not change the position of these lines in the $(n, m)$ plane. Figure 4.1 shows the result if fluctuation corrections are taken into account. The length of the repeat unit (diblock) is fixed
Figure 4.1: Plot of the ratio $\chi N/\chi_s N$ versus the number of diblocks in the multiblock $n$, $N = 50$. Letters L and S denote large and short length scale respectively.

for all graphs, $N = 50$. We plot the ratio of the transition $\chi$-parameter value to the value obtained in the mean-field, which corresponds to the spinodal $\chi_s$. The regions of different stable phases are depicted with corresponding letters. The second order phase transitions convert to first order ones with a small but finite amplitude $A$. For the structures with large length scale (SC, FCC, and SG) separation occurs at a scale of the whole macromolecule and therefore fluctuation effects decrease as $1/N_{tot}^{1/3}$. At the top right corner of Figure 4.1 the lamellar structure with short length scale is the stable one. In this case the system behaves essentially like a regular multiblock copolymer melt and fluctuation effects decrease as $1/N^{1/3}$ with increasing length $N$ of the repeat diblock. It was shown in ref. [73] that fluctuations are large due to increase
of the inter-block correlations with increasing \( n \) and approach some limiting level at \( n \to \infty \). The dotted line is calculated along the equimaxima line when only one (large) length scale is taken into account. This line is shown just for a qualitative illustration of the border between large scale BCC and short scale LAM phase.

**Figure 4.2:** Fluctuation phase diagram inside the region where the scattering function has two maxima for \( n = 15, N = 50 \). The border (crossover) between two disordered phases is depicted by the dashed line. The insertion shows the part of the diagram close to the region of large length scale BCC phase. Vertical dotted line indicates the value of \( m \), which corresponds to the equimaxima line, and illustrates the shift of the BCC-L region compared to the mean-field phase diagram.

The fluctuation corrections are determined by parameter \( s \), which is proportional to the critical value \( q^* \), see (4.14). Therefore, fluctuation corrections
are rather different for different length scales: they are larger for the short length scale, since \( q_2^2 > q_1^* \). Recently, the mean-field weak segregation theory, which correctly accounts for two maxima of the scattering function for the calculation of phase diagrams inside the bifurcation region, was developed by Kuchanov and Pichugin [21, 22]. The development of an appropriate fluctuation theory would require essential modification of the existing one, accounting for one length scale only. In this case, for example, the expression for the trial function (4.8) needs to be modified. Here we restrict ourselves to the situation of one maximum only and therefore we can apply existing theory. It is possible, at least on a semi-quantitative level, to study how one-length-scale structures are influenced by fluctuations inside the bifurcation region. Note that 1) the two length scales should be sufficiently different to consider them independently, 2) we are not demanding that the change of the length scale occurs at the equimaxima line. Figure 4.2 shows the fluctuation diagram for \( n = 15 \), for which the mean-field phase diagram was calculated in chapter 2. Strikingly, fluctuations create a large region of the disordered phase, moving the region with large scale BCC phase away from the short LAM and short BCC transition lines. This effect of shifting of the transition lines and appearing of an ordered phase ”island” in the ”sea” of the disordered phase in the \((\chi N, m)\) plane will probably not change much if one incorporates two-length-scale structures. The disordered phase DIS-L is calculated for the large length scale (small \( q_1^* \)), whereas DIS-S is calculated for the short length scale (large \( q_2^* \)). Therefore, these disordered phases differ by their scattering properties. (In the mean field approximation DIS-L and DIS-S are indistinguishable.)

The point where the borders of the large length scale BCC phase merge is located at the equimaxima line in the mean field (see Figure 2.7). If fluctuation corrections are taken into account the situation changes. Apart from the \( s \)-dependence, the fluctuation free energy depends also on \( \xi \sim \beta \). We noticed (see chapter 3) that \( \beta_1(q_1^*) \) is always larger than \( \beta_2(q_2^*) \). \( \xi \) and \( s \) enter the expression for the free energy (4.9) in a product and both depend on the architectural parameters. Therefore the final effect on the phase behavior will depend on parameters \( n \) and \( m \) as well. Indeed, for \( n = 15 \) fluctuations shift the borders of the BCC-L phase towards larger \( m \) values (towards larger length
scale), while for \( n = 17 \) the effect is opposite. This shift of the transition lines from the equimaxima line is shown in Figure 4.3.

![Graph](image)

**Figure 4.3:** The dashed line is the equimaxima line. The solid line is the line of the points where the borders of the BCC-L phase merge if fluctuation corrections are taken into account.

