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Collective and single-chain correlations near the block copolymer order–disorder transition

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The concentration pair correlation function and the order–disorder transition in a diblock copolymer melt are studied in the framework of a self-consistent one-loop approximation. In contrast with earlier work, no simplifying assumption on the wave vector dependence of the correlation functions is made. This allows us to calculate the shift in the peak of the fluctuation spectrum recently observed in neutron scattering experiments. Quantitative agreement with experimental results is found. We also present a new calculation of how the collective concentration fluctuations influence single chain statistics in the copolymer melt. It is shown that even in the disordered phase, strong deviations from Gaussian statistics can be expected for finite molecular weights. A local segregation between monomers of the two different blocks results in an increase in the copolymer radius of gyration.

I. INTRODUCTION

A diblock copolymer[1] is a macromolecule made up of two polymerized sequences (blocks) of chemically different monomers, A and B, chemically bonded to each other. At high temperatures, a melt of such chains has a uniform composition. As the temperature is lowered, the incompatibility between A and B monomers causes the melt to undergo an order–disorder transition (ODT) towards a microphase characterized by long range order in its composition. This ODT is the counterpart for copolymers of the more usual demixing transition observed in A–B homopolymer blends. Due to the connectivity constraint between the A and B blocks, the demixing in copolymers can occur only on the scale of a chain, with the formation of inhomogeneous concentration patterns. In particular, for the case of nearly symmetric copolymers, the ordered microphase is a lamellar one, characterized by a one-dimensional oscillation of the concentration field with a period of order R, the chain radius of gyration.

A comprehensive theoretical study of the ODT was first performed by Leibler.[2] Using the random phase approximation (RPA) method, he computed the spectrum of composition fluctuations in the disordered phase, and used a Landau-type mean-field approximation to estimate the location of the ODT and the nature of the ordered phase as a function of composition. In particular, for symmetric diblocks, the transition to a lamellar phase was predicted to be of second order, with diverging composition fluctuations at the transition point. Leibler pointed out, however, that this prediction was an artifact of his mean-field approximation, and that inclusion of fluctuation contributions to the free-energy would modify this result to a first-order phase transition. This inclusion was carried out by Fredrickson and Helfand[3] following a method developed by Brazovskii.[4] According to

their theory, the transition is in fact weakly first order, and the mean-field results of Leibler become exact only in the limit of infinitely long chains.

Although many general features of the ODT appear to be well described by the Leibler and Fredrickson–Helfand theories[5,6] several discrepancies between theory and experiment remain. In strict application of the RPA, as in Leibler's calculation, the individual copolymer chains are assumed to remain Gaussian, characterized by an unperturbed radius of gyration that scales as $R \sim N^{1/2}$ (N is the degree of polymerization). It follows that the peak wave vector q^* in the fluctuation spectrum is predicted to scale as $q^* \sim R^{-1} \sim N^{-1/2}$. The Fredrickson–Helfand theory, due to some simplifying assumptions made in the calculation, retained these features of the traditional RPA. Recent experiments[7] and numerical simulations[8] indicate deviations from this behavior. In small angle neutron scattering experiments on a nearly symmetric poly(ethylene–propylene)-poly(ethyl-ethylene) (PEP-PEE) system, the position of the structure factor peak (q^*) was found to exhibit an N dependence stronger than $N^{-1/2}$.[7] In the simulations, copolymer chains on a lattice show a strong departure from Gaussian statistics. It is the purpose of this work to show how the Fredrickson–Helfand calculation can be improved to account for this variation of the structure factor peak, and how single chain statistics are affected by the large concentration fluctuations in the disordered phase. We note that two recent studies have appeared which address the behavior of q^* in the vicinity of the transition[9] and far below the ODT.[10] As discussed below, we find results that differ from those of Ref. 9 for the collective parameter q^* and, moreover, provide new predictions for single chain statistics.

The paper is organized as follows: the theoretical methods used to study concentration fluctuations, compute the location of the ODT and investigate the single chain statistics are described in the next section. Section III presents our numerical results, including a quantitative comparison with

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the neutron scattering data of Refs. 6 and 7. The paper ends with a short discussion. Although the paper is self-contained, the reader interested in understanding the computational details will need some familiarity with the earlier work of Refs. 2, 3, and 5.

II. THEORY

A. Description of the model

Our starting point is the straightforward extension of Edwards' Hamiltonian for a homopolymer[11] to a diblock copolymer melt as formulated by Ohta and Kawasaki.[12] The Hamiltonian for $P + 1$ diblock copolymers, each consisting of $N_A = fN$ monomers of species A and $N_B = (1 - f)N$ monomers of species B is

$$H_0 = \sum_{\alpha=0}^{P} \frac{3}{2a^2} \int_0^N ds \left(\frac{d\mathbf{r}^{(\alpha)}}{ds} \right)$$

$$+ \frac{1}{2} \int \int d\mathbf{r}\, d\mathbf{r}' \, \hat{\rho}_i(\mathbf{r}) v_{ij}(\mathbf{r} - \mathbf{r}') \hat{\rho}_j(\mathbf{r}). \qquad (1)$$

Throughout the paper, the Greek superscripts refer to the chains while Roman indices label the two different species ($i,j = $ A,B). Summation over repeated Roman indices is implied. The microscopic monomer densities $\hat{\rho}_{A,B}$ are defined as

$$\hat{\rho}_A(\mathbf{r}) = \sum_\alpha \int_0^{fN} ds\, \delta[\mathbf{r} - \mathbf{r}^{(\alpha)}(s)],$$

$$\hat{\rho}_B(\mathbf{r}) = \sum_\alpha \int_{fN}^N ds\, \delta[\mathbf{r} - \mathbf{r}^{(\alpha)}(s)] \qquad (2)$$

and a is the statistical segment length, which for simplicity is assumed to be independent of the species. The 2×2 matrix $v(\mathbf{r})$ describes the monomer–monomer interactions. At this stage no particular form is assumed for these interactions. In practical calculations, we shall, however, specialize to the case of an incompressible melt, which is obtained by writing $v_{ij}(\mathbf{r}) = u_{ij}\delta(\mathbf{r})$, with $u_{AA} = u_{BB} = U$ and $u_{AB} = u_{BA} = U + \chi\rho^{-1}$, and taking the limit $U \to \infty$ to ensure incompressibility. The quantity $\rho = N(P + 1)/V$ is the monomer number density and the Flory interaction parameter χ has its usual meaning of a per monomer energy penalty associated with A–B contacts. Finally, we note that we work in units of energy where $k_B T = 1$.

