

## Single-chain statistics and the upper wave-vector cutoff in polymer blends

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We derive the equation for the single-chain correlation function in polymer blends. The chains in the incompressible blend have a radius of gyration smaller than the radius of gyration for ideal chains. The chains shrink progressively as we approach the critical temperature  $T_c$ . The correction responsible for shrinking is proportional to  $1/\sqrt{N}$ , where  $N$  is the polymerization index. At  $T = T_c$  and for  $N = 1000$ , the size of the chain has been estimated to be 10% smaller than the size of the ideal coil. The estimate relies on the appropriate cutoff. In the limit of  $N \rightarrow \infty$  the chains approach the random walk limit. Additionally, we propose in this paper a self-consistent determination of the radius of gyration and the upper wave-vector cutoff. Our model is free from any divergences such as were encountered in the previous mean-field studies; we make an estimate of the chain size at the true critical temperature and not the mean-field one.

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### I. INTRODUCTION

In this paper we are mainly concerned with the behavior of a single chain in the binary mixture of two homopolymers. It is a well known fact that in the limit of  $N \rightarrow \infty$  (the infinite length of the chain) the self-interactions of a chain are screened by the presence of other chains [1,2] and thus the chain adopts the Gaussian statistics as an ideal coil. Moreover, in this limit the collective structure factor for all the chains can be calculated from the random phase approximation (RPA) of de Gennes [3]. And last but not least the coexistence curve is obtained from the well-known Flory-Huggins free energy. As has been shown elsewhere the one-loop corrections to the collective structure factor and the Flory-Huggins expression for the critical temperature of mixing are of the order of  $\sqrt{N}$  [4]. As has been shown there, the corrections are still appreciable even for chains as long as  $10^3 l$ , where  $l$  is the monomer size. Moreover, it has been pointed out that the results of the loop expansion strongly rely on the appropriate choice of the cutoff; in particular, it was shown that if the real-space cutoff is of the order of  $l$  neither RPA nor the Flory-Huggins results would have been retrieved in the limit of large  $N$ . We have been able to estimate the correct cutoff as roughly proportional to  $\sqrt{N}l$ . The purpose of this paper is twofold. First we want to derive the equation for the monomer-monomer correlation function in the single chain and in particular, find the radius of gyration for a single coil in a polymer blend. Secondly we would like to discuss the problem of the cutoff in polymer physics and propose a mean for the self-consistent determination of the cutoff in the theory.

Previous studies of the chain statistics in polymer blends have been done in the Gaussian limit only, whereas here we present a self-consistent one-loop approximation scheme. In particular, our results are free from any spurious divergences encountered in the previous study [5]. Indeed the singularity at  $T = T_c$  of the effective monomer potentials derived in [5,6] can be treated by an effective renormalized theory [7]. Our method is very similar to, although not identical to, the one used by Barrat and Fredrickson [8]; here we will compare the two methods in terms of the technical details as well as obtained results.

The paper is organized as follows. In Sec. II we present the basic scheme for the calculations. In Sec. III we find the approximate equation for the single-chain correlation function as well as for the collective structure factor. In this section we also make an analytical estimate of the radius of gyration at infinite temperature and at the critical temperature. Section IV contains the discussion of the cutoff in polymer blends and the proposition for its self-consistent determination. Section V contains the concluding remarks.

### II. THE PARTITION FUNCTION FOR A POLYMER BLEND

We consider a mixture of  $n_A$   $A$ -type flexible polymers with  $N_A$  monomers in each molecule, and  $n_B$   $B$ -type flexible polymers with  $N_B$  monomers in each molecule inside a volume  $V$ . The external field  $U_A$  couples to only one chain of  $A$  monomers. The formula for the partition function for this system can be conveniently written in the following form [4,8,9]:

$$Z[U_A] = \int D\phi_A \int D\phi_B \exp(-H_I[\phi_A, \phi_B]) \int DJ_A \int DJ_B \exp \left[ i \int \frac{d\mathbf{q}}{(2\pi)^3} \phi_A J_A + i \int \frac{d\mathbf{q}}{(2\pi)^3} \phi_B J_B + F_A^{(n_A)}[J_A] + F_A^{(1)}[J_A + iU_A] - F^{(1)}[J_A] + F_B^{(n_B)}[J_B] \right]. \quad (2.1)$$

