

Dynamics of Ring Polymers in the Presence of Fixed Obstacles

Michael Rubinstein

Corporate Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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The configurations and dynamics of a polymer ring (R) inside a strongly crosslinked polymer gel (G) are discussed and compared to those of linear (L) and branched (B) polymers in G . R is not topologically connected to G in the sense that the contour line of R can be reduced to a point without crossing any of the chains of G . This topological requirement leads to the correspondence between the configurations of R in G and the set of lattice trees (randomly branched polymers). But the dynamics of R in G is much faster than that of entangled B , and is similar to the dynamics of entangled L .

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Ring polymers (R) constitute an interesting and important class of macromolecules.¹ DNA molecules are often found in the form of very high-molecular-weight R . Gel electrophoresis is a common method of separation and characterization of DNA.² The existing theories of gel electrophoresis apply only to linear polymers (L)³⁻⁸ and are based on the reptation model⁹; therefore, they are not directly applicable to R . It is important to develop a theory for the static and dynamic properties of high-molecular-weight R in a gel (G). This theory would be a starting point toward the understanding of the experimental results of the R diffusion into a matrix of L ¹⁰ and, possibly, the dynamics of a melt of R .¹¹

In this paper, we propose a theory for the configurations and dynamics of R in G . We compare our theoretical predictions with those for L in G and branched polymers (B) in G , and with some experimental results. The unexpected predictions of the present theory are that the configurations of R and G can be mapped onto those of randomly branched unlooped polymers (lattice trees), but the dynamics are similar to those of entangled L . In order to explain these predictions clearly, we review the results of the dynamic theories of L in G and B in G .

The dynamic properties of G are determined by chemical crosslinks and topological entanglements. Permanent (temporary) entanglements are topological interactions which permanently (temporarily) reduce available configurational space.¹²

We have confined the scope of this paper to the dynamics of polymers in an array of fixed obstacles; therefore, we assume that networks have no dangling ends and loops (no temporary entanglements). The network of primitive paths of G has crosslinks and permanent entanglements at its vertices and divides space into cells of average size a . For a polymer diffusing through G , this distance a defines a length scale, called the tube width, at which topological constraints become important.

A polymer diffusing through a network has no permanent entanglements (otherwise, it would not be diffusible). The distance between the temporary entanglements of a flexible polymer in a network is determined by the cell size a of this network. In θ solvents and in

the absence of solvent, the section of the polymer between entanglements can be modeled by a random walk, and the molecular weight of this section $M_e \sim a^2$. For a network in a good solvent $M_e \sim a^{1/\nu}$, where $\nu = 3/(d+2)$ is the Flory exponent (0.6 in $d=3$ dimensions). If the molecular weight of the polymer is much larger than that of the chains of G between crosslinks, the polymer will be swollen by G .¹³ This effect is similar to the swelling of long chains in a melt of shorter ones.¹⁴ Thus, in d dimensions, the radius of gyration of L (or star polymers) diffusing through G is

$$R_G^{(L)} \sim M^{3/(d+2)}, \quad (1a)$$

and for randomly branched polymers¹⁵

$$R_G^{(B)} \sim M^{5/(2d+4)}. \quad (1b)$$

The confining tube can be defined as a region with a high-average-density profile of a diffusing polymer, where averaging is taken over a much longer time than the relaxation time of the sections of mass M_e , but much shorter than the equilibration time of the whole chain.¹² The central line of the tube (the line of maximum average density) is called the primitive path of the polymer. In Fig. 1, we present a two-dimensional sketch of entangled L and B (solid lines) in G . The topological constraints (primitive paths) of G are denoted by circles. Primitive paths of L and B are represented by dashed lines.

A polymer can be divided into its primitive path and a set of unentangled loops, called defects.⁹ A few of these defects are represented by dotted lines in Fig. 1. The dynamic properties of a primitive path and unentangled loops are very different. Unentangled loops relax quickly (Rouse-type relaxation time $\sim M_e^2$) and diffuse along the primitive path. This diffusion of the unentangled loops of stored length (defects) along the primitive path of the polymer was considered originally by de Gennes⁹ for L in G .

The equilibration time τ_e for the density of defects along the primitive path is proportional to M^2 :

$$\tau_e \sim M^2 \quad (2)$$

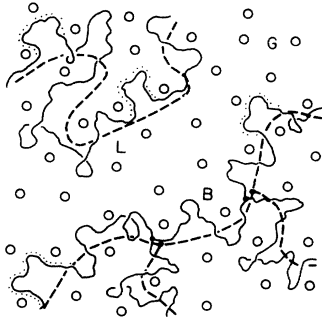


FIG. 1. Entangled linear (L) and branched (B) polymers (solid lines) in a gel (G) (primitive paths of G , open circles). L and B can be divided into their primitive paths (dashed lines) and a set of unentangled loops (four of them are outlined by dashed lines).

(it is of the order of diffusion time of defects along the primitive path). At this time, the length of the primitive path reaches its equilibrium value, unless there are branch points at both ends (e.g., central chain of an H polymer in Fig. 1).

The above description applies to a polymer of any topology. Below, we consider relaxation and diffusion of L , B , and R in G separately.

If a gel containing an unattached polymer is stressed, the polymer can relax by moving out of its original stressed tube into a completely new, unstressed one. For L , this process is called reptation.⁹ The relaxation time of L , called reptation time, is proportional⁹ to M^3 :

$$\tau_r^{(L)} \sim M^3. \quad (3)$$

During this time, the center of mass of L moves a distance on the order of $R_G^{(L)}$; therefore, the diffusion coefficient of L in G is

$$D^{(L)} \sim (R_G^{(L)})^2 / \tau_r^{(L)} \sim M^{-3d/(d+2)}. \quad (4)$$

Notice the difference between the exponent 1.8 (for $d=3$) of Eq. (4) and exponent 2 of Ref. 9. This difference comes from the assumption of swelling of L in G [Eq. (1a)]. L are not swollen in the melt of other L , and the diffusion coefficient for L in L is $\sim M^{-2}$, as is experimentally observed.¹⁶

A branched polymer cannot reptate along its tube the way L does, because unentangled loops (defects) cannot pass the branch point. This difference in the boundary condition dramatically affects polymer dynamics. The dynamics of the simplest type of B [the symmetric star polymer (S)] in G was originally solved by de Gennes.¹⁷ The solution was later modified,^{18,19} but the exponential dependence of relaxation time on molecular weight M_a of the arm of S still remains intact:

$$\tau_r^{(S)} \sim \exp(\alpha M_a). \quad (5)$$

The reason for this dependence is that, in order for an

f -arm S to relax (completely change its configuration), all of its arms must retract all the way to the branch point (to form huge unentangled loops with the branch point in the same cell of G as the tips of the arms). The retracted arms are then pushed out through the gates of the cell (faces between adjacent cells) into completely new configurations. The probability of a large unentangled loop in G is exponentially small¹²; hence Eq. (5).

Diffusion of an f -arm star consists of a set of steps of its center between neighboring cells of G (steps of order a). To make such a step, S needs to vacate all but (at most) two gates of the cell. The probability of this in the z -gate cell is

$$c(z, f) = \frac{[1 + (z-1)(f-1)/2]z!f!}{(z+f-1)!}.$$

The diffusion coefficient is therefore an exponentially decaying function of M_a :

$$D^{(S)} \sim c(z, f)a^2/\tau_r^{(S)} \sim c(z, f)\exp(-\alpha M_a). \quad (6)$$

We would like to stress that the factor α in the exponential does not depend on the number f of arms of the star polymer. (An opposing point of view with $\alpha \sim f-2$ has appeared in some recent papers.^{20,21}) To move the center of S , the $f-2$ arms need not be retracted simultaneously! Following the retraction, it is only necessary that the tips of these arms leave the cell containing the branch point through the same gate as one of the two remaining arms of S . Thus, the functionality of the branch point f enters a combinatorial prefactor $c(z, f)$ in Eq. (6), but not the exponent. This is to be contrasted with the other relaxation mechanism described by Klein,²¹ where the branch point together with $f-1$ arms of the star move along the tube of the remaining arm. The relaxation time associated with it is proportional to $\exp[(f-2)\alpha' M_a]$, where $\alpha' \gtrsim \alpha$. Thus the relaxation of a three-arm star is a combination of the two mechanisms—the retraction of the arms and the fluctuations in the position of the branch point, as described by Klein.²¹ But for the number of arms $f > 3$ the first mechanism clearly dominates.

