New Method for Phase Transitions in Diblock Copolymers: 
– The Lamellar Case

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Abstract

A new mean-field type theory is proposed to study order-disorder transitions (ODT) in block copolymers. The theory applies to both the weak segregation (WSL) and the strong segregation (SSL) regimes. A new energy functional is proposed without appealing to the random phase approximation (RPA). We find new terms unaccounted for within RPA. We work out in detail transitions to the lamellar state and compare the method to other existing theories of ODT and numerical simulations. We find good agreements with recent experimental results and predict that the intermediate segregation regime may have more than one scaling behavior.

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1 Introduction

Predicting morphologies of block copolymers continues to be a very challenging problem from the computational point of view. To make this latter task more feasible ‘nice’ energy functionals are needed and this is the goal of this paper. For linear copolymers, the self-consistent field method (SCFT) developed by Helfand and others [1–7] is considered to be the method of choice. It applies quite well to all regimes of segregations. Recently it was successfully used to predict different morphologies of linear triblock copolymers [6]. The method is based on a naive mean field approximation to the partition function. Fluctuation effects can also be added but at the expense of complicating the method [8].

Around the order-disorder transition point, Leibler’s [9] field theory for diblock copolymers is superior to the self-consistent field theory. For this reason there have been attempts to generalize it to all types of segregations, intermediate as well as strong segregations. Ohta and Kawasaki [10–12] were the first to propose a free energy functional of Leibler’s form that treats the strong segregation case of a diblock copolymer. It gives comparable results as the self-consistent method and its predictions are well supported by experiment [13, 14]. Fluctuation effects were later added to Leibler’s theory by Fredrickson, Helfand and Barrat [15–19] who showed that the peak of the scattering function not only depends on $\chi N$, the Flory-Huggins parameter, but also on the average segment length and volume. The Leibler free energy functional was also shown to be useful in the strong segregation case if the wave vector dependence of the energy functional is fully kept, since higher order spatial harmonics of the order parameter become more and more important as the temperature is lowered in the ordered phase [20, 21].

Here, we set to find a similar, but simpler, energy functional for incompressible diblock copolymers that is valid for both the weak and strong segregation regimes. Our work has the same spirit as the recent work of Stepanow [22] where he used graphical methods to obtain an improved self-consistent expression for the structure factor of a diblock copolymer. He avoided using the random phase approximation (RPA) [23], i.e., Leibler’s theory, and instead finds an expansion of the partition function in terms of an effective potential [24–26]. Here we adopt the same goal of developing an expression of the free energy based also on an effective potential. The random phase approximation will not be used to get our energy functional.

Besides succeeding in finding a new expression for the energy of a diblock copolymer, we also find new “ideal” terms missed by RPA and already found by Holyst and Vilgis [27] in the polymer mixture case.

Our method is strictly functional; we do not use any graphs. Our results to lowest order are similar to Stepanow result [22] and our energy functional is qualitatively the same as Leibler’s. The quartic term is similar to Leibler’s fourth order term but is much simpler to work with.

The paper is organized as follows. In section II, we develop the formalism. The details are left to the Appendix. In section III, we solve the transition to the lamellar...
morphology of a symmetric diblock. In section IV, we compare our results with those of the self-consistent method, Leibler’s method, and simulations \[28\].

2 Free Energy of a Block Copolymer

We start by deriving a new expression for the free energy of a block copolymer melt. Even though in this paper we are mainly interested in incompressible diblock copolymers, it can be easily generalized to, e.g., triblocks. The method we use bypasses the random phase approximation and the use of virtual sources, as was done originally by Leibler \[9\]. The Hamiltonian we use for our system is that of Edwards \[24\] generalized to copolymers and can be taken of the form:

\[
H = H_0 + V,
\]

\[
H_0[r_i] = \frac{3}{2N\sigma^2} \sum_{i=1}^{n} \int_0^N d\tau \left( \frac{d\mathbf{r}_i(\tau)}{d\tau} \right)^2
\]

\[
V[r_i] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \sum_{i,j=1}^{2} \rho_i(\mathbf{r})\rho_j(\mathbf{r}') V_{ij}(\mathbf{r}, \mathbf{r}'),
\]

\[i, j = A, B\] (1)

