Discretized Model of Entangled-Polymer Dynamics

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(Received 1 June 1987)

A discretized version of the reptation model is proposed. The tube is modeled by a one-dimensional lattice and the polymer is modeled by a cluster of walkers, called reptons, on this lattice. Each repton represents a part of the chain. Reptons are allowed to hop between neighboring sites, but the cluster always remains connected. This model is solved analytically and numerically. In the experimentally accessible range of molecular weights M it predicts the diffusion coefficient $D \sim M^{-2} + O(M^{-3})$ and viscosity $\eta_0 \sim M^{3.4 \pm 0.1}$.

PACS numbers: 61.41.+e, 62.10.+s, 64.60.Ht, 66.10.Cb

There has been substantial progress in our understanding of the dynamics of entangled polymers during the last two decades. It was based on the concepts of the confining tube[1] and reptation.[2]

In the de Gennes reptation model,[2] sections of stored length were described by noninteracting defects diffusing along the contour of the tube and collectively causing the displacement of the whole chain. The fluctuations in the density of randomly diffusing defects and the resulting fluctuations in tube length were preaveraged in conventional treatments of the reptation model[2,3] leading to the dependence of the diffusion coefficient D_{3D} and the longest relaxation time τ_r on polymer molecular weight M,

$$D_{3D} \sim M^{-2}, \tag{1}$$

$$\tau_r \sim M^3. \tag{2}$$

Prediction (1) is considered to be experimentally verified,[4] while for the longest relaxation time τ_r and related viscosity η_0, the experimentally measured exponent[5] is 3.4 ± 0.1. This difference between predicted and observed exponents is one of the biggest remaining mysteries in polymer physics.

There have been a number of attempts to explain this mystery.[6-12] Doi argued[6,7] that the observed 3.4 exponent is a finite-size effect due to fluctuations in tube length. He proposed the expression for viscosity

$$\eta_0 \sim M^3[1 - \nu(M_e/M)^{1/2}]^3, \tag{3}$$

where M_e is the molecular weight between entanglements and ν was estimated from the variational principle[7] to be around 1.47. The right-hand side of Eq. (3) is approximately proportional to $M^{3.4}$ over a limited range of molecular weights. This explanation was challenged analytically by des Cloizeaux[8] and numerically by Needs.[9] They argued that the effect of fluctuations in tube length on viscosity should be smaller than predicted by Doi.

Other explanations of the 3.4-power law have been proposed,[10-12] but none is completely satisfactory.

In the present Letter, I propose and solve a simple model of the dynamics of the single entangled chain. This model exhibits fluctuations in tube length similar to those described by Doi.[6,7] It follows in detail the diffusion of defects of stored length[2] along the contour of the confining tube.

I restrict my discussion to the motion of a single polymer. The effect of other chains is assumed to be limited to the formation of an entanglement net by their primitive paths.[13] If the system we are dealing with is a melt or a concentrated solution (rather than a gel), the dynamics of any chain would be affected by the motion of other chains (by constraint release). This effect has to be self-consistently taken into account.[14] But in order to do that one has to start from a reliable theory of the single-chain dynamics. I propose a candidate for such a theory below.

The entanglement net formed by primitive paths of surrounding chains divides space into cells.[13,15] A primitive path (an axis of a confining tube) of a chosen chain can be considered as a walk between centers of these cells. A polymer consists of its primitive path and a set of unentangled loops.[13,16] The amount of chain length stored in unentangled loops varies from cell to cell along the primitive path of the chain. The objective is to solve the dynamics of these loops, called defects by de Gennes.[2]

The "repton" model is a discretized version of the reptation model. I represent the set of cells of the entanglement net traversed by the primitive path of a chosen chain by a one-dimensional lattice. Let us model the sections of the chain, stored in each cell in the form of unentangled loops and the primitive path, by objects called "reptons" on the sites of this lattice (the number of reptons being roughly proportional to the length of these sections). For example, the entangled chain in Fig. 1(a) is mapped onto a connected cluster of 7 reptons in Fig. 1(b). The coordinates of N reptons x_i always obey $x_1 \le x_2 \le \cdots \le x_N$. The system can also be modeled by a one-dimensional directed random walk [Fig. 1(c)]. Representing a section of a chain by a single repton, I discard high-frequency modes and concentrate on low-frequency (long-time) behavior of the polymer.

Next, I define the simplest axioms to model the dy-

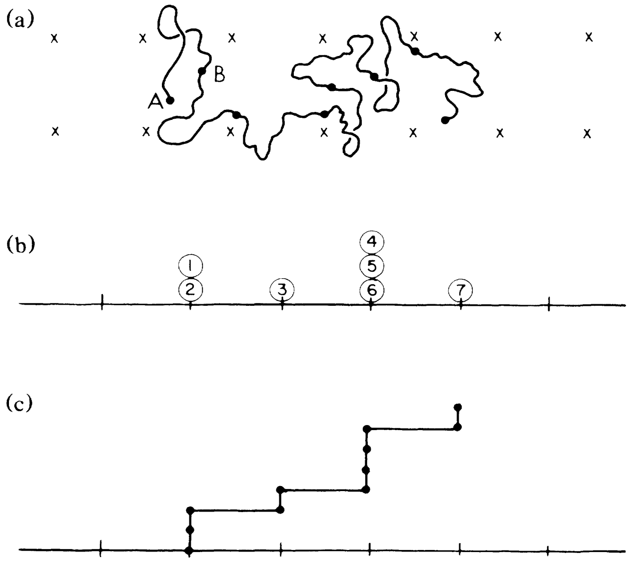

FIG. 1. (a) A polymer in an entanglement net is confined to a tube. Filled circles divide the chain into segments of stored length. (b) Repton-model representation of the configuration of 1(a). Cells of the entanglement net along the confining tube are represented by a one-dimensional lattice. Sections of chain length stored in these cells are modeled by walkers (reptons) on the lattice sites. (c) Directed-random-walk representation of the same configuration.

namics of unentangled loops.

Rule 1.—Never vacate a site in the middle of the cluster and preserve the order of reptons: $x_{i+1}-x_i$ is either 0 or 1 for $i=1,2,\ldots,N-1$.

The second rule is related to the fact that we are mapping a higher-dimensional problem onto the (one-dimensional) repton model. Let us assume that each cell has z faces (gates). Then, for a section of a chain at the end of a polymer [e.g., section AB in Fig. 1(a)], there are $z-1$ possible gates to enter an empty cell and only one gate to go into an already occupied one. Since in one-dimensional lattice representation [Fig. 1(b)] all of these $z-1$ empty cells are mapped on one empty site, we have to assume that the probability of a repton hopping onto this empty site is $z-1$ times higher than for hopping onto an already occupied one.

Rule 2.—If allowed by rule 1, the probability of a repton hopping between neighboring occupied sites is $1/z$, while the probability of hopping onto an empty site is $(z-1)/z$.

Consider the subset of all allowed states of the system that correspond to K-occupied sites ($K=1,2,\ldots,N$). The detailed balance of the transitions between different states implies that states within each subset have the same probability p_K, while the probabilities of states from different subsets are related by $p_L/p_K=(z-1)^{L-K}$.

It is easy to show that any connected cluster of N reptons on K sites can be mapped to a unique combination of $K-1$ zeros and $N-K$ ones [see Fig. 1(c)]. Zeros correspond to the boundaries between occupied lattice points and ones correspond to multiple reptons. Indeed, we can put K reptons (out of N) on K sites (one at each) to satisfy the connectivity requirement. The remaining $N-K$ reptons (or corresponding ones) can be placed in any combination on K sites (can be spaced by $K-1$ zeros). The total number of such combinations is

$$S(K,N)=\begin{bmatrix}N-1\\K-1\end{bmatrix}=\frac{(N-1)!}{(K-1)!(N-K)!}. \tag{4}$$

States from different subsets have different probabilities; therefore, the probability of N reptons to occupy K sites is

$$P(K,N)=\frac{(z-1)^{K-1}(N-1)!}{z^{N-1}(K-1)!(N-K)!}. \tag{5}$$

From this probability distribution we can calculate the average size of the cluster,

$$\langle L\rangle=\textstyle\sum_{K=1}^{N}KP(K,N)=N-(N-1)/z. \tag{6}$$

As expected for a directed random walk, the average size of the cluster $\langle L\rangle$ grows linearly with the number N of reptons in it. Another conclusion from Eq. (6) is that the entropic "tension" and average cluster size increase with the coordination number z.

