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Rouse Dynamics of Block Copolymers

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ABSTRACT: We present rigorous analysis for the dynamic intrachain correlations of block copolymers within the Rouse model, which uncovers current misunderstandings of the dynamics of unentangled block copolymers in solutions and melts. Analytic predictions are made for the dynamic correlations at large and small distances, respectively, providing a critical test for the theory of Benmouna *et al.* which ignores memory effects and is based on a "dumbbell" model. At large distances, differences exist with regard to the k and composition dependence of the internal mode relaxation time. At small distances, on the other hand, we find non-Markovian stretched exponential decay, as opposed to their Markovian simple exponential decay, and for the correlation between two dynamically asymmetric blocks, a single mode with an intermediate decay constant, in contrast to the linear combination of the two intrablock correlation decay modes obtained by Benmouna *et al.* Furthermore, for structurally and dynamically symmetric but composition asymmetric diblock copolymers, they do not formally recover their predictions for homopolymers.

I. Introduction

During the last two decades, block copolymers have attracted considerable attention for the rich variety of phenomena associated with them. For instance, the dynamics of concentration fluctuations in block copolymer solutions involves multiple relaxation modes.[1] In dilute solutions, there is single chain relaxation with diffusive and internal modes. Increasing polymer concentrations give rise to additional cooperative matrix relaxation and polydispersity-induced long range composition fluctuations.

Single chain dynamics may be described by either the Rouse[2] or the Zimm[3] model. The former considers noninteracting Gaussian chains, appropriate for unentangled polymers in semidilute and concentrated solutions and melts, whereas the latter also includes hydrodynamic interactions, which are important in dilute polymer solutions. Theoretical predictions for the Rouse normal modes of block copolymers[4−7] have been confirmed by dielectric spectroscopy experiments.[8] Based on the Rouse model and a Markovian approximation (i.e., neglecting memory effects), the dynamic intrachain correlations, which are approximately reduced to block−block correlations in the spirit of a "dumbbell" model, are derived by Benmouna *et al.*[9] Two relaxation modes are obtained, which appear to represent diffusion and internal relaxation, respectively, at large distances and long times. These results are consistent with Zimm model calculations and Brownian dynamics simulations for structurally, dynamically, and composition symmetric diblock copolymers carried out by Rey and Freire,[10] and also with dynamic light scattering experiments.[1,11−13] However, strictly speaking, memory effects are negligible only at short times. The predictions of Benmouna *et al.* need to be tested at long times by rigorous analysis of the corresponding Rouse model. In fact, it is well-known that at small distances, the dynamic intrachain correlations of homopolymers obtained within the Markovian approximation[14] fail to exhibit the non-Markovian stretched exponential decay deduced from the Rouse model.[15] Oversimplification due to the use of the dumbbell-like model may also be a cause of concern. The collective relaxation modes have also been studied theoretically[16,17] and experimentally,[1,11−13] but only single chain dynamics is considered here.

This paper provides such a test, which should improve our understanding of the dynamics of unentangled block copolymers. We generalize the Rouse model studies of homopolymers in ref 15 to diblock copolymers, which enables rigorous calculations for the dynamic intrachain correlations. The normal mode analysis by Stockmayer and Kennedy[6] is reformulated in section II. On the basis solutions to the normal modes, section III evaluates the dynamic correlations and makes analytic predictions at large and small distances, which are our main results. These results are then compared with those of Benmouna *et al.*[9] in section IV, revealing a number of cases where their theory becomes inappropriate. The present analysis may be straightforwardly extended to the Zimm model of diblock copolymers in dilute solutions. It also provides a starting point for the renormalized Rouse model and the mode-coupling theory of diblock copolymer melts and solutions,[18] appropriate for entangled dynamics and unentanglement−entanglement crossover.

After submitting this paper, I received a preprint by Molina and Freire.[19] They also point out the inadequacy of Benmouna *et al.*'s predictions at small distances, based on Zimm model calculations and dynamic Monte Carlo simulations.

II. Normal Modes

This section reformulates the Stockmayer−Kennedy analysis for the Rouse model of block copolymers and summarizes the main results,[6] with more details given in Appendices A and B.

Consider an AB diblock copolymer with N segments, of which a fraction f consists of the A species. The chain is labeled such that the first fN segments make up the A block and the remaining $(1 - f)N$ monomers constitute the B block. The continuum limit Langevin equation

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for a Gaussian diblock copolymer may be written as[15]

$$\zeta_n \frac{\partial \mathbf{R}_n(t)}{\partial t} = K_n \frac{\partial^2 \mathbf{R}_n(t)}{\partial n^2} + \mathbf{f}_n(t) \qquad (2.1)$$

where the label n is treated as a continuous variable, the friction coefficient is

$$\zeta_n = \begin{cases} \zeta_{\mathrm{A}}, & \text{for } 0 \le n < Nf \\ \zeta_{\mathrm{B}}, & \text{for } Nf < n \le N \end{cases} \qquad (2.2)$$

$\mathbf{R}_n(t)$ is the position of the nth segment at time t, the elastic constant is

$$K_n = 3k_{\mathrm{B}}T/\sigma_n^{\,2} = \begin{cases} K_{\mathrm{A}} = 3k_{\mathrm{B}}T/\sigma_{\mathrm{A}}^{\,2}, & \text{for } 0 \le n < Nf \\ K_{\mathrm{B}} = 3k_{\mathrm{B}}T/\sigma_{\mathrm{B}}^{\,2}, & \text{for } Nf < n \le N \end{cases} \qquad (2.3)$$

with $\sigma_{\mathrm{A(B)}}$ the statistical segment length for A(B) and $\mathbf{f}_n(t)$ the random force exerted on the nth monomer at time t. The random force is assumed to follow

$$\langle \mathbf{f}_n(t)\mathbf{f}_m(t')\rangle = 2k_{\mathrm{B}}T\zeta_n\delta(n-m)\delta(t-t')\mathbf{I} \qquad (2.4)$$

where "$\langle\,\rangle$" denotes an equilibrium statistical average and $\mathbf{I}$ is the unit tensor of rank 2. The boundary conditions are

$$\frac{\partial \mathbf{R}_n}{\partial n} = 0, \qquad \text{at } n = 0, N \qquad (2.5)$$

$$\mathbf{R}_n \text{ and } K_n\frac{\partial \mathbf{R}_n}{\partial n} \text{ are continuous at } n = Nf \qquad (2.6)$$

where eq 2.5 is due to the vanishing of the elastic forces at the free ends and eq 2.6 arises from chain connectivity and force balance at the interblock junction.

The motions of different segments are correlated due to chain connectivity, as represented by the elastic force $K_n\partial^2\mathbf{R}_n/\partial n^2$ in eq 2.1. To understand the Rouse dynamics of diblock copolymers, we must obtain the *full* spectrum of mutually independent normal modes and the dynamic intrachain correlations, which are studied in this section and section III, respectively.

