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Simulation of Diffusion of Asymmetric Diblock and Triblock Copolymers in a Spherical Domain Structure

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ABSTRACT: Diffusion of asymmetric diblock and triblock copolymers in a three-dimensional periodic potential field with body centered cubic (bcc) symmetry is simulated numerically using Langevin dynamics. To simulate unentangled copolymer melts, a spring and bead model (*Rouse*) is introduced. To simulate entangled polymer melts, a copolymer chain is only allowed to move along its contour, following a *strict reptation* algorithm, with fixed segment length and no contour length fluctuations. For an AB diblock copolymer with a short A block, we compute a normalized diffusion coefficient, D/D_0, where D_0 is the diffusion coefficient in the absence of potential fields. We find that D/D_0 scales according to $\exp(-\alpha N_A)$ for fairly large αN_A regardless of the mechanism of the diffusion (Rouse or strict reptation), where α is the amplitude of the potential field and N_A is the number of segments in the A block. In this asymmetric regime (fraction of minority block, $f = 0.1$), the product αN_A evidently determines the diffusion of the diblock copolymer. The diffusion of ABA triblock copolymers by the Rouse mechanism also scales with αN_A in the same way as for diblock copolymers, where N_A for the triblock copolymer is the number of segments in *each* A block. That suggests that the triblock copolymer diffuses by activating only one A block at a time (*walking* diffusion), which is consistent with experiments. However, the strict reptation calculations show larger reduction of diffusion coefficients for triblock copolymers in the bcc potential field. Apparently, entanglements inhibit such a *walking* diffusion mechanism and reduce the diffusion more strongly for triblock copolymers than for diblock copolymers.

Introduction

Diblock and triblock copolymers can order into a variety of structures depending on the asymmetry of the block copolymer molecules. Phase behaviors of diblock copolymers have been extensively studied.[1,2] However, the kinetics of microphase separation leading to these interesting microstructures is not well understood. Understanding the diffusion of block copolymers in the ordered state is the key to understanding the kinetics of microphase separation as well as the fundamental dynamics of block copolymers.

Lodge and co-workers have performed a series of experiments with symmetric diblock copolymers that have a lamellar structure.[3] They shear-aligned lamellae in a particular direction and measured diffusion in the directions parallel and perpendicular to the lamellae. They found an exponential decrease of the normalized diffusion coefficient, D/D_0, with the product χN, where χ is the interaction parameter between units of the two blocks and N is the number of segments. The exponential dependence was ascribed to the thermodynamic barrier that individual diblock copolymer chains experience as they move through the diblock copolymer ordered structure.

For lamellar structures, the diffusion depends on the direction relative to the lamellae and also the mechanism of diffusion, that is, reptation or Rouse. Experimentally, aligning lamellae by shear is limited to entangled melts. Lodge et al. found that well-entangled diblock copolymer chains diffuse by thermodynamic activation in the direction perpendicular to the lamellae. On the other hand, the diffusion of well-entangled diblock copolymers parallel to the lamellae is not simple. In a relatively weak field (relatively small χN but in the ordered state), a diblock copolymer chain pulls one of its blocks into the domain of the other block, for example, the A block is exposed to the B block domain, and hops parallel to the lamellae, resulting an exponential decrease of D/D_0 with χN. However, in a relatively strong field (relatively large χN), the diblock copolymer retracts a block from its initial “tube” without exposing it to the other block domain and extends it into a new “tube”, resulting in an exponential decrease with N but little or no dependence on χ. This parallel diffusion mechanism at large χN is reminiscent of the diffusion of star polymers.[15] In contrast to the diffusion of entangled diblock copolymers, unentangled diblock copolymers in shear-aligned lamellae showed temperature-dependent anisotropy of diffusion coefficients.[4] The diffusion in the direction perpendicular to the lamellae was up to 40 times slower than that in the direction parallel to the lamellae.

The diffusion of an entangled asymmetric diblock copolymer across the order−order transition (OOT) (cylindrical to spherical domain structure) in a shear-aligned matrix was measured.[5] No anisotropy of diffusion in either the cylindrical or spherical domain structure was observed with no indication of an OOT in the temperature dependence of diffusivity.

The diffusion of unentangled diblock copolymers in cylinder and gyroid structures was recently measured.[6] The authors took advantage of the hysteresis of the order−order transition (depending on the thermal history, the structure can be either cylinder or gyroid at the same temperature) and measured the diffusion of diblock copolymer in both cylinder and gyroid structures at the same temperature. The diffusion in a gyroid structure is much faster than that in a cylinder structure at the same temperature, indicating that the

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diffusion along the interface dominates and that the diblock copolymer chains explore three-dimensional space more effectively solely by diffusion along interfaces in a gyroid structure.

For a spherical domain structure, the mechanism of the diblock copolymer diffusion differs from that in lamellae, cylinders, or gyroid structures.[7,8] Due to the discontinuous minority domains, diblock copolymer chains have to expose the minority A block to the surrounding majority B block in order to diffuse in any direction. The diffusion of a whole spherical domain is another possibility, but experimentally it has been shown that D/D_0 exponentially decreases with χN_A, indicating that diffusion is controlled by a thermodynamic barrier. In general, the thermodynamic barrier should be described by a function of χN and f. In the limit of high asymmetry, $\chi N_A = \chi N f$ is a good approximation to the effective activation barrier since a core A block experiences almost full contact with the surrounding B block domain in an activated state, while a core A block has almost no contact with B blocks in a stable trapped state.

An experimental comparison between diffusion in lamellar and spherical domain structures shows different prefactors for the thermodynamic barrier. For a lamellar structure of a symmetric diblock copolymer, the barrier is found to be $0.25\chi N$ (or $0.5\chi N_A$), while for a spherical domain structure, $1.2\chi N_A$ is found instead.[7] The reason for this difference has not yet been clarified theoretically.

Theoretical efforts to include periodic potential fields in the diffusion of diblock copolymer chains have been limited to some simple cases. The diffusion of diblock copolymer with no entanglements in a weak one-dimensional potential field was solved as a perturbation expansion.[9] It was found that the reduction of diffusion coefficients has a maximum when the wavelength of the potential field is approximately the same as the radius of gyration of the diblock copolymer chain. This work was further extended to more general one-dimensional potential fields, for example, a square wave, by Barrat and Fredrickson[10] and solved by a perturbation expansion for weak fields and activation process theory for strong fields. They also introduced a numerical simulation of a Rouse Langevin equation in a periodic potential field and compared it to the approximate analytical solutions. Leibig[11] applied a reptational algorithm to simulate diffusion of symmetric entangled diblock copolymers in a one-dimensional periodic potential field.

There have been several other theoretical studies on diffusion of diblock copolymers; however, the theory directly applicable to asymmetric diblock copolymers with a spherical domain structure is very limited. A polymer mode coupling (PMC) theory can be applied to asymmetric diblock copolymers.[13,14] The PMC theory predicts an isotropic diffusion coefficient, and the result agrees with the experimental result of diffusion of PEP−PEE in a lamellar structure in the direction parallel to the lamellae. However, PMC predicts that the reduction of the normalized diffusion coefficient, D/D_0, saturates as the interaction between blocks becomes strong, while experimentally in a spherical domain structure, D/D_0 decreases exponentially as $\exp(-1.2\chi N_A)$.

Recently, the tracer diffusion of triblock copolymers in a spherical domain structure was measured.[16] Surprisingly, the D/D_0 of the triblock copolymer was almost the same as that of a diblock copolymer with half the molecular weight, suggesting that the triblock copolymer activates only one end core block at a time, leading to a "walking" diffusion mechanism. There is no theoretical work on the diffusion of triblock copolymers that illuminates the experimental findings.

In this paper, we apply both the Langevin dynamics simulation with a simple spring and bead model (Rouse) and the reptational Langevin dynamics simulation method developed by Leibig[11] to diffusion in a three-dimensional periodic potential field with body center cubic (bcc) symmetry that is intended to simulate the diffusion of highly asymmetric diblock copolymers in a bcc ordered spherical domain structure. The diffusion of a symmetric diblock copolymer in a one-dimensional periodic potential was also simulated to provide a comparison with the results for the asymmetric diblock copolymers. The simulations are further extended to asymmetric triblock copolymers in the same potential fields. These simulation results are finally compared with the relevant experimental findings.

Model and Calculations

Periodic Potential Field. We introduce a *static* potential field, $\nu(\mathbf{r})$, given by

$$\nu(\mathbf{r}) = \gamma \tanh[C \sum_{i=1}^{6} \cos(\mathbf{q}_i \cdot \mathbf{r}) + D] \qquad (1)$$

where $\nu(\mathbf{r})$ is a dimensionless periodic function of position $\mathbf{r}$ in three-dimensional space, $\mathbf{q}_i$ are wave vectors that specify the symmetry of a bcc structure, C is a parameter that changes the width of interface between a spherical core domain and the continuous corona domain, and D introduces an compositional asymmetry into the periodic potential field. The $\mathbf{q}_i$ are given by $\mathbf{q}_1 = (2\pi/L)(1,1,0)$, $\mathbf{q}_2 = (2\pi/L)(0,1,1)$, $\mathbf{q}_3 = (2\pi/L)(1,0,1)$, $\mathbf{q}_4 = (2\pi/L)(1,-1,0)$, $\mathbf{q}_5 = (2\pi/L)(0,1,-1)$, and $\mathbf{q}_6 = (2\pi/L)(-1,0,1)$. C is changed to explore the effect of interfacial thickness on the diffusivity, while D is fixed at a value consistent with the A-block fraction, f. L is the lattice parameter. For self-diffusion in a weakly segregated sample, we set $L \simeq 2a\sqrt{N}$, where a is the statistical segment length of the polymer and N is the total number of segments. The nondimensional potential field was normalized by the parameter γ such that the maximum amplitude of the potential is 1. The dimensional potential field is such that monomers are subjected to the external potential $V(\mathbf{r}) = \epsilon\alpha k_B T\nu(\mathbf{r})$, where $\epsilon = +1$ for A monomers and -1 for B monomers, α is an amplitude of the potential field proportional to χ in the strong segregation limit, k_B is Boltzmann's constant, and T is the temperature.

Bead-Spring Simulation. In our Rouse-like simulations, diblock or triblock copolymer chains are constructed by assembling N beads, each with a friction coefficient, ζ, and connected by springs with spring coefficient $3k_B\, T/a^2$. The Hamiltonian for a block copolymer chain is given by

$$H = \frac{3k_B T}{2a^2}\int_0^N \mathrm{d}s\left(\frac{\mathrm{d}\mathbf{r}(s)}{\mathrm{d}s}\right)^2 + \alpha k_B T\int_0^N \mathrm{d}s\,\epsilon(s)\nu(\mathbf{r}(s)) \qquad (2)$$

where s is the curvilinear coordinate, which is 0 at the A-block chain end and N at the other chain end. Specifically, we chose $f = 0.1$, so for diblock copolymers $\epsilon(s) = +1$ for $s < 0.1N$, $\epsilon(s) = -1$ for $s > 0.1\ N$, while for triblock copolymers $\epsilon(s) = +1$ for $s < 0.05N$ or $s > N - 0.05N$, $\epsilon(s) = -1$ for $0.05N < s < N - 0.05N$. In eq 2, a is the statistical segment length, which is assumed to be the same for A and B monomers for simplicity. The same assumption is made for the friction coefficients ζ of A and B monomers. The equation of motion is

$$\frac{\mathrm{d}\mathbf{r}(s)}{\mathrm{d}t} = -\frac{1}{\zeta}\frac{\delta H}{\delta\mathbf{r}(s)} + \theta(s,t) \qquad (3)$$

where $\theta(s, t)$ is the usual Gaussian white noise that satisfies

$$\langle\theta_i(s,t)\theta_j(s',t')\rangle = 2k_B T\zeta^{-1}\,\delta(s-s')\delta(t-t')\delta_{ij} \qquad (4)$$

In an absence of the potential field, the Rouse diffusion coefficient is given by

$$D_0 = \frac{k_B T}{N\zeta} \qquad (5)$$

Barrat and Fredrickson introduced Rouse modes to remove the coupling of spring force between beads and truncated it to several Rouse modes. That method is not appropriate, however, for the case of high asymmetry in the chain structure. The position of the joint in the diblock copolymer is crucial in determining the total potential energy of the diblock copolymer. For asymmetric diblock copolymers, many Rouse modes are required to describe accurately where the joint of the diblock copolymer chain is as well as the configurations of the small A block. Instead, we numerically solved the coupled Langevin equation in real (i.e., s) space. We discretize s to a discrete variable n, for which the Langevin equation is given for small Δt by

$$\mathbf{r}_n(t+\Delta t) - \mathbf{r}_n(t) = -\frac{3k_B T\Delta t}{a^2\zeta}(2\mathbf{r}_n - \mathbf{r}_{n+1} - \mathbf{r}_{n-1}) - \frac{\alpha k_B T\epsilon(n)\Delta t}{\zeta}\nabla v(\mathbf{r}_n) + \mathbf{f} \qquad (6)$$

where the boundary condition is $\mathbf{r}_{N+1} = \mathbf{r}_N$ and $\mathbf{r}_0 = \mathbf{r}_1$. Δt is chosen so that the algorithm is stable and of sufficient accuracy to reproduce known results ($k_B T\, a^{-2}\zeta^{-1}\Delta t = 0.1$). The random force $\mathbf{f}$ is defined as a Gaussian white noise with the following first and second moments: $\langle\mathbf{f}\rangle = 0$ and $\langle f_i f_j\rangle = 2k_B T\zeta^{-1}a^{-2}\Delta t\delta_{ij}$. Mean square displacements are measured and the diffusion coefficients are calculated according to

$$D = \frac{\langle(\mathbf{r}(t) - \mathbf{r}(0))^2\rangle}{6t} \qquad (7)$$

where $\mathbf{r}(t)$ is the position of the center of mass of the block copolymer at time t.

Strict Reptational Simulation. In the strict reptation simulation, the tube model is accounted for in the algorithm.[11] One primitive chain in the system is forced to move along its contour in the presence of a periodic potential field. Moreover, the primitive chain length is held constant, so there are no contour length fluctuations. Therefore, the elastic energy in the Hamiltonian is neglected. The diffusion is essentially one-dimensional diffusion in which a chain can move forward or backward along a curvilinear coordinate. Only the chain ends can explore outside of the tube. In a discrete expression, the Langevin equation is defined by

$$\Delta Y_0 = -\frac{D_R\Delta t}{k_B T a^2}\frac{\partial V}{\partial Y_0} + f \qquad (8)$$

where f is a random displacement defined by the first and second moments as $\langle f\rangle = 0$ and $\langle f^2\rangle = 2D_R\, a^{-2}\Delta t$. Y_0 is the curvilinear position of the center of mass of the polymer, ΔY_0 is the number of entanglement units by which the chain is displaced in a single time step along the contour, and V is the potential energy of the polymer. ΔY_0 is rounded to an integer value, and the remainder is stored for the next time step. (If a remainder exists from a previous step, the remainder is added to ΔY_0 and then ΔY_0 is rounded.) The position of the nth segment at time $t + \Delta t$ is connected to that at time t:

$$\mathbf{r}_n(t+\Delta t) = \mathbf{r}_{n+\Delta Y_0}(t) \qquad (9)$$

It should be noted that, in this strict reptation algorithm, the position of entanglements can be set to the position of corresponding monomers, since there is no motion except that along the chain contour. The chain end at the forward direction moves by a random walk in three dimensions with a fixed step length and a number of steps ΔY_0.

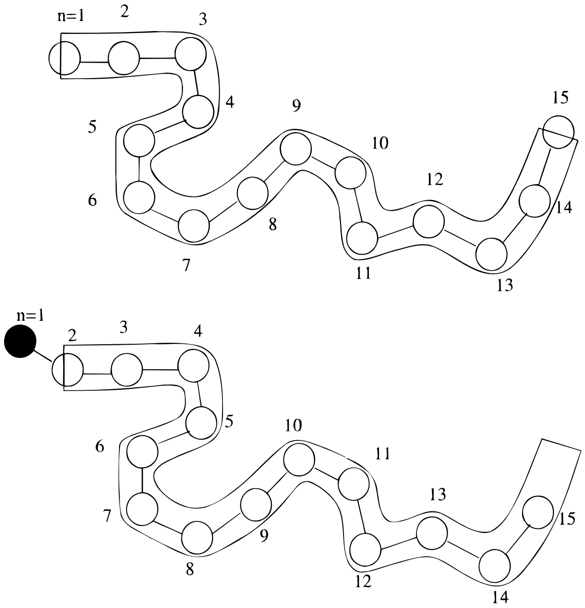

Figure 1. Illustration of the strict reptation algorithm. An example for the 15-mer (homopolymer) is shown here. The configurations at time t_0 (above) and $t_0 + \Delta t$ (below) are compared to determine the free energy difference ΔV. We approximate $V_1(t_0 + \Delta t) \approx V_1(t_0)$ so that ΔV starting from the configuration at $t = t_0$ is given by $\Delta V = V_1(t_0) - V_{15}(t_0)$.

At a given time t, the change in the potential energy of a homopolymer corresponding to a time step t is given by

$$\Delta V = \sum_{n=0}^{N} V\{\mathbf{r}_n(t+\Delta t)\} - \sum_{n=0}^{N} V\{\mathbf{r}_n(t)\} = \sum_{n=0}^{\Delta Y_0}[V\{\mathbf{r}_{N-n}(t+\Delta t)\} - V\{\mathbf{r}_n(t)\}] \qquad (10)$$

where $\mathbf{r}_n(t + \Delta t)$ represents the new position of the nth monomer at time $t + \Delta t$. The second expression arises because all the monomers except that moving out of the tube are at positions previously occupied by the other monomers. It is enough to take the sum only over the new and vacated monomer positions. An illustration for the simple example of a homopolymer is shown in Figure 1. To compute the difference in free energy between time t_0 and $t_0 + \Delta t$, $V_1(t_0 + \Delta t)$ is an unknown parameter that must be evaluated. When the change in potential field is small enough over the distance of one segmental step, the approximation

$$V_1(t_0 + \Delta t) = V_1(t_0) \qquad (11)$$

is possible and can reduce the computation for $\partial V/\partial Y_0$ significantly. The potential energies of those newly occupied positions are approximated to the potential energy of the chain end of the previous configuration so that we can compute $\partial V/\partial Y_0$ without knowing the future configuration at $t_0 + \Delta t$.

For block copolymers under the above approximations, we need to calculate the difference in the potential energies of the joints of the block copolymer in addition to that of the chain ends discussed in the last paragraph. Therefore, we obtain the approximate gradient of the potential energy for a diblock copolymer:

$$\frac{\partial V}{\partial Y_0} = V\{\mathbf{r}_N\} + V\{\mathbf{r}_0\} - 2V\{\mathbf{r}_{f_A N}\} \qquad (12)$$

For a triblock copolymer,

$$\frac{\partial V}{\partial Y_0} = V\{\mathbf{r}_N\} - V\{\mathbf{r}_0\} - 2V\{\mathbf{r}_{1/2f_\mathrm{A}N}\} + 2V\{\mathbf{r}_{(1-1/2f_\mathrm{A})N}\} \quad (13)$$

The simulation is performed in the following sequence. (1) At a given configuration in the potential field, the external force is computed. (2) The Brownian random force is calculated by selecting a random number from an appropriate Gaussian distribution. (3) The direction and distance (along its contour) for the block copolymer to move is calculated from the 1-D Langevin equation (eq 8). (4) The integer value of the distance to move is retained, and the remainder is stored for the next iteration. (5) The chain then reptates the approximate number of steps in the identified direction. The forward end of the chain moves by a 3-D random walk displacement, and the rest of the chain monomers simply follow their neighbors along the chain contour. (6) Finally, we redefine the configuration for the next step in the iteration.

It has been confirmed that this algorithm gives a diffusivity proportional to N^{-2} that is consistent with reptation theory in absence of potential fields.[11] Diffusion coefficients are calculated from the long time limit of the center of mass mean-squared displacement,

$$D = \lim_{t\to\infty}(1/6t)\,\langle(\mathbf{r}_0(t) - \mathbf{r}_0(0))^2\rangle$$

where $\mathbf{r}_0(t)$ is the position of the center of mass at time t. In general, the diffusion is described by a tensor diffusivity D_{ij}, but the tensor is reduced by the symmetry of a cubic lattice to a scalar value D.

Results and Discussion

Reptation Simulation of Asymmetric Diblock Copolymer Diffusion. *N* and α Dependence of Diblock Copolymers. In this section, we show the universal scaling of the normalized diffusion coefficients, D/D_0, by the product αN that results from the reptational simulation. A periodic potential field is defined by the following parameters: The width of the interface between the A spherical domain and the B continuous domain relative to the periodicity of the bcc lattice is fixed by setting the parameter C to 10. The asymmetry parameter D is set to 0.25 to give a volume fraction f_A of the A spherical domain of 0.1. The A volume fraction can be obtained by integration of the potential field. The spacing of the periodic potential field is scaled to the spacing ($2\pi/q^*$) predicted by Leibler[18] for the diblock copolymer chain at a $f_\mathrm{A} = 0.1$, so that the spacing is always consistent with the dimensions of the copolymer that is diffusing. This condition ensures that we simulate self-diffusion. We have simulated the diffusion of three different diblock copolymers, $N = 200$, 500, and 1000 with $f_\mathrm{A} = 0.1$. In all cases, the number of monomers is large enough (the movement of the chain is slow enough) so that the approximation of eq 11 is valid. The amplitude of the potential field is varied so as to test whether D/D_0 varies only with the product αN_A (universal scaling).

In Figure 2, the normalized diffusion coefficient, D/D_0, is plotted against the product αN_A. Recent experiments have shown that D/D_0 decreases exponentially with αN_A whether N_A is varied by polymer synthesis or α is varied by changing temperature.[7,8] We find that the results for all three diblock copolymers collapse to a single curve when the two parameters α and N are changed independently. It is also interesting that this universal relation is evidently not a single exponential, but the slope increases from almost 0 in the small αN_A region to 1 in the region where $\alpha N_\mathrm{A} \geq 6$. The slope of unity in the latter region indicates that the diffusion is controlled by an activation energy for the diblock copolymer to pull its A core block from an A spherical domain and drag the A block through the B corona domain, exposing the N_A monomers of the A block fully to B monomers with an energy cost of $\chi k_\mathrm{B}T$ per monomer.

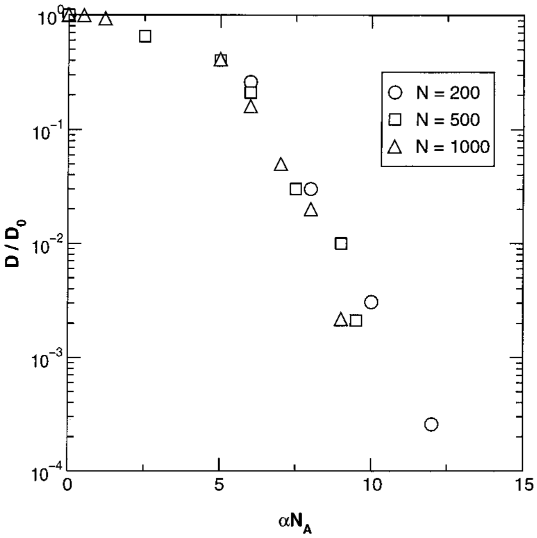

Figure 2. Universal dependence of D/D_0 on the product of α and N_A for various values of N, the total number of segments in the block copolymer. Asymmetry was held constant at $f_\mathrm{A} = 0.1$. The strict reptation algorithm was used. For each value of N ($N_\mathrm{A} = N \times f_A$), the amplitude of the potential field, α was varied. The results show that D/D_0 is a function only of the product αN_A.

This behavior is qualitatively similar to the recent experimental measurements of diffusion of an asymmetric diblock copolymer in a spherical domain structure, although the conversion between the amplitude of the periodic potential field α and the interaction parameter χ is not trivial. In both the experiment and simulation, D/D_0 decreases exponentially for χN_A or αN_A above a certain value. Below this value, D/D_0 decreases with χN_A or αN_A much less strongly. One difference, however, is that the experiment showed a somewhat larger slope of 1.2, which cannot be explained by a simple activation theory. It should be noted that in the experiment, the shape of the potential field, for example, the interfacial width, changes as χ or N_A increases/decreases while, in the simulations, the width is held constant. We look into the effect of the interfacial thickness of the potential field in the next section.

The Effect of Interfacial Thickness of the Spherical Domains on Diffusion. In this section, we examine the effect of the width of the interface between a spherical A domain and the continuous B domain. The parameter controlling the interfacial width, C, is changed from 1 to 100, while the other parameters except α are fixed. D is held at 0 to ensure that only C changes the width of the interface. The potential field with $C = 1$ is almost sinusoidal, which is physically meaningful when the amplitude of the periodic potential field is small. The potential field with $C = 100$ is almost a step function and represents a periodic potential field in the limit of strong segregation. In real systems, the interfacial width should fall between those two limiting cases. D/D_0 is plotted against αN_A in Figure 3. N_A is held constant (1000), and the α dependence is plotted for a series of different C values. For $C = 1$, the

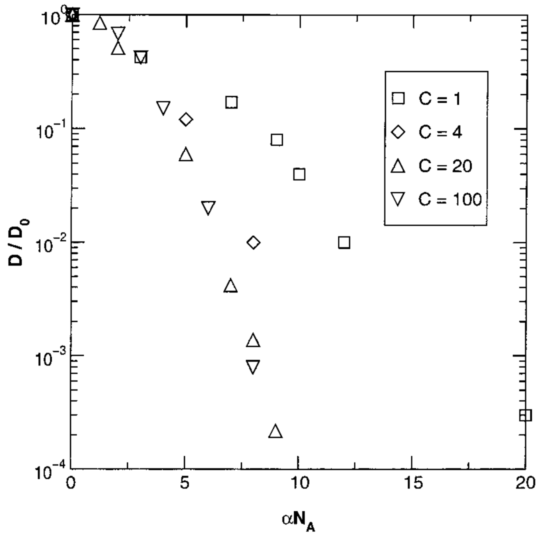

Figure 3. The effect of interfacial width on the normalized diffusion coefficient, D/D_0, in a three-dimensional bcc potential field with the strict reptation algorithm. The asymmetric parameter D was set equal to 0 so that the interfacial width is only a function of the parameter C. N is fixed at 1000, f_A is fixed at 0.1, and α was varied for various values of C.

reduction of D/D_0 is small, and the slope does not reach −1, the slope characteristic of simple activation-controlled diffusion. For $C = 4$, the reduction becomes stronger and more significant. For $C = 20$ and 100, the reduction becomes even stronger and evidently approaches a limiting curve, as no difference in D/D_0 is observed for these two different values of C.

In a potential field with a large interfacial width, an A block of a diblock copolymer chain is not fully surrounded by A monomers in a spherical A domain. Moreover, the A block does not have full contact with B monomers in the B domain during activated movement to another A domain. Therefore, the difference in the potential energy is smaller than in the simple activation picture, in which an A monomer of an A block has full contact with A monomers in a spherical A domain and with B monomers in the B domain, leading to a potential barrier of χN_A. As C increases, the shape of the potential field becomes step function-like, and this simple activation picture becomes more accurate.

In a real system, C is not an independent parameter but a function of χN. χ or N change both the amplitude of the potential field α and the width of the potential field C. Qualitatively, we can draw a curve that follows the points for small C in the small αN_A region and follows the points for large C in the large αN_A region. In that case, the slope of −1.2 that is experimentally observed for self-diffusion may be still compatible with the results of the simulation.

Comparison between Reptation and Rouse Simulation of Asymmetric Diblock Copolymer Diffusion. The mechanism of diffusion may have some effects on the reduction of diffusion by a periodic potential field. For instance, when the diffusing chain is governed by Rouse dynamics, the diffusion perpendicular to lamellae should be much slower than the diffusion parallel to the lamellae since there is no potential barrier in the direction parallel to the lamellae. The diffusion of an entangled diblock copolymer in a lamellar structure, however, does not show such strong anisotropy. The slowing down of diffusion in the direction parallel to the lamellae has been observed experimentally to be exponential in χN. In Rouse dynamics, the three equations of motion in the three orthogonal directions are independent; therefore, the diffusion parallel to a one-dimensional potential field (lamellae) is not reduced. The reptational dynamics, however, has off-diagonal terms in the mobility tensor that couple the force acting on the chain in all three directions. In such a case, the mechanism of diffusion in an absence of the potential field strongly influences the reduction of diffusion in a potential field in a particular direction.

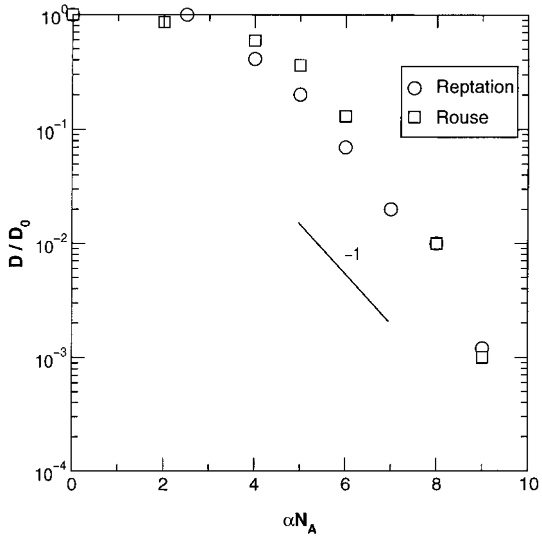

Figure 4. A comparison between the reptational simulation and the Rouse simulation in a three-dimensional bcc potential field. $C = 5.5$, $D = 0.25$, $f_A = 0.1$, and $N = 1000$. α was varied, and D/D_0 was plotted against α.

We compare the two different algorithms for simulation of diffusion in a three-dimensional potential field with bcc symmetry. The shape of the potential field, which is defined by the parameters C and D, is fixed throughout this comparison. The set of parameters, $C = 5.5$ and $D = 0.25$, fit the interfacial width of the asymmetric PS−PVP diblock copolymer used in the corresponding experiments in our group.[7,8] PS and PVP have an interaction parameter of approximately 0.1, and the PVP fraction is about 0.1. N_A is also held constant, and α is varied to identify the dependence of the diffusion coefficient on the potential amplitude. In Figure 4, we plot D/D_0 as a function of αN_A. The two diffusion algorithms show almost the same order of magnitude of the reduction of the diffusion coefficient throughout the αN_A range. It should be noted that this is a comparison of *normalized* diffusion coefficients. The raw diffusion coefficient, D, of reptation must be smaller than D of Rouse under the same conditions, but the D_0's are also different by a similar ratio. The slope of D/D_0 as a function of αN_A gradually increases as αN_A becomes larger and reaches approximately −1 in the range $\alpha N_A \geq 5$, irrespective of the mechanism of diffusion in the absence of a potential field.

The above comparison suggests that the thermodynamic activation process controls the diffusion of diblock copolymers over a fairly large range of αN_A. This is primarily due to the discrete spherical domain structure that allows no short-cut path to neighboring domains. Therefore, neither the internal structure nor the mechanism of diffusion compete with the thermodynamic activation process in the spherical domain structure. In contrast, a diblock chain in a lamellar structure may retract one of its blocks from a tube and stretch into a

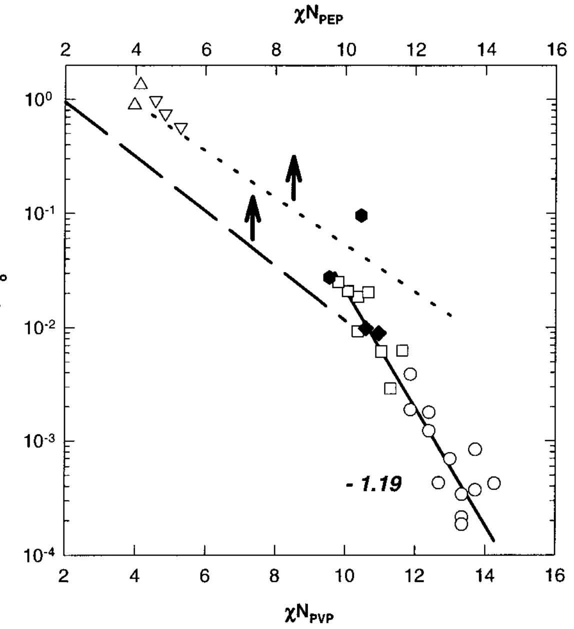

Figure 5. Experimental universal χN_A dependence of the normalized diffusion coefficients $\langle D\rangle/D_0$ of poly(styrene-*b*-2-vinylpyridine) (PS−PVP) diblock copolymers.[7] χN_{PVP} and χN_{PEP} are the product of χ and the degree of polymerization of the minority block. Symbols are PS−PVP32 (upward triangle), PS−PVP46 (downward triangle), PS−PVP70 (hexagon), PS−PVP77 (square), PS−PVP97 (diamond), and PS−PVP114 (circle). The number following each "PS-PVP" is the number-average molecular weight/1000. The dotted and dashed lines represent the data of Lodge and co-workers on symmetric PEP−PEE diblock copolymer diffusing parallel to and perpendicular to the lamellae, respectively.[3]

new tube without paying an enthalpic penalty to move parallel to the lamellae, resulting in diffusion with χ independence.[3]

Simulation of Diblock Copolymer Self-diffusion: Symmetric versus Asymmetric Diblock Copolymers. Recently, an experimental comparison between diblock copolymer diffusion in a lamellar structure and a spherical ordered structure has shown that there is a difference in the prefactor β in the exponential dependence $D/D_0 \sim \exp(\beta\chi N_A)$, where N_A is defined as the number of segments in the minority block. ($N_A = 1/2N$ for symmetric diblock copolymer in a lamellar structure.) Here, we reproduce the plot in Figure 5. The value of β for symmetric diblock copolymers in a lamellar structure is approximately −0.5, and for asymmetric diblock copolymers in a spherical domain, structure β is approximately −1.2. Since the experimental range is neither in weak segregation nor in strong segregation, it is difficult to understand the difference theoretically.

Four series of simulations are compared: (1) a Rouse simulation of asymmetric diblock copolymers in a spherical domain structure with a bcc symmetry, (2) a reptation simulation of asymmetric diblock copolymers in a spherical domain structure with a bcc symmetry, (3) a Rouse simulation of symmetric diblock copolymers in a lamellar structure, and (4) a reptation simulation of symmetric diblock copolymers in a lamellar structure.

For the simulations of diffusion in lamellar structures, the diffusion coefficients parallel to and perpendicular to the lamellae may differ. The diffusion coefficients of symmetric diblock copolymers in lamellar potential fields with two diffusion mechanisms, that is, Rouse or reptation, in the directions perpendicular and parallel to the lamellae are compared with the diffusion of asymmetric diblock copolymers in a spherical domain structure in Figure 6. *D* from a Rouse simulation of diffusion in a lamellar structure in the direction parallel to the lamellae is equal to D_0, since the off-diagonal term of the mobility tensor for the Rouse model is zero; it is not plotted in Figure 6. In Figure 6, D/D_0 is plotted as a function of αN_A where N_A is held constant at 1000 and α is varied. The potential field for the spherical domain structure is defined by $C = 5.5$ and $D = 0.25$ in eq 1. The potential field for the lamellar structure is given by

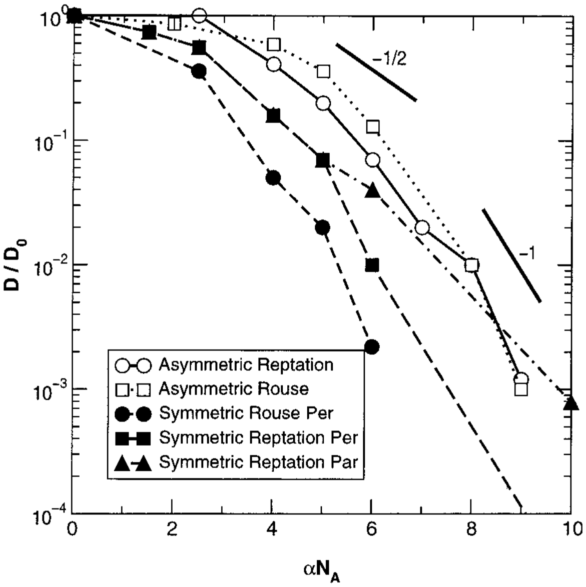

Figure 6. A comparison between the simulations of symmetric diblock copolymers in lamellar potential fields and the simulations of asymmetric diblock copolymers in bcc potential fields. For asymmetric diblock copolymer chains ($f_A = 0.1$), the diffusion is simulated in the bcc potential field by both the reptation and Rouse algorithms. For symmetric diblock copolymer chains ($f_A = 0.5$), the diffusion is simulated in the lamellar potential field by both the reptation and Rouse simulations. The diffusion in a perpendicular direction is represented by "per" and that in a parallel direction is represented by "par" in the figure. The "Symmetric Rouse Per" result is omitted because D/D_0 is 1 regardless of the presence of a potential field. The details of the parameters specifying the potential fields can be found in the text.

$$\nu(x) = \gamma \tanh[C \cos(x)] \tag{14}$$

where *C* is set to 3, which gives a reasonable interfacial thickness for the system investigated by Dalvi et al.,[3] and *x* is the coordinate perpendicular to the lamellae. γ normalizes the amplitude of the potential to 1.

The diffusion of symmetric diblock copolymers in lamellae simulated by the reptational diffusion algorithm is almost the same in the directions perpendicular and parallel to the lamellae up to $\alpha N_A = 5$, which is consistent with corresponding experimental results by Dalvi et al.[3] However, when $\alpha N_A > 5$, the perpendicular diffusion becomes slower than the parallel diffusion. The ratio D/D_0 in the perpendicular direction drops below 10^{-4} at $\alpha N_A = 10$ but could not be determined accurately due to a lack of statistics.

The slowing down of diffusion in the direction parallel to the lamellae is explained by a mechanism in which a diblock copolymer chain has to pull one of the blocks, say an A block, from a tube in the A domain through the B domain by executing motion only along its contour. Dalvi et al. also observed that D/D_0 eventually crossed over (at $\alpha \gg 1$) to αN_A independent diffusion. This crossover is explained by a star polymer-like chain retraction mechanism associated with contour length fluctuations. In the present *strict* reptation algorithm, however, there is no mechanism that changes the length of contour. Such a motion is prohibited in the simulation.

The Rouse simulation of the diffusion of symmetric diblock copolymers shows a smaller value of D/D_0 than does the reptation simulation. Note that this does not imply that D from a Rouse simulation is smaller than D from a reptational simulation, but that the normalized effect of the potential field on the diffusivities, D/D_0, is stronger for the Rouse simulation. A possible interpretation is the following. In a lamellar 1-D potential field, diblock chains are oriented along the direction perpendicular to the lamellae. On small scales (on the order the dimensions of a diblock copolymer chain), the reptational diffusion in the direction of an oriented tube of the diblock copolymer is faster than in the other directions.[11] Therefore, the lamellar potential field slows the diffusion in the perpendicular direction energetically but also enhances the diffusion by orienting the polymer chain in the direction perpendicular to the lamellae. The two effects work against each other, thus producing less reduction of D/D_0 by the potential field than the case where the tube is unoriented. On the other hand, for the Rouse simulation, the diffusion is reduced purely through the potential field acting only on the diffusion in the perpendicular direction.

For diffusion of symmetric diblock copolymers in a lamellar structure, the mechanism of diffusion parallel to the interface is strongly affected by entanglements. Molecular dynamic simulations of such diffusion by Murat et al.[12] in the crossover regime from Rouse diffusion to diffusion under fully entangled conditions reveals a complicated picture. As the chain length increases, entanglement effects are reduced from those expected in an isotropic melt due to chain stretching normal to the interface. Neither our Rouse diffusion simulations nor our strict reptation simulations can capture such effects, and we must rely on the more accurate molecular dynamics simulations for accurate results in this regime. On the other hand, such effects on diffusion of the asymmetric copolymers along the sphere interface should have little effect on the long-range diffusion. Our simulation of diffusion in such structures show that the entanglements enter only in their effects on D_0, that is, D/D_0 shows nearly the same dependence on αN for both the Rouse and strict reptation simulations.

The PEP−PEE materials of previous experiments[3] with oriented lamellar structures have molecular weights well above the molecular weight between entanglements M_e, which is consistent with the reptational simulation. The PS−PVP diblock copolymers with spherical domain structures have molecular weights above, but not far above M_e ($2 \times M_e < M < 6 \times M_e$). The simulations show, however, that entanglements have a weak effect on the diffusion of asymmetric diblock copolymers in spherical domain structures. We can qualitatively compare the reptational simulation of a symmetric diblock copolymer in a lamellar potential field and the reptational simulation of an asymmetric diblock copolymer in a bcc potential field with experiments on PEP−PEE (lamellar) and PS−PVP (spherical), respectively. The mapping of the interaction parameter χ into an amplitude of the potential field α requires a numerical self-consistent field calculation for a quantitative comparison. Here, we qualitatively compare the simulations and experiments. From Figure 4 and Figure 5, the following similarities are found. The diffusion of symmetric diblock copolymers in the region where D/D_0 is greater than 0.01 in the plot shows the approximate slope of −1/2, which is consistent with experimental results. It should be noted that the slope approaches −1 for the direction perpendicular to the lamellae but does not reach −1 for the direction parallel to them, even at fairly large αN. Experimentally, however, diffusion coefficients have not been measured in the large χN_A regime. With the strict reptation simulation, we cannot simulate the *block-retraction* mechanism proposed by Dalvi et al.,[3] in which the diblock copolymer chain retracts one of the blocks and stretches it into a new configuration without paying any potential energy penalty but with an entropic penalty similar to that involved in the mechanism of diffusion of branched polymers.[15] On the other hand, the slope of D/D_0 for asymmetric diblock copolymers approaches −1 for both the simulation and the experiment. The slope of −1.2 obtained in the experiment might be interpreted as a shape change of the potential, which changes from a sinusoidal to steplike shape as the parameter χN_A increases. Clearly, the shapes of the potential fields do not change in our simulation. The effect of the shape of the potential (or the thickness of the interface) has been previously discussed. It is noteworthy that we found in our simulation a significant difference in diffusivity depending on the presence of entanglements in lamellae, but not in spherical domains. A recent experiment[4] on unentangled symmetric poly(styrene−isoprene) (PS−PI) block copolymer in shear-aligned lamellae showed qualitatively[17] that the diffusion in the direction perpendicular to the lamellae decreases 40 times more than that in the direction parallel to the lamellae. The PS−PI has an order−disorder transition at 160 °C, and the significant reduction of the diffusion is observed at 90−110 °C; therefore, the reduction of diffusivity begins at fairly small χN, although χN was not calculated in the reference. The experimental findings agree very well with our simulation result. In our simulation, the diffusion of symmetric unentangled (Rouse) diblock copolymer in the direction perpendicular to the lamellae decreases significantly at fairly small αN_A, while the diffusion of entangled diblock copolymer starts to slow at larger αN_A and with a smaller dependence on αN_A.

Diffusion of Triblock Copolymers. The experimental study of the diffusion of diblock copolymers was extended to ABA triblock copolymers (PVP−PS−PVP triblock copolymers) in a spherical domain structure.[16] The experiment showed that the D/D_0 of ABA triblock copolymers decreases exponentially with χN_A at fairly large χN_A, where N_A is the number of segments of each A block. The result is attributed to the mechanism in which an ABA triblock copolymer activates only a single block at a time and executes a *walk* through a lattice of spherical domains. It is possible for ABA triblock copolymers to detach only one A block from an A spherical domain and to move the A block to another A spherical domain as a fundamental step of the diffusion mechanism. The thermodynamic barrier for this mechanism of ABA triblock copolymers is χN_A, which is same

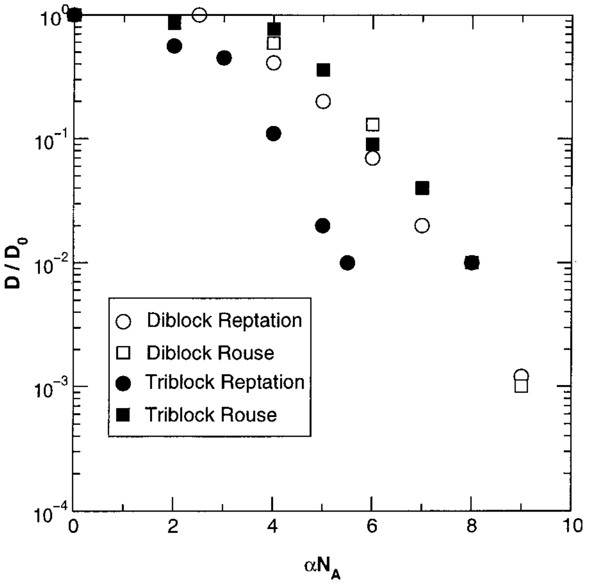

Figure 7. A comparison of diblock copolymer and triblock copolymer diffusion in a bcc potential field by both the reptation and Rouse algorithms. The potential field used in this simulation is the same as in Figure 4. N_A for ABA triblock copolymer is defined as the number of segments of each A block.

as that of diblock copolymers. As a result, D/D_0 of the triblock copolymer can be almost same as that of the diblock copolymers and exhibits the same decrease with χN_A, given approximately by

$$D/D_0 \sim \exp(-\chi N_A) \tag{15}$$

Both the reptation and Rouse simulation algorithms were extended to ABA triblock copolymers in a bcc potential field. The result of the ABA triblock copolymers is compared with that of the diblock copolymers. For ABA triblock copolymers, we define N_A as the number of segments in *each* A block in the ABA triblock copolymer. Thus, when comparing a diblock copolymer and triblock copolymer with the same N_A, the total number of segments of the triblock copolymer is twice that of the corresponding diblock copolymer. The potential field is the same as that used in Figure 4. The results of the simulations are shown in Figure 7. For this comparison, N_A was held constant, and α was varied. It is clearly seen that D/D_0 for the triblock copolymer in the Rouse simulation agrees with that of the diblock copolymer. On the other hand, D/D_0 for the reptational simulation of the triblock copolymer differs significantly from that of the diblock copolymer.

The Rouse simulation for the triblock copolymer also produces a D/D_0 that depends on αN_A as $\exp(-\alpha N_A)$ in the fairly large αN_A regime. That result agrees with the experimental observations quite well.[16] A consistent mechanism that leads to the $\exp(-\alpha N_A)$ dependence is a *walking* diffusion of the triblock copolymer, where a single A block is thermodynamically activated at a time to move one A block from one potential well to another. Other evidence of *walking* diffusion in this simulation is the presence of copolymers that bridge between A domains that is detectable during the simulation. We monitored an end-to-end distance of a triblock copolymer as a function of time during the diffusion simulation and computed the mean square end-to-end distance, $\langle R \rangle \equiv \sqrt{\langle r(t)^2 \rangle}$, where $r(t)$ is the end-to-end distance at time t and the brackets represent the time average. Two sets of potential fields are used: (1) the spacing of the potential field is set to the value consistent with the size of the diffusing triblock or diblock copolymer (self-diffusion) and (2) the spacing of the potential field is three times larger than that of (1) (tracer diffusion). The result of this set of simulations is shown in Figure 8.

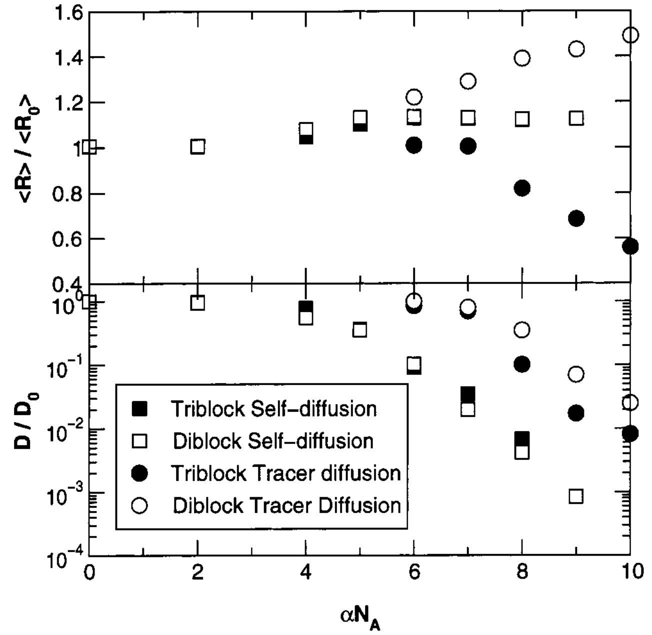

Figure 8. A comparison of diblock copolymer and triblock copolymer diffusion in a bcc potential field using the Rouse simulation. The potential field used in this simulation is the same as in Figure 4 except for the spacing parameter L. For the self-diffusion simulation, L is estimated from the $2\pi/q^*$ predicted by Leibler,[18] while for tracer diffusion, L is three times larger than the natural lattice spacing of the predicted value, i.e., the spacing of the lattice is larger than the diffusing diblock or triblock chains. N_A for ABA triblock copolymer is defined as the number of segments of an each A block.

The value $\langle R \rangle / \langle R \rangle_0$ is always greater than 1 when the potential field is consistent with the chain dimension, where $\langle R \rangle_0$ is the end-to-end distance of the triblock copolymer in the absence of the potential field, indicating the presence of bridging conformations during the Rouse simulation. Again, the D/D_0 of diblock and triblock copolymers are indistinguishable. If both chains ends reside in the same spherical domain, $\langle R \rangle / \langle R \rangle_0$ would be smaller than 1. Such an extreme case is seen in tracer diffusion of the triblock copolymer. $\langle R \rangle / \langle R \rangle_0$ decreases as the potential field becomes strong. The rapid decrease of $\langle R \rangle / \langle R \rangle_0$ indicates that as the potential field becomes strong, the end blocks reside most of the time in the same spherical domain, since the distance between spherical domains is too far for the triblock copolymer chain to bridge. In such a case, D/D_0 of the triblock copolymer also decreases more than that of diblock copolymers. It should be noted that the direct comparison between self-diffusion and tracer diffusion is not appropriate since the increase in spacing with the other parameters fixed causes the interfacial thickness to widen markedly, which makes the diffusion faster (see Figure 3).

The reptation simulation of the triblock copolymer shows different behavior from the others. The potential field slows the diffusion strongly. It could be that the triblock chains are not allowed to walk through in the potential field, since the triblock chain is completely confined in a tube and the contour length fluctuation is prohibited in this strict reptation algorithm. The chain has to execute the motion only along the tube; therefore, it is not possible to activate a single A block and move it to another domain with the other end of A block fixed in a potential well. Therefore, "walking" diffusion, which gives $\exp(-\alpha N_A)$, is totally prohibited. A triblock copolymer chain has to expose both A blocks to the B continuous domain to diffuse, giving a much higher thermodynamic barrier to diffusion. The experiment[16] used triblock copolymers which were only sparsely entangled; therefore, it may be more reasonable to compare them with the Rouse simulation rather than with the *strict* reptation simulation.

Conclusions

We find that the normalized diffusion coefficients D/D_0 of AB diblock copolymers with a short A block ($f_A = 0.1$) decrease exponentially with the product of the amplitude of the potential field and the number of segments of A (shorter) block independent of the type of simulation, that is, Rouse or strict reptation. Both results are compatible with a simple *activated hopping* diffusion mechanism, where thermodynamic activation of a diblock copolymer chain from a potential well (spherical domain) controls the diffusion.

Simulations that compare diffusion of symmetric and asymmetric diblock copolymers qualitatively agree with results of experiments. The simulation is able to show the effect of entanglements on the anisotropy and reduction of diffusion in lamellae.

The Rouse simulation of triblock copolymer diffusion gives almost the same D/D_0 as for a diblock copolymer with the same N_A in each A block but double the total molecular weight. That agrees well with the recent experimental results and the physical picture that triblock copolymers activate only one A block at a time and *walk* in the potential field.

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