A thermodynamically admissible reptation model for fast flows of entangled polymers

A THERMODYNAMICALLY ADMISSIBLE REPTATION MODEL FOR FAST FLOWS OF ENTANGLED POLYMERS

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ABSTRACT

Numerical predictions of a previsouly proposed thermodynamically consistent reptation model for linear entangled polymers are presented for shear and extensional flows. Comparisons with experimental data and two alternative molecular-based models are given in detail. The model presented in this contribution incorporates the essence of double reptation, convective constraint release and chain stretching, and it avoids the independent alignment approximation. Simulation results reveal that the model at a highly simplified level with few structural variables, i.e., four degrees of freedom, is able to capture qualitatively all features of the available experimental observations and is highly competitive with recently proposed models in describing rheological properties of linear entangled polymers.

KEYWORDS: POLYMER MELT, RHEOLOGY, REPTATION, CONSTRAINT RELEASE, CHAIN STRETCHING, FAST FLOWS

INTRODUCTION

Stress-strain relationships for polymer melts are the main ingredient for the flow simulation of polymer processing. The reliability and accuracy of these simulations depends crucially on the constitutive equations which describe the nonlinear viscoelastic properties of the underlying model polymer. Although the closed-form phenomenological models have been widely used in research and commercial codes, their degree of success is limited because of a lack of physical ingredient on the molecular level. For the purpose of realistic modelling, molecular-based models are uniquely suited. A molecular model was elaborated by Doi and Edwards [1] who extended the reptation idea introduced by de Gennes [2] to a tube idea in order to describe the viscoelastic behavior of entangled polymers in the presence of 'obstacles'. In addition to the reptation mechanism, Doi and Edwards originally assumed instantaneous and complete chain retraction, affine tube deformation by the flow, and independent alignment of tube segments. By doing so, they obtained a closed-form constitutive equation which only involves the second moment of the orientation vector for a tube segment. For highly entangled, linear polymers, the original Doi-Edwards (DE) model has been extended to incorporate chain contour length fluctuations [3, 4] and constraint release due to the motion of the surrounding chains (so called 'double reptation') [5]. The combination of these two effects lead to a refined description of the linear viscoelastic properties [6], however, the model is much less successful for the nonlinear properties. The major experimental observations that the original DE theory fails to describe in the nonlinear regime are the following:

1. There exist irreversible effects in double-step strain experiments with flow reversal;
2. Over a wide range of shear rates γ above the inverse disentanglement time $1/\tau_d$ the steady shear stress is nearly constant for very highly entangled melts or solutions or increases slowly with shear rate for less highly entangled ones. The first normal stress difference N_1 increases more rapidly with shear rate than does the shear stress over the same range of shear rates. The slope of N_1 versus γ increases as the molecular weight decreases;
3. The steady-state shear viscosity of different molecular weights merge into a single curve in the high shear rate, power-law regime;
4. The shear stress shows transient overshoots in the start-up of steady shear flow at low shear rates. The strain at which the maximum in the overshoot occurs increases with shear rate at high rates;
5. The first normal stress difference exhibits transient overshoots in the start-up of steady shear flow at moderate shear rates;
6. The rate of stress relaxation following cessation of steady shear flow is shear rate dependent;
7. The steady-state extinction angle decreases more gradually with shear rate than predicted by the DE model;
8. The transient extinction angle shows an undershoot at the start-up of steady shear at high shear rates; it also shows an immediate undershoot when the shear rate is suddenly decreased after a steady state has been reached, finally it reaches a higher steady-state value;
9. Steady-state values of the dimensionless uniaxial extensional viscosity are non-monotonic functions of extension rate;

In order to improve the situation, several attempts of modifying the original DE model have been made during the last years. The next section summarizes the basic equations of our model which is able to capture qualitatively, or quantitatively in most cases, in particular the nonlinear properties observed for shear and elongational flows from item 1 to 9 above.

MODEL DESCRIPTION

The structural state variables chosen are the configurational distribution function $f(\mathbf{u}, s\mathbf{r})$ and the stretching ratio of the chain contour length $\lambda = L/L_0$ where $\mathbf{u}$ is a unit vector describing the orientation of a tube segment, s is the position label of a tube segment in the interval [0,1] (the values $s = 0$ and $s = 1$ and correspond to the chain ends), $\mathbf{r}$ is the space position vector, and L_0 denotes the equilibrium contour length of the chain. After determining all the state variables (the hydrodynamic variables and the above structural state variables), the model has been formulated in the GENERIC formalism by constructing its 'building blocks' step by step [7]. Here we summarize the final time-evolution equations for the structural variables. The equation for the chain contour length stretching and relaxation reads $D\lambda/Dt = \dot{\lambda}_{\rm convect} + \dot{\lambda}_{\rm dissip}$, where D/Dt denotes the material time derivative, and the total stretching rate is split into convective and dissipative contributions,