\(r_i\) is a curve along the \(i\)'th macromolecule that has two types of monomers \(A\) and \(B\) with densities \(\rho_A(\mathbf{r})\) and \(\rho_B(\mathbf{r})\), respectively. We assume both monomers to have the same Kuhn length \(\sigma\). There are \(n\) chains in the melt, each with \(f\) \((f = fN)\) monomers of type \(A\) and \((N - f)\) of type \(B\). The interaction potential \(V\) is taken to have the simple form

\[
V(\mathbf{r}, \mathbf{r}') = \rho_0 \left( \begin{array}{cc} 0 & \chi \\ \chi & 0 \end{array} \right) \delta(r_i(s) - r_j(s')), \quad (2)
\]

where \(\chi\) is the Flory-Huggins constant and \(\rho_0\) is the total average density of monomers. The partition function of this incompressible system of macromolecules is then given by

\[
\mathcal{Z} = \int d(\mathbf{r}_i) \delta(1 - \rho_A(\mathbf{r}) - \rho_B(\mathbf{r})) \exp \left[ - \left( H_0 + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \mathbf{\rho}^T(r) V(\mathbf{r}, \mathbf{r}') \mathbf{\rho}(\mathbf{r}') \right) \right].
\]

(3)

In the above we have set the Boltzmann constant to one and used a vector notation for the densities, i.e.

\[
\mathbf{\rho}(\mathbf{r}) = \left( \begin{array}{c} \rho_A(\mathbf{r}) \\ \rho_B(\mathbf{r}) \end{array} \right).
\]

(4)
The densities are given by

\[ \rho_A(r) = \frac{N}{\rho_0} \sum_{\alpha=1}^{n} \int_{0}^{f} ds \, \delta(r - r_\alpha(s)), \]  

(5)

and

\[ \rho_B(r) = \frac{N}{\rho_0} \sum_{\alpha=1}^{n} \int_{1}^{f} ds \, \delta(r - r_\alpha(s)). \]  

(6)

In \( \mathcal{Z} \), the second term in the exponential is a quadratic symmetric form and hence it can be diagonalized. This diagonalization allows us to deal with a new virtual set of monomers that are ‘decoupled’. We therefore introduce a new set of variables \( \rho_1 \) and \( \rho_2 \) such that:

\[ \rho_1(r) = \frac{1}{2}(\rho_A(r) + \rho_B(r)), \]  

(7)

\[ \rho_2(r) = \frac{1}{2}(\rho_A(r) - \rho_B(r)). \]  

(8)

In this new set of variables the potential becomes diagonal with

\[ V_{11} = 2\rho_0 \chi, \]  

(9)

\[ V_{22} = -2\chi \rho_0, \]  

(10)

\[ V_{12} = V_{21} = 0. \]  

(11)

Ignoring the incompressibility condition for now and after isolating the free energy of the disordered state we have

\[ \mathcal{Z} = \int \mathcal{D}r_i \exp\{ -\frac{1}{2} \Delta \rho_\alpha \mathbf{V}_{\alpha\beta} \Delta \rho_\beta - \rho_0^0 \mathbf{V}_{\alpha\beta} \Delta \rho_\beta \} \times \exp\{ -\frac{1}{2} \rho_0^0 \mathbf{V}_{\alpha\beta} \Delta \rho_\beta^0 \}, \]  

(12)

where

\[ \mathcal{D}r_i = d(r_i) \exp(-H_0), \]

and

\[ \Delta \rho_\alpha(r) = \rho_\alpha(r) - \rho_\alpha^0, \quad \alpha = 1, 2. \]
For a symmetric diblock,
\[ \rho^0 = \begin{pmatrix} \frac{1}{2} \\ 0 \end{pmatrix} \] (13)

Upon introducing a two-component Hartree-type field \( \varphi_\alpha \) with which these new virtual molecules are interacting, the partition function becomes
\[
Z = \int \mathcal{D}(r_i) \mathcal{D} \varphi \exp\left\{ -\frac{1}{2} \int \mathcal{D}r \mathcal{D}r' \varphi_\alpha(r) V_{\alpha\beta}^{-1}(r, r') \varphi_\beta(r') + i \int \mathcal{D}r \left[ \varphi_\alpha(r) + i \rho^0_\beta V_{\alpha\beta} \right] \cdot \Delta \rho_\alpha(r) \right\}. \tag{14}
\]

