Microphase separation in two-length-scale multiblock copolymer melts
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In this chapter the phase behavior of $A_{mN/2}$-$b$-$B_{N/2}$-$b$-$A_{N/2}$-$b$-$B_{mN/2}$ multiblock copolymer melts is studied with the weak segregation theory. The interplay between ordering on different length scales is shown to cause dramatic changes both in the ordered phase symmetry and the periodicity upon small variations of the architectural parameters $n$ and $m$ of the macromolecules. It turns out that long-length-scale cubic phases, such as face-centered cubic (FCC), simple cubic (SC), double gyroid (DG) and single gyroid (SG) (so-called BCC$_2$) all are found to be stable for certain values of $n$ and $m$. In this fully symmetric situation, the lamellar (LAM) morphology is shown to be replaced by SG, FCC or SC as the most stable low-temperature phase.
2.1. Introduction

Many block copolymer melts undergo so-called (ODT) order-disorder transitions resulting in the formation of ordered morphologies with the symmetry of a crystal lattice [5, 23–25]. The physical reason for this ordering, also called "microphase separation", is the competition between the short-range segregation and long-range stabilization tendencies. Indeed, with a reduction in temperature the energy gain upon local segregation grows as compared to the entropic loss accompanying such a segregation. At the same time large scale demixing is obviously forbidden due to covalent bonding of the different blocks. As a result, below a certain (spinodal) temperature the disordered state becomes unstable with respect to the growth of the amplitudes $A$ of those local concentration fluctuations, described by an order parameter, $\Psi(r) = A \cos(qr)$, whose wave numbers $q$ are close to a certain critical value $q^* \neq 0$ [5, 26, 27]. Varying the system parameters different morphologies may appear at the order-disorder and order-order phase transitions [8] and the aim of the theory is to determine the symmetry and geometry of the most stable ordered phases for a copolymer given its architecture and temperature.

In a more general context, the theory of microphase separation in block copolymer systems provides a unique opportunity to test the general phenomenological concepts of the statistical theory of solid-liquid transition via a rigorous microscopic consideration. Indeed, the universal (Gaussian) conformational behavior of the long polymer blocks makes it possible to develop a microscopic theory of microphase separation in block copolymer melts, which was first accomplished by Leibler[5] for diblock copolymers. Using the mean-field approximation Leibler found that the thermodynamically stable ordered morphologies for diblock copolymers $A_n$-$b$-$B_m$ are the body-centered cubic lattice (BCC), hexagonal (HEX) and lamellar (LAM) structures. All the first order phase transition lines between these ordered phases and between the BCC and disordered phase (DIS) merge at a critical point in the $(\tilde{\chi}, f)$ plane (as usual, here $f = n/N$ is the composition of the A monomers, $N = n + m$ is the total degree of polymerization of the diblock copolymer, $\tilde{\chi} = N\chi$, where $\chi$ is the Flory-Huggins interaction parameter). If the statistical segment lengths and excluded volumes are the same for all the monomer species, which is
assumed hereafter for simplicity, then the critical point is located at $f = 0.5$, which corresponds to the symmetric diblock copolymer melt. The order-disorder transition at this point is a second order phase transition into the lamellar phase [5].

The Leibler theory [5] has been generalized by Fredrickson and Helfand [28] with due regard for fluctuation corrections and by other authors to melts of block copolymers with more complicated architectures [29, 30] (see also refs. [23–25] and references therein). It is referred to as the weak segregation theory (WST) and is the first (and, up to our knowledge, the only) microscopic consideration implementing the Landau idea of the second-order solid-liquid transition [31]. (The latter is also referred to as the weak crystallization theory [32–34].)

Unfortunately, the region of the WST applicability corresponds to a rather narrow vicinity of the critical point. Besides, the WST employs so-called first harmonics approximation and it is often believed that within this approximation ”the predictions about ordered structures are limited to classical phases of lamellar, hexagonal and body-centered cubic structures, and consequently the possibility of other structures such as bicontinuous structures, e.g. double gyroid, is excluded... To overcome this limitation the so-called harmonic correction is used by including higher harmonic” [35]. Because of this, during the last decade the so-called self consistent field theory (SCFT) by Matsen, [36, 37], which is free of these shortcomings, became the dominant approach to investigate the microphase behavior of block copolymer systems. In contrast to the WST, the SCFT has a much broader region of applicability, which enabled Matsen and Schick [36] to explain the stability of the double gyroid (DG) phase, just observed experimentally [38, 39] at some distance from the critical point.

The application of the WST requires calculation of cumbersome expressions for so called higher structural correlators, still, the SCFT is no less technically involved and much more time consuming (in terms of numerical calculations) than the WST. Besides, unlike the SCFT, a considerable part of the calculations necessary to build the phase diagrams within the WST can be done analytically. Most importantly, however, a general WS analysis [40, 41] has demonstrated that, contrary to the aforementioned belief, under certain
conditions the most stable phases around the critical point are not necessarily the classic ones. Instead, some others cubic phases such as double gyroid (DG), simple cubic (SC), face-centered cubic (FCC) and single gyroid (SG) (the so-called BCC \(_2\) [40]) (we refer to all the phases but BCC, HEX and LAM as the non-conventional ones) may be stable, whereas the classic phases are metastable only. The conditions for the non-conventional phases to be stable even within the 1st harmonics approximation have been found [41]. (These conditions ensure that the phase transition lines DG – HEX, on the one side, and DG – LAM (or DG – SG, DG – FCC, DG – SC) on the other side, extend, unlike in the case of diblock copolymers, up to the very critical point.)