$$\dot{\lambda}_{\rm convect} = \lambda\,(\nabla\mathbf{v}) : \langle \mathbf{u}\,\mathbf{u}\rangle \tag{1}$$

and

$$\dot{\lambda}_{\rm dissip} = \frac{1}{\tau_s}\frac{c(\lambda)}{3Z}(\lambda - 1), \tag{2}$$

where $\nabla\mathbf{v}$ is the velocity gradient tensor, $\langle \mathbf{u}\,\mathbf{u}\rangle$ is the spatial dependent symmetric second rank alignment tensor defined by

$$\langle \mathbf{u}\,\mathbf{u}\rangle \equiv \int_0^1 \mathrm{d}s \int \mathrm{d}^3 f(\mathbf{u}, s, \mathbf{r})\mathbf{u}\,\mathbf{u}\ , \tag{3}$$

Z is the number of entanglement segments per chain which is given by $M/\bar{M}_e$ (M is the molecular weight of the chain and $\bar{M}_e$ is the average molecular weight between entanglement points along one chain), τ_s is the characteristic stretching time, $c(\lambda)$ is the effective spring coefficient assumed as [7]

$$c(\lambda) = \frac{3\,c_1 Z}{1 - [(\lambda-1)/(\lambda_{\rm m}-1)]^2} + \frac{\lambda^2+\lambda+1}{\lambda^2 c_2^{-1}}, \tag{4}$$

which has the standard FENE type spring behavior for large extensions and the term proportional to c_2 ensures that the contour length is always positive. While $\lambda_{\rm m}$ is the maximum possible stretching ratio of the chain contour length which is equal to the square root of the number of Kuhn steps per entanglement $N_{\rm K}^e$: $\lambda_{\rm m} = d_T/b_{\rm K}$, where $d_T^2 \equiv R^2(N^e) = b_{\rm K}^2 N_{\rm K}^e$ is the 'tube diameter' and average end-to-end distance of the entanglement segment at equilibrium and $b_{\rm K}$ is the length of the Kuhn step (which is twice the persistence length), c_1 can be estimated from the probability of small deviations from the equilibrium contour length.

If we denote the molecular weight between entanglements for polymer melts as M^e, then $\bar{M}^e$ for polymer solutions can be estimated by using the relation $\bar{M}^e \approx M^e/\phi^{1.2}$, where ϕ is the volume fraction of polymer [8]. The values of d_T and $b_{\rm K}$ for some polymer melts can be calculated from the relevant experimental data tabulated in the literature where the values of M^e are also given. The value of $b_{\rm K}$ is calculated from the characteristic ratio C_∞. Based on these available data, the values of $\lambda_{\rm m}$ for several important melts are used.

The diffusion equation for the configurational distribution function takes the form

$$\begin{aligned}\frac{D\,f}{D\,t} = & -\frac{\partial}{\partial\mathbf{u}}\cdot\left[\left(\mathbf{1} - \frac{\mathbf{u}\,\mathbf{u}}{u^2}\right)\cdot(\nabla\mathbf{v})^{\dagger}\cdot\mathbf{u}f\right] \\ & -\frac{\partial}{\partial s}(\dot{s}_{\rm tot}f) - \frac{\dot{\lambda}_{\rm dissip}}{\lambda}f \\ & +\frac{1}{\pi^2\tau_d}\frac{\partial^2 f}{\partial^2 s} + \frac{\partial}{\partial\mathbf{u}}\cdot D\left(\mathbf{1} - \frac{\mathbf{u}\,\mathbf{u}}{u^2}\right)\cdot\frac{\partial}{\partial\mathbf{u}}f\ ,\end{aligned} \tag{5}$$

where

$$\dot{s}_{\rm tot} = -\frac{1}{\lambda}\left(s - \frac{1}{2}\right)\dot{\lambda}_{\rm dissip} \tag{6}$$

