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Dynamics of Ternary Polymer Solutions

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ABSTRACT: Hydrodynamic interaction is included in the description of ternary polymer solutions (two polymers or a block copolymer mixed with a solvent). The effect of hydrodynamic interaction on the two decay rates (of the so called "slow" and "fast" modes) is assessed for dilute and semidilute solutions where Rouse dynamics are not appropriate. The Kubo formula was used to express the generalized mobilities in terms of the Oseen tensor and the static structure factors (convolution integral). The random phase approximation was used to express the interacting system static structure factors. A concentration blob concept allows the incorporation of hydrodynamic interaction inside each blob. Specific cases are discussed.

Introduction

There has been a great deal of attention given to the dynamics of ternary polymer mixtures involving two polymers in dilute/semidilute solution.[1–10] Experimental data have been reported using quasielastic light or neutron scattering from either two homopolymers or a block copolymer in solution. Two modes are observed and are referred to as the "slow" (or "interdiffusion") mode and the "fast" (or "cooperative diffusion") mode. These two modes are not in general pure normal modes[11] except in special cases (matched degrees of polymerization, common good solvent, etc.). In order to interpret such data, a model[1] based on Rouse dynamics (i.e., neglecting hydrodynamic interaction) has been used. Since hydrodynamic interaction may be important in dilute and semidilute solutions, it is included here using a simple approach. A concentration blob concept allows the incorporation of hydrodynamic interaction inside each blob. The approach used to include hydrodynamic interaction is a straightforward application of the Kubo formula expressing the generalized mobilities in terms of a convolution (in reciprocal space) over the Oseen tensor and the interacting structure factors. The random phase approximation (RPA) is used to express the various interacting structure factors in terms of excluded volumes and ideal (bare) structure factors. The formalism is developed first for an incompressible multicomponent polymer mixture in solution, and then it is applied to the ternary cases of two homopolymers or a block copolymer in solution.

General Formalism

Consider a multicomponent polymer mixture consisting of n different polymers and a solvent. In the homogeneous one-phase region, the dynamics of this system are characterized by n modes. Defining the static structure factor matrix $\mathbf{S}(q)$ composed of the n^2 partial structure factors $S_{AA}(q)$, $S_{AB}(q)$, etc., and the first cumulant matrix $\Lambda(q)$ (n^2 components also), the dynamic structure factor matrix $\mathbf{S}(q,t)$ is given by the general relation[12]

$$\mathbf{S}(q,t) = \exp[-\Lambda(q)t]\mathbf{S}(q) \tag{1}$$

and the generalized mobility matrix is $\mathbf{m}(q) = \Lambda(q)\mathbf{S}(q)/k_BTq^2$.

In order to describe intermediate concentrations (such as in semidilute solutions) it is common to introduce concentration "blobs" (of size ζ) where hydrodynamic interaction is important within each blob but becomes screened for monomers that belong to different blobs. The polymer solution can therefore be described as a mixture of concentration blobs. The two extreme limits in concentration (dilute solution and melt limits) are readily recovered when the blob size gets large (of the order of the radius of gyration R_g) for the dilute solution limit and when the blob size is equal to the monomer size (statistical segment length b) for the melt limit (i.e., when no solvent is present).

A correlation length of the form

$$\zeta = (b - R_g\phi^{*4/3})/(1 - \phi^{*4/3}) + (R_g - b)(\phi^*/\phi)^{4/3}/(1 - \phi^{*4/3}) \tag{2}$$

could be used in order to estimate the blob size (here ϕ is the total polymer volume fraction and ϕ^* is the overlap volume fraction). Equation 2 represents an interpolation formula that gives $1/\phi^{4/3}$ and reproduces the desired limits at the semidilute and melts limits.

Because the focus of this paper is on dilute and semidilute polymer solutions (where hydrodynamic interaction is important), the formalism presented here does not apply to the melt limit whereby the dynamic RPA[13] should be used in order to recapture the inverse superposition rule for mobilities.

At intermediate concentrations, the mobility matrix $\mathbf{m}$ can be expressed in terms of a convolution of the Oseen tensor and of the static structure factors matrix (Kubo formula) as

$$\mathbf{m}(q) = \mathbf{m}_R + [1/(2\pi)^3]\int d^3k T_{33}(\mathbf{k}-\mathbf{q})\{\mathbf{S}(k) - \delta\} \tag{3}$$

where $T_{33}(q)$ is the longitudinal component of the Oseen tensor (i.e., along the $\mathbf{q}$ direction):

$$T_{33}(k) = [1 - (\mathbf{k}\cdot\mathbf{q})^2/q^2]/\eta k^2 \tag{4}$$

$\mathbf{m}_R$ is the Rouse term contribution, η is the viscosity, and δ is an $n \times n$ diagonal matrix with elements $\delta_{AB}\phi_A v_A$ where δ_{AB} is the Kronecker δ function and ϕ_A and v_A are the volume fraction and monomer volume for component A. Rouse mobilities are expressed in terms of the volume fractions (ϕ_A) and friction coefficients (ξ_A) as $m_A{}^R = \phi_A v_A/\xi_A$. The static RPA can be used to express the structure factor matrix $\mathbf{S}(k)$

$$\mathbf{S}(k) = \mathbf{S}_0(k)[\mathbf{I} + \mathbf{V}\mathbf{S}_0(k)]^{-1} \tag{5}$$

in terms of the excluded volume matrix $\mathbf{V}$ and ideal (also called "bare") structure factor matrix $\mathbf{S}_0(k)$ (here $\mathbf{I}$ is the identity matrix). Combining these two equations, the generalized mobility matrix becomes

$$\mathbf{m}(q) = \mathbf{m}_R + [1/(2\pi)^3]\int d^3k\, T_{33}(\mathbf{k}-\mathbf{q}) \times \{\mathbf{S}_o(k)[\mathbf{I} + \mathbf{V}\mathbf{S}_o(k)]^{-1} - \delta\} \quad (6)$$

The k integration is split into two parts,[14] $[\mathbf{m}(q) - \mathbf{m}_R = \mathbf{m}_L(q) + \mathbf{m}_H(q)]$: one "low-$k$" part, $\mathbf{m}_L(q)$ (for $k < 2\pi/\zeta$), to account for interblob interactions and one "high-k" part, $\mathbf{m}_H(q)$ (for $k > 2\pi/\zeta$), to account for interactions within each blob. Note that for $k < 2\pi/\zeta$ the interaction parameters, degrees of polymerization, and molar volumes refer to blobs, not monomers, and the mixture viscosity η_m should be used in the expression of the Oseen tensor whereas for $k > 2\pi/\zeta$ the solvent viscosity η_s should be used. Since $\eta_m \gg \eta_s$, hydrodynamic interaction plays a minor role between blobs while it is important inside the blobs. For simplicity, a sudden jump from η_m to η_s is assumed for $k = 2\pi/\zeta$ (smoother variations could be used instead). The polymer mixture viscosity can be related to the solvent viscosity as $\eta_m = \eta_s R_g/\zeta$ where R_g is an average polymer radius of gyration.

Inside each blob, single-chain, and interchain contributions can be separated out:

$$\mathbf{m}_H(q) = [1/(2\pi)^3]\{\int d^3k\, T_{33}(\mathbf{k}-\mathbf{q})\{\mathbf{S}_o(k) - \delta\} - \int d^3k T_{33}(\mathbf{k}-\mathbf{q})\mathbf{S}_o(k)\mathbf{V}\mathbf{S}(k)\} \quad (7)$$

For dilute solutions (linear virial expansion) a known result[15]

$$\mathbf{m}_H(q) = [1/(2\pi)^3]\{\int d^3k T_{33}(\mathbf{k}-\mathbf{q})\{\mathbf{S}_o(k) - \delta\} - \int d^3k T_{33}(\mathbf{k}-\mathbf{q})\mathbf{S}_o(k)\mathbf{V}\mathbf{S}_o(k)\} \quad (8)$$

is recovered.

In concentrated polymer solutions, hydrodynamic interaction becomes small (because $\mathbf{m}_L(q)$ has a small contribution and $\mathbf{m}_H(q)$ becomes negligible). It should be noted that $\mathbf{m}_H(q) > \mathbf{m}_L(q)$ except at the melt limit or close to a critical point (where critical slowing down makes $\mathbf{m}_H(q)$ very small).

Ternary Polymer Mixtures

The general formalism can be applied to an incompressible ternary polymer mixture (two homopolymers or a block copolymer in solution). Dropping the momentum transfer q for notation convenience, the various intermediate scattering functions are given by[16]

$$S_{AA}(t) = [1/(1-\alpha_1\alpha_2)]\{(S_{AA} - \alpha_2 S_{BA})\exp(-\lambda_1 t) + (-\alpha_1\alpha_2 S_{AA} + \alpha_2 S_{BA})\exp(-\lambda_2 t)\}$$

$$S_{AB}(t) = [1/(1-\alpha_1\alpha_2)]\{(S_{AB} - \alpha_2 S_{BB})\exp(-\lambda_1 t) + (-\alpha_1\alpha_2 S_{AB} + \alpha_2 S_{BB})\exp(-\lambda_2 t)\}$$

$$S_{BA}(t) = [1/(1-\alpha_1\alpha_2)]\{(\alpha_1 S_{AA} - \alpha_1\alpha_2 S_{BA})\exp(-\lambda_1 t) + (-\alpha_1 S_{AA} + S_{BA})\exp(-\lambda_2 t)\}$$

$$S_{BB}(t) = [1/(1-\alpha_1\alpha_2)]\{(\alpha_1 S_{AB} - \alpha_1\alpha_2 S_{BB})\exp(-\lambda_1 t) + (-\alpha_1 S_{AB} + S_{BB})\exp(-\lambda_2 t)\} \quad (9)$$

where

$$\lambda_1 = \Lambda_{av} + [\Lambda_{av}^2 - \det(\Lambda)]^{1/2}$$

$$\lambda_2 = \Lambda_{av} - [\Lambda_{av}^2 - \det(\Lambda)]^{1/2}$$

$$\Lambda_{av} = (\Lambda_{AA} + \Lambda_{BB})/2, \quad \det(\Lambda) = \Lambda_{AA}\Lambda_{BB} - \Lambda_{AB}\Lambda_{BA} \quad (10)$$

and

$$\alpha_1 = (\lambda_1 - \Lambda_{AA})/\Lambda_{AB}, \quad \alpha_2 = \Lambda_{AB}/(\lambda_2 - \Lambda_{AA})$$

These equations have been reported previously[12,16] and have been applied to the interpretation of dynamic scattering measurements from ternary polymer mixtures (two polymers in solution) using a Rouse model (i.e., neglecting hydrodynamic interaction).[1-10] The elements of Λ

$$\Lambda_{AA} = q^2 k_B T[m_{AA}S_{BB} - m_{AB}S_{BA}]/(S_{AA}S_{BB} - S_{AB}S_{BA})$$

$$\Lambda_{AB} = q^2 k_B T[-m_{AA}S_{AB} + m_{AB}S_{AA}]/(S_{AA}S_{BB} - S_{AB}S_{BA})$$

$$\Lambda_{BA} = q^2 k_B T[m_{BA}S_{BB} - m_{BB}S_{BA}]/(S_{AA}S_{BB} - S_{AB}S_{BA})$$

$$\Lambda_{BB} = q^2 k_B T[-m_{BA}S_{AB} + m_{BB}S_{AA}]/(S_{AA}S_{BB} - S_{AB}S_{BA}) \quad (11)$$

are given in terms of the various mobilities and structure factors. Note that the matrix Λ is not symmetric (i.e., $\Lambda_{AB} \neq \Lambda_{BA}$).

The various mobilites are given by

$$m_{AA}(q) = m_{AA}{}^R + m_{AA}{}^H(q) + m_{AA}{}^L(q)$$

$$m_{AB}(q) = m_{AB}{}^H(q) + m_{AB}{}^L(q)$$

$$m_{BB}(q) = m_{BB}{}^R + m_{BB}{}^H(q) + m_{BB}{}^L(q) \quad (12)$$

and

$$m_{AA}{}^H(q) = [1/(2\pi)^3]\int d^3k T_{33}(\mathbf{k}-\mathbf{q})S_{AA}(k) \quad \text{for } k > 2\pi/\zeta, \text{ etc.}$$

$$m_{AA}{}^L(q) = [1/(2\pi)^3]\int d^3k T_{33}(\mathbf{k}-\mathbf{q})S_{AA}(k) \quad \text{for } k < 2\pi/\zeta, \text{ etc.} \quad (13)$$

The angular integrations (Ω_k) can be performed

$$[1/(2\pi)^3]\int d^3k T_{33}(\mathbf{k}-\mathbf{q})F(k) = \int dk\, (1/4\pi^2\eta)\, Z(k/q)F(k)$$

$$Z(x) = \{x(1+x^2)/2\}Ln\{|x+1|/|x-1|\} - x^2 \quad (14)$$

and the remaining integration (over the magnitude k) is performed numerically.

When A and B are homopolymers, the static RPA gives

$$S_{AA} = S_{AA}{}^o(1 + V_{BB}S_{BB}{}^o)/[(1 + V_{AA}S_{AA}{}^o)(1 + V_{BB}S_{BB}{}^o) - V_{AB}V_{BA}S_{AA}{}^o S_{BB}{}^o]$$

$$S_{AB} = -S_{AA}{}^o V_{AB} S_{BB}{}^o/[(1 + V_{AA}S_{AA}{}^o)(1 + V_{BB}S_{BB}{}^o) - V_{AB}V_{BA}S_{AA}{}^o S_{BB}{}^o]$$

$$S_{BB} = S_{BB}{}^o(1 + V_{AA}S_{AA}{}^o)/[(1 + V_{AA}S_{AA}{}^o)(1 + V_{BB}S_{BB}{}^o) - V_{AB}V_{BA}S_{AA}{}^o S_{BB}{}^o] \quad (15)$$

and $S_{AA}{}^o$ and $S_{BB}{}^o$ are given by the Debye function

$$S_{AA}{}^o(q) = N_A v_A \phi_A P_A(q)$$

$$P_A(q) = 2\{\exp(-q^2R_{gA}{}^2) - q^2R_{gA}{}^2 + 1\}/q^4R_{gA}{}^4, \text{ etc.}$$

which describes θ conditions fairly well. Here N_A, v_A, and ϕ_A are the degree of polymerization, molar volume, and volume fraction respectively. Under good solvent conditions, a swollen radius of gyration is often used. V_{AA}, V_{BB}, and V_{AB} are the polymer A–solvent, polymer B–solvent and polymer A–polymer B excluded volumes respectively. Defining the Flory–Huggins interaction parameter χ_{AB} between the two kinds of monomers, one can express V_{AB} as $V_{AB} = \chi_{AB} + (V_{AA} + V_{BB})/2$ where we have assumed unit monomer volumes ($v_A = v_B = 1$) for simplicity.

If the two polymer components form an A–B block copolymer instead, then

$$S_{AA}(q) = \{S_{AA}{}^{\circ}(1 + V_{BA}S_{AB}{}^{\circ} + V_{BB}S_{BB}{}^{\circ}) - S_{AB}{}^{\circ}(V_{BA}S_{AA}{}^{\circ} + V_{BB}S_{BA}{}^{\circ})\}/D$$

$$S_{BB}(q) = \{S_{BB}{}^{\circ}(1 + V_{AB}S_{BA}{}^{\circ} + V_{AA}S_{AA}{}^{\circ}) - S_{BA}{}^{\circ}(V_{AB}S_{BB}{}^{\circ} + V_{AA}S_{AB}{}^{\circ})\}/D$$

$$S_{AB}(q) = \{-S_{AA}{}^{\circ}(V_{AA}S_{AB}{}^{\circ} + V_{AB}S_{BB}{}^{\circ}) + S_{AB}{}^{\circ}(1 + V_{AA}S_{AA}{}^{\circ} + V_{AB}S_{BA}{}^{\circ})\}/D \quad (16)$$

where

$$D = (1 + V_{AA}S_{AA}{}^{\circ} + V_{AB}S_{BA}{}^{\circ})(1 + V_{BA}S_{AB}{}^{\circ} + V_{BB}S_{BB}{}^{\circ}) - (V_{AA}S_{AB}{}^{\circ} + V_{AB}S_{BB}{}^{\circ})(V_{BA}S_{AA}{}^{\circ} + V_{BB}S_{BA}{}^{\circ})$$

with

$$S_{AB}{}^{\circ}(q) = (N_A N_B v_A v_B \phi_A \phi_B)^{1/2} P_{AB}{}^{\circ}(q)$$

and $P_{AB}{}^{\circ}(q)$ is the structure factor which corresponds to the proper copolymer block sequence (diblock, triblock, alternating, etc). Beyond the spinodal line (obtained by setting $D = 0$), the present formalism does not apply.

All of the ingredients are available in order to estimate the two decay rates λ_1 and λ_2 and the amplitudes of the various dynamic structure factors $S_{AA}(q,t)$, $S_{AB}(q,t)$ etc. The scattered intensity (scattering cross section) is then obtained as

$$d\Sigma(q,t)/d\Omega = B_{AS}{}^2 S_{AA}(q,t) + B_{BS}{}^2 S_{BB}(q,t) + 2B_{AS}B_{BS}S_{AB}(q,t) \quad (17)$$

where $B_{AS}{}^2$ and $B_{BS}{}^2$ are the contrast factors between components A and solvent (S) and B and solvent respectively. In the case of light scattering, these are expressed in terms of refractive indices while for neutron scattering (neutron spin echo) they depend on the scattering length densities.

Specific Cases

Considering typical parameters for a ternary mixture of two homopolymers in solution, a number of figures have been generated based on the formalism described above. Figure 1 represents the effect of hydrodynamic interaction on the variation of the decay rates λ_1 and λ_2 with the wavenumber q.

If hydrodynamic interaction is neglected, the Benmouna et al. approximation[1] assumes the simple case of matched molecular weights ($N_A = N_B = N$), equal friction coefficients ($\xi_A = \xi_B = \xi$), segment lengths ($b_A = b_B = b$) and solvent quality ($V_{AA} = V_{BB} = V$) as well as compatible polymers in good solvent ($\chi_{AB}/V \ll 1$), which simplifies the expressions for the two decay rates as follows:

$$\lambda_1(q) = q^2\{k_BT/N\xi P(q)\}\{1 + V\phi NP(q)\}$$

$$\lambda_2(q) = q^2\{k_BT/N\xi P(q)\}\{1 - 2\phi_A\phi_B\chi_{AB}NP(q)/\phi\} \quad (18)$$

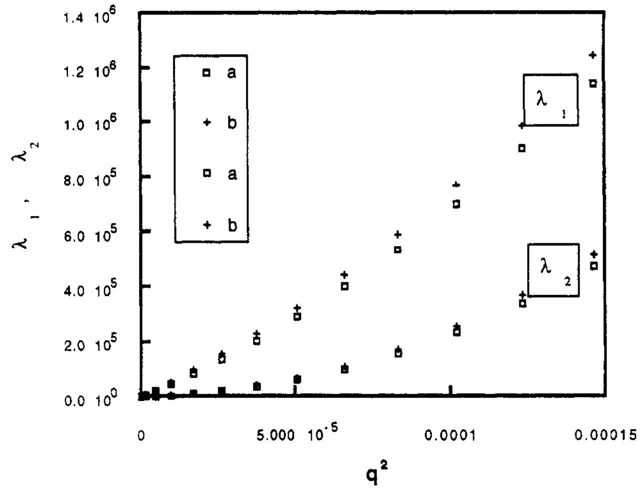

Figure 1. Variation of the decay rates $\lambda_1(q)$ and $\lambda_2(q)$ with q^2 for two homopolymers in solution when hydrodynamic interaction is increased. Parameters used: $N_A = N_B = 7000$, $b_A = b_B = 8$ A, $v_A = v_B = 1$, $\phi_A = 0.006$, $\phi_B = 0.007$, $\phi^* = 0.0013$, $V_{AA} = V_{BB} = 0.08$, $V_{AB} = 0.088$, $D_A = D_B = 4 \times 10^{12}$ A^2/s. Key: (curve a) $\eta_s/k_BT = 4 \times 10^{-10}$ s/A^3, $\eta_m/k_BT = 4 \times 10^{-8}$ s/A^3; (curve b) $\eta_s/k_BT = 4 \times 10^{-14}$ s/A^3, $\eta_m/k_BT = 4 \times 10^{-12}$ s/A^3. Curve a corresponds to negligible hydrodynamic interaction.

Here ϕ_A and ϕ_B are the volume fractions for components A and B respectively, ϕ is the total polymer volume fraction ($\phi = \phi_A + \phi_B$) and $P(q)$ represents the Debye function. λ_1 and λ_2 are referred to as the cooperative and interdiffusion modes respectively. This approximation works better for high concentrations since it neglects hydrodynamic interaction.

Figure 2a,b show the variation of λ_1/q^2 and λ_2/q^2 with the relative volume fraction ϕ_A/ϕ for increasing hydrodynamic interaction. Two cases corresponding to the Benmouna et al approximation (curve a) and to the exact result with no hydrodynamic interaction (curve b) have also been included. It can be seen that the Benmouna et al approximation is very good for λ_2/q^2 but misses the slight curvature of λ_1/q^2. The effect of hydrodynamic interaction is seen to increase both λ_1/q^2 and λ_2/q^2. Figure 3 summarizes the effect of increasing total polymer concentration ϕ (but still in the semidilute region) with fixed hydrodynamic interaction while Figure 4 shows that the effect of hydrodynamic interaction becomes more important at low ϕ as expected. What was not expected was the fact that the ratio of λ_2/λ_1 seems to remain constant for increasing hydrodynamic interaction. Note that the intermonomer interactions were weakened (χ_{AB} made smaller) in order to reach substantial polymer concentrations without hitting the spinodal condition.

Benmouna et al.[1] have also considered the case of a bimodal mixture of two identical homopolymers with different molecular weights in solution. If we set $\xi_A = \xi_B = \xi$, $b_A = b_B = b$, $V_{AA} = V_{BB} = V_{AB} = V$ (i.e., $\chi_{AB} = 0$) in the above general formalism for ternary mixtures, the following decay rates were derived[1]

$$\lambda_1 = \Lambda_{av} + [\Lambda_{av}{}^2 - \det(\Lambda)]^{1/2}$$

$$\lambda_2 = \Lambda_{av} - [\Lambda_{av}{}^2 - \det(\Lambda)]^{1/2}$$

with

$$\Lambda_{av} = (q^2k_BT/\xi)\{1/N_AP_{AA}{}^{\circ} + 1/N_BP_{BB}{}^{\circ} + V\phi\}/2$$

$$\Lambda_{av}{}^2 - \det(\Lambda) = (q^2k_BT/\xi)^2\{[1/N_BP_{BB}{}^{\circ} - 1/N_AP_{AA}{}^{\circ} + V\phi]^2/4 - \phi_AV(1/N_BP_{BB}{}^{\circ} - 1/N_AP_{AA}{}^{\circ})\} \quad (19)$$

Figure 5 shows the case of such a bimodal homopolymer mixture in solution. It is interesting to note that in the

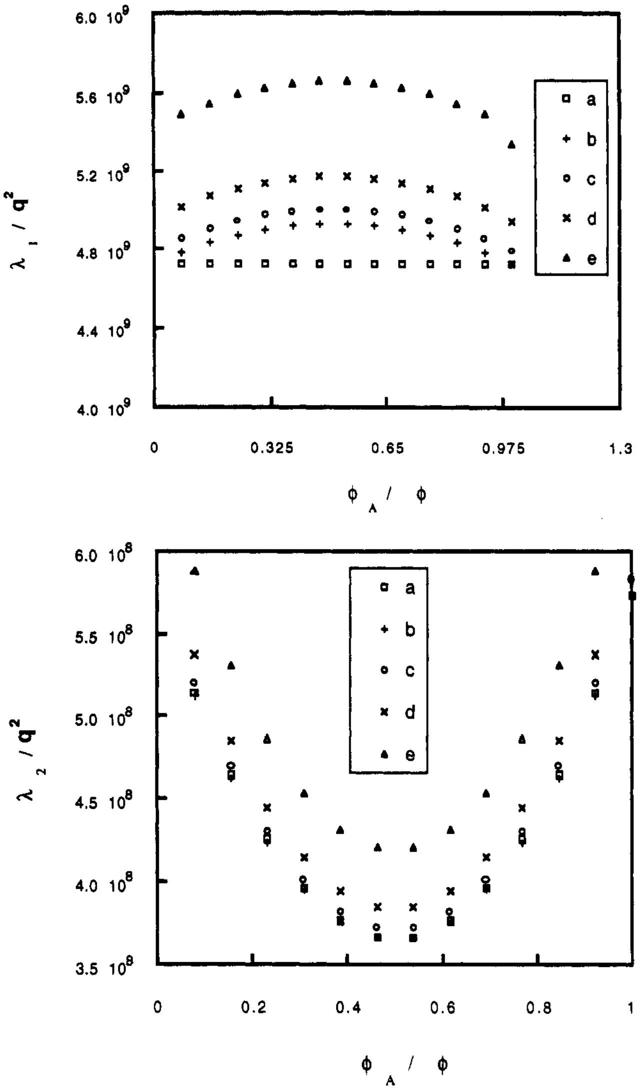

Figure 2. (a) Top: Variation of the diffusion constant $\lambda_1(q)/q^2$ with the relative volume fraction ϕ_A/ϕ for two homopolymers in solution when hydrodynamic interaction is increased. Parameters used: $N_A = N_B = 7000$, $b_A = b_B = 8$ A, $\upsilon_A = \upsilon_B = 1$, $\phi = 0.013$, $\phi^* = 0.0013$, $V_{AA} = V_{BB} = 0.08$, $V_{AB} = 0.088$, $D_A = D_B = 4{\times}10^{12}$ A^2/sec, q = 0.0004 A^{-1}. Key: (curve a) the Benmouna et al. approximation (no hydrodynamic interaction); (curve b) $\eta_s/k_BT = 4 \times 10^{-10}$ s/A^3, $\eta_m/k_BT = 4 \times 10^{-8}$ s/A^3; (curve c) $\eta_s/k_BT = 40 \times 10^{-13}$ s/A^3, $\eta_m/k_BT = 4 \times 10^{-11}$ s/A^3; (curve d) $\eta_s/k_BT = 1.2 \times 10^{-13}$ s/A^3, $\eta_m/k_BT = 1.2 \times 10^{-11}$ s/A^3; (curve e) $\eta_s/k_BT = 4 \times 10^{-14}$ s/A^3, $\eta_m/k_BT = 4 \times 10^{-12}$ s/A^3. (b) Bottom: Variation of the diffusion constant $\lambda_2(q)/q^2$ with the relative volume fraction ϕ_A/ϕ for two homopolymers in solution when hydrodynamic interaction is increased. Same parameters used.

