

Diffusion of a reptating polymer interacting with a random matrix

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(Received 15 April 1993)

The diffusion of a long polymer chain in a random matrix is investigated using a discrete Ising-like reptation model which has been modified to include a weak random chain-matrix interaction. While reptation's usual inverse-length dependence of the diffusion constant is not changed, the interaction engenders a long-lived transient with a characteristic time proportional to the square of the chain length.

PACS number(s): 36.20.-r, 82.45.+z, 87.15.-v

INTRODUCTION

Diffusion of polymers through random networks is frequently described with the reptation model introduced by de Gennes [1] and elaborated by Doi and Edwards [2]. A fundamental tenet of the model is that the chain's friction coefficient along its random curvilinear path is proportional to chain length. Accordingly reptation predicts that the chain's diffusion constant along the same curvilinear path must depend inversely on chain length and after projection along an external direction, like that of an applied external field, for example, the diffusion will depend inversely on chain length squared [1,2]. The frequently observed inverse-length dependence of the gel-electrophoretic mobility of polyelectrolytes such as DNA is consistent with these predictions [3,4], but significant departures from this prediction have been observed [5-8]. Also recent experiments [9-14] and computer simulations with long polymer chains [15-17] show a different dependence of diffusion on chain length and support the view that other modes of motion, more complex than simple reptation, can contribute significantly to the motion. Within the framework of simple reptation theory, however, it has been suggested that some neglected interaction between chain and matrix could also alter the diffusion's length dependence, and long chains might be localized or trapped by rare low-energy states [18]. In this paper we investigate analytically the effect of a weak random chain-matrix interaction on the diffusional motion of a long chain. To do this we extend a discrete, Ising-like, reptation model previously described [19]. The precise form of the interaction is not specified, but weak elastic bending of the chain as it migrates or a van der Waals-type interaction between chain and network would be consistent with our formulation. Principally, we find that, while the length dependence of the diffusion constant predicted by reptation is not changed, the chain-lattice interaction can give rise to a long-lived transient, decaying inversely with time, with a characteristic time proportional to the square of the chain length. Regardless of chain length, we find that trapping states only exist in the limit of very large interactions.

In Sec. I we outline the discrete reptation model and perform several simple illustrative calculations which set the stage for our main calculation. In Sec. II we formu-

late the master equation which describes the time dependence of the chain's diffusive motion and obtain the time dependence of the diffusion. In Sec. III our results are summarized, discussed, and possible future extensions indicated.

I. REPTATION MODEL AND PRELIMINARIES

In the discrete reptation model employed here the chain is replaced by a sequence of + or - signs, which roughly denote orientation with respect to some external axis [16]. The total number of signs, always an even number N , is taken to represent the length of the chain. The projection of the chain along the external direction is assumed proportional to the discrete random variable $x = n_+ - n_-$, where n_+ is the number of positive signs and n_- , the number of negative signs in the sequence. Since N is even, possible x values are all even values, from $-N$ to N , and 0. For $N = 8$, for example, a possible chain sequence is $_T(+ + + - - + +)_H$, where H and T denote arbitrarily but permanently labeled head and tail ends of the chain. When the chain makes an H (T) move the sign at the T (H) end is dropped and another is added at the H (T) end. More details can be found in Ref. [16]. For this calculation we extend the model and schematize the chain with two superimposed sequences of + and - signs, which we assume to be independent. (For the case of elastic energy this last assumption might be modified, but since we will only consider weak interactions in this calculation we will omit that complication.) One sequence, the x sequence, represents the projection along an external axis of the chain's spatial configuration that we have just discussed. (Since we only consider diffusion in this calculation, we will not need the x sequence.) The other sequence, which we will call the g sequence, is a discrete, two-valued, rendering of the chain's interaction with the matrix. Negative signs are assigned to links with no interaction (e.g., a relaxed link of the chain for elastic energy), and the interactions energy is always $-\epsilon$ (in units of kT) and + signs are assigned to links whose interaction is nonzero (e.g., a bent link) and they have energy ϵ . In case the interaction is the chain's elastic energy, the energy to bend a single link is therefore 2ϵ . Like x , we define a discrete random variable $g = n_+ - n_-$, where n_+ and n_- are sign counts in the g sequence. A

possible $N=8$ g sequence is $_T(- - - + + + +)_H$, where H and T refer to head and tail ends of the chain, just as for the x sequence. For each g sequence the total chain-matrix interaction energy is $g\epsilon$. The energy of the lowest state is $-N\epsilon$, and as the chain moves $\Delta g=0$, or ± 2 .