In general, the best strategy to build theoretically phase diagrams of block copolymers is to base the SCFT analysis in a broad range of the system parameters on the results of the WST analysis close to the critical point(s), where both theories are expected to provide identical results. Consistent with this strategy, in this and the next chapter we apply the WST to the new class of copolymer systems that are the subject of study for this thesis. We report a new type of phase behavior: an abrupt and tremendous increase of the period of the supercrystal morphologies as well as the occurrence of non-conventional morphologies with a gradual change of the architecture for some specially designed binary block copolymers.

This prediction is based on two recent observations, the first of which is the discovery of so-called two-length-scale behavior. Up to our knowledge, it was first described by Holyst and Schick [42] who considered a symmetric ternary mixture of A and B homopolymers and AB block copolymers. They found that there is a line, which they called equimaxima line, where the homopolymer A – homopolymer B correlation function reveals two peaks of the same height, one of which being always located at \(q = 0\) and the other one at certain \(q^* \neq 0\). However, this equimaxima line was found to be located entirely within the stability region of the disordered phase, one of the peaks being eliminated when approaching the spinodal. We refer to such a behavior as a virtual two-length-scale one. The real two-length-scale behavior has been first discovered by ten Brinke et al.,[17, 18] who found that melts of some specially designed multiblock and comb-coil macromolecules, whose architecture is characterized by two intrinsic lengths, may become
2.1. Introduction

unstable *simultaneously* with respect to critical fluctuations with two rather different characteristic wave numbers $q_1^*$ and $q_2^*$. (It is worthwhile to note that real two-length-scale behavior has been found also in blends of ABC and AC block copolymers [43] and solutions of multiblock copolymers [44].) The phase diagrams obtained by ten Brinke et al.[18, 19, 45] within both the WST and SCFT demonstrated that such a two-length-scale instability results in order-order transitions between lattices with different periods. The second observation that is relevant to our work is the finding[46] that, due to symmetry, the WS theory is applicable to the symmetric ternary A$_N$-b-B$_{(1-f)N}$-b-C$_N$ triblock copolymers with an arbitrary value of $f$ if the middle block is non-selective with respect to the end blocks. Here non-conventional phases SG, FCC and SC appear with increasing middle block composition $f_B = 1 - 2f$.

In this thesis we consider monodisperse melts of AB multiblock copolymers, whose architecture is shown in Figure 2.1. The multiblock copolymer is build up of a middle part consisting of $n$ diblock units $(A_{N/2}$-b-$B_{N/2})$ of size $N$. At the resp. ends of the multiblock homopolymers $A_f m N$ resp. $B_{(1-f)m N}$ ($0 \leq f \leq 1$) are attached. Hence, the parameter $m$ characterizes the relative total length of the tails with respect to that of the diblock unit, while the parameter $f$ characterizes the asymmetry ratio of the end blocks. For $f = 0.5$ the system has equal amounts of A and B monomers and is perfectly symmetric. The most asymmetric case corresponds to $f = 0$ (or $f = 1$), when the macromolecules contain only one homopolymer block B (or A). The total degree of polymerization reads, $N_{tot} = nN + Nmf + Nm(1-f) = N(n + m)$. In the rest of this chapter we will restrict ourselves to the symmetric case of $f = 0.5$ leaving the investigation of the influence of the asymmetry parameter $f$ for the next chapter.

Experimentally, there is always a distribution of the described multiblock copolymer macromolecules over the lengths and number of the blocks since real macromolecules are obtained via an intrinsically statistical polymerization process. Accordingly, both ordering (microphase separation) and macro-phase separation can occur. In the latter case coexistence of phases with different crystal symmetry or between ordered and disordered (homogeneous) phases may take place. However, the region of such a coexistence occupies a
Figure 2.1: The architecture of the macromolecules considered (here $n = 3$).

rather narrow region on the corresponding phase diagrams [47, 48] if only the molecular structure distribution is not too broad. Therefore, here we disregard the effect of the structural polydispersity (and, thus, the effects of the phase coexistence) and focus only on the architecture caused peculiarities of the phase diagrams. Of course, this is fully validated if the system is monodisperse, i.e. consists of identical macromolecules whatever complicated their structure is.