This drift velocity for s reflects a rescaling of the position label for the tube segment when the chain relaxes in the tube. The third term (creation/destruction term) on the right side of Eq. 5 compensates for configurations lost or gained at the boundaries. The terms involving second-order derivatives in Eq. 5 are of irreversible nature and express the erratic reptational motion along the chain contour (second-order derivative with respect to $\mathbf{u}$ with the orientational diffusion coefficient D), respectively. The form of D is

$$D = \frac{1}{6}\left[\delta_1\frac{1}{\tau_d} - \delta_2\frac{\dot{\lambda}_{\rm dissip}}{\lambda}\,\mathrm{H}(\frac{-\dot{\lambda}_{\rm dissip}}{\lambda})\right], \tag{7}$$

where $\mathrm{H}(x)$ denotes the Heaviside step function. The δ_1-term is interpreted as representing 'double reptation', and the δ_2-term represents the convective constraint release mechanism. The quantities $1/\tau_d$ and $-\dot{\lambda}_{\rm dissip}/\lambda$ determine the constraint release rate due to the loss of entanglements caused by reptation motion and chain retraction of side chains, respectively. The parameters $\delta_{1,2}$ determine the transfer rate from the constraint release rate to the relaxation rate of chain orientation, here we take $\delta_1 = \delta_2 = 1/\lambda$. This choice is motivated by the work of Mead et al. [9] in connection with the appearance of their switch function. The argument is that the constraint release causes not only chain segments reorientation, but also contour length shortening (this effect is not explicitly taken into account here). The role of the parameters $\delta_{1,2}$ is to apportion the effects of constraint release between these two effects.

When the chain is unstretched, the constraint release causes only chain segments reorientation; when the chain is highly stretched, the constraint release causes mainly chain contour length shortening. Hence, the parameters must be chosen in such a way that they approach unity when λ is near unity, and approach zero when λ is large. To our knowledge current research is performed to offer a refined interpretation of the switch function, which then should better reflect the stretch hardening factor in our FENE chain. Such a modification is expected to be of relevance when non-Gaussian effects become dominant, in particular for strong elongational flows.
Conservation of the total probability implies the boundary conditions

$$\frac{\partial \tilde{f}}{\partial s}|_{s=0} = \frac{\partial \tilde{f}}{\partial s}|_{s=1} = 0, \qquad (8)$$

where $\tilde{f}(s,r) = \int f(\mathbf{u},s,\mathbf{r})\mathrm{d}^3u = 1$. At the chain ends, we assume random orientation by specifying the distribution

$$f(\mathbf{u},s,\mathbf{r}) = \frac{1}{4\pi}\,\delta(|\mathbf{u}|-1), \quad s = 0,1\,, \qquad (9)$$

which is common practice, but has been opened to discussion in Ref. [10]. The extra stress tensor consists of two contributions, namely, the original Doi-Edwards contribution, plus a contribution associated with the chain stretching,

$$\tau(\mathbf{r}) = n_p k_\mathrm{B} T\,[3Z + c(\lambda)\lambda(\lambda-1)]\,\langle \mathbf{u}\,\mathbf{u}\rangle\,. \qquad (10)$$

In these expressions, n_p is the number density of polymers. The plateau modulus G_N^0, is still given by the Doi-Edwards expression $G_N^0 = \frac{3}{5} Z n_p k_\mathrm{B} T$.
The model accounts for double reptation, convective constraint release, and chain stretching and avoids the IA approximation by the drift term and the creation/destruction term. It has been verified to possess the full structure of GENERIC, in particular, the time-structure invariance of reversible dynamics.
Numerical results for shear and elongational flows obtained from the stochastic model summarized above are going to be published.

CONCLUSIONS

A thermodynamically admissible reptation model [7] that includes chain stretching, double reptation, and convective constraint release, and that avoids IA approximation is numerically investigated for transient and steady properties in shear and extensional flows. Quantitative comparisons are made with experimental data of entangled polystyrene solution in shear flows. We find that the model is able to capture qualitatively, or quantitatively in most cases, all the nonlinear properties observed for shear flows summarized in the introduction from item 1 to item 9.

It has been verified to possess the full structure of GENERIC, in particular, the time-structure invariance of reversible dynamics. The model has only four structural degrees of freedom, one from the position label s, two from the unit orientation vector $\mathbf{u}$, and one from the chain stretching λ. We assume $\tau_d/\tau_s = 3Z$ for our model. In addition to the plateau modulus G_N^0 and the reptation time τ_d, our model has two basic parameters, namely Z, the number of entanglements per chain which is proportional to the molecular weight (and can be expressed in terms of the Rouse and reptation time), and the maximum stretch λ_m, being equal to the square root of the number of Kuhn steps per entanglement segment. Remaining four model parameters have been introduced but actually assigned with the values $\lambda\delta_{1,2} = c_{1,2} = 1$.
Comparison with two recently formulated models by Hua et al. [11] and Mead et al. [9], respectively, in shear flows are presented.

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