For a normal mode p, the normal coordinate $\mathbf{X}_p(t)$ is a linear combination of $\mathbf{R}_n(t)$,

$$\mathbf{X}_p(t) = \int_0^N \mathrm{d}n\, \phi_{pn}\mathbf{R}_n(t) \qquad (2.7)$$

where ϕ_{pn} is chosen so as to satisfy

$$\zeta_p \frac{\partial X_p(t)}{\partial t} = K_p\mathbf{X}_p(t) + \mathbf{f}_p(t) \qquad (2.8)$$

$$\langle \mathbf{f}_p(t)\mathbf{f}_{p'}(t')\rangle = 2k_{\mathrm{B}}T\zeta_p\delta_{pp'}\delta(t-t')\mathbf{I} \qquad (2.9)$$

with ζ_p, K_p, and $\mathbf{f}_p$ the effective friction coefficient, elastic constant, and random force for the normal modes, respectively.

The normal coordinates are obtained in Appendix A below as

$$\phi_{pn} = \begin{cases} S_{p\mathrm{A}}\cos(q_{p\mathrm{A}}n), & \text{for } 0 \le n < Nf \\ S_{p\mathrm{B}}\cos[q_{p\mathrm{B}}(N-n)], & \text{for } Nf < n \le N \end{cases} \qquad (2.10)$$

where

$$\frac{K_p}{\zeta_p} = \frac{K_{\mathrm{A}}}{\zeta_{\mathrm{A}}}q_{p\mathrm{A}}^{\;2} = \frac{K_{\mathrm{B}}}{\zeta_{\mathrm{B}}}q_{p\mathrm{B}}^{\;2} \qquad (2.11)$$

Hence,

$$q_{p\mathrm{B}} = \mu_{\mathrm{r}}q_{p\mathrm{A}} \qquad (2.12)$$

$$\mu_{\mathrm{r}} = \left(\frac{K_{\mathrm{A}}\zeta_{\mathrm{B}}}{K_{\mathrm{B}}\zeta_{\mathrm{A}}}\right)^{1/2} = \frac{\sigma_{\mathrm{B}}}{\sigma_{\mathrm{A}}}\left(\frac{\zeta_{\mathrm{B}}}{\zeta_{\mathrm{A}}}\right)^{1/2} \qquad (2.13)$$

Additional constraints on the normal modes are

$$\frac{S_{p\mathrm{A}}}{\zeta_{\mathrm{A}}}\cos(q_{p\mathrm{A}}Nf) = \frac{S_{p\mathrm{B}}}{\zeta_{\mathrm{B}}}\cos[q_{p\mathrm{B}}N(1-f)] \qquad (2.14)$$

$$\frac{K_{\mathrm{A}}}{\zeta_{\mathrm{A}}}S_{p\mathrm{A}}\sin(q_{p\mathrm{A}}Nf) = -\frac{K_{\mathrm{B}}}{\zeta_{\mathrm{B}}}S_{p\mathrm{B}}\mu_{\mathrm{r}}\sin[q_{p\mathrm{B}}N(1-f)] \qquad (2.15)$$

Equation 2.15 divided by eq 2.14 reduces to

$$\tan(q_{p\mathrm{A}}Nf) = -\mu\tan[q_{p\mathrm{A}}\mu_{\mathrm{r}}N(1-f)] \qquad (2.16)$$

$$\mu = \mu_{\mathrm{r}}K_{\mathrm{B}}/K_{\mathrm{A}} = \left(\frac{K_{\mathrm{B}}\zeta_{\mathrm{B}}}{K_{\mathrm{A}}\zeta_{\mathrm{A}}}\right)^{1/2} = \frac{\sigma_{\mathrm{A}}}{\sigma_{\mathrm{B}}}\left(\frac{\zeta_{\mathrm{B}}}{\zeta_{\mathrm{A}}}\right)^{1/2} \qquad (2.17)$$

where eq 2.12 has been utilized.

The results in eqs 2.10−2.17 are equivalent to those in ref 6. Solutions to eq 2.16, discussed in detail in Appendix A, correspond to the series $q_{p\mathrm{A}}$, $p = 0, 1, 2, ...$ These further yield $q_{p\mathrm{B}}$ from eq 2.12, K_p/ζ_p from eq 2.11, and $S_{p\mathrm{A}}/S_{p\mathrm{B}}$ from eq 2.14. Note that K_p, ζ_p, $S_{p\mathrm{A}}$, and $S_{p\mathrm{B}}$ are not uniquely defined, as one of them is adjustable. However, there is no ambiguity with regard to physical variables, such as the intrachain correlations.

An always existent solution to eq 2.16 is $q_{0\mathrm{A}} = q_{0\mathrm{B}} = 0$ for the diffusive mode $p = 0$. Setting $S_{0\mathrm{A}} = \zeta_{\mathrm{A}}/(N\bar{\zeta})$, with the average friction coefficient $\bar{\zeta}$ $f\zeta_{\mathrm{A}} + (1-f)\zeta_{\mathrm{B}}$, we obtain $S_{0\mathrm{B}} = \zeta_{\mathrm{B}}/(N\bar{\zeta})$ from eq 2.14, and

$$\phi_{0n} = \frac{\zeta_n}{N\bar{\zeta}} \qquad (2.18)$$

$$\mathbf{X}_0 = \int_0^N \mathrm{d}n\,\phi_{0n}\mathbf{R}_n = \frac{1}{N\bar{\zeta}}\int_0^N \mathrm{d}n\,\zeta_n\mathbf{R}_n \qquad (2.19)$$

$$\zeta_0 = \left(\int_0^N \mathrm{d}n\,\phi_{0n}^{\;2}/\zeta_n\right)^{-1} = N\bar{\zeta} \qquad (2.20)$$

from eqs 2.10, 2.7, and A8 in Appendix A below, respectively. The coordinate $\mathbf{X}_0$ is the position of the center of "mass", if ζ_n is regarded as an effective mass.

Other modes ($p \neq 0$), generally nontrivial, are analyzed in detail in Appendix B. Here we relate ζ_p to $S_{p\mathrm{A}}$ and $S_{p\mathrm{B}}$, using eqs A8 and 2.10,

$$\zeta_p^{\;-1} = \int_0^N \mathrm{d}n\,\phi_{pn}^{\;2}/\zeta_n = Nf\frac{S_{p\mathrm{A}}^{\;2}}{2\zeta_{\mathrm{A}}} + N(1-f)\frac{S_{p\mathrm{B}}^{\;2}}{2\zeta_{\mathrm{B}}} \qquad (2.21)$$

Standard exercise[15] leads to

$$\langle[\mathbf{X}_0(t) - \mathbf{X}_0(0)]^2\rangle = 6Dt \tag{2.22}$$

$$D = \frac{k_\mathrm{B}T}{\zeta_0} = \frac{k_\mathrm{B}T}{Nf\zeta_\mathrm{A} + N(1-f)\zeta_\mathrm{B}} \tag{2.23}$$

$$\langle\mathbf{X}_p(t)\cdot\mathbf{X}_{p'}(0)\rangle = \frac{3k_\mathrm{B}T}{K_p}\mathrm{e}^{-t/\tau_p}\delta_{pp'}, \qquad \text{for } p \neq 0 \tag{2.24}$$

where D is the center-of-mass diffusion constant and $\tau_p = \zeta_p/K_p$ is the relaxation time for mode $p \neq 0$.