Once again, an H (T) move drops the sign at the T (H) end of the g sequence and adds a sign at the H (T) end. In our model we assume that $\frac{1}{2}$ is the probability of adding either a $+$ or $-$ sign. In other words, when the random lattice was constructed, at each position which a chain link might occupy the sign of the chain-lattice interaction was permanently fixed by the flip of a coin. The distribution of possible chain energies in the matrix is therefore binomial. Therefore, for a chain which can move freely about the matrix, as will be the case in the limit $\epsilon \rightarrow 0$, the equilibrium distribution of g values must also be binomial, just as the distribution of x values is binomial in the absence of an external force field [19].

It is easy to calculate the equilibrium statistics of the discrete random variable g . In thermal equilibrium the probability of a given value of $g = n_+ - n_-$ is just given by

$$p(g) = (2^{-N} \cosh^{-N} \epsilon) N! / (n_+! n_-!) e^{-g\epsilon}, \quad (1)$$

where the first set of parentheses contains the normalization. That is, using $N = n_+ + n_-$ and $g = n_+ - n_-$, it is easy to prove that $\sum_g N! / (n_+! n_-!) e^{-g\epsilon} = 2^N \cosh^N \epsilon$, where $N! / (n_+! n_-!)$ is just the degeneracy of each g state and the sum is over all possible g values, that is, $g = -N, -N+2, \dots, -2, 0, 2, \dots, N-2, N$. The mean value is then

$$\langle g \rangle = \sum_g p(g) g = -N \tanh(\epsilon). \quad (2)$$

Similarly we find that $\langle g^2 \rangle = N[(N-1) \tanh^2 \epsilon + 1]$ and the variance $\langle g^2 \rangle - \langle g \rangle^2 = N(1 - \tanh^2 \epsilon)$. These results show that as ϵ increases the equilibrium changes from a binomial distribution of g values centered at $g=0$ to a state in which the chain is trapped at a place where the interaction energy is lowest and $g=-N$. The important point though is that both the scaled mean $\langle g \rangle / N$ and the scaled variance $(\langle g^2 \rangle - \langle g \rangle^2) / N$ depend only on ϵ and not, for example, on the product $N\epsilon$. Further, only in the limit $\epsilon \rightarrow \infty$ is the chain trapped in its lowest-energy state with the variance equal to zero. For diffusion this behavior of the variance is especially revealing since the variance measures how widely the chain samples the whole set of g values. Also, since the scaled variance is determined solely by the interaction energy ϵ , we expect the diffusion constant to show new dependence on ϵ but no modification of the size dependence required by reptation. These expectations are borne out by explicit calculation in Sec. II.

To illustrate our general approach we now calculate how the chain approaches the equilibrium state as each forward (H move) or backward (T move) move increases the move number from i to $i+1$, with $i=0$ and $g=g_0$ initially. To solve this problem we first write the recurrence relation satisfied by the discrete probabilities

that the chain has configuration g after i moves. Denoting these probabilities by $P_i(g)$, if initially $P_{i=0}(g) = \delta_{g,g_0}$, the recurrence relation to be solved is

$$P_{i+1}(g) = W_0(g) P_i(g) + W_2(g-2) P_i(g-2) + W_{-2}(g+2) P_i(g+2), \quad (3)$$

