6. Multiblock copolymers with an arbitrary block length distribution

6.1 Introduction

In this chapter we calculate the general expression for the Landau free energy for a broad class of polydisperse multiblock copolymers, and calculate the mean-field phase diagram in the first harmonics approximation for a few examples. The class of copolymers for which our analysis is valid comprises all linear multiblock copolymers with an arbitrary length distribution of the A-blocks and the B-blocks (these distributions may be different), the only restriction being that the average number of blocks per molecule, as well as the average number of monomers per block is large. The large number of blocks per molecule gives a simplification in the calculation of the correlation functions, as will become clear in paragraph 6.2. The large number of monomers per block assures that the mean-field approximation is reasonable, so that the fluctuation corrections can be ignored. In order to keep the calculations tractable, we will not derive the general expressions for the correlation functions, but only those which are relevant for the first harmonics approximation. For the third order correlation this means that we restrict ourselves to the situation where at least two of its three arguments have the same length; see 2.2.4 and 2.2.20. For the fourth order term it means that we restrict ourselves to the calculation of the quantity $M_h^2$ (equation 2.2.22; remember that the definition 2.2.20 of $M_h^2$ only involves second and third order correlation functions).

There are two reasons why the multiblock copolymer with a Flory distribution (the correlated random copolymer) was treated separately. First, by taking into account phase coexistence and fluctuation corrections we have analyzed this system more deeply than we will the general systems considered in this chapter. Second, the equations given in this chapter are rather lengthy and deriving them is tedious. For the correlated random copolymer, chapter 3 presented a much faster and more elegant way to arrive at the same expression. Strictly speaking, the polymer system analyzed in chapters 3, 4 and 5 (referred to as system 1) is not completely the same as the system described in this chapter (referred to as system 2), even if we give the block lengths a Flory distribution. In system 1, there is a considerable polydispersity in the number of blocks per molecule, whereas in system 2 all molecules have the same (large) number of blocks. However, the Landau free energy of multiblock copolymers
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converges if the average number of blocks per molecule increases, and becomes independent of the distribution of the number of blocks. Therefore, system 1 and system 2 are equivalent with regard to their phase behavior, which remains true even if the possibility of macrophase separation is taken into account. In chapter 3 we chose deliberately a model which is polydisperse in the number of blocks per molecule, because this resulted in a considerable simplification in the calculation of the correlation functions.

6.2 The vertex functions

**The second order correlation function**

Consider an AB-multiblock copolymer melt, and let $Q$ be the number of $A$-blocks per molecule (which equals the number of $B$-blocks). It is assumed that $Q$ is very large, and that the lengths of the blocks are independent of each other. All blocks of the same type (i.e. $A$ or $B$) have the same length distribution. Let $P_\alpha(n)dn$ be the probability that a block of type $\alpha$ has a length between $n$ and $n+dn$. This distribution is normalized according to

$$\int_{0}^{\infty} P_\alpha(n) dn = 1$$  \hspace{1cm} (6.2.1)

According to chapter 1, in order to find an expression for the Landau free energy we have to calculate the correlation functions. We start with the second order one. According to paragraph 1.3 the proper way to average it over the composition $\{\rho_s\}$ is given by

$$g_{\alpha\beta}(q) = \sum_s \rho_s \sum_{i,j} \sigma_\alpha^i \sigma_\beta^j e^{-q^2|i-j|}$$  \hspace{1cm} (6.2.2)

First we have to identify the molecule types $s$ in the model under consideration, and then we have to find an expression for $\rho_s$ (which is the number of molecules of type $s$ per unit of volume) as a function of $s$. A molecule-type $s$ is fixed if the lengths of all blocks in the molecule are fixed:

$$s = \left(N_A^1, N_B^1, N_A^2, N_B^2, \ldots, N_A^0, N_B^0\right)$$  \hspace{1cm} (6.2.3)
where \( N^i_\alpha \) denotes the length of the \( i^{th} \) block of type \( \alpha \) in the molecule. The quantity \( \rho_s \) is proportional to the product of the probabilities of all the blocklengths:

\[
\rho_s = c P_s = c P_A(N^i_A) P_B(N^i_B) P_A(N^2_A) P_B(N^2_B) \cdots P_A(N^0_A) P_B(N^0_B)
\]  

The normalization constant \( c \) is determined by the constraint that the monomer density is unity, i.e.

\[
\sum_s \rho_s N_s = 1
\]  

where the total molecule length \( N_s \) is given by

\[
N_s = \sum_{i=1}^{Q} \left( N^i_A + N^i_B \right)
\]  

The value of the normalization \( c \) can straightforwardly be determined via

\[
I = \sum_s \rho_s N_s = c \int_0^\infty d(N^i_\alpha) \left[ \sum_{i,\alpha} N^i_\alpha \right] \prod P_\alpha(N^i_\alpha)
\]  

Taking the summation out of the integration and using the identities

\[
\int_0^\infty P_\alpha(n) \, dn = 1 \quad \int_0^\infty n P_\alpha(n) \, dn = n_\alpha
\]  

where \( n_\alpha \) is the average length of a block of type \( \alpha \), we find for the value of \( c \)

\[
c = \frac{I}{Q(n_A + n_B)}
\]  

In the definition 6.2.2 of the second order correlation function, there are three summations present. First one chooses a certain realization of the blocklengths, and after that \( i \) is summed over all monomers of type \( \alpha \), and \( j \) over all monomers of type \( \beta \). Then take another realization of the blocklengths, etc. It is, however, more convenient to rearrange this summation, using the fact that the blocklengths are independent. First take a block of type \( \alpha \) and a different block
of type $\beta$. Choose a monomer $i$ in the first block, and a monomer $j$ in the second one. These two blocks will divide the chain into three parts: a middle part and two tails. Choose the number of blocks in the middle part. If e.g. $\alpha = A$ and $\beta = B$, this number will range from zero till $Q - 2$. The remaining blocks have to be distributed over the two tails. At this point the fact that $Q$ is very large will simplify matters, in the following way. As mentioned before, the relevant $q$-values are those corresponding to fluctuations on the length scale of the radius of gyration of the blocks. Therefore,

$$q_{\text{rel}}^2 = (n_A + n_B)^{-1}$$

(6.2.10)

Since according to 6.2.2 all bonds between the monomers $i$ and $j$ get a factor $e^{-q^2}$, the weight factor $e^{-\|i-j\|^2}$ will have decayed by a factor two if $i$ and $j$ are about one block apart, and so the situations where $i$ and $j$ are many blocks apart will give a negligible contribution to the correlation function. Therefore, one gets a contribution only if the number of blocks in between $i$ and $j$ is of order unity, and correspondingly the total number of blocks in the tails will be of order $Q$. Summing over the lengths of the blocks in the tails will give factor unity (the blocks lengths are independent), and summing over the ways to divide the remaining blocks over the two tails will give a factor $Q$. This factor $Q$ can be interpreted as the number of blocks in which monomer $i$ can be present. Monomer $j$ must be near monomer $i$ in order to get a significant contribution to the correlation function, and therefore one gets this factor $Q$ only once. The same reasoning applies for the higher order correlation functions, i.e. they all are proportional to $Q$. The next thing to do is to sum over all possible lengths of the blocks in the middle part, over the lengths of the blocks containing $i$ and $j$, and finally over $i$ and $j$ within the two blocks. If $\alpha = \beta$, then also the possibility that $i$ and $j$ are in the same block needs to be considered.

Now the above will be worked out in more detail. We start with the AA-correlation. In the summation over all pairs $i, j$ of monomers in 6.2.2, the selfcorrelation part $i = j$ can be ignored because the average number of monomers per block is large. In the rest of the sum, the situation $i < j$ gives the same contribution as $i > j$. This symmetry will be accounted for by a factor 2. First consider the case that $i$ and $j$ are in the same block. This situation is represented by 6.2.11. The thin lines represent $A$-blocks, the thick lines represent $B$-blocks. There will be a lot more blocks to the left and to the right of $i$ and $j$ than shown in the figure, but their only contribution to the final answer is the factor $Q$ which is the number of blocks where monomer $i$ can be situated. Monomers over which should be summed are represented by a dot. The number $i, j, k, \cdots$ of the monomer is shown below the diagram, where the numbering restarts...
from unity in every block, unless specified otherwise. The relevant blocklengths are given above the line representing the molecule.

\[ n_i \quad n_j \]

(6.2.11)

The factor \( Q \) due to translational invariance will cancel against the factor \( Q \) present in the normalization constant \( c \).

\[
\frac{1}{Q(n_A+n_B)} 2Q \int_0^\infty dn P_n(n) \int_0^n dt \int_{-t}^{t} e^{-x(i-j)} =
\]

\[
\frac{2}{(n_A+n_B)} \int_0^\infty dn P_n(n) \left( \frac{n + e^{-nx} - 1}{x^2} \right) = (n_A+n_B) \left( -\frac{2(1-\alpha(y))}{y^2} + \frac{2f}{y} \right)
\]

(6.2.12)

The following definitions have been made:

\[
f = \frac{n_A}{n_A+n_B} \quad x = q^2 \quad y = (n_A+n_B)x \quad \alpha(y) = \int_0^\infty dn e^{-nx} P_n(n)
\]

(6.2.13)

In analogy, the function \( \beta(y) \) is defined as the Laplace transform of the length distribution of the \( B \)-blocks. Note that in the calculations in this chapter the wave vector is rescaled with the average total block length \( N \), while in chapters 3, 4 and 5 it was rescaled with \( \ell \). Both quantities give an indication for the block lengths in the system, but they are defined differently:

\[
N = n_A + n_B \quad \ell = \left( (n_A^{-1} + n_B^{-1}) \right)^{-1}
\]

(6.2.14)

Relation 6.2.14 should be kept in mind when results from this chapter are compared to those of chapter 3. Although \( \alpha \) is a function of \( y \), this dependence will not be made explicit in our notation in order to keep the formulas as transparent as possible. Therefore, in the future if \( \alpha \) has been written without its argument it is understood that the argument is \( y \).
The second contribution to $g_{AA}$ 6.2.2 arises if $i$ and $j$ are in different blocks. Again, there will be a factor 2 because $j$ can be either larger or smaller than $i$, and a factor $Q$ because of the choice of the block where e.g. $i$ is present. Let $n_1$ be the length of the $A$-block where monomer $i$ is situated, and $n_2$ the length of the $A$-block where monomer $j$ is situated. Assume that between the $A$-block where $i$ is situated, and the $A$-block where $j$ is situated, there are $k$ $A$-blocks and $(k + l)$ $B$-blocks, with $k \geq 0$. The lengths of the $A$-blocks are $\nu_1, \ldots, \nu_k$, and the lengths of the $B$-blocks are $\mu_1, \ldots, \mu_{k+l}$, see 6.2.15. Then the contribution to the correlation function $g_{AA}$ is equal to

$$
\left( \frac{2}{n_A + n_B} \sum_{k=0}^{\infty} \left[ d\nu_0 P_0(n_1) \cdots d\nu_k P_k(n_k) \right] \right)
\int d\mu_1 P_1(\mu_1) \cdots \int d\mu_{k+l} P_{k+l}(\mu_{k+l})
\int d\nu_0 e^{-x(n_i + \nu_0 + \nu_1 + \cdots + \nu_k + \mu_1 + \cdots + \mu_{k+l})} = (n_A + n_B)^2 \frac{2\beta(I - \alpha)^2}{(I - \alpha\beta)y^2}
$$

Combining the equations 6.2.12 and 6.2.15 gives as final result for the $AA$-component of the second order correlation function

$$
g_{AA}(y) = 2(n_A + n_B) \left( \frac{(I - \alpha)(I - \beta)}{(I - \alpha\beta)y^2} + \frac{f}{y} \right)
$$

Clearly the $BB$-component will be given by

$$
g_{BB}(y) = 2(n_A + n_B) \left( \frac{(I - \alpha)(I - \beta)}{(I - \alpha\beta)y^2} + \frac{1 - f}{y} \right)
$$

To calculate the $AB$-component, only one situation needs to be considered, because $i$ and $j$ cannot be in the same block. Assume that $i$ is present in an $A$-block with length $n_1$, and $j$ in a
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$B$-block of length $n_2$. Perform the calculation for the case that monomer $i$ is to the left of monomer $j$, and add a factor 2. Again add a factor $Q$ for the position of the two blocks in the molecule. Let $k$ be the number of blocks in between $i$ and $j$, where $k \geq 0$. This situation can be represented by the diagram

\[ \begin{array}{c}
\bullet & \mu_i & \nu_i & \cdots & \mu_k & \nu_k & n_2 & \bullet \\
\text{i} & & & & & & & \text{j}
\end{array} \]  

(6.2.18)

which stands for the expression

\[ \overline{g_{AB}(y)} = \frac{2Q}{Q(n_A + n_B) \sum_{k=0}^{\infty} \int d\mu_i P_A(n_i) \int d\nu_i P_B(n_i) \cdots \int d\nu_k P_A(n_k)} \]

\[ \overline{g_{AB}(y)} = \int d\mu_i P_B(\mu_i) \cdots \int d\mu_k P_B(\mu_k) \int_0^{n_i} \int_0^{n_2} e^{-x(n_i-i+\nu_1+\cdots+\nu_k+\mu_i+\cdots+\mu_k)} = \]

\[ = \frac{2}{(n_A + n_B)(1-\alpha \beta)} \int_0^{n_i} \int_0^{n_2} e^{-x(n_i-i)} \int_0^{n_2} e^{-x \nu} = \]

\[ = 2(n_A + n_B) \frac{(1-\alpha)(1-\beta)}{(1-\alpha \beta) y^2} \]  

(6.2.19)

The second order vertex $\gamma_2$ can now be calculated, using equation 1.3.52

\[ \gamma_2 = \frac{g_{AA} + 2g_{AB} + g_{BB}}{g_{AA} g_{BB} - g_{AB}^2} \quad \Rightarrow \quad \gamma_2 = \frac{I}{2(n_A + n_B)} \frac{f(I-f)}{y} - \frac{I}{(1-\alpha)(1-\beta) y^2} \]  

(6.2.20)

The third order correlation function

The third order correlation function is necessary both for the calculation of the third order vertex, and for the calculation of $M_2(h)$, which is part of the fourth order vertex, see 2.2.20. For the third order vertex we need its value only for the situation where all three arguments have the same length. We start with the calculation of $g_{AAA}(y,y,y)$ (use 1.2.13 and 1.2.9)
where the summations over \( i \), \( j \) and \( k \) extend over the whole chain. Now there are several contributing situations. If \( i \), \( j \) and \( k \) are all three present in the same block, the summation can be split into \( 3! \) contributions \( \langle i,j,k \rangle \), \( \langle j,k,i \rangle \), \( \langle k,i,j \rangle \), etc., which each give the same contribution. Therefore, we will do the calculation only for \( \langle i,j,k \rangle \), and add a factor 6. Let \( n \) be the length of the A-block containing \( i \), \( j \) and \( k \). The integrand does not depend on the position of the middle monomer, which is due to the fact that all three vectors have the same length. The contribution is

\[
g_{\text{AAA}}(q,q,q) = \sum_{s} \rho_{s} \sum_{i,j,k} \sigma_{s}^{A} \sigma_{s}^{A} \sigma_{s}^{A} e^{[\max(i,j,k) - \min(i,j,k)]q^2} \tag{6.2.21}
\]

