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Comprehensive comparisons with nonlinear flow data of a consistently unconstrained Brownian slip-link model

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Synopsis

A consistently unconstrained Brownian slip-link model (CUBS) with constant chain friction is used to predict the nonlinear rheological behavior of linear, entangled, polymeric liquids. The model naturally incorporates primitive-path-length fluctuations, segment connectivity, monomer density fluctuations, entanglement fluctuations, and constraint release without making any closure approximations. Constraint release is imposed on the level of the dynamics of the chain, and the relaxation modulus follows from these rigorously. The model is a mean-field, single-chain slip-link model, or temporary network model, with a single phenomenological time constant, $\tau$, fit by linear viscoelasticity. The nonlinear flow predictions are made without adjusting any additional parameters. We find that the addition of constant chain friction noticeably improves the model predictions in all the flows considered. In contradiction with tube models, the results suggest that the additional physics of constraint release and convective constraint release are not very important in predicting the nonlinear shear properties, except at low shear rates close to the LVE regime.

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I. INTRODUCTION

Quantitative agreement with experimental data has become increasingly accurate for tube models. However, most such models are restricted to either linear viscoelasticity or to flow, and to a single kind of chain architecture. If chain branching is considered, the mathematical model is modified substantially from the linear case, or is unknown altogether.

These tube models exist on various levels of description. Doi and Edwards tensor model [Doi and Edwards (1978a, 1978b, 1978c)] can be written as six three-dimensional integrals: one dimension for time history and two over segment orientation; tube models with stretch have seven coupled ordinary differential equations, including one dimension for average stretch [Ianniruberto and Marrucci (2001)]; the preaveraged tube model of [Graham et al. (2003)] uses six coupled partial differential equations. The last model is sometimes considered to be the most accurate tube model available.

Ideally, one seeks a model on the least-detailed level possible that makes accurate

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predictions for the problem at hand. For example, continuum mechanics equations—coupled ordinary differential equations—have been a primary goal, historically. If more complicated equations arise, calculation of nonhomogeneous flows becomes more difficult. For example, implementation of the coupled partial differential equations of Graham et al. in finite element codes is presumably computationally prohibitive. Even so, the use of uncontrolled closure approximations in these models can lead to unexpected errors. For example, the latter model predicts zero second-normal stress difference in shear flow.

In order to avoid uncontrolled closures, it is necessary to account for fluctuations more rigorously. Toward this end stochastic models are ideally suited. This is the approach taken, for example, by Öttinger using a single-segment model [Fang et al. (2000); Öttinger (1999)], by Hua and Schieber for a full chain model [Hua and Schieber (1998a); Hua et al. (1998, 1999); Neergaard et al. (2000)], and by Masubuchi et al. using interacting chains inside a simulation box [Masubuchi et al. (2003)]. Not surprisingly, these models show agreement with data over a broader range of experiments—for example, a reasonable second normal-stress difference. However, only the first of these models has been used in complex geometries [Gigras and Khomami (2002)].

Nonetheless, all tube models to date exhibit a maximum in the steady shear stress versus shear rate curve, which is not observed experimentally. Only through tuning parameters for excessive convective constraint release, or too-early onset of chain stretching is the maximum avoided in the single-segment tube models. When no such adjustable parameters are available, the maximum is seen for sufficiently entangled tube models.

More recent work has seen the advance of slip-link models. The first slip-link picture was drawn by Doi and Edwards. However, it was used only to motivate a certain network-model expression for the stress tensor in their tube model. The repton model of Rubinstein (1987) more closely resembles the slip-link picture than the tube picture, but here the constraining mesh of chains surrounding the test chain was considered to be regular. Flow was not considered. Neergaard and Schieber introduced the idea of using the monomer density between slip-links as a stochastic variable in a stochastic, full chain model [Neergaard and Schieber (2000); Schieber (2003a); Schieber et al. (2003)], and a similar multichain simulation was introduced independently by [Masubuchi et al. (2001)]. Greco considered a similar stochastic, single-segment model, in which an infinitely long chain possessed two entanglements, and the (infinitely long) ends were in a chemical potential bath [Greco (2002)]. Only step strains have been considered to date for this latter model.

Likhtman considered a Rouse chain sliding through slip links that are themselves attached by elastic springs to an affinely deforming background [Likhtman (2005)]. The picture is a more-detailed depiction of a similar model developed by Panyukov and Rubinstein for lightly cross-linked elastomers [Rubinstein and Panyukov (2002)]. Likhtman’s model has been used to study dynamic equilibrium only, to date.

In a previous article, we generalized the slip-link model of Neergaard and Schieber to include constraint release—the idea that the matrix of constraining chains are relaxing on the same spectrum of time scales as the probe chain [Nair and Schieber (2006)]. Comprehensive comparison was made there with linear viscoelastic experiments and reasonable agreement was found with data. Here we make comparisons with flow. We will show that the slip-link model is able to describe accurately all observations (known to us) in shear flow, including a monotonic steady shear stress growth with shear rate for linear chains.

An added benefit to slip-link models is a more natural connection to atomistic level simulations. Recently, several groups have created and tested algorithms to predict entanglement statistics from equilibrated, long-chain, melt polymers on such a level [Ever-
More than one algorithm has been able to predict entanglement density; however, recent attempts have included calculation of more-detailed statistics, such as primitive-path length distribution, or entanglement number distribution \cite{foteinopoulou2006,shanbhag2007,tzoumanekas2006,zhou2005}. These comparisons have shown excellent agreement with our slip-link theories, offering a path for true \textit{ab initio} calculation of stresses and dynamics in entangled polymers.

A third advantage to slip-link models is that branched systems or even cross-linked systems \cite{eskandari2006} can be modeled without significant modification to the mathematics.

\section*{II. THE CUBS MODEL}

In the consistently unconstrained Brownian slip-link (CUBS) model (Fig. 1), entanglements are represented as small rings called “slip links” along the contour length of the chain. As in the reptation theory, the chain is free to move along its contour length but the transverse motion is restricted due to the presence of slip links or entanglements. The end segments which are not constrained by any slip links are free to explore all conformations in space. The chain is allowed to slide through these entanglements and, hence, the number of Kuhn steps in an entangled strand fluctuates stochastically. Without constraint release, the entanglements are assumed to move affinely.

The entanglements are created and destroyed only at the ends of the chain when an end strand completely slips out of a slip link and the dangling end has zero Kuhn steps. In reality, a new entanglement is created when a surrounding chain entangles the test chain at the end. We model this process by an entanglement creation probability that satisfies detailed balance with entanglement destruction. In the previously proposed model, entanglements are assumed to be fixed in the medium—i.e., reptation of the surrounding chains was not considered (no constraint release). In this model, we consider the diffusion of the surrounding chains, thereby mimicking the creation and destruction of entanglements in the middle of the chain (constraint release). In the previous model it
was also assumed that friction is proportional to the number of entanglements and, hence, total friction in the chain fluctuated with the creation and destruction of entanglements. In the present model, friction is assumed to be proportional to the number of monomers or Kuhn steps in the chain. Hence, total friction in the chain is a constant quantity since the total number of monomers or Kuhn steps in the chain is a constant.

