

Simple, Accurate and User-Friendly Differential Constitutive Model for the Rheology of Entangled Polymer Melts and Solutions from Non-Equilibrium Thermodynamics

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Abstract

In a recent reformulation of the Marrucci-Ianniruberto constitutive equation for the rheology of entangled polymer melts in the context of non-equilibrium thermodynamics, rather large values of the convective constraint release parameter β_{crr} had to be used in order not to violate the second law of thermodynamics. In this work, we present an appropriate modification of the model which avoids the splitting of the evolution equation for the conformation tensor into an orientation and a stretching part. Then, thermodynamic admissibility dictates simply that $\beta_{crr} \geq 0$, thus allowing for more realistic values of β_{crr} to be chosen. Moreover, and in view of recent experimental evidence for a transient stress undershoot (following the overshoot) at high shear rates whose origin may be traced back to molecular tumbling, we have incorporated in the model additional terms accounting, at least in an approximate way, for non-affine deformation through a slip parameter ξ . Use of the new model to describe available experimental data for the transient and steady-state shear and elongational rheology of entangled polystyrene melts and solutions shows close agreement. Overall, the modified model proposed here combines simplicity with accuracy, which renders it an excellent choice for managing complex viscoelastic fluid flows in large-scale numerical calculations.

Keywords: entangled polymer melts, concentrated polymer solutions, non-equilibrium thermodynamics, polymer tumbling, transient shear viscosity undershoot.

1. Introduction

Using accurate constitutive models to describe the complex rheological response of high molecular weight (MW) polymers (melts or solutions) to an applied flow field allows for the more economic, rational design of new polymer-based products as well as for the better description of processing operations as these models are key ingredients in large-scale numerical calculations of viscoelastic fluid flows. A successful such model should be able to accurately predict changes in the rheology

of the material during processing as a function of chemical structure and composition, molecular architecture, and morphology (possible co-existence of crystalline and amorphous domains).

Since its introduction and after several modifications and improvements, the tube model [1,2] has offered a remarkable conceptual framework for formulating theories that can explain and quantitatively describe the behavior of entangled, high-MW polymer melts and concentrated polymer solutions both under equilibrium and non-equilibrium (flow) conditions. It relies on the idea that due to chain uncrossability and development of entanglements with other chains, the lateral motion of a reference chain is effectively constrained within a curvilinear tube-like region (a mean-field tube), which develops around the primitive path of the chain and has a diameter whose magnitude reflects the strength of these topological interactions. In the simplest case of a linear chain being restricted within such a tube-like region, relaxation is achieved through backward and forward diffusion (i.e., through reptation) along the axis of the confining tube [1,2]. Today, chain reptation within the mean-field tube is not simply a mathematical invention; it has been directly observed in molecular level simulations [3]. However, it is also well-known that for the tube model to be able to quantitatively describe the equilibrium dynamics of actual polymeric systems, it has to account for additional mechanisms, such as contour length fluctuations (CLF) due to the “breathing” motion of chain ends, and constraint release (CR) due to the destruction of topological constraints as a result of the simultaneous (collective) relaxation of chains surrounding the reference chain.

In the regime of strong flows, a mechanism that the original theory failed to consider is that of convective constraint release (CCR). In this case, when the shear rate exceeds $1/\tau_d$ where τ_d is the inverse chain reptation or disentanglement time, the simultaneous motion of the surrounding chains comprising the mean-field tube leads to release of entanglements, thus inducing a faster relaxation [4,5]. Self-consistently, this means that the number of entanglements should be a decreasing function of the strength of the flow field, a notion that was originally missed by polymer physicists and rheologists. This has been directly demonstrated in the non-equilibrium molecular dynamics (NEMD) simulations of Baig et al. [6] with an entangled polyethylene melt under shear flow, as well as in several other NEMD simulation studies afterwards [7–10]. The direct observation of flow-induced chain disentanglement was incorporated a few years later into a novel and very successful constitutive rheological model by Ianniruberto and Marrucci accounting explicitly for the CCR mechanism [11]. Chain stretching was also incorporated into the model [12] by considering separate evolution equations for the tensor \mathbf{S} describing the average orientation of tube segments and the scalar variable λ accounting for the average chain stretch. However, Wapperom et al. [13] argued that such a model leads to anomalous behavior when employed in numerical simulations of complex flows. This motivated Ianniruberto and Marrucci [14] to propose a suitable modification that unified the two different equations into a single one by making use of a single conformation tensor that can describe both effects (tube orientation and chain stretch).

Another important mechanism that was originally neglected but was again pointed out by NEMD simulations to be of relevance is rotation or tumbling even of entangled chains under shear [6–8,15]. Shear-induced tumbling of entangled polymer chains was incorporated into a constitutive model by Costanzo et al. [16] by introducing a “tumbling” function. In fact, the authors showed that this tumbling behavior is responsible for the appearance of a transient stress undershoot (following the overshoot) at high shear rates in the case of polymer solutions but not in the case of polymer melts. A similar conclusion was reached by Stephanou et al. [17,18] who revisited the kinetic theory of Curtiss-Bird [19–21] and solved the corresponding model equations [22] in the presence of rotational diffusion. They showed that the tumbling-snake model for polymeric systems, as they coined the kinetic theory of Curtiss-Bird, predicts pronounced undershoots in the

time-dependent shear viscosity arising from the rotational Brownian diffusion term in the equation of motion for polymer segments, but not in the transient normal stress coefficients. Obviously, such undershoots should be absent in the transient extensional viscosities, since elongational flows are by default free of any rotational contributions to the velocity gradient tensor, and this was indeed verified to be the case [16,23,24]. Additional results from NEMD simulations demonstrated that the overshoot and undershoot in the shear viscosity upon flow startup are correlated to tube orientation and chain tumbling, respectively [9,10].

In a recent contribution [25], we formally re-derived the Ianniruberto-Marrucci [14] and Rolie-Poly [26] models in the context of the generalized bracket [27] and GENERIC [28–30] formalisms of non-equilibrium thermodynamics (NET), and appropriately extended them to account in a self-consistent manner for a second normal stress difference. However, by applying the 2nd law of thermodynamics and requiring the evolution equation to preserve the positive semi-definite nature of the conformation tensor between successive entanglement points along a chain for all times and all flow fields was found to constrain the so-called CCR parameter β_{ccr} to rather large values (larger than one), which seems to be too restrictive. In the present article, we provide a reformulation of that model that allows the use of more realistic values of the CCR parameter. We also introduce in the model a term that accounts for non-affine motion of entanglement strands (allowing for chain tumbling) through a slip parameter ξ . The use of nonequilibrium thermodynamics guarantees that this extra mechanism is self-consistently incorporated in the constitutive model, which also ensures the internal consistency of the final set of transport equations.

The structure of the rest of the paper is as follows: in the next section we present the nonequilibrium thermodynamics formulation of the new model in the context of the generalized bracket formalism [27]; the proof of its thermodynamic admissibility is detailed in the Appendix. We note here that at the level of description of interest in this work, the generalized bracket and the GENERIC [28–30] formalisms are equivalent and may be used interchangeably. In Section 3 we derive asymptotic solutions of the model in the cases of steady-state and transient shear and elongational flows, in the limit of low shear rates. We also discuss how closely the new model can describe experimental rheological data already reported in the literature over the years both for entangled polymer melts and entangled polymer solutions. We conclude with Section 4 presenting a summary of the most important results of our study and a brief discussion of future plans.

