# Polymer Reptation in Disordered Media

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The effect of ambient disorders and sequence heterogeneities on the reptation of a long polymer is studied with the aid of a disordered tube model. The dynamics of a random heteropolymer is found to be much slower than that of a homopolymer due to collective pinning effects. The asymptotic properties belong to the universality class of a directed path in (1 + 1)-dimensional random media. [S0031-9007(98)05771-8]

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The stochastic motion of a polymer chain entangled in a disordered medium such as a gel is of much scientific and technological interest. A convenient starting point for understanding the polymer dynamics is de Gennes' reptation model, which describes the polymer's wormlike motion along a fictitious tube threaded through an array of fixed obstacles [1–3]. In the original reptation model, the polymer was assumed to be homogeneous, and effects due to randomness in the medium (e.g., spatial variations in the pore size of a gel) were neglected. A later argument by Harris [4] showed that the static configuration of a self-avoiding polymer is, in fact, not affected by the randomness, a result supported by numerical simulations [5,6]. However, extensive numerical [6–8] and experimental [9,10] studies found the *dynamics* of polymers in random media to be much slower than the classical reptation dynamics [1–3]. These results are understood qualitatively within an "entropic trapping" framework [6,11].

It should be noted that although some of the best known applications of reptation theory are concerned with the behavior of biopolymers which are inherently *heterogeneous*, there has been little theoretical work on the reptation of heteropolymers beyond a restricted model analyzed by de Gennes many years ago [12]. In this Letter, we address the combined effect of the heterogeneity of the polymer and the randomness of the media. Polymer motion is separated into two components: reptation within a tube and diffusive motion of the center of mass. For a homopolymer, the disorder does not affect the reptational motion, but the center-of-mass motion is drastically slowed down due to entropic trapping. For a heteropolymer, the reptational motion is also drastically affected: The well-known algebraic reptation time becomes exponentially long, making the dynamics of the heteropolymer even much slower. Our results are obtained with the aid of a disordered tube model, which we find to be analogous to the well-known problem of a directed path in random media [13].

Consider first a long, flexible homopolymer entangled in a covalently cross-linked gel matrix, characterized by a typical pore size $a$. We shall take $a > \xi \gg b$, $\xi$ being the persistence length of the polymer and $b$ being the monomer size. (For example, double-stranded DNA in agarose gel has $a \sim 5000$ Å, $\xi \approx 500$ Å, and $b = 3.4$ Å [14]; pore sizes are typically much smaller in polyacrylamide gels [10].) Since the equilibrium configuration of the polymer is that of a self-avoiding walk, described by the size exponent $\nu \gtrsim 1/2$ even in the presence of disorders [4–6], we shall describe the dynamics of the polymer by the reptation tube model [3]. In this model, the polymer is confined to a tube of diameter $\sim a$ [1], and modeled as "beads" linearly connected by (entropic) springs of spring constant $K = \frac{3}{2} k_B T/\xi^2$. Configurational entropy associated with the exponential number of (self-avoiding) tube trajectories results in an effective tensile force acting on the two ends of the bead-spring chain as in the disordered-free case [3]. This effect is incorporated into the model by letting the springs acquire a finite equilibrium length of the order $a$ [3]. Each link of this bead-spring chain therefore represents an elementary "blob" of $M_{\text{blob}} \sim a^2/b\xi$ monomers whose physical size is $\sim O(a)$. Confinement of the polymer to the tube costs a free energy (per blob) of the order $\overline{V} = k_B T(\xi/a)^2$ [2]. Since the diameter of the reptation tube embedded in the disordered gel matrix is nonuniform along its length, we describe the variable confinement entropy by a "random potential" $V(s)$, where $s$ denotes the curvilinear coordinate along the tube. For a typical self-avoiding tube trajectory, $V$ may be modeled by a short-range correlated random variable, characterized by the variance $\overline{\delta V(s)\delta V(s')} = \Delta_V \delta_a(s - s')$, where $\delta V(s) \equiv V(s) - \overline{V}$, $\delta_a(s)$ is an exponentially damped function of range $a$, and the overline denotes average over the ensemble of tubes. Assuming that the fractional variance in tube diameter variation is $O(1)$, we have $\Delta_V \sim \overline{V}^2$.

