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Diffusion of a Symmetric Block Copolymer in a Periodic Potential

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ABSTRACT: The tracer diffusion of a symmetric diblock copolymer with Rouse dynamics in a periodic external potential is studied by using numerical simulation, a perturbation expansion valid for weak potentials, and a thermally activated process theory valid for large potentials. In all cases, diffusion is slowed by the potential. If the theory is taken as a model for self-diffusion of a copolymer in a lamellar mesophase, the amount of slowing down predicted in the vicinity of the order–disorder transition is relatively small, at most 40%.

1. Introduction

Diblock copolymer melts exhibit a complex phase behavior, characterized by phase transitions between a disordered melt existing at high temperature and various ordered mesophases that appear as the temperature is lowered. Such mesophases arise as a result of the incompatibility between the two blocks (A and B) of the copolymers (this would trigger a macroscopic phase separation in a homopolymer blend) and of the connectivity constraints that hinder this phase separation. The mesophases are characterized by the existence of a periodic modulation in the concentration, with a period comparable to the radius of gyration R_g of a polymer chain in the melt.

The thermodynamics of these order–disorder transitions (ODT) is now reasonably well understood theoretically.[1] A mean-field theory due to Leibler[2] indicated that, for copolymers with degree of polymerization N and composition f, ordered phases would become stable for temperatures T such that $\chi(T)\, N > C(f)$. Here $\chi(T) \sim 1/T$ is the (A–B) Flory interaction parameter and $C(f)$ is a concentration-dependent function. Of particular interest is the case of symmetric copolymers ($f = {}^1/_2$), for which the mean-field theory predicts a second-order transition into a lamellar mesophase at $\chi(T)\, N \simeq 10.5$. Although later calculations[3] have shown that due to fluctuation effects the transition is actually first-order, one of its characteristics remains the existence of large concentration fluctuations near the transition point for wavevectors of magnitude $q_l \sim R_g^{-1}$. Close to the transition point, the inhomogeneous concentration field in the lamellar phase can be described by a sinusoidal wave of wavevector q_l. As the temperature is lowered, higher order harmonics start contributing to the concentration inhomogeneities, until the concentration profile eventually becomes well described by a square wave of period $2\pi/q_l$.[4]

The present understanding of the dynamical properties of copolymers near their ODT is, however, much more limited. In particular, despite several promising attempts,[5-7] a quantitative theory of the viscometric anomalies observed near the ODT[8] is still missing. Our goal in this paper will be a more modest one, in that we shall be concerned only with the study of diffusion of a copolymer in an ordered lamellar phase. Such studies were initiated in a recent theoretical paper[9] and are the subject of current experimental interest.[10] One of the motivations for studying tracer diffusion in ordered phases is that it might shed some light on the transport properties of the disordered phase, where (due to the large concentration fluctuations) the local environment experienced by a chain is similar to the one existing in the ordered phase.

Following ref 9, we shall adopt a simple, "single-chain" model for tracer diffusion in the lamellar phase. The existence of an inhomogeneous concentration field is accounted for in a mean-field fashion. The diffusing tagged chain under consideration experiences a time-independent chemical potential inhomogeneity proportional to the concentration inhomogeneity (the proportionality coefficient being $\chi k_B T/\rho$, where ρ is the monomer density). This chemical potential field is equivalent to an external potential that would act with opposite signs on the monomers of the two species A and B. Apart from this external potential, the chain obeys standard Rouse dynamics, a reasonable assumption since many copolymer melts studied experimentally are below the entanglement threshold (this is not the case, however, for the melt studied in ref 10). The model is described in more detail in the next section.

In order to study this diffusion problem, we used a combination of three approaches, described in section 3: a perturbation calculation[9] valid for small amplitudes of the external potential, a generalization of Kramer's theory of activated processes[11] valid for large amplitudes of the potential, and numerical simulation. The results of these calculations for a sinusoidal and a square wave external potential are presented in section 4. Although our main interest is in self-diffusion, we also discuss results for tracer diffusion, i.e., for a symmetric chain whose molecular weight differs from that of the host copolymer.

