Flow instabilities in complex fluids: Nonlinear rheology and slow relaxations

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Abstract. We here present two simplified models aimed at describing the long-term, irregular behaviours observed in the rheological response of certain complex fluids, such as periodic oscillations or chaotic-like variations. Both models exploit the idea of having a (non-linear) rheological equation, controlling the temporal evolution of the stress, where one of the participating variables (a ‘structural’ variable) is subject to a distinct dynamics with a different relaxation time. The coupling between the two dynamics is a source of instability.

Introduction

Complex fluids are known to exhibit a wide range of unconventional behaviour when forced to flow, due to the intricate couplings between their structure at the mesoscopic scale and the imposed flow. In this work, we investigate theoretically certain situations where, under steady external drive, the long-term behaviour of the fluids is intrinsically unstable: the fluids never reach a steady state, and rather respond in an unsteady way (as shown by time measurements of e.g., the shear stress or the shear rate). Such situations include the appearance of sustained temporal oscillations in surfactant solutions [1, 2] as well as polymer solutions [3]. In other cases, some apparently totally erratic temporal responses have been found, in dense colloidal suspensions [4] and several surfactant systems [5, 6]. In the latter, there are some indications [5, 6] that the obtained signal is in fact the result of a deterministic chaotic dynamics. Such a chaotic behaviour at virtually zero Reynolds number (and thus no inertia) must stem from a nonlinearity within the constitutive properties of the material, and has thus been dubbed “rheological chaos”, or “rheochaos”.

General principles

These unsteady behaviours raise numerous questions from the theoretical viewpoint. Various hypotheses can be made as to what mechanisms give rise to such temporal instabilities (oscillations or rheochaos). The path that we are currently exploring relies on two main physical features shared by many complex fluids:

(i) An underlying tendency to form shear-banded flows.

(ii) A dependence of the present state of the fluid on past history, due to the presence of slow-relaxing structural modes.

The appearance of shear-bands in shear flows is indeed one of the most frequent mechanical instability observed in complex fluids. Slow-relaxing “structural modes”, on the other hand, are directly linked to the commonly observed memory effects – i.e., long-term metastability – in complex fluids, where the shear history of a sample can be remembered for a surprisingly long time. One way to interpret this is that the previous flow has disturbed in some way one or several quantities characterizing the structure of the fluid (for instance, the micellar length in a worm-like micelle system, or the local density in colloidal systems, etc.), and that these structural variables then only relax over long periods, because they involve, e.g., collective motions, or are controlled by a slow, independent physico-chemical process.

In this article, we give a short overview of our ongoing work on this subject, presenting two related models which include the above-mentioned physical ingredients, as well as some preliminary results.

A shear-thickening model with memory

The first model is a toy rheological equation which describes a shear-thickening fluid with memory, within a purely scalar approach where only the shear component \( \sigma \) of the stress tensor is considered. Imagining that the fluid is sheared in a Couette cell, we take \( \sigma \) as the vorticity direction (the axial direction), and will consider spatial variations in that direction only. In the proposed model, the evolution with time \( t \) of the shear stress \( \sigma(\xi, \mu) \) is then
given by (in units where the elastic modulus is one)

\[ \dot{\sigma}(\xi, t) = \dot{\gamma} R(\sigma) + \lambda M \psi \int_{-\infty}^{t} \sigma(\xi, t') \, dt' + \kappa \nabla^2 \sigma(\xi, t) \]

with \( \dot{\sigma} = \partial \sigma / \partial t \). The shear rate, \( \dot{\gamma} \), is supposed uniform in the z-direction (this is related to a low- Reynolds assumption). The positive term \( R(\sigma) = a \sigma \dot{\gamma} + b \sigma + c \sigma^3 \) is a non-linear, instantaneous relaxation term, with \( a, b, c \) positive constants chosen so that \( R(\sigma) \) has a decreasing portion. This creates a tendency for the fluid to form “vorticity” shear bands (stacked in the z-direction). The integral term over past states of the stress represents the sum of relaxation times much shorter than \( \tau_s \). Finally, the inclusion of a non-local term, in the form of stress diffusion with diffusivity \( \kappa \), is required to describe interfaces between different bands in inhomogeneous flows.

The original version of this model, proposed by Cates et al. [7], was purely temporal (no space variable \( z \), \( \kappa = 0 \) ) and already proved capable of long-term unsteady responses: when \( \dot{\gamma} \) is externally fixed in a certain range, the stress displays sustained (space-homogeneous) oscillations akin to those of the van der Pol oscillator. With the spatially-resolved version presented here, we are able to study the spatio-temporal dynamics of such unstable behaviour.

Qualitative features of the model

The qualitative features of the model are best explained by rewriting the integro-differential equation as an equivalent differential system:

\[ \dot{\sigma} = \dot{\gamma} R(\sigma) + \lambda \dot{m} + \kappa \nabla^2 \sigma \quad ; \quad \dot{m} = \frac{m \sigma}{\tau_s} \]

The memory integral within eq. (1) now appears as an auxiliary variable \( m(\xi, t) \), which follows its own dynamics and at each instant tries to relax towards the current value of the stress \( \sigma(\xi, t) \).

