Dynamics of a Ring Polymer in a Gel

Sergei P. Obukhov,[1] Michael Rubinstein,[2] and Thomas Duke[3]
[1]*Department of Physics, University of Florida, Gainesville, Florida 32611*
and Institute for Theoretical Physics, Moscow, Russia
[2]*Imaging Research and Advanced Development, Eastman Kodak Company, Rochester, New York 14650-02116*
[3]*Departments of Physics and Molecular Biology, Princeton University, Princeton, New Jersey 08544*

(Received 19 April 1994)

We present a simple scaling theory of the dynamics of a ring polymer in a gel. In the absence of excluded volume interactions, we predict that the translational diffusion coefficient D varies with the molecular weight M as $D \sim M^{-2}$ and the longest relaxation time T scales as $T \sim M^{5/2}$. The results of numerical simulations support these findings.

PACS numbers: 82.70.Gg, 61.41.+e

The motion of polymer molecules in a gel has proved to be a problem of enduring interest. While the behavior of both linear [1–3] and branched [3,4] species has been rather thoroughly examined, there have been relatively few theoretical treatments of the dynamics of ring polymers [5–7]. Yet the problem is an important one. DNA often occurs naturally in a circular form and such molecules are frequently characterized by the technique of gel electrophoresis. An understanding of the electrophoretic mobility of circular DNA requires, as a starting point, a theoretical description of the diffusive motion of the molecules in thermal equilibrium. In this Letter we demonstrate that previous conjectures on the dynamics of cyclic polymers overlooked important modes of motion available to the molecule and consequently underestimated the rate of evolution of polymer configurations. The longest relaxation time T of a ring polymer in a gel scales with its molecular weight M as $T \sim M^{5/2}$, and not as $T \sim M^3$ as formerly supposed [5–7].

We restrict our discussion to a model gel, represented by a cage that divides space into a connected network of open regions (pores), each of linear dimension a. Furthermore, we suppose that the gel contains no dangling ends that could skewer a circular molecule. We confine our attention to ring polymers that are neither knotted nor supercoiled (e.g., nicked circular DNA) and that are introduced into the gel subsequent to their manufacture so that they are not concatenated with the network. A polymer has contour length L, Kuhn length b, and a fluid friction ζ associated with each Kuhn segment. It is assumed that $b < a$ so that the polymer is flexible on the scale of the gel pores. To begin, we shall neglect the excluded volume interaction of the molecule with itself. Then the polymer may be modeled by a chain of $N = Lb/a^2$ segments, each of linear dimension a and representing a blob comprised of $N_e = (a/b)^2$ Kuhn segments. The Rouse relaxation time of each blob is $\tau_0 \sim a^4\zeta/b^2kT$. In this Letter, we are concerned only with the case of long chains, $N \gg 1$.

Since the polymer cannot encompass any material part of the gel, it must double up on itself and adopt a conformation similar to that shown in Fig. 1(a). Such a configuration is equivalent [5–8] to one of the ensemble of lattice trees [Fig. 1(b)]. The statistics of ring polymers in a gel at thermal equilibrium, then, are the same as those of (ideal) randomly branched polymers or "lattice animals." Consequently the radius of gyration R scales [9] as $R \sim N^{1/4}a$.

de Gennes [1] pictured the reptation of a linear polymer in a gel as the consequence of the diffusion of numerous "length defects" or kinks along the polymer contour. Three groups of authors [5–7] independently proposed that this idea could be adapted to ring molecules. They envisaged the migration of kinks around the perimeter of the conformation, as shown in Fig. 1(a), and supposed that the kinks diffuse just as they do on a linear chain. By considering the time required for a kink to diffuse halfway around the perimeter, and noting that in this period the kink moves a spatial distance R, they concluded that the relaxation time of the polymer scales as $T \sim N^3$ and its translational diffusion coefficient as $D \sim N^{-5/2}$ (in

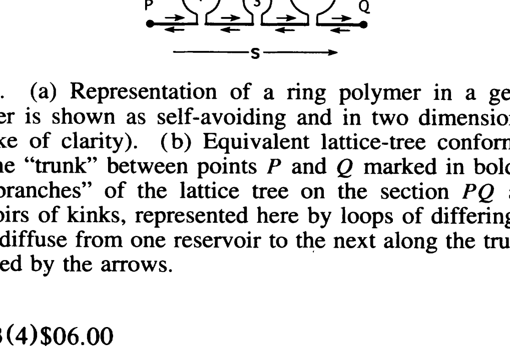

FIG. 1. (a) Representation of a ring polymer in a gel (the polymer is shown as self-avoiding and in two dimensions for the sake of clarity). (b) Equivalent lattice-tree conformation with the "trunk" between points P and Q marked in bold. (c) The "branches" of the lattice tree on the section PQ act as reservoirs of kinks, represented here by loops of differing size. Kinks diffuse from one reservoir to the next along the trunk, as indicated by the arrows.

0031-9007/94/73(9)/1263(4)$06.00

three dimensions, with no excluded volume). The validity of this argument is doubtful, however, for it fails to take into account the evolution of the shape of the perimeter as one kink moves around it (the shape change, of course, is due to the motion of other kinks). Indeed, the variability of the perimeter provides a mechanism whereby the local density of kinks can be altered and, as we shall see, this affects the kink diffusion so that it differs from that on a linear chain. Since the conformation is perpetually changing, we propose that a more reliable approach to determining the long-time diffusion of the molecule is to focus attention on the most durable feature of the polymer configuration. If one considers the lattice-tree representation [Fig. 1(b)], it is clear that kink diffusion will first rearrange the leaves, then the branches, and finally the trunk. The crux of our approach, then, is to investigate the dynamical evolution of the tree trunk.

Consider a general section of the polymer such as the part between points P and Q (moving clockwise around the ring) in Fig. 1(a). The portion of the lattice tree corresponding to this section may unambiguously be divided into a trunk and branches [Fig. 1(b)], with each branch representing a closed loop of the molecule. The trunk corresponds to the "backbone" of a lattice animal and its statistics are well known. It has the conformation of a random walk of length $m \sim n^{1/2}$ segments, where n is the number of chain segments in the section PQ. Now consider kink diffusion on this portion of the molecule. Again, a division into two components can be made: (i) migration of kinks within the branches; and (ii) diffusion of kinks along the trunk. We argue that the first process just rearranges the conformation of a closed loop and does not contribute significantly to overall transport of the section PQ. Each loop, however, acts as a reservoir of kinks which participate in the second process; the transport of kinks along the trunk can be thought of as the transfer of kinks between adjacent loops [Fig. 1(c)]. Consider a time interval τ_0, which is the typical time for a kink to move through one pore, i.e., through a mean-square displacement along the trunk $\Delta s^2 = a^2$. The motion of a single kink causes the center of mass of PQ to move through $\Delta s^2_{\mathrm{c.m.}} = a^2/n^2$ along the trunk. Since there are of order m loops, and the direction in which each of them transfers a kink is random, the overall mean-square displacement of the center of mass along the trunk is $\Delta s^2_{\mathrm{c.m.}} \sim ma^2/n^2$. Thus the curvilinear diffusion coefficient of the section PQ, measured along the trunk, is $D_s(n) = \Delta s^2_{\mathrm{c.m.}}/\tau_0 \sim D_0 n^{-3/2}$, where $D_0 = a^2/\tau_0$ is the diffusion coefficient of kinks around the ring. The self-similar nature of the polymer conformation ensures that this result holds on all length scales.

Considering now the entire ring (or, more precisely, one undoubled half of it), its trunk contains $M \sim N^{1/2}$ segments and has length $S = Ma$. The longest relaxation time T of the polymer corresponds to the modification of all segments of the trunk and is therefore given by $T \sim S^2/D_s(N)$. Thus

$$T \sim N^{5/2}\tau_0 . \tag{1}$$

In this time, the polymer moves through a spatial distance of order its radius of gyration so that its translational diffusion coefficient is given by $D \sim R_g^2/T$ and scales as

$$D \sim N^{-2}D_0 . \tag{2}$$

Coincidentally, the diffusion coefficient of a ring polymer scales with length in the same way as that of a reptating linear chain [1]. The relaxation behavior is very different, however. As a linear chain reptates out of its tube, only the segments close to its ends relax rapidly, the majority of segments relaxing on the time scale of the longest relaxation time. For a ring polymer, on the other hand, a substantial proportion of the segments (those corresponding to the leaves of the tree) relax almost immediately and only a small fraction of the molecule remains to be relaxed on the time scale of the longest relaxation time. Furthermore, this time is shorter than that of the equivalent linear chain [1].

The above arguments rationalize results that we have obtained from numerical simulations using a variant of the repton model [10,11]. The gel is represented by a regular cubic grid of impenetrable lines and the polymer modeled as a chain of N_a segments forming a closed ring on the dual lattice (Fig. 2). Each segment may be in one of two states: either extended, connecting two adjacent lattice points, or looped on a single lattice point, in which case it represents a length defect. The dynamics is specified by three "exchange rules" which are, in effect, rules for defect motion. *Rule 1:* A loop and an extended segment adjacent to it may exchange identities, the extended segment becoming a loop and vice versa (the effect of this move is that the loop hops one unit along the chain). *Rule 2:* A pair of loops that are adjacent on the chain may extend together towards a new lattice point, chosen at random from amongst the nearest neighbors. *Rule 3:* The reverse of rule 2, a pair of adjacent extended segments that connect the same two lattice points may contract to form two loops. For simplicity, the rates of each of these three

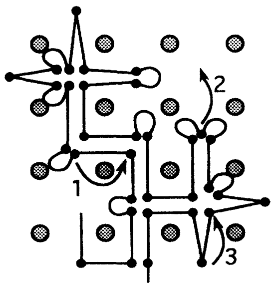

FIG. 2. Model for the numerical simulation of the polymer dynamics [represented here is the upper right portion of the molecule in Fig. 1(a)]. The numbered hopping moves indicated by the arrows correspond to the three rules stated in the text.

transitions are set equal. This model is essentially similar to the cage model of Evans and Edwards [5,12], but is more efficient to simulate, permitting a full investigation of the length dependence of the polymer dynamics.

We have examined the equilibrium statistics of the polymers generated using these dynamical rules. We find that the radius of gyration scales as $R \sim N_a^\nu$ with $\nu = 0.28 \pm 0.02$ for $N_a > 100$ (not shown). There is apparently only a very slow approach to asymptotic behavior, for the exponent is significantly larger at smaller N_a. The diffusion coefficient of the center of mass was measured over a period in which the polymer moved through a displacement at least 1 order of magnitude greater than its radius of gyration (Fig. 3). It scales with the polymer length as $D \sim N_a^{-2.1\pm0.1}$, in agreement with Eq. (2). The relaxation behavior was investigated by determining the fraction f of original lattice-tree bonds that still remain after time t has elapsed. A substantial fraction of bonds relax very quickly, but at long times there is a single exponential decay $f = f_0 \exp(-t/T)$ (see Fig. 4). The measured time constant, which corresponds to the longest relaxation time of the polymer, scales as $T \sim N_a^{2.6\pm0.1}$, consistent with Eq. (1). Furthermore, extrapolation of the exponential part of the curve back to the axis yields an intercept f_0 that scales as $f_0 \sim N_a^{0.5\pm0.1}$, supporting the association of the long-time decay with the relaxation of the tree trunk of length $M \sim N_a^{0.5}$. We have also investigated the curvilinear transport of a tagged segment along the chain at early times. Consider the point P on the polymer in Fig. 1(a), which corresponds to an interior part of the tree in Fig. 1(b). After time $t \ll T$ has elapsed, the polymer will still pass through the pore that originally housed P, but the point P itself will have diffused away. Let l be the distance (measured along the chain) between P and its initial location. We find that $\langle l^2 \rangle \sim t^\gamma$ with $\gamma = 0.80 \pm 0.04$. The value of this exponent lies between the values obtained for tracer diffusion on a linear chain [1], $\gamma = \frac{1}{2}$, and for free diffusion of noninteracting particles, $\gamma = 1$. It follows from Eq. (1), valid on all length scales due to the self-similarity of the polymer conformation. Inversion of (1) implies that the typical contour length through which the chain has diffused at time t is $l \sim t^{2/5}$ so that the mean-square length of chain that has passed through a pore scales with time as $\langle l^2 \rangle \sim t^{4/5}$.

