Dynamics of Diblock Copolymers in Dilute Solutions

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ABSTRACT: In the present work we consider the dynamics of freely translating and rotating diblock (A−B), Gaussian copolymers, in dilute solutions. Using the previously developed multiple scattering technique [*J. Chem. Phys.* **1978**, *69*, 2657, 2088; **1979**, *70*, 5875 (refs 1−3)]—applied to the study of suspensions of spheres and polymers—we have computed the diffusion and the friction coefficients D_{AB} and ζ_{AB}, respectively, and the change $\delta\eta_{AB}$ in the viscosity of the solution as functions of $x = N_A/N$ and $t = l_B/l_A$, where N_A and N are the number of segments of the A block and of the whole copolymer, respectively, and l_A and l_B are the Kuhn lengths of the A and B blocks. Specific regimes that maximize the difference between the diffusion constants of copolymers with distinct t values, which lead to increasing the efficiency of separation processes, have been identified.

1. Introduction

Currently, due to both the practical significance and the theoretical challenge, there is a sustained interest in the study of transport properties of copolymers in solution, mainly in relation to electrophoresis and associated phenomena. Basically, one wishes to tag the macromolecules of interest with a neutral chain to make the friction coefficient of the resulting object molecular weight dependent for all measurement conditions, in order to increase the efficiency of the separation process.[4] As there are experimental regimes for which the molecular weight dependence is lost and the separation is very weak if not impossible (for a recent calculation for polyelectrolytes, see Muthukumar[5]), a broader understanding of the dynamics of composite objects in solution becomes critical.

To gain insight into the dynamical behavior of an arbitrary heterogeneous polymer in solution, we will address a simpler, nevertheless illuminating problem: consider two linear, Gaussian polymers A and B, with lengths/number of segments L_A/N_A and L_B/N_B, respectively, and Kuhn lengths l_A and l_B, joined to form a composite chain (A−B) of total length $L = L_A + L_B$ and total number of monomers $N = N_A + N_B$. In this paper we calculate the self-diffusion and the friction coefficients of the diblock copolymer A−B and the change in the viscosity of the solution due to the copolymer in dilute solutions, as functions of the dimensionless variables $t = l_B/l_A$ and $x = N_A/N$.

Our calculations are based on the cluster expansion theory and on the effective medium hypothesis.[1,6−9] The main simplifying assumption is the absence of excluded volume interaction. Other approximations and features of our model are (a) no interaction between the polymer chains except the hydrodynamic interaction is present, (b) the solvent is incompressible and the steady state limit is considered, (c) the solution is assumed infinitely diluted (one chain limit), (d) the usual preaveraging approximation,[10] where one replaces the Oseen tensor $\mathbf{G}(\mathbf{r},\mathbf{r}')$ with its configurational average $\langle\mathbf{G}(\mathbf{r},\mathbf{r}')\rangle$, is employed, and (e) the hydrodynamic interaction is enforced by using stick boundary condition.

The model is not limited by the Gaussian nature of the two polymer components, because the Kuhn lengths

l_A and l_B could be effective quantities modeling chains with excluded volume and Coulombic interactions (assertion valid in the hydrodynamic limit; at short distances the fractal structure of the polymer becomes transparent). Also, even if the diblock copolymer could be regarded as a particular example of a branched polymer, extensively studied in the literature,[10,11] the important distinction in our work is that we allow for unequal Kuhn lengths for the two branches, with interesting consequences in the calculations—the structure factor of the copolymer must be computed now using a bivariate Gaussian probability distribution function. Finally, the present approach allows for obtaining exact results, albeit numerical except some limits, and no approximation of Kirkwood−Riseman type is necessary.

Concerning the outline of the paper, we next develop schematically—emphasizing the new elements—the underlying theory; then we show explicitly the calculation of D_{AB}, ζ_{AB}, and $\delta\eta_{AB}$. We conclude with a discussion of the results.

II. Calculation of the Steady-State Velocity Field: Infinite Dilution Limit

The dynamical properties of the system can be deduced from the knowledge of the average velocity field at any point in the solution. As this type of computation is already very well documented,[6] we will show detailed derivations only when necessary.

Briefly, the main steps of our computations are (1) we write the velocity field in the solution in the presence of the copolymer, (2) we apply the boundary condition to eliminate the unknown friction forces between the polymer and the fluid and then we average over the random position and the configuration of the chain, (3) we construct the cluster expansion in terms of the self-energy (Hartree−Fock diagrams) Σ of the fluid and we express it as a function of the known (measurable) physical parameters of the system, and (4) we use the self-energy to extract—both analytically and numerically—the quantities of interest.

Assuming that the diblock copolymer A−B with total number of segments N is immersed in an ideal, incompressible fluid obeying the linearized, time independent Navier−Stokes equation (with the solvent density equal

to 1), we can write the equation followed by the velocity field $\mathbf{v}(\mathbf{r})$ everywhere in the suspension as

$$-\eta_0 \Delta \mathbf{v}(\mathbf{r}) + \nabla p(\mathbf{r}) = \mathbf{F}(\mathbf{r}) + \int_0^L \mathrm{d}s\, \delta(\mathbf{r} - \mathbf{R}_s)\sigma_s \quad (1)$$

where $\mathbf{F}(\mathbf{r})$ and $p(\mathbf{r})$ are some external force producing the flow and the pressure, respectively, η_0 is the kinematic shear viscosity coefficient, and $\sigma_s = \sigma(s)$ is the force exerted by the bead located at $\mathbf{R}_s = \mathbf{R}(s)$ upon the fluid, s being the arc length along the chain (for notational convenience we will subsequently write s as a subscript). The formal solution of eq 1 is readily given by the integral representation (equivalent to the single layer solution of standard boundary methods)

$$\mathbf{v}(\mathbf{r}) = \mathbf{v}_0(\mathbf{r}) + \int_0^L \mathrm{d}s\, \mathbf{G}(\mathbf{r} - \mathbf{R}_s)\cdot\sigma_s \quad (2)$$

in which $\mathbf{v}_0(\mathbf{r}) = \int \mathrm{d}\mathbf{r}'\, \mathbf{G}(\mathbf{r} - \mathbf{r}')\cdot\mathbf{F}(\mathbf{r}')$ is the externally imposed velocity field and $\mathbf{G}$ is the Oseen tensor:

$$\mathbf{G}(\mathbf{k}) = \frac{\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}}{\eta_0 k^2}$$

$$\mathbf{G}(\mathbf{r} - \mathbf{r}') = \frac{1}{8\pi\eta_0|\mathbf{r} - \mathbf{r}'|}\left(\mathbf{I} + \frac{(\mathbf{r} - \mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^2}\right) \quad (3)$$

Here, $\mathbf{I}$ is the unit tensor and $\hat{\mathbf{k}}$ is the unit vector pointing in the $\mathbf{k}$ direction and the Fourier transform is given by

$$\mathbf{G}(\mathbf{r}) = \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\, \mathbf{G}(\mathbf{k})\, \exp(-i\mathbf{k}\cdot\mathbf{r}) \quad (4)$$

As mentioned, the dynamics of the copolymer chain and of the fluid are coupled through the no-slip boundary condition

$$\dot{\mathbf{R}}_s = \dot{\mathbf{R}}_0 + \omega \times \mathbf{S}_s = \mathbf{v}(\mathbf{R}_s) \quad (5)$$

where the velocity of the center-of-mass $\dot{\mathbf{R}}_0$ is constant and we further assume that the angular velocity ω is constant and equal to the configuration averaged angular velocity of the chain. To this equation we attach the physical constraints of force-free and torque-free motion (neglecting the inertial terms) of the diblock chain:

$$-\mathbf{f}\ (\text{total force}) = \int_0^L \mathrm{d}s\, \sigma_s = 0$$

$$-\mathbf{M}\ (\text{total torque}) = \int_0^L \mathrm{d}s\, \mathbf{S}_s \times \sigma_s = 0 \quad (6)$$

Above we used the relation $\mathbf{R}_s = \mathbf{R}_0 + \mathbf{S}_s$, where $\mathbf{S}_s$ represents the position vector of the monomer at s about the center-of-mass ($\mathbf{R}_0$) of the copolymer.

Next one needs to eliminate the unknown forces σ_s, a task accomplished by using the boundary condition (5) and defining the single-chain inverse operator $\mathbf{G}^{-1}$ as

$$\int_0^L \mathrm{d}s'\, \mathbf{G}^{-1}(\mathbf{R}_s, \mathbf{R}_{s'})\cdot\mathbf{G}(\mathbf{R}_{s'} - \mathbf{R}_{s''}) = \delta_{ss'}\mathbf{I} \quad (7)$$

We obtain then

$$\sigma_s = \int_0^L \mathrm{d}s'\, \mathbf{G}^{-1}(\mathbf{R}_s, \mathbf{R}_{s'})\cdot(\dot{\mathbf{R}}_0 + \omega \times \mathbf{S}_{s'} - \mathbf{v}_0(\mathbf{R}_{s'})) \quad (8)$$

where the variables s and s' should be read as the arc length arguments of $\mathbf{R}(s)$ and $\mathbf{R}(s')$. Inserting σ back into (6) we can calculate the total force $\mathbf{f}$ and torque $\mathbf{M}$ acting upon the polymer as

$$-\mathbf{f} = \mathbf{g}_{\mathrm{T}}\cdot\dot{\mathbf{R}}_0 + \mathbf{g}_{\mathrm{TR}}\cdot\omega - \int\int_0^L \mathrm{d}s\, \mathrm{d}s'\, \mathbf{G}_{ss'}^{-1}\cdot\mathbf{v}_0(s') \quad (9a)$$

$$-\mathbf{M} = \mathbf{g}_{\mathrm{RT}}\cdot\dot{\mathbf{R}}_0 + \mathbf{g}_{\mathrm{R}}\cdot\omega - \int\int_0^L \mathrm{d}s\, \mathrm{d}s'\, \mathbf{S}_s \times \mathbf{G}_{ss'}^{-1}\cdot\mathbf{v}_0(s') \quad (9b)$$

where we manipulated $\mathbf{G}_{ss'}^{-1}$ as a dyadic tensor. The newly introduced tensors $\mathbf{g}_{T,R}$ provide, upon averaging over the distribution of the segments s and s', the translational and rotational friction coefficients of the copolymer:

$$\zeta_{\mathrm{AB}} = \langle\mathbf{g}_{\mathrm{T}}\rangle = \langle\int\int_0^L \mathrm{d}s\, \mathrm{d}s'\, \mathbf{G}_{ss'}^{-1}\rangle \quad (10a)$$

$$\zeta_{\mathrm{AB}}^{\mathrm{rot}} = \langle\mathbf{g}_{\mathrm{R}}\rangle = -\langle\int\int_0^L \mathrm{d}s\, \mathrm{d}s'\, \mathbf{S}_s \times \mathbf{G}_{ss'}^{-1} \times \mathbf{S}_{s'}\rangle \quad (10b)$$

The remaining coefficients $\mathbf{g}_{\mathrm{TR,RT}}$ (the cross translational–rotational and rotational–translational terms) vanish upon preaveraging, and so will be further discarded. For future reference, their expressions are

$$\mathbf{g}_{\mathrm{TR}} = -\int\int_0^L \mathrm{d}s\, \mathrm{d}s'\, \mathbf{G}_{ss'}^{-1} \times \mathbf{S}_{s'} \quad (11a)$$

$$\mathbf{g}_{\mathrm{RT}} = \int\int_0^L \mathrm{d}s\, \mathrm{d}s'\, \mathbf{S}_s \times \mathbf{G}_{ss'}^{-1} \quad (11b)$$

Returning to the constraints (6), we now eliminate the unknowns $\dot{\mathbf{R}}_0$ and ω using

$$\dot{\mathbf{R}}_0 = \mathbf{g}_{\mathrm{T}}^{-1}\cdot\int\int_0^L \mathrm{d}s\, \mathrm{d}s'\, \mathbf{G}_{ss'}^{-1}\cdot\mathbf{v}_0(s')$$

$$\omega = \mathbf{g}_{\mathrm{R}}^{-1}\cdot\int\int_0^L \mathrm{d}s\, \mathrm{d}s'\, \mathbf{S}_s \times \mathbf{G}_{ss'}^{-1}\cdot\mathbf{v}_0(s') \quad (12)$$

where the inverse operators $\mathbf{g}_{\mathrm{T}}^{-1}$ and $\mathbf{g}_{\mathrm{R}}^{-1}$ are defined by the relations $\mathbf{g}_{\mathrm{T,R}}^{-1}\cdot\mathbf{g}_{\mathrm{T,R}} = \mathbf{I}$. Inserting the values obtained for $\dot{\mathbf{R}}_0$ and ω in eq 8 we find that

$$\sigma_s =$$
$$-\int_0^L \mathrm{d}s'\, \{\mathbf{G}_{ss'}^{-1} - \int\int_0^L \mathrm{d}t\, \mathrm{d}t'\, \mathbf{G}_{st}^{-1}\cdot\mathbf{g}_{\mathrm{T}}^{-1}\cdot\mathbf{G}_{t's'}^{-1} +$$
$$\int\int_0^L \mathrm{d}t\, \mathrm{d}t'\, \mathbf{G}_{st}^{-1} \times \mathbf{S}_t\cdot\mathbf{g}_{\mathrm{R}}^{-1}\cdot\mathbf{S}_{t'} \times \mathbf{G}_{t's'}^{-1}\}\cdot\mathbf{v}_0(s') \quad (13)$$

By introducing this expression back into eq 2, we get the solution for the velocity field $\mathbf{v}(\mathbf{r})$:

$$\mathbf{v}(\mathbf{r}) = \mathbf{v}_0(\mathbf{r}) + \int\int\int \mathrm{d}\mathbf{r}'\, \mathrm{d}\mathbf{r}''\, \mathrm{d}\mathbf{r}'''\, \mathbf{G}(\mathbf{r} - \mathbf{r}')\cdot$$
$$\mathbf{T}(\mathbf{r}',\mathbf{r}'')\cdot\mathbf{v}_0(\mathbf{r}'') \quad (14)$$

$\mathbf{T}$, the flow propagator that embodies the effect of the polymer chain upon the solution, is given by

$$\mathbf{T}(\mathbf{r},\mathbf{r}') = -\int\int_0^L \mathrm{d}s\, \mathrm{d}s'\, \delta(\mathbf{r} - \mathbf{R}_s)\mathbf{T}_{ss'}\delta(\mathbf{r}' - \mathbf{R}_{s'})$$

$$\mathbf{T}_{ss'} = \mathbf{T}(\mathbf{R}_s,\mathbf{R}_{s'}) =$$
$$\mathbf{G}_{ss'}^{-1} - \int\int_0^L \mathrm{d}t\, \mathrm{d}t'\, \mathbf{G}_{st}^{-1}\cdot\mathbf{g}_{\mathrm{T}}^{-1}\cdot\mathbf{G}_{t's'}^{-1} +$$
$$\int\int_0^L \mathrm{d}t\, \mathrm{d}t'\, \mathbf{G}_{st}^{-1} \times \mathbf{S}_t\cdot\mathbf{g}_{\mathrm{R}}^{-1}\cdot\mathbf{S}_{t'} \times \mathbf{G}_{t's'}^{-1} \quad (15)$$

where, as previously mentioned, the subscripts s, s', ... represent the arguments $\mathbf{R}_s$, $\mathbf{R}_{s'}$, ... of the operators. $\mathbf{T}$ depends in general upon the position, the structure, and the geometry of the copolymer.

Finally, we obtain the equation for the macroscopic velocity field by averaging eq 14 with respect to the random distribution of $\mathbf{R}_0$:

$$\mathbf{u}(\mathbf{r}) = \langle \mathbf{v}(\mathbf{r}) \rangle_0 = \mathbf{v}_0(\mathbf{r}) + \mathbf{G}^* \langle \mathbf{T} \rangle_0^* \mathbf{v}_0|_{\mathbf{r}} \qquad (16)$$

where we introduced the notations $*$ and $|_{\mathbf{r}}$ to denote the convolution operation and its final argument: $A^*B|_{\mathbf{r}} = \int d\mathbf{r}' \, A(\mathbf{r},\mathbf{r}') \cdot B(\mathbf{r}')$.

The connection with the experimentally measurable quantities is made by introducing the self-energy tensor $\Sigma(\mathbf{r},\mathbf{r}')$ defined by

$$\int d\mathbf{r}' \, \Sigma(\mathbf{r},\mathbf{r}') \cdot \langle \mathbf{v}(\mathbf{r}') \rangle_0 = \Sigma^* \langle \mathbf{v} \rangle_0 = \langle \int_0^L ds \, \delta(\mathbf{r} - \mathbf{R}_s) \sigma_s \rangle_0 \qquad (17)$$

Next we average directly eq 2 over $\mathbf{R}_0$ and we insert the expression of Σ from above, which yields

$$\mathbf{u}(\mathbf{r}) = \mathbf{v}_0(\mathbf{r}) + \int\int d\mathbf{r}' \, d\mathbf{r}'' \, \mathbf{G}(\mathbf{r} - \mathbf{r}') \cdot \Sigma(\mathbf{r}',\mathbf{r}'') \cdot \mathbf{u}(\mathbf{r}'') \qquad (18)$$

Taking into account that $\mathbf{v}_0(\mathbf{r}) = \mathbf{G}^* \mathbf{F}|_{\mathbf{r}}$, we can formally manipulate this equation to obtain

$$\mathbf{u}(\mathbf{r}) = \mathcal{G}^* \mathbf{F}|_{\mathbf{r}} = \int d\mathbf{r}' \, \mathcal{G}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}') \qquad (19)$$

in which $\mathcal{G}$—the effective Oseen tensor—is given by

$$\mathcal{G}(\mathbf{r},\mathbf{r}') = (\mathbf{I} - \mathbf{G}^*\Sigma)^{-1}{}^*\mathbf{G}|_{(\mathbf{r},\mathbf{r}')}$$

$$\mathcal{G}(\mathbf{k}) = \frac{\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}}{\eta_0 k^2 - \Sigma_\perp(k)} \qquad (20)$$

Here, by taking the inner-product with the projectors $\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}$ and $\hat{\mathbf{k}}\hat{\mathbf{k}}$ that obey $(\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}) \cdot (\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}) = \mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}$ and $\hat{\mathbf{k}}\hat{\mathbf{k}} \cdot (\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}) = 0$, we decomposed the tensors in their transverse and longitudinal parts as in $\mathbf{A} = A_\perp(\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}) + A_\| \hat{\mathbf{k}}\hat{\mathbf{k}}$, with $\mathbf{A}$ a symmetric tensor. After Fourier transforming and projecting the transversal and longitudinal components of the tensors, we can calculate the self-energy as a function of the flow propagator $\mathbf{T}$ by equating the expressions of $\mathbf{u}(\mathbf{r})$ from eqs 16 and 18. These operations yield

$$\Sigma(\mathbf{k}) = \frac{T_\perp(k)}{1 + G_\perp(k)T_\perp(k)} (\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}) + T_\|(k)\hat{\mathbf{k}}\hat{\mathbf{k}} \qquad (21)$$

where $\mathbf{T}(\mathbf{k})$ is the Fourier transform of $\langle \mathbf{T}(\mathbf{r} - \mathbf{r}') \rangle_0$ and $G_\| = 0$ (eq 3). Note that the equation for Σ is exact. In the dilute limit we work with, we can further approximate

$$\Sigma(\mathbf{k}) \simeq \mathbf{T}(\mathbf{k}) \qquad (22)$$

where preaveraging upon $\mathbf{T}(\mathbf{k})$ is understood.

From the structure of the effective Oseen tensor (20) we identify the change $\delta\eta_{AB}$ in the viscosity of the solution due to the added copolymer, in the hydrodynamic limit $|\mathbf{k}| \to 0$, as

$$\frac{\eta_{AB}}{\eta_0} - 1 = -\frac{1}{\eta_0} \lim_{k \to 0} \frac{\partial}{\partial k^2} \Sigma_\perp(k) \qquad (23)$$

III. Calculation of D_{AB}, ζ_{AB}, and $\delta\eta_{AB}$

In this section we present the detailed derivation of the transport properties of the system. The essential aspect is the computation of the structure factor, which involves, for the diblock copolymer case, the use of a bivariate Gaussian probability distribution function. This calculation is presented in Appendix A. For any operator $\mathbf{A}(s,s')$ depending on the arc length variables s, s' we will use the following Fourier representation (Rouse modes expansion in polymer language):

$$\mathbf{A}(s,s') = \frac{1}{L^2} \sum_{p=-\infty}^{\infty} \sum_{p'=-\infty}^{\infty} \mathbf{A}_{pp'} \, e^{(2i\pi/L)ps - (2i\pi/L)p's'}$$

$$\mathbf{A}_{pp'} = \int\int_0^L ds \, ds' \, \mathbf{A}(s,s') \, e^{-(2i\pi/L)ps + (2i\pi/L)p's'} \qquad (24)$$

where we remind that L is the total length of the polymer chain. Also, the inverse of $\mathbf{A}$ is defined by

$$\int_0^L ds' \, \mathbf{A}^{-1}(s,s') \cdot \mathbf{A}(s',s'') = \delta(s - s')\mathbf{I}$$

$$\sum_{p'=-\infty}^{\infty} \mathbf{A}_{pp'}{}^{-1} \cdot \mathbf{A}_{p'p''} = L^2 \delta_{pp'}\mathbf{I} \qquad (25)$$

A. Diffusion Coefficient D_{AB}. From eqs 9a and 10a we obtain immediately—after preaveraging (which is equivalent to replacing all instances of the Oseen tensor $\mathbf{G}(s,s')$ with its configurational average $\langle \mathbf{G}(s,s') \rangle$)—that $\mathbf{D}_{AB}$, a tensor quantity in general, is just the inverse of the friction coefficient ζ_{AB} (Einstein relation). Thus we write

$$\frac{\mathbf{D}_{AB}}{k_B T} = D_{AB}\mathbf{I} = \frac{1}{L^2} \int\int_0^L ds \, ds' \, \langle \mathbf{G}(s,s') \rangle$$

$$= \frac{1}{L^2} \mathbf{G}_{00} = \frac{1}{3\pi^2 \eta_0 L^2} \int_0^\infty dk \int\int_0^L ds \, ds' \times$$

$$\langle \exp[i\mathbf{k} \cdot (\mathbf{S}_s - \mathbf{S}'_{s'})] \rangle \mathbf{I} \qquad (26)$$

where we used the Fourier expansions (4) and (24) and the integral $\int d\Omega_k \, (\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}) = (8\pi/3)\mathbf{I}$. Splitting the double integral over the arc length variables s and s' in the regions $[0, L_A]$; $[L_A, L]$, inserting the value of the exponential term (the structure factor of the diblock copolymer) from Appendix A, and integrating over k, we get

$$\frac{D_{AB}}{k_B T} = \frac{16}{\pi\sqrt{\pi}} \frac{1}{L^2} \frac{1}{\eta_0} \frac{1}{l_A l_B} \left[R_A{}^3 \left(\frac{l_B}{l_A} - 1 \right) + R_B{}^3 \left(\frac{l_A}{l_B} - 1 \right) + (R_A{}^2 + R_B{}^2)^{3/2} \right] \qquad (27)$$
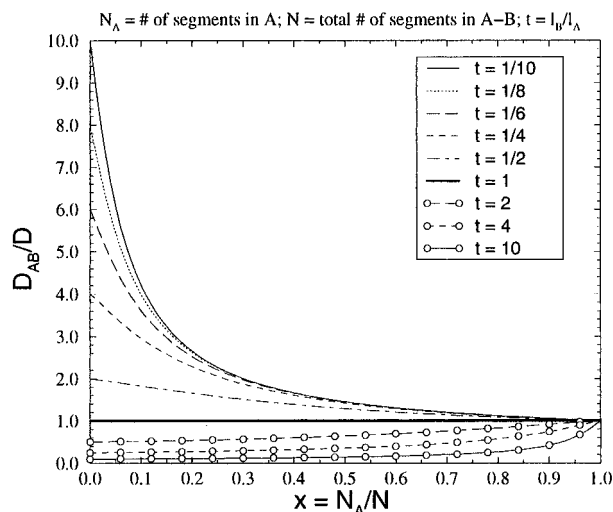
Figure 1. Diffusion coefficient D_{AB}/D as a function of $x = N_A/N$ and $t = l_B/l_A$ (D is the diffusion coefficient of a homogeneous chain with length $L_N = Nl_A$): (solid line) $t = {}^1/_{10}$; (dotted line) $t = {}^1/_8$; (long dashed line) $t = {}^1/_6$; (dashed line) $t = {}^1/_4$; (dot-dashed line) $t = {}^1/_2$; (thick solid line) $t = 1$; (○-long dashed line-○) $t = 2$; (○- dashed line-○) $t = 4$; (○-solid line-○) $t = 10$.

where $R_A = \sqrt{L_A l_A/6}$, $R_B = \sqrt{L_B l_B/6}$ are the radii of gyration of the two segments A and B, respectively, of the copolymer. It is readily checked that D_{AB} reduces to the classical Kirkwood−Riseman (K−R) result[12]

$$\frac{D}{k_B T} = \frac{1}{\zeta} = \frac{8\sqrt{2}}{3} h = \frac{4}{9\pi\sqrt{\pi}\eta_0 R_g} \quad (28)$$

with $1/h = \eta_0 l\sqrt{12\pi^3 N} = 6\pi\sqrt{2\pi}\eta_0 R_g$ and $R_g = \sqrt{Nl^2/6}$, in the limits $l_A = l_B$, $N_A = 0$, or $N_B = 0$.

The dimensionless variables that control the diffusion of the copolymer are made apparent by normalizing the expression (27) for D_{AB} to the classical value (28) of D of a polymer with the length $L_N = Nl_A$, where $N = N_A + N_B$. Defining $t = l_B/l_A$ and $x = N_A/N$ yields, upon normalization,

$$\frac{D_{AB}}{D} = \frac{t^2(1-x)^{3/2}(1-t) - x^{3/2}(1-t) + [x + t^2(1-x)]^{3/2}}{t[x + t(1-x)]^2} \quad (29)$$

which is the expression plotted in Figure 1 as a function of x and t, where t has values both smaller and larger than 1. When $t = 1$, $x = 1$, or $x = 0$, we obtain the meaningful limits 1, 1, and $1/t$, respectively, the last result (when $x = 0$) representing just the diffusion coefficient of a polymer of length $L_B = Nl_B$ normalized to the corresponding value of a chain with length $L_N = Nl_A$. When $t = 0$, the limit of (29) is $1/\sqrt{x}$. From Figure 1 we notice that a slight increase in the monomer fraction of the A block in the A−B copolymer when $t = l_B/l_A < 1$ has a much stronger effect on D_{AB} than an even larger increase of x in the regime with $t > 1$.

A more relevant relation—particularly from an experimental point of view—is obtained by computing the ratio between D_{AB} and the diffusion coefficient D_A of the block A given by the standard result (28) (with N
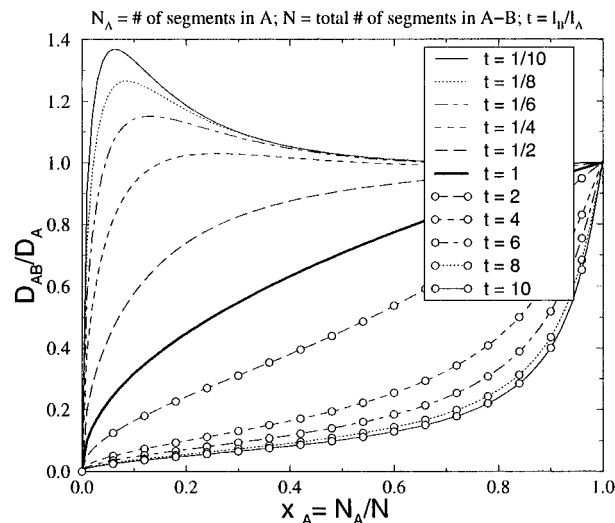

Figure 2. Diffusion coefficient D_{AB}/D_A as a function of $x = N_A/N$ and $t = l_B/l_A$ (D_A is the diffusion coefficient of a homogeneous chain with length $L_A = N_A l_A$): (solid line) $t = {}^1/_{10}$; (dotted line) $t = {}^1/_8$; (dot-dashed line) $t = {}^1/_6$; dashed line $t = {}^1/_4$; (long dashed line) $t = {}^1/_2$; (thick solid line) $t = 1$; (○-long dashed line-○) $t = 2$; (○-dashed line-○) $t = 4$; (○-dot-dashed line-○) $t = 6$; (○-dotted line-○) $t = 8$; (○-solid line-○) $t = 10$.

replaced by N_A), which immediately gives

$$\frac{D_{AB}}{D_A} = \sqrt{x}\,\frac{t^2(1-x)^{3/2}(1-t) - x^{3/2}(1-t) + [x + t^2(1-x)]^{3/2}}{t[x + t(1-x)]^2} \quad (30)$$

This expression is plotted as a function of x and t in Figure 2 for a sequence of values of t in the range $[{}^1/_{10}-10]$, the points with $t > 1$ being marked by circles joined by lines. Now at each fixed value of x (correspondingly N_A) one can compare the change in the diffusion coefficient of the diblock copolymer with respect to the diffusion constant of one of its components, which has direct implications in separation techniques.

We remark that at small x values and $t \leq {}^1/_4$ a maximum in D_{AB}/D_A occurs. Also, D_{AB} exhibits a change in curvature when the t parameter goes from $t < 1$ to $t > 1$, which motivated us in calculating the separation curves $\Delta(D_{AB}/D_A)$, defined as the difference between two values of the ratio D_{AB}/D_A corresponding to distinct values of t, as a function of x. These curves are displayed in Figure 3. Physically, the behavior of the diffusion coefficient of the diblock copolymer opens the way to control the process of separation of macromolecules by tagging the targets with other weight-controlled polymers. In particular, one can think of modifying the diffusion coefficient of a given polymer chain A by attaching to it another polymer B, with t having a prescribed value. This is illustrated in Figure 3 by the maxima occurring in the $\Delta(D_{AB}/D_A)$ function. There is also a range of the x values that offers an increased efficiency of the separation. This domain is much more localized for $t < 1$ than for $t > 1$, but the absolute value of the peak of $\Delta(D_{AB}/D_A)$ is highest when one compares—at the same x ratio—two copolymers with t greater and smaller than 1. This is reasonable—t small means l_A big, so even small variations in x have more significant effects than for pairs of copolymers with t comparable to 1.
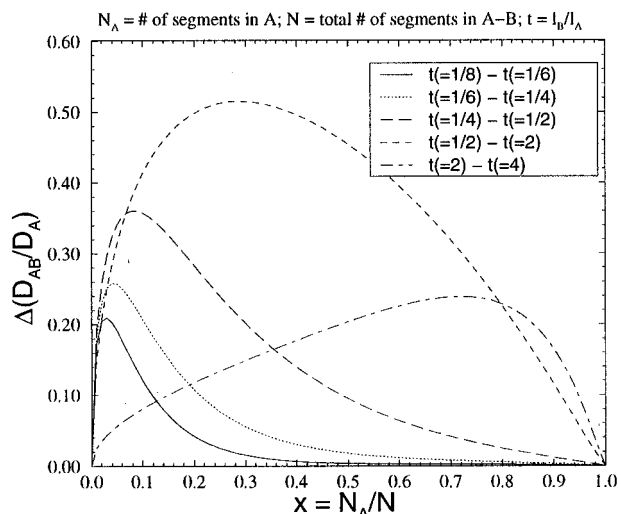
Figure 3. Separation curves as $\Delta(D_{AB}/D_A)(x) = (D_{AB}/D_A)(x,t_1) - (D_{AB}/D_A)(x,t_2)$: (solid line) $t_1 = \frac{1}{8}$, $t_2 = \frac{1}{6}$; (dotted line) $t_1 = \frac{1}{6}$, $t_2 = \frac{1}{4}$; (long dashed line) $t_1 = \frac{1}{4}$, $t_2 = \frac{1}{2}$; (dashed line) $t_1 = \frac{1}{2}$, $t_2 = 2$; (dot-dashed line) $t_1 = 2$, $t_2 = 4$.

B. Friction Coefficient ζ_{AB}. From eq 10a, expanding the inverse Oseen tensor $\mathbf{G}_{ss'}^{-1}$ in double Fourier series (24), we find that $\zeta_{AB} = \mathbf{G}_{00}^{-1}$. Because the $\mathbf{G}_{pp'}$ tensor, due to the diblock structure of the copolymer with different Kuhn lengths, is not diagonal in the p index, the calculation of the friction coefficient is more difficult. In general, one needs to decompose the $\mathbf{G}_{ss'}^{-1}$ matrix in its diagonal and nondiagonal parts and then to use a Born expansion up to the desired order.[3] Fortunately, next we will show that the $\mathbf{G}_{00}^{-1}$ factor can be computed by direct numerical inversion.

We start with the expression of $\mathbf{G}_{pp'}$ elements given by eq 24:

$$\mathbf{G}_{pp'} = \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}}{\eta_0 k^2} \int \int_0^L ds\, ds' \, \langle \exp[i\mathbf{k}\cdot(\mathbf{S}_s - \mathbf{S}_{s'})]\rangle \exp\left[-\frac{2i\pi}{L}ps + \frac{2i\pi}{L}p's'\right] \quad (31)$$

To evaluate the integrals, first we split the domain of integration $(0, L) \times (0, L)$ over s and s' into four regions: $(0, L_A) \times (0, L_A)$, $(0, L_A) \times (L_A, L)$, $(L_A, L) \times (0, L_A)$, and $(L_A, L) \times (L_A, L)$, and then we insert the expression of the structure factor from Appendix A. As the remaining integrations are rather intricate, we present the computation of $\mathbf{G}_{pp'}$ elements in Appendix B. The final result is

$$\mathbf{G}_{pp}|_{p\neq 0} = L^2 \frac{1}{\pi \sqrt{6\pi}\eta_0} \frac{1}{\sqrt{L|p|}} \left[\frac{L_A}{L}\frac{1}{\sqrt{l_A}} + \left(1 - \frac{L_A}{L}\right)\frac{1}{\sqrt{l_B}}\right]\mathbf{I} \quad (32a)$$

$$\mathbf{G}_{pp'}|_{p\neq 0} = L^2 \frac{1}{2\pi^2\sqrt{6\pi}\eta_0} \frac{1}{\sqrt{L|p|}} \frac{1}{i(p'-p)}\left[\frac{1}{\sqrt{l_B}} - \frac{1}{\sqrt{l_A}}\right] [1 - e^{(2\pi i L_A/L)(p'-p)}]\mathbf{I} \quad (p,p' \in \mathbb{Z}) \quad (32b)$$

From eqs 26 and 27 the $\mathbf{G}_{00}$ element is just $L^2\mathbf{D}_{AB}/(k_BT)$. The $\mathbf{G}_{pp'}$ matrix is hermitian ($\mathbf{G}_{pp'} = \mathbf{G}_{p',p}^*$) and diagonally dominant, thus securing a well-behaved inverse. We remark that only when $l_A = l_B$, $L_A = 0$, or $L_A = L$ do the nondiagonal elements of $\mathbf{G}_{pp'}$ vanish.

To further proceed with the numerical inversion, we need to reduce the $\mathbf{G}_{pp'}$ tensor to a dimensionless form. This task is accomplished by noticing that the Rouse

coefficients $\mathbf{G}_{pp'}$ can be written as

$$\mathbf{G}_{pp'} = L^2 \frac{1}{4\pi^2\sqrt{6\pi}\eta_0} \frac{1}{\sqrt{Ll_A}}\mathbf{K}_{pp'}(x,t) \quad (33)$$

where $\mathbf{K}$ is a purely numerical tensor, function of the dimensionless parameters $x = N_A/N$ and $t = l_B/l_A$ and with the matrix representation (hermitian) given by

$$\mathbf{K}_{00}(x,t) = \frac{32\pi}{3} \frac{t^2(1-x)^{3/2}(1-t) - x^{3/2}(1-t) + [x + t^2(1-x)]^{3/2}}{t[x + t(1-x)]^{3/2}}\mathbf{I} \quad (34a)$$

$$\mathbf{K}_{pp}(x,t)|_{p\neq 0} = \frac{4\pi}{\sqrt{|p|}}\left[y + \frac{1-y}{\sqrt{t}}\right]\mathbf{I}; \qquad y = \frac{x}{x + t(1-x)} \quad (34b)$$

$$\mathbf{K}_{pp'}(x,t)|_{p\neq 0} = \frac{2}{i(p'-p)} \frac{1}{\sqrt{|p|}}\left(\frac{1}{\sqrt{t}} - 1\right)[1 - e^{2i\pi(p'-p)y}]\mathbf{I} \quad (34c)$$

where we employed $L = L_A + L_B = Nl_A (x + t(1-x))$. Note that for our choice of t the limit of $t \to 0$ for $\mathbf{K}_{pp'}$ is not immediate. Next, applying the definition (25) we construct the inverse $\mathbf{G}_{pp'}^{-1}$ as

$$\sum_{p'=-\infty}^{+\infty} \mathbf{G}_{pp'}^{-1}\cdot\mathbf{G}_{p'p''} = L^2\delta_{pp'}\mathbf{I} \quad (35)$$

and substituting $\mathbf{G}_{pp'}$ from eq 33, we find that

$$\mathbf{G}_{pp'}^{-1} = 4\pi^2\sqrt{6\pi}\eta_0\sqrt{Ll_A}\mathbf{K}_{pp'}^{-1}(x,t) \quad (36)$$

where the $\mathbf{K}^{-1}$ operator is defined by the equation

$$\sum_{p'=-\infty}^{\infty} \mathbf{K}_{pp'}^{-1}(x,t)\cdot\mathbf{K}_{p'p''}(x,t) = \delta_{pp'}\mathbf{I} \quad (37)$$

Eventually, recalling that $\zeta_{AB} = \mathbf{G}_{00}^{-1}$ and after normalizing to the friction coefficient $\zeta = 9\pi\sqrt{\pi}\eta_0 R_g/4$ (see eq 28) of a homogeneous polymer of length $L = Nl_A$, we obtain

$$\frac{\zeta_{AB}}{\zeta}(x,t) = \frac{32}{3}\pi\sqrt{x + t(1-x)}K_{00}^{-1}(x,t) \quad (38)$$

where we dropped the unit dyad from the formulas, as inessential. The limiting cases when the tensor $\mathbf{K}_{pp'}^{-1}$ is diagonal can be readily checked analytically. We then get

$$K_{00}(x,1) = \frac{32\pi}{3}; \qquad K_{pp}(x,1) = \frac{4\pi}{\sqrt{|p|}}$$

$$K_{00}(0,t) = \frac{32\pi}{3}\frac{1}{\sqrt{t}}; \qquad K_{pp}(x,1) = 0 \quad \text{for} \quad p \neq p'$$

$$K_{00}(1,t) = \frac{32\pi}{3}; \qquad K_{pp}(x,0) = \frac{32\pi}{3} \quad (39)$$

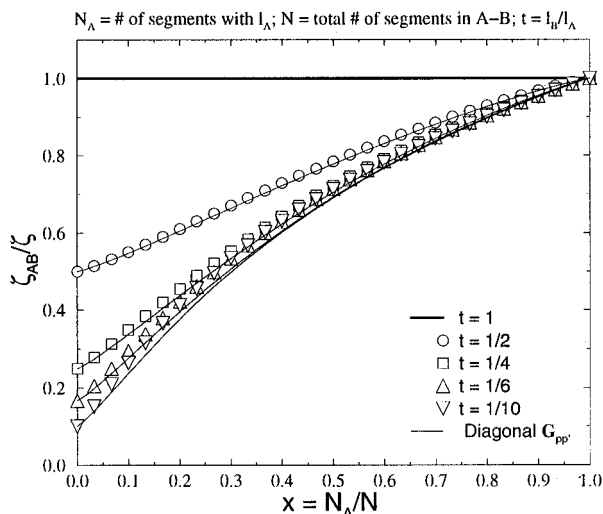For these limits the inverse of K_{00} is just $K_{00}^{-1} = (K_{00})^{-1}$

N$_A$ = # of segments with l$_A$; N = total # of segments in A–B; t = l$_B$/l$_A$

Figure 4. Friction coefficient ζ_{AB}/ζ as a function of x and t (ζ is the K–R friction coefficient for a chain with length $L_N = Nl_A$). Thin lines show the results obtained when using only the diagonal elements of $\mathbf{G}_{pp'}$ for the t values corresponding to the following symbols: (thick solid line) $t = 1$; ($\bigcirc$) $t = 1/2$; ($\square$) $t = 1/4$; ($\triangle$) $t = 1/6$; ($\triangledown$) $t = 1/10$; (—) diagonal $\mathbf{G}_{pp'}$.

N$_A$ = # segments in A; N = total # of segments in A–B; t = l$_B$/l$_A$
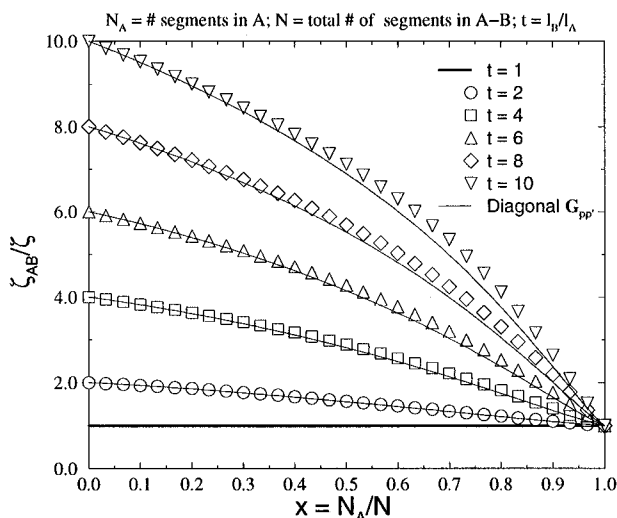
Figure 5. Friction coefficient ζ_{AB}/ζ as a function of x and t (ζ is the K–R friction coefficient for a chain with length $L_N = Nl_A$). Thin lines show the results obtained when using only the diagonal elements of $\mathbf{G}_{pp'}$ for the t values corresponding to the following symbols: (thick solid line) $t = 1$; ($\bigcirc$) $t = 2$; ($\square$) $t = 4$; ($\triangle$) $t = 6$; ($\diamond$) $t = 8$; ($\triangledown$) $t = 10$; (—) diagonal $\mathbf{G}_{pp'}$.

and the friction coefficient $\zeta_{AB}/\zeta(x,t)$ reduces accordingly to the physically correct values:

$$\frac{\zeta_{AB}}{\zeta}(x,1) = 1; \qquad \frac{\zeta_{AB}}{\zeta}(0,t) = t; \qquad \frac{\zeta_{AB}}{\zeta}(1,t) = 1 \quad (40)$$

The explicit inversion of $K_{00}(x,t)$ is carried out by first fixing the values of the parameters x and t. Then we iterate the dimensions of the $K_{pp'}(x,t)$ and we numerically invert it for each $|p| = 1, p_{max}$ until $K_{00}^{-1}(x,t)$ converges to the desired precision—we have chosen 10^{-7} for computational convenience—at a certain p_{max}.

The final results for ζ_{AB}/ζ calculated from eq 38 have been plotted in Figures 4 and 5 against the fraction x of A beads, for values of t smaller and greater than 1. Points where a numerical evaluation was carried out are marked by symbols, their shape corresponding to different values of t.

An illuminating aspect of the result is that neglecting the off-diagonal components of the Rouse tensor $\mathbf{G}_{pp'}$ and

inverting it directly (then ζ_{AB} is just $L^2 (G_{00})^{-1}$) still leads to the qualitatively correct behavior of ζ_{AB}, as displayed by the continuous lines in Figures 4 and 5.

C. Intrinsic Viscosity [η_{AB}]. As seen from eq 23, the information regarding the change in the viscosity of the solution is contained in the self-energy $\Sigma(\mathbf{k})$. To find it, we proceed by averaging over the random position $\mathbf{R}_0$ of the center-of-mass of the polymer and Fourier transforming eq 15, which yields

$$\Sigma(\mathbf{k}) \simeq \mathbf{T}(\mathbf{k}) = -\frac{1}{V}\int d(\mathbf{r} - \mathbf{r}')\int d\mathbf{R}_0 \exp[i\mathbf{k}\cdot$$

$$(\mathbf{r} - \mathbf{r}')]\int\int_0^L ds\,ds'\,\delta(\mathbf{r} - \mathbf{R}_0 - \mathbf{S}_s)\mathbf{T}_{ss'}\delta(\mathbf{r}' - \mathbf{R}_0 - \mathbf{S}_{s'})$$

$$= -\frac{1}{V}\int\int_0^L ds\,ds'\,\mathbf{T}_{ss'}\exp[i\mathbf{k}\cdot(\mathbf{S}_s - \mathbf{S}_{s'})] \tag{41}$$

where V is the volume of the suspension. Inserting the full form of $\mathbf{T}_{ss'}$ from (15) produces

$$\Sigma(\mathbf{k}) = -\frac{1}{V}[\mathbf{T}^{(1)}(\mathbf{k}) - \mathbf{T}^{(2)}(\mathbf{k}) + \mathbf{T}^{(3)}(\mathbf{k})] \tag{42}$$

with the new factors being given by

$$\mathbf{T}^{(1)}(\mathbf{k}) = \int\int_0^L ds\,ds'\,\mathbf{G}_{ss'}^{-1}\exp[i\mathbf{k}\cdot(\mathbf{S}_s - \mathbf{S}_{s'})] \tag{43a}$$

$$\mathbf{T}^{(2)}(\mathbf{k}) = \int\int\int\int_0^L ds\,ds'\,dt\,dt'\,\mathbf{G}_{st}^{-1}\cdot\mathbf{g}_T^{-1}\cdot\mathbf{G}_{t's'}^{-1}$$
$$\exp[i\mathbf{k}\cdot(\mathbf{S}_s - \mathbf{S}_{s'})] \tag{43b}$$

$$\mathbf{T}^{(3)}(\mathbf{k}) = \int\int\int\int_0^L ds\,ds'\,dt\,dt'\,\mathbf{G}_{st}^{-1}\times\mathbf{S}_t\cdot\mathbf{g}_R^{-1}\cdot\mathbf{S}_{t'}\times$$
$$\mathbf{G}_{t's'}^{-1}\exp[i\mathbf{k}\cdot(\mathbf{S}_s - \mathbf{S}_{s'})] \tag{43c}$$

Here, we recall that $\mathbf{G}_{ss'}^{-1}$ is defined by eq 7 and should actually read $\mathbf{G}^{-1}(\mathbf{S}_s - \mathbf{S}_{s'})$. From (10) we calculate—within the preaveraging approximation—the frictional coefficients $\mathbf{g}_T$ and $\mathbf{g}_R$ as

$$\langle\mathbf{g}_T\rangle = \int\int_0^L ds\,ds'\,\langle\mathbf{G}_{ss'}^{-1}\rangle = \mathbf{G}_{00}^{-1} \tag{44a}$$

$$\langle\mathbf{g}_R\rangle = -\int\int_0^L ds\,ds'\,\langle\mathbf{G}_{ss'}^{-1}\rangle\cdot\langle\mathbf{S}_s\times\mathbf{I}\times\mathbf{S}_{s'}\rangle$$

$$= \frac{2}{3}\int\int_0^L ds\,ds'\,\langle\mathbf{G}_{ss'}^{-1}\rangle\cdot\langle\mathbf{S}_s\cdot\mathbf{S}_{s'}\rangle =$$

$$\frac{2}{3}\frac{1}{L^2}\sum_{p=-\infty}^{+\infty}\sum_{p'=-\infty}^{+\infty}\mathbf{G}_{pp'}^{-1}\cdot\mathbf{F}_{pp'}^* \tag{44b}$$

where we used $\langle S_s^{(i)} S_{s'}^{(j)}\rangle = 1/3\langle\mathbf{S}_s\cdot\mathbf{S}_{s'}\rangle\delta_{ij}$ that implies $\langle(\mathbf{S}_s\cdot\mathbf{r})(\mathbf{S}_{s'}\cdot\mathbf{r})\rangle = 1/3 r^2\langle\mathbf{S}_s\cdot\mathbf{S}_{s'}\rangle$ for any vector $\mathbf{r}$. Note that the double summation over p and p' is equivalent to taking the trace of $\mathbf{G}^{-1}\cdot\mathbf{F}$. We also developed all quantities in the double Fourier series (24) and (25). The $\mathbf{F}$ elements are computed from

$$\mathbf{F}_{pp'} = F_{pp'}\mathbf{I} = \int\int_0^L\langle\mathbf{S}_s\cdot\mathbf{S}_{s'}\rangle\exp\left[-\frac{2i\pi}{L}ps + \frac{2i\pi}{L}p's'\right]\mathbf{I} \tag{45}$$

We remark that $\mathbf{F}$ is a hermitian operator. Averaging $\mathbf{S}_s\cdot\mathbf{S}_{s'}$ over the distribution of the segments s and s' for the diblock copolymer is a rather involved operation, and the details are presented in Appendix C.

Next we can simplify the calculations by taking directly the k^2 components of $\mathbf{T}^{(i)}(\mathbf{k})$ in (43). Then $\mathbf{T}^{(1)}$

becomes, upon preaveraging,[6]

$$\mathbf{T}_{k^2}^{(1)} = \int\int_0^L ds\,ds'\,\langle\mathbf{G}_{ss}^{-1}\rangle\cdot\langle(\mathbf{k}\cdot\mathbf{S}_s)(\mathbf{k}\cdot\mathbf{S}_s)\rangle$$

$$= \frac{1}{3}k^2\int\int_0^L ds\,ds'\,\langle\mathbf{G}_{ss'}^{-1}\rangle\cdot\langle\mathbf{S}_s\cdot\mathbf{S}_s'\rangle = \frac{1}{2}k^2\langle\mathbf{g}_R\rangle \quad (46)$$

where $\mathbf{g}_R$ is given by eq 44b. In a similar manner, it follows that $\mathbf{T}_{k^2}^{(2)}$ can be written as

$$\mathbf{T}_{k^2}^{(2)} = \frac{1}{3}k^2\int\int\int\int_0^L ds\,ds'\,dt\,dt'\,\langle\mathbf{G}_{st}^{-1}\rangle\cdot\langle\mathbf{g}_T^{-1}\rangle\cdot\langle\mathbf{G}_{t's'}^{-1}\rangle$$
$$\langle\mathbf{S}_s\cdot\mathbf{S}_s'\rangle$$

$$= \frac{1}{3}\frac{1}{L^2}k^2\langle\mathbf{g}_T^{-1}\rangle\sum_{pp'}\mathbf{G}_{0p}^{-1}\cdot\mathbf{F}_{pp'}'\cdot\mathbf{G}_{p'0}^{-1} \quad (47)$$

where the Fourier expansions (24) and (25) were once again utilized. For a homogeneous polymer ($t = 1$), $\mathbf{G}_{pp'}^{-1}$ becomes diagonal and $\mathbf{F}_{00} = 0$ (Appendix C) so $\mathbf{T}_{k^2}^{(2)}$ vanishes as required.[6]

Finally, the k^2 part of $\boldsymbol{T}^{(3)}(\mathbf{k})$ results from

$$\mathbf{T}_{k^2}^{(3)} = \langle\mathbf{g}_R^{-1}\rangle\int\int\int\int_0^L ds\,ds'\,dt\,dt'\,\langle\mathbf{G}_{st}^{-1}\rangle\cdot(\mathrm{I}\times$$
$$\langle\mathbf{k}\cdot\mathbf{S}_s\mathbf{S}_t\rangle)\cdot(\langle\mathbf{k}\cdot\mathbf{S}_{s'}\mathbf{S}_{t'}\rangle\times\mathrm{I})\cdot\langle\mathbf{G}_{t's'}^{-1}\rangle$$

$$= -\frac{1}{9}\langle\mathbf{g}_R^{-1}\rangle k^2(\mathrm{I}-\hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\int\int\int\int_0^L ds\,ds'\,dt\,dt'$$
$$\langle\mathbf{G}_{st}^{-1}\rangle\cdot\langle\mathbf{S}_t\cdot\mathbf{S}_s\rangle\cdot\langle\mathbf{S}_{s'}\cdot\mathbf{S}_{t'}\rangle\cdot\langle\mathbf{G}_{t's'}^{-1}\rangle \quad (48)$$

where we pulled out the $\mathbf{g}_R^{-1}$ factor as it is just a number multiplying the unit tensor and we applied the relation $(\mathrm{I}\times\mathbf{a})\cdot(\mathbf{a}\times\mathrm{I}) = -a^2(\mathrm{I}-\hat{\mathbf{a}}\hat{\mathbf{a}})$, valid for any vector $\mathbf{a}$. Developing all factors in double Fourier (Rouse modes) series, we obtain

$$\mathbf{T}_{k^2}^{(3)} = -\frac{1}{9}\frac{1}{L^4}\langle\mathbf{g}_R^{-1}\rangle k^2(\mathrm{I}-$$
$$\hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\sum_{pq}\mathbf{G}_{pq}^{-1}\cdot\mathbf{F}_{pq}^*\cdot\sum_{p'q'}\mathbf{G}_{q'p'}^{-1}\cdot\mathbf{F}_{q'p'}^* \quad (49)$$

in which all the summation indices run over the $(-\infty,+\infty)$ interval. Replacing the sums in terms of the $\langle\mathbf{g}_R\rangle$ coefficient (eq 44b) and noticing that in our approximation $\langle\mathbf{g}_R^{-1}\rangle\cdot\langle\mathbf{g}_R\rangle = 1$, we get the simpler form

$$\mathbf{T}_{k^2}^{(3)} = -\frac{1}{4}\langle\mathbf{g}_R\rangle k^2(\mathrm{I}-\hat{\mathbf{k}}\hat{\mathbf{k}}) \quad (50)$$

Collecting all the components of $\mathbf{T}_{k^2}$ from eqs 46, 47, and 50 and inserting them in eq 42, we find that

$$\Sigma_{k^2}(\mathbf{k}) = -\frac{1}{V}\left[\frac{1}{2}k^2\langle\mathit{g}_R\rangle\mathrm{I} - \frac{1}{3}k^2\langle\mathit{g}_T^{-1}\rangle\frac{1}{L^2}\sum_{p=-\infty}^{+\infty}\sum_{p'=-\infty}^{+\infty}\times\right.$$
$$\left. G_{0p}^{-1}F_{pp'}G_{p'0}^{-1}\mathrm{I} - \frac{1}{4}k^2\langle\mathit{g}_R\rangle(\mathrm{I}-\hat{\mathbf{k}}\hat{\mathbf{k}})\right] \quad (51)$$

where we used the fact that all quantities are scalar multiples of the unit dyad I (e.g., $\langle\mathit{g}_R\rangle$ and $\langle\mathit{g}_R^{-1}\rangle$ are now some functions to be computed and $G_{pp'}^{-1}$ and $F_{pp'}$ are the matrix elements of the Fourier representation of G^{-1} and F). The change in viscosity follows from eq 23 by

applying the transverse projector $\mathrm{I}-\hat{\mathbf{k}}\hat{\mathbf{k}}$ to the previous expression:

$$\frac{\delta\eta_{AB}}{\eta_0}(\mathrm{I}-\hat{\mathbf{k}}\hat{\mathbf{k}}) = \frac{1}{V\eta_0}\left[\frac{1}{4}k^2\langle\mathit{g}_R\rangle - \frac{1}{3}k^2\times\right.$$
$$\left.\langle\mathit{g}_T^{-1}\rangle\frac{1}{L^2}\sum_{p,p'}G_{0p}^{-1}F_{pp'}G_{p'0}^{-1}\right](\mathrm{I}-\hat{\mathbf{k}}\hat{\mathbf{k}}) \quad (52)$$

Introducing the concentration of the copolymer $c_{AB} = M_{AB}/VN_{AV}$, with N_{AV} Avogadro's number and M_{AB} the molecular mass, we calculate the intrinsic viscosity $[\eta_{AB}]$ from

$$[\eta_{AB}] = \frac{\eta_{AB}-\eta_0}{c_{AB}\eta_0} = \frac{\delta\eta_{AB}}{\eta_0}\frac{VN_{AV}}{M_{AB}} \quad (53)$$

Formally, we have the desired expression. Practically, we need to reduce it to a dimensionless form amenable to numerical evaluation. To this end, we write $\mathbf{G}^{-1}$ in terms of the $\mathbf{K}^{-1}$ operator from eq 36 obeying also (37), with $\mathbf{K}(x,t)$ introduced in eq 33. Then we express $\mathbf{F}_{pp'}$ as

$$\mathbf{F}_{pp'} = \frac{(Nl_A)^4}{2N}f_{pp'}(x,t)\mathrm{I} \quad (54)$$

where $x = N_A/N$, $t = l_B/l_A$ and $f_{pp'}$, is a dimensionless function of x and t (see Appendix C). Inserting back into eq 44b, we obtain the rotational friction coefficient as

$$\langle\mathit{g}_R\rangle = 4\,\pi^2\,\sqrt{\frac{2\pi}{3}}\eta_0(Nl_A^2)^{3/2}\frac{1}{[x+(1-x)t]^{3/2}}\sum_{p,p'=-\infty}^{+\infty}\times$$
$$K_{pp'}^{-1}(x,t)\,f_{pp'}^*(x,t) \quad (55)$$

To check the result, we quote some particular values of the $f_{pp'}(x,t)$ function:

$$f_{00}(x,1) = 0; \qquad f_{00}(0,t) = 0; \qquad f_{00}(1,t) = 0$$

$$f_{pp}(x,1) = \frac{1}{\pi^2p^2}; \qquad f_{pp'}(x,1) = \frac{1}{2\pi^2pp'};$$
$$f_{pp}(x,0) = \frac{x^3}{\pi^2p^2} \quad (56)$$

When $t = 1$ (the homogeneous case), the $K_{pp'}$ matrix is diagonal, $K^{-1} = (K)^{-1}$ and using (39) $\langle\mathit{g}_R\rangle$ reduces to the known result

$$\langle\mathit{g}_R\rangle|_{t=1} = \frac{24}{\sqrt{\pi}}\eta_0\left(\frac{Nl_A^2}{6}\right)^{3/2}\sum_{p=1}^{\infty}\frac{1}{p^{3/2}} \quad (57)$$

Now, as $\langle\mathit{g}_T^{-1}\rangle$ is just the inverse of the translational friction coefficient $\langle\mathit{g}_T\rangle$ given by (44a), we can calculate

$$\langle\mathit{g}_T\rangle = D_{AB} = \frac{8}{3\pi\sqrt{6\pi}\eta0}\frac{1}{\sqrt{Nl_A^2}}\times$$
$$\frac{t^2(1-x)^{3/2}(1-t)-x^{3/2}(1-t)+[x+t^2(1-x)]^{3/2}}{t[x+t(1-x)]^2}$$
$$(58)$$

from which we recover the Kirkwood−Riseman result when $t\to 1$, as already discussed.

Going back to the viscosity formula (52), we use eqs 36, 54, 55, and 58 to express everything in dimensionless variables and, after normalizing to the non-free draining result[6,12]

$$\frac{\delta\eta}{\eta_0} = \frac{1}{V}\frac{6}{\sqrt{\pi}}\left(\frac{Nl_A^2}{6}\right)^{3/2} Zeta(3/2) \quad (59)$$

where $Zeta(3/2) = \sum_{p=1}^{\infty} 1/p^{3/2}$ (the Riemann function), we finally obtain

$$\frac{\delta\eta_{AB}}{\delta\eta}(x,t) = \frac{2\pi^3}{Zeta(3/2)}\frac{1}{[x+t(1-x)]^{3/2}} \times$$

$$\left[\sum_{p,p'=-\infty}^{+\infty} K_{pp'}{}^{-1}(x,t)\, f_{pp'}^*(x,t) - \frac{64\pi}{3} \times \right.$$

$$\frac{t^2(1-x)^{3/2}(1-t) - x^{3/2}(1-t) + [x+t^2(1-x)]^{3/2}}{t[x+t(1-x)]^{3/2}} \times$$

$$\left. \sum_{p,p'=-\infty}^{+\infty} K_{0p}{}^{-1}(x,t)\, f_{pp'}(x,t)\, K_{p'0}{}^{-1}(x,t) \right] \quad (60)$$

Once again, we can check analytically some limits of this expression by using the matrix elements $K_{pp'}$ and $f_{pp'}$ from eqs 39 and 56:

$$\frac{\delta\eta_{AB}}{\delta\eta}(x,1) = 1; \qquad \frac{\delta\eta_{AB}}{\delta\eta}(1,t) = 1; \qquad \frac{\delta\eta_{AB}}{\delta\eta}(0,t) = t^3 \quad (61)$$

To compare directly the increase in viscosity due to the A-B copolymer to the change due to polymer A only (computed from the K−R result), we only need to multiply (60) with $1/x^{3/2}$, which then yields

$$\frac{\delta\eta_{AB}}{\delta\eta}(x,t) = \frac{1}{x^{3/2}}\frac{\delta\eta_{AB}}{\delta\eta}(x,t) \quad (62)$$

The relative intrinsic viscosity of the suspension follows readily from (53):

$$\frac{[\eta_{AB}]}{[\eta]} = \frac{M_{AB}}{M}\frac{\delta\eta_{AB}}{\delta\eta}(x,t) \quad (63)$$

where M and $[\eta]$ are the molecular mass and the intrinsic viscosity of a solution of a polymer with $N = N_A + N_B$ beads and l_A Kuhn length.

In Figure 6 the viscosity calculated from (60) is plotted against $x = N_A/N$ for different values of the parameter $t = l_B/l_A$. From a practical point of view, it is reassuring that, checking once again the validity of the Kirkwood−Riseman approximation by computing $\delta\eta_{AB}$ by neglecting all the nondiagonal elements of $\mathbf{G}_{pp'}$, we obtain a very good agreement with the exact numerical evaluations. This aspect is illustrated in Figure 6, where the continuous lines represent the calculation done using only the diagonal elements $\mathbf{G}_{pp}$.

On the basis of this finding, in Figure 7 the viscosity calculated from (60) but employing the Kirkwood− Riseman approximation is plotted against x at various t values. Similar to the observations in the diffusion case, we notice that the intrinsic viscosity $[\eta_{AB}]/[\eta_A]$ attains a minimum matching the maximum of D_{AB}/D_A from Figure 2. This should be useful for some techno-
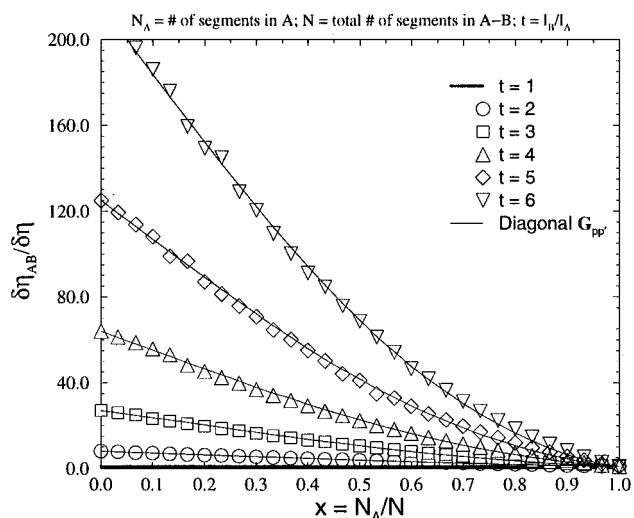

Figure 6. Change in the viscosity $\delta\eta_{AB}/\delta\eta$ as a function of x and t ($\delta\eta$ is the K−R non-free draining result for the change in viscosity due to a polymer with length $L = Nl_A$). Thin lines show the results obtained when using only the diagonal elements of $\mathbf{G}_{pp'}$ for the t values corresponding to the following symbols: (thick solid line) $t = 1$; (○) $t = 2$; (□) $t = 3$; (△) $t = 4$; (◇) $t = 5$; (▽) $t = 6$; (−) diagonal $\mathbf{G}_{pp'}$.
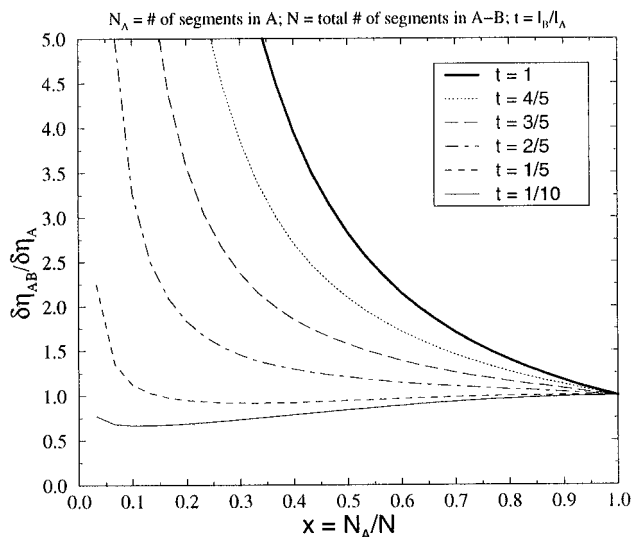

Figure 7. Change in the viscosity $\delta\eta_{AB}/\delta\eta_A$ as a function of x and t using the Kirkwood−Riseman approximation ($\delta\eta_A$ is the K−R non-free draining result for the change in viscosity due to a polymer with length $L_A = N_A l_A$): (thick solid line) $t = 1$; (dotted line) $t = 4/5$; (long dashed line) $t = 3/5$; (dot-dashed line) $t = 2/5$; (dashed line) $t = 1/5$; (solid line) $t = 1/10$.

logical processes where a control of the viscosity of a solution is desired.

IV. Conclusions

In this paper we have considered the stationary dynamics of an infinitely diluted solution of freely translating and rotating Gaussian diblock copolymers. The copolymer chain consists of two components A and B, with Kuhn lengths l_A and l_B and number of segments N_A and N_B, respectively. There is no excluded-volume interaction, and the solution is described by the linearized Navier−Stokes equation. The hydrodynamics is coupled to the chain dynamics by the no-slip boundary condition.