The partition function of the system Z is the trace over all monomer coordinates of $\exp(-H)$. This integral can be rewritten in several different ways, depending on the quantity one wants to estimate. In the next section, we shall be interested in computing concentration correlation functions and Z will be written as

$$Z = \int D\psi \exp(-H_c[\psi]), \qquad (3)$$

where $\psi(\mathbf{r}) = [(1 - f)\rho_A(\mathbf{r}) - f\rho_B(\mathbf{r})]/\rho$ is a coarse-grained concentration field and the effective Hamiltonian H_c is defined by

$$\exp(-H_c[\psi]) = \langle \delta(\psi - \hat{\psi}) \rangle_{H_0}. \qquad (4)$$

The brackets on the right-hand side of Eq. (4) denote an ensemble average with statistical weight $\exp(-H_0)$. For

the purpose of studying the internal correlations of a tagged single chain, in Sec. II B it proves convenient to introduce a new expression for Z, using a generalization of the standard Edwards transformation:[13]

$$Z = \langle \exp(-F_{ni}[i\phi]) \rangle_\phi. \qquad (5)$$

Here the average is taken over a "random field" $i\phi(\mathbf{r}) = [i\phi_A(\mathbf{r}), i\phi_B(\mathbf{r})]$ with Fourier components $\phi(\mathbf{k})$ distributed according to the Gaussian distribution

$$Q[\phi] = \prod_k \{V \det [v(\mathbf{k})]/(2\pi)\}^{-1/2} \exp$$

$$- \left\{ \frac{1}{2V}\phi_i(\mathbf{k})[v^{-1}(\mathbf{k})]_{ij}\phi_j(-\mathbf{k}) \right\}, \qquad (6)$$

(where V is the volume of the system) and $F_{ni}[\phi]$ is the free energy for a system of noninteracting copolymers in the external potential $\phi(\mathbf{r})$.

B. Concentration fluctuations

The concentration–concentration structure factor $S_{cc}(\mathbf{q})$ is defined by

$$S_{cc}(\mathbf{q}) = Z^{-1}\rho \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}}$$

$$\times \int D\psi \exp(-H_c[\psi])\psi(\mathbf{r})\psi(0) \qquad (7)$$

and its calculation thus requires a knowledge of the effective Hamiltonian H_c. Such an expression was derived in Ref. 12. To fourth order in ψ, H_c is given by

$$H_c[\psi] = \frac{1}{2!}V^{-1}\sum_q \rho\Gamma_2(q,f)\psi(\mathbf{q})\psi(-\mathbf{q}) + \frac{1}{3!}V^{-2}$$

$$\times \sum_{\mathbf{q}_1,\mathbf{q}_2} \rho\Gamma_3(\mathbf{q}_1,\mathbf{q}_2,-\mathbf{q}_1-\mathbf{q}_2,f)\psi(\mathbf{q}_1)\psi(\mathbf{q}_2)\psi(-\mathbf{q}_1$$

$$-\mathbf{q}_2) + \frac{1}{4!}V^{-3}\sum_{\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3} \rho\Gamma_4(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,-\mathbf{q}_1-\mathbf{q}_2$$

$$-\mathbf{q}_3,f)\psi(\mathbf{q}_1)\psi(\mathbf{q}_2)\psi(\mathbf{q}_3)\psi(-\mathbf{q}_1-\mathbf{q}_2-\mathbf{q}_3) \qquad (8)$$

where the vertex functions Γ_2, Γ_3, Γ_4 are given explicitly in Refs. 2 and 12. Indeed, if the partition function (3) is computed in a mean-field approximation (i.e., saddle points), Eq. (8) becomes the expression for the free energy obtained by Leibler.[2] $\Gamma_2(q)$ is the inverse of Leibler's structure factor:

$$\Gamma_2(q,f) = N^{-1}[F(q^2Na^2/6,f) - 2\chi N], \qquad (9)$$

where $F(x,f)$ is a combination of Debye functions.[2] The higher order vertex functions do not depend on the monomer–monomer interactions, and are expressible solely in terms of the concentration correlation functions of ideal polymer chains.

According to Leibler's mean-field theory, the disordered phase ($\langle \psi(\mathbf{r}) \rangle = 0$) becomes unstable when $\Gamma_2(q,f)$ vanishes. This condition is thus sufficient to locate the spinodal for the ODT in mean-field theory. For symmetric diblocks ($f = 0.5$) $\Gamma_2(q,f)$ first vanishes for a single q when (χN) reaches the critical value 10.495. The ordered phase has a lamellar structure, with a period that is determined by the wave vector at which $\Gamma_2(q,f)$ has a minimum [or equiv-

alently, at which $S_{cc}(q)$ in the disordered phase has a peak]. This wave vector $q_0(f)$ is determined solely by the function F, and is therefore independent of χ. For $f = 0.5$, $q_0 = 4.78 N^{-1/2} a^{-1}$.

As mentioned in the introduction, it was already realized by Leibler that mean-field theory was inadequate for describing symmetric block copolymer melts close to the transition point. In such systems presenting an instability at finite wave vector, Brazovskii[4] showed that a proper inclusion of fluctuations transforms the mean-field second-order phase transition into a first-order one, and suppresses the divergence of the concentration fluctuations in the disordered phase. Fredrickson and Helfand[3] used Brazovskii's method to calculate the corrections to mean field theory for copolymers. In order to obtain analytically tractable results, they made the simplifying assumption that the vertex functions Γ_3 and Γ_4 have no wave vector dependence. Their method, however, can readily be generalized to include such a dependence. Using the self-consistent one loop approximation described in,[3,4] we obtain the following integral equation for $S_{cc}(q)$:

$$S_{cc}(q,f)^{-1} = \Gamma_2(q,f)$$
$$+ \frac{1}{2V\rho} \sum_{\mathbf{k}} \Gamma_4(\mathbf{q}, -\mathbf{q}, \mathbf{k}, -\mathbf{k}, f) S_{cc}(\mathbf{k}, f). \quad (10)$$

The wave vector dependence of Γ_4 in this equation is the only difference with the result of Ref. 3. This, however, turns out to be of crucial importance for predicting the shift in the structure factor peak induced by the fluctuations. Were this dependence not present, the integral on the right-hand side of (10) would be wave vector independent, and therefore the maximum in S_{cc} would remain the mean-field value $q = q_0$. For this reason, we believe the calculation presented in Ref. 9, which predicts a shift in the peak without using a wave vector dependent Γ_4, to be in error.

The integral equation (10) can be reduced to a set of algebraic equations if for the purpose of calculating the integral on the right-hand side of Eq. (8), S_{cc} is approximated by a Lorentzian sharply peaked around its maximum q^*:

$$S_{cc}(q,f)^{-1} = N^{-1}r + \alpha a^2 (q - q^*)^2. \quad (11)$$

This approximation is justified by the fact that the transition is weakly first order, so that $S_{cc}(q,f)$ is theoretically expected[3] and experimentally found[6] to be well described by Eq. (11) in the relevant wave vector region. The three parameters (that still depend on the composition f) α, q^*, and r are determined by the consistency conditions [obtained by demanding that close to q^*, the right-hand side of Eq. (10) must have the form (11)]:

$$r = N\Gamma_2(q^*, f) + \frac{Na^2 q^{*2}}{4\pi(\overline{N}r\alpha)^{1/2}} N\gamma_4(q^*, q^*, f),$$

$$0 = \Gamma_2'(q^*, f) + \frac{Na^2 q^{*2}}{4\pi(\overline{N}r\alpha)^{1/2}} \gamma_4'(q^*, q^*), \quad (12)$$

$$2\alpha = \Gamma_2''(q^*, f) + \frac{Na^2 q^{*2}}{4\pi(\overline{N}r\alpha)^{1/2}} \gamma_4''(q^*, q^*, f),$$

where the primes indicate partial derivatives with respect to q, $\overline{N} = N(\rho a^3)^2$ and $\gamma_4(q,k,f)$ is an angular average of $\Gamma_4(\mathbf{q}, -\mathbf{q}, \mathbf{k}, -\mathbf{k}, f)$

$$\gamma_4(q,k,f) = \frac{1}{4\pi k^2} \int d\mathbf{k}' \, \delta(|\mathbf{k}'| - |\mathbf{k}|)$$
$$\times \Gamma_4(\mathbf{q}, -\mathbf{q}, \mathbf{k}', -\mathbf{k}', f). \quad (13)$$