Now we proceed to the general case of multiblock copolymer melts, where the tail blocks have not necessary the same number of chain segments. We plot phase diagrams with due regard for fluctuation effects for larger values of \( m \), which are far beyond the region where the scattering function has two maxima (see Figures 4.4 – 4.6). Dashed lines indicate the mean-field transition lines. The number of repeat units is fixed, \( n = 10 \). The main observation here is that first order transitions from the disordered phase to lamellar (LAM), hexagonal (HEX) and several cubic phases (FCC, SC, DG, SG) are possible inside certain intervals of composition and architectural parameters.
Figure 4.4: Phase diagrams for the systems with $n = 10$ and (a) $N = 10^9$, $m = 1.6$, and (b) $N = 50$, $m = 3.5$. Dashed lines depict the mean-field phase diagrams. Solid lines correspond to the phase diagrams with fluctuation corrections taken into account.
Figure 4.5: Phase diagrams for the systems with \( n = 10, N = 50, \) and (c) \( m = 4.2, \) (d) \( m = 5. \) Dashed lines depict the mean-filed phase diagrams. Solid lines correspond to the phase diagrams with fluctuation corrections taken into account.
Figure 4.6: Phase diagrams for the systems with \( n = 10 \) and (e) \( N = 50, m = 6 \), (f) \( m = 10, \) and \( N = 10^5 \) (solid lines), \( N = 50 \) (dotted line). Dashed lines depict the mean-filed phase diagrams. Solid lines correspond to the phase diagrams with fluctuation corrections taken into account.
Figure 4.4a presents the phase diagram for the system with multiblock-like behavior where microphase separation occurs at a short length scale (with $m = 1.6$ and $N = 10^9$). In this case large values of $N$ are required in order to stabilize the BCC phase. Several examples are presented in Figures 4.5 – 4.6, for which we take $N = 50$. Figure 4.6f corresponds to $m = 10$, where the middle multiblock has the same length as both tail blocks together. This phase diagram belongs to the same universality class as that for diblock copolymers. The border of the BCC phase in the latter system is very close to the border of the HEX phase. Therefore, fluctuations destroy the BCC and HEX phases and only the LAM phase survives for $N = 50$.

**Figure 4.7:** Plot of the ratio $\chi N/\chi_s N$ versus $m$ for the systems of Figures 4.4 – 4.6 with $f = 0.5$. 
To illustrate that fluctuation effects indeed decrease with increasing parameter \(m\), we fix \(f = 0.5\), \(N = 50\), and plot the ratio \(\chi N / \chi_s N\) for the systems shown in Figures 4.4a – 4.6f, see Figure 4.7.

### 4.4. Concluding remarks

In this chapter the influence of fluctuation effects on the phase behavior of two-length-scale multiblock copolymer melts described by the general formula \(A_{fmN-b-(B_{N/2-b-A_{N/2}})_n-b-B_{(1-f)mN}}\) was investigated. Fluctuations affect the system behavior differently at different length scales. We found that in certain parameter regions first order phase transitions from the disordered phase to the large length scale cubic structures such as simple cubic (SC), face centered cubic (FCC), single gyroid (SG), and double gyroid (DG) are possible. For the symmetric systems, inside the region where two length scales are important, we considered only one-length-scale structures and fluctuation effects at different length scales. This analysis revealed quite unusual fluctuation behavior, regarding shift of the transition lines and occurrence of a large window of the disordered phase with an ordered phase "island". It is of interest to incorporate fluctuation effects for two-length-scale structures, since the mean-field weak segregation theory for the systems with two coexisting length scales has been already addressed [21, 22].

### Appendix

#### 4.A. Angle dependence of \(\xi\)

Accounting for the angle dependence in the integral for \(\xi\) (see (4.13)) leads to an increase of the fluctuation effects and decrease of the transition temperature. Let us consider the LAM phase for example. From the solution of eqs.
(4.18), (4.19) we obtain

\[
\tau = \frac{r}{1 - \xi/(2\beta)} - \frac{s\xi}{2\sqrt{r}}
\]  

(4.20)

This function attains its maximum at \( r_0 = (s\xi^2/(2\beta) - s\xi)^{2/3} \) which is equal to

\[
\tau_{\text{max}} = -\frac{3(s\xi)^{2/3}}{2(\xi/(2\beta) - 1)^{1/3}}
\]  

(4.21)

The partial derivative of \( \tau_{\text{max}} \) with respect to \( \xi \) is given by

\[
\frac{\partial \tau_{\text{max}}}{\partial \xi} = \tau_{\text{max}}\left(\frac{2}{3\xi} - \frac{1}{3\xi - 6\beta}\right)
\]  

(4.22)

This function is positive for \( \xi > 4\beta \) and \( \xi < 4\beta \), and has its minimum at \( \xi = 4\beta \).