Effect of topological constraints on the dynamics of polymer solutions

A. N. Semenov

M. V. Lomonosov State University, Moscow

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The effect of topological constraints on the dynamics of a long polymer macromolecule is analyzed. The slowest relaxation process results from the presence of local simple nodes and local entanglements. The corresponding relaxation time is significantly longer than the time for the diffusion of a macromolecule over a distance on the order of its own size. For a polymer solution at the Θ temperature, a critical concentration c^* is predicted at which an infinite cluster of entangled macromolecules arises. The concentration c^* is shown to separate two regions in which the viscosity depends in very different ways on the concentration. The theoretical predictions are compared with experimental data.

I. INTRODUCTION

The dynamic properties of polymer solutions are presently being studied intensely by both theoreticians and experimentalists.[1–3] The classical theories based on the approaches of Rouse[4] and Zimm[5] have proved incapable of describing the behavior of many important dynamic characteristics. According to the present understanding,[2] the primary deficiency of those theories is that they ignore the prohibition against mutual intersection of the polymer chains as they move. This prohibition, very important to the dynamics of polymer systems, has been termed the "entanglement effect." In reptation theory,[6–8] a comparatively recent development, an attempt has been made to incorporate entanglement phenomenologically on the basis of a "tube" model.[9] This theory successfully explains many dynamic properties of polymer systems, but many effects still remain unexplained. Despite its successes, reptation theory is unsatisfactory from an internal standpoint, since it is based on an unproved model. It is therefore a very important problem to derive a systematic dynamic theory incorporating entanglements (topological constraints). In the present paper we attempt to point out a way to derive such a theory.

In Section 2 of this paper we analyze some known approaches to the problem of the dynamics of an isolated polymer ball. In Section 3 we propose a new method for describing the topological state of a polymer chain. Working from some intuitively obvious ideas which emerge from that description, we draw a conclusion regarding how the maximum relaxation time $\tau_{\max}$ depends on the number N of units in the polymer chain. Section 4 analyzes the dynamics of a semidilute polymer solution. The example of the dependence of the viscosity of a solution on the polymer concentration is used to determine the new consequences of the conclusions reached in the preceding section. The basic theoretical results are compared with experimental data.

2. BASIC THEORETICAL APPROACHES TO THE PROBLEM OF THE DYNAMICS OF A POLYMER BALL

Historically the first dynamic model of a polymer chain was the Rouse model,[4] in which the macromolecule is represented by a sequence of $N+1$ beads with coordinates $\mathbf{r}_0, \mathbf{r}_1, \ldots, \mathbf{r}_N$, connected by massless bonds. Each bond corresponds to a potential $U(\mathbf{r}_j - \mathbf{r}_{j-1})$ of the form

$$U(\mathbf{r}) = Tr^2/4a^2, \tag{1}$$

where a is the scale length of one unit of the chain (Fig. 1). As a bead moves, the external medium (the solvent molecules) exerts a force on it, given by

$$\mathbf{f}_j = -\zeta_0 \dot{\mathbf{r}}_j + \boldsymbol{\xi}_j(t), \quad \boldsymbol{\xi}_j = \sum_\alpha \xi_{j\alpha} \mathbf{e}_\alpha, \tag{2}$$

where ζ_0 is the viscous friction coefficient, and $\boldsymbol{\xi}_j$ is the random component of the force exerted on bead j (the $\mathbf{e}_\alpha$ are unit vectors); here

$$\langle \xi_{j\alpha}(t) \xi_{j'\alpha'}(t') \rangle = 2T\zeta_0 \delta_{\alpha\alpha'} \delta_{jj'} \delta(t-t'). \tag{3}$$

The equation of motion of the chain is[1)]

$$\zeta_0 \dot{\mathbf{r}}_j = T(\mathbf{r}_{j+1} + \mathbf{r}_{j-1} - 2\mathbf{r}_j)/2a^2 + \boldsymbol{\xi}_j(t), \quad j = 0, 1, \ldots, N. \tag{4}$$

Analyzing system (4), we can easily find the maximum relaxation time of the internal modes of a "ball" [10]:

$$\tau_R = 2a^2N^2/\pi^2 D_0, \quad D_0 = T/\zeta_0. \tag{5}$$

This time agrees in order of magnitude with the time for the diffusion of the ball over a distance on the order of its own size:

$$R = N^{1/2} a. \tag{6}$$

Actually, each bead will interact with the external medium in a manner independent of the other entanglements [see (2) and (3)], so that the translational diffusion coefficient of an entanglement is $D = D_0/N$, i.e.,

$$\tau_R \sim R^2/D. \tag{7}$$

Rouse's theory has the serious deficiency that it ignores the hydrodynamic interaction caused by the motion of the solvent. This deficiency can be remedied by explicitly incor-

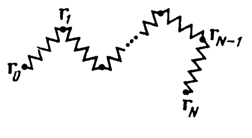

FIG. 1. Rouse's model of a polymer chain.

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porating thermodynamic degrees of freedom in the theoretical description, as in the ordinary quasisteady approach.[11] As a result one can obtain Zimm's model.[5] The translational diffusion coefficient D of a sufficiently long chain in this model agrees in order of magnitude with the diffusion coefficient of a sphere of radius R (Ref. 10):

$$D\sim T/6\pi\eta_s R, \tag{8}$$

where η_s is the viscosity of the solvent. The maximum relaxation time of the internal modes of the ball can again be estimated from (7):

$$\tau_z\sim R^2/D\sim 6\pi\eta_s R^3/T, \tag{9}$$

i.e.,

$$\tau_z\propto N^{3/2}. \tag{10}$$

These theories ignore the exchange interactions of the beads, so that they can be used only under Θ conditions, when the effective second virial coefficient of the interaction of the beads is zero. In a good solvent, this coefficient is larger than zero, so that the ball will swell to a size[10]

$$R=aN^\nu,\quad \nu\approx{}^3/_5. \tag{11}$$

If we generalize Zimm's model by incorporating the exchange interaction, we find that expressions (8) and (9) remain valid, as is shown by the analysis of Ref. 10, if we use in them the value of R given in (11). In this case we thus have

$$\tau_{max}\propto N^{3\nu}\approx N^{9/5}. \tag{12}$$

A serious deficiency of all of these theories is that they ignore topological restrictions. Such restrictions should have a particularly strong effect on the dynamics of a ball under Θ conditions, with the concentration of chain units higher than in a swollen ball.

Obviously, entanglements could not have a strong effect just on the diffusion of a single ball as a whole, since the "topology" of the ball would remain constant in the course of such a motion. Consequently, Zimm's theory does yield correct values for the translational diffusion coefficient of a ball [see (8)]. On the other hand, the topological restrictions undoubtedly retard the relaxation of the internal modes of the ball, so we have

$$\tau_{max}\gg R^2/D.$$

3. DESCRIPTION OF THE DYNAMICS OF A POLYMER BALL IN TERMS OF TOPOLOGICAL VARIABLES

The prohibition against self-intersection of parts of the chain imparts a new quality to the chain: a topology. This is strictly correct for a closed chain.[12] An unclosed chain (which is what we will be talking about below) can be closed by connecting its ends with a straight line segment. The length of this segment is on the order of $R=N^{1/2}a$ (under Θ conditions) and is much smaller than the total contour length of the chain, $L\sim Na$. It is thus clear that the introduction of a closing line segment of this sort will not change anything substantially (cf. Ref. 13).

From the mathematical standpoint, it is a fairly simple matter to characterize a topology, i.e., the type of knot at which a chain is tied. We know[12] that knots can be combined by tying one behind another and that an arbitrary knot Q can be represented unambiguously as a composition of simple nodes P_k:

$$Q=N_1P_1+N_2P_2+\dots, \tag{13}$$

where N_1 and N_2 are the multiplicities of the simple knots; P_1 is the simplest of the simple knots (a trefoil); etc.

The probability that some simple knot (e.g., a trefoil) is tied in a region of, e.g., ten units is some fixed numerical factor. Consequently, the average number of simple knots of a given type must be proportional to the number of units in the chain:

$$N_k\propto N,\quad k=1,2,\dots. \tag{14}$$

Simple knots which are tied to a small part of the chain could naturally be called "local knots." In addition to these local knots, there can of course be knots which can be seen only over rather large parts of the chain, consisting of $g>1$ units. The number of such larger-scale simple knots, N'_k, will evidently be considerably smaller than the number of simple knots, $N'_k\sim N_k/g$, so that we can ignore the effect of the large-scale knots in the order-of-magnitude calculations below.