The factor \( Q \) is, like in the calculation of the second order correlation function, the number of possible choices for the A-block containing the monomers, and \( \alpha' \) is the derivative of \( \alpha \) with respect to \( y \):

\[
\alpha'(y) = \frac{d}{dy} \int_{0}^{\infty} dn e^{-n \alpha} P_{A}(n) = \frac{-1}{n_{A} + n_{B}} \int_{0}^{\infty} dn n e^{-n \alpha} P_{A}(n) \tag{6.2.23}
\]

In the equations to follow the dependence of the correlation functions on the average total blocklength \( (n_{A} + n_{B}) \) will not be shown explicitly. Every summation over the monomers will add a factor \( (n_{A} + n_{B}) \), and taking into account the normalization 6.2.9 it follows that the \( k \)th order correlation function is proportional to

\[
g_{k} \propto (n_{A} + n_{B})^{k-1} \tag{6.2.24}
\]
As a consequence, all vertices (and therefore the free energy) are inversely proportional to

\[ \Gamma_k \propto (n_A + n_B)^{-1} \]  

(6.2.25)

which is analogous to the situation for monodisperse diblock copolymers. The next contribution to \( g_{AAA}(y,y,y) \) arises when two monomers are in the same block, and the third is not. Assume that \( i < j < k \) and \( i \) and \( j \) are in the same block. Then a symmetry factor \( 12 \) should be added, a factor \( 6 \) due to the order of \( i, j \) and \( k \) and a factor \( 2 \) for the choice whether the middle monomer is in the same block as the right one or as the left one. In between the two \( A \)-blocks there could be a sequence of blocks. In this sequence the number of \( B \)-blocks exceeds the number of \( A \)-blocks by one. As shown above, summing over all possibilities for this sequence gives a factor which is equal to

\[ \frac{\beta}{l - \alpha \beta} \]  

(6.2.26)

In the following this factor will be incorporated without further explanation. Returning to \( g_{AAA} \) the contribution is

\[
\left. \begin{array}{c}
\underline{n_1} \\
\bullet \\
i \\
\bullet \\
j \\
\underline{n_2} \\
\bullet \\
k
\end{array} \right\} 
= \frac{12\beta}{l - \alpha \beta} \int dn_1 P_A(n_1) \int dn_2 P_A(n_2) \int_0^{n_1} d_i \int_0^{n_2} d_j \int_0^{n_1 + n_2} d_k e^{-x(n_1 + n_2 - i + k)} = \\
= \frac{12\beta}{l - \alpha \beta} \left( \frac{(l - \alpha)^2}{y^3} + \frac{\alpha (l - \alpha)}{y^2} \right) 
\]

(6.2.27)

Finally there is the possibility that \( i, j \) and \( k \) are all in different blocks. The symmetry factor is \( 6 \), and there will be 2 factors of the form 6.2.26 present.
Therefore the final expression for $g_{AAA}$ is the sum of these 3 contributions. Next we calculate $g_{AAB}$. Since the ideas behind the calculation are the same as in the case of $g_{AAA}$, we will just give the diagram with the accompanying symmetry factor, the integral represented by the diagram and the final answer. The numerical factor in front of the integral is the symmetry factor due to the fact that the same integral can be reached by interchanging the order of the indices.
It is clear that the expressions for \( g_{ABB} \) and \( g_{BBB} \) can be obtained from the above expressions just by interchanging \( \alpha \) and \( \beta \). Next we calculate the third order correlation function for the case that 2 arguments have the same square length \( y \), but the third argument has square length \( hy \):

\[
\begin{align*}
g_{\alpha\beta\gamma}(\vec{q}_1, \vec{q}_2, \vec{q}_3) &= (n_A + n_B) q_1^2 = (n_A + n_B) q_2^2 = (n_A + n_B) q^*_3 \\ &= (n_A + n_B) h q^*_z = hy
\end{align*}
\]

This correlation function is needed for the calculation of \( M_2(h) \) (equation 2.2.20). The diagrams and the corresponding expressions will be given without further comments. The monomer denoted by \( k \) is the one corresponding to \( q^*_3 \).
\[\begin{align*}
\int_{i}^{n} \int_{k}^{n} \int_{j}^{n} e^{-x(j-i)} \, dx \, dk \, dj = -\frac{4(1-\alpha)}{y^3} + \frac{2f}{y^2} - \frac{2\alpha'}{y^2} \quad (6.2.34) \\
\int_{i}^{n_{1}} \int_{k}^{n_{1}} \int_{j}^{n_{2}} e^{-x(n_{1}-i+j)} = \frac{4\beta}{1-\alpha\beta} \left( \frac{(1-\alpha)^2}{y^3} + \frac{(1-\alpha)\alpha'}{y^3} \right) \quad (6.2.35) \\
\int_{k}^{n_{1}} \int_{i}^{n_{1}} \int_{j}^{n_{2}} e^{-h x(i-k)-x(n_{1}-i+j)} = \frac{4\beta(1-\alpha)}{1-\alpha\beta} \left( \frac{\alpha}{(1-h)y^3} + \frac{1}{hy^3} + \frac{\alpha_h}{h(h-1)y^3} \right) \quad (6.2.36)
\end{align*}\]
where we introduced the notation

\[ \alpha_h \equiv \alpha(hy) = \int_0^\infty dn \ e^{-nhx} P_A(n) \]  

(6.2.38)

