Chain Diffusion in Lamellar Block Copolymers

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Abstract

Diffusion of symmetric diblock copolymer chains in macroscopically oriented lamellar block copolymers are studied in a molecular dynamics simulation. Results for diffusion constant both parallel $D_{\parallel}$ and perpendicular $D_{\perp}$ to the lamellar planes are compared to results in the disordered one phase region. For diblocks of length $N = 40 (1.1 N_e)$ and $100 (3 N_e)$, where $N_e$ is the entanglement length of a homopolymer melt at the same density, $D_{\parallel}$ is nearly independent of $\chi$, while $D_{\perp}$ is strongly suppressed as $\chi$ is increased. These results are in agreement with theoretical predictions based on the Rouse model. The isotropic diffusion constant of quenched disordered systems is approximated fairly well by $(2D_{\parallel} + D_{\perp})/3$ of the corresponding lamellar system.
The question whether lamellar ordering modifies self diffusion in a symmetric diblock melt has been the subject of several recent theoretical and experimental studies. Barrat and Fredrickson [1] argued that for chains obeying Rouse dynamics, the diffusion within a lamellar plane is unaffected by the lamellar structure, while perpendicular diffusion is retarded by an amount determined by the degree of segregation. Measurements on quenched, unoriented samples [2,3] indicated that there is no discontinuity for the diffusion constant at the order-disorder transition (ODT). The samples used in these studies were polycrystalline, without macroscopic ordering, so that the separate components of the diffusion coefficient could not be determined. Such a separation was achieved [4] for entangled chains by macroscopically orienting the sample using oscillatory shear. Measurements on such mono domain samples showed less anisotropy than predicted by the Rouse model. For well entangled chains, both parallel and perpendicular diffusion have to involve translation of the A segments of the chains into the B domains, so that both components are reduced by the lamellar structure, though not necessarily to the same extent. Such an activated reptation mechanism in which the diffusion constant $D$ decays as $\exp(-\chi N)$ was observed by Lodge and Dalvi [5] for highly entangled melts of poly(ethylene-propylene)-poly(ethylene) diblock copolymers. The difference between the diffusion constants parallel $D_\parallel$ and perpendicular $D_\perp$ to the interface was found to decrease as the ODT is approached. Block-retraction mechanism, similar to arm-retraction known from star polymers, is also found to play a role in the diblock diffusion and also gives rise to an exponential decay of $D$ with increasing $N$.

Computer simulations of diblock copolymer systems have been mostly restricted to studying the statics and thermodynamics of such systems [6]. The only simulation which studied diffusion in a diblock system is by Pan and Shaffer [7], who studied a symmetric diblock in the strong segregation regime ($\chi N = 45$) for several chain lengths $N$ using the bond fluctuation method on a lattice. They found that $D_\parallel$ was roughly two times smaller than $D$ for a homopolymer melt and the critical chain length at which entanglements became important was comparable in the two systems. No perpendicular diffusion was observed for this value of $\chi N$. Since these simulations were done on a lattice, there was no a priori way to
determine the equilibrium lamellar spacing $d_l$.

Here we study by continuum space molecular dynamics simulations the diffusion constants of perfectly oriented lamellar systems both in the plane of the lamella and in the perpendicular direction, for chains of length 40 and 100, corresponding to about 1.1 and $3N_e$ respectively. $N_e \simeq 35$ is the entanglement length for a homopolymer melt [8], at the same average density ($\rho \simeq 0.85\sigma^{-3}$). $d_l$ is determined from a constant pressure simulation. It is then fixed and $D_\parallel$ and $D_\perp$ are determined at constant volume. The results are compared to simulations in the isotropic disordered phase.

