5. Fluctuation corrections

5.1 Introduction

In chapter 1 the partition function of a polydisperse copolymer melt has been written in the general form

$$Z = \int d\psi e^{-F_L(\psi)}$$

(5.1.1)

where $F_L$ is the Landau free energy. In mean-field theory it is assumed that one profile $\tilde{\psi}$ (the one that maximizes the integrand) is completely dominant over all other profiles. In that case the free energy $F$ of the system is given by

$$F \equiv -\ln \int d\psi e^{-F_L(\psi)} = F_L(\tilde{\psi})$$

(5.1.2)

Physically this would mean that (on a coarse grained level) the concentration profile is completely smooth and static, and given by $\tilde{\psi}$. In reality, however, the instantaneous profile $\psi(\bar{x},t)$ (where $t$ is time) can be fluctuating according to

$$\psi(\bar{x},t) = \langle \psi(\bar{x}) \rangle + \delta\psi(\bar{x},t)$$

$$\langle \psi(\bar{x}) \rangle = \frac{\int d\psi \, \psi(\bar{x}) e^{-F_L(\psi)}}{\int d\psi \, e^{-F_L(\psi)}}$$

(5.1.3)

where the average profile $\langle \psi \rangle$ can be different from the most probable profile $\tilde{\psi}$. As will become clear later on, for multiblock copolymers the mean-field assumption becomes more accurate if the average block length increases. For moderate values of the block length, however, the deviations from the mean-field approximation can be considerable. Quite generally one can say that the fluctuations are the most important in the vicinity of the critical point. Study of the fluctuation corrections is not only important for the calculation of the phase diagram, it also gives additional information, such as the amplitude of the fluctuations in the profiles, the scattering properties of the disordered phase and of the various ordered phases (see paragraph 5.5), and the deviation of the chain conformations from the random walk.
For monodisperse diblock copolymers the fluctuation corrections were calculated for the first time in ref 44, where it was shown that due to the presence of fluctuations it is possible to get a direct phase transition from the disordered state into the lamellar state for asymmetric diblock copolymers (i.e. for \( f \neq 0.5 \)). This was also observed experimentally, and not predicted by the mean-field theory. Another consequence of the presence of the fluctuations is that the phase transition becomes a first order transition everywhere along the phase transition line, whereas mean-field theory predicts the transition to be second order in the critical point \( f = 0.5 \). A third implication of the presence of fluctuations is an increase in the region of stability of the disordered phase. More precisely, the transition value of the rescaled interaction parameter \( N\chi \) increases with decreasing chain length \( N \) according to

\[
\Delta(N\chi) \propto N^{-1/3}
\]

(5.1.4)

This is in accordance with the assertion that the saddle point approximation (mean-field theory) becomes exact in the limit of infinitely long blocks. Equation 5.1.4 is also valid for monodisperse multiblock copolymers, provided that \( N \) is taken to be the block length (not the total length of the molecule). For random copolymers, the fluctuation corrections were taken into account for the first time in ref 76. It is intuitively clear that for these systems, due to their intrinsic randomness, the fluctuations will be stronger than for the regular diblock copolymers. This is confirmed by the fact that the fluctuation region shrinks more slowly with increasing average block length \( N \) according to

\[
\Delta(N\chi) \propto N^{-1/4}
\]

(5.1.5)

This relatively slow decay of the fluctuations is due to a particular property of the free energy of the (un-)correlated random copolymers: the dominant contribution \( F_L^0 \) to their Landau free energy \( F_L \) is degenerate with respect to the morphology of the microstructure: all morphologies have exactly the same value for \( F_L^0 \) (see equation 3.4.8). If the subdominant contributions to \( F_L \) are neglected, the fluctuation corrections destroy completely the stability of the ordered phases, and the disordered phase becomes thermodynamically stable everywhere, which was proven mathematically in refs 46, 57, 77 and 78 and via Monte Carlo simulations in ref 79. For \( T < T_s \) this disordered phase has an anomalously large correlation length.\(^57\) Moreover, although \( \langle \psi \rangle = 0 \), the system is far from homogeneous due to the strong fluctuations. In this respect the disordered phase for \( T < T_s \) resembles a disordered microstructure\(^40\) (random wave structure).
As was shown by Erukhimovich and Dobrynin\textsuperscript{77,79} by studying a phenomenological Hamiltonian, the presence of a small degeneracy-breaking term makes the transition to the ordered phase possible. Nevertheless, it was shown that also a near-degeneracy has implications for the phase behavior: due to the fluctuations the region of stability of the disordered phase increases if the degeneracy-breaking term becomes smaller. For random copolymers the relative magnitude of this term decreases to zero on approaching the spinodal, making the system completely degenerate at the spinodal itself. This effect accounts for the slow decrease of the fluctuations in the correlated random copolymer as expressed by 5.1.5. As in the case of monodisperse diblock copolymers, the fluctuation corrections disappear if \( N \) approaches infinity. However, since the \( N \)-dependence of 5.1.5 is weaker than that of 5.1.4, they disappear more slowly, meaning that the fluctuation corrections remain large even if the blocks are relatively long. Therefore, the study of the fluctuation effects is even more important for the correlated random copolymer than it is for the monodisperse diblock copolymer.

In paragraph 5.2 we present a general theory\textsuperscript{71} which incorporates the fluctuation corrections for block copolymers having a general architecture and sequence distribution (apart from architectures with closed loops). Paragraphs 5.3, 5.4 and 5.5 are devoted to the fluctuation behavior of the correlated random copolymer. In paragraph 5.3 we present a preliminary analysis, which enables to derive the scaling result 5.1.5, and gives information concerning the order of magnitude of various parameters near the disorder-order transition. In paragraph 5.4 the scattering properties of the melt in the limit of infinitely long blocks is investigated. In paragraph 5.5 the phase diagram in the vicinity of the critical point is calculated, as well as the amplitude of the fluctuations in the profiles.

### 5.2 General theory

The configurational partition function \( Z \) as given by 5.1.1 is a function of the interaction strength \( \chi \) and the composition (remember that the temperature \( k_{\text{B}}T \), the statistical segment length \( a \), and the excluded volume per segment \( \upsilon \) can be rescaled to unity; see equations 1.1.10 and 1.1.11). Knowledge of \( Z \) alone is not sufficient to calculate the phase diagram. More information about the system can be extracted by considering the system in the presence of external fields, because differentiation with respect to these fields will enable us to calculate all kinds of averages. As external fields we take a field \( h \) coupling to \( \psi \), and a field \( J \) coupling to \( \psi^2 \). The partition function in the presence of these fields becomes
\[ Z[h, J] = \frac{\int d\psi \exp\left(-h \cdot \psi - \frac{1}{2} J \cdot \psi^2 - \frac{1}{4} \Gamma_2 \cdot \psi^2 - \frac{1}{6} \Gamma_3 \cdot \psi^3 - \frac{1}{24} \Gamma_4 \cdot \psi^4\right)}{\int d\psi \exp\left(-\frac{1}{2} \Gamma_2 \cdot \psi^2\right)} \]  
(5.2.1)

where the dot is a short-hand notation for

\[ h \cdot \psi = \int d\bar{x} h(\bar{x}) \psi(\bar{x}) \]  
(5.2.2)

\[ \Gamma_2 \cdot \psi^2 = \int d\bar{x} d\bar{y} \Gamma_2(\bar{x}, \bar{y}) \psi(\bar{x}) \psi(\bar{y}) \]

etc. The denominator in 5.2.1 is added as a normalization; it is constant in the sense that it does not depend on the external fields. As usual, the free energy \( F \) of the system is defined by

\[ F[h, J] = -\ln Z[h, J] \]  
(5.2.3)

In appendix B it is explained how \( F \) can be calculated, and represented by a series of diagrams. Summarizing, these are the results derived in appendix B:

- The diagrams consist of dots and lines. Each dot represents one of the vertices \( h, J, \Gamma_3 \) or \( \Gamma_4 \). A dot representing an \( n \)th order vertex has \( n \) shoots. Via the shoots, the dots are connected by lines. Each line represents the inverse of the second order vertex \( \Gamma_2 \). Every shoot is connected with exactly one line. For a line it is allowed to connect two shoots belonging to the same dot. Only the connected diagrams are included in the series representing \( F \). A diagram is called connected if it is possible to go from any dot to any other dot via the lines. Diagrams having an odd number of dots get a plus sign, whereas diagrams having an even number of dots get a minus sign. In addition every diagram \( E \) gets a front factor \( 1/N_E \), where the integer \( N_E \) is the symmetry factor of the diagram, which has been defined in appendix B. For more details, and for the proof of the correctness of this diagram representation, the reader is referred to appendix B.

**The correlation function**

Differentiation of the free energy 5.2.3 with respect to the external fields leads to the equations of motion
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\( a) \ \frac{\partial F[h,J]}{\partial h(\vec{x})} = \langle \psi(\vec{x}) \rangle \)

\( b) \ \frac{\partial F[h,J]}{\partial J(\vec{x}, \vec{y})} = \frac{1}{2} G(\vec{x}, \vec{y}) + \frac{1}{2} \langle \psi(\vec{x}) \rangle \langle \psi(\vec{y}) \rangle \)  

\( G(\vec{x}, \vec{y}) = \langle \psi(\vec{x}) \psi(\vec{y}) \rangle - \langle \psi(\vec{x}) \rangle \langle \psi(\vec{y}) \rangle \)

\( G(\vec{x}, \vec{y}) \) is the second order correlation function which tells how the thermal fluctuations \( \delta \psi(\vec{x}, t) = \psi(\vec{x}, t) - \langle \psi(\vec{x}) \rangle \) at two different points \( \vec{x} \) and \( \vec{y} \) are correlated. It is defined in such a way that it is zero if \( \vec{x} \) and \( \vec{y} \) are far apart. In polymer multiblock copolymers the correlation is positive: if at a certain point the A-monomer fraction is larger than average, then in nearby points it is also expected to be larger than average. This is the so-called “correlation hole effect.”

Note that there is an important difference between this correlation function \( G \) and the correlation functions \( G_{\alpha\beta} \) defined in paragraph 1.2: the functions \( G_{\alpha\beta} \) describe the correlations in the ideal system, i.e. in the compressible system without interactions, whereas the function \( G \) describes the correlations in the real incompressible system. If the disordered state (characterized by \( \langle \psi(\vec{x}) \rangle = 0 \) ) is almost homogeneous, that is, if the instantaneous profile \( \psi(\vec{x}) \) is small, then the connection between \( G \) and \( G_{\alpha\beta} \) is straightforward. In this situation the dominant contribution to the Landau free energy comes from the second order term (in the ordered states the second and fourth order terms are of the same order of magnitude). So, if the conditions are such that the disordered state is stable and nearly homogeneous, the partition function and the correlation function can be approximated by

\( Z = \int d\psi \ e^{-\frac{1}{2} \int d\vec{x} \int d\vec{y} \ T_2(\vec{x}, \vec{y}) \psi(\vec{x}) \psi(\vec{y})} \)

\( G(\vec{x}, \vec{y}) = \langle \psi(\vec{x}) \psi(\vec{y}) \rangle \approx \frac{\int d\psi \ \psi(\vec{x}) \psi(\vec{y}) e^{-\frac{1}{2} \int d\vec{x} \int d\vec{y} \ T_2(\vec{x}, \vec{y}) \psi(\vec{x}) \psi(\vec{y})}}{\int d\psi \ e^{-\frac{1}{2} \int d\vec{x} \int d\vec{y} \ T_2(\vec{x}, \vec{y}) \psi(\vec{x}) \psi(\vec{y})}} \)

The Gaussian integrals in 5.2.5 can be calculated analytically. To this end, define the functional \( S[h(\vec{x})] \) by

\( S[h] = \int d\psi \ e^{-\frac{1}{2} \int d\vec{x} \int d\vec{y} \ T_2(\vec{x}, \vec{y}) \psi(\vec{x}) \psi(\vec{y})} \left[ d\vec{x} h(\vec{x}) \right] - \int d\vec{x} h(\vec{x}) \psi(\vec{x}) \)

\( S[h] = \int d\psi \ e^{-\frac{1}{2} \int d\vec{x} \int d\vec{y} \ T_2(\vec{x}, \vec{y}) \psi(\vec{x}) \psi(\vec{y})} = e^{\frac{1}{2} \int d\vec{x} \int d\vec{y} \ T_2^{-1}(\vec{x}, \vec{y}) h(\vec{x}) h(\vec{y})} \)
In order to verify this result, the most convenient way is first to skip from the continuous indices $\bar{x}$ and $\bar{y}$ to discrete ones $i$ and $j$, and then to diagonalize the matrix $\Gamma_2$, after which the functional integral over $\psi$ changes into a product of $l$-dimensional Gaussian integrals. Combining 5.2.5 with 5.2.6 leads to

$$G(\bar{x}, \bar{y}) = \frac{\partial^2 S[h]}{\partial h(\bar{x}) \partial h(\bar{y})} = \Gamma^{-1}_2(\bar{x}, \bar{y})$$

(5.2.7)

Rewrite equation 5.2.7 as

$$\int d\bar{z} \ G(\bar{x}, \bar{z}) \Gamma_2(\bar{z}, \bar{y}) = \delta_D(\bar{x} - \bar{y})$$

(5.2.8)

Taking Fourier transforms, and using 1.2.14 and 1.3.58 (which express translational invariance), we arrive at

$$g(q) = \frac{1}{\gamma_2(q)} = \frac{1}{g_{AA} + 2g_{AB} + g_{BB}} - 2\chi$$

(5.2.9)

where in the last step expression 1.3.52 has been used. Because of 5.2.9, which is valid only in the nearly homogeneous disordered state, the inverse of the second order vertex function is sometimes called the “bare correlation function.” In the microphase separated state, where the right hand side of 5.2.9 may become negative for some values of $q$, the expression 5.2.9 for $g(q)$ is not valid any more, and should be replaced by the so-called Dyson equation, to be derived and discussed later.

