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Electrophoresis in strong fields

M. Olvera de la Cruz,* J. M. Deutsch,† and S. F. Edwards
Cavendish Laboratory, Cambridge CB3 0HE, England
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We present a computer simulation on a lattice of a long charged polymer diffusing in a topologically restricted environment in the presence of an electric field. The problem is related to that of a set of self-attracting particles diffusing in a random environment. For strong fields the polymer gets trapped in metastable configurations, so that the relaxation time of the polymer has an exponential dependence on chain length. Various correlation functions such as the mean square displacement vary logarithmically with time.

INTRODUCTION

Diffusion of long polymers in gels is restricted by the topological constraints of the network structure of the gel. Although the dynamics of these configurations are complicated, the snakelike-motion or "reptation" model easily explains the dynamical properties of such systems.[1]

A chain trapped in a network moves around obstacles by Brownian motion. A chain can only move freely at its ends and at portions free of entanglements. The reptation model takes this into account by constraining the polymer to move in a tube whose diameter is the average distance between network junction points. The polymer is unhindered within a certain length scale called the tube diameter, since the polymer moves freely over distances of the order of the pore size of the gel. For larger diffusion distances, the polymer is constrained to move along the path of the random tube.

In this paper, the effects on chain dynamics in gels in the presence of an electric field are discussed. Consider a long charged polymer embedded in a gel when an electric field is suddenly switched on. Charge cannot migrate along a polymer so that the motion of charge is restricted to the motion of the monomers. If the field is small the transfer of charge through the network is by fluctuations on a length scale smaller than the tube diameter. This results in a process that proceeds by a continuous diffusive drift. However, for sufficiently strong fields, there is a nontrivial Boltzmann penalty associated with the motion of the smallest "crankshafts" along the chain. For the entire polymer to move, some crankshafts must move against the electric field, out of local minima. Thus we expect the polymer tube to be in a metastable configuration. In other words, the longer the polymer and the stronger the electric field the longer the relaxation time from the initial configuration. From a computer simulation of a polymer in a gel it is found that when a sufficiently strong electric field is switched on metastability does arise.

An outline of this paper is as follows: Section I discusses a computer simulation for a polymer diffusing in a gel in the absence of an external field. Section II relates the effect of a constant electric field in the above situation to the problem of a particle diffusing in a random environment. The problem is discussed in terms of Sinai's results for a random walk in a random potential.[2,3] Section III describes the computer simulation for this problem and analyzes the results. Finally, in Sec. IV the validity of the simulation is discussed and experimental evidence that could confirm the results is suggested.

I. A COMPUTER SIMULATION FOR A POLYMER DIFFUSING IN A GEL

We will first review the work of Evans and Edwards.[4] It is assumed that the polymer in the gel is at its Θ temperature, i.e., at the temperature at which the binary excluded-volume parameter vanishes such that the polymer statistics are nearly Gaussian.

We represent the gel by a fixed cage. For computational advantages the pore size of the gel is set equal to the step length of the polymer, which corresponds to the cage model with unit spacing.[4] In these circumstances one has the polymer chain as a random walk of N steps on a cubic lattice embedded in a network which consists of infinitely long bars forming a perfect lattice with spacings equal to the step length of the random walk. The points where the random walk comes directly back onto itself correspond to the portions of polymer free of entanglements, hereafter referred to as kinks. The dynamics of this model allow free movement of the ends of the polymer and of the kinks; otherwise the monomers are frozen due to the presence of the bars.

In the computer simulation the dynamics are set by iterations. At each iteration the program chooses a point j on the polymer at random; if the point is not a kink, that is if $\bar{r}_{j+1} \neq \bar{r}_{j-1}$, it carriers on iterating. Otherwise the kink is displaced one lattice spacing along one of the six possible directions, chosen randomly. Figure 1 shows some possible moves.

In the cage model one can vary the separation of the bars allowing the movement of all monomers which are not crossed by a bar. For any spacing of the cage between 0 and N the same phenomenological results are obtained in the absence of a field.

The computed quantities are the center-of-mass and the monomer-monomer correlation functions. The center-of-mass correlation function is defined as

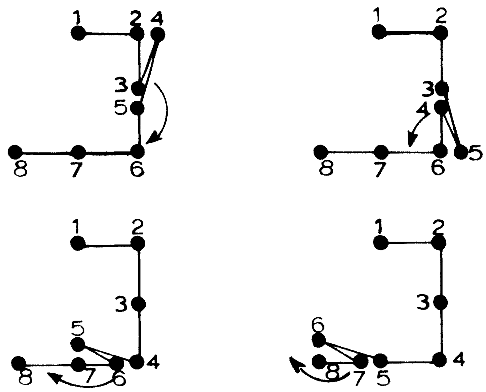

FIG. 1. Movement of the kinks along the backbone of the polymer.

$$g_{\text{c.m.}}=\langle R^2_{\text{c.m.}}(t)\rangle=\frac{1}{N^2}\left\langle\left[\sum_{j=1}^{N}[\bar{r}_j(t)-\bar{r}_j(0)]\right]^2\right\rangle .$$

The monomer-monomer correlation function is defined as

$$g_i=\langle R_i^2(t)\rangle=\frac{1}{N}\left\langle\sum_{j=1}^{N}[\bar{r}_j(t)-\bar{r}_j(0)]^2\right\rangle .$$

The monomer-monomer correlation function for this model has different power laws in time.[4] At $t=t_{\text{rep}}$ the internal modes have relaxed,[5] and

$$g_i\propto t \text{ for } t>t_{\text{rep}}\propto N^3 .$$

The relaxation time t_{rep} is the time it takes the polymer to form a new random tube, uncorrelated with the original configuration.