2. Methods

2.1 Non-equilibrium thermodynamics refinement of the Stephanou et al. model [25]

Following [25], in the modified version of our model we make use of only one structural parameter, the conformation tensor \mathbf{c} , which is made dimensionless through $\tilde{\mathbf{c}} = K \mathbf{c} / k_B T$ where K denotes the spring constant of the Hookean dumbbells representing entanglement strands, k_B the Boltzmann constant, and T the absolute temperature. The conformation tensor $\tilde{\mathbf{c}}$ refers to one entanglement strand and at equilibrium (zero flow field applied) coincides by definition with the unit tensor \mathbf{I} . Contrary to our previous model, however, we consider an extra contribution to the dissipative bracket, in addition to relaxation phenomena at the level of the structural variable, namely chain non-affine motion, introduced through a fourth-rank tensor \mathbf{L} . Then, using the well-known procedure of the generalized bracket [27], the resulting evolution equation for the entanglement strand conformation tensor reads

$$\tilde{\dot{\mathbf{c}}}_{\alpha\beta,[1]} = -\Lambda_{\alpha\beta\gamma\epsilon} \frac{\delta \mathcal{A}}{\delta \mathbf{c}_{\gamma\epsilon}} + L_{\alpha\beta\gamma\epsilon} \nabla_\gamma \frac{\delta H_m}{\delta \mathbf{M}_\epsilon}, \quad (1)$$

where the left hand-side defines the upper-convected Maxwell time derivative

$$\tilde{\mathbf{c}}_{\alpha\beta,[1]} \equiv \frac{\partial \tilde{c}_{\alpha\beta}}{\partial t} + \mathbf{u}_\gamma \nabla_\gamma \tilde{c}_{\alpha\beta} - \tilde{c}_{\alpha\gamma} \nabla_\gamma \mathbf{u}_\beta - \nabla_\gamma \mathbf{u}_\alpha \tilde{c}_{\gamma\beta}, \quad (2)$$

A denotes the Helmholtz free energy of the system, H_m the mechanical part of the system Hamiltonian, $\mathbf{\Lambda}$ the relaxation fourth-rank matrix, and \mathbf{L} a fourth-rank matrix associated with the non-affine motion mechanism. The corresponding expression for the stress tensor is obtained from the momentum balance equation and provides the relation between the extra or polymer contribution to the stress tensor and the conformation tensor [27]:

$$\sigma_{\alpha\beta} = 2c_{\gamma\beta} \frac{\delta H_m}{\delta c_{\alpha\gamma}} + L_{\alpha\beta\gamma\epsilon} \frac{\delta H_m}{\delta c_{\gamma\epsilon}}. \quad (3)$$

In Eqs. (1)-(3), we have assumed Einstein's implicit summation convention for any repeated Greek indices (and this will be followed throughout this work). We will also restrict our analysis to incompressible and isothermal fluids.

The mechanical part of the Hamiltonian is simply equal to the kinetic energy plus the Helmholtz free energy:

$$H_m = \int \frac{\mathbf{M}^2}{2\rho} dV + A(\mathbf{C}). \quad (4a)$$

The latter is given as [25,31,32]

$$A(\tilde{\mathbf{c}}) = \frac{G_e}{2} \int [\Phi(\text{tr}(\tilde{\mathbf{c}} - \mathbf{I})) - \ln \det \tilde{\mathbf{c}}] dV \quad (4b)$$

and includes two contributions: the dimensionless potential $\Phi(\text{tr}(\tilde{\mathbf{c}} - \mathbf{I}))$ accounting for chain stretching, and an entropic contribution through a (dimensionless) term involving the logarithm of the determinant of the conformation tensor. In Eq. (4b), G_e is the entanglement modulus given by $G_e = n_e k_B T$ where n_e is the entanglement density (assumed to be constant in this work). The partial derivative of the potential $\Phi(\text{tr}(\tilde{\mathbf{c}} - \mathbf{I}))$ with respect to the first invariant (the trace) of $\tilde{\mathbf{c}}$ defines the (dimensionless) effective spring constant h [27,30,33]:

$$h(\text{tr}(\tilde{\mathbf{c}} - \mathbf{I})) = 2 \frac{\delta \tilde{A}(\tilde{\mathbf{c}})}{\delta \text{tr}(\tilde{\mathbf{c}} - \mathbf{I})} = \frac{\partial \Phi(\text{tr}(\tilde{\mathbf{c}} - \mathbf{I}))}{\partial \text{tr}(\tilde{\mathbf{c}} - \mathbf{I})}. \quad (5)$$

where with $\tilde{A} = A/G_e$ we have denoted the dimensionless free energy. The corresponding Volterra derivative of the dimensionless free energy with respect to $\tilde{\mathbf{c}}$ is

$$\frac{\delta \tilde{A}(\tilde{\mathbf{c}})}{\delta \tilde{\mathbf{c}}} = \frac{1}{2} [h(\text{tr}(\tilde{\mathbf{c}} - \mathbf{I})) \mathbf{I} - \tilde{\mathbf{c}}^{-1}]. \quad (6)$$

In Ref. [25], we had employed the FENE-P (Cohen) approximation [34] rather than the FENE-P (Warner) one, because it provides a better approximation to the inverse Langevin function [33,34]. However, Varchanis et al. [35] have found that the FENE-P (Cohen) force law leads to two different solutions, both stable and both preserving the positive definite nature of the conformation tensor, with one being aphysical. Motivated by this finding, in the present study we chose to work with the FENE-P (Warner) approximation for which [33]:

$$\Phi(\text{tr}(\tilde{\mathbf{c}} - \mathbf{I})) = -(b_e - 3) \ln \left(1 - \frac{\text{tr}(\tilde{\mathbf{c}} - \mathbf{I})}{b_e} \right), \quad (7a)$$

$$h(\text{tr}(\tilde{\mathbf{c}} - \mathbf{I})) = \frac{b_e - 3}{b_e - \text{tr}\tilde{\mathbf{c}}}. \quad (7b)$$

Note that Eq. (7a) differs from Eq. (23a) in Stephanou et al. [33]: although both equations lead to the same expression for the force law, Eq. (7b), Eq. (7a) also vanishes at equilibrium as it should, whereas Eq. (23a) in Stephanou et al. [33] does not. Here, b_e is the extensibility parameter defined as $b_e \equiv 3L_e^2/\langle a_e^2 \rangle$ with L_e denoting the maximum length of the entanglement strand (the length of an entanglement strand is equal to $L/(Z+1)$ where L is the primitive path contour length and Z the number of entanglements per chain). For given polymer chemistry, the extensibility parameter should not be considered an adjustable (free) parameter but rather as a known constant, equal to $b_e \equiv [3(0.82)^2/C_\infty](M_e/M_0)$ where C_∞ is the characteristic ratio at infinite chain length, M_e the entanglement molecular weight, and M_0 the monomer molecular weight. For example, for polystyrene (PS): $M_0 = 52$ g/mol and $C_\infty = 9.6$ (Ref. [36], Table 3.3), hence $b_e \equiv M_e/248$ g/mol. Consequently, for PS melts for which we know that $M_e \approx 13300$ g/mol (Ref. [36], Table 3.3), we find $b_e = 54$, whereas for entangled polymer solutions the value of b_e will depend on the polymer concentration of the solution (see Sec. 3.2.2).

Non-affine deformation effects in Eq. (1) are introduced through the tensor \mathbf{L} , and in our work here is assumed to have the following form:

$$L_{\alpha\beta\gamma\epsilon} = -\frac{\xi}{2}(\tilde{c}_{\alpha\gamma}\delta_{\beta\epsilon} + \tilde{c}_{\alpha\epsilon}\delta_{\beta\gamma} + \tilde{c}_{\beta\gamma}\delta_{\alpha\epsilon} + \tilde{c}_{\beta\epsilon}\delta_{\alpha\gamma}), \quad (8)$$

where ξ denotes the non-affine or slip parameter. The same form has been used by Beris et al. [37] to capture the thixotropic behavior of concentrated star polymer suspensions.