If $m = 0$ or $m = 1$ with $f = 0.5$, then the system is just a melt of symmetric multiblock copolymers consisting of $n$ or $n + 1$ diblock units ($A_{N/2}-b-B_{N/2}$), respectively. In this case, on reducing the temperature, lamellar A- and B-domains are formed. In general, for regular multiblock copolymers the phase diagram is shown [30] within the WST to be topologically equivalent to that of diblock copolymer melts. However, the situation changes drastically for larger $m$. In this case with a temperature decrease the long tail blocks are expected first to segregate into separate A- and B-domains whereas the shorter blocks of the alternating middle block are still mixed. We show below that these expectations are fully justified. For $m$ large, on a further reduction of the temperature the shorter blocks will also start to phase separate. This is, however, beyond the scope of the present WST analysis (see chapter 5).

The architecture of the polymer of interest does resemble the structure of the ACB triblock, the middle part ($A_{N/2}-b-B_{N/2}$) corresponding to the
nonselective block C. We expect that, at least for $f = 0.5$ considered here, the WST is applicable and the above mentioned complicated cubic structures can be stable. At the same time the middle part $(A_{N/2} - b - B_{N/2})_n$ has its own intrinsic characteristic length, which may, in turn, dictate another period of microphase separation. Hence, this polymer has two different length scales, one related to the size of the diblock $N$ and another to the total size of the macromolecules. Therefore, we expect rather complicated phase behavior of these melts, which we study here using the weak segregation theory.

2.2. Theory

To describe microphase separation it is convenient to introduce the order parameter $\Psi_i(r) = \phi_i(r) - f_i$, 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.

Given a distribution $\phi_i(r)$, the free energy $F$ of a binary incompressible system is conventionally assumed to be the sum

$$F = F_{str}\{\phi_i(r)\} + \chi \int \phi_A(r)\phi_B(r)dr$$

(2.1)

where the first contribution is related to the entropy of the inhomogeneous distribution of the Gaussian macromolecules characterized by the order parameter $\Psi(r)$ and the second (monomer-monomer interaction) part of the free energy is accounted for via a specified value of the $\chi$-parameter ($\chi > 0$) within the Flory-Huggins lattice approach [4].

In Fourier space the order parameter $\Psi(q) = \int \Psi(r)e^{iqr}dr$ is the amplitude of the harmonic concentration wave with the wave vector $q$ and a finite period $D = 2\pi/|q|$. In the vicinity of the critical point the order parameter is sufficiently small and the free energy may be expanded in terms of the order parameter. The fourth order Landau expansion reads [5]

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

(2.2)
Here the $n$th-order vertex functions $\Gamma_n$ are related to the $n$th order Gaussian single-chain correlation functions $g_{\alpha_1...\alpha_n}(r_1...r_n)$ as first shown by Leibler [5]. The explicit expressions for these correlators are rather cumbersome even in the simplest case of diblock copolymers. For more complicated architectures (asymmetric triblock and trigrift, polyblock and polygraft and star copolymers) the list of the correlators already occupies 24 pages of the supplementary material available for ref. [30]. In particular, the second order vertex function $\Gamma_2(q_1, q_2)$ reads

$$\Gamma_2(q_1, q_2) = V\delta(q_1 + q_2)\gamma_2(q_1) = V(\tilde{g}^{-1}(q_1) - 2\chi)$$ (2.3)

where

$$\tilde{g}(q) = \frac{g_{AA}(q)g_{BB}(q) - g_{AB}^2(q)}{g_{AA}(q) + 2g_{AB}(q) + g_{BB}(q)}$$ (2.4)

and the functions $g_{AA}(q)$, $g_{BB}(q)$ and $g_{AB}(q)$ for our system are defined in the appendix A.

For polydisperse systems one more, so called non-local fourth-order term, which implicitly describes the effects of macromolecules redistribution between the coexisting phases, should be included into the Landau expansion (2.2). The non-local term was first calculated for long random AB copolymer chains by Shakhnovich and Gutin [49]. For arbitrary molecular structural distributions it was found by Panyukov and Kuchanov [50], Fredrickson et al. [51], and Erukhimovich and Dobrynin [47]. The phase diagrams of such polydisperse systems with due regard for the non-local term were calculated in refs. [47, 48, 52, 53] For monodisperse systems, where obviously no macrophase separation can occur, the non-local term is identically zero [47, 50, 51].

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],

$$\min \Gamma_2(q) = \Gamma_2(q^*) = 0$$ (2.5)
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It follows from the spinodal equation (2.5) that the spinodal value of $\chi$-parameter reads

$$\chi_s = \tilde{g}^{-1}(q^*)/2$$

(2.6)

where $q^*$ is the location of the global minimum of the function $\Gamma_2(q)$ (or $\tilde{g}^{-1}(q)$).