where $W_0(g)$ is the probability that the chain makes a $\Delta g=0$ transition from configuration g during the $i+1$ move and the W_2 and W_{-2} are defined analogously for $\Delta g = \pm 2$ transitions during the $i+1$ move. Equation (3) is completely general, but the exact form of each W is prescribed by the model adopted to describe the polymer's motion. Here we can obtain the W 's by considering diagrams like those in Fig. 1. Consider Fig. 1(a), for example. The chain is in state g after the i th move and both H and T moves are $\Delta g = +2$ transitions. The chain-matrix configuration after the i th move is therefore $+_T(- \dots -)_H +$, where the signs outside the parentheses refer to the matrix position that the chain moves into. The probability that the chain sequence is as above is just $n_- / N(n_- - 1) / N - 1$, while the probability for the matrix is $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$. Two additional probabilities are needed: the probabilities W_H and W_T that thermal energy will cause a head (H) jump or a tail (T) jump, respectively. In this case, since the energy changes are equal for both jumps, $W_H = W_T = \frac{1}{2}$. So the contribution of diagram 1 (a) to $W_2(g-2)$ is

$$W_H [n_- / N(n_- - 1) / N - 1] \frac{1}{4} + W_T [n_- / N(n_- - 1) / N - 1] \frac{1}{4} = [n_- / N(n_- - 1) / N - 1] \frac{1}{4},$$

with $n_- / N = \frac{1}{2} [1 - (g-2) / N]$. In general, $W_H \neq W_T$ and further, either the H or T move, but not both, contributes to the probability W . Consider Fig. 1(c), for ex-

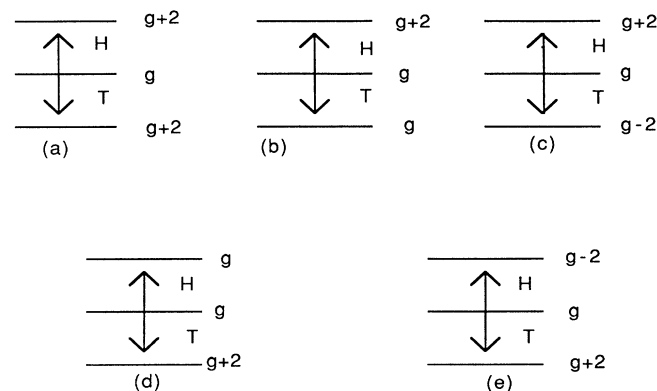


FIG. 1. Diagrams which show $\Delta g=2$ moves available to a chain initially in configuration g . In (a), for example, both H and T are $\Delta g=2$ moves. The remaining four diagrams occur in pairs, with H and T outcomes exchanged. Corresponding to each diagram is a chain-matrix configuration from which the probability of a $\Delta g=2$ outcome can be calculated. The sum of the probabilities is $W_2(g)$, the total probability that the chain makes a $\Delta g=2$ move from configuration g .

ample. Here the required chain-matrix configuration is $-_T(-\cdots+)_H+$, which occurs with probability $[n_-/Nn_+/(N-1)]^{1/4}$, and only the H move, with probability $W_H=e^{-2\varepsilon}/(e^{-2\varepsilon}+e^{+2\varepsilon})$ contributes to the $\Delta g=+2$ probability. The more favorable T move has probability $W_T=e^{+2\varepsilon}/(e^{-2\varepsilon}+e^{+2\varepsilon})$, and of course, $W_H+W_T=1$. The diagram 1(c) contribution to W_2 is therefore

$$e^{-2\varepsilon}/(e^{-2\varepsilon}/(e^{-2\varepsilon}+e^{+2\varepsilon})(n_-/N)[n_+/(N-1)]^{1/4}.$$

