$\mathbf{R}(s')]^2\rangle$ were used instead [calculation (a)], the $t = t'$ limit of (C2) would be utilized in (C1), resulting in a value twice as large. Hence, calculation (b) is too small by a factor of 2.

In order to consider calculation (c) it is necessary to employ a discrete notation as is done in ref 8 and 9. In these calculations the finite chain length corrections involve terms of the form $\exp(-k^2Ll/6) - 1$ which would yield a predicted viscosity twice too large if retained. Consequently, if approximations (1) and (2) are not simultaneously employed, the appropriate overall factors of 2 or 0.5 must be appended. At infinite dilution calculations may be done precisely, but at finite concentrations the approximations (1) and (2) become invaluable. Present understanding of the intricacies of the ordering of the limits, arising from approximation (1), may enable us to alleviate the necessity of applying these correction factors.

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# The Onset of Entangled Behavior in Semidilute and Concentrated Polymer Solutions

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*Received August 17, 1977*

ABSTRACT: It is proposed that the onset of entangled behavior with increasing $N$ (degree of polymerization) in polymer solutions of concentration $c > c^*$ (overlap concentration) corresponds to the point where molecular diffusion becomes restricted to reptation alone. An internally self-consistent model for reptation in such solutions, based on a reptation and "tube"-reorganization concept, is developed. By treating the relaxation of molecules as a cooperative phenomenon the onset of reptation is identified as a second-order, ferromagnetic-like transition occurring at a critical $N$ and entanglement density. It is possible to compare some predictions of our treatment with experiments on the variation of $N_c$ (critical $N$ for onset of entangled behavior) with $c$, by incorporating results of previous studies on static-correlation properties in semidilute polymer solutions. The agreement is surprisingly good.

## I. Introduction

There is a well-known transition in the time-dependent properties of polymer solutions occurring at concentrations well above the overlap concentration[14] $c = c^*$ (indeed, in undiluted polymer) as a function of molecular weight $M$: this is the onset of "entangled" behavior,[1,2a] which manifests itself in a number of properties. The variation of steady-flow viscosity $\eta$ for $c > c^*$ as a function of molecular weight $M$ (or $N$, the degree of polymerization) shown in Figure 1 is an example.[1,2a] Experimentally, a rather sharp change in the slope of the log $N$ vs. log $\eta$ plot is observed to occur at some critical polymer length $N = N_c$. The value of $N_c$ varies with the concentration $c$; for undiluted polymers $N_c$ is the equivalent of around 300–600 backbone units, the value depending on the polymer. The experimental situation has been extensively reviewed.[1,2a]

The precise nature of entanglements and the role they play in modifying the dynamic properties of concentrated polymer systems are not well understood. It is customary to consider[3] the critical point at $N = N_c$ (or $M = M_c$) as that at which entanglement couplings between different molecules form; as molecules drag past each other there is enhanced friction at the coupling points, leading, for example, to the higher $N$ dependence of $\eta$ (Figure 1) as-

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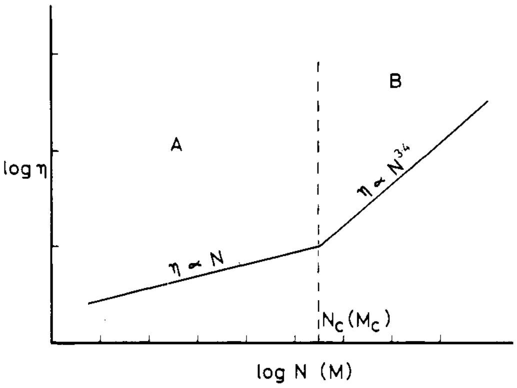

**Figure 1.** Typical variation of the steady-flow viscosity $\eta$ with degree of polymerization $N$ (or molecular weight $M$) for a linear polymer in solution at fixed polymer concentration $c$ ($>>c^*$, the "overlap" concentration[14]). The value of $N_c$, the critical degree of polymerization for the onset of entangled behavior, varies with $c$ but is typically the equivalent of some 300–600 backbone units for undiluted polymer.

sociated with entanglements. Calculations based on the above picture, as well as on variations of it such as the relaxation of a transient network[2a] (formed by the couplings), have been given. It has been recognized for some time, however, that this classical picture is not adequate[4,5] and that the essence of the problem, rather, is one of topological constraints on the motion of molecules.

De Gennes first proposed that the effect of topological constraints on the motion of polymer molecules in a concentrated system (resulting from the noncrossability of the contours of adjacent chains) could be treated in terms of a tube constraint.[4] The "tube" is defined about any given molecule by the locus of its intersections with neighboring molecules, and translation within the tube was seen as proceeding by worm-like wriggling of the molecules along their own length. This motion was termed reptation (from reptile). More recently calculations of the viscosity $\eta$, based on the reptation model, have been given.[6a,7] Very recently substantive support for the reptation concept was provided by a series of measurements on the variation of $D$ with diffusant molecular weight, for deuterated polyethylene diffusing in a normal (protonated) polyethylene matrix of $M >> M_c$.[8]

The current position may be summarized as follows:

(a) For $c > c^*$ and $M < M_c$ (region A of Figure 1) the situation is quite complex. In fact, the Rouse equation[10] gives a good account of the experimental situation concerning the behavior of $\eta$ as a function of $M$ in this regime.[1,2]

(b) At $M = M_c$ the behavior of $\eta$ changes from $\eta \propto M$ to $\eta \propto M^{3.4}$ and remains so for $M > M_c$ (region B of Figure 1). The transition occurs over a narrow range of $M$.[1,2a]

(c) Calculations[6a,7] of $\eta$ based on the reptation model predict $\eta \propto M^3$.

(d) Direct support for the reptation concept has been provided by measurements of $D$ as a function of $M$ in an entangled polymer matrix.[8] These show $D \propto M^{-2.0\pm0.1}$, compared with $D \propto M^{-2}$ as predicted for reptating molecules.[4]

Consideration of these points has led[8] to the following proposal: the onset of entangled behavior corresponds to the point at which the translational self-diffusion of a polymer molecule (which may be identified with the slowest relaxation mode, essentially) in a concentrated solution becomes constrained to take place by reptation.

This proposal will be explored in the following sections. In section II an internally self-consistent model for reptation in a polymer solution is developed, and in section III the transition between Rouse-like and reptative relaxation modes is considered. Numerical factors in the present treatment are approximate throughout.

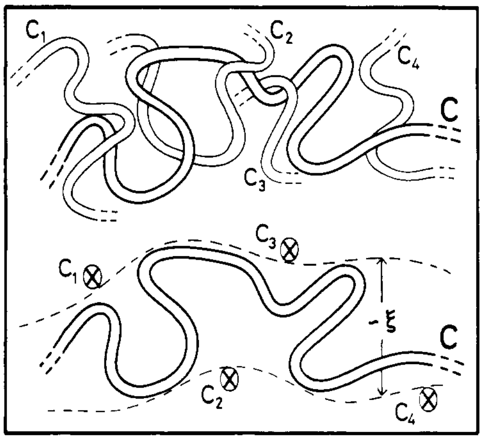

**Figure 2.** A given polymer chain C entangled with other chains $C_1$–$C_4$ (top) may be regarded as enclosed within a virtual pipe (bottom), defined by the locus of the constraints imposed on its motion by the other chains. $\xi$ is the mean permitted displacement of a segment of C in a direction normal to the "pipe axis", and the points (⊗) in the lower figure represent cross sections through $C_1$–$C_4$ in a plane parallel to the paper. Since each of the chains $C_1$–$C_4$ may itself be regraded as being in a similar pipe, the mean separation of the cross sections (⊗) is also $\sim\xi$.

## II. A Self-Consistent Model for Reptation

A polymer molecule (with $N$ monomers) in a semidilute or concentrated solution may be regarded as being within a virtual "tube" defined by its intersections with adjacent molecules, as in Figure 2. $\xi$, as shown in Figure 2, represents the root mean square permitted displacement of a point on the molecule of interest. It is essentially the interentanglement separation.

In a real polymer system the configuration of the virtual tube will change with time, as the molecules which define it ($C_1$–$C_4$ in Figure 2) are also mobile. Two characteristic times may be defined: $\tau_{\mathrm{rep}}$, which is the time a given molecule (the labeled molecule, say) takes to reptate along the length $L$ of its confining tube, and $\tau_{\mathrm{R}}$, which is the time taken by a tube to renew its configuration in some sense, to be defined later. In completely frozen surroundings (i.e., a rigidly fixed "tube") $\tau_{\mathrm{rep}}$ will be the relaxation time for the labeled molecule: in this time it will completely renew its configuration by wriggling out of its old "tube" and "generating" a new one.

$\tau_{\mathrm{rep}}$ may be estimated by treating the labeled molecule as a Rouse chain enclosed within a fixed tube:[7] taking the size of a submolecule as $\xi$ (i.e., the size of the interentanglement region), there will be $\boldsymbol{N} = N/g$ entanglement points and also $\boldsymbol{N}$ submolecules, where $g$ is the mean number of labeled chain monomers between entanglements. The mobility $B_s$ of a submolecule in the tube is related to the curvilinear diffusion coefficient $D_c$ of the whole chain along the tube as $D_c = B_s kT/\boldsymbol{N}$ ($k$ is Boltzmanns constant, $T$ being the temperature) by Einsteins relation:[15] if a Rouse chain with $\boldsymbol{N}$ beads of mobility $B_s$ is pulled inside a tube, the friction will be proportional to the number of beads, and the overall mobility of the chain along the tube will be $B_s/\boldsymbol{N}$. The time taken for the chain to diffuse along the tube length $L \simeq \boldsymbol{N}\xi$ is just

$$\tau_{\mathrm{rep}} \simeq \frac{L^2}{2D_c} \simeq \frac{\boldsymbol{N}^3\xi^2}{2B_s kT} \tag{1}$$

Any internally self-consistent model for reptation must require that $\tau_{\mathrm{R}} \gtrsim \tau_{\mathrm{rep}}$, so that molecules are always moving

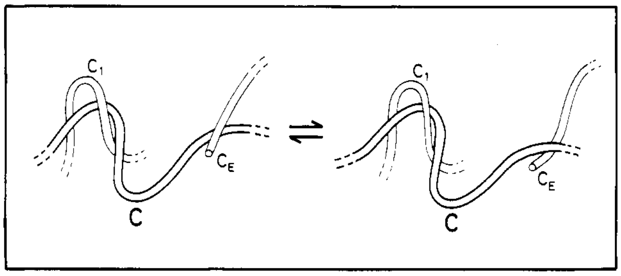

**Figure 3.** The basic tube renewal step as proposed by De Gennes.[7,9] The chain end $C_E$ jumps to a new position relative to the chain of interest C, leading to a change in tube topology at that point. Chains such as $C_1$ whose ends are far from the particular "tube" of interest do not participate in this process.

within effectively fixed surroundings, i.e., reptating. Mechanisms for tube reorganization have been considered by De Gennes[7,9] and, briefly, by Doi.[6a] The former considered the fundamental "tube" renewal step to take place only at points where the tube is defined by the end part of a molecule, such as $C_E$ in Figure 3. Changes in "tube" topology at those points occurred by flipping of the chain end, as shown in Figure 3. This sort of process will in fact cause local fluctuations in the tube topology, but it cannot lead to an overall renewal of configuration. This is because only a small fraction ($\simeq 1/N$) of the points of intersection defining a tube can participate in this renewal mode, while the bulk of the points defining the tube (such as $C_1$ in Figure 3) remain unchanged. Doi assumed[6a] that the tube relaxation time $\tau_R$ was the characteristic time for cooperative relaxation calculated for polymer melts by Edwards and Grant:[5] these authors, however implicitly excluded reptation from their calculations, so that this assumption is not consistent with a reptation model. These inconsistencies clearly do not invalidate the calculations for $\eta$, since in these a fixed tube constraint, i.e., reptation, is assumed.

An internally self-consistent model for reptation may be set up as follows: suppose that, for a concentrated polymer solution of sufficiently high molecular weight, diffusion of the molecules is in fact constrained to reptation. Then, with reference to Figure 2, the only way whereby topological changes may take place all along the length of a "tube" is for chains such as $C_1$, $C_2$, ... to reptate along their length until they have passed the position of intersection with the labeled chain C. The constraint at that point is then relaxed, to be replaced by another one due to an adjacent segment of some other molecule. Figure 4 shows this basic step schematically, indicating also the way in which the "tube" deforms upon relaxation of a constraint. The characteristic distance involved is the interentanglement length $\xi$.

There will be a characteristic time associated with the relaxation of "tube" constraints, which we call $\tau_c$. In a purely reptating system $\tau_c$ will clearly be associated with $\tau_{rep}$, the time taken for a molecule to reptate along its length. This is because it is only by the reptating away of the molecule (as $C_1$, $C_2$, ...), with which the constraint is associated, that such a constraint may relax; in the Appendix it is shown that in fact $\tau_c = \tau_{rep}/6$. There is a further assumption implicit in taking the constraint relaxation mechanism described above as the fundamental tube distortion step: this is that the time taken by the labeled molecule to "sample" the new "tube" topology is much shorter than $\tau_c$. This will be justified later.

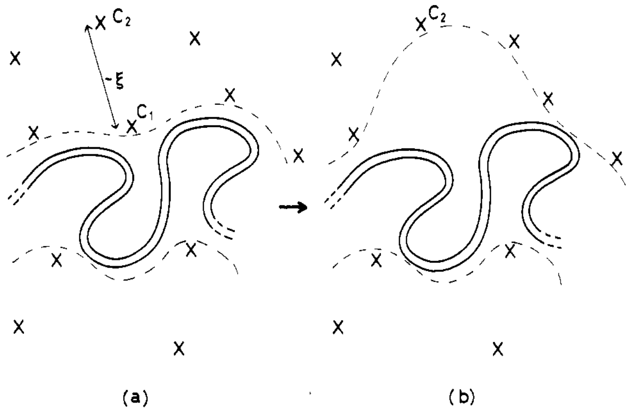

**Figure 4.** The fundamental "tube" renewal step in the present model. The constraining chain $C_1$ shown schematically in section (a) has reptated away in (b) and the tube is now defined by the constraint due to the chain $C_2$, a mean distance $\xi$ away. All "tube"-defining constraints participate in this process. The segment of enclosed chain near the newly created "hole" "samples" it in a time $\sim\theta_s << \tau_c$, the mean lifetime of a constraint.

We now follow Edwards and Grant[5] and De Gennes[7,9] in treating the virtual tube as an equivalent Rouse chain,[10] where the constraints (i.e., the points of intersection of our labeled chain with adjacent chains) correspond to ends of submolecules in Rouse's terminology. Since there are $\boldsymbol{N}$ constraints defining a virtual "tube" about any molecule, there will be $\boldsymbol{N}$ submolecules in the equivalent Rouse chain. Following De Gennes[7] we take the longest relaxation time $\tau_1$ of the equivalent Rouse chain as the characteristic time for renewal of tube configuration, $\tau_R$. In a time $t \simeq \tau_1$ the configuration of a Rouse chain loses, through diffusion, its correlation with its value at time $t = 0$.[10] We then have

$$\tau_1 \simeq \boldsymbol{N}^2\xi^2/6\pi^2BkT \tag{2}$$

where $B$ is in some sense the "mobility" of a tube constraint. Since in a time $\tau_c$ such a constraint is replaced by another a mean distance $\xi$ away (Figure 4), we may write $\tau_c \simeq \xi^2/2BkT$, so that from (2)

$$\tau_R \simeq \boldsymbol{N}^2\tau_c/3\pi^2 \tag{3}$$

Where constraints relax by reptation alone $\tau_c = \tau_{rep}/6$ (see Appendix), so that in a reptating system

$$\tau_R \simeq \boldsymbol{N}^2\tau_{rep}/18\pi^2 \tag{4}$$

Now $\boldsymbol{N} = N/g$. The value of $g$, the mean number of monomers between intersection points, will be some function of the polymer concentration[11] (see, for example, section IV), so that for a given concentration, $\tau_R >> \tau_{rep}$ for sufficiently high $N$. This implies that the "tube" is essentially unchanged over the time a molecule takes to reptate along it; i.e., molecules move in fixed surroundings. This fulfills the internal consistency requirement for reptation to take place. Equation 4 may be written $\tau_R \propto \boldsymbol{N}^2\tau_{rep}$ for fixed $c$ ($c >> c^*$), and this may be contrasted with De Gennes' result,[7] $\tau_R \simeq \tau_{rep}$, and Doi's assumption[6a] of $\tau_R \propto N\tau_{rep}$ on the basis of the work by Edwards and Grant.[5] The very much slower rate of tube reorganization (for $N >> 1$) in our model (in the reptation regime) is a consequence of imposing a self-consistency requirement on the relaxation of the tube constraints.

It is important to appreciate that the relaxation of the virtual tube configuration cannot in general[16] be observed in studies of the relaxation properties of entangled polymers (as, for example, low-frequency mechanical measurements[1]). This is because the relaxation rate measured in such studies corresponds to the *overall* relaxation of a molecule, of characteristic time $\tau_r$ (see also eq 6), and is the sum of two relaxation processes, namely reptation and virtual tube reorganization. We have, for the two characteristic times,

$$\tau_{\mathrm{R}} \propto \boldsymbol{N}^5 \qquad \text{(tube reorganization)}$$

and

$$\tau_{\mathrm{rep}} \propto \boldsymbol{N}^3 \qquad \text{(reptation)}$$

so that for entangled systems (high $\boldsymbol{N}$) $\tau_{\mathrm{R}} >> \tau_{\mathrm{rep}}$, and thus the overall relaxation proceeds almost entirely by reptation. In these circumstances the contribution of the slow tube-reorganization component to the overall relaxation cannot be observed.

Consider now the time taken by a segment of the labeled molecule to "sample" a newly created "hole" in its surrounding "tube" (Figure 4), produced by the disappearance of a constraint. The size of the segment involved is necessarily $\sim\xi$, so that its mobility is $B_s$ as before. The time such a segment takes to "sample" the newly created space (itself of size $\sim\xi$) is $\theta_s \simeq \xi^2/2B_skT$. For reptation, $\tau_c = \tau_{\mathrm{rep}}/6$ and from (1) $\tau_{\mathrm{rep}} \simeq \boldsymbol{N}^3\xi^2/2B_skT$; since $\boldsymbol{N} >> 1$, we have $\tau_c >> \theta_s$. Thus the labeled molecule samples the "hole" created by the relaxation of a "tube" constraint in a time very much shorter than the time scale of the latter. This justifies our previous assumption.

It is appropriate at this stage to point out some of the simplifications made in the above model. Hydrodynamic interactions between parts of the labeled molecule over distances $<\xi$ have been ignored (for distances $>\xi$, these will be screened out by the entanglements), i.e., we have used the free draining approximation at all distances. Our treating of portions of the labeled molecule between entanglements as Rouse-like submolecules also implies $\xi >>$ monomer size, so that the model applies better in the semidilute regime than in concentrated or undiluted polymer systems. There is a more subtle point which we have not considered: the constraints along the length of our labeled molecule may not all be independent of each other. For example, two or more of the constraints such as $C_1$–$C_4$ in Figure 4 may belong to a single molecule, or indeed be "distant" segments of the labeled molecule itself. The consequence of this in terms of our model would be to reduce the effective number of independent constraints $\boldsymbol{N}$ defining the virtual "tube". To the accuracy of the present discussion, however, the consequences of these simplifications are ignored: this is equivalent in a sense to a "mean field approximation". It will not substantially alter the main conclusions of our treatment.

## III. Breakdown of Reptation

The analysis of the previous section showed that for sufficiently high $N$ and $c$ an internally self-consistent picture of reptation is possible, with

$$\tau_{\mathrm{R}} \simeq \boldsymbol{N}^2\tau_{\mathrm{rep}}/18\pi^2 >> \tau_{\mathrm{rep}}$$

Consider now what happens as $\boldsymbol{N}$ is lowered (by reducing either $N$ or $c$) from some high value for which

$$\boldsymbol{N}^2/18\pi^2 >> 1 \tag{5}$$

As the tube renewal time $\tau_{\mathrm{R}}$ approaches (from above) the value of $\tau_{\mathrm{rep}}$, i.e., when the inequality in (5) begins to break down, there will be a rapid cooperative effect tending to reduce $\tau_{\mathrm{R}}$ even more rapidly. This may be qualitatively visualized as follows: as long as $\tau_{\mathrm{R}} >> \tau_{\mathrm{rep}}$, any given chain will be moving in essentially fixed surroundings and its relaxation will be purely reptative; the overall relaxation time $\tau_{\mathrm{r}} = \tau_{\mathrm{rep}}$. As the value of $\boldsymbol{N}$ decreases so that the "tube" can no longer be considered fixed on the time scale of reptative renewal, the overall relaxation will become more rapid than that due to reptation alone. Thus the constraint relaxation time $\tau_c$ becomes shorter than its value for pure reptation (since the constraining molecules are also relaxing faster), leading to a further decrease in $\tau_{\mathrm{R}}$, and so on.

The effect is similar in some sense to a second-order transition, e.g., the ferromagnetic–paramagnetic transition in ferromagnetic materials. Though the physical processes involved are different, both effects may be viewed as resulting from cooperative interaction between the elements of the respective systems: magnetic interaction on the one hand and intertangled molecules, or topological interaction, on the other. In ferromagnetism the interaction between the magnetic moments (pictured as an internal field) is perturbed as the temperature approaches the critical temperature $T_c$ (Curie temperature) from below; because of the cooperative, or interdependent, nature of the magnetic interaction, a rapid breakdown of the ordered domains occurs as $T_c$ is reached. Beyond $T_c$ one has only paramagnetism and diamagnetism. The ferromagnetism phenomenon and the occurence of a critical temperature are often explained by a graphical method;[17] in the remainder of this section we make use of a similar graphical approach to illustrate more quantitatively the onset of reptative behavior for the case of concentrated polymer systems.