Rouse limit (no hydrodynamic interaction), λ_2/q^2 first increases and then decreases while when hydrodynamic interaction is included, λ_2/q^2 decreases for low ϕ.

Discussion

Ternary incompressible polymer mixtures (two polymers in solution) can sustain two modes; one of which (the cooperative mode) is dominated by polymer–solvent interactions while the other one (the interdiffusion mode) is dominated by polymer–polymer interactions. Hydrodynamic interaction is important in dilute and semidilute solutions whereas it becomes screened in concentrated solutions and melts. The formalism used here still cannot account for entanglement (viscoelastic) effects which may contribute at high polymer concentrations and in melts.

The static RPA has been used in order to express the interacting static structure factors. Keeping in mind the usual drawbacks of the static RPA when applied to polymer solutions (due to the neglect of density fluctuations), the approach outlined here is an improvement over the Rouse dynamics model that has been used so far in order to interpret the experimentally observed trends of the slow/fast modes.

It is interesting to note two features that can be observed in Figures 2a and 4. Figure 2a shows a curvature to the variation of λ_1/q^2 with ϕ_A/ϕ which is not predicted by the Benmouna et al. model and which is enhanced by hydrodynamic interaction. Figure 4 also shows that the initial variation of λ_2/q^2 with ϕ has a curvature to it whereas this variation is linear in the original Benmouna et al. theory.

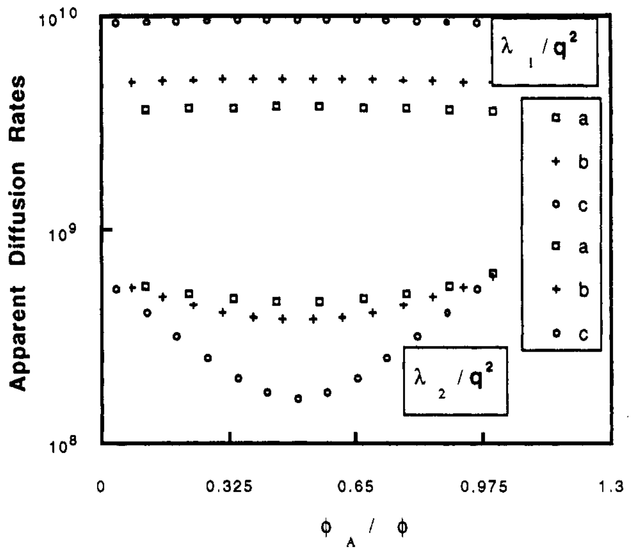

Figure 3. Variation of the diffusion constants $\lambda_1(q)/q^2$ and $\lambda_2(q)/q^2$ with the relative volume fraction ϕ_A/ϕ for two homopolymers in solution when the total polymer volume fraction is increased. Parameters used: $N_A = N_B = 7000$, $b_A = b_B = 8$ A, $\upsilon_A = \upsilon_B = 1$, $\phi^* = 0.0013$, $V_{AA} = V_{BB} = 0.08$, $V_{AB} = 0.088$, $D_A = D_B = 4 \times 10^{12}$ A^2/s, $\eta_s/k_BT = 1.2 \times 10^{-13}$ s/A^3, $\eta_m/k_BT = 1.2 \times 10^{-11}$ s/A^3, $q = 0.0004$ A^{-1}. Key: (curve a) $\phi = 0.009$; (curve b) $\phi = 0.013$; (curve c) $\phi = 0.026$.