For a local knot we introduce the coordinate n, the index of the unit near which this knot is positioned. We can thus consider a gas of local knots which interact weakly with each other and which can, in particular, pass by each other. The diffusion coefficient of a local knot for diffusion along the chain must be on the order of the translational diffusion coefficient of a single unit, D_0, regardless of whether the hydrodynamic interaction is taken into account (i.e., regardless of whether we are dealing with the Rouse model with topological restrictions or the Zimm model). We denote by $f(n)$ the distribution function of the simple local knots of a definite type k along the polymer chain. The time evolution of this distribution function is described by the diffusion equation

$$\partial f/\partial t=\Gamma\partial^2 f/\partial n^2,\quad f(0)=f(N)=f_0, \tag{15}$$

where $f_0=N_k/N$ is the equilibrium density of simple knots of type k, and $\Gamma\sim D_0/a^2$ is the reciprocal of the time for diffusion over the scale size, a, of a single unit. It follows from Eq. (15) that the maximum relaxation time for the function f is

$$\tau_f=\pi^2N^2/\Gamma\sim a^2N^2/D_0. \tag{16}$$

The maximum relaxation time of the polymer ball as a whole must obviously exceed the relaxation time corresponding to any individual variables: $\tau_{\max}\gg\tau_f$. Comparing (16) with (10) and (12), we conclude that incorporating topological restrictions leads to a substantial change in the N dependence of $\tau_{\max}$ for both a ball under Θ conditions and a swollen ball.

If we assume that the functional dependence $\tau_{\max}(N)$ is a power law at $N>1$,

$$\tau_{max}\propto N^{z},\tag{17}$$

we conclude from (16) that the exponent is $z\geqslant 2$. Let us attempt to amplify this estimate for the case of a ball under Θ conditions.

We assume that two regions of a macromolecule which contain, say, ten units each and which are far apart along the chain come spatially close together. If each of these regions is closed by a straight line segment between its ends, we obtain a local entanglement, which is analogous in meaning to the concept of a local knot. Entanglements, like knots [see (13)], can be divided into simple components.[12] We select the two outer thirds of the macromolecule, and we examine their mutual topological state. The total number M of simple local entanglements between them must be proportional to the number $\widetilde{N}$ of contacts between small regions of these thirds and to the probability p_1 for the formation of an entanglement at each contact: $M\sim p_1\widetilde{N}$. The probability p_1 is a constant numerical factor which does not depend on the number of units in the chain (N). The average number of contacts of units which are far apart along the chain, for a ball under Θ conditions, is on the order of[10] $N^{1/2}$, so we can write

$$\langle M\rangle\sim p_1N^{1/2}\propto N^{1/2}.\tag{18}$$

The position of each local simple entanglement on the chain can be characterized by the two coordinates n and m: the indices of those units whose closing on each other results in the formation of the given entanglement (n and m are counted from the corresponding ends: $0<n<N/3$, $0<m<N/3$). Local entanglements can move; i.e., their coordinates n and m can change. The corresponding diffusion coefficient is determined by friction between the solvent and a small number of close-lying units, so it is given in order of magnitude by $\Gamma\sim D_0/a^2$ (the dimensionality of the diffusion coefficient is determined by the circumstance that the coordinates n and m are dimensionless). In contrast with the case of local knots, however, the diffusion of entanglements is not a free diffusion, since entanglements interact strongly with each other. To demonstrate this point, we consider two local entanglements which are close together along the chain: (n,m) and $(n+x,m+y)$. Two regions of the chain—one between n and $n+x$ and one between m and $m+y$—form a ring as a result of these entanglements (Fig. 2). This ring makes a contribution to the configuration integral of the chain which is determined by the factor

$$P(x,y)=[4\pi a^2(x+y)]^{-3/2},\tag{19}$$

which corresponds to an interaction energy

$$U(x,y)=-T\ln P=\tfrac{3}{2}T\ln|x+y|+\mathrm{const}.\tag{20}$$

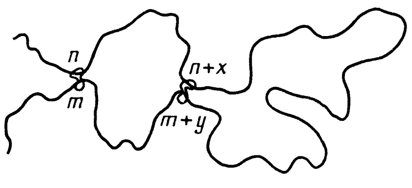

FIG. 2. A ring $(n, n+x, m+y, m)$ between two neighboring local entanglements.

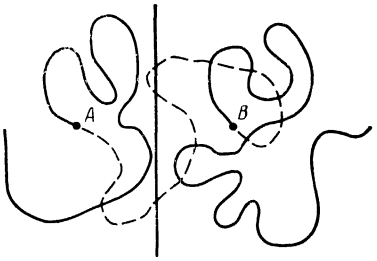

FIG. 3. Polymer chain in a state in which its end thirds are definitely not entangled (the central third is represented by the dashed line).

Expression (20) describes a long-range attraction between local entanglements. We can show that this attraction substantially increases the relaxation times because of anomalous growth of fluctations.

Despite the fact that the mean number of local entanglements between the thirds of the chain which we have selected, $\langle M\rangle$, is large [see (18)], the probability W for the case $M=0$ is some number of order unity. This assertion can be proved in the following way. We consider the units of indices $N/3$ and $2N/3$, which we label A and B, respectively (Fig. 3). In the typical state, the distance r between these units is, in order of magnitude, $R=N^{1/2}a$. We focus on a plane which intersects the line segment AB at its midpoint and is oriented perpendicular to this line segment. By directly evaluating the corresponding configuration integral we find the probability that all the units of the first third of the chain (with indices ranging from 0 to $N/3$) are on the same side of this plane, while all the units of the last third (from $2N/3$ to N) are on the other side. It is not difficult to show that this probability, Φ, is a function of exclusively the ratio r/R, which is independent of N at $N\gg 1$: $\Phi=f(r/R)$. We have $\Phi\sim 1$ at $r\sim R$. To complete the proof we note that in the spatially separated state described here there are clearly no entanglements between the end thirds.

The possible topological states of the end thirds can thus be described roughly as follows: There is a probability $W\sim 1/2$ that these thirds are not coupled at all, and there is a probability $1-W\sim 1/2$ that the number of local entanglements between them is large, in accordance with (18). If the end thirds are initially in a highly tangled state, during relaxation to total equilibrium the free energy of a ball will decrease by an amount

$$\Delta F=-T\ln(1-W)\sim T,\tag{21}$$

which must be exactly equal to the amount of energy which is dissipated in the course of the relaxation:

$$\Delta F=\int\mathscr{D}\,dt,\tag{22}$$

where $\mathscr{D}$ is the dissipation rate. We denote by $\mathscr{D}_e$ that part of the dissipation rate which is a consequence of the friction as local entanglements move along the chain (i.e., as the coordinates n and m change). We can find a lower estimate of $\mathscr{D}_e$ by considering only the local friction between units which are spatially close together:

$$\mathscr{D} \geqslant \mathscr{D}_e \geqslant \sum_a \frac{T}{\Gamma}\left[\left(\frac{\partial n_a}{\partial t}\right)^2+\left(\frac{\partial m_a}{\partial t}\right)^2\right], \tag{23}$$

where n_a and m_a are the coordinates of the entanglement with index a, and the quantity Γ does not depend on M.

The number of simple entanglements of one type or another is a topological invariant for closed chains, so that this number cannot change during "collisions" of local entanglements. If the end thirds which we are considering here are to be completely unentangled, each local entanglement must reach one of the ends of these thirds. One of the coordinates of each entanglement (e.g., n) must change by an amount $\Delta n_a \sim N$, since in the original state these coordinates have random values over the interval $0 < n < N/3$. Denoting by τ_e the relaxation time, we can estimate the integral of the right side of Eq. (3) over the time as follows:

$$\int dt \frac{T}{\Gamma} \sum_a \left[\left(\frac{\partial n_a}{\partial t}\right)^2+\left(\frac{\partial m_a}{\partial t}\right)^2\right]$$

$$\geqslant \frac{\tau_e T}{\Gamma} \sum_a \left(\frac{\Delta n_a}{\tau_e}\right)^2 \sim \frac{TN^2}{\Gamma \tau_e}\langle M\rangle. \tag{24}$$

This estimate uses the relation $\Delta n_a \sim N$, and a number of entanglements $a_{\max} \sim \langle M \rangle$.

From (18) and (21)–(24) we find

$$Tp_1 N^{5/2}/\Gamma\tau_e \lesssim T,$$

i.e.,

$$\tau_e \gtrsim (p_1/\Gamma) N^{5/2}. \tag{25}$$

Using $\tau_{\max} \geqslant \tau_e$, and comparing (25) with (17), we find that for a polymer ball under Θ conditions the dynamic index is

$$z \geqslant 5/2. \tag{26}$$

The results on the index z are shown in Table I.

4. DYNAMICS OF A SEMIDILUTE Θ SOLUTION OF FLEXIBLE-CHAIN POLYMERS

We consider a solution of long polymer chains at the Θ temperature. We denote by c the number of chains per unit volume. If the condition $cR^3 \lesssim 1$ holds, then the balls formed by the chains will essentially not overlap. We call such a solution "dilute." The viscosity of a dilute solution depends on the concentration c in accordance with[2]

$$\eta/\eta_s = f_\eta(cR^3), \quad f_\eta(x) = 1 + \alpha x + \dots, \tag{27}$$

where f_η is a function which is regular at the origin (α is a numerical coefficient). If the condition $cR^3 \ll 1$ holds, then we have

$$\eta = \eta_s + \Delta\eta, \quad \Delta\eta = \alpha \eta_s c R^3. \tag{28}$$

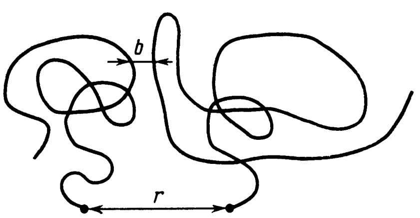

FIG. 4. Two polymer chains whose ends are separated by a distance r, while the minimum distance between the units of these chains is b.

Expression (28) may be interpreted in the following way. We use the scaling[10]

$$\Delta\eta \sim G_0 \tau, \tag{29}$$

where G_0 is a typical dynamic shear modulus of the polymer component, and τ is a typical relaxation time of the shear stress. We have[10]

$$G_0 \sim cT. \tag{30}$$

In the case of a shear strain, the "topology" of each ball remains the same, so that the topological restrictions have no effect on the relaxation. The relaxation time τ can therefore be calculated from (9); substituting the latter along with (30) into (29), we find

$$\Delta\eta \sim cT(6\pi\eta_s/T)R^3 \sim \eta_s c R^3,$$

in agreement with expression (28).

We turn now to a study of the dynamics of a polymer solution at a higher concentration. We consider two polymer chains whose ends are separated by a distance r (Fig. 4). We denote by $W_N(r,b)$ the probability that no two units of these chains come closer to each other than a distance b:

$$|\mathbf{r}_{1n} - \mathbf{r}_{2n'}| \geqslant b, \quad n, n' = 1, \dots, N$$

(n and n' are the indices of the units of the first and second chains, respectively). Using the standard scaling relations, we can easily show that $W_N(r,b)$ is a universal function of the reduced distance r/R,

$$W_N(r, b) = \Phi(r/R), \tag{31}$$

if the scale value b satisfies the inequalities

$$RN^{-2/3} = aN^{-1/6} \ll b \ll R = N^{1/2}a. \tag{32}$$

The quantity b in (31) can thus be increased nearly up to the size of the ball, R, so that the quantity $\Phi(r/R)$ is the probability for an unentangled state of the two chains. On the other hand, we could choose $b \sim A$ and thereby interpret $1 - \Phi(r/R)$ as the probability that at least two of the units

TABLE I.