We use a coarse grained bead-spring model similar to that used in our earlier studies of polymer melts and networks [8] and tethered chains [9]. Each chain consists of $N$ beads (monomers), connected to form a linear chain. For diblocks, the model is generalized to two types of polymer species, say $A$ and $B$, which are connected in a block of $fN$ beads of type $A$ connected to a block of $(1 - f)N$ beads of type $B$. Here we consider only symmetric diblocks, $f = 1/2$. The interaction potential $U_{IJ}(r)$ between two beads of types $I, J = \{A, B\}$ separated by a distance $r$ is taken as the repulsive part of a Lennard Jones 6 : 12 potential,

$$U_{IJ}(r) = \begin{cases} 4\epsilon_{IJ} \left[ \left( \frac{\sigma_{IJ}}{r} \right)^{12} - \left( \frac{\sigma_{IJ}}{r} \right)^6 + \frac{1}{4} \right] & r \leq r_c; \\ 0 & r > r_c, \end{cases}$$

where the cutoff distance $r_c = 2^{1/6}\sigma_{IJ}$. Here, $\epsilon_{IJ}$ and $\sigma_{IJ}$ are, respectively, parameters fixing the energy and length scale for monomers of type $I$ and $J$. Adjacent monomers along the chains are coupled through an anharmonic FENE potential, chosen to eliminate unphysical bond crossings or breaking [8,9]. All the interactions are short ranged and the model is very efficient computationally. For symmetric copolymers, we set $\epsilon_{AA} = \epsilon_{BB} = \epsilon$, $\epsilon_{AB}/\epsilon = 1 + \tilde{\epsilon}$, and $\sigma_{AA} = \sigma_{BB} = \sigma_{AB} = \sigma$. The latter choice simply means that all monomers have the same interaction range and thus the two species have the same molar volume. All of our results are reported in terms of $\sigma$ and $\epsilon$, with $\tau = \sigma(m/\epsilon)^{1/2}$ for the time scale, where $m$ is the mass of a monomer. The energy parameters are a special case of ($\epsilon = 1$) $\tilde{\epsilon} = \epsilon_{AB} - \frac{1}{4}(\epsilon_{AA} + \epsilon_{BB})$, used in simple lattice models such as in Flory-Huggins theory. In ref. [10], we showed that...
simply introducing this difference in the repulsive interaction strength between like and unlike monomers was sufficient to drive phase separation. By varying $\tilde{\epsilon}$, while leaving the temperature $T$ constant, one can induce a phase transition from a homogeneous blend to a system with two segregated coexisting phases $[\tilde{\epsilon}_c = 3.40(5)k_BT/N]$ [14]. This approach also has the advantage of overcoming a problem inherent in experimental studies: namely, the dependence of the monomeric friction constant on the temperature. It is somewhat reminiscent of recent elegant experiments by Gehlsen et al. [11] in which the phase separation of binary mixtures is studied as a function of the difference in deuterium content between two otherwise identical polymer species.

We study $M$ chains of length $N$ by solving Newton’s equations of motion using a velocity-Verlet algorithm [12] with a time step $\Delta t = 0.013\tau$ [9,10]. Two different starting states were used: disordered and lamellar. In the former case, we studied cubic systems at density $\rho = 0.85\sigma^3$ [8]. The lamellar state was constructed as described in ref. [10]. Since $d_l$ depends on $\tilde{\epsilon}$ and is not known a priori, we first ran a constant pressure simulation [10] at a $P = 5\epsilon\sigma^{-3}$ in which the dimensions of the simulation cell, parallel $L_\parallel$ and perpendicular $L_\perp$ to the lamellar plane varied independently [13] for each value of $\tilde{\epsilon}$. $d_l$ adjusts itself rather rapidly (a few hundred thousand time steps). With increasing $\tilde{\epsilon}$, $L_\perp$ increases and the cross sectional area $L_\parallel^2$ decreases, such that the overall density remains fairly constant. The equilibrium lamellar spacing increases rapidly with $\tilde{\epsilon}$ and then saturates as shown in Fig. 1. The results scale with $N$ as predicted by self-consistent field theory [14–16]. For large $\tilde{\epsilon}$ the chains are highly stretched and the number of $AB$ contacts is small. Thus, further increase in the repulsive energy between the two species does not strongly affect $d_l$. In this regime $\chi$ is no longer proportional to $\tilde{\epsilon}$ as often incorrectly assumed in many previous lattice simulations of diblock copolymer systems [14].

