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Simple constitutive equation for linear polymer melts derived from molecular theory: Rolie–Poly equation

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Abstract

Recently we developed a theory for fast flows of entangled polymer melts which includes the processes of reptation, convective and reptation-driven constraint release, chain stretch and contour length fluctuations. The theory is derived from a stochastic microscopic equation of motion of the chain inside the tube and of the tube itself. As a result we obtain a partial differential equation for the tube tangent correlation function, the solution of which requires quite intensive calculations. At the same time the application of this theory to realistic flows (which is anything other than the laboratory rheometer) requires a simple and less computationally intensive set of equations for the stress tensor similar to the Giesekus, PTT, Larson or Pom–Pom equations. In particular, the last was derived from molecular theory for a generic type of branched polymer. In this paper we demonstrate that molecular tube theory can also provide a route to constructing a family of very simple differential constitutive equations for linear polymers. They capture the full model quite well and therefore can be used in flow solving software to model spatially inhomogeneous flows. We present a comparison of the proposed equations with our full model and with experimental data.

Keywords: Polymer melts; Reptation; Tube theory; Constraint release; Constitutive equations; Entangled polymers

1. Introduction

The dynamics of entangled polymer melts are described most successfully by the tube model of Doi and Edwards [1]. In this theory the main mechanism or stress relaxation in the linear regime is assumed to be reptation out of the original tube. Important additional mechanisms, such as the self-consistent constraint release (CR) and contour length fluctuations (CLF), make significant, though sub-dominant, contributions to the rheology observed in monodisperse linear materials (for the most recent review of linear theory see [2]).

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However in non-linear flows or large step strain experiments the situation changes: the main mechanism of stress relaxation becomes convective constraint release (CCR), which was introduced by Marrucci [3]. However, the other mechanisms still play an important role. As was shown in recent work on CCR theories [4–8], a successful theory must properly describe the delicate interplay between chain stretch inside the tube, CCR and contour length fluctuations.

The aim of this short paper is to obtain a simple constitutive equation for fast flows of entangled polymer melts from our full theory [8]. This kind of simple "one-mode" equation is required for simulations of complex flows, see for example [9,10], where only the rheological response is required without needing information about molecular structure. We will show that this method of derivation is promising and, in particular, it suggests a new structure of single equation for the stress tensor with two relaxation times—stretch relaxation and orientation relaxation.

This is in contrast to previous work where one had to decouple the stretch and orientation variables in order to capture this characteristic behaviour of polymer melts. The main results of this paper were first reported in [11].

2. The full model

We start with a brief description of our full model [8]. We introduce a stochastic variable $\boldsymbol{R}(s,t)$ which describes the vector position of the tube segment. The variable s labels monomers inside the tube, measured in entanglement segments from one end of the chain ($s = 0, \ldots, Z$, where $Z = N/N_e$ and N_e is the number of monomers in entanglement segment) and t is time. Then we derive a stochastic equation of motion for the tube through a microscopic consideration of the relaxation mechanisms discussed above:

$$\boldsymbol{R}(s,t+\Delta t) = \boldsymbol{R}(s+\Delta\xi,t) + \Delta t\left(\boldsymbol{\kappa}\cdot\boldsymbol{R} + \frac{3}{2}\frac{\nu}{|R'|}\boldsymbol{R}'' + \boldsymbol{g}(s,t) + \frac{1}{2\pi^2\tau_e}\frac{(\boldsymbol{R}''\cdot\boldsymbol{R}')\boldsymbol{R}'}{\boldsymbol{R}'^2}\right).$$

The first term describes reptation, the second represents deformation by the flow ($\boldsymbol{\kappa}$ is the velocity gradient tensor), the third and fourth describe CCR, and the last term models retraction along the tube contour due to the stretch relaxation. There are two terms in this stochastic equation that generate noise and for which we make assumptions concerning only their second moments. Here $\Delta\xi$ is the random noise due to reptation, $\langle\Delta\xi(t)\Delta\xi(t')\rangle = 2D_c\delta(t-t')$, $g(s,t)$ is the random noise due to CCR, $\langle\boldsymbol{g}(s,t)\boldsymbol{g}(s',t')\rangle = \boldsymbol{I}\nu a^2\delta(s-s')\delta(t-t')/|R'|$, where $\boldsymbol{I} = \delta_{\alpha\beta}$ is isotropic tensor (α and β are Cartesian coordinates) and ν is the frequency of constraint release, which must be determined self-consistently from the motion of the chain ends. The timescales are as following: τ_e is the Rouse relaxation time of one entanglement segment, and $D_c = 1/(3Z\pi^2\tau_e)$ is the reptation diffusion constant. This notation is described in detail in our previous paper [5].

From this stochastic equation we then derive a regular partial differential equation for the tangent correlation function

$$f_{\alpha\beta}(s,s',t) \equiv \left\langle\frac{\partial R_\alpha}{\partial s}\frac{\partial R_\beta}{\partial s'}\right\rangle,$$

which contains information about both tube orientation and the chain stretch inside the tube (in fact the local chain stretch is just $\sqrt{\mathrm{tr}\,\boldsymbol{f}(s,s)}$). This function contains full information about the average chain

trajectories, which is enough to calculate the stress and structure factor. In particular, the *polymeric* contribution to the stress tensor is

$$\sigma_{\alpha\beta} = \frac{3G_e}{Z}\int_0^Z f_{\alpha\beta}(s,s)\,\mathrm{d}s. \tag{1}$$

To proceed with the derivation of an evolution equation for $\boldsymbol{f}(s,s',t)$ we use several decoupling approximations. The net result is the following equation:

$$\begin{aligned}\frac{\partial \boldsymbol{f}}{\partial t} &= D_c\left(\frac{\partial}{\partial s}+\frac{\partial}{\partial s'}\right)^2 \boldsymbol{f} + \boldsymbol{\kappa}\cdot\boldsymbol{f} + \boldsymbol{f}\cdot\boldsymbol{\kappa}^{\mathrm{T}} \\ &+\frac{3\nu}{2}\left(\frac{\partial}{\partial s}\frac{1}{\sqrt{\mathrm{tr}\,\boldsymbol{f}(s,s)}}\frac{\partial}{\partial s}(\boldsymbol{f}-\boldsymbol{f}_{\mathrm{eq}}) + \frac{\partial}{\partial s'}\frac{1}{\sqrt{\mathrm{tr}\,\boldsymbol{f}(s',s')}}\frac{\partial}{\partial s'}(\boldsymbol{f}-\boldsymbol{f}_{\mathrm{eq}})\right) \\ &+\frac{1}{2\pi^2\tau_e}\left(\frac{\partial}{\partial s}\boldsymbol{f}(s,s')\frac{\partial}{\partial s}\ln\,\mathrm{tr}\,\boldsymbol{f}(s,s) + \frac{\partial}{\partial s'}\boldsymbol{f}(s,s')\frac{\partial}{\partial s'}\ln\,\mathrm{tr}\,\boldsymbol{f}(s',s')\right),\end{aligned} \tag{2}$$

where $\boldsymbol{f}_{\mathrm{eq}}(s,s') \equiv ((\boldsymbol{I}a^2)/3)\delta(s-s')$ is equilibrium tangent correlation function without flow. The frequency of constraint release is defined from the retraction rate

$$\nu = c_\nu\left(\frac{1}{3Z^3\tau_e\beta_{\mathrm{rcr}}} + \frac{1}{aZ^*}\frac{\partial}{\partial t}\int_0^Z \sqrt{\mathrm{tr}\,\boldsymbol{f}(s,s)}\,\mathrm{d}s\bigg|_{\mathrm{retr}}\right), \tag{3}$$

where the first term is a constant contribution due to reptation (β_{rcr} is a constant of order unity) and the second is the rate of change of the tube length due to retraction. The restriction ($|_{\mathrm{retr}}$) to the time dependence of $\boldsymbol{f}(s,s')$ in Eq. (3), accounting for retraction process only, is achieved by computing $\partial f/\partial t$ with only the last term in Eq. (2). Here $Z^* = \int_0^Z \sqrt{\mathrm{tr}\,\boldsymbol{f}(s,s)}\,\mathrm{d}s$ is the new number of entanglements under stretch and c_ν is a dimensionless parameter of order one, regulating relative "strength" of constraint release. Note that Eq. (2) is different from our non-stretching theory [5] only by the last term and by several renormalizations of CCR terms due to stretch. Details can be found in [8] but are not important for the following derivation. We also developed the concept of a position-dependent diffusion coefficient $D_c(s,s')$ to describe contour length fluctuations and choose $D_c(s,s')$ and β_{rcr} in a way that our non-linear theory agrees well with the more precise linear theory of [2]. These details also do not impact the derivation of a simple one-mode equation.

3. Single mode equation

There are several ways of deriving a one-mode equation from the full model of Eq. (2). One is to neglect all s-dependence of $\boldsymbol{f}(s,s')$. Another is to perform a Fourier transformation analogous to [5], and to assume that all Fourier components are unperturbed by the flow except for the first. This method is described in Appendix A. The third way is to develop a dumbbell CCR model, which contains terms analogous to CCR terms in Eq. (2). Fortunately all three methods lead to equations of the same structure, which we give below in Eq. (4). Each method generates slightly different form for the "transition functions" in Eq. (4) f_{retr} and f_{ccr}. In particular, it can be easily seen that if we neglect all s-dependencies of $\boldsymbol{f}(s,s')$ in