The equilibrium flow curve \( \sigma(\dot{\gamma}) \) for the model is obtained when \( \dot{\sigma} = \dot{m} = 0 \). Flowing states on this curve are spatially uniform, and on each point of the curve, the memory \( m \) has had time to relax to the equilibrium value of the stress \( m = \sigma \). However, when \( \tau_s \) is large (slow memory relaxation), this equilibrium flow curve may only be observed on long enough timescales. On timescales much shorter than \( \tau_s \), the fluid will behave as if the memory \( m \) were static: one has therefore also to consider a set of “instantaneous” flow curves which correspond to the relaxation of the stress (i.e., \( \dot{\sigma} = 0 \)) at fixed \( m \). As the memory slowly evolves, the fluid will then accordingly “jump” from one instantaneous flow curve to the other.

It is then easy to understand qualitatively why the fluid has an unstable behaviour in a certain range of stress. In Figure 1, the long-term, equilibrium flow curve is drawn together with the set of instantaneous curves: the sole inspection of the equilibrium curve, which has no decreasing portion (for the choice of parameter values considered), could let one think that all states are stable, but one observes that there is a region where the long-term curve is in fact crossed by decreasing parts of short-term curves. Consequently, at these intersection points, the fluid has an instantaneous tendency to destabilize, thereby precluding the establishment of the equilibrium state [7].

Numerical study of the model

We now briefly present some of the results that have been found so far on the spatio-temporal dynamics of the model.

The model was studied numerically through a spectral Galerkin truncation [8], where \( \sigma(\xi, t) \) and \( m(\xi, t) \) are decomposed as a finite sum of spatial Fourier modes, of the form \( \sigma_n(\xi) \cos(q_n z) \) with wave-vector \( q_n = n \pi / H \) for the stress (\( H \) is the total height of our imaginary Couette device), plus a similar set of memory modes \( m_n(\xi) \). (We usually take the first ten modes into account in our numerics.) The system of equations then reduces to a...
set of coupled ordinary differential equations governing the temporal evolution of \( \sigma_n \dot{\gamma} \) and \( m_n \dot{\gamma} \).

As is the case for conventional shear bands, two different protocols can be followed in the numerical study of the instability (details will appear elsewhere [9]): either working at fixed shear rate \( \dot{\gamma} \) (i.e., with a shear-controlled Couette cell), or working at fixed torque, or equivalently at fixed average stress \( \tau \dot{\gamma} \) (stress-controlled Couette). These two protocols lead to rather different results, as we shall now see.

**Working at fixed \( \dot{\gamma} \)**

We here work with a fixed, externally imposed value of \( \dot{\gamma} \), and compute the values of the different modes \( \sigma_n \dot{\gamma} \) and \( m_n \dot{\gamma} \), from which we reconstruct \( \sigma \) and \( m \dot{\gamma} \). For numerical solutions carried within the unstable window, our results show that, in the vast majority of cases, the spatio-temporal dynamics of the instability is in fact essentially purely temporal: regardless of their initial magnitude, all the modes rapidly decay and disappear, except for the spatially uniform mode \( \sigma_0 \dot{\gamma} \). This mode then oscillates alone, with a fixed period and a regular shape, as in the temporal version of ref. [7].

In a few, small regions of the parameter space explored, it has been possible to obtain a slightly richer dynamics, where some of the lower modes survive and undergo small-scale periodic oscillations, alongside a large uniform mode oscillation which still dominates.

**Working at fixed \( \tau \dot{\gamma} \)**

We now work at imposed average stress \( \tau \dot{\gamma} \) in terms of Fourier modes, this corresponds to fixing the value of the uniform Fourier mode \( \sigma_0 \dot{\gamma} = \text{const.} \), which will thus not be able to oscillate at all. A very rich spatio-temporal behaviour then arises, as the higher spatial modes will now, by necessity, be involved in the instability.

Different unstable features may appear [9], in Figure 2-a, we present a most striking one, called “flip-flop shear-bands”: a shear-banded profile appears, with a low shear band and a high shear band separated by an interface; but these bands are unstable, and periodically flip, the higher band becoming the lower and vice-versa. The “flipping time” is very short as compared to the latency time between two flips. Figure 2-b shows the corresponding temporal evolution of the total stress \( \sigma \dot{\gamma} \).

Much more irregular-looking time variations can also be obtained for different parameter choices, as Fig. 2-c shows for the stress. We emphasize however that these patterns remain time-periodic; so far no chaotic response has been found in the present model.