Here  $\phi_A$  and  $\phi_B$  are the Fourier transforms of the local concentrations of  $A$  and  $B$  monomers respectively.  $H_I$  is the interaction Hamiltonian,

$$H_I = \frac{\rho_0}{k_B T} \int \frac{d\mathbf{q}}{(2\pi)^3} \left[ \frac{1}{2} w_{AA} |\phi_A(\mathbf{q})|^2 + \frac{1}{2} w_{BB} |\phi_B(\mathbf{q})|^2 + w_{AB} \phi_A(\mathbf{q}) \phi_B(-\mathbf{q}) \right], \quad (2.2)$$

$\omega_{ij}$  are the effective interaction parameters and  $\rho_0$  is the total density of monomers. The free-energy density for the system of  $n_\gamma$  noninteracting Gaussian chains in the external field  $J_\gamma$ ,  $F_\gamma^{(n_\gamma)}[J_\gamma]$  ( $\gamma = A, B$ ), is given in the form of the cumulant expansion [4,9], i.e.,

$$F_\gamma^{(n_\gamma)}[J_\gamma] = \sum_{n=1}^{\infty} \frac{(-i)^n}{n!} \int \frac{d\mathbf{q}_1}{(2\pi)^3} \cdots \int \frac{d\mathbf{q}_n}{(2\pi)^3} \langle \hat{\phi}_\gamma^{(n_\gamma)}(\mathbf{q}_1) \cdots \hat{\phi}_\gamma^{(n_\gamma)}(\mathbf{q}_n) \rangle_0^c J_\gamma(-\mathbf{q}_1) \cdots J_\gamma(-\mathbf{q}_n), \quad (2.3)$$

where the concentration operators  $\hat{\phi}_\gamma^{(n_\gamma)}(\mathbf{q})$  for  $n_\gamma$  chains are given by the following formulas:

$$\hat{\phi}_A^{(n_A)}(\mathbf{q}) = \frac{1}{\rho_0} \sum_{\alpha=1}^{n_A} \sum_{i=1}^{N_A} \exp(\mathbf{q} \mathbf{r}_i^{(\alpha)}), \quad (2.4)$$

$$\hat{\phi}_B^{(n_B)}(\mathbf{q}) = \frac{1}{\rho_0} \sum_{\beta=1}^{n_B} \sum_{j=1}^{N_B} \exp(\mathbf{q} \mathbf{r}_j^{(\beta)}) \quad (2.5)$$

and the average  $\langle \cdot \rangle_0^c$  (subscript  $c$  stands for cumulants) is taken with respect to the ideal chain statistics which in our case is taken to be a Gaussian statistic. Here  $\mathbf{r}_i^{(\alpha)}$  denotes the position vector of the  $i$ th monomer in the  $\alpha$ th chain. The free energy of our labeled chain  $F_A^{(1)}[J_A + iU_A]$  is simply given by the above equations with  $n_\gamma$  set equal to 1 and the potential equal to  $J_A + iU_A$ . Finally if we integrate out the fields  $J_A, J_B$  we find the partition function in the following form:

$$Z[U_A] = \int D\phi_A \int D\phi_B \exp(-\Gamma_A[\Psi_A] - \Gamma_B[\Psi_B] - H_I), \quad (2.6)$$

where only  $\Gamma_A[\Psi_A]$  depends on the external potential  $U_A$ . First we find

$$\begin{aligned} \Gamma_A[\Psi_A] &= \sum_{n=2}^{\infty} \frac{1}{n!} \int \frac{d\mathbf{q}_1}{(2\pi)^3} \cdots \int \frac{d\mathbf{q}_n}{(2\pi)^3} \Gamma_n^{(A)}(\mathbf{q}_1 \cdots \mathbf{q}_n) \Psi_A(-\mathbf{q}_1) \cdots \Psi_A(-\mathbf{q}_n) - \int \frac{d\mathbf{q}_1}{(2\pi)^3} \langle \hat{\phi}_A^{(1)}(\mathbf{q}_1) \rangle_0^c U(\mathbf{q}_1) \\ &\quad - \frac{1}{2} \int \frac{d\mathbf{q}_1}{(2\pi)^3} \int \frac{d\mathbf{q}_2}{(2\pi)^3} \langle \hat{\phi}_A^{(1)}(\mathbf{q}_1) \hat{\phi}_A^{(1)}(\mathbf{q}_2) \rangle_0^c U_A(\mathbf{q}_1) U_A(\mathbf{q}_2). \end{aligned} \quad (2.7)$$

Next we find  $\Psi_A$  expanded up to the second order in the external potential  $U_A$ :

$$\begin{aligned} \Psi_A(\mathbf{q}_1) &= \Psi(\mathbf{q}_1) - \int \frac{d\mathbf{q}_2}{(2\pi)^3} \langle \hat{\phi}_A^{(1)}(\mathbf{q}_1) \hat{\phi}_A^{(1)}(\mathbf{q}_2) \rangle_0^c U_A(\mathbf{q}_2) \\ &\quad - \frac{1}{2} \int \frac{d\mathbf{q}_2}{(2\pi)^3} \int \frac{d\mathbf{q}_3}{(2\pi)^3} \langle \hat{\phi}_A^{(1)}(\mathbf{q}_1) \hat{\phi}_A^{(1)}(\mathbf{q}_2) \hat{\phi}_A^{(1)}(\mathbf{q}_3) \rangle_0^c U_A(\mathbf{q}_2) U_A(\mathbf{q}_3). \end{aligned} \quad (2.8)$$

Here  $\Psi(\mathbf{q}) = \phi_A(\mathbf{q}) - \langle \hat{\phi}_A^{(n_A)}(\mathbf{q}) \rangle_0$ ,  $q \neq 0$ , represents the Fourier transform of the deviations of the concentration of  $A$  monomers from the average concentration. Additionally we shall need the second-order vertex function as a functional of the external field. It has the following form:

$$\Gamma_2^{(A)} = (S_2^{(A)})^{-1}, \quad (2.9)$$

$$\begin{aligned} S_2^{(A)} &= \langle \hat{\phi}_A^{(n_A)}(\mathbf{q}_1) \hat{\phi}_A^{(n_A)}(\mathbf{q}_2) \rangle_0^c + \int \frac{d\mathbf{q}_3}{(2\pi)^3} \langle \hat{\phi}_A^{(1)}(\mathbf{q}_1) \hat{\phi}_A^{(1)}(\mathbf{q}_2) \hat{\phi}_A^{(1)}(\mathbf{q}_3) \rangle_0^c U_A(\mathbf{q}_3) \\ &\quad + \frac{1}{2} \int \frac{d\mathbf{q}_3}{(2\pi)^3} \int \frac{d\mathbf{q}_4}{(2\pi)^3} \langle \hat{\phi}_A^{(1)}(\mathbf{q}_1) \hat{\phi}_A^{(1)}(\mathbf{q}_2) \hat{\phi}_A^{(1)}(\mathbf{q}_3) \hat{\phi}_A^{(1)}(\mathbf{q}_4) \rangle_0^c U_A(\mathbf{q}_3) U_A(\mathbf{q}_4). \end{aligned} \quad (2.10)$$

Finally if we use the incompressibility formula we will find  $\Psi_B = -\Psi$  and  $\Gamma_B[\Psi_B]$  in the form known from the RPA [10]. Here we note that Barrat and Fredrickson [8], who used the same type of analysis, have performed this step differently, namely, they integrated over the monomer concentrations  $\phi_A, \phi_B$ , whereas we integrated over the coupling fields  $J_A, J_B$ . This difference will show up in the approximate equation for the single-chain correlation function.

