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Inhomogeneous Flows of Complex Fluids: Mechanical Instability Versus Non-Equilibrium Phase Transition

Grégoire Porte (*), Jean-François Berret and James L. Harden

Groupe de Dynamique des Phases Condensées (**), Case 026, Université Montpellier II,
34095 Montpellier Cedex 05, France

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Abstract. — We briefly review and re-interpret recent experimental results on shear-induced inhomogeneous flows in complex fluids. These are usually explained in terms of a mechanical instability of the non-linear flow regime. However, in at least two respects, the robustness of the two-state banded-flow regime and the kinetics of band formation under shear, they present striking analogies with ordinary field-induced phase transitions in equilibrium systems. We propose a phenomenological explanation of these effects in terms of an effective non-equilibrium potential that accounts for the free energy stored in a viscoelastic material under steady-shear conditions. Within this picture, a shear-thinning non-homogeneous flow can be shown to be a manifestation of some underlying hidden structural transition.

1. Introduction

A number of publications dealing with solutions of giant micelles under shear [1–9] have reported the existence of shear-banded inhomogeneous stationary flows above some characteristic shear rate $\dot{\gamma}_t$. A mechanical signature of this behaviour is the onset of a stress plateau at $\dot{\gamma}_t$ where the stress σ abruptly becomes independent of the shear rate. In some cases [2, 3], this behavior is reported for concentrated solutions close to the domain of stability of an oriented nematic phase in the absence of flow. But in other cases, similar plateaus were observed at much lower concentration in the semidilute regime [1, 4, 7–9]. Several experimental studies, involving neutron scattering under shear and flow birefringence, have supported the picture of bands of strongly oriented micelles coexisting in the plateau regime with bulk regions of weakly oriented, entangled micelles.

The well-known “spurt effect” observed during the extrusion of polymer melts, first reported by Bagley *et al.* [10] and subsequently investigated by Vinogradov [11], is believed to originate from the same basic physical mechanism. Similar onsets of a stress plateau have also been reported for complex fluids consisting of totally different self-assembling microstructures, namely the “onion” texture of lamellar lyotropic phases under stationary shear [12–15]. In this

(*) Author for correspondence (e-mail: porte@gdpc.univ-montp2.fr)

(**) Unité Mixte de Recherche CNRS Université Montpellier II n°5581

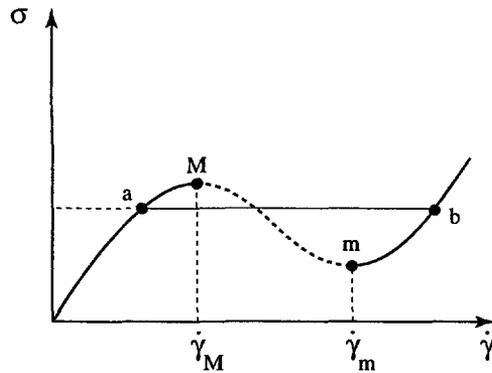


Fig. 1. — Schematic representation of a non-monotonic constitutive relation for the shear stress σ as a function of the rate of strain $\dot{\gamma}$.

latter case, the plateau takes place at the shear-induced layering transition in a sample with an initially disordered onions population. Once again, the stress plateau was described in terms of an inhomogeneous flow consisting of bands of ordered layers of onions coexisting with disordered regions of the flow. The occurrence of similar mechanical signatures for materials with such different microstructures indeed demands a unifying description and interpretation.

In the case of unidimensional objects such as giant micelles and polymers, explanations have been proposed [16–18] which are based on a non-monotonic constitutive relation for the shear stress σ as a function of the rate of strain $\dot{\gamma}$ (see Fig. 1 for a schematic picture). If the applied strain rate $\dot{\gamma}$ lies in the region of decreasing stress (the dotted part of the curve in Fig. 1), an initially homogeneous flow becomes mechanically unstable. Such a flow will evolve in time until some stationary state is reached where bands of highly sheared liquid of low viscosity coexist with more viscous fluid subjected to a lower shear rate. In this banded regime, the stress is uniform throughout the material and only the relative volume fraction of the high *versus* low shear-rate bands varies, so to adjust to changes in the applied strain rate.

Such models account for the existence of a stress plateau. Note however that in this picture, all pairs of stable states in the plateau regime (one lying on the low shear stable branch, the other on the high shear one; for example states a and b in Fig. 1) are equally stable mechanically. Hence in a strain-rate controlled experiment, the set of possible stationary banded flows is highly degenerate. As a result, it seems likely that the final stationary state of flow will depend strongly on the shear history of the sample. In particular, hysteresis would be expected when switching from increasing strain rates to decreasing strain rates, an expectation which is not confirmed by available data.

