cules strengthened the above conclusions. In addition, it indicated that upon large deswelling, macrosyneresis appears in the flexible gels.

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Generalized Reptation Model

Horst Wendel

Universität Ulm, Abteilung für Biophysik, 7900 Ulm, West Germany

Jaan Noolandi*

Xerox Research Centre of Canada, 2480 Dunwin Drive,
Mississauga, Ontario, Canada L5L 1J9. Received December 29, 1980

ABSTRACT: The reptation model is generalized on the basis of a theory that accounts for hindered defect diffusion along the chain. A basic ingredient of the theory is a waiting time distribution for the hops of elementary defects that store length. Important rheological quantities are found to generally depend on fractional powers of the molecular mass rather than on integer powers as in the conventional reptation picture.

Recently, de Gennes proposed a theory[1] that attempts to explain the long-time dynamics of entangled polymer systems on a molecular basis. According to his reptation hypothesis, a linear polymer is restricted to a snake-like motion within a virtual tube that simulates the topological restrictions due to entanglements with other polymers. The theory was augmented by Doi and Edwards.[2] Still it exhibits some major difficulties. For example, the terminal relaxation time τ_t and the static shear viscosity $\mu(0)$ are found to depend on the third power of the molecular weight M while experiment yields $\tau_t \sim \mu(0) \sim M^{\alpha}$, with α in the range 3.3–3.4.[3] This discrepancy may not be explained by polydispersity effects, as is widely believed, or by fluctuations, which lead to a fractional *molecular weight* dependent exponent.[3]

From a theoretical point of view the discrepancy is very fundamental. At worst it implies a different model, i.e., a molecular mechanism different from the reptation concept since "there is no obvious correction which might increase the exponent from 3 to the experimental value of 3.3.[4] Recently, the situation has become even more confusing due to the measurements of the polymer diffusion coefficient D_3,[5] which was found to obey the law $D_3 \sim M^{-2}$ as predicted by the conventional reptation model.

Here we propose an extension of the reptation model that, depending on the time scale of interest, yields the fractional power dependences required by some experiments as well as the integer dependence required by others.

The essence of the reptation hypothesis[1] lies in the confinement of a polymer to one-dimensional diffusion. Diffusion is effected by density fluctuations of a dilute defect gas, i.e., by defects migrating freely along the chain. Each defect stores length b. The corresponding diffusion coefficient D_1 is a microscopic constant characteristic of local jump processes and is independent of the molecular mass M. The equilibration time τ_d of the defect gas is the time for a single defect to perform a mean-square displacement equal to the square of the contour length of the polymer; i.e., $\tau_d \sim (Na)^2/D_1$. Here a is the separation of two adjacent "monomers", of which there are N. Because of its M^2 dependence, τ_d cannot be identified with the terminal relaxation time τ_t. Thus de Gennes introduced the time τ_r a polymer needs to disengage completely from its initial tube. For ρb defects per length b (ρ is the defect density per unit length) it takes a time $\tau_r = \tau_d(Na/\rho b^2) \sim (Na)^3/D_1\rho b^2$ for the chain to renew its surroundings. Thus τ_r depends on the third power of M and is identified with τ_t, which is found to be proportional to $M^{3.4}$.[3]

The nature and spatial extension of a reptation defect have not been discussed. Yet, larger scale fluctuation processes can be excluded because of the large energies involved. As an example, we restrict ourselves to discussing elementary defects, gt$\bar{g}$ defects or kinks, respectively. The typical kink defect energy for polyethylene is $\Delta E \sim 1.2$ kcal/mol[6] and a conservative estimate yields a defect density of 14% at room temperature[7] compared to a saturation concentration of 25%. Thus, except for experiments on the scale of time $t \rightarrow \infty$, the assumption of a dilute freely moving defect gas is not entirely justified. This combined with the fact that the tube topology imposes strong temporary restrictions on the defect distribution, especially around points of entanglement, casts

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doubts on the Ansatz of free defect diffusion in general.

In the following we propose a model based on the picture of hindered diffusion. An important ingredient of the theory is a waiting time distribution $\psi(t)$ for defect hops from one segment to a neighboring one.

We divide the contour line of the polymer into cells labeled l. A defect is then considered as a walker performing random forward and backward hops to neighboring cells. Usual assumptions in the theory of a random walk are that at regular time intervals (a) the walker must jump to a new point and (b) the transition probability for a jump from cell l' to l, $p(l,l')$, is the same anytime a walker is at l'. In our case the steps do not occur at regular time intervals. Instead we assume that the probability for a defect to make a next step $l' - l$ in the time interval $t...t + \delta t$ is given by $\psi(l' - l, t)\delta t$.[8]

Let $R_n(l',t)\Delta t$ be the probability for a defect to just arrive at l' between time t and $t + \Delta t$ in n steps if it started at $l_0 = 0$ for $t = 0$. Then the probability $P(l,t)$ for the defect being found at l at time t, if initially at l_0, is given by

$$P(l,t) = \sum_n \int_0^t R_n(l,t')\phi(t - t')\, d\tau \qquad (1)$$

where $\sum_n R_n(l,t')\phi(t - t')$ accounts for the fact that the defect arrived at l earlier than t and waited there at least until t; i.e., the relaxation function ϕ is defined via

$$\phi(t) = 1 - \int_0^t \psi(t')\, dt' \qquad (2)$$

where

$$\psi(t) = \sum_{l \neq 0} \psi(l,t) \qquad (3)$$

is the waiting time distribution mentioned above.

The formal solution for $P(l,t)$ may be found via the relation for its Laplace transform (LT) $\tilde{P}(l,u)$.[8] Here we are interested in the mean-square displacement of a defect for long times. Coherent transport effects are then negligible and the LT $\tilde{\psi}(l,u)$ factorizes into u- and l-dependent terms,[9] respectively; i.e.

$$\tilde{\psi}(l,u) = p(l)\tilde{\psi}(u) \qquad (4)$$

The mean-square displacement is thus[8]

$$\langle l^2(u)\rangle = \sum_l l^2 \tilde{P}(l,u) = \sum_l l^2 p(l) \frac{1 - u\tilde{\phi}(u)}{u^2\tilde{\phi}(u)} \qquad (5)$$

At this point, we have to specify the spectral density of the waiting time distribution function $\psi(t)$ or the relaxation function $\phi(t)$, respectively. For the discussion later on, two classes are of special relevance. The respective small u behaviors are given by

$$\tilde{\phi}(u) \sim \text{constant} \qquad (6)$$

and

$$\tilde{\phi}(u) \sim u^{-\gamma}, \qquad 0 \leq \gamma < 1 \qquad (7)$$

Equation 6 corresponds to an exponential time dependence of the waiting time distribution function; i.e.

$$\psi(t) \sim e^{-\alpha t} \qquad (8)$$

with $\alpha > 0$. For this choice, $\langle l^2(u)\rangle \sim u^{-2}$, which is the LT of the usual diffusion law

$$\langle l^2(t)\rangle \sim t \qquad (9)$$

It is this law that is exploited in the conventional reptation model to yield the dependence of rheological quantities on integral powers of the polymer mass.[1,2]

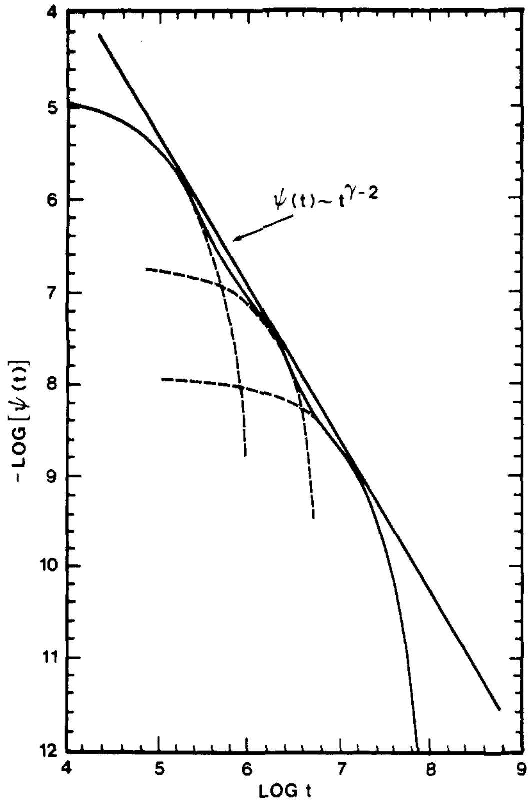

Figure 1. Waiting time distribution function $\psi(t)$ showing decomposition of apparent power law into a small number of exponentials over almost 3 decades of time.

In order to understand the physics of the choice of eq 7, it is helpful to recall the equivalence of the continuous-time random walk to the multiple trapping model (MTM).[10] The MTM separates the states of a system into transport states and traps with capture and release probability ω_i and r_i (with i labeling different traps). This means that a random walker in a transport state diffuses freely, and there is a probability ω_i for the free walker to become trapped upon leaving a site. For an immobilized walker, there is a probability r_i of being released into a transport state.

Most importantly, the set $\{\omega_i, r_i\}$ uniquely determines $\psi(t)$. Indeed it has been demonstrated[10] (i) that

$$\psi(t) \sim \sum_i A_i \exp(-r_i t) \qquad (10)$$

with A_i being a simple function of ω_i and r_i, and (ii) that the superposition of a small number of trapping states in eq 10 suffices to generate eq 7 over a large interval of times or frequencies, respectively. This finding is schematized in Figure 1. Physically, all that is necessary for eq 7 to hold is that conformational changes in the polymer allow also for times that are comparable to the time scale of the experiment. We point out that for times $t > \max\{r_i^{-1}\}$, eq 10 turns into eq 8. This means on this time scale we find the common nondispersive diffusive behavior.

In the spirit of the MTM, defects on a polymer chain now belong to either of two classes: (i) freely diffusing defects or (ii) trapped defects that are temporarily immobilized. Note that if a certain defect is trapped, the chain as a whole is *not* immobilized during this time. Defects of different "wavelengths" can pass through one another, a situation well-known for spin waves in solids. Thus in the present model the random walk of a defect is envisaged as superposition of random motion (diffusion) and random stopping (trapping).

With the choice of eq 7, we obtain[8]

$$\langle l^2(t)\rangle \sim c(\gamma)t^{1-\gamma} \qquad (11)$$

with

$$c(\gamma) = \frac{1}{\Gamma(2-\gamma)}\sum_{l} l^2 p(l)$$

Equation 11 represents a superlinear diffusion law for $0 \leq \gamma < 1$, where for $\gamma = 0$ we recover the diffusion law (9). Thus eq 11 is the basic relation upon which we will dwell in the following.

Given a chain of contour length Na, the defect must undergo a mean-square displacement of $(Na)^2$ to make the whole chain move curvilinearly by the length b stored in the defect; i.e., from eq 11, $(Na)^2 = \langle l^2(\tau_d)\rangle \sim \tau_d^{1-\gamma}$, or

$$\tau_d \sim (Na)^{2/(1-\gamma)} \tag{12}$$

τ_d is the shortest time during which the chain can move as a whole. τ_d in eq 12 in general depends on a fractional power of Na (molecular weight M). Now de Gennes assumes that defects diffuse freely along the chain; i.e., he implies $\gamma = 0$. By postulating disengagement of the chains from their tubes on the time scale of interest, he defines a disengagement time τ_r, which for $\gamma = 0$ turns out to be proportional to M^3.

For a density of one defect per length b it takes on the order of $\tau_d(Na/b)$ for the chain to disengage from its original tube. Equation 12 thus leads to

$$\tau_r \sim \tau_d\frac{Na}{b} \sim \frac{Na}{b}(Na)^{2/(1-\gamma)} \tag{13}$$

The curvilinear diffusion coefficient D_c derives from the fact that upon disengagement the chain must perform a displacement of the order of its contour length L $(=Na)$. Thus

$$D_c = \frac{L^2}{\tau_r} \sim \frac{(Na)^2}{(Na/b)(Na)^{2/(1-\gamma)}} \tag{14}$$

The translational diffusion coefficient D_3 is obtained by replacing L in eq 14 by the radius of gyration R_0 of an ideal polymer

$$D_3 = \frac{R_0^2}{\tau_r} \sim \frac{Na^2}{(Na/b)(Na)^{2/(1-\gamma)}} = ab(Na)^{-2/(1-\gamma)} \tag{15}$$

The complex dynamic viscosity $\mu(\omega)$ can be derived in exactly the same manner as by Doi and Edwards.[2] The only difference arises by replacing their disengagement time by the relation eq 13; i.e.

$$\mu(\omega) = \frac{G_0}{5}\sum_{p_{\mathrm{odd}}}\frac{8}{p^4\pi^2}\,\frac{\tau_r}{1 + i\omega\tau_r/p^2} \tag{16}$$

where $G_0 = 3ck_BT(L/a)$, with c being the number density of polymers, k_B the Boltzmann constant, and T the absolute temperature. The steady-state viscosity $\mu(0)$ is then given by

$$\mu(0) = \frac{G_0}{5}\sum_{p_{\mathrm{odd}}}\frac{8}{p^4\pi^2}\tau_r = \frac{\pi^2}{60}G_0\tau_r \tag{17}$$

Since G_0 is independent of the molecular weight, we note the proportionality

$$\mu(0) \sim \tau_r \sim (Na)(Na)^{2/(1-\gamma)} \tag{18}$$

Let us assume $\gamma = {}^1/_6$. Then theory gives $\tau_r \sim N^{3.4}$, $D_3 \sim N^{-2.4}$, and $\mu(0) \sim N^{3.4}$. These results compare favorably with experiment, which finds $\tau_r \sim N^{3.4}$,[3] $\mu(0) \sim N^{3.4}$,[3] and $D_3 \sim N^{-2.1\pm0.1}$.[5]

The apparent discrepancy of theory and experiment with respect to D_3 deserves some comment. We note that the experiment had been performed on the scale of days ($\sim10^5$–10^6 s). This time scale clearly renders the waiting time distribution of eq 10 underlying our evaluation above to the form of eq 8. On this time scale, eq 9 or equivalently the choice $\gamma = 0$ will lead to $D_3 \sim N^{-2}$, in perfect agreement with experiment.[5] On the other hand, the stimulated Rayleigh scattering experiments of Leger et al. involve times of the order of 1 s,[5] which may be marginal to observe the effects of hindered diffusion. The most reliable zero shear rate viscosity measurements involve times of the order of 10 s or longer, and it would be interesting to carry out the stimulated Rayleigh scattering work on this time scale.

In conclusion, we have generalized de Gennes' reptation model by accounting for occasional trapping of defects that otherwise diffuse freely along the polymer chain. This picture has been described by a waiting time distribution function $\phi(t)$, which was understood to include a combination of capture and release processes of defects. For the special choice $\phi(t) = t^{\gamma-1}$ we derived the molecular weight dependences of the terminal relaxation time, the translational diffusion coefficient, and the dynamic and static shear viscosities. Their weight dependences were predicted to follow fractional power laws in general. For $\gamma = {}^1/_6$ agreement with some experiments was demonstrated. Other experiments were described well by choosing $\gamma = 0$. The change from $\gamma = {}^1/_6$ to $\gamma = 0$ was naturally explained on the basis of different time scales during which the experiments were performed.

Finally, we note that in order to give a strict explanation of the problems discussed, the task remains of proving the universality of $\gamma = {}^1/_6$. Here we communicated only some physical reasoning and we are not sure whether $\phi(t) = t^{\gamma-1}$ might be an effective single-particle projection of a complicated many-body phenomenon. Still, we could imagine a test of our ideas by introducing artificial "traps" into a polymer by synthesizing long polymer chains with small nonflexible parts or by using polymers that exhibit fluctuations toward crystallinity in the melt.

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