We introduce now two more fields, \( \Phi \) and \( \mu \). Since
\[
\int \mathcal{D} \Phi \alpha \delta(\Phi_\alpha(r) - \Delta \rho_\alpha(r)) = 1, \tag{15}
\]
then we have
\[
Z = \exp(-F_0) \int \mathcal{D} \varphi \mathcal{D} \Phi \mathcal{D} \mu \mathcal{D}(r_i) \exp\left\{ -i \mu_\alpha \Phi_\alpha \right\} \times \exp\left\{ -\frac{1}{2} \varphi_\alpha V_{\alpha\beta}^{-1} \rho_\beta + i (\rho_\alpha + \mu_\alpha + i \rho^0_\beta V_{\alpha\beta}) \Delta \rho_\alpha \right\}, \tag{16}
\]
where
\[ F_0 = n\chi N f (1 - f). \tag{17} \]
is the energy of the disordered state. Now, we make a change of variables and let
\[
\varphi_\alpha(r) = \varphi_\alpha(r) + \mu_\alpha(r) + i \int dr V_{\alpha\beta}(r) \rho^0_\beta(r). \tag{18}
\]

We also define a new functional
\[
F[\varphi] \equiv \ln \left( \int \mathcal{D}(r_i) \exp\left[ -\left( H_0(r_i) + i \int \mathcal{D} r \varphi(r) \cdot \rho(r) \right) \right] \right). \tag{19}
\]
This functional can be expanded in \( \varphi \) around a homogeneous state
\[
F[\varphi] = \sum_{m=0}^\infty \frac{1}{m!} \sum_{\{\alpha\}} \int \ldots \int \mathcal{D}r_1 \mathcal{D}r_2 \ldots \mathcal{D}r_m C_{\alpha_1 \alpha_2 \ldots \alpha_m} (r_1, r_2, \ldots, r_m) \times \varphi_{\alpha_1} (r_1) \varphi_{\alpha_2} (r_2) \ldots \varphi_{\alpha_m} (r_m) \tag{20}
\]
\[ \alpha_i = 1, 2. \]
The coefficients $C_{\alpha\beta...}$ are given in Appendix A. In the following we keep only terms up to the fourth order. After some rearrangements and writing $\varphi$ in place of $\overline{\varphi}$, we have the following expression for the partition function,

\[
Z = \int \mathcal{D}\Phi \mathcal{D}\mu \mathcal{D}\varphi \exp\left\{ -\frac{1}{2} \varphi_\alpha (V^{-1}_{\alpha\beta} + C_{\alpha\beta}) \varphi_\beta \\
- \frac{1}{4!} C_{\alpha\beta\lambda\gamma} \varphi_\alpha \varphi_\beta \varphi_\lambda \varphi_\gamma + i \Xi_\alpha \varphi_\alpha \right\} \times \int \mathcal{D}\Psi \exp\left\{ \frac{1}{4!} C_{\alpha\beta\lambda\gamma} (\Psi_{\alpha\beta} - \varphi_\alpha \varphi_\beta)(\Psi_{\lambda\gamma} - \varphi_\lambda \varphi_\gamma) \right\}.
\]

Here we have introduced a new pairing field $\Psi_{\alpha\beta}$ so we can cancel the quartic term in $\varphi_\alpha$. We have also set

\[
i \Xi(\mathbf{r}) = i \rho_\alpha^0 + V^{-1}_{\alpha\beta} \mu_\beta(\mathbf{r}),
\]

and have not written the space integrals explicitly. Then, we can integrate the $\varphi$ field and then the $\mu$ field exactly. We are left with only two fields $\Phi$ and $\Psi$ (see Appendix B)

\[
Z = \int \mathcal{D}\Phi \mathcal{D}\Psi \exp\{ -\mathcal{F}(\Phi, \Psi) \},
\]