Diagram 1(e) is the T jump version of 1(c) and its contribution to the $\Delta g=+2$ probability is identical to that just calculated. Similarly, diagrams 1(b) and 1(d) are paired and both contribute $e^{-2\varepsilon}/(e^{-2\varepsilon}+1)(n_-/N)^{1/4}$. To calculate this note that two chain-matrix configurations contribute to this diagram: $+_T(-\cdots+)_H+$ and $-_T(-\cdots-)_H+$. For each sequence a T jump is a $\Delta g=0$ transition and the probabilities are $\frac{1}{4}(n_-/N)[n_+/(N-1)]$ and $\frac{1}{4}(n_-/N)(n_- - 1)/(N-1)$ respectively. The total probability of the $\Delta g=+2$ channel is thus

$$\begin{aligned} W_2(g-2) &= (n_-/N)(n_- - 1)/[4(N-1)] \\ &+ e^{-2\varepsilon}/[2(e^{-2\varepsilon}+1)](n_-/N) \\ &+ e^{-2\varepsilon}/[2(e^{-2\varepsilon}+e^{+2\varepsilon})] \\ &\times (n_-/N)[n_+/(N-1)], \end{aligned} \quad (4a)$$

with $n_-/N = \frac{1}{2}[1 - (g-2)/N]$. The diagrams needed to calculate the probabilities W_{-2} and W_0 are given in Figs. 2 and 3. The results are

$$\begin{aligned} W_0(g) &= \frac{1}{4} + 1/[2(1+e^{2\varepsilon})](n_+/N) \\ &+ 1/[2(1+e^{-2\varepsilon})](n_-/N), \end{aligned} \quad (4b)$$

with $n_{\pm}/N = \frac{1}{2}(1 \pm g/N)$ and

$$\begin{aligned} W_{-2}(g+2) &= (n_+/N)(n_+ - 1)/[4(N-1)] \\ &+ e^{2\varepsilon}/[2(1+e^{2\varepsilon})](n_+/N) \\ &+ e^{2\varepsilon}/[2(e^{2\varepsilon}+e^{-2\varepsilon})] \\ &\times (n_+/N)[n_-/(N-1)], \end{aligned} \quad (4c)$$

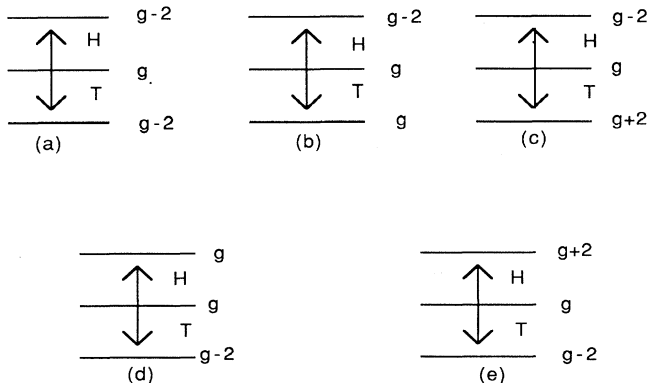


FIG. 2. $\Delta g = -2$ diagrams.

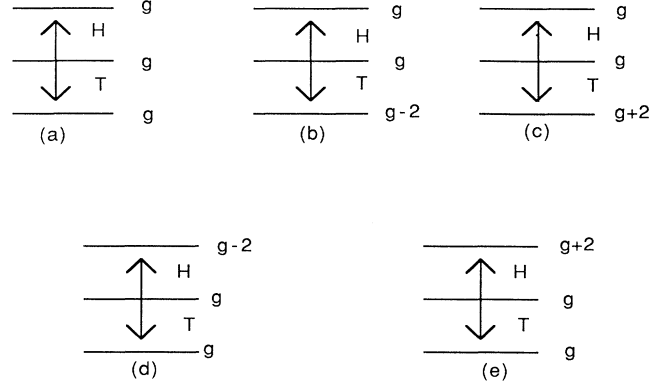


FIG. 3. $\Delta g = 0$ diagrams.

with $n_{\pm}/N = \frac{1}{2}[1 \pm (g+2)/N]$. Note also that $W_0(g) + W_2(g) + W_{-2}(g) = 1$, since the W 's partition probability among the three transition channels available to a configuration g .