Now the overall relaxation of a given molecule in our model (with a characteristic time $\tau_{\mathrm{r}}$) may be considered as due to the sum of two relaxation processes: reptation within a surrounding tube (with characteristic time $\tau_{\mathrm{rep}}$) and relaxation due to the reorganization of the tube itself (with characteristic time $\tau_{\mathrm{R}}$). *If these two processes are independent of each other*, then we may quite generally write

$$\frac{1}{\tau_{\mathrm{r}}} \approx \frac{1}{\tau_{\mathrm{rep}}} + \frac{1}{\tau_{\mathrm{R}}} \tag{6}$$

Treating the "tube" as a Rouse tube, as before, its relaxation time may always be written as in eq 3,

$$\tau_{\mathrm{R}} = \boldsymbol{N}^2\tau_c/3\pi^2$$

so that (6) becomes

$$\frac{1}{\tau_{\mathrm{r}}} \simeq \frac{1}{\tau_{\mathrm{rep}}} + \frac{3\pi^2}{\boldsymbol{N}^2\tau_c} \tag{7}$$

Equation 7 is a general relation expressing an overall relaxation rate for a system relaxing by two independent modes. To proceed, we make use of our model of the previous section. When the polymer solution or melt is highly entangled, the overall relaxation is constrained to proceed by reptation alone:

$$\tau_{\mathrm{r}} = \tau_{\mathrm{rep}} \tag{8a}$$

We now impose the self-consistency requirement that in fact each of the constraining segments defining a tube itself belongs to a molecule which is surrounded by a similar tube, and that the relaxation of constraints thus also proceeds by reptation (see section II and also the Appendix); in this case

$$\tau_c = \tfrac{1}{6}\tau_{\mathrm{rep}} \tag{8b}$$

From eq 8 we obtain a simple self-consistency relation (in the entangled regime) between the overall relaxation of a given molecule and the relaxation time of the constraints about it; this takes account of the fact that both the given molecule and its adjacent neighbors relax in an

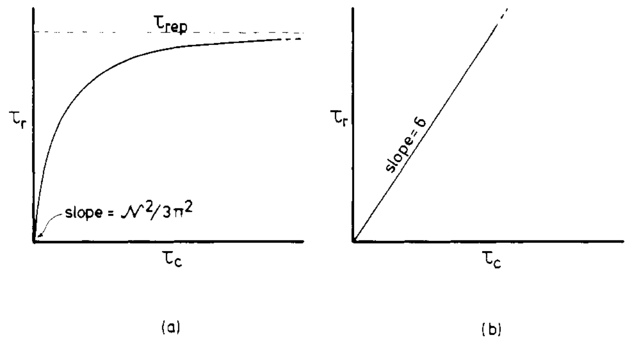

**Figure 5.** (a) Plot of eq 7a. (b) Plot of eq 9.

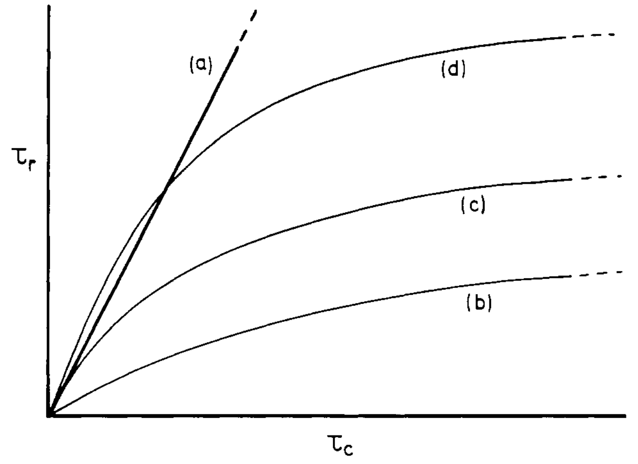

**Figure 6.** Equations 9 (curve (a)) and 7a (curves (b–d)) plotted on the same graph. Curve (b): $N < N_c$; there is only one solution consistent with both (7a) and (9), at $\tau_c = 0$. This solution corresponds to unconstrained or Rouse-like relaxation. Curve (c): $N = N_c$; the slopes in the limit $\tau_c \rightarrow 0$ are equal, i.e., $N_c^2/3\pi^2 = 6$. Curve (d): $N > N_c$; there is a second solution, at a finite value of $\tau_c$, satisfying both equations. This solution corresponds to constrained relaxation. The relative values of the abcissa and ordinate scales are equal for the three $N$ values, so that eq 9 is represented by curve (a) in all three cases. The absolute values are different for the different curves, for clarity of exposition.

identical way (in other words, we are using a self-consistent mean-field approach):

$$\tau_r = 6\tau_c \qquad (9)$$

Recasting eq 7, we have

$$\tau_r = \frac{N^2\tau_{rep}\tau_c}{(N^2\tau_c + 3\pi^2\tau_{rep})} \qquad (7a)$$

Figure 5a,b shows $\tau_r$ plotted against $\tau_c$ from eq 7a and 9. With reference to Figure 5a we note that the asymptotic limit of $\tau_r$ ($=\tau_{rep}$) is proportional to $N^3$, and that the slope near the origin is $N^2/3\pi^2$.

Plotting eq 7a and 9 together, we distinguish three cases, as shown in Figure 6. We note at once that there is always a solution satisfying both (7a) and (9), at all values of $N$. This is the solution at $\tau_c = 0$. In our model this formally corresponds to $\tau_r = 0$. *Physically*, however, we know there is a *lower limit* associated with the relaxation time of a polymer molecule, which is the Rouse relaxation limit of the enclosed molecule: a free polymer molecule *cannot relax any faster*. This limit of characteristic time $\tau_{Rouse}$ does not appear explicitly in our model, since our equations were based on the reptation/tube-reorganization picture. However, it is evident that the limit $\tau_c \rightarrow 0$ must correspond to the progressive disappearance of effective topological constraints, and the solution at $\tau_c = 0$ (infinitely fast relaxation of constraints) must implicitly be identified with the relaxation of an effectively unconstrained or free polymer molecule, i.e., with the Rouse relaxation limit.

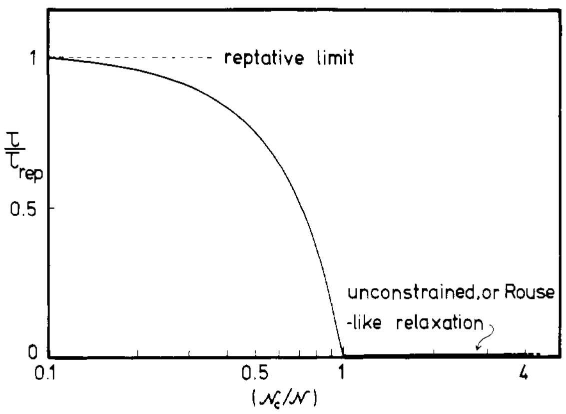

**Figure 7.** The variation of the reduced relaxation time ($\tau/\tau_{rep}$) with $N$ from eq 12.

Thus there will always be a solution (for all $N$ values) common to both eq 7a and 9, corresponding to the Rouse relaxation. Reference to Figure 6 shows, however, that *it is only above some critical value* of $N = N_c$ *that a second solution appears*. This second solution corresponds to the onset of constrained relaxation (finite $\tau_c$ values) and rapidly approaches the reptative limit as $N$ increases beyond $N_c$. The critical value of $N$ is that for which the slopes of the curves, describing eq 7a and 9 as $\tau_c \rightarrow 0$, are equal (curves (a) and (c) of Figure 6); thus $N_c = (18\pi^2)^{1/2}$.

Eliminating $\tau_c$ between (7a) and (9) for $N > N_c$, we obtain

$$\tau_r = \left(1 - \frac{N_c^2}{N^2}\right)\tau_{rep} \quad N \geq N_c \qquad (10)$$

Bearing in mind that the solution at $\tau_c = 0$ corresponds to the Rouse relaxation, we may now write for the overall relaxation time $\tau$:

$$\tau = \tau_{Rouse} \qquad N < N_c$$

$$\tau = \tau_{Rouse} + (1 - [N_c^2/N^2])\tau_{rep} \qquad N \geq N_c \qquad (11)$$

In our model we deal with a Rouse molecule of $N$ submolecules, each of size $\xi$ and mobility $B_s$, so that (see (2))

$$\tau_{Rouse} = N^2\xi^2/6\pi^2B_skT = N^2\theta_s/3\pi^2$$

where $\theta_s = \xi^2/2B_skT$; note that, for a given value of $c$, $\theta_s$ is independent of $N$.[11] From (1), therefore, we have

$$\tau_{rep} = N^3\theta_s$$

and (11) becomes

$$\tau = N^2\theta_s/3\pi^2 \qquad N < N_c$$

$$\tau = \frac{N^2\theta_s}{3\pi^2} + \left(1 - \frac{N_c^2}{N^2}\right)N^3\theta_s c \qquad N \geq N_c \qquad (12)$$

The variation of $\tau$ with $N$ (eq 12) is indicated in Figure 7, where a "reduced" relaxation time ($\tau/\tau_{rep}$) is plotted against ($N_c/N$). For $N > N_c$ rapid transition from uncontrained or Rouse-like behavior is evident. For $N = 1.5N_c$, the relaxation time is already over half that associated with pure reptation, whereas at $N = 3N_c$, $\tau$ has attained a value some 90% of that associated with purely reptative relaxation.

To summarize this section: a critical value of $N$ ($=N_c$) at which the relaxation of a polymer molecule in a concentrated system begins to behave in a constrained manner is identified, using a graphical approach similar to that used to explain ferromagnetism. For $N < N_c$, only a solution corresponding to unconstrained relaxation, i.e., the Rouse mode, is possible, with a second solution corresponding to constrained relaxation appearing at $\mathbf{N} \geq \mathbf{N}_c$. With increasing $\mathbf{N}$ the value of the relaxation time rapidly attains the limit associated with pure reptation. The value of $\mathbf{N}_c$ in the present model is $(18\pi^2)^{1/2}$.

## IV. Discussion and Conclusions

The topological constraints imposed on a given polymer molecule by its neighbors in semidilute and concentrated solutions have been treated in terms of reptation within a virtual "tube" and "tube reorganization", first introduced by De Gennes.[7,9] For a sufficiently high value of the parameter $\mathbf{N}$ an internally self-consistent model for reptation may be set up; $\mathbf{N}$ here is $N/g$, where $N$ is the degree of polymerization and $g$ is the mean number of monomers between entanglement points, and may be regarded as the number of entanglements along a chain.

By considering the relaxation of molecules in entangled polymer systems as a cooperative phpenomenon, the onset of reptation may be identified as a second-order transition from unconstrained or Rouse-like behavior, occurring at a critical value of $\mathbf{N} = \mathbf{N}_c$. In the present rather unsophisticated model the value of $\mathbf{N}_c$ is $(18\pi^2)^{1/2}$;[18] it corresponds in a sense to the Curie temperature in ferromagnets, where the spontaneous alignment of magnetic spins is the corresponding cooperative phenomenon. A better description in this case is the locking in of a log jam as the length and density of logs exceeds some critical value.