**FIGURE 2.** (a) “Flip-flop” shear-bands for \( \tau \dot{\gamma} = 7 \dot{\gamma} \): From top to bottom, successive snapshots of the stress \( \sigma \dot{\gamma} \) vs. position \( z \), at times \( t = 8800 \) to \( 8960 \). (b) Time series of the stress at position \( z = 0 \) for the same value of \( \tau \dot{\gamma} \). (c) Time series of the stress at position \( z = 0 \) for \( \tau \dot{\gamma} = 9 \dot{\gamma} \). The time window corresponds to two periods of the signal. (Parameters same as Fig. 1.)

**A model with “fluidity”**

We would now like to introduce another fluid model, based on the same general ideas as previously, but more specifically oriented towards solutions of wormlike micelles and polymers. The shear stress \( \Sigma \) in the fluid is locally the sum of a polymer or micellar part, \( \sigma \), and a Newtonian part \( \eta \dot{\gamma} \) corresponding to the solvent:

\[
\Sigma = \sigma + \eta \dot{\gamma}
\]  

The model’s equations are as follows:

\[
\sigma = \frac{\sigma}{\tau} + \frac{G(\tau)}{\tau} \dot{\gamma}^2 + \kappa \nabla^2 \sigma
\]  

(4)

\[
\dot{\gamma} = \frac{\tau}{\tau_0} \dot{\gamma}
\]  

(5)

The stress evolution equation (4) has a classical form, and describes the relaxation (with a timescale \( \tau \)) of the “polymer” stress towards a value which, at a given \( \dot{\gamma} \), is controlled by \( G(\tau) \dot{\gamma} \). \( G(\tau) \) is the elastic modulus and generally depends on the value of \( \tau \) (see below). The function \( g \) is hump-shaped, hence conferring on the fluid a tendency to shear-thinning, and shear-banding, with bands in the velocity gradient direction (i.e., the radial direction of the Couette cell).

Similarly to the model with memory, one of the variables involved in the stress equation is subject to a distinct dynamics: this is now the Maxwell time \( \tau \) of the fluid, which, as stated by eq. (5), relaxes towards a shear-rate dependent equilibrium value \( \tau_0 \dot{\gamma} \) with a characteristic time \( \tau_0 \). We note that having a dynamical Maxwell
time is indeed very similar to the “fluidity” model introduced by Derec et al. in the context of paste flow (see [10]).

Here again, $\tau$ is a “structural” variable in the sense that it reflect variations in the local structure of the fluid: for semi-dilute solutions of wormlike micelles, it will typically relate to local variations of the mean chain length of the micelles. In this interpretation, the chain length distribution, and consequently the mean chain length, may change only through the action of some micelle-micelle chemical reactions, which will have their own timescale $\tau_s$ — this time will thus control the relaxation of $\tau$, as in eq. 5. On the other hand, the dependence of the equilibrium value $\tau_{eq}$ on the shear rate can be interpreted as a displacement of the chemical equilibrium by the mechanical shearing (for example, decreasing $\tau_{eq}$, by helping chain scission, or, increasing $\tau_{eq}$, by helping polymerisation). For more dilute solutions (non-entangled), one may rather interpret the variations of $\tau_{eq}$ as related to the strong shear-thickening transition usually observed upon varying $\dot{\gamma}$: the structural changes occurring at the transition (gelation) will then strongly alter $\tau_{eq}$.

In accord with the model with memory of the previous section, we have focussed on slow relaxations of the structural variable: $\tau_s \approx 1$. Then one can again construct a “long-term”, master flow curve where all variables are equilibrated ($\dot{\sigma} = 0$), and an underlying set of “short-term” curves where $\tau$ is fixed (quasi-static) and the stress is equilibrated with respect to that value of $\tau$. As seen in the previous model, an increasing portion of the “long-term” curve is here also made unstable when crossed by decreasing portions of underlying curves.

Two variants of the model can be studied, depending on whether the elastic modulus $G$ is affected or not by changes in the structure of the fluid, that is, changes in $\tau$. Variant 1 corresponds to $G(\tau) = G_0$, being constant, which would be suitable for a semi-dilute, entangled solution of micelles, where (reasonable) changes in the mean micellar length leave the modulus unchanged. In variant 2, $G$ varies with $\tau$, as would e.g. be the case in the shear-thickening transition of dilute micelles, where the significant structural changes affecting $\tau$ will affect $G$ as well. Work on both variants of the model is currently in progress, but results so far are promising. Figure 3 shows an example of results in variant 2.

To conclude, we would like to mention extremely interesting results by S. Fielding and P. Olmsted [1]: working independently on essentially the same model as eqs. 4-5, they have been able, within variant 1, to obtain chaotic-like signals in a regime where both the underlying curves and the master flow curve have decreasing portions, and where the structural relaxation occurs on timescales comparable to the stress relaxation ($\tau_s \approx 1$).

Many questions are still open in the study of the type of models which have been described in this article. Are the existence of distinct “structural” relaxations really the origin of the instabilities observed in experiments? Is the regime just described the only one displaying chaotic-like behaviour, and relatedly, what is required for regular or irregular-looking periodic motion to destabilize into chaos?

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