JOURNAL OF CHEMICAL PHYSICS VOLUME 109, NUMBER 6 8 AUGUST 1998

Transient relaxation of a charged polymer chain subject to an external field in a random tube

S. F. Burlatsky[a] and John M. Deutch[b]
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 12 August 1997; accepted 4 May 1998)

Transient relaxation of a charged polymer chain in a random media is studied theoretically. We consider a chain in a random tube and present scaling results for relaxation times, for displacement of the chain segments inside the tube, and for the dynamics of leaking from the tube ends. © *1998 American Institute of Physics.* [S0021-9606(98)51230-5]

I. INTRODUCTION

There has been considerable progress during the past several years in the analytical description of diffusion in random media. One of the most striking results was obtained by Sinai[1] for the dynamics of a particle on a discrete one-dimensional infinite lattice with random uncorrelated hopping probabilities at each site. Sinai has proven rigorously that the mean-square displacement, L, in such a system is

$$L \propto (\ln t)^4, \tag{1}$$

where t is the time. Sinai's work has stimulated interest in the relevance of this slowing down to a variety of diffusion phenomena. For instance, it was shown that Sinai-type diffusion is relevant to $1/f$-noise,[2] slow spin dynamics in random-field magnets and dynamics of dislocations in doped crystals.[3] Another example of Sinai diffusion is provided by a charged particle diffusing on a linear random structure, e.g., polymer chain or random pore, in presence of an uniform electric field.[4,5] In this paper, we show that relaxation of charged polymer in a tube randomly oriented in a constant external field corresponds to the Sinai type model—relaxation of a polymer chain in a 1D (one-dimensional) random potential.

The motion of charged polymer chains in an external electric field has been extensively studied experimentally and theoretically, see recent reviews,[6–16] and references therein. When this motion takes place in a random medium the physical situation corresponds to gel electrophoresis—an important experimental tool for separating charged polymers, especially DNA.[17] Pulsed field electrophoresis[18] improves the separation of large DNA molecules in a gel matrix or a polymer solution.[19] In this technique, an electric field that is applied alternately in two or more different directions and separation is achieved because the relaxation time required to reorient chains depends on their lengths.[19,20–22]

Current understanding of gel electrophoresis is substantially based on the reptation model introduced by de Gennes,[23] and extended by Doi and Edwards.[24–26] The reptation or tube model was first applied to electrophoresis by Lerman and Frisch,[27] and more extensively in Refs. 28 and 29, and later expanded in Refs. 30–35.

Pulsed field electrophoresis of a point particle confined in a random tube has been theoretically studied[36] as has the steady electrophoretic mobility of charged particles (monomers or short chains) subject to a constant field in a medium with random curved interconnected channels.[37] Zimm introduced the Lakes–Straits model;[38] in this model, segments of a large polymer chain in a random media accumulate in lakes connected by random straits and the chain leaks from the lakes at higher energy for the segment, through straits to lakes at lower energy. The theory of gel electrophoresis in the large field transient regime where polymer chains escape from their tubes by formation of hernias (loops) was recently developed in Ref. 39 and the steady-state mobility for a similar type of motion was studied in Refs. 40 and 41. The barrier to loop formation in a porous matrix was theoretically and experimentally studied in Ref. 42.

In this paper we consider the motion of the charged polymer in a random media subject to a moderate external field

$$E \ll \frac{k_B T}{qa}, \tag{2}$$

neglecting loop formation. Here E is the strength of the external electric field and a is the diameter of a random pore determined by the matrix. The opposite limit was considered in Refs. 40 and 41. We disregard the solid friction effects which may significantly change the relaxation of long chains.[43–47] In the present model, the polymer is confined in a random pore or tube. We assume each tube is sufficiently large to accommodate at any point along its length complicated conformations of the polymer chain and there is only one polymer chain per tube.

We consider two types of initial distributions of the chain which correspond, respectively, to two models. In the first *model (model* A*)*, the random media is represented by an array of channels[48] which are not interconnected.[36,48,49] The configuration of the tube which confines the polymer chain is determined by channels in a random porous matrix so ''the chain could only move backward and forward in one, unchanging tube.'' [48] Within this model we consider a phantom

---

[a] On leave of absence from Institute of Chemical Physics, Russian Academy of Science.
[b] E-mail: jmd@mit.edu

chain and disregard excluded volume effects. In the second *model (model* B*)*, we adopt a more common picture for the motion of a polymer chain in a gel: The chain creates its own channel in an array of obstacles, renewing its own tube as it moves.

We examine the internal relaxation of the polymer confined in a random tube for both models, A and B, in the limit of a long chain, and analytically estimate the relaxation times and corresponding scaling displacement on time dependencies which are governed by the segments exchange between local minima of the chain energy prescribed by the tube configuration (between ''lakes'' in the terms of Ref. 38). In Sec. II we present the general equations governing the motion of the charged polymer in presence of an external field. In Sec. III we show how the relaxation scenario for the infinite length chain in a random tube can be mapped onto the relaxation of a chain in a one-dimensional Sinai—type random potential. In Sec. IV we calculate the characteristic internal relaxation time for a polymer which is stretched into ropelike fragments between the potential minima (inside ''straits'' in the terms of Ref. 38) and in Sec. V we calculate the characteristic internal relaxation time for a polymer whose segments are joined by purely elastic forces. The leaking of the polymer out of the tube end is considered in Sec. VI.

