Segment connectivity, chain-length breathing, segmental stretch, and constraint release in reptation models. I. Theory and single-step strain predictions

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A self-consistent reptation theory that accounts for chain-tube interactions, segment connectivity, chain-length breathing, segmental stretch, and constraint release is proposed. Simulation results are compared semiquantitatively to experimental observations in single-step strain flows. Since stochastic simulation techniques are used, no approximations, such as independent alignment or consistent averaging are needed to obtain results. The simulation results show excellent agreement with experimental trends in shear and normal stress relaxations, including the second normal stress difference, well into the nonlinear regime. For most of these experiments, the original Doi and Edwards theory, which incorporates independent alignment or consistent averaging, is not satisfactory. In the following companion paper, we show how the model is capable of describing double-step-strain flows for all stress components. Subsequent papers show excellent agreement for the inception of steady shear flow, and steady shear flow. © 1998 American Institute of Physics. [S0021-9606(98)52746-8]

I. INTRODUCTION

To describe the effects of topological constraints on chain motion in concentrated systems, de Gennes introduced the idea of reptation to find scaling laws for a polymer chain in a gel. The idea was later extended by Doi and Edwards (DE) to describe the viscoelastic behavior of entangled polymer chains. Roughly speaking, because of entanglements, it is proposed that it is easier for a polymer chain to move in the direction along its backbone than in the transverse direction, except for its two ends which can move in any possible direction. de Gennes called this idea “reptation.”

In addition to the proposed reptation mechanism, the original calculations by Doi and Edwards made the following assumptions: (i) the effects of chain connectivity are neglected (“single-segment theory”), (ii) the tube is a static object that relaxes at the ends only, even though it is made of other reptating chains (“neglect of constraint release”), (iii) the contour length of the coarse-grained chain does not stretch during flow (no “segmental stretch”), (iv) the distance between entanglements in the tube does not change during flow (“independent alignment”), (v) the velocity of the tube is neglected in calculating the frictional forces between the chain and the tube (accounted for approximately in the “rigorous” model of Doi and Edwards), and (vi) there is no fluctuation in the chain length (no “chain breathing”).

Note that most of these assumptions are made for mathematical convenience, typically in order to decouple the motions of the individual segments in the same chain. Subsequent workers have tried to improve on some of these assumptions, as discussed in Sec. IB.

A. Doi–Edwards model with independent alignment

Within the reptation picture and these assumptions, the dynamics of a single tube segment was assumed by Doi and Edwards to be

\[
\dot{u} = (\delta - uu) \cdot \kappa : u,
\]

where \( u \) is the unit vector describing the orientation of the tube segment, \( \kappa = (\nabla u)^T \) is the transpose of the velocity gradient, and \( \delta \) is the unit tensor. One sees that the tube segment first deforms affinely with the imposed flow, and then the projection operator in the parentheses returns the length of the vector back to unity. Hence, the length of each tube segment is held constant, so that the distance between entanglement points stays constant. This assumption is consistent with the assumption of constant contour length, but not consistent with the assumption of affine motion for entanglement points followed by chain retraction.

It is often pointed out that the model assumes instantaneous retraction of the chain length. However, the physical picture does not suggest that each tube segment retracts back to its equilibrium length; this assumption is made only for mathematical convenience.

The dynamics of the chain within the tube are described by a force balance on the chain, where inertia is neglected. The only two forces on the chain are the friction of the chain with the tube, and the Brownian forces. If \( s \) is the distance along the contour to a point on the chain that occupies the tube segment, measured from an arbitrarily chosen point on the tube, then the dynamics are described by the Langevin equation.
\[ 0 = -\xi_{\text{segment}} Z ds + \sqrt{2kT\xi_{\text{segment}}} dW_t, \]  

where, \( \xi_{\text{segment}} \) is the friction coefficient between a segment in the primitive chain and the tube, \( Z \) is the number of tube segments, \( k \) is Boltzmann’s constant, \( T \) is the absolute temperature, and \( W_t \) is a Wiener process. Note that the total friction coefficient of the chain is \( Z\xi_{\text{segment}} \). We see that the friction force contains the chain segment velocity \( ds \), instead of the chain velocity relative to the deformation-induced tube velocity. For further discussion, see the “rigorous” model below, and the equation of motion in the model suggested here—Eq. (5).

Finally, these two motions are coupled through the boundary condition,

\[ u \text{ takes random orientation when } s = 0, Za, \]

where \( a \) is the equilibrium length between entanglement points. This boundary condition specifies that the chain takes random orientation when it reptates out of the tube.

### B. Modifications

Many of these assumptions have been reconsidered in subsequent works, usually only in approximate ways. We give a short summary of the modifications important for the model considered here.

#### 1. “Rigorous” model

Doi and Edwards\(^5\) derived another equation for the dynamics of the chain in the tube that takes into account the tube velocity in the chain-tube friction, called the “rigorous” reptation model,

\[ 0 = -\xi_{\text{segment}} Z \int_{s_{ad}}^{s} \kappa \langle u(s')u(s') \rangle ds' dt \]

\[ + \sqrt{2kT\xi_{\text{segment}}} dW_t, \]

where the angular brackets \( \langle \cdots \rangle \) indicate an ensemble average. The integral is meant to account for the relative motion from the stretching of the tube. Again, for mathematical convenience, Doi and Edwards wished to decouple the dynamics of the different segments along the chain. Hence, they made a consistent-averaging approximation, and used the average orientations of segments, and not the instantaneous values taken along the chain. Few calculations have been made for this model.

#### 2. Additional chain-tube interactions

Jongschaap and Geurts (see Ref. 6, for example) considered more detailed interactions between the chain and the confining tube. In particular, they considered the increased tension in the chain that is caused by the friction between the chain and the tube. A lucid description of the physical model formulated by the mathematics can be found in Öttinger.\(^7\)

Pearson et al.\(^8\) considered the effect of chain stretching in predictions of the Doi–Edwards model. Their calculations showed that the overshoot in first normal stress, which is observed experimentally, could be described by reptation models when chain stretching is taken into account. However, the model they used is still a single-segment theory only, and certain consistent-averaging and decoupling assumptions were necessary in the derivation, for mathematical tractability. Despite these assumptions, the model is difficult to calculate. Also, the approximations used in the derivation have led some workers to draw incorrect conclusions.\(^9\) For example, as we show in a subsequent paper, chain stretching plays an important role in predicting reasonable values for the power-law region of the viscosity and first-normal-stress-coefficient curves.

### 3. Segment connectivity

Doi\(^10\) first recognized that segment connectivity was essential for describing reversing flows. Osaki et al.,\(^11\) Venerus and Kahvand\(^12,13\) and Brown and Burghardt,\(^14\) carried out double-step-strain experiments where the second step was taken in the reverse direction. These data showed that the original Doi–Edwards model (and presumably also the “rigorous” model) failed at describing the stresses following the second step. Doi\(^10\) recognized that segment connectivity was important in flows with strain reversals for the following reasons: Following the first step, chain segments on the ends of the chain relax first from the retraction and reptation mechanisms, while the inner segments remain untouched at early times following the strain. If the second step has the same magnitude in strain, but the opposite sign, the inner segments are now returned to their original configuration, hence their contribution to stress is once again isotropic (on average). However, the outer segments have relaxed to an isotropic state following the first step, and now contribute once again to the stress following the second step. Using these ideas Doi\(^10\) derived an equation that was able to describe the shear stress and the first normal stress measured by Osaki et al.,\(^11\) Venerus and Kahvand,\(^12,13\) and Brown and Burghardt\(^14\) very well, when the second step is imposed after the “retraction” time of the chains. However, the derived equation is valid only in double-step strains, and did not describe the second normal stress difference satisfactorily; also, if the second step was made before the “retraction,” comparison with data was unsatisfactory. Hence, chain stretching appears to be important for some rapid, multidirectional strains.

A model that incorporates segment connectivity was considered in a full-chain model by Hua et al.\(^15\) They found that the number of entanglements felt by a chain could be dramatically decreased by an imposed flow field. The equation derived by Doi for double-step strain was confirmed by the full-chain theory. However, the chain lengths neither stretched nor fluctuated in flows.

Ianniruberto and Marrucci called such a loss of entanglements observed in the full-chain theory “convective constraint release” (CCR). They included this effect in a single-segment theory that added loss of entanglements in an \textit{ad hoc} way.\(^16\) They studied the effect of CCR on the power-law region and found an improvement over the original Doi–Edwards constitutive equation. However, the theory has no chain stretching or chain-length fluctuations, and the CCR mechanism is only approximate. Also, since the theory does not contain information about the full chain, it could not be expected to perform well in double-step strain predictions.
4. Chain-length breathing

It is well known that reptation models predict the incorrect scaling law for the dependence of the longest relaxation time constant on molecular weight. Doi was the first to recognize that chain-length breathing could be important in correcting the discrepancy between the original model and experiment. Thus, he considered a Rouse chain trapped in a tube at equilibrium. Using a variational technique, he estimated the new time constant for the model, and indeed found an improvement in the scaling prediction. Ketzmerick and Öttinger performed an “exact” numerical solution of Doi’s model (a generalized Brownian dynamics simulation), and found results that were consistent with the experimentally observed scaling exponent of 3.4. However, both of these works consider chains only at equilibrium.

5. Constraint release

Finally, many workers have also considered the importance of relaxation mechanisms in the tube that do not arise from motion of the probe chain, but rather motion from the surrounding chains. We point out only the works of Tsenoglou and des Cloizeaux (see also Ref. 20), who derived a very successful polydispersity mixing rule based on the idea of “constraint release.” However, these derivations are very crude, since constraint release dynamics require information about segment connectivity, and chain-chain interactions that are not present in the model. More important, the model is used only for chains at equilibrium, or for linear viscoelasticity predictions.

We note that the work of Curtiss and Bird (see Ref. 21, and references therein) appears to have been motivated, at least in part, by an attempt to create a single, self-consistent model with stochastic dynamics similar to that proposed for the original Doi and Edwards model. However, since a different physical picture was used for the derivation, their model does not contain the modifications enumerated above.

From this short synopsis one can see that there exists a number of different reptation models that are valid only in certain cases, that make different approximations, and that can describe only some sets of data. To date, there is no single, self-consistent reptation theory that can describe all of the major trends in data even qualitatively. Hence, it is impossible to judge the merits of the reptation picture, since one can never be sure if the approximations or the picture itself is to blame for discrepancies with experiment.

Here we wish to reconstruct the model based on the original physical picture for reptation, but we remove those assumptions and approximations employed in previous works described above. That is, while still sticking with the picture of a coarse-grained, elastic polymer chain confined in a tube, we incorporate into the model the effects of chain-tube interactions, segment connectivity, segmental stretching, chain-length fluctuations and constraint release in a self-consistent manner without introducing any approximation to solve the model.

Using the simulations, we are then in a position to make discerning comparisons with data. Importantly, the calculations we show have only two adjustable parameters: the number of entanglements at equilibrium, and the number of beads in the elastic chain. There exist other parameters; however, all but one of these can be estimated a priori from the chemistry of the chains—and these two are obtainable from linear viscoelasticity. The results that we show here are made dimensionless by the single input time constant, and a characteristic length scale. Section II B describes the parameters in greater detail.

Here we consider only single-step-strain flows. Different strain histories, including double-step strains, and the inception of steady shear flow will be discussed in subsequent articles. We show that, surprisingly, the simulations are able to describe every observed steady and transient trend in these data for shear stress, first normal stress, and second normal stress. We tentatively conclude, awaiting quantitative comparison and elongational flow calculations, that the reptation picture is correct.

II. THEORY

Construction of the model consists of two parts: The first part describes the chain motion, which is governed by a set of Langevin equations; the second part prescribes the tube motion, which consists of two superimposed motions—a simple, deterministic, convection process, and a random, instantaneous constraint release process. The tube, which confines the motions of the polymer chain, is assumed to be convected with flow and be deformed affinely by the flow field. In addition, the tube can undergo a constraint release process anywhere along its contour. Its orientation is described by a finite set of connector vectors \( \{\mathbf{u}_i\} \), whose number is stochastic. The chain is described by \( N \) position scalars \( \{s_i\} \), which define the location of all beads within the tube. These scalars indicate the distance of each bead along the contour length measured along the path of the tube from an arbitrarily chosen origin.

A. Governing equations

The orientation of a polymer chain, which is modeled as a bead-and-spring chain, is defined by the orientation of its confining tube. The only way a chain can escape from its confining tube is by random motion, or reptation, at the two ends. The length of the chain is determined by a Langevin equation. Note that, whereas the tube deforms affinely, the chains are not convected affinely with the flow because of the assumed frictional force with the tube. Thus, to find the length and orientation of a chain, one must solve the equations of motion for both the chain and the tube simultaneously.

First, we write the stochastic equation of motion (Langevin equation) for the \( N \) elastic chain beads:

\[
0 = -\zeta [\dot{s}_1 - v_T(s_1)] + F_S^1 + F_{1\text{s}} + F_{1\text{B}},
\]

\[
0 = -\zeta [\dot{s}_\nu - v_T(s_\nu)] + F_S^\nu - F_S^{\nu-1} + F_{\nu\text{s}} + F_{\nu\text{B}},
\]

\[
\nu = 2, \ldots, N-1
\]

\[
0 = -\zeta [\dot{s}_N - v_T(s_N)] - F_S^{N-1} + F_{N\text{s}} + F_{N\text{B}},
\]

where

\( \{s_i\} \) is the contour length measured along the path of the tube from an arbitrarily chosen origin.

\( \nu \) is the index for the beads of the chain.

\( F_{1\text{B}}, F_{\nu\text{B}} \) are the frictional forces.

\( F_S^i \) is the force due to segmental stretching.

\( F_{\nu\text{s}} \) is the force due to the constraint release at bead \( \nu \).

\( F_{1\text{s}} \) is the force due to the constraint release at bead 1.

\( \zeta \) is the friction coefficient.

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where \( s_i \) is the position of the \( n \)th bead measured along the contour length of the tube from an arbitrarily chosen origin on the tube; \( v_T(s_i) \) is the tube velocity in the tangential direction along the tube relative to the chosen origin at the location of bead \( n \); \( F^S \) is the spring force connecting the \((n+1)\)th and \(n\)th beads; \( F^B \) is the Brownian force acting on bead \( n \); \( W_p \) describes the Wiener process for bead \( n \) and satisfies \( \langle W_p \rangle = 0 \) and \( \langle W_p(t)W_p(t') \rangle = \min(t,t') \delta_{tt'} \); the friction coefficient between an elastic-chain bead and the tube is \( \zeta \); \( F^E \) is the excluded volume force that prevents the beads from passing through one another in the tube, and \( N \) is the number of beads in the elastic chain. Here we assume that the excluded-volume potential is a hard-sphere well, and treat it with a reflecting boundary condition. Note that the spring constant \( H \) can be a function of the relative extension between the two adjacent beads [for example, as with a finitely extensible nonlinear elastic (FENE) spring].

We subtract the \( n = n \)th equation from the \( n = (n-1) \)th one to construct another set of equations:

\[
0 = -\zeta [s_i - v_T(s_i)] + F^S_i + F^B_i,
0 = -\zeta [Q^k_i - (v_T(s_{i+1}) - v_T(s_i))] + (F^S_{i+1} - 2F^S_i + F^B_{i+1} - F^B_i), n = 1, ..., N-2,
0 = -\zeta [Q^k_{i-1} - (v_T(s_{i-1}) - v_T(s_i))]
+ (2F^S_{i-1} - 2F^S_i - F^B_{i-1} + F^B_i),
\]

where \( Q^k_i := s_{i+1} - s_i \) is the connecting scalar for the \( i \)th spring. Conceptually, Eq. (6) can be divided into two parts: The first equation describes the chain motion relative to the tube at one end, and the remaining equations describe the motion of the springs connecting two adjacent beads.

The relative tube-stretching velocity at two beads, \( v_T(s_{i+1}) - v_T(s_i) \), can be determined analytically from the imposed flow field and the instantaneous orientation of the tube where the beads are located. For convenience, we give here the general formula for the velocity for a continuous chain \((N \rightarrow \infty)\) relative to the chosen origin, even though the chain is actually discrete:

\[
v_T(s) = \kappa \int_0^s \frac{u(s')u(s')}{|u(s')|^2} ds'.
\]

For example, for the case sketched in Fig. 1, the relative tube velocity of the two beads is given by

\[
v_T(s_{i+1}) - v_T(s_i) = \kappa \left[ \frac{u_{i+k} - u_{i+k-1}}{|u_{i+k-1}|^2} Q^k_i + \frac{u_{i+k} - u_{i+k+1}}{|u_{i+k+1}|^2} Q^{k+1}_i \right],
\]

where \( u_k \) is the orientation vector of the \( k \)th tube segment; and \( Q^k_i \) is the part of \( Q_i \) confined in the \( k \)th tube segment.

The orientation of the tube segment during deformation from time \( t' \) to time \( t \) can be found by the deterministic time evolution described by

\[
u_k(t) = E(t,t') \cdot u_k(t'),
\]

where \( E(t,t') := \exp[\int_{t'}^{t} \kappa(t') dt'] \) is the deformation gradient tensor. The hooks \([\cdot] \) indicate a time-ordering operator (see Ref. 22, p. 389, for an example).

To be consistent with the original picture, we assume a Kramers-type expression for the polymer contribution to the stress (again for a continuous chain),

\[
\varphi = (N-1)nkT \delta - n \left( \int HQ(s) \frac{u(s)u(s)}{|u(s)|^2} ds \right),
\]

where \( \delta \) is the unit tensor, \( n \) is the number density of polymer, and the integral is over the entire length of the chain. For example, the integral evaluated over the length of the tube occupied by chain segment \( i \) of the discrete chain shown in Fig. 1 is given by

\[
HQ_i \left[ \frac{Q^k_i}{|u_{i+k-1}|^2} + \frac{Q^{k+1}_i}{|u_{i+k+1}|^2} \right]
\]

We have obtained a complete set of equations for the chain and tube dynamics, Eqs. (6)–(9). In the simulation, one can first find the tube orientation via Eq. (9), and then solve Eqs. (6) and (7) to obtain the new chain lengths and bead locations.