The treatment provides some insight into the nature of the onset of entangled behavior in semidilute and concentrated polymer solutions. The existence of a critical $\mathbf{N}$ value, below which relaxation of the molecules is unperturbed (or Rouse-like), and above which it is rapidly constrained to proceed by reptation alone, provides support for the suggestion[8] that the onset of entangled behavior corresponds to the onset of reptative behavior. The model also predicts that in highly entangled ($\mathbf{N} >> \mathbf{N}_c$) systems the "tube" constraint about any molecule changes very slowly relative to the time of reptative renewal (i.e., $\tau_R >> \tau_{rep}$). This provides support for recent theoretical treatments[6] of the properties of concentrated polymer systems in which a fixed tube constraint is assumed.

The rather sharp transition from Rouse-like to constrained, and ultimately reptative, relaxation predicted by the model is consistent with the sharp changeover observed in the dependence of the steady flow viscosity $\eta$ on $N$, as noted earlier. One difficulty which remains unresolved, however, is that in the entangled regime one has $\tau \propto N^3$ (for fixed $c$) and thus one expects $\eta \propto \tau \propto N^3$ rather than $\eta \propto N^{3.4}$ as observed experimentally. This discrepancy is a feature of all models of relaxation which are based on reptation;[6,7] it has been discussed at some length by De Gennes.[7]

We may compare some predictions of our model with experimental data by adopting results from studies on static correlation properties of semidilute polymer systems. If, for example, we follow the treatment of Daoud et al.[11] in their interpretation of neutron scattering data, we have $\mathbf{N} = N/g = ANc^{5/4}$, where $c$ is the polymer concentration (in a good solvent) and $A$ is a constant depending on the monomer size, its specific partial volume, and the characteristic ratio for the polymer.[19] We then expect[20]

$$N_c \simeq \frac{(18\pi^2)^{1/2}}{A} c^{-1.25} \tag{13}$$

on our model, where $N_c$ is the critical degree of polymerization for the onset of entangled behavior at concentration $c$. The only extensive set of results we have found measuring the variation of $N_c$ with $c$ in the semidilute regime (where our treatment is expected to be better applicable) is in the study by Schurz and Hochberger[13] on the steady flow viscosity $\eta$ of polyisobutylene (PIB) in toluene, a good solvent. These authors measured the critical $c$ for a given value of $N$ by varying $c$ and plotting $\log \eta$ vs. $\log c$. The critical $c$ was then the point at which the slope of the plot showed a discontinuity. In their experiments, $c$ varied between $10^{-3}$ and 0.5 g/cm$^{-3}$ of PIB in toluene, and the molecular weight varied between $4 \times 10^4$ and $7 \times 10^6$. Their results showed

$$N_c = (\text{constant}) c^{-1.28\pm0.04} \tag{14}$$

which is to be compared with eq 13. The value of the constant in eq 14 was ~55. The value of $A$ in eq 13 for PIB is about 0.2, so that $(18\pi^2)^{1/2}/A \simeq 65$. In view of the approximations inherent in our model, however, this rather close agreement must be regarded as fortuitous.

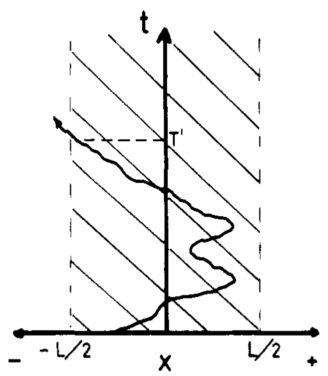

**Figure 8.** A particle at a random position $x$ $(-^1/_2 < x < {}^1/_2)$ at $t = 0$ will "escape" the shaded region after some expected time $T = \langle T' \rangle$.

**Acknowledgment.** I thank Professor Sir S. F. Edwards for critical discussions and comments on the manuscript, and Dr. J. Hannay for help with the calculation in the Appendix. I also thank Dr. M. Doi and Mr. R. Ball for useful comments. The receipt of a Research Fellowship from St. Catharine's College, Cambridge, is gratefully acknowledged.

## Appendix

We require the relaxation time ($\tau_c$) of a tube constraint in a regime where reptation is the only diffusion mode. That is equivalent to calculating the mean time over which the local topological relationship between a constraint and the labeled chain remains invariant. The "tube" of which the constraints are part lies situated at a random point along the contours of the constraining molecules (Figure 2), and these molecules may themselves diffuse by curvilinear motion, or reptation, alone. Thus, we wish to calculate the expected time before either end of a chain of length $L$ diffusing parallel to its own length with a curvilinear diffusion coefficient $D_c$ crosses a point (i.e., the position of the labeled chain) situated at random along its length at $t = 0$. If we recast the problem by "fixing" the chain and allowing the point to diffuse, we want to find the expected time that a particle diffusing along $x$ from a random starting position $(-^1/_2 < x < {}^1/_2)$ "escapes" by reaching $x = \pm{}^1/_2 L$ (Figure 8).

The probability of finding the particle at $x$ at time $t$ is the solution of

$$\frac{\partial P}{\partial t} = D_c \frac{\partial^2 P}{\partial x^2} \tag{A1}$$

where $P(x,t)$ obeys

$$P(x,0) = 1/L$$

$$P(\tfrac{1}{2}L,t) = P(-\tfrac{1}{2}L,t) = 0 \text{ for } t > 0 \qquad \text{(A2)}$$

Let

$$P(\mathrm{x},0) = \sum_{n\ \mathrm{odd}} a_n \cos\frac{n\pi x}{L} \qquad \text{(A3a)}$$

with $a_n$ to be found, and

$$P(x,0) = 1/L \qquad \text{(A3b)}$$

from (A2). Then from (A1),

$$P(x,t) = \sum_{n\ \mathrm{odd}} a_n \cos\frac{n\pi x}{L} e^{-(n\pi/L)^2 D_c t}$$

To find $a_n$ multiply both sides of (A3) by $\cos(m\pi x/L)$ and integrate,

$$\int_{-L/2}^{L/2} \cos\frac{m\pi x}{L}\cdot\frac{1}{L}\,\mathrm{d}x = \int_{-L/2}^{L/2} a_m \cos^2\frac{m\pi x}{L}\,\mathrm{d}x$$

$$\frac{2L}{m\pi}\cdot\frac{1}{L} = \tfrac{1}{2}La_m$$

$$\therefore a_m = \frac{4}{m\pi L}$$

Now the probability that the diffusing particle is still in the range $-L/2$ to $L/2$ at time $t$ is

$$\int_{-L/2}^{L/2} P(x,t)\,\mathrm{d}x$$

The expected time $T$ before "escape" is therefore

$$T = \int_{t=0}^{\infty}\int_{-L/2}^{L/2} P(x,t)\,\mathrm{d}x\,\mathrm{d}t$$

giving

$$T = \sum_{n\ \mathrm{odd}}\int_0^{\infty}\int_{-L/2}^{L/2}\frac{4}{n\pi L}\cos\frac{n\pi x}{L}\cdot e^{-(n\pi/L)^2 D_c t}\,\mathrm{d}x\,\mathrm{d}t = \sum_{n\ \mathrm{odd}}\frac{4}{n\pi L}\cdot\frac{2L}{n\pi}\left(\frac{L}{n\pi}\right)^2\frac{1}{D_c} = \frac{8L^2}{\pi^4 D}\sum_{n\ \mathrm{odd}}\frac{1}{n^4} \qquad \text{(A4)}$$

Now

$$\sum_1^{\infty}\frac{1}{n^4} = \frac{\pi^4}{90} = \sum_{n\ \mathrm{even}}\frac{1}{n^4} + \sum_{n\ \mathrm{odd}}\frac{1}{n^4} = \sum_1^{\infty}\frac{1}{(2n)^4} + \sum_{n\ \mathrm{odd}}\frac{1}{n^4} = \frac{1}{16}\sum_1^{\infty}\frac{1}{n^4} + \sum_{n\ \mathrm{odd}}\frac{1}{n^4}$$

i.e.,

$$\sum_{n\ \mathrm{odd}}\frac{1}{n^4} = \frac{15}{16}\cdot\frac{\pi^4}{90}$$

so from (A4)

$$T = \frac{1}{12}\frac{L^2}{D_c}$$

But $L^2/2D_c$ = mean time for chain to diffuse along its own length $\equiv \tau_{\mathrm{rep}}$.

$$\therefore T \equiv \tau_c = \tfrac{1}{6}\tau_{\mathrm{rep}}$$

## References and Notes

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(14) $c^*$ is here loosely defined as that concentration at which individual coils begin to overlap each others' pervaded volume. For a more detailed discussion of the concentration limits of dilute, semidilute, and concentrated solutions, see, for example, ref 11.

(15) We follow here the approach of ref 7.

(16) One might observe the effects of tube relaxation in the case where reptation of the labeled molecule is suppressed. For example, if the diffusion coefficient of a closed polymer *ring* molecule in a matrix of entangled *linear* polymer were being measured, one might expect its translational diffusion to proceed by "tube" reorganization alone; this is because a closed ring molecule cannot reptate. In this case, the model predicts the diffusion coefficient of the ring molecule, $D_{\mathrm{R}}$, to scale as

$$D_{\mathrm{R}} \propto 1/M_{\mathrm{R}}M_{\mathrm{m}}^3$$

for a given matrix concentration, where $M_{\mathrm{R}}$ and $M_{\mathrm{m}}$ are the ring-polymer and matrix molecular weights, respectively. The corresponding overall relaxation time for the ring molecule is predicted to scale as

$$\tau_{\mathrm{r}} \propto M_{\mathrm{R}}^2 M_{\mathrm{m}}^3$$

(17) For a simple description of ferromagnetism see, for example, B. E. Bleaney and B. Bleaney, "Electricity and Magnetism", 3rd ed, Oxford University Press, London, 1976.

(18) Care must be taken in applying the present *numerical* factors to the case of very concentrated polymer solutions or polymer melts. Thus for undiluted polymer the value of $N_c$ (eq 13) appears too low when compared with experimental data. The reasons for this have been discussed briefly at the end of section II; in addition, the analysis of ref 11 (on which eq 13 is partly based) does not extend to the case of very high concentrations. The physical picture associated with the model, however (the cooperative nature of the Rouse-to-reptation transition), remains unchanged in the melt regime.

(19) Specifically, for a C–C backbone polymer with $j$ backbone units/monomer

$$A = (0.83)^2 j(\bar{v})^{+5/4}/c_{\infty}$$

where $c_{\infty}$ is the characteristic ratio for the polymer, $\bar{v}$ is the monomer partial specific volume, and the numerical factor arises from the angle between C–C bonds. See, for example, ref 12, and also ref 11.

(20) The prediction $N_c \propto c^{-5/4}$ was first made in a footnote to ref 7.