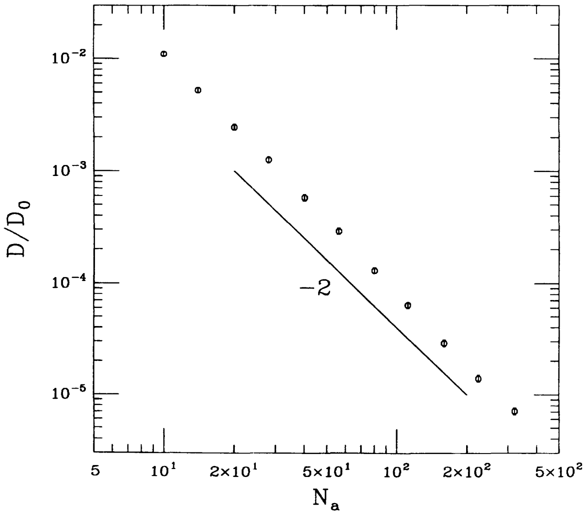

FIG. 3. Diffusion coefficient D as a function of the number of chain segments N_a. The solid line is the theoretical scaling Eq. (1).

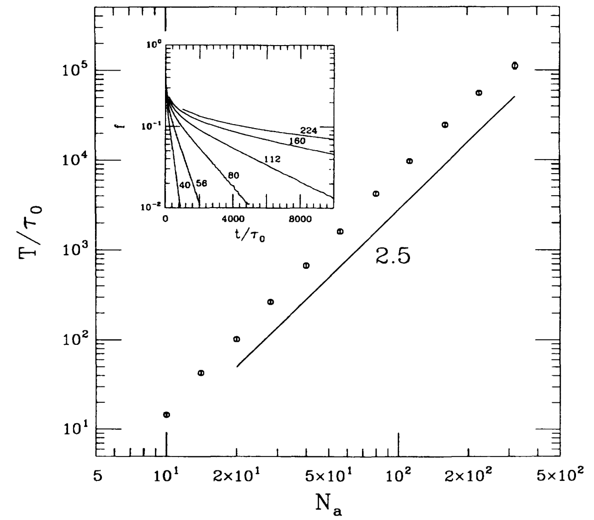

FIG. 4. Longest relaxation time T as a function of the number of chain segments N_a. The solid line is the theoretical scaling Eq. (2). Inset: Fraction f of original bonds remaining after time t, for polymers of different length N_a (labeled).