For $\chi > \chi_s$ an ordered structure with period $D = 2\pi/q^*$ appears. Therefore, the one component order parameter acquires the symmetry of a crystal lattice with this period and can be expanded in a Fourier series

$$\Psi(r) = \sum_{q_i} A(q_i) \exp i(q_i r + \varphi(q_i))$$

(2.7)

where $q_i$ is the set of vectors, which 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 (2.7) only $2k$ vectors belonging to the first coordination sphere of the length $q^*$. Due to the symmetry all amplitudes of the first harmonic are the same, and it is convenient to normalize the amplitudes via the relationship $A(q_i) \equiv A/\sqrt{k}$ (see also [54, 55]). Substituting (2.7) into (2.2) we obtain for the free energy

$$\Delta F/(VkB) = \tau A^2 + \alpha A^3 + \beta A^4$$

(2.8)

The following designations are introduced

$$\tau = \gamma_2(q^*)$$

(2.9)

$$\alpha_k = \gamma_3 \frac{3}{k^{3/2}} \sum \cos \Omega^{(3)}_j$$

(2.10)

and

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

(2.11)

In Eqs. (2.9)–(2.11) we used the Leibler designations and parameters [5]

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

(2.12)
\[ \gamma_3 = \Gamma_3(q_1, q_2, q_3)/V \] (2.13)

and

\[ \lambda_0(h) = \lambda(0, h, 4 - h), \quad \lambda(h_1, h_2, h_3) = \Gamma_4(q_1, q_2, q_3, q_4)/V \] (2.14)

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 noncoplanar 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 eq. (2.11) is over all pairs of noncollinear vectors \( q_i \) and \( q_j \).

Finally, we minimize the free energy (2.8) with respect to the amplitude \( A \) (the resulting amplitude is required to be small enough to ensure validity of the WST) and compare the free energy values for different lattices to determine the most stable phase. For those phases, whose stability are studied in this thesis, the explicit expressions for the coefficients \( \alpha \) and \( \beta \) are listed below, see also appendix B for some details about the structures considered.

First, the well-known expressions for the classic lamellar (LAM), hexagonal (HEX) and body-centered cubic (BCC) phases read[5]

\[ \alpha_{\text{LAM}} = 0, \quad \beta_{\text{LAM}} = \lambda_0(0)/4 \] (2.15)

\[ \alpha_{\text{HEX}} = 2\gamma/3^{3/2}, \quad \beta_{\text{HEX}} = [\lambda_0(0) + 4\lambda_0(1)]/12 \] (2.16)

\[ \alpha_{\text{BCC}} = 8\gamma/6^{3/2}, \quad \beta_{\text{BCC}} = [\lambda_0(0) + 8\lambda_0(1) + 2\lambda_0(2) + 4\lambda(1, 2)]/24 \] (2.17)

We take into account also a non-conventional phase, which surprisingly appears to be stable in the weakly segregated multiblock copolymers within an interval of the relative tail length \( m \). This phase was first introduced by Brazovskii et al. [40] and is closely related to the BCC phase, which was the reason to refer to it as the BCC\(_2\) phase. Indeed, the BCC\(_2\) is formed if one keeps in the order parameter (2.7) the same six vectors (and the opposite ones) of the first harmonic

\[ q_1 = \frac{q^*}{\sqrt{2}} (0, 1 - 1), \quad q_2 = \frac{q^*}{\sqrt{2}} (-1, 0, 1), \quad q_3 = \frac{q^*}{\sqrt{2}} (1, -1, 0), \]

\[ q_4 = \frac{q^*}{\sqrt{2}} (0, -1 - 1), \quad q_5 = \frac{q^*}{\sqrt{2}} (-1, 0, -1), \quad q_6 = \frac{q^*}{\sqrt{2}} (-1, -1, 0) \] (2.18)
which are known to correspond to the conventional BCC morphology if all the phase shifts $\varphi(q_i)$ appearing in the trial function (2.7) are zero. However, the phase shifts necessary to form the BCC lattice are different:

$$\varphi_1 = \varphi_2 = \varphi_3 = \pi/2, \quad \varphi_4 = \varphi_5 = \varphi_6 = 0 \quad (2.19)$$

Note that in original paper by Brazovskii [40] all phases of the BCC lattice are the same and equal to $\pi/2$. If one eliminates this restriction the phases can be chosen in accordance with (2.19), which is equivalent to a transformation of the coordinate system.

As consistent with the definitions [(2.18) and (2.19)], the order parameter (2.7) for BCC reads

$$\Psi(r) = 2A/(\sqrt{6}) \left[ \cos(\bar{x} + \bar{y}) + \cos(\bar{y} + \bar{z}) + \cos(\bar{z} + \bar{x}) \\
- \sin(\bar{x} - \bar{y}) - \sin(\bar{y} - \bar{z}) - \sin(\bar{z} - \bar{x}) \right], \quad (2.20)$$

where the waved coordinates are scaled as compared to the original ones according to the rule $\bar{s} = sq^*/\sqrt{2}$. The fact that the series (2.20) contains both cosines and sines implies [56] that the BCC morphology is non-centrosymmetric. Thus, it seems to be the simplest (and the only one up to now) cubic non-centrosymmetric morphology that can be described (and for some cases predicted as shown below) within the WS theory.