Equation (12) was solved numerically to obtain r, q^*, and α, and the full $S_{cc}(q)$ was then obtained from the right-hand side of Eq. (10), calculated with the representation (11) inserted into the second term. The evaluation of γ_4 requires a calculation of $\Gamma_4(\mathbf{q}, -\mathbf{q}, \mathbf{k}, -\mathbf{k}, f)$, which for completeness is summarized in Appendix A.

C. Transition to the lamellar phase

For nearly symmetric diblock copolymers, it is known from experiments and from previous theoretical studies[2,3] that the ordered microphase which appears at large enough values of χN has a lamellar, or one dimensional, structure. Close to the transition, the order parameter $\bar{\psi}$ in this phase can be approximated by a single harmonic:

$$\bar{\psi}(\mathbf{r}) = 2A \cos(\mathbf{q}_l \cdot \mathbf{r}). \quad (14)$$

This approximation is known to break down in the "strong segregation limit," i.e., for $\chi N \gg 10$,[10,12,14,15] but is justified near the transition by the fact that S_{cc} is a sharply peaked function of q. The wave vector $\mathbf{q}_l$ characterizes the oscillation period of the concentration wave in the ordered phase, and in general differs from q^*. The free energy difference per monomer $f_m(A)$ between the ordered phase described by Eq. (14) and the disordered phase can be calculated as a power series in the amplitude A. Here we merely outline the main steps of this calculation, and refer the reader to Refs. 4 and 5 for details. The procedure is to write the partition as a functional of the order parameter field $\bar{\psi}(\mathbf{r})$ (that can in principle be realized by applying an external field to the system) and to obtain the desired expansion by taking functional derivatives with respect to $\bar{\psi}(\mathbf{r})$ at $\bar{\psi}(\mathbf{r}) = 0$. For the particular case (14), the functional derivatives are actually ordinary derivatives with respect to A, and the result can be summarized by the equation:

$$\frac{df_m}{dA} = 2A\Delta_2(\mathbf{q}_l, A, F)$$
$$- A^3 \Gamma_4(\mathbf{q}_l, -\mathbf{q}_l, \mathbf{q}_l, -\mathbf{q}_l, f), \quad (15)$$

where $\Delta_2(\mathbf{q}, A, f)$ is the inverse of the susceptibility in the ordered phase and is given in the self-consistent one loop approximation by an integral equation similar to Eq. (10):

$$\Delta_2(\mathbf{q}, A, f) = \Gamma_2(q, f) + A^2 \Gamma_4(\mathbf{q}, -\mathbf{q}, \mathbf{q}_l, -\mathbf{q}_l, f)$$
$$+ \frac{1}{2V\rho} \sum_{\mathbf{k}} \Gamma_4(\mathbf{q}, -\mathbf{q}, \mathbf{k}, -\mathbf{k}, f)$$
$$\times \Delta_2(\mathbf{k}, A, f)^{-1}. \quad (16)$$

A complication arises at this point due to the fact that Δ_2 is not an isotropic function of $\mathbf{q}$. This is due to the fact that the ordered phase has selected the particular direction along $\mathbf{q}_l$. It turns out, however, that the dependence of $\Gamma_4(\mathbf{q}, -\mathbf{q}, \mathbf{k}, -\mathbf{k}, f)$ on the angle between $\mathbf{q}$ and $\mathbf{k}$ is very weak, so that a good approximation is to replace Γ_4 by γ_4 in Eq. (16), thus restoring the isotropy of Δ_2. By taking successive derivatives of Eqs. (15) and (16) with respect to A,

setting $A = 0$ in the final results, and using the representation (11) for $S_{cc}(q)^{-1} = \Delta_2(q, A = 0)$ we obtain the following expansion for f_m:

$$f_m(A) = \tau(q_l)A^2 + \frac{u(q_l)}{4}A^4 + \frac{w(q_l)}{36}A^6, \qquad (17)$$

where the coefficients τ, u, v are given by

$$\tau(q_l) = r + \alpha Na^2(q^* - q_l)^2,$$
$$u(q_l) = [1 + BN\gamma_4(q^*,q^*)]^{-1}[N\gamma_4(q_l,q_l)$$
$$+ BN^2\gamma_4(q_l,q_l)\gamma_4(q^*,q^*) \qquad (18)$$
$$- 2BN^2\gamma_4(q^*,q_l)^2],$$
$$w(q_l) = 9Br^{-1}[1 + BN\gamma_4(q^*,q^*)]^{-3}N^3\gamma_4(q^*,q_l)^3,$$

where $B = Na^2q^{*2}/[8\pi(\bar{N}r\alpha)^{1/2}]$. Note that to simplify the notation we have dropped the f dependence of the coefficients. From Eq. (17) it is easily seen[5] that a first order transition to a lamellar phase of period $2\pi/q_l$ will take place whenever the two conditions $u(q_l) < 0, u(q_l)^2 = 16\tau(q_l)w(q_l)/9$ are fulfilled. In practice, we find that the value of q_l that minimizes the free energy is always very close to q^*: the ordering takes place at the wave vector for which the fluctuations in the disordered phase are maximum. This conclusion, however, would be modified by the inclusion of higher order harmonics in the representation of the ordered phase, which becomes increasingly important as the temperature is lowered below the ODT.[10]

D. Tagged chain correlations

In order to study the internal correlations of a tagged chain, we add to the Hamiltonian given in Eq. (1) an external potential $U(\mathbf{r}) = [U_A(\mathbf{r}), U_B(\mathbf{r})]$ that couples to the microscopic density of this particular chain, labeled (0). The new Hamiltonian is thus

$$H_U = H_0 + \int d\mathbf{r}\, U_i(\mathbf{r})\hat{\rho}_i^{(0)}(\mathbf{r}). \qquad (19)$$

The density–density correlation functions of the tagged chain are obtained by taking functional derivatives of the corresponding partition function $Z[U]$ with respect to U, evaluated at $U = 0$:

$$\langle \hat{\rho}_i^{(0)}(\mathbf{r})\hat{\rho}_j^{(0)}(\mathbf{r}')\rangle = \frac{1}{Z[0]}\frac{\delta^2 Z[U]}{\delta U_i(\mathbf{r})\delta U_j(\mathbf{r}')}\bigg|_{U=0}. \qquad (20)$$