II. GENERAL EQUATIONS

The motion of a charged polymer chain in a random tube in the presence of a constant external field can be described by the following equation:

$$\beta \frac{\partial r(n,t)}{\partial t} = F(n,n+1) + F(n,n-1) + qE\cos[\theta(r)] + f_r(n,t), \tag{3}$$

where $r(n,t)$ is the position of nth segment at time t along tube axis, β is the friction coefficient of the segment, $F(n,n+1)$ is the intermolecular force which the segment $(n+1)$ acts on the segment n, $\theta(r)$ is the angle between the local tube axis and the field direction, and $f_r(n,t)$ is the random Langevin force (arising from thermal motion) acting on segment n. The displacement along the tube is proportional to the squared displacement in real space coordinates $\langle r^2/3\rangle = \langle x^2\rangle = \langle y^2\rangle = \langle z^2\rangle = a^2N$, since the tube configuration in space can be described by a random walk with step length a, and number of steps N.

For relaxation of sufficiently large chain fragments the chain motion is determined by the external electric field and the random thermal force $f_r(n,t)$ can be neglected (the quantitative criteria is presented below), and Eq. (3) becomes

$$\beta \frac{\partial r(n,t)}{\partial t} = F(n) + F(n-1) + qE\cos[\theta(r)], \tag{4}$$

where we have defined the chain tension $F(n) \equiv F(n,n+1)$, and used the fact that $F(n,n+1) = -F(n+1,n)$.

The external force $qE\cos[\theta(r)]$, which acts on the nth segment located at point r inside the tube, does not explicitly depend on n and time. This external force depends only on the angle between the external field E and the tube axes in the point r. This external force is random as a consequence of the random orientation that the tube makes with the external field; see Fig. 1.

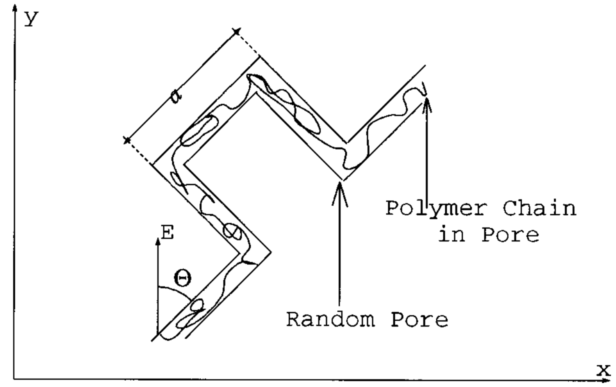

FIG. 1. The configuration of the random pore in the presence of the external electric field fixed in space. The polymer chain lying in the pore is illustrated in a random configuration within the tube.

One can associate a random one-dimensional potential $U(r)$ with the random force $f_r(r)$. In a lattice model, with spacing a

$$U(r) = a[f_r(0) + f_r(1) + \cdots f_r(m)], \tag{5}$$

for $m > 0$

$$U(r) = 0, \tag{6}$$

for $r = 0$ (the origin can be chosen in arbitrary point of tube), and

$$U(r) = a[f_r(0) + f_r(-1) + \cdots f_r(-m)], \tag{7}$$

for negative r.

For d-dimensional cubic lattice, at each step the tube has a random orientation with respect to the external field. Thus, the random force f_r, at each tube step (lattice bond), is equal to qE or $-qE$ with probability $1/(2d)$ and it is equal to zero with probability $(1-1/d)$. The resulting random potential $U(r)$ is the sum of r/a identically distributed independent random variables with zero mean value and dispersion equal to $(qEa)^2$. Thus

$$\langle U^2(r)\rangle = (qE)^2 ar. \tag{8}$$

This ''deterministic'' description based on omission of thermal force $f_r(n,t)$ is valid when

$$\sqrt{\langle U^2(r)\rangle} \gg k_B T. \tag{9}$$

We consider the relaxation of polymer chains that are initially either randomly distributed inside the tube, or distributed as expected for a reptation configuration, see Fig. 1, before the field is turned on. For the *random initial distribution* which corresponds to a chain in a tube defined by a random porous matrix (model A), the number of segments $N(L)$ on length scale L is given by the dependence of the random walk displacement on the number of steps

$$L = bN^{1/2}, \tag{10}$$

where b is the chain segment size (Kuhn length, which is determined by polymer properties and does not depend on