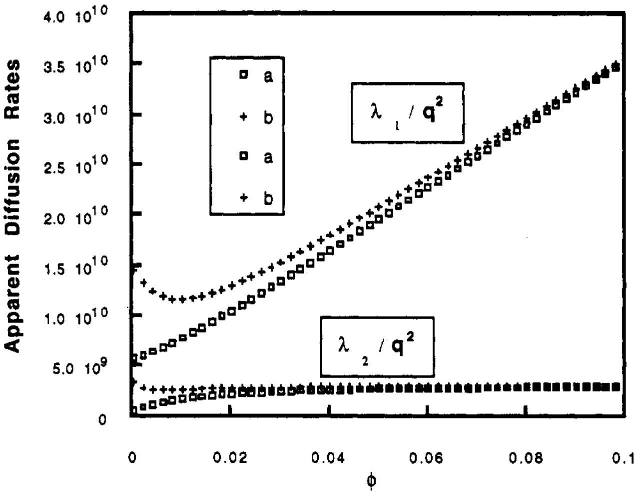

Figure 4. Variation of the diffusion constants $\lambda_1(q)/q^2$ and $\lambda_2(q)/q^2$ with the total polymer volume fraction ϕ for two homopolymers in solution when hydrodynamic interaction is increased. Parameters used: $N_A = N_B = 7000$, $b_A = b_B = 8$ A, $\upsilon_A = \upsilon_B = 1$, $\phi_A/\phi = \phi_B/\phi = 0.5$, $\phi^* = 0.013$, $V_{AA} = V_{BB} = 0.008$, $V_{AB} = 0.010$, $D_A = D_B = 4 \times 10^{12}$ A^2/s, $\eta_s/k_BT = 1.2 \times 10^{-13}$ s/A^3, $\eta_m/k_BT = 1.2 \times 10^{-11}$ s/A^3, $q = 0.0004$ A^{-1}. Key: (curve a) $\eta_s/k_BT = 4 \times 10^{-8}$ s/A^3, $\eta_m/k_BT = 4 \times 10^{-4}$ s/A^3; (curve b) $\eta_s/k_BT = 1 \times 10^{-13}$ s/A^3, $\eta_m/k_BT = 1 \times 10^{-9}$ s/A^3. Curve a corresponds to negligible hydrodynamic interaction.

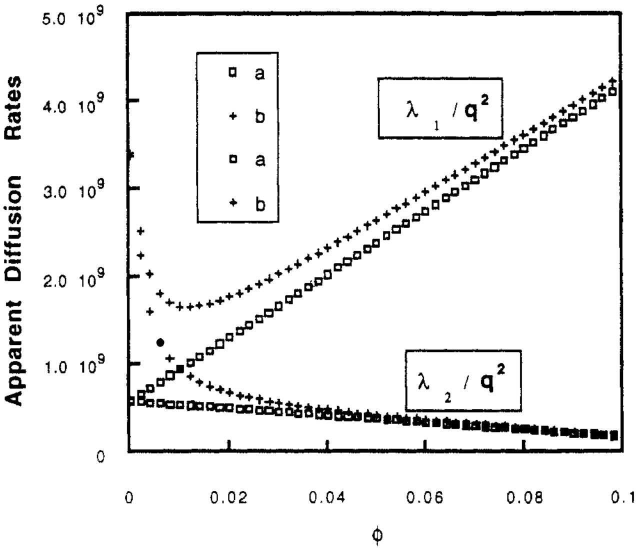

Figure 5. Variation of the diffusion constants $\lambda_1(q)/q^2$ and $\lambda_2(q)/q^2$ with the total polymer volume fraction ϕ for two homopolymers in solution when hydrodynamic interaction is increased. Parameters used: $N_A = 7000$, $N_B = 700$, $b_A = b_B = 8$ A, $v_A = v_B = 1$, $\phi_A/\phi = \phi_B/\phi = 0.5$, $\phi^* = 0.013$, $V_{AA} = V_{BB} = V_{AB} = 0.08$, $D_A = D_B = 4 \times 10^{12}$ A^2/s, $\eta_s/k_BT = 1.2 \times 10^{-13}$ s/A^3, $\eta_m/k_BT = 1.2 \times 10^{-11}$ s/A^3, $q = 0.0004$ A^{-1}. Key: (curve a) Benmouna et al. result (no hydrodynamic interaction); (b) $\eta_s/k_BT = 1 \times 10^{-13}$ s/A^3, $\eta_m/k_BT = 1 \times 10^{-9}$ s/A^3.

Benmouna et al.[17] have recently considered hydrodynamic interaction in a study of critical fluctuations in ternary polymer solutions using an approach similar to the one taken in this paper. Because they were interested in investigating scaling trends and avoiding numerical integrations, they used expansions of the various structure factors in the low or high q limits. Our paper focuses on generating specific results in the noncritical region.

References and Notes

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