### III. THE SINGLE-CHAIN CORRELATION FUNCTION

The correlation function for the single chain labeled by the external potential  $U_A$  is simply given by

$$S_{AA}(\mathbf{q}_1, \mathbf{q}_2) = \langle \hat{\phi}_A^{(1)}(\mathbf{q}_1) \hat{\phi}_A^{(1)}(\mathbf{q}_2) \rangle = \frac{\delta^2 Z[U_A]}{Z[U_A] \delta U_A(\mathbf{q}_1) \delta U_A(\mathbf{q}_2)}. \quad (3.1)$$

Now using this equation at  $U_A=0$  we find the following approximate equation for the single-chain structure factor in the incompressible blend:

$$VS_{AA}(\mathbf{q}, -\mathbf{q}) = \langle \hat{\phi}_A^{(1)}(\mathbf{q}) \hat{\phi}_A^{(1)}(-\mathbf{q}) \rangle_0 + \frac{1}{2\rho_0} \int \frac{d\mathbf{k}}{(2\pi)^3} [ \langle \hat{\phi}_A^{(1)}(\mathbf{q}) \hat{\phi}_A^{(1)}(-\mathbf{q}) \hat{\phi}_A^{(1)}(\mathbf{k}) \hat{\phi}_A^{(1)}(-\mathbf{k}) \rangle_0 - \langle \hat{\phi}_A^{(1)}(\mathbf{q}) \hat{\phi}_A^{(1)}(-\mathbf{q}) \rangle_0 \langle \hat{\phi}_A^{(1)}(\mathbf{k}) \hat{\phi}_A^{(1)}(-\mathbf{k}) \rangle_0 ] \Gamma_2^{(A)}(\mathbf{k}) \Gamma_2^{(A)}(\mathbf{k}) S_c(\mathbf{k}). \quad (3.2)$$

It includes the ideal term and the first nonvanishing correction to it. Here  $S_c(\mathbf{k}) = \langle \Psi(\mathbf{k}) \Psi(-\mathbf{k}) \rangle / V$  is the collective structure factor for the polymer blend [4] and  $\Gamma_2^{(A)}$  is given by Eqs. (2.9) and (2.10) with  $U_A=0$ . The averages with the subscript 0 are taken over the configurations of noninteracting system (ideal averages) whereas those without the subscript are taken over the configurations of the interacting system. As can be seen from this equation the upper wave-vector cutoff is crucial in this equation. Here we simply set it equal to  $2\pi/\sqrt{N}$  [4]. Due to the cutoff the ideal term is  $\sqrt{N}$  larger than the correction and thus dominates in the limit  $N \rightarrow \infty$ . Other corrections divided by the ideal term are of the order  $1/N$  and smaller and thus have not been included in Eq. (3.2). The longer discussion concerning the cutoff is contained in the following section. The equation for the single-chain correlation function in Ref. [8] is similar in structure to Eq. (3.2), only instead of having  $\Gamma_2^{(A)}(\mathbf{k}) \Gamma_2^{(A)}(\mathbf{k}) S_c(\mathbf{k})$  one has  $\langle J_A(\mathbf{k}) J_A(-\mathbf{k}) \rangle$ . The latter is exactly equal to  $\chi(1 + 2\chi S_c(\mathbf{k}))/2$ , where the Flory-Huggins parameter  $\chi = w_{AB} - (w_{AA} + w_{BB})/2$  and this form has been used in Ref. [8]. Note that if we use the linear approximate relation between  $J_A$  and  $\Psi_A$ , i.e.,  $J_A = \Gamma_2^{(A)} \Psi_A$  we would get the same result from both approaches as evident from the form of Eq. (3.2). This equation for the single-chain correlation function should be supplemented by the self-consistent equations for the collective structure factor,  $S_c(\mathbf{k})$  [4]. Since we are only interested in the first-order corrections to the Gaussian structure factor for a single chain we shall not use them here; instead we will make some simple approximation to  $S_c$ .

The radius of gyration [11]

$$R^2 = \frac{1}{2N_A^2} \left\langle \sum_{i=1}^{N_A} \sum_{j=1}^{N_A} (\mathbf{r}_i^{(1)} - \mathbf{r}_j^{(1)})^2 \right\rangle \quad (3.3)$$

is obtained from Eq. (3.2) by differentiating both sides twice with respect to  $q$  and taking the limit of  $q \rightarrow 0$ . We find (compare with the Appendix)

$$2N_A^2 R^2 / 3 = 2N_A^2 R_0^2 / 3$$

$$- \frac{1}{2\rho_0} \int \frac{d\mathbf{k}}{(2\pi)^3} f(\mathbf{k}) \Gamma_2^{(A)}(\mathbf{k}) \Gamma_2^{(A)}(\mathbf{k}) S_c(\mathbf{k}), \quad (3.4)$$

where  $R_0^2 = N_A l^2 / 6$  is the radius of gyration for the ideal chain [Eq. (3.3) with the ideal average] and  $f(\mathbf{k})$  is explicitly given in the Appendix. Since  $f(\mathbf{k})$  is always positive we find the first intuitively obvious result that *chains in a blend shrink*. Additionally it is also clear that chains shrink progressively as we lower the temperature. Now we can estimate how much they shrink at the infinite temperature and at the critical temperature. For simplicity we shall take the symmetric case ( $N = N_A = N_B$ ,  $\phi = n_A N_A / (n_A N_A + n_B N_B) = \frac{1}{2}$ ) and we will be interested in the first-order correction to the Gaussian result. For all temperatures we can use the following approximation [11]:

$$\Gamma_2^{(A)}(\mathbf{k}) = \frac{2}{N} + \frac{\mathbf{k}^2 l^2}{6}. \quad (3.5)$$

At the infinite temperature we can simply set  $S_c = 2/\Gamma_2^{(A)}$  while at the critical temperature we can approximate  $S_c(\mathbf{k})$  by  $3/(\mathbf{k}^2 l^2)$ . These two approximations are in accordance with the self-consistent loop equations for  $S_c$  [4]. Now at  $T = \infty$  we have

$$R^2 \approx R_0^2 \left[ 1 - \frac{1.6}{\rho_0 l^3 \sqrt{N}} \right] \quad (3.6)$$

while at the critical temperature  $T = T_c$ :

$$R^2 \approx R_0^2 \left[ 1 - \frac{2.7}{\rho_0 l^3 \sqrt{N}} \right]. \quad (3.7)$$

The role of the cutoff is clear here. If not for the  $\sqrt{N}$  in the upper wave-vector cutoff the correction to the Gaussian radii of gyration would be nonzero even in the limit of  $N \rightarrow \infty$  and thus RPA would not be a correct description in this limit. It is interesting to note here that  $1/\sqrt{N}$  corrections are also obtained for the polymer chain immersed in a good solvent [12].

#### IV. THE UPPER WAVE-VECTOR CUTOFF

As we have seen in the previous section the fluctuation corrections to the radius of gyration strongly depend on the upper wave-vector cutoff. Although it is ubiquitous in statistical mechanics there are no ready recipes for the choice of the cutoff. In low molecular mass liquids we usually have one natural length scale, which corresponds to the size of a molecule and the cutoff is usually made proportional to this length scale. In the polymer mixtures the problem is more complicated since we have three different length scales: the total length of a polymer molecule,  $Nl$ , the size of the region occupied by a polymer molecule (proportional to the radius of gyration),  $\sim\sqrt{N}l$ , and finally, the microscopic length scale  $l$ , which is determined by the size of a single monomer. We believe that  $\Lambda$  should be proportional to the radius of gyration, that is to  $\sqrt{N}l$ . Here we repeat the same arguments as given elsewhere [4]. At high temperatures, where the interactions between the monomers are irrelevant, the monomer-monomer correlation function decays exponentially with the characteristic correlation length which is proportional to the radius of gyration. Moreover, in all our calculations the specific structure of monomers has not been taken into account. The microscopic length scale is irrelevant here. Finally, if we chose the microscopic length scale as the cutoff the fluctuation corrections would survive in the limit of  $N\rightarrow\infty$  and thus the RPA would not be the correct description in this limit. We believe this is not the case. We note that since the size of the polymer molecule in the blend is roughly proportional to  $\sqrt{N}l$ , this choice is also in accordance with the prescription known from low molecular mass systems where the cutoff is made proportional to the size of a molecule. Since in the polymer system this size changes with temperature and concentration, it would be desirable here to determine it self-consistently from the theory. The equation for the radius of gyration  $R$  [Eq. (3.4)] offers a simple way for the self-consistent determination of the cutoff if we set it equal to  $2\pi C/R$  where  $C$  is some numeric constant. Thus apart from this constant the cutoff would be determined from the theory. In this way the equation for the collective structure factor  $S_C$  [Eq. (3.12) in Ref. [4]] and the single-chain structure factor  $S_{AA}$  would be mutually coupled via the self-consistently determined radius of gyration and the cutoff. This prescription is good for the symmetric mixture. In the case of asymmetric mixture we postulate that the cutoff should be equal to  $2\pi/[\Lambda(R_A, R_B)]$ , where  $\Lambda$  is the symmetric function of the two radii of gyration for  $A$  and  $B$  chains. *Finally, we assume the scaling form for  $\Lambda$ :*

$$\Lambda(R_A, R_B) = R_A f(x), \quad (4.1)$$

where  $x = R_B/R_A$ . From the symmetry properties of  $\Lambda$ , we have the following equation for  $f(x)$ :

$$\frac{1}{x} f(x) = f\left(\frac{1}{x}\right). \quad (4.2)$$

The general solution of this functional equation is

$$f(x) = \left[ C_1 \frac{1+x^3}{1+x} + C_2 x \right]^{1/2}. \quad (4.3)$$

Here  $C_1$  and  $C_2$  are two constants which depend on the microscopic details of the system. We cannot determine them from the present theory, thus in the interpretation of experimental results, they should be the fitting parameters.

From our self-consistent prescription for the cutoff and Eq. (3.4) for the radius of gyration we see that both quantities are always positive, the property which was not guaranteed by the perturbative expansion.

#### V. DISCUSSION

One of the goals of this paper was to compare our method with the generalization of the Edwards method [1,13] applied to dense polymer system by Barrat and Fredrickson [8]. Close to the critical temperature we obtain qualitatively the same results as one would get from their method, namely, that the chains shrink. At a high temperature Barrat and Fredrickson obtain the intuitively correct result, i.e., that chains approach the Gaussian limit (expansion of the chains above the Gaussian limit would be expected only if the system was not incompressible [14]), while we find an unphysical result that the radius of gyration is smaller than the Gaussian radius of gyration. We believe that our unphysical result comes from the usage of the Landau expansion far away from the critical point, where it is not supposed to work.

As far as the technical details are concerned both methods are almost the same except for the order of integration and further treatment of the field-field correlation function  $\langle J_A J_A \rangle$ . We use the natural order of integrations, first with respect to the field  $J_A, J_B$  and next with respect to the order parameter, whereas in Ref. [8] the order of integrations is inverted. Although it is easier to integrate out the order parameter first the question arises whether the change of the order in which the integrals are performed is a correct step. Moreover integrating over the concentrations is not particularly easy in the incompressible system since then the concentration fields are constrained as follows  $\phi_A(\mathbf{q}) + \phi_B(\mathbf{q}) = 0$ . Barrat and Fredrickson integrate without imposing this condition; instead they use the artificial potential  $V_0$  ( $w_{AB} = V_0 + \chi$ ,  $w_{AA} = w_{BB} = V_0$ ) between monomers which in the limit  $V_0 \rightarrow \infty$  imposes incompressibility, once again there is an interchange of the limit  $V_0 \rightarrow \infty$  and the integration. The limit  $V_0 \rightarrow \infty$  has been investigated in detail in Ref. [6]. The physical meaning of  $V_0$  is indeed the inverse of the vacancy concentration. In the limit of vanishing vacancy concentration  $V_0$  tends to infinity and the results can be interpolated to the case of the original incompressibility condition when the total fluctuation of the concentration field vanishes. It can be easily seen that in the case of the Gaussian approximation the interchange of the order of integrations and  $V_0 \rightarrow \infty$  does not change the results at all. Beyond the Gaussian limit these details change the results and matter significantly, as we have shown in this paper. Finally we note that in order to integrate over the concentration

fields one must invert the matrix  $w_{ij}$ . For purely attractive van der Waals interactions (with the same ionization potential for  $A$  and  $B$  monomers) the matrix has a vanishing determinant [see Eqs. (1)–(3) in Ref. [15]] and thus cannot be inverted.

Summarizing, both methods give the same qualitative results near the phase transition in polymer blends, but the Edwards method generalized by Barrat and Fredrickson rests on a number of assumptions which might not be correct. At the same time it gives a reasonable result at high temperature, while our method does not. Which of the two approaches is a better one for polymer systems should be a matter of meticulous study which we hope to perform in the future.