Eq. (2) and associate it with the *polymer* contribution to the stress $\boldsymbol{\sigma}$ in units of G_e (see Eq. (1)), we will get an equation of the form

$$\frac{d\boldsymbol{\sigma}}{dt} = \boldsymbol{\kappa}\cdot\boldsymbol{\sigma} + \boldsymbol{\sigma}\cdot\boldsymbol{\kappa}^T - \frac{1}{\tau_d}(\boldsymbol{\sigma} - \boldsymbol{I}) - f_{retr}(tr\boldsymbol{\sigma})\boldsymbol{\sigma} - f_{ccr}(tr\boldsymbol{\sigma})(\boldsymbol{\sigma} - \boldsymbol{I}), \tag{4}$$

where $f_{retr}(x)$ and $f_{ccr}(x)$ are some scalar functions describing retraction and CCR, and $\boldsymbol{I} \equiv \delta_{\alpha\beta}$ is the equilibrium value of the stress tensor in these units. Eq. (4)has a transparent physical interpretation: the reptation term (with τ_d) is a single time relaxation towards equilibrium, the CCR term is also a relaxation towards the equilibrium, but with the rate dependent on the amount of stretch $tr\boldsymbol{\sigma}$, and retraction is relaxation to zero, also with the rate dependent on $tr\boldsymbol{\sigma}$.

The second and the third methods of derivation of a simple equation provide slightly different expressions for the functions f_{retr} and f_{ccr}, but with the same asymptotic behaviour. In Appendix A we discuss Fourier transform derivation. However, this behaviour may be derived from some general physical arguments that we will use here. We must consider two regimes: small stretch $tr\boldsymbol{\sigma} - 3 \ll 1$ and large stretch $tr\boldsymbol{\sigma} - 3 \gg 1$, which occur when the deformation is correspondingly slower or faster than the stretch or Rouse relaxation time, $\tau_R = Z^2\tau_e$. In the first regime retraction must be proportional to the amount of stretch, i.e. $f_{retr}(tr\boldsymbol{\sigma}) \sim tr\boldsymbol{\sigma} - 3$, so that retraction relaxes $tr\boldsymbol{\sigma}$ to its equilibrium value of 3. Since the typical relaxation time is the Rouse time, we may write $f_{retr}(tr\boldsymbol{\sigma}) \sim (tr\boldsymbol{\sigma} - 3)/\tau_R$. The CCR rate, ν, in this regime must be proportional to the retraction rate (if one neglects reptation constraint release, see Eq. (3)). Therefore we write $f_{ccr}(tr\boldsymbol{\sigma}) \sim \beta(tr\boldsymbol{\sigma} - 3)/\tau_R$, where β is CCR coefficient analogous to c_ν in our full theory and to the coefficient β introduced by Marrucci in his original CCR paper [3].

In the limit of large stretch we recall that, in the absence of any other mechanisms, retraction in a one-mode approximation should lead to the following simple relaxation for the stretch, $d\lambda/dt = -(\lambda - 1)/\tau_R$. This form was used in both the Pom–Pom [12] and MLD models [4]. In our model $\lambda = \sqrt{tr\boldsymbol{\sigma}/3}$, and therefore we conclude that only the choice $f_{retr}(tr\boldsymbol{\sigma}) \to 2/\tau_R$ in this limit will lead to the desired result. Indeed if we have $d\boldsymbol{\sigma}/dt = -2(\boldsymbol{\sigma} - \boldsymbol{I})/\tau_R$, then taking trace of this equation will lead to $d\lambda/dt = -\lambda/\tau_R$ for large λ, as required.

The CCR term at large stretch can, however, depend on the stretch. In particular, if one assumes constant tube diameter, we expect an effective suppression of CCR because the number of entanglements per chain increases, and also because one needs more CR events to move the same number of monomers compared to a unstretched chain. We therefore assume that $f_{ccr}(tr\boldsymbol{\sigma}) \sim \beta(tr\boldsymbol{\sigma}/3)^\delta/\tau_R$, where δ is some negative power, which can be obtained by fitting to our full theory. If one wants to model the effect of the tube diameter changing with stretch, both f_{retr} and f_{ccr} could be further modified. We summarize their asymptotic behaviour once again

$$f_{retr}(tr\boldsymbol{\sigma}) = \begin{cases} \dfrac{2(tr\boldsymbol{\sigma} - 3)}{\tau_R}, & tr\boldsymbol{\sigma} - 3 \ll 1 \\ \dfrac{2}{\tau_R}, & tr\boldsymbol{\sigma} - 3 \gg 1 \end{cases}; \qquad f_{ccr}(tr\boldsymbol{\sigma}) = \begin{cases} \dfrac{2\beta(tr\boldsymbol{\sigma} - 3)}{\tau_R}, & tr\boldsymbol{\sigma} - 3 \ll 1 \\ \dfrac{2\beta(tr\boldsymbol{\sigma}/3)^\delta}{\tau_R}, & tr\boldsymbol{\sigma} - 3 \gg 1 \end{cases}.$$

Our final step is choosing suitable interpolation functions between two regimes. We propose to use $f_{retr}(tr\boldsymbol{\sigma}) = 2(1 - \sqrt{3/tr\boldsymbol{\sigma}})/\tau_R$ and $f_{ccr}(tr\boldsymbol{\sigma}) = 2\beta(tr\boldsymbol{\sigma})^\delta(1 - \sqrt{3/tr\boldsymbol{\sigma}})/\tau_R$. The form without square roots also has the correct asymptotes, but it provides slightly less accurate agreement with the full theory. The particular choice of transition functions and prefactors was motivated by the equation for the stretch relaxation $d\lambda/dt = -(\lambda - 1)/\tau_R$, which is satisfied by Eq. (5) in all regimes.

This leads to our main result

$$\frac{\mathrm{d}\boldsymbol{\sigma}}{\mathrm{d}t} = \boldsymbol{\kappa}\cdot\boldsymbol{\sigma} + \boldsymbol{\sigma}\cdot\boldsymbol{\kappa}^{\mathrm{T}} - \frac{1}{\tau_{\mathrm{d}}}(\boldsymbol{\sigma}-\boldsymbol{I}) - \frac{2(1-\sqrt{(3/\mathrm{tr}\boldsymbol{\sigma})})}{\tau_{\mathrm{R}}}\left(\boldsymbol{\sigma} + \beta\left(\frac{\mathrm{tr}\boldsymbol{\sigma}}{3}\right)^{\delta}(\boldsymbol{\sigma}-\boldsymbol{I})\right), \tag{5}$$

which we call the Rolie–Poly constitutive equation, standing for ROuse LInear Entangled POLYmers (the reference to Rouse is appropriate—the tube of entanglements becomes a Rouse-like object under the operation of CCR).

It is possible to take the limit of $\tau_{\mathrm{R}} \to 0$, which corresponds to the old non-stretching theory. This limit exists because $\left(1-\sqrt{3/\mathrm{tr}\boldsymbol{\sigma}}\right)$ goes to zero as fast as τ_{R} keeping the ratio constant. Thus by taking $\mathrm{tr}\boldsymbol{\sigma} = 3 + \Delta$ in the non-stretching limit and assuming that $\Delta \to 0$ as $\tau_{\mathrm{R}} \to 0$ we obtain

$$\frac{2(1-\sqrt{(3/\mathrm{tr}\boldsymbol{\sigma})})}{\tau_{\mathrm{R}}} \to \frac{2}{3}\mathrm{tr}(\boldsymbol{\kappa}\cdot\boldsymbol{\sigma}), \quad \text{as } \tau_{\mathrm{R}} \to 0,$$

and therefore we get the following non-stretching version of Rolie–Poly equation:

$$\frac{\mathrm{d}\boldsymbol{\sigma}}{\mathrm{d}t} = \boldsymbol{\kappa}\cdot\boldsymbol{\sigma} + \boldsymbol{\sigma}\cdot\boldsymbol{\kappa}^{\mathrm{T}} - \frac{1}{\tau_{\mathrm{d}}}(\boldsymbol{\sigma}-\boldsymbol{I}) - \frac{2}{3}\mathrm{tr}(\boldsymbol{\kappa}\cdot\boldsymbol{\sigma})(\boldsymbol{\sigma} + \beta(\boldsymbol{\sigma}-\boldsymbol{I})). \tag{6}$$

One can regroup terms as

$$\frac{\mathrm{d}\boldsymbol{\sigma}}{\mathrm{d}t} = \boldsymbol{\kappa}\cdot\boldsymbol{\sigma} + \boldsymbol{\sigma}\cdot\boldsymbol{\kappa}^{\mathrm{T}} - \frac{1}{\tau_{\mathrm{d}}^{\mathrm{eff}}}(\boldsymbol{\sigma}-\boldsymbol{I}) - \frac{2}{3}\mathrm{tr}(\boldsymbol{\kappa}\cdot\boldsymbol{\sigma})\boldsymbol{\sigma}; \qquad \frac{1}{\tau_{\mathrm{d}}^{\mathrm{eff}}} = \frac{1}{\tau_{\mathrm{d}}} + \frac{2}{3}\beta\mathrm{tr}(\boldsymbol{\kappa}\cdot\boldsymbol{\sigma}),$$

which now looks very similar to the original Marrucci equation [3]. The difference is, however, that our derivation provides a natural introduction of stretch into the system, obtaining a non-stretch equation as a limiting case of a more general equation. In contrast, the generalization of Eq. (6) to the stretching case is not unique.

We now discuss the properties of the obtained equation in comparison with the full model and experiment. Fig. 1 shows steady-state shear predictions of the full theory [8] and the Rolie–Poly equation. The full theory predictions are for $Z = 20$ and $c_\nu = 0.1$, which are the typical values used to describe experimental data. The Rouse time was the same for both versions of the model, $\beta = 1$ approximately

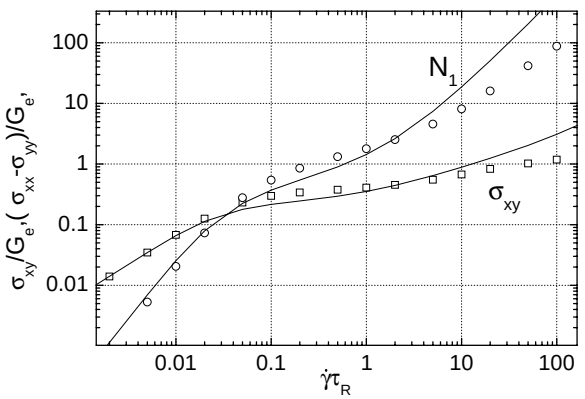

Fig. 1. Steady-state shear predictions of the full model (symbols) and Rolie–Poly equation (lines) for $Z = 20$.

corresponds to $c_\nu = 0.1$ and $\delta = -0.5$ is the optimal value to fit both transient and steady-state predictions of the full theory. To fix G_e and τ_d, we fitted the terminal region of the linear spectrum G', G'', produced by our linear theory [2]. One can see that the single mode Rolie–Poly equation has qualitatively similar behaviour to that of the full theory. In particular, it has three regimes as a function of shear rate: linear regime $\dot\gamma < \tau_d^{-1}$, CCR regime $\tau_d^{-1} < \dot\gamma < \tau_R^{-1}$, and CCR + stretch regime $\dot\gamma > \tau_R^{-1}$. The largest quantitative disagreement is at high rates, where the single mode equation produces faster stress growth compared to the full theory. The reason is that the full theory contains a spectrum of stretch relaxation times, reflecting different stretch of different parts of the chain, whereas the single mode equation assumes uniform stretch. The discrepancy can be reduced by introducing finite extensibility, for example by replacing $\tau_R \to \tau_R(1 - (\mathrm{tr}\boldsymbol{\sigma}/3\lambda_{max}^2))$. We do not consider it here for two reasons: one is that a change of spring constant would require appropriate change in the stress definition, and therefore new terms in Eq. (5). The second reason is that for the 7% polybutadiene solutions which we discuss later, the finite extensibility parameter, λ_{max}, is expected to be very large and therefore should not be relevant under shear. This is, of course, not true for polymer melts or extensional measurements. The smoother crossover of the full theory from the first to the second regime is also explained by the broad spectrum of linear relaxation of the full theory due to contour length fluctuations.

However, fitting steady-state stresses is a much simpler task than fitting transient data, as was also noted in [13]. This is illustrated in Fig. 2, where we compare the transient predictions for start-up of shear flow for the full theory and the single mode Rolie–Poly equation with the same parameters as in Fig. 1. One can see that, although the overshoots have the same qualitative behaviour, the agreement is not satisfactory mainly because of a large discrepancy in the linear regime.

To improve the situation, we add several faster modes to the main mode, described by Eq. (5). To do this we fit the linear spectrum, G' and G'', by a set of several modes (one per decade), up to the high frequency crossover, i.e. up to about $\omega \sim \tau_e^{-1}$. This procedure gives a set of G_e^i and τ_d^i. Then we model the slowest mode (and if necessary the second slowest—for extremely fast flow rates) by Eq. (5), and all faster modes by Eq. (6). Note that one can model all modes by Eq. (5) with small Rouse times, but it will require a very small timestep. We have to determine only one Rouse time, which is the Rouse time of the slowest mode. This procedure results in Fig. 3, where we used $\tau_R^{\text{Rolie–Poly}} = \tau_R^{\text{full}}$, and $\delta = -0.5$

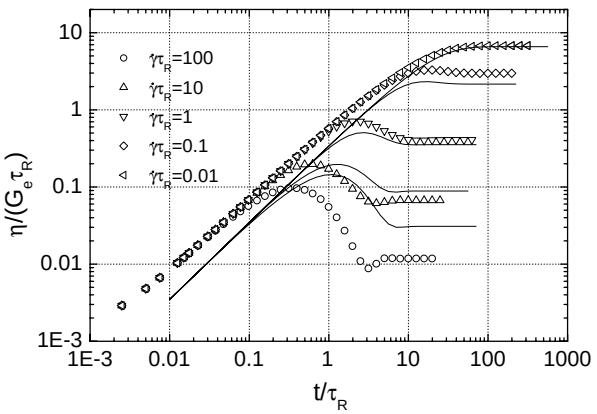

Fig. 2. Transient start-up shear predictions of the full model (symbols) and Rolie–Poly equation (lines) for $Z = 20$.

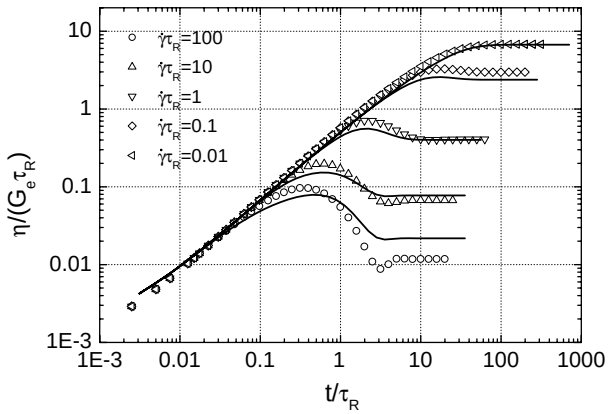

Fig. 3. Transient start-up shear predictions of the full model (symbols) and multi-mode Rolie–Poly equation (lines) for $Z = 20$.

and $\beta = 0.5$. The agreement now is improved everywhere apart from the overprediction of steady-state at very high shear rates discussed above.

Recently, the authors of [15] discovered some artifacts at high shear rates of the Ianniruberto and Marrucci model [7,13] with two separate equations for the stretch and orientation tensor. We checked our model up to very high rates and found no such artifacts. Therefore we agree with authors of [16] that the artifacts are caused by decoupling of stretch and orientation, and in order to avoid them one has to use the form of the Rolie–Poly equation. We note that the only difference between equation proposed in [16] and our equation (proposed earlier in [11]) is that in the Rolie–Poly equation CCR does relax some stretch ($\mathrm{tr}\boldsymbol{\sigma}$), in agreement with our full model.

Fig. 4 shows comparison of the two theories for transient uniaxial elongation with the same parameters as Fig. 3. Apart from the fact that the Rolie–Poly equation has larger extension thinning, the agreement is satisfactory. Note that neither theory has finite extensibility included, which would limit the degree of strain hardening in the stretching regime $\dot{\epsilon} > \tau_{\mathrm{R}}^{-1}$.

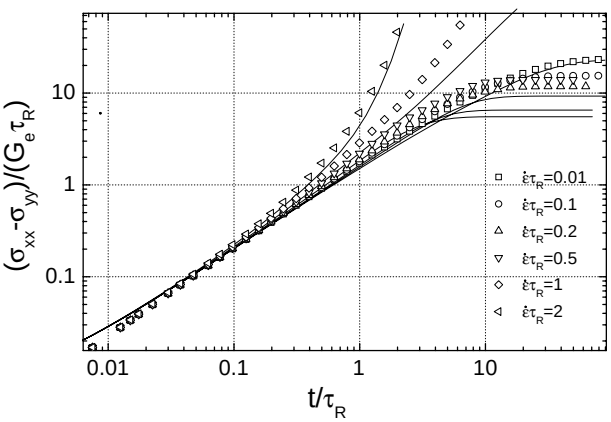

Fig. 4. Transient start-up elongational predictions of the full model (symbols) and multi-mode Rolie–Poly equation (lines) for $Z = 20$.

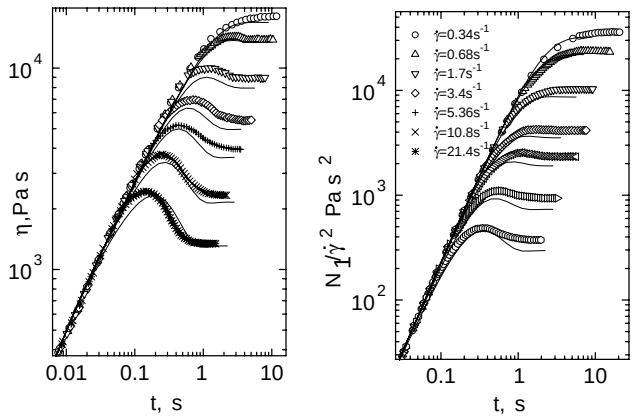

Fig. 5. Start-up shear viscosity measurements for 7% PB solution of $Mw = 350\,\mathrm{K}$, measured in [14] (symbols) and fits by multi-mode Rolie–Poly equation (lines).

In Figs. 5 and 6 we demonstrate that the Rolie–Poly equation, in the multi-mode formulation described above, is capable of fitting experimental transient shear data. We plot shear stress (left) and normal stress difference (right) for two 7% polybutadiene solutions of $Mw = 350\,\mathrm{K}$ (Fig. 5) and $Mw = 813\,\mathrm{K}$ (Fig. 6), as reported in [14]. Using only τ_R and β as fitting parameters (we always set $\delta = -0.5$) we can fit the whole dataset with sufficient precision for complex flow modeling. The fitting shows that the optimum value of τ_R in the Rolie–Poly model is always 1.5–2 times smaller than those predicted by the linear theory [2], and the β parameter must be chosen to be very small (it was set to zero for this particular dataset). This does not mean of course that CCR is unimportant—the approximate one-mode theory is not a tool to make such a conclusion. Here setting $\beta = 0$ is just a technical trick in order to compensate for the overprediction of steady-state stress at large rates (see Fig. 1 and discussion thereafter). Note that the ratio of fitted Rouse times for two polymers is only 2.5, whereas in the full theory Rouse time scales as M^{w^2} and we expect the ratio of Rouse times to be 5.4. This shows definite advantages of the full theory.