where

\[
\mathcal{F}(\Phi, \Psi) = -\frac{1}{4!} \Psi_{\alpha\beta} C_{\alpha\beta\lambda\gamma} \Psi_{\lambda\gamma} + \frac{1}{2} \rho_\alpha^0 A^{-1}_{\alpha\beta} \rho_\beta^0 \\
+ \frac{1}{2} \zeta_0^0 B^{-1}_{\alpha\beta} \zeta_0^0 + \frac{1}{2} \log \det A_{\alpha\beta} + \frac{1}{2} \log \det B_{\alpha\beta},
\]

and

\[
\zeta_\alpha(\mathbf{r}) = \Phi_\alpha(\mathbf{r}) + \rho_\alpha^0 - V^{-1}_{\alpha\beta} A^{-1}_{\beta\lambda} \rho_\lambda^0,
\]

\[
A = (1 + \frac{1}{6} \Delta U) U^{-1}, \\
B = V^{-1} - V^{-1} A^{-1} V, \\
\Delta_{\alpha\beta} = \Psi_{\lambda\gamma} C_{\lambda\gamma\alpha\beta}, \\
U_{\alpha\beta} = (V_{\alpha\beta} + C_{\alpha\beta})^{-1}.
\]

In the above $A$, $B$, $\Delta$, and $U$ are spatial dependent matrices. $U_{\alpha\beta}$ is the desired effective potential \[24\]. We expand the logarithmic terms in powers of $U$. We do the same when we seek an expression for $B$. In all expansions, we keep only quadratic terms in $\Psi$. The final lowest order expression we get from this expansion is our expression for the energy.
\[ H(\Phi) = \frac{1}{2\text{vol}} \sum_q \Phi(q) \left( \frac{1}{C_{22}(q)} - 2\chi \rho_0 \right) \Phi(-q) \]  

\[ -\frac{1}{3!} \frac{1}{\text{vol}^2} \sum_p \Phi(q) \frac{C_{2222}(q, -q, p, -p)}{[C_{22}(q)]^2 C_{22}(p)} \Phi(-q) \]  

\[ -\frac{1}{4!} \frac{1}{\text{vol}^3} \sum_{q_1q_2q_3} \frac{C_{2222}(q_1, q_2, q_3, -q_1 - q_2 - q_3)}{C_{22}(q_1)C_{22}(q_2)C_{22}(q_3)C_{22}(q_1 + q_2 + q_3)} \times \Phi(q_1)\Phi(q_2)\Phi(q_3)\Phi(q_1 + q_2 + q_3). \]  

It can be easily shown that \( \text{vol}/(2nC_{22}(q)) \) is actually Leibler’s structure function. Leibler’s structure function \( S(q) \) is given by (Appendix A)

\[ S^{-1}(q) = \frac{S_{AA}(q) + 2S_{AB}(q) + S_{BB}(q)}{S_{AA}(q)S_{BB}(q) - S_{AB}^2(q)}. \]  

This is indeed equivalent to \( C_{22}^{-1}(q) \) with the proper normalization. However it is easier to see this graphically and in fig.1, we plot this function. Hence the first and the second terms are the usual RPA result for the inverse scattering function. The third term is new and is not captured by the RPA approximation. It is not due to fluctuations. It has been first pointed out by Holyst and Vilgis in their study of polymer blends [27]. The fourth term is familiar but the coefficient is much simpler to calculate and behaves differently than Leibler’s term for large wave vectors. In fig.2, we plot both terms for a subset of wavenumbers. Our fourth order coefficient is given by
Figure 1: The two body correlation function, $C_{22}(q)$, in our diagonalized system of collective densities.
Figure 2: Comparison of fourth order coefficients of this theory and Leibler's RPA theory.
\[ C^{(4)}(q_1, q_2, q_3, -q_1 - q_2 - q_3) = \frac{C_{2222}(q_1, q_2, q_3, -q_1 - q_2 - q_3)}{C_{22}(q_1)C_{22}(q_2)C_{22}(q_3)C_{22}(q_1 + q_2 + q_3)}. \] (28)