Now the partition function $Z[U]$ can be calculated by using the Edwards transformation. The result is

$$Z = \langle \exp(-f_{ni}[i\phi + U] - Pf_{ni}[i\phi])\rangle_\phi, \qquad (21)$$

where $f_{ni}[\phi]$ is the free energy for a single Gaussian chain in the potential ϕ. The first term in the exponential corresponds to the chain (0), which is subjected to the external potential $U + i\phi$. $f_{ni}[\phi]$ can be expanded as a series in ϕ, the coefficients being the connected Green's functions of a Gaussian chain. To fourth order in ϕ, one has

$$f_{ni}[\phi] = \int d\mathbf{r}\, G_{Ci}^{(1)}(\mathbf{r})\phi_i(\mathbf{r}) - \frac{1}{2!}\int\int d\mathbf{r}\, d\mathbf{r}'\, G_{Cij}^{(2)}(\mathbf{r},\mathbf{r}')\phi_i(\mathbf{r})\phi_j(\mathbf{r}')$$

$$+ \frac{1}{3!}\int\int\int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, G_{Cijk}^{(3)}(\mathbf{r},\mathbf{r}',\mathbf{r}'')\phi_i(\mathbf{r})\phi_j(\mathbf{r}')\phi_k(\mathbf{r}'')$$

$$- \frac{1}{4!}\int\int\int\int d\mathbf{r}\, d\mathbf{r}',d\mathbf{r}''\, d\mathbf{r}'''\, G_{Cijkl}^{(4)}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''')\phi_i(\mathbf{r})\phi_j(\mathbf{r}')\phi_k(\mathbf{r}'')\phi_l(\mathbf{r}''') + O[\phi^5]. \qquad (22)$$

Inserting this expansion in Eq. (21), and performing the two derivatives in Eq. (20), we obtain after some straightforward algebra the following result for the correlation functions:

$$\langle \hat{\rho}_i^{(0)}(\mathbf{r})\hat{\rho}_j^{(0)}(\mathbf{r}')\rangle = \langle \hat{\rho}_i^{(0)}(\mathbf{r})\hat{\rho}_j^{(0)}(\mathbf{r}')\rangle_{ni} + \frac{1}{2}\int\int d\mathbf{r}''\, d\mathbf{r}'''$$
$$\times [\langle \hat{\rho}_i^{(0)}(\mathbf{r})\hat{\rho}_j^{(0)}(\mathbf{r}')\hat{\rho}_k^{(0)}(\mathbf{r}'')\hat{\rho}_l^{(0)}(\mathbf{r}''')\rangle_{ni}$$
$$- \langle \hat{\rho}_i^{(0)}(\mathbf{r})\hat{\rho}_j^{(0)}(\mathbf{r}')\rangle_{ni}\langle \hat{\rho}_k^{(0)}(\mathbf{r}'')\hat{\rho}_l^{(0)}$$
$$\times (\mathbf{r}''')\rangle_{ni}]\langle i\phi_i(\mathbf{r}'')i\phi_j(\mathbf{r}''')\rangle_0 + O[\phi^3], \qquad (23)$$

where $\langle \cdots \rangle_{ni}$ indicates an ensemble average over the configurations of a Gaussian (noninteracting) chain (0). The index 0 on the last average indicates that this average is taken with the weight $Q[\phi]\exp(-F_{ni}[i\phi])$, where $F_{ni}[i\phi] = (P+1)f_{ni}[i\phi]$. Transforming to Fourier space, and making use of the unconnected Green's functions $G^{(n)}$ defined by Leibler (see Appendix A) Eq. (23) becomes

$$F_{ij}^{(0)}(q) \equiv \frac{V}{N}\int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}}\langle \hat{\rho}_i^{(0)}(\mathbf{r})\hat{\rho}_j^{(0)}(0)\rangle$$

$$= G_{ij}^{(2)}(q) + \frac{1}{2V}\sum_{\mathbf{k}}[G_{ijkl}^{(4)}(\mathbf{q}, -\mathbf{q}, \mathbf{k}, -\mathbf{k})$$
$$- NG_{ij}^{(2)}(q)G_{ij}^{(2)}(k)]\Phi_{kl}(k), \qquad (24)$$

where

$$\Phi_{ij}(q) = \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}}\langle i\phi_i(\mathbf{r})i\phi_j(0)\rangle_0. \qquad (25)$$

Note that when $q = 0$ the second term on the right-hand side of Eq. (24) vanishes, so that the normalization $F_{ij}^{(0)}(0) = G_{ij}(0) = N_iN_j/N$ is preserved.

The correlation functions Φ_{ij} of the field ϕ conjugate to the density are related to the density–density correlations by the following exact equation:

$$\rho S_{ij}(\mathbf{q}) = V^{-1}\langle \hat{\rho}_i(\mathbf{q})\hat{\rho}_j(-\mathbf{q})\rangle$$

$$-2\frac{\delta \log(Z)}{\delta v_{ij}(\mathbf{q})}$$

$$= [v^{-1}(\mathbf{q})]_{ij} + [v^{-1}(\mathbf{q})\cdot\Phi(\mathbf{q})\cdot v^{-1}(\mathbf{q})]_{ij}, \quad (26)$$

where $v^{-1}(\mathbf{q})$ is the inverse of the Fourier transform of the 2×2 matrix $v(\mathbf{r})$, and the dots denote matrix products. The last line in Eq. (26) is obtained by making use of the Edwards representation (3,4) of the partition function. In the particular case of an incompressible melt, $S_{ij}(q) = (2\delta_{ij} - 1)S_{cc}(q)$ and $[v^{-1}(q)]_{ij} = (1 - 2\delta_{ij})\rho/(2\chi)$. Therefore Eq. (26) reduces to

$$\Phi_{ij}(q) = \frac{\chi}{2\rho}[1 + 2\chi S_{cc}(q)](2\delta_{ij} - 1). \quad (27)$$

Finally, we make the usual assumption that $S_{cc}(q)$ is sharply peaked around $q = q^*$, and that the contribution from this peak dominates the integral on the right-hand side of Eq. (24). Making use of the Lorentzian approximation for $S_{cc}(q)$ given in Eq. (11) we obtain

$$N^{-1}F_{ij}^{(0)}(q) \simeq N^{-1}G_{ij}^{(2)}(q) + 2B(\chi N)^2[N^{-3}g_{ijkl}^{(4)}(q,q^*)$$

$$- N^{-2}G_{ij}(q)G_{kl}(q^*)](2\delta_{kl} - 1), \quad (28)$$

where as in Eq. (16) $B = Na^2q^{*2}/[8\pi(\bar{N}r\alpha)^{1/2}]$, and $g_{ijkl}^{(4)}(q,k)$ is the angular average of $G_{ijkl}^{(4)}(\mathbf{q}, -\mathbf{q}, \mathbf{k}, -\mathbf{k})$ defined in strict analogy with Eq. (13).