A key advantage of the original tube model [3] is that the nonlocal excluded-volume interaction between the beads can be neglected. This results from the entropy-generated stretching forces, which makes the chain *extended* in the tube, i.e., the contour length of the chain being linearly proportional to the number of beads. Consequently, the large scale dynamics of the polymer is obtained simply as the 1D Rouse dynamics of the beads. Let us assume that the nonlocal interaction between the beads (confined in the self-avoiding tube) can be neglected also for the disordered case. Then the statistical mechanics of a long polymer with degree of polymerization $M \gg M_{\text{blob}}$ is given by a bead-spring chain of $N \simeq M/M_{\text{blob}} \gg 1$ links, with the "Hamiltonian"

$$\mathcal{H}_0 = \sum_{n=0}^{N} \left\{ \frac{K}{2} (s_{n+1} - s_n - a)^2 + V(s_n) \right\}, \quad (1)$$

where $s_n$ denotes the coordinate of the $n$th bead along the tube.

The legitimacy of neglecting the nonlocal bead-bead interaction certainly deserves scrutiny: As in the disorder-free case, the approximation is justified provided the chain is in an extended conformation. On the other hand, a Gaussian chain in a tube can, in principle, collapse [15] to a region where $\delta V$ is large and negative, corresponding to a section of the tube with wider openings. If the chain described by (1) collapses, then the tube model would not be self-consistent. What opposes the collapse of the Gaussian chain are again the tensile stretching forces generated by the configurational entropy of the self-avoiding tube. This physics is reflected in the model (1) as a competition between the "elastic energy" cost against chain collapse, of the order $\frac{K}{2} a^2$ per spring, and the disorder energy gain, of the order $\sqrt{\Delta_V}$. The outcome of this competition has been obtained recently in the context of "non-Hermitian quantum mechanics" [16]: A discontinuous phase transition between the collapsed and the extended state is found at a certain critical point given by the condition $\frac{K}{2} a^2 \sim \sqrt{\Delta_V}$. Using the expressions given above for $K$ and $\Delta_V$ for the polymer problem at hand, we find that *the extended state is always preferred* under the presumed condition $a \gtrsim \xi$. Thus, the disordered tube model (1) is justified self-consistently. It will be used from here on to generate the large scale dynamics of self-avoiding polymers in random media.

Classical reptation dynamics is characterized by the reptation time $\tau_{R,0} \sim N^3$, which is the time it takes for the polymer to reptate from a given tube to a completely different tube in the adjacent neighborhood. For time scales much exceeding $\tau_{R,0}$, the polymer behaves as a point particle undergoing Brownian motion. This leads to a diffusion coefficient $D_0(N) \sim N^{2\nu}/\tau_{R,0}(N)$. In the presence of randomness, the reptation time $\tau_R$ is modified (see below); but more significantly, the large scale motion becomes one of thermally activated barrier hopping, since adjacent tubes may be narrower and hence higher in energy [11]. The typical barrier height $E_b(N)$ can be taken as the free energy variation of a polymer confined to cells of size $\sim N^\nu$. This variation is bounded to be within the order of $\pm N^{1/2}$ and is found numerically [17] to scale as $N^\omega$, with $\omega \approx 0.15$ in 3D and $\omega \approx 0.28$ in 2D. Thus the overall diffusion coefficient is reduced drastically to $D \sim [N^{2\nu}/\tau_R(N)] e^{-E_b(N)/k_B T}$ for large $N$.

To estimate the reptation time $\tau_R(N)$ itself for the random system, it is necessary to separate the sliding motion of a polymer along its prescribed tube from the thermally activated barrier hopping. This can be accomplished within the disordered tube model (1) by artificially imposing a *periodic boundary condition* on the random potential $V$, i.e., $V(s) = V(s + Na)$. With this simplification, the extended state of the chain can be obtained straightforwardly, by observing a discrete translational symmetry $s_n \to s_{n+1}$ which the model (1) possesses even in the presence of disorder: The polymer can move along the tube by the propagation of a longitudinal "defect" or "kink" (e.g., a configuration with $s_n = s_{n+1}$) much like what was proposed in the original reptation model [1]. Thus, the random potential is irrelevant in the extended state [16], and the scaling properties in the sliding regime are the same as those in the disorder-free case. For example, $\tau_R \sim \tau_{R,0}$, accompanied by a contour length fluctuation $\delta L_0(N) \approx [(k_B T/K)N]^{1/2}$.

The above analysis clarifies the role of entropic trapping for a homopolymer: The very slow motion of a long homopolymer in random media is dominated by the exponentially long waiting time $\sim \tau_{R,0} e^{N^\omega/k_B T}$ needed to overcome large spatial variations in the *mean* confinement potential. It is not a result of local "bottlenecks" which impedes the reptational motion along the tube. To study this behavior experimentally or numerically, it is necessary to have sufficiently long polymers such that each polymer threads through *many* local bottlenecks.

We next consider a heteropolymer which may carry sidegroups of vastly different sizes, or may have different degrees of partial charges, hydrophobicities, etc. Following de Gennes [12], we model the coarse-grained effect of the sidegroups by assigning a "charge" $q_n \in \{\pm Q\}$ to each bead $n$. Then the interaction energy $V$ in Eq. (1) becomes explicitly $n$ dependent, with the form

$$V(s_n, n) = V_0(s_n) + q_n V_1(s_n), \quad (2)$$

where $V_0(s) \pm Q V_1(s)$ is, respectively, the free energy cost of placing a beam of ± charge at the coordinate $s$ along the tube. We will take the random potentials $V_0$ and $V_1$ to be short-range correlated, with variances of the order $\Delta_V$. To model a heteropolymer, we choose the charges $\{q_n\}$ randomly, with probability $p$ for $q = +Q$ and $1 - p$ for $q = -Q$, such that $[q] = (2p - 1)Q$, and $[\delta q_m \delta q_n] = \Delta_q \delta_{m,n}$, $\Delta_q = 4p(1 - p)Q^2$. (Here, $[\cdots]$ denotes average over the ensemble of random sequences.) The magnitude of $Q$ depends on the coarse-graining scale $a$ and variations of the monomer-tube interaction. Let the latter be characterized by a fractional variance $\sigma$, then we have $Q^2 = \sigma M_{\text{blob}}$.

As in the homopolymer case, a Gaussian chain described by the Hamiltonian (1) with the interaction (2) may be in either the collapsed or the extended state depending on the magnitude of the elastic energy $\frac{K}{2} a^2$. However for a random heteropolymer (RHP), different monomers tend to prefer different sections of the tube. Hence the extended state is even more preferred, and we are again justified to neglect the nonlocal bead-bead interaction.

Let us consider now the reptational motion of an extended RHP, again by imposing periodic boundary condition on the $V$'s. Heterogeneity in sequence composition has profound effects on the dynamics, as the random $q_n$'s remove the translational symmetry $s_n \to s_{n+1}$ described above for the homopolymer. Thus, larger beads prefer to occupy segments of the tube with wider cavities, etc. de Gennes demonstrated the existence of such a heteropolymeric effect by considering a singular limit of the RHP model [12], where the longitudinal elasticity of the polymer is suppressed by taking $K \to \infty$. Below, we will show that a significant heteropolymer effect can exist generically for an elastic RHP.

To proceed, we introduce a longitudinal displacement field, $u_n = s_n - na$, and write the Hamiltonian as

$$\mathcal{H} = \sum_{n=1}^{N} \left\{ \frac{K}{2} (u_{n+1} - u_n)^2 + W(u_n, n) \right\}, \tag{3}$$

where $W(u_n, n) = \delta q_n \cdot \delta V_1(u_n + na, n)$. [There are actually two additional terms in $\mathcal{H}$: $\sum_n q_n \overline{V_1}$ and $\sum_n \{V_0(s_n) + [q] V_1(s_n)\}$. The first term is simply an overall energy shift and does not affect the motion of the polymer along the tube. The second term is just like the random potential of the homopolymer problem (1); it is irrelevant as discussed above.] The Hamiltonian (3) then describes a fictitious "directed path" with "transverse" coordinates $\{u_n\}$, embedded in a $(1 + 1)$-dimensional random medium $W(u, n)$ [18]. The randomness results from a combination of sequence heterogeneity and medium disorder. To elucidate the properties of this system, we first perform a naive pertubative analysis for small randomness $\Delta \equiv \Delta_q \Delta_V$. We find the randomness to have a negligible effect on the classical reptation results for chains below a crossover scale $N_\times \approx (k_B T)^5/(K \Delta^2 a^2)$. The perturbative analysis fails for long chains with $N > N_\times$, indicating that the *asymptotic reptation properties are qualitatively affected by arbitrarily weak sequence heterogeneities*. Note the dependence of the polymer's crossover length $M_\times \equiv N_\times M_{\text{blob}}$ on the tube size $a$: Using expressions for $K$ and $\Delta$ given above for the simple RHP model, we find $M_\times \sim a^4 b/\sigma^2 \xi^5$, which increases quickly with increasing $a/\xi$ as suggested in Ref. [12], but is nevertheless accessible for sufficiently heterogeneous polymers in typical gels.

To obtain the asymptotic behavior of the polymer with $M \gg M_\times$ regime, let us examine more closely the effective random potential $W(u, n)$: The statistics of $W$ is easily obtained in terms of the statistics of $q_n$ and $V_1(s)$, with $\overline{[W]} = 0$ and

$$\overline{[W(u, n) W(u', n')]} = \Delta \delta_a(u - u') \delta_{n,n'} \,. \tag{4}$$

The correlator (4) indicates that an effective *two-dimensional* random "point" potential is *generated*, even though $W$ itself, being a product of two *one-dimensional* random variables, must contain long-range correlations. The latter is manifested in the higher moments of $W$. For instance, $W^2(u, n)$ contains a term $[(\delta q)^2] \delta V_1^2(u_n + na)$ which is correlated along the direction $u_n = -na$. But such terms are just like the random potential $V(s)$ of the homopolymer case and are irrelevant. Thus, we conjecture that *the system (3) belongs to the universality class of a directed path in (1 + 1)-dimensional uncorrelated Gaussian random potential.*

This universality class is well known [13]. In the asymptotic regime, the polymer exhibits glassy dynamics which is characterized by two exact scaling laws: The sample-to-sample free energy variation scales as $\delta F(N) \approx k_B T \cdot (N/N_\times)^{1/3}$, and the contour length fluctuation scales as $\delta L(N) \approx s_\times (N/N_\times)^{2/3}$, where $s_\times = \delta L_0(N_\times) = (k_B T)^3/K \Delta a$. The conjectured equivalence between RHP reptation and the directed path problem was tested, by numerically computing $\delta F(N)$ and $\delta L(N)$ from the model (1) and the interaction (2), treating $K$, $\Delta$ as arbitrary parameters. We used the transfer matrix method [13], and examined particularly the "zero-temperature" limit of the model, whose small crossover length $N_\times$ enables us to access the asymptotic scaling regime. The zero-temperature problem is an optimization problem. It is necessary to place the bead-spring chain on a discrete lattice. To simplify the numerics, we restrict the displacement of beads such that $s_{n+1} - s_n$ can take on only the values $\{a, a \pm 1\}$ at each step $n$ of the transfer matrix. A random potential $V_1(s)$ of zero mean and unit variance is assigned to each lattice point, and a charge $q_n$ is assigned independently to each bead. The numerical results for the disorder-averaged contour length fluctuation $\delta L = \overline{[(u_N^*)^2]}^{1/2}$ of the optimal configuration $u_n^*$ (with the $n = 0$ end fixed at the origin) and the sample-to-sample variation $\delta E^*(N)$ of the total energy of the optimal configuration $E^*(N)$ [19] are shown in Fig. 1(a). It is seen that fluctuations rapidly approach those expected of the directed path, $\delta L \sim N^{2/3}$ and $\delta E^* \sim N^{1/3}$, suggesting that the RHP is indeed in the same universality class as the $(1 + 1)$-dimensional directed path. Similar behaviors have recently been found in a number of related studies [20,21].

Another useful quantity to examine is variation in the polymer's "energy landscape," which we obtain by fixing the $n = 0$ end of the polymer to an arbitrary coordinate $s$, and then computing the energy $E(s, N)$ of the optimal configuration (of the constrained polymer) for each $s$. The landscape is characterized by the correlation function $C_E(s - s', N) \equiv \{\overline{[E(s, N) - E(s', N)]^2}\}$, which is expected [13] to have the scaling form $C_E(s, N) = N^{2/3} g(|s|/N^{2/3})$, with the scaling function $g(x \lesssim 1) \sim x$ and $g(x \gtrsim 1) \sim$ const. This scaling form is verified by our numerics as shown in Fig. 1(b).

The zero-temperature behavior described here corresponds to the asymptotic regime of the RHP, beyond

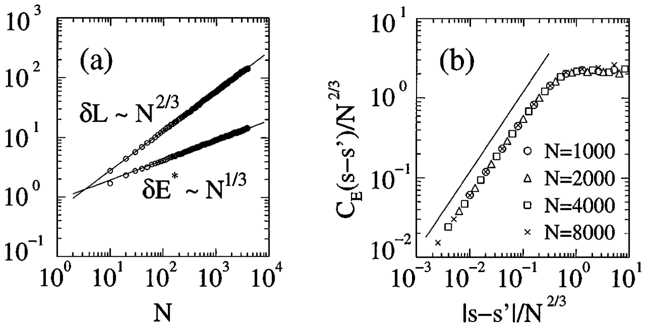

FIG. 1. Heteropolymers confined in a tube: (a) Scaling of the contour length fluctuation $\delta L$, and the sample-to-sample minimal energy variation $\delta E^*$, for bead-spring chains of $N = 4000$, $a = 4$, $K = 1$, and $[q] = 0.1$, averaged over 1500 samples. (b) Autocorrelation of the energy landscape $E(s,N)$; the straight line has slope 1.

the crossover scale $N_\times$. For the finite temperature problem at hand, the RHP dynamics along the tube is governed by variations in the *free-energy* landscape $F(s,N)$, whose form is obtained easily from $E(s,N)$. It is described by the correlation function $C_F(s - s', N) = (k_B T)^2 |s - s'|/s_\times$, for $s_\times < |s - s'| < \delta L(N)$, saturating to $C_F \sim (\delta F)^2 \approx (k_B T)^2 (N/N_\times)^{2/3}$ for larger displacements $|s - s'|$.

Dynamics of the chain in such a rough free energy landscape cannot proceed by the propagation of a few isolated kinks. It requires instead *collective* movement of large pieces of the chain such that the chain always remains in local optimal configurations [22]. The resulting "collective creep" dynamics can be modeled by the motion of one of the chain ends in the 1D Brownian random potential $F(s,N)$ [23]. The latter is a well-studied classical problem [24]. The time it takes for the particle to move by a distance $s > s_\times$ along the tube is $\tau_{R,0}(N_\times) \exp[C_F(s)/(k_B T)^2] \sim e^{s/s_\times}$. Since $C_F(s)/(k_B T)^2$ saturates at $(N/N_\times)^{2/3}$ for $\delta L < s < L$, the reptation time is

$$\tau_R(N) \approx \tau_{R,0}(N_\times) \exp[(N/N_\times)^{2/3}], \qquad (5)$$

which greatly exceeds the classical reptation time $\tau_{R,0}(N)$ if the polymer is sufficiently long. Note that $\tau_R$ also exceeds the waiting time $\sim e^{N^\omega/k_B T}$ needed for the activated barrier hopping by the homopolymer. Hence we conclude that *the dynamics of a long random heteropolymer is much slower than that of a homopolymer.*

The extraordinary slow dynamics of the RHP is a *collective phenomenon* resulting from a global "resonance" of the randomness in the polymer composition with the randomness in the tube structure; it is not a local effect, say, an increase of the microscopic friction. This can be tested by comparing an RHP with a *ABAB* copolymer consisted of the same monomers. Upon coarse graining by a finite scale, the copolymer becomes equivalent to a homopolymer, while heterogeneities of an RHP cannot be coarse grained away. Thus we expect a long RHP to exhibit much slower dynamics than a periodic copolymer of the same length and monomer content.

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