A. Mathematical description

The evolution equation for the probability density has four contributions, from, respectively, affine motion of the entanglements, sliding of the chain through the entanglements, constraint release, and creation/destruction of the entanglements at the chain ends

$$\frac{\partial p}{\partial t} = \dot{p}_{\text{affine}} + \dot{p}_{\text{steps}} + \dot{p}_{\text{CR}} + \dot{p}_{\text{ends}},$$

(1)

We give each contribution in turn.

The dynamics of the Kuhn steps in the chain are driven by both Brownian forces and free energy minimization. Free energy minimization requires the sliding of Kuhn steps from the strands of higher chemical potential \(\frac{\partial F}{\partial N_i}T_{(R),j}\(N_{j+}\)) to those of lower chemical potential. A friction or mobility for this Kuhn-step-shuffling process is also required, which introduces the single phenomenological parameter of the theory

\[
\dot{p}_{\text{steps}} = \sum_{i,j=1}^{Z} \frac{\partial}{\partial N_i} k_B T (\{N_k\}) \hat{A}_{ij} \left[ \left( \frac{\partial F}{\partial N_j} \right) T_{(R),j}\(N_{j+}\) \frac{p}{\partial N_j} + k_B T \frac{\partial p}{\partial N_j} \right],
\]

(2)

where

\[
\hat{A}_{ij} := \begin{cases} 
-\frac{1}{\tau_{i-1}}, & i = j + 1 \\
\frac{1}{\tau_{i}} + \frac{1}{\tau_{i-1}}, & i = j \\
-\frac{1}{\tau_{i}}, & i = j - 1 \\
0, & \text{otherwise}
\end{cases}
\]

(3)

We have considered two possible implementations for this friction: constant-entanglement friction and constant-chain friction. For constant-entanglement friction, we set \(\tau_i = \tau_K - \text{constant}\), in which case \(\hat{A}_{ij}\) is the Rouse matrix divided by \(\tau_K\). Nondimensionalizing the dynamical equations also leads to a more natural fundamental time scale \(\tau_e = N_e^2 \tau_K\).

Since the number of entanglements on a chain fluctuate, the total friction experienced by the chain will also fluctuate in this case. For various mathematical reasons, tube models typically assume that the friction of a chain is constant. Hence, we also consider the possibility that \(\tau_i = \tau_K (N_i + N_{i-1})/2N_e\), which we call constant-chain friction. Comparison with experiment below suggests that constant-chain friction is a better assumption.

In the absence of constraint release, the entanglements are assumed to move affinely during flow. Hence, we write
\[ \dot{p}_{\text{affine}} = - \sum_{i=1}^{Z-1} \frac{\partial}{\partial \mathbf{R}_i} \cdot [\kappa \cdot \mathbf{R}_i] p, \]

where \( \kappa = (\nabla \mathbf{v})^T \) is the transpose of the velocity gradient. Note that, due to the shuffling of Kuhn steps through the slip links, the chains themselves do not deform affinely.

The effect of constraint release is incorporated in a self-consistent mean-field way. Constraint release is mimicked by a diffusive process of the entanglements, which makes the entanglement motion no longer affine. Hence, we write

\[ \dot{p}_{\text{CR}} = \sum_{i,j=1}^{Z-1} \frac{\partial}{\partial \mathbf{R}_i} \cdot \frac{N_e a_k^2}{12k_B T \tau_{\text{CR}}^i A_{ij}} \left[ p \left( \frac{\partial F}{\partial \mathbf{R}_j} \right) + k_B T \frac{\partial p}{\partial \mathbf{R}_j} \right], \]

where \( \tau_{\text{CR}}^i \) is the constraint release time scale and \( A_{ij} \) is the Rouse matrix [Bird et al. (1987)]. Here we use a dimensionless prefactor, which determines the strength of the constraint release mechanism. We calculate the value of this prefactor to be 1/12. Details of this calculation may be found in the supplementary materials of [Nair and Schieber (2006)]. Thus, by considering the diffusion of the surrounding chains, we are mimicking the birth and destruction of slip links in the middle of the chain. The time constants \( \tau_{\text{CR}}^i \) are obtained in a self-consistent way by keeping track of the fraction of surviving entanglements during an equilibrium simulation. Note that this assumption of Rouse-like motion for the slip links is not necessary for this model, since creation and destruction of entanglements in the middle of the chain could be implemented rigorously. However, such an assumption is typically made in tube models, which we will follow here. More rigorous formulation is left for future work.

During flow, the rate of entanglement destruction can increase—so-called “convective constraint release” [Ianniruberto and Marrucci (2000)]. Hence, during flow we replace \( \tau_{\text{CR}}^i \) with \( \tau_{\text{CCR}}^i \), where

\[ \frac{1}{\tau_{\text{CCR}}^i} = \frac{1}{\tau_{\text{CR}}^i} + \langle w_d \rangle - \langle w_d \rangle_{\text{eq}}, \quad i = 1, \ldots, Z - 1, \]

where \( \langle w_d \rangle \) is the average rate of destruction of entanglements at the dangling ends during flow and \( \langle w_d \rangle_{\text{eq}} \) is that at equilibrium.

Ideally, the destruction of entanglements would be given by boundary conditions—i.e., the entanglement dies when the chain reaches the entanglement. However, such an implementation creates subtle numerical and thermodynamical problems, because the chain statistics are no longer determined by the entropy of the chain. On the other hand, the model is not designed to distinguish length and time scales on the order of when the final, single Kuhn step passes through the entanglement. To obviate these problems, we instead give the dangling end an entropy that prevents the last Kuhn step from passing through the entanglement. Then, we give a probability for entanglement destruction that increases with decreasing number of Kuhn steps in the last strand

\[ w_d = \frac{1}{\tau_e} \sqrt{\frac{3N_e}{N_E}}, \]

where \( N_E \) is the number of Kuhn steps in the end strands. Note that Eq. (44) of [Schieber et al. (2003)] contains a typographical error, whereas Eq. (20) of [Nair and Schieber (2006)] is correct. This allows us to control the proper statistics of the chain through the entropy and avoid the problems mentioned. Since the short time scales are most affected, we do not expect this approximation to have a significant effect. Nonetheless, we are
currently studying a more fundamental implementation of entanglement destruction that avoids these problems entirely, in order to study the effect of the approximation rigorously.

Related to the above problem, we impose the restriction that the length of an entanglement segment should always be greater than the length of a Kuhn step. The strand length is kept greater than the length of a Kuhn step ($a_k$), through a reflecting boundary condition. We have studied the sensitivity of predictions to this cutoff length and find that results are indistinguishable within statistical error as long as it remains below the average equilibrium entanglement spacing [Kitkrailard (2005)].