The center-of-mass correlation function is given at all times as

$$g_{\text{c.m.}}=D_{\text{c.m.}}t ,$$

where $D_{\text{c.m.}}\propto 1/N^2$ is the diffusion coefficient of the center of mass.[5]

II. A POLYMER IN AN ELECTRIC FIELD

Let us suppose that the chain trapped in the network is charged, as in the case of DNA, and a constant electric field is suddenly switched on. In order to understand the behavior of the monomer-monomer correlation function it is necessary to look at the diffusion of the kinks along the backbone of the polymer. When a constant electric field is switched on we will see that the potential along the backbone is random.

Let the coordinates of the backbone of the polymer be parametrized by a curve $\overline{R}(S)$, where S goes from 0 to $L=Na$. A constant electric field gives a potential energy at each point $\overline{R}(S)$,

$$V(\overline{R}(S))=\overline{E}\cdot\overline{R}(S) .$$

As a kink is restricted to move along the backbone, it feels only the component of $\overline{E}$ along the chain. Since $\overline{R}(S)$ is a random walk, such that $\langle\overline{R}^2(S)\rangle=aS$, then the potential over S is random, and

$$\langle V(S)\rangle=0 ,$$
$$\langle[V(S)-V(S')]^2\rangle=E^2a\,|S-S'| . \tag{1a}$$

It then follows that the force on a kink as a function of S, $F(S)=-(\partial V/\partial S)$, is such that

$$\langle F(S)\rangle=0 ,$$
$$\langle F(S)F(S')\rangle=E^2a\delta\,|S-S'| , \tag{1b}$$

for

$$|S-S'|<L .$$

Assume for the moment that the backbone $\overline{R}(S)$ is static; then the problem is that of a particle moving in a one-dimensional space S with the probability of hopping from s_i to s_{i+1}, $p(s_i)$, randomly distributed over S. This problem has been studied rigorously by Sinai[2] who constructed the probability functional for a particular realization of the force $F(S)$ and then averaged over all possible realizations to find that the mean square distance traveled by a particle in such circumstances,

$$\langle S^2\rangle\propto(\ln t)^4 . \tag{2}$$

de Gennes has approached this problem in a different way.[6] He was interested instead in calculating the average time it takes a particle diffusing in a random potential with a mean given by (1a) to move a distance S. He showed that in such circumstances,

$$\langle t\rangle=D^{-1}\int_0^S dm\int_0^m dp\,\langle\exp[v(m)-v(p)]\rangle\propto\exp(E^2S). \tag{3a}$$

Therefore, inverting this equation,

$$S^2\propto(\ln\langle t\rangle)^2 . \tag{3b}$$

The discrepancies between the results of (2) and (3) show the breakdown of scaling laws in this problem.[7] Let us compare Kramer's criterion—$t(S)\propto\exp(\Delta V(S))$, where $\Delta V(S)$ is the maximum barrier height between 0 and S—with both Eqs. (2) and (3) to find out which realizations of the potential are significant in determining the average quantities in each case. If the time a particle stays in the interval $[0,S]$ is calculated using (2) the most significant barrier height is the maximum barrier height one typically finds between 0 and S,

$$t\propto\exp\langle[V(S)-V(0)]^2\rangle^{1/2}=\exp(ES^{1/2}) . \tag{4}$$

On the other hand, (3a) would state that the time a particle stays in an interval $[0,S]$ is dominated by the time it takes to surmount atypically large maximum barriers of the potential in the interval. Let $P(V_m,S)$ be the probability that in the interval $[0,S]$ the maximum potential is V_m, which one expects to decay very rapidly for $V_m\gg ES^{1/2}$. In order to find the average time we average over all realizations of V_m,

$$\langle t\rangle\propto\int e^{V_m}P(V_m,S)dV_m .$$

Consider the realization for a maximum potential along S to be $V_m=El$; then the probability of such a realization is the probability that a random walk of $N=S/a$ steps $(a=1)$ has a maximum displacement of l, $P(l,N)$. This resembles the problem of a random walk with an absorbing wall at l. Chandrasekhar[8] found the probability $W(x,N;l)$ that a particle executing a random walk of N steps arrives at x given that there is an absorbing wall at $x=l$. So the probability that a random walk has its maximum displacement at l,

$$P(l,N)=\frac{d}{dl}\int_{-\infty}^{l} W(x,N;l)dx ,$$

can be obtained, and this leads to

$$\langle t\rangle \propto \exp\left[\frac{E^2}{2}S\right] . \tag{5}$$

Although there are discrepancies between (4) and (5), both results are correct. Sinai's result (2) gives the mean-square displacement of the particle $\langle S^2\rangle$, while if the average time $\langle t\rangle$ is of interest, de Gennes's result (3) should be used. The differences between them show that a typical realization of the potential is not enough to find the average time the particle spends in an interval since the time it spends surmounting the highest potential barriers is much longer than the time it spends crossing the mean barriers.

The case of an entangled chain in the presence of an electric field is slightly different as here the problem is one of metastability. It is expected that after a kink has diffused over the whole path S and is no longer confined to a particular random walk the monomer-monomer correlation function is given by the power law for diffusion of a particle in a constant field:

$$\langle[\bar R(S,t)-\bar R(S,0)]^2\rangle \propto t^2 . \tag{6}$$

An additional difference from the problem described above is that $V(S)$ is not really static. As the kinks tend to move more in the direction of the field than against it, they aggregate, as shown schematically in Fig. 2. The particles aggregate at minima of the potential, further increasing the height of the barriers. In order for a segment to straighten out, there will be intermediate configurations where all the kinks have clustered together, forming several potential barriers with height of order ES. This suggests that the time the particle spends in the interval $[0,S]$ is typically

$$t \propto \exp(ES\times \text{const}) . \tag{7}$$

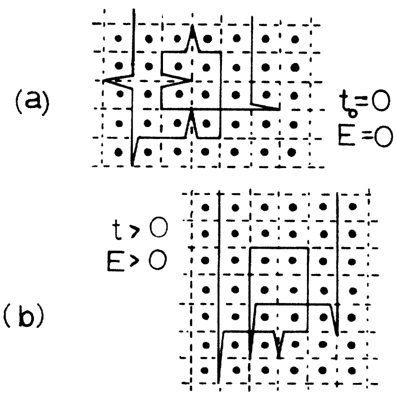

FIG. 2. (a) Initial random configuration $(E=0$ at $t=0)$ of the chain in the unit cage. The dots represent the cage. (b) The kinks have moved along the polymer backbone at $t>0$.

III. A COMPUTER SIMULATION OF A POLYMER IN AN ELECTRIC FIELD

The effects of a constant electric field were included in the computer program for the cage model with the unit spacing, as describing in Sec. I. As there, the initial configuration of the polymer is a random walk. The dynamics of the polymer after the electric field is switched on were represented by a Monte Carlo algorithm. At each iteration the energy associated with the movement was computed. Let

$$\bar r^{\,i}=(\bar r^{\,i}_1,\bar r^{\,i}_2,\dots,\bar r^{\,i}_N)$$

be the coordinates of the $N=L/a$ monomers in the chain at the ith iteration and $H(\bar r^{\,i})$ the energy associated with this configuration. The program randomly chooses a point on the chain, and if this point is not a kink the program carries on to the next iteration. If it is a kink it chooses one of the six possible directions of movement and it compares energies: If moving to the new configuration $\bar r\,'$ lowers the energy of the system it accepts it, i.e., if $H(\bar r')<H(\bar r^{\,i})$, it flips the kink by setting $\bar r^{\,i+1}=\bar r\,'$; otherwise it accepts it with probability

$$e^{-[H(\bar r')-H(\bar r^{\,i})]/T} . \tag{8}$$

After completing a required number of iterations the whole process is repeated for different initial random configurations until adequate statistics are obtained.

The computed quantities in this paper are the monomer-monomer and center-of-mass correlation functions. The relaxation time, the time it takes the polymer to lose its correlation with the original entangled configuration, is dominated by the time it takes a kink to diffuse the entire length of the polymer backbone. As the kinks aggregate, forming long sections of polymer aligned in the direction of the field, the potential barriers are of the order of the length S of these stretched sections. The relaxation time is expected to be, as in (7),

$$\tau=b\exp(ELc) , \tag{9}$$

where b has some much slower algebraic dependence on L. The constant c in (9) is a numerical factor less than 1 which is given by the maximum potential barrier to surmount in the interval $[0,L]$. The maximum potential height is $L/2$, corresponding to the final configuration where the polymer is trapped by a single entanglement. Nevertheless, as Eq. (7) is an asymptotic form for when $ES\gg 1$ and the aggregation effect has a characteristic time depending on the value of E, we expect substantial corrections for chain lengths considered here.

The relaxation will be logarithmic only if the relaxation time at $E=0$, L^3, is less than $\exp(ELc)$. Otherwise, the diffusion of the kinks along S is dominated by thermal noise with a constant drift in the direction of the field.[9]

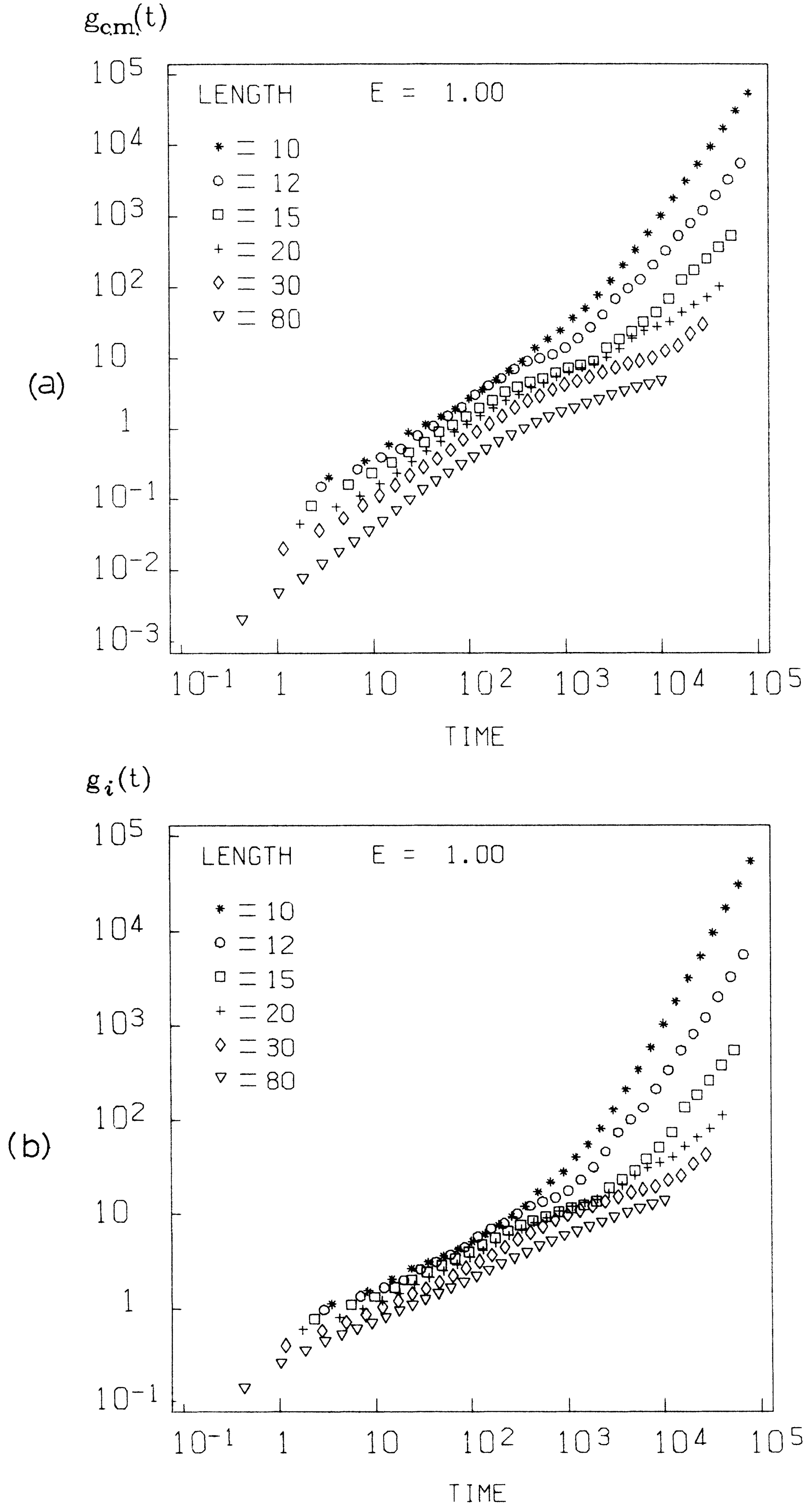

FIG. 3. (a) Plot of $\log(g_{\text{c.m.}})$ against $\log(t)$ for $E=1$ and $L=10$, 12, 15, 20, 30, and 80. (b) Plot of $\log(g_i)$ against $\log(t)$ for $E=1$ and $L=10$, 12, 15, 20, 30, and 80.