In order for thermodynamic equilibrium, Eq. (1), to be the stationary state of Eq. (3) (that is, when $i \rightarrow \infty$ and $P_{i+1} = P_i$) the W 's must satisfy detailed balance. Since in equilibrium $n_g W_2(g) = n_{g+2} W_{-2}(g+2)$, where n_g is the number of chains in configuration g and n_{g+2} the number in configuration $g+2$, this requires that the W 's satisfy

$$W_{-2}(g+2)/W_2(g) = [z(g)/z(g+2)]e^{\Delta}, \quad (5)$$

where $z(g) = N!/(n_+!n_-!)$ is just the number of sign permutations associated with configuration g [similarly for $z(g+2)$] and $\Delta (=2\varepsilon)$ is the chain's energy increase (in units of kT) in a $\Delta g=+2$ transition. Using the W 's from Eqs. (4) we find, in fact, that

$$\begin{aligned} W_{-2}/W_2 &= z(g)/z(g+2) \\ &\times [1 + \Delta + (2n_+ + N - 1)[4(N-1)]\Delta^2 \\ &+ \cdots], \end{aligned} \quad (6)$$

where $n_+ = (1+g)/N$. This result shows that only for $\Delta \ll 1$ will the model's stationary state satisfy thermodynamic equilibrium. Important for this investigation though, this will be true for any length N ; hence the product $N\varepsilon$ may be large without violating detailed balancing. Since the focus of this investigation is a long chain with a weak interaction, the simple W 's derived above will be adequate.

Combining Eqs. (4) and (3) and defining a new random variable $k = g/2$, whose range is the consecutive integer values $(-N/2, -N/2+1, \dots, -1, 0, 1, \dots, N/2)$, we can rewrite Eq. (3) as

$$\begin{aligned} P_{i+1}(k) &= (a_1 + b_1 k)P_i(k) \\ &+ [a_2 + b_2(k-1) + c_2(k-1)^2]P_i(k-1) \\ &+ [a_3 + b_3(k+1) + c_3(k+1)^2]P_i(k+1), \end{aligned} \quad (7)$$

where the coefficients a_1, b_1, a_2, b_2 , etc. depend only on N and the energy ε . Their expressions are given in the Appendix. To solve Eq. (7) we define a generating func-

tion $F_i(s) = \sum_k P_i(k) s^k$. The derivatives of F evaluated at $s=1$ give the moments of the probability distribution, that is, $\langle k \rangle = (dF/ds)_{s=1}$ and $(d^2F/d^2s)_{s=1} = \langle k^2 \rangle - \langle k \rangle^2$. The differential-difference equation for $F_i(s)$ is

$$s^2 \frac{d^2 F_i}{ds^2} (c_2 s + c_3 / s) + s \frac{dF_i}{ds} [b_1 + (b_2 + c_2)s + (b_3 + c_3)/s] + (a_1 + a_2 s + a_3 / s) F_i = F_{i+1}. \quad (8)$$

Setting $s=1$ in Eq. (8) and using the coefficient values in the Appendix, one finds that $F_i(s=1) = F_{i+1}(s=1) = \sum_k P_i(k) = 1$, since the $P_i(k)$'s are normalized for all values of the move index i . The stationary state of Eq. (8) for $\epsilon=0$ is obtained by setting $F_{i+1}(s) = F_i(s) = F(s)$. One finds

$$2 \frac{s}{N} \frac{dF}{ds} + F(1-s)/(1+s) = 0, \quad (9)$$

whose solution is $F(s) = (\frac{1}{2})^N (1+s)^N / s^{N/2}$. Using the binomial theorem to expand $F(s)$ and setting $g=2k$ we find that g 's steady-state probability distribution is binomial, that is, $P(g) = N! / [(N+g)/2]! [(N-g)/2]!$, and that $\langle g \rangle = 0$ and $\langle g^2 \rangle = N$, as expected. It is also straightforward to show from Eq. (8) for $\epsilon=0$ (that g 's mean value after step i) $\langle g(i) \rangle = g_0 [(N-1)/N]^i$, or for large N , $\langle g(i) \rangle \approx g_0 e^{-1/N}$, which shows that the duration of the transient phase of the motion depends on the chain length N . In fact, in Sec. II we show that the temporal duration of the transient phase of the diffusion is proportional to N^2 . Steady-state solutions of Eq. (8) for arbitrary ϵ can be written in terms of polynomials derived from hypergeometric series, but we will not discuss those results here.