2. Model

Our starting point will be the Hamiltonian for a symmetric Rouse diblock copolymer chain whose monomers are subjected to the external potential $\epsilon\alpha k_B T v(X)$, where $\epsilon = +1$ for A monomers and -1 for B monomers. $v(X)$ is a dimensionless periodic function of the space coordinate X, which is assumed to vary in the direction of the concentration modulation in the lamellar phase. The period of this modulation is $2\pi/q_0$. In the following, $v(X)$ was normalized so that its first Fourier component is unity and the amplitude α is χ times the amplitude of the lamellar-phase concentration profile. Finally, we note that, due to the scalar character of the Rouse mobility matrix, the diffusion in the Y and Z spatial directions is unaffected by the periodic potential and can be described by the standard Rouse equations. It is therefore sufficient

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to consider a one-dimensional model whose Hamiltonian reads

$$H = \frac{3k_BT}{2a^2}\int_0^N \mathrm{d}s \left(\frac{\mathrm{d}X(s)}{\mathrm{d}s}\right)^2 + \alpha k_BT\int_0^N \mathrm{d}s\ \epsilon(s)\ v(X(s)) \qquad (1)$$

where $\epsilon(s) = +1$ for $s < N/2$, $\epsilon(s) = -1$ for $s > N/2$, and a is the statistical segment length, which for simplicity is assumed to be identical for the two species. The same assumption is made for the Rouse friction coefficient ζ that enters the equation of motion

$$\frac{\mathrm{d}X(s)}{\mathrm{d}t} = -\frac{1}{\zeta}\frac{\delta H}{\delta X(s)} + \theta(s,t) \qquad (2)$$

where $\theta(s,t)$ is the usual Gaussian white noise satisfying $\langle\theta(s,t)\theta(s',t')\rangle = 2k_BT\zeta^{-1}\delta(s-s')\delta(t-t')$. The diffusion constant of the chain in the absence of the external potential is therefore $D_0 = k_BT(N\zeta)^{-1}$. It will also prove convenient to introduce the dimensionless parameter $x_0 = q_0^2(Na^2/6)$ that gives a measure of the external potential wavelength in units of the unperturbed chain radius of gyration. If one takes for q_0 the value computed by Leibler[2] for the periodicity of the lamellar phase, one finds that the case of self-diffusion corresponds to $x_0 \simeq 4$. Larger or smaller values of x_0 describe tracer diffusion in a melt of copolymers respectively smaller or larger than the tracer.[9]

The Hamiltonian (1) can be transformed by the introduction of the Rouse modes y_p, defined as

$$y_0 = \frac{1}{N}\int_0^N \mathrm{d}s\ X(s)$$

$$y_p = \frac{\sqrt{2}}{N}\int_0^N \mathrm{d}s\ X(s)\cos\left(\frac{p\pi s}{N}\right),\quad p \geq 1 \qquad (3)$$

With this definition, the Hamiltonian and equation of motion now read

$$H = k_BT\sum_{p\geq 1}\frac{{y_p}^2}{2{b_p}^2} + \alpha k_BT\int_0^N \mathrm{d}s\ \epsilon(s)\ v(X(s)) \qquad (4)$$

$$\frac{\mathrm{d}y_p}{\mathrm{d}t} = -\frac{1}{N\zeta}\frac{\partial H}{\partial y_p} + \theta_p(t) \qquad (5)$$

with $b_p^2 = Na^2/(3p^2\pi^2)$ and $X(s)$ being given as a function of the y_p by

$$X(s) = y_0 + \sqrt{2}\sum_{p\geq 1}\cos\left(\frac{p\pi s}{N}\right)y_p \qquad (6)$$

The normalization of the Rouse modes in eq 3 has been chosen so that the mobility matrix entering eq 5 retains its scalar character under the Rouse transformation, a feature that will prove convenient for applying the theory described in section 3.2.

The essential reason for making this transformation to Rouse modes (which, in contrast to the case of a free Rouse chain, does not diagonalize the Hamiltonian) is that we can now define a *truncated Rouse model*. Specifically, the truncated Rouse model with p_m modes is defined by eqs 4–6, in which the sums over p appearing in eqs 4 and 6 are truncated at an upper value $p_m - 1$. Obviously, such a model with p_m degrees of freedom is easier to handle in numerical calculations than the original model defined by eqs 1 and 2, but it also retains the important feature that the interaction with the external potential is distributed continuously along the chain. The latter feature would not be preserved in a discrete "bead–spring" model involving a similar number of degrees of freedom. Physically, the truncation at p_m modes amounts to a coarse-graining of the original Rouse model on a scale $R_g/p_m^{1/2}$.

In summary, our model is completely specified by the parameters p_m, the maximum number of Rouse modes considered, x_0, αN, and by a choice of potential function $v(X)$. These last three quantities are in principle experimentally measurable, α being equal to the amplitude of the concentration inhomogeneity in the lamellar phase multiplied by the Flory parameter χ. Two different expressions for the function $v(X)$ were employed in our calculations: a cosine wave $v_1(X) = \cos(q_0X)$ and a "square wave" function $v_2(X) = 0.251\tanh[10\cos(q_0X)]$, where the amplitude is such that the first component in a Fourier expansion of v_2 is 1.

3. Theoretical Treatments

3.1. Perturbation Expansion. In ref 9, a perturbation expansion for the diffusion tensor $[D]$ of a copolymer chain in a periodic potential was obtained using field-theoretical methods. The expansion parameter is the amplitude α of the potential, and the calculation, valid for any value of x_0, was carried out to order α^2. Due to the decoupling between the different spatial directions that characterizes the Rouse model, only the XX element of $[D]$, which we denote by D_X, is nontrivial. Its relation to the quantity D defined in ref 9 is $D = (2/3)D_0 + (1/3)D_X$.

Here we present a simplified derivation of the perturbation expansion for D_X, starting from the exact Green–Kubo formula[12]

$$D_X = \int_0^\infty \mathrm{d}t\left\langle\frac{\mathrm{d}y_0(t)}{\mathrm{d}t}\frac{\mathrm{d}y_0(0)}{\mathrm{d}t}\right\rangle \qquad (7)$$

where y_0 is the center of mass position (eq 3) and the broken brackets indicate an average taken over the trajectories generated by the Langevin equation (5). Using the latter equation, eq 7 can be transformed into

$$D_X = D_0 - \frac{1}{(N\zeta)^2}\int_0^\infty \mathrm{d}t\ \langle F(t)\ F(0)\rangle \qquad (8)$$

where $F(t)$ is the total force acting on the chain center of mass, i.e.

$$F(t) = -\alpha k_BT\int_0^N \mathrm{d}s\ v'(X(s,t))\ \epsilon(s) \qquad (9)$$

and the prime denotes a derivative with respect to X. By introducing the Fourier expansion of the periodic force $-v'(X)$ (assuming, without loss of generality, that $v(X)$ is an even function)

$$-v'(X) = q_0\sum_{m\geq 1} f_m\sin(mq_0X) \qquad (10)$$

the correlation function appearing in eq 9 can be written as

$$\langle F(t)\ F(0)\rangle = \frac{1}{2}(\alpha k_BTq_0)^2\sum_{m\geq 1}{f_m}^2\int_0^N\int_0^N \mathrm{d}s\ \mathrm{d}s'\ \epsilon(s)\ \times$$
$$\epsilon(s')\ \langle\exp(imq_0(X(s,t) - X(s',0)))\rangle \qquad (11)$$

In order to get a small α expansion of D_X exact to second order in α, it is sufficient to replace the correlation function in the integrand by its unperturbed (i.e., Rouse) value. The calculation is straightforward (ref 13, eq 4-III-7) and yields[14]

$$\frac{D_X}{D_0} = 1 - \frac{1}{2}(\alpha N)^2 \sum_{m \geq 1} f_m{}^2 K(m^2 x_0) + O(\alpha^4) \qquad (12)$$

where

$$K(x_0) = \int_0^\infty \mathrm{d}s \int_0^1 \mathrm{d}\tau_1 \int_0^1 \mathrm{d}\tau_2 \, \epsilon(\tau_1)\, \epsilon(\tau_2) \times \exp[-s - \phi(\tau_1,\tau_2,s,x_0)]$$

$$\phi(\tau_1,\tau_2,s,x_0) = x_0|\tau_1 - \tau_2| + \frac{4x_0}{\pi^2} \sum_{p=1}^{p_m} p^{-2} \cos(p\pi\tau_1) \times \cos(p\pi\tau_2)(1 - \exp(-p^2\pi^2 s/2x_0)) \qquad (13)$$

Due to the invariance of D_X under the transformation $\alpha \rightarrow -\alpha$, the first neglected term in eq 12 is of order α^4. The properties of the function $K(x_0)$ were discussed in ref 9. Its rather fast decay at large x_0 ($K(x_0) \sim x_0^{-2}$) implies in particular that the series in eq 12 converges rapidly, so that only the first few harmonics of the potential contribute significantly to the slowing down of the diffusion.

3.2. Activated Process Theory. Although the perturbation theory described above can in principle be systematically improved, at finite order it would never produce the exponential, Arrhenius-like decrease of the diffusion coefficient that we intuitively expect for large values of the potential amplitude α. In the large α limit, we expect the center of mass of the chain to spend most of its time localized at the nodes of the function $v(X)$, so that the chain can lower its energy by having its A monomers in a $v(X) \leq 0$ region and its B monomers in a $v(X) \geq 0$ region. In order to diffuse, the chain has to jump over an energy barrier separating two such minimal energy configurations. If the rate at which a barrier separating two neighboring minima is crossed is $1/\tau$, the diffusion constant will be given by

$$D_X = (\pi/q_0)^2 \tau^{-1} \qquad (14)$$

where π/q_0 is the distance separating the positions of the tracer chain center of mass in the neighboring minimal energy configurations.

The problem of calculating the escape rate of overdamped Brownian particles from a potential minimum across a barrier was first solved by Kramers[11] in the simplest case involving only 1 degree of freedom. Several workers[15,16] generalized his approach to multidimensional systems, as required for the treatment of a Rouse chain with p_m modes. The main result of this theory, which for completeness is summarized in the appendix, is the following: if the chain can escape from a minimum M in its multidimensional energy surface (defined by eq 4) through a saddle point S, the rate at which this escape occurs is given by

$$\tau^{-1} = \frac{|\alpha_1|}{2\pi N\zeta}\left(\frac{\det(Q(M))}{|\det(Q(S))|}\right)^{1/2} \exp((U(M) - U(S))/k_B T) \qquad (15)$$

where $U(A)$ and $Q(A)$ are respectively the value of the energy function and of its Hessian matrix at the point A ($A = M$ or S), and α_1 is the negative eigenvalue of $Q(S)$. The eigenvector associated with α_1 gives the direction of passage of S (i.e., the reaction coordinate).

In order to use eq 15, we first have to identify the relevant minima and saddle points of eq 4 in the space spanned by the Rouse modes ($y_0, ..., y_{p_m-1}$). As discussed above, the minima will be periodically spaced with a period π/q_0 along the y_0 axis in this space. The values of the y_p at a minimum M are obtained by numerically solving the coupled equations

$$v(y_0(M)) = 0$$

$$y_p/b_p{}^2 = \sqrt{2}\alpha \int_0^N \mathrm{d}s\, \epsilon(s) \cos\left(\frac{p\pi s}{N}\right) v'(X(s)) \qquad p \geq 1 \qquad (16)$$

and both $U(M)$ and $Q(M)$ can be obtained from these solutions. An obvious saddle point connecting two minima corresponds to a configuration S where $v'(y_0) = 0$ and $y_p = 0$, $p \geq 1$. In most cases, this saddle point turns out to be a satisfactory one; i.e., only one of the eigenvalues of $Q(S)$ is negative, as required for a direct application of eq 15. When x_0 becomes larger than about 5, however, a complication arises because this trivial saddle point turns out to have more than one negative eigenvalue. This indicates the existence of other saddle points with a lower energy. In such cases, i.e., when a second eigenvalue of $Q(S)$ became small, we adopted the approximate procedure of replacing its contribution to det ($Q(S)$) by an integral of the Boltzmann factor along the corresponding eigenvector direction, as discussed in the appendix. The approximation is, however, quite crude, and the results should therefore not be trusted for large values of x_0. Furthermore, this difficulty is clearly indicative of the fact that the whole approach becomes inappropriate for large x_0. Use of eq 14 and 15 relies on a "pointlike" picture of the diffusion process, in which the configuration of the chain is determined only by the position of its center of mass. Complex configurations in which the chain extends over more than one oscillation of the potential thus do not contribute in this picture. For $x_0 \simeq 5$, the radius of gyration of the unperturbed chain becomes of the order of the distance π/q_0 between energy minima, and the "pointlike diffusion" description is expected to break down.

A further limitation of the activated process theory is the assumption that the energy surface is well represented by a quadratic form in the vicinity of both the saddle points and the minima. Obviously, such an approximation should be more accurate for the cosine potential $v_1(X)$ than for the square-wave-like potential $v_2(X)$.

3.3. Numerical Simulation. For any finite number of modes p_m, the set of coupled Langevin equations (eq 5) can easily be simulated numerically[17] using the finite difference integration formula

$$y_p(t + \Delta t) = y_p(t) - \frac{\Delta t}{N\zeta}\frac{\partial H}{\partial y_p(t)} + (\Delta(y_p))_R + O((\Delta t^2)) \qquad (17)$$

where the random displacement $(\Delta(y_p))_R$ is sampled from a Gaussian distribution with zero mean and variance $2(\Delta t)k_B T/N\zeta$. The diffusion constant can then be determined from the long time limit of the center of mass mean-squared displacement, $D_X = \lim_{t\rightarrow\infty}(1/2t)\langle(y_0(t) - y_0(0))^2\rangle$. An alternative way of computing D_X, which is more accurate for large-amplitude potentials when the jump diffusion picture described in the preceding section applies, is to use eq 14. The hopping time τ is then equal to $4\tau_1$, where τ_1 is the decay time of the correlation function $\langle y_1(t)\, y_1(0)\rangle$. Note that y_1 characterizes the orientation of the end to end vector of the chain and changes sign whenever the chain jumps from one energy minimum to a neighboring one.

Simulations were carried out for a four-mode Rouse chain ($p_m = 3$). The time step was $10^{-4}t_0$, where $t_0 = 1/(D_0 q_0{}^2)$ is the time needed for a free Rouse chain to diffuse over a distance $q_0{}^{-1}$. For long enough simulation

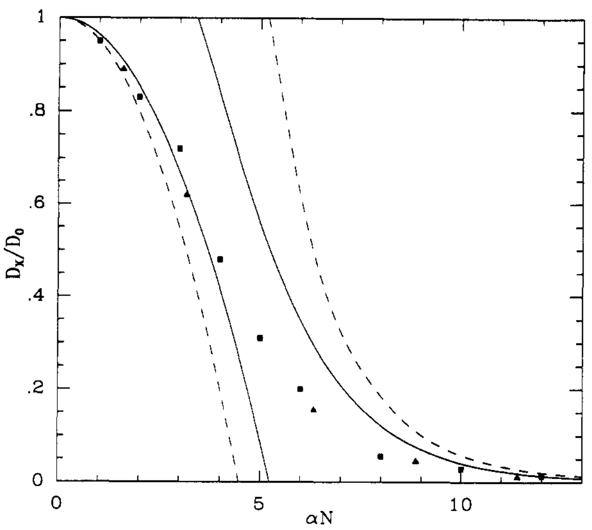

Figure 1. Comparison of simulations and theories for the self-diffusion case ($x_0 = 4$), as a function of the amplitude of the potential, for a four-mode Rouse chain. The full curves and the squares are obtained for the cosine potential $v_1(X)$; the dashed curves and the triangles are for the square wave potential $v_2(X)$. The squares are simulation results; the two inverted parabolas and convex curves are results respectively from the perturbation theory (eq 12) and from the activated process theory.

runs, the center of mass mean-squared displacement shows a clear linear behavior at long times and the diffusion constant can be extracted without difficulties.

4. Results and Discussion

4.1. Rouse Chain with Four Modes. In this section, we shall compare results from the two approximate calculations presented in sections 3.1 and 3.2 with the "exact" simulation results obtained as described in section 3.3 for a four-mode Rouse chain. Three series of simulation runs where carried out: in the first and second series, a chain with $x_0 = 4$ (corresponding to the case of self-diffusion in a diblock copolymer) is subjected respectively to a cosine or a square wave potential of variable amplitudes αN. In the third series, we study the diffusion of a chain at various x_0 (potential wavelength) in a cosine potential of amplitude $\alpha N = 10$.

The results of the self-diffusion study are displayed in Figure 1. From the comparison of the simulation results obtained for the square wave and the cosine potential, it appears that the slowing down of the diffusion is relatively insensitive to the shape of the potential and is to a good approximation a function only of the first Fourier coefficient of the potential. Both approximate calculations perform quite well in their respective domain of validity (small αN for the perturbation theory, large αN for the activated process theory), especially for the cosine wave potential. In this case, the perturbation theory agrees with the simulation results for $\alpha N \leq 5$, while the activated process theory gives good results for $\alpha N \geq 10$. The intermediate crossover region is unfortunately not well described by either theory. For the square wave potential, the predictions of the activated process theory are less satisfactory, as could be expected for such a strongly anharmonic energy surface.

Figure 2 presents a comparison between simulation results and activated process theory for the third series of runs. Clearly the large amplitude chosen for the cosine potential ($\alpha N = 10$) makes the perturbation theory inapplicable in this case. The agreement between theory and simulation is excellent for small x_0 but gets less satisfactory as x_0 increases. The difficulties encountered with the activated rate theory for large x_0 and discussed in section 3.2 are likely responsible for this discrepancy. Note that both the simulation and theoretical results present a shallow minima for $x_0 \simeq 3$. Perturbation theory[9] also predicts the existence of such a minimum in D_X as x_0 is increased at a fixed amplitude of the potential, however for a higher value of x_0 ($x_0 \simeq 5$).

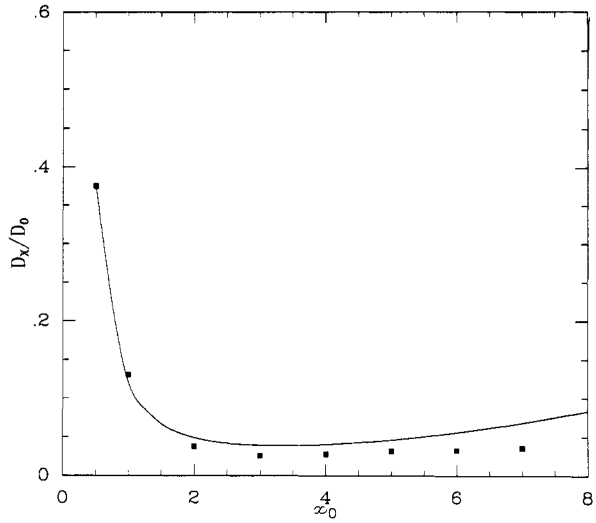

Figure 2. Comparison of simulation results (squares) and activated process theory (full curve) for chains of variable x_0 in a cosine potential of given amplitude, $\alpha N = 10$.

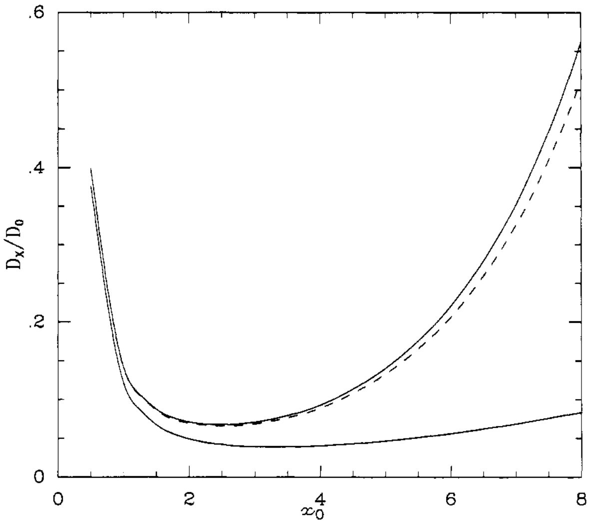

Figure 3. Influence of the number of modes included in the activated process theory for a cosine potential of fixed amplitude $\alpha N = 10$, as a function of x_0. The upper full curve is obtained for $p_m = 18$, the dashed curve for $p_m = 15$, and the lower full curve for $p_m = 4$.

4.2. Influence of the Number of Rouse Modes. For practical reasons the comparison between simulation and theory was made for a rather small number of Rouse modes. The parameter p_m, however, is not relevant for a comparison to experimental results, and the theories are meaningful only if their predictions become independent of p_m as p_m gets large. We find numerically that this is the case for both theories presented here. The sensitivity of the activated theory to p_m is shown in Figure 3, where it is seen that in the region where the theory is reliable ($x_0 \leq 5$) the results are insensitive to p_m for $p_m \geq 15$. This is also true for the perturbation theory, due to the rather fast convergence of the sum in eq 13.

Finally, Figure 4 displays the results of both theories for the self-diffusion ($x_0 = 4$) of an 18-mode Rouse chain.

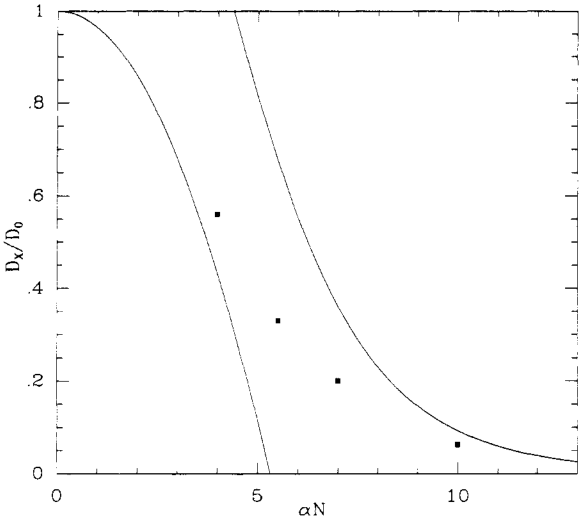

Figure 4. Perturbation and activated process theories results for the self-diffusion ($x_0 = 4$) of an 18-mode chain in a cosine potential as a function of the potential amplitude. The inverted parabola is the perturbation theory result. The squares are simulation results.

From the results obtained in the 4-mode case, we infer that the actual diffusion coefficient should smoothly crossover from one curve to the other in the region $5 \leq \alpha N \leq 10$. Some simulation results obtained for an 18-mode chain in this crossover region are also shown in Figure 4.

4.3. Discussion. As mentioned in the Introduction, the model studied in this paper can be considered as a crude one for the tracer diffusion of a labeled copolymer in a monocrystalline lamellar mesophase. Not surprisingly, we find that the diffusion in the direction perpendicular to the lamellae is slowed down. Due to the use of Rouse dynamics, however, the diffusion in the lamellar plane is unaffected. The amount of slowing down and the theory appropriate to describe the diffusion are strongly dependent on the amplitude of the concentration inhomogeneity existing in the lamellar phase. The potential $\alpha N k_B T v(X)$ in the model can be identified with $\chi N k_B T \psi(X)$, where $\psi(X) = (\rho_A(X) - \rho_B(X))/\rho$ is the monomer concentration difference in the lamellar phase. Consideration of Figure 4 then leads to the following conclusions:

(i) Close to the order–disorder transition, the amplitude of the concentration inhomogeneity ψ_0 is small. Typical values of ψ_0 estimated from a theory appropriate for this regime[18] are of order 0.30 for symmetric copolymers of moderate molecular weight, such as those studied by Bates and Rosedale.[19] Since χN in this region is of order 10, perturbation theory is expected to apply. The slowing down of diffusion attributed to the inhomogeneous potential will be relatively modest under such circumstances, at most 40%. In the disordered phase, concentration patterns of comparable amplitude are expected to survive for quite long times. The above estimate shows, however, that they should not influence self-diffusion in a dramatic fashion.

(ii) As χN is raised, the conditions of complete segregation will rapidly be approached, and the activated process theory will become appropriate. Our prediction is that when the product $\chi N \psi_0$ reaches a value of about 10, the diffusion perpendicular to the lamellae will be slowed by an order of magnitude. Therefore, in strongly segregated phases, diffusion is expected to be extremely slow and to decrease exponentially with χN.

The analysis in the present paper was restricted to the case of symmetric copolymers but could easily be extended to compositionally asymmetric diblocks or to copolymers of different architectures. Indeed, the perturbation theory for diblock tracers of arbitrary composition, f, was already given in ref 9. For long-wavelength potentials, the present activated process theory can be straightforwardly extended to such cases, but the identification of the relevant minima and saddle points may become problematic as x_0 is increased.

Finally, we emphasize that the above conclusions are meaningful only for weakly entangled chains, for which a Rouse model can be applied. For chains obeying reptation dynamics, the diffusion will be slowed in all directions since excursions of the test chain into the potential are required to release entanglements, even for lateral motion.[20]

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Appendix

In this appendix, we briefly summarize the extension of Kramers' escape rate theory[11] to multidimensional systems due to Landauer and Swanson.[16] We consider a system of independent particles each described by N degrees of freedom $(x_1, ..., x_N)$ and moving on an energy surface given by a function $V(x_1,...,x_N)$. This energy surface possesses two deep wells M and M', separated by a saddle point S. The dynamics of the pth degree of freedom of a particle is governed by the Langevin equation

$$\frac{dx_p}{dt} = -\frac{D_0}{k_B T}\frac{\partial V}{\partial x_p} + \theta_p(t) \qquad \text{(A1)}$$

where the noise θ_p satisfies the usual fluctuation–dissipation relation $\langle \theta_p(t)\ \theta_q(t') \rangle = 2D_0\delta_{pq}\delta(t-t')$. The arguments given below can be extended to the case where D_0 is not a scalar,[21] but this complication is unnecessary in the present case.

Following Kramers, we shall adopt "source and sink" boundary conditions: particles that leave the vicinity of M are instantly replaced, and particles that arrive in the vicinity of M' are taken away from the system. Under such conditions, a steady-state situation is achieved in which the wells M and M' contain populations respectively of $N_0 + N_1$ and $N_0 - N_1$ particles in a state of local thermodynamic equilibrium, and a small constant current flows from M to M' across the saddle point S. The "escape rate" from one well τ^{-1} is then given by the number of particles per unit time crossing the saddle point divided by the population imbalance between the two wells, $2N_1$. Obviously, this situation can be achieved only if the time required for establishing local thermodynamic equilibrium in the well M is much shorter than τ, so that the theory is applicable only if $V(S) - V(M) \gg k_B T$.

Following Landauer and Swanson, we shall write the steady-state particle density $n(x_1,...,x_N)$ in the saddle-point region in the form

$$n = \beta \exp(-V/k_B T) \qquad \text{(A2)}$$

where for simplicity the argument $(x_1, ..., x_N)$ to the functions n and β has been omitted. The function β would be a constant for a system in thermal equilibrium. Therefore, in the well M where local thermodynamic equilibrium exists, β must assume a constant value.

The particle current associated with the density (A2) is given by[22]

$$\mathbf{j} = -D_0(\nabla\beta) \exp(-V/k_B T) \qquad \text{(A3)}$$

The steady-state assumption implies $\nabla\cdot\mathbf{j} = 0$. In the vicinity of S, the energy function V can be written as a quadratic form:

$$V = V(S) + \frac{1}{2}\sum_{i=1}^{N}\alpha_i x_i^2 \tag{A4}$$

Here we have, without loss of generality, assumed that this quadratic form is diagonal for the variables $(x_1, ..., x_N)$ and have taken S as the origin of coordinates. We further choose the variable x_1 to be associated with the negative eigenvalue α_1 of the Hessian matrix of V at S. Using this expression for V together with the stationarity condition, we obtain

$$\sum_{i=1}^{N}\left(\frac{\partial^2\beta}{\partial x_i^2} - \frac{\alpha_i x_i}{k_B T}\frac{\partial\beta}{\partial x_i}\right) = 0 \tag{A5}$$

A trivial solution to eq A5 is $(x_1 \geq 0)$

$$\beta = \beta_0\int_0^{x_1}\mathrm{d}u\,\exp(\alpha_1 u^2/2k_B T) \tag{A6}$$

This solution (where β_0 is a constant) satisfies all the necessary requirements: in the vicinity of S, β depends only on x_1, and the resulting current (directed along the x_1 axis) satisfies the continuity equation in the steady-state situation. Since α_1 is negative, β rapidly goes to a constant $\beta_0(\pi k_B T/(2|\alpha_1|))^{1/2}$ far from the saddle point, so that the resulting density n correctly describes thermodynamic equilibrium in the wells M and M'.

Using this solution, it is then a simple matter to compute the escape rate τ: the number of particles per unit time crossing the saddle point is given by the flux of **j** across a plane orthogonal to the x_1 direction at S, i.e.

$$\frac{-\mathrm{d}N_M}{\mathrm{d}t} = D_0\beta_0\int \mathrm{d}x_2 ... \int \mathrm{d}x_N \exp(-V(0,x_2,...,x_N)/k_B T) \tag{A7}$$

and the number of particles in excess in the well M where $\beta = \beta_0\ (\pi k_B T/(2|\alpha_1|))^{1/2}$ is given by

$$N_1 = \beta_0(\pi/\alpha_1)^{1/2} \times \int_{\mathrm{well}\,M} \mathrm{d}x_1 ... \mathrm{d}x_N \exp(-V(x_1,...,x_N)/k_B T) \tag{A8}$$

If in order to compute the integrals in eqs A7 and A8 one makes the assumption that the function V can be expanded to quadratic order around both M and S, the result quoted in the text (eq 15) for $\tau^{-1} = -(2N_1)^{-1}\mathrm{d}(N_M)/\mathrm{d}t$ is obtained. This might, however, not be a satisfactory approximation if the potential is strongly anharmonic. In particular, the method described in the text for dealing with the case where $Q(S)$ has a second negative eigenvalue constitutes an attempt to estimate the integral in eq A7 without making this assumption: instead, it is assumed that if x_2 is the new unstable direction, $V(0,x_2,...,x_N)$ can be approximated by $V(0,x_2,0...,0) + (1/2)\sum_{i=3}^{N}\alpha_i x_i^2$, which amounts to exactly integrating the Boltzmann factor in the x_2 direction.

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