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Reptation of a polymer chain by conformal transitions in the entangled regime

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We study a model for reptation, where motion along the contour of the chain is due to displacements caused by singlet- or double-bond rotations (local jumps) followed by rearrangements of the neighboring units, rather than "kink motion." We recover the usual scaling behavior of the diffusion coefficients and relaxation times with the chain mass. Moreover, the effective activation energy that is found from the local jump model for translational motion of the chain center of mass compares favorably with experiment and is independent of the molecular weight for large enough chains.

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I. INTRODUCTION

Dynamical properties of flexible linear polymers are still poorly understood. In the entangled regime the reptation concept [1–3] is the most successful in describing the dynamical behavior of a single chain. The reptation model is used for representing the low-frequency motions of a chain in a fluid of entangled chains, neglecting rapid relaxation processes that are attributed to local conformal transitions of the backbone. Within the reptation model, a flexible linear polymer chain composed of N links diffuses via a slithering motion of the chain along its contour, as shown in Fig. 1, through an effective tube whose walls are formed by sections of other chains. Motion of the chain along its contour has been pictured as due to the random motion along the chain contour of "kinks," or defects, where a certain length of chain is "stored" [1,4].

Helfand and collaborators [5–9] have studied the kinetics of conformational transitions in chain molecules, and they find that single-bond rotations followed by the compensating rearrangement of neighboring units are predominantly responsible for local motions. Such models have also been considered by Erman and co-workers [10]. In this paper, we investigate single- and double-bond transitions as a possible mechanism for reptation in the entanglement regime. This is a slightly modified microscopic picture for reptation, where local conformations, which may be single- or double-bond transitions, are constrained by the entanglements and give rise only to a slithering motion along the chain.

FIG. 1. The chain moves to the right, and a certain portion (A,B) of the original tube disappears; a new part of the tube (C,D) is created.

In Sec. II we compute the curvilinear diffusion coefficient D_{tube} and the translation diffusion coefficient for the polymer center of mass D_{tr} in terms of the polymer mass and the probability per unit time for single-bond transitions. We recover the scaling results of de Gennes [1] and Doi and Edwards [2,3] for the dependence of these quantities and of the renewal time on the polymer mass. A comparison with experimentally obtained activation energies leads us to construct, in Sec. III, a model involving two rotameric transitions bracketing chain segments of arbitrary size. The effective activation energies found in this way can be much larger than the monomer activation energies and are therefore more in line with those found experimentally. Moreover, a possible source for deviation from the Arrhenius form for the transition rates and the temperature dependence of these effective activation energies is indicated.

II. REPTATION VIA SINGLE-BOND TRANSITIONS

We consider the following model for diffusion by reptation.

(a) The mobile links belong to very long chains (the end effects are neglected).

(b) A single-bond rotational transition takes place at a given time (in Fig. 2, the transition takes place at the bond I_k). This transition affects the position of the other links so that the direction of their displacements along the contour is random.

(c) The transition affects only a contour S of finite length along either side of I_k. The parts of the chain beyond S are referred to as the *tails.* A transition takes place without any rearrangement of the tails.

(d) For a rotameric transition, the root mean square of the displacements along the chain contour averaged over the affected links is taken to be a constant, b. At a given temperature, a single-bond transition rate is expressed in terms of the Boltzmann factor as

$$p=\nu_0 e^{-E/k_B T}, \tag{1}$$

where ν_0 is the intrinsic frequency of molecular vibration, k_B is the Boltzmann constant, T is the temperature, and

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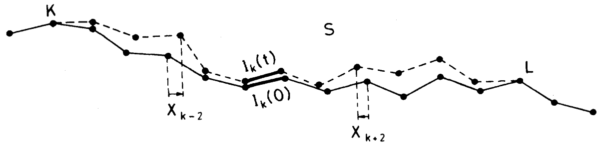

FIG. 2. A rotameric transition of the I_k bond changes the conformation of the contour from the solid line to the dashed line between points K and L. We shall denote the part of the chain between points K and L by the contour S. The vector for the kth bond is shown as $I_k(0)$ at the time 0 and as $I_k(t)$ at t. In the figure x_{k-2} and x_{k+2} are the displacement vectors of I_{k-2} and I_{k+2}th bonds, respectively. The direction of the displacement vectors x_k of the bond are random along the contour S.

E is the transition activation energy. The average number of single-bond transitions along a chain composed of N links, during a time t, is given by

$$Y_N = tN\nu_0 e^{-E/k_BT} . \tag{2}$$

If we assume this number to be small in comparison with N, the displacements caused by each transition are confined to nonoverlapping contours S. Then Z_N, the number of links that are displaced within a time t, is on the average

$$\bar{Z}_N = t\mathcal{S}N\nu_0 e^{-E/k_BT} . \tag{3}$$

Here, $\mathcal{S}$ stands for the average number of links in the contour S affected by a single-bond transition. The direction of a displacement x_k in curvilinear coordinates along the chain contour is random (see Fig. 2). We take each monomer mass to be m, and the chain mass to be $M = mN$.

The average displacement of the center of mass of the chain within a time t is, of course, zero. The mean square value of the displacement of the center of mass along the contour is

$$\langle X_{\text{c.m.}}^2 \rangle = \frac{1}{N^2} \left\langle \sum_{k=1}^{Z_N} \sum_{l=1}^{Z_N} x_k x_l \right\rangle = \frac{b^2}{N^2} \bar{Z}_N , \tag{4}$$

with $N = M/m$, and where

$$\langle x_k x_l \rangle = b^2 \delta_{kl} .$$

Substitution of Eq. (3) into Eq. (4) yields a relation between the chain displacement in curvilinear coordinates along the chain contour, the chain length, the temperature, and the transition activation energy, viz.,

$$\langle X_{\text{c.m.}}^2 \rangle = \frac{b^2 t \mathcal{S} \nu_0}{N} e^{-E/k_BT} . \tag{5}$$

Fick's law for diffusion gives

$$\langle X^2 \rangle = Dt . \tag{6}$$

Comparing Eqs. (5) and (6), we may write down the tube diffusion coefficient,

$$D_{\text{tube}} = \frac{b^2 \nu_0 \mathcal{S}}{N} e^{-E/k_BT} . \tag{7}$$

We can find the renewal time τ_r if we set

$$D_{\text{tube}} \tau_r = (Na)^2 . \tag{8}$$

The right-hand side is the square of the contour length, with a being the bond length. Then from Eqs. (7) and (8),

$$\tau_r = \frac{N^3 a^2}{b^2 \nu_0 \mathcal{S}} e^{E/k_BT} . \tag{9}$$

This result is quite striking because it incorporates the de Gennes scaling result $\tau_r \sim N^3$ [11], as well as the temperature dependence of the relaxation time. For a Gaussian walk of N steps with step size a, one would have for the mean square displacement $\langle X^2 \rangle = Na^2$. The translation diffusion coefficient $D_{\text{tr}} = Na^2/\tau_r$ is then

$$D_{\text{tr}} = \frac{b^2 \nu_0 \mathcal{S}}{N^2} e^{-E/k_BT} . \tag{10}$$

Equation (10) is in the Arrhenius form and includes the de Gennes scaling result for the translational diffusion coefficient [12] $D_{\text{tr}} \sim N^{-2}$.

The diffusion activation energy per mole is defined as

$$E_{\text{diff}} = -N_0 k_B \frac{\partial \ln D_{\text{tr}}}{\partial (1/T)} , \tag{11}$$

where N_0 is Avogadro's number. From Eqs. (10) and (11) one finds $E_{\text{diff}} = N_0 E$, the single-bond transition activation energy per mole. If one measures D_{tr} experimentally as a function of T, then one can obtain the diffusion activation energy E_{diff} by plotting $\ln D_{\text{tr}}$ vs $1/T$ [13,14]. The E_{diff} found in this way turns out to be much larger than $N_0 E$ [15–17]. This leads us to construct the double-bond transition model for reptation, which we now proceed to do in the next section.

III. "LOCAL JUMP" MODEL

In this model, instead of only single-bond transitions, both double- and single-bond transitions are considered, and these types of transitions are called *local jumps*. Shown in Fig. 3 is a *local jump* caused by *two* rotameric transitions at the links labeled T and U. The part of the chain between T and U flips over, and the monomers, respectively, on the *left* and *right* of T and U get slightly rearranged. Let α be the number of links in the part of the chain between T and U that makes the jump. We have assumed that a local jump *of length* α affects only a finite contour of length P_α on either side of it. Note that crankshaft [18] motion is only a special kind of double-bond transition. The number of links that flip over between two rotating bonds is variable and is limited by N_e, the number of links between two entanglement points. On a chain of length N, the average number of local jumps involving α links within time t at a given temperature T is

$$Y_\alpha = tNA_\alpha e^{-E_\alpha/k_BT} .$$

Here E_α is the activation energy of a local jump involv-

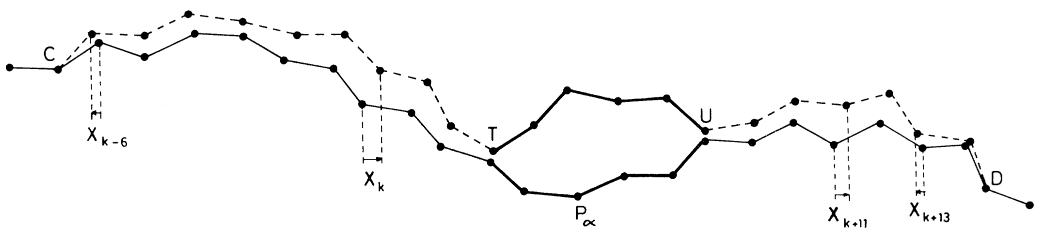

FIG. 3. A double-bond transition of the chain between T and U changes the conformation of the contour from the solid line to the dashed line between points C and D. We shall denote by the contour P_α the part of the chain between points C and D. The direction of the displacement vectors x_k of the links are random along the contour P_α.

ing α links, and A_α is a proportionality constant with dimensions of inverse time. The total number of links that are displaced within a time t as a result of local jump transitions involving α links is, on the average,

$$\bar{Z}_\alpha = NtP_\alpha A_\alpha e^{-E_\alpha/k_BT} . \tag{12}$$

After a local jump involving α links, the root mean square of the displacements along the chain contour averaged over the affected links is taken to be c_α. The average displacement of the center of mass of the chain along its contour within a time t is

$$\langle X_{\text{c.m.}} \rangle = \frac{1}{M} \left\langle \sum_{\alpha=1}^{N_e} m \left[\sum_{j=1}^{Z_\alpha} x_j^\alpha \right] \right\rangle = 0 . \tag{13}$$

Here we have summed over contributions from local jumps of different *length* α. The mean square value of the displacement of the center of mass is

$$\langle X_{\text{c.m.}}^2 \rangle = \frac{1}{N^2} \left\langle \left[\sum_{\alpha=1}^{N_e} \sum_{i=1}^{Z_\alpha} x_i^\alpha \right]^2 \right\rangle . \tag{14}$$

Here the brackets stand for an average over all realizations of local jumps and the displacements they cause on either side of them. The displacements along the chain contour are again statistically independent,

$$\langle x_i^\alpha x_j^\beta \rangle = c_\alpha^2 \delta_{ij} \delta_{\alpha\beta} , \tag{15}$$

and therefore,

$$\langle X_{\text{c.m.}}^2 \rangle = \frac{1}{N^2} \sum_{\alpha=1}^{N_e} \bar{Z}_\alpha c_\alpha^2 , \tag{16}$$

which, upon substituting for $\bar{Z}_\alpha$ from Eq. (12), yields

$$\langle X_{\text{c.m.}}^2 \rangle = \frac{t}{N} \sum_{\alpha=1}^{N_e} c_\alpha^2 P_\alpha A_\alpha e^{-E_\alpha/k_BT} .$$

The tube diffusion coefficient in curvilinear coordinates along the chain contour is then found from Fick's Law [Eq. (6)] to be

$$D_{\text{tube}} = \frac{1}{N} \sum_{\alpha=1}^{N_e} c_\alpha^2 P_\alpha A_\alpha e^{-E_\alpha/k_BT} . \tag{17}$$

We may find the renewal time, as in the previous model, from Eqs. (8) and (17) to be

$$\tau_r = \frac{N^3 a^2}{\sum_{\alpha=1}^{N_e} c_\alpha^2 P_\alpha A_\alpha e^{-E_\alpha/k_BT}} . \tag{18}$$

The translation diffusion coefficient is therefore

$$D_{\text{tr}} = \frac{1}{N^2} \sum_{\alpha=1}^{N_e} c_\alpha^2 P_\alpha A_\alpha e^{-E_\alpha/k_BT} . \tag{19}$$

From Eqs. (11) and (19) we find the diffusion activation energy per mole of the polymer chain as

$$E_{\text{diff}} = \frac{N_0 \sum_{\alpha=1}^{N_e} P_\alpha A_\alpha E_\alpha e^{-E_\alpha/k_BT}}{\sum_{\alpha=1}^{N_e} P_\alpha A_\alpha e^{-E_\alpha/k_BT}} = N_0 \langle E \rangle , \tag{20}$$

where the brackets indicate an average over the length of the segment involved in the double-bond transition. Note that the sum extends to N_e, the entanglement length.

Since we expect the activation energies E_α to be quite large for jump transitions involving many links, the Boltzmann weights of the terms with relatively large α appearing in the sums in Eq. (20) are negligibly small. Thus the sums are effectively truncated at some $\alpha_{\max}(T)$, possibly much smaller than N_e. This means that the apparent activation energy per mole for the diffusing polymer chains in an entangled regime does not depend on the chain length, if this length is greater than the average entanglement length; it depends weakly on the chain length N_e between two entanglement points and strongly on the temperature. This result is supported by experimental findings [19], which indicate that the apparent diffusion activation energy per mole is independent of the chain length for long chains and can be fit by an empirical formula of the type

$$E_{\text{diff}} = \frac{AT^2}{(B+T)^2} , \tag{21}$$

where A and B are constants that do not depend on T.

We can understand this temperature dependence on the basis of Eq. (19). Let us assume $E_\alpha = E_0 \alpha^x$ and that $P_\alpha \sim \exp(\alpha^y)$, say. Also let A_α and c_α depend weakly on α. Then, going to the continuum limit and performing a saddle point approximation to the integral over α, one finds

$$D_{\mathrm{tr}} \sim \frac{1}{N^2} c_{\alpha_0} A_{\alpha_0} e^{-[(y-x)/x]\alpha_0^y} ,$$

where

$$\alpha_0 = \left[\frac{x E_0}{y k_B T} \right]^{1/(y-x)} .$$

E_{diff} can now be computed from Eq. (11),

$$E_{\mathrm{diff}} \cong N_0 k_B \left[\frac{E_0}{k_B} \right]^{y/(y-x)} \left[\frac{x}{yT} \right]^{x/(y-x)} \tag{22}$$

$$\sim A T^{x/(x-y)} .$$

The empirical result in Eq. (21) calls for the $x=2y$. Finally, let us remark that we expect x to be equal to the fractal dimension of the entanglement network, since E_α should grow with the number of links that have to be displaced within the volume swept out by a local jump of length α.

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