There are two contributions left:

\[ = \frac{4 \beta_h}{(1 - \alpha \beta)(1 - \alpha_h \beta_h)} \int d\eta_1 P_A(\eta_1) \int d\eta_2 P_A(\eta_2) \int d\eta_3 P_A(\eta_3) \]

(6.2.39)
Next we calculate $g_{AAB}(y, y, hy)$. Since the way to construct the integral from the diagram will be clear by now, we only give the diagrams and their values. There are no additional difficulties compared to the previous case.

\[ g_{ABA}(y, y, hy) \]

Let $k$ be the monomer associated with $hy$, and let $j$ be the $B$-monomer.

\[ g_{ABA}(y, y, hy) \]

Next consider $g_{ABA}(y, y, hy)$. Let $k$ be the monomer associated with $hy$, and let $j$ be the $B$-monomer.
The third order correlations containing two or three $B$’s can easily be deduced from the above formulas by interchanging $\alpha$ and $\beta$.

**The fourth order correlation function**

Finally the fourth order correlation functions have to be calculated. According to paragraph 2.2, in the first harmonics approximation it is sufficient to calculate the quantity $M_f(h)$ defined by

$$M_f(h) = 8 \sum_{\alpha \beta \gamma \delta} M_{\alpha \beta \gamma \delta} \zeta_\alpha \zeta_\beta \zeta_\gamma \zeta_\delta$$

$$M_{\alpha \beta \gamma \delta} = \sum_s \rho_s \sum_{i<j<k<l} \sigma_{ij}^{\alpha} \sigma_{jk}^{\beta} \sigma_{kl}^{\gamma} \sigma_{il}^{\delta} \exp[-(j-i)q_z^2 - (k-j)q_x^1 - (l-k)q_x^2]$$

(6.2.49)

The summation over $i, j, k$ and $l$ in the expression for $M_{\alpha \beta \gamma \delta}$ can be split into parts, according to which of the monomers $i, j, k$ and $l$ are present in the same block. As an example, consider $M_{ABBA}$ which can be split into two parts, because monomers $j$ and $k$ can either be present in the same block or in different blocks. Each of these parts can be represented by a diagram:

$$M_{ABBA} = \bullet \bullet \bullet \bullet + \bullet \bullet \bullet \bullet$$

(6.2.50)

The amount of work is reduced by noting the symmetry

$$M_{AAAB} = M_{BAAA} \quad M_{ABAB} = M_{BABA}$$

(6.2.51)
etc., and by noting that we need only to calculate $M_{ab\gamma\delta}$ for the case where the number of $A$-monomers is 0, 1 or 2, because the expression for e.g. $M_{ABBB}$ follows from the expression for $M_{BAAA}$ by interchanging $\alpha$ with $\beta$. There is, however, one complication. Although $M_{ab\gamma\delta}(h)$ is continuous at $h = 1$, it is not possible to insert this value into the expressions to follow. Therefore, we give the expressions for $h = 1$ separately. The calculations of the diagrams for arbitrary value of $h \neq 0, 1$ resembles much the calculation of the third order correlation functions. We start with the calculation of $M_{AAAA}$, which can be written as a sum of 8 diagrams, 6 of them are essentially different.

$$M_{AAAA} = \text{Diagram} \leftrightarrow \frac{\alpha'}{(h-1)y^3} + \frac{\alpha_h}{(h-1)^2h^2y^3} +$$

$$+ \frac{\alpha(-3+2h)}{(h-1)^2y^4} + \frac{f}{hy^3} \frac{(1+2h)}{h^2y^3} +$$

$$+ 2 \text{Diagram} \leftrightarrow 2\beta(I-\alpha) \left( \frac{\alpha'}{(h-1)y^3} + \frac{\alpha_h}{(h-1)^2hy^3} + \frac{(2-h)\alpha}{(h-1)^2y^3} + \frac{l}{hy^3} \right) +$$

$$+ \text{Diagram} \leftrightarrow \beta_h \frac{(-l+\alpha_h+h(l-\alpha))^2}{(1-\alpha_h\beta_h)(h-1)^2h^2y^4} +$$

$$+ \text{Diagram} \leftrightarrow \beta^2(I-\alpha)^2(-\alpha+\alpha_h+(1-h)\alpha' \frac{h}{1-\alpha\beta}) \frac{1}{(1-\alpha\beta)^2(h-1)^2y^4} +$$

$$+ 2 \text{Diagram} \leftrightarrow 2\beta\beta_h \frac{(l-\alpha)(\alpha_h-\alpha)}{(1-\alpha\beta)(1-\alpha_h\beta_h)(h-1)^2y^4} \left( \frac{l-\alpha_h}{h} - l + \alpha \right) +$$

$$+ \text{Diagram} \leftrightarrow \frac{\beta^2\beta_h}{(1-\alpha\beta)^2(1-\alpha_h\beta_h)(h-1)^2y^4} \text{ (6.2.52)}$$

Now we turn to the calculation of $M_{AAAB} \ (= M_{BAAA})$. The $A$-monomers can be either in the same block, or in different blocks, leading to the following contributions.
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\[ M_{AAAB} = \begin{array}{c}
\bullet\bullet\bullet\bullet\bullet
\end{array} \leftrightarrow \frac{\beta \beta_h (1 - \alpha)(1 - \beta)(\alpha_h - \alpha)^2}{(1 - \alpha \beta)^2 (1 - \alpha h \beta_h) (h - I)^2 y^4} +
\]

\[ + \begin{array}{c}
\bullet\bullet\bullet\bullet\bullet
\end{array} \leftrightarrow \frac{\beta (1 - \alpha)(1 - \beta)(-\alpha + \alpha_h + \alpha \gamma (1 - h))}{(1 - \alpha \beta)^2 (h - I)^2 y^4} +
\]

\[ + \begin{array}{c}
\bullet\bullet\bullet\bullet\bullet
\end{array} \leftrightarrow \frac{\beta_h (\alpha - \alpha_h)(1 - \beta)(-1 + \alpha_h + h(1 - \alpha))}{(1 - \alpha \beta)(1 - \alpha h \beta_h) (h - I)^2 h y^4} +
\]

\[ + \begin{array}{c}
\bullet\bullet\bullet\bullet\bullet
\end{array} \leftrightarrow \frac{l}{(1 - \alpha \beta)} \left( \frac{\alpha' (1 - \beta)}{(h - I) y^2} - \frac{\alpha_h (1 - \beta)}{(h - I)^2 h y^4} + \frac{\alpha (1 - \beta)(2 - h)}{(h - I)^2 y^4} + \frac{l - \beta}{h y^4} \right) \quad (6.2.53)
\]

\[ M_{AABA} = \begin{array}{c}
\bullet\bullet\bullet\bullet\bullet
\end{array} \leftrightarrow \frac{\beta (1 - \alpha)^2 (\alpha_h - \alpha)(\beta_h - \beta)}{(1 - \alpha \beta)^2 (1 - \alpha h \beta_h) (h - I)^2 y^4} +
\]

\[ + \begin{array}{c}
\bullet\bullet\bullet\bullet\bullet
\end{array} \leftrightarrow \frac{(1 - \alpha)(\beta - \beta_h)(-1 + \alpha_h + h(1 - \alpha))}{(h - I)^2 h y^4} \quad (6.2.54)
\]

\[ M_{AABB} = \begin{array}{c}
\bullet\bullet\bullet\bullet\bullet
\end{array} \leftrightarrow \frac{\alpha \beta (1 - \alpha)(1 - \beta)(\alpha_h - \alpha)(\beta_h - \beta)}{(1 - \alpha \beta)^2 (1 - \alpha h \beta_h) (h - I)^2 y^4} +
\]

\[ + \begin{array}{c}
\bullet\bullet\bullet\bullet\bullet
\end{array} \leftrightarrow \frac{\alpha (1 - \beta)(\beta_h - \beta)(1 - \alpha_h - h(1 - \alpha))}{(1 - \alpha \beta)(1 - \alpha h \beta_h) (h - I)^2 h y^4} +
\]

\[ + \begin{array}{c}
\bullet\bullet\bullet\bullet\bullet
\end{array} \leftrightarrow \frac{\beta (1 - \alpha)(\alpha_h - \alpha)(1 - \beta_h - h(1 - \beta))}{(1 - \alpha \beta)(1 - \alpha h \beta_h) (h - I)^2 h y^4} +
\]

\[ + \begin{array}{c}
\bullet\bullet\bullet\bullet\bullet
\end{array} \leftrightarrow \frac{(\alpha_h - 1 + h(1 - \alpha))(\beta_h - 1 + h(1 - \beta))}{(1 - \alpha h \beta_h) h^2 (1 - h)^2 y^4} \quad (6.2.55)
\]

\[ M_{ABAB} = \begin{array}{c}
\bullet\bullet\bullet\bullet\bullet
\end{array} \leftrightarrow \frac{(1 - \alpha)(1 - \beta)(\alpha_h - \alpha)(\beta_h - \beta)}{(1 - \alpha \beta)^2 (1 - \alpha h \beta_h) (h - I)^2 y^4} \quad (6.2.56)
\]
In order to obtain the expressions for \( h = 1 \) the most easy way is not to take the limit \( h \to 1 \), but to recalculate the diagrams. In the expressions the double derivative of \( \alpha \) appears, which is defined as

\[
\alpha'' = \frac{d^2 \alpha(y)}{dy^2} = \frac{1}{(n_A + n_B)} \int_0^\infty dn \, n^2 \, e^{-n \xi} \, P_A(n)
\]  

\( (6.2.58) \)

\[
M_{AAAA}(1) = \leftrightarrow -\frac{3(1-\alpha)}{y^4} + \frac{f}{y^5} - \frac{2\alpha'}{y^3} + \frac{\alpha''}{2y^2} +
\]

\[
+2 \leftrightarrow \frac{2(1-\alpha)}{1-\alpha\beta} \left( \frac{(1-\alpha)}{y^4} + \frac{\alpha'}{y^3} - \frac{\alpha''}{2y^2} \right) +
\]

\[
\leftrightarrow \frac{\beta}{1-\alpha\beta} \left( \frac{(1-\alpha)^2}{y^4} + \frac{2\alpha' (1-\alpha)}{y^3} + \frac{(\alpha')^2}{y^2} \right) +
\]

\[
\leftrightarrow \frac{\alpha'' \beta^2 (1-\alpha)^2}{2y^2 (1-\alpha\beta)^2} +
\]

\[
+2 \leftrightarrow \frac{-2(1-\alpha)\alpha'}{(1-\alpha\beta)^2} \left( \frac{1-\alpha}{y^4} + \frac{\alpha'}{y^3} \right) +
\]

\[
\leftrightarrow \frac{\beta^3 (1-\alpha)^2 (\alpha')^2}{(1-\alpha\beta)^3 y^3}
\]  