To address this apparent degeneracy, the formation of shear-banded flows has been theoretically examined using linear stability analysis [18, 19]. In these approaches, the Navier-Stokes equation is written in combination with a phenomenological non-monotonic constitutive relation. An initially homogeneous flow is taken as the starting state onto which a small perturbation is added. Those perturbations which are amplified in time indicate the emergence of inhomogeneous flows. In the absence of coupling to other degrees of freedom, such linear analysis produces banded flows that have structures at all scales and hence fails to identify a characteristic length scale for structural inhomogeneity under flow. In particular, this implies the existence of unphysical bands of arbitrarily narrow width. Numerical calculations for uni-dimensional flows extending this analysis beyond the quasi-uniform linear regime [18] also

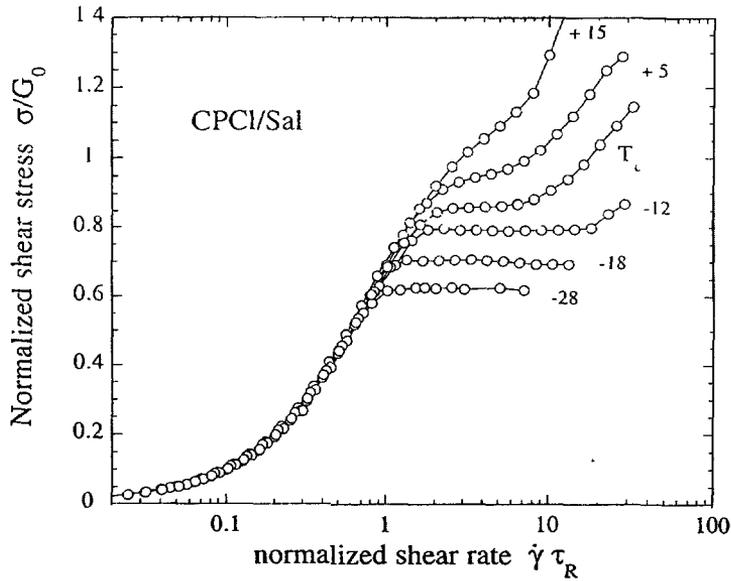


Fig. 2. — Plot of σ/G_0 vs. $\dot{\gamma}\tau_r$ for the CPCI-Sal system with 0.5 M NaCl. The critical flow curve is designated by T_c . The other curves correspond to situations above (plus signs) and below (minus signs) the critical temperature.

resulted in unphysically narrow bands. The introduction of an additional term into the constitutive equation accounting for the energy cost of band interfacial structure yielded bands of finite width and a selection mechanism for the viscoelastic portion of the stress in the banded flow regime [18, 20]. On the other hand, phenomenological theories for which the stress is coupled to a conserved internal order parameter (such as solute concentration [19]) can predict a characteristic length scale of flow inhomogeneities within the framework of linear stability analysis. However, such approaches still depend on an assumed form for the non-monotonic constitutive relation.

On the experimental side, the system CPCI + Na-salicylate in brine (0.5 M NaCl) is certainly the system for which the most extensive set of rheological data in the non-linear regime have been reported to date [4]. Shear-banded flows with a well-characterized stress plateau were reported for a very large concentration range (from 6% to 31% at 30 °C). These materials are nearly perfect Maxwell fluids in the linear regime; the rheological response of a given sample with surfactant volume fraction ϕ and at temperature T to linear oscillatory shear is well-characterized by a single elastic modulus $G_0(\phi, T)$ and relaxation time $\tau_r(\phi, T)$. Furthermore, the (non-linear) steady-state stress response σ to a constant imposed strain rate $\dot{\gamma}$ for all samples and temperatures could be plotted in dimensionless reduced units $\sigma^* = \sigma/G_0$ versus $\dot{\gamma}^* = \dot{\gamma}\tau_r$, as shown in Figure 8 of reference [4]. In Figure 2, we show a more complete set of recent data on the same system [5] in which both concentration and temperature have been systematically varied. As discussed at length in reference [5], for each concentration ϕ there is a “critical” temperature $T_c(\phi)$ for which the plateau reduces to one flat inflection point and above which inhomogeneous flow is no longer observed. For this data, a single set of mastercurves for all samples at all temperatures is obtained in Figure 2 provided that the appropriate reduced units (σ^* , $\dot{\gamma}^*$, and $T^* = T - T_c$) are used. Note that samples of different concentrations but at temperatures deviating from $T_c(\phi)$ by the same amount have

identical flow curves in our reduced units. The analogy of Figure 2 with the phase diagram of an equilibrium system undergoing a typical phase separation process is quite striking. This is indeed not in contradiction with the above description of a mechanical instability. Many bifurcation patterns of dynamical systems follow the same general scheme [21], including the observed progressive evolution of the order parameter from a discontinuous jump (*e.g.* the shear-banded flows below T_c in Fig. 2) to a continuous evolution (the homogeneous flow above T_c) through a flat critical point (at T_c).

