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Investigation of the inhomogeneous shear flow of a wormlike micellar solution using a thermodynamically consistent model

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ABSTRACT

By using the generalized bracket approach of nonequilibrium thermodynamics, we recently developed a new two-species model for wormlike micelles based on the flow-induced breakage of the longer species. In this work, we complete the model by adding diffusion in a thermodynamically consistent manner. Furthermore, we discuss the behavior of a limiting case of the model in transient Couette flow between two coaxial cylinders, which is a flow that exhibits spatial inhomogeneities and has widely been studied for wormlike micellar solutions. The flow problem was spatially discretized using a Chebyshev method. A Crank–Nicolson scheme was employed for time discretization. At each time step, the nonlinear system of discretized flow equations was solved using a preconditioned Newton–Krylov solver. The model parameters were obtained by fitting experimental data of a previously studied wormlike micellar system. We found that the model can capture the trends observed in steady simple shear, small-amplitude oscillatory shear, and step strain. The main feature of the model is a strong elastic recoil during the start-up of simple shear flow.

1. Introduction

Wormlike micelles are flexible cylindrical aggregates of surfactant molecules in solution. They are extensively used as rheological modifiers in consumer products such as paints, cosmetics, pharmaceuticals, and foods. When undergoing strong shearing deformations, the mixtures can develop inhomogeneities in the flow field, including multiple localized bands with different shear rates, known as shear bands. The resulting experimental signature is a stress plateau, drawn as a function of the applied shear rate in steady simple shear. The unusual rheological behavior of wormlike micelles has been the focus of many theoretical and experimental investigations; see Refs. [1–5] for recent comprehensive reviews.

In theory, the shear banding of wormlike micelles is thought to arise from a nonmonotonic curve of the shear stress versus the applied shear rate for steady homogeneous flow. Solutions along the decreasing part of this curve are unstable. The flow therefore separates into zones with different shear rates that coexist at identical values of the stress.

Among the most popular constitutive models for wormlike micelles are those single-species models originally developed for polymeric materials [6–9]. Numerous theoretical studies on shear banding have been performed using the Johnson–Segalmann model [10,6,11,12] and the Rolie–Poly model [13–18]. Most single species models, Johnson–Segalman for example, aggregate all other elements of the mixture into one Newtonian (as opposed to viscoelastic) contribution. A disadvantage of the Johnson–Segalman model is that it exhibits unphysical oscillations in step strain [19] and an unbounded viscosity in extensional flows [19]. The Rolie–Poly model can capture the behavior of wormlike micelles in step stress, strain ramp, and shear start-up [17]. For an anisotropy factor of $\alpha > 0.5$, the Giesekus model predicts shear banding. The Giesekus model has the limitation that it plateaus at high extension rates. Therefore, it cannot describe the extreme extension thinning behavior as experimentally observed for wormlike micellar solutions [20,21]. The main drawback of the models mentioned above is that they do not explicitly take into account the continuous breakage and reformation of the micelles.

Using kinetic theory, Vasquez et al. [22] developed a model for wormlike micelles that is based upon a discrete version of the Cates model [23]. In the Vasquez–Cook–McKinley (VCM) model, the wormlike micelles are represented by two species

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of Hookean dumbbells of molecular weights M_A and $M_B = M_A/2$, respectively. The micelles that are longer than the statistical average in the equilibrium state of rest form species A, and those that are shorter form species B. Further, one constituent of species A can break in half to form two constituents of species B, which themselves can recombine to one constituent of species A. The VCM model can capture the experimental trends observed not only in simple shearing flows [24,25] but also in step strain [26], large-amplitude oscillatory shear [27], and extension [28]. A drawback of the VCM model is the choice of the functional form of the breakage and reforming rates. The flow-induced breakage of the longer species was described by a term similar to that in the PEC model which accounted for flow-induced alignment [8], the reforming rate was assumed constant. With this nonlinearity, the VCM model predicts shear banding. The hypothesis that shear banding is a result of the breakage and reformation processes is unique to VCM model. This is in contrast to other models for shear banding that are based on other hypotheses, for example, the flow-induced alignment of the micelles [9]. A limitation of the VCM model is that it is not thermodynamically consistent. Nonequilibrium thermodynamics requires the transport coefficients appearing in the time evolution equations for the state variables to depend only on the state variables of the system and their spatial derivatives. The explicit dependence of the breakage rate on the velocity gradient tensor renders the VCM model thermodynamically inconsistent.