The polymer contribution to the stress tensor is given by [Nair and Schieber (2006); Schieber (2003a, 2003b)]

$$\tau^p = -n \sum_{Z=3}^{\infty} \sum_{j=1}^{Z-1} \int \int R_j \left( \frac{\partial F}{\partial R_j} \right)_{T,[N_i],[R]} p([R], [N_i], Z; t) dR_j dN_i, \quad (8)$$

where $n$ is the number density of the polymer chains.

**B. Brownian dynamics simulation**

Solution of the evolution Eq. (1) for the conformational probability density is, in general, not possible analytically. Numerical solution of the probability density is also not feasible given the large number of dimensions possible to describe the conformations. Therefore, Brownian dynamics is used to calculate the model’s predictions for stress (or other quantities). Finding the equivalent stochastic differential equations and other stochastic dynamics from the evolution equation for $p$ are straightforward [Gardiner (1982); Honerkamp (1983); Öttinger (1996)].

The evolution equation for the number of Kuhn steps in strand $i$ can be written as

$$dN_i = \frac{1}{k_BT_i} (\mu_{i+1} - \mu_i) dt - \frac{1}{k_BT_{i-1}} (\mu_i - \mu_{i-1}) dt + \sqrt{\frac{2}{\tau_i}} dW_i - \sqrt{\frac{2}{\tau_{i-1}}} dW_{i-1}, \quad i = 1, \ldots, Z, \quad \text{(9)}$$

where $\mu_i := (\partial F / \partial N_i)_{T,[R],i,[N_{i+1}]}$ is the chemical potential of the $i$th strand, except for the end strands, where $\mu_0 = \mu_1, \mu_{Z+1} = \mu_{Z}$, and $\tau_0 = \tau_Z = \infty$. An ensemble of chains whose dynamics are described by this SDE are simulated in discrete time, by using a semi-implicit stepping algorithm. Details are given in Nair and Schieber (2006).

The evolution equation for the position of entanglements is given as

$$dR_i = \kappa \cdot R_i dt - \frac{N_i a_k^2}{12k_BT_i^{CR}} \left( \frac{\partial F}{\partial R_i} \right)_{T,[N_i],[R]} dt + \sqrt{\frac{N_i a_k^2}{6\tau_i^{CR}}} dW_i. \quad \text{(10)}$$

The ensemble size used is 5000–10 000 chains and time-step size ($\Delta t$) is selected as 0.02$\tau_c$. Chain conformations are generated from the equilibrium probability density assuming zero cutoff length in $Q$ and then segments smaller than $a_k$ are reflected. This procedure gives the proper statistics for $Q$, but distorts the statistics for the $\{N_i\}$ somewhat. In order to correct the Kuhn-step-number statistics, it is necessary to equilibrate a few time steps. We equilibrate $\langle Z \rangle_{eq} / \Delta t$ time steps, which is sufficient to create an equilibrium ensemble. Simulations with and without constraint release (CR) are performed and the effect of convective constraint release (CCR) is incorporated as shown by Eq. (6).
TABLE I. Summary of experimental systems compared with theory in this article: \(M_w\)=weight-averaged molecular weight in kDa, \(PDI=M_w/M_n\), polydispersity index (where \(M_n\) is the number-averaged molecular weight), \(T\)=temperature in degrees Celsius, \(\langle Z\rangle_{eq}\)=average number of entanglements per chain plus one; \(\tau_e\) (NCR)=characteristic strand relaxation time assuming no constraint release in seconds; \(\tau_e\) (CR)=characteristic strand relaxation time with constraint release in seconds. WLC indicates use of the worm-like chain free energy; otherwise, the Gaussian free energy expression was used.

<table>
<thead>
<tr>
<th>System</th>
<th>(M_w) (kDa)</th>
<th>PDI</th>
<th>(T) (°C)</th>
<th>(\langle Z\rangle_{eq})</th>
<th>(\tau_e) (NCR) (s)</th>
<th>(\tau_e) (CR) (s)</th>
<th>Source(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1 sol.</td>
<td>1920</td>
<td>1.20</td>
<td>23</td>
<td>10</td>
<td>0.84</td>
<td>1.7</td>
<td>Venerus and Kahvand (1994a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Nair (2004)</td>
</tr>
<tr>
<td>PS2 melt</td>
<td>200</td>
<td>1.05</td>
<td>160</td>
<td>11</td>
<td>0.4</td>
<td>0.78</td>
<td>Venerus and Kahvand (1994b)</td>
</tr>
<tr>
<td>PS3 melt</td>
<td>500.5</td>
<td>1.02</td>
<td>170</td>
<td>28</td>
<td>0.375</td>
<td></td>
<td>Neergaard et al. (2000)</td>
</tr>
<tr>
<td>PS4 melt</td>
<td>200</td>
<td>1.06</td>
<td>175</td>
<td>11</td>
<td>0.137</td>
<td></td>
<td>Collis et al. (2005)</td>
</tr>
<tr>
<td>PS5 melt</td>
<td>200</td>
<td>1.05</td>
<td>130</td>
<td>14</td>
<td>56.4</td>
<td></td>
<td>Schweizer et al. (2004)</td>
</tr>
<tr>
<td>PS6 melt</td>
<td>390</td>
<td>1.06</td>
<td>130</td>
<td>28</td>
<td>23.4 (WLC)</td>
<td></td>
<td>Bach et al. (2003)</td>
</tr>
<tr>
<td>PS7 soln</td>
<td>3900</td>
<td>1.05</td>
<td>21</td>
<td>27.5</td>
<td>0.023 (WLC)</td>
<td></td>
<td>Bhattacharjee et al. (2003)</td>
</tr>
<tr>
<td>PB soln</td>
<td>813</td>
<td>&lt;1.05</td>
<td>25</td>
<td>21</td>
<td>0.15</td>
<td></td>
<td>Menezes and Graessley (1980)</td>
</tr>
</tbody>
</table>

The shear rates used in the simulations are made dimensionless using \(\tau_e\). The largest value of \(N_e\) used for calculations is 50, since theoretical predictions are insensitive to \(N_e\) when greater than 50, at fixed \(\langle Z\rangle_{eq}\).

### III. EXPERIMENTAL SYSTEMS

Seven polymer systems are compared with the CUBS model: a polystyrene solution, a polybutadiene solution, and five polystyrene melts. The different systems are summarized in Table I.