The shift $\bar{x} = X + \pi/4$, $\bar{y} = Y + \pi/4$, $\bar{z} = Z + \pi/4$ of the origin of the co-ordinate system reduces the order parameter profile (2.20) to the form

$$\Psi(r) = \tilde{A} \left[ \sin X \cos Y + \sin Z \cos X + \sin Y \cos Z \right] \quad (2.21)$$

The level surfaces of the order parameter (2.21), i.e. the surfaces satisfying the condition

$$\sin X \cos Y + \sin Z \cos X + \sin Y \cos Z = C \quad (2.22)$$

are known [57] to be representatives of the triple periodic bicontinuous surfaces having the symmetry $I4_132$ of the space group No. 214. In particular, the surface (2.22) with $C = 0$ is well known [57, 58] as the gyroid surface because it is similar to the Schoen’s gyroid minimal surface. We also refer
Figure 2.2: Schematic representation of morphologies with Miller indices [321] (a) the single gyroid (SG) morphology with a single network, (b) the double gyroid (DG) morphology with two separate interpenetrating networks, which are mirror images of one another. The volume is filled with the majority component and the tunnels with the minority component. The DG structure forms only in asymmetric systems, whereas the SG morphology forms also in the symmetric multiblock, where each of the tail blocks (A and B) forms its own network.

According to the BCC\textsubscript{2} lattice as the single gyroid (SG) in contrast to the popular non-conventional cubic lattice having the symmetry \textit{Ia\bar{3}d} of the space group No. 230, which is also called gyroid or doubled gyroid (DG), see Figure 2.2. For the two gyroid phases the coefficients \(\alpha\) and \(\beta\) read [40, 41, 59]

\[
\alpha_{SG} = 0, \quad \beta_{SG} = \frac{[\lambda_0(0) + 8\lambda_0(1) + 2\lambda_0(2) - 4\lambda(1, 2)]}{24} \quad (2.23)
\]

\[
\alpha_{DG} = \frac{\gamma}{3^{3/2}}, \quad \beta_{DG} = \frac{[\Lambda_1 - 2\Lambda_2 - 4\lambda(1/3, 2/3)]}{48} \quad (2.24)
\]

where the designations \(\Lambda_1 = \lambda_0(0) + 2[\lambda_0(4/3) + 2[\lambda_0(1/3) + \lambda_0(2/3) + \lambda_0(1) + 2\lambda_0(5/3)]]\) and \(\Lambda_2 = 2\lambda(2/3, 5/3) - \lambda(2/3, 2/3)\) are introduced. Finally, for the face-centered cubic (FCC), simple square (SQ) and simple cubic (SC) phases, which we also include in the list of the competing phases, the coefficients \(\alpha\)
and \( \beta \) read

\[
\alpha_{SQ} = 0, \quad \beta_{SQ} = \frac{[\lambda_0(0) + 2\lambda_0(2)]}{8} \tag{2.25}
\]
\[
\alpha_{SC} = 0, \quad \beta_{SC} = \frac{[\lambda_0(0) + 4\lambda_0(2)]}{12} \tag{2.26}
\]
\[
\alpha_{FCC} = 0, \quad \beta_{FCC} = \frac{[\lambda_0(0) + 6\lambda_0(4/3) - 2\lambda(4/3, 4/3)]}{16} \tag{2.27}
\]

In ref. [60] photonic properties of bicontinuous cubic microphases were studied. It was shown that a complete band gap exists for the single network morphologies such as simple cubic (\( Pm\bar{3}m \)), single gyroid (\( I4_132 \)) and single diamond (\( Fd\bar{3}m \)), whereas the double network variants such as body centered cubic (\( Im\bar{3}m \)), double gyroid (\( Ia\bar{3}d \)), and double diamond (\( Pn\bar{3}m \)) possess no complete gaps at any volume fraction for the range of dielectric constant \( \varepsilon \) from 1 to 20.

There exists a so-called critical surface in the space \((f, n, m)\)

\[
\Gamma_3(q_1, q_2, q_3, f, n, m) = 0 \quad (|q_i| = q^*, \quad q_1 + q_2 + q_3 = 0) \tag{2.28}
\]

where the coefficient \( \alpha \) in the free energy (2.8) equals zero. At any critical point (set of parameters, which belongs both to the critical surface and spinodal) the phase transition is continuous and, therefore, starts with zero order parameter. Thus, the WS theory is expected to be valid in the vicinity of the critical points.

For simple block copolymer systems like diblock [5], triblock and trigraft [29, 30], multiblock and multigraft (comb-like) as well as various star [30] copolymers the WST predicts that only the lamellar, hexagonal, and body-centered cubic structures are stable, which is due to fact that for these systems the fourth-order vertices can be well approximated [28] as

\[
\Gamma_4(q_1, q_2, q_3, q_4) = \Gamma_4(q_1, q_2, q_3, q_4) \tag{2.29}
\]

However, one can check straightforwardly that for the two-length scale multiblock copolymers under consideration the approximation (2.29) is not valid since the values of the fourth-order structural correlators depend strongly on the angles between the vectors \( q_i \). It is the consequence of this strong angle dependence that some other, more complicated structures (which are only metastable for simple diblock copolymers) become stable. The phase diagrams obtained are presented in the next section.
2.3. Results and discussion