Finally, the stress tensor is obtained by substituting Eqs. (6) and (8) into Eq. (3) and reads:

$$\sigma_{\alpha\beta} = (1 - \xi)G_e [h(\text{tr}(\tilde{\mathbf{c}} - \mathbf{I}))\tilde{c}_{\alpha\beta} - \delta_{\alpha\beta}]. \quad (9)$$

The only remaining task is to define the relaxation matrix $\mathbf{\Lambda}$. To this, we consider two relaxation times, the disentanglement or reptation time τ_d , and the Rouse time τ_R , implying that two relaxation matrices $\mathbf{\Lambda}$ should be defined:

$$\begin{aligned} \Lambda_{\alpha\beta\gamma\epsilon}^{\tau_d} &= \frac{f_{\tau_d}(\text{tr}\tilde{\mathbf{c}})}{\tau_d G_e} (\tilde{c}_{\alpha\gamma}\tilde{\beta}_{\beta\epsilon} + \tilde{c}_{\alpha\epsilon}\tilde{\beta}_{\beta\gamma} + \tilde{c}_{\beta\gamma}\tilde{\beta}_{\alpha\epsilon} + \tilde{c}_{\beta\epsilon}\tilde{\beta}_{\alpha\gamma}) \\ \Lambda_{\alpha\beta\gamma\epsilon}^{\tau_R} &= \frac{f_{\tau_R}(\text{tr}\tilde{\mathbf{c}})}{2\tau_R G_e} (\tilde{c}_{\alpha\gamma}\tilde{\beta}_{\beta\epsilon} + \tilde{c}_{\alpha\epsilon}\tilde{\beta}_{\beta\gamma} + \tilde{c}_{\beta\gamma}\tilde{\beta}_{\alpha\epsilon} + \tilde{c}_{\beta\epsilon}\tilde{\beta}_{\alpha\gamma}) \end{aligned} \quad (10)$$

In Eq. (10), $\tilde{\beta}$ is the (dimensionless) mobility tensor (see Ref. [25]) and f_{τ_d} and f_{τ_R} scalar functions of the trace of $\tilde{\mathbf{c}}$ defined as:

$$f_{\tau_R}(\text{tr}\tilde{\mathbf{c}}) = 1 - f_{\tau_d}(\text{tr}\tilde{\mathbf{c}}) = \frac{\beta_{ccr} [h(\text{tr}(\tilde{\mathbf{c}} - \mathbf{I}))\text{tr}\tilde{\mathbf{c}} - 3]}{3 + \beta_{ccr} [h(\text{tr}(\tilde{\mathbf{c}} - \mathbf{I}))\text{tr}\tilde{\mathbf{c}} - 3]}. \quad (11)$$

The (total) relaxation matrix $\mathbf{\Lambda}$ needed in Eq. (1) is then $\mathbf{\Lambda} = \mathbf{\Lambda}^{\tau_d} + \mathbf{\Lambda}^{\tau_R}$.

On inserting Eqs. (4a), (6), (8), and (10) in Eq. (1), we obtain the following evolution equation for the dimensionless conformation tensor:

$$\dot{\tilde{c}}_{\alpha\beta, [JS]} = -\frac{1}{\tau_{ccr}(\text{tr}\tilde{\mathbf{c}})} \left\{ h(\text{tr}(\tilde{\mathbf{c}} - \mathbf{I}))\tilde{c}_{\alpha\gamma}\tilde{\beta}_{\beta\gamma} - \tilde{\beta}_{\alpha\beta} \right\}, \quad (12a)$$

where the left hand-side defines the Johnson-Segalman time-derivative

$$\tilde{\dot{c}}_{\alpha\beta,[JS]} \equiv \tilde{\dot{c}}_{\alpha\beta,[I]} + \frac{\xi}{2} \left(\dot{\gamma}_{\alpha\gamma} \tilde{c}_{\gamma\beta} + \tilde{c}_{\alpha\gamma} \dot{\gamma}_{\gamma\beta} \right), \quad (12b)$$

and the CCR relaxation time is

$$\frac{1}{\tau_{ccr}(\text{tr}\tilde{\mathbf{c}})} = \frac{2}{\tau_d} + \left(\frac{1}{\tau_R} - \frac{2}{\tau_d} \right) \frac{\beta_{ccr} \left[h(\text{tr}(\tilde{\mathbf{c}} - \mathbf{I})) \text{tr}\tilde{\mathbf{c}} - 3 \right]}{3 + \beta_{ccr} \left[h(\text{tr}(\tilde{\mathbf{c}} - \mathbf{I})) \text{tr}\tilde{\mathbf{c}} - 3 \right]}, \quad (12c)$$

with β_{ccr} being the effective CCR parameter. Note that in order to account for both reptation and constraint release, at least in a crude way, we have invoked the *double reptation* approximation and considered the disengagement time to be half the corresponding disengagement time when only reptation is considered, i.e. $\frac{1}{2} \tau_d$ [14]. When a non-zero value of the CCR parameter is considered, the CCR relaxation time, τ_{ccr} , will exhibit a flow-induced reduction from its equilibrium value (i.e., $\frac{1}{2} \tau_d$) towards its value at large flow rates (i.e., the Rouse time). Finally, for the mobility tensor, we invoke Giesekus' postulate that $\tilde{\boldsymbol{\beta}} = \mathbf{I} + \alpha \tilde{\boldsymbol{\sigma}}$ [25,33], where α is the anisotropic mobility parameter and $\tilde{\boldsymbol{\sigma}} = \boldsymbol{\sigma}/G_e$ denotes the dimensionless stress tensor. Thus, the evolution equation, Eq. (12a), becomes (henceforth, for notation simplicity, we shall drop the arguments in the functions $h(\text{tr}(\tilde{\mathbf{c}} - \mathbf{I}))$ and $\tau_{ccr}(\text{tr}\tilde{\mathbf{c}})$):

$$\tilde{\dot{c}}_{\alpha\beta,[JS]} = -\frac{1}{\tau_{ccr}} \left\{ \alpha(1-\xi) h^2 \tilde{c}_{\alpha\gamma} \tilde{c}_{\beta\gamma} + [1-2\alpha(1-\xi)] h \tilde{c}_{\alpha\beta} - [1-\alpha(1-\xi)] \delta_{\alpha\beta} \right\}. \quad (13)$$

As far as the conditions that should be obeyed for the model to be thermodynamically admissible and preserve the positive-definite character of the conformation tensor, these are elaborated in the Appendix and require that:

$$0 \leq \alpha \leq (1-\xi)^{-1} \text{ and } \beta_{ccr} \geq 0. \quad (14)$$

According to these, the proposed revised model allows for any non-negative value of the CCR parameter to be used without violating the laws of NET, which should be contrasted with the earlier version [25] wherein β_{ccr} had to be strictly larger than unity. Finally, note that in deriving the above constitutive model we have assumed that the contribution of solvent to the total stress is too small compared to the contribution of polymer (although it can be easily incorporated if needed).

2.2. Asymptotic solutions

We proceed next to analyze the asymptotic behavior of the model in the limit of low strain rates for the following three cases: inception of simple shear flow (SSF) described by the kinematics $\mathbf{u} = (\dot{\gamma}_0 y, 0, 0)$, inception of uniaxial elongation flow (UEF) described by the kinematics $\mathbf{u} = (\dot{\epsilon}_0 x, -\frac{1}{2} \dot{\epsilon}_0 y, -\frac{1}{2} \dot{\epsilon}_0 z)$, and small amplitude oscillatory flow (SAOF) described by the kinematics $\mathbf{v} = (\dot{\gamma} \cos(\omega t) y, 0, 0)$. The material functions to analyze are: a) the shear viscosity η ($= \sigma_{xy} / \dot{\gamma}_0$) and the two normal stress coefficients Ψ_1 ($= (\sigma_{xx} - \sigma_{yy}) / \dot{\gamma}_0^2$) and Ψ_2 ($= (\sigma_{yy} - \sigma_{zz}) / \dot{\gamma}_0^2$) in the case of shear, b) the extensional viscosity η_{1E} ($= (\sigma_{xx} - \sigma_{yy}) / \dot{\epsilon}_0$) in the

case of uniaxial elongation, and c) the storage $G'(\omega)$ and loss $G''(\omega)$ moduli in the case of SAOF.