Extending to our case the cluster expansion theory[1,7−9,13] previously used to study the hydrodynamics of suspensions of polymers and spheres, we developed explicitly the necessary theoretical elements and

we obtained analytically and calculated numerically the following physical quantities of interest: the diffusion coefficient D_{AB}, the friction coefficient ζ_{AB}, and the intrinsic viscosity $[\eta_{AB}]$. The results have been displayed graphically as functions of the dimensionless variables characterizing the problem, $x = N_A/N$ and $t = l_B/l_A$.

Even for the simple system studied here, an interesting behavior of D_{AB} and implicitly of the other quantities, emerged. The main finding of the present work is that by adjusting x (the molecular mass ratio) and t parameters, we can control the process of separation of diblock copolymers (or, more generally, combined objects) under hydrodynamic flow. To illustrate this aspect we constructed separation curves by taking the difference $\Delta(D_{AB}) = D_{AB}(x,t_1) - D_{AB}(x,t_2)$ and representing it as a function of x and the pair $t_1 - t_2$, which allows us to identify both the absolute maxima and the ranges of x that maximize the difference $\Delta(D_{AB})$ for given t_1 and t_2. As an immediate extension of the present work, an application of our approach to the process of electrophoretic separation is in progress. Our results also complement previous theoretical work[14−16] on the cooperative diffusion coefficient of diblock copolymers.

The formalism presented is applicable in more general contexts not limited to Gaussian chains. For example, when excluded-volume or Coulombic interactions are present we can capture their effects—in certain conditions—by renormalizing the Kuhn lengths l_A and l_B to some effective values. As an additional observation, the usual Kirkwood−Riseman approximation is not necessary. But, rather surprisingly, our calculations have shown rigorously that one can still safely apply it.

Appendix A: Computation of $\langle \exp[i\mathbf{k}(\mathbf{S}_s - \mathbf{S}_{s'})]\rangle$

Consider a Gaussian polymer chain consisting of N links each of mean-square length l_k, with $k \in \overline{1,N}$. Following Yamakawa,[10] we can construct the probability distribution function $P(\mathbf{S}_i - \mathbf{S}_j)$ of the distance between two beads i and j located at $\mathbf{S}_i$ and $\mathbf{S}_j$, respectively, about the center-of-mass of the chain as

$$P(\mathbf{S}_i - \mathbf{S}_j) = \left(\frac{3}{2\pi\langle l^2\rangle}\right)^{3/2}\exp\left[-\frac{3|\mathbf{S}_i - \mathbf{S}_j|^2}{2\langle l^2\rangle}\right] \quad (A1)$$

with $\langle l^2\rangle = \sum_{m\geq j+1}^{i} l_k^2$. Then, $\langle \exp[i\mathbf{k}\cdot(\mathbf{S}_i - \mathbf{S}_j)]\rangle$ is the generating function of the moments of the $P(\mathbf{S}_i - \mathbf{S}_j)$ distribution and is given by

$$M[\mathbf{k}] = \langle \exp[i\mathbf{k}\cdot(\mathbf{S}_i - \mathbf{S}_j)]\rangle = \exp\left(-\frac{1}{6}k^2\langle l^2\rangle\right) \quad (A2)$$

In our problem we have only two types of links, A and B, with average lengths l_A and l_B and the calculation of the structure factor averaged over the distribution of beads yields

$$\langle e^{i\mathbf{k}\cdot(\mathbf{S}_s-\mathbf{S}_{s'})}\rangle =$$
$$\begin{cases} e^{-(1/6)k^2|s-s'|l_{A,B}} & \text{if } s, s' < L_A \text{ or } s, s' > L_A \\ e^{-(1/6)k^2[(L_A-s)l_A+(s'-L_A)l_B]} & \text{if } s < L_A \text{ and } s' > L_A \\ e^{-(1/6)k^2[(L_A-s')l_A+(s-L_A)l_B]} & \text{if } s > L_A \text{ and } s' < L_A \end{cases} \quad (A3)$$

In the expressions above we introduced the arc length variables s and s' instead of the numbers i and j (e.g., $s = il_A$ if $s < L_A$) and $L_A = N_A l_A$ and $L_B = N_B l_B$.

Appendix B: Computation of the Matrix Elements $\mathbf{G}_{pp'}$

As previously shown, the Fourier coefficients of the Oseen tensor are given by

$$\mathbf{G}_{pp'} = \int \frac{d\mathbf{k}}{(2\pi)^3}\frac{\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}}{\eta_0 k^2}\int\int_0^L ds\, ds'\, \langle \exp[i\mathbf{k}\cdot(\mathbf{S}_s -$$
$$\mathbf{S}_{s'})]\rangle \exp\left[-\frac{2i\pi}{L}ps + \frac{2i\pi}{L}p's'\right] \quad (B1)$$

Introducing the structure factor from (A3) and performing the angular integral utilizing $\int d\Omega_k\,(\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}) = (8\pi/3)\mathbf{I}$, we arrive at

$$\mathbf{G}_{pp'} = \frac{1}{3\pi^2\eta_0}\int_0^\infty dk[\int\int_0^{L_A}ds\, ds'\, e^{-(1/6)k^2|s-s'|l_A} +$$
$$\int\int_{L_A}^L ds\, ds'\, e^{-(1/6)k^2|s-s'|l_B} +$$
$$\int_0^{L_A}\int_{L_A}^L ds\, ds'\, e^{-(1/6)k^2[(L_A-s)l_A+(s'-L_A)l_B]} +$$
$$\int_{L_A}^L\int_0^{L_A}ds\, ds'\, e^{-(1/6)k^2[(L_A-s')l_A+(s-L_A)l_B]}]$$
$$\exp\left[-\frac{2i\pi}{L}ps + \frac{2i\pi}{L}p's'\right]\mathbf{I} \quad (B2)$$

The evaluation of the integrals goes as follows. First we compute the $\mathbf{G}_{00}$ factor:

$$\mathbf{G}_{00} = \frac{16}{\pi\sqrt{\pi}\eta_0}\frac{1}{l_A l_B}\left[R_A^3\left(\frac{l_B}{l_A} - 1\right) + R_B^3\left(\frac{l_A}{l_B} - 1\right) + (R_A^2 + R_B^2)^{3/2}\right]\mathbf{I} \quad (B3)$$

where $R_{A,B} = (L_{A,B}l_{A,B}/6)^{1/2}$ are the radii of gyration of the A and B components of the copolymer and the integral $\int_0^\infty dx\,[(1/x^2) - (1/x^4)(1 - e^{-x^2})] = 2\sqrt{\pi}/3$ was used.

Next, making $p = p' \neq 0$ and integrating over s and s' yields

$$\mathbf{G}_{pp} = \frac{1}{3\pi^2\eta_0}\int_0^\infty \times$$
$$dk\left\{\frac{2L_A^2(kR_A)^2}{(kR_A)^4 + \left(\frac{2\pi L_A}{L}p\right)^2} + \frac{2(L-L_A)^2(kR_B)^2}{(kR_B)^4 + \left(\frac{2\pi(L-L_A)}{L}p\right)^2} +\right.$$
$$\frac{L_A(L-L_A)}{\left[(kR_A)^2 - \frac{2\pi L_A}{L}p\right]\left[(kR_B)^2 - \frac{2\pi(L-L_A)}{L}p\right]}\left[1 -\right.$$
$$\exp\left(\frac{2i\pi L_A}{L}p - k^2R_A^2\right)\right]\left[1 - \exp\left(-\frac{2i\pi L_A}{L}p - k^2R_B^2\right)\right] +$$
$$\frac{L_A(L-L_A)}{\left[(kR_A)^2 + \frac{2\pi L_A}{L}p\right]\left[(kR_B)^2 + \frac{2\pi(L-L_A)}{L}p\right]}\left[1 -\right.$$
$$\left.\exp\left(-\frac{2i\pi L_A}{L}p - k^2R_A^2\right)\right]\left[1 - \exp\left(\frac{2i\pi L_A}{L}p - k^2R_B^2\right)\right]\right\}\mathbf{I}$$
$$(B4)$$

Integrating over k in the complex plane the third and fourth factors of the integral vanish and we find that $\mathbf{G}_{pp}$ is given by

$$\mathbf{G}_{pp} = L^2 \frac{1}{\pi \sqrt{6\pi}\eta_0} \frac{1}{\sqrt{L|p|}} \left[\frac{1}{\sqrt{l_A}} \frac{L_A}{L} + \frac{1}{\sqrt{l_B}} \left(1 - \frac{L_A}{L} \right) \right] \mathbf{I} \quad (B5)$$

The computation of the remaining elements $\mathbf{G}_{pp'|p\neq p'}$ and $\mathbf{G}_{0p}$ is accomplished in a similar manner and involves a rather lengthy calculus. A simplification occurs if it is noticed that the $\mathbf{G}_{pp'}$ operator given by (B1) is hermitian ($\mathbf{G}_{pp'} = \mathbf{G}_{p'p}^*$). Then we only need to calculate

$$\mathbf{G}_{pp'} = \frac{1}{3\pi^2\eta_0} \int_0^\infty dk \left\{ \frac{L_A L}{i\pi(p'-p)} \frac{(kR_A)^2}{(kR_A)^4 + \left(\frac{2\pi L_A}{L}p\right)^2} \right.$$
$$[e^{(2i\pi L_A/L)(p'-p)} - 1] + \frac{L(L-L_A)}{i\pi(p'-p)}[1 -$$
$$\left. e^{(2i\pi(L_A-L)/L)(p'-p)}] \frac{(kR_B)^2}{(kR_B)^4 + \left(\frac{2\pi(L-L_A)}{L}p\right)^2} \right\} \mathbf{I} \quad (B6)$$

which yields the final result

$$\mathbf{G}_{pp'} = L^2 \frac{1}{2\pi^2\sqrt{6\pi}\eta_0} \frac{1}{\sqrt{L|p|}} \frac{1}{i(p'-p)} \left(\frac{1}{\sqrt{l_B}} - \frac{1}{\sqrt{l_A}} \right) [1 -$$
$$e^{(2i\pi L_A/L)(p'-p)}] \mathbf{I} \quad (B7)$$

Letting $p' \to 0$ gives $\mathbf{G}_{p0}$, and from hermiticity we obtain $\mathbf{G}_{0p} = \mathbf{G}_{p0}^*$.

Appendix C: Evaluation of the Average $\langle \mathbf{S}_s \cdot \mathbf{S}_s' \rangle$

We consider a Gaussian diblock copolymer A−B consisting in N_A links of Kuhn length l_A and N_B links of Kuhn length l_B, with $N_A + N_B = N$. Let $\mathbf{r}_k$ be the bond vector (along the segment) of the kth link. Our goal is to construct the bivariate probability distribution function $P(\mathbf{S}_i, \mathbf{S}_j)$.[10] This can be done by expressing the positions $\mathbf{S}_i$ and $\mathbf{S}_j$ of the ith and jth beads about the center-of-mass as

$$\mathbf{S}_i = \sum_{k=1}^N \Psi_{ik}\mathbf{r}_k; \qquad \mathbf{S}_j = \sum_{k=1}^N \Psi_{jk}\mathbf{r}_k \quad (C1)$$

where

$$\Psi_{ik} = \theta(i - k) + \frac{k}{N+1} - 1;$$
$$\Psi_{ik} = \theta(j - k) + \frac{k}{N+1} - 1 \quad (C2)$$

and $\theta(x)$ is the step function. Also, we introduce the symmetric matrix C

$$\mathbf{C} = \begin{pmatrix} C_{ii} & C_{ij} \\ C_{ji} & C_{jj} \end{pmatrix} \quad (C3)$$

with its components given by

$$C_{mn} = \frac{1}{\langle l^2 \rangle}(l_A^2 \sum_{k=1}^{N_A} \Psi_{mk}\Psi_{nk} + l_B^2 \sum_{k=N_A+1}^{N} \Psi_{mk}\Psi_{nk})$$
$$m, n \in \{i,j\} \quad (C4)$$

and $\langle l^2 \rangle = (1/N)[N_A l_A^2 + (N - N_A)l_B^2] = l_A^2(x + t^2(1 - x))$.

With these notations, we can calculate in a well documented fashion[10] the bivariate probability distribution function of the Gaussian diblock copolymer A−B as

$$P(\mathbf{S}_i, \mathbf{S}_j) = \left(\frac{3}{2\pi\langle l^2 \rangle} \right)^3 \frac{1}{(\det \mathbf{C})^{3/2}} \exp[-C_1 \mathbf{S}_i \cdot \mathbf{S}_i -$$
$$C_2 \mathbf{S}_i \cdot \mathbf{S}_j - C_3 \mathbf{S}_j \cdot \mathbf{S}_j] \quad (C5)$$

where

$$C_1 = \frac{3C_{jj}}{2\langle l^2 \rangle \det \mathbf{C}}; \qquad C_2 = -\frac{3C_{ij}}{\langle l^2 \rangle \det \mathbf{C}};$$
$$C_3 = \frac{3C_{ii}}{2\langle l^2 \rangle \det \mathbf{C}} \quad (C6)$$

The generating function for the moments is equal to

$$M[\mathbf{k},\mathbf{k}'] = \exp\left[-\frac{1}{6}\langle l^2 \rangle (C_{ii}\mathbf{k}^2 + 2C_{ij}\mathbf{k}\cdot\mathbf{k}' + C_{jj}\mathbf{k}'^2) \right]$$
$$(C7)$$

The sought average $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ results immediately from

$$\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle = \lim_{\substack{k\to 0 \\ k'\to 0}} l^2 \nabla_k \nabla_{k'} M[\mathbf{k},\mathbf{k}'] = \langle l^2 \rangle C_{ij} \quad (C8)$$

It is clear that the value of the C_{ij} factor depends on where the beads i and j are located with respect to the two sections of the copolymer. We have three cases: both beads in block A (C_{ij}^A), both beads in block B (C_{ij}^B), or the ith bead in A and the jth bead in B ($C_{ij}^{AB} = C_{ji}^{BA}$). Inserting the values of $\Psi_{(i,j)k}$ from eq C2 into eq C4 and carrying out the summation keeping only terms of order N, we obtain

$$C_{ij}^A = \frac{l_A^2}{\langle l^2 \rangle} \left\{ \frac{i^2}{2N} + \frac{j^2}{2N} - i\theta(i - j) - j[1 - \theta(i - j)] + \right.$$
$$\left. N_A\left(1 - x + \frac{x^2}{3}\right) + t^2\frac{N}{3}\left[1 - 3x\left(1 - x + \frac{x^2}{3}\right)\right] \right\} \quad (C9a)$$

$$C_{ij}^B = \frac{l_A^2}{\langle l^2 \rangle} \left\{ \frac{N}{3}[t^2 + (1 - t^2)x^3] + \right.$$
$$\left. t^2\left[\frac{i^2}{2N} + \frac{j^2}{2N} - i\theta(i - j) - j[1 - \theta(i - j)] \right] \right\} \quad (C9b)$$

$$C_{ij}^{AB} = \frac{l_A^2}{\langle l^2 \rangle} \left\{ \frac{i^2}{2N} - \frac{1}{2}N_A x\left(1 - \frac{2}{3}x \right) + \right.$$
$$\left. t^2\left[\frac{j^2}{2N} - j + \frac{N}{3}\left(1 + \frac{3}{2}x^2 - x^3 \right) \right] \right\} \quad (C9c)$$

where we recall that $x = N_A/N$ and $t = l_B/l_A$. Returning to the arc length variables s and s' (e.g., $s = il_A$ when s

$\leq L_A$ or $s = N_A l_A + (i - N_A) l_B$ for $s > N_A$), we complete the computation of $\langle \mathbf{S}_s \cdot \mathbf{S}_{s'} \rangle$ by inserting the C_{ij} factors in (C8). In the three mentioned cases of distribution of the beads s (former i) and s' (former j) in the blocks A and B we find

$$\langle \mathbf{S}_s \cdot \mathbf{S}_{s'} \rangle^A = \frac{1}{2N} \Big[s^2 + s'^2 - 2s N l_A \theta(s - s') - 2s' N l_A (1 - \theta(s - s')) + 2(N l_A)^2 \Big(x(1 - t^2) \Big(1 - x + \frac{1}{3} x^2 \Big) + \frac{1}{3} t^2 \Big) \Big] \quad \text{(C10a)}$$

$$\langle \mathbf{S}_s \cdot \mathbf{S}_{s'} \rangle^B = \frac{1}{2N} \Big[s^2 + s'^2 - 2N l_A [x(1 - t) - t\theta(s - s')] s - 2N l_A [x(1 - t) + t(1 - \theta(s - s'))] s' + 2(N l_A)^2 \Big(\frac{1}{3} x^2 (1 - t^2) + \frac{t^2}{3} + xt(1 - t) + x^2 (1 - t)^2 \Big) \Big] \quad \text{(C10b)}$$

$$\langle \mathbf{S}_s \cdot \mathbf{S}_{s'} \rangle^{AB} = \frac{1}{2N} \Big[s^2 + s'^2 - 2N l_A (t + x(1 - t)) s' + 2(N l_A)^2 \Big(\frac{1}{2} x^2 (1 - t)^2 + xt(1 - t) + \frac{t^2}{3} - \frac{1}{2} x^2 (1 - t^2) \Big(1 - \frac{2}{3} x \Big) \Big) \Big] \quad \text{(C10c)}$$

with $\langle \mathbf{S}_s \cdot \mathbf{S}_{s'} \rangle^{BA} = \langle \mathbf{S}_s \cdot \mathbf{S}_{s'} \rangle^{AB} |_{s \leftrightarrow s'}$.

Having calculated these averages, we introduce them back into

$$\mathbf{F}_{pp'} = F_{pp'} \mathbf{I} = \int \int_0^L \langle \mathbf{S}_s \cdot \mathbf{S}_{s'} \rangle \exp\Big[-\frac{2i\pi}{L} ps + \frac{2i\pi}{L} p' s' \Big] \mathbf{I} \quad \text{(C11)}$$

and after evaluating the resulting integrals we arrive at the Fourier coefficients $\mathbf{F}_{pp'}$. We show the f_{00}, f_{pp}, and f_{0p} elements (where $f_{pp'}$ is the dimensionless part of $\mathbf{F}_{pp'}$

from eq 54):

$$f_{00}(x, t) = \frac{2}{3} (1 - t)^2 (1 - x)^2 x^2 (t^2 + x - t^2 x) \quad \text{(C12a)}$$

$$f_{pp}(x, t) = \frac{1}{4p^3 \pi^3} e^{-2ip\pi x/(t + x - tx)} (-t - x + tx)^2 (-it + ie^{4ip\pi x/(t + x - tx)} t + it^2 - ie^{4ip\pi x/(t + x - tx)} t^2 + 4e^{2ip\pi x/(t + x - tx)} p\pi t^2 - ix + ie^{4ip\pi x/(t + x - tx)} x + 4e^{2ip\pi x/(t + x - tx)} p\pi x + 2itx - 2ie^{4ip\pi x/(t + x - tx)} tx - it^2 x + ie^{4ip\pi x/(t + x - tx)} t^2 x - 4e^{2ip\pi x/(t + x - tx)} p\pi t^2 x) \quad \text{(C12b)}$$

$$f_{0p}(x, t) = \frac{1}{4\pi^3 p^3} (-1 + t)(-t - x + tx)(it^2 - ie^{2i\pi px/(t + x - tx)} t^2 + 2itx - 2ie^{2i\pi px/(t + x - tx)} tx - 2e^{2i\pi px/(t + x - tx)} \pi ptx - 2it^2 x + 2ie^{2i\pi px/(t + x - tx)} t^2 x + 2e^{2i\pi px/(t + x - tx)} \pi pt^2 x + 2i\pi^2 p^2 x + ix^2 - ie^{2i\pi px/(t + x - tx)} x^2 - 2e^{2i\pi px/(t + x - tx)} \pi px^2 + 2i\pi^2 p^2 x^2 - 2itx^2 + 2ie^{2i\pi px/(t + x - tx)} tx^2 + 6e^{2i\pi px/(t + x - tx)} \pi ptx^2 + it^2 x^2 - ie^{2i\pi px/(t + x - tx)} t^2 x^2 - 4e^{2i\pi px/(t + x - tx)} \pi pt^2 x^2 - 4i\pi^2 p^2 t^2 x^2 + 2e^{2i\pi px/(t + x - tx)} \pi px^3 - 2i\pi^2 p^2 x^3 - 4e^{2i\pi px/(t + x - tx)} \pi ptx^3 + 2e^{2i\pi px/(t + x - tx)} \pi pt^2 x^3 + 2i\pi^2 p^2 t^2 x^3) \quad \text{(C12c)}$$

Unfortunately, $f_{pp'}(x, t)$ is too long to be reproduced here. Limits of $f_{pp'}(x, t)$ when $x = \{0, 1\}$ and $t = 1$ were quoted in the text (see eq 56).

References and Notes

(1) Freed, K. F.; Muthukumar, M. *J. Chem. Phys.* **1978**, *69*, 2657.
(2) Freed, K. F.; Muthukumar, M. *J. Chem. Phys.* **1978**, *68*, 2088.
(3) Muthukumar, M.; Freed, K. F. *J. Chem. Phys.* **1979**, *70*, 5875.
(4) Long, D.; Ajdari, A. *Electrophoresis* **1996**, *17*, 1161.
(5) Muthukumar, M. *Electrophoresis* **1996**, *17*, 1167.
(6) Muthukumar, M. *J. Phys. A* **1981**, *14*, 2129.
(7) Muthukumar, M.; Freed, K. F. *J. Chem. Phys.* **1982**, *76*, 6195.
(8) Muthukumar, M. *J. Chem. Phys.* **1982**, *77*, 959.
(9) Freed, K. F.; Muthukumar, M. *J. Chem. Phys.* **1982**, *76*, 6186.
(10) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(11) Stockmayer, W. H.; Fixman, M. *Ann. N. Y. Acad. Sci.* **1953**, *57*, 334.
(12) Kirkwood, J. G.; Riseman, J. *J. Chem. Phys.* **1948**, *16*, 565.
(13) Mondescu, R. P.; Muthukumar, M. *J. Chem. Phys.* **1996**, *105*, 4846.
(14) Benmouna, M.; Duval, M.; Borsali, R. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 1839.
(15) Hammouda, B.; Akcasu, A. Z.; Benmouna, M. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 853.
(16) Benmouna, M.; Borsali, R. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 981.