The weak-field electrophoretic mobility μ of a ring polymer in a gel is related to its equilibrium diffusion coefficient by the Nernst-Einstein relation. Since the electrostatic driving force, proportional to the total charge, varies linearly with the degree of polymerization, Eq. (1) implies than $\mu \sim N^{-1}$. The inverse-linear dependence is coincidentally the same as the law that has been observed [13] for linear polymers and rationalized in terms of the reptation model [14]. There is some circumstantial evidence that the gel-electrophoretic mobility of circular DNA [15,16] does obey this scaling in weak electric fields, but more extensive experimental data are required to confirm this. It is known that long linear polymers display nonequilibrium behavior in a moderate electric field: their mobility deviates from the prediction of the Nernst-Einstein relation, becoming field dependent and independent of molecular weight [13]. This has been attributed to perturbation of the chain configuration from the equilibrium Gaussian coil to a conformation elongated in the field direction [17–19]. Presumably, a similar effect will occur for ring molecules too, although the mechanism must differ in detail. At still higher field strengths, ring polymers have been predicted to behave in the same way as linear polymers, adopting a treelike conformation aligned along the field [20]. In practice, circular DNA molecules get trapped in gels when electrophoresis is attempted at elevated field strengths [15], apparently because they are caught by dangling gel fibers, like a hoop on a stick. Replacing the gel by a microfabricated array of obstacles [21] would eliminate this problem and allow the experimental investigation of the electrophoretic mobility in strong fields.

Since the segment density of an ideal lattice animal increases with its size (in three or fewer dimensions), the self-interaction of a ring polymer in a gel must eventually become significant for long enough molecules. If the cross-sectional radius of the polymer is r, the excluded volume of a pair of Kuhn segments [2] is $v \sim b^2 r$. Then the typical number of Kuhn segments that interact with another can be estimated as $n_{\text{int}} \sim (NN_e)^2 v/R^3$. The excluded volume interaction may be neglected only when n_{int} is smaller than unity, and consequently must be taken into account when $N > (b^2/ar)^{4/5}$. For DNA in an agarose gel ($b \approx 100$ nm, $r \approx 1.5$ nm, $a \approx 300$ nm) this corresponds to molecules longer than about 30 kilobases. To describe this situation, the above arguments for the dynamics may be repeated for a chain that has the statistics of a self-avoiding lattice animal. The radius of gyration scales as $R \sim N^\nu$ with $\nu = 5/2(d + 2)$ in the Flory approximation [22] (the Flory exponent is known [23] to coincide with the exact result in $d = 3$). The backbone length m scales with the total number n of segments as $m \sim n^\rho$ where $\rho = (d + 6)/(3d + 4)$ [24]. For these values of the static exponents, the arguments that led to Eqs. (1) and (2) yield $T \sim N^{2+\rho}$ and $D \sim N^{2\nu-2-\rho}$. In three dimensions, one obtains $T \sim N^{2.69}$, $D \sim N^{-1.69}$. The excluded volume interaction slows down the relaxation of the polymer but, by swelling the chain, increases its diffusion coefficient.

The description of the dynamics of an individual ring polymer in a gel presented here may be useful as the basis of a theory of the viscoelastic behavior of a melt of cyclic polymers [25,26]. But two additional effects have to be considered. First, in a melt, the constraints to motion imposed by the surrounding polymers change as the molecules diffuse. This dynamic dilution of constraints [27] has to be evaluated self-consistently, taking into account the different relaxation times of different sections of the lattice tree. Second, in our analysis we have neglected the purely topological interaction of the polymer with itself. One loop of the molecule may pass through another; and when this happens the penetrated loop cannot retract until the first loop has moved back out. This interaction is expected to slow down the dynamics significantly. Such events will be more common in a melt of rings where the loops of neighboring molecules are also involved, so the transport properties are likely to depend more strongly on molecular weight than Eqs. (1) and (2).

We thank J. L. Viovy for helpful discussions.

---

[1] P. G. de Gennes, J. Chem. Phys. **55**, 572 (1971).

[2] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University, Oxford, 1986).

[3] T. P. Lodge, N. A. Rotstein, and S. Prager, Adv. Chem. Phys. **79**, 1 (1990).

[4] P. G. de Gennes, J. Phys. (Paris) **36**, 1199 (1975).

[5] M. E. Cates and J. M. Deutsch, J. Phys. (Paris) **47**, 2121 (1986).

[6] M. Rubinstein, Phys. Rev. Lett. **57**, 3023 (1986).