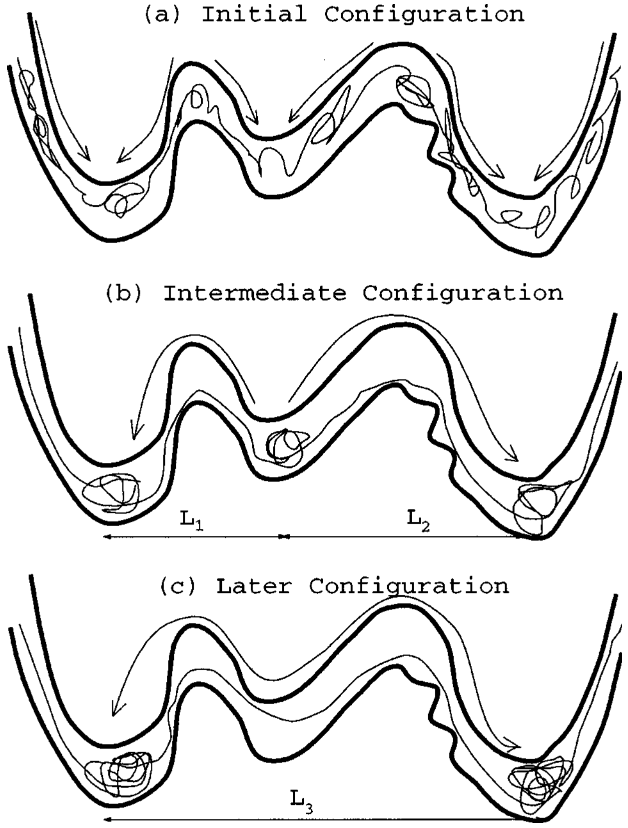

FIG. 2. Relaxation scenario: (a) Initial configuration of chain in random tube; (b) relaxation of chain segments to local minima—relaxation occurs on length scales L_1 and L_2; (c) later configuration—relaxation on length scale L_3. Arrows indicate the direction of the flow of chain segments.

random matrix). For a *reptation type initial condition*, which corresponds to reptation in a tube created by the chain (model B), the entropy—induced tensile forces stretch the chain in the tube[50] and

$$L=b^2N/a. \tag{11}$$

Our model implicitly assumes that the segment size b is small compared to the characteristic tube step size a.

III. RELAXATION SCENARIO

At $t=0$, the external electric field is switched on. The polymer chain in an initial configuration finds itself distributed in a random potential with many local potential minima and maxima. Portions of the chain will be pulled from a higher local minimum to a lower local minimum. In the region between two subsequent local minima the polymer chain will be highly stretched. The situation is depicted in Fig. 2(a).

As time progresses, the segments will migrate to the local energy minima in the potential. Segments present in the neighborhood of the minima will have a random configuration; segments present in the regions between the minima will be stretched. This situation is illustrated in Fig. 2(b).

In the subsequent time, segments in the higher potential will flow, as indicated by the arrows, to the lower neighboring minima that are characterized by length scales L_1 and L_2. At later times, segments will move between the next neighboring lower minima in the potential on the length scale L_3 as indicated in Fig. 2(c). At this point, the chain fragment located along the higher minimum is stretched. Segments in minima do not interact until all the intervening higher relative minima have been ‘‘emptied’’ and the intervening chain length is stretched. Note that at some points along the random tube, the local direction of flow can change sign as time proceeds.

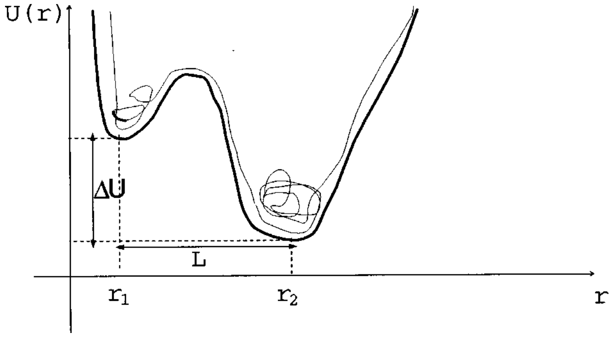

FIG. 3. Relaxation model depicting stretched polymer chain between two minima. The minima are separated by a distance of the order L and are of the order $\Delta U \propto \sqrt{L}$ different in energy.

Our interest is in determining the characteristic relaxation time $t(L)$ for the chain to relax when the characteristic length between extrema is of order L and, as a consequence of our assumption of the random potential, Eq. (8), the strength of the random potential is

$$U(L)\approx qE\sqrt{aL}. \tag{12}$$

We proceed to calculate this relaxation time for two different cases. In the first case, we assume that the chain is stretched in a ropelike configuration in the region between local minima. In the second case, we assume that only harmonic forces exist between neighboring segments and that these intermolecular forces in combination with the external random potential, cause segment motion.

IV. RELAXATION TIME ESTIMATE FOR ROPELIKE STRETCHING

We consider the flow of chain segments from one local minimum to a neighboring local minimum, of lower energy. We assume that the polymer is not stretched in local minima and the polymer is stretched to a ropelike configuration in the region between the minima, see Fig. 3.

The equation of motion, Eq. (4), for the segments is

$$\beta\,\frac{\partial r(n,t)}{\partial t}=\frac{\partial F(n)}{\partial n}+f(r). \tag{13}$$

We seek a steady-state solution that satisfies the relation

$$r(n,0)=r(n-Jt,t), \tag{14}$$

where J is the steady flux of segments flowing between the two neighboring wells. Continuity requires vanishing of the total differential with respect to time

$$\frac{dr(n,t)}{dt}=-J\,\frac{\partial r(n,t)}{\partial n}+\frac{\partial r(n,t)}{\partial t}=0, \tag{15}$$

and substitution into Eq. (13) leads to the expression

$$\beta J\,\frac{dr(n,t)}{dn}=\frac{dF(n)}{dn}+f(r). \tag{16}$$

The assumption in this case is that the segment density is stretched over the entire distance between the adjoining minima. Thus, we assume

$$dn/dr\equiv\rho=1/b, \tag{17}$$

integrate both sides of Eq. (16) between positions of two adjoining minima and find

$$\frac{\beta JL}{\rho}=U(r_1)-U(r_2)=qE\sqrt{aL}. \tag{18}$$

In obtaining Eq. (18), we have made use of the fact that the chain is not stretched in either of the two minima so that $F(n)$ vanishes at both the initial and final point of the integral.

This expression immediately leads to the following result for the steady-state flux J:

$$J=\frac{\rho qE}{\beta}\sqrt{\frac{a}{L}}. \tag{19}$$

The relaxation time is determined by the initial number of segments $N(L)$ in the region of size L divided by the flux

$$t(L)=\frac{N(L)}{J}. \tag{20}$$

For a random initial segment distribution, [model A, Eq. (10)] the relaxation for motion between two adjoining minima when the chains are stretched is

$$t(L)=\frac{\beta b}{qE}\sqrt{\frac{b}{a}}\left(\frac{L}{b}\right)^{5/2}, \tag{21}$$

and the corresponding mean-squared displacement

$$L(t)=b\left(\frac{qEt}{\beta b}\right)^{2/5}\left(\frac{a}{b}\right)^{1/5}. \tag{22}$$

For a reptation like initial condition, [model B, Eq. (11)]

$$t(L)=\frac{\beta b}{qE}\sqrt{\frac{b}{a}}\left(\frac{L}{b}\right)^{3/2}, \tag{23}$$

with the corresponding displacement that varies according to

$$L(t)=b\left(\frac{qEt}{\beta b}\right)^{2/3}\left(\frac{a}{b}\right)^{1/3}. \tag{24}$$

Recall that $L(t)$ is displacement along the random tube; displacement in real space is proportional to $\sqrt{L(t)}$.

V. RELAXATION TIME ESTIMATE FOR PERFECTLY ELASTIC CHAIN

We now consider the case where the flow of polymer segments in the case when the force between the segments is perfectly elastic. For elastic chain

$$F(n)=\gamma[r(n+1)-r(n-1)], \tag{25}$$

where $\gamma=3k_BT/b^2$ is the elastic constant and Eq. (4) yields

$$\beta\,\frac{\partial r(n,t)}{\partial t}=\gamma\,\frac{\partial^2 r(n,t)}{\partial^2 n}+f(r). \tag{26}$$

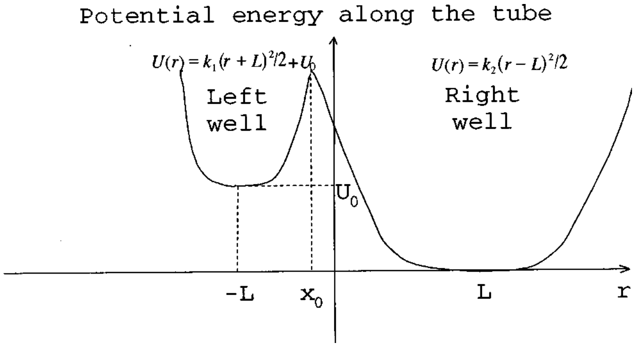

FIG. 4. Polymer chain in adjoint minima of random potential. Each potential minimum is approximated by a parabola and the minimum of the right hand parabola lies below the minimum of the left hand side parabola by an amount U_0. The position coordinate along the tube is indicated by r, two parabolas intersect at $r=x_0$. Initially, the segment $n=0$ is at x_0.

In order to extract the relaxation behavior we again consider the flow from one potential well to another; see Fig. 4. In this case, for simplicity, we assume that the two potential wells in the external random potential $U(r)$ are parabolic wells separated by distance $2L$ between their minima along the r coordinate and by the amount U_0 along the U coordinate. The force constant is k_1 for the left well, and k_2 for the right well, $k_1<k_2$, as indicated in Fig. (4). Thus, $U_L(r)=k_1(r+L)^2/2$ for the left potential well in the coordinate system with its origin in its minimum and $U_R(r)=k_2(r-L)^2/2$ for the right potential well. In a fixed coordinate system the force at position r is $f(r)=-k\Delta r$, where Δr denotes the deviation from potential minimum along tube coordinate and $k_1(k_2)$ is the force constant in the left (right) potential well.