### B. Model parameters

The model contains five fundamental parameters: the friction coefficient \( \zeta \), the number of beads \( N \), the Kuhn step length \( a_k \), the number of Kuhn steps \( N_k \), and the length of an equilibrium tube segment \( a \). Of these, \( a_k \) and \( N_k \) can be estimated \( a \) priori from knowledge about the chemistry of the chain. The parameters \( a \) and \( \zeta \) are found from the average number of entanglements at equilibrium \( \langle Z \rangle \) and the reptation time constant \( \tau_a \), given by Eq. (20). Only \( N \) does not appear in the original Doi–Edwards theory.

We find the average number of entanglements from the average elastic chain length at equilibrium \( \langle L \rangle \),

\[
\langle Z \rangle = \frac{\langle L \rangle}{a}.
\]

We need to find the average length of the chain at equilibrium. For the moment we assume Hookean connector springs that are confined to the tube. The equilibrium distribution function for a connector is the Maxwell–Boltzmann relation,
The result shows how the chain length grows with excluded volume, which acts as a kind of "pressure" inside the tube.

Therefore, the average length of a connector at equilibrium is

\[
\langle Q \rangle_{eq} = \int_{0}^{\infty} Q \exp \left[ -\frac{H}{2kT} Q^2 \right] dQ = \sqrt{\frac{2kT}{\pi H}}.
\]

The Hookean spring constant is given by

\[
H = \frac{3kT(N-1)}{N_K a_K^2},
\]

when we assume that the Kuhn steps are evenly distributed among elastic chain segments. Combining these last two equations with Eq. (12), we find

\[
\langle Z \rangle_{eq} = \frac{(N-1)\langle Q \rangle_{eq}}{a} = \frac{(N-1)}{a} \sqrt{\frac{2kT}{\pi H}} = \sqrt{\frac{2}{3\pi}} \left( \frac{a_K}{a} \right) \sqrt{N_K(N-1)}.
\]

Note that the chain length grows with \( N \) as well as with \( N_K \).

Therefore, our five fundamental parameters are determined by specification of \( a_K, N_K, N, \langle Z \rangle_{eq}, \) and \( \tau_d \). We find \( \langle Z \rangle_{eq} \) from the ratio of molecular weight to entanglement molecular weight: \( \langle Z \rangle_{eq} = M/M_e \). We can estimate \( \tau_d \) from a linear viscoelastic experiment, such as \( G(t) \). We treat \( N \) as an adjustable parameter, also while fitting \( G(t) \).

However, we do not expect any quantitative dependence on \( N \), since the beads simply provide a discretized approximation to a continuous elastic chain. The discretization provides an additional length scale that is smaller than that resolved accurately by the model.

Therefore, our two adjustable parameters are fit from linear viscoelasticity alone. Finally, if we use finitely extensible connectors in the chain, we introduce the parameter \( b \), which is specified by the already-determined parameters: \( b = 3N_K(N-1) \).

III. SIMULATION ALGORITHM

In this section, we describe the stochastic simulations used to obtain rheological properties. We first introduce the stochastic algorithm for finding the chain length and orientation, followed by a discussion of how constraint release is accomplished in the simulation.

A. Stochastic algorithm

The discretized equations corresponding to Eq. (6) employing first order, Eulerian forward schemes are:

\[
f_{eq}(Q) = \sqrt{\frac{2H}{\pi kT}} \exp \left[ -\frac{H}{2kT} Q^2 \right], \quad 0 \leq Q = \infty.
\]

Therefore, the equation of motion is

\[
\Delta \tilde{s}_i = -\frac{H}{\xi} Q_i \Delta t + \sqrt{2kT \xi \Delta t} \xi_1.
\]

The algorithm is simulated in the following way.

(i) First, we make the length and time dimensionless by the characteristic length \( \sqrt{kT/H} \) and the characteristic time \( \lambda_H := \xi/4H \), respectively. We have already found that the average equilibrium length of a chain segment, which, when made dimensionless is \( \sqrt{2/\pi} \) if a Hookean spring is used as the connector. The ratio \( N/(Z)_{eq} \) is chosen to be 3 for most of the simulations, or is otherwise specified. Thus, once we pick a value for \( N \), the total equilibrium chain length can be found, and the average length of each tube segment can be calculated. For a chain of FENE connectors, a numerical procedure is used. Since the equilibrium chain length is stochastic, we first average the chain length over the whole ensemble of chains, and then divide the average chain length by \( \langle Z \rangle_{eq} \) to obtain the average equilibrium tube segment length. For the same reason, the number of tube segments for each chain is stochastic and can be slightly different from the

\[
Q_i(t+\Delta t) = Q_i(t) + (v_T(s_2) - v_T(s_1)) \Delta t + \frac{H}{\xi} (Q_2 - Q_1) \Delta t + \sqrt{2kT \xi \Delta t} \xi_2.
\]

where \( \Delta \tilde{s}_i := [s_i - v_T(s_1)] \Delta t \), and \( \xi_i \) is a random number whose distribution satisfies zero mean and unit variance. Note that \( \Delta \tilde{s}_1 \) is the movement of the chain in the confining tube relative to one end. This quantity can be used to determine the chain reptation at that end of the tube. For example, when \( \Delta \tilde{s}_1 < 0 \), the chain reptates out of the tube by an amount of \( -\Delta \tilde{s}_1 \) at that end.

Since the governing equation for a chain segment length, \( Q_i \), is stochastic, the total chain length will also fluctuate with time. Such a situation is different from most previous works that assume constant contour length by neglecting the Brownian forces on the beads. Also note that the information concerning chain connectivity, chain retraction, reptation, and the chain-length fluctuations are all consistently incorporated into Eq. (17). These processes follow from the mechanical model and are not put in by hand. Also note that no Maxwell demons are employed to prevent the chain from collapsing to a point in the tube. Finally, predictions are made for general flow fields, unlike most previous modifications, which are either limited to equilibrium state or only a few types of flow fields.

The algorithm is simulated in the following way.
specified value of \((\langle Z \rangle)_{eq}\), even at equilibrium. During flow, the average number of entanglements can decrease dramatically.

(ii) The dimensionless time step size is chosen to be 2/5 for most of the simulations. Smaller values of the time step size have been tested, and the differences in predictions are found to be insignificant. During each time step, \(N\) uniform random numbers that satisfy the distribution of \(\xi_i\) are created by a pseudorandom number generator, and the equation set in Eq. (17) is solved to find \(\Delta s_j\) and \(Q_i\) for a new time step for each polymer chain. Note that during each time step, bead overlap can occur, and these beads are relocated according to the hard-sphere, excluded-volume potential by a simple reflection algorithm which takes into account multiple bead overlaps.

(iii) The length and orientation of each tube segment at a new time step is determined by Eq. (9).

(iv) If \(\Delta s_j\) found from step (ii) is less than zero, that end of the chain will reorient out of the tube by an amount \(-\Delta s_j\), in a random direction, and a new tube segment of that end should be created; otherwise, the chain segment on that end retracts and the tube segment at that end should be cut by an amount \(\Delta s_j\). Note that in order not to introduce artificial effects from the chosen time step size, when a new tube segment is created, we will first fill out the tube segment to its full length before another new tube segment is created. For a more detailed discussion concerning this issue, the reader is referred to Hua et al.\(^{15}\)

(v) After step (iv), if the new chain length turns out to be greater than the new tube length, then the chain segment on the other end will reorient out of the tube in a random direction, and a new tube segment should be created by an amount such that the total tube length equals the chain length. All beads are relocated hereafter using a redistribution subroutine such that the Langevin equation is solved, and no bead overlap occurs. Each bead could reside in a different tube segment at the new time step.

(vi) Having information of both the bead locations and the tube segment orientations, we can evaluate the polymer contribution to stress by Eq. (10).

### B. Constraint release

Constraint release has been found to be very important in describing experimental data for stress relaxation (see Refs. 18 and 19 and their subsequent papers), particularly for polydisperse systems. Marrucci\(^{23}\) accounted for constraint release in a reptation model by letting the tube diameter increase when the surrounding chains reptate. In the works of Tsenoglou\(^{16}\) and des Cloizeaux,\(^{17}\) the stress relaxation is assumed to result from the reptation of entanglement points (or the destruction of network junctions), and the idea is called “double reptation.” Both Tsenoglou’s and des Cloizeaux’s works were based on a single-step strain. Below, we consider a stochastic algorithm for constraint release that can be applied in general flow fields. It is important to note that our physical picture is new, and not a part of the original reptation picture. However, we believe it provides a dynamics whose picture is self-consistent with a chain in a matrix of other reptating chains. Nonetheless, other self-consistent constraint release mechanisms are possible.