III. Dynamic Intrachain Correlations

The dynamic intrachain correlations may be obtained on the basis of the normal modes. For Gaussian chains, the block–block correlations are[15]

$$\hat{\omega}_{\alpha\beta}(k,t) \equiv \frac{1}{N}\int_{\alpha\mathrm{block}} \mathrm{d}m \int_{\beta\mathrm{block}} \mathrm{d}n \times \langle\exp\{i\mathbf{k}\cdot[\mathbf{R}_m(t) - \mathbf{R}_n(0)]\}\rangle$$
$$= \frac{1}{N}\int_{\alpha\mathrm{block}} \mathrm{d}m \int_{\beta\mathrm{block}} \mathrm{d}n \exp\left[-\frac{k^2}{6}\psi_{mn}(t)\right], \quad \text{for } \alpha, \beta = \mathrm{AorB} \tag{3.1}$$

$$\psi_{mn}(t) = \langle[\mathbf{R}_m(t) - \mathbf{R}_n(0)]^2\rangle \tag{3.2}$$

Light scattering experiments measure $\sum_{\alpha\beta}f_\alpha f_\beta\hat{\omega}_{\alpha\beta}(k, t)$ where f_α is the scattering factor for α monomers.

Inserting eqs A9 and 2.18–2.24 into eq 3.2 produces

$$\psi_{mn}(t) = \sum_p \zeta_p^{\,2}\left\langle\left[\frac{\phi_{pm}}{\zeta_m}\mathbf{X}_p(t) - \frac{\phi_{pn}}{\zeta_n}\mathbf{X}_p(0)\right]^2\right\rangle$$
$$= 6Dt + 3k_\mathrm{B}T\sum_{p\neq0}\zeta_p\tau_p\left(\frac{\phi_{pm}}{\zeta_m} - \frac{\phi_{pn}}{\zeta_n}\right)^2 + \frac{6k_\mathrm{B}T}{\zeta_m\zeta_n}\sum_{p\neq0}\zeta_p\tau_p\phi_{pm}\phi_{pn}(1 - \mathrm{e}^{-t/\tau_p}) \tag{3.3}$$

where $\langle|\mathbf{X}_p(t)|^2\rangle = \langle|\mathbf{X}_p(0)|^2\rangle = 3k_\mathrm{B}T/K_p$ for $p \neq 0$, obtainable from eq 2.24, has been used. Comparing the known results $\psi_{mn}(0) = |\int_m^n \mathrm{d}s\ \sigma_s^{\,2}|$ with eq 3.3 yields

$$3k_\mathrm{B}T\sum_{p\neq0}\zeta_p\tau_p\left(\frac{\phi_{pm}}{\zeta_m} - \frac{\phi_{pn}}{\zeta_n}\right)^2 = \left|\int_m^n \mathrm{d}s\ \sigma_s^{\,2}\right| \tag{3.4}$$

$$\psi_{mn}\left(t\right) = 6Dt + \left|\int_m^n \mathrm{d}s\ \sigma_s^{\,2}\right| + \frac{6k_\mathrm{B}T}{\zeta_m\zeta_n}\sum_{p\neq0}\zeta_p\tau_p\phi_{pm}\phi_{pn}\left(1 - \mathrm{e}^{-t/\tau_p}\right) \tag{3.5}$$

Substituting eqs 2.10 and 3.5 into eq 3.1 gives the dynamic intrachain correlations. At long time, exponential expansions[10,19,20] may be used to deduce

$$\hat{\omega}_{\alpha\beta}(k,t) = \frac{1}{N}\int_{\alpha\mathrm{block}} \mathrm{d}m \int_{\beta\mathrm{block}} \mathrm{d}n \times \exp\left(-Dk^2t - \frac{k^2}{6}\left|\int_m^n \mathrm{d}s\ \sigma_s^{\,2}\right| - \frac{k_\mathrm{B}Tk^2}{\zeta_m\zeta_n}\sum_{p\neq0}\zeta_p\tau_p\phi_{pm}\phi_{pn}\right) \times \sum_{j=0}^{\infty}\frac{1}{j!}\left(\frac{k_\mathrm{B}Tk^2}{\zeta_\alpha\zeta_\beta}\sum_{p\neq0}\zeta_p\tau_p\phi_{pm}\phi_{pn}\mathrm{e}^{-t/\tau_p}\right)^j \tag{3.6}$$

For $k \ll N^{-1/2}\sigma^{-1}$, eq 3.6 further reduces to

$$\hat{\omega}_{\alpha\beta}(k,t) \approx [\hat{\omega}_{\alpha\beta}(0) + O(k^2)]\mathrm{e}^{-Dk^2t} + \frac{1}{N}\sum_{p\neq0}\left[\frac{k_\mathrm{B}Tk^2}{\zeta_\alpha\zeta_\beta}\zeta_p\tau_p + O(k^4)\right]\mathrm{e}^{-(Dk^2+1/\tau_p)t}\int_{\alpha\mathrm{block}} \mathrm{d}m\ \phi_{pm}\int_{\beta\mathrm{block}} \mathrm{d}n\ \phi_{pn}$$
$$= [\hat{\omega}_{\alpha\beta}(0) + O(k^2)]\mathrm{e}^{-Dk^2t} + \frac{\epsilon_{\alpha\beta}}{N}\sum_{p\neq0}\frac{k_\mathrm{B}Tk^2}{\zeta_\alpha\zeta_\beta}\zeta_p\tau_p\frac{S_{p\mathrm{A}}^{\,2}}{q_{p\mathrm{A}}^{\,2}}\sin^2(q_{p\mathrm{A}}fN)\mathrm{e}^{-(Dk^2+1/\tau_p)t}$$
$$\approx [\hat{\omega}_{\alpha\beta}(0) + O(k^2)]\mathrm{e}^{-Dk^2t} + \frac{\epsilon_{\alpha\beta}}{N}\frac{k_\mathrm{B}Tk^2}{\zeta_\alpha\zeta_\beta}\zeta_{p=1}\tau_1\frac{S_{1\mathrm{A}}^{\,2}}{q_{1\mathrm{A}}^{\,2}}\sin^2(q_{1\mathrm{A}}fN)\mathrm{e}^{-(Dk^2+1/\tau_1)t} \tag{3.7}$$

where eqs 2.10–2.15 are used in evaluating the integrals, $\epsilon_\mathrm{AA} = \epsilon_\mathrm{BB} = 1$, $\epsilon_\mathrm{AB} = -1$, the static block–block correlations are

$$\hat{\omega}_{\alpha\beta}(k) = \frac{1}{N}\int_{\alpha\mathrm{block}} \mathrm{d}m \int_{\beta\mathrm{block}} \mathrm{d}n \exp\left[-\frac{k^2}{6}\left|\int_m^n \mathrm{d}s\ \sigma_s^{\,2}\right|\right] \tag{3.8}$$

or

$$\hat{\omega}_\mathrm{AA}(k) = \frac{2f^2N}{x_\mathrm{A}^{\,2}}(x_\mathrm{A} - 1 + \mathrm{e}^{-x_\mathrm{A}}) \tag{3.9}$$

$$\hat{\omega}_\mathrm{BB}(k) = \frac{2(1-f)^2N}{x_\mathrm{B}^{\,2}}(x_\mathrm{B} - 1 + \mathrm{e}^{-x_\mathrm{B}}) \tag{3.10}$$

$$\hat{\omega}_\mathrm{AB}(k) = f(1-f)N\frac{1 - \mathrm{e}^{x_\mathrm{A}}}{x_\mathrm{A}}\frac{1 - \mathrm{e}^{-x_\mathrm{B}}}{x_\mathrm{B}} \tag{3.11}$$

with $x_\mathrm{A} = k^2fN\sigma_\mathrm{A}^{\,2}/6$ and $x_\mathrm{B} = k^2(1-f)N\sigma_\mathrm{B}^{\,2}/6$, and for sufficiently long time $t \gg \tau_1$, the sum over $p \neq 0$ is dominated by the first mode $p = 1$. While the first term in eq 3.7 is the diffusion mode, the second term, with a much smaller amplitude, resembles the "breathing" mode predicted by Benmouna *et al.*[9] However, our results have important differences from theirs, as discussed in section IV below.

Analytic expressions are available for the internal modes only in limiting cases. Structurally and dynamically symmetric diblock copolymers, where $\sigma_\mathrm{A} = \sigma_\mathrm{B} = \sigma$ and $\zeta_\mathrm{A} = \zeta_\mathrm{B} = \zeta$, are equivalent to homopolymers in the Rouse model and, therefore, have the same normal modes,[15] i.e., $D = k_BT/(N\zeta)$, $q_{1A} = \pi/N$, $\zeta_{p=1}S_{1A}{}^2 = 2\zeta/N$, and $\tau_1 = \zeta N^2\sigma^2/(3\pi^2 k_BT)$. Hence, eq 3.7 reduces to

$$\hat{\omega}_{\alpha\beta}(k,t) \approx [\hat{\omega}_{\alpha\beta}(0) + O(k^2)]\exp\left(-\frac{k_BTk^2t}{N\zeta}\right) + \epsilon_{\alpha\beta}\frac{2N^2k^2\sigma^2}{3\pi^4}\sin^2(\pi f)\exp\left[-\left(1 + \frac{Nk^2\sigma^2}{3\pi^2}\right)\frac{3\pi^2k_BTt}{N^2\sigma^2\zeta}\right] \tag{3.12}$$

On the other hand, for strongly dynamically asymmetric diblock copolymers, e.g., $\zeta_A \ll \zeta_B$, and f not approaching 0 or 1, the long time dynamics is mainly controlled by the B block, i.e., $D \approx k_BT/[(1 - f)N\zeta_B]$, $q_{1A} \approx \pi/[(1 - f)N\mu_r]$, $\zeta_{p=1}S_{1A}{}^2 \approx 2\zeta_A{}^2/[(1 - f)N\zeta_B]$, and $\tau_1 \approx \zeta_B(1 - f)^2N^2\sigma_B{}^2/(3\pi^2k_BT)$. Thus, eq 3.7 becomes

$$\hat{\omega}_{\alpha\beta}(k,t) \approx [\hat{\omega}_{\alpha\beta}(0) + O(k^2)]\exp\left[-\frac{k_BTk^2t}{(1-f)N\zeta_B}\right] + \epsilon_{\alpha\beta}\frac{2f^2(1-f)N^2k^2\sigma_B{}^2\zeta_A{}^2}{3\pi^2\zeta_\alpha\zeta_\beta} \times \exp\left\{-\left[1 + \frac{(1-f)Nk^2\sigma_B{}^2}{3\pi^2}\right]\frac{3\pi^2k_BTt}{(1-f)^2N^2\sigma_B\zeta_B}\right\} \tag{3.13}$$

For $N^{-1/2}\sigma^{-1} \ll k \ll \sigma^{-1}$, on the other hand, the dynamics is dominated by local modes with large p, when eq 3.1 simplifies to

$$\hat{\omega}_{AA}(k,t) \approx \frac{1}{N}\int_0^{fN}\mathrm{d}m\int_0^{fN}\mathrm{d}n\,\exp\left\{-\frac{k^2\sigma_A{}^2}{6}\left|n - m\right| - \frac{k^2}{2}\frac{k_BT}{\zeta_A{}^2}\sum_{p\neq 0}\zeta_p\tau_pS_{pA}{}^2[\cos(q_{pA}(m+n)) + \cos(q_{pA}(m-n))](1 - \mathrm{e}^{-t/\tau_p})\right\} \tag{3.14}$$

Within the Rouse relaxation time τ_1, the integral in eq 3.14 is dominated by large q_{pA} modes with $p \gg 1$, for which the rapidly oscillating term $\cos[q_{pA}(m + n)]$ has little contribution, and $\cos[q_{pA}(m - n)]$ is strongly peaked at $m = n$. For $\tau_e \ll t \ll \tau_1$, where $\tau_e \sim \zeta\sigma^2/(3\pi^2k_BT)$ is a microscopic time scale, we may drop $\cos[q_{pA}(m + n)]$ and replace $\cos[q_{pA}(m - n)]$ by 1,[15] which reduces eq 3.14 to

$$\hat{\omega}_{AA}(k,t) \approx \hat{\omega}_{AA}(k)\exp\left[-\frac{k^2}{2}\frac{k_BT}{\zeta_A{}^2}\sum_{p\neq 1}\zeta_p\tau_pS_{pA}{}^2(1 - \mathrm{e}^{-t/\tau_p})\right] \quad \text{for } \tau_e \ll t \ll \tau_1 \tag{3.15}$$

A similar expression holds for $\hat{\omega}_{BB}(k, t)$.

The interblock correlation $\hat{\omega}_{AB}(k, t)$ in the large k limit arises mainly from segments near the junction between the A and B blocks. Thus, we replace ϕ_{pm} and ϕ_{pn} by $\phi_{p,fN}$ in eq 3.5, which yields

$$\hat{\omega}_{AB}(k,t) \approx \hat{\omega}_{AB}(k) \times \exp\left[-k^2\frac{k_BT}{\zeta_A{}^2}\sum_{p\neq 1}\zeta_p\tau_pS_{pA}{}^2(1 - \mathrm{e}^{-t/\tau_p})\cos^2(q_{pA}fN)\right], \quad \text{for } \tau_e \ll t \ll \tau_1 \tag{3.16}$$

As shown in Appendix B, the intrablock correlations have the same time dependence as the intrachain correlations of the corresponding homopolymers,[21-23] whereas the interblock correlation has an intermediate relaxation time, i.e.,

$$\hat{\omega}_{\alpha\beta}(k,t) \approx \hat{\omega}_{\alpha\beta}(k)\exp\left[-2k^2\left(\frac{k_BTt}{3\pi}\right)^{1/2}\left(\frac{\zeta_\alpha{}^{1/2}}{\sigma_\alpha} + \frac{\zeta_\beta{}^{1/2}}{\sigma_\beta}\right)^{-1}\right] \tag{3.17}$$

for t much greater than this relaxation time implied by the equation. Note that parameters such as N and f do not appear in the time dependence in eq 3.17.

Hence, except when $\zeta_A/\zeta_B = (\sigma_A/\sigma_B)^2$, the three correlation functions generally have different decay constants at large k. An interesting consequence is that the Fourier or Laplace spectrum of the dynamic scattering function may contain *three* peaks, rather than two predicted by Benmouna *et al.*[9] (also see section IV below), although the interblock peak is expected to be much weaker than the intrablock peaks. In dynamically strongly asymmetric cases, e.g., $\zeta_A \ll \zeta_B$, the A block relaxes much faster than the B block, while the interblock correlation relaxes 4 times as fast as the B block.

The dynamic correlations for structurally and dynamically symmetric diblock copolymers may be approximated as

$$\hat{\omega}_{\alpha\beta}(k,t) \approx \hat{\omega}_{\alpha\beta}(k)\exp\left[-\frac{k^2k_BTt}{\zeta\hat{\omega}_{\mathrm{tot}}(k)}\right] \tag{3.18}$$

$$\hat{\omega}_{\mathrm{tot}}(k) = \sum_{\alpha\beta}\hat{\omega}_{\alpha\beta}(k) = \frac{2N}{x^2}(x - 1 + \mathrm{e}^{-x}) \approx \frac{N}{1 + x/2} \tag{3.19}$$

where $\hat{\omega}_{\mathrm{tot}}(k)$ is the total static intrachain correlations, $x = k^2N\sigma^2/6$, and the internal mode is ignored because its amplitude is much smaller than that of the diffusive mode. Equation 3.18 gives the correct relaxation time in both large and small k limits and is adequate when used in a time integral, such as the evaluation of the diffusion constant from the polymer mode-coupling theory.[18,24,25] Note that these symmetric diblock copolymers are equivalent to homopolymers within the Rouse model. Indeed, the total intrachain correlation in eq 3.18 recovers the proper analytic form for that of the homopolymer,

$$\hat{\omega}_{\mathrm{tot}}(k,t) \equiv \sum_{\alpha\beta}\hat{\omega}_{\alpha\beta}(k,t) = \hat{\omega}_{\mathrm{tot}}(k)\exp\left[-\frac{k^2k_BTt}{\zeta\hat{\omega}_{\mathrm{tot}}(k)}\right] \tag{3.20}$$

which is derived by Akcasu and Gurol within the Markovian approximation.[14] For asymmetric diblock copolymers, the interpolation form is

$$\hat{\omega}_{\alpha\beta}(k,t) \approx \hat{\omega}_{\alpha\beta}(k) \times \exp\left\{-k^2k_BTt\left[\frac{1}{N\bar{\zeta}} + \frac{k^2}{3}\left(\frac{\zeta_\alpha{}^{1/2}}{\sigma_\alpha} + \frac{\zeta_\beta{}^{1/2}}{\sigma_\beta}\right)^{-2}\right]\right\} \tag{3.21}$$

IV. Comparison with the Theory by Benmouna *et al.*

We now compare our rigorous results with those obtained within the Markovian approximation by Benmouna *et al.*[9] Their dynamic correlations are

$$\hat{\omega}_{\alpha\beta}(k,t) = a_{\alpha\beta} \exp\left[-\frac{k_B T k^2 \Gamma_a t}{\hat{\omega}(k)}\right] + b_{\alpha\beta} \exp\left[-\frac{k_B T k^2 \Gamma_b t}{\hat{\omega}(k)}\right] \quad (4.1)$$

where

$$\boldsymbol{\Omega} = \begin{pmatrix} f\hat{\omega}_{BB}(k)/\zeta_A & -f\hat{\omega}_{AB}(k)/\zeta_A \\ -(1-f)\hat{\omega}_{AB}(k)/\zeta_B & (1-f)\hat{\omega}_{AA}(k)/\zeta_B \end{pmatrix} \quad (4.2)$$

$$2\Gamma_{a,b} = \mathrm{Tr}\,\boldsymbol{\Omega} \pm [(\mathrm{Tr}\,\boldsymbol{\Omega})^2 - 4 \det \boldsymbol{\Omega}]^{1/2} \quad (4.3)$$

$$\hat{\omega}(k) = \hat{\omega}_{AA}(k)\hat{\omega}_{BB}(k) - \hat{\omega}_{AB}{}^2(k) \quad (4.4)$$

$$a_{AA} = [(\Gamma_a - \Omega_{22})\hat{\omega}_{AA}(k) + \Omega_{12}\hat{\omega}_{AB}(k)]/(\Gamma_a - \Gamma_b) \quad (4.5)$$

$$a_{BB} = [(\Gamma_a - \Omega_{11})\hat{\omega}_{BB}(k) + \Omega_{21}\hat{\omega}_{AB}(k)]/(\Gamma_a - \Gamma_b) \quad (4.6)$$

$$a_{AB} = [(\Gamma_a - \Omega_{22})\hat{\omega}_{AB}(k) + \Omega_{12}\hat{\omega}_{BB}(k)]/(\Gamma_a - \Gamma_b) \quad (4.7)$$

with Tr $\boldsymbol{\Omega}$ and det $\boldsymbol{\Omega}$ denoting the trace and determinant of the matrix $\boldsymbol{\Omega}$, respectively, and $b_{\alpha\beta}$ may be obtained by exchanging Γ_a with Γ_b in eqs 4.5–4.7.

We first point out the self-*inconsistency* that occurs for structurally and dynamically symmetric diblock copolymers, which are identical to homopolymers in the Rouse model. Here the total intrachain correlation calculated from eqs 4.1–4.7 depends unphysically on f and is unequal to that of homopolymers in eq 3.20 derived within the same approach if $f \neq 1/2$. In the small k limit, however, eqs 4.1–4.7 approximately simplify to

$$\hat{\omega}_{\alpha\beta}(k,t) \approx [\hat{\omega}_{\alpha\beta}(0) + O(k^2)] \times \exp\left(-\frac{k_B T k^2 t}{N\zeta}\right) + \frac{\epsilon_{\alpha\beta}}{9} f^2(1-f)^2 N^2 k^2 \sigma^2 \times \exp\left\{-\left[1 + \frac{5 - 2f(1-f)}{72} N k^2 \sigma^2\right] \frac{9 k_B T t}{f(1-f)N^2\sigma^2\zeta}\right\} \quad (4.8)$$

which is consistent with eq 3.20. Equation 4.8 also qualitatively agrees with eq 3.12. However, the internal mode decay constant is independent of f in eq 3.12, just the opposite of eq 4.8, where it approaches infinity as f goes to 0 or 1, the homopolymer limit. Furthermore, the k dependence of the internal mode decay constant in eq 3.12 is only about half as strong as that in eq 4.8.

For structurally symmetric but dynamically strong asymmetric diblock copolymers, where $\sigma_A = \sigma_B = \sigma$ but, e.g., $\zeta_A \ll \zeta_B$, eqs 4.1–4.7 lead, in the small k limit, to

$$\hat{\omega}_{\alpha\beta}(k,t) \approx [\hat{\omega}_{\alpha\beta}(0) + O(k^2)] \times \exp\left[-\frac{k_B T k^2 t}{(1-f)N\zeta_B}\right] + \frac{\epsilon_{\alpha\beta}}{9} f^2 N^2 k^2 \sigma^2 \frac{\zeta_A{}^2}{\zeta_\alpha \zeta_\beta} \times \exp\left\{-\left[1 + \frac{9 - 4(1-f)}{72} N k^2 \sigma^2\right] \frac{9 k_B T t}{f N^2 \sigma^2 \zeta_A}\right\} \quad (4.9)$$

where f is assumed not to approach 0 or 1. Aside from the same diffusion terms in eqs 3.13 and 4.9, the internal mode relaxation time here ($\propto \zeta_A$) is much shorter and has a much stronger k dependence (about 6 times at $f = 1/2$) than that ($\propto \zeta_B$) in eq 3.13. The two time scales also exhibit dramatically different variations with f.

In the large k limit, eqs 4.1–4.7 become

$$\hat{\omega}_{\alpha\alpha}(k,t) \approx \hat{\omega}_{\alpha\alpha}(k) \exp\left(-k^4 \sigma_\alpha{}^2 \frac{k_B T t}{12\zeta_\alpha}\right) \quad (4.10)$$

$$\hat{\omega}_{AB}(k,t) \approx \begin{cases} \hat{\omega}_{AB}(k) \exp\left(-k^4 \sigma_A{}^2 \dfrac{k_B T t}{12\zeta_A}\right), & \text{if } \zeta_A \sigma_A{}^{-2} = \zeta_B \sigma_B{}^{-2} \\ \dfrac{\hat{\omega}_{AB}(k)}{\zeta_A \sigma_A{}^{-2} - \zeta_B \sigma_B{}^{-2}} \left[\zeta_A \sigma_A{}^{-2} \exp\left(-k^4 \sigma_A{}^2 \dfrac{k_B T t}{12\zeta_A}\right) - \zeta_B \sigma_B{}^{-2} \exp\left(-k^4 \sigma_B{}^2 \dfrac{k_B T t}{12\zeta_B}\right)\right], & \text{if } \zeta_A \sigma_A{}^{-2} \neq \zeta_B \sigma_B{}^{-2} \end{cases} \quad (4.11)$$

In contrast to the non-Markovian stretched exponential decay in eq 3.17, a simple exponential decay arises in eqs 4.10 and 4.11 due to the Markovian approximation. The two theories have comparable relaxation times for intrablock correlations but differ drastically on the interblock correlation when $\zeta_A \sigma_A{}^{-2} \neq \zeta_B \sigma_B{}^{-2}$: a single mode with an intermediate decay constant in eq 3.17 vs two modes with the two intrablock decay constants in eq 4.11.

Apart from the absence of the stretched exponential decay due to the Markovian approximation, the inadequacy of the predictions by Benmouna *et al.* stems from their use of the dumbbell-like model, which oversimplifies the dynamic intrachain correlations of diblock copolymers to a 2 × 2 matrix of block–block correlations and ignores intrablock motions. Hence, their intrachain dynamics is artificially restricted to interblock relaxation, whereas rigorous solutions to the Rouse model in refs 4–7 and Appendix A below give a full spectrum of normal modes that generally do not correspond to just interblock relaxation, especially with significant mismatch for the sizes and friction coefficients of the two blocks.

In summary, a number of differences are found between our rigorous analysis for the dynamic correlations of diblock copolymers within the Rouse model and the approximate counterpart by Benmouna *et al.*[9] At small k, while both retain the same diffusion mode, the internal mode relaxation constant of the former has a much weaker k dependence and very different composition dependence than that of the latter. The disagreement is enhanced by the dynamic asymmetry of the two blocks. For large k, we find non-Markovian stretched exponential decay as opposed to their Markovian simple exponential decay, and a single mode with an intermediate decay constant for the correlation between two dynamically asymmetric blocks, in contrast to theirs as a linear combination of the two intrablock correlation decay modes. Furthermore, their results for structurally and dynamically symmetric but compositionally asymmetric diblock copolymers do not formally agree with those for homopolymer[14] obtained from the same approach. Our predictions, and hence, the Rouse model, may be tested by dynamic light scattering experiments and computer simulations on unentangled block copolymer solutions and melts. Although the continuous Gaussian chain model employed in the theories may not be quantitatively adequate, especially in the large k regime, for the short chains with $N < 100$ in the simulations,[10] this is not expected to affect our results qualitatively. The discrepancy between the two theories is expected to persist when hydrodynamic and excluded volume interactions are also considered (the Zimm model[3]), as the approximations adopted by Benmouna *et al.* remain problematic.

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Appendix A: Derivation of the Normal Modes

To determine the normal modes, we obtain by using eqs 2.1−2.7

$$\begin{aligned}\frac{\partial \mathbf{X}_p}{\partial t} &= \int_0^N \mathrm{d}n\, \phi_{pn}\frac{\partial \mathbf{R}_n}{\partial t} = \int_0^N \mathrm{d}n\, \phi_{pn}\left(\frac{K_n}{\zeta_n}\frac{\partial^2 \mathbf{R}_n}{\partial n^2} + \frac{\mathbf{f}_n}{\zeta_n}\right)\\ &= \frac{K_\mathrm{A}}{\zeta_\mathrm{A}}\left(\phi_{pn}\frac{\partial \mathbf{R}}{\partial n}\right)_{n=0}^{n\to Nf-0} + \frac{K_\mathrm{B}}{\zeta_\mathrm{B}}\left(\phi_{pn}\frac{\partial \mathbf{R}}{\partial n}\right)_{n\to Nf+0}^{n=N} - \frac{K_\mathrm{A}}{\zeta_\mathrm{A}}\left(\frac{\partial \phi_{pn}}{\partial n}\mathbf{R}\right)_{n=0}^{n\to Nf-0} - \frac{K_\mathrm{B}}{\zeta_\mathrm{B}}\left(\frac{\partial \phi_{pn}}{\partial n}\mathbf{R}\right)_{n\to Nf+0}^{n=N} +\\ &\qquad \int_0^N \frac{\mathrm{d}n}{\zeta_n}\left(K_n\frac{\partial^2 \phi_{pn}}{\partial n^2}\mathbf{R}_n + \phi_{pn}\mathbf{f}_n\right)\\ &= [\phi_{pn}(n\to Nf-0)/\zeta_\mathrm{A} - \phi_{pn}(n\to Nf+0)/\zeta_\mathrm{B}]\times \left(K\frac{\partial \mathbf{R}_n}{\partial n}\right)_{n=Nf} - \left(\frac{K_\mathrm{A}}{\zeta_\mathrm{A}}\frac{\partial \phi_{pn}}{\partial n}\bigg|_{n\to Nf-0} - \frac{K_\mathrm{B}}{\zeta_\mathrm{B}}\frac{\partial \phi_{pn}}{\partial n}\bigg|_{n\to Nf+0}\right)\mathbf{R}_{Nf} +\\ &\qquad \frac{K_\mathrm{A}}{\zeta_\mathrm{A}}\frac{\partial \phi_{pn}}{\partial n}\bigg|_{n=0}\mathbf{R}_0 - \frac{K_\mathrm{B}}{\zeta_\mathrm{B}}\frac{\partial \phi_{pn}}{\partial n}\bigg|_{n=N}\mathbf{R}_N + \int_0^N \frac{\mathrm{d}n}{\zeta_n}\left(K_n\frac{\partial^2 \phi_{pn}}{\partial n^2}\mathbf{R}_n + \phi_{pn}\mathbf{f}_n\right) \end{aligned} \quad \text{(A1)}$$

where, e.g., $[F(x)]_{x=a}^{x=b} = F(x=b) - F(x=a)$.

Comparing eqs 2.8 and A1 yields

$$\frac{\zeta_p}{\zeta_n}K_n\frac{\partial^2 \phi_{pn}}{\partial n^2} = -K_p\phi_{pn} \quad \text{(A2)}$$

$$\mathbf{f}_p = \zeta_p\int_0^N \mathrm{d}n\, \phi_{pn}\mathbf{f}_n/\zeta_n \quad \text{(A3)}$$

with the boundary conditions

$$\frac{\partial \phi_{pn}}{\partial n} = 0, \quad \text{at } n = 0, N \quad \text{(A4)}$$

$$\frac{\phi_{pn}}{\zeta_n} \text{ and } \frac{K_n}{\zeta_n}\frac{\partial \phi_{pn}}{\partial n} \text{ are continuous at } n = Nf \quad \text{(A5)}$$

The orthogonality of ϕ_{pn} is proved using eqs A2−A5,

$$\begin{aligned}\left(\frac{K_p}{\zeta_p} - \frac{K_{p'}}{\zeta_{p'}}\right)\int_0^N \mathrm{d}n\, \phi_{pn}\phi_{p'n}/\zeta_n &= \int_0^N \mathrm{d}n\, \frac{K_n}{\zeta_n^{\,2}}\left(\phi_{pn}\frac{\partial^2 \phi_{p'n}}{\partial n^2} - \phi_{p'n}\frac{\partial^2 \phi_{pn}}{\partial n^2}\right) = \frac{K_\mathrm{A}}{\zeta_\mathrm{A}^{\,2}}\left(\phi_{pn}\frac{\partial \phi_{p'n}}{\partial n} - \phi_{p'n}\frac{\partial \phi_{pn}}{\partial n}\right)_{n=0}^{n\to Nf-0} +\\ &\qquad \frac{K_\mathrm{B}}{\zeta_\mathrm{B}^{\,2}}\left(\phi_{pn}\frac{\partial \phi_{p'n}}{\partial n} - \phi_{p'n}\frac{\partial \phi_{pn}}{\partial n}\right)_{n\to Nf+0}^{n=N} = 0 \end{aligned} \quad \text{(A6)}$$

Therefore, $\int_0^N \mathrm{d}n\, \phi_{pn}\phi_{p'n}/\zeta_n = 0$ except when $p = p'$. Combining this and eqs 2.4 and A3 produces

$$\langle \mathbf{f}_p(t)\mathbf{f}_{p'}(t')\rangle = 2k_\mathrm{B}T\zeta_p^{\,2}\delta_{pp'}\delta(t-t')\mathbf{I}\int_0^N \mathrm{d}n\, \phi_{pn}^{\,2}/\zeta_n \quad \text{(A7)}$$

Comparing eqs 2.9 and A7 gives

$$\int_0^N \mathrm{d}n\, \phi_{pn}\phi_{p'n}/\zeta_n = \zeta_p^{\,-1}\delta_{pp'} \quad \text{(A8)}$$

With eq A8, we may convert eq 2.7 into the inverse transformation

$$\mathbf{R}_n = \zeta_n^{\,-1}\sum_p \zeta_p\phi_{pn}\mathbf{X}_p \quad \text{(A9)}$$

Solving eq A2 yields the normal coordinates in eq 2.10. While the boundary condition in eq A4 is automatically satisfied by the solution in eq 2.10, substituting eq 2.10 into eq A5 produces eqs 2.14 and 2.15.

Appendix B: Solutions to the Normal Modes and the Dynamic Intrachain Correlations

The key of this appendix is to solve eq 2.16.

The parameter $\lambda = \mu_\mathrm{r}(1 - f)/f$ is assumed to be rational, as an irrational λ may always be approximated by a rational number to within any given accuracy. Let $\lambda = n_1/n_2$, where n_1 and n_2 are relatively prime integers, and $\theta = q_{p\mathrm{A}}fN/n_2$. Thus, eq 2.16 becomes

$$\tan(n_2\theta) = -\mu\tan(n_1\theta) \quad \text{(B1)}$$

Substituting

$$\tan(n\theta) = \frac{n\tan\theta - \binom{n}{3}\tan^3\theta + \binom{n}{5}\tan^5\theta - \ldots}{1 - \binom{n}{2}\tan^2\theta + \binom{n}{4}\tan^4\theta - \ldots} \quad \text{(B2)}$$

where $\binom{n}{m} = n!/[m!(n-m)!]$, changes eq B1 to a polynomial of order $n_1 + n_2$ in $\tan\theta$, which is easily solvable either analytically or numerically. As shown below, the advantage of dealing with eq B1 is that it directly gives the full spectrum of normal modes, whereas the roots to eq 2.16 must be sought one by one.

Equation B1 generally has $n_1 + n_2$ solutions. When one of n_1 and n_2 is even while the other is odd, eq B1 has the following solutions:

$$\theta = s\pi, \quad \pm\theta_i + s\pi, \quad \text{for } s = 0, \pm1, \pm2, \ldots; \quad i = 1, 2, \ldots, (n_1 + n_2 - 1)/2; \quad 0 < \theta_i < \pi/2 \quad \text{(B3)}$$

Equation 2.11, 2.14, and 2.21 yield, for $\theta = s\pi$ ($s \neq 0$),

$$S_{p\mathrm{B}} = (-1)^s \frac{\zeta_\mathrm{B}}{\zeta_\mathrm{A}} S_{p\mathrm{A}} \tag{B4}$$

$$\zeta_p = \frac{2{\zeta_\mathrm{A}}^2}{N\bar{\zeta}{S_{p\mathrm{A}}}^2} \tag{B5}$$

$$\tau_p = \frac{f^2 N^2 {\sigma_\mathrm{A}}^2 \zeta_\mathrm{A}}{3\pi^2 {n_2}^2 k_\mathrm{B} T s^2} \tag{B6}$$

and for $\theta = \pm\theta_i + s\pi$,

$$S_{p\mathrm{B}} = (-1)^s \frac{\zeta_\mathrm{B} \cos(n_2\theta_i)}{\zeta_\mathrm{A} \cos(n_1\theta_i)} S_{p\mathrm{A}} \tag{B7}$$

$$\zeta_p = \frac{2{\zeta_\mathrm{A}}^2}{N{S_{p\mathrm{A}}}^2}\left[f\zeta_\mathrm{A} + (1-f)\zeta_\mathrm{B}\frac{\cos^2(n_2\theta_i)}{\cos^2(n_1\theta_i)}\right]^{-1} \tag{B8}$$

$$\tau_p = \frac{f^2 N^2 {\sigma_\mathrm{A}}^2 \zeta_\mathrm{A}}{3{n_2}^2 k_\mathrm{B} T\,(\pm\theta_i + s\pi)^2} \tag{B9}$$

The first nondiffusive mode $p = 1$ corresponds to $\theta = \theta_\mathrm{min} = \min\{\theta_i | i = 1, 2, ...\}$, for which substituting eqs B4−B6 into eq 3.7 produces

$$\begin{aligned}\hat{\omega}_{\alpha\beta}(k,t) \approx{}& [\hat{\omega}_{\alpha\beta}(0) + O(k^2)]\mathrm{e}^{-Dk^2t} + \\ & \epsilon_{\alpha\beta}\frac{2k^2{\zeta_\mathrm{A}}^3 f^4 N^2 {\sigma_\mathrm{A}}^2}{3{n_2}^4 {\theta_\mathrm{min}}^4 \zeta_\alpha\zeta_\beta}\left[f\zeta_\mathrm{A} + (1-f)\zeta_\mathrm{B}\frac{\cos^2(n_2\theta_\mathrm{min})}{\cos^2(n_1\theta_\mathrm{min})}\right]^{-1} \times \\ & \sin^2(n_2\theta_\mathrm{min}) \exp\left[-\left(Dk^2 + \frac{3{n_2}^2 k_\mathrm{B} T {\theta_\mathrm{min}}^2}{f^2 N^2 {\sigma_\mathrm{A}}^2 \zeta_\mathrm{A}}\right)t\right], \\ & \text{for } k \ll N^{-1/2}\sigma^{-1} \text{ and } t \gg \tau_1\end{aligned} \tag{B10}$$

On the other hand, for $k \gg N^{-1/2}\sigma^{-1}$, inserting eqs 2.11−2.13 and B3−B9 into eqs 3.15 and 3.16, changing the summation over p to that over θ_i, and integrating over s yield

$$\hat{\omega}_{\alpha\beta}(k,t) \approx \hat{\omega}_{\alpha\beta}(k) \exp\left[-k^2 f\sigma_\mathrm{A}\left(\frac{k_\mathrm{B} T \zeta_\mathrm{A} t}{3\pi}\right)^{1/2} \kappa_{\alpha\beta}\right] \tag{B11}$$

$$n_2\kappa_\mathrm{AA} = \frac{1}{\bar{\zeta}} + 2\sum_i\left[f\zeta_\mathrm{A} + (1-f)\zeta_\mathrm{B}\frac{\cos^2(n_2\theta_i)}{\cos^2(n_1\theta_i)}\right]^{-1} \tag{B12}$$

$$n_2\kappa_\mathrm{BB} = \frac{1}{\bar{\zeta}} + 2\sum_i\left[f\zeta_\mathrm{A}\frac{\cos^2(n_1\theta_i)}{\cos^2(n_2\theta_i)} + (1-f)\zeta_\mathrm{B}\right]^{-1} \tag{B13}$$

$$n_2\kappa_\mathrm{AB} = \frac{2}{\bar{\zeta}} + 4\sum_i\left[\frac{f\zeta_\mathrm{A}}{\cos^2(n_2\theta_i)} + \frac{(1-f)\zeta_\mathrm{B}}{\cos^2(n_1\theta_i)}\right]^{-1} \tag{B14}$$

where t is much greater than the relaxation time in eq B11.

If both n_1 and n_2 are odd, on the other hand, the solutions to eq B1 are

$$\begin{aligned}\theta = s\pi, \quad & (s + {}^1\!/_2)\pi, \quad \pm\theta_i + s\pi, \\ & \text{for } s = 0, \pm1, \pm2, ...; \quad i = 1, 2, ..., \\ & (n_1 + n_2)/2 - 1; \quad 0 < \theta_i < \pi/2\end{aligned} \tag{B15}$$

where the solutions $\theta = (s + {}^1\!/_2)\pi$, for which eq B1 diverges, are obtained from the original eqs 2.14 and 2.15. For $\theta = s\pi$ $(s \neq 0)$, $S_{p\mathrm{B}} = (\zeta_\mathrm{B}/\zeta_\mathrm{A})S_{p\mathrm{A}}$, while eqs B5 and B6 still hold. For $\theta = (s + {}^1\!/_2)\pi$, eqs 2.11, 2.15, and 2.21 yield

$$S_{p\mathrm{B}} = (-1)^{1+(n_1-n_2)/2}\frac{\zeta_\mathrm{B}}{\mu\zeta_\mathrm{A}} S_{p\mathrm{A}} \tag{B16}$$

$$\zeta_p = \frac{2{\zeta_\mathrm{A}}^2}{N{S_{p\mathrm{A}}}^2}[f\zeta_\mathrm{A} + \mu^{-2}(1-f)\zeta_\mathrm{B}]^{-1} \tag{B17}$$

As for $\theta = \pm\theta_i + s\pi$, $S_{p\mathrm{B}} = (\zeta_\mathrm{B}/\zeta_\mathrm{A})S_{p\mathrm{A}} \cos(n_2\theta_i)/\cos(n_1\theta_i)$, while eqs B8 and B9 are still valid. Thus, eqs B10, B11, and B14 remain applicable, except that $\theta_\mathrm{min} = \min\{\pi/2, \theta_i | i = 1, 2, ...\}$, and κ_AA and κ_BB are changed to

$$\begin{aligned}n_2\kappa_\mathrm{AA} ={}& \frac{1}{\bar{\zeta}} + \frac{1}{f\zeta_\mathrm{A} + \mu^{-2}(1-f)\zeta_\mathrm{B}} + \\ & 2\sum_i\left[f\zeta_\mathrm{A} + (1-f)\zeta_\mathrm{B}\frac{\cos^2(n_2\theta_i)}{\cos^2(n_1\theta_i)}\right]^{-1}\end{aligned} \tag{B18}$$

$$\begin{aligned}n_2\kappa_\mathrm{BB} ={}& \frac{1}{\bar{\zeta}} + \frac{1}{\mu^2 f\zeta_\mathrm{A} + (1-f)\zeta_\mathrm{B}} + \\ & 2\sum_i\left[f\zeta_\mathrm{A}\frac{\cos^2(n_1\theta_i)}{\cos^2(n_2\theta_i)} + (1-f)\zeta_\mathrm{B}\right]^{-1}\end{aligned} \tag{B19}$$

where θ_i are shown in eq B15.

Although we are unable to *analytically* prove eq 3.17 for an arbitrary λ based on the above results, we have done so for certain values of λ(=1, $^3/_2$, 2, 3, 4, 5, *etc.*, and their inverses), where eq B1 is *analytically* solvable, while other parameters are not fixed. For other values of λ, numerical results also agree with eq 3.17.

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