The scattering behavior of \( A_{fmN} - b - (B_{N/2} - b - A_{N/2})_n - b - B_{(1-f) mN} \) block copolymers is rather different from that of the simple copolymer melts (e.g., diblock copolymer \( A_{fN} - b - B_{(1-f)N} \), which is the particular case of the architecture of the multiblock with \( n = 0, m = 1 \)). For the latter only one maximum is observed in the structure factor \( S(q) \sim (\Gamma_2(q))^{-1} \) and, accordingly, the function \( \Gamma_2(q) \), which determines the spinodal, has only one minimum. In contrast, for the multiblock copolymers of interest there is a region in the \((n, m)\) plane called the bifurcation region, where the structure factor exhibits two maxima. The presence of a maximum of \( S(q) \) [i.e., a minimum of \( \Gamma_2(q) \) at \( q = q^* \)] indicates the existence of a characteristic length scale \( D = 2\pi/q^* \) of the weekly modulated ordered morphology occurring in the weak segregation regime. The presence of two maxima indicates that two different length scales may arise [17, 18, 43]. One of these scales is determined by the radius of gyration of the basic diblock unit AB of the multiblock middle part of the molecule, and the other one by the radius of gyration of the macromolecule as a whole.

The so-called classification diagram [17] delineating the bifurcation region for the symmetric systems \( A_{mN/2} - b - (B_{N/2} - b - A_{N/2})_n - b - B_{mN/2} \) is shown in Figure 2.3. Even though \( n \) is an integer, by definition, for convenience we treat it as a continuous variable and plot, accordingly, continuous lines in the classification and phase diagrams. The border lines of the bifurcation region merge at the point \((n = 5.17, m = 2.18)\) called the bifurcation point [17, 18]. The equimaxima line where both maxima of the structure factor diverge at the same value of \( \chi \) is shown by the dashed line. On this line a dramatic change of the length scale occurs: the dominant fluctuations destroying the spatially uniform disordered state have considerably longer wave length above the line than below it.

Now, let us compare the phase behavior of the \( A_{fmN} - b - (B_{N/2} - b - A_{N/2})_n - b - B_{(1-f) mN} \) copolymers in the whole \((n, m)\) plane and that of the particular case of diblock copolymers \( A_{fN} - b - B_{(1-f)N} \). For the latter the ODT is typically a discrete first-order phase transition and it is a continuous second-order phase transition (within the mean-field approximation of the WST) in the only crit-
Figure 2.3: (a) Classification diagram for the symmetric system. Solid lines delineate the bifurcation region. Dashed line inside the bifurcation region is the equimaxima line, where a dramatic change of length scales occurs: below this line the scattering function has a dominant maximum at $q_2^* (q_2^* > q_1^*)$, and above this line it has a dominant maximum at $q_1^*$. Inserts show characteristic scattering functions.

Critical point $f = 0.5$, where the coefficient $\alpha$ of the third order term in the expansion of free energy (2.8) vanishes due to the copolymer symmetry. Similarly, the ODT is a second-order phase transition for the symmetric $A_{mN/2-b-(B_{N/2}-b-A_{N/2})n-b-B_{mN/2}}$ copolymers for any physical value of $m \geq 0$ and integer $n > 0$. Indeed, the state of the symmetric systems is not changed after interchange of A and B monomers and, therefore, the free energy (2.2) should remain unchanged after replacing $\Psi_A$ by $\Psi_B = -\Psi_A$, which is only
possible if all the terms of the free energy with odd powers of the order parameter vanish. Vanishing of the cubic term can, of course, be checked also via straightforward calculation.

All the critical points are located on the spinodal surface in the space \((n, m, \chi_s)\). The ODT in the critical point is the DIS – LAM transition for the case of diblock copolymers, but for the symmetric \(A_{mN/2} - b - (B_{N/2} - b - A_{N/2})_n - b - B_{mN/2}\) multiblock copolymers the ordered phase arising in the critical point can have the symmetry of the LAM, BCC, SC, FCC or SG phases depending on the values of the structural parameters \(n, m\). The resulting phase diagram for the symmetric copolymers can be calculated straightforwardly and its projection on the \((n, m)\) plane is shown in Figure 2.4a. One can see from Figure 2.4b, which focuses on the region near near the bifurcation point, that there are different sequences of self-assembled structures upon increasing \(m\) along a line crossing the bifurcation region for fixed \(n\). For \(n \leq 3\) the only ordered phase below the critical temperature is the lamellar one, its periodicity being strongly \(m\)-dependent. With increase of the relative length of the tails \(m\) the sequences (LAM-S) – (SC-L) – (FCC-L) – (SG-L) – (LAM-L) and (LAM-S) – (BCC-S/L) – (SC-L) – (FCC-L) – (SG-L) – (LAM-L) of stable morphologies occur for \(n = 4\) and \(n \geq 5\), respectively. Here L resp. S refers to long resp. short, so that e.g. the periodicity of LAM-S being much smaller than that of LAM-L (see Figures 2.4 and 3.7 further on). Figure 2.5 shows the sequence of morphologies which become stable with increasing \(m\) for fixed value of \(n\), say \(n = 4\). For \(n > 4\) the sequence of morphologies will be similar, except that after the short length scale lamellar the large (or short) length scale BCC phase becomes stable as the spinodal temperature is reached.