II. DIFFUSIONAL MOTION

Suppose the discrete probability $P_i(t)$ that the chain make i moves during the time interval $(0, t)$ is known. If each move's length is a and if forward (H) and backward (T) moves occur with equal frequency, the mean-square displacement during $(0, t)$ is

$$\langle S^2 \rangle = a^2 \sum_i i P_i(t) = a^2 \langle i(t) \rangle, \quad (10)$$

where $\langle i(t) \rangle$ is the average number of moves during $(0, t)$. Since the chain's one-dimensional diffusion constant is just the long time limit of $\langle S^2 \rangle / 2t$, the transient

and steady state of the diffusion are obtained by calculating $\langle i(t) \rangle$. To do this consider the discrete joint probability $P_i(g, t)$, which during $(0, t)$ the chain makes i moves and is in state g at time t . A recurrence relation for $P_i(g, t)$ is

$$P_{i+1}(g, t + \Delta t) = P_{i+1}(g, t) [1 - (R_0 + R_2 + R_{-2}) \Delta t] + P_i(g, t) R_0 \Delta t + P_i(g-2, t) R_2 \Delta t + P_i(g+2, t) R_{-2} \Delta t. \quad (11)$$

This recurrence relation enumerates all the channels that lead to configuration g and move $i+1$ during interval $(t, t + \Delta t)$. $R_0 \Delta t$ is the probability of a $\Delta g = 0$ move during $(t, t + \Delta t)$ and $R_2 \Delta t$ and $R_{-2} \Delta t$ are similarly defined for $\Delta g = +2$ and -2 moves. The first term in Eq. (11) is the probability that at time t the chain is in state g and has already made $i+1$ moves and then makes no move during $(t, t + \Delta t)$. The other terms are similarly defined. Rearranging terms, dividing by Δt and letting $\Delta t \rightarrow 0$, we obtain the differential-difference equation

$$\frac{dP_{i+1}(g, t)}{dt} = -P_{i+1}(g, t)(R_0 + R_2 + R_{-2}) + P_i(g, t) R_0 + P_i(g-2, t) R_2 + P_i(g+2, t) R_{-2}. \quad (12)$$

To calculate the rates R_0 , R_2 , and R_{-2} we return to the diagrams in Figs. 1-3 and use an approach based on first-passage times [16]. To calculate R_0 , for example, the probability of each $\Delta g = 0$ process in Fig. 3 should be multiplied by the inverse mean-first-passage time for the process diagrammed and then added. For Fig. 3(a), for example, the mean-first-passage time is just the mean time between jumps in free diffusion t_d . This is also the case for diagram 3(c), but a new first-passage time t_{-2} must be calculated for 3(b). Since the ratio t_d / t_{-2} can only depend on the energy change 2ϵ and not on N and since we are only interested in the case of $\epsilon \ll 1$ when $t_{-2} \approx t_d$ must hold, we will set $t_{-2} = t_d$. This approximation, which simplifies the calculation, can lead to incorrect numerical factors in calculated results but will not change their N or ϵ dependence for $\epsilon \ll 1$. Approximating the ratio t_{-2} / t_d by the Boltzmann factor $e = -2\epsilon$, for example, does not change the N or ϵ dependence of our results when $\epsilon \ll 1$. Thus we set $R_0 = W_0 / t_d$, $R_2 = W_{+2} / t_d$, and $R_{-2} = W_{-2} / t_d$, where the W 's are defined in Eq. (8). Defining dimensionless time t' by setting $t = t' t_d$ and also using the random variable $k = g/2$, which takes consecutive integer values from $-N/2$ to $N/2$, we find that Eq. (12) becomes

$$\frac{dP_{i+1}(k, t')}{dt'} = -P_{i+1}(k, t') [a_1 + a_2 + a_3 + (b_1 + b_2 + b_3)k + (c_2 + c_3)k^2] + P_i(k, t') (a_1 + b_1 k) + P_i(k-1, t') [a_2 + b_2(k-1) + c_2(k-1)^2] + P_i(k+1, t') [a_3 + b_3(k+1) + c_3(k+1)^2], \quad (13)$$

where the coefficients are given in the Appendix. To solve Eq. (13) define the generating function

$$F(r, s, t') = \sum_i \sum_k P_i(k, t') r^i s^k, \quad (14)$$

which in addition to $F(r=1, s=1, t')=1$ has the following useful properties:

$$\left[\frac{\partial F}{\partial r} \right]_{r=s=1} = \sum_i \sum_k i P_i(k, t') = \langle i(t') \rangle, \quad (15a)$$

$$\left[\frac{\partial F}{\partial k} \right]_{r=s=1} = \sum_i \sum_k k P_i(k, t') = \langle k(t') \rangle. \quad (15b)$$

From Eqs. (13) and (14) the partial differential equation satisfied by $F(r, s, t')$ is

$$s^2 \frac{\partial^2 F}{\partial s^2} [c_2(rs-1) + c_3(r/s-1)] + s \frac{\partial F}{\partial s} [b_1(r-1) + (b_2+c_2)(rs-1) + (b_3+c_3)(r/s-1)] \\ + F[a_1(r-1) + a_2(rs-1) + a_3(r/s-1)] = \frac{\partial F}{\partial t'}. \quad (16)$$

To obtain $\langle i(t') \rangle$ and $\langle k(t') \rangle$ from Eq. (16) first we switch to new variables using $s=e^v$ and $r=e^u$. We then replace e^v and e^u by $1+v$ and $1+u$, respectively, since we are only interested in Eq. (16) in the neighborhood of $s=r=1$. The resulting equation is

$$\frac{\partial^2 F}{\partial t'^2} [(c_2-c_3)v + (c_2+c_3)u] + \frac{\partial F}{\partial t'} [(b_1+b_2+b_3+c_2+c_3)u + (b_2-b_3+c_2-c_3)v] \\ + F[(a_1+a_2+a_3)u + (a_2-a_3)v] = \frac{\partial f}{\partial t'}. \quad (17)$$

Then since $\langle i(t') \rangle = (\partial F / \partial u)_{v=u=0}$ and $\langle k(t') \rangle = (\partial F / \partial v)_{v=u=0}$, we differentiate both sides of Eq. (17), set $v=u=0$, and obtain the following coupled equations:

$$\frac{\partial \langle k \rangle}{\partial t'} = (a_2 - a_3) + \langle k \rangle (b_2 - b_3 + c_2 - c_3) \\ + (c_2 - c_3) \left[\frac{\partial^2 F}{\partial t'^2} \right]_0, \quad (18a)$$

$$\frac{\partial \langle i \rangle}{\partial t'} = (a_1 + a_2 + a_3) + \langle k \rangle (b_1 + b_2 + b_3 + c_2 + c_3) \\ + (c_2 + c_3) \left[\frac{\partial^2 F}{\partial t'^2} \right]_0. \quad (18b)$$

For $\epsilon=0$, evaluation of the coefficients given in the Appendix shows that Eqs. (18) reduce to

$$\frac{\partial \langle k \rangle}{\partial t'} = -\langle k \rangle / N, \quad (19a)$$

$$\frac{\partial \langle i \rangle}{\partial t'} = 1. \quad (19b)$$

The solution of Eq. (19a) is the temporal equivalent of $\langle g \rangle \approx g_0 e^{t/N}$ discussed Sec. I and from Eq. (19b) $\langle i(t) \rangle = t/t_d$, the expected free-diffusion result.