Consider a cyclic polymer inside a network, but not permanently entangled with it, so that it can diffuse without breaking any chemical bonds [Fig. 2(a)]. The fact that only temporary entanglements of the R with the G are present means that the R is topologically equivalent to a point (can be reduced to a point without crossing any other chains). As mentioned above, primitive paths of G divide space into cells of average size a . The set of the centers of these cells forms a lattice dual to that of crosslinks and permanent entanglements of G . The gates of G correspond to the bonds of the dual lattice. The absence of permanent entanglements implies that the R crosses each gate an even number of times. If we replace this even number of crossings by a single bond, we obtain a lattice tree [Fig. 2(b)]. Thus, the

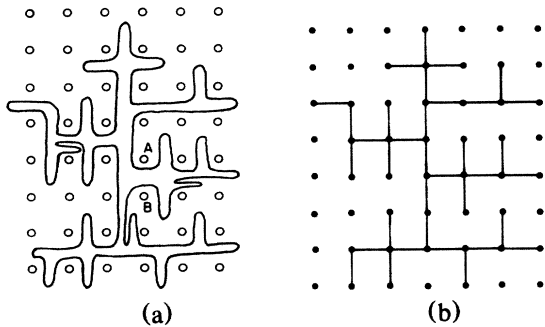


FIG. 2. (a) Ring polymer in a gel can be mapped onto (b) a lattice tree on a dual lattice.

statistics of R in G are similar to the statistics of lattice trees. This point was suggested by Khokhlov and Nechaev,²² and independently by us for the present work. In Ref. 22 the term "lattice animals" was used. It includes closed loops forbidden for temporarily entangled R in G . Closed loops are irrelevant for the static properties of lattice animals,²³ but they make R diffusion in G impossible.

Thus, any R in G can be mapped onto a lattice tree on a dual lattice, but a lattice tree corresponds to many configurations of R in G . Mapping of R in G onto lattice trees neglects configurational details on scales smaller than a . This simplification is justified by the fact that short-time dynamics is not affected much by large-scale topology; therefore, the nontrivial aspects of the dynamics of R in G come from motion on the scale of a and larger. In fact, instead of our mapping the R itself, it would be more appropriate to map the line of maxima of the density of R averaged over short times (see the definition of the confining tube above). This would eliminate the branches of the lattice tree appearing and disappearing with very high frequency, corresponding to a few monomers of R getting in and out of new cells of G , and leave only relevant large-scale motion.

Lattice trees model randomly branched unlooped polymers. Therefore, the configurations of R in G are similar to those of randomly branched polymers. This similarity implies that the radius of gyration of R in G has the same dependence on molecular weight as Eq. (1b):

$$R_G^{(R)} \sim M^{5/(2d+4)}. \quad (7)$$

The dynamics of R in G are introduced in a way similar to the dynamics of L in G .⁹ The motion of R in G results from elementary displacements (by distance of the order of a) of small unentangled loops (of size $\sim M_e$).⁹ These displacements correspond to the hopping of the lattice tree branches between the adjacent bonds. Unentangled loops (defects) undergo one-dimensional diffusion along the contour of R as they move along the contour of L .⁹ The only difference is in the geometry of the contours. This implies that the longest relaxation

times for the two systems are proportional²⁴ [Eq. (3)]:

$$\tau_r^{(R)} \sim M^3. \quad (8)$$

Despite the similarity in conformations the dynamics of R in G differs from that of B in G . The unentangled loops diffusing along B cannot pass branch points and are reflected from them, causing an exponential dependence of relaxation time on the molecular weight of the arms [Eq. (5)]. The R has no chemical branch points and the branch points of the lattice-tree representation of R in G do not restrict the motion of unentangled loops along the contour of R .

The dynamics of the lattice tree on the dual lattice can be described in the following way. The motion starts with the leaves of the tree jumping to adjacent bonds. Later, the combined motion of leaves corresponds to a displacement of the branches of the tree. Finally, the motion of the larger branches transforms into a diffusion of the trunk of the lattice tree (and of R). This dynamic picture is similar to the way artists make cartoons; therefore, this model is called the lattice-tree animation model.

This picture is to be compared with the reptation of nonramified R in G proposed by Klein.²¹ The probability of a nonramified configuration (linear lattice tree with no branches) is exponentially low, and the probability of staying in this configuration long enough to reptate in the same manner as a L in G does is still lower. Therefore, this diffusion method of R in G seems less likely than the proposed lattice-tree animation model.