To get asymptotic expressions for the conformation tensor and consequently for the material functions in the limit of small strain rates, we invoke a linearization of the evolution equation for the conformation tensor, which in a second step is solved analytically to provide also the stress tensor components. Then, the following results are obtained for the relevant viscometric or material functions:

Inception of shear:

$$\eta^+(t) = \eta_0 \left[1 - \exp(-2t/\tau_d) \right], \quad (15a)$$

$$\Psi_1^+(t) = \Psi_{1,0} \left[1 - \left(1 + \frac{2t}{\tau_d} \right) \exp\left(-\frac{2t}{\tau_d}\right) \right], \quad (15b)$$

$$\begin{aligned} \Psi_2^+(t) = & -\frac{1}{2} \Psi_{1,0} \left\{ \left[\xi + \alpha(1-\xi)^2 \right] \left[1 - \left(1 + \frac{2t}{\tau_d} \right) \exp\left(-\frac{2t}{\tau_d}\right) \right] \right. \\ & \left. + \alpha(1-\xi)^2 \exp\left(-\frac{2t}{\tau_d}\right) \left[1 - \frac{2t}{\tau_d} - \exp\left(-\frac{2t}{\tau_d}\right) \right] \right\}, \end{aligned} \quad (15c)$$

where $\eta_0 = (1-\xi)^2 \frac{1}{2} \tau_d G_e$ and $\Psi_{1,0} = \tau_d \eta_0$ are also the zero-shear rate steady-state values of the shear viscosity and of the first normal stress coefficient:

$$\lim_{\dot{\gamma}_0 \rightarrow 0} \frac{\eta}{\eta_0} = 1, \quad (16a)$$

$$\lim_{\dot{\gamma}_0 \rightarrow 0} \frac{\Psi_1}{\Psi_{1,0}} = 1, \quad (16b)$$

$$\lim_{\dot{\gamma}_0 \rightarrow 0} \frac{\Psi_2}{\Psi_{1,0}} = -\frac{\alpha}{2} \left[\alpha(1-\xi)^2 + \xi \right]. \quad (16c)$$

Inception of uniaxial elongation:

$$\eta_E^+(t) = 3\eta_0 \left[1 - \exp(-2t/\tau_d) \right], \quad (17)$$

and thus Trouton's law holds, since:

$$\lim_{\dot{\epsilon}_0 \rightarrow 0} \frac{\eta_E}{\eta_0} = 3. \quad (18)$$

Small Amplitude Oscillatory flow:

$$G''(\omega) = \frac{\eta_0 \omega}{1 + \left(\frac{1}{2} \tau_d \omega \right)^2}; \quad G'(\omega) = \eta_0 \frac{1}{2} \tau_d \frac{\omega^2}{1 + \left(\frac{1}{2} \tau_d \omega \right)^2}. \quad (19)$$

3. Results and Discussion

All predictions provided here have been obtained with the FENE-P (Warner) approximation for the function h [Eq. (7b)]. In Section 3.1, we will also employ the relation $\tau_d = 3Z\tau_R$ [2], we will take $b_e = 100$, and will keep the number of entanglements Z equal to 20.

3.1. Material functions in shear

In Figure 1 we depict model predictions for the steady-state shear viscosity [Fig. 1(a)] and the first [Fig. 1(b)] and second [Fig. 1(c)] normal stress coefficients (appropriately scaled with the zero-rate viscosity η_0 and the first normal stress coefficient $\Psi_{1,0}$), as a function of the applied shear rate; results for various values of the model parameters are shown. When a vanishing value of the anisotropic parameter α is considered, then a vanishing second normal stress coefficient is predicted [the corresponding curves are missing from Fig. 1(c)]. As the CCR parameter increases, both η and Ψ_1 exhibit a faster shear thinning behavior, which is the expected behavior given that the CCR parameter introduces a shear-induced reduction of the relaxation time.

However, and irrespective of the value of the CCR parameter assumed, the power-law behavior at large shear rates remains unaltered, with the corresponding exponents equal to $-2/3$ for the shear viscosity and equal to $-4/3$ for the first normal stress coefficient. Then, while keeping β_{ccr} constant, upon increasing the value of α from 0 to 0.1 the power-law exponent at large shear rates changes to -1 and $-5/3$ for η and Ψ_1 , respectively. By further increasing the value of α to 0.2, the shear viscosity is affected only by very little while the

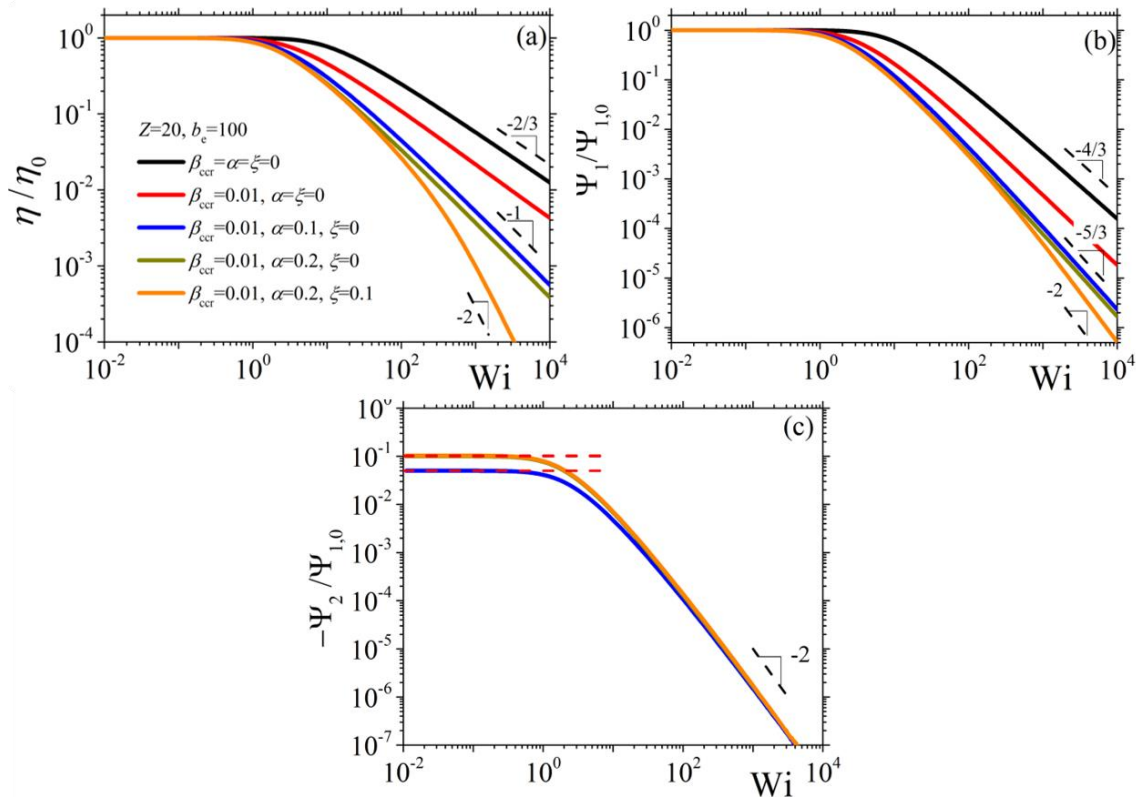


Figure 1. Model predictions for the three material functions (in scaled units) in shear, and dependence on the parameters α , ξ , and β_{ccr} : (a) shear viscosity, (b) first normal stress coefficient, and (c) second normal stress coefficient.

first normal stress coefficient is not affected at all. In the case of the second normal stress coefficient we note a non-vanishing value which at small shear rates reaches the zero-rate value dictated by Eq. (16c). Thus, as α increases, the zero-rate value increases. However, the large shear rate power-law exponent is equal to -2 irrespective of the values of the parameters. Finally, for non-zero values of the non-affine parameter ξ , we note that until about $Wi=100$ the predictions for η and Ψ_1 are the same as when $\xi = 0$, but after that, the power-law behavior differs as the corresponding exponents for both η and Ψ_1 become now equal to -2. On the other hand, the prediction for Ψ_2 remains the same.

In Figures 2 and 3 we present the model predictions for the growth of the shear viscosity and first normal stress coefficient, respectively, upon inception of the shear flow at three different values of the dimensionless shear rate Wi ($= 1, 10$, and 100), along with the prediction of the LVE behavior given by Eq. (15) (dotted orange line). Irrespective of the shear rate and the parameter values assumed, at sufficiently short times all viscometric curves follow the LVE prediction, which is the expected theoretical prediction. At small shear rates ($Wi=1$), both functions are seen to approach their steady-state values monotonically, whereas at larger shear rates ($Wi=10$) they go through an overshoot before they reach their steady-state values. Finally, at large shear rates ($Wi=100$) and for a non-zero value of the non-affine parameter, the shear viscosity goes through an undershoot right after the overshoot, which is more pronounced in the curves shown in Fig. 2(b). Of course, this is only a rather small undershoot; more pronounced undershoots will be reported in the next section when we will discuss how the model can fit true experimental data [see Figs. 7(a) and 11(b)]. Furthermore, note that both the intensity and the position of this undershoot are controlled by the parameters of the model. Such a behavior is not noticed for the first normal stress coefficient. Overall, the same trend is noticed also for the second normal stress coefficient (Fig. 4) whereas, contrary to the other two viscometric functions, the transient curves go over (instead of below) the LVE predictions.