This term is independent of any three-body correlation functions. Leibler’s \( \Gamma^{(4)} \) term does however depend on three body correlation terms, and this greatly complicates computations involving it; it is given by

\[ \Gamma^{(4)}(q_1, q_2, q_3, -q_1 - q_2 - q_3) = \gamma_{ijkl}(q_1, q_2, q_3, -q_1 - q_2 - q_3) \left( S_{iA}^{-1}(q_1) - S_{iB}^{-1}(q_2) \right) \left( S_{jA}^{-1}(q_2) - S_{jB}^{-1}(q_3) \right) \left( S_{kA}^{-1}(q_3) - S_{kB}^{-1}(q_4) \right). \] (29)

with \( i, j, k, l = A, B \). \( \gamma_{ijkl} \) is a function of two-point, three-point and four-point correlation functions. In fig.2, we plot both coefficients for \( q_1 = -q_2 = q_3 = -q_4 \).

To lowest order, the propagator of this theory also agrees with that of Stepanow [22], except that our self-energy term has additional contributions from the fourth term, \( Tr(\Lambda U) \), of the free energy in Eq.(B-7). Hence to consider any fluctuations this term must be included from the outset and therefore the work in [22] is more thorough than the one presented, e.g., in [16] and others based on RPA. In the next section where we use our functional to study transitions from a disordered state to a lamellar state, we will not include the quadratic non-RPA term in order to compare our functional with that of Leibler’s.

### 3 The Lamellar Solution

Following Melenkevitz and Muthukumar [20], we conjecture a solution that minimizes the energy functional. Knowing that in SCFT the densities are found by solving a modified heat equation, we choose a function of the following form

\[ \Phi(x) = \sum_{l=1,3,...} \frac{2}{\pi l} \exp[-\frac{1}{2}(q_l \lambda)^2] \sin(q_l x). \] (30)

This choice is also dictated by the fact that

\[ \int dx \Phi(x) = 0, \] (31)

and the solution must be periodic. The wave vector \( q \) is given by

\[ q_l = \frac{2\pi l}{D}, \] (32)

where \( D \) is the lamellar periodicity. \( \lambda \) is another parameter besides \( D \) that is related to the wall thickness of the interface region between the two components of the diblock.
copolymers. Both parameters are to be found by minimizing the energy \( H \) with respect to them. Actually, we solve for \( \lambda \) for a given \( D \) and then calculate the corresponding energy and choose the solution with the lowest energy. We rescale dimensions in terms of the radius of gyration so the energy per chain is given by

\[
H/n = \frac{1}{2} \sum_{m=1,3,\ldots} b_m^2 \left( \frac{\text{vol}}{2nC_{22}(m)} - \chi N \right) - \frac{1}{384} \sum_{m=\pm1,\pm3,\ldots} b_m b_p b_r b_s C_{2222}(m, p, r, s) \frac{C_{22}(m) C_{22}(p) C_{22}(r) C_{22}(s)}{C_{22}(m) C_{22}(p) C_{22}(r) C_{22}(s)},
\]

where

\[
b_m = \frac{2}{\pi m} \exp\left(-\frac{1}{2}(2\pi m\lambda/D)^2\right).
\]

Figures 3-8 summarize all the results about this particular solution. In particular, we observe that this solution predicts that the order-disorder transition (ODT) occurs for \( \chi N \) right below 10.5. Immediately below the transition temperature, our energy functional shows that the behavior of the polymer chains is no longer Gaussian. For Gaussian chains, the scaling factor \( \delta \) between \( \ln(D) \) and \( \ln(\chi N) \) is zero. In our case, we find that for \( \chi N \) less than 13, \( \delta \) is approximately equal to 0.26. For \( \chi N \) between 13 and 30, \( \delta = 0.52 \), and for \( \chi N \) above 30, \( \delta \) becomes about 0.19. Hence the 2/3-power law between \( D \) and \( N \) in the SSL is also verified by this solution. So far only one intermediate region has been observed [13]. Here, this solution suggests that the intermediate region is really more than one. Since the behavior below the ODT is believed to be nonuniversal, it will be interesting to see if this predicted behavior is also observed in some symmetric diblock copolymers other than the one treated in [13]. The inclusion of the non-RPA term that we omitted in this solution will not change this overall picture. It has only a moderate effect at high values of \( \chi N \) where higher and higher wavenumbers are needed in the energy.
Figure 3: Density profiles for the lamellar morphology given by Eq.(30) for $\chi N = 10.5, 11, 12, 25, 50, 100$. 
4 Comparison and discussion:

