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Modeling the thixotropic behavior of structured fluids

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ABSTRACT

A novel approach for modeling the mechanical behavior of thixotropic viscoplastic fluids is presented. Non-monotonic flow curves, stress overshoot during microstructure breakdown flows at constant shear rate, and viscosity bifurcation are some of the common aspects of structured fluids that are predicted by the new model. It involves two evolution equations, one for the stress and the other for the structure parameter. Simple ideas are employed to describe the microstructure, and, as a result, a model with a clear physical basis is obtained. In addition to the flow curve, which by construction is exactly predicted, it is shown that the model is able to predict correctly the behavior observed in the usual rheometric transient flows, among which abrupt changes in shear rate (microstructure buildup or breakdown experiments) and abrupt changes in shear stress (viscosity bifurcation experiments). The model is frame-indifferent and applicable to complex flows.

1. Introduction

Structured fluids are found in a wide range of human activities. Most suspensions, emulsions, and foams are structured fluids, and some examples are: personal care products, cosmetics, different foods, nanocomposites, paints, inks, cements, adhesives, greases, natural muds, drilling muds, crude oils, gels, and mining, coal and metal slurries.

Structured fluids exhibit non-Newtonian mechanical behavior. At small stress levels, their microstructure often confers them an elastic behavior. In this case, beyond a certain stress threshold, usually called *yield stress*, a major microstructure collapse occurs which causes dramatic drops in viscosity and elasticity.

While under constant stress conditions for some long enough period of time, the microstructure of a structured fluid usually acquires a stable configuration, which is the result of the equilibrium between the microstructure buildup and breakdown rates. If the microstructure changes do not occur instantaneously after a stress change, the structured fluid is said to be time-dependent. A time-dependent fluid is said to be *thixotropic* if its viscosity decreases/increases with time as it undergoes a shear rate increase/decrease, and if in addition these viscosity changes are reversible. On the other hand, a time-dependent fluid is said to be *antithixotropic* if its viscosity increases/decreases with time as it undergoes a shear rate increase/decrease, and if in addition these viscosity changes are reversible.

Most structured fluids that exhibit a yield stress are time-dependent, especially in the small stress range. Some extent of irreversibility in the microstructure changes is also often observed, but modeling and characterizing the mechanical behavior of irreversible structured fluids are rather difficult tasks (e.g. [20]). Actually, as far as their mechanical behavior is concerned, even thixotropic fluids are far from being thoroughly understood [15].

Barnes [4] published a detailed review of thixotropy, where he described the phenomenon, discussed numerous examples, summarized its history, and gave an overview of the state of the art. In this review, Barnes [4] pointed out that most of the then available theories only described the viscous thixotropic phenomenon, and that only a few attempted to describe viscoelastic effects. He grouped the viscous theories into three different categories: first those that employ the so-called structure parameter, usually λ, a scalar quantity that typically varies in the interval $[0, 1]$ and represents an indirect measure of the level of structuring (these are usually called *structural kinetics* models); second those that use some direct information of the microstructure, usually called *microstructural* models; and third those just based on viscosity-time data.

As an example of viscoelastic model, Barnes [4] cited the one set forth by Acierno et al. [1–3], although these workers focused on low-density polyethylene rather than on thixotropic fluids. They proposed a multimode Maxwell-type differential equation set for stress whose relaxation times and shear moduli depend on a structure parameter.

Mujumdar et al. [17] also gave a thorough discussion of the thixotropy literature, including a quite complete comparison between the various structural kinetics models then found in the literature. These models consist essentially of an evolution equation

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for the structure parameter and an algebraic constitutive equation that relates the stress (or viscosity) to the structure parameter.

The constitutive equation of the structural kinetics models usually comprises three additive terms, one for the yield stress (usually taken as structure-parameter-dependent), one involving a structure-parameter-dependent viscosity (the so-called structural viscosity), and the last involving the viscosity of the completely unstructured fluid. In most models, both the yield stress and the structural viscosity terms are assumed, for simplicity, to depend linearly on the structure parameter. In the more recent models, a maximum elastic strain is included in the yield stress term, rendering it the capability of predicting elastic effects (e.g. [13,17]).

Recently Mewis and Wagner [15] published a valuable text explaining in detail the fundamentals of thixotropy as it is nowadays understood. Among other helpful discussions, the explanation on the difference between thixotropic and viscoelastic behavior is particularly elucidative. In this connection, these authors point out that one shortcoming of the viscoelastic thixotropic models available in the literature that are derived from the Maxwell model (e.g. [3,7,11,18]) is their incapability of predicting what distinguishes experimentally thixotropy from viscoelasticity, namely an instantaneous drop in shear stress when the shear rate is suddenly decreased. Another important limitation of the presently available Maxwell-type viscoelastic models is the absence of yield stress in the model predictions [15].

As Mewis and Wagner [14,15] point out, despite the recent advances in predictive methods and in the general understanding, a unified treatment of thixotropy is still lacking. In fact, due to the intricacy of the subject, assumptions made just for the sake of simplicity, rather than based on physical arguments, abound in the thixotropy models presently available in the literature. As a result, the predictive capability of these models is usually rather limited.

In fact, the whole problem of thixotropy modeling seems to need thinking out afresh. This paper is intended as a contribution, however humble, to this task. Below I describe a novel Maxwell-type viscoelastic model that follows different paths, guided by rather simple physical arguments. The drawbacks presented by the previously published Maxwell-type models are removed altogether. The model is employed in different rheological test flows, and the results demonstrate its good predictive capability.

2. The model

In this section I describe the assumptions and derive the equations that compose the proposed constitutive model for thixotropic materials. One of the key assumptions is the existence of a microstructure whose state can be described by a single scalar parameter. Let λ be this parameter that expresses the state of the structure. By definition, it ranges from 0 to 1, 0 corresponding to a completely unstructured state and 1 corresponding to a completely structured state.

2.1. The mechanical model

I now develop a differential equation for the shear stress τ with basis on the mechanical analog shown in Fig. 1. In this figure, $G(\lambda)$ is the shear modulus of the microstructure; $\eta_v(\lambda)$ is the structural viscosity, a function that describes the purely viscous response of the material; γ_e is the elastic shear strain of the microstructure when it is submitted to the shear stress τ; γ_v is the viscous shear strain; and γ is the total shear strain. This analog corresponds to the simplest viscoelastic constitutive model, namely, the well known Maxwell fluid model, except that here both G and η_v are assumed to be functions of the structure parameter λ. It is clear that, according to this analog, a very large value of η_v combined with a finite value of G implies an essentially elastic behavior; conversely, a very large value of G combined with a finite value of η_v implies an essentially viscous behavior. Alternatively, one may think in terms of a microstructure-dependent relaxation time, η_v/G, which when large implies important elastic effects and vice-versa.

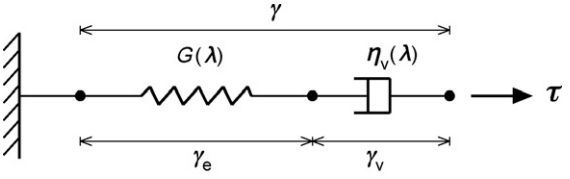

Fig. 1. The mechanical analog of the material's mechanical behavior.

It is easy to see from the model represented in Fig. 1 that

$$\gamma_e + \gamma_v = \gamma \Rightarrow \dot{\gamma}_e + \dot{\gamma}_v = \dot{\gamma} \tag{1}$$

where the dot on top of the variables denotes differentiation with respect to time t.

Moreover, the following three expressions can be written for the stress:

$$\tau = \eta(\dot{\gamma}, t)\dot{\gamma} \tag{2}$$

$$\tau = \eta_v \dot{\gamma}_v \tag{3}$$

$$\tau = G(\gamma_e - \gamma_{e,n}) \tag{4}$$

where $\eta(\dot{\gamma}, t)$ is the viscosity function. γ_e and $\gamma_{e,n}$ are deformations measured from an arbitrary fixed reference configuration of the microstructure. γ_e is the elastic deformation corresponding to the current configuration, and $\gamma_{e,n}$ is the deformation corresponding to the natural or neutral configuration, i.e. the configuration assumed when $\tau = 0$. The neutral configuration is a characteristic of the microstructure, and hence it is expected to change if (and only if) the microstructure changes. Consequently, $\gamma_{e,n}$ is expected to be a sole function of the microstructure parameter λ. Differentiation of Eq. (4) with respect to time gives

$$\dot{\tau} = \dot{G}(\gamma_e - \gamma_{e,n}) + G(\dot{\gamma}_e - \dot{\gamma}_{e,n}) \tag{5}$$

I now postulate that changes in $\gamma_{e,n}$ are solely due to changes in the microstructure, i.e. $\dot{\gamma}_{e,n} = 0 \Leftrightarrow \dot{G} = 0$, while changes in γ_e are solely due to changes in stress, i.e. $\dot{\gamma}_e = 0 \Leftrightarrow \dot{\tau} = 0$.

Thus, Eq. (5) can be decomposed into two independent expressions:

$$0 = \dot{G}(\gamma_e - \gamma_{e,n}) - G\dot{\gamma}_{e,n} \quad \text{or} \quad \dot{\gamma}_{e,n} = \frac{\dot{G}}{G}(\gamma_e - \gamma_{e,n}) \tag{6}$$

and

$$\dot{\tau} = G\dot{\gamma}_e \tag{7}$$

The above considerations grant the desired behavior of the model. For example, when G increases due to a microstructure breakdown at constant stress, the elastic strain γ_e does not change, but the difference $(\gamma_e - \gamma_{e,n})$ decreases at the same rate, so that the stress is kept unchanged. Another example is the case in which the material microstructure is initially completely destroyed due to a long exposure to high shear stresses, and then at a given instant of time the stress is set to zero so that the microstructure starts building up. In this case, the model predicts that $\gamma_{e,n} = \gamma_e$ (see Eq. (4)), $\dot{\gamma}_e = 0$ (see Eq. (7)), and thus $\dot{\gamma}_{e,n} = 0$, despite the fact that $\dot{G} \neq 0$ (see Eq. (6)). Therefore, in this case the model predicts that the building up of the microstructure will render the material elastic while keeping it in its relaxed configuration $\gamma_{e,n}$, as it should.