Last but not least we have postulated in this paper the way of determining the upper wave vector cutoff in the theory of polymers. As discussed here the dependence of the cutoff on  $N$  is crucial for the theory of polymer blends. It is also clear that in Ref. [8] the cutoff is introduced indirectly via the approximate treatment of the integrals involving  $k^2\Gamma_4(q, k)$  [e.g., Eqs. (10) and (12) in Ref. [8]], where it is approximated by  $(q^*)^2\Gamma_4(q^*, q^*)$ . Since  $q^* \sim 1/R_g$ , this approximation is similar to the in-

roduction of the cutoff roughly at  $1/R_g$ , as proposed here. Without this approximation the integrals would be ultraviolet divergent. Even if we set the cutoff there at the microscopic scale the corrections would be large and independent of  $N$ . In particular we would not retrieve in this case the Leibler results [10] in the limit of large  $N$ . Thus we may also conclude that the cutoff of  $1/R_g$  is necessary in the case of diblock copolymers and in general in all polymer mixtures including copolymers as well. The usefulness of our prescription for these different systems will be a matter of our future study.

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#### APPENDIX

Here we shall follow the equations given in Ref. [8]. For the fourth-order correlation function we have

$$\langle \hat{\phi}_A^{(1)}(\mathbf{q})\hat{\phi}_A^{(1)}(-\mathbf{q})\hat{\phi}_A^{(1)}(\mathbf{k})\hat{\phi}_A^{(1)}(-\mathbf{k}) \rangle_0 = 8g_1(q, 0, k) + 2[g_1(q, \mathbf{q} + \mathbf{k}, q) + g_1(q, \mathbf{q} - \mathbf{k}, q) + g_1(k, \mathbf{q} + \mathbf{k}, k) + g_1(k, \mathbf{q} - \mathbf{k}, k)] + 4[g_1(q, \mathbf{q} + \mathbf{k}, k) + g_1(q, \mathbf{q} - \mathbf{k}, k)]. \quad (\text{A1})$$

Here

$$g_1(q_1, q_2, q_3) = \frac{N_A}{x_1 x_2 x_3} + \frac{g(x_1)}{x_1(x_1 - x_2)(x_1 - x_3)} + \frac{g(x_2)}{x_2(x_2 - x_3)(x_2 - x_1)} + \frac{g(x_3)}{x_3(x_3 - x_2)(x_3 - x_1)}, \quad (\text{A2})$$

where  $x_i = q_i^2 l^2 / 6$  and  $g(x) = [\exp(-xN_A) - 1] / x$ . For the two-point correlation function we find

$$\langle \hat{\phi}_A^{(1)}(\mathbf{q})\hat{\phi}_A^{(1)}(-\mathbf{q}) \rangle_0 = 2(N_A + g(x)) / x, \quad (\text{A3})$$

and  $x = q^2 l^2 / 6$ .

In order to obtain the radius of gyration one has to differentiate

$$h(\mathbf{k}, \mathbf{q}) = \langle \hat{\phi}_A^{(1)}(\mathbf{q})\hat{\phi}_A^{(1)}(-\mathbf{q})\hat{\phi}_A^{(1)}(\mathbf{k})\hat{\phi}_A^{(1)}(-\mathbf{k}) \rangle_0 - \langle \hat{\phi}_A^{(1)}(\mathbf{q})\hat{\phi}_A^{(1)}(-\mathbf{q}) \rangle_0 \langle \hat{\phi}_A^{(1)}(\mathbf{k})\hat{\phi}_A^{(1)}(-\mathbf{k}) \rangle_0 \quad (\text{A4})$$

twice with respect to  $q$  and finally take the limit of  $q \rightarrow 0$  [see Eq. (3.2)]. The MATHEMATICA software package comes in handy at this point. We find

$$h''(\mathbf{k}, 0) = f(\mathbf{k}) = 4N_A^5 \cos^2\theta [-120 + 120 \exp(y) - 96y - 24 \exp(y)y - 24y^2 - 12 \exp(y)y^2 + 4 \exp(y)y^3 + y^4] / [3 \exp(y)y^5], \quad (\text{A5})$$

where  $y = N_A k^2 l^2 / 6$  and  $\theta$  is the angle between the  $\mathbf{q}$  and  $\mathbf{k}$  vector. This formula is used in Sec. III for the computation of the radius of gyration.

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