Test fluid PS1 is a 12 wt % solution in tricresyl phosphate nearly monodisperse (polydispersity index = 1.2) polystyrene with a molecular weight \(M_w\) of \(1.92 \times 10^6\) Da at a polymer density of \(0.135 \text{ g/cm}^3\) [Venerus and Kahvand (1994a)]. In the case of polymer solutions, the entanglement molecular weight is calculated as

\[
M_e^{\text{solution}} = \frac{M_e^{\text{melt}}}{\phi^{1.3}},
\]

where \(\phi\) is the volume fraction of the polymer and \(M_e^{\text{melt}}\approx 18 000\) g/mol. At any rate, the entanglement molecular weight is confirmed in LVE comparisons by examination of the height of the plateau modulus. We use the same fluid for making data comparisons in reversing double-step strain flow [Brown and Burghardt (1996); Venerus and Kahvand (1994a, 1994b)], inception of steady shear flow, steady shear flow, cessation of steady shear flow [Kahvand (1995)], and exponential shear flow [Neergaard et al. (2000)]. \(M_e\) for the solution is calculated as given by Eq. (11) and the value of \(\langle Z\rangle_{eq}\) is estimated (\(\langle Z\rangle_{eq}=M_w/M_n\)) to be 10. From the linear viscoelastic comparisons, \(\tau_e\) for the solution is obtained as, \(\tau_e^{\text{NCR}}=0.84\) s and \(\tau_e^{\text{CR}}=1.7\) s at 23 °C.

Comparison between \(G^*\) data and theory to determine \(\tau_e\) for this system is given in Nair and Schieber (2006).

The experimental sample used for data comparisons in single-step strain experiments is the polystyrene melt PS2 of molecular weight 200 kDa [Nair (2004)]. Using \(M_e\)
= 18100 g/mol [Ferry (1980)], the \( \langle Z \rangle_{eq} \) for the melt is estimated to be 11 at 160 °C. The value of \( \tau_e \) for the melt is obtained as, \( \tau_e^{NCR} = 0.4 \) s and \( \tau_e^{CR} = 0.78 \) s at 160 °C and \( N_e \) is taken as 22.

Data for a nearly monodisperse polybutadiene in Flexon 391 solution (PB/Flexon391, polydispersity index <1.05) with a concentration of 7 wt % and \( M_w = 813 \) kDa is taken from [Menezes and Graessley (1980)]. The experiment was done at 25 °C with a polymer density of 0.972 g/cm³.

As is typically done, we first estimated the number of entanglements by using the plateau modulus. However, further refinement was necessary after comparison with LVE data. Therefore, we performed a detailed fit of the linear viscoelastic prediction with the experimental data in order to fix the value of \( \langle Z \rangle_{eq} \) at approximately 21 (see Fig. 6). The estimated value of \( N_e \) for polystyrene solution is 545. However, we take \( N_e = 50 \) in order to save computational time. The value of \( \tau_e \) for the melt is estimated as \( \tau_e^{NCR} = 0.15 \) s from the LVE comparison. Fits for PS1 and PS2 are given elsewhere [Nair and Schieber (2003)].
The remaining fits are shown in Figs. 2–6. Some predictions are found using the worm-like chain (WLC) free energy, which is discussed below. We find no difference between predictions using the Gaussian free energy and the WLC for LVE, which is expected for small deformation flows.


FIG. 5. A comparison of the storage and loss moduli predictions and those measured by [Bhattacharjee et al. (2003)] for PS7 solution.

A high-molecular-weight polystyrene melt of [Collis et al. (2005)] at 170 °C with $M_w=500.5$ kDa and PI index of 1.02 is PS3. By using $M_e \approx 18000$, the average number of entangled strands, $\langle Z \rangle_{eq}$, is 28. The $G^*$ data/theory comparisons are shown in Fig. 7 without constraint release. A low-molecular-weight polystyrene melt of [Schweizer et al. (2004)], $M_w = 200$ kDa, is called PS4. The estimated value of $\langle Z \rangle_{eq}$ is 11. In both systems, the average number of Kuhn steps, $N_e$, is 22.

From the predictions obtained from the CUBS model without constraint release, the characteristic time for the high molecular weight and the low molecular weight system are 0.0375 and 0.137 s, respectively.

IV. COMPARISON IN FLOW

We now study in detail the nonlinear predictions of CUBS with constant chain friction. All the flow predictions made here are without adjusting any parameters.

![FIG. 7. A comparison between the storage $G'$ and loss $G''$ moduli predictions of the model without constraint release and that for polystyrene melt PS3 [Collis et al. (2005)], $M_w = 500.5$ kDa, $\langle Z \rangle_{eq} = 28$ at 170 °C.](image)

![FIG. 8. Ratio of nonlinear to linear shear modulus as functions of dimensionless time for different assumptions in the model and an approximate, analytic result found by assuming a separation of time scales between retraction and chain reorientation. In this comparison, the chain has an average of 35 entanglements, $N_e = 22$, and the strain is $\gamma = 6.3$.](image)
A. Single-step strain

The earliest tube model derived by Doi and Edwards made a remarkable parameter-free comparison with the strain-dependent part of single-step strain data. However, future refinements seemed to worsen this very favorable comparison. Earlier, one of us derived an analytic expression for the damping function based on the slip-link model under certain assumptions [Schieber (2003a)]. We now check this analytic result through numerical solution of the model.

A step strain is imposed on a material instantaneously at time $t=0$. The relaxation of shear stress can be expressed in terms of the nonlinear relaxation modulus, $G(t, \gamma)$, defined as

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

where $\gamma$ is the magnitude of the imposed strain. Beyond a certain time $\tau_l$ that depends on the polymer system, the nonlinear relaxation modulus shows separability into time- and strain-dependent parts over a wide range of strains.

FIG. 9. Shear stress relaxation following single-step strain as functions of time for several strains predicted by the model with and without CR/CCR and PS2 data [Nair (2004)].

FIG. 10. Shear stress relaxation following double-step strain of the type-B flow with $\gamma_1=4$ and $\gamma_2=-2$ at several values of $t_1$ predicted by the model with and without CR/CCR and PS1 data [Venerus and Kahvand (1994a)].
where $G(t)$ is the relaxation modulus of linear viscoelasticity and $h(\gamma)$ is the damping function. In the limit of small strains, the nonlinear relaxation modulus becomes $G(t)$. The damping function is a monotonically decreasing function of strain.

Figure 8 shows a comparison of the ratio of nonlinear to linear shear modulus predicted by different models for $Z_{\text{eq}}=36$ and the analytic result. We see that the model with CR/CCR and constant chain friction shows better agreement with the analytic $h(\gamma)$. In Fig. 9 we show comparisons of shear stress relaxation of PS melt ($M_w=200$ K, $Z_{\text{eq}}=11$) as functions of time for several strains. Except for the highest strain, the model predictions with convective constraint release look good. A previous article compared the damping function predictions with data, and the curves were a bit more strain softening than either of Doi and Edwards’ predictions. Therefore, our theory appears to continue the venerable tradition of degrading the Doi–Edwards-model prediction of the damping function, but improving all other comparisons, as we now show.

B. Reversing double-step strain

Double-step strain experiments provide a more severe test for evaluating the rheological constitutive theories for concentrated polymer systems. In these experiments, a strain of $\gamma_1$ is imposed at time $t=0$, followed by a strain of $\gamma_2$ after a time $t_1$, in the same ($\gamma_2>0$) or opposite ($\gamma_2<0$) direction to the first step strain. In this study, we consider only reversing double-step strain flows where the second strain is applied in a direction opposite to the first. Our model is used here for predicting two types of reversing flows, type-B ($\gamma_2=-\gamma_1/2$) and type-C ($\gamma_2=-\gamma_1$).

It is known that the Doi–Edwards (DE) model with the independent alignment (IA) assumption [Doi and Edwards (1986)] which is a particular case of, and performs identically to the K-BKZ model [Bernstein et al. (1963); Kaye (1962)] in step strains does not perform well in predicting reversing double-step strain deformation. Double-step strain experiments have also been used to test the DE model with and without the IA assumption [Brown and Burghardt (1996); Osaki et al. (1981); Osaki and Kurata (1982); Venerus and Kahvand (1994a, 1994b); Venerus et al. (1990)].

Doi derived a rigorous constitutive equation by avoiding the IA assumption [Doi (1980)] but still assuming instantaneous chain retraction, which was able to explain reversing double-step strain deformation as long as the time between the two steps is...
much larger than the retraction time ($\tau_R$). However, when $t_1 \leq \tau_R$, the model fails [Brown and Burghardt (1996); Venerus and Kahvand (1994a, 1994b)]. Also, the equation derived by Doi is not applicable to any other flows.

Model predictions for type-B flows with $\gamma_1=4$ and $\gamma_2=-2$ are compared with PS1 in Fig. 10. We see that except at short times, the model shows good agreement with experimental data and the results are not strongly sensitive to constraint release. The discrepancy shown at short times might be attributed to the coarse-graining introduced in the model. As mentioned before, the model cannot capture the relaxations taking place below the strand size. Figure 11 shows the comparison of first normal stress ($N_1$) relaxation at $t_1=4$ s. Here the model without CR/CCR gives better predictions compared to the predictions of K-BKZ and DE theories shown in Fig. 11 of the article by Venerus and Kahvand (1994b).

Figure 12 shows comparison of the second normal stress ($N_2$) relaxation at $t_1=1$ s. As in the case of $N_1$, we see that the model without CR/CCR gives better predictions for $N_2$, except at short times.

In Fig. 13, we show the comparisons of the shear stress relaxation for type-C flows with $\gamma_1=4$ and $\gamma_2=-4$ at $t_1=2$ and 32 s. Here the data seem to show a similar shape for
different waiting times, and just a vertical displacement. The model without CCR show
the same feature, but CCR does not. Nonetheless, the model does predict the correct
magnitudes for the shear stress. Figure 14 shows the transient normal stress ratio for
type-C flows at $t_1 = 1, 4, \text{and } 16 \text{ s}$. Here, we see that the normal stress ratio is time
dependent and also $t_1$ dependent. The trend is shown by experimental data in Fig. 6(a) of
Brown and Burghardt (1996).

C. Inception of steady shear flow

Figures 15 and 16, compare the model predictions to the PS1 solution data for tran-
sient growth of shear viscosity and first normal stress difference, respectively, at several
shear rates. In both cases, at high shear rates the model without CR and CCR captures the
features of the data quantitatively, whereas, at low shear rates the model with CR and
CCR predicts the data well. The linear viscoelastic limit forms an upper envelope for all
the shear rates and the transient overshoot occur at medium and high shear rates, in
accordance with experiments. It is interesting to note that at high shear rates, the model
without CR/CCR captures both the overshoot and undershoot, while CR/CCR makes the
undershoot disappear.

FIG. 14. Second- to first-normal-stress ratio for type-C flow with $y_1 = 4$ and $y_2 = -4$ at $t_1 = 1, 4, \text{and } 16 \text{ s}$ (from
top to bottom) predicted by the model with and without constraint release.

FIG. 15. Transient viscosities as functions of time under start up of steady shear at several shear rates predicted
by the model with and without constraint release, and he experimental data of polystyrene solution PS1
[Kahvand (1995)].
These data can also be examined in terms of the extinction angle, Fig. 17. We estimate the extinction angle as $\chi = \frac{1}{2} \tan^{-1}(2\tau_{\eta}/N_1)$, which is valid within our Gaussian approximation. Here also, the model without CR/CCR shows better agreement at high shear rates, while the model with CR/CCR gives better predictions at low shear rates. We can see that the theory is able to capture the undershoot in extinction angle at high shear rates.

High deformation rate appears to suppress the effect of constraint release. At any rate, constraint release does not have a large effect on predictions, which contradicts the predictions of tube models [Ianniruberto and Marrucci (1996, 2000); Marrucci (1996)].

We also examine polystyrene melts PS3 and PS4. Figure 18 shows a comparison between the CUBS model and the experimental viscosities of PS4. There is some discrepancy between the LVE predictions and the data at small strains, suggesting some experimental difficulties in this range. Taking this inconsistency into account the theoretical predictions are reasonable, especially at the higher Deborah numbers.

Figure 19 shows a similar comparison for PS3. These data show an even larger discrepancy with the LVE curve at small strains, suggesting some experimental error, possibly an overestimate of sample size. Interestingly, the difference between the data
FIG. 18. Transient viscosities as functions of time under start up of steady shear at several shear rates predicted by the model with and without constraint release, and the experimental data of polystyrene melt PS4 [Schweizer et al. (2004)].

FIG. 19. Transient viscosities as functions of time under start up of steady shear at several shear rates predicted by the model with and without constraint release and the experimental data of polystyrene melt PS3 [Collis et al. (2005)].

FIG. 20. Transient viscosities as functions of time under start up of steady shear at several shear rates predicted by the model with and without constraint release, and the experimental data of the polybutadiene solution [Menezes and Graessley (1980)].
and theory is nearly identical to the discrepancy between data and the LVE curve, which would also agree with our speculation about the sample’s being somewhat smaller than assumed.

Predictions from the CUBS model also show good agreement with the experimental results for the PB solution data in Figs. 20 and 21.

D. Steady shear flow

The original Doi–Edwards model predicts a maximum in the shear stress with shear rate at steady state, whereas experiments predict a monotonic increase of shear stress with shear rate. The DE model predicts a power-law index of $3/2$ for the steady-state viscosity in shear flow [Doi and Edwards (1979)].

Öttinger considered a modification of the Doi–Edwards and Curtiss–Bird models to include the effect of constraint release. This modified reptation model predicts an improved power-law index of $3/4$ for the steady-state viscosity [Öttinger (1994)]. Ianniruberto and Marrucci suggested a modification of the Doi–Edwards tube model to include the mechanism of convective constraint release which is claimed to be important during fast flows of polymer melts. This model predicted that the steady-state shear stress asymptotically approaches a plateau at high shear rates [Ianniruberto and Marrucci (1996)], and it has been widely believed that CCR is a necessary mechanism to avoid a local maximum. More about this point is discussed in the conclusions.

Before making quantitative comparisons with data, we looked at the question of monotonicity in the steady-state shear-stress curve for a more highly entangled chain: $\langle Z\rangle_{eq}=30$ and $N_e=22$. Figure 22 shows the result in dimensionless form. It should be noted that the Deborah number is not in terms of the longest relaxation time, but rather $De=\dot{\gamma}\tau_e$.

Note that things like constraint release and Rouse timescales arise from the model, rather than being added to the model. Therefore, the monotonic growth of the shear stress is a result of the assumed physics. In fact, in this calculation constraint release is switched off. Therefore, we can conclude that CCR is unnecessary to avoid the maximum. Second, the effect of stretch can clearly be seen for De values greater than approximately 0.2. From the same curve we can estimate the onset of the longest relaxation time at about...
De = 3 \times 10^{-3}. This gives us a ratio of \sim 67 for the longest relaxation time to the Rouse time, in accord with the usual estimate of 3\langle Z\rangle_{eq} for tube models, realizing that primitive-path length fluctuations should lower this estimate.

Figure 23 shows the shear stress predictions and data for PS1. Only a slight dependence is seen on CR. As expected, no maximum is visible. The steady-state viscosity η and the first normal stress difference coefficient \Psi_1 for PS1 have power-law indices of 0.79 and 1.4, respectively. The model shows excellent agreement, independent of constraint release, with power-law indices of 0.82 and 1.37, respectively, when CR/CCR is present and 0.82 and 1.38 when CR/CCR are switched off. The small discrepancy could be due to the small amount of polydispersity present in the polystyrene system used here. The shear rates used to evaluate the power-law indices range from 0.1 to 40 s^{-1}.

Similarly good agreement in the power-law indices are found (not shown) for the steady state viscosity as a function of shear rate for PS4, with a power-law index of 0.84 for η when CR/CCR is not present in the model. The polybutadiene solution data exhibit power-law indices of 0.87 and 1.65 respectively, for η and \Psi_1 when CR is not present in the model, in agreement with predictions.

FIG. 22. Dimensionless steady-state shear stress as a function of dimensionless shear rate De = \tau_\dot{\gamma} predicted by the theory without constraint release, \langle Z\rangle_{eq} = 30 and \nu = 22. The solid line is the linear viscoelastic prediction obtained from the CUBS model.

FIG. 23. Steady-state values of shear stress as functions of shear rate under steady shear flow predicted by the model with and without constraint release, and experimental data of polystyrene solution PS1 [Kahvand (1995)].
E. Cessation of steady shear flow

Figure 24 shows the relaxation of shear stress following cessation of steady shear flow at two shear rates for PS1. We can see that the relaxation is faster at the higher shear rate than at the smaller shear rate, which is due to the faster chain retraction. These trends are consistent with theory. At higher shear rate (1.0 s\(^{-1}\)), the models with and without CR/CCR shows good predictions at shorter times since relaxation is mainly due to monomer density fluctuation and contour-length fluctuation. At larger times, the model with CR/CCR shows better agreement since relaxation is mainly due to reptation and double reptation.

F. Exponential shear flow

In exponential shear flow the shear strain increases exponentially with time, given by

\[ \gamma(t) = \exp(\alpha t) - \exp(-\alpha t), \]

where \( \alpha \) is a parameter governing the shear acceleration.

Several experimental [Demarquette and Dealy (1992); Doshi and Dealy (1987); Samurkas et al. (1989); Sivashinsky et al. (1984); Venerus (2000); Zülle et al. (1987)] and theoretical [Kwan and Shaqfeh (1999); Neergaard et al. (2000); Graham et al. (2001)] studies on exponential shear flow have been reported during the past two decades. Neergaard et al. used the full chain reptation model [Hua and Schieber (1998b)] to interpret the exponential shear flow data for entangled polystyrene solution. Based on their model predictions, they reached the conclusion that exponential shear flow stretches the chains no more than does inception of steady shear [Neergaard et al. (2000)]. In fact, that work showed that all exponential shear flow data could be described by steady shear flow data when plotted versus instantaneous shear rate. Hence, we show all comparisons in that form here.

In Figs. 25 and 26, we show the comparisons of unadulterated shear stress and first normal stress difference, respectively, as functions of instantaneous shear rates for PS1. We can see that the model gives excellent predictions of shear stress except at high \( \alpha \), where the model with CR/CCR slightly overpredicts stretch. In the \( N_1 \) predictions, the model shows good agreement at low \( \alpha \), but again somewhat overpredicts stretch at high \( \alpha \).
**FIG. 25.** Shear stress as functions of instantaneous shear rate for exponential shearing flow at several values of \( \alpha \) predicted by the model with and without constraint release, and PS1 data [Neergaard et al. (2000)].

**FIG. 26.** First normal stress difference as functions of instantaneous shear rate for exponential shear flow at several values of \( \alpha \): model predictions with and without constraint release, and PS1 data [Neergaard et al. (2000)].

**FIG. 27.** Transient elongational stress as a function of time, predicted by the CUBS model with Gaussian and wormlike chain free energy and PS5 melt, Bach et al. (2003) \( M_w = 200 \, \text{kDa} \).
G. Elongational flow

Only recently has it been possible to achieve rheometric control for uniaxial extension of entangled, linear polymers. Concentrated solutions (PS7) have been examined at Monash University [Bhattacharjee et al. (2003)], and melts (PS5 and PS6) at the Danish Technical University [Bach et al. (2003)]. Note that systems PS6 and PS7 are particularly interesting, because they have nearly identical entanglement number, but only one is solution. We first examine the transient melt data, PS5, in Fig. 27. Here we see the first clear failure of the model. Whereas the data show a monotonic approach to steady state, the model exhibits oscillation until very large strains.

Nonetheless, if we compare the steady elongational stresses, we see in Fig. 28, that the slip-link model is able to capture the steady elongational stresses very well.

It is natural to guess that the infinite-extensibility assumption in the model is the cause of the discrepancy with the elongational data. Therefore, we also considered a free energy that prevents any segment from being stretched past its contour length. Namely, we use a free energy that becomes infinitely large as \( Q \rightarrow N \alpha K \). Here we use an approximation to the worm-like chain free energy for an entangled strand

\[
\frac{F_S(Q,N,T)}{k_B T} = \frac{3 N l_p - 2 Q}{4 (N l_p - Q) N l_p^2} \log J(N),
\]

which we derive from the approximate tension expression of [Marko and Siggia (1995)]. The function \( J(N) \) is a normalization factor dependent upon the number of persistence lengths in the strand, \( l_p = \alpha K / 2 \) is the persistence length and now \( N \) is the number of persistence lengths instead of the number of Kuhn steps. The function \( J \) is defined as

\[
J(N) := \left[ 4 \pi (N l_p)^3 \int_0^{N l_p} Q^2 \exp \left( \frac{3 N l_p - 2 Q}{4 (N l_p - Q) N l_p^2} \right) dQ \right]^{-1}.
\]

Since we cannot perform the integration analytically, we use a minimax approximation to obtain a numerical expression for \( J \). Details about the numerical expression can be found in the Appendix.