From the small wave vector expansion of $N^{-1}F_{ij}^{(0)}(q)$,

$$N^{-1}F_{ij}^{(0)}(q) = \frac{(N_iN_j)}{N^2}\left[1 - \frac{q^2R_{ij}^2}{3} + O(q^4)\right], \quad (29)$$

we extract the three "partial radii of gyration" of the tagged chain:

$$R_{ij}^2 = \frac{1}{2N_iN_j}\sum_{I=1}^{N_i}\sum_{J=1}^{N_j}\langle (\mathbf{r}_I^{(0)} - \mathbf{r}_J^{(0)})^2\rangle. \quad (30)$$

$R_{ii}^2(i = A,B)$ is the radius of gyration of the i part of the diblock. The overall radius of gyration R^2 is given by the combination

$$R^2 = f^2R_{AA}^2 + 2f(1 - f)R_{AB}^2$$

$$+ (1 - f)^2R_{BB}^2. \quad (31)$$

For a Gaussian diblock, $R_{AA}^2 = Na^2f/6, R_{AB}^2 = Na^2/4$, and $R_{BB}^2 = Na^2(1 - f)/6$.

Before we describe the results of our calculations, it is useful to briefly comment on the similarities and differences between our calculation of the tagged chain correlations and the classical approach of Edwards for calculating the size of a homopolymer chain in a melt.[13] Although the two calculations might at first sight look quite different, they are in fact intimately related. Let us first consider a homopolymer melt: in this case it is evident from Eq. (26) that *if the melt structure factor is calculated by using the random phase approximation*, the function $\Phi(q)$ is exactly the "screened potential" derived by Edwards. Moreover, Eq. (24) is a perturbation expansion to first order for the correlation function of a chain whose monomers interact through the screened potential $\Phi(q)$. The well-known result of Edwards for the radi-

us of gyration can be recovered from the small q expansion of the resulting $F^{(0)}(q)$.

These remarks emphasize the fact that our calculation is actually a perturbative one in the strength of the (screened) potential, as was already clear when we neglected terms of order higher than ϕ^2 in Eq. (23). In the case of the homopolymer melt, neglecting higher order terms is justified by the weakness of the screened potential. The situation for block copolymers, however, is quite different: the screened potential Φ is dominated by the contribution of $S_{cc}(q)$ close to q^*, which becomes very large as the microphase separation is approached [in fact, in writing Eq. (28), only this contribution has been accounted for, and we have neglected a smaller term that would yield Edwards' swelling effect]. The integrated effect, however, amounts to an expansion in the variable $(\chi N)/\bar{N}^{1/2}$. Therefore neglecting the higher order terms [which would be proportional to $(\chi N)^4/\bar{N}$] is not always justified, as will become evident from the numerical results presented in the next section. The expansion can nevertheless be controlled near the ODT by making $\bar{N}$ arbitrarily large.

III. RESULTS

A. General features

Unfortunately, the equations obtained in the preceding sections can only be solved numerically. In order to display the general features of the results, we have solved these equations for various values of $\bar{N}$ and χN, for $f = 0.5$. The values of $\bar{N}$ ranged from $\bar{N} = 100$ to $\bar{N} = 16\,000$. As mentioned above, our theory amounts to an expansion in $\bar{N}^{-1/2}$, hence is not expected to be accurate (see Ref. 3 for a discussion) for small $\bar{N}$, while for large $\bar{N}$ it asymptotically approaches the mean-field theory.
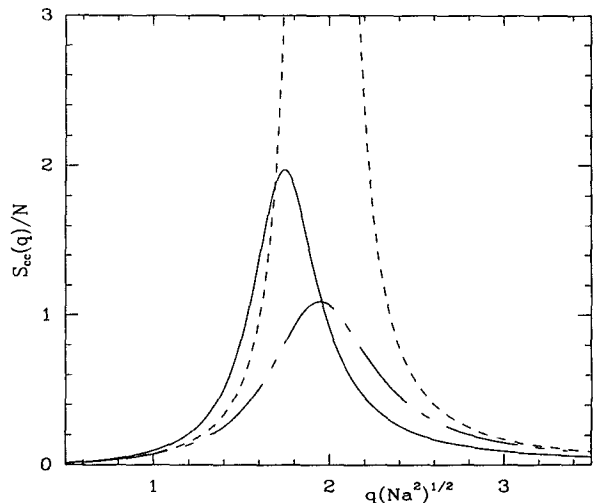
Figure 1 compares a representative concentration–con-

FIG. 1. The concentration–concentration structure factor $S_{cc}(q)$ for a symmetric copolymer melt with $\bar{N} = 1000$ at the ODT point. Full line: present work. Short dashes: Leibler's theory. Long dashes: Fredrickson–Helfand theory.

centration structure factor obtained by solving Eqs. (12) to the corresponding results obtained from the fluctuation theory[3] and from the mean-field theory of Ref. 2. The comparison is made for $\overline{N} = 1000$ at the ODT. The modifications compared to the result of Ref. 3 are a shift in the peak position, a larger peak intensity, and a smaller peak width, which (except for the shift) bring our new result closer to the mean-field structure factor. The reason for this evolution can be traced to the wave vector dependence of the function $\gamma_4(q,q)$: this quantity is an increasing function of q, so that the shift of the peak towards smaller wave vectors will have the tendency to decrease the strength of the fluctuation term that smears out the diverging mean-field structure factor. The same effect is displayed in more detail in Fig. 2, which shows the inverse peak intensity as a function of χN in the different theories.

Figure 3 shows the variation of the peak position q^* as a function of χN for different values of $\overline{N}$. For small χN, q^* scales like $N^{-1/2}$, as in the mean-field or Fredrickson–Helfand theory. As the ODT is approached, deviations from this "Gaussian" behavior become manifest. The peak position is shifted towards smaller values. The extent of this effect, and the range of values of χN for which it is observable before the ODT takes place, are a decreasing function of the molecular weight, as is natural for such a fluctuation induced phenomenon. For the smaller chains considered, $\overline{N} = 100$, the deviation from Gaussian behavior reaches about 10% at the ODT. Note that even in the $\chi N \to 0$ limit, the peak is shifted compared to the mean-field value q_0. This is due to the existence of correlations associated with the incompressibility constraint (the "correlation hole" effect[2,16]) that contribute to the second term in the right-hand side of Eq. (10).

Due to the increased magnitude of the concentration fluctuations compared with the Fredrickson–Helfand theory, one can expect that the transition to the lamellar phase
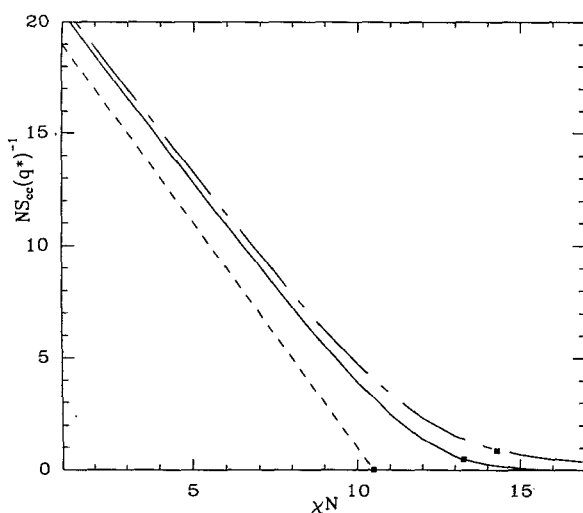

FIG. 3. Variation of the structure factor peak position q^* multiplied by $(Na^2/6)^{1/2}$ with χN for different values of $\overline{N}$. From bottom to top, the full curves correspond to values of $\overline{N}$ of 100, 500, 1000, 8000, and 16 000, respectively. For each $\overline{N}$, the filled square indicates the location of the ODT. The horizontal dashed line gives the position of the peak in the Leibler and Fredrickson–Helfand theories, and the vertical one the location of the ODT according to Leibler's theory.

will be shifted towards smaller values of χN. This expectation is borne out by the calculation of the transition point $(\chi N)_t$ as a function of $\overline{N}$, following the procedure outlined in Sec. II C. The result is displayed in Fig. 4. For the smaller chains, our results for $(\chi N)_t$ are seen to lie about halfway between the mean-field and the Fredrickson–Helfand predictions. For large $\overline{N}$, the difference between the Fredrickson–Helfand result and ours becomes small, and both asymptotically tend to the mean-field result.

