Elastic scattering from diblock copolymer chains in dilute solution

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The elastic scattering structure factor of a single diblock copolymer chain is calculated up to first order in $\epsilon(=4-d$, with d the dimensionality of the space) with the conformational space renormalization group method. The influence of several thermodynamic conditions on the scattering intensity is analyzed. Our results are compared with small-angle neutron scattering experiments under variable contrast conditions and numerical simulations of the zero average contrast case. © *1996 American Institute of Physics.* [S0021-9606(96)51914-0]

I. INTRODUCTION

The conformation of macromolecules in solution is very often studied with scattering methods, either elastic or quasielastic, with different techniques to probe the microscopic details affored at the scale lengths relevant to the experiment. The literature is plentiful of experiments on linear or branched homopolymers in the whole range of temperature and concentration, and a satisfactory agreement between theory and experiment has been achieved. In the last years, attention was focused in diblock copolymers because of the richness of structures discovered in the semidilute and concentrated regimes.[1]

Nevertheless, the very dilute regime has not been fully explored, and the question about the microsegregation at the level of a single chain remains open from the experimental point of view. To our knowledge, only two small-angle neutron scattering (SANS) experiments were performed with diblock copolymers, and with rather low molecular weight fractions. Ionescu *et al.*[2] studied the radii of gyration of polystyrene-*block*-polyisoprene copolymers in two solvents with the variable contrast method. Their tentative conclusion is that their findings can be explained without assuming segregation, when compared with an approximate theory of the excluded volume. Some years later, Duval *et al.*[3] applied the results of the random phase approximation (RPA) (appropriate to study dense systems) to the interpretation of the scattering intensity of polystyrene-*block*-poly(deuterated styrene) solution of varying concentration. Under zero-average contrast conditions they were able to show that the maximum of the scattering intensity behaved as predicted by RPA, even in the dilute regime ($c<c^*$, where c^* is the overlap concentration). Both in theta and good solvent conditions, the z-averaged radius of gyration was fitted by a relation valid in the low molecular weight range.

Theoretically, the statistical and thermodynamical properties of high polymer solutions are rigorously described by renormalized field theory[4] or alternative realizations of the scale invariance symmetry of the system. Block copolymers were carefully studied some years ago by Joanny *et al.*[5] with des Cloizeaux's direct renormalization method.[4] In the infinite chain length limit, the only stable fixed point of the renormalization group (RG) equations is that of the symmetric state with equal values of the intra- and interblock excluded volume parameters, i.e., the homopolymer fixed point. This result shows that block copolymers and homopolymers belong to the same universality class and share the same critical exponents. In the neighborhood of the other fixed points, the copolymer swells with Gaussian-type exponents, but the nonuniversal prefactors depend on the case considered. The several average dimensions of block copolymers were later analyzed by Douglas and Freed[6] and more recently by Vlahos *et al.*[7]

In this work, we focus our attention on the elastic scattering function $S(k)$ of dilute copolymer solutions as predicted by the renormalization group method. The homopolymer system was originally studied by Ohta *et al.*[8] up to first order in $\epsilon=4-d$. Their conclusion is well known. The scattering function at the excluded volume fixed point is almost identical to the Debye function, the classical result from Gaussian statistics. We develop here a similar analysis at the eight fixed points of the copolymer system. The incorporation of the contrast factor in the formalism makes it possible to compare our predictions with experiments, in particular with the zero-average contrast case where the forward scattering contribution vanishes.

This paper is organized as follows: In Sec. II we review the formalism for treating the structure factor, describe the model and calculation and give the analytical results. In Sec. III we apply the results to special cases and compare with experimental and simulation results. Our conclusions are summarized in Sec. IV.

II. MODEL AND RG CALCULATION

A. The structure factor

For a system of independent point scatterers, the intensity of the scattered radiation is proportional to[9]

$$S(k)=\sum_{i,j}\langle\chi_i\chi_j e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)}\rangle, \tag{1}$$

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where χ_i is the form factor of element i and $\mathbf{k}$ the scattering vector, $k=4\pi/\lambda \sin(\theta/2)$, λ the wavelength of incident radiation in the scattering medium, and θ the scattering angle. $\langle\cdots\rangle$ means average over all possible chain conformations. Light as well as neutron scattering can be treated with the same formalism, the only difference being the expressions for the form factors. In the case of light scattering, they are the polarizabilities of the point scatterers, and can be written (at infinite dilution) as[9]

$$\chi_i=\frac{\hat{M}_i}{2\pi}\frac{n_0}{N_A}\left(\frac{\partial n}{\partial c_i}\right)_0 . \tag{2}$$

Here $\hat{M}_i$ is the molecular weight of the ith monomer, c_i its weight concentration, N_A Avogadro's number, n_0 the solvent refraction index, and $(\partial n/\partial c_i)_0$ the refraction index increment due to monomer i, at infinite dilution. In the case of neutron scattering, χ_i is the excess scattering length[10]

$$\chi_i=b_i-\hat{M}_i\frac{v_i}{v_s}b_s , \tag{3}$$

with b_i and b_s the coherent scattering lengths of monomer and solvent, and v_i and v_s the corresponding specific volumes.

In the case of diblock copolymers, we have two blocks, p_1 and p_2, formed by monomers of kind A and B. We can write

$$S(k)=\sum_{\alpha,\beta}\chi_\alpha\chi_\beta S_{\alpha\beta}(k) \tag{4}$$

$$=\sum_{\alpha,\beta}\chi_\alpha\chi_\beta N_\alpha N_\beta P_{\alpha\beta}(k), \tag{5}$$

$$P_{\alpha\beta}(k)=\frac{1}{N_\alpha N_\beta}\sum_{\substack{i\in p_\alpha\\ j\in p_\beta}}\langle e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)}\rangle, \tag{6}$$

where N_α is the length of block α. Clearly, $P_{\alpha\beta}=P_{\beta\alpha}$, and $P_{\alpha\beta}(0)=1$. It is convenient to follow Ref. 11 and define

$$\bar{\chi}=\frac{\chi_1 N_1+\chi_2 N_2}{\hat{M}_1 N_1+\hat{M}_2 N_2}, \tag{7}$$

$$y=\frac{\chi_1 N_1}{\chi_1 N_1+\chi_2 N_2}. \tag{8}$$

With this, one can write (we put P_1 and P_2 for P_{11} and P_{22})

$$S(k)=M^2\bar{\chi}^2[y^2P_1(k)+(1-y)^2P_2(k)$$
$$+2y(1-y)P_{12}(k)], \tag{9}$$

where $M=\hat{M}_1N_1+\hat{M}_2N_2$. In the special case $\bar{\chi}=0$ (zero mean contrast) the above equation is not valid, and we must write instead

$$S(k)=N_1^2\chi_1^2[P_1(k)+P_2(k)-2P_{12}(k)]. \tag{10}$$

B. Model and perturbation calculation

The chain is modeled with Edwards' Hamiltonian,[12]

$$\mathscr{H}[\mathbf{c_1},\mathbf{c_2}]=\frac{1}{2}\int_0^{N_1^0}\left(\frac{\partial\mathbf{c}_1}{\partial\tau}\right)^2 d\tau+\frac{1}{2}\int_0^{N_2^0}\left(\frac{\partial\mathbf{c}_2}{\partial\tau}\right)^2 d\tau$$
$$+\frac{u^0}{2}\int_0^{N_1^0}d\sigma\int_0^{N_1^0}d\tau\,\delta[\mathbf{c}_1(\sigma)-\mathbf{c}_1(\tau)]$$
$$+\frac{v^0}{2}\int_0^{N_2^0}d\sigma\int_0^{N_2^0}d\tau\,\delta[\mathbf{c}_2(\sigma)-\mathbf{c}_2(\tau)] \tag{11}$$

$$+w^0\int_0^{N_1^0}d\sigma\int_0^{N_2^0}d\tau\,\delta[\mathbf{c}_1(\sigma)-\mathbf{c}_2(\tau)]. \tag{12}$$

$\mathbf{c}_1$ and $\mathbf{c}_2$ are continuous curves describing the chain conformation, u, v and w the excluded volume parameters, and the superscript 0 denotes bare quantities. The condition $\mathbf{c}_1(N_1^0)=\mathbf{c}_2(0)$ is imposed, and a cutoff length a is implicit in all divergent integrals.

Averages are computed as

$$\langle\cdots\rangle=\frac{1}{\mathscr{Z}}\int\mathscr{D}[\mathbf{c_1},\mathbf{c_2}](\cdots)e^{-\mathscr{H}},$$

$$\mathscr{Z}=\int\mathscr{D}[\mathbf{c}_1,\mathbf{c}_2]e^{-\mathscr{H}}. \tag{13}$$

The reciprocal variable of $\mathbf{c}$ is $\mathbf{q}=\sqrt{l/d}\,\mathbf{k}$, with l Kuhn's length.

We use the conformation space renormalization group technique developed by Oono *et al.*[13] The structure factors in d dimensions up to first order in the excluded volume interaction are computed first. The resulting expression is expanded in powers of ϵ, and then a renormalized expansion is obtained by the use of renormalization factors. Finally, the renormalized scattering functions is studied at the fixed points of the RG equation.

We summarize the relevant steps of the calculation. The partition function is

$$\mathscr{Z}=\mathscr{Z}_0-\mathscr{Z}_0\left\{\frac{u}{4\pi^2}\left[\frac{N_1^0}{a}-\ln\left(\frac{N_1^0}{a}\right)-1\right]+\frac{v}{4\pi^2}\left[\frac{N_2^0}{a}\right.\right.$$
$$\left.\left.-\ln\left(\frac{N_2^0}{a}\right)-1\right]+\frac{w}{4\pi^2}\left[1+\ln\left(\frac{N_1^0N_2^0}{a(N_1^0+N_2^0)}\right)\right]\right\}, \tag{14}$$

$$\mathscr{Z}_0=\int D[\mathbf{c_1},\mathbf{c_2}]\ \exp\left\{\frac{1}{2}\int_0^{N_1^0}\left(\frac{\partial\mathbf{c}_1}{\partial\tau}\right)^2 d\tau\right.$$
$$\left.+\frac{1}{2}\int_0^{N_2^0}\left(\frac{\partial\mathbf{c}_2}{\partial\tau}\right)^2 d\tau\right\}. \tag{15}$$

The bare perturbation to first order for the structure factors gives (S_{22} can be obtained from S_{11} by the exchange $N_1^0\leftrightarrow N_2^0, u^0\leftrightarrow v^0$),

$$S_{11}=2(N_1^0)^2A(\varphi_1^0)-u^0[R_{11}^u+\alpha_1A(\varphi_1^0)]-v^0\left[R_{11}^v+\alpha_1\left(1+\ln\frac{N_2^0}{N_1^0}\right)A(\varphi_1^0)\right]-w^0\left[R_{11}^w-\alpha_1\left(1+\ln\frac{N_2^0}{N^0}\right)A(\varphi_1^0)\right]$$
$$-u^0\alpha_1[A(\varphi_1^0)+B(\varphi_1^0)]\ln\frac{N_1^0}{a}, \tag{16}$$

$$S_{12}=(N^0)^2Q(\varphi_1^0,\varphi_2^0)-u^0\left[R_{12}^u+\frac{\alpha}{2}\,Q(\varphi_1^0,\varphi_2^0)\right]-v^0\left[R_{12}^v+\frac{\alpha}{2}\,Q(\varphi_1^0,\varphi_2^0)\right]-w^0\left[R_{12}^w-\frac{\alpha}{2}\left(1+\ln\frac{N_2^0}{N^0}\right)\right.$$
$$\left.\times Q(\varphi_1^0,\varphi_2^0)+\frac{\alpha}{2}\,\frac{e^{-\varphi_2^0}}{(\varphi^0)^2}\ln\frac{N_1^0}{N_2^0}\right]-u^0\,\frac{\alpha}{2}\left[\frac{N_1^0}{N^0}\,\frac{e^{-\varphi_2^0}-1}{\varphi^0}\,e^{-\varphi_1^0}+Q(\varphi_1^0,\varphi_2^0)\right]\ln\frac{N_1^0}{a}$$
$$-v^0\,\frac{\alpha}{2}\left[\frac{N_2^0}{N^0}\,\frac{e^{-\varphi_1^0}-1}{\varphi^0}\,e^{-\varphi_2^0}+Q(\varphi_1^0,\varphi_2^0)\right]\ln\frac{N_2^0}{a}, \tag{17}$$

where

$$A(\varphi)=\frac{e^{-\varphi}-1+\varphi}{\varphi^2}, \tag{18}$$

$$B(\varphi)=\frac{e^{-\varphi}}{\varphi^2}+\frac{e^{-\varphi}}{\varphi}-\frac{1}{\varphi^2}, \tag{19}$$

$$Q(\varphi_1^0,\varphi_2^0)=\frac{(e^{-\varphi_1^0}-1)(e^{-\varphi_2^0}-1)}{(\varphi^0)^2}, \tag{20}$$

$$N^0=N_1^0+N_2^0, \tag{21}$$

$$\varphi_i^0=\frac{N_i^0q^2}{2}, \tag{22}$$

$$\alpha_i=\frac{2(N_i^0)^2}{4\pi^2}, \tag{23}$$

and α and φ^0 are equivalent to α_i and φ_i^0 with N^0 in place of N_i^0. The functions R_{11}^u, R_{11}^v, R_{11}^w, R_{12}^u, R_{12}^v, and R_{12}^w are given in Appendix A. These functions are the regular part of the bare expansion, i.e., they remain finite in the limit $a\rightarrow 0$. Note that singular parts (proportional to $\ln N^0/a$) appear associated with the intrablock interactions (u,v), but not with the interblock interaction (w).

The following relations are proposed between bare and renormalized quantities:

$$N_1=Z_NN_1^0,$$
$$N_2=Z_MN_2^0,$$
$$S_{11}=Z_{S_{11}}^{-1}S_{11}^B,$$
$$S_{22}=Z_{S_{22}}^{-1}S_{22}^B,$$
$$S_{12}=Z_{S_{12}}^{-1}S_{12}^B. \tag{24}$$

The factors Z are chosen so that the singularities in the structure factors are absorbed into the renormalization factors. At this stage, it is necessary to introduce the fenomenological scale L.[13] When this is done, one obtains

$$S_{11}=2N_1^2A(\varphi_1)-u[R_{11}^u+\alpha_1A(\varphi_1)]-v\left[R_{11}^v+\alpha_1\left(1\right.\right.$$
$$\left.\left.+\ln\frac{N_2}{N_1}\right)A(\varphi_1)\right]-w\left[R_{11}^w-\alpha_1\left(1+\ln\frac{N_2}{N}\right)A(\varphi_1)\right]$$
$$-u\alpha_1[A(\varphi_1)+B(\varphi_1)]\ln\frac{N_1}{L},$$

$$S_{12}=N^2Q(\varphi_1,\varphi_2)-u\left[R_{12}^u+\frac{\alpha}{2}\,Q(\varphi_1,\varphi_2)\right]-v\left[R_{12}^v+\frac{\alpha}{2}\,Q(\varphi_1,\varphi_2)\right]-w\left[R_{12}^w-\frac{\alpha}{2}\left(1+\ln\frac{N_2}{N}\right)Q(\varphi_1,\varphi_2)\right.$$
$$\left.+\frac{\alpha}{2}\,\frac{e^{-\varphi_2}}{\varphi^2}\ln\frac{N_1}{N_2}\right]-u\,\frac{\alpha}{2}\left[\frac{N_1}{N}\,\frac{e^{-\varphi_2}-1}{\varphi}+Q(\varphi_1,\varphi_2)\right]\ln\frac{N_1}{L}-v\,\frac{\alpha}{2}\left[\frac{N_2}{N}\,\frac{e^{-\varphi_1-1}}{\varphi}+Q(\varphi_1,\varphi_2)\right]\ln\frac{N_2}{L}, \tag{25}$$

and for the renormalization constants,

$$Z_N=1+\frac{u}{4\pi^2}\ln\frac{L}{a}, \tag{26}$$

$$Z_M=1+\frac{v}{4\pi^2}\ln\frac{L}{a}, \tag{27}$$

$$Z_{S_{11}}=1-\frac{u}{2\pi^2}\ln\frac{L}{a}, \tag{28}$$

$$Z_{S_{22}}=1-\frac{v}{2\pi^2}\ln\frac{L}{a}, \tag{29}$$

$$Z_{S_{12}}=1-\frac{u}{4\pi^2}\ln\frac{L}{a}-\frac{v}{4\pi^2}\ln\frac{L}{a}. \tag{30}$$

To find the nontrivial fixed points of the RG equations requires a second order expansion in ϵ. Since the fixed points do not depend on the property being computed, we rely on the calculation of Joanny *et al.*,[5] who studied osmotic pressure and radii of gyration of solutions of copolymers and mixtures of polymers. They found eight fixed points for the interaction,

$$\begin{aligned}
(u^*,v^*,w^*)&=(G,G,G),\\
(u^*,v^*,w^*)&=(V,G,G),\\
(u^*,v^*,w^*)&=(G,V,G),\\
(u^*,v^*,w^*)&=(V,V,G),\\
(u^*,v^*,w^*)&=(G,G,W),\\
(u^*,v^*,w^*)&=(V,G,W),\\
(u^*,v^*,w^*)&=(G,V,W),\\
(u^*,v^*,w^*)&=(V,V,V),
\end{aligned} \tag{31}$$

where $G=0$, $V=\pi^2\epsilon/2$, $W=\pi^2\epsilon$ in our units.

C. RG equation

We now study the renormalization group equation at the fixed points to find the scaling behaviour of the structure factor. The equation is

$$L\left.\frac{dS_\alpha}{dL}\right|_{\text{fixed point}}=\left(L\frac{\partial}{\partial L}+\gamma_{S_\alpha}+\gamma_{N_1}N_1\frac{\partial}{\partial N_1}+\gamma_{N_2}N_2\frac{\partial}{\partial N_2}\right)S_\alpha=0, \tag{32}$$

where $\alpha=11$, 22 or 12, and

$$\gamma_{N_1}=\frac{u^*}{4\pi^2}, \tag{33}$$

$$\gamma_{N_2}=\frac{v^*}{4\pi^2}, \tag{34}$$

$$\gamma_{S_{11}}=-\frac{u^*}{2\pi^2}, \tag{35}$$

$$\gamma_{S_{22}}=-\frac{v^*}{2\pi^2}, \tag{36}$$

$$\gamma_{S_{12}}=-\frac{u^*}{4\pi^2}-\frac{v^*}{4\pi^2}. \tag{37}$$

By Euler's theorem, S_α must have the property

$$S_\alpha(q,\lambda L,\lambda^{\gamma_{N_1}}N_1,\lambda^{\gamma_{N_2}}N_2)=\lambda^{-\gamma_{S_\alpha}}S(q,L,N_1,N_2) \tag{38}$$

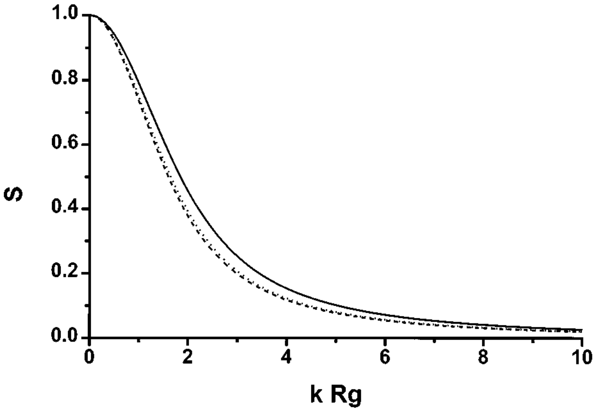

FIG. 1. Total structure factor for Gaussian homopolymers. The plot shows the differences among the result for $d=4$ (full line), the exact Debye function in $d=3$ (dashed line), and the ϵ expansion at the Gaussian fixed point in $d=3$ (dotted line).

for all $\lambda>0$. Choosing $\lambda=L^{-1}$ and changing the unit length we find

$$S_\alpha=s^{-2-\gamma_{S_\alpha}}f[s^{-1/2}q,s^{-\gamma_{N_1}+1}N_1,s^{-\gamma_{N_2}+1}N_2], \tag{39}$$

with $s>0$ and f an unspecified function. Setting $s=N^{-1}$, we find for S_α the following scaling form:

$$S_\alpha=N^2\left(\frac{N}{L}\right)^{\gamma_{S_\alpha}}f\left[N^{1/2}q,\left(\frac{N}{L}\right)^{\gamma_{N_1}}\frac{N_1}{N},\left(\frac{N}{L}\right)^{\gamma_{N_2}}\frac{N_2}{N}\right]. \tag{40}$$

So the partial structure factors can be written in terms of the variables N, $\hat{x}=(N/L)^{\gamma_{N_1}}N_1/N$ and $\hat{z}=(N/L)^{\gamma_{N_2}}N_2/N$, *at the eight fixed points*. However, in the terms of order zero in the renormalized expansion [Eq. (25)] they appear only as the products $N\hat{x}$ and $N\hat{z}$, so it is better to define

$$\eta=\left(\frac{N}{L}\right)^{\gamma_{N_1}}N_1,\quad \xi=\left(\frac{N}{L}\right)^{\gamma_{N_2}}N_2, \tag{41}$$

$$\varphi_\eta=\eta q^2/2,\quad \varphi_\xi=\xi q^2/2. \tag{42}$$

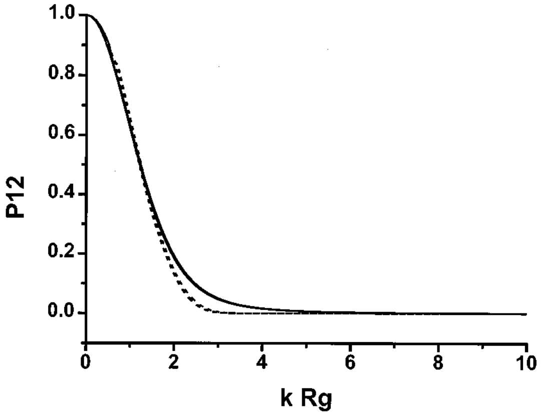

FIG. 2. Interblock scattering. The full curves represent the Debye function and the ϵ expansion at fixed points VGG and VVG, while the dashed curves correspond to the GGW, VGW, and VVV fixed points. As seen, the first three curves are practically undistinguishable among themselves, as are the last three. Thus most of the excluded volume effect is contained in the w (interblock) interaction.

In the first order terms we can write $N=\eta+\xi$, $x=\hat{x}=\eta/(\eta+\xi)$. Finally we extend the expansion into an exponential function, in order to obtain positive function, as a structure factor should be. The final result is

$$S_{11}=\left(\frac{N}{L}\right)^{-u^*/2\pi^2} 2\eta^2 A(\varphi_\eta)\exp\left\{-\frac{u^*}{4\pi^2}\left[\frac{4\pi^2 R_{11}^u}{2\eta^2 A(\varphi_\eta)} +1+\ln x+\frac{B(\varphi_\eta)}{A(\varphi_\eta)}\ln x\right]-\frac{w^*}{4\pi^2}\left[\frac{4\pi^2 R_{11}^w}{2\eta^2 A(\varphi_\eta)}-1 -\ln(1-x)\right]\right\}, \tag{43}$$

$$S_{22}=\left(\frac{N}{L}\right)^{-v^*/2\pi^2} 2\xi^2 A(\varphi_\xi)\exp\left\{-\frac{v^*}{4\pi^2}\left[\frac{4\pi^2 R_{11}^v}{2\xi^2 A(\varphi_\xi)}+1 +\ln(1-x)+\frac{B(\varphi_\xi)}{A(\varphi_\xi)}\ln(1-x)\right]-\frac{w^*}{4\pi^2}\left[\frac{4\pi^2 R_{11}^w}{2\xi^2 A(\varphi_\xi)} -1-\ln x\right]\right\}, \tag{44}$$

$$S_{12}=N^2 Q(\varphi_\eta,\varphi_\xi)\exp\left\{-\frac{u^*}{4\pi^2}\left[\frac{4\pi^2 R_{12}^u}{N^2 Q(\varphi_\eta,\varphi_\xi)}+\frac{\eta^2}{\varphi_\eta}\frac{e^{-\varphi_\eta}(e^{-\varphi_\xi}-1)}{N^2 Q(\varphi_\eta,\varphi_\xi)}\ln x+1+\ln x\right] -\frac{v^*}{4\pi^2}\left[\frac{4\pi^2 R_{12}^v}{N^2 Q(\varphi_\eta,\varphi_\xi)}+\frac{\xi^2}{\varphi_\xi}\frac{e^{-\varphi_\xi}(e^{-\varphi_\eta}-1)}{N^2 Q(\varphi_\eta,\varphi_\xi)}\ln(1-x)+1+\ln(1-x)\right]-\frac{w^*}{4\pi^2}\left[\frac{4\pi^2 R_{12}^w}{N^2 Q(\varphi_\eta,\varphi_\xi)} +\frac{\eta\xi}{\varphi_\eta\varphi_\xi}\frac{e^{-\varphi_\xi}}{Q(\varphi_\eta,\varphi_\xi)}\ln\frac{x}{1-x}-1-\ln(1-x)\right]\right\}. \tag{45}$$

These expressions are the exponentiated renormalized expansions for the structure factors, in terms of the scaling variables.

Expanding the structure factors in powers of q^2 (Guinier expansion), one can obtain the radius of gyration of both blocks, as well as the mean distance between the centers of mass. These expressions are given in Appendix B; they were first computed by Douglas and Freed[6] by an alternative method.

D. Plots

The structure factor is plotted against the adimensional variable $\rho=kR_g$. We have $R_g=lr$, where $r=r(\eta,\xi)$ is given in Appendix B. Then

$$\varphi_\eta=\frac{\eta}{2}\frac{\rho^2}{r}\frac{1}{d}\approx\frac{\eta}{8}\frac{\rho^2}{r}\left(1+\frac{\epsilon}{4}\right), \tag{46}$$

$$\varphi_\xi=\frac{\xi}{2}\frac{\rho^2}{r}\frac{1}{d}\approx\frac{\xi}{8}\frac{\rho^2}{r}\left(1+\frac{\epsilon}{4}\right). \tag{47}$$

The order 0 term of the structure factors depends on the space dimension d only through the relation between φ_η, φ_ξ and the plot variable ρ. To be consistent, we deem it necessary to expand this term in ϵ and exponentiate. This causes minor differences in $d=3$ between ϵ-expanded structure factor at the Gaussian fixed point and the Debye function, which we illustrate in Fig. 1 for a linear homopolymer. [In our notation, the Debye function is $2A(\varphi)$.] At this fixed point, $\varphi=3\rho^2/d$. The plot compares the curves for $d=4$ (where the Debye function and ϵ expansion are identical), and for $d=3$, which shows the difference between Debye and the $O(\epsilon)$ expansion. The maximum difference is less than 4%.

III. APPLICATIONS

We now apply the foregoing general results [Eqs. (43)–(45)] to the case of 50/50 ($x=1/2$, or $\eta/\xi=1$) diblock copolymers. As discussed above, we use the full ϵ expansion, and give as reference the (exact) Debye function for $d=3$.

We focus first on the partial structure factors P_1 and P_{12} (P_2 is identical to P_1 for $x=1/2$). P_{12} gives the contribution to scattering resulting form the interference between radiation scattered by different blocks. Accordingly, its contribution goes to 0 faster than P_1 for short wavelengths (it almost vanishes for $\rho>5$). The u and v interactions barely have any effect in its shape; however when w takes the excluded volume fixed point value P_{12} has a steeper descent, and almost vanishes for $\rho\approx3$ (Fig. 2).

By contrast, P_1 is nonvanishing up to $\rho\approx10$, and differs for the six fixed points shown in Fig. 3. The difference, however, is small, and one can see than most of the change brought to the total structure factor by the excluded volume effect is due to the interblock (P_{12}) scattering. This is also the case in homopolymers (though here we do not refer to blocks but to far-away monomers along the chain).

Turning now to the total structure factor, the contrast factor y must be brought into consideration. The GGG and VVV fixed points describe a polymer with equal u, v, and w interactions. This corresponds to an homopolymer as regards conformational properties, but in radiation scattering the (different) scattering lengths of the A and B monomers come into play. In some cases, as that depicted in Fig. 4, the shape

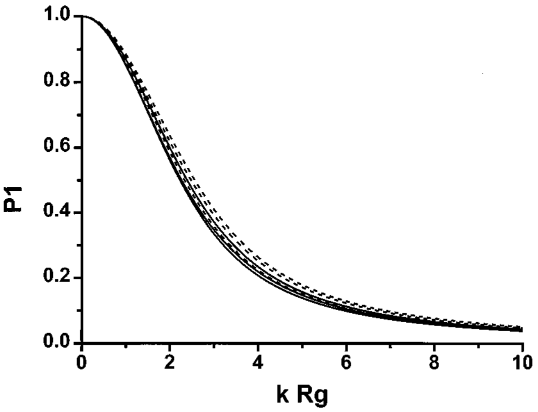

FIG. 3. Intrablock scattering. The same fixed points as in Fig. 2 are shown. In this case all three interaction parameters have equivalent (though small) effect in the difference in scattered intensity.

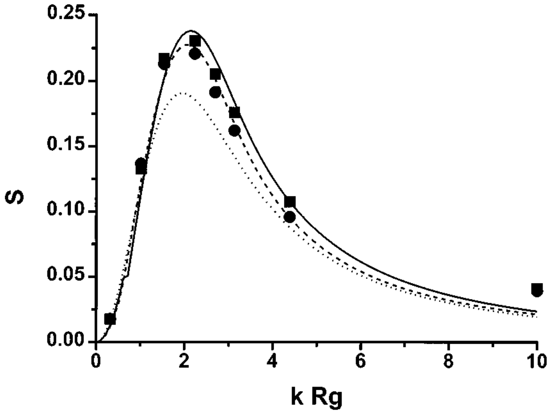

FIG. 5. Comparison with the Brownian dynamics simulation (Ref. 14) results. Discrete points are the simulation results, and continuous curves the present theoretical results. Squares, segregating blocks; circles, excluded volume; full line, *GGW* fixed point; dashed line, *VVV* fixed point; dotted line, Debye function. The small kink in the *GGW* curve is a numerical artifact.

of the structure factor is significantly altered and the difference between excluded volume and Gaussian regimes is increased.

Two special values of the contrast factor have attracted researchers' attention, namely zero average contrast and $y=1$. In the first case, there is no scattering for $\theta=0$. In the second, the B block is isorefractive with the solvent, and only the A block is visible in the scattering experiment.

Duval *et al.*[3] did SANS measurements on polystyrene-*block*-poly(deuterated sytrene) at zero average contrast conditions. Unfortunately, their results are not fit for comparison with our calculation, because of the polydispersity of their samples. Zero average contrast scattering was also considered by Rey and Freire,[14] who performed Brownian dynamics simulations for excluded volume and segregated Gaussian chains, corresponding to our *VVV* and *GGW* fixed points, respectively. In Fig. 5 we compare their simulation results with the theoretical curves for the *VVV* and *GGW* fixed points. There is fair agreement in the excluded volume case, and *GGW* curve shows the correct tendency. In both cases, there is a noticeable improvement over the Debye function.

Ionescu and co-workers[2] did SANS measurements on poly(deuterated styrene)-*block*-polyisoprene (PDS-PI) of molecular weight 66 000 (weight average) in cyclohexane at 20 °C and 40 °C. By mixing normal and deuterated solvent they achieved several different contrast conditions. Their aim was to establish the existence or absence of segregation, and so they do not give the full scattering curve, but only the apparent radius of gyration. In Fig. 6 we plot their data together with the theoretical result (Appendix B) for the *GGG* and *GGW* fixed points. The curves were drawn by fixing the composition and the radius of gyration of the PDS block (precursor). Based on the uniform expansion theory of the excluded volume, the authors concluded that "there is no segregation." However, we find no reason to choose either of the RG theoretical curves.

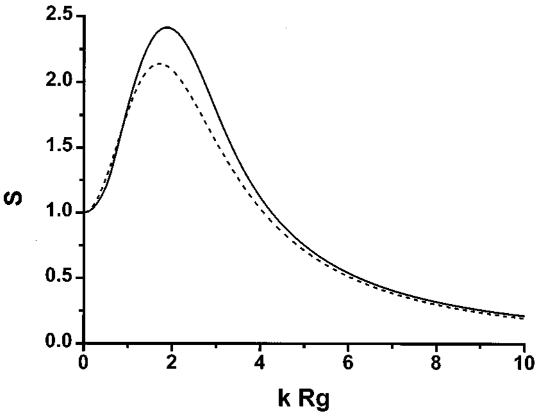

FIG. 4. Total scattering for the case $y=2$. The difference in scattering lengths enhances the difference between Gaussian (dashed curve) and excluded volume (full curve) chains.

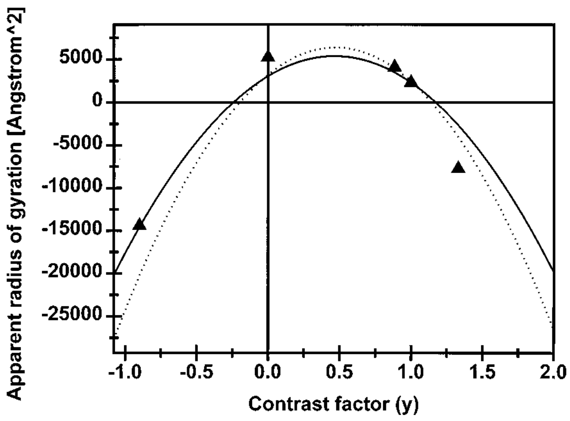

FIG. 6. Apparent radius of gyration of PDS-PI in cyclohexane at 40 °C for different contrasts. The points are experimental values of Ref. 2. Full line, *GGG* fixed point; dashed line, *GGW* fixed point. Neither of the theoretical curves can be preferred.

IV. CONCLUSION

We have applied the renormalization group technique to study the structure factor of dilute solutions of diblock copolymers, extending the results of Ohta *et al.*[8] Though first order corrections to scattering are small for homopolymers, the contrast factor makes the difference more important in the case of copolymers with very different scattering lengths.

Our results compare well with the Brownian dynamics simulation of Rey and Freire.[14] The experiments available for comparison are scarce, and do not allow to distinguish among the different fixed points.

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APPENDIX A: REGULAR PART OF PERTURBATION EXPANSION

We give here the functions R_{11}^{u}, etc. which contain only terms that remain finite in the limit $a \rightarrow 0$. The following definitions are used:

$$N = N_1 + N_2,$$

$$x = N_1/N,$$

$$z = (1-x)/x.$$

Terms $D2$, $D3$, $D4$, $D5$, $D6$, $D8$, and $D9$ were taken from Ref. 15,

$$R_{11}^{u} = \frac{2N_1^2}{4\pi^2}\,(D1_R + D2_R + D3_R + D4_R + D5_R + D6_R),$$

$$D1_R = \frac{1}{\varphi_1^2} - \frac{e^{-\varphi_1}}{\varphi_1^2} - \frac{e^{-\varphi_1}}{\varphi_1^2}\int_0^1 \frac{e^{\varphi_1 s} - 1}{s}\,ds, \tag{A1}$$

$$D2_R = -\frac{2}{\varphi_1}\int_0^1 ds\,\frac{e^{-\varphi_1 s/4}}{s}\int_0^{s/2} dt\, e^{\varphi_1 t^2/u} + 2\int_0^1 ds\left[\frac{1}{\varphi_1} - \frac{1}{\varphi_1^2} + \frac{e^{-\varphi_1(1-s)}}{\varphi_1^2}\right]\frac{e^{-\varphi_1 s/4}}{s^2}\int_0^{s/2}(e^{\varphi_1 t^2/2} - 1)\,dt + \int_0^1\left(\frac{1}{\varphi_1} - \frac{1}{\varphi_1^2}\right)\frac{e^{-\varphi_1 s/4} - 1}{s}\,ds + \frac{e^{-\varphi_1}}{\varphi_1^2}\int_0^1 \frac{e^{3\varphi_1 s/4} - 1}{s}\,ds, \tag{A2}$$

$$D3_R = \frac{2}{\varphi_1^3} - \frac{1}{\varphi_1^2} - \frac{e^{-\varphi_1}}{\varphi_1^2} - 2\frac{e^{-\varphi_1}}{\varphi_1^3} + \frac{e^{-\varphi_1}}{\varphi_1^2}\left(\frac{2}{\varphi_1} + 1\right) \times \int_0^1 \frac{e^{\varphi_1 s} - 1 - \varphi_1 s}{s^2}\,ds - \frac{e^{-\varphi_1}}{\varphi_1^2}\int_0^1 \frac{e^{\varphi_1 s} - 1}{s}\,ds, \tag{A3}$$

$$D4_R = \int_0^1 ds\int_0^{s/2} dt\left(\frac{1}{s} - 1\right)e^{-\varphi_1 s/4}e^{\varphi_1 t^2/s}, \tag{A4}$$

$$D5 = D2, \tag{A5}$$

$$D6 = D1, \tag{A6}$$

$$R_{11}^{v} = \frac{2N_1^2}{4\pi^2}\,D7_R,$$

$$D7_R = -\left[\frac{e^{-\varphi}}{\varphi_1^2} - \frac{1}{\varphi_1^2} + \frac{1}{\varphi_1}\right]\left[1 + \ln\left(\frac{N_2}{N_1}\right)\right], \tag{A7}$$

$$R_{11}^{w} = \frac{2N_1^2}{4\pi^2}\,(D8_R + D9_R + D10_R),$$

$$D8_R = \left[\frac{1}{x\varphi_1} - \frac{1}{\varphi_1^2}\right]\ln(1-x) + \frac{e^{-\varphi_1}}{\varphi_1^2}\int_0^1 \frac{e^{\varphi_1 s} - 1}{s}\,ds - \frac{e^{-\varphi}}{\varphi_1^2}\int_{1-x}^1 \frac{e^{\varphi s}}{s}\,ds - \frac{1}{\varphi_1^2} + \frac{1}{\varphi_1} + \frac{e^{-\varphi_1}}{\varphi_1^2}, \tag{A8}$$

$$D9_R = -\frac{1 - e^{\varphi_1}}{\varphi_1}\,\frac{1-x}{x}\,\ln(1-x) - \frac{e^{-\varphi_1}}{\varphi_1^2}\int_0^1 ds\int_0^{1-s} dt\,\frac{e^{\varphi_1[s + t^2/(s+t)]} - 1 - \varphi_1[s + t^2/(s+t)]}{t^2} + \frac{e^{-\varphi_1}}{\varphi_1^2}\int_0^1 ds\int_0^{1-s} dt\,\frac{e^{\varphi_1[u + t^2/(z+s+t)]} - 1 - \varphi_1[u + t^2/(z+s+t)]}{t^2} + \frac{1}{\varphi_1^2}\int_0^1 ds\int_0^{1-s} dt\,\frac{e^{-\varphi_1 st/(s+t)} - 1 + \varphi_1 st/(s+t)}{t^2} - \frac{1}{\varphi_1^2}\int_0^1 ds\int_0^{1-s} dt\,\frac{e^{-\varphi_1(z+s)t/(z+s+t)} - 1 + \varphi_1(z+s)t/(z+s+t)}{t^2}, \tag{A9}$$

$$D10_R=\frac{1}{\varphi_1}\int_0^1 ds\int_0^{1-s}dt\int_0^{1-s-t}dy\;\frac{1}{t^2}\times\left\{\exp\left[-\varphi_1\,\frac{t(s+y)}{s+t+y}\right]-\exp\left[-\varphi_1\,\frac{t(z+s+y)}{z+s+t+y}\right]\right\}\tag{A10}$$

$$R_{12}^u=\frac{N_1^2}{4\pi^2}\,(D11_R+D12_R+D13_R),$$

$$D11_R=\frac{e^{-\varphi_2}-1}{\varphi_1^2}\left\{\frac{1}{\varphi_1}-e^{-\varphi_1}-\frac{e^{-\varphi_1}}{\varphi_1}-e^{-\varphi_1}\times\int_0^1\frac{e^{\varphi_1 s}-1}{s}\,ds\right\}+e^{-\varphi_1}\left(1+\frac{1}{\varphi_1}\right)\times\int_0^1\frac{e^{\varphi_1 s}-1-\varphi_1 s}{s^2}\,ds,\tag{A11}$$

$$D12_R=\frac{1-e^{-\varphi_2}}{\varphi_1^2}\left\{\int_0^1 ds\int_s^1 dt\;\frac{e^{\varphi_1(s^2/t-s)}-1}{t^2}-e^{-\varphi_1}\int_0^1 ds\int_s^1 dt\;\frac{e^{\varphi_1(t-s+s^2/t)}-1}{t^2}\right\},\tag{A12}$$

$$D13_R=\frac{e^{-\varphi_2}-1}{\varphi_1^2}\left\{1-e^{-\varphi_1}-e^{-\varphi_1}\int_0^1\frac{e^{\varphi_1 s}-1}{s}\,ds\right\},\tag{A13}$$

$$R_{12}^w=\frac{N^2}{4\pi^2}\,(D14_R+D15_R+D16_R+D17_R),$$

$$D14_R=\frac{1}{\varphi^2}\left\{xe^{-\varphi}\int_0^1 dt\int_{xt}^{xt+1-x}\frac{e^{\varphi s}-1-\varphi s}{s^2}\,ds-e^{-\varphi_1}\int_0^1\frac{e^{\varphi_1 s}-1}{s}\,ds-e^{-\varphi_2}\int_0^1\frac{e^{\varphi_2 s}-1}{s}\,ds+e^{-\varphi}\int_{1-x}^1\frac{e^{\varphi s}}{s}\,ds+e^{-\varphi}\int_x^1\frac{e^{\varphi s}}{s}\,ds+e^{-\varphi}\times\ln(1-x)-\varphi e^{-\varphi}[(1-x)\ln(1-x)+x\ln x]+e^{-\varphi}-e^{-\varphi_1}-e^{-\varphi_2}+1\right\},\tag{A14}$$

$$D15_R=\frac{1}{\varphi_2}\left\{e^{-\varphi_1}\ln(1-x)-e^{-\varphi_1}\int_0^1\frac{e^{\varphi_1 s}-1}{s}\,ds+e^{-\varphi_1}\int_0^x\frac{e^{\varphi s}}{s+1-x}\,ds-\int_{1-x}^1 ds\int_{s-(1-x)}^{s}dt\;\frac{e^{\varphi(t^2/s-t)}-1}{t^2}+e^{-\varphi_1}\int_0^x ds\int_s^{s+1-x}dt\;\frac{e^{\varphi[s-t+t^2/(s+1-x)]}-1}{t^2}\right\},\tag{A15}$$

$D16_R$ is obtained from $D15_R$ by $N_1\leftrightarrow N_2$ and $x\leftrightarrow 1-x$,

$$D17_R=\frac{1}{\varphi}\left\{\int_0^x ds\int_0^{x-s}dt\int_s^{1-x+s}dy\;\frac{e^{-\varphi ty/(t+y)}-1}{y^2}-\int_0^x ds\int_0^{x-s}dt\int_s^{1-x+s}dy\times\frac{e^{-\varphi y}e^{\varphi y^2/(s+t+1-x)}-1}{y^2}\right\}.\tag{A16}$$

APPENDIX B: RADIUS OF GYRATION

By expanding the total structure factor in powers of $\varphi\propto q^2$, one obtains

$$S(q)=S(0)\left[1-\frac{\langle Rg_{Ap}^2\rangle}{l}\,q^2+\cdots\right],\tag{B1}$$

$$\langle Rg_{Ap}^2\rangle=y^2\langle Rg_{11}^2\rangle+(1-y)^2\langle Rg_{22}^2\rangle+2y(1-y)\langle Rg_{12}^2\rangle.\tag{B2}$$

This gives

$$\langle Rg_{11}^2\rangle=-l\left\{\frac{-\eta}{6}+\frac{u\eta[13-12\log\eta+12\log(\eta+\xi)]}{288\pi^2}+w\xi[-5\eta^3-18\eta^2\xi-12\eta\xi^2-12\eta^2\xi\log\xi-24\eta\xi^2\log\xi-12\xi^3\log\xi+12\eta^2\xi\log(\eta+\xi)+24\eta\xi^2\log(\eta+\xi)+12\xi^3\log(\eta+\xi)]/[96\pi^2\eta^2(\eta+\xi)]\right\},\tag{B3}$$

$$\langle Rg_{22}^2\rangle=-l\left\{\frac{-\xi}{6}+\frac{v\xi(13-12\log\xi+12\log(\eta+\xi))}{288\pi^2}+\eta w[-12\eta^2\xi-18\eta\xi^2-5\xi^3-12\eta^3\log\eta-24\eta^2\log\eta-12\eta\xi^2\log\eta+12\eta^3\times\log(\eta+\xi)+24\eta^2\xi\log(\eta+\xi)+12\eta\xi^2\times\log(\eta+\xi)]/[96\pi^2(\eta+\xi)\xi^2]\right\},\tag{B4}$$

$$
\begin{aligned}
\langle Rg_{12}^2\rangle = {} & l\{96\eta^3\pi^2\xi^2+96\eta^2\pi^2\xi^3+u[-29\eta^3\xi^2+24\eta^3\xi^2\ \log\ \eta-24\eta^3\xi^2\ \log(\eta+\xi)]+v[-29\eta^2\xi^3+24\eta^2\xi^3 \\
& \times\log\ \xi-24\eta^2\xi^3\ \log(\eta+\xi)]+w[-36\eta^4\xi-66\eta^3\xi^2-66\eta^2\xi^3-36\eta\xi^4-36\eta^5\ \log\ \eta-84\eta^4\xi\ \log\ \eta \\
& -72\eta^3\xi^2\ \log\ \eta-72\eta^2\xi^3\ \log\ \xi-84\eta\xi^4\ \log\ \xi-36\xi^5\ \log\ \xi+36\eta^5\ \log(\eta+\xi)+84\eta^4\xi\ \log(\eta+\xi) \\
& +72\eta^3\xi^2\ \log(\eta+\xi)+72\eta^2\xi^3\log(\eta+\xi)+84\eta\xi^4\ \log(\eta+\xi)+36\xi^5\ \log(\eta+\xi)]\}/(288\eta^2\pi^2\xi^2).
\end{aligned}
\tag{B5}
$$

[1] V. T. Bartels, V. Abetz, K. Mortensen, and M. Stamm, Europhys. Lett. **27**, 371 (1994).

[2] I. Ionescu, C. Picot, R. Duplessix, M. Duval, H. Benoit, J. P. Lingelser, and Y. Gallot, J. Polym. Sci. Polym. Phys. Ed. **19**, 1033 (1981).

[3] M. Duval, C. Picot, M. Benmouna, and H. Benoit, J. Phys. (France) **49**, 1963 (1988).

[4] J. des Cloizeaux and G. Jannink, *Les Polymères en Solution: leur Modélisation et leur Structure* (Editions de Physique, Paris, 1987).

[5] J.-F. Joanny, L. Leibler, and R. Ball, J. Chem. Phys. **81**, 4640 (1984).

[6] J. F. Douglas and K. F. Freed, J. Chem. Phys. **86**, 4280 (1987).

[7] C. H. Vlahos, A. Horta, L. A. Molina, and J. J. Freire, Macromolecules **27**, 2726 (1994).

[8] T. Ohta, Y. Oono, and K. F. Freed, Phys. Rev. A **25**, 2801 (1982).

[9] H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper & Row, New York, 1971).

[10] J. P. Cotton and H. Benoit, J. Phys. (France) **36**, 905 (1975).

[11] I. Ionescu, C. Picot, M. Duval, R. Duplessix, and H. Benoit, J. Polym. Sci. Polym. Phys. Ed. **19**, 1019 (1981).

[12] S. F. Edwards, Proc. Phys. Soc. **85**, 613 (1965).

[13] Y. Oono, T. Ohta, and K. F. Freed, J. Chem. Phys. **74**, 6458 (1981).

[14] A. Rey and J. J. Freire, J. Chem. Phys. **101**, 2455 (1994).

[15] J. L. Alessandrini and M. A. Carignano, Macromolecules **25**, 1157 (1992).