\( (6.2.59) \)
\[ M_{\text{AAAB}}(I) = \begin{array}{c}
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet
\end{array} \leftrightarrow \frac{(1-\beta)}{(1-\alpha\beta)} \left( \frac{1-\alpha}{y^3} + \frac{\alpha'}{y^2} - \frac{\alpha''}{2y^2} \right) + \]

\[ + \begin{array}{c}
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet
\end{array} \leftrightarrow \frac{-\beta(1-\beta)\alpha}{(1-\alpha\beta)^2} \left( \frac{1-\alpha}{y^3} + \frac{\alpha'}{y^2} \right) + \]

\[ + \begin{array}{c}
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet
\end{array} \leftrightarrow \frac{\beta(1-\alpha)(1-\beta)\alpha''}{2(1-\alpha\beta)^2 y^2} + \]

\[ + \begin{array}{c}
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet
\end{array} \leftrightarrow \frac{\beta^2 (1-\alpha)(1-\beta)\alpha^2}{(1-\alpha\beta)^3 y^2} \]  

(6.2.60)

\[ M_{\text{AABA}}(I) = \begin{array}{c}
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet
\end{array} \leftrightarrow \frac{(1-\alpha)\beta'}{(1-\alpha\beta)} \left( \frac{1-\alpha}{y^3} + \frac{\alpha'}{y^2} \right) + \]

\[ + \begin{array}{c}
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet
\end{array} \leftrightarrow \frac{\beta(1-\alpha)^2 \alpha' \beta'}{(1-\alpha\beta)^3 y^2} \]  

(6.2.61)

\[ M_{\text{AABB}}(I) = \]

\[ \begin{array}{c}
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet
\end{array} \leftrightarrow \frac{1}{1-\alpha\beta} \left( \frac{(1-\alpha)(1-\beta)}{y^3} + \frac{\alpha' (1-\beta)}{y^3} + \frac{\beta'(1-\alpha)}{y^3} + \frac{\alpha' \beta'}{y^2} \right) + \]

\[ + \begin{array}{c}
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet
\end{array} \leftrightarrow \frac{-\beta(1-\alpha)\alpha'}{(1-\alpha\beta)^2} \left( \frac{1-\beta}{y^3} + \frac{\beta'}{y^2} \right) + \]

\[ + \begin{array}{c}
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet
\end{array} \leftrightarrow \frac{-\alpha(1-\beta)\beta'}{(1-\alpha\beta)^2} \left( \frac{1-\alpha}{y^3} + \frac{\alpha'}{y^2} \right) + \]

\[ + \begin{array}{c}
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet \\
\bullet \bullet \bullet \bullet
\end{array} \leftrightarrow \frac{\alpha\beta\alpha' \beta'}{(1-\alpha\beta)(1-\beta)} \]  

(6.2.62)
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\[ M_{ABAB}(I) = \leftrightarrow \frac{2\alpha' \beta' (1-\alpha)(1-\beta)}{(1-\alpha\beta)^2 y^2} \quad (6.2.63) \]

\[ M_{ABBA}(I) = \leftrightarrow \frac{\beta' (1-\alpha)^2}{2(1-\alpha\beta)^2 y^2} + \]

\[ + \leftrightarrow \frac{\alpha (1-\alpha)^2 \beta^2}{(1-\alpha\beta)^2 y^2} \quad (6.2.64) \]

6.3 The Schultz-Zimm distribution

The Schultz-Zimm distribution

In this paragraph the expressions for the vertex functions derived in the previous paragraphs are used to determine the mean-field phase diagram in the first harmonics approximation of multiblock copolymers where the block lengths have a Schultz-Zimm distribution. The normalized Schultz-Zimm distribution is defined by

\[ P_n = \frac{k^k e^{-kn/n_n} n_n^{k-1}}{\Gamma(k)n_n^k} \quad (6.3.1) \]

where \( k > 0 \), and \( n_n \) is the number average block length. A usefull indication for the polydispersity of any distribution is the value of the parameter \( U \geq 0 \), which was defined in 3.1.2 by

\[ U = \frac{\langle (\Delta n)^2 \rangle}{\langle n \rangle^2} = \frac{n_w}{n_n} - 1 \quad (6.3.2) \]

where \( n_w \) is the weight averaged block length. Only for a monodisperse distribution we have \( U = 0 \), and its value becomes larger if the polydispersity increases. For the Schultz-Zimm distribution 6.3.1 one obtains

\[ U = \frac{1}{k} \quad (6.3.3) \]
Therefore, the polydispersity decreases with increasing $k$. For $k = 1$, the Schultz-Zimm distribution reduces to the exponential Flory distribution, studied in the previous chapters. In the limit $k \to \infty$, it becomes infinitely narrow, and the value of $U$ approaches zero. This corresponds to regular, monodisperse multiblock copolymers. In fig 6.1 the Schultz-Zimm distribution has been plotted for various values of $k$.