Finally, Fig. 5 presents the evolution of the radius of

FIG. 2. Inverse of the structure factor peak intensity for symmetric copolymers with $\overline{N} = 1000$ as a function of χN. The symbols are the same as in Fig. 1. The squares indicate the location of the ODT according to the different theories.
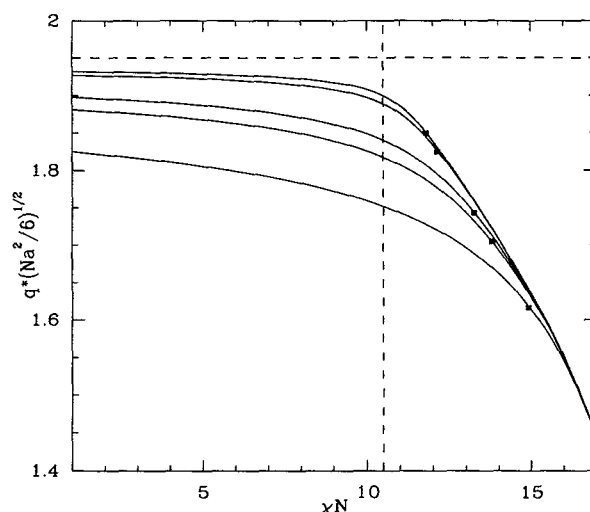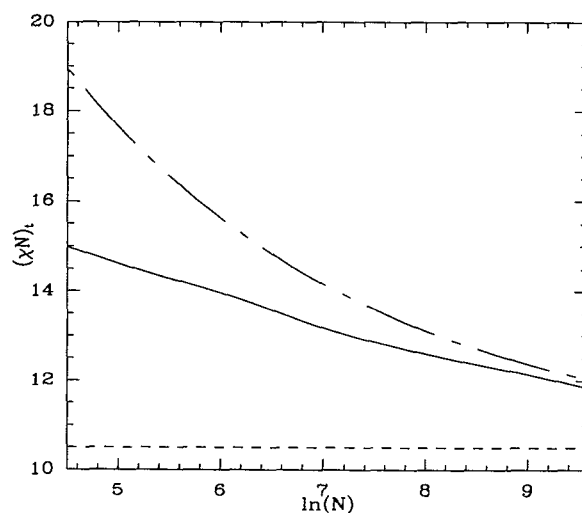

FIG. 4. Location of the ODT as a function of $\overline{N}$ in the different theories. The symbols have the same meaning as in Fig. 1.
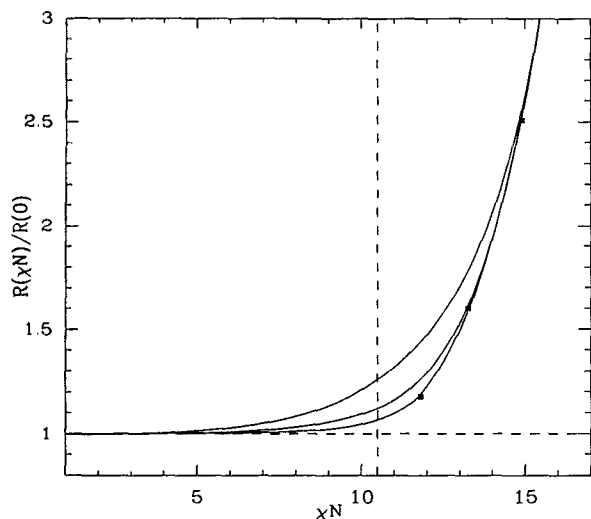
FIG. 5. Radius of gyration of the chain divided by its unperturbed value as a function of χN for three values of $\bar{N}$. From top to bottom $\bar{N} = 100, 1000, 8000$. The squares and the dashed lines have the same meaning as in Fig. 3.

gyration R divided by its unperturbed value $(Na^2/6)^{1/2}$ as a function of χN, for three values of $\bar{N}$. R^2 is seen to present a very dramatic increase as the ODT is approached. It must be remembered, however, that our calculation of R is a perturbative one. Thus, the increase of R well beyond its unperturbed value exhibited in Fig. 5 is unphysical, and is merely indicative of the fact that our approximation breaks down for large (χN). Other methods are required to analyze the low temperature (large χN) microphases.[14,15] The inadequacy of our method for large χN becomes even clearer if the different contributions to R^2 [Eq. (29)] are studied separately. One finds then that while R^2_{AB} exhibits a positive departure from its Gaussian value $(Na^2/4)$, this deviation is negative for R^2_{AA} and R^2_{BB}, and these quantities eventually become negative for large enough χN, a clearly unphysical result. In spite of this limitation, several interesting conclusions can be drawn from the calculation, which is expected to be accurate as long as the deviations from Gaussian behavior remain small: first, these deviations start quite far from the ODT, deep inside the disordered phase. Secondly, the study of the different contributions to R^2 shows that concentration fluctuations affect single chain statistics in two different ways: a segregation effect between A and B monomers yields an increase in R_{AB}, and what can be described as an effective attractive interaction between monomers of the same species results in a decrease of R_{AA} and R_{BB}. This last effect was anticipated in Ref. 17 on the basis of an RPA calculation of the screened potentials for a copolymer chain, but the authors erroneously inferred from it that the whole chain would contract as χN increases. Our calculation displays the opposite effect. In fact, our result indicates that as χN increases, the chain will look more and more like a dumbbell made up of two separate coils of pure A and B monomers. Even though each of these coils is more compact than a Gaussian coil, the increasing separation between them results in an increase of the chain radius of gyration.

B. Comparison with neutron scattering results

As mentioned in the introduction, this work was in part motivated by the recent experimental results of Ref. 7. In this study, the position of the peak in $S_{cc}(q)$ was studied as a function of the polymerization index N at fixed temperature $(T = 296$ K) for a series of PEP-PEE diblocks with $f = 0.55$. It was shown that for the larger molecular weights, the peak position q^* did not conform to the mean-field and Fredrickson-Helfand result $q^* \sim N^{-1/2}$ but displayed a stronger N dependence that was approximately represented as $q^* \sim N^{-0.8}$. Figure 6 shows a comparison between the experimental results for q^* as a function of N and the prediction of our theory. The procedure used to independently determine the parameters (χ, ρ, and a) required for this comparison is outlined in Appendix B, and is similar to that followed in Ref. 6. We merely mention here that no adjustable parameters are used in the comparison. The nearly quantitative agreement between theory and experiment is therefore quite remarkable.