We estimate the force constant by estimating $U(L)$ from the Eq. (8) and find

$$k_1\propto k_2\propto qE\sqrt{a/L^3}. \tag{27}$$

We seek a steady-state solution of Eq. (26) according to Eq. (15) and arrive at the following relaxation equation:

$$J\beta\,\frac{dr(n)}{dn}=\gamma\,\frac{d^2 r(n,t)}{d^2 n}-k_{1,2}\Delta r, \tag{28}$$

where $k_{1,2}$ refers to the force constants in each of the two potential wells. Thus, for $-\infty<r<0$, in the left well

$$\gamma r_L''-J\beta r_L'-k_1(r_L+L)=0 \tag{29}$$

and for $0<r<\infty$, in the right well

$$\gamma r_R''-J\beta r_R'-k_2(r_R-L)=0. \tag{30}$$

We seek a solution in each well with the position measured from the well minima. These solutions have the form

$$\Delta r(n)=A_\pm\,\exp(\lambda_\pm n), \tag{31}$$

where $\lambda_\pm$ are the eigenvalues given by

$$\lambda_\pm(k_{1,2})=\frac{\beta J}{2\gamma}\pm\sqrt{\left(\frac{\beta J}{2\gamma}\right)^2+\frac{k_{1,2}}{\gamma}}, \tag{32}$$

and the constants $A_\pm$ are determined by matching the solutions for the left and the right wells.

We designate the segment located at the point of intersection of the two wells $n=0$. There are two continuity conditions for the chain at $n=0$. These are

$$r_L(0)=r_R(0) \tag{33}$$

and

$$\left.\frac{dr_L(n)}{dn}\right|_{n=0}=\left.\frac{dr_R(n)}{dn}\right|_{n=0}. \tag{34}$$

The crossover point (the point of intersection of the two wells, where the $n=0$ segment is located) is

$$x_0=r_L(0)=r_R(0), \tag{35}$$

which is determined from the equation

$$\frac{k_1(x_0+L)^2}{2}+U_0=\frac{k_2(x_0-L)^2}{2}, \tag{36}$$

(see Fig. 4 for the definition of the parameters of the potential.)

In the left well located at the distance L from the segment zero, the solution is

$$r_L(n)+L=(x_0+L)\exp[\lambda_+(k_1)n], \tag{37}$$

one must choose the eigenvalue $\lambda_+(k_1)$ since the segments as $n\rightarrow\infty$ bunch up in the left well, located at $r_L=-L$.

In the well located at the right, the solution is

$$r_R(n)-L=(x_0-L)\exp[\lambda_-(k_2)n], \tag{38}$$

one must choose the eigenvalue $\lambda_-(k_2)$ since $r_L\rightarrow L$ as $n\rightarrow\infty$.

These solutions describe the steady flux of an infinite chain, moving from one minimum to another one and satisfy the continuity condition at x_0. The value of the flux J is determined from Eq. (34)

$$(x_0+L)\lambda_+(k_1)=(x_0-L)\lambda_-(k_2), \tag{39}$$

with x_0 from Eq. (36). As an example, we consider the case $k_1=k_2=k$. From Eq. (36) one finds

$$x_0=-\frac{U_0}{2Lk}. \tag{40}$$

Substitution into Eq. (39) leads to the expression for J

$$\begin{aligned} J&=-\operatorname{sign}(x_0)\,\frac{2\sqrt{k\gamma}}{\beta}\,\sqrt{\frac{(x_0/L)^2}{1-(x_0/L)^2}}\\ &=\operatorname{sign}(x_0)\,\frac{2\sqrt{k\gamma}}{\beta}\,\sqrt{\frac{(U_0/2kL^2)^2}{1-(U_0/2kL^2)^2}}. \end{aligned} \tag{41}$$

The quantity (x_0/L) is limited to lie in the range $-1<(x_0/L)<+1$ if the barrier is to lie between the two minima; this in turn leads to the condition $-1<(U_0/2kL^2)<+1$. The sign for the flux has been chosen to give the correct direction for J as $x_0\rightarrow 0$. Note that the flux tends to infinity as the barrier height disappears.

Use of Eqs. (12), (27), and (41), leads to the following scaling relation for J:

$$J\propto\frac{(qE\gamma)^{1/2}a^{1/4}}{\beta L^{3/4}}. \tag{42}$$

The more general case for intersecting quadratic potentials with different force constants can be analyzed in a similar way and leads to a comparable, but more complicated, result to the one exhibited in Eq. (42).

In order to determine the relaxation time, it is necessary to estimate the chain density. According to Eqs. (37) and (38) the segment number as a function of r in each well, has the form

$$n(r)=\frac{1}{\lambda}\ln\left(\frac{\Delta r}{x_0\pm L}\right), \tag{43}$$

and consequently the density $r(r)=|dn/dr|$ is equal to

$$\rho=\frac{1}{\lambda\Delta r}. \tag{44}$$

Note that as Δr tends to zero, i.e., to the well minimum, the density tends to infinity indicating the buildup of polymer segments in the potential minimum.