	Phantom chains	Chains with topological restrictions
Θ conditions	$z=1{,}5$	$z \geqslant 2{,}5$
Good solvent	$z=3\nu\approx 9/5$	$z \geqslant 2$

of the different chains will come within a distance on the order of a with each other. In other words, this is the probability for a highly entangled state (since if two units come close together, an even greater number of additional contacts should arise, and the number of entanglements will be on the order of $p_1 N^{1/2}$). The probability for a highly entangled state of two balls is thus a well-defined function $\Phi'(r/R) = 1 - \Phi(r/R)$:

$$\begin{aligned} &\Phi'(r/R) \to 0, \quad r \gg R, \\ &\Phi'(r/R) \to 1, \quad r \ll R. \end{aligned} \tag{33}$$

Macromolecules which are entangled end-to-end in a solution can form clusters of various sizes. In a dilute solution ($cR^3 \ll 1$) the average distance between neighboring balls will be $r \gg R$, so that the clusters must be small. As the concentration is increased, to $cR^3 \sim 1$, the number and average dimensions of the clusters should increase, with the result that there will be a sharp increase in the viscosity of the solution. However, the particular way in which the viscosity η depends on c, as described by expression (27), does not itself change. The situation changes qualitatively at $c = c^* = \varkappa/R^3$, where an infinite cluster forms ($\varkappa$ is a numerical coefficient). If a shear deformation causes an infinite cluster to be in a stressed state, it will not be able to relax through an inverse deformation, in the way that an individual ball could. For the relaxation of an infinite cluster, there would have to be a substantial change in its "topology": Some of the macromolecules would have to "get disentangled" and then "get entangled" again in a new way. It follows that the relaxation time τ must be on the order of the "topological" time $\tau_{\max} \gg \tau_e$ [see (17) and (25)].

At $c > c^*$ we should thus replace τ in (29) by $\tau_{\max}$, and we should replace G_0 by the characteristic elastic modulus of an infinite cluster. We obviously have

$$G_0 = c^* T f_G(c/c^*),$$

where f_G is a universal function with the value $f_G(1) = 0$. The viscosity of the solution at $c > c^*$ is therefore

$$\eta = A\eta_s N^{z-3/2} h(c/c^*), \tag{34}$$

where A is a nonuniversal constant, z is the dynamic index introduced in the preceding section of the paper, and h is a universal function which vanishes at $c = c^*$. At $c < c^*$, expression (27) holds and can be rewritten as

$$\eta = \eta_s f(c/c^*). \tag{35}$$

We would expect that the universal function f would become infinite at $c = c^*$. Expressions (34) and (35) of course cannot be used in a certain small neighborhood of c^* in which there is a transition from one asymptotic behavior to another. The c dependence of η is shown schematically in Fig. 5. In the interval between $c^*/2$ and $2c^*$ the viscosity of the solution increases by a large factor, proportional to $N^{z-3/2} \gg 1$.

The conclusions of this section of the paper can be compared with some experimental results. The universal dependence in (27) agrees well with experimental data at $cR^3 \lesssim 1$; the functional dependence $f_\eta(cR^3)$ is indeed very sharp at $cR^3 \sim 1$ (Ref. 2). At large values of cR^3, expression (27) is no longer valid; it has been found empirically that the maximum concentration at which expression (27) still holds is determined by the condition[2]

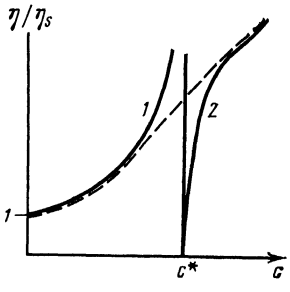

FIG. 5. Schematic plot of the viscosity η as a function of the concentration c (dashed line) and universal curves for $c < c^*$ and $c > c^*$: 1—$f(c,c^*)$; 2—$N^{z-3/2}h(c/c^*)$.

$$c^*[\eta] \sim 5-15, \quad [\eta] = 6^{3/2}\Phi_\infty R^3,$$

where $[\eta]$ is a characteristic viscosity, and $\Phi = 0.47$ (Ref. 14).

The behavior of η as a function of the reduced concentration c, $[\eta] \sim cR^3$, which has been found experimentally for $c > c^*$ turns out to be different for polymers with different molecular masses.[15] The results found in Ref. 15 satisfy a generalizing expression of the type (34); the empirical index $x = z - 3/2$ is

$$x = 0.9 \pm 0.2,$$

in good agreement with the estimate found in the present paper,

$$x = z - {}^3/_2 \geqslant 1.$$

I wish to thank A. R. Khokhlov for useful discussions of these results.

[1)] We should formally set $\mathbf{r}_{-1} \equiv \mathbf{r}_0$, $\mathbf{r}_{N+1} \equiv \mathbf{r}_N$ in expression (4).

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