The existence of two lamellar morphologies with rather different periodicity illustrates the presence and interplay of two competing length scales in the system. The phase transition lines (BCC-L) – (SC-L) and (LAM-S) – (BCC-L) are close to the upper boundary of the bifurcation region and the equimaxima line, respectively, and merge on the scale of Figure 2.4a. The enlarged plot shown in Figure 2.4b demonstrates that at the point \((n = 10.52, m = 2.65)\) the (LAM-S) – (BCC-S) line crosses the equimaxima line and for larger values of \(n\) the transition from short scale LAM to long scale BCC phase occurs along the equimaxima line.
2.3. Results and discussion

Figure 2.4: (a) Phase diagram in the \((n, m)\) plane. (b) Enlarged region of this diagram. Solid lines show the phase transition lines, dotted lines depict the bifurcation region and dashed line indicates the equimaxima line. Dashed-dotted line depicts transition between short scale LAM and short scale BCC structures occurring at \(\chi N > \chi_s N\) values.
Figure 2.5: Schematic representation of the sequence of morphologies of the symmetric multiblock copolymer melts. No attempts have been made to indicate the increase in periodicity length scale except qualitatively for the two lamellar structures.
2.3. Results and discussion

Figure 2.6: (a) Spinodal $\chi_s N$ values. (b) Characteristic dimensionless inverse length scale $Q^* = (q^* R_g(N))^2$, $D/R_g(N) = 2\pi/\sqrt{Q^*}$, where $R_g(N)$ is the radius of gyration of the repeat unit.

The values of the $\chi$-parameter corresponding to the order-disorder transitions as well as the reduced critical wave length $Q^* = (q^* R_g(N))^2$ are shown in Figures 2.6a and 2.6b, respectively, as functions of $m$ and $n$. The bifurcation region border and equimaxima line are depicted with dashed lines. For $m =$
0 the system corresponds to a symmetric multiblock copolymer melt. It demonstrates the standard asymptotic behavior of $Q^*$ and $\chi_s N$ with increasing $n$ [3, 61–63]. For larger $m$ the system behaves like a symmetric ABC triblock melt with a nonselective middle block B [46] (due to the structure symmetry the effective interactions between the middle multiblock part and two tail blocks are the same). Asymptotically, with increasing value of $m$ both surfaces of Figure 2.6 approach the zero-level plane, which is quite natural. Indeed, the number of monomers involved in ordering on the short length scale is $N$, whereas for the ordering on the long length scale is $N_{tot} = N(n + m)$. The transition temperatures for the first and the second case are $\chi_s N$ and $\chi_s N(n + m)$ respectively. Hence, with increasing $m$ the ODT of the long length scale occurs at $\chi_s N = const/(n + m)$.

It is worthwhile to compare one-length-scale structures with different periodicity inside the bifurcation region. Here the scattering function has two maxima at $q = q_1$ and $q = q_2$ ($0 < q_1 < q_2$), therefore we can write, $\tilde{g}^{-1}(q_2) - 2\chi = \tau$, $\tilde{g}^{-1}(q_1) - 2\chi = \tau + \Delta$. The mean-field free energies for $q_1$ and $q_2$ are the following:

$$\frac{\Delta F_1}{V k_B T} = \begin{cases} \frac{-(\tau + \Delta)^2}{4\beta_1}, & \tau < -\Delta \\ 0, & \tau > -\Delta \end{cases}$$  

(2.30)

$$\frac{\Delta F_2}{V k_B T} = \begin{cases} \frac{-\tau^2}{4\beta_2}, & \tau < 0 \\ 0, & \tau > 0 \end{cases}$$

(2.31)

If $\beta_1 > \beta_2$ and $\Delta > 0$ then the two plots of the free energy never intersect and the second phase (with $q_2$) always wins. On the other hand, if $\beta_1 < \beta_2$ and $\Delta > 0$ then there is a value $\tau_0(\beta_1, \beta_2, \Delta)$ such that for $0 > \tau > \tau_0$ the second phase wins, whereas for $\tau < \tau_0$ the first phase wins. Since all the quantities $\beta_1, \beta_2, \Delta$ depend on $m, n$ the actual phase transition temperature depends on the structural parameters as well. There is always a phase transition on the equimaxima line, but there is also an additional phase transition at somewhat lower temperature. Since for the two competing phases (BCC and LAM) $\beta_1(q_1) > \beta_2(q_2)$, the transition is always from a long to a short length scale (see the dashed-dotted line in Figure 2.4b). To
2.3. Results and discussion

Figure 2.7: Phase diagram in the \((m, \chi N)\) plane for the symmetric system with \(n = 15\) inside the bifurcation region. Only one-length-scale structures are considered.