The diffusion coefficient of R in G can be determined from Eqs. (7) and (8),

$$D^{(R)} \sim (R_G^{(R)})^2 / \tau_r^{(R)} \sim M^{-(3d+1)/(d+2)}. \quad (9)$$

This prediction agrees with recent computer simulations.²⁴ The difference in the molecular-weight dependence of L in G [Eq. (4)] and R in G [Eq. (9)] implies a similar difference in electrophoretic mobility,³⁻⁸ which is consistent with experiments.²

In our treatment of the dynamics of R in G , we assumed that overlapping branches of the lattice tree do not interact in the sense that unentangled loops do not penetrate one another too deeply. This would slow the dynamics, because for one such loop to retract, another loop that penetrated through it must move out first. We believe that this effect cannot be neglected for the melt of R in R . It is probably the major cause for significant slowing of the dynamics of R in R . Thus, going from R in G to R in R , we predict an increase in relaxation time τ_r as a result of the trapping of unentangled loops, whereas when we go from L in G to L in L τ_r should decrease because of constraint release.

The results presented in this paper are directly applicable only to R in G . The equilibrium conformations of R in L do not correspond to lattice trees, but for very high-molecular-weight L , diffusion of R in L is due

mainly to an exponentially small fraction of R (non-threaded ones).²¹ Their configurations and dynamics, until they encounter the ends of L , are similar to R in G . Therefore, the dynamic theory of R in L can be constructed analogously to that of Ref. 21 by use of the lattice-tree animation model instead of the nonramified R reptation model. The contribution from the majority of R in L , the threaded ones, can be described by the Orwoll-Stockmayer²⁵ model with bond-flip rates equal to the constraint release rates, determined by the molecular weight of L .

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¹*Cyclic Polymers*, edited by J. A. Semlyen (Elsevier, New York, 1986).

²S. Mickel, V. Arena, and W. Bauer, *Nucleic Acids* **4**, 1465 (1977).

³L. S. Lerman and H. L. Frisch, *Biopolymers* **21**, 995 (1982).

⁴O. J. Lumpkin and B. H. Zimm, *Biopolymers* **21**, 2315 (1982).

⁵O. J. Lumpkin, P. Dejardin, and B. H. Zimm, *Biopolymers* **24**, 1573 (1985).

⁶G. W. Slater and J. Noolandi, *Phys. Rev. Lett.* **55**, 1579 (1985), and *Biopolymers* **24**, 2181 (1985), and *Europhys. Lett.* **1**, 347 (1986), and *Biopolymers* **25**, 431 (1986).

⁷M. Olvera de la Cruz, J. M. Deutsch, and S. F. Edwards, *Phys. Rev. A* **33**, 2047 (1986).

⁸D. Adolf, "Dynamics of Entangled Chain in an External Field," to be published.

⁹P. G. de Gennes, *J. Chem. Phys.* **55**, 572 (1971).

¹⁰P. J. Mills, J. W. Mayer, E. J. Kramer, G. Hadziioannou, P. Lutz, C. Strazielle, P. Rempp, and A. Kovacs, "Diffusion of Polymer Rings in the Linear Matrices," to be published.

¹¹J. Roovers, *Macromolecules* **18**, 1359 (1985).

¹²M. Rubinstein and E. Helfand, *J. Chem. Phys.* **82**, 2477 (1985).

¹³K. Kremer, *Z. Phys. Chem. Abt. B* **45**, 149 (1981).

¹⁴P. J. Flory, *J. Chem. Phys.* **17**, 303 (1949).

¹⁵J. Isaacson and T. C. Lubensky, *J. Phys. (Paris)* **41**, L469 (1980).

¹⁶M. Tirrell, *Rubber Chem. Technol.* **57**, 523 (1984).

¹⁷P. G. de Gennes, *J. Phys. (Paris)* **36**, 1199 (1975).

¹⁸M. Doi and N. Y. Kuzuu, *J. Polym. Sci. Polym. Lett. Ed.* **18**, 775 (1980).

¹⁹D. S. Pearson and E. Helfand, *Macromolecules* **17**, 888 (1984).

²⁰W. W. Graessley, *Adv. Polym. Sci.* **47**, 67 (1982).

²¹J. Klein, *Macromolecules* **19**, 105 (1986).

²²A. R. Khokhlov and S. K. Nechaev, *Phys. Lett.* **112A**, 156 (1985).

²³T. C. Lubensky and J. Isaacson, *Phys. Rev. Lett.* **41**, 829 (1978), and *Phys. Rev. A* **20**, 2130 (1979).

²⁴M. E. Cates and J. M. Deutsch, "Conjectures on the Statistics of Ring Polymers," to be published.

²⁵R. A. Orwoll and W. H. Stockmayer, *Stochastic Processes in Chemical Physics* (Wiley, New York, 1969).