**The Legendre transformation**

The free energy $F$ 5.2.3 is given as a function of $h$ and $J$, but by means of a Legendre transformation it can be rewritten as a function of $\psi$ and $G$ (from now on, we will often simply write $\psi$ instead of $\langle \psi \rangle$). This Legendre transformation is defined by

$$\tilde{F}(\psi, G) = F(h_{\psi G}, J_{\psi G}) - \psi h_{\psi G} - \frac{1}{2} \left(G + \psi^2\right) J_{\psi G}$$

(5.2.10)
where the space-dependence of the variables \( h, J, \psi \) and \( G \) has not been written down explicitly. The pair \((h_{qG}, J_{qG})\) is the inverse of the equation of motion 5.2.4. Differentiation of 5.2.10 with respect to \( \psi \) or \( G \) leads to the conjugated equation of motion

\[
\frac{\partial \hat{F}}{\partial \psi} = -h - J\psi \\
\frac{\partial \hat{F}}{\partial G} = -\frac{J}{2}
\]  

(5.2.11)

Since in the polymer system the auxiliary fields \( h \) and \( J \) are equal to zero, 5.2.11 shows that we have to look for an extremal point (in fact for a minimum) of the conjugated free energy \( \hat{F} \). Since the expression for \( F \) is known, the expression for \( \hat{F} \) can in principle be obtained by inverting 5.2.4 in order to find \((h_{qG}, J_{qG})\), followed by the integration of 5.2.11.

**The expression for the conjugated free energy**

Inverting 5.2.4 can be accomplished using diagram techniques (see also appendix B). Translated to diagram language, equation 5.2.4a tells that \( \psi(x) \) is equal to the sum of all diagrams having one loose end (a loose end is a line attached to only one vertex; before differentiating with respect to \( h \) the other end of the line was attached to a dot representing \( h \)). See fig 5.1. The minus sign appears, because the number of vertices has been reduced by 1 after the differentiation (see our convention with respect to the sign of a diagram). For the following, we will need the notion of \( n \)-point irreducibility. A diagram having no more than one loose end is called \( n \)PI (\( n \)-point irreducible), if it is not possible to split the diagram into two disconnected pieces by cutting \( k \leq n \) lines. Now return to the diagrammatic representation fig 5.1 of \( \psi \). We will rewrite it as a sum of IPI diagrams, in the following way. Choose a diagram having one loose end which is not IPI. This diagram will be of the general form given in fig 5.2: attached to the loose end there is a IPI part, which has one or more “external lines” by which it is connected to parts of the diagram which become completely detached if this external line is cut. In the summation representing \( \psi \), take the IPI part fixed, and sum over all possible diagrams attached to the external lines. For each external line this summation leads to the sum of all diagrams having one loose end, and this is just equal to \( \psi \). See fig 5.3 for clarification. The dotted lines in this figure do not represent \( \Gamma_2^{-I} \), because according to fig 5.1, \( \Gamma_2^{-I} \) is part of \( \psi \). Therefore, \( \psi \) is
directly attached to a vertex. Note that even if the number of factors $\psi$ is odd, no additional minus signs arise.

![Fig 5.2](image)

![Fig 5.3](image)

Fig 5.3 has to be applied as often as possible, until all diagrams are $1PI$. Since in the original diagram series all 1-point vertices $h$ are linked to the rest of the diagram by just one line, all diagrams containing $h$ are not $1PI$, except for the simple diagram depicted in fig 5.4. Therefore, after making all diagrams $1PI$ by repeated application of fig 5.3, all explicit $h$-dependence has disappeared from the diagrams, except for the diagram in fig 5.4. During the process the notion of “diagram” has been extended: the vertices can now have “free shoots,” which are not connected to a line, but to $\psi$ instead. The sign of a diagram is still determined by its number of vertices. Diagrams of the old type depend on the fields $h$ and $J$, and we will refer to them as $(h,J)$-diagrams. These diagrams are connected, but not necessarily $1PI$. Diagrams of the new type depend on $\psi$ and $J$, but not on $h$ (the diagram in fig 5.4 is excluded), and will be referred to as $(\psi,J)$-diagrams. These diagrams are all $1PI$. A $(\psi,J)$-diagram can be considered as a collection of $(h,J)$-diagrams. If a $(\psi,J)$-diagram contains no factors $\psi$, then this collection contains only one $(h,J)$-diagram, otherwise it contains infinitely many $(h,J)$-diagrams. The equation depicted in fig 5.1 has now been rewritten as

$$\psi = -\Gamma_2^{-1}h - \sum_{\psi,J}$$

where $\sum_{\psi,J}$ is the sum of all $(\psi,J)$-diagrams having one loose end (the loose end is denoted by a dot).
Our goal is inverting equation 5.2.4, i.e. to find the expression for $h$ and for $J$ in terms of $\psi$ and $G$. Although the $h$-dependence of 5.2.12 is now trivial, the vertex $J$ is still present in a complicated way. To isolate $J$, use must be made of equation 5.2.4b. Consider an $(h,J)$-diagram in $F$ which contains $k$ vertices $J$. When this diagram is differentiated with respect to $J$, then, after applying the product rule, one obtains a sum of $k$ diagrams. In each diagram one of the vertices $J$ has been taken away. Considering one of these diagrams, there are two possibilities: either the diagram falls apart into two disconnected pieces, or it remains connected; fig 5.5 shows these possibilities. The disconnected diagrams in $\partial F/\partial J$ cancel exactly against the disconnected diagrams in $\psi^2/2$; see equation 5.2.4b. Therefore, $G/2$ is equal to the sum of all connected diagrams having two loose ends, including the trivial diagram consisting of just one single line (we assign a symmetry factor unity to this diagram); see fig 5.6. For diagrams having two loose ends we will adopt the rule that they get a plus sign if their number of vertices is even, and a minus sign otherwise, which is contrary to the rule for diagrams having zero or one loose end. The reason for this will become clear in a minute: diagrams having two loose ends will be considered as part of a diagram having zero or one loose ends, and adding an even number of vertices will not change the sign of such a diagram.

For the following, we need to generalize the notion of $n$-point irreducibility to diagrams having two loose ends: such a diagram is called $n$PI if the diagram obtained after connecting the loose ends is $n$PI. Fig 5.7 gives an example: the lower diagram is 1PI, but the upper one is not.

The right hand side of fig 5.6 can be rewritten as a sum of $(\psi,J)$-diagram’s by application of the rule shown in fig 5.3. Therefore, $G$ is equal to $\Gamma - J$1, plus twice the sum of all $(\psi,J)$-diagram’s having two loose ends. Using this new interpretation of fig 5.6, it is possible to rewrite $\Sigma_{\psi,J}$ as a sum of 2PI $(\psi,G)$-diagrams, by grouping the $(\psi,J)$-diagram’s, and representing each group by one $(\psi,G)$-diagram, in the following way. Consider a diagram in $\Sigma_{\psi,J}$ which is not 2PI. Fig 5.8 shows the general form of such a diagram. Take part $A$ fixed, sum over all possibilities for $B$, and add the diagram where $B$ is absent (note that the latter diagram could be 2PI). Using fig 5.6, the sum of
all \((\psi, J)\)-diagrams having the same \(A\) can be represented by just one diagram, where the part containing \(B\) is replaced by \(G\). In a diagram this \(G\) is denoted by a thick line, in order to distinguish it from \(\Gamma^{-1}_2\), which is denoted by a thin line. See fig 5.9. This process is repeated as often as possible. In the 2PI diagram series thus obtained, the diagram depicted in fig 5.10 is exceptional in the sense that it is the only diagram which still contains \(J\). The other diagrams, which do not depend on \(J\), will be referred to as \((\psi, G)\)-diagrams. Each of these diagrams stands for infinitely many \((\psi, J)\)-diagrams. If \(\Sigma_{\psi,G}\) is the sum of all \((\psi, G)\)-diagrams having one loose end, then equation 5.2.12 can be rewritten as

\[
\psi = -\Gamma^{-1}_2 h - \Gamma^{-1}_2 J \psi - \dot{\Sigma}_{\psi,G}
\]  

(5.2.13)

and, therefore, according to 5.2.11

\[
\frac{\partial \hat{F}}{\partial \psi} = -h - J \psi = \Gamma_2 \psi + \Gamma_2 \dot{\Sigma}_{\psi,G}
\]  

(5.2.14)

The factor \(\Gamma_2\) in front of \(\dot{\Sigma}_{\psi,G}\) eliminates the loose ends of the diagrams. The expression for \(\hat{F}\) can now be obtained by the integration of 5.2.14. Integration of \(\Gamma_2 \dot{\Sigma}_{\psi,G}\) with respect to \(\psi\) comes down to attaching a factor \(\psi\) to the free shoot which remained after the elimination of the loose end. The front factor arising when a monomial \(x^n\) is integrated with respect to \(x\), is automatically accounted for by a change in the symmetry factor of the diagram.

\[
\hat{F} = \frac{1}{2} \Gamma_2 \psi^2 + \psi \frac{\partial}{\partial \psi} \Sigma_{\psi,G} + f_j(G)
\]  

(5.2.15)

\(\Sigma_{\psi,G}\) is the sum of all \((\psi, G)\)-diagrams having no loose ends. The operator \(\psi \frac{\partial}{\partial \psi}\) deletes all diagrams which do not depend on \(\psi\). To find \(f_j(G)\), consider again fig 5.6, which tells that \(G\) is equal to \(\Gamma^{-1}_2\), plus twice the sum of all \((\psi, J)\)-diagrams having two loose ends. Although
these diagrams are $IPI$, some of them can be split into two parts by cutting just one line, such
that each part contains one loose end. Take a fixed integer value for $k \geq 0$, and consider the set of all
$(\psi, J)$-diagrams having two loose ends, which, by cutting one line, can be split into two parts,
each part containing one loose end, at exactly $k$ places. See fig 5.11 for an example with $k = 3$.
For fixed $k$, sum over all these diagrams. Between two neighboring “splitting places” the result of the summation will be twice the sum of all
$(\psi, J)$-diagrams with two loose ends (plus sign if the number of vertices is even) which cannot be split into two parts (each part containing one loose end) by cutting just one line. These $(\psi, J)$-diagrams are not all $2PI$, because they can be of the form given in fig 5.12. However, using the generalization of fig 5.9, the sum between two splitting places can be represented by twice the sum of all $2PI$ $(\psi, G)$-diagrams having two loose ends, plus twice the diagram depicted in fig 5.13. After summing over $k \geq 0$, and adding the “bare correlator” $\Gamma_{2,1}^{-1}$, the expression for $G$ becomes

$$G = \cdots + \frac{\Gamma_2}{2} \cdot J + 2 \tilde{\Sigma}_{\psi,G}$$

This geometrical series gives a closed expression (the Dyson equation) for the inverse of $G$

$$G^{-1} = \Gamma_2 + J - 2 \tilde{\Sigma}_{\psi,G}$$

If the external field is absent, and the first term is dominant over the diagram summation, then the Dyson equation 5.2.17 reduces to equation 5.2.7. Combining 5.2.17 with the conjugated equation of motion 5.2.11 leads to

$$\frac{\partial \hat{F}}{\partial G} = -\frac{1}{2} J = \frac{1}{2} \Gamma_2 - \frac{1}{2} G^{-1} - \tilde{\Sigma}_{\psi,G}$$

If a diagram belonging to $\tilde{\Sigma}_{\psi,G}$ is integrated with respect to $G$, then the loose ends will become connected by a thick line, and the result is a $2PI$ diagram belonging to $\Sigma_{\psi,G}$. However, our convention for the sign of diagrams having two loose ends is different from our convention for the sign of diagrams having no loose ends, and so a minus sign has to be added. Integrating the
first term of the right hand side of 5.2.18 is trivial, but the integration of the second term needs some explanation. Consider a real symmetric matrix $A_{ij}$. Let $\lambda_i$ be its eigenvalues. Then

$$\text{Tr} \ln A = \sum \ln \lambda_i = \ln \prod \lambda_i = \ln \det A$$  \hspace{1cm} (5.2.19)$$

Differentiating this with respect to the component $A_{ij}$ leads to

$$\frac{\partial \text{Tr} \ln A}{\partial A_{ij}} = \frac{\partial \ln \det A}{\partial A_{ij}} = \frac{I}{\det A} \frac{\partial \det A}{\partial A_{ij}} = \frac{I}{\det A} (\text{cof } A)_{ij} = A_{ji}^{-1} = A_{ji}^{-1}$$  \hspace{1cm} (5.2.20)$$

where cof denotes the cofactor matrix. Therefore, the expression for the Legendre transform of the free energy, following from 5.2.18, is

$$\tilde{F} = \frac{I}{2} \Gamma_2 G - \frac{I}{2} \text{Tr} \ln G + G \frac{\partial}{\partial G} \Sigma_{\psi,G} + f_2(\psi)$$  \hspace{1cm} (5.2.21)$$

Combination of 5.2.15 with 5.2.21 leads to the final expression \textsuperscript{71} for $\tilde{F}$

$$\tilde{F} = \frac{I}{2} \Gamma_2 \psi^2 - \frac{I}{2} \text{Tr} \ln G + \frac{I}{2} \Gamma_2 G + \Sigma_{\psi,G}$$  \hspace{1cm} (5.2.22)$$

According to equation 5.2.11, the corresponding minimization condition in the absence of the external fields reads

$$\frac{\partial \tilde{F}}{\partial \psi} = \frac{\partial \tilde{F}}{\partial G} = 0$$  \hspace{1cm} (5.2.23)$$

Remember that the diagrams in $\Sigma_{\psi,G}$ are 2PI, and that they contain only third and fourth order vertices. For the analysis in this chapter, only a limited number of terms in 5.2.22 will be needed. All these terms are proportional to the volume $V$ of the system. In the rest of this chapter, expression 5.2.24 will form the basis for the analysis of the fluctuation behavior of the correlated random copolymer.

$$F \equiv C_1 + C_2 + C_3 + D_1 + D_2 + D_3$$  \hspace{1cm} (5.2.24)$$

$$C_1 = \frac{I}{2V} \int d\vec{x}_j d\vec{x}_2 \Gamma_j(\vec{x}_j,\vec{x}_2) \psi(\vec{x}_j) \psi(\vec{x}_2)$$
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\[ C_2 = \frac{1}{6V} \int d\vec{x}_1 d\vec{x}_2 d\vec{x}_3 \Gamma_3(\vec{x}_1, \vec{x}_2, \vec{x}_3) \psi(\vec{x}_1) \psi(\vec{x}_2) \psi(\vec{x}_3) \]

\[ C_3 = \frac{1}{24V} \int d\vec{x}_1 d\vec{x}_2 d\vec{x}_3 d\vec{x}_4 \Gamma_4(\vec{x}_1, \vec{x}_2, \vec{x}_3, \vec{x}_4) \psi(\vec{x}_1) \psi(\vec{x}_2) \psi(\vec{x}_3) \psi(\vec{x}_4) \]

\[ D_1 = \frac{1}{8V} \int d\vec{x}_1 d\vec{x}_2 d\vec{x}_3 d\vec{x}_4 \Gamma_4(\vec{x}_1, \vec{x}_2, \vec{x}_3, \vec{x}_4) G(\vec{x}_1, \vec{x}_2) G(\vec{x}_3, \vec{x}_4) \]

\[ D_2 = \frac{1}{4V} \int d\vec{x}_1 d\vec{x}_2 d\vec{x}_3 d\vec{x}_4 \Gamma_4(\vec{x}_1, \vec{x}_2, \vec{x}_3, \vec{x}_4) \psi(\vec{x}_1) \psi(\vec{x}_2) G(\vec{x}_3, \vec{x}_4) \]

\[ D_3 = \frac{1}{2V} \int d\vec{x}_1 d\vec{x}_2 \Gamma_2(\vec{x}_1, \vec{x}_2) G(\vec{x}_1, \vec{x}_2) - \frac{1}{2V} \mathrm{Tr} \ln G(\vec{x}_1, \vec{x}_2) \]

The diagrams representing \( C_2, C_3, D_1 \) and \( D_2 \), which belong to \( \Sigma_{\psi, G} \), have been drawn in fig 5.14. The dashed lines in fig 5.14 indicate only the connection between the vertex and \( \psi \); they do not represent the bare correlator \( \Gamma_2^{-1} \). In paragraph 5.4 it will be shown that the approximation 5.2.24 is sufficient for our purposes.

### 5.3 The trial function for \( G \)

As expressed by equation 5.2.11, in the absence of the external fields the free energy \( \tilde{F} \) has to be minimized with respect to \( \langle \psi \rangle \) and \( G \). It is not possible to do this rigorously. Instead, one has to make an educated guess for the trial functions for \( \langle \psi \rangle \) and \( G \) containing a couple of
adjustable parameters, insert this into the expression for \( \bar{F} \), and minimize with respect to the parameters. The usual trial function for \( \langle \psi \rangle \) in the first harmonics approximation has already been given in equation 2.2.2. The situation with the choice of a trial function for \( G \) is not trivial. Assuming that \( G(\bar{x}, \bar{y}) \) depends only on the difference between the vectors \( \bar{x} \) and \( \bar{y} \), i.e. \( G(\bar{x}, \bar{y}) = g(\bar{x} - \bar{y}) \), its Fourier transform takes the form

\[
G(\bar{q}_1, \bar{q}_2) = \int d\bar{x} d\bar{y} e^{i\bar{q}_1 \cdot \bar{x} + i\bar{q}_2 \cdot \bar{y}} G(\bar{x}, \bar{y}) = \\
\int d\bar{\mathbf{r}} e^{i\bar{q}_1 \cdot \bar{\mathbf{r}} + i\bar{q}_2 \cdot \bar{\mathbf{r}}} g(\bar{\mathbf{r}}) = V G_D(\bar{q}_1 + \bar{q}_2) g(\bar{q}_1)
\]

The usual trial function for \( g(\bar{q}) \) is

\[
g^{-1}(\bar{q}) = c(q - q_*)^2 + r
\]

This choice of trial function will be used in paragraph 5.4, in order to give a preliminary (simplified) analysis of the fluctuation behavior of the correlated random copolymer. In paragraphs 5.5 and 5.6, however, we will use a more detailed expression for \( g \), namely

\[
\begin{align*}
g^{-1}(\bar{q}) &= 2 \left( q^2 + \frac{\alpha^2}{q^2 - q_*^2 + \alpha} - q_*^2 - \alpha + \beta \right) \\
&= 2 q_*^2 \left( p^2 + \frac{s^2}{p^2 - I + s} - I - s + \rho \right) \\
&\equiv 2 q_*^2 \tilde{g}^{-1}(\tilde{p})
\end{align*}
\]

The rescaled wave vector \( p \), and the adjustable parameters \( s \) (which must be larger than unity) and \( \rho \) are defined by

\[
\begin{align*}
s &= \frac{\alpha}{q_*^2} \\
\rho &= \frac{\beta}{q_*^2} \\
p &= \frac{q}{q_*}
\end{align*}
\]

The important simplifying assumption for both trial functions 5.3.2 and 5.3.3 is their isotropic form. This means that possible anisotropy of the concentration fluctuations in the ordered phases is neglected. The advantages of the trial function 5.3.3 are that it enables to evaluate the position, the height and the width of the correlation function as independent parameters. Moreover, 5.3.3 makes it possible to calculate the integrals in 5.2.24 analytically. It is clear
that in order to write down a suitable trial function one has to know in advance what the real correlation function looks like. The bare correlation function \( g_{\text{bare}}(q) = \gamma_2^{-1}(q) \) attains its maximum value for \( q = 0 \). If \( t < 0 \) (i.e. \( \chi < \chi_s \)) the full correlation function can be approximated by the bare correlation function, at least in the limit \( \ell \to \infty \). For \( t > 0 \), however, the maximum of the correlation function shifts to a non-zero value of \( q \), which can be shown by solving the Dyson equation iteratively by inserting the bare correlation function into its right hand side. However, some residual forward scattering \( g(q = 0) \neq 0 \) remains due to the polydispersity in composition. For larger values of \( q \) the correlation function has to be proportional to \( q^{-2} \) because of the random walk nature of the chain. All these properties are present in the trial function 5.3.3. In what way the parameters \( \rho \) and \( s \) determine the shape of \( g(q) \) (the amount of forward scattering, and the height and width of the scattering peak) is shown in fig 5.15. Note that changing the value of \( q_* \) gives just a rescaling of the horizontal and vertical dimensions of the graph of \( g(q) \), and has no influence on its shape. We assume that in the microphase separated state the radius of the first harmonics sphere coincides with the position \( q_* \) of the peak in the correlation function. Although these parameters could be considered as independent, it is to be expected that they differ not too much.

Since 5.3.3 is a rational function, most of the integrals over Fourier space involved in the definition of the terms 5.2.24 can be calculated exactly. As explained in chapter 1, in a coarse grained description (characteristic for Landau theory) there is a cut-off value \( \Lambda \) present for the length of the vectors in Fourier space. Therefore, after rewriting the integrals represented by the terms \( D_1, D_2 \) and \( D_3 \) (these are the only terms in 5.2.24 which depend on the correlation function) as integrals over Fourier space, and using the trial function 5.3.3, the integrals should
be restricted to the area $|\tilde{q}| < \Lambda$. This is, however, technically difficult. Instead, one usually ignores the cut-off and deals afterwards with the contributions from high $q$-values. There are three possibilities. The first and most easy possibility is that the integral is convergent even after removing the cut-off. In that case, usually the contribution coming from the high $q$-values is negligible. The second possibility is that the integral is divergent in the limit $\Lambda \to \infty$, but this divergence can be removed by adding to the integrand a function which does not depend on the adjustable parameters. Clearly adding such a term has no influence on the minimization condition for the free energy. The last possibility is that the divergence cannot be removed in a simple way. Then one has to assign a value to the integral by ignoring somehow the contribution from high $q$-values. In the calculation of the diagrams for the correlated random copolymer in appendix E all three possibilities occur. In order to keep the divergency of the integral $D_3$ manageable, the behavior of 5.3.3 for large $q$-values has been chosen such that it coincides with the behavior of the bare correlation function $\Gamma_2^{-1}$ for $f = 0.5$, as given in 3.3.7 (remember that in the WSR the vertices can be expanded in powers of $\varepsilon \equiv f - 0.5 \approx t$).

**The correlation function in real space**

The spatial correlation function $g(\tilde{x})$ can be obtained from 5.3.3 by means of a Fourier transformation.

$$g(\tilde{x}) = \frac{1}{(2\pi)^3} \int d\tilde{q} e^{-i\tilde{q} \cdot \tilde{x}} g(\tilde{q}) = \frac{1}{2(2\pi)^2 i \tilde{x}} \int_{-\infty}^{\infty} dp e^{i p \cdot \tilde{x}} p \tilde{g}(p)$$

(5.3.5)

The integral in 5.3.5 can be calculated analytically by rewriting expression 5.3.3 for $g(\tilde{q})$ into the following form:

$$\tilde{g}(p) = \frac{p^2 + s - 1}{((p-a)^2 + b^2)((p+a)^2 + b^2)}$$

(5.3.6)

$$a = \frac{\sqrt{1-\rho/2} + \sqrt{1-\rho + \rho s}}{\sqrt{2}} \quad b = \frac{\sqrt{-1+\rho/2} + \sqrt{-1-\rho + \rho s}}{\sqrt{2}}$$

By closing the integration contour in 5.3.5 in the upper half of the complex plane, one obtains finally
This equation shows that \( g(\vec{x}) \) is characterized by two length scales: \( R_{\text{osc}} = l/a_q \), which is proportional to the period of the oscillations, and \( R_{\text{cor}} = l/b_q \), which is the distance over which the correlations vanish, i.e. the correlation length.

### 5.4 A preliminary analysis

**Introduction**

A detailed analysis of the fluctuation behavior of the correlated random copolymer, which will enable us to draw the phase diagram in the vicinity of the critical point, will be postponed to paragraph 5.6, where, using the trial function 5.3.3 for \( g(q) \), the free energy will be expanded according to 5.2.24. In order to be able to minimize the resulting complicated expression analytically, it is vital to know which terms are relevant, and which terms can be neglected. Since the analysis will be done under the assumption that the block length \( \ell_{c} \) is large, the magnitude of a certain term can be judged if it is known how the various parameters scale with \( \ell \). Moreover, we will have to know beforehand at what value of the interaction parameter \( t \) the disorder-order transition occurs, because the relative magnitude of the terms in the free energy expansion depends on \( t \). On the other hand it is clear that this transition value will be the result of the analysis, and so we are in an impasse. To solve the problem, in this section a more simple and transparent fluctuation analysis is presented for the case \( f = 0.5 \). This analysis reveals the transition value for \( t \), and the relative magnitudes of the adjustable parameters at the transition. These results were also obtained for instance in ref 45. Further on, in paragraphs 5.5 and 5.6, they will be used as the starting point for a more detailed analysis.

**A simplified expression for the trial function for G**

In this paragraph we will not take equation 5.3.3 as trial function for the correlation function, but the simpler (and more often used) 5.4.1:

\[
g^{-1}(q) = c(q - q_s)^2 + r
\]  

(5.4.1)
This trial function approximates the real correlation function only in the vicinity of its minimum \( q = q_s \). The trial function 5.3.3, which is used in paragraphs 5.5 and 5.6, can be approximated by 5.4.1 under the correspondence

\[
c = \frac{8}{s} \quad r = 2pq_s^2
\]  

(5.4.2)

The integral of 5.4.1 over space is equal to

\[
\int dq \, g(q) = \int dq \, \frac{1}{c(q - q_s)^2 + r} = \int_0^\infty \frac{4\pi q^2 dq}{c(q - q_s)^2 + r}
\]  

(5.4.3)

This representation of the integral shows clearly that it is divergent, since the integrand reaches a finite, non-zero value for \( q \to \infty \). However, according to the discussion in paragraph 1.1, there is a cut-off value \( \Lambda \) present in Fourier space, which is due to the fact that the random walk model breaks down at length scales smaller than \( \Lambda^{-1} \). Therefore, strictly speaking the integral 5.4.3 should be replaced by

\[
\int dq \, g(q) = \int_0^\Lambda \frac{4\pi q^2 dq}{c(q - q_s)^2 + r}
\]  

(5.4.4)

This is illustrated in fig 5.16 for the situation where the maximum height \( 4\pi q_s^2/r \) is large compared to the limiting value \( 4\pi/c \). In this case the contribution from the tail (shaded area in fig 5.16) should be ignored, even though it is infinite. Having this in mind, expression 5.4.4 can be approximated in the following way.

\[
\int dq \, g(q) \cong 4\pi q_s^2 \int_0^\infty \frac{dq}{c(q - q_s)^2 + r} = 4\pi q_s^2 \int_{-\infty}^\infty \frac{dq}{c(q - q_s)^2 + r} = \frac{(2\pi)^2 q_s^2}{\sqrt{cr}}
\]  

(5.4.5)

Using the analysis in this paragraph, the value of the parameter \( c \) (which is the curvature of \( g^{-1} \) in its minimum) cannot be obtained from the minimization condition for the free energy. Therefore, it will be considered as a constant, and not as an adjustable parameter. From the results obtained in the next paragraphs it follows that \( c \approx 4 \). However, the conclusions obtained in this paragraph do not depend on its precise value, although we have to use the fact that \( c \) does not depend on the block scale \( \ell \), or on the distance \( t \) to the spinodal.\(^{45} \)
Now we can calculate the various contributions to the free energy, listed in 5.2.24. We start with the logarithmic contribution to $D_3$, which can, as explained in appendix E, be rewritten as

$$-\frac{1}{2V} \text{Tr} \ln G(\tilde{x}_1, \tilde{x}_2) = -\frac{1}{2} \frac{1}{(2\pi)^3} \int d\bar{q} \ln g(\bar{q})$$  \hspace{1cm} (5.4.6)

In reference 71 it was shown how the divergency of this integral can be handled in the case of monodisperse block copolymers, in which case the logarithmic contribution contains only one adjustable parameter $r$, since the value of $q_*$ is determined from the shape of the second order vertex function. Then, it is possible to assign a value to the divergent integral 5.4.6 by calculating its derivative with respect to $r$, and subsequently integrate the obtained expression. This comes down to subtracting an infinite constant (constant means: independent of $r$) from the free energy, which has no influence on the results. In formulas (use 5.4.1 and 5.4.6):
\[
\frac{\partial}{\partial r} \left( \int dq \ln g(q) \right) = -\int dq \frac{g(q)}{G(q)} \approx -\frac{4\pi^2 q^*_r}{\sqrt{cr}} \Rightarrow \\
-\frac{1}{2V} \ln G(\tilde{q}_1, \tilde{q}_2) \approx \frac{q^*_r \sqrt{r}}{2\pi \sqrt{c}} 
\]

(5.4.7)

However, for the polydisperse block copolymers considered here, \(q_*\) is an adjustable parameter, and we should differentiate 5.4.6 with respect to \(q_*\) as well. However, the crude expression 5.4.1 for \(g(q)\) does not allow us to do this. Therefore, if we take 5.4.7 as the expression for the logarithmic term, it has to be understood that it represents only its \(r\)-dependence. However, in the analysis of this paragraph this term is negligible anyway, as can be seen by substituting the final results for \(r\), \(q_*\) and \(c\) into 5.4.7, and compare its magnitude with that of the other terms. Therefore, in the analysis of this paragraph the logarithmic contribution to \(D_3\) (see 5.2.24) can be neglected. So, there are only three relevant terms in the free energy expansion 5.2.24. The first one is

\[
\frac{1}{2V} \int d\tilde{x}_1 d\tilde{x}_2 \Gamma_2(\tilde{x}_1, \tilde{x}_2) G(\tilde{x}_1, \tilde{x}_2) = \frac{1}{2V^2} \sum_{\tilde{q}_1, \tilde{q}_2} \Gamma_2(\tilde{q}_1, \tilde{q}_2) G(-\tilde{q}_1, -\tilde{q}_2) = \\
= \frac{1}{2V} \sum_{\tilde{q}} \gamma_2(\tilde{q}) g(\tilde{q}) = \frac{1}{2(2\pi)^3} \int dq \gamma_2(q) g(q) = \frac{\gamma_2(q_*)}{2(2\pi)^3} \int dq g(q) \equiv \\
\approx \frac{2(q_*^2 - t/\ell)}{2(2\pi)^3} \frac{(2\pi)^2 q_*^2}{\sqrt{cr}} = \frac{q_*^4}{2\pi \sqrt{cr}} - \frac{tq_*^2}{2\pi \ell \sqrt{cr}} 
\]

(5.4.8)

where we inserted \(f = 0.5\). For the remaining two terms \(D_1\) and \(D_2\), we need the expression 3.3.13 for the fourth order vertex for the case that its arguments are pairwise opposite. Inserting \(f = 0.5\) and taking along only the dominant term (dominant with respect to its \(t\)-dependence), one obtains

\[
\gamma_4(\tilde{q}_1, -\tilde{q}_1, \tilde{q}_2, -\tilde{q}_2) \approx \frac{16}{\ell^2 (q^2_1 + q^2_2)} 
\]

(5.4.9)

Therefore, the second relevant contribution to the free energy is
The disordered phase

The free energy of the disordered phase is the sum of \(5.4.8\) and \(5.4.10\).

\[
\ell F_{dis} = \frac{\ell q_*^2}{4\pi^2 \ell^2 cr} + \frac{\ell^2 q_*^4}{2\pi \ell^2 \sqrt{cr}} - \frac{\nu \ell q_*^2}{2\pi \ell \sqrt{cr}}
\]

(5.4.12)

This has to be minimized with respect to \(r\) and \(q_*\). The minimization with respect to \(r\) gives a balance between the first term and the third term. In the minimum, these terms are of the same order of magnitude, i.e.

\[
\frac{1}{\ell^2 r} \approx \frac{t}{\ell \sqrt{r}} \quad \Rightarrow \quad r \propto \frac{1}{\ell^2 t^2}
\]

(5.4.13)

Next one should minimize with respect to the wave vector \(q_*\). In the minimum there is a balance between the second term and, say, the first one (the third has the same order of magnitude as the first due to the minimization with respect to \(r\)). After neglecting numerical factors, we get

\[
1 \approx \frac{\ell^2 r}{t} \quad \Rightarrow \quad r \propto \frac{1}{\ell^2 t^2}
\]
Using the scaling relation 5.4.13, this yields

\[ q_t^2 \propto \frac{t}{\ell} \]  \hspace{1cm} (5.4.15)

Inserting 5.4.13 and 5.4.15 into 5.4.12 shows that

\[ F_{\text{dis}} \propto \frac{t^3}{\ell} \]  \hspace{1cm} (5.4.16)

The scalings 5.4.15 and 5.4.16 are the same as for the ordered states. If expression 5.4.12 is analyzed in more detail, one can find that the free energy of the disordered state equals that of the ordered states up till the third (and leading) order in \( t \).

**The ordered states**

The dominant contribution to the free energy of the lamellar structure at \( f = 0.5 \) is given by the sum of the Landau free energy 3.4.4 and the fluctuation corrections 5.4.8, 5.4.10 and 5.4.11:

\[ \ell F_{\text{lam}} = \frac{\ell q_t^2}{4\pi^2 \ell^2 cr} + \frac{\ell^2 q_s^4}{2\pi \ell \sqrt{cr}} - \frac{t\ell q_t^2}{2\pi \ell \sqrt{cr}} + \frac{4A^2}{2\pi \ell \sqrt{cr}} + 2(\ell q_s^2 - t)A^2 + \frac{4A^4}{\ell q_s^2} \]  \hspace{1cm} (5.4.17)

In this approximation the free energy is degenerate with respect to the type of structure. If the fluctuation corrections are neglected, only the last two terms remain, and the equilibrium values for \( A \) and for \( q_s \) are given by

\[ \ell q_s^2 \approx \frac{t}{3} \quad A \approx \frac{t}{3\sqrt{2}} \]  \hspace{1cm} (5.4.18)

We want to find out at what point (i.e. at what value of the interaction parameter \( t \)) the fluctuations become important. Judging from equation 5.4.17 they become important when the fluctuation contribution to the coefficient of \( A^2 \) has the same order of magnitude as the mean-
Field contribution. When the fluctuation correction just start to give a contribution, it is safe to assume that the scalings 5.4.18 are still valid, and so we obtain the condition

\[ \frac{A^2}{\ell \sqrt{r}} \approx \frac{tA^2}{\ell^2 t^2} \quad \Rightarrow \quad r \propto \frac{1}{\ell^2 t^2} \]  

(5.4.19)

It is important to note that 5.4.19 does not tell how in the ordered states the value of \( r \) changes when (at fixed \( t \)) the value of \( t \) is changed, like equation 5.4.13 does for the disordered state. Instead, 5.4.19 is a condition telling when fluctuations become important. Next we rewrite equation 5.4.17 in a more transparent way:

\[ \ell F_{\text{num}} = yx^2 + y^2 x - ty + 4xA^2 + 2yA^2 - 2tA^2 + \frac{4A^4}{y} \]

\[ y \equiv \ell q_s^2, \quad x \equiv \frac{1}{2\pi \ell \sqrt{cr}} \]  

(5.4.20)

When condition 5.4.19 is fullfilled, all three parameters \( x, y \) and \( A \) are of the same order of magnitude (use also 5.4.18), and proportional to \( t \). Minimizing the free energy given in 5.4.20 shows that in the chosen approximation the values of \( y \) and \( A \) are given by

\[ y = \frac{t}{3}, \quad A^2 = \frac{1}{4}(t - 2x - y)y \]  

(5.4.21)

but the value of \( x \) cannot be determined in this way, because minimization of 5.4.20 would lead to \( x = 0 \Rightarrow r = \infty \). In order to get an expression for \( x \) (or, equivalently, for \( r \)) without going beyond the approximations made here, one has to follow a different route. According to equation 5.2.23, the equilibrium values of \( \psi \) and \( G \) satisfy

\[ \frac{\partial \hat{F}[\psi, G]}{\partial G} = 0 \]  

(5.4.22)

Instead of integrating this, filling in trial functions and differentiate with respect to the adjustable parameters (as was our strategy so far), it is also possible to consider equation 5.4.22 by itself. As explained in paragraph 5.2, equation 5.4.22 leads to the Dyson equation 5.2.17. In approximation used here it has the form
\[ G^{-1}(\tilde{x}_1, \tilde{x}_2) = \Gamma_2(\tilde{x}_1, \tilde{x}_2) + \frac{1}{2} \int d\tilde{x}_1 \cdots d\tilde{x}_4 \Gamma_4(\tilde{x}_1, \cdots, \tilde{x}_4) G(\tilde{x}_3, \tilde{x}_4) + \]
\[ + \frac{1}{2} \int d\tilde{x}_1 \cdots d\tilde{x}_4 \Gamma_4(\tilde{x}_1, \cdots, \tilde{x}_4) \psi(\tilde{x}_3) \psi(\tilde{x}_4) \]  \hfill (5.4.23)

Filling in the expressions for \( \Gamma_4 \) given in 5.4.9 and for \( G \) given in 5.4.1, leads to

\[ c(q - q_*)^2 + r = 2q^2 - \frac{2t}{\ell} + \frac{4q_*^2}{\pi \ell^2 (q_*^2 + q^2)} + \frac{16A^2}{\ell^2 (q_*^2 + q^2)} \] \hfill (5.4.24)

Insert \( q = q_* \), multiply with \( \ell \) and switch to the new variables \( x \) and \( y \) which were defined in 5.4.20:

\[ \ell r = 2y - 2t + 4x + \frac{8A^2}{y} \] \hfill (5.4.25)

Inserting the solution 5.4.21 into the Dyson equation 5.4.25 shows that

\[ r = 0 \] \hfill (5.4.26)

This fact, which was obtained for the first time in ref 45, means that in order to find an expression for \( r \), one should take into account the terms which are subdominant in \( t \), both in the expression 5.4.17 for \( F_{lam} \), and in the Dyson equation 5.4.24. However, this need not be done explicitly in order to obtain the desired result. Instead, it suffices to note the following. All terms on the right hand side of 5.4.25 are polynomials in \( t \), starting at first order. We have seen that the linear part of the right hand side vanishes. Direct calculation shows that the quadratic term does not vanish. Therefore, 5.4.25 gives the relation

\[ \ell r \propto t^2 \] \hfill (5.4.27)

Equation 5.4.27 reveals, how in the ordered states the equilibrium value of \( r \) changes with \( t \). Equation 5.4.19, on the other hand, gives the condition on \( r \) where the fluctuations start giving an important contribution. Combining these equations shows that the value of \( t \) for which the fluctuations become important satisfies the scaling relation \(^{45}\)

\[ t \propto \ell^{-1/4} \] \hfill (5.4.28)
It is to be expected that the transition from the disordered state to the lamellar state occurs for \( t \)-values satisfying 5.4.28. Next we determine how the parameters \( \rho, q_*, s \) (appearing in the trial function 5.3.3 for \( G \)) and \( A \) scale with \( \ell \), because we need this information in the following paragraphs. These scalings are the same for the disordered state and for the ordered states (apart from the amplitude \( A \), of course). To relate \( \rho \) to \( r \), and \( s \) to \( c \), use 5.4.2. For the ordered states, the scalings follow from 5.4.18 and 5.4.27, whereas for the disordered state they follow from 5.4.13 and 5.4.15 (use also 5.4.28 in both cases):

\[
t_{ODT} \propto \ell^{-1/4} \quad \rho \propto \ell^{-1/4} \quad s \propto \ell^0 \quad q_* \propto \ell^{-5/8} \quad A \propto \ell^{-1/4} \quad (5.4.29)
\]

These relations are taken as a starting point for the more detailed analysis in paragraph 5.6.

**The relative magnitude of the diagrams near the phase transition point**

The results obtained can be used to determine which terms in the free energy expansion 5.2.22 should be included and which can be neglected in the vicinity of the order-disorder transition for near-symmetric copolymers (i.e. for \( \varepsilon \propto t \) or smaller). It is possible to obtain the order of magnitude of a diagram (that is, its scaling with \( \ell \)) by approximating the correlation function by a spherical delta function (which is infinite on the shell \(|\bar{q}| = q_*\) and zero outside and inside), after which the diagrams factorize into separate contributions coming from the vertices and lines it consists of. The third and fourth order vertices give a factor

\[
\psi = \frac{\varepsilon}{\ell} \propto \ell^{-5/4} \quad \bar{\psi} = \frac{1}{\ell^2 q_*^2} \propto \ell^{-3/4} \quad (5.4.30)
\]

whereas the factors due to the lines and the \( \psi \)'s can be found according to

\[
\psi = A \approx \ell^{-1/4} \quad \approx \int d\bar{q} g(\bar{q}) = \frac{q_*^2}{\sqrt{r}} \approx \frac{q_*}{\sqrt{\rho}} \propto \ell^{-1/2} \quad (5.4.31)
\]

Using this, the scaling of the diagrams in the free energy expansion can be obtained easily; for instance
It is clear that in the limit $\ell \to \infty$ the upper four diagrams are completely dominant over the rest. Also, $\int \Gamma_2 \psi^2 \propto \ell^{-7/4}$ (because $\Gamma_2 \approx q^2 + t/\ell \propto \ell^{-5/4}$), $\int \Gamma_2 G \propto \ell^{-7/4}$, and $\int \ln g = q^2 \sqrt{r} = q^3 \sqrt{\beta} \propto \ell^{-8/4}$ (use 5.4.2 and 5.4.7). Since in paragraph 5.6 we show that in the limit $\ell \to \infty$ it is necessary and sufficient to take along all terms up till order $\ell^{-8/4}$, the approximation 5.2.24 is justified.

### 5.5 The phase behavior in the limit of infinite chemical correlation length

In this section we study the ordered phases and of the supercooled metastable disordered phase in the region of the phase diagram, which is defined by the following two criteria: 1) the system is only weakly segregated; 2) the fluctuations in the ordered phases are negligible. The first condition implies that the distance to the critical point is not too large, whereas the second implies that it is not too small. The first can be satisfied by taking small values for $\varepsilon$ and $t$, however the second can only be satisfied at the same time if the fluctuation region is small, which will be the case if $\ell$ is large. Therefore, in this section we will consider the limit $\ell \to \infty$, in which case the second criterion is satisfied for all $\varepsilon > 0$, $t > 0$. The purpose of this paragraph is to find the shape of the correlation function $g(q)$, and to describe the supercooled metastable disordered phase (the phase diagram itself in the limit $\ell \to \infty$ has already been calculated in chapter 3). Although for the ordered phases the mean-field theory is exact in the considered limit, in order to obtain information about the correlation function it is nevertheless necessary to take the (negligible) fluctuation corrections into account, because the mean-field free energy does not depend on $g(q)$. 

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**The ordered states**

Since \( \varepsilon = f - 0.5 \) and \( t = \ell (\chi - \chi_c) = \ell \Delta - 1 \) are small, the vertex functions can be expanded in powers of \( \varepsilon \). Since we consider the limit \( \ell \to \infty \), the scaling with \( \ell \) of the various terms in the free energy expansion is important in order to be able to judge which terms have to be included, and which can be neglected. We assume that for the ordered phases the adjustable parameters \( A, q, \rho \) and \( s \) satisfy the scaling laws

\[
A \propto \ell^0, \quad q_* \propto \ell^{-1/2}, \quad \rho \propto \ell^0, \quad s \propto \ell^0
\]  

(5.5.1)

The scaling laws for \( A \) and \( q_* \) were shown to be valid in chapter 3, equations 3.4.6 and 3.4.8 (the parameter \( t \) is fixed, and does not depend on \( \ell \)). The assumptions concerning the scaling of \( \rho \) and \( s \) will be verified by the fact that the subsequent calculations result in explicit expressions for the parameters \( \rho \) and \( s \), which indeed satisfy 5.5.1. In the free energy expansion in powers of \( \ell^{-1} \) we keep, apart from the leading saddle point contribution \( F_0 \) (which is independent of \( \rho \) and \( s \)), only the next term \( F_1 \)

\[
F = F_0 + F_1 + O(\ell^{-2})
\]

\[
F_0 = F_0(A, q_*) \quad F_1 = F_1(A, q_*, \rho, s)
\]  

(5.5.2)

\[
F_0 \propto \ell^{-1} \quad F_1 \propto \ell^{-3/2}
\]

Note that although \( F_1 \) is completely negligible as compared to \( F_0 \), it has to be taken into account in order to obtain information about \( g(q) \). The expression for \( F_0 \), which is nothing but the Landau free energy, was derived in chapter 3. For convenience, we will write down its expression 3.4.4 once again:

\[
\ell F_0 = 2(\ell q_*^2 - t)A^2 + \frac{4A^4}{\ell q_*^2} - 24\mu|\epsilon|A^2 + \lambda A^4
\]  

(5.5.3)

For the relevant structures, the values of the parameters \( \mu \) and \( \lambda \) were given in equation 3.4.5. The minimum \( A = A_0, q_* = q_0 \) of 5.5.3 was given in 3.4.6 and 3.4.8:

\[
A_0 = \frac{t}{3\sqrt{2}} + \mu|\epsilon|t - \frac{\lambda t^2}{54\sqrt{2}} \quad \ell q_0^2 = A_0 \sqrt{2}
\]  

(5.5.4)
Inserting this solution for \( A_0 \) and \( q_0 \) into the expression 5.5.3, we obtain

\[
\ell F_0 = -\frac{t^3}{27} + \frac{\lambda t^4}{324} - \frac{2\sqrt{2}\mu|\epsilon|t^3}{9}
\]  

(5.5.5)

which was also given in 3.4.8. To find the leading order fluctuation correction \( F_1 \) defined in 5.5.2, note that it is the sum of the contributions \( D_2 \) and \( D_3 \) defined in 5.2.24, and calculated using the trial function 5.3.3 in appendix E, eqs E7, E8 and E17. The diagram \( D_1 \) can be neglected in this section, because it is proportional to \( \ell^2 \), which, on using 5.5.1, follows from equations E4 and E5. The expressions for \( D_2 \) and \( D_3 \) are given in terms of the integrals \( I_4, I_6 \) and \( I_9 \), which are evaluated in appendix F:

\[
F_1 = \frac{q_*}{8\pi^2\ell} \left( q_*^2\ell I_4 - t I_6 \right) + \frac{A^2}{\pi^2\ell^2 q_*} \left( I_9 + 2q_*^2\ell I_6 \right)
\]  

(5.5.6)

According to the assumption 5.5.1, \( \rho \) reaches a finite value in the limit \( \ell \to \infty \), and so the exact expressions \( F_7, F_8 \) and \( F_9 \) for \( I_4, I_6 \) and \( I_9 \) have to be used. The equilibrium values \( \rho_0 \) and \( s_0 \) for the parameters \( \rho \) and \( s \) can be found from the equations obtained by inserting the values 5.5.4 for \( A \) and \( q_* \) into \( F_1 \), and subsequent minimizing with respect to \( \rho \) and \( s \):

\[
\frac{\partial F_1(A_0, q_0, \rho, s)}{\partial \rho} = 0 \quad \frac{\partial F_1(A_0, q_0, \rho, s)}{\partial s} = 0
\]  

(5.5.7)

Solving eqs 5.5.7 gives for all phases under consideration

\[
\rho_0 = 8A_0\sqrt{2} + 3 - \frac{t}{A_0\sqrt{2}} \quad s_0 = 2
\]  

(5.5.8)

which after substitution of the expression 5.5.4 for \( A_0 \) gives, up to leading order in \( t \)

\[
\rho_0 = \frac{(16 - \lambda)t}{6} + 9\mu|\epsilon|\sqrt{2} \quad s_0 = 2
\]  

(5.5.9)

This solution satisfies the original assumption 5.5.1 concerning the scaling with \( \ell \). For the lamellar and the hexagonal structures, the value of \( \rho \) increases with increasing value of \( t \), which means that the profile becomes less fluctuating if the interaction becomes stronger. For the bcc structure, however, \( \lambda = 19 > 16 \), so the value of \( \rho \) decreases with increasing value of \( t \).
This means that the bcc structure prefers the region near the phase transition line, which is in accordance with both experimental and theoretical findings. According to 5.5.9, the value of $\rho$ would become zero at $t/\varepsilon = 8\sqrt{3}$, however, long before this could happen, there will be a transition to another structure. To discuss the obtained results, consider as an example the lamellar structure for symmetric copolymers (i.e. $f = 0.5 \Leftrightarrow \varepsilon = 1$). Then the solutions 5.5.4 and 5.5.9 reduce to

$$A_0 = \frac{t}{3\sqrt{2}}, \quad \ell q_0^2 = \frac{t}{3}, \quad \rho_0 = t, \quad s_0 = 2 \quad (5.5.10)$$

Figure 5.15 shows that the equality $s = 2$ means that the system exhibits a residual forward scattering $g(q = 0) \neq 0$, which is due to the presence of concentration fluctuations on arbitrary long length scales. In monodisperse incompressible copolymer melts this kind of scattering is suppressed completely. The parameter $\rho$ determines the height of the scattering peak (fig 5.15). According to 5.5.10, the peak is infinitely high at the critical point itself, and becomes lower as the segregation increases (however, close to the critical point the analysis presented in this paragraph will break down; see paragraph 5.6). This means that if the degree of segregation $\chi$ increases, the profile becomes less fluctuating, and in equation 5.2.24 the fluctuation terms $D_i$ become negligible with respect to the saddle point terms $C_i$. The amplitude of the fluctuations $\delta \psi$ in the profile can be found as follows. Using the definition 5.2.4 for the correlation function we get

$$\langle \delta \psi(\hat{x})^2 \rangle = \langle \psi^2(\hat{x}) \rangle - \langle \psi(\hat{x}) \rangle^2 = G(\hat{x}, \hat{x}) =$$

$$= \frac{1}{V^2} \sum_{\vec{q}_1, \vec{q}_2} e^{-i(\vec{q}_1 + \vec{q}_2) \cdot \vec{x}} V \delta(\vec{q}_1 + \vec{q}_2) G(\vec{q}_1) =$$

$$= \frac{1}{(2\pi)^{2}} \int d\vec{q} \ g(\vec{q}) = \frac{q_*}{8\pi^2} \int_{-\infty}^{\infty} dp \ p^2 \tilde{g}(p) = \frac{q_* L_6}{8\pi^2} \approx \frac{s^{1/2} q_*}{8\pi r^{1/2}} \approx \frac{1}{4\sqrt{6} \pi \ell^{1/2}}$$

where in the fifth step 5.3.3 has been used, in the sixth step F5, in the seventh step F14, and in the last step 5.5.10. Since the amplitude of the profile reaches a finite value in the considered limit, 5.5.11 shows that in the microphase separated state the relative magnitude of the fluctuations is proportional to
\[
\frac{\Delta \psi}{\psi} \propto \ell^{-1/4}
\]  
(5.5.12)

Strictly speaking, the integral over Fourier space of the trial function 5.3.3 for \( g(\tilde{q}) \) is divergent for large \( q \)-values. However, after introducing a cut-off value \( \Lambda \) for the vectors in Fourier space (paragraph 1.1), it is possible to assign a value to it. This was illustrated in fig 5.16.

**The disordered state**

Next we calculate the free energy and the correlation function of the disordered phase for \( f = 0.5 \) in the same limit \( \ell \chi > \ell \chi_s \) = fixed, \( \ell \rightarrow \infty \). Since \( \langle \psi(\tilde{x}) \rangle = 0 \), the free energy \( F_{\text{dis}} \) is just the sum of the fluctuation corrections \( D_j \) and \( D_3 \) (equation 5.2.24). Let the \( \ell \)-scaling of the parameters \( \rho \), \( q_s \) and \( s \) characterizing the correlations in the disordered phase be

\[
\rho \propto \ell^{-1} \quad q_s \propto \ell^{-1/2} \quad s \propto \ell^0
\]  
(5.5.13)

Then, up to leading order in \( \ell^{-1} \), the free energy of the disordered phase is (see equations E4, E5 and E17)

\[
F_{\text{dis}} = \frac{s}{64\pi^2 \ell^2 \rho} + \frac{s q_s^2}{16\pi^2 \ell \rho} + \frac{3s^{1/2} q_s^3}{8\pi \rho^{1/2}} - \frac{13}{8\pi \rho^{1/2}}
\]  
(5.5.14)

Minimization with respect to the adjustable parameters is straightforward. The resulting equilibrium values of these parameters and the free energy expanded to the fourth order in \( t \) are equal to

\[
\ell q_{\text{dis}}^2 = \frac{t}{3} \quad \rho_{\text{dis}} = \frac{27s}{64\pi^2 \ell t^3} \quad \ell F_{\text{dis}} = -\frac{t^3}{27} + \frac{4t^4}{81}
\]  
(5.5.15)

which satisfies 5.5.13. We see that the disordered phase remains metastable for \( t > 0 \). The peak in the correlation function of the disordered state becomes sharper the more the system is moving off the spinodal \( t = 0 \) into the region of stability of the ordered phases, and broadens when approaching the spinodal. As mentioned before when discussing the ordered states, for finite (though large) values of \( \ell \) the above analysis is only valid for \( t \)-values satisfying \( t \gg \ell^{-1/4} \) and, therefore, due to the \( \ell^{-1} t^{-3} \) dependence of \( \rho_{\text{dis}} \), the scattering peak stays sharp
Fluctuation corrections

in the whole region where this analysis is valid. When expression 5.5.15 is compared with expression 5.5.5, it is apparent that there is a difference between structures with \( \lambda < 16 \) (such as the lamellar and the cylindrical phase) and those with \( \lambda > 16 \) (such as the bcc phase). Structures with \( \lambda < 16 \) remain stable with respect to the disordered phase in the whole region \( t > 0 \), while structures with \( \lambda > 16 \) become unstable with respect to the disordered phase if the segregation \( t \) is increased. Also in equation 5.5.9 the value \( \lambda = 16 \) is special. Note that for the random wave structure \( \lambda = 16 \).

Remarkably, for \( \ell \to \infty \), \( \ell \chi > \ell \chi^* \) fixed, the free energy 5.5.15 of the disordered phase and the free energy 5.5.5 of the ordered phases not only have the same \( \ell \)-dependence, but are even equal to leading order in \( t \). Moreover, the free energy of the disordered phase turns out to coincide with the free energy of the random wave structure to fourth order in \( t \). This similarity between the supercooled disordered phase and the random wave structure can be extended even more. Consider the quantity \( \int d\bar{x} \langle \psi^2(\bar{x}) \rangle \), which is a measure of the amplitude of the concentration inhomogeneities. For all ordered phases it is given by

\[
\frac{1}{V} \int d\bar{x} \langle \psi^2(\bar{x}) \rangle \equiv \frac{1}{V} \int d\bar{x} \langle \psi(\bar{x}) \rangle^2 = \frac{A^2}{n} \sum_{Q,Q_1} \frac{1}{V} \int d\bar{x} \exp\left(i(\bar{Q}_1 + \bar{Q}_2) \cdot \bar{x}\right) = 2A^2 \equiv \frac{t^2}{9} (5.5.16)
\]

The first step is justified by the fact that the ordered phases are hardly fluctuating in the considered limit (see equation 5.5.12), and in the last step 5.5.10 has been inserted. For the disordered state we obtain in a similar way

\[
\frac{1}{V} \int dx \langle \psi^2(x) \rangle = \langle \psi^2(x) \rangle = \langle \psi^2(x) \rangle - \langle \psi(x) \rangle^2 = \frac{1}{(2\pi)^3} \int d\bar{q} G(\bar{q}) = \frac{q_*}{8\pi^2} \int_{-\infty}^{\infty} dp^2 \tilde{G}(p) = \frac{q_* I_6}{8\pi^2} \equiv \frac{s^{1/2} q_*}{8\pi \rho^{1/2}} \equiv \frac{t^2}{9} (5.5.17)
\]

where in the last step we inserted 5.5.15. Equations 5.5.16 and 5.5.17 show that the amplitude of the concentration inhomogeneities in the disordered phase is of the same order of magnitude as that in the ordered phases.
5.6 The fluctuations in the profiles and their influence on the phase diagram

Introduction

In this section we incorporate the fluctuation corrections for nearly symmetric copolymers in the vicinity of the order-disorder transition, both for the disordered phase, and for the ordered phases. In this situation the fluctuation corrections are expected to be considerable. In paragraph 5.4 it was shown that on approaching the critical point the fluctuation corrections become important at values of $t$ scaling according to $t \propto t_{ODT}^{-1/4}$. Since the fluctuations stabilize the disordered state, it is to be expected that the order-disorder transition takes place in the same region:

$$t_{ODT} \propto t_{ODT}^{-1/4}$$

(5.6.1)

The purpose of this paragraph is the construction of the phase diagram near the critical point, and the determination of the magnitude of the fluctuations in the profiles. In order to be able to do rigorous calculations we assume that $\ell$ is large, and in the calculations we take the limit $\ell \to \infty$. However, there is an important difference with the previous paragraph, where this limit was taken keeping the point $(\varepsilon, t)$ fixed. Under these circumstances the point leaves the fluctuation region if $\ell$ increases. In this paragraph, however, we move the point $(\varepsilon, t)$ towards the critical point if $\ell$ increases to ensure that it stays in the fluctuation region. This can be accomplished by taking the limit $\ell \to \infty$ under fixed values of the rescaled parameters $\tilde{\ell}$ and $\tilde{\varepsilon}$, which are defined by

$$\tilde{\ell} = \ell^{1/4} \ell_{ODT}$$ $$\tilde{\varepsilon} = \ell^{1/4} \varepsilon$$

(5.6.2)

In view of 5.6.1 it is to be expected that in the limit $\ell \to \infty$ the order-disorder transition will take place for a finite, non-zero value of $\tilde{\ell}$. To know the relative importance of the various terms in the free energy expansion, we will make use of the scaling relations for the parameters $A$, $q_s$, $\rho$ and $s$ derived in paragraph 5.4, and given in 5.4.29:

$$\rho \propto \ell^{-1/4} \quad s \propto \ell^{0} \quad q_s \propto \ell^{-5/8} \quad A \propto \ell^{-1/4}$$

(5.6.3)

These scaling relations are valid both for the disordered state, and for the ordered states. Their validity will be confirmed by the results to be obtained later on, in the sense that the
minimalization condition 5.2.23 leads to expressions of the parameters which indeed satisfy 5.6.3.

\textbf{The disordered state}

We start our analysis with the disordered state. Near the order-disorder transition the free energy $F_{\text{dis}}$ can be written as a power series in $\ell^{-1/8}$:

\[ F_{\text{dis}} = F_{0,\text{dis}} + F_{1,\text{dis}} + F_{2,\text{dis}} \]

\[ F_{0,\text{dis}} \propto \ell^{-14/8} \quad F_{1,\text{dis}} \propto \ell^{-15/8} \quad F_{2,\text{dis}} \propto \ell^{-16/8} \]  

(5.6.4)

To keep all these terms is necessary since, as is shown below, the free energies of the disordered state and the various ordered states turn out to differ only by the terms of the order $\ell^{-16/8}$. The only contributions to $F_{\text{dis}}$ are $D_1$ and $D_3$. Since $\rho$ approaches zero when $\ell$ approaches infinity (equation 5.6.3), it is justified to use the expansion of the diagrams in powers of $\rho$ (appendix E equations E4, E5, E17, and appendix F equations F10–F14).

\[ F_{\text{dis}}^0 = \frac{s}{64\pi^2 \ell^3} + \frac{q_3 s^{1/2}}{8\pi \rho^{1/2}} + \frac{q_4 s^{1/2}}{8\pi \rho^{1/2}} \]  

(5.6.5)

In order to make the $\ell$-dependence of the parameters explicit, it is convenient to define rescaled parameters $\tilde{x}, \tilde{q}$ and $\tilde{\rho}$, which reach a finite limit for $\ell \to \infty$, as follows

\[ \tilde{\rho} = \ell^{1/4} \rho \quad \tilde{x} = \frac{s^{1/2}}{8\pi \tilde{\rho}^{1/2}} \quad \tilde{q} = \ell^{5/8} q_0 \]  

(5.6.6)

In terms of these quantities, the expression for $F_{0,\text{dis}}^0$ becomes

\[ F_{0,\text{dis}}^0 = \frac{1}{\ell^{1/4}} \left( \tilde{x}^2 + \tilde{q}^3 \tilde{x} - \tilde{q} \tilde{x} \tilde{x} \right) \]  

(5.6.7)

Minimization with respect to $\tilde{q}$ and $\tilde{x}$ yields

\[ \tilde{q}^2 = \frac{\tilde{\tau}}{3} \quad \tilde{x} = \tilde{q}^3 \]  

(5.6.8)
\[ F_0^{\text{dis}} = -\frac{\tilde{t}^3}{27 \ell^{14/8}} \] (5.6.9)

The second contribution \( F_1^{\text{dis}} \) is proportional to \( \ell^{-15/8} \). Using the expressions for the diagrams given in appendices E and F the following result is obtained

\[ F_1^{\text{dis}} = \frac{1}{8\pi \ell^{15/8}} \left( (1-s)\tilde{x} + \frac{\tilde{x}}{s} + \frac{(s-1)\tilde{x}}{s} + \frac{2\tilde{q}^3(s-1)^{3/2}}{3} \right) \] (5.6.10)

After substitution of the solution 5.6.8 for \( \tilde{x} \), this rearranges to

\[ F_1^{\text{dis}} = \frac{\tilde{q}^3}{8\pi \ell^{15/8}} \left( 2-s + \frac{2(s-1)^{3/2}}{3} \right) \] (5.6.11)

Minimization with respect to \( s \) leads to

\[ s = 2 \quad F_1^{\text{dis}} = \frac{\tilde{t}^{3/2}}{36\pi \sqrt{3} \ell^{15/8}} \] (5.6.12)

Since up to this order the free energies of the disordered state and the ordered states will turn out to be equal, it is necessary to calculate \( F_2^{\text{dis}} \) as well, containing the terms proportional to \( \ell^{-16/8} \). There are two contributions. The first one \( F_2^{\text{dis}} \) consists just of those terms in the expansion of \( D_1 \) and \( D_3 \) which have the proper scaling with \( \ell \). Filling in the results for \( s, \tilde{q} \) and \( \tilde{x} \) gives

\[ F_2^{\text{dis}} = \frac{1}{\ell^2} \left( \frac{7}{128\pi^2} + \frac{4\tilde{t}^4}{81} \right) \] (5.6.13)

The second contribution \( F_2^{\text{dis}} \) arises from the fact that the equilibrium values 5.6.8 and 5.6.12 for the parameters \( s, \tilde{q} \) and \( \tilde{x} \) providing the minimum of the isolated addenda 5.6.7 and 5.6.11 should be corrected to give the minimum of their sum 5.6.4. The magnitude of the correction as compared to the major contribution is of the order \( \ell^{-1/8} \). The effect of this discrepancy is
\[ F_{2s}^{\text{dis}} = -\frac{1}{2} \sum_{i,j} \frac{\partial F_{1}^{\text{dis}}}{\partial x_{i}} \left( \frac{\partial^{2} F_{0}^{\text{dis}}}{\partial x_{i} \partial x_{j}} \right)^{-1} \frac{\partial F_{1}^{\text{dis}}}{\partial x_{j}} = -\frac{1}{192\pi^{2}\ell^{2}} \] (5.6.14)

with \( x_{i} = s \), \( x_{2} = \tilde{q} \) and \( x_{j} = \tilde{x} \). Finally, for the disordered state, the equilibrium values for the rescaled parameters 5.6.6 are finite (which confirms the scaling relations 5.6.3), and given by

\[ s_{\text{dis}} = 2 \quad \tilde{p}_{\text{dis}} = \frac{27}{32\pi^{2}\ell^{3}} \quad \tilde{q}_{\text{dis}}^{2} = \frac{\ell}{3} \] (5.6.15)

The complete expression for \( F_{\text{dis}} \) up till order \( \ell^{-2} \) is given as follows:

\[ F_{\text{dis}} = -\frac{\ell^{3}}{27\ell^{14/8}} + \frac{\ell^{3/2}}{36\pi\sqrt{3}\ell^{15/8}} + \frac{19}{384\pi^{2}\ell^{2}} + \frac{4\ell^{4}}{81\ell^{2}} \] (5.6.16)

**The lamellar state**

Next we calculate the free energy of the lamellar state. Generally, the free energy of the ordered states contains the saddle point contribution \( F_{L} = C_{1} + C_{2} + C_{3} \), as well as the fluctuation corrections \( D_{1}, D_{2} \) and \( D_{3} \) (see 5.2.24). Since it was shown in paragraph 5.4 that the scaling relations 5.6.3 of the parameters \( A, q_{*}, \rho \) and \( s \) are also valid for the ordered states, we can write, similarly to 5.6.4,

\[ F_{\text{lam}}^{\text{dis}} = F_{0}^{\text{lam}} + F_{1}^{\text{lam}} + F_{2}^{\text{lam}} \] (5.6.17)

\[ F_{0}^{\text{lam}} \propto \ell^{-14/8} \quad F_{1}^{\text{lam}} \propto \ell^{-15/8} \quad F_{2}^{\text{lam}} \propto \ell^{-16/8} \]

The minimization with respect to the amplitude \( A \) is straightforward. The free energy contains terms proportional to \( A^{2} \), arising from the saddle point contribution \( F_{L} \) and the fluctuation correction \( D_{2} \), and terms proportional to \( A^{4} \) arising from \( F_{L} \). Very important is the sign of the quadratic coefficient. If it is positive, minimization with respect to \( A \) leads to \( A = 0 \), which returns to the analysis for the disordered phase. In the following it will be assumed that it is negative, leading to a non-zero value for \( A \). Afterwards it will be checked under which conditions this assumption is correct. To leading order in \( \ell \), this quadratic coefficient (we will refer to it as \( \tau_{\text{eff}} \)) is given by
\[ \tau_{\text{eff}} = \left( 2(\tilde{q}^2 - \tilde{r}) + \frac{s^{1/2}}{2\pi \tilde{q} \tilde{\rho}^{1/2}} \right) \ell^{-5/4} \] (5.6.18)

Under the assumption that 5.6.18 is negative, the minimization with respect to \( A \) is straightforward, and leads to

\[ F^{\text{lam}}_0 = -\frac{\tilde{q}^2 (\tilde{r} - \tilde{q}^2)^2}{4 \ell^{14/8}} \] (5.6.19)

\[ F^{\text{lam}}_i = \frac{\tilde{q} (\tilde{q}^2 (-6 + 4(s - 1)^{3/2} + 3s) + 3\tilde{r} (2 - s))}{48 \pi \ell^{15/8}} \] (5.6.20)

\[ F^{\text{lam}}_2 = \frac{5 \tilde{q}^4 (\tilde{r} - \tilde{q}^2)^2}{8 \ell^2} + \frac{2 \pi - 8s + 4 \pi s + 4s^2 - \pi s^2}{256 \pi^3 \ell^2} - \frac{3s \tilde{q}^2}{128 \pi^2 \ell^2 \tilde{\rho}} \]

\[ + \frac{3 \tilde{q}^3 s^{1/2} (\tilde{r} - \tilde{q}^2)}{16 \pi \ell^2 \tilde{\rho}^{1/2}} + \frac{\tilde{q} s^{1/2} (-\tilde{q}^2 - 2s \tilde{q}^2 + 3\tilde{r}) \tilde{\rho}^{1/2}}{32 \pi \ell^2} \] (5.6.21)

\( F_0 \) depends only on \( \tilde{q} \), \( F_i \) depends both on \( \tilde{q} \) and \( s \), while \( F_2 \) depends on all three parameters \( \tilde{q} \), \( s \) and \( \tilde{\rho} \). This fact simplifies the minimization procedure. Since \( F_0 \) is the dominant contribution to the free energy, the value of \( \tilde{q} \) is determined by \( F_0 \) alone. Minimization of \( F_0 \) with respect to \( \tilde{q} \) leads to

\[ \tilde{q}_{\text{lam}}^2 = \frac{\tilde{r}}{3} \quad F^{\text{lam}}_0 = -\frac{\tilde{r}^3}{27 \ell^{14/8}} \] (5.6.22)

which is the same result as for the disordered phase (equation 5.6.9). Inserting this value for \( \tilde{q} \) into the expression for \( F^{\text{lam}}_i \), and then minimizing with respect to \( s \) yields

\[ s_{\text{lam}} = 2 \quad F^{\text{lam}}_i = \frac{\tilde{r}^{3/2}}{36 \pi \sqrt{3} \ell^{15/8}} \] (5.6.23)

Again the same result as for the disordered phase (equation 5.6.12), which is the reason why we have to calculate the terms proportional to \( \ell^{-2} \) as well. Now there are three contributions. The first one is calculated by inserting the expressions for \( \tilde{q} \) and \( s \) (equations 5.6.22 and 5.6.23) into the first two terms of 5.6.21:
\[ F_{2a}^{\text{lam}} = \frac{5\tilde{\ell}^4}{162\ell^2} + \frac{3}{128\pi^2\ell^2} \]  
(5.6.24)

The second one is (see the comment preceding equation 5.6.14)

\[ F_{2b}^{\text{lam}} = -\frac{1}{2} \partial_i \left( \partial^2 F_0^{\text{lam}} \right) \frac{\partial F_i^{\text{lam}}}{\partial x_j} = -\frac{1}{192\pi^2\ell^2} \]  
(5.6.25)

The third contribution comes from the \( \tilde{\rho} \)-dependent terms in 5.6.21. Using the expressions for \( \tilde{\rho} \) and for \( s \) (equations 5.6.22 and 5.6.23), this contribution is

\[ F_{2c}^{\text{lam}} = \frac{\tilde{\ell}}{12\sqrt{6}\ell^2\pi} \left( -\frac{3\sqrt{6}}{16\pi} \frac{1}{\tilde{\rho}} \tilde{\ell}^{3/2} + \tilde{\ell}^{1/2} \tilde{\rho}^{1/2} \right) \]  
(5.6.26)

Collecting all the terms one obtains the total free energy \( F_{\text{lam}} \) as a function of \( \tilde{\ell} \) and \( \tilde{\rho} \), which has to be minimized with respect to \( \tilde{\rho} \):

\[ F_{\text{lam}} = -\frac{\tilde{\ell}^3}{27\ell^{14/8}} + \frac{\tilde{\ell}^{3/2}}{36\pi\sqrt{3}\ell^{13/8}} + \frac{5\tilde{\ell}^4}{162\ell^2} + \frac{7}{384\pi^2\ell^2} + \frac{\tilde{\ell} g(\tilde{\rho})}{12\sqrt{6}\ell^2\pi} \]  
(5.6.27)

\[ g(\tilde{\rho}) = -\frac{3\sqrt{6}}{16\pi} \frac{1}{\tilde{\rho}} \tilde{\ell}^{3/2} + \frac{\tilde{\rho}^{1/2}}{\tilde{\ell}^{1/2}} + \tilde{\ell}^{1/2} \tilde{\rho}^{1/2} \]

It is important to note that the domain of definition of the function \( g(\tilde{\rho}) \) is bounded by the condition (see equation 5.6.18)

\[ \tau_{\text{eff}} \leq 0 \]  
(5.6.28)

which is necessary to have a non-zero equilibrium value of the amplitude \( A \). Using the expression 5.6.18 for \( \tau_{\text{eff}} \), together with the values of \( s_{\text{lam}} \) and \( q_{\text{lam}} \), shows that condition 5.6.28 is equivalent to

\[ \tau_{\text{eff}} \leq 0 \iff \tilde{\rho} \geq \frac{27}{32\pi\tilde{\ell}^{13/8}} = \tilde{\rho}_{\text{dis}} \]  
(5.6.29)
The function \( g(\tilde{\rho}) \) (see 5.6.27) is shown in fig 5.17 for selected values of \( \tilde{t} \). The point on the curve corresponding to the disordered phase is marked with \( dis \), whereas the point corresponding to the lamellar phase is marked with \( lam \). In fig 5.17a the disordered phase is metastable, in 5.17b the lamellar phase is metastable, and in 5.17c the lamellar phase looses stability.

The \( \tilde{t} \)-value for which the lamellar state looses global stability, and the \( \tilde{t} \)-value for which it becomes unstable can be extracted from equations 5.6.16 and 5.6.27. Going back from \( \tilde{t} \) to the original parameter \( \chi \), the results can be summarized as follows:

\[
\chi - \chi_c > 0.909 \ell^{-5/4}
\]
the lamellar phase is globally stable

\[
0.909 \ell^{-5/4} > \chi - \chi_c > 0.872 \ell^{-5/4}
\]
the lamellar phase is metastable

\[
\chi - \chi_c = 0.872 \ell^{-5/4}
\]
the lamellar phase looses stability

In order to prove that the disordered state remains metastable even for \( \tilde{t} > 0.909 \), we calculate the slope of the function \( g(\tilde{\rho}) \) at the point \( \tilde{\rho} = \tilde{\rho}_{dis} \). Since this slope is positive for all values of\( \tilde{t} \).
Fluctuation corrections

\( \tilde{t} \), there is always an energy barrier between the disordered state and the lamellar state (see also fig 5.17):

\[
\left. \frac{dg(\tilde{\rho})}{d\tilde{\rho}} \right|_{\tilde{\rho}=\tilde{\rho}_c} = \frac{2\pi \tilde{t}^2 \sqrt{2}}{3\sqrt{3}} > 0
\] (5.6.30)

For the range of \( \tilde{t} \)-values \( \tilde{t} > 0.872 \) for which the lamellar phase is (meta-)stable, the \( \tilde{\rho} \)-dependent part \( g(\tilde{\rho}) \) of the free energy 5.6.27 can be minimized rigorously. The result is

\[
F_{\text{lam}} = -\frac{\tilde{t}^3}{27\ell^{14/8}} + \frac{\tilde{t}^{3/2}}{36\pi\sqrt{3}\ell^{15/8}} + \frac{7}{384\pi^2\ell^2} + \frac{5\tilde{t}^4}{162\ell^2} + \frac{\tilde{t}^2}{24\pi\sqrt{6}\ell^2} \left( J + \frac{1}{J} \right)
\]

\[
q_{\text{lam}}^2 = \frac{t}{3\ell}, \quad s_{\text{lam}} = 2, \quad \rho_{\text{lam}} = \frac{tJ^2}{3}, \quad A_{\text{lam}} = \ell^{-1/4} \left( \frac{\tilde{t}^2}{18} - \frac{\tilde{t}^{1/2}}{8\sqrt{6}\pi\tilde{\rho}^{1/2}} \right)^{1/2}
\] (5.6.31)

\[
J = 2\cos \left[ \frac{\pi}{3} - \frac{1}{3} \arctan \sqrt{\frac{128\pi^2\tilde{\rho}^4}{729} - 1} \right], \quad \tilde{t} > 0.872
\]

For large values of \( \tilde{t} \) the expression for \( \rho \) simplifies to

\[
\rho \to \frac{4t}{3} \cos \left[ \frac{\pi}{3} - \frac{l}{3} \frac{\pi}{2} \right] = t
\] (5.6.32)

which is in accordance with equation 5.5.10.

**Structures other than lamellar**

In order to calculate the free energies for other morphologies, note that they can be expanded in powers of \( \ell^{-1/8} \) as well:

\[
F = F_0 + F_1 + F_2
\]

\[
F_0 \propto \ell^{-14/8} \quad F_1 \propto \ell^{-15/8} \quad F_2 \propto \ell^{-16/8}
\] (5.6.33)

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After minimization with respect to the amplitude $A$ the expressions for $F_0$ and $F_1$ prove to be morphology independent and given by expressions 5.6.19 and 5.6.20. Therefore, the parameters $q_*$ and $s$ determined by the minimization of $F_0$ and $F_1$, respectively, have the same values for all morphologies (to leading order in $\ell$). Thus, the differences in free energies of the various morphologies are completely due to $F_2$. Inserting the values for $q_*$ and $s$, one obtains $F_2$ as a function of $\tilde{\rho}$ for general values of $\mu$ and $\lambda$.

\[
\ell^2 F_2(\tilde{\rho}) = \frac{7}{384\pi^2} + (\lambda - 16) \left( \frac{\tilde{t}}{384\pi^2 \tilde{\rho}} - \frac{\tilde{t}^{5/2}}{72\sqrt{6\pi}\tilde{\rho}^{3/2}} \right) + \\
\frac{\tilde{t}^{3/2}}{12\sqrt{6}\pi} + \frac{\lambda\tilde{t}^4}{324} - 24\mu|\tilde{\xi}|\tilde{A}_0^3(\tilde{\rho})
\]

(5.6.34)

where the (rescaled) amplitude value $\tilde{A}_0(\tilde{\rho})$ for the partial equilibrium state of the system (given a fixed value for the parameter $\tilde{\rho}$) is given by

\[
\tilde{A}_0(\tilde{\rho}) = \left( \frac{\tilde{t}^2}{18} - \frac{\tilde{t}^{1/2}}{8\sqrt{6}\pi\tilde{\rho}^{3/2}} \right)^{1/2}
\]

(5.6.35)

For the random wave structure ($\lambda = 16, \mu = 0$) the second and the fifth term on the right hand side of 5.6.34 vanish, and the only $\tilde{\rho}$-dependence comes from the third term. Therefore, both $F_2(\tilde{\rho})$ and $\tilde{A}_0(\tilde{\rho})$ decrease continuously with decreasing values of $\tilde{\rho}$ down to the left bound of its domain of definition 5.6.28, where $A_0$ disappears, and the values of $\tilde{\rho}$ and of the free energy equal those for the disordered state 5.6.16. Therefore, the random wave structure is completely unstable.

In general, $F_2$ must be minimized with respect to $\tilde{\rho}$. For $\tilde{\rho} = \tilde{\rho}_c$ one obtains the free energy of the disordered phase. For the shape of $F_2$ as a function of $\tilde{\rho}$ there are two possibilities: either $F_2$ is a monotonously increasing function, in which case the ordered phase under consideration is completely unstable, or it has a minimum, in which case it is at least metastable. To construct the phase diagram on the plane $(\tilde{\xi}, \tilde{t})$ the minimum values of $F_2$ were calculated numerically and compared for the various morphologies, which resulted in the phase diagram shown in fig 5.18.
To visualize the fluctuation corrections better, the mean-field phase transition lines \textit{lam-hex} and \textit{hex-bcc} are presented in the same figure as dashed lines. As is seen from this picture, the larger the distance to the critical point, the closer the phase transition lines are to their mean-field approximations, and, therefore, the less pronounced the fluctuation corrections are. For the phase transition lines between various ordered phases these corrections decay much faster than for the transitions from the disordered phase into the bcc phase. It is worthwhile to note also that for the correlated random copolymers the “windows” where the disorder-order transition occurs into the cylindrical or lamellar state (resp. for \(0.0624 < |\bar{\epsilon}| < 0.1332\) and for \(|\bar{\epsilon}| < 0.0624\)) are fairly small when compared with the corresponding windows found in ref 44 for the monodisperse diblock copolymer melt.

**The relative amplitude of the fluctuations \(\delta\psi(x)\) in the profile**

The phase diagram fig 5.18 presents the results for the average concentration profile \(\langle \psi(\bar{x}) \rangle\), which is obtained after averaging the instantaneous profile over a sufficiently long time interval. The instantaneous profile differs from the average profile due to the presence of the fluctuations. The above analysis provides information about the magnitude of these fluctuations. It is to be expected that they are strongest in the neighborhood of the phase
transition line. For symmetric copolymers \( f = 0.5 \) close to the transition point \( \tilde{T} = 0.909 \), we will calculate the amplitude of the fluctuations both in the lamellar and in the disordered phase, and compare the result with the amplitude of the average profile. The calculation is analogous to the one in equations 5.5.16 and 5.5.17. For the lamellar phase one obtains

\[
\langle \psi^2 \rangle_{\text{lam}} = \frac{1}{V} \int d\tilde{x} \langle \psi^2(\tilde{x}) \rangle = \frac{1}{V} \int d\tilde{x} \left( \langle \psi^2(\tilde{x}) \rangle - \langle \psi(\tilde{x}) \rangle^2 + \langle \psi(\tilde{x}) \rangle^2 \right) = \\
= \frac{1}{(2\pi)^3} \int d\tilde{q} G(\tilde{q}) + \frac{1}{V} \int d\tilde{x} \langle \psi(\tilde{x}) \rangle^2 = \frac{s^{1/2} q_s}{8\pi \rho^{1/2}} + 2A^2 \bigg|_{\tilde{T} = 0.909} = (0.046 + 0.046) \ell^{-1/2}
\]  

(5.6.37)

where the first part is due to the fluctuations, and the second part is due to the average profile. This result shows that in the lamellar phase right after the transition the amplitude of the fluctuations \( \delta \psi \) is equal to the amplitude of the average profile. This means that the concentration profile will appear to be rather irregular. For the disordered phase the corresponding result is

\[
\langle \psi^2 \rangle_{\text{dis}} = \langle \psi^2(\tilde{x}) \rangle = \frac{1}{(2\pi)^3} \int d\tilde{q} G(\tilde{q}) = \frac{s^{1/2} q_s}{8\pi \rho^{1/2}} = 0.092 \ell^{-1/2}
\]  

(5.6.38)

The comparison of equation 5.6.37 with equation 5.6.38 shows that the amplitude of the concentration inhomogeneities in the disordered phase is the same as the amplitude of the concentration inhomogeneities in the lamellar phase. From these observations one can conclude that snapshot pictures taken from both phases might be rather similar near the disorder-order transition. There is another point which confirms this conclusion. In equation 5.3.7 an expression was given for the spatial correlation function \( g(\tilde{x}) \). It was shown that \( g(\tilde{x}) \) is an exponentially decaying sine, characterized by two length scales: the period \( R_{\text{osc}} \) of the oscillations, and the distance \( R_{\text{cor}} \) over which the correlations vanish. These length scales are given by

\[
R_{\text{osc}} = l/|aq_s|, \quad R_{\text{cor}} = l/bq_s
\]

\[
a = \sqrt[\sqrt{2}]{1 - \rho/2 + \sqrt{1 - \rho + \rho s}} \quad \quad b = \sqrt[\sqrt{2}]{-1 + \rho/2 + \sqrt{-1 + \rho + \rho s}}
\]  

(5.6.39)

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In the disordered phase, near the phase transition line \( t \propto \ell^{-1/4} \), the values of \( s \) and \( \rho \) satisfy \( s = 2 \) (equation 5.6.15), and \( \rho \propto \ell^{-1/4} \ll 1 \) (equation 5.6.3). Inserting this into 5.6.39 leads to \( a \ll 1 \), \( b \ll \sqrt{\rho}/2 \ll 1 \), and so

\[
R_{osc} \ll R_{cor} \quad (5.6.40)
\]

Therefore, the correlation function exhibits many oscillations before it vanishes, which means that locally the disordered phase will appear to have some kind of ordering (see also ref 57, where the same result was obtained for a melt of uncorrelated random copolymers).

**Disordered phase versus random wave structure**

Although the disordered phase (having \( \langle \psi \rangle = 0 \)) is essentially different from the random wave structure (having \( \langle \psi \rangle \neq 0 \)), the analysis in this chapter reveals that there is a remarkable similarity between these phases. First of all, in the limit \( \ell \to \infty \) both phases have the same free energy. Second, the amplitude of the concentration inhomogeneities in the disordered phase is equal to that in the random wave structure, both near the order disorder transition, and for stronger segregations. And third, the disordered phase has an anomalously long correlation length, making it indistinguishable from the random wave structure on length scales which may be much larger than \( 1/q_* \). In conclusion we can say that it is very well possible that the experimentally observed “disordered microstructure” (which can theoretically be described by the random wave structure) is in fact the strongly fluctuating disordered phase.\(^{41}\)