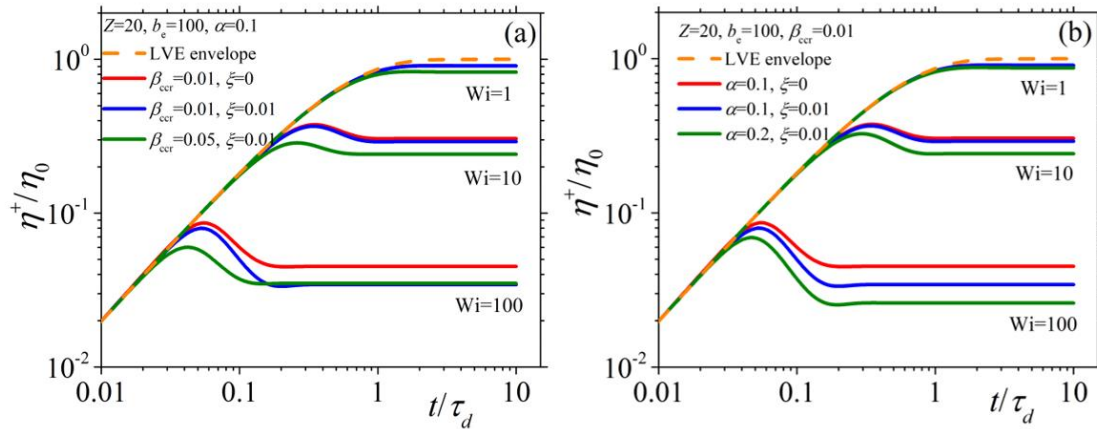


Figure 2. Growth of the shear viscosity upon inception of the shear flow at different shear rates for several values of the model parameters (α , ξ , and β_{crr}). The LVE envelope is depicted as a dashed orange line.

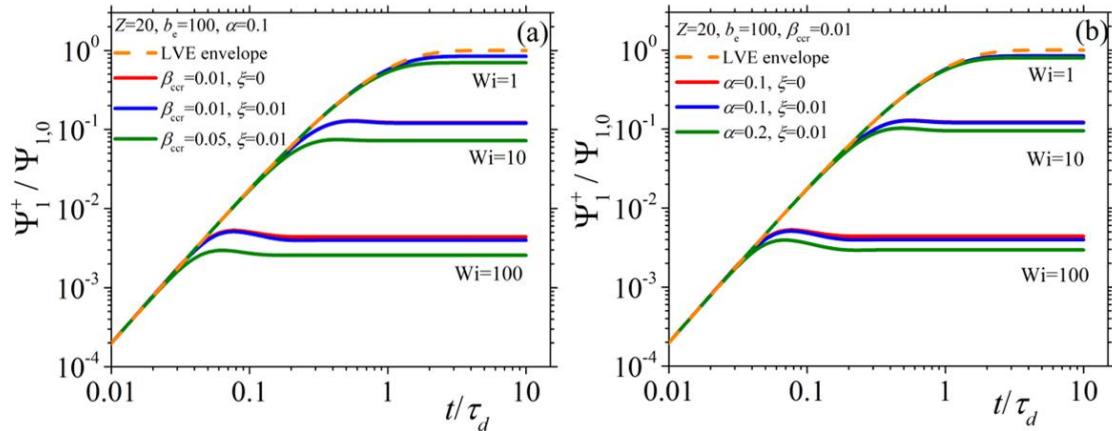


Figure 3. Same as with Fig. 2 but for the first normal stress coefficient.

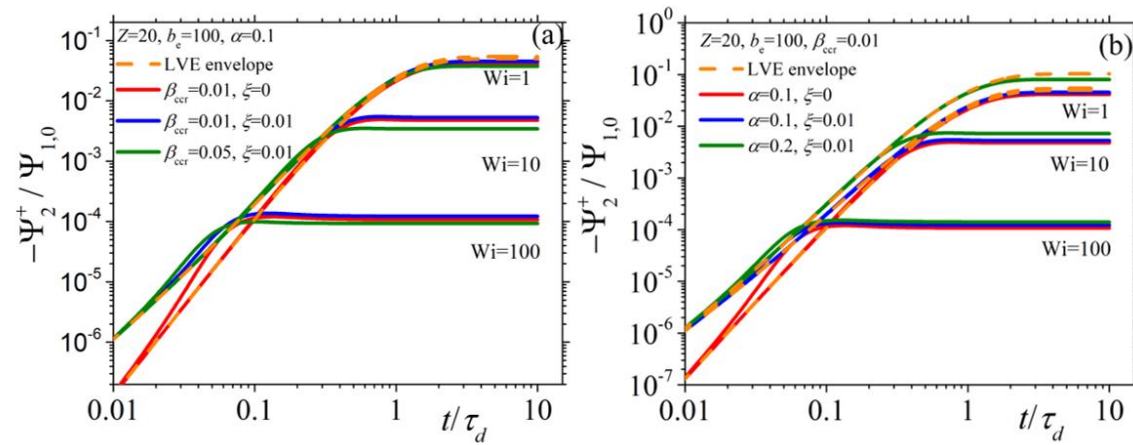


Figure 4. Same as with Fig. 2 but for the second normal stress coefficient.

3.2. Comparison with experimental data for entangled polystyrene melts and solutions

3.2.1. Comparison with the experimental data presented in Stephanou et al. [17]

Figure 5 shows how the new model can fit the experimental data for the spectra of the storage and loss moduli discussed in Ref. [17] in conjunction with the earlier version of this model; the model predictions were obtained with the help of Eqs. (19). To carry out the fitting, we first need to specify two of the model parameters: the reptation time τ_d , and either the entanglement modulus G_e or the zero-rate viscosity η_0 . The values that were found to describe the data best are $\tau_d = 11$ s and $\eta_0 = 68$ kPa.s. The fitting is particularly good for small frequencies, which is the expected behavior. This is particularly pleasing given the use of only one mode in the model and the neglect of fast (Rouse) mode contributions.

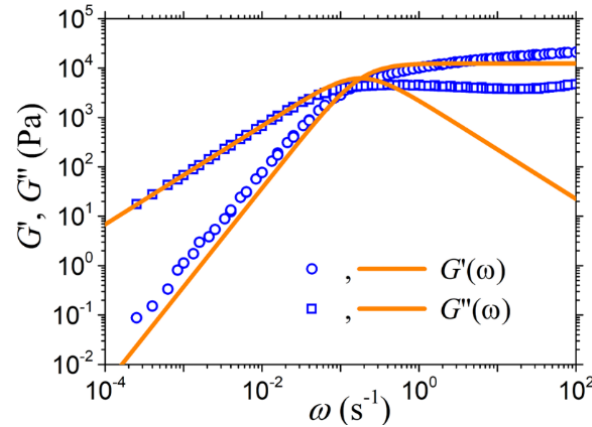


Figure 5. Model predictions and comparison with the experimental data considered also in Ref. [17], for the storage and loss moduli at 30 °C of a nearly monodisperse PS solution with 899 kDa and polymer volume fraction 36.7% ($Z = 13.9$) characterized by $\tau_d = 11$ s and $\eta_0 = 68$ kPa.s.

Next, in Figure 6, we present the fittings for the steady-state values of the shear viscosity and of the two normal stress coefficients, whereas in Figures 7 and 8 we present the corresponding fittings in the case of the inception of shear flow. There, the Rouse time was calculated through $\tau_R \equiv \tau_d / 3Z$ and, since the entanglement molecular weight of the PS in the solution is equal to 64.6 kDa (see Table S-1 of Ref. [17], then $b_e = 260$. Then, and in order to choose the values of the rest of the model parameter, we used that: a) the parameter α effectively controls the transient second normal stress coefficient, and b) the undershoot observed at large shear rates in the transient shear viscosity is highly sensitive to the value of the non-affine parameter ξ [see Fig. 7(b)]. Thus, we came up with the following values: $\alpha = 0.4$, $\beta_{ccr} = 0.06$, and $\xi = 0.03$. The graphs show that the model offers a very good description of all three steady-state viscometric functions. In addition, it can predict quite accurately the growth of the shear viscosity and of the first normal stress coefficient to flow start-up; even the position of the shear viscosity undershoot, t_u , at large shear rates is predicted quite accurately [Fig. 7(b)]. The description of the relative undershoot, d_u , (undershoot depth divided by the steady-state value), on the other hand, is less satisfactory [Fig. 7(c)]. Finally, for the growth of the second normal stress coefficient in the start-up of shear flow, we note that the prediction comes with an offset, even in the LVE envelope. We hypothesize that this is due to the consideration of only a single mode in the present analysis.