As the crossover point is approached the density approaches

$$\rho(x_0)=\frac{1}{x_0\lambda}. \tag{45}$$

Taking advantage of the Eqs. (27), (32), and (41), we obtain

$$\rho(x_0)=\sqrt{\frac{\gamma}{qE}}\frac{1}{(aL)^{1/4}}. \tag{46}$$

The density $\rho(x_0)$ is determined by the equilibrium between electric forces and chain elasticity and thus it does not depend on β. We note that $\rho(x_0)\rightarrow 0$ when $L\rightarrow\infty$ so that we may conclude that the chain is anomalously stretched on large L scale at the points of local potential minima.

We estimate the relaxation time of the chain according to Eq. (20). If the initial chain configuration is *random (model* A*)*, then $N(L)=(L/b)^2$ and the relaxation time predicted on the basis of Eq. (42)

$$t(L)\propto\beta\sqrt{\frac{b}{qE\gamma}}\left(\frac{b}{a}\right)^{1/4}\left(\frac{L}{b}\right)^{11/4}, \tag{47}$$

which determines the typical displacement

$$L(t)\propto b\left(\frac{t}{\beta}\right)^{4/11}\left(\frac{qE\gamma}{b}\right)^{2/11}\left(\frac{a}{b}\right)^{1/11}. \tag{48}$$

If the initial chain configuration is of the *reptation form (model* B*)*, then $N(L)=(La/b^2)$ and one finds

$$t(L)\propto\beta\sqrt{\frac{b}{qE\gamma}}\left(\frac{a}{b}\right)^{3/4}\left(\frac{L}{b}\right)^{7/4}, \tag{49}$$

which corresponds to

$$L(t)\propto b\left(\frac{t}{\beta}\right)^{4/7}\left(\frac{qE\gamma}{b}\right)^{2/7}\left(\frac{b}{a}\right)^{3/7}. \tag{50}$$

We recall again that L in Eq. (49) represents the typical displacement along the tube, corresponding to time t. The displacement in real space is proportional to $\sqrt{L}$. Finally, we

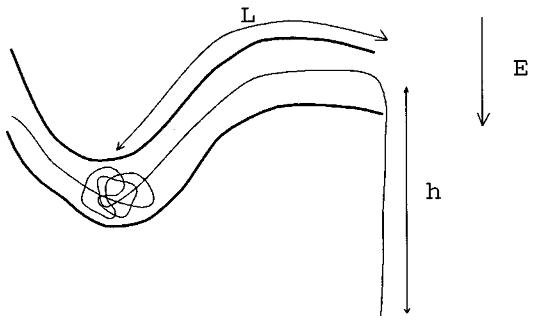

FIG. 5. The end of the polymer chain moves out of the tube. The polymer occupies a distance L inside the tube and a distance h outside the tube.

note that there is no limit that takes the results for the elastic chain considered in this section over to the results for the rigid chain considered in the previous section. In particular, the limit $\gamma\rightarrow 0$ leads to an infinite relaxation time in Eq. (49) because there is no force between the segments to pull them from one minima to another.

VI. LEAKING OF ROPELIKE POLYMER FROM THE END OF THE TUBE

We next consider the motion of the polymer chain when it leaks out of the end of the tube. The physical situation is depicted in Fig. 5 where a distance h of the polymer chain has moved out of the tube and with a distance L from the end of the tube to the energy minimum within the tube that acts as a source of polymer segments flowing out. For a ropelike polymer, the steady-state dynamics is described exactly as in Sec. IV according to Eq. (16). For large h, the chain is stretched from the minimum to the free end and we assume constant density of the chain segments along the length.

Integration of the Eq. (16) from the minimum to the end of the chain leads to the result

$$\frac{\beta J(h+L)}{\rho}=U(r_2)-U(r_1), \tag{51}$$

in analogy to Eq. (18). In this expression, r_1 is the location of the chain end and, therefore,

$$U(r_1)=qEh, \tag{52}$$

r_2 is the location of the segment reservoir. Because the tube is randomly configured

$$U(r_2)=Eq\sqrt{aL}. \tag{53}$$

The resulting expression for the flux is

$$J=\frac{\rho qE}{\beta}\left(\frac{h-\sqrt{aL}}{h+L}\right). \tag{54}$$

At a particular moment, h is growing with time and the number of segments left in the tube is decreasing. We seek to establish a relationship between J, h, and the changing length scale L. For the ropelike chain with constant density ρ

$$bJ=\frac{dh(t)}{dt}. \tag{55}$$

The number of chain segments which were pulled out of the part of the tube with the length L during time t, $h(t)/b$, equals the initial number of segments in this part of the tube, $N[L(t)]$. *For the random initial distribution* (model A), $N[L(t)]$ is determined by Eq. (10), thus

$$L(t)=\sqrt{bh(t)} \tag{56}$$

and

$$\frac{dh(t)}{dt}=\frac{qE}{\beta}\left(\frac{1-(a^2b/h^3)^{1/4}}{1+\sqrt{b/h}}\right). \tag{57}$$