After $d_l$ is determined, we fixed the volume to study the dynamics in the lamellar phase. The results presented here are for $M = 1600$ chains of length $N = 10$, $M = 800$ chains of $N = 20$ and $40$ and $M = 200$ chains of $N = 100$. The $N = 40$ and $100$ systems were studied in both the disordered and lamellar regions of phase space, while $N = 10$ and $20$ systems
were only simulated in the disordered phase. The lamellar systems contained 100 chains per layer for \( N = 40 \) and 50 chains per layer for \( N = 100 \), giving \( L_\perp = 4d_l \) for \( N = 40 \) and \( 2d_l \) for \( N = 100 \). From our study of the order parameter in the ordered phase as a function of \( \tilde{\epsilon} \), we estimate that \( \tilde{\epsilon}_{ODT}(40) = 0.85 \pm 0.05 \) and \( \tilde{\epsilon}_{ODT}(100) = 0.28 \pm 0.03 \) [10].

To study the diffusion in both phases, long runs were necessary to obtain good statistics. Typical runs for \( N = 40 \) were of length \((5.2 - 10.0) \times 10^4 \tau\) while for \( N = 100 \), they were of order \((3.9 - 6.5) \times 10^5 \tau\). In addition, lamellar systems for \( N = 200 \) and \( N = 400 \) were also simulated for visualization of the chain motion. However, these simulations were too large to run long enough to obtain the diffusive constants. These results will be presented in a later paper.

We follow the motion of the chains’ center of mass through \( g_3(t) \), whose components are defined by

\[
g_{3\alpha}(t) = \left\langle [r_{cma}(t) - r_{cma}(0)]^2 \right\rangle, \tag{2}
\]

with \( \alpha = x, y, \) or \( z \). Here \( r_{cma}(t) \) are the components of the center of mass of a chain and \( \langle \cdots \rangle \) denotes both an ensemble average over all the chains in the system and an average over different starting states. At sufficiently long times, \( g_{3\alpha}(t) \) exhibits diffusive motion with \( g_{3\alpha} \rightarrow 2D_\alpha t \). In the disordered phase, the three diffusion constants are identical and equal to \( D \), the isotropic diffusion constant. In the lamellar phase, the motion in the \( xy \) plane (plane of the lamella) is expected to be faster than the motion between the lamellar planes (\( z \) direction). The parallel diffusion constant \( D_\parallel = (D_x + D_y)/2 \), and \( D_\perp = D_z \).

The behavior of \((g_{3x}(t) + g_{3y}(t))/2\) for some of the \( N = 40 \) systems is shown in Fig. [2]. For the isotropic systems (homopolymers and the disordered diblocks), the quantity shown is \( g_3(t)/3 \). For times longer than about \( 10^4 \tau \), all the systems show diffusive behavior. The same quantity for a homopolymer melt and a lamellar system of chain length \( N = 100 \) is shown in Fig. [3]. The transition to the diffusive regime in the lamellar system takes place around \( t \approx 10^4 \tau \), somewhat later than in the homopolymer melt. This delay in the onset of the diffusive motion is common to all lamellar systems studied. The diffusion constants were
calculated from the slope of \((g_{3y}(t)+g_{3y}(t))/2\) in the diffusive regime. Perpendicular diffusion is observed only for systems sufficiently close to the ODT. For large \(\tilde{\epsilon}\), \(g_{3z}(t)\) saturates at about the square of the thickness of the interface region, within which the junction points of the chains are localized.

Chains of length 40 (1.1\(N_c\)) are clearly in the Rouse regime and are expected to obey Rouse dynamics. Barrat and Fredrickson modelled the self diffusion of a Rouse chain in a lamellar system as tracer diffusion of such a chain in a periodic potential varying in one dimension, perpendicular to the lamella planes [1]. According to this study, diffusion in the plane is not affected by the periodic potential, while diffusion perpendicular to the lamella is slowed down by an amount dependent upon the magnitude of the concentration fluctuations. Near the ODT, \(D_\perp\) is expected to decrease by less than 40% compared to \(D_\parallel\), while in the strongly segregated phases it should decay exponentially with \(\chi N\) [1]. To check these predictions, we plot in Fig. 4 both \(D_\parallel\) and \(D_\perp\) as a function of \(\tilde{\epsilon}\) for lamellar systems as well as the isotropic \(D\) for disordered systems. \(D_\parallel\) in the lamellar \(N = 40\) systems is only very weakly dependent on \(\tilde{\epsilon}\). At the ODT, \(D_\parallel/\tau/\sigma^2 \simeq 9.5 \times 10^{-4}\), while in the strong segregation limit (\(\tilde{\epsilon} = 9.0\), not shown in Fig. 4), \(D_\parallel/\tau/\sigma^2\) decreases only to \(8.0 \times 10^{-4}\). For a homopolymer melt (\(\tilde{\epsilon} = 0\)), the isotropic diffusion constant is about \(1.5 \times 10^{-3}\sigma^2/\tau\), so that the diffusion constant in the isotropic phase close to ODT is lower by about 50% compared to the diffusion constant in the homopolymer melt. This reduction results from the increased friction from the local motion of the monomers. \(D_\perp\), on the other hand, decays rapidly with \(\tilde{\epsilon}\). While near the ODT the ratio \(D_\perp/D_\parallel \simeq 0.8\), it is reduced to about 0.03 for \(\tilde{\epsilon} = 1.4\). The reduction of about 20% near ODT is consistent with the Barrat-Fredrickson prediction. For higher values of \(\tilde{\epsilon}\), we could not observe any perpendicular diffusion during the time scale of our simulations.

The four non-zero values of \(D_\perp\) for \(N = 40\) can be fitted nicely with an exponential decay of the form \(D_\perp/D_o = 0.57 \exp[-0.16N(\tilde{\epsilon} - \tilde{\epsilon}_{ODT})]\), where \(D_o\) is the value the diffusion constant in the homopolymer melt. To make a quantitative comparison with the theory of Barrat and Fredrickson [1], we note that they predict that when \(\chi\psi_0 \approx \chi_{ODT}\), where \(\psi_0\) is
the amplitude of the density variation in the lamella, $D_\perp$ is reduced by a factor of about 10. For our system at $\tilde{\epsilon} = 1.0 > \tilde{\epsilon}_{ODT}$, $\psi_0 = 0.83$, so that $\tilde{\epsilon}\psi_0 = 0.83 \approx \tilde{\epsilon}_{ODT}$. For this system, $D_\perp$ is about 1/3 of the ODT value or about 3 times less suppression than predicted.

The situation for the $N = 100$ chains is qualitatively similar. This length corresponds to about $3N_e$, and entanglements are not expected to play a major role. In a homopolymer of $N = 100$ chains, crossover to reptation motion is barely observed [8]. For stretched chains, $N_e$ might even increase. The systems near the ODT all have essentially the same $D_\parallel$ (about $2.1 \times 10^{-4}\sigma^2/\tau$). The reduction in $D$ at the ODT compared to the homopolymer melt is about 40%, comparable to that seen for $N = 40$. For very high values of $\tilde{\epsilon}$, the reduction in $D_\parallel$ is comparable to that for $N = 40$ chains. In the most strongly stretched system studied ($\tilde{\epsilon} = 9.0$, not shown in Fig. 4), $D_\parallel$ is about 0.75 of $D_\parallel$ near ODT, while the same ratio is about 0.85 for $N = 40$. The perpendicular motion is significantly reduced in comparison to the parallel one. For $\tilde{\epsilon} = 0.3$ (close to the ODT), we found $D_\perp = 7 \times 10^{-5}\sigma^2/\tau$, or about 1/3 of the corresponding $D_\parallel$. We note that the suppression of $D_\perp$ near ODT is higher than for the $N = 40$ diblocks and the Barrat-Fredrickson prediction. However, for these longer chains, a more precise determination of the ODT is needed before a reliable comparison can be made. For larger values of $\tilde{\epsilon}$, no measurable perpendicular diffusion was found. For the system with $\tilde{\epsilon} = 0.5$, only two chains succeeded in translating their junction points from one interface to another during the whole course of the simulation, with no measurable $D_\perp$. For larger $\tilde{\epsilon}$, no chain exchange occurred between the interfaces.

It is also interesting to note that for quenched disordered systems (those with $\tilde{\epsilon} > \tilde{\epsilon}_{ODT}$), the isotropic $D \simeq (2D_\parallel + D_\perp)/3$ of the corresponding lamellar system [17]. Fredrickson [18] had suggested that for small anisotropy, the diffusion constant of a quenched system should be slightly larger than $(2D_\parallel + D_\perp)/3$. We do not see an evidence of the predicted enhancement. However, this prediction is only for systems very close to the ODT. Since the exact ODT of our model system is not known to a high accuracy, we cannot rule out this result.

We also studied the diffusion in the disordered regime for shorter, unentangled chains...
of length $N = 10$ and 20. For $N = 10$ and 20, the isotropic diffusion constant scales $D \sim N^{-1} f(\bar{\epsilon}/\bar{\epsilon}_{ODT})$, where $f(x)$ is a decreasing function of $x$. A comparison of these results with the theoretical predictions of Leibig and Fredrickson [19] for tracer diffusion in the disordered regime will be presented in a later paper.

Our results demonstrate that for lamellar systems of short chains (of length $N = 40$ and 100), self diffusion in the lamellar plane near the ODT is essentially unaffected by the amount of chain stretching. This is in accordance with the Rouse-like motion of chains. Perpendicular diffusion is strongly suppressed by the lamellar structure. Our results are qualitatively consistent with the Barrat-Fredrickson theory, although the amount of suppression is somewhat less than predicted. In the limit of strong stretching, some reduction in $D_{\parallel}$ is observed, possibly indicating the onset of entanglement effects. Further studies on long chains are needed to study the effect of entanglements.

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FIG. 1. The equilibrium lamellar spacing $d_l$ scaled by $N^{2/3}$ as a function of the excess AB interaction parameter $\tilde{\epsilon}$, for $N = 40$ ($\triangle$), 100 ($\circ$), 200 ($\square$), and 400 ($\bullet$).

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FIG. 2. Mean squared displacement of the center of mass parallel to the lamellar plane,
\[ \left[ \left( g_{3x}(t) + g_{3y}(t) \right) / 2 \right] \] versus \( t/\tau \) for \( N = 40 \) systems: lamellar with \( \bar{\epsilon} = 0.9 \) (\( \triangle \)) and 3.0 (\( \circ \)), homopolymer melt (\( \blacksquare \)), isotropic near the ODT, \( \bar{\epsilon} = 0.8(\square) \), and at \( \bar{\epsilon} = 3.0(\bullet) \).

FIG. 3. \( \left( g_{3x}(t) + g_{3y}(t) \right) / 2 \) versus \( t/\tau \) for a homopolymer melt (\( \circ \)) and a lamellar system with \( \bar{\epsilon} = 1.0 \) (\( \square \)) for \( N = 100 \). The lines have a slope of 1, characteristic of the diffusive regime.
FIG. 4. Diffusion coefficients as a function of the excess AB interaction parameter, $\tilde{\varepsilon}$: $D_\parallel (\circ)$ and $D_\perp (\Box)$ for $N = 40$ lamella, isotropic $D (\triangle)$ for disordered $N = 40$ melt, $D_\parallel (\diamond)$ for $N = 100$ lamella and isotropic $D (\triangledown)$ for disordered $N = 100$ melt. The lines for the $N = 40$ systems are only a guide to the eye.