Extension of the Theory of Microphase Separation in Block Copolymer Melts beyond the Random Phase Approximation

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ABSTRACT: By using the diagram technique method, we introduce the collective variables in the theory of copolymer melts without appealing to the random phase approximation. The main result of this work is that the fluctuations in the collective structure factor directly couple to the individual structure factors of the block copolymer chain entering the Leibler expression of the collective structure factor. The expansion parameter, which controls the fluctuations, is found to be proportional to the Flory−Huggins χ parameter. We apply our method to compute the collective structure factor of a diblock copolymer melt above the microphase separation (MST) in a self-consistent way. Below the MST, we predict that the individual quantities of the copolymer melt (gyration radius, R_g; mean-square end-to-end distance of the block copolymer, R^2) become explicitly dependent on the order parameter and compute this dependence for R^2 up to the lowest order.

I. Introduction

The phenomenon of the microphase separation of a diblock polymer melt has been the subject of investigations over the last 30 years (refs 1−7 and the references cited therein). The understanding of the weak segregation limit is based on the mean-field theory developed by Leibler[2] and its extension by Fredrickson and Helfand[3] to include the fluctuations of the order parameter. The theory of Leibler is based on the method of Edwards (see ref 8) of introducing the "collective" coordinates instead of the coordinates of polymer chains and the random phase approximation (RPA) introduced previously by de Gennes[9] (see also ref 10). By using this method, Leibler derived a free energy function as an expansion in powers of the order parameter, enabling the study of the weak segregation limit in the context of the Landau theory of phase transitions. This mean-field theory and its extension by Fredrickson and Helfand, who have taken into account the fluctuations in the order parameter in the framework of the Hartree approach developed previously by Brasovskii,[11] have been able to explain the different morphologies of the ordered phase and to describe qualitatively the scattering data in the disordered phase. Thus, the Leibler−Fredrickson−Helfand theory of microphase separation in block copolymer melts achieved considerable success in understanding the phenomenon of the microphase separation. However, this theory uses the random phase approximation, which contains uncontrolled approximations, which so far have not been analyzed in the literature. This circumstance makes it appropriate to analyze the basis of the theory of microphase separation, especially the random phase approximation. The establishment of new phases in recent experiments by Bates and co-workers (ref 12 and the references cited therein), which are not explained by present theories, is an additional and more practical reason to analyze the assumptions of the existing theories of microphase separation.

The most striking discrepancy between RPA and experiment concerns the behavior of the collective structure factor of the copolymer melt. The RPA predicts that the collective structure factor of the diblock copolymer melt $S_{cc}(q) = \langle \delta\Phi_A(q)\delta\Phi_A(-q)\rangle$ [$\delta\Phi_A(r) = \rho_A(r) - f\rho_m$, $\rho_A(r)$ is the monomer density of the A monomers, ρ_m is the average monomer density of the melt, and f is the polymer composition] achieves its maximum at the momentum q^*, obeying the condition $x^* = q^*R_g = 1.945$ for $f = 1/2$ (R_g is the unperturbed gyration radius of the copolymer chain), with x^* being independent of both temperature and molecular weight. This prediction of RPA disagrees with the experimental findings[13−18] and the results of Monte Carlo simulations[19,20] showing a dependence of x^* on both temperature and molecular weight. Moreover, Monte Carlo simulations have shown that the collective length associated with q^* increases faster than the single-chain length associated with single-chain properties, such as the gyration radius of a copolymer chain in the melt, and that the dependence of q^* on the temperature appears gradually with decreasing temperature. In addition, the recent experiments of Bates et al.[16] and the Monte Carlo simulations by Fried and Binder[20] have shown that a region exists above the MST where q^* shows the following power law dependence on N: $q^* \sim N^{-0.8}$. There are only a few theoretical investigations on the problem of T and N dependence of q^*.[21−23] Barrat and Fredrickson[21] extended the Fredrickson and Helfand theory to take into account the q dependence of the vertex function. Their approach is still based on RPA. David and Schweizer[23] recently developed a theory of microphase separation in block copolymer melts based on the extension of the theory of low molecular liquids developed by Chandler and Andersen[24] to polymer systems. Their work goes beyond RPA, but because the basis of their theory is quite different from that of the Leibler−Fredrickson−Helfand theory, it does not contain an analysis of RPA.

The aim of this article consists of extending the theory of microphase separation in block copolymer melts without the use of the random phase approximation (RPA). The essential point of the present approach consists of introducing the collective variables in the theory of polymer melts by using the diagram technique, which enables one to avoid the use of the random phase approximation. In this way, we are able to analyze the terms missed in RPA and study their effects. The main result of our article is the prediction of the manner in

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which fluctuation effects couple to the mean-field theory and of the expansion parameter controlling the fluctuations. In contrast to the previous study, where the fluctuations essentially modify the Flory–Huggins parameter χ in the Leibler expression of the collective structure factor $S_{cc}(q)$ for an incompressible melt,

$$S_{cc}(q) = \rho_m/(S^{-1}_{0,11}(q) + S^{-1}_{0,22}(q) - 2S^{-1}_{0,12}(q) - 2\chi) \quad (1)$$

with $S^{-1}_{0,\alpha\beta}(q)$ being the inverse of the matrix (with respect to the indices α and β) of the unperturbed scattering functions of a copolymer chain, we have shown that the fluctuations directly couple to the structure factors of the copolymer chains entering $S_{cc}(q)$. Within RPA the expansion parameter is essentially the coefficient in front of the Φ^4 term in Leibler's free energy expansion, which is independent of the temperature, taking into account the corrections to RPA modify the expansion parameter so that it becomes proportional to χ and thus becomes explicitly dependent on the temperature.

This article is organized as follows. Section II introduces to the diagrammatics of introducing the collective variables in the theory of block copolymer melts. Section III presents the results of the self-consistent computation of the collective structure factor of the copolymer melt. Section IV presents the results of computing the structure factor of the copolymer chain in the melt and the gyration radius. Section V treats the jump in the mean-square end-to-end distance of the copolymer chain at the order–disorder transition. Sections VI and VII contain the discussion and conclusions.

II. The Formalism

In studying dense systems such as polymer melts, it is convenient to introduce the collective densities instead of the positions of the polymer chains. In introducing the collective description, we mainly follow Edwards.[8] In contrast to previous studies,[2,3,10] we carry out the procedure of introducing the collective variables by using the method of diagrams. The Edwards free energy (in units of kT) associated with n copolymer chains confined to a volume V is given by

$$F = \frac{3}{2l}\sum_{i=1}^{n}\int_0^L ds\ (\partial r_i/\partial s)^2 +$$

$$\frac{1}{2}\sum_{ij=1}^{n}\int_0^{fL} ds_i \int_0^{fL} ds_j\ V_{11}(r_i(s_i) - r_j(s_j)) +$$

$$\frac{1}{2}\sum_{ij=1}^{n}\int_{fL}^{L} ds_i \int_0^{fL} ds_j\ V_{21}(r_i(s_i) - r_j(s_j)) +$$

$$\frac{1}{2}\sum_{ij=1}^{n}\int_0^{fL} ds_i \int_{fL}^{L} ds_j\ V_{12}(r_i(s_i) - r_j(s_j)) +$$

$$\frac{1}{2}\sum_{ij=1}^{n}\int_{fL}^{L} ds_i \int_{fL}^{L} ds_j\ V_{22}(r_i(s_i) - r_j(s_j)) \quad (2)$$

where the matrix of interactions between the s_ith segment of the ith copolymer chain and the s_jth segment of the jth chain, $V_{\alpha\beta}(r_i(s_1) - r_j(s_2))$ ($\alpha, \beta = 1, 2$) is given by

$$V(r_i(s_1) - r_j(s_2)) = \begin{pmatrix} V & V+\chi \\ V+\chi & V \end{pmatrix} \delta^{(3)}(r_i(s_1) - r_j(s_2))$$

Following Edwards, we introduce, instead of individual coordinates of polymer chains $r_i(s)$ ($i = 1, ..., n$, $s \in [0, L]$, where L is the arc length of the chain), the collective densities of the polymer $\rho_1(r) = l^{-1}\sum_{i=1}^{n}\int_0^{fL} ds\ \delta(r - r_i(s))$ and $\rho_2(r) = l^{-1}\sum_{i=1}^{n}\int_{fL}^{L} ds\ \delta(r - r_i(s))$, where n is the number of polymer chains in the melt, l is the statistical segment length, and $L = Nl$. The interaction energy between the segments can be represented with help of the densities $\rho_1(r)$ and $\rho_2(r)$ as follows:

$$F_{int} = \frac{1}{2}\int dr_1 \int dr_2\ \rho_\alpha(r_1) V_{\alpha\beta}(r_1 - r_2)\rho_\beta(r_2)$$

where summation over α and β, which take the values 1 and 2, is assumed. The partition function is given by

$$Z = \int Dr_i(s)\ \exp(-F_{el} - F_{int}) \quad (3)$$

where F_{el} is the elastic part of the free energy given by the first term of eq 2. By introducing an auxiliary field $\Phi_\alpha(r)$, we represent the partition function as follows:

$$Z = \int Dr_i(s) \int D\Phi\, \delta^{(\infty)}(\Phi - \rho)\ \exp\left(-F_{el} - \frac{1}{2}\Phi V \Phi\right) = \int D\Phi\ \exp\left(-\frac{1}{2}\Phi V \Phi\right) \langle \delta^{(\infty)}(\Phi - \rho)\rangle_0 \quad (4)$$

where the abbreviation $\langle \delta^{(\infty)}(\Phi - \rho)\rangle_0 = \int Dr_i(s)\ \exp(-F_{el})\delta^{(\infty)}(\Phi - \rho)$ is introduced. The factor $1/\mathcal{V}$, where $\mathcal{V}$ is the volume of the system, is included in the measure $Dr_i(s)$. In both the preceding and the following expressions, we do not write explicitly the matrix indices of the quantities Φ, V, and ρ. The infinite product of Dirac's delta functions $\delta^{(\infty)}(\Phi - \rho)$ is in fact a double product: $\delta^{(\infty)}(\Phi_1 - \rho_1)\delta^{(\infty)}(\Phi_2 - \rho_2)$. The average of the delta function in the preceding expression can be represented as follows

$$\langle \delta^{(\infty)}(\Phi - \rho)\rangle_0 = \int DQ\ \exp(iQ\varphi)\ \langle \exp(-iQ\rho)\rangle_0$$

The average of $\langle \exp(-iQ\rho)\rangle_0$ can be carried out within the perturbation theory. It is useful to represent it by means of diagrams. Examples of the diagrams contributing to $\langle \exp(-iQ\rho)\rangle_0$ are shown in Figure 1. The continuous lines represent the copolymer chains. The dotted lines are associated with the expression $-iQ_\alpha(k_i)$. The integrations over the wave vectors k_i and the "positions" s_i of the insertions $-iQ_\alpha(k_i)$ along the continuous line have to be carried out. We note that we are using canonical formalism with a fixed number of copolymer chains n. The theorems of the graph theory enabling one to carry out partial summations of the diagrams in Figure 1 can be applied in the limits $n \to \infty$, $\mathcal{V} \to \infty$, and $n/\mathcal{V} =$ constant. An important part of our approach consists of the following partial summation of diagrams in Figure 1. We perform a partial summation of the diagrams in Figure 1 possessing not more than two insertions (dotted lines) in one continuous line. It is easy to see that in the limit mentioned previously, these diagrams sum to an exponential factor. As a result, we obtain

$$Z = \int D\Phi\ \exp\left(-\frac{1}{2}\Phi V \Phi\right) \int DQ\ \exp\left(iQ(\Phi - \rho_m) - \frac{1}{2}Q\rho_m S_0 Q\right)(1 + L(iQ)) \quad (5)$$

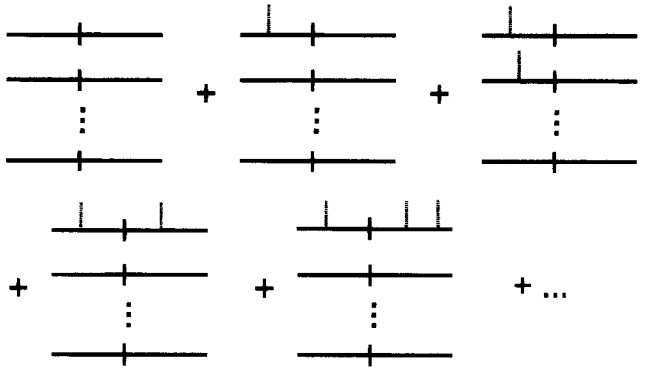

Figure 1. Examples of diagrams contributing to $\langle \exp(-iQ\rho)\rangle_0$.

where $L(iQ)$ is a series in powers of Q and is diagrammatically represented by a series of all (nonconnected) diagrams having more than two insertions in one continuous line (see Figure 1). ϱ_m is the average monomer density.

We now will carry out the integration over Q in eq 5. Up to the zero order in powers of Q in $L(iQ)$ [$L(iQ) = 0$], the integration over Q gives

$$\left(\frac{1}{\prod 4\pi \det S_0}\right)^{1/2} \exp\left(-\frac{1}{2}\delta\Phi\rho_m^{-1}S_0^{-1}\delta\Phi\right)$$

where $\delta\Phi_1 = \Phi_1 - f\rho_m$ and $\delta\Phi_2 = \Phi_2 - (1-f)\rho_m$ were introduced and $S^{-1}_{0,\alpha\beta}(k_1, k_2)$ are the elements of the matrix, which is the inverse of the matrix with matrix elements $S_{0,\alpha\beta}(k_1, k_2) = (2\pi)^3\delta^{(3)}(k_1 + k_2)P_{\alpha\beta}(k_1)$, where $P_{\alpha\beta}(k_1)$ are the unperturbed structure factors of a block copolymer. The latter can be expressed through the Debye function, $g_1(f, x) = 2(fx + \exp(-fx) - 1)/x^2$, as

$$P_{11}(k) = Ng_1(f, x)$$

$$P_{22}(k) = Ng_1(1-f, x)$$

$$P_{12}(k) = \frac{1}{2}N(g_1(1, x) - g_1(f, x) - g_1(1-f, x))$$

where $x = k^2R_g^2$ (R_g is the gyration radius of the Gaussian coil).

We now carry out the integration over Q in eq 5 to all orders in Q. Each Q in the integrand of eq 5 can be represented as a functional derivative of the integral with respect to $\delta\Phi$. As a result, the integral over Q in eq 5 is obtained as

$$\left(1 + L\left(\frac{\delta}{\delta\Phi}\right)\right)\exp\left(-\frac{1}{2}\delta\Phi\rho_m^{-1}S_0^{-1}\delta\Phi\right) \quad (6)$$

We note here that we differ from the random phase approximation. While in RPA the integration over Q is carried out approximately using the saddle point method,[10] the expression in eq 6 is exact. The diagrammatic representation of eq 6 is straightforward and can be pursued with the help of Figures 1 and 2.

The formula analogous to eq 6 bears some resemblance to the functional form of the Wick theorem[25] in quantum-field theory. The expression for the partition function is obtained from eqs 5 and 6 as

$$Z = \int D\Phi \exp\left(-\frac{1}{2}\Phi V\Phi\right)\left(1 + L\left(\frac{\delta}{\delta\Phi}\right)\right) \exp\left(-\frac{1}{2}\delta\Phi\rho_m^{-1}S_0^{-1}\delta\Phi\right) \quad (7)$$

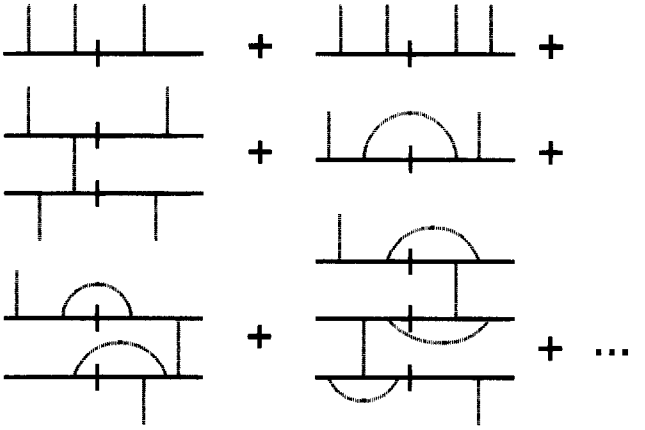

Figure 2. Examples of diagrams contributing to the interaction part of the free energy, $F_i(\delta\Phi)$. The dotted lines are associated with $S^{-1}_{0,\alpha\beta}(r_1, r_2)$. The free ends of the dotted lines are associated with $\delta\Phi_\alpha(r)$.

The diagrams appearing in eq 7 are generally nonconnected. Again, for $n \to \infty$, $\mathcal{V} \to \infty$, and $n/\mathcal{V}$ = constant, we can apply the graph connectivity theorem. According to this theorem, the perturbation expansion of nonconnected diagrams in eq 7 can be represented as the exponential of connected diagrams. As a result we get, instead of eq 7,

$$Z = \int D\Phi \exp\left(-\frac{1}{2}\Phi V\Phi - \frac{1}{2}\delta\Phi\rho_m^{-1}S_0^{-1}\delta\Phi - F_i(\delta\Phi)\right) \quad (8)$$

where $F_i(\delta\Phi)$ is represented by a series of connected diagrams. The examples of diagrams contributing to $F_i(\delta\Phi)$ are shown in Figure 2. We note that eq 8 can be written as

$$Z = \int D\Phi \exp(-F(\delta\Phi)) \quad (9)$$

with

$$\exp(-F(\delta\Phi)) = \exp\left(-\frac{1}{2}\Phi V\Phi\right)\left(1 + L\left(\frac{\delta}{\delta\Phi}\right)\right)\exp\left(-\frac{1}{2}\delta\Phi\bar{\rho}^{-1}S_0^{-1}\delta\Phi\right) = \exp\left(-\frac{1}{2}\delta\Phi(V + S_0^{-1})\delta\Phi - F_i(\delta\Phi)\right) \quad (10)$$

The first and the second and third diagrams in Figure 2 are proportional to $\delta\Phi^3$ and $\delta\Phi^4$, respectively, and coincide with those obtained in RPA. The analytical expressions associated with these diagrams give the vertex functions of the free energy function of the Leibler theory. There are also terms in $F_i(\delta\Phi)$ that are proportional to $\delta\Phi^2$ (the fourth, fifth, ... diagrams in Figure 2). These terms are missed in RPA. We note that the quantity $F_i(\delta\Phi)$ is interpreted within RPA as a free energy. This is due to the fact that within RPA $F_i(\delta\Phi)$ is the saddle point solution of the integral over Q. This is no longer the case in the present approach. To elucidate the meaning of the terms in $F_i(\delta\Phi)$, which are missed in RPA, we should consider a physical quantity, for example, the density–density correlation function, which is defined as follows:

$$G_{\alpha\beta}(r_1, r_2) = \langle\delta\rho_\alpha(r_1)\delta\rho_\beta(r_2)\rangle = \int D\Phi\ \delta\Phi_\alpha(r_1)\delta\Phi_\beta(r_2) \exp(-F(\delta\Phi))/\int D\Phi \exp(-F(\delta\Phi)) \quad (11)$$

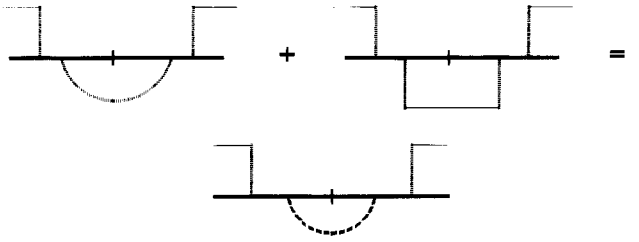

Figure 3. First-order correction to the density–density correlation function $\langle\delta\rho_\alpha(r_1)\delta\rho_\beta(r_2)\rangle$. The dotted lines are associated with $S^{-1}_{0,\alpha\beta}$. The thin continuous lines are associated with the propagator, $(V + S_0^{-1})^{-1}$. The dashed line is associated with the effective potential, $V^{\text{eff}} = (V^{-1} + S_0)^{-1}$. The free ends of the thin lines are fixed at r_1, α and r_2, β, respectively.

with $\exp(-F(\delta\Phi))$ given by eq 10. The Fourier transform of $\langle\delta\rho_1(r_1 - r_2)\delta\rho_1(0)\rangle$ is connected to the collective structure of the melt. The diagrams contributing to $G(r_1, r_2)$ are obtained from those contributing to the partition function by multiplying the latter by $\delta\Phi_\alpha(r_1)\delta\Phi_\beta(r_2)$ and averaging over $\delta\Phi(r)$. The average over $\delta\Phi(r)$ has to be carried out by using the statistical weight

$$\exp\left(-\frac{1}{2}\delta\Phi(V + S_0^{-1})\delta\Phi\right) \tag{12}$$

where the average monomer density of the copolymer melt, ρ_m, is absorbed into S_0. Up to the lowest order, the Fourier transform of the density–density correlation function $G(q)$ is obtained as

$$G_0(q) = (V + S_0^{-1}(q))^{-1}$$

Note that, in the case of incompressible melts, $G_0(q)$ results in the Leibler expression of the collective structure factor given by eq 1. Due to the denominator in eq 11, the nonconnected diagrams cancel in the perturbation expansion of the scattering function G. An example of diagrams of interest are shown in Figure 3.

The second diagram in Figure 3 appears from the average over $\delta\Phi$ of the second diagram in Figure 2, which is part of the vertex function, as is obvious from the picture. This diagram is taken into account in RPA. On the contrary, the first diagram in Figure 3 does not appear in RPA. The latter appears from the average over $\delta\Phi$ of the fourth diagram in Figure 2. Both diagrams in Figure 3 can be unified to one diagram with an internal line associated with the expression

$$-S_0^{-1}(q) + S_0^{-1}(q)(V + S_0^{-1}(q))^{-1}S_0^{-1}(q) = -(S_0(q) + V^{-1})^{-1} = -V^{\text{eff}}(q) \tag{13}$$

which is nothing but the effective potential introduced by Edwards[8] and studied for copolymers previously in refs 26 and 27. We remind the reader that the quantities S_0, V, and S_0^{-1} in eq 13 are matrices. This procedure, which we have explained by using the diagrams in Figure 3, can be applied to more complicated diagrams. As a result, the diagrams in the perturbation series of the density–density correlation function having internal lines associated with $-S_0^{-1}$ and $S_0^{-1}(V + S_0^{-1})^{-1}S_0^{-1}$ can be unified to diagrams with internal lines associated with the effective potentials. Thus, in contrast to the theories based on RPA, taking into account the terms missed in RPA enables one to represent the perturbation expansions of the physical quantities as series in powers of the effective potentials!

We note that, although in the vicinity of the pole of the structure factor the second term on the left-hand side of eq 13 dominates, the first term in eq 13, $-S_0^{-1}$, influences the behavior of the whole expression for small and large momenta. In addition, this term influences the dependence of the perturbation expansion on the temperature. The analytical expression associated with the diagram in Figure 3, which gives the first-order correction to the collective structure factor, can be written in abbreviated form as

$$G_0\Sigma G_0$$

where the self-energy, Σ, is given by

$$\Sigma_{\alpha\beta}(r - r') = -\int d^3r_1 \int d^3r_2\, S^{-1}_{0,\alpha\gamma}(r - r_1)\bar{S}_{\gamma\delta}(r_1, r_2)S^{-1}_{0,\delta\beta}(r_2 - r') \tag{14}$$

The quantity $\bar{S}$ in eq 14 is defined by

$$\bar{S}_{\alpha\beta}(r_1, r_2) = \int dr_3 \int dr_4\, V^{\text{eff}}_{\gamma\delta}(r_3, r_4)S_{4,\alpha\gamma\delta\beta}(r_1, r_2, r_3, r_4) \tag{15}$$

with

$$S_{4,\alpha\beta\gamma\delta}(r_1, r_2, r_3, r_4) = l^{-4}N^{-1}\rho_m \left[\int ds_1^\alpha \int ds_2^\beta \int ds_3^\gamma \int ds_4^\delta \langle\delta(r_1 - r_\alpha(s_1^\alpha))\,\delta(r_2 - r_\beta(s_2^\beta))\delta(r_3 - r_\gamma(s_3^\gamma))\delta(r_4 - r_\delta(s_4^\delta))\rangle_0\right] \tag{16}$$

being essentially the unperturbed four-point structure factor of the copolymer chain. The summation over repeated Greek indices is assumed in eq 15. The integrations over s_i^α occur in the interval $(0, fL)$ when $\alpha = 1$ and in the interval (fL, L) when $\alpha = 2$. The integration over several s_i^α within the same interval is ordered.

In addition to the diagram shown in Figure 3, there is a series of connected diagrams in the perturbation expansion of the density–density correlation function (eq 11) consisting of an arbitrary number of diagrams shown in Figure 3 being consecutively connected by lines, which are associated with the unperturbed density–density correlation function $\langle\delta\Phi_\alpha(r)\delta\Phi_\beta(r')\rangle_0$. These diagrams can be summed up to give the effective propagator as follows

$$G = (G_0^{-1} - \Sigma)^{-1} = (V + S_0^{-1} - \Sigma)^{-1} \tag{17}$$

Let us now consider the expression $S_0^{-1} - \Sigma = S_0^{-1} + S_0^{-1}\bar{S}\,S_0^{-1}$ appearing in eq 17. The last term in this expression is represented by a diagram consisting of one polymer chain. The preceding expression can be extended to a series by taking into account the diagrams consisting of many chains (continuous line) connected consecutively by lines associated with S_0^{-1}. Examples of such diagrams are shown in Figure 4. The first diagram in Figure 4 is associated with the expression $S_0^{-1}\bar{S}_0^{-1}$. The summation of the series of these diagrams, which is nothing but a geometrical series, results in

$$G = (V + S^{-1})^{-1} \tag{18}$$

with

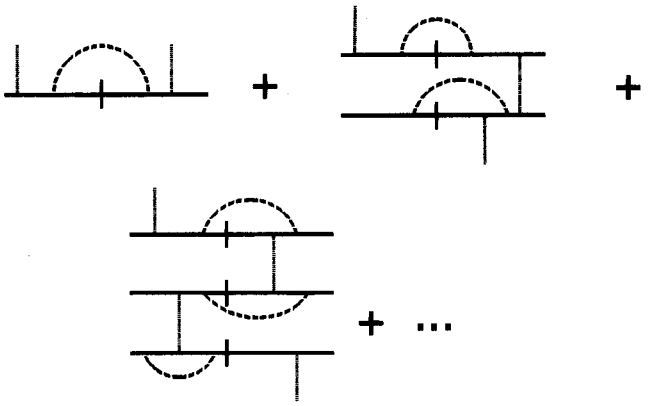

Figure 4. Examples of diagrams contributing to $S_0^{-1} - \Sigma$. The thick continuous lines are associated with copolymer chains. The dotted lines are associated with $S_{0,\alpha\beta}^{-1}$. The dashed lines are associated with the effective potential, $V^{\text{eff}} = (V^{-1} + S_0)^{-1}$.

$$S = S_0 - \bar{S} \tag{19}$$

being the perturbed structure factor of a copolymer chain in the melt. Equation 19 is nothing but the first-order correction to the structure factor of the copolymer chain in the melt in powers of the effective potential, V^{eff}. So far, we have considered the collective structure factor of the copolymer melt up to the linear order of the effective potentials. We expect that taking into account the terms of higher order in V^{eff} will again result in eq 18, where S will be given as a perturbation expansion in powers of the effective potentials. Thus, we expect that eq 18 is exact and gives a relation between the collective structure factor of the copolymer melt, $G(q)$, and the scattering functions of the copolymer chains in the melt, $S_{\alpha\beta}(q)$ (we are considering a compressible melt). An independent measure of $G(q)$ and $S_{\alpha\beta}(q)$ will enable one to check eq 18. We note that, in the case of an incompressible melt, eq 18 will reduce to eq 1 with S_0 replaced by the perturbed scattering factors of a copolymer chain in the melt.

Let us compare eqs 18 and 19 with the result predicted by RPA. The first difference from RPA consists of the following. Taking into account the first diagram in Figure 3, which is missed in RPA, enables one to represent the perturbation expansion of the collective structure factor as an expansion in powers of the effective potential. In the limit $V_{\alpha\beta} \to 0$, which in the case of the enthalpic origin of bare interactions corresponds to the limit $T \to \infty$, the effective potentials tend to the bare potentials $V_{\alpha\beta}$ and disappear when the latter disappear. As a consequence, the self-energy Σ (see eq 14) tends to zero for high temperatures. We note that Σ has a final limit for $T \to 0$ ($\chi \to \infty$) due to the fact that the effective potentials $V_{\alpha\beta}^{\text{eff}}(p)$ tend to $S_{0,\alpha\beta}^{-1}(p)$ for $T \to 0$ (see eq 13). This prediction is also in contrast to the theories based on RPA. The further difference from RPA and the Fredrickson–Helfand theory consists of the manner in which the fluctuations couple to the mean-field theory. In the theories based on RPA, as it follows from eq 17, the corrections to the mean-field theory due to fluctuations occur to S_0^{-1} or what is essentially the same as the Flory–Huggins χ parameter. The additional summation of diagrams carried out in order to go from eq 17 to eq 18 has the consequence that the corrections to the mean-field theory change S_0 and not S_0^{-1}, as is the case in the theories based on RPA. Thus, the fluctuations to the collective structure appear through the structure factors of the copolymer chains in the melt. This result, which has been proved here up to the first order in powers of the effective potential, is very natural and is expected to hold to all orders in powers of the effective potential.

Let us compare the character of the fluctuation effects of the present theory and those in the theory of David and Schweizer. In contrast to the present theory, where the fluctuation effects on the collective structure factor arise due to the perturbed single-chain structure factors, the fluctuation effects in their theory arise from microscopic modifications of the interchain packing, which lead to physical cluster formation and which couple to domain scale correlations in a finite size manner. The fact that the perturbation expansion occurs in powers of the effective potential also has consequences on the parameter controlling the fluctuation effects. This question will be considered in the next section.

We know from the theory of polymer solutions that the perturbation expansions in powers of the bare excluded volume interaction contain so-called "mass divergences" (see refs 8 and 28), appearing above two dimensions. These divergences are nonphysical and do not contribute, for example, to the collective structure factor. The cancellation of the latter is due to the fact that the collective structure factor (see eq 11) is given by a ratio of two quantities, and the regularization of the numerator and the denominator with respect to the mass divergences results in the same counterterm for both the numerator and the denominator in eq 11. Supposing that eq 11 is regularized from the beginning, we find that the first-order correction to the structure factor of the copolymer chain, $S_0 \to S = S_0 - \bar{S}$, will be free of the mass divergences. To our knowledge, the theories based on the RPA do not treat these divergences explicitly. Thus, it seems that the latter contribute to the coefficients of the free energy function in these theories.

III. The Cooperative Scattering Function

In this section, we will apply the results derived in the preceding section to calculate the collective structure factor of the copolymer melt. The starting point to evaluate $G_{11}(q)$ is eq 18, giving the first-order correction to the scattering function of the copolymer chain in powers of the effective potential. We see from the latter that the computation of the collective structure factor is based on the calculation of the structure factors of a copolymer chain in the melt. The method presented here enables one to compute the structure factor in a self-consistent way. The procedure is as follows. According to eq 18, the structure factor $G_{11}(q)$ is expressed through the effective potentials. The latter is expressed again through the propagator as follows:

$$V^{\text{eff}} = V(V + S_0^{-1})^{-1} S_0^{-1} = VG_0S_0^{-1} \tag{20}$$

By replacing the bare structure factor G_0 in eq 20 with the effective one, G, we obtain the effective potential as

$$V^{\text{eff}} = VGS_0^{-1} \tag{21}$$

Equation 21, together with eq 18, gives a self-consistent equation for the collective structure factor. From a theoretical point of view, it appears more reasonable to obtain a self-consistent equation on the level of the scattering functions of the copolymer chain. We will obtain such an equation by replacing the bare structure factor S_0 in eq 20 with the effective structure

factor of the copolymer chain S. At the one-loop level, we expect that both approaches would be essentially equivalent. Equation 20 generally applies for compressible melts. In the case of incompressible melts, the collective structure factor can be written as $G_{\alpha\beta} = (2\delta_{\alpha\beta} - 1)G_{11}$, which results in the following expression for the effective potential:

$$V^{\text{eff}}_{\alpha\beta}(p) = \chi\rho_m^{-1}(2\delta_{\alpha\beta} - 1)G_{11}(p)(S^{-1}_{0,11}(p) - S^{-1}_{0,12}(p)) \quad (22)$$

In the following, we will denote $G_{11}(q)$ by $S_{cc}(q)$. Note that we consider the symmetric case $f = 1/2$. To study the effect of incompressibility on the fluctuation effects, we have to study the fluctuation effects for both compressible and incompressible melts. From a general point of view, we would expect that the incompressibility suppresses the fluctuation effects. In the vicinity of the order–disorder transition, the scattering function $G(p)$ has a pronounced maximum at the wave vector p^*. Leibler's mean-field theory predicts $x^* = p^*R_g = 1.945\,56$. The value of the Flory–Huggins χ parameter at which the structure factor diverges is $\chi_{c,0} = 10.495$. Following Brasovskii[11] and Fredrickson and Helfand,[3] we will approximate the cooperative structure factor as

$$S_{cc,appr}(p) = \rho_m/(2(\chi_c - \chi) + 4a\rho_m(p - p^*)^2) \quad (23)$$

with $a\rho_m = \chi_c/p^{*2}$. In the vicinity of the order–disorder transition, the most important contribution in the integration over p in the first-order correction to the structure factor of the copolymer chain appears from the momenta in the vicinity of p^*, so that in carrying out the integration over p, we follow Brasovskii[11] and Fredrickson and Helfand[3] and put $p = p^*$ in the expression associated with $\tilde{S}$ (see eq 15), excepting $S_{cc,appr}(p)$. Then the integral over the absolute value of p can be performed to give

$$\int_p S_{cc,appr}(p) = \frac{1}{4\pi}\rho_m\frac{p^{*2}}{(a\rho_m)^{1/2}}(2(\chi_c - \chi))^{-1/2} \quad (24)$$

Thus, the one-loop correction to $S(q)$ reduces to the integration over the angle between the momenta q and p. So far, χ_c and p^* in eqs 23 and 24 are considered as free parameters and may differ from their bare values given by Leibler.

Before we compute the collective structure factor, let us first consider the expansion parameter of the perturbation expansion in powers of the effective potentials. The expression associated with $\tilde{S}$ can be written after introducing the dimensionless quantities as $\rho_m N z f(\rho_m VN, qR_g)$, with z being the dimensionless expansion parameter, $z = \rho_m^{-1}NR_g^{-d}$ ($d = 3$ is the space dimension). The function $f(\rho_m VN, qR_g)$ is given by an integral over the dimensionless wave vector $\mathbf{p}' = \mathbf{p}R_g$. In the limit of small V the function $f(x)$ is linear in x, so that the expansion parameter will become

$$z = VN^2R_g^{-d} \quad (25)$$

which coincides with the expansion parameter of the two-point contact interaction.[28] In the vicinity of the order–disorder transition, we use the approximate procedure of carrying out the integration over the momentum $|\mathbf{p}|$, which we explained earlier, and obtain the expansion parameter of the first-order correction to the individual structure factor as

$$z = \frac{\chi NR_g^{-3}(x^*)^3(2(\chi_c - \chi))^{-1/2}}{8\pi\rho_m(\chi_c)^{1/2}} \quad (26)$$

with $x^* = p^*R_g$ being a dimensionless quantity.

We note that according to eqs 25 and 26 there are two expansion parameters controlling the fluctuations. It is interesting if these regimes can be observed experimentally. The proportionality of z to the Flory–Huggins χ parameter means that, in contrast to the Fredrickson–Helfand theory, the enthalpic interactions have a significant effect on the fluctuation effects. This conclusion is in agreement with the results of David and Schweizer obtained within their theory of copolymer melts, which is a generalization of the reference interaction site model theory of low molecular liquids developed by Chandler and Andersen[24] to copolymer melts. By neglecting the dependence of x^* and χ_c in eq 26 on N and T, it follows that both parameters given by eqs 25 and 26 scale in the same way as $\chi NN^{-1/2}$. The perturbation parameter predicted by David and Schweizer also scales in the same way.

The effective scattering factors of a copolymer chain in the melt, $S_{\alpha\beta}(q)$, depend on the parameters χ_c and x^*. In the case of an incompressible melt, the collective structure factor is expressed by the inverse of the matrix $S_{\alpha\beta}(q)$, with S given by eq 19, as follows:

$$S_{cc}(q) = \rho_m N/(N(S^{-1}_{11}(q) + S^{-1}_{22}(q) - 2S^{-1}_{12}(q)) - 2\chi N) \quad (27)$$

where $S^{-1}_{\alpha\beta}(q)$ are the elements of the matrix, which is the inverse of the matrix whose elements are the scattering functions of the copolymer chain, $S_{\alpha\beta}(q)$, in the melt. According to eqs 19 and 22, the scattering functions of the copolymer chains in the melt, $S_{\alpha\beta}(q)$, are expressed through the collective structure factor of the melt, $S_{cc}(q)$. Thus, eqs 19, 22, and 27 give a self-consistent equation for the collective structure factor of the melt. We will approximate the collective structure factor by eq 23. The parameters χ_c and $x^* = p^*R_g$ are determined by approximating eq 27 with eq 23. To determine χ_c and x^*, we used the least-squares method. In fitting eq 23 to eq 27, we took only values in the vicinity of the maximum of $S_{cc}(q)$. The results of computing $\chi_c N$ and x^* as a function of χN for two values of the quantity $1/(8\pi\rho_m)NR_g^{-3}$ are given in Figures 5 and 6, respectively. We note that the quantity $1/(8\pi\rho_m)$-NR_g^{-3} decreases with increasing monomer density ρ_m and degree of polymerization N, so that for large ρ_m and N, Leibler's mean-field theory will be recovered.

The dependence of the position of the maximum of the structure factor on χN is in qualitative agreement with the results of the Monte Carlo simulations and the theoretical calculations. Figure 7 shows the result of computing the inverse of the maximum of the collective structure factor as a function of χN.

The behavior of $1/S_{cc}(q^*)$ qualitatively agrees with the results of previous investigations. The qualitative behavior of the maximum of the collective structure factor $S_{cc}(q^*) \simeq 1/(\chi_c - \chi)$ can be obtained by comparing the expansion parameter in eq 26 with $N(\chi_c - \chi)$. The maximum of $S(q^*)$ is obtained to scale as $N^{4/3}$, which is in agreement with the predictions of the Fredrickson–Helfand theory and the David–Schweizer theory.

IV. Structure Factor of a Copolymer Chain in the Melt

According to eq 18, the computation of the collective structure factor is based on the calculation of the

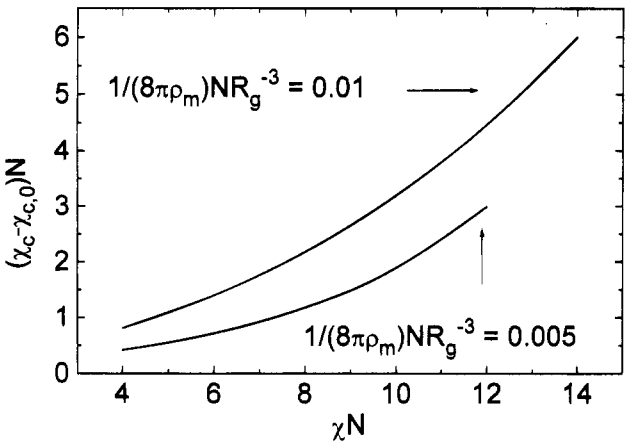

Figure 5. Effective value of χ_c as a function of χN.

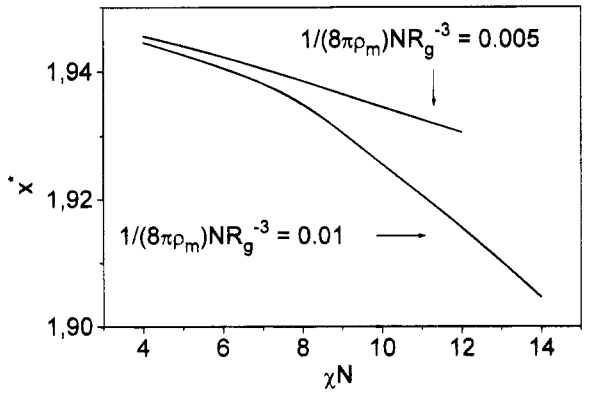

Figure 6. Position of the maximum of the scattering function $x^* = q^*R_g$ as a function of χN.

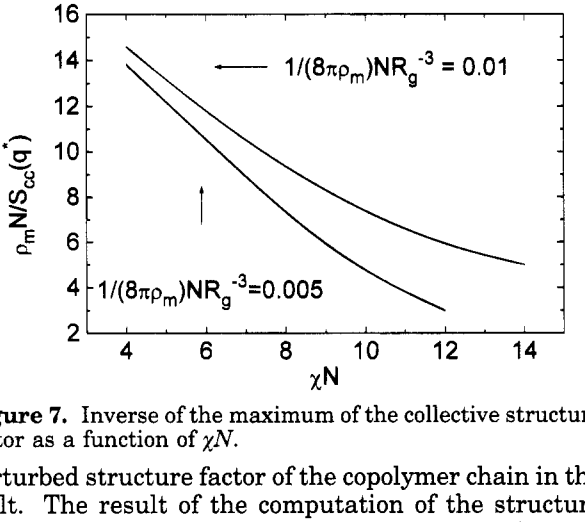

Figure 7. Inverse of the maximum of the collective structure factor as a function of χN.

perturbed structure factor of the copolymer chain in the melt. The result of the computation of the structure factor, $S_{11}(q)$, is shown in Figure 8. For comparison we also show the corresponding structure factor of a Gaussian copolymer chain. As follows from Figure 8, interactions in the melt decrease the structure factor of the copolymer chain. The perturbed structure factors of a copolymer chain enable one to compute the gyration radius of a copolymer chain. The gyration radius is computed by using the formula

$$R_g^2 = -3\partial \ln S(q)/\partial q^2|_{q=0} \qquad (28)$$

where the whole structure factor of the diblock copolymer chain, $S(q)$, is expressed by the structure factors, $S(q)_{\alpha\beta}$, of the blocks as $S(q) = S_{11}(q) + 2S_{12}(q) + S_{22}(q)$. The result of the computation of R_g^2 as a function of χN is given in Figure 9.

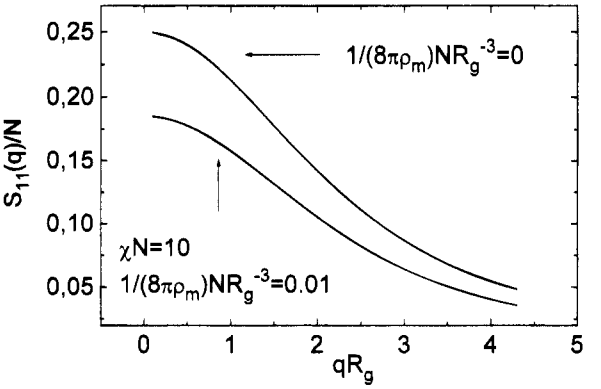

Figure 8. Structure factor of the copolymer chain, $S_{11}(q)$, in the melt.

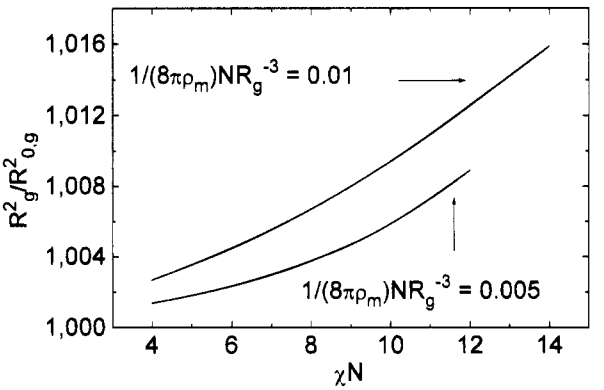

Figure 9. Gyration radius of a copolymer chain in the melt.

We note that the computation of the gyration radius carried out here does not deviate significantly from that carried out in refs 21 and 22. In contrast to these authors, who computed the collective structure factor (eq 23) by using the Fredrickson–Helfand theory, we have used the result of the self-consistent computation of the parameters χ_c and x^* of the structure factor (eq 23) within the present approach. We note that the structure factors $S(q)_{\alpha\beta}$ in eq 29 are regularized and are free of the mass divergences discussed earlier. The numerical results presented in Figures 5–9 are found for quite a small expansion parameter ($\simeq 1/(8\pi\rho_m)NR_g^{-3}$), so that the deviations of different quantities from the predictions of Leibler theory (among others the gyration radius of a copolymer chain shown in Figure 9) are found to be quantitatively rather small.

V. Jump in the Copolymer Size at the Order–Disorder Transition

The technique used in this article leads to the prediction that the individual quantities of copolymer chains, such as the gyration radius and the mean-square end-to-end distance of a copolymer chain, explicitly depend on the average value of the order parameter. Since the order–disorder transition is the first-order phase transition,[3] such a dependence implies that the individual properties have a jump at the transition. In this section, we will compute the jump in the mean-square end-to-end distance of a copolymer chain, R^2, at the order–disorder transition. The mean-square end-to-end distance has to be computed by using the following formula:

$$R^2 = \frac{\int d^3r \int d^3r_0\, (r - r_0)^2 \langle P(r, L; r_0, 0; \delta\Phi)\rangle_\Phi}{\int d^3r \int d^3r_0\, \langle P(r, L; r_0, 0; \delta\Phi)\rangle_\Phi} \quad (29)$$

where $P(r, L; r_0, 0; \delta\Phi)$ is the correlation function of the end-to-end distance of a copolymer chain in the melt without carrying out the average over the field $\delta\Phi$. Examples of diagrams contributing to $P(r, L; r_0, 0; \delta\Phi)$ are shown in Figure 10.

The average $\langle ... \rangle_\Phi$ in eq 29 means an average over Φ that has to be carried out with the help of the statistical weight $\exp(-F(\delta\Phi))$ given by eq 10. The average over Φ in the disordered state ($\langle\delta\Phi\rangle = 0$) gives the expansion of $\langle P(r, L; r_0, 0; \delta\Phi)\rangle_\Phi$ in powers of the effective potential $V^{\text{eff}} = (S_0 + V^{-1})^{-1}$ up to the first order in V^{eff}. At and below the transition, $\langle\delta\Phi\rangle \neq 0$. In carrying out the average of $P(r, L; r_0, 0; \delta\Phi)$ over $\delta\Phi$, this circumstance should be taken into account. The result is that R^2 becomes explicitly dependent on $\langle\delta\Phi\rangle$. The first diagram in Figure 10 does not contribute to R^2. Taking into account the contribution from the second diagram gives the mean-square end-to-end distance of a copolymer chain in the ordered state as

$$R^2/R_0^2 = 1 + 7.286(\langle\delta\Phi\rangle/\rho_m)^2 + ... \quad (30)$$

where R_0^2 is the mean-square end-to-end distance of the copolymer chain in the disordered state. Thus, the mean-square end-to-end distance of a copolymer chain has a discontinuity at the transition. This jump is proportional to the square of the order parameter and is expected to be small. In the ordered state, $\langle R^2\rangle$ explicitly depends on the order parameter.

VI. Discussion

Let us discuss some general aspects of our approach to the theory of microphase separation. The theory presented here is based on the diagrammatic reformulation of the description of the polymer melt in terms of the coordinates of the polymer segments (bare theory) by using the collective variables (effective theory). While in the bare theory the perturbation expansion occurs in powers of the bare interactions between the segments, the expansion in the theory reformulated in terms of the collective variables occurs in powers of the effective potentials. For high temperatures (small χ), the effective potential tends to the bare segment–segment interactions, so that in this limit the present theory reproduces the bare theory. We have also found that the effective potentials have a nonzero limit for deep temperatures. It appears that the mass divergences appearing in the bare theory are also significant in the reformulated theory. The structure factors of a copolymer chain in the melt, which are represented as a perturbation series in powers of the effective potentials, should be regularized with respect to the mass divergences.

The procedure of introducing the collective variables in the theory of polymer melts as well as the effective potentials was introduced by Edwards (see ref 8). The effective potentials for block copolymer melts were studied in detail in refs 26 and 27. The effective potentials possess the unpleasant property to diverge for large momenta for incompressible copolymer melts. It appears that use of the approximate formula (eq 22) has the consequence that the effective potentials tend to constant values for large momenta.

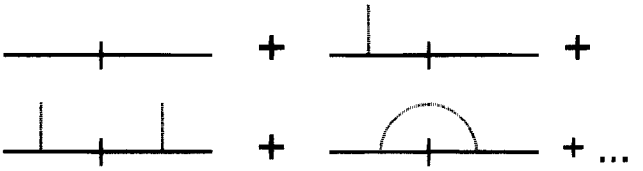

Figure 10. Correlation function of the end-to-end distance of a copolymer chain in the melt.

One of the general outputs of our approach concerns the prediction of the parameter controlling the fluctuation effects. The Leibler–Fredrickson–Helfand theory predicts that the physical quantity depends on two parameters χN and the quantity (Ginzburg number) $\bar{N} = 6^3(R_g^3\rho_c)^2$ (ρ_c is the chain density), which controls the fluctuation effects. The fluctuation effects disappear for $\bar{N} \to \infty$. Thus, the fluctuation effects in this theory essentially are of entropic origin. On the contrary, we predict that the fluctuation effects (in the regime where the maximum of the collective structure factor is pronounced) are controlled by the parameter $z = \chi N R_g^{-3}(x^*)^3(2(\chi_c - \chi))^{-1/2}/(4\pi\rho_m(\chi_c)^{1/2}) \sim \chi N\bar{N}^{-1/2}$. Therefore, we conclude that the enthalpic interactions between the monomers in the melt essentially influence the fluctuation effects. We note that this conclusion is in accordance with the prediction made by David and Schweizer[23] within their polymer reference interaction site model theory (PRISM) of copolymer melts. We note that, in contrast to the theory of David and Schweizer, the present approach has the same basis as the Leibler–Fredrickson–Helfand theory and is nothing but an extension of the latter beyond the random phase approximation.

In this paper, we have only considered the collective structure factor of the diblock copolymer melt in the disordered state. Equations 18 and 19 enable one to study the thermodynamics of microphase separation without appealing to RPA. Below the transition, the structure factor of the copolymer chain (eq 19) does explicitly depend on the average value of the order parameter, $\bar{\Phi} \equiv \overline{\delta\Phi}$. The inverse of the collective structure factor given by eq 18 can be identified with the second derivative of the thermodynamic potential:

$$\frac{\delta^2\Gamma(\bar{\Phi})}{\delta\bar{\Phi}(1)\delta\bar{\Phi}(2)} = G^{-1}(1, 2, \bar{\Phi}) \quad (31)$$

Integration of the latter would enable one to derive the thermodynamic potential of the copolymer melt.

The method presented in this work is not restricted to diblock copolymers. It can be applied to consider polymer blends and stochastic polymers.

VII. Conclusions

We have extended the theory of microphase separation beyond the random phase approximation. Carrying out the procedure of introducing the collective variables with the help of diagrams has enabled us to avoid the use of the random phase approximation. Taking into account the terms missed in RPA has the consequence that the perturbation expansions of the theory reformulated in terms of collective variables occur in powers of the effective potentials. The main difference from the previous theories consists of the manner in which the fluctuation effects couple to the mean-field theory. We have shown that the fluctuation effects on the collective structure factor of the copolymer melt couple through the structure factors of the copolymer chain in the melt.

By expressing the effective potentials through the collective structure factor, we have proposed a self-consistent scheme to compute the collective structure factor of the copolymer melt in the disordered state. By using this self-consistent scheme, we have computed the collective structure factor of an incompressible copolymer melt in the disordered state. We have shown that the individual quantities of copolymer chains have a jump at the order–disorder transition and have computed the latter for the mean-square end-to-end distance of a copolymer chain in the melt to the lowest order in powers of the order parameter.

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