In fig.3, we plot density profiles for different $\chi N$’s. We observe that the order-disorder transition occurs below $\chi N = 10.5$. The segregation amplitude grows much faster for $\chi N$ just above the ODT temperature $\chi N_c$ and less than 30. Hence in this theory, the strong segregation regime is attained much faster than the self-consistent method (SCFT) predicts [5]. This is also confirmed by recent experiments on symmetric diblock copolymers [13]. Figure 4 compares our results to that of the SCFT calculations at $\chi N = 12.5$ and simulations [28]. The simulation was done with chains of forty-eight segments. Assuming that the critical temperature, $\chi N_c$, for these chains is also close to 10.495 as is the case for infinite chains, we find that the simulation gives a result that falls between our result and the SCFT result. However the ODT temperature for these short chains is expected to be less than in the ideal case. The SCFT curves were found by solving Eqs.(3-7), that appear in [5], using a finite difference method and using a random configuration as an input. Our results agree well with those given in [7]. In fig.5, we instead predict the $\chi N$ value for which our theory coincides with the simulation results. We find a $\chi N$ value of approximately 11.15. Assuming now that $\chi N/\chi N_c = 1.2$ corresponds to $\chi N = 11.15$ in our theory, we plot in fig.6 and fig.7 density profiles for $\chi N = 22.3$ and $\chi N = 44.5$ and compare our results against those of simulation. We find relatively good agreements between theory and simulation especially far from the interfaces. Finally, in fig.8, we check if our theory predicts the observed scaling behavior. Clearly, we can distinguish three regimes from the plot. The intermediate regime extends from about $\chi N = 13$ and to about $\chi N = 27$, has a scaling factor $\delta$ of about 0.52. Above $\chi N = 30$, the scaling factor is about 0.19, in agreement with observations [13]. Compared to Leibler’s energy functional [21], our results are much closer to the SCF. This is due to the fourth order term which is smaller than Leibler’s fourth order term for large wavenumbers. For large $\chi N$, our energy functional gives closer periods to the SCFT method than the full Leibler Hamiltonian [21] that overestimates periods by as much as 30 %. Moreover, our theory predicts that transition to the strong segregation regime occurs at $\chi N \approx 30$. In complete agreement with the experimental results in [13]. In the SCFT, the SSL is believed to occur around $\chi N = 50$. Ref. [20] suggests that the SSL starts to occur for $\chi N$ larger than 90.
Figure 4: Density profiles of the symmetric lamellar solution for $\chi N = 12.5$. The Simulation is done for $\chi N / \chi N_c = 1.2$. 
Figure 5: Comparison of density profiles for $\chi N/\chi N_c = 1.2$. The simulation curve is at $\chi N/\chi N_c = 1.15$. The simulation curve is at
Figure 6: Comparison of density profiles for $\chi_N = 22.3$. The simulation curve is at $\chi_N/\chi_N^c = 2.4$. 

Equation 30 (SCFT) and simulation results are shown in the graph.
Figure 7: Comparison of density profiles for $\chi_N = 44.5$. The simulation curve is at $\chi_N/\chi_{N_c} = 4.8$. 

Equation 30

Simulation

SCFT
Figure 8: log of $\ln D$ vs. $\ln(\chi N)$ for a symmetric lamellar morphology. For high $\chi N$, the scaling factor is approximately 0.69. $\delta$ is the slope of the best fit segment to the data in three different regions. The weak segregation limit (WSL), the intermediate segregation configuration (ISC) and the strong segregation limit (SSL).
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Appendix

Appendix A

Let \( Q \) be a partition function of a melt of polymer chains in external fields \( \varphi_1 \) and \( \varphi_1 \)

\[
Q[\varphi_i] = \int D(r) \exp\{-i\varphi_1\Sigma\phi - i\varphi_2\Delta\phi\} \tag{A-1}
\]

where

\[
\Delta\phi = (1 - f)\varphi_1 - f\varphi_2 \tag{A-2}
\]

\[
\Sigma\phi = \varphi_1 + \varphi_2 - 1
\]

\( \varphi_1, \varphi_2 \) are densities.

We next expand \( \log Q \) in terms of \( \varphi_1 \) and \( \varphi_2 \). Since \( Q \) should be invariant under \( \Delta\phi \rightarrow -\Delta\phi \) and \( \Sigma\phi \rightarrow -\Sigma\phi \), only even powers of \( \varphi_i \) are present, hence we write:

\[
\log Q = -\frac{1}{2!} \int dx_1 dx_2 \ C_{\alpha\beta}(x_1, x_2) \varphi_\alpha(x)\varphi_\beta(y) + \frac{1}{4!} \int dx_1...dx_4 C_{\alpha\beta\gamma\delta}(x_1, ..., x_4) \varphi_\alpha(x_1)...\varphi_\delta(x_4) + ...
\]

where, e.g.,

\[
C_{22}(x_1, x_2) = <\Delta\varphi(x_1)\Delta\varphi(x_2)>_0 \tag{A-4}
\]

\[
C_{2222}(x_1...x_4) = <\Delta\varphi(x_1)...\Delta\varphi(x_4)>_0 \tag{A-5}
\]

\[- C_{22}(x_1, x_2)C_{22}(x_3, x_4)
\]

\[- C_{22}(x_1, x_3)C_{22}(x_2, x_4)
\]

\[- C_{22}(x_1, x_4)C_{22}(x_2, x_4)
\]

The averages \( <...>_0 \) are evaluated with a Gaussian distribution. Hence we find

\[
C_{22}(q) = S_{AA}(q) - 2S_{AB}(q) + S_{BB}(q)
\]

with

\[
S_{AA}(x) = \frac{2}{x^2}(f_A(x) + \exp(-f_A(x)) - 1)
\]

\[
S_{AB}(x) = -\frac{1.0}{x^2}(\exp(-f_B(x)) - 1 - \exp(-x) + \exp(-f_A(x))
\]

and \( x = q^2\sigma^2N/6 \)

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Similar expressions for the other correlation functions, such as $C_{2222}$, can straightforwardly derived, but with much more labor. It amounts to calculating all correlation functions, $G_{\alpha\beta\gamma\delta}(x_1, x_2, x_3, x_4)$, in the Gaussian distribution of the form

$$G_{\alpha\beta\gamma\delta}(x_1, x_2, x_3, x_4) = \int ds_{1,\alpha} \int ds_{2,\beta} \int ds_{3,\gamma} \int ds_{4,\delta} \left\langle \delta(x_1 - x(s_{1,\alpha}))\delta(x_2 - x(s_{2,\beta}))\delta(x_3 - x(s_{3,\gamma}))\delta(x_4 - x(s_{4,\delta})) \right\rangle_0$$

where $\alpha, \beta, \gamma, \delta = 1, 2$. Hence $C_{2222}$ will be a linear combination of all these functions.

**Appendix B**

We start from

$$Z = \int D\Phi D\Psi \exp\{-i\mu_\alpha \Phi_\alpha - \frac{1}{2} \mu_\alpha V_{\alpha\beta}^{-1} \mu_\beta - i\rho_0^\alpha \mu_\alpha\}$$

$$\times \int D\varphi \exp\{-\frac{1}{2} \varphi_\alpha (V_{\alpha\beta}^{-1} + C_{\alpha\beta}) \varphi_\beta + i\Xi_\alpha \varphi_\alpha - \frac{1}{12} \Psi_{\alpha\beta} C_{\alpha\beta\lambda\delta} \varphi_\lambda \varphi_\delta\}$$

The integral over $\varphi$ is Gaussian and can be done exactly. If we set

$$A_{\alpha\beta} = V_{\alpha\beta}^{-1} + C_{\alpha\beta} + \frac{1}{6} \Psi_{\lambda\delta} C_{\alpha\beta\lambda\delta}$$

we have:

$$Z = \int D\Phi D\Psi \exp\{-\frac{1}{4!} \Psi_{\alpha\beta} C_{\alpha\beta\lambda\gamma} \Psi_{\lambda\gamma} - \frac{1}{2} \rho_\alpha^0 A_{\alpha\beta}^{-1} \rho_\beta^0 - \frac{1}{2} \text{Tr} \log A_{\alpha\beta}\}$$