For reptation-type initial distribution (model B), $N[L(t)]$ is determined by Eq. (11), thus

$$L(t)=\frac{bh(t)}{a} \tag{58}$$

and

$$\frac{dh(t)}{dt}=\frac{qE}{\beta}\left(\frac{1-\sqrt{b/h}}{1+b/a}\right). \tag{59}$$

Equation (57) indicates that for random initial distribution the dangling ends smaller then $(a^2b)^{1/3}$ will not expand. Similarly, Eq. (59) indicates that for reptation type initial distribution, dangling ends smaller than b do not expand. In the pore fixed by a random matrix the small dangling end will be absorbed into the nearest minimum and the evolution will follow the scenario described in Sec. III until the chain length accumulated in the closest to the pore end minimum is large enough to establish a stable leakage from the pore end. The leakage of the chain from its own tube starts after the thermal fluctuations create large enough dangling ends. Large dangling ends expand with a constant rate in agreement with Ref. 51.

VII. RESULTS AND DISCUSSION

We obtained expressions for relaxation times and corresponding typical displacements for a charged polymer chain in a random tube for different initial configurations of the chain and for the case of stretched (ropelike) and elastic chains. For the times smaller then overall relaxation time of the chain, a chain segment moves inside the tube from one local energy minimum to another. The motion of a segment in the tube is deterministic and the rate is determined by the ratio of total electric force acting on the chain fragment between the minima to the corresponding total friction force. The overall random displacement results from random positions of the energy minima along the tube. For the stretched chain, the relaxation times and displacements are given in the Eqs. (21)–(24); for the *random* and *reptation*like initial conditions the typical displacement is proportional to

$$L\propto b\left(\frac{qEt}{\beta b}\right)^{2/5}\left(\frac{a}{b}\right)^{1/5} \tag{60}$$

and to

$$L\propto b\left(\frac{qEt}{\beta b}\right)^{2/3}\left(\frac{a}{b}\right)^{1/3}, \tag{61}$$

respectively. For the elastic chain, the relaxation times and displacements are given in the Eqs. (47)–(50); for the *random* and *reptationlike* initial conditions the typical displacement is proportional to

$$L \propto b\left(\sqrt{\frac{qE\gamma}{\beta^2 b}}\,t\right)^{4/11}\left(\frac{a}{b}\right)^{1/11} \tag{62}$$

and to

$$L \propto b\left(\sqrt{\frac{qE\gamma}{\beta^2 b}}\,t\right)^{4/7}\left(\frac{b}{a}\right)^{3/7}, \tag{63}$$

respectively.

This scaling behavior should be compared to the result for the time dependence of the displacement of a segment of the Rouse chain[50]

$$\frac{L}{b} \propto \left(\frac{t}{\tau_R}\right)^{1/4}, \tag{64}$$

where $\tau_R = \beta b^2/k_B T$.

The dependence in Eq. (64) is understood as follows: For short times, a segment moves as an individual particle so $L \propto \sqrt{D_0 t}$, where D_0 is the diffusion coefficient of the segment. As time increases, $n \propto \sqrt{D_0 t}$ segments move together and the center-of-mass displacement moves as $L \propto \sqrt{D_n t}$, where D_n is the diffusion coefficient of n segments moving in concert. Since $D_n = D_0/n$, one finds $L \propto t^{1/4}$.

The results for a charged chain in a random tube presented above also include collective effects. However, the driving force of the motion is the random potential instead of the thermal fluctuations. The significant difference in our results compared to Eq. (64) is not only the difference of the time dependence but also in the amplitudes which reflect the very different physics leading to the relaxation. For example, from Eqs. (60) and (61) for the relaxation for the stretched case $\tau_{\mathrm{stretch}} \propto \beta b/qE$ which differs considerably from τ_{Rouse}.

According to our relaxation scenario, a finite chain in an external fixed tube collapses into the deepest potential well. We have described the relaxation times for this problem. Once in the deepest energy well, further relaxation of the chain is described by Sinai type diffusion, Eq. (1), because the collapsed chain behaves as a single aggregate. This continues until a piece of the chain leaks outside the matrix, then the dynamics is described according to Sec. VI. For large dangling ends, the leakage rate is constant.

[1] Y. G. Sinai, Theor. Probab. Appl. **27**, 247 (1982).
[2] E. Marinari, G. Parisi, D. Ruelle, and P. Windey, Phys. Rev. Lett. **50**, 1223 (1983).
[3] J. P. Bouchaud, A. Comtet, A. Georges, and P. L. Doussal, Ann. Phys. (NY) **201**, 285 (1990).
[4] H. E. Roman, M. Schwartz, A. Bunde, and S. Havlin, Europhys. Lett. **7**, 389 (1988).
[5] S. Havlin, J. Stat. Phys. **58**, 653 (1990).
[6] E. Lai, B. W. Birren, S. M. Clark, M. I. Simon, and L. Hood, BioTechniques **7**, 34 (1989).
[7] H. J. S. Dawkins, J. Chromatogr. **492**, 616 (1989).
[8] J. Noolandi, G. W. Slater, H. A. Lim, and J. L. Viovy, Science **243**, 1456 (1989).
[9] J. Maddox, Nature (London) **345**, 381 (1990).
[10] J. Maddox, Phys. Today **240**, 20 (1990).
[11] C. R. Calladine, C. M. Collis, H. R. Drew, and M. R. Mott, Science **243**, 203 (1991).
[12] B. Norden, C. Elvingson, M. Jonsson, and B. Akerman, Q. Rev. Biophys. **24**, 103 (1991).
[13] B. H. Zimm and S. D. Levene, Q. Rev. Biophys. **25**, 171 (1992).
[14] J. L. Viovy, T. Duke, and F. Caron, Contemp. Phys. **33**, 25 (1992).
[15] A. E. Barron and H. W. Blanch, Sep. Purif. Methods **24**, 1 (1995).
[16] B. Kozulic, Anal. Biochem. **321**, 1 (1995).
[17] H. V. Thorne, J. Mol. Biol. **24**, 203 (1967).
[18] C. R. Cantor and D. C. Schwartz, Electrophoresis Using Alternating Transverse Electric Fields, U.S. Patent, 1984, patent Number: 442580.
[19] Y. Kim and M. D. Morris, Electrophoresis **17**, 152 (1996).
[20] D. C. Schwartz and C. R. Cantor, Cell **37**, 67 (1984).
[21] G. F. Carle, M. Frank, and M. V. Olson, Science **232**, 65 (1986).
[22] D. C. Schwartz, Pulsed Oriented Electrophoresis, U.S. Patent, 1995, patent Number: 5,405,519.
[23] P. De Gennes, J. Chem. Phys. **55**, 575 (1971).
[24] M. Doi and S. Edwards, Faraday Trans. **74**, 1789 (1978).
[25] M. Doi and S. Edwards, Faraday Trans. **74**, 1802 (1978).
[26] M. Doi and S. F. Edwards, Faraday Trans. **74**, 1818 (1978).
[27] L. S. Lerman and H. L. Frisch, Biopolymers **21**, 995 (1982).
[28] O. J. Lumpkin and B. H. Zimm, Biopolymers **21**, 2315 (1982).
[29] O. J. Lumpkin, P. DeJardin, and B. H. Zimm, Biopolymers **24**, 1573 (1985).
[30] G. W. Slater and J. Noolandi, Biopolymers **24**, 2181 (1985).
[31] G. W. Slater and J. Noolandi, Biopolymers **25**, 431 (1986).
[32] J. L. Viovy, Phys. Rev. Lett. **60**, 855 (1988).
[33] J. Noolandi, J. Rousseau, and G. W. Slater, Phys. Rev. Lett. **58**, 2428 (1987).
[34] A. Diwan and T. Schuster, Anal. Biochem. **183**, 122 (1989).
[35] A. N. Semenov, T. A. J. Duke, and J.-L. Viovy, Phys. Rev. E **51**, 1520 (1995).
[36] J. P. Bouchaud and A. Georges, J. Phys. A **23**, L1003 (1990).
[37] S. Fridrikh, Y. Gotlib, and B. Belenkij, Electrophoresis **18**, 26 (1997).
[38] B. H. Zimm, J. Chem. Phys. **94**, 2187 (1991).
[39] D. Long and J. L. Viovy, Phys. Rev. E **53**, 803 (1996).
[40] S. P. Obukhov and M. Rubinstein, J. Phys. II **3**, 1455 (1993).
[41] N. Lee, S. Obukhov, and M. Rubinstein, Electrophoresis **17**, 1011 (1996).
[42] B. Akerman, Phys. Rev. E **54**, 6685 (1996).
[43] S. Burlatsky and J. Deutch, Science **260**, 1782 (1993).
[44] S. F. Burlatsky and J. M. Deutch, J. Chem. Phys. **103**, 8216 (1995).
[45] J. M. Deutsch and Y. Hyoungsoo, J. Chem. Phys. **106**, 9376 (1997).
[46] K. Gisselfalt, B. Akerman, and M. Jonsson, Electrophoresis **18**, 663 (1997).
[47] B. Akerman, Electrophoresis **17**, 1027 (1996).
[48] B. H. Zimm, Electrophoresis **17**, 996 (1996).
[49] B. H. Zimm and O. Lumpkin, Macromolecules **26**, 226 (1993).
[50] M. Doi and S. F. Edwards, in *International Series of Monographs on Physics*, edited by S. F. Edwards, H. Ehrenreich, C. H. L. Smith, and M. Rees (Oxford University Press, New York, 1986), Vol. 1.
[51] H. A. Lim, G. W. Slater, and J. Noolandi, J. Chem. Phys. **92**, 709 (1990).