The second order vertex

In order to obtain the expressions for the vertices, we have to calculate the Laplace transforms $\alpha(y)$ and $\beta(y)$, which were defined in equation (6.2.13). First we assume that the value of $k$ is the same for both the A-blocks and the B-blocks. In that case one finds

$$\alpha(y) = \left(1 + \frac{f y}{k}\right)^{-k} \quad \beta(y) = \left(1 + \frac{(1-f) y}{k}\right)^{-k} \quad (6.3.4)$$
To see whether the position $q_*$ of the minimum of the second order vertex is positive or zero, it is sufficient to determine the slope of $\gamma_2$ at $y = 0 \iff q_* = 0$. If this slope is negative then $q_* > 0$, otherwise $q_* = 0$. Using 6.2.20 in combination with 6.3.4 one obtains

$$\left. \frac{d\gamma_2}{dy} \right|_{y=0} = \frac{1 + 12f - 12f^2 - k^2}{24(n_A + n_B)f^2(1-f)^2}$$

(6.3.5)

This result is illustrated in fig 6.2. Remember that the example of the correlated random copolymer (obtained by taking $k = 1$) shows that even if $q_* = 0$, the system can still undergo a transition to a microphase separated state.

**The influence of the polydispersity on the phase diagram**

The general expressions for the third and fourth order vertices were given in paragraph 6.2. For general values of $k$ the final expressions for the vertices cannot be presented in an elegant way. The phase diagrams shown in fig 6.3 were obtained by minimizing the free energy numerically with respect to the parameters $A$ and $y$. 
Fig 6.3 Mean-field phase diagrams for multiblock copolymers if the lengths of the A-blocks and the lengths of the B-blocks have the same Schultz-Zimm distribution, characterized by the value of $k$ given in the figures. For all these phase diagrams, the order in which the various structures appear if the segregation $N_{\chi}$ is increases, is given by: disordered–bcc–hexagonal–lamellar.

Fig 6.4 $q_*$ as a function of the rescaled distance to the spinodal for symmetric multiblock copolymers for various values of the inverse polydispersity $k$.

Fig 6.3 shows a series of phase diagrams for the situation where the A-blocks and the B-blocks have the same Schultz-Zimm distribution. Going from left to right, and from top to bottom, the value of $k$ increases, which corresponds to a decrease in polydispersity. This decrease in polydispersity has the following consequences for the phase diagram. First of all, the disorder-order transition line shifts upwards. This means that the polydispersity destabilizes the system. Second, for finite values of $k$ the border lines between the various ordered phases are linear functions of $f$ near the critical point, whereas they are parabolic if $k = \infty$. Another trend which is clear from fig 6.3 is the fact that the region of stability of the bcc structure shrinks considerably if the blocks become more monodisperse.
Fig 6.4 shows how, for symmetric co-polymers, the period of the arising micro-structure changes with the degree of segregation (the period $D$ is related to the radius $q_*$ of the first harmonics sphere via $D = l/q_*$). Two conclusion can be made from fig 6.4. First, if the average block length is kept constant, then the period will increase with increasing polydispersity. Second, if the polydispersity is large, then the period will decrease with increasing segregation, while if the polydispersity is small, the opposite will happen.

Fig 6.5, finally, shows the phase diagram for the situation where the $A$-blocks are monodisperse, while the $B$-blocks have a Flory distribution. The critical point shifts towards compositions where the polydisperse block type is in excess.

6.4 Concluding remarks

The analysis presented in this chapter can be extended in several ways. For instance, by taking into account the fluctuation corrections it is possible to consider chains with finite block lengths. In particular, it might be interesting to answer the following question. Both the correlated random copolymer, and the monodisperse regular multiblock copolymer belong to the same class of multiblock copolymers with blocks having a Schultz-Zimm distribution. For the monodisperse copolymer, characterized by $k = \infty$, the fluctuations-induced shift of the phase transition line scales like $\Delta N\chi \propto N^{-1/3}$, whereas for the correlated random copolymer, characterized by $k = 1$, it scales like $\Delta N\chi \propto N^{-1/4}$. Using the expressions derived in this chapter, it should be possible to determine the dependence of the scaling exponent on the value of the parameter $k$. Another possible extension of the presented analysis would be to take into account the higher harmonics, which makes the study of the phase behavior for stronger segregations possible. An rather restricting drawback of the first harmonics approximation
used in this chapter is that it predicts only the classical structures lamellar, hexagonal and bcc. Taking into account the higher harmonics could reveal regions of stability of more complex structures, such as the gyroid one. Although the expressions for the vertices given in paragraph 6.2 are not general since we imposed already at that point the first harmonics approximation, it seems that the generalization of these expressions can be obtained in a straightforward (although rather tedious) way. Another suggestion to continue this research is to investigate the consequences of a finite number of blocks per chain. However, this requires a lot more work, and would only be interesting if the possibility of macrophase separation is taken into account, since the microphase behavior converges rapidly with increasing number of blocks. Another way of proceeding from this point is to examine more closely the expressions for the vertices. For instance, it might be interesting to calculate, either analytically or numerically, the expression for the non-local term for multiblock copolymers having Schultz-Zimm block length distributions, and see if these expressions have the same physical origin as in the case of the correlated random copolymer (see the introduction of chapter 3). Of course, it would also be interesting to construct the phase diagrams for polymer melts consisting of molecules having more exotic architectures, such as comb copolymers, but it is clear that in that case one should restart the calculations from the beginning.