illustrate this we plot in Figure 2.7 the phase diagram for \(n = 15\). (Note that the two length scales should be sufficiently different in order to consider them independently.) Upon cooling from the disordered phase to below the spinodal temperature the system first separates (a second order transition) into short length scale LAM or long length scale BCC phase, depending on the tail length parameter \(m\). Eventually, when the temperature is low enough the system undergoes a first order transition to the short length scale structure (LAM or BCC). If one takes into account morphologies with two incommensurate length scales the transitions (BCC-L) – (LAM-S) and (BCC-L) – (BCC-S) will become metastable, but eventually a transition to the short length scale structure is anticipated, see [22].
To understand the validity of the phase diagrams presented it is important to note that the equilibrium free energy has been calculated by taking into account the dominant maximum only. Considering also that the WST is applicable close to the critical points, we conclude that this approximation is, obviously, valid outside the bifurcation region but becomes questionable close to the equimaxima line, where both maxima are important [22].

Appendix

2.A. The second order structural correlators

The second order structural correlators appearing in eq. (2.4) read

\[ g_{AA}(x) = \frac{2}{N_{\text{tot}}} [n F_D(x, 0.5) + F_D(x, mf) + \exp(-xN/2)p(x, 0.5) \times [p(x, 0.5) S_2(x, n) + p(x, mf) S_1(x, n)]] \]  

(2.32)

\[ g_{AB}(x) = \frac{1}{N_{\text{tot}}} [p(x, 0.5) S_1(x, n)p(x, mf) + p(x, m(1 - f))] + p(x, mf)p(x, m(1 - f)) \exp(-xnN) + p^2(x, 0.5) \times [S_2(x, n) + S_2(x, n + 1)] \]  

(2.33)

Here \( x = (aq)^2/6 \) and we introduce the auxiliary functions

\[ p(x, f) = [1 - \exp(-xfN)]/x, \]  

(2.34)

\[ F_D(x, f) = [\exp(-xfN) - 1 + xfN]/x^2, \]  

(2.35)

\[ S_1(x, n) = [1 - \exp(-xnN)]/[1 - \exp(-xN)], \]  

(2.36)

\[ S_2(x, n) = [\exp(-xnN) - n \exp(-xN) + n - 1]/[1 - \exp(-xN)]^2 \]  

(2.37)

The correlation function \( g_{BB}(x) \) can be obtained from the expression for \( g_{AA}(x) \) if one substitutes \((1 - f)\) instead of \( f \).

The third and fourth order correlation functions are rather cumbersome and can not be represented in a compact way. The procedure to calculate
correlators becomes especially effective if one applies the diagram technique described in detail for example in refs. [54, 55, 64].

2.B. Structural symmetries

For 3D periodic structures studied in this thesis the group numbers, designations, and first harmonics are listed in the table below.

<table>
<thead>
<tr>
<th>number</th>
<th>group</th>
<th>designation</th>
<th>harmonics</th>
</tr>
</thead>
<tbody>
<tr>
<td>214</td>
<td>$I4_1\bar{3}2$</td>
<td>SG (or BCC$_2$)</td>
<td>[110], [211], [220], etc.</td>
</tr>
<tr>
<td>221</td>
<td>$Pm\bar{3}m$</td>
<td>SC</td>
<td>[100], [110], [111], [200], etc.</td>
</tr>
<tr>
<td>225</td>
<td>$Fm\bar{3}m$</td>
<td>FCC</td>
<td>[111], [200], [220], etc.</td>
</tr>
<tr>
<td>229</td>
<td>$Im\bar{3}m$</td>
<td>BCC</td>
<td>[110], [200], [211], [220], etc.</td>
</tr>
<tr>
<td>230</td>
<td>$Ia\bar{3}d$</td>
<td>DG</td>
<td>[211], [220], [321], [400], etc.</td>
</tr>
</tbody>
</table>

Unnormalized basis functions for SC, FCC, and BCC structure, which will be important for the analysis carried in chapter 5, are proportional to

$$\mu_{[hkl]}(x, y, z) \propto \sum_{hkl} F(h, k, l) \cos(hX) \cos(kY) \cos(lZ)$$ (2.38)

with $X = 2\pi x/D$, $Y = 2\pi y/D$, $Z = 2\pi z/D$ ($D$ is the periodicity), and reflection conditions defined as

- **SC** $F(h, k, l) \neq 0, \ \forall h, k, l$
- **FCC**
  $$\begin{cases} F(h, k, l) \neq 0, & h, k, l \text{ all even or all odd} \\ F(h, k, l) = 0, & h, k, l \text{ mixed even and odd} \end{cases}$$ (2.39)
- **BCC**
  $$\begin{cases} F(h, k, l) \neq 0, & h + k + l = 2n \\ F(h, k, l) = 0, & h + k + l = 2n + 1 \end{cases}$$
For the single gyroid (SG) and double gyroid (DG) the expressions for the basis functions rather cumbersome and can be found in the tables for crystallography [56]. The normalized basis functions are ordered with increasing the indices $h, k, l$. For example, for the SC mesophase we have $\mu_1 = \mu_{[000]} = 1$, $\mu_2 = \mu_{[100]}$, $\mu_3 = \mu_{[110]}$, etc.