The fluctuations in the cluster size K around the average can be represented asymptotically by the Gaussian

$$P(K,N)\simeq\{z/[2(z-1)\pi N]^{1/2}\}\exp\{-[z^2/2(z-1)N][K-(z-1)N/z]^2\}, \tag{7}$$

which is very similar to the fluctuations in tube length described in earlier work.[13,16,17]

The probability of an attempted repton jump to succeed is calculated from rules 1 and 2 to be

$$J=[2(z-1)/z^3]\{1+2(z-1)/N\}. \tag{8}$$

Therefore, the diffusion coefficient of the center of mass of the cluster of N reptons is

$$D=(z-1)a^2/z^3N\tau_m+O(N^{-2}), \tag{9}$$

where a is the lattice spacing (average cell size) and τ_m is the average microscopic time between attempted hops. Note that the relative correction from the second term of Eq. (9) can be smaller than that of Eq. (8) because of correlations between steps. The one-dimensional diffusion coefficient of the repton model [Eq. (9)] corresponds to the curvilinear diffusion coefficient of a polymer in a tube. If we assume Gaussian random walk configuration of a chain, the three-dimensional diffusion coefficient is $D_{3\mathrm{D}}\simeq D/N$, and the experimentally observed result [Eq. (1)] is asymptotically recovered.

In Fig. 2, the numerically calculated diffusion coefficients of the repton model for $z=2$, 6, and 12 are compared with the asymptotic expression $D_z(N)=(z-1)a^2/(z^3N\tau_m)$. The asymptotic behavior is reached relatively quickly (between $N=30$ and 50 reptons). Equation (9) suggests a more negative effective exponent $D \sim N^{-2-O(1/N)}$ for smaller N, but in order to describe correctly the behavior of shorter chains, one has to include higher-frequency modes neglected by the repton model. This crossover region from entangled to disentangled polymers (small N) is beyond the scope of the present Letter.

Consider the stress-relaxation behavior of the repton model. If a step strain is imposed on a system of an unattached chain in an array of fixed obstacles, such as an ideal network, the resulting stress decays as the chain reptates into an undeformed configuration. The cells of the network that sustain stress are the ones that have not been vacated by the chain since the time of the step strain.[2,3]

Let us model this relaxation process by following the rates at which a cluster of reptons vacates initially occupied sites. Assume that step strain was imposed at time $t=0$. Denote by $x_R(t)$ the leftmost propagation of the right end of the cluster between initial time and t. Similarly, let $x_L(t)$ be the rightmost propagation of the left end of the cluster. Then those and only those sites x_i of the lattice that satisfy $x_L(t) \le x_i \le x_R(t)$ have been continuously occupied between time 0 and t. The stress is proportional to the number of these sites,

$$\mu(t)=\langle L\rangle^{-1}\langle x_R(t)-x_L(t)+1\rangle, \tag{10}$$

where the angular brackets denote the ensemble average and the normalization factor $1/\langle L\rangle$ is chosen so that $\mu(0)=1$. [See Eq. (6) for the value of the average cluster size $\langle L\rangle$.]

Zero-shear-rate viscosity is equal to the integral of the stress-relaxation function[5]:

$$\eta_0=\int_0^\infty \mu(t)\,dt, \tag{11}$$

where the units are chosen to set plateau modulus $G_0=1$. An analytical expression for $\mu(t)$ for $N>2$ is still an open question. The numerically calculated values of η_0 for $z=2$, 6, and 12 are presented in Fig. 3. The straight lines are the best fits to the viscosities for larger N. The slopes of these lines on the doubly logarithmic scale are 3.22 for $z=2$, 3.36 for $z=6$, and 3.52 for $z=12$.

The case with two gates per cell ($z=2$) corresponds to a polymer confined to a one-dimensional pipe. In the case of $z=6$, the obstacles form either a two-dimensional triagonal lattice or a three-dimensional cubic lattice. The case $z=6$ also corresponds to the average coordination number of 3D random packing of spheres,[18] while $z=12$ is closer to the highest coordination numbers observed in random systems.[19] The average number z of gates per entanglement net cell in most experimental

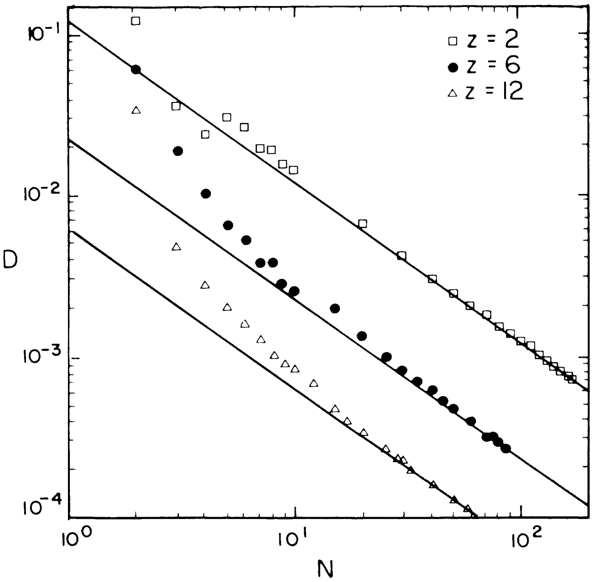

FIG. 2. Diffusion coefficient of the center of mass of the cluster of N reptons along the contour of the tube as a function of N for three different average coordination numbers of the entanglement net, $z=2$, 6, and 12. Straight lines correspond to the asymptotic behavior $D_z(N)=(z-1)a^2/(z^3N\tau_m)$.

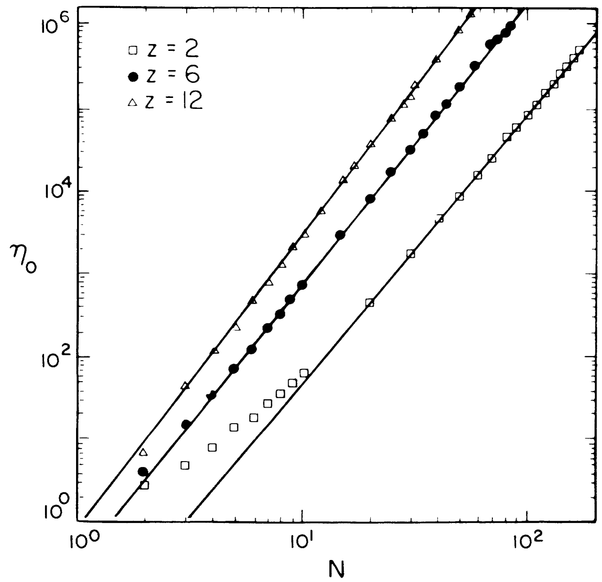

FIG. 3. Repton-model predictions of the viscosity η_0 as a function of cluster size N. Straight lines are best fits of the higher-N parts of the plot. Their slopes are 3.22 for coordination number $z=2$, 3.36 for $z=6$, and 3.52 for $z=12$.

systems is close to 6, and therefore the repton model predicts an effective exponent $\eta_0 \sim M^{3.4 \pm 0.1}$, while $D \sim M^{-2} + O(M^{-3})$ for those systems.

From diffusion coefficients D_z and average cluster sizes, one estimates the time it takes the cluster to diffuse its own length, $\tau_z \simeq \langle L \rangle^2 / D_z \simeq z(z-1) N^3 \tau_m$. The prefactor $z(z-1)$ quantitatively explains the vertical shift between the viscosity curves for different z (Fig. 3) and suggests that asymptotically $\eta_0 \sim \tau_z$ as $N \to \infty$.

In the proposed model there are no interactions between reptons occupying the same site. The probability of an unentangled loop decreases exponentially with the size of this loop.[13,16] The algebraic prefactor of this dependence introduces weak interaction between reptons occupying the same site, and could be included in a more elaborate version of the model.

The above demonstrates that a simple model of single-chain dynamics can exhibit nontrivial crossover behavior in the experimentally relevant range of molecular weights. The many chain effects, such as constraint release, may modify[14] the molecular-weight dependence, but the origin of the phenomena is in the single-chain dynamics.

The results of the repton model qualitatively agree with the conclusions of Doi,[6,7] but represent a more accurate treatment of tube-length fluctuations and are in better agreement with experiments[20,21] at intermediate molecular weights, where Doi's expression [Eq. (3)] overpredicts the curvature. The two models probably coincide in the high-molecular-weight region where $M^{-1/2}$ expansion used by Doi is accurate, but this region is currently inaccessible both experimentally and numerically.

I thank E. Helfand for introducing me to the problem, C. L. Henley for a number of suggestions that led to the analytical solution of the model, and M. E. Cates, R. Colby, M. Doi, J. M. Deutsch, P. G. de Gennes, W. W. Graessley, K. Kremer, D. S. Pearson, L. A. Ray, and T. A. Witten for useful discussions.

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