In our previous paper [29], we recast the VCM model into a thermodynamically consistent form. To describe the breakage and reformation kinetics of the micelles, we extended the mass action treatment of chemical reaction kinetics that originally appeared in [30] to multicomponent systems with an internal viscoelastic structure. The thermodynamic description is general and could be used in the future to model more complex reaction processes. The new model validates the fact that a nonlinear term must appear in the expression of the breakage rate. In addition, we also showed that for the two-species model to be thermodynamically consistent, a similar nonlinear expression is needed for the recombination rate. The reaction rates that appear in the new model have a stronger nonlinearity than those in the VCM model. Therefore, the elastic recoil in inhomogeneous shear flow is stronger, as will be shown in this paper. More importantly, the validation of the reaction rates confirms the hypothesis that shear banding occurs because of the breakage and recombination processes.

Cylindrical Couette geometry has been widely used for studying the shear banding behavior of wormlike micelles. For instance, Helgeson et al. [31] used the Giesekus model to compare the rheology, flow kinematics, and some ensemble-averaged microstructural quantities with experimental data obtained for a concentrated CTAB solution. Hu and Lips [32] and Hu et al. [33] studied the spatio-temporal development of the wormlike micellar mixture using a combination of particle tracking velocimetry, small-angle light scattering, microscopic visualization, and flow birefringence. The overshoot of the wall shear stress during the start-up of simple shear flow was explained by chain disentanglement. According to their opinion, shear banding is caused by the re-entanglement of the wormlike micelles. Recently, the simultaneous occurrence of shear banding and other types of instabilities such as elastic instabilities has attracted considerable interest [34–36]. Elastic recoil is a transient feature of not only polymeric materials but also wormlike micelles [37–39]. To the best of the authors' knowledge, Zhou et al. [40] were the first to report the theoretical finding of a negative azimuthal velocity as a result of the elastic recoil of the wormlike micelles. Numerous researchers have experimentally studied the spatio-temporal evolution of the velocity field using flow visualization techniques [32,41,42,38]. In Miller and Rothstein [41], transient damped inertio-elastic shear waves propagating across the Couette cell were observed. As a result of the interaction of these waves with the shear band formation, velocity profiles with three distinct bands were obtained. In a numerical analysis performed for the VCM model, Zhou et al. [25] demonstrated that the presence of inertia can lead to multiple banded solutions in transient and even steady-state shear flow. When a constitutive model is augmented with nonlocal terms, additional boundary conditions must be imposed. These conditions must be carefully selected because they can impact the results. In Adams et al. [14], it was shown that, depending on the type of boundary conditions, multiple banded states can be generated.

The goal of this work is to complete the new model by adding Fickian and stress-induced diffusion. Diffusion is allowed to take place not only between the two species but also between the micellar mixture and the viscous solvent. Another objective is to investigate the spatio-temporal features of the new model in a shear flow allowing for inhomogeneous behavior, including the formation of the shear bands. The behavior of the model will be discussed using the hypothesis that shear banding is the result of the breakage and recombination events taking place between the wormlike micelles. Experimentalists may find the quantitative results useful when having to select a model for comparison. Although the characteristic length of a macroscale rheometer is too large for stress and/or number density diffusion to play a physically important role, nonlocal terms are usually added to obtain a unique stress plateau [27,6,13,31]. At this stage of the work, we performed the computation in the diffusionless limit.

The remainder of this paper is organized as follows. In Section 2, we describe how to incorporate Fickian and stress-induced diffusion in the new model. In Section 3, we describe the circular Couette flow problem. The numerical methodology used to solve the problem is described in Section 4. In Section 5, we discuss the transient and steady-state behavior of the model. The final conclusions are drawn in Section 6.

2. Thermodynamically consistent model

2.1. Extension of the two-fluid approach to viscoelastic multicomponent systems

In this section, we add Fickian and stress-induced diffusion to the new model. For this purpose, we had to extend the standard two-fluid approach described in Beris and Edwards [30] to viscoelastic multicomponent systems.

Let us assume that the total system under investigation is closed, isothermal, and incompressible. The total system consists of three components, namely, two species of Hookean dumbbells of molecular weights M_A and $M_B = M_A/2$ and a viscous solvent. For each species $i = A, B$, the following state variables are defined: the mass density ρ_i, the momentum density $\mathbf{m}^i = \rho_i \mathbf{v}^i$, with $\mathbf{v}^i$ being the velocity field, and a structural tensorial parameter density $\mathbf{C}^i = n_i \mathbf{c}^i$, where n_i is the number density and $\mathbf{c}^i$ is the conformation tensor. Here, the conformation tensor is defined as the average second moment of the end-to-end connection vector of the microstructural constituents. The number density of component i is given as $n_i = (\rho_i/M_i)N_A$, where M_i is the molecular weight of component i and N_A is the Avogadro constant. For the viscous solvent, we define the following state variables: the mass density ρ_s and the momentum density $\mathbf{m}^s = \rho_s \mathbf{v}^s$, with $\mathbf{v}^s$ being the velocity field.

The following expression for the mechanical part of the Hamiltonian is used to characterize the total system energy: