Microscopic theory of convective constraint release

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Synopsis

We develop a microscopic description of the contribution to stress relaxation in entangled polymer melts of convective constraint release, which is the release of entanglement constraints due to the effects of convective flow on chains surrounding a given chain. Our theory resolves three of the main shortcomings of the Doi–Edwards model in nonlinear rheology, in that it predicts (1) a monotonically increasing shear stress as a function of shear rate, (2) shear stress independent of molecular weight at sufficiently high shear rates, and (3) only modest anisotropies in the single chain scattering function, in agreement with experiment. In addition, our approach predicts that a stress maximum and resulting shear-banding instability would occur for living micelle solutions, as observed. © 2001 The Society of Rheology. [DOI: 10.1122/1.1349122]

I. INTRODUCTION

The model of Doi and Edwards (DE) (1986) of stress relaxation by reputation is a remarkably successful microscopic model, given its simplicity, in describing the flow properties of entangled polymer melts. Its shortcomings in the regime of linear viscoelasticity have largely been addressed by a recent quantitative treatment of contour-length fluctuations [Milner and McLeish (1998)] inspired by a microscopic theory for stress relaxation in star polymer melts [Milner and McLeish (1997)].

Substantial discrepancies remain between the DE model and experiment in nonlinear rheology. The simplest of these is that in steady shear, the DE model predicts a viscosity $\eta(\dot{\gamma})$ for large shear rates shear thinning more strongly than $\dot{\gamma}^{-1}$, in fact, scaling as $\eta \sim \dot{\gamma}^{-3/2}$ [Doi and Edwards (1986)]. This behavior implies a maximum in the shear stress as a function of shear rate, with the consequence that flows with shear rates $\dot{\gamma}$ slightly above an inverse reputation time $\tau_d^{-1}$ would be hydrodynamically unstable to shear banding. This striking behavior is not observed in experiment.

In contrast, entangled solutions of “living micelles,” while exhibiting many of the same rheological signatures as conventional polymer melts, do, in fact, present a shear-banding instability, which is associated with a stress maximum [Grand et al. (1997)]. A credible microscopic theory of the nonlinear rheology of entangled polymers ought to be

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able to distinguish between the case of unbreakable and living polymers, predicting a stress maximum and shear banding for the latter case only.

Marrucci (1996) has in a recent series of papers described a mechanism for stress relaxation in entangled polymers under flow that would be absent from linear viscoelasticity, which he called convective constraint release (CCR). The release of entanglement constraints arises from the continual retraction of extra chain contour length generated by the flow. An affinely deforming chain, initially an ensemble of random coils, will on average increase in length in a shear flow, the first correction to its length coming at second order in strain. Because entangled chains are nonetheless free to relax back to their equilibrium length by retracting along their “tubes,” this means that in steady flow chains are continually being stretched and relaxing back.

As they do so, entanglements that the ends of a chain impose on other chains are continually being relaxed, at a rate equal to the rate at which chain contour length would increase if chain retraction were suddenly turned off. This mechanism requires chain conformations to be anisotropic in steady state to operate, and so it first appears at second order in strain rate.

Following these ideas, Ianniruberto and Marrucci (1996) and Mead et al. (1998) have both constructed nonlinear constitutive models in which it is assumed at the outset that because of CCR, the renewal rate of the entire tube conformation of a chain is a function of the shear rate, becoming of order the shear rate for highly aligned chains. This strong assumption makes some progress towards avoiding the unphysical stress maximum, but it does so by delaying it to higher strain rates and molecular weights and weakening its amplitude, not by eliminating it altogether. A maximum is still present, for example, at a value of $N/N_e = 50$, which is well within the range of existing experiments. The assumption that CCR acts directly on the overall chain conformation via the effective terminal time also has the drawback that no prediction can be made for the single-chain structure factor. This is because the extra relaxation is applied directly to the relaxation of stress, rather than via the local chain conformation. A proper simultaneous treatment of chain conformation and stress is becoming increasingly important in the light of the strong links between small angle neutron scattering and molecular theories of rheology [McLeish et al. (1999)], and of a long-standing lack of explanation of the relatively mild anisotropy observed in sheared polymer melts [Müller et al. (1993)] compared to predictions of the tube model of Doi and Edwards (1986).

However, a careful microscopic consideration by Viovy et al. of constraint release by reputation of surrounding chains [Viovy et al. (1991)], strongly suggests an alternative microscopic view of the effect of CCR. Namely, constraint release motion may be regarded as hopping motion of the tube itself, on a time scale set by the frequency of constraint release events, with a hopping distance of order the tube diameter. In effect, the tube itself undergoes Rouse motion mediated by constraint release.

According to this picture, the renewal rate for the entire tube conformation is the “constraint release Rouse time,” which scales as the hopping time (inverse constraint release rate) times $n^2$, where $n = N b^2/a^2 = 5/4 N/N_e$ is the number of steps of the primitive path, $N$ is a chain length, $a$ and $b$ are the tube diameter and the chain Khun segment, and $N_e$ is defined by the plateau modulus $N_e = c k_B T / G^{(0)}$. This is evidently much longer than the constraint release time for highly entangled chains, and the tube conformation is not completely renewed until this much longer time passes. This picture has been the subject of a recent series of stochastic chain simulations by Hua and Schieber (1998) and Hua et al. (1999), that seek to combine the ingredients of reputation, path length fluctuation, and CCR. However, these calculations also fail to eliminate the shear stress maximum completely. We need a complementary analytic approach that allows
incorporation of the missing physics. It should contain sufficient information to be able to calculate both stress tensor and single chain structure factor \( S(q) \), at least on length scales greater than the tube diameter \( q < 2 \pi a^{-1} \).

In this paper, we shall develop a microscopically based nonlinear constitutive equation incorporating CCR, that does not simply assume the tube conformation is renewed at a rate of order \( \dot{\gamma} \). Instead, we shall describe the effects of CCR on the tube conformation in terms of its Rouse motion. We shall work with the imposed constraint of fixed tube length, corresponding to the DE assumption that the relaxation of the contour length of a chain inside its tube is rapid.

We are thus limited to shear rates less than the inverse Rouse time of the chain inside the tube, \( \dot{\gamma} \tau_R < 1 \). Because \( \tau_R \) is smaller than the reputation time by a factor of \( 3n \), for long entangled chains there is an interesting regime \( \tau_d^{-1} < \dot{\gamma} < \tau_R^{-1} \) in which the tube conformations may be considerably anisotropic but the chains remain unstretched. This is the regime to which our theory pertains.

Within our theory, the distinction between conventional unbreakable polymers and living micelles appears naturally, because of the different mechanisms for stress relaxation in the absence of CCR. Stress in conventional entangled polymers relaxes via reputation; in contrast, stress in living polymers relaxes primarily as breaks occur near a given section of the chain. In living polymers, there are no permanent chain ends, and no permanent arc-length labeling of the monomers along the chain. This ultimately leads to a nearly single-exponential stress relaxation function for living polymers, with the relaxation time determined by the rate at which chain breaks occur sufficiently near a given monomer for it to reptate to the break point and relax its stress. When we modify our theory of CCR to apply to living micelles, a stress maximum appears without adjustable parameters.

The remainder of this paper is organized as follows. In Sec. II, we introduce a generalized stochastic model for the motion of the tube itself, which combines the effects of reputation, constraint release Rouse motion, advection by the macroscopic flow, and the constant-length constraint imposed by rapid chain retraction. In Sec. III, we introduce the quantities we shall compute, namely the stress tensor and single-chain structure factor, which can both be expressed in terms of the tube tangent correlation function. In Sec. IV, we develop an equation of motion for the tube tangent correlation function from the stochastic equation of motion for the tube, with an approximate treatment of the constraint of fixed tube length and contour-length fluctuations. In Sec. V, we explore the model predictions for chain conformations and stress for shear flows in startup and steady state. In Sec. VI, we extend our theory to the case of living micelles. In Sec. VII, we discuss the implications of our model for the so-called “damping function” describing the stress amplitude immediately following a large-amplitude step strain. We present final conclusions and discussion in Sec. VIII.

II. TUBE DYNAMICS

We seek a model for constraint release in flow that is compatible with the tube-confined processes of reputation, chain length fluctuation, and retraction [Doi and Edwards (1986)], but which also describes the insight that chain ends passing through the entanglement volume of a chain segment may result in a local reorganization of its effective tube. Like other work reviewed in the introduction above, we shall adopt the framework that the tube itself may be viewed as a Rouse object under the action of these processes, with a local hopping rate determined self-consistently by the disentanglement dynamics of the real chains.
Other recent work has pointed out possible differences between Rouse-tube and standard Rouse dynamics. In particular, it is tempting to allow a strong biasing of the local hopping motion [Hua and Schieber (1998)], so that removal of a constraint by convection of a neighboring chain allows the chain to “straighten out” locally kinked configurations, but not to create them. This would also be the conclusion of a strictly “two-body” theory of “entanglement points,” which would imply that constraint release by retraction of neighboring strands under flow would always annihilate entanglements, never creating them. Chains progressively align, and the tubes actually dilate in such a picture. Perhaps unsurprisingly, this asymmetry in the Rouse hops of the tube does not remove the stress maximum, although it may weaken it [Hua and Schieber (1998), Mead et al. (1998)].

In fact, such a picture is inconsistent with what we know about entanglements in melts. The scaling of the plateau modulus with concentration is not consistent with a two-body theory of entanglements [Colby and Rubinstein (1990)]. Theoretical ideas also suggest that entanglements arise via the mutual, delocalized topological interaction of many structures [Rubinstein and Panyukov (1997)]. Very recently Ianniruberto and Marrucci (2000) have proposed an accounting for local chain reorientation in CCR. Furthermore, empirical evidence on a wide range of melts [Fetters et al. (1999)] implies that the tube diameter (or equivalently the value of $M_e$) is determined by universal criteria on the local melt structure (of order 10 distinct chains are required to be present in the volume of one entanglement). We will see that strong convective constraint release occurs for deformation rates of the order of $\dot{\gamma} \approx \tau_{d}^{-1}$, yet the melt structure will not be strongly perturbed at the level of an entanglement length until $\dot{\gamma} \approx \tau_{e}^{-1}$. So at deformation rates that would be expected to lead to CCR, the local criteria that govern the nature of the effective confining tube are hardly perturbed from those of an equilibrium melt.

This leads to a model for CCR in which the local tube diameter is kept constant, but where the local tube contour is permitted a random hopping motion, coupled to the average rate of constraint release. The $O(1)$ constant that describes tube motion induced by constraint release (how many constraint release events within a tube volume are needed to provide one lateral hop of the tube of size $a$) will be the one new parameter of this theory. We may, however, expect it to be related to the number of chains ($\sim 10$) defining the entanglement volume itself. So constraint release induces local Rouse-like tube motions that both straighten and buckle the primitive path.

In one respect the motion of the tube is not quite that of a Rouse polymer: the tube is actually defined by the chain it contains. Because of retraction, the primitive path retains a constant contour length, in contrast to a real Rouse chain whose contour length can change by stretching. We will need to include the constraint of constant length in the Rouse-like description on the dynamics.

So we need to derive an equation of motion for the tube that includes four types of motion: (1) reptation, (2) convection by the flow, (3) retraction, which maintains a fixed tube length, and (4) Rouse-like motion due to convective constraint release. Because of the very different nature of reptation and retraction motion on the one hand (motion along the tube) and Rouse-like motion on the other hand (isotropic motion), it is impossible to reduce a description of this richer tube motion to a coordinate set that “diagonalizes” the equation of motion, analogous to Rouse coordinates for pure Rouse motion. In the remainder of this section we will derive a stochastic equation of motion for the tube trajectory itself, which is described by coordinates of each point $R(s,t)$ as a function of dimensionless curvilinear distance $s$ from the end along the tube ($s = 0$ and $s = n$ are the ends) and time $t$. In Sec. III we will recast this stochastic dynamics for $R(s,t)$ as an
ordinary (nonstochastic) equation of motion for convenient averages of $\mathbf{R}(s,t)$, which are more suitable for direct solution.

We want to express the position of the tube at time $t + \Delta t$ via position of the tube at time $t$. Reptation and convection by the flow terms are well known [see Doi and Edwards (1986)]

$$\mathbf{R}(s,t+\Delta t) = \mathbf{R}(s+\Delta \xi(t),t) + \Delta t \kappa \mathbf{R}(s,t) + \ldots,$$

where $\kappa$ is the deformation rate tensor, which for simple shear has a single nonzero entry $\kappa_{xy} = \dot{\gamma}$. The random noise $\Delta \xi(t)$ has zero average and white noise correlation function

$$\langle \Delta \xi(t) \Delta \xi(t') \rangle = 2D_e \delta(t-t')$$

with $D_e$ the curvilinear diffusion coefficient

$$D_e = \frac{1}{\pi^2 n \tau_e}$$

and is related to the reptation time $\tau_d$ as $\tau_d = n^2/(\pi^2 D_e)$. Note that throughout this paper diffusion constants have the dimensions of $s^{-1}$, since contour length variables $(s,s')$ are given in terms of the tube diameter $a$. Our ‘microscopic’ time scale $\tau_e$ is the extrapolated reptation time of one tube segment consisting of $(4/5)N_e$ monomers (equivalently, three times the Rouse time for such a chain).

Constraint release motion results from a random release of entanglement constraints on the tube. Each constraint release event permits the tube to move locally a distance of order the tube diameter, whereupon it finds itself once again constrained by entanglements. As constraints are released at the same rate on all portions of the tube, this implies Rouse motion for the tube. We therefore write the constraint release terms in an equation of motion for $\mathbf{R}(s,t)$ by using a Rouse model

$$\mathbf{R}(s,t+\Delta t) = \ldots + \Delta t \left( \frac{3\nu}{2} \frac{\partial^2 \mathbf{R}}{\partial s^2} + \mathbf{g}(s,t) \right) + \ldots,$$

where $\mathbf{g}(s,t)$ is a delta-correlated, zero-mean noise term.

By the fluctuation-dissipation theorem, the noise amplitude is related to the coefficient $\nu$ by

$$\langle g_{\alpha}(s,t) g_{\beta}(s',t) \rangle = \nu \tau_e^2 \delta(t-t') \delta(s-s') \delta_{\alpha\beta}$$

(Greek indices signify Cartesian coordinates $\{x, y, z\}$ in this paper). Thus we see that $\nu$ is the frequency of constraint release events in the model.

Finally, we derive the term in the equation of motion responsible for retraction of the chain, which maintains the total length of the tube constant. Assume that at time $t$ the chain is not stretched and at the next moment $t + \Delta t$ convection stretches each segment at $s$ along the tube by a factor of $(1 + \lambda(s)\Delta t)$. To get back to its previous position, each segment must move a distance $\Delta s = \int_s^{s'} (1 + \lambda(s)\Delta t) ds$ along the tube towards its center because due to constraints the chain can move only along its own path.

The formalism and computation are eased by assuming that the stretching rate $\lambda(s)$ does not depend on the position along the chain; we get $\Delta s = (n/2-s)\lambda \Delta t$. This assumption was checked in (single-chain ensemble) Brownian simulations of our formalism and works well when constraint release is present. In fact, it is possible to lift this assumption, deriving a set of equations with $n$ Lagrange multipliers $\lambda_i$ instead of one $\lambda$. This was done and we show that the constant-$\lambda$ assumption does not affect the stress
behavior at all, so we proceed with it here (but in some cases it does have minor effects on predictions of the single-chain scattering, so we have used this full formalism to produce the relevant Figs. 7–9 below).

Therefore the retraction part of the equation of motion could be written as

$$ R(s, t+\Delta t) \rightarrow R(s+\lambda \Delta t(n/2-s), t) \approx R(s, t) + \Delta t \lambda \frac{\partial R}{\partial s} (n/2-s). \quad (6) $$

Here $\lambda$ is a functional of $R(s)$, to be determined ultimately (see Sec. III A) from the condition of the constant chain length $E_0 = \int_0^a ds \ U(R(s), t)$. 

From the definition of $\lambda$ Eq. (6) and the fact that $|\partial R/\partial s| \approx a$ everywhere it follows that $\lambda an/2$ is a speed of each chain end during retraction. We will thus call $\lambda$ the retraction rate.

We assemble these terms [Eqs. (1), (4), (6)] to obtain the stochastic dynamical equation for the tube

$$ R(s, t+\Delta t) = R(s+\Delta \xi(t), t) + \Delta t \left( \kappa R + \frac{3 \nu}{2} \frac{\partial^2 R}{\partial s^2} + g(s, t) + \lambda \left( \frac{n}{2} - s \right) \frac{\partial R}{\partial s} \right). \quad (8) $$

The four terms on the right-hand side correspond, respectively to reptation, convection, CCR (third and fourth terms), and retraction. Equation (8) is a nonlinear stochastic partial differential equation with two noise terms $\Delta \xi(t)$ and $g(s, t)$. Because we are only concerned with terms of first order in $\Delta t$ (because equations of motion will be first order in $\partial/\partial t$), we can consider separately the different types of motion of the tube (since each contribute at $O(\Delta t)$, cross terms are negligible).

The constraint-release rate $\nu$ should be in fact related to $\lambda$. Because constraints of a given tube arise from other chains, we assume that the retraction of two ends of a given chain by a distance $a/2$ should on average release a constraint somewhere on another chain. From Eq. (6) we therefore conclude that the frequency of convective constraint release should be proportional to the retraction rate.

Independent of convective effects, constraints on a given chain segment are released by reptation of the other chains. Therefore the total constraint release rate should be the sum of the rate of CCR and the rate of ordinary “reptative” constraint release, which should be inversely proportional to the mean lifetime $(\pi^2/12)n^3 \tau_c$ of chain segments from the theory of Doi and Edwards (1986). Note that since CCR only becomes significant when $\gamma n^3 \tau_c > 1$, the reptative constraint release term does not change our qualitative predictions for large shear rates.

Summing the reptative constraint release and CCR contributions as described above, we have

$$ \nu = c_\nu \left( \lambda + \frac{12}{\pi^2 n^3 \tau_c} \right). \quad (9) $$

Here $c_\nu$ is a phenomenological coefficient of order unity; $c_\nu = 1$ would mean that one tube retracting by one entanglement length releases one tube segment of some other chain. We expect $c_\nu \ll 1$. Together, Eqs. (7), (8), and (9) are sufficient to determine $R(s, t)$, $\lambda$ and $\nu$. We note that the only new parameter in this development of the tube model is the constant $c_\nu$ itself.
III. STRESS TENSOR, STRUCTURE FACTOR

Our goal in this work is to compute the nonlinear, time-dependent flow behavior of monodisperse entangled polymer melts, including the effects of convective constraint release. First and foremost, we compute the stress tensor $\sigma_{\alpha\beta}$, developing methods that apply for an arbitrary time-dependent flow history, although we will focus on startup of shear flow.

But together with purely rheological investigations of stress relaxation in entangled polymer melts, it is also useful to ask how the chains in the melt are situated in space, by means of scattering experiments. We therefore calculate the single-chain structure factor $S(q)$, which can be observed by neutron scattering from a dilute admixture of labeled chains.

We imagine experiments in which scattering is performed after a given startup flow, and a subsequent rapid quench below the glass transition. This corresponds exactly to the experiments of Müller et al. (1993). Thus the relevant $S(q; t)$ is an equal-time density–density correlation function a time $t$ after starting the flow. We restrict ourselves to scattering wave numbers satisfying $qa < 2\pi$; that is, we do not look inside the tube. Therefore the chain structure factor and the tube structure factor are taken to be identical.

The stress tensor $\sigma_{\alpha\beta}$ is given in terms of the chain-path $R(s)$ by

$$\sigma_{\alpha\beta} = \frac{c}{N} \frac{3T}{a^2} \int_0^n ds \left( \frac{\partial R_\alpha}{\partial s} \frac{\partial R_\beta}{\partial s} \right).$$  \hspace{1cm} (10)

Here $c/N$ is the polymer concentration, and the arclength variable $s$ ranges from zero to the total chain length $n$.

Later it will turn out to be convenient to introduce Rouse coordinates for the tube

$$X_p = (1/n) \int_0^n ds R(s) \cos(p\pi s/n),$$  \hspace{1cm} (11)

$$R(s) = X_0 + 2 \sum_{p=1}^n X_p \cos(p\pi s/n).$$  \hspace{1cm} (12)

The number of tube Kuhn segments $n$ in the entire chain serves as an appropriate cutoff for the number of tube Rouse modes.

In terms of tube Rouse modes the stress tensor is

$$\sigma_{\alpha\beta} = \frac{c}{N} \frac{3T}{2\pi^2} \frac{2\pi}{n} \sum_{p=1}^n p^2 \langle (X_p)_\alpha (X_p)_\beta \rangle,$$  \hspace{1cm} (13)

where the angle brackets denote an average over the system.

To compute the structure factor, we begin with its formal definition

$$S(q) = \int_0^n ds \int_0^n ds' \langle e^{iq \cdot R(s)} e^{-iq \cdot R(s')} \rangle.$$  \hspace{1cm} (14)

With the separation $R(s) - R(s')$ between tube segments at $s$ and $s'$ taken to be Gaussian random variables, we have

$$S(q) = \int_0^n ds \int_0^n ds' \exp[-(q_a q_\beta/2)(R_a(s) - R_a(s'))(R_\beta(s) - R_\beta(s'))].$$  \hspace{1cm} (15)

The structure factor may be expressed as
\[ S(q) = \int_0^L ds \int_0^L ds' \exp\left[-(q_{\alpha\beta}/2) \int_s^{s'} ds_1 \int_s^{s'} ds_2 \left( \frac{\partial R_\alpha}{\partial s}(s_1) \frac{\partial R_\beta}{\partial s}(s_2) \right) \right]. \] (16)

Using the expansion of chain coordinates in Rouse modes, we may rewrite the structure factor as

\[ S(q) = \int_0^L ds \int_0^L ds' \exp \left[-2q_{\alpha\beta} \sum_{\rho,\rho'} \langle (X_\rho)_\alpha (X_{\rho'})_\beta \rangle \right] \times \left[ \cos \left( \frac{p \pi s}{n} \right) - \cos \left( \frac{p \pi s'}{n} \right) \right] \left[ \cos \left( \frac{p' \pi s}{n} \right) - \cos \left( \frac{p' \pi s'}{n} \right) \right]. \] (17)

(Note that in the quiescent limit, the structure factor of Eq. (17) reduces to a Debye function as it should.)

**IV. TUBE TANGENT CORRELATION FUNCTION**

From Eqs. (10) and (16) for the stress tensor and structure factor, we see that knowledge of the tube tangent correlation function

\[ f_{\alpha\beta}(s, s', t) = \langle (\partial R_\alpha/\partial s)(s, t) (\partial R_\beta/\partial s)(s', t) \rangle \] (18)

would be sufficient to compute both \( \sigma_{\alpha\beta} \) and \( S(q) \). We now proceed to derive an equation of motion for \( f_{\alpha\beta}(s, s', t) \).

First, we derive an equation of motion for the related quantity \( F_{\alpha\beta}(s, s', t) = \langle R_\alpha(s, t) R_{\beta}(s', t) \rangle \). This is obtained from Eq. (8) by (1) expanding to first order in \( \Delta t \); (2) expanding to second order in \( \Delta \xi(t) \); (3) averaging over \( \Delta \xi(t) \) using Eq. (2) for the correlations of the reptative noise (and the fact that the reptative noise is uncorrelated with the conformation); (4) averaging over \( g(s, t) \) using the Ito–Stratonovich relation

\[ \langle g_\alpha(s, t) R_{\beta}(s', t) \rangle = \frac{\nu a^2}{2} \delta(s - s') \delta_\alpha\beta \] (19)

for the cross correlation between \( g(s, t) \) and \( R(s, t) \); and (5) assuming that \( \lambda \) is uncorrelated with the chain conformation. The result after a few pages of algebra is

\[ \frac{\partial F}{\partial t} = (3\nu/2) \left( \frac{\partial^2}{\partial s^2} + \frac{\partial^2}{\partial s'^2} \right) F + \kappa \cdot F + F \cdot \kappa^T + \nu a^2 \delta_{\alpha\beta} \delta(s - s') + D_c \left( \frac{\partial}{\partial s} + \frac{\partial}{\partial s'} \right)^2 F \\
+ \lambda \left[ (n/2 - s) \frac{\partial}{\partial s} + (n/2 - s') \frac{\partial}{\partial s'} \right] F. \] (20)

The sole assumption made in deriving Eq. (20), that the retraction rate \( \lambda(t) \) is uncorrelated with the tube coordinate \( R_\alpha(s, t) \), or

\[ \langle R_\alpha(s, t) R_{\beta}(s', t) \rangle \lambda(t) \rangle = \lambda(t) \langle R_\alpha(s, t) R_{\beta}(s', t) \rangle \] (21)

can be checked by direct simulation of Eq. (8). A large ensemble of single chains were subjected to the deterministic and Brownian noise terms, but were individually retracted to maintain fixed contour length. Preliminary results show that it turns out to be a good approximation when CCR is present. We leave more detailed comparison of stochastic and analytical approaches to future publications.
Now we apply the operator \((\partial l/\partial s)(\partial l/\partial s')\) to the equation to obtain an equation of motion for \(f_{ab}\)

\[
\frac{\partial f}{\partial t} = \kappa \cdot f + T + D_c \left( \frac{\partial}{\partial s} + \frac{\partial}{\partial s'} \right)^2 (f - f_{eq}) + (3 \nu/2) \left( \frac{\partial^2}{\partial s^2} + \frac{\partial^2}{\partial s'^2} \right) (f - f_{eq})
\]

\[-\lambda \left[ 2 + (s-n/2) \left( \frac{\partial}{\partial s} \right) + (s' - n/2) \left( \frac{\partial}{\partial s'} \right) \right] f. \tag{22}\]

Here the equilibrium value \(f_{ab}^{(eq)}\) of the tube tangent correlation function is given by

\[
f_{ab}^{(eq)} = (a^2/3) \delta(s-s') \delta_{ab}. \tag{23}\]

A. Discussion of the equation of motion

The equation of motion Eq. (22) for \(f_{ab}(s,s';t)\) is a partial differential equation in which \(s\) and \(s'\) range over the interval \([0,n]\). The convective terms \(\kappa \cdot f + T\) (of the usual form for a second-rank covariant tensor) act on \(f\) “in place,” at a fixed \(\{s,s'\}\). The reptative diffusion acts only along diagonal lines \(s-s' = \text{const}\), while the constraint release Rouse diffusion acts isotropically.

The terms enforcing the fixed-length constraint give rise to a “current” flowing along the diagonal direction, with speed proportional to the distance from the center point \([n/2,n/2]\). This expresses the effect of relabeling the monomers along the chain following a small retraction; the term \(2 \lambda f_{ab}\) arises from the effect of this relabeling on the tangent vectors themselves, i.e., from the effect on the derivatives \(\partial l/\partial s\) and \(\partial l/\partial s'\) in the definition of \(f_{ab}\).

We shall see below that typically \(D_c \gg D_R = 3 \nu/2\), so that the region where \(f\) is non-negligible remains confined to a narrow ridge close to \(s-s' = 0\).

Even with constraint release being a perturbation on reptation, these equations contain a mechanism by which a maximum in the shear stress as a function of shear rate is avoided. Constraint release gives rise to a local relaxation towards the isotropic \(f_{eq}\) all along the diagonal spine, corresponding to the slight misalignment of tube segments that have been able to make a local hop. These isotropic misaligned segments then give a source term (via the convective deformation, \(\kappa \cdot f + T\)) for shear stress.

Without this mechanism (i.e., in the Doi–Edwards model), the shear stress catastrophically “aligns away,” resulting in a maximum in shear stress as a function of shear rate, and consequent flow instabilities. In the present model, because the hop rate for nearly aligned tubes becomes proportional to \(\dot{\gamma}\) (see below), the amount of tube misalignment becomes constant in the limit of high extension rates, leading ultimately to an asymptotically constant value of shear stress.

One may ask whether a more restricted set of degrees of freedom than the full function \(f_{ab}(s,s')\) is sufficient to describe a tube undergoing both Rouse and reptative motion. However, this is not possible; we must retain the full function. To see this, consider the following. In equilibrium, \(f_{ab}(s,s')\) is isotropic, local [proportional to \(\delta(s-s')\)], and constant, by Eq. (23). After a rapid step strain, \(f_{ab}(s,s')\) becomes anisotropic (proportional to some tensor \(A_{ab}\)), but is still local and constant. Now the terms in Eq. (22) arising from reptation preserve the locality of \(f_{ab}(s,s')\). This is because pure reptation moves all parts of the chain along the tube together, so that the chain path at different \(s\) and \(s'\) remains uncorrelated.
If only reptation was operative, we could write \( f_{\alpha\beta}(s,s',t) = A_{\alpha\beta} \delta(s-s') \psi((s + s')/2,t) \) and thus describe stress relaxation with a simpler function \( \psi(s,t) \) —which would be the tube survival probability of Doi and Edwards. Unfortunately, the terms in Eq. (22) describing Rouse motion are of the form of an isotropic diffusion operator in the \( \{s,s'\} \) plane, and spoil the locality of \( f_{\alpha\beta}(s,s') \), forcing us to abandon \( \psi(s,t) \) as a description of the tube motion.

Likewise, if only Rouse motion were operative, the resulting diffusion operator in Eq. (22) would be diagonalized in Fourier space, i.e., by transforming to Rouse modes. Unfortunately, the reptation terms are not diagonal in Fourier space, so again we are stuck with the full equation.

**B. Fourier-space equation of motion**

It turns out to be numerically simpler to solve Eq. (22) in Fourier space, i.e., by transforming to Rouse modes, than to solve directly in real space. This is because transforming gives us a set of coupled ordinary differential equations to solve rather than a partial differential equation; (2) cutting off the number of Rouse modes at \( n \) is a natural way to impose a short-distance cutoff in the theory, which would be problematic in real space; and (3) for realistic polymer molecular weights, the number of Rouse modes is typically not very large (\( n < 50 \), say).

Using Eq. (12) for the Rouse modes, we have a Fourier-transformed tangent correlation function \( (C_{pq})_{\alpha\beta} \), related to \( f_{\alpha\beta}(s,s') \) by

\[
(C_{pq})_{\alpha\beta} = \langle (X_p)_\alpha (X_q)_\beta \rangle = \frac{1}{\pi^2 pq} \int_0^n ds \, ds' \sin \left( \frac{p \pi s}{n} \right) \sin \left( \frac{q \pi s'}{n} \right) f_{\alpha\beta}(s,s')
\]

with an inverse relation

\[
f_{\alpha\beta}(s,s') = \frac{4 \pi^2}{n^2 pq} \sum_{p,q > 0} p q \sin \left( \frac{p \pi s}{n} \right) \sin \left( \frac{q \pi s'}{n} \right) (C_{pq})_{\alpha\beta}.
\]

The equilibrium value of \( (C_{pq})_{\alpha\beta} \) is

\[
(C_{pq})_{\alpha\beta}^{eq} = \frac{n a^2}{6 \pi^2 p^2} \delta_{pq} \delta_{\alpha\beta}.
\]

Now we Fourier transform Eq. (22) using Eq. (24). After a few pages of algebra we obtain

\[
\frac{\partial}{\partial t} (c_{pq}) = (\kappa + \kappa^T) \delta_{pq} + \kappa \cdot c_{pq} + c_{pq} \cdot \kappa^T - \frac{1}{n^3} (1 + c_h n \lambda)(p^2 + q^2) c_{pq}
\]

\[+ \frac{8}{\pi^2 n^3} \sum_{p',q'} M_{pp'} M_{qq'} c_{p'q'} + \lambda \left( \sum_p \tilde{M}_{pp'} c_{p'q'} + \sum_{q'} \tilde{M}_{qq'} c_{pq'} - \delta_{pq} \right)\]

in which \( c_h = 3 \pi^2 c_v/2 \), and the 1 in the last term denotes the Cartesian unit tensor \( \delta_{\alpha\beta} \).

In Eq. (27) we have made for convenience some rescalings and changes in notation. We measure time in units of \( \tau_e = \tau_d/n^3 \) and defined a scaled deviatoric mode amplitude \( c_{pq} \) by
Thus \( c_{pq} = 0 \) in equilibrium.

The coupling constant matrices \( M \) and \( \bar{M} \) are given by

\[
M_{pp'} = \begin{cases} 
-pp'[-(-1)^{p+p'} - 1] & p \neq p' \\
\frac{p^2 - p'^2}{p^2 - p'^2} & p = p' 
\end{cases},
\]

\[
\bar{M}_{pp'} = \begin{cases} 
-pp'[(-1)^{p+p'} + 1] & p \neq p' \\
\frac{p^2 - p'^2}{p^2 - p'^2} & p = p' 
\end{cases}.
\]

Note that \( f_{\alpha\beta}(s,s') \) is symmetric under the interchange of \( \{\alpha,s\} \) and \( \{\beta,s'\} \); indeed, only becomes nonlocal in \( s - s' \) because of Rouse diffusion \( f \) should be symmetric under separate interchange of \( \alpha \) and \( \beta \), and \( s \) and \( s' \). This implies that \( (C_{pq})_{\alpha\beta} \) must be symmetric under separate interchange of \( \alpha \) and \( \beta \), and \( p \) and \( q \). Also, because the two ends of a chain are the same, \( f_{\alpha\beta}(s,s') \) is equal to \( f_{\alpha\beta}(n-s,n-s') \), which implies that \( C_{pq} \) vanishes unless \( [p,q] \) are both odd or both even. These symmetries reduce the number of degrees of freedom by a factor of about 4. For \( n \) modes and \( n \) even (odd), we have \( 3n(n+2)/4[3(n+1)^2/4] \) of freedom, or 330\(^2\) of freedom for \( n = 20 \). (The factor of 3 corresponds to the three tensor components \( xx,xy \), and \( yy \) in simple shear.)

In terms of the new variables \( (c_{pq})_{\alpha\beta} \), the deviatoric part of the stress tensor takes the simple form

\[
\delta\sigma_{\alpha\beta} = \frac{cT}{N_c} (1/n) \sum_{p=1}^{n} (c_{pp})_{\alpha\beta}.
\]

The front factor \( cT/N_c \) is in fact the plateau modulus \( G_0 \) (recall that \( c \) is the monomer concentration, and the plateau modulus is "\( kT \) per displaced volume of an entanglement segment"). In what follows, we shall present stress values in units of \( G_0 \).

C. Hopping rate

We turn now to determine the retraction rate \( \lambda \). Our procedure is approximate in that we do not choose \( \lambda \) to fix the contour length Eq. (7), but the more convenient quantity

\[
\int ds \sum_{n} f_{\alpha\alpha}(s,s) = na^2,
\]

which is proportional to the sum of the mean-square lengths of each tube segment. In the Fourier-transform variables, the constraint reads

\[
\frac{2\pi^2}{n} \sum_{p=1}^{n} \sum_{\alpha=1}^{3} p^2 (C_{pp})_{\alpha\alpha} = na^2.
\]

Replacing the true constant-length constraint Eq. (7) by the approximate relation Eq. (32) can be checked for accuracy at any point in a calculation, i.e., at any moment, knowing \( c_{pq} \) we calculate the segment lengths \( R^2(s,t) \). In the calculations presented below this was done routinely. We found that no segment length deviates from a more...
than 5%. This approximation is valid ultimately for the same reason that taking $\lambda$ independent of $x$ works: the local operation of CCR endows each segment with approximately the same stretch $\lambda$ and length $a$. It is perhaps worth noting that this is not itself a form of the "independent alignment approximation" of Doi and Edwards (1986), a version of which is instead implicit in the decoupling approximation of Eq. (21) when CCR is absent or very small (see Sec. VII on damping functions below).

We obtain an expression for $\lambda$ that precisely maintains Eq. (33) by applying the trace operator $\sum p q \delta_{p q} \sum_{\alpha \beta} \delta_{\alpha \beta}$ to the equation of motion, to obtain

$$
\lambda = \frac{2 \kappa c_{p p} - (2/n^2) \left(1 + \frac{12c_h}{n^2 \pi^2}\right) p^2 \text{tr} c_{p p} + 8/(\pi^2 n^3) M_{p p} M_{p q} \text{tr} c_{p', q'}}{3n + (2c_h/n^2) q^2 \text{tr} c_{q q}}
$$

with all indices $\{p, p', q, q'\}$ summed over.

Consider how the hopping rate in shear flow depends on the shear rate. From Eq. (34), $\lambda$ evidently vanishes in the limit of low deformation rates, for which $f_{\alpha \beta}$ is isotropic. Since $\lambda$ is an even analytic function of $\dot{\gamma}$, for small shear rates $\lambda$ is second order in shear rate.

At shear rates much higher than the inverse reptation time, if the average tube alignment with respect to the velocity direction reaches an asymptotically constant small angle (as in experiments), then $\int ds f_{\alpha \beta}(s, s)$ approaches some tensor that is not quite aligned with the flow (and correspondingly, the shear stress approaches some constant value). In this scenario, the hopping rate would asymptotically become linear in shear rate, with a possibly small coefficient because of the near alignment of the tubes.

Now we may ask whether convective constraint release is a big or a small effect with respect to reptation. Recall that the reptation time $\tau_d$ scales as $\tau_d \sim \tau_s n^3$. We expect significant tube alignment, resulting in shear thinning and a retraction rate $\lambda$ of order $\dot{\gamma}$, when $\dot{\gamma} \tau_d$ exceeds unity. Note that the stretch relaxation time $\tau_s$ of the chains, i.e., the Rouse time corresponding to contour-length fluctuations inside the tube, scales as $\tau_s \sim \tau_s n^2$. Therefore, the condition that we have shear thinning but not chain stretching inside the tube is $n \gg \dot{\gamma} \tau_d \gg 1$.

Now the constraint release Rouse time $\tau_R$ scales as $\tau_R \sim n^2/(c \dot{\gamma})$, with $c$ possibly quite small. Thus we may have $\tau_R \gg \tau_d$, i.e., constraint release Rouse motion is a perturbation compared to reptation, if $n^2/c \gg \dot{\gamma} \tau_d$. That is, constraint release Rouse motion is never sufficient to completely relax the tube conformation, whenever the shear rate is low enough that chain stretching is negligible.

However, the highest Rouse modes of the tube will be relaxed by constraint release before reptation renews the tube. Equating the constraint release Rouse time of the $p$th mode $\tau_R(p) \sim n^2/(c \dot{\gamma} p^2)$ to the reptation time to find the lowest $p^* \approx 1$ relaxed, we find $p^* \sim n^2/(c \tau_d) > n/c$. If $c$ happened to be as small as $1/n$, only the top few Rouse modes would relax ($p^* \sim n$) before reptation; if $c$ were of order unity, $p^*$ would be of order $n^{1/2}$, and all Rouse modes between $n^{1/2}$ and $n$ would be relaxed by CCR.

### D. Contour-length fluctuations

For entangled polymers of practical molecular weights, the number of entanglements is usually quite modest, ranging from 5 to 50 or so. For such small $n$, rapid relaxation of the ends of the chain by contour-length fluctuations is quite significant. Indeed, these faster processes are responsible for the dynamic modulus $G''(\omega)$ displaying a power law
greater than $-1/2$ above the terminal frequency, and ultimately for the apparent 3.4 power law dependence of the zero-shear viscosity on molecular weight [Doi (1983), Milner and McLeish (1998)].

We may treat these fast processes approximately by including a local relaxation term on the right-hand side of Eq. (22) to make the ends of the chain relax more quickly. This approach is quite similar to our previous work on contour-length fluctuations and linear dynamic rheology [Milner and McLeish (1998)]. The term we add takes the form

$$\frac{\partial \mathbf{A}}{\partial t} = \ldots \left( \frac{1}{\tau(s)} + \frac{1}{\tau(s')} \right) (\mathbf{f} - \mathbf{f}_{eq}).$$

If either of the points $s$ or $s'$ is sufficiently near a free end of the chain, contour-length fluctuations will quickly relax the correlation function $f(s,s')$ to its equilibrium isotropic value.

Fourier transforming this term leads to a final term in Eq. (27)

$$\frac{\partial \mathbf{c}_{pq}}{\partial t} = \ldots - \sum_{p'} L_{pp'} c_{p'q} - \sum_{q'} L_{qq'} c_{pq'}.$$

Here we have defined the matrix $L_{pp'}$ as

$$L_{pp'} = (1/2) \sum_r K_r (\delta_{p+r,p} + \delta_{p'+r,p} - \delta_{p+p',r})$$

and we have written a Fourier series for $1/\tau(s)$ as

$$\frac{1}{\tau(s)} = \sum_{r \geq 0} K_r \cos \left( \frac{r \pi s}{n} \right)$$

in which $K_r$ vanishes by symmetry for $r$ odd.

For $\tau(s)$, we used expressions developed in our previous work [Milner and McLeish (1997)] on stress relaxation in star polymers, and effects of contour-length fluctuations in linear polymer melts [Milner and McLeish (1998)]. Essentially, these expressions for $\tau(s)$ interpolate between the fast contour-length fluctuation rate for monomers near the chain end, and exponentially slow activated retractions for monomers more distant from the chain end. The reader is referred to Milner and McLeish (1997) and Milner and McLeish (1998) for details.

V. RESULTS FOR STARTUP SHEAR FLOWS

We now explore the consequences of the model developed in the previous section, in startup shear flows. [We solved the equations of motion Eq. (27) numerically on a Macintosh G3 using Bulirsch–Stoer routines from Numerical Recipes in C, called from Mathematica via MathLink.]

First, the shear stress shows substantial overshoots, as shown in Fig. 1. The first normal stress shows no overshoot, because our treatment does not contain any chain stretching. The shear-stress overshoots for different representative values of shear rate are shown in Fig. 2. The overshoot appears at $\dot{\gamma} \tau_{el} \geq 1$ and then grows with increasing shear rate, reaching about 20% at large shear rates. The shear strain at the maximum is approximately constant, $\dot{\gamma} \approx 1.6$, as is clear from Fig. 2 where the shear stress is plotted versus strain.
The steady-state viscosity \( \eta(\dot{\gamma}) \) and first normal stress difference \( N_1(\dot{\gamma}) \) are found by integrating the equations of motion to a sufficiently late time. The steady-state shear stress as a function of shear rate for different values of the hopping parameter \( c_h \) is shown in Fig. 3. The case of \( c_h = 0 \) corresponds to pure reptation without constraint release. In this case the shear stress decreases for large \( \dot{\gamma} \), giving rise to a shear stress maximum, in contradiction with experiment. This behavior is very similar to the predictions of the Doi–Edwards theory, in which shear thinning becomes unstable at \( \dot{\gamma} \tau_d^{-1} \approx \dot{\gamma} \approx \tau_s^{-1} \).

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We obtain this qualitative behavior whether or not we include the effects of contour-length fluctuations on the stress relaxation. Stress as a function of shear rate for different values of \( c_h \) with contour-length fluctuations included is shown in Fig. 4. Contour-length fluctuations alone are not sufficient to eliminate the stress maximum, although they do...
displace the stress maximum to higher shear rate. When contour-length fluctuations are added to CCR, the approach to the asymptotic stress plateau is shifted to higher rates, with very little change in slope. A range of values for $c_n$ gives a large region over which the shear-thinning exponent is in the range 0.8–0.9, as observed experimentally for nearly monodisperse polymer melts. In principle, the value of $c_n$ could be determined by comparing the detailed shape of the shear-thinning curve to experiment, but in fact this does not pin down the value too precisely once the stress maximum is eliminated. Hence we take $c_n = 0.1$ unless otherwise specified. This corresponds to the case that ten chains are needed to create one entanglement.

The chain-length dependence of the steady-state viscosity is displayed in Fig. 5, for $n = 10, 20, 40$. Note the $n$ independence of the viscosity in the strong shear-thinning region, in agreement with the experiment of Bercea et al. (1993). The zero-shear viscosities for these three values of $n$ scale with an apparent exponent of $\eta(0) \sim n^{3.4–3.5}$, in agreement with experiment [Berry and Fox (1968)]. This behavior is reproduced because of the contour-length fluctuations included via Eq. (35); without them, the zero-shear viscosity in our theory scales as $n^3$. Indeed, the shapes of the shear-thinning curves for

**FIG. 3.** Steady-state shear stress vs shear rate, for $n = 20$ and $c_n = 0, 0.01, 0.1, 1$.

**FIG. 4.** Steady-state shear stress vs shear rate, for $n = 20$ and $c_n = 0, 0.01, 0.1, 1$, including the effects of contour length fluctuations. Note that shear rate is made dimensionless with the “bare” reptation time $\gamma_d$, calculated in the absence of fluctuations.
different $n$ are such that they can be brought to a universal curve by scaling by the zero-shear viscosity and a characteristic time which scale the same way with $n$, i.e., by "sliding" the curves along the common high-shear asymptote of slope $-1$ (inset to Fig. 5). The corresponding first normal-stress coefficients as a function of shear rate are shown in Fig. 6. They too can be similarly collapsed to a common universal curve (see inset to Fig. 6).

In our treatment we can also examine the single chain structure factor $S(q)$, as observable in neutron-scattering experiments from selectively deuterated chains. We have in mind an experiment in which a flow is suddenly stopped by quenching below the glass transition, and neutron scattering performed afterwards, as has been performed by Müller et al. (1993). A typical structure factor computed from our theory is shown in Fig. 7. Note that constraint release drastically changes the overall picture: the degree of orientation decreases, and the $q$ dependence of the orientation angle appears; contour lines of $S(q)$ at smaller $q$ are more oriented than at larger $q$.
To compare these results with neutron scattering experiments, we can extract various quantities including the characteristic dimensions $R_{\text{max}}^2(\dot{\gamma})$ and $R_{\text{min}}^2(\dot{\gamma})$ in the major and minor principal directions, as well as the $q$-dependent alignment angle $\beta(q, \dot{\gamma})$ between the major principal axis contours of $S(q)$ and the flow ($x$) direction. These quantities summarize the changes in dimension and orientation of typical chain conformations as a result of the flow, assuming that the contours of $S(q)$ are elliptical.

Our predictions for $q$-dependent alignment angle are in qualitative agreement with existing experiments [Müller et al. (1993)]. The typical $q$-dependence $\beta(q)$ is shown in the inset to Fig. 8 for $n = 20$. The dependence on shear rate of the limiting values $\beta_{\text{max}} = \beta(q = 0)$ and $\beta_{\text{min}} = \beta(q = 2\pi/a)$ are shown in Fig. 8 for different chain lengths. Note the slow approach to an apparent limiting angle. This is a direct result of

**FIG. 7.** Single-chain structure factor, for $n = 20$, $c_v = 0.1$ and high shear limit. Inset: the same structure factor in the same scale without CCR ($c_v = 0$).

**FIG. 8.** Alignment angles $\beta_{\text{max}}$ and $\beta_{\text{min}}$ vs shear rate, for $n = 20$ and $n = 10$, $c_v = 0.1$ and $c_v = 0$. Inset: $q$ dependence of alignment angle.
CCR, and the value of this angle is in effect a measure of the hopping parameter $c_{\nu}$. The original Doi–Edwards theory ($c_{\nu} = 0$) predicts $\beta_{\text{max}} = \beta_{\text{min}} = 90$. Increasing $c_{\nu}$ leads to decreasing both $\beta_{\text{max}}$ and $\beta_{\text{min}}$ and increasing the gap between them. The angle $\beta$ also depends on chain length: increasing $n$ leads to an increase of the gap between $\beta_{\text{max}}$ and $\beta_{\text{min}}$. The arrows in Fig. 8 indicate experimental results of Müller et al. (1993). However, in the paper, the authors did not specify the shear rate and did not reach steady-state shear (total strain was 2.4, but to reach steady flow one needs more than ten strain units). Therefore one needs more neutron scattering data for a detailed comparison to our predictions.

The major and minor radii of gyration are shown in Fig. 9; note again the apparent limiting anisotropy. In fact, neither Müller et al. nor any subsequent analysis have discussed the strong disagreement between the single-chain structure factor measured in this work and the tube-based theory without CCR. The real chains are much less oriented than the simple theory would suggest. But on incorporating CCR into the model, we are able simultaneously to account for the chain anisotropy and the rotation of the principal axis of the scattering pattern with $q$. The latter is a striking feature of the data, and is a direct consequence of the local Rouse motion of the tube, and the convection of the perturbed structures so formed to longer length scales by the flow.

Note that the deformations of the chains from isotropic random coils are never extremely large. Specifically, in all we have discussed so far, the tube conformations remain fixed-length random walks, albeit anisotropic, described by the tube orientation tensor $\langle (\partial R_{\alpha}/\partial s) (\partial R_{\beta}/\partial s) \rangle$. Therefore, even if the tube orientation tensor becomes "completely aligned" with the flow, the mean-square end-to-end radius in the flow direction $R_z^2$ never gets more than three times larger than its equilibrium value of $na^2/3$.

We might imagine that the tube would align completely with the flow, i.e., stretch out to its fully extended length along the flow direction, if only the tube convection and length truncation processes were active, such that eventually only the center portion of the tube is highly stretched to give rise to an aligned tube. However, with constraint release motion active, the center portion of the tube continually misaligns, and the small loops so formed are continually stretched out to form the anisotropic random walk that is the asymptotic state of the present model in the high shear rate limit.
VI. LIVING MICELLES

For living micelles, the stress relaxation term in the absence of CCR is not diffusive reptation along the tube, but is instead well approximated by local, single-exponential relaxation [Cates (1990)]. There is no distinguished place along the chain as the chain end for reptation, since a tube segment must wait for a break to occur sufficiently near it to relax.

Likewise, the fixed-length constraint may be regarded as killing off segments randomly, depending on whether or not they are currently near an end. Indeed, the fixed-length constraint itself collapses down from \( f_d \text{str}(s.s) = \text{const} \) to \( \text{str}(0) = (0) = \text{const} \).

The living micelle tube does undergo constraint release Rouse motion. Note that the CCR term in Eq. (22) in fact makes no reference to chain length, nor does the coefficient of isotropic diffusion in the \((s.s')\) plane depend on monomer position. Thus for living micelles, we expect a collapse of Eq. (22) to a one-dimensional partial differential equation in which \( x = s - s' \) is the dependent variable.

The resulting equation of motion is in fact much simpler than Eq. (22)

\[
\frac{\partial f}{\partial t} = \kappa \cdot f + f \cdot \kappa^T - \tau^{-1}(f - f_{\text{eq}}) + (3/2) \frac{\partial^2}{\partial x^2} (f - f_{\text{eq}}) - \lambda \left( 2 + x \frac{\partial}{\partial x} \right) f. \tag{39}
\]

The first two terms of this equation are evidently the same convective terms as before; the third term is the simple exponential relaxation to equilibrium; the fourth term is CCR Rouse diffusion in the difference coordinate \( x \). The final term expresses the effects of the constant-length constraint on the tube tangent correlator as a function of the difference variable \( x = s - s' \), in which small differences in \( x \) are continually advected to larger differences under the relabeling that follows retraction. The term \( 2\lambda f \) arises from the “stretching” of the tangent vectors, i.e., from the effect of relabeling after retraction on the derivatives \( \partial / \partial s \) and \( \partial / \partial s' \), just as in Eq. (22).

We expand the deviatoric part of \( f_{\alpha\beta}(x) \) in a Fourier series about the equilibrium stress \( f_{\alpha\beta}^{\text{(eq)}}(x) = (a^2/3) \delta(x) \delta_{\alpha\beta} \)

\[
f_{\alpha\beta}(x) - f_{\alpha\beta}^{\text{(eq)}}(x) = a^2/3 \sum_{p > 0} (f_p)_{\alpha\beta} \cos(p \pi x / n)
\]

\[
(f_p)_{\alpha\beta} = 3/(na^2) \left\{ \int_{-n}^{n} dx \cos(p \pi x / n) [f_{\alpha\beta}(x) - f_{\alpha\beta}^{\text{(eq)}}(x)] \right\}
\]

and Fourier transform the equation of motion to obtain

\[
\frac{\partial f_p}{\partial t} = (\kappa + \kappa^T) + \kappa \cdot f_p + f_p \cdot \kappa^T - \tau^{-1} f_p - \lambda \left( 2 \delta + 2 f_p + \frac{c_h p^2}{n^2} f_p + \sum_{p'} J_{pp'} \left( \delta + f_{p'} \right) \right). \tag{41}
\]

Here the coupling matrix \( J_{p,q} \) is given by

\[
J_{pp'} = \begin{cases} \frac{2p^2(-1)^{p+p'}}{p^2-p'^2} & p \neq p' \\ 1/2 & p = p' \end{cases}
\]

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\]
The fixed-tube-length constraint becomes $\Sigma \text{tr} f_p = 0$, since the equilibrium part of $f$ already fulfills the constraint. By applying the operator $\Sigma f_p (\text{tr})$ to the equation of motion, we obtain an explicit expression for $\lambda$

$$\lambda = \frac{2\kappa \Sigma f_p}{6n + c_h/n^2 \Sigma f_p \text{tr} f_p + \Sigma f_p J_{p,p'} (3 + \text{tr} f_p)}.$$  

Following the approach of Sec. II, we obtain an expression in this case for the deviatoric part of the stress tensor as

$$\delta \sigma_{\alpha\beta} = \frac{c T}{N_p n} \sum_{p=1}^{n} (f_p)_{\alpha\beta}$$

and for the structure factor as

$$S(q) = \int_0^{n} ds\, ds' \exp \left[ -a^2 q_{\alpha\beta} (6n \left[ (\delta_{\alpha\beta} + (f_p)_{\alpha\beta}) (s' - s)^2 ight. 

\left. + 4(n/\pi)^2 \sum_p (\delta_{\alpha\beta} + (f_p)_{\alpha\beta}) (1 - \cos(p \pi (s' - s)/n)/p^2) \right. \right].$$

Our model again takes the form of coupled ordinary differential equations for mode amplitudes, which we solve numerically. The results are qualitatively similar to the conventional unbreakable polymer case, with one important exception: the shear thinning is now strong enough to induce a maximum in the shear stress. Figure 10 shows the steady-state shear stress $\sigma_{xy}(\dot{\gamma})$ for the living micelles with $n = 20$ and various values of $c_h$. For $c_h$ less than about $c_h = 4$ (or $c_p = 0.27$), the viscosity exhibits a region of shear thinning with exponent less than $-1$. Hence there is a range of values $1 < c_h < 4$ of the phenomenological parameter $c_p$, which describes how often a tube segment actually hops when a constraint is released, for which we predict the absence of a stress maximum for conventional polymers and the presence of a stress maximum for living micelles.
VII. STEP STRAIN; DAMPING FUNCTION

Step strains are never instantaneous. We may consider "ultrafast" or "fast" step strains, at shear rates always large compared to the reptation time $\tau_s$. If the step strain is ultrafast, the chains are initially stretched and then quickly retract in their tubes. There are issues of principle to be resolved in extending a tube-based picture of stress relaxation to this regime, yet this is the regime typical of measurements of the damping function. If we confine ourselves to merely fast step strains, the chains do not stretch, but maintain fixed tube length adiabatically. It seems initially plausible that the state of the system reached a time $t_s$ after an ultrafast step strain which must be the same as the state reached after a fast step strain of the same amplitude. However, we will find both evidence and arguments in the following that CCR is effective during the step strain only in the fast case.

The present model implies that convective constraint release is operative during a fast step strain. Thus the damping function $h(\gamma)$, which is the factor $\sigma(\gamma)/\{\gamma \sigma'(0)\}$ by which the stress after the step strain is lower than expected from linear response, must differ from the Doi–Edwards result. Since the Doi–Edwards result for $h(\gamma)$ is in good agreement with experiment (over a range of strains up to 10 [Doi and Edwards 1986]), we might hope that the new damping function incorporating the effects of convective constraint release is not too different.

To compute the damping function, we drop all terms in the equation of motion Eq. (22) resulting from reptation. Then, because the constraint release Rouse rate is explicitly of order the shear rate (from $\kappa$), we may regard the equation of motion as describing evolution with strain rather than with time. We may then compute a new tube orientation "$Q$ function" to replace that of Doi–Edwards, which incorporates not only the processes of affine tube convection (via the terms $\kappa \cdot f + f \cdot \kappa^T$) and fixed tube length (via the constraint terms), but also constraint release Rouse motion. From this, we may compute the damping function $h(\gamma)$.

As a preliminary, if we drop not only the reptation terms but also the constraint release terms, Eq. (22) can be solved exactly, with the isotropic initial condition of Eq. (23). The result is

$$\mathbf{f}(s, s', t) = \mathbf{E}(t) \cdot \mathbf{E}^T(t) / \mathbf{E}(t) : \mathbf{E}^T(t) a^2 \delta(s - s'), \quad (46)$$

where $\mathbf{E}(t)$ is the deformation tensor ($\partial \mathbf{E}/\partial t = \kappa \cdot \mathbf{E}$), with initial condition $\mathbf{E}(0) = 1$. (This approximate dynamical implementation of the constant tube length constraint is the same as in the Larson equation for stress evolution [Larson (1988)].)

The result Eq. (46) is equivalent to a factorization of the Doi–Edwards $Q$ function similar to the independent alignment (IA) approximation [Doi and Edwards (1986)]

$$Q_{\alpha\beta}^*(\mathbf{E}) = \langle (\mathbf{E} \cdot \mathbf{u})_\alpha (\mathbf{E} \cdot \mathbf{u})_\beta \rangle / \langle |\mathbf{E} \cdot \mathbf{u}|^2 \rangle, \quad (47)$$

where the brackets denote averaging of the vector $\mathbf{u}$ over the unit sphere.

Recall that the Doi–Edwards expressions for $Q$ with and without IA approximation are [Doi and Edwards (1986)]

$$Q_{\alpha\beta}^{(DE)}(\mathbf{E}) = \langle (\mathbf{E} \cdot \mathbf{u})_\alpha (\mathbf{E} \cdot \mathbf{u})_\beta / |\mathbf{E} \cdot \mathbf{u}| \rangle / \langle |\mathbf{E} \cdot \mathbf{u}| \rangle, \quad Q_{\alpha\beta}^{(IA)}(\mathbf{E}) = \langle (\mathbf{E} \cdot \mathbf{u})_\alpha (\mathbf{E} \cdot \mathbf{u})_\beta \rangle / \langle |\mathbf{E} \cdot \mathbf{u}|^2 \rangle. \quad (48)$$
From each $Q$ function a corresponding approximation to the damping function $h(\gamma)$ is obtained, by

$$h(\gamma) = \frac{Q_{xy}(\gamma)}{\gamma Q_{xy}'(0)}. \quad (49)$$

From this and Eq. (46) we have $h^*(\gamma) = 1/(1 + \gamma^3/3)$. Both $h^{(DE)}(\gamma)$ and $h^{(IA)}(\gamma)$ must be numerically evaluated. All three functions are quite close to each other, as shown in Fig. 11. All three approach a $-2$ power law for large shear strains. Experimental data of Osaki et al. (1982) are in rather good agreement with this general trend, up to total strains of 10–20, as shown in Fig. 11.

Calculating the damping function with and without CCR is instructive (see Fig. 12). Clearly, for the same reason that CCR remove the stress maximum in steady flow, the predicted values for the stress in step strain are also larger, and the damping function consequently weaker, than in Doi–Edwards theory. At high strains the prediction seems no longer to agree with data on model polymers. However, the calculation of the damping function with CCR refers to a very particular condition: the forward step strain is done

![FIG. 11. Doi–Edwards (DE, solid), independent alignment (IA, dotted) and Larson-model (L, dashed) damping functions vs shear rate, compared to data of Osaki et al. (1982).](image1)

![FIG. 12. Early-time damping function vs shear rate for $c_h = 0$ and $c_h = 1$, compared to Doi–Edwards damping function (dashed) and data of Osaki et al. (1982).](image2)
much faster than reptation, but also much slower than the Rouse time, since the contour length has been kept constant here. In practice, experiments in step strain are not typically done at this fast rate, but at an ultrafast rate in which the chain stretches throughout the strain almost affinely. In these circumstances there will be NO CCR during the forward strain, since there is no retraction. There is the possibility of CCR during the subsequent fast chain retraction, but in this phase of the dynamics there is no forward shear to convect the new tube conformations and produce extra shear stress. So although CCR occurs, the mechanism for translating it into extra stress is absent. Without further calculation at this stage, it is possible that a full theory incorporating stretch actually predicts a STRONGER damping function than Doi–Edwards, since the Rouse tube relaxation will only add to the overall stress relaxation on retraction. As Mead et al. (1998) have pointed out, in the case of strong stretch it is likely that the tube Rouse steps are suppressed by the higher tension in the retracting chain. Experiments on step strain in the fast (but not ultrafast) case would therefore be an interesting test of this work, but also point forward to the need to incorporate stretch. This we leave to the future.

VIII. CONCLUSIONS

We have presented a microscopic theory of the mechanism introduced by Marrucci called convective constraint release (CCR), and its effect on the nonlinear rheology of polymer melts and concentrated solutions of living micelles. In CCR, entanglements are released when the free end of a chain retracts past an entangling chain. Flows of finite amplitude would typically stretch chains were it not for the fast retraction of chains within their tubes; this continuing retraction gives rise to a finite rate of CCR.

Our theory applies to general flow types, so long as the deformation rates are not sufficient to stretch the chains, i.e., for deformation rates smaller than the inverse Rouse time $1/\tau_r n^2$ [$\tau_r$ is the relaxation time of one tube segment, and $n$ is the number of tube segments in the chain]. Since the reptation time scales as $\tau_r n^3$, this gives a range of deformation rates of width $n$ for which the flow behavior is non-Newtonian and our theory applies.

It is not correct to assume, as previous authors have done, that a single CCR event completely relaxes stress on an entangled segment. This was made clear by Viovy et al. (1991) in another context, who pointed out the existence of the constraint release Rouse time. The time for a tube conformation to completely relax by constraint release motion is $n^2$ times inverse hop rate.

Nonetheless, our more careful treatment gives very similar rheological behavior to the previous work. This is because only a few CCR events per entanglement segment are needed to stave off the catastrophic shear thinning of the Doi–Edwards model. The operative mechanism is that CCR events misalign tube segments, and keep them from becoming completely aligned along the flow direction. Thus there can be some remaining shear stress held by the tube even at high shear rates.

The details of the stress relaxation mechanism that competes with the alignment are important. When we extend our theory to the case of living micelles, for which stress relaxation is essentially a local process of waiting for a break in the chain to occur sufficiently nearby, we find a stress maximum. This result is also in agreement with experiments, which find shear banding and other phenomena in living micelles consistent with a stress maximum, but no such behavior in conventional polymer melts.

The prediction of a maximum in the shear stress for living polymers holds for the hopping rate efficiency $c_p$ (the only adjustable parameter in our theory) less than about 0.27. In contrast, there is no stress maximum in the case of conventional polymers for $c_p$. 

greater than about 0.07; thus for any choice of $c_\gamma$ in the range $0.07 < c_\gamma < 0.27$, we
have no stress maximum for conventional polymers and a stress maximum for living
polymers, as observed.

In addition to rheological information, our calculations give the instantaneous structure
factor of chains in the flow. Neutron-scattering measurements have been made of
$S(q)$ for deuterated chains in melts frozen in the act of flowing. These results give
additional information about the way the chains move and relax in the flow that cannot be
determined from the stress tensor alone. We can also compute scattering from chains with
labeled ends or centers, which could reveal even more detail, such as the greater extent to
which the middle of a chain is aligned by flow as compared to the ends.

Several authors have proposed in various contexts mechanisms by which the tube
diameter or cross section becomes dependent on the applied strain in the entanglement
network [Mhetar and Archer (1999) and Rubinstein and Panyukov (1997)]. We have
explicitly neglected any such mechanisms, in order to examine the consequences of CCR
in isolation. According to these authors, effects on the tube cross section would set in at
shear rates of order the inverse reptation time (i.e., when the tubes become significantly
aligned). Therefore, if these effects are real, they would be active in the same regime of
deformation rates as CCR. Combining these effects remains a subject for future work.

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