It should be emphasized that the vertical line indicating the location of the ODT in Fig. 6 is the result of a theoretical calculation based on the formalism presented here and is not an experimental line. The same was true in the corresponding figure of Ref. 7 (where the line was based on the Fredrickson-Helfand theory). In fact, the experimental point that lies closest to this line in Fig. 6 corresponds to a polymerization index $N = 791$, and the corresponding sample was found from rheological measurements to be within a few degrees of its ODT at $T = 296$ K.[18] For $N = 791$, the theoretical prediction (using the parameters derived in Appendix B) is $T_{ODT} = 287$ K, again a nearly quantitative agreement.

IV. SUMMARY AND CONCLUSIONS

In this work, we have added a third level of sophistication to the previously existing descriptions of the ODT in
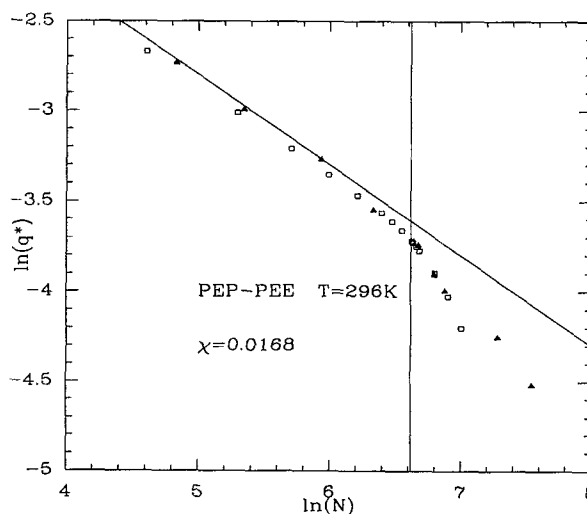

FIG. 6. Peak position of the structure factor (in inverse Å) vs polymerization index for a PEP-PEE sample at $T = 296$ K. Open squares: theoretical prediction. Full triangles: experimental result of Ref. 7. The full vertical line indicates the theoretical prediction for the ODT location. A straight line of slope $-1/2$ was drawn as a guide to the eye.

diblock copolymers. In the mean-field approach of Ref. 2, the free energy of the system is computed by taking into account only the most probable value of the order parameter ψ. This results into a second-order phase transition, with a susceptibility peaked at a temperature independent wave vector q_0. In Ref. 3, it was shown how the ODT is modified when the contributions from fluctuating patterns consisting of superpositions of plane waves with wave vectors having *random directions and phases, but fixed magnitude q_0*, are accounted for. These fluctuations induce a first-order phase transition, but the restriction on the magnitude of the fluctuations wave vectors implies that the susceptibility remains peaked at the mean-field wave vector q_0. Our calculation shows how this last deficiency can be corrected by incorporating isotropic concentration fluctuations, but without restriction on the magnitude of the wave vectors. The result is a shift in the susceptibility peak that brings the theory in quantitative agreement with experimental results.

Another aspect of this paper is a consistent calculation of how the single chain statistics are affected by concentration fluctuations. From a perturbative calculation to order $(\chi N)^2/\bar{N}^{1/2}$ we deduce that for finite molecular weights, the typical single chain configurations differs strongly from those of a Gaussian coil even quite far from the ODT. The chain can be qualitatively pictured as a dumbbell consisting of two coils (one for each block) that are more densely packed than Gaussian coils, but the chain as a whole is stretched above Gaussian dimensions. At present, no experimental results on single chain statistics in the disordered phase are available. Simulation results[8] indicate an increase of the radius of gyration with χN that is in qualitative agreement with our prediction. A more quantitative comparison of the present theory with simulation, however, is complicated by the fact that the simulations were performed with short diblock copolymer chains dissolved in a neutral solvent, rather than a melt of long chains. We hope that our predictions will stimulate additional experimental work and simulations on this class of interesting polymeric materials.

In summary, our calculations show that the traditional idea underlying the RPA approach for polymer melts, namely that concentration response functions can be computed as if the individual chains adopt Gaussian configurations, has to be reconsidered for the case of block copolymers. Strong fluctuations in concentration influence both collective and single chain properties, and can strongly modify the associated length scales $1/q^*$ and R for chains of finite size.

ACKNOWLEDGMENTS

APPENDIX A

This appendix presents an outline of the calculation of the coefficients $\Gamma_4(\mathbf{q}, -\mathbf{q}, \mathbf{k}, -\mathbf{k})$. Our starting point will be

Eqs. (III-24) and (III-25) of Ref. 2 [see also Eq. (A22) of Ref. 12] which we reproduce here without derivation:

$$\Gamma_4(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4) = \gamma_{ijkl}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)$$
$$\cdot [G_{iA}^{(2)-1}(\mathbf{q}_1) - G_{iB}^{(2)-1}(\mathbf{q}_1)]$$
$$\times [G_{jA}^{(2)-1}(\mathbf{q}_2) - G_{jB}^{(2)-1}(\mathbf{q}_2)]$$
$$\cdot [G_{kA}^{(2)-1}(\mathbf{q}_3) - G_{kB}^{(2)-1}(\mathbf{q}_3)]$$
$$\times [G_{lA}^{(2)-1}(\mathbf{q}_4) - G_{lB}^{(2)-1}(\mathbf{q}_4)], \quad \text{(A1)}$$

$$\gamma_{ijkl}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4) = -G_{ijkl}^{(4)}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)$$
$$+ V^{-1}\sum_{\mathbf{k}} G_{nm}^{(2)-1}(\mathbf{k})$$
$$\times [G_{ijm}^{(3)}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{k})G_{nkl}^{(3)}(-\mathbf{k},\mathbf{q}_3,\mathbf{q}_4)$$
$$+ G_{ikm}^{(3)}(\mathbf{q}_1,\mathbf{q}_3,\mathbf{k})G_{njl}^{(3)}(-\mathbf{k},\mathbf{q}_2,\mathbf{q}_4)$$
$$+ G_{ilm}^{(3)}(\mathbf{q}_1,\mathbf{q}_4,\mathbf{k})G_{nkj}^{(3)}(-\mathbf{k},\mathbf{q}_3,\mathbf{q}_2)].$$
$$\text{(A2)}$$

Here $\mathbf{q}_4$ is shorthand for $-\mathbf{q}_1 - \mathbf{q}_2 - \mathbf{q}_3$. The quantities $G^{(2)}, G^{(3)}, G^{(4)}$ are the density–density correlation functions for a noninteracting (Gaussian) copolymer. In particular,

$$G_{ijkl}^{(4)}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)$$
$$= \langle \hat{\rho}_i^{(0)}(\mathbf{q}_1)\hat{\rho}_j^{(0)}(\mathbf{q}_2)\hat{\rho}_k^{(0)}(\mathbf{q}_3)\hat{\rho}_l^{(0)}(\mathbf{q}_4)\rangle_{ni}. \quad \text{(A3)}$$

The detailed recipe for calculating these functions is given in appendix B of Ref. 2. Here we shall merely quote the results obtained for $G^{(3)}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)$ $(\mathbf{q}_3 = -\mathbf{q}_1 - \mathbf{q}_2)$ and $G_4(\mathbf{q}, -\mathbf{q}, \mathbf{k}, -\mathbf{k})$ which are useful for calculating $\Gamma_4(\mathbf{q}, -\mathbf{q}, \mathbf{k}, -\mathbf{k})$. The result for $G^{(4)}$ is also required for the single chain calculations of Sec. II D.