$$\times \int D\mu \exp\{-\frac{1}{2} \mu_\alpha V_{\alpha\beta}^{-1} \mu_\beta - i\mu_\alpha \Phi_\alpha - i\rho_0^\alpha \mu_\alpha + \frac{1}{2} \mu_\alpha V_{\alpha\beta}^{-1} A_{\alpha\beta}^{-1} V_{\gamma\lambda}^{-1} \mu_\gamma$$

$$+ i\mu_\alpha V_{\alpha\beta}^{-1} A_{\beta\lambda}^{-1} \rho_\lambda^0\}$$

Again the $\mu$–integral is Gaussian. After integrating out $\mu$, we have

$$Z = \int D\Phi D\Psi \exp\{-\frac{1}{4!} \Psi_{\alpha\beta} C_{\alpha\beta\lambda\gamma} \Psi_{\lambda\gamma}$$

$$- \frac{1}{2} \rho_\alpha^0 A_{\alpha\beta}^{-1} \rho_\beta^0 - \frac{1}{2} \text{Tr} \log A_{\alpha\beta}$$

$$- \frac{1}{2} \zeta_\alpha B_{\alpha\beta}^{-1} \zeta_\beta - \frac{1}{2} \text{Tr} \log B_{\alpha\beta}\}$$

$$:= \int D\Phi D\Psi \exp\{-F(\Phi, \Psi)\}$$

If we set

$$T^{-1} = V^{-1} - V^{-1} UV^{-1},$$

$$21$$
leave out terms of order \((C_{\alpha\beta\lambda\gamma})^2\); and use the incompressibility constraint, i.e.,

\[
\begin{align*}
\rho_2^0 &= 0 \\
\Phi_1 &= 0
\end{align*}
\]  
(B-6)

we get after some quite heavy algebra the following simple form:

\[
\mathcal{F}(\Phi, \Lambda) = \frac{1}{2} \int dx_1 dx_2 \Phi(1) T(1, 2) \Phi(2) - \frac{1}{4!} \int dx_1 \ldots dx_4 \Lambda(1, 2) C_{2222}^{-1}(1, 2, 3, 4) \Lambda(3, 4)
\]

\[
- \frac{1}{2} \int dx_1 \ldots dx_8 \Phi(1) (TV^{-1}U)(1, 3) \Lambda(4, 5)(UV^{-1}T)(5, 8) \Phi(8)
\]

\[
+ \frac{1}{12} \int dx_1 dx_2 \Lambda(1, 2) U(2, 1)
\]

\[
+ \frac{1}{12} \int dx_1 \ldots dx_6 (TV^{-1}U)(1, 4) \Lambda(4, 5)(UV^{-1}T)(6, 1)
\]

where

\[
\Lambda(x_1, x_2) = \int dx_3 dx_4 C_{2222}(1, 2, 3, 4) \Psi(3, 4)
\]  
(B-8)

and

\[
\Phi(x) = \Phi_2(x)
\]

Now we can integrate over \(\Lambda\) since the integral is only Gaussian, and we find that

\[
Z = \int \mathcal{D}\Phi \exp\{-\mathcal{F}(\Phi)\}
\]  
(B-9)

where

\[
\Delta\mathcal{F}(\Phi) = \mathcal{F}(\Phi) - \mathcal{F}_0
\]  
(B-10)

\[
= \frac{1}{2\text{vol}} \sum_q \Phi(q)[T(q)
\]

\[
- \frac{1}{6 \text{vol}} \sum_p C_{2222}(q, -q, p, -p) C_{22}(p) C_{22}(q) C_{22}(p) \Phi(-q)
\]

\[
- \frac{1}{24 \text{vol}^3} \sum_{q, p, k} C_{2222}(q, p, k, -(q + p + k)) C_{22}(q) C_{22}(p) C_{22}(k) C_{22}(q + p + k)
\]

\[
\times \Phi(q) \Phi(p) \Phi(k) \Phi(-p - q - k)
\]

and

\[
T(q) = \frac{1}{C_{22}(q)} + V_{22}(q)
\]  
(B-11)

is now the effective potential for the two-component incompressible copolymer melt.
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