[7] S. K. Nechaev, A. N. Semenov, and M. K. Koleva, Physica (Amsterdam) **140A**, 506 (1987).

[8] A. R. Khoklov and S. K. Nechaev, Phys. Lett. **112A**, 156 (1985).

[9] B. H. Zimm and W. H. Stockmayer, J. Chem. Phys. **17**, 1301 (1949).

[10] M. Rubinstein, Phys. Rev. Lett. **59**, 1946 (1987).

[11] T. A. J. Duke, Phys. Rev. Lett. **62**, 2877 (1989).

[12] K. E. Evans and S. F. Edwards, J. Chem. Soc. Faraday Trans. II **77**, 1929 (1981).

[13] E. M. Southern, Anal. Biochem. **100**, 309 (1979).

[14] L. S. Lerman and H. L. Frisch, Biopolymers **21**, 995 (1982).

[15] S. Mickel, V. Arena, and W. Bauer, Nucl. Acids Res. **4**, 1465 (1977).

[16] D. A. Hoagland and M. Muthukumar, Macromolecules **25**, 6696 (1992).

[17] O. J. Lumpkin, P. Dejardin, and B. H. Zimm, Biopolymers **24**, 1573 (1985).

[18] G. W. Slater and J. Noolandi, Phys. Rev. Lett. **55**, 572 (1985).

[19] T. A. J. Duke, A. N. Semenov, and J. L. Viovy, Phys. Rev. Lett. **69**, 3260 (1992).

[20] S. P. Obukhov and M. Rubinstein, J. Phys. II (France) **3**, 1455 (1993).

[21] W. Volkmuth and R. H. Austin, Nature (London) **358**, 600 (1992).

[22] J. Isaacson and T. Lubensky, J. Phys. (Paris), Lett. **41**, L469 (1980).

[23] G. Parisi and N. Sourlas, Phys. Rev. Lett. **46**, 871 (1981).

[24] A. M. Gutin, A. Y. Grosberg, and E. I. Shakhnovich, Macromolecules **26**, 1293 (1993).

[25] J. Roovers, Macromolecules **21**, 1517 (1988).

[26] G. B. McKenna, B. J. Hostetter, N. Hadjichristidis, L. J. Fetters, and D. J. Plazek, Macromolecules **22**, 1834 (1989).

[27] J. L. Viovy, M. Rubinstein, and R. H. Colby, Macromolecules **24**, 3587 (1991).

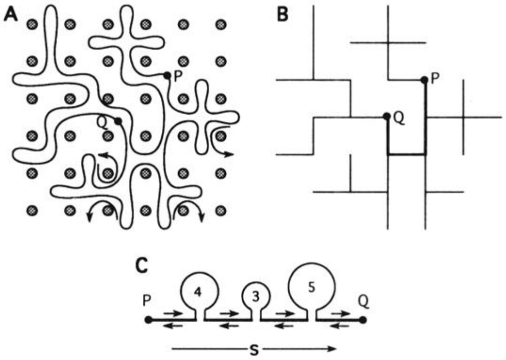

FIG. 1. (a) Representation of a ring polymer in a gel (the polymer is shown as self-avoiding and in two dimensions for the sake of clarity). (b) Equivalent lattice-tree conformation with the "trunk" between points *P* and *Q* marked in bold. (c) The "branches" of the lattice tree on the section *PQ* act as reservoirs of kinks, represented here by loops of differing size. Kinks diffuse from one reservoir to the next along the trunk, as indicated by the arrows.

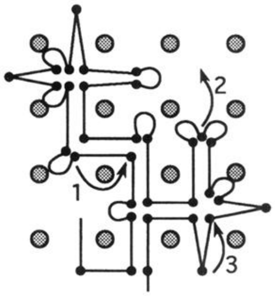

FIG. 2. Model for the numerical simulation of the polymer dynamics [represented here is the upper right portion of the molecule in Fig. 1(a)]. The numbered hopping moves indicated by the arrows correspond to the three rules stated in the text.