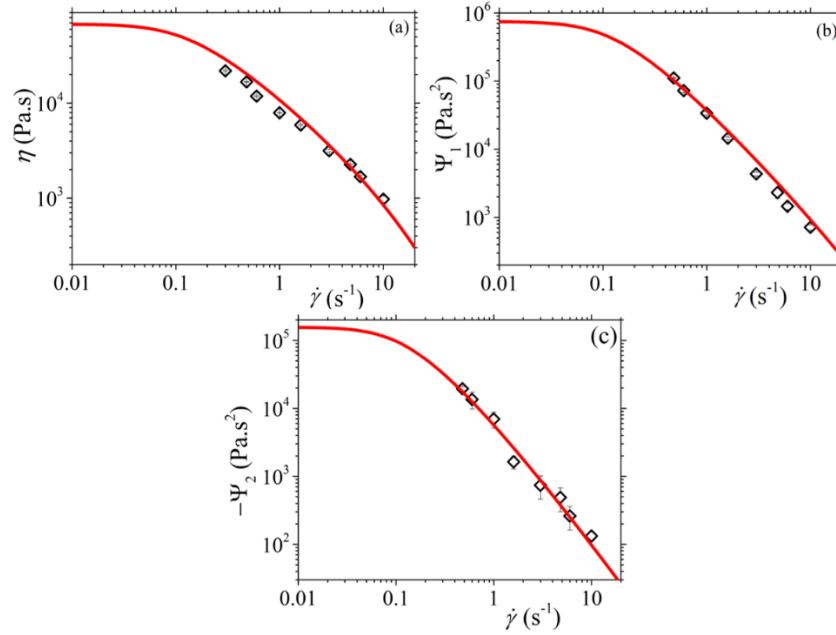


Figure 6. Model predictions and comparison with the experimental data considered in Ref. [17] for: (a) the shear viscosity, (b) the first normal stress coefficient, and (c) the second normal stress coefficient, at steady state. Model parameters: $\alpha=0.4$, $b_e=54$, $\beta_{ccr}=0.06$, and $\xi=0.03$ (the rest are the same as in Fig. 5).

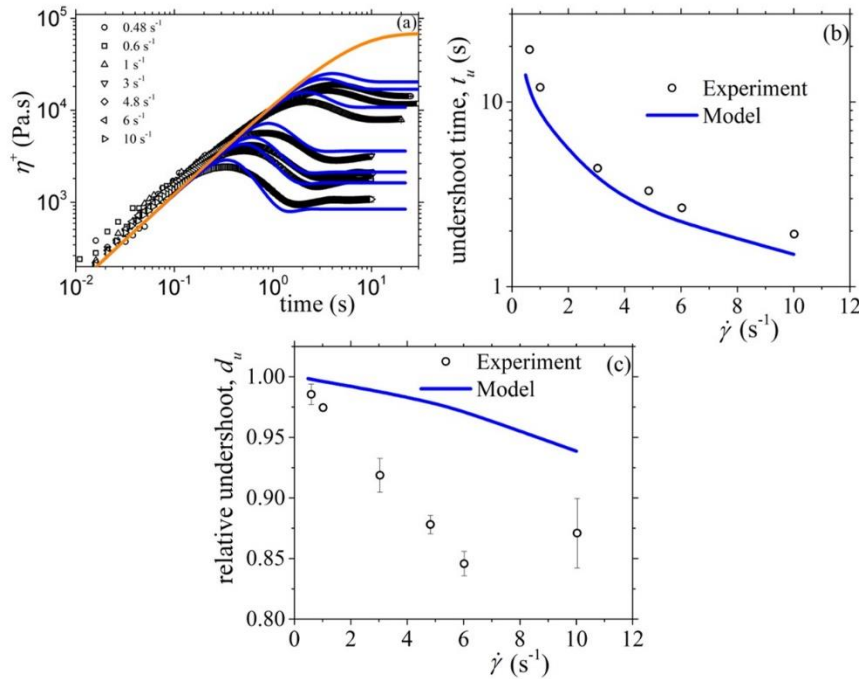


Figure 7. Model predictions and comparison with the experimental data considered in Ref. [17] for: (a) the growth of the shear viscosity, (b) the undershoot time, and (c) the relative undershoot, upon inception of shear flow. The thick orange line in Fig. 1(a) depicts the LVE envelope, Eq. (15). Same parameter values as in Fig. 6.

3.2.2. Comparison with the experimental data of Costanzo et al. [16]

We next use the new model to describe the experimental data of Costanzo et al. [16] for the polystyrene melt PS185k and the polystyrene solution PS285k/2k-65, both of which have the same number of entanglements, $Z = 13.9$. For the reptation time we consider the values depicted as τ_m in their Table 2 (5.10 s for the melt, and 5.32 s for the solution). And the same for the Rouse time and the zero-rate viscosity; we adopt the values also given in their Table 2: $\tau_R = 0.271$ s and $\eta_0 = 2.28 \times 10^5$ Pa.s for the PS185k melt, and $\tau_R = 0.319$ s and $\eta_0 = 1.04 \times 10^5$ Pa.s for the PS285k/2k-65 solution. Finally, as mentioned before, for the melt $b_e = 54$, whereas for the solution $b_e = 83$ (since $M_e = 20.5$ kDa as calculated through $M_e^{\text{solution}} = M_e^{\text{melt}} / \phi$ with ϕ being the polymer volume fraction [16]). Moreover, for the melt, and since no undershoots are observed at large shear rates in the transient shear viscosity, we consider $\xi = 0$. For the remaining parameters, both for the melt and the solution, we follow the same strategy as above the only difference being that now we use the model to fit the steady-state and transient elongational viscosities for the two systems, which are depicted in Figs. 12 and 13. Overall, the following model parameters are used: $\alpha = 0.15$, $\beta_{ccr} = 0.2$, and $\xi = 0$ for the melt; and $\alpha = 0.47$, $\beta_{ccr} = 0.001$, and $\xi = 0.0015$ for the solution. The comparison is again very good for all (steady-state and transient) shear

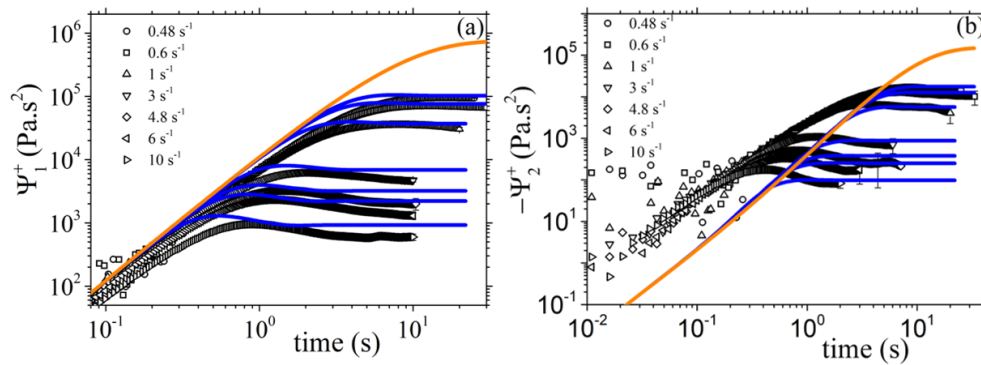


Figure 8. Model predictions and comparison with the experimental data of Ref. [17] for the growth of the first (a) and second (b) normal stress coefficients, upon inception of shear flow. The thick orange lines depict the LVE envelope, Eq. (15). Same parameter values as in Fig. 6.

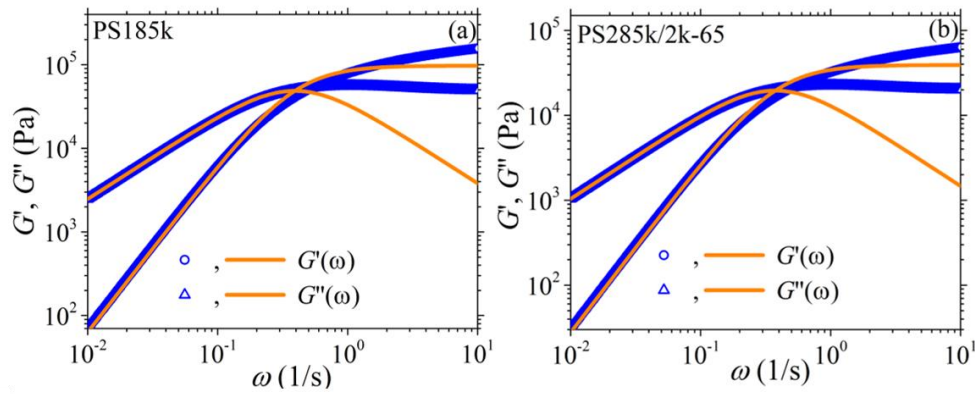


Figure 9. Model predictions for the storage and loss moduli and comparison with the experimental data of Costanzo et al. [16] for: (a) a nearly monodisperse PS melt with $M = 185$ kDa at 160 °C characterized by $\tau_d = 5.1$ s and $\eta_0 = 2.28 \times 10^5$ Pa.s, and (b) a nearly monodisperse PS solution with $M = 285$ kDa and polymer volume fraction 64.9% at 160 °C characterized by $\tau_d = 5.32$ s and $\eta_0 = 1.04 \times 10^5$ Pa.s.

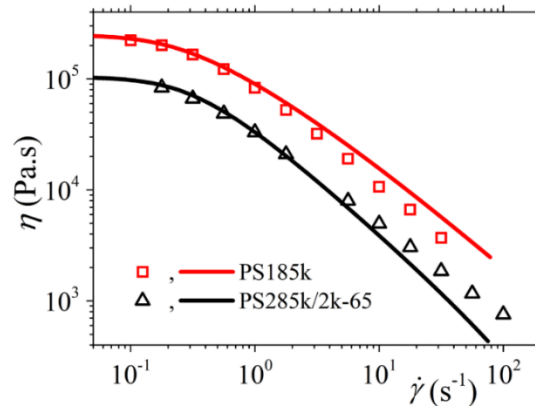


Figure 10. Model predictions and comparison with the experimental data of Costanzo et al. [16] for the shear viscosity of the PS185k melt and the PS285k/2k-65 solution, at steady state. Model parameters: $\alpha = 0.15$, $b_e = 54$, $\beta_{crr} = 0.2$, and $\xi = 0$ for the melt; $\alpha = 0.47$, $b_e = 83$, $\beta_{crr} = 0.001$, and $\xi = 0.0015$ for the solution (the rest are the same as in Fig. 9).

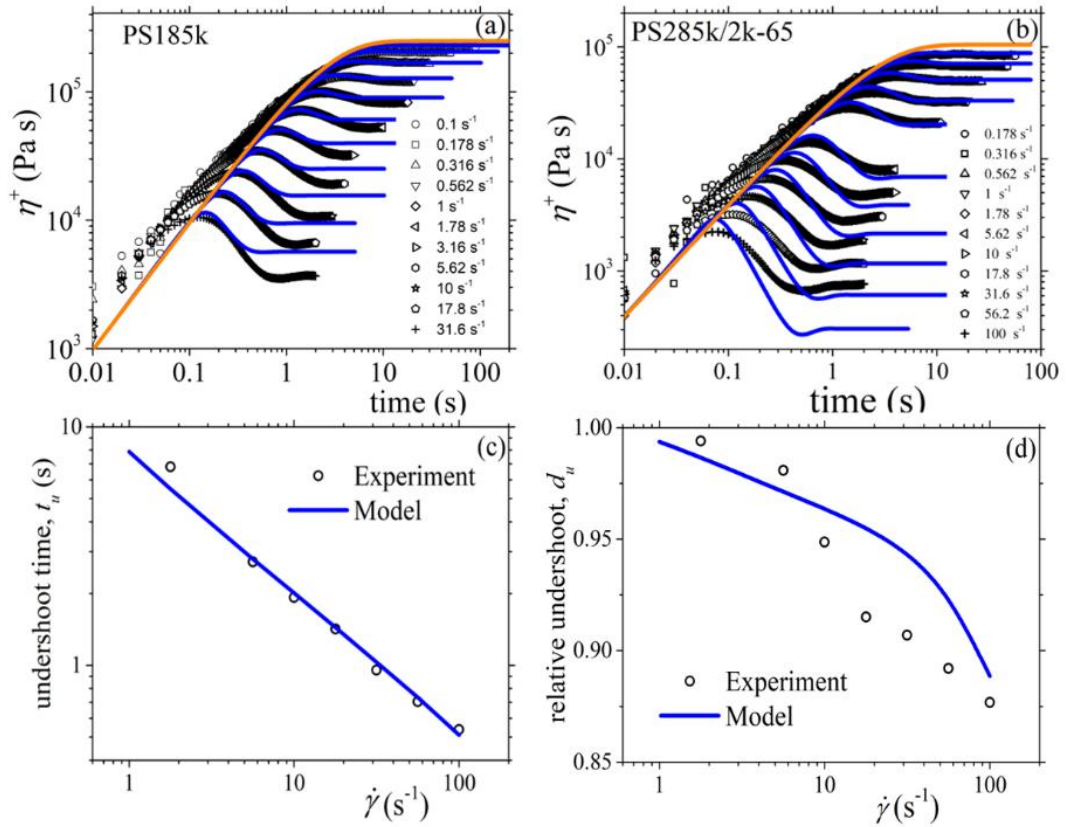


Figure 11. Model predictions and comparison with the experimental data of Costanzo et al. [16] for: (a) the growth of the shear viscosity of the PS185k melt, (b) the growth of the shear viscosity of the PS285k/2k-65 solution, (c) the undershoot time of the PS285k/2k-65 solution, and (d) the relative undershoot of the PS285k/2k-65 solution, upon inception of shear flow. The thick orange line in Fig. 11(a) and (b) depicts the LVE envelope, Eq. (15a). Same parameter values as in Fig. 10.

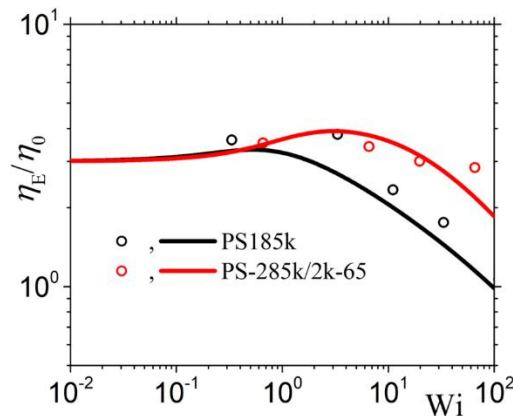


Figure 12. Model predictions and comparison with the experimental measurements of Costanzo et al. [16] for the steady uniaxial extensional viscosity. Same parameter values as in Fig. 11 but in all cases $\xi = 0$.