The kinetics of formation of the inhomogeneous flows in response to strain rates in the plateau range were also studied in reference [4]. A sigmoidal evolution of $\sigma(t)$ towards a steady-state plateau value was found with a characteristic time often much longer than the viscoelastic time τ_r . Such kinetics are characteristic of nucleation and growth processes, usually associated with first order phase transitions. For one particular system (CPCL in hexanol + brine), it has even been possible to observe the evolution from nucleation and growth kinetics (in response to the startup of low shear rate flows) to a “spinodal” instability (in response to the startup of high shear rate flows) [22]. Moreover, the robust character of the plateau in the shear-banded state was verified with great care and confirmed for all samples: the plateau value of the stress was found to be remarkably constant and completely independent of the shear history of the sample [4, 5]. In particular, provided that enough time is allowed for the system to reach its stationary state, hysteresis was never observed when switching from increasing to decreasing rates of shear in the plateau regime. Furthermore, for at least one sample we checked carefully that the measured transition stress is the same in both control stress and controlled strain rate experiments [23]. This robustness with respect to the variable under control is again a distinctive feature of usual first order phase transitions. These two characteristics, robustness of the plateau and slow sigmoidal onset kinetics, are somewhat inconsistent with the above theoretical description in terms of a mechanical flow instability. Rather, this behavior is reminiscent of the thermodynamically driven isotropic-to-nematic transition observed at rest above 35% concentration.

This quasi-thermodynamic behavior is not restricted to this particular giant micelle system. We also checked the behavior of the system of reference [1], consisting of 100 mM CPCL and 60 mM NaSal in salt-free D₂O [6]. This system is currently considered as model example of a complex fluid which undergoes a true mechanical instability in flows [17]. However, we found evidence for both the robustness of the plateau and the slow onset kinetics in this system as well. Figure 3 shows an example plot of the onset kinetics of the plateau in $\sigma(t)$ for this system. The solid curve represents the best fit of the data with a function of the form $\sigma(t) = \sigma_{pl} + \Delta\sigma \exp[-(t/\tau_{ng})^2]$, where τ_{ng} is the characteristic time for the nucleation and growth process and $\Delta\sigma$ is the excess stress of the initial homogeneous flow compared to that of the fully developed inhomogeneous flow in the plateau regime [4]. After a brief elastic overshoot of duration $t \simeq \tau_r$, all data points closely follow the theoretical sigmoidal curve characteristic of the nucleation and 1D-growth discussed at length in [4]. In contrast, for a true mechanical instability one would expect relaxation behavior with a finite relaxation rate at $t = 0$. Furthermore, very recent experimental studies of the layering transition in “onion” phases also revealed a robust response of the two-state coexistence plateau regime to changes in shear rate. So, in our opinion, an alternative interpretation of the inhomogeneous flows is needed which can account for these unexpected features shared in common by such very different systems.

In the following section, we present a phenomenological “quasi-thermodynamic” treatment of systems exhibiting banded flows that is based on the free energy stored in a viscoelastic material in steady shear flows. We will show that, within this framework, the mechanical instability of viscous flow may be preempted by the metastable response of this internal elastic-like degree of

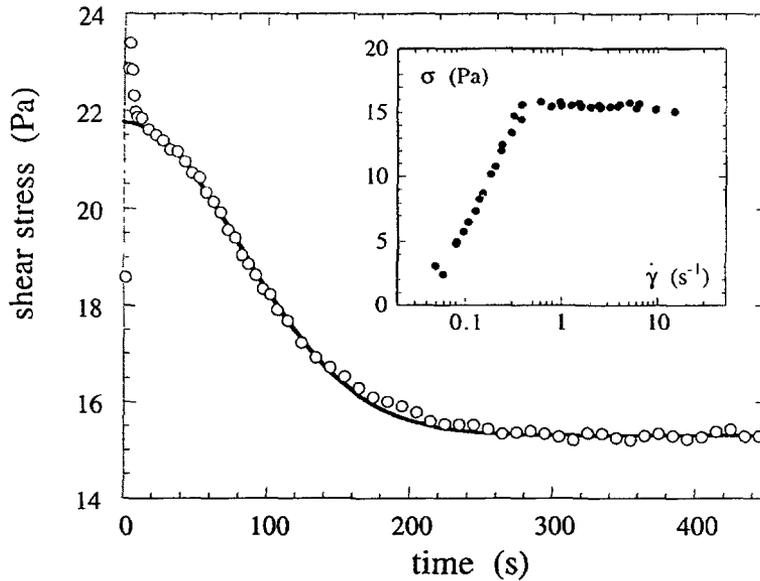


Fig. 3. — Sigmoidal transient response of giant micelle solutions consisting of 100 mM CPCL and 60 mM NaSal in salt-free D₂O in response to steady shear at a rate $\dot{\gamma} = 0.5 \text{ s}^{-1}$ [1, 6]. Note the brief elastic overshoot of duration $t = \tau_r \simeq 3 \text{ s}$. The solid curve represents the best fit of the data with a function of the form $\sigma(t) = \sigma_{pl} + \Delta\sigma \exp[-(t/\tau_{ng})^2]$, where $\tau_{ng} = 115 \text{ s} \gg \tau_r$ is the characteristic time for the nucleation and growth process and $\Delta\sigma = 6.5 \text{ Pa}$ is the excess stress of the initial homogeneous flow compared to that of the fully developed inhomogeneous flow in the plateau regime (see [4] for more details on the theoretical curve). The inset represents the stationary response of σ versus $\dot{\gamma}$. Note the sharp slope discontinuity at $\dot{\gamma} \simeq 0.3 \text{ s}^{-1}$ marking the beginning of the plateau region.

freedom in the sheared material. This inherent metastability can explain both the robustness of the stationary banded state and the nucleation and growth kinetics of its formation.

2. Quasi-Thermodynamic Approach

In the case of an equilibrium system, the phase behavior and the associated metastability barriers may be obtained through the analysis of an appropriate thermodynamic potential. The difficulty with flow-induced states is that the system is not at equilibrium: in steady-state conditions, energy is injected in the system and dissipated at a constant rate by the viscous flow. Hence, there is no fundamental principle that can guarantee the existence of such a potential in flow conditions. However, the empirical evidence for the robust behavior of these complex fluid systems in steady flows, both in the homogeneous and in the two-phase banded regimes, is an indication that the observed stationary flows are indeed true attractors for the non-equilibrium state of the system. Moreover, the nucleation and growth kinetics show that the power of attraction expresses itself even when some effective “barrier of metastability” must be overcome. In these respects, the two coexisting states of flow under constant shear is strikingly analogous to the two-phase coexistence in an equilibrium system induced by some constant applied field.

The issue of an effective potential governing the behavior of non-equilibrium systems has been addressed by many authors [24–38]. It has been shown in particular that in the restricted case

of elongational flows, the viscous forces exerted by the solvent on individual macromolecules do admit a description in terms of a potential and are thus indistinguishable from conservative field forces [24–26]. However, this favourable condition does not apply to shear flows at the molecular level. Nevertheless, this does not preclude a phenomenological approach based on a coarse-grained effective potential that is defined on a *mesoscopic* scale. To introduce this potential we proceed as follows.

First we note that for any viscoelastic medium, some free energy is stored in the material submitted to a constant strain rate, due to the perturbation of various internal degrees of freedom. This is simply the total amount of free energy F_s that will be thermalised after switching off the shear. In principle, it is given by the integral of the total entropy production over the time interval required for the internal structure of the fluid to go from steady-state to quiescent conditions. Using this stored energy F_s and the measured shear stress σ , one can introduce a strain-like order parameter γ_s . In analogy with the differential definition of the entropy in equilibrium thermodynamics ($dS = dQ/T$), we define the “stored strain” γ_s in a formal manner as the quantity conjugate to σ with respect to F_s : $d\gamma_s = dF_s/\sigma$, giving

$$\sigma = \frac{dF_s}{d\gamma_s} \quad (1)$$

This choice reflects the fact that in a quasi-thermodynamic approach the shear stress is an intensive variable which, for rheological flows without inertial effects, should be spatially uniform in multi-phase flow conditions. Note that γ_s is not defined at a microscopic micellar scale but rather describes the effective state of the medium averaged over mesoscopic scales (in the same spirit as the thermodynamic limit is used to define thermodynamic variables). A clear indication that some stationary state of “deformation” is supported by a viscoelastic material in flow is provided by the steady birefringence measured under constant shear rate. However, we know of no way to measure γ_s directly in the general case, and so we will regard it as an internal order parameter which parameterizes F_s .

This γ_s is reminiscent of the quasi-hydrodynamic local network strain variable used in recent two-fluid descriptions of semi-dilute polymer solutions in flow [38]. Moreover, our notion of the “stored strain” is in much the same spirit as the recoverable elastic strain introduced by Leonov to derive constitutive equations for polymeric liquids from a non-equilibrium thