Supplementary Information: Theory of the center-of-mass diffusion and viscosity of microstructured and variable sequence copolymer liquids

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1. Intramolecular correlation function $\omega_{\alpha\gamma}(k)$

The intramolecular pair correlation function, $\omega_{\alpha\gamma}(k)$, is the Fourier transform of the probability distribution function of distances between two sites along the chain averaged over the sites of the same chemical pairs (neglecting chain end effects). It enters the PRISM equations (Eq. 1 in the main text) through the matrix $\Omega(k)$, and carries the copolymer sequence information. For the Freely Jointed Chain (FJC) model [1,2] considered in the present study (fixed bond length $l = 4\sigma/3$ which equals persistence length), $\omega_{\alpha\gamma}(k)$ for any given sequence of A/B copolymer is given by [3],

$$\omega_{\alpha\gamma}(k) = \frac{1}{N_{\alpha\gamma}} \sum_{i \in J_\alpha} \sum_{j \in J_\gamma} (sin(kl)/(kl))^{|i-j|} \qquad (1)$$

where $N_{\alpha\gamma} = N_\alpha + N_\gamma$ if $\alpha \neq \gamma$ and $N_{\alpha\gamma} = N_\alpha$ if $\alpha = \gamma$, where N_α and N_β are the number of interaction sites of types α and γ, respectively, $N_\alpha + N_\gamma = N$ is the total chain length and J_α and J_γ denote the

sets of the indices for sites of type α and γ, respectively. Eq. (1) provides a numerical method for calculating $\omega_{\alpha\gamma}(k)$ for arbitrary A/B copolymer sequences.

2. Derivation of $\Delta\zeta$

In this section, we summarize some technical details of our calculations for the "collective" part of friction, $\Delta\zeta$. Recall from Eq.6 in the main text that

$$\Delta\zeta = \frac{\beta^{-1}}{3}\int_0^\infty dt \sum_{\alpha,\gamma} \int \frac{dk}{(2\pi)^3} k^2 \tilde{\omega}_{\alpha\gamma}(k,t)[C \cdot \tilde{S}(k,t) \cdot C]_{\alpha\gamma}$$

. The dimensionless collective dynamic structure factors $S(k,t)$ can be obtained by solving Eq. 8 in the main text using Laplace transforms [4,5]. The form of solution is expressed as,

$$S_{\alpha\gamma}(k,t) = a_{\alpha\gamma}exp(-\Lambda_I t) + b_{\alpha\gamma}exp(-\Lambda_C t) \qquad (2)$$

where $a_{\alpha\gamma}$, $b_{\alpha\gamma}$, Λ_I, Λ_C are given as,

$$a_{11} = \frac{(\Lambda_I - \Theta_{22})S_{11} + \Theta_{12}S_{21}}{\Lambda_I - \Lambda_C}$$

$$a_{12} = \frac{(\Lambda_I - \Theta_{22})S_{12} + \Theta_{12}S_{22}}{\Lambda_I - \Lambda_C}$$

$$a_{21} = \frac{(\Lambda_I - \Theta_{11})S_{21} + \Theta_{21}S_{11}}{\Lambda_I - \Lambda_C}$$

$$a_{22} = \frac{(\Lambda_I - \Theta_{11})S_{22} + \Theta_{21}S_{12}}{\Lambda_I - \Lambda_C} \qquad (3)$$

and

$$b_{11} = \frac{(\Lambda_C - \Theta_{22})S_{11} + \Theta_{12}S_{21}}{\Lambda_C - \Lambda_I}$$

$$b_{12} = \frac{(\Lambda_C - \Theta_{22})S_{12} + \Theta_{12}S_{22}}{\Lambda_C - \Lambda_I}$$

$$b_{21} = \frac{(\Lambda_C - \Theta_{11})S_{21} + \Theta_{21}S_{11}}{\Lambda_C - \Lambda_I}$$

$$b_{22} = \frac{(\Lambda_C - \Theta_{11})S_{22} + \Theta_{21}S_{12}}{\Lambda_C - \Lambda_I} \qquad (4)$$

and

$$\Lambda_I = \frac{\Theta_{11} + \Theta_{22}}{2} - \sqrt{(\frac{\Theta_{11} + \Theta_{22}}{2})^2 - (\Theta_{11}\Theta_{22} - \Theta_{12}\Theta_{21})}$$

$$\Lambda_C = \frac{\Theta_{11} + \Theta_{22}}{2} + \sqrt{(\frac{\Theta_{11} + \Theta_{22}}{2})^2 - (\Theta_{11}\Theta_{22} - \Theta_{12}\Theta_{21})}$$

$$(5)$$

with

$$\Theta_{11} = k^2 D_s S_{22}/\Delta(S)$$
$$\Theta_{12} = \Theta_{21} = - k^2 D_s S_{12}/\Delta(S)$$
$$\Theta_{22} = k^2 D_s S_{11}/\Delta(S)$$

$$(6)$$

where $\Delta(S) = S_{11}S_{22} - S_{12}S_{21}$. Note that all the variables are functions of wavevector k, which has been notationally suppressed for better readability. The dimensional dynamic partial collective structure factors $\tilde{S}_{\alpha\gamma}(k,t)$ are obtained as $\tilde{S}_{\alpha\gamma}(k,t) = \rho_{\alpha\gamma}S_{\alpha\gamma}(k,t)$ where $\rho_{\alpha\gamma} = \rho_\alpha$ if $\alpha = \gamma$ and $\rho_{\alpha\gamma} = \sqrt{\rho_\alpha \rho_\gamma}$ otherwise. Eq. (2) and Eq. (7) of the main text can then be substituted into Eq. (6) of the main text to obtain the solution for $\Delta\zeta_{CM}$. We exchange the order of integration and perform the integration over time t first in Eq. (6) in the main text analytically and thus obtain,

$$\int_0^\infty dt \tilde{\omega}_{\alpha\gamma}(k,t)[C(k)\tilde{S}(k,t)C(k)]_{\alpha\gamma} = \frac{A_{\alpha\gamma}G_{\alpha\gamma}}{\Gamma + \Lambda_I} + \frac{B_{\alpha\gamma}G_{\alpha\gamma}}{\Gamma + \Lambda_C}$$

$$(7)$$

where $\Gamma = k^2 D_s \omega^{-1}(k)$ and $A_{\alpha\gamma}, B_{\alpha\gamma}, G_{\alpha\gamma}$ are,

$$A_{11} = C_{11}^2\rho_{11}a_{11} + C_{11}C_{12}\rho_{12}a_{21} + C_{12}C_{11}\rho_{12}a_{12} + C_{12}^2\rho_{22}a_{22}$$
$$B_{11} = C_{11}^2\rho_{11}b_{11} + C_{12}C_{11}\rho_{12}b_{21} + C_{12}C_{11}\rho_{12}b_{12} + C_{12}^2\rho_{22}b_{22}$$
$$A_{12} = C_{11}C_{12}\rho_{11}a_{11} + C_{11}C_{22}\rho_{12}a_{12} + C_{12}^2\rho_{21}a_{21} + C_{12}C_{22}\rho_{22}a_{22}$$
$$B_{12} = C_{11}C_{12}\rho_{11}b_{11} + C_{11}C_{22}\rho_{12}b_{12} + C_{12}^2\rho_{21}b_{21} + C_{12}C_{22}\rho_{22}b_{22}$$
$$A_{21} = C_{11}C_{21}\rho_{11}a_{11} + C_{21}^2\rho_{12}a_{12} + C_{11}C_{22}\rho_{21}a_{21} + C_{21}C_{22}\rho_{22}a_{22}$$
$$B_{21} = C_{11}C_{21}\rho_{11}b_{11} + C_{21}^2\rho_{12}b_{12} + C_{11}C_{22}\rho_{21}b_{21} + C_{21}C_{22}\rho_{22}b_{22}$$
$$A_{22} = C_{12}C_{21}\rho_{11}a_{11} + C_{21}C_{22}\rho_{12}a_{12} + C_{12}C_{22}\rho_{21}a_{21} + C_{22}^2\rho_{22}a_{22}$$
$$B_{22} = C_{12}C_{21}\rho_{11}b_{11} + C_{21}C_{22}\rho_{12}b_{12} + C_{12}C_{22}\rho_{21}b_{21} + C_{22}^2\rho_{22}b_{22}$$
$$G_{11} = n_{11}\omega_{11}$$
$$G_{12} = n_{12}\omega_{12}$$
$$G_{21} = n_{21}\omega_{21}$$
$$G_{22} = n_{22}\omega_{22}$$

$$(8)$$

3

Here, $C_{\alpha\gamma} \equiv C_{\alpha\gamma}(k)$ are the site-site direct correlation functions, $a_{\alpha\gamma}$, $b_{\alpha\gamma}$ are given by Eqs. (3-6), the $\omega_{\alpha\gamma}$ matrix elements are given by Eq. (1), and $n_{\alpha\gamma} = n_{\alpha}$ if $\alpha = \gamma$ and $n_{\alpha\gamma} = n_{\alpha} + n_{\gamma}$ otherwise. Finally, the per-monomer collective friction is calculated as,

$$\Delta\zeta = \frac{\Delta\zeta_{CM}}{N} = \frac{\beta^{-1}}{6\pi^2 N}\int_0^\infty dk k^4 \sum_{\alpha\gamma}\frac{A_{\alpha\gamma}G_{\alpha\gamma}}{\Gamma + \Lambda_I} + \frac{B_{\alpha\gamma}G_{\alpha\gamma}}{\Gamma + \Lambda_C} \equiv \frac{\beta^{-1}}{6\pi^2}\int_0^\infty dk V(k) \tag{9}$$

where $V(k)$ is the defined as the dynamic vertex.

For homopolymer fluids, straightforward analytic analysis reveals that the above equation reduces to a simpler expression given by,

$$\Delta\zeta = \frac{\rho\beta^{-1}}{6\pi^2 D_s}\int_0^\infty dk k^2 C^2(k)\frac{S^2(k)\omega^2(k)}{S(k) + \omega(k)} \tag{10}$$

3. Structure factors and radial distribution functions

The SI Figure 1 shows the A-A and A-B structure factors and radial distribution functions associated with their B-B counterparts that are shown in the main text Figure 3.
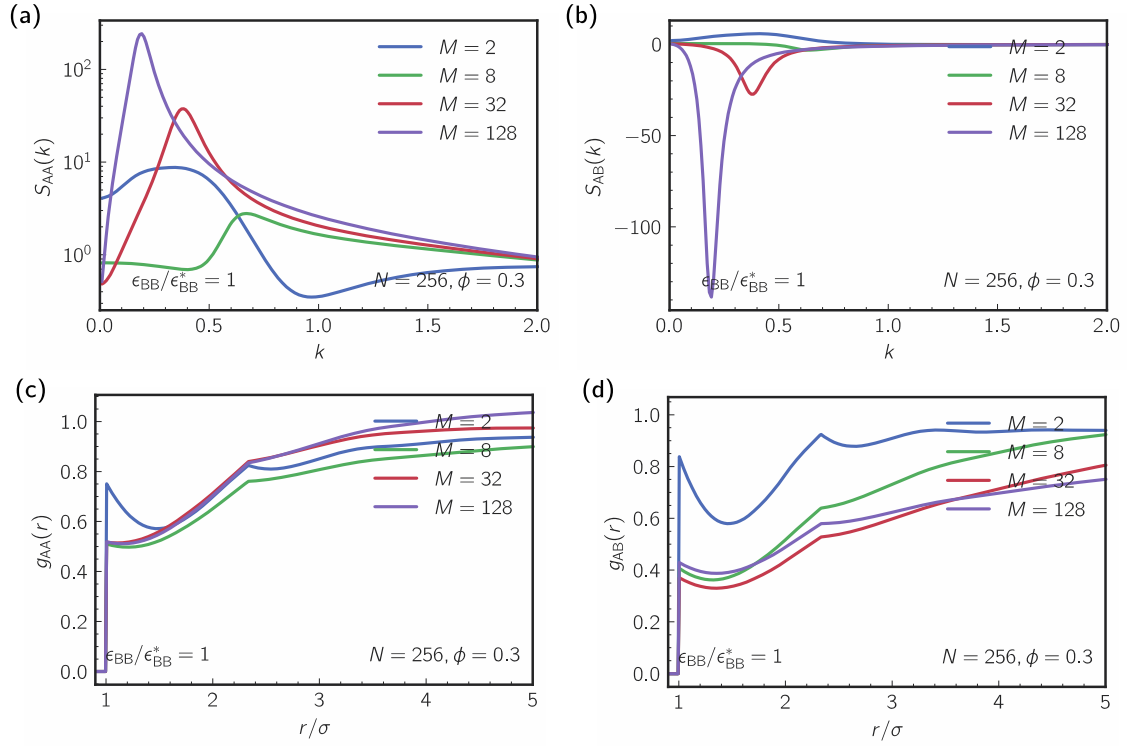
Figure 1: ***(a)*** *Partial A-A structure factor at the microemulsion crossover boundary* $\epsilon_{BB}/\epsilon_{BB}^* = 1$.

(b) *Partial A-B structure factor at the microemulsion crossover boundary* $\epsilon_{BB}/\epsilon_{BB}^* = 1$. ***(c)*** *Partial*

A-A radial distribution functions at the microemulsion crossover boundary $\epsilon_{BB}/\epsilon_{BB}^* = 1$. ***(d)*** *Partial*

A-B radial distribution functions at the microemulsion crossover boundary $\epsilon_{BB}/\epsilon_{BB}^* = 1$.

4. Athermal copolymer friction.

SI Figure 2 shows that the expression for the friction constant formulated for the copolymer system (Eq. 6 in the main text) reduces naturally in the athermal (no attractions) limit to the homopolymer case by setting $\beta\epsilon_{BB} = 0$.
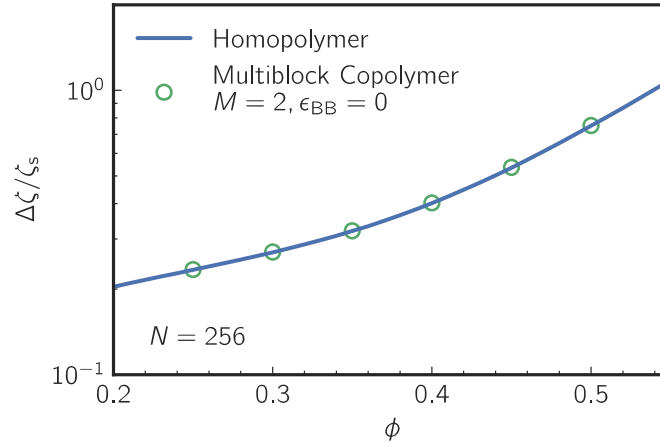

Figure 2: Per-segment collective friction ($\Delta\zeta$) normalized by the elementary local segmental friction (ζ_s), $\Delta\zeta/\zeta_s$, as a function of ϕ. Circles are results for multiblock copolymer with block length $M = 2$ and at athermal condition by setting B-B attraction to be zero, $\beta\epsilon_{BB} = 0$.

5. Correlation between friction and wavevector normalized structure factor peak

SI Figure 3a shows the growth of the wavevector normalized structure factor peak in a manner complementary to Figure 8a of the main text. SI Figure 3b shows the correlation between the non-dimensionalized per-monomer collective friction and wavevector normalized structure factor peak, which is complementary to Figure 8b in the main text.
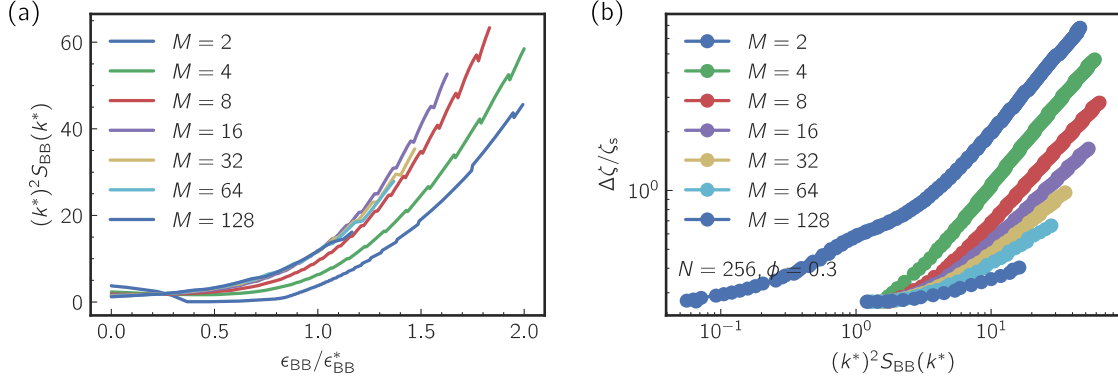

*Figure 3: **(a)** Growth of microdomain length scale normalized low wavevector structural factor peak, $(k^*)^2 S_{BB}(k^*)$, as as function of normalized interaction strength $\epsilon_{BB}/\epsilon^*_{BB}$. **(b)** Non-dimensional per-monomer collective friction, $\Delta\zeta/\zeta_s$, as a function of $(k^*)^2 S_{BB}(k^*)$. $N = 256, \phi = 0.3$.*

6. Dynamic vertex and its approximations

SI Figure 4 shows the comparison between the dynamic vertex and its two approximate simplified

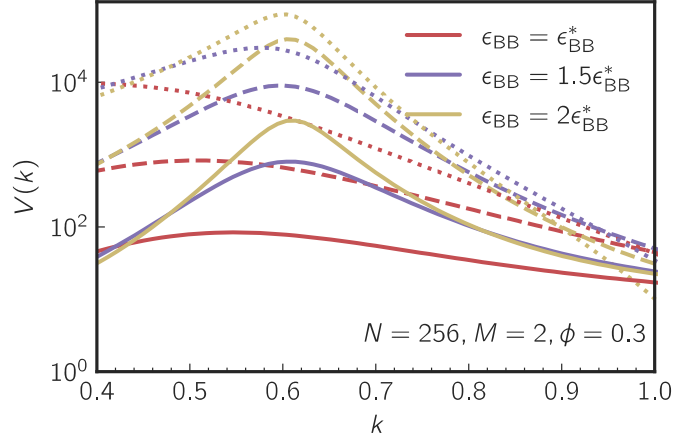forms discussed in the main text.

Figure 4: Comparison between vertex $V(k)$ and two approximations, $V_1(k)$ and $V_2(k)$ (see main

text). $V_1(k)$ *is shown in dotted lines and* $V_2(k)$ *is shown in dashed lines.*

$$V_1(k) = \rho_B(N_B/N)k^2 C_{BB}^2(k) S_{BB}^2(k) \omega_{BB}^2(k)/(S_{BB}(k) + \omega_{BB}(k))$$

and

$$V_2(k) = \rho k^2 \bar{C}^2(k) S^2(k) \omega^2(k)/(S(k) + \omega(k))$$

7. References

1   K. Schweizer and J. Curro, Atomistic Modeling of Physical Properties, 2006, 319–377.

2   K. S. Schweizer and J. G. Curro, in Advances in Chemical Physics, John Wiley & Sons, Ltd, 1997, pp. 1–142.

3   G. Shi and K. S. Schweizer, The Journal of Chemical Physics, 2023, 159, 044904.

4   D. C. Viehman and K. S. Schweizer, The Journal of Chemical Physics, 2008, 128, 084509.

5   Y. Zhou and K. S. Schweizer, The Journal of Chemical Physics, 2020, 153, 114901.