Defining

$$P(I,J,q) = \exp(-q^2a^2|I-J|/6), \quad \text{(A4)}$$
$$f_1(q_1,q_2,f) = \int_0^{fN} dI \int_0^I dJ \int_0^J dK\, P(I,J,q_1)P(J,K,q_2), \quad \text{(A5)}$$
$$f_2(q_1,q_2,f) = \int_{fN}^N dI \int_0^{fN} dJ \int_0^J dK\, P(I,J,q_1)P(J,K,q_2), \quad \text{(A6)}$$
$$g_1(q_1,q_2,q_3,f) = \int_0^{fN} dI \int_0^I dJ \int_0^J dK \int_0^K dL\, P(I,J,q_1)$$
$$\times P(J,K,q_2)P(K,L,q_3), \quad \text{(A7)}$$
$$g_2(q_1,q_2,q_3,f) = \int_{fN}^N dI \int_0^{fN} dJ \int_0^J dK \int_0^K dL$$
$$\times P(I,J,q_1)P(J,K,q_2)P(K,L,q_3), \quad \text{(A8)}$$
$$g_3(q_1,q_2,q_3,f) = \int_{fN}^N dI \int_{fN}^I dJ \int_0^{fN} dK \int_0^K dL\, P(I,J,q_1)$$
$$\times P(J,K,q_2)P(K,L,q_3), \quad \text{(A9)}$$

we obtain

$$G_{AAA}^{(3)}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)$$
$$= 2[f_1(q_1,q_2,f) + f_1(q_2,q_3,f) + f_1(q_3,q_1,f)],$$
$$G_{AAB}^{(3)}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3) = f_2(q_3,q_1,f) + f_2(q_3,q_2,f), \quad \text{(A10)}$$

$G_{AAAA}^{(4)}(\mathbf{q}, -\mathbf{q}, \mathbf{k}, -\mathbf{k})$

$$= 8g_1(q,0,k,f) + 2[g_1(q,\mathbf{q}+\mathbf{k},q,f) + g_1(q,\mathbf{q}-\mathbf{k},q,f)$$
$$+ g_1(k,\mathbf{q}+\mathbf{k},k,f) + g_1(k,\mathbf{q}-\mathbf{k},k,f)]$$
$$+ 4[g_1(q,\mathbf{q}+\mathbf{k},k,f) + g_1(q,\mathbf{q}-\mathbf{k},k,f)],$$

$G_{AAAB}^{(4)}(\mathbf{q}, -\mathbf{q}, \mathbf{k}, -\mathbf{k})$

$$= 2g_2(k,0,q,f) + g_2(k,\mathbf{q}-\mathbf{k},k,f) + g_2(k,\mathbf{q}+\mathbf{k},k,f)$$
$$+ g_2(k,\mathbf{q}-\mathbf{k},q,f) + g_2(k,\mathbf{q}+\mathbf{k},q,f), \qquad (A11)$$

$G_{AABB}^{(4)}(\mathbf{q}, -\mathbf{q}, \mathbf{k}, -\mathbf{k}) = 4g_3(k,0,q,f),$

$G_{ABAB}^{(4)}(\mathbf{q}, -\mathbf{q}, \mathbf{k}, -\mathbf{k})$

$$= g_3(q,\mathbf{q}+\mathbf{k},q,f) + g_3(q,\mathbf{q}+\mathbf{k},k,f)$$
$$+ g_3(k,\mathbf{q}+\mathbf{k},k,f) + g_3(q,\mathbf{q}+\mathbf{k},k,f).$$

The functions that are not explicitly listed in Eqs. (A10) and (A11) can be easily obtained by making appropriate changes such as $f \leftrightarrow (1-f)$ or $\mathbf{q} \leftrightarrow \mathbf{k}$, as is clear from the definition (A3). In principle, the evaluation of functions g_1, g_2, g_3, f_1, f_2 is a completely straightforward task, although the algebra involved is quite formidable. We have found these calculations are greatly facilitated by the use of a symbolic mathematics software package. A FORTRAN code for calculating $G^{(3)}$, $G^{(4)}$, and Γ_4 is available from the authors (e-mail address: jlb@squid.ucsb.edu,ghf@squid.ucsb.edu).

APPENDIX B

In this appendix, we discuss the procedure used to carry out the comparison between the experiments of Ref. 7 and the theory presented in Sec. III B. This procedure is quite similar to the one used in Ref. 6 (see in particular the appendix) from which we shall borrow some relations without discussion.

In the present theoretical calculations, a copolymer melt is characterized by five independent quantities: the segment length a, the Flory parameter χ, the polymerization index N, the volume per segment $v = 1/\rho$, and the composition f. The relevant combinations that actually enter the calculation are f, the unperturbed radius of gyration $Na^2/6, \chi N$ and the parameter $\overline{N} = N\rho^2 a^6$.

The main difficulty in comparing the calculation and the experiments lies in the fact that the two blocks in a real copolymer have different statistical segment lengths. From independent measurements on PEP and PEE *homopolymers*,[19] the two relevant segment lengths for PEP–PEE diblocks are[6] (lengths in Å, temperature T in Kelvin):

$$\ln a_A^2 = -1.0 \times 10^{-3} T + 4.24,$$
$$\ln a_B^2 = -2.3 \times 10^{-3} T + 3.90, \qquad (B1)$$

when the segments are defined as having a 56 g/mol weight.[6] In our comparison, we make the simplifying assumption that the statistical segment length a used in the theory can be computed as $a = 6R_0^2/N$, where R_0^2 is the radius of gyration of a Gaussian chain made up of fN segments of length a_A and $(1-f)N$ segments of length a_B. This simple approximation results in the expression for a:

$$a^2 = f^2(3 - 2f)a_A^2 + (1-f)^2(1 + 2f)a_B^2, \qquad (B2)$$

where $f = 0.55$ for the homologous series of samples investigated in Ref. 7. The other parameters are the volume per segment, which has been estimated in Ref. 6,

$$\ln v = 6.5 \times 10^{-4} T + 4.489 \qquad (B3)$$

and the Flory parameter χ. In order to determine the latter, we follow Ref. 6 in assuming a simple temperature variation, $\chi = A/T + B$. We then calculate χ_{ODT} for the three samples ($N = 957$, $N = 1026$, and $N = 1523$) for which the ODT temperature is known from rheological measurements. The parameters A and B are then adjusted to yield a best fit. The result is

$$\chi = 5.12/T - 5.28 \times 10^{-4}. \qquad (B4)$$

Once the parametrizations (B2), (B3), and (B4) are established, comparison between the theory and the experiments can be carried out in the absence of any adjustable parameter.

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