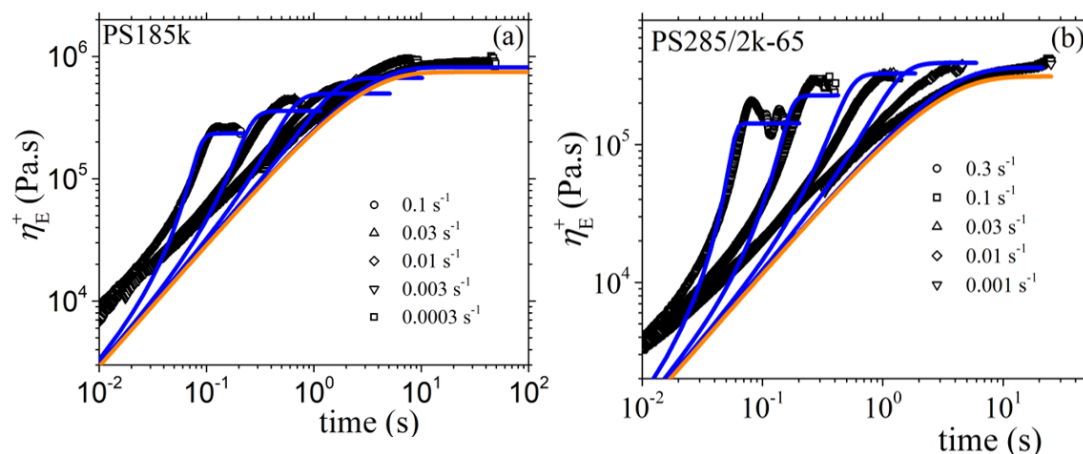


Figure 13. Model predictions and comparison with the experimental measurements of Constanzo et al. [16] for the extensional stress growth coefficient as a function of time for several stretch rates. The thick orange line depicts the LVE envelope, Eq. (17). Same parameter values as in Fig. 12.

and elongational viscosities. Note also that in the case of elongational flow, we have used $\xi = 0$ both for the melt and the solution, since no chain tumbling occurs in extensional flows. Again, the description of the growth of the shear viscosity is quite gratifying, especially of the position of the undershoot at large shear rates in the case of the polymer solution [Fig. 11(c)]; the relative undershoot, on the other hand, is described again less accurately.

4. Conclusions

Some time ago, we presented a reformulation of the Marrucci-Ianniruberto constitutive equation [14] for the rheology of entangled polymer melts and concentrated solutions in the context of nonequilibrium thermodynamics [25]. However, rather large values of the CCR parameter had to be invoked so as not to violate the second law of thermodynamics. Here, we have presented an appropriate modification of that model that avoids the splitting of the evolution equation for the conformation tensor into an orientation and a stretching part; as a result, thermodynamic admissibility allows for a more friendly range of values of the CCR parameter to be used (they must only be non-negative). In addition, and in view of recent experimental evidence for the appearance of undershoots in the transient stress (following the overshoot) at high shear rates whose origin may be traced back to molecular tumbling at high shear rates, the new model contains additional terms accounting for non-affine chain deformation through a slip parameter.

The capability of the new model to describe very satisfactorily rheological data was demonstrated by using it to fit available experimental data for the transient and steady-state shear and elongational rheology of entangled PS melts and solutions. Remarkable success was observed for all viscometric functions checked, given also the use of only a single mode. Given its simplicity, this is a remarkable feature of the new model. It can thus be used as an excellent alternative to other successful constitutive models such as the Rolie-Poly [26] to characterize the rheological response of polymeric fluids or to carry out large scale numerical calculations of complex viscoelastic flows.

Of course, the new version of the model is far from being considered complete. There is a few more features and mechanisms of relevance to the flow of entangled polymer fluids that must be accounted for in the corresponding constitutive and transport equations. First, we mention the need to implement a configuration dependent friction coefficient as has been proposed by Mead et al. [38], as well as the proper extension to a multi-mode formulation. Second, and given the wealth

of information provided by recent NEMD studies [6–8,15] at the level of individual chains and their conformations, it would be highly desirable to check how well the model can describe the conformational properties of entangled polymer melts under flow (and not just the viscometric functions). For example, Sefiddashti et al. [9] have already carried out such a first MD-test of several constitutive models. In turn, such a direct comparison would help fully parameterize the model on the outcome of these direct NEMD simulations. It is by bringing together simulations and theory that one can achieve a more complete description of polymer flows, which can then be encoded in the form of friendly and easy-to-use, yet powerful and accurate constitutive laws for the subsequent use in numerical calculations of viscoelastic flows through geometries of practical relevance.

Author Contributions: Conceptualization, P.S.S. and V.G.M.; Methodology, P.S.S.; Software, I.C.T.; Validation, I.C.T.; Investigation, I.C.T.; Data Curation, I.C.T.; Writing-Original Draft Preparation, P.S.S.; Writing-Review & Editing, P.S.S. and V.G.M.; Visualization, P.S.S. and I.C.T.; Supervision, P.S.S. and V.G.M.; Project Administration, P.S.S.; Funding Acquisition, P.S.S.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix

In this Appendix we discuss the thermodynamic admissibility of the new model. To this, we need first to guarantee that the conformation tensor is positive-definite. A sufficient (but not necessary) condition for $\tilde{\mathbf{C}}$ to be positive definite is that the prefactor of the unit tensor in the evolution equation must be positive [27,39]. This requires that

$$\frac{1 - \alpha(1 - \xi)}{\tau_{ccr}} > 0. \quad (\text{A1})$$

Since the CCR relaxation time is always positive (see also below), then the new model guarantees a positive definite conformation tensor (non-negative eigenvalues) provided that $\alpha < (1 - \xi)^{-1}$. Thermodynamic admissibility further requires that the model be compatible with the 2nd law of thermodynamics, according to which the total rate of entropy production within the system must be non-negative. For incompressible and isothermal flows, such a requirement is expressed as $[H_m, H_m] \leq 0$ [27], for which a necessary and sufficient condition to hold is

$$\frac{\delta H_m}{\delta \tilde{\mathbf{C}}_{\alpha\beta}} \Lambda_{\alpha\beta\gamma\epsilon} \frac{\delta H_m}{\delta \tilde{\mathbf{C}}_{\gamma\epsilon}} \geq 0 \quad (\text{A2})$$

This implies that

$$\begin{aligned} & \frac{\delta \tilde{A}}{\delta \tilde{\mathbf{C}}_{\alpha\beta}} \left(\Lambda_{\alpha\beta\gamma\epsilon}^{\tau_d} + \Lambda_{\alpha\beta\gamma\epsilon}^{\tau_R} \right) \frac{\delta \tilde{A}}{\delta \tilde{\mathbf{C}}_{\gamma\epsilon}} \geq 0 \Rightarrow \\ & \frac{1}{2\tau_{ccr}(\text{tr}\tilde{\mathbf{C}})} \left\{ \left[h^2 \text{tr}\tilde{\mathbf{C}} - 6h + \text{tr}\tilde{\mathbf{C}}^{-1} \right] + \alpha(1 - \xi) \left[h^3 \text{tr}\tilde{\mathbf{C}}^2 - 3h^2 \text{tr}\tilde{\mathbf{C}} + 9h - \text{tr}\tilde{\mathbf{C}}^{-1} \right] \right\} \geq 0 \end{aligned} \quad (\text{A3a})$$

which can also be written as

$$\frac{1}{2\tau_{ccr}} \sum_{i=1}^3 \frac{(h\mu_i - 1)^2}{\mu_i} \{1 + \alpha(1 - \xi)(h\mu_i - 1)\} \geq 0, \quad (\text{A3b})$$

where $\mu_i, i = \{1, 2, 3\}$ denote the eigenvalues of the conformation tensor. Given that the conformation tensor is positive-definite (thus, $\mu_i \geq 0, \forall i$), the sum in Eq. (A3b) is always non-negative. On the other hand, the CCR relaxation time, i.e., the prefactor in Eq. (A3b), is non-negative provided that:

$$\frac{1}{\tau_{ccr}(\text{tr}\tilde{\mathbf{c}})} \geq 0 \Rightarrow \left(\frac{1}{\tau_R} - \frac{2}{\tau_d} \right) \frac{\beta_{ccr} [h(\text{tr}(\tilde{\mathbf{c}} - \mathbf{I}))\text{tr}\tilde{\mathbf{c}} - 3]}{3 + \beta_{ccr} [h(\text{tr}(\tilde{\mathbf{c}} - \mathbf{I}))\text{tr}\tilde{\mathbf{c}} - 3]} \geq 0. \quad (\text{A4})$$

Note that both the reptation and Rouse times are positive quantities. First, we need to check whether $\tau_d > 2\tau_R$. Since a relation of the form $\tau_d = 3Z_{eq}\tau_R$ with $Z_{eq} > 1$ (otherwise the polymeric system studied is below the entanglement threshold) is usually employed, this condition is always true. Second, we note that the fraction in Eq. (A4) is always positive (it ranges between 0 and unity) for all non-negative values of the CCR parameter. Thus, thermodynamic admissibility is guaranteed, provided that $\beta_{ccr} \geq 0$.

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