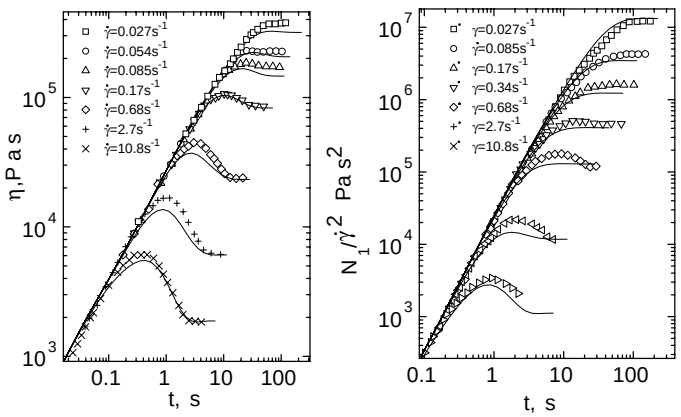

Fig. 6. Same as Fig. 5, but for $Mw = 813\,\mathrm{K}$.

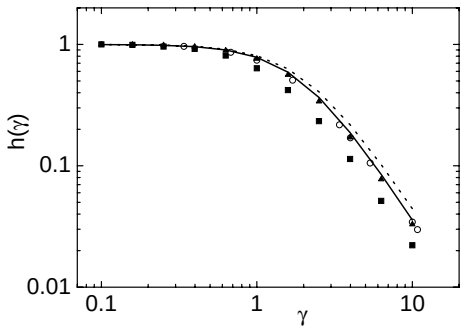

Fig. 7. Damping function prediction of the full model (open circles), Rolie–Poly equation with $\beta = 0$ (triangles) and $\beta = 1$ (squares), compared with Doi–Edwards predictions with the independent alignment approximation (dashed line) and without it (solid line).

Finally we present predictions of the Rolie–Poly equation and the full model for the step shear damping function $h(\gamma)$, which is effectively the fraction of the stress which is relaxed by slow processes (reptation) in a step strain experiment (Fig. 7). The experimental data are known to be in very good agreement with the original Doi–Edwards theory [1], and therefore any new theory should ensure that the damping function predictions are not spoiled by the new relaxation mechanisms. The agreement of the full theory with the Doi–Edwards predictions is very good, as well as the agreement with the Rolie–Poly equation without constraint release. The later is quite surprising since our form of equation is much simpler than the Doi–Edwards Q-tensor. We think that this agreement between the Rolie–Poly model and the Doi–Edwards model is merely a fortuitous coincidence.

The addition of CCR to a Rolie–Poly equation spoils this agreement, which again suggests that in practice one should use small value for the CCR parameter β. The addition of faster modes in the multi-mode version does not change the damping function predictions, but does help to eliminate a maximum in $\sigma_{xy}(\dot{\gamma})$ plot. We note also that the presence of CCR in the full theory does not spoil the agreement with the Doi–Edwards damping function, and the agreement with $c_\nu = 1$ is even better than with $c_\nu = 0.1$.

In conclusion, we have proposed a very simple one-mode differential constitutive equation for the stress tensor, which describes entangled linear polymers with sufficient accuracy yet simplicity of calculation for complex flow modeling. Contrary to previous approaches, we have derived this equation from a more detailed molecular theory [8], then justified the simplifications by comparison between the two theories. To test this equation in the future one can compare complex flow simulations with experimental flow visualization, as well as by purely viscometric experiments.

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Appendix A

One way of derivation of a one-mode equation from the full theory Eq. (2) is via its Fourier transform, which can be introduced as

$$\boldsymbol{C}_{pq} = \frac{1}{\pi^2 pq}\int_0^Z\int_0^Z \sin\left(\frac{\pi p s}{Z}\right)\sin\left(\frac{\pi q s'}{Z}\right)\left(\boldsymbol{f}(s,s') - \boldsymbol{f}_{\mathrm{eq}}(s,s')\right)\mathrm{d}s\,\mathrm{d}s'.$$

This transforms Eq. (2) to a system of algebraic equations using similar approach to [5]

$$\begin{aligned}\dot{\boldsymbol{C}}_{pq} = {}& \boldsymbol{\kappa}\cdot\boldsymbol{C}_{pq} + \boldsymbol{C}_{pq}\cdot\boldsymbol{\kappa}^{\mathrm{T}} + \frac{Z}{6\pi^2 p^2}(\boldsymbol{\kappa}+\boldsymbol{\kappa}^{\mathrm{T}}) - \left(\frac{3\nu}{2}+\frac{D}{Z}\right)\frac{\pi^2(p^2+q^2)}{Z^2}\boldsymbol{C}_{pq} + 8\frac{D}{Z^3}R_{pm}R_{ql}\boldsymbol{C}_{ml}\\ &+\frac{D\boldsymbol{I}}{2Z^2}\left(\frac{1}{q}\gamma_{pq}+\frac{1}{p}\gamma_{qp}\right) + \frac{3D\pi^2}{Z^3}\sum_m m[\gamma_{pm}\boldsymbol{C}_{mq}+\gamma_{qm}\boldsymbol{C}_{mp}],\end{aligned} \tag{A.1}$$

where R_{pq} is known constant matrix, $D = (k_{\mathrm{B}}T/N_{\mathrm{e}}\zeta_0)$ is the diffusion constant of one entanglement segment,

$$\gamma_{ab} = \int_0^Z \ln(\mathrm{tr}\,\boldsymbol{f}(s,s))\left(b\cos\left(\frac{a\pi s}{Z}\right)\cos\left(\frac{b\pi s}{Z}\right) - a\sin\left(\frac{a\pi s}{Z}\right)\sin\left(\frac{a\pi s}{Z}\right)\right)\mathrm{d}s$$

and

$$\nu = \frac{c_\nu 12\pi^3 D}{Z^4}\sum_{p,q} pq\,\mathrm{tr}\boldsymbol{C}_{pq}\left[p\cos\left(\frac{p\pi s}{Z}\right)\sin\left(\frac{q\pi s}{Z}\right) + q\sin\left(\frac{p\pi s}{Z}\right)\cos\left(\frac{q\pi s}{Z}\right)\right]. \tag{A.2}$$

Now one can assume that all modes but the first one $\boldsymbol{C}_{11}$ are unperturbed. This is not true of course, but it leads to correct functional form of a simple equation. We will therefore omit all prefactors and replace $\boldsymbol{C}_{11}$ by the stress $\boldsymbol{\sigma} - \boldsymbol{\sigma}_{\mathrm{eq}}$, where $\boldsymbol{\sigma}_{\mathrm{eq}} = \boldsymbol{I}$ since the stress is measured in units of the plateau modulus. The first line of Eq. (A.1) is easily transferred to

$$\dot{\boldsymbol{\sigma}} = \boldsymbol{\kappa}\cdot\boldsymbol{\sigma} + \boldsymbol{\sigma}\cdot\boldsymbol{\kappa}^{\mathrm{T}} - \nu(\boldsymbol{\sigma}-\boldsymbol{I}) - \frac{1}{\tau_{\mathrm{d}}}(\boldsymbol{\sigma}-\boldsymbol{I}) + \cdots,$$

where the term with ν is CCR, and the term with τ_{d} is reptation. Note that both effects relax $\boldsymbol{\sigma}$ to its equilibrium value.

To simplify the retraction part (second line of Eq. (A.1)) we first evaluate γ_{11}:

$$\gamma_{11} = \int_0^Z \ln\left(\mathrm{tr}\boldsymbol{C}_{11}\sin^2\left(\frac{\pi s}{Z}\right)+1\right)\cos\left(\frac{2\pi s}{Z}\right)\mathrm{d}s \equiv \Gamma(\mathrm{tr}\boldsymbol{C}_{11}),$$

where the function $\Gamma(x)$ has the following asymptotes

$$\Gamma(x) = \begin{cases} -\frac{1}{4}x, & x \ll 1\\ -1, & x \gg 1\end{cases}.$$

Now the second line of Eq. (A.1) simplifies to

$$\dot{\boldsymbol{\sigma}} = \frac{\cdots \Gamma(\mathrm{tr}\boldsymbol{\sigma} - 3)\boldsymbol{\sigma}}{\tau_\mathrm{R}}$$

The frequency of constraint release ν must be proportional to the rate of stretching reduction due to retraction, and chain stretch is $\lambda = \sqrt{\mathrm{tr}\boldsymbol{\sigma}}$:

$$\nu \sim \left.\frac{\partial\lambda}{\partial t}\right|_\mathrm{retr} \sim \frac{1}{\sqrt{\mathrm{tr}\boldsymbol{\sigma}}}\mathrm{tr}\dot{\boldsymbol{\sigma}}|_\mathrm{retr} = \frac{\sqrt{\mathrm{tr}\boldsymbol{\sigma}}}{\tau_\mathrm{R}}\Gamma(\mathrm{tr}\boldsymbol{\sigma} - 3), \tag{A.3}$$

which leads to

$$\boldsymbol{\sigma} = \boldsymbol{\kappa}\boldsymbol{\sigma} + \boldsymbol{\sigma}\boldsymbol{\kappa}^\mathrm{T} - \frac{1}{\tau_\mathrm{d}}(\boldsymbol{\sigma} - \boldsymbol{I}) - \frac{1}{\tau_\mathrm{R}}\Gamma(\mathrm{tr}\boldsymbol{\sigma} - 3)(\boldsymbol{\sigma} + \beta\sqrt{\mathrm{tr}\boldsymbol{\sigma}}(\boldsymbol{\sigma} - \boldsymbol{I})).$$

This equation corresponds to Eq. (5) with $\delta = 1/2$ within prefactors. If one includes CCR suppression by stretch, the power δ changes to 0 or $-1/2$ (see [8] for details).

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