Because k 's probability distribution is binomial for $\epsilon=0$, $(\partial^2 F / \partial t'^2)_0 = \langle k^2 \rangle \approx N/4$ in Eqs. (18) for $\epsilon \ll 1$. Expanding the numerical coefficients about $\epsilon=0$ shows that the final term in Eq. (18a) must be of order ϵ^2/N and the final term in Eq. (18b) of order ϵ/N . Therefore we neglect these terms. To first order in ϵ then, Eq. (18a) gives

$$\langle k(t) \rangle = k_0 e^{-t/t_d} N - \frac{3}{4} N \epsilon (1 - e^{-t/t_d} N), \quad (20)$$

which predicts that the steady-state value of $\langle k \rangle$ for small ϵ is $-\frac{3}{4} N \epsilon$, instead of the exact value of $\frac{1}{2} N \epsilon$ [see Eq. (2)]. This erroneous numerical factor is the result of approximation all mean-first-passage times by t_d . More importantly, however, the dependence of $\langle k \rangle$'s steady-state value on N and ϵ is correct. Note also that $\langle k(t) \rangle$'s characteristic time $t_d N$ is proportional to N^2 , since t_d is proportional to the chain's friction coefficient, which is proportional to N . Returning to Eq. (18b) we find that

$$\frac{d \langle i \rangle}{dt'} = (1 - \epsilon/4) + \langle k(t') \rangle \epsilon / 2N. \quad (21)$$

Using Eq. (20) we calculate to lowest power in ϵ that

$$\langle i(t) \rangle / t = (1 - \epsilon/4) / t_d \\ + [\epsilon k_0 / (2N)] (1 - e^{-t/t_d} N) / (t / t_d N). \quad (22)$$

The first term in Eq. (22) shows that the diffusion constant is altered from its free-diffusion value by the chain-matrix interaction, but the inverse N dependence, from t_d , is the same as for simple reptation. The size of the diffusional transient in Eq. (22) depends on the initial value k_0/N , which may be positive, negative, or zero. In general, the transient starts from an initial value of $\epsilon k_0 / (2N)$ and then decreases towards zero, inversely with time for long times, with a characteristic time proportional to N^2 .

III. DISCUSSION AND CONCLUSION

The principal conclusion of our study is that a weak chain-matrix interaction does not alter the inverse-length

dependence of the chain's diffusion constant predicted by reptation, even for very long chains. While the specifics of the molecular mechanism behind the interaction have not been specified, our formulation would seem to apply to either weak elastic bonding of chain segments or van der Waals-like interactions between chain and matrix. It is less certain that our conclusion applies to the random entropic forces encountered by the diffusing chain [15–17], since a realistic model of these effects must also include significant fluctuations in the reptation tube length, which we have neglected [20]. An approximate way of including such length fluctuations in our discrete reptation model has been proposed [21], and their effect on diffusion will be considered in a future investigation.

ACKNOWLEDGMENTS

We are indebted to our colleague Bruno H. Zimm for many useful discussions. Part of this work was supported by NIH Grant No. GM 11916.

APPENDIX

$$\begin{aligned}
 a_1 &= 1/4[1 + 1/(1 + e^{2\epsilon} + 1/(1 + e^{-2\epsilon}))], \\
 b_1 &= 1/(2N)[1/(1 + e^{2\epsilon}) - 1/(1 + e^{-2\epsilon})], \\
 a_2 &= 1/(4N)\{(N - 2)/[4(N - 1)] + e^{-2\epsilon}/(e^{-2\epsilon} + 1) \\
 &\quad + e^{-2\epsilon}/(e^{-2\epsilon} + e^{2\epsilon})N/(N - 1)\}, \\
 b_2 &= -1/(4N)[1 + 2e^{-2\epsilon}/(e^{-2\epsilon} + 1)], \\
 c_2 &= 1/[4N(N - 1)][1 - 2e^{-2\epsilon}/(e^{-2\epsilon} + e^{2\epsilon})], \\
 a_3 &= 1/(4N)\{(N - 2)/[4(N - 1)] + e^{2\epsilon}/(e^{2\epsilon} + 1) \\
 &\quad + e^{2\epsilon}/(e^{2\epsilon} + e^{-2\epsilon})N/(N - 1)\}, \\
 b_3 &= 1/(4N)[1 + 2e^{2\epsilon}/(e^{2\epsilon} + 1)], \\
 c_3 &= 1/[4N(N - 1)][1 - 2e^{2\epsilon}/(e^{2\epsilon} + e^{-2\epsilon})].
 \end{aligned}$$

In the above expressions N is any positive even value.

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