Consistent with our mean-field picture and the time discretization of our simulation algorithm, we assume that whenever a tube segment is destroyed by reptation, constraint release for some other chain segment might result. To add the constraint release mechanism in our algorithm, we first note that the entanglements are continuously renewed and destroyed because of chain reptation. Thus, we must find a criterion determining whether or not the constraint on a certain chain segment should be released when another tube segment reptates. In order to do that, we first recognize that a newly created tube segment presumably will not impose any new constraint on those tube segments already existing, as is illustrated in Fig. 2. Based on this idea, we can implement the constraint release mechanism in our simulation algorithm by adding one extra step between steps (iv) and (v); whenever an end tub segment \(u_i\) is destroyed by reptation, we randomly pick a kink formed by two tube segments, \(u_{i}^j\) and \(u_{i+1}^j\), where \(i\) and \(j\) denote two different polymer chains. If the time of creation of the chosen tube segments by reptation, \(L_{u_{i}^j, u_{i+1}^j}\), is prior to that of the destroyed end segment, \(L_{u_{i}^j, u_{i+1}^j}\), then a constraint release will result; otherwise, there will be no constraint release. Once the constraint release occurs, we specify a new tube segment \(u_{i+1}^j\) according to

\[
u_{i+1}^j = u_{i}^j + u_{i+1}^j,\]

as is sketched in Fig. 3. We expect the results to be independent of ensemble size, since the number of tube segments being destroyed by reptation increases linearly with the ensemble size, whereas the probability of a tube being selected at random from a single destruction decreases inversely with ensemble size. Hence, the probability for a single tube segment to be selected for constraint release, which is the product of these two probabilities, is independent of ensemble size.

Note that during flow, the slip links, or entanglement points, in a single chain are destroyed by two mechanisms: CCR and double constraint release (DCR). However, the entanglement points are simultaneously created by both chain reptation and chain-length fluctuations. The number of entanglements for a single chain fluctuates, and the average number results from a competition of these processes. Dur-
The relaxation of shear stress, $\tau_{yx}$, is described by the nonlinear relaxation modulus, $G(t, \gamma)$, defined as

$$G(t, \gamma) := -\frac{\tau_{yx}}{\gamma},$$

(21)

where $\gamma$ is the magnitude of the imposed step strain. For most polymeric fluids, the nonlinear relaxation modulus is found to show separability into time- and strain-dependent parts over a wide range of strains:

$$G(t, \gamma) = G(t)h(\gamma),$$

(22)

where $G(t)$ is the (linear) “relaxation modulus” which contains information on the linear viscoelasticity of the fluid, and $h(\gamma)$ is the “damping viscoelasticity” representing the nonlinear part of the stress relaxation.

The single-step strain experiment is the simplest case to simulate, since both the tube and the chain are deformed affinely with flow under step strain, and the length and orientation of a chain can be determined analytically. Furthermore, the flow velocity terms, $u_{f}T_{f}$, in Eq. (17) drop out for $t>0$.

First, we compare the predictions of $G(t)$ obtained by the DE model, and by the simulation model with and without constraint release, where $G_{c} := (N-1)nkT$ is the plateau modulus. From Fig. 4 one can see that the stress relaxation predicted by the DE model drops off more quickly than those of the simulation model. This sudden drop is because the DE model has only a single relaxation mechanism (reptation), whereas in the simulation model several relaxation mechanisms including reptation, chain-length fluctuations and constraint release all contribute to the stress relaxation. We also observe that the incorporation of constraint release in the model enhances the stress relaxation. In fact, the predictions of zero-shear-rate viscosity, obtained by integrating $G(t)$ with respect to time shows that when constraint release is included, the value of the zero-shear-rate viscosity is found to decrease by a factor of approximately $3/5$.

To demonstrate the importance of constraint release, in particular for polydisperse polymer systems, we simulate a binary system, $N=11$ and 21 with equal weight density, and
compare the result with that obtained by the mixing rule.\textsuperscript{18,19}
Note that there is a subtle difference in the systems that Tsenoglou and des Cloizeaux have considered (see the discussions in Ref. 20). In our simulation, since constraint release occurs for both the mono- and polydisperse systems, we use Tsenoglou’s formula for the stress relaxation in a binary system:

\[ G(t_{\text{mix}}) = (w_1 \sqrt{G_1(t)} + w_2 \sqrt{G_2(t)})^2, \]

where \( w_i \) is the weight fraction for species \( i \); \( G_i \) is relaxation modulus for species \( i \) in a monodisperse system, and \( G_{\text{mix}} \) is the relaxation modulus for the mixture. In Fig. 5 we show the relaxation modulus for a binary mixing system obtained directly from the simulation (the solid line), and from Eq. (23) (the dotted line) using the simulation results of two monodisperse systems. From the comparison we find that the mixing rule agrees very well with the simulation result. That is, the simulation model should be capable of describing polydisperse system data in any flow once the relaxation modulus for the monodisperse systems are fit quantitatively. From here on, we consider only the cases where constraint release is included.

To show the effects of chain retraction on the shear stress relaxation, we plot \( G(t, \gamma)/G_e \) as functions of time for several different magnitudes of strains. From Fig. 6, we find that the shear stress relaxation exhibits two distinct regimes at early and long times for large strains. In these cases, the initial stress decay corresponds mostly to the chain retraction, and the decay at long times is mainly due to chain reptation. The results in Fig. 6 are in remarkably good agreement with the experimental results reported by Venerus and Kahvand.\textsuperscript{12}

The individual effect of chain retraction and reptation on stress relaxation is clear if one looks at the curve of \( G(t, \gamma)/G_e \) divided by the damping function \( h(\gamma) \) as shown in Fig. 7 using the same set of data as in Fig. 6. Here we see that the separability (or factorizability) is observed after a certain time, \( t/\tau_d \sim 0.3 \), which is roughly five times the Rouse relaxation time (or retraction time) range. A curve similar to Fig. 6 has also been obtained experimentally by Osaki \textit{et al.}\textsuperscript{11} Note that in a later version of the Doi and Edwards model\textsuperscript{5} a simple, but not self-consistent modification for chain retraction dynamics was introduced to describe the trend one observes in step-strain flows shown in Fig. 6. The modified DE model gives predictions in qualitative agreement with observed behavior in step strain flows, but cannot be applied to other flows.

In Fig. 8, we show predictions of the damping function for the DE models with and without IA approximation and the simulation model from Eq. (22). We see very close predictions for these models, and the predictions have been

\[ FIG. 5. \text{Stress relaxation modulus as functions of dimensionless time predicted by the simulations and the mixing rule.} \]

\[ FIG. 6. \text{Shear stress relaxation as functions of dimensionless time predicted by the simulations for several different magnitudes of strains: } \gamma = 0.25, 0.5, 1, 2, 5, 8 \text{ and 10.} \]

\[ FIG. 7. \text{Shear stress relaxation divided by the damping function as functions of dimensionless time using the same set of simulation data as in Fig. 6.} \]

\[ FIG. 8. \text{Damping function as functions of strain predicted by the DE models with and without IA approximation and by the simulations.} \]
found to be in fairly good agreement with experimental data for linear, narrow-molecular-weight-distribution systems (for example, see the comparison with a polystyrene in Ref. 25—p. 141).

Both the DE models with and without independent alignment approximation predict time-independent behavior of the normal stress ratio $-N_2/N_1$ for the single-step strain, where $N_1$ and $N_2$ are the first and second normal stress differences, respectively. However, it has been found experimentally that this ratio is actually time dependent and monotonically increasing.\(^{14,24}\) Furthermore, the value of the normal stress ratio at some later time was found to fall between the analytical values predicted by the DE models with and without IA approximation. In Fig. 9 we show a typical transient plot for the normal stress ratio, $-N_2/N_1$, where the shear strain $\gamma = 8$. From Fig. 9 we indeed find that the normal stress ratio is time dependent and increases with time at the early stage. When we plot the average values of $-N_2/N_1$ between the time interval $t/\tau_d = 0.01$ and 1.0 against the shear strains in Fig. 10, we find that the values of normal stress ratio always fall between the two limits given by the DE models, in close agreement with experiment.

In Fig. 11, we check the Lodge–Meissner consistency relation\(^{25}\) which states that during the stress relaxation, the ratio of the normal stress difference and the shear stress remains unchanged (equal to the magnitude of the imposed strain). The Lodge–Meissner relation is satisfied by most concentrated polymer systems.\(^{12,26}\) From Fig. 11, we find that such a relation is also verified by the simulations.

The comparisons made so far for single-step strain are particularly encouraging. The simulation model is capable of capturing all known important features of experimental data, and encourage future quantitative comparison. In the adjacent companion paper, double-step strain comparisons are also made. Shear flow is tackled in a subsequent paper.

### V. CONCLUSION

We propose a self-consistent reptation theory that accounts for segment connectivity, chain-length breathing, segmental stretch and constraint release, all of which are omitted in the Doi and Edwards models. Simulation results from the new theory for single-step strain are compared to experimental observations. Since stochastic simulation techniques were used, no approximations, such as independent alignment or consistent averaging are needed for calculations. Only one adjustable parameter, the ratio of the number of chain segments to the number of tube segments, need be specified. We find that the theory is able to describe qualitatively all known experimental observations.

For example, the theory predicts a shoulder region for shear stress relaxation following a step strain for large magnitudes of strains; it also predicts separability of stress relaxation into time- and strain-dependent parts after a ‘‘retraction’’ time following the imposition of a step strain. Both observations are in agreement with experiments. The normal stress ratio from the simulations is found to be increasing with time, and its dependence on strain agrees very well with experimental data.

Moreover, the theory can also predict the mixing rule of Tsenoglou for the shear stress relaxation of a mixture. These results indicate that the failure of the Doi and Edwards models to predict many experimental results is due to the assumptions and approximations employed in their theory. The success of the new theory greatly encourages further studies for other types of flow fields. These are accomplished in subsequent papers.
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