Figures 27 and 28 also show the results for the slip-link model with finite extensibility. Surprisingly, we see that finite extensibility (or, more accurately in this case, “finite monomer density”) plays only a small role in the transient elongational stresses, and
almost no role in steady elongational stresses. Similar comparisons are made for the more highly entangled sample, PS6, in Figs. 29 and 30, with similar conclusions.

We now turn to the elongational data for the entangled solution, PS7. Recall that this sample has the same number of entanglements per chain as the earlier melt, PS5, whose steady elongational data the theory was able to capture (though not the transients). Except for the smallest elongation rate, the slip-link model with finite extensibility is unable to capture the transient data (Fig. 31). However, unlike the melt comparison, the predictions substantially underpredict the steady stress data in Fig. 32, and even show the wrong shape.

To examine this discrepancy further, we place the solution and melt data on the same plot by making the strain rate dimensionless by $\dot{\varepsilon}$, and the elongational viscosity dimensionless by the zero-shear-rate viscosity. Recall that both of these dimensional quantities are determined by comparison at LVE. Figure 33 clearly shows that the melt and the solution trends are opposite: the solution is strain hardening and the melt is strain softening at high strain rates.

Theories for concentrated systems to date have assumed an equivalence between entangled solutions and entangled melts, at least implicitly by assuming that entanglements determine the dynamics. Clearly, such an assumption is not in agreement with our final

![Figure 29](image-url) **FIG. 29.** Transient elongational stress as a function of time, predicted by the CUBS model with worm-like chain model and PS6 melt, Bach *et al.* (2003) $M_w = 390$ kDa.

![Figure 30](image-url) **FIG. 30.** Steady state elongational stress, predicted by the CUBS model with worm-like chain model and PS melt, Bach *et al.* (2003) $M_w = 390$ kDa.
There are three possibilities: (1) one of the data sets is (or both are) incorrect, (2) additional physics is important in distinguishing solutions from melts, or (3) an assumption in the model is incorrect.

Since the elongational data have not yet been reproduced in other labs, the first option cannot be ruled out—easily said for a theoretician.

![Figure 31](image1.png)

**FIG. 31.** Transient elongational stress as a function of time, predicted by the CUBS model with worm-like chain model and PS7, Bhattacharjee *et al.* (2003) $M_w=3900$ kDa.

![Figure 32](image2.png)

**FIG. 32.** Steady state elongational stress, predicted by the CUBS model with Gaussian chain model and worm-like chain model and PS7, Bhattacharjee *et al.* (2003) $M_w=3900$ kDa.

![Figure 33](image3.png)

**FIG. 33.** Dimensionless steady state elongational viscosities comparison between polystyrene melt, Bach *et al.* (2003) (390 kDa at 130 °C), and polystyrene solution, Bhattacharjee *et al.* (2003) (3.9 MDa at 21 °C).
We also note that polymer density fluctuations are much larger for the solutions than they are for the melts. Such fluctuations are not considered in the model, since entanglements are considered fixed in space for LVE, and to move affinely for flows. These fluctuations might explain the second option. A straightforward way to examine this assumption is in a multichain simulation of the sort used by Masubuchi et al. (2001).

There are a number of assumptions made in the model: constant chain friction; mimicking constraint release through slip-link diffusion, instead of creation and destruction of entanglements in the middle of the chain; destruction of the entanglements at the end of the chain through a probability, instead of as a boundary condition; slip links are deformed affinely. Discrepancy with data because of the first of these assumptions seems unlikely because constant-entanglement friction has also been tested and found to be somewhat inferior at predicting shear and elongational stresses. The second and third assumptions are currently being examined in a more rigorous formulation of the model. The fourth assumption is more problematic to examine in a mean-field model, such as assumed here. Again, a simulation similar to that of Masubuchi et al. (2003) might be more appropriate to examine this assumption, since the motion of the entanglements could be followed rather than assumed. We do note in passing that we have also examined alternative assumptions about entanglement motion in light of thermodynamic considerations. However, these calculations found that fluctuating entanglement motion yielded affine motion, on average.

V. CONCLUSIONS

We introduce a consistently unconstrained Brownian slip-link model with constant chain friction to study the nonlinear properties of linear entangled polymer melts. The model uses a single phenomenological parameter $\tau_e$, which is fit by the linear viscoelasticity data and all the flow predictions are made without any adjustable parameters.

We found good to excellent agreement with all shear flows studied: single step, reversing double step, inception of steady shear, steady shear, cessation of steady shear, and exponential shear. Results were not very sensitive to CR—in contrast with tube models. Studies using various formulations of tube models consistently show that constraint release substantially reduces the shear thinning seen in steady shear flow. However, the studies do not make clear whether CCR is sufficient to avoid the maximum altogether.

For example, Marrucci and Ianniruberto (2003) include a prefactor $\beta$ that should be order 1, but is set to 2 to avoid the maximum. The original article including CCR Ianniruberto and Marrucci (2000) does not use the factor of 2 and exhibits a plateau in the shear stress—still implying flow instabilities. The more recent model of Leygue et al. (2006) also predicts a local maximum in the shear stress and the authors point out that the $\beta$ parameter of Marrucci et al. could be used as a fix, but decline to do so and write “We nevertheless believe that a better understanding of convective constraint release, especially in reversing flows, could lead to improved formulations where such modifications would not be necessary.” Fang et al. (2000) decrease the stretching time constant in their stochastic, single-segment model by a factor greater than 2 to give an onset of stretch at smaller shear rates to avoid the maximum. Mead et al. (1998) decrease the ratio $\tau_s/\tau_e$ by approximately 80% to describe their polystyrene solution of 17 entanglements. They argue that primitive-path length fluctuations justify the change, but the predictions show a change in slope of stress with shear rate (from stretch) that are not evident in either the shear-stress or normal-stress data. In a more-detailed formulation, Milner et al. (2001) adjust their parameter $c_s$ to a value of 0.1 in order to avoid the maximum. The physical reasoning given for the parameter’s being less than one is that more than two
chains might make up an entanglement [see the Appendix of Nair and Schieber (2006) for an alternative explanation]. However, ten chains would be inconsistent with the number predicted by the packing criteria of Fetters et al. (1999a, 1999b) using Rault’s argument [Rault (1987)], or of the binary interactions found in more recent atomistic simulations [Everaers et al. (2004)]. Our earlier full-chain stochastic model with convective constraint release [Hua et al. (1999)] (which mixes tubes and slip links) also predicts a plateau in the shear stress curve. Since the constraint release is found in a self-consistent way, there are no adjustable parameters like $\beta$ or $c_\nu$. It is possible that tube models predict instability even with convective constraint release.

On the other hand, in the dual slip-link model [Doi and Takimoto (2003)], the shear stress increases monotonically with shear rate in steady shear flow but they do not make any quantitative comparison with experiments.

Tubologists might wonder why our slip-link model shows something different from tube models. We mention here three possible explanations. First, we note that tube models typically assume that the number of entanglements on a chain are fixed at a single number—there are no fluctuations at equilibrium, and flow does not change it. At equilibrium, the tube is a random walk with constant step length. It is unclear how this assumption is modified with flow, given that most tube models are on the level of a single step in the primitive path.

On the other hand, our slip-link formulation has a distribution of entanglement numbers at equilibrium, and a distribution of strand lengths; flow modifies both of these distributions in well defined ways. An earlier formulation of the model with constant entanglement friction [Schieber et al. (2003)] gives results qualitatively similar to this one, but shows how shear flow modifies the entanglement number distribution. In that plot we show that the distribution remains Poissonian, but decreases to about half at high Deborah numbers. The observed disentanglement has two effects that lead in opposite directions. First, chains with fewer entanglements have longer strands that are largely aligned with the flow. These would be expected to contribute to more shear thinning. However, when these chains become dangling ends, they reëntangle rather quickly, leading to disordered strands, reducing shear thinning.

We mention that the flow stress curves in that paper are in error, though all equations and dynamic results are correct. This was due to a bug in the portion of the code that calculated stress from chain conformations. When this bug is fixed, all results we have studied for constant-entanglement friction vary only slightly from those with constant-chain friction. However, these results are slightly better for the latter.

It is also possible that the difference might be connected to the fact that the dynamics in the slip-link model are connected to the stress through different derivatives of the free energy, whereas in tube models, chain tension itself determines both stress and dynamics. In other words, in the formulation proposed here the derivative of free energy with respect to monomer number is the chemical potential, which determines dynamics; the derivative with respect to slip-link position is tension, which determines stress. As a result, tension along the chain is not equilibrated for strain rates between the inverse of the longest relaxation time, and the inverse of the Rouse time—not true for tube models. For these strain rates, the chemical potential of the chain ends stays near the equilibrium value of $-1/2 N_e$. Hence, chemical potential balance gives the number of Kuhn steps in the strand as approximately $N/N_e \approx (3/2)[\sqrt{1+(8Q^2/3NQa_K^2)} - 1]$. Therefore, the monomer density $N/Q$ is not constant along the chain, but varies in a nonlinear way with $Q$. In tube models, equating the tension $T=3k_BTQ/Na_K^2$ with the equilibrium Maxwell-demon
tension $k_BT/\sqrt{N_a a_k}$ requires that the monomer density $N/Q$ stay constant. The maximum observed in tube models might be because the tension—and, hence, the monomer density—is constant along the chain at these strain rates.

A third possibility is that the local maximum is avoided because the strands have a sort of built-in polydispersity in lengths, which smooths out the stress curve. One might imagine trying to test these ideas by creating chains with more monodisperse lengths. However, such a formulation would violate the equilibrium conformation statistics valid for concentrated chains. It is also difficult to imagine a test for the second hypothesis that would not violate thermodynamics. The first postulate might be tested by imposing more entanglements in the middle of the chain in order to keep the entanglement density constant. We have examined these dynamics, but obtained stress predictions that were very far from those observed, and different from tube model predictions.

The model was able to describe steady elongational data for polystyrene melts, but was unable to describe the transient melt elongational data, nor the solution elongation data. The former discrepancy is likely due to the assumption of how entanglements are destroyed in the model. Evidence of this is seen in the phase-space plot of Fig. 34, where the transient elongational viscosity is plotted versus the average number of entangled strands, and time is parametric. Here we see that disentanglement precedes a drop in the viscosity, followed by réentanglement that precedes a rise in the viscosity.

The latter discrepancy between solution and melt data is more puzzling. If the data hold, it suggests that entangled melts and solutions are not universal and that local polymer concentration fluctuations can play an important role. A more-detailed model would be necessary to examine this hypothesis.

ACKNOWLEDGMENT

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To Eq. (16), we fit a numerical expression for $J$,  
\[ J[y(N)] = \exp \left[ \frac{A_1 + A_2 y + A_3 y^2 + A_4 y^3 + A_5 y^4}{1 + A_6 y + A_7 y^2 + A_8 y^3 + A_9 y^4} \right], \tag{A1} \]
where $y(N) = \log N$. Values for the constants are given in Table II.

The chemical potential for this free energy is found by taking the differential of the free energy with respect to $N$; hence, a derivative of $J$ is necessary. Rather than take a derivative of our numerical approximation, we first take the derivative analytically

\[
\mu(Q, N, T) = \frac{3Nl_p - 2Q}{4(l_p - Q)} - \frac{Q^2(6N^2l_p^2 - 9Nl_pQ + 4Q^2)}{4N^2l_p^2(l_p - Q)^2} + \frac{3}{N} - \frac{\int_0^1 \left( \frac{Q}{Nl_p} \right)^2 g\left( \frac{Q}{Nl_p} \right) \exp \left[ -g\left( \frac{Q}{Nl_p} \right) N \right] dQ}{\int_0^1 \left( \frac{Q}{Nl_p} \right)^2 \exp \left[ -g\left( \frac{Q}{Nl_p} \right) N \right] dQ}. \tag{A2} \]

TABLE II. Constants for the numerical approximation to the normalization function $J$, Eq. (A1).

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TABLE III. Constants for the numerical approximation to integral term in the chemical potential expression $\mu_0$, Eq. (A4).

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<tr>
<td>$M_{10}$</td>
<td>0.018962828443251357</td>
</tr>
</tbody>
</table>
where we define $g(x)$ as

$$g(x) = \frac{3 - 2x}{4(1 - x)} x^2.$$  \hspace{1cm} (A3)

Then, from Eq. (A2) we fit a numerical approximation to the ratio of integrals, which we call $\mu_0$.

$$\mu_0 = \exp \left[ \frac{M_1 + M_2 y + M_3 y^2 + M_4 y^3 + M_5 y^4 + M_6 y^5}{1 + M_7 y + M_8 y^2 + M_9 y^3 + M_{10} y^4} \right],$$  \hspace{1cm} (A4)

where again $y = \log N$. Values for the constants are given in Table III.

In Figs. 35 and 36, respectively, we check our expressions by plotting the relative residual $(J_{\text{fit}} - J) / J$ between the numerical solutions obtained from MATHEMATICA for the integrals and the numerical expression of normalization factor, Eq. (A1), and the integral term in the chemical potential expression, Eq. (A4).
References


Schieber, J. D., J. Neergaard, and S. Gupta, “A full-chain, temporary network model with sliplinks, chain-length fluctuations, chain connectivity and chain stretching,” J. Rheol. 47, 213–233 (2003). Although all dynamical calculations were verified to agree with analytic results at equilibrium, we later discovered that stress calculations contained a bug. Hence, stress curves in this manuscript should be ignored.