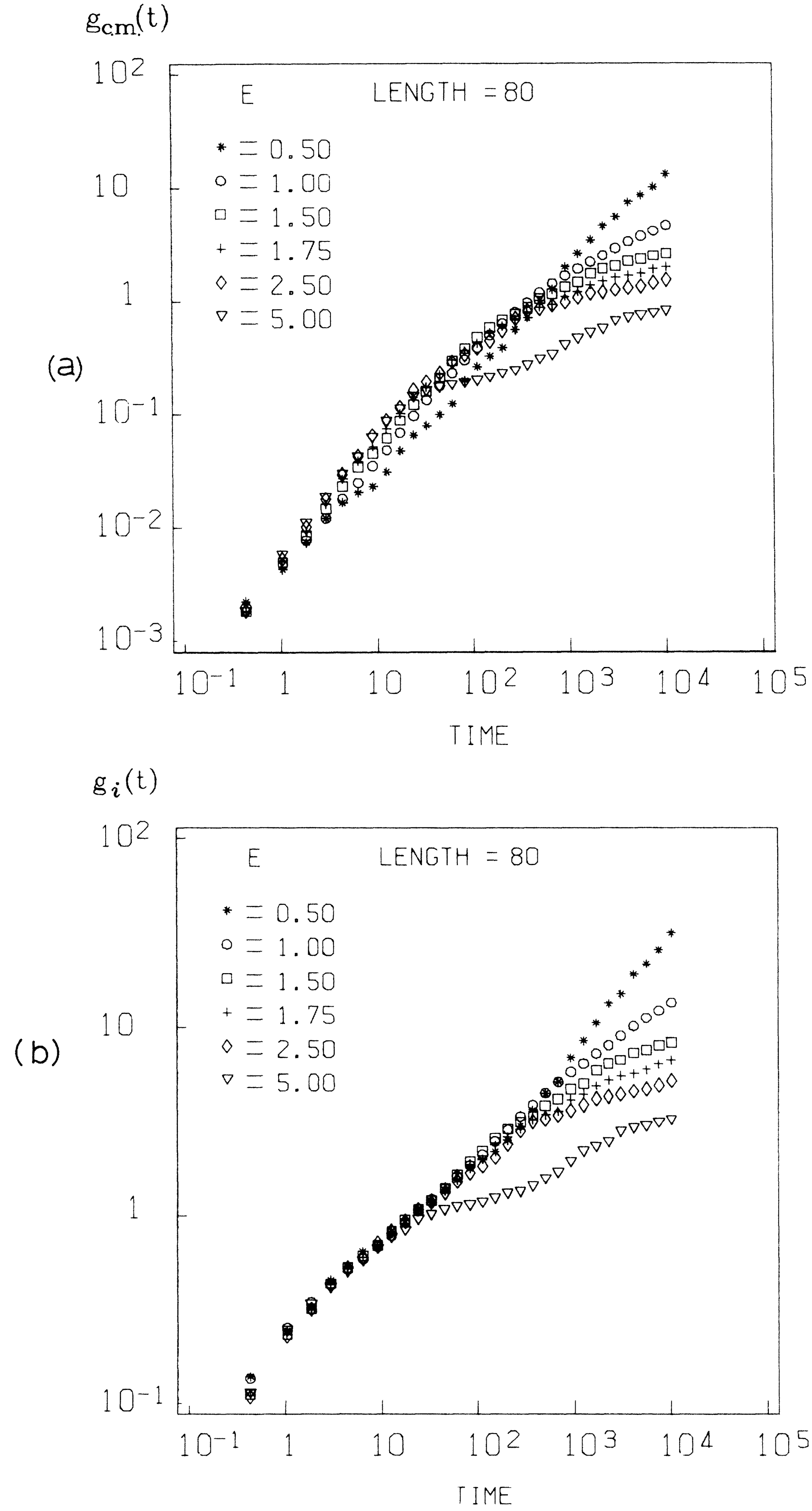

FIG. 4. (a) Plot of $\log(g_{\text{c.m.}})$ against $\log(t)$ for $L = 80$ and $E = 0.5$, 1.0, 1.5, 1.75, 2.5, and 5. (b) Plot of $\log(g_i)$ against $\log(t)$ for $L = 80$ and $E = 0.5$, 1.0, 1.5, 1.75, 2.5, and 5.

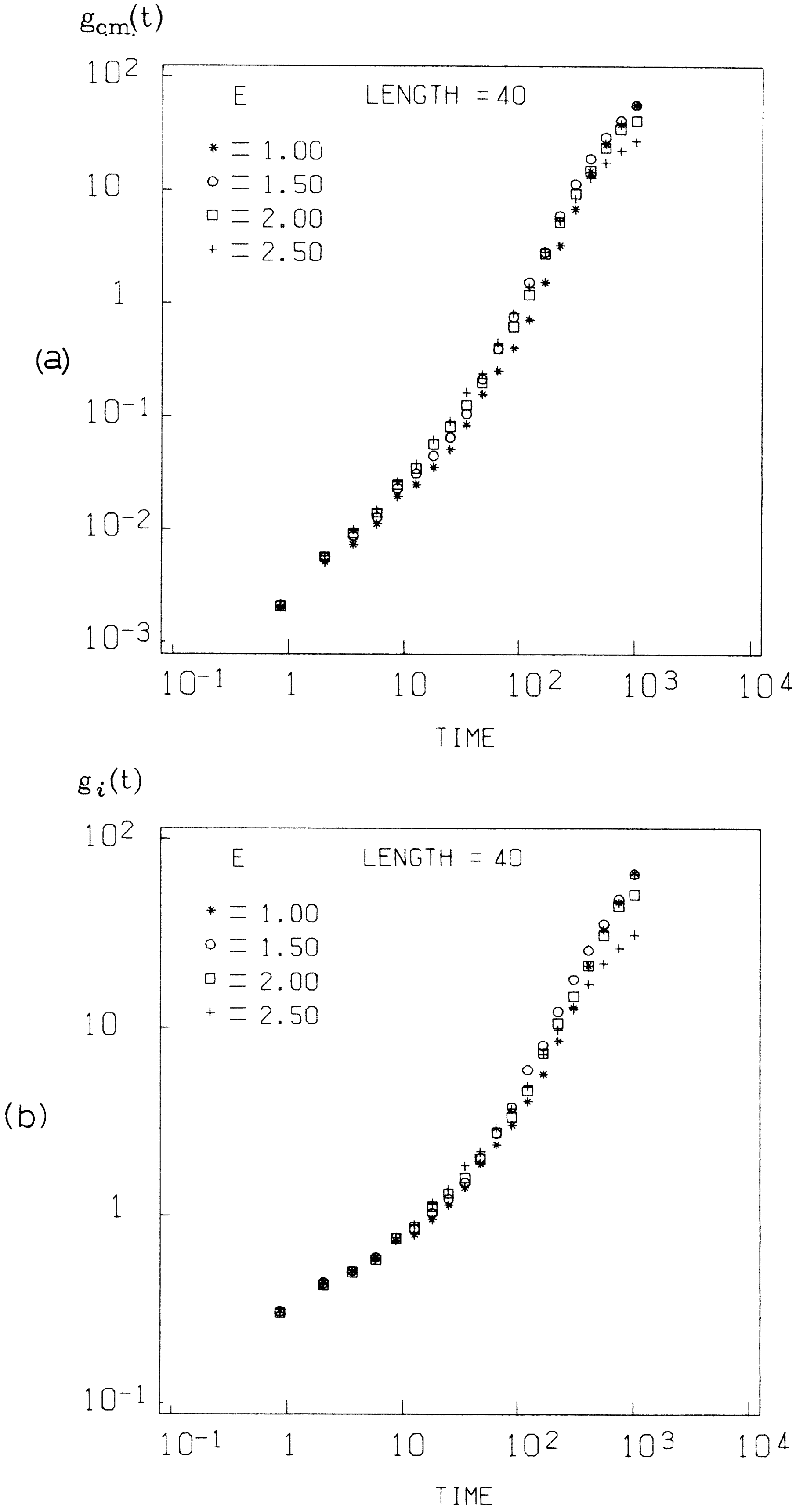

FIG. 5. (a) Plot of log($g_{\text{c.m.}}$) against log(t) for a stretched chain of $L = 40$ for $E = 1.0$, 1.5, 2.0, and 2.5. (b) Plot of log(g_i) against log(t) for a stretched chain of $L = 40$ for $E = 1.0$, 1.5, 2.0, and 2.5.

The case where E is very small is not considered here, as explained in Sec. IV.

The logarithm of the center-of-mass and monomer-monomer correlation functions are plotted against the logarithm of time for different polymer lengths at constant electric field $E=1$ in Figs. 3(a) and 3(b), respectively. As L is increased the plots show the expected logarithmic relaxation in time. Also plots of $\log\langle R_i^2(t)\rangle$ and $\log\langle R_{\mathrm{c.m.}}^2(t)\rangle$ against $\log(t)$ were computed for $L=80$ [Figs. 4(a) and 4(b)] but this time varying the electric field.

It would be of interest to find the steady-state configuration of the polymer, which is not obtained from equilibrium statistical mechanics. It is also accessible experimentally by light scattering. It was found in the computer simulation that for EL sufficiently large the polymer stretches from its random configuration with $R_g \propto \sqrt{L}$ to $R_g \propto L$ in a time which goes as e^{ELc}. On the other hand, the time it takes a stretched chain to curl back to its original random configuration should be roughly e^{LEc}. In order to observe the behavior of the polymer once it is stretched, the program was run starting from a straight chain and varying the electric field and the length of the chain. Figure 5 shows the correlation functions for $L=40$ for different electric fields. It is observed that there is a crossover effect, such that the polymer moves slower at higher fields which indicates that the polymer gets caught by entanglements even if it is straight, as one might expect.

The present work is not extensive enough to conclude that the equilibrium configuration of the polymer is no longer a random walk, especially in the limit where the length of the polymer is much greater than the pore size, as then the topological constraints increase the probability that a straight chain gets entangled again in the gel.

In the simulation it was assumed that the pore size is equal to the step length of the polymer. This assumption was made to simplify the computational task. It is expected that within the assumptions of this simulation metastability will be observed for any pore size bigger than the step length of the polymer.

A computer simulation was also performed for a Rouse chain in the presence of an electric field. In this model the chain is free of entanglements so all monomers are free to move. It was found that the equilibrium configuration of the chain was a random walk. That is, the polymer does not stretch, as shown by plotting the difference between the radius of gyration at $t=0$ and t (see Fig. 6). The results for the correlation functions are given in Fig. 7. In this case one has a linear diffusion process: the stronger the field the faster the polymer relaxation.

The center of mass moves at constant speed at all times for any value of E,

$$\langle R_{\mathrm{c.m.}}^2(t)\rangle \propto t^2 .$$

Thus the polymer does not change its equilibrium configuration even for $EL \gg 1$ if it does not entangle in the gel.

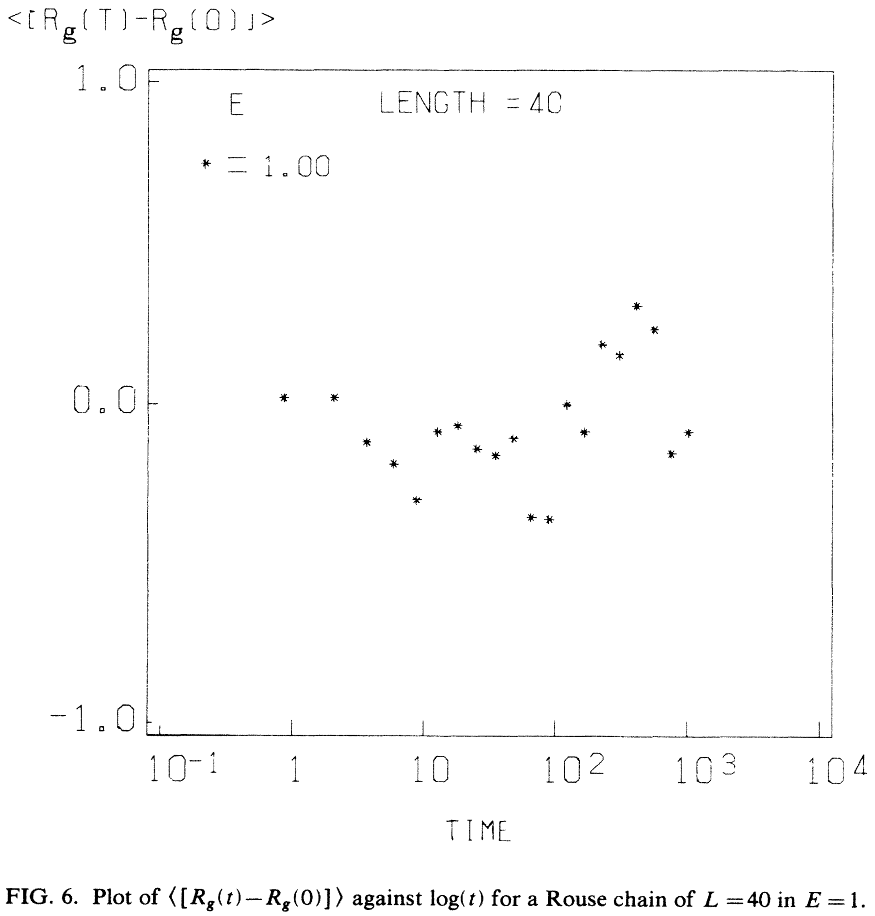

FIG. 6. Plot of $\langle [R_g(t)-R_g(0)]\rangle$ against $\log(t)$ for a Rouse chain of $L=40$ in $E=1$.

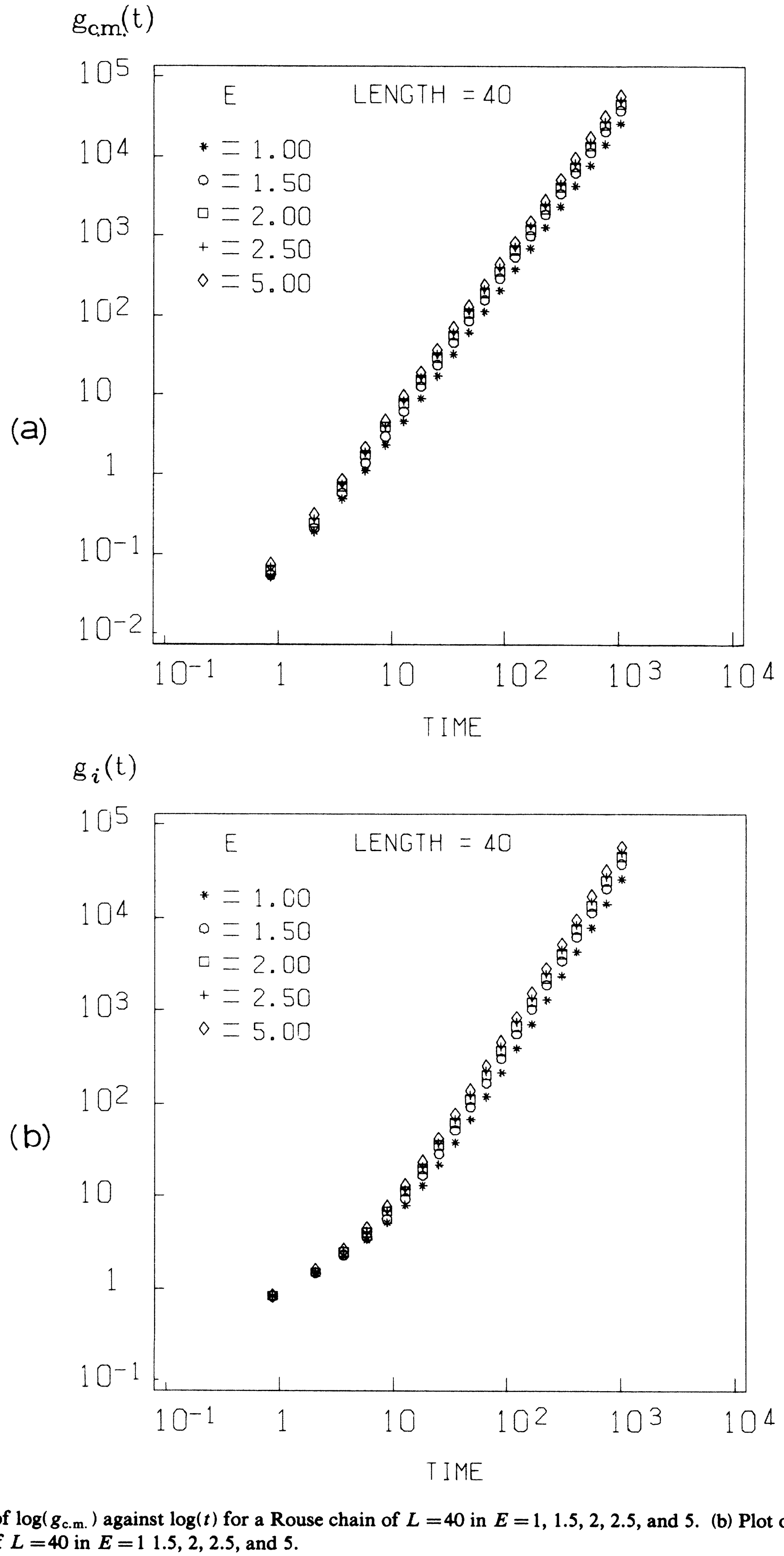

FIG. 7. (a) Plot of log($g_{\text{c.m.}}$) against log(t) for a Rouse chain of $L=40$ in $E=1$, 1.5, 2, 2.5, and 5. (b) Plot of log(g_i) against log(t) for a Rouse chain of $L=40$ in $E=1$ 1.5, 2, 2.5, and 5.

IV. DISCUSSION

In this section we discuss the applicability of our lattice model to a real system. Instead of considering an entire cage as we did previously, consider only one thin "bar." We label the lengths of string initially hanging on the two sides of the bar by L_1 and L_2.

In the lattice model, the average velocity v of the string decreases with increasing E. Setting the charge per unit length equal to unity we have that $v \sim \exp(-EL_1)$.

Now consider a continuous charge string that is inextensible but locally flexible, also with unit charge per length. In this circumstance we have to apply some boundary conditions at the surface of the bar. If we assume that there is a frictionless contact between the bar and the string, then the velocity of the string is an increasing function of the field strength with

$$v \sim E(L_2 - L_1)/(L_2 + L_1) .$$

(Here we are making the additional assumption of a local bead friction due to the viscosity of the solvent, although inclusion of hydrodynamic effects also give a similar dependence on E.) So there is no metastability induced by the electric field.

However, one can construct off-lattice models that do show metastability akin to the lattice case. If we bind many rigid hook-shaped side chains onto the continuous string, then the hook will tend to get caught and hang from the bar. Once a hook is hanging, the probability of it becoming unhooked is proportional to $\exp(-ELh)$ where h is the vertical distance necessary to lift the hook in order to disengage it, and L is the total length of the string. Therefore this model shows strong metastability.

We can relax the assumption that the chain possesses hook-shaped side chains and consider a flexible but "bumpy" chain. If the local corrugations of the chain are sufficiently large, then we might expect a behavior similar to that of the hooked chain. If the height of the corrugations is not large enough to stop the chain from sliding over the top of the bar, we still might expect the chain to get stuck if it was knotted around the bar. This is because when two portions of chain slide against each other, then tend to get trapped in local corrugations. In order for them to slide, they must overcome an energy barrier proportional to the chain tension times the height of the corrugation.

The above two examples of metastable behavior depend crucially on having a small but finite length that gives rise to an energy barrier proportional to it. The chain must overcome this barrier in order to move. This is similar to the lattice case since kinks must hop a small but finite distance. In all three cases, if this small length goes to zero—or the E goes to zero—while we maintain a fixed charge per unit length, then energy barriers disappear and configurations cease to be metastable.

Any real system does contain an analogous length necessary for metastability, namely the distance between monomers. Therefore we believe that the metastability discussed above could be observed experimentally in some real system. Nevertheless a sufficiently strong field is required; for a temperature T and a charge per monomer q, $ELq/2kT > 1$, where k is Boltzmann's constant (in the simulation Eq/kT is set equal to E). Otherwise the motion is driven by a continuous diffusion drift. For example, in DNA electrophoresis experiments the charge per monomer is very small, and a very strong field is required in order to observe metastability (we estimate of the order of 200 V/cm for a chain of length 1×10^5 Å). In these experiments the electric field varies from 1 to 10 V/cm.[10] Nevertheless, experiments with pulsed field gradients of around 200 V/cm have recently been used to separate DNA of different lengths;[11] the results may provide evidence for the applicability of the work present here.

CONCLUSIONS

It has been shown that a linear chain in a network becomes trapped when under the influence of a strong electric field. The relaxation time increases exponentially with the strength of the field times the length of the polymer.

In these circumstances the polymer stretches and once it is stretched, it will eventually entangle again. It was not possible to find the steady-state configuration. However, in the case of a chain free of entanglements it was shown that the chain in equilibrium preserves its radius of gyration in the presence of an electric field.

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[*] Present address: National Bureau of Standards, Gaithersburg, MD 20899.

[†] Present address: Institute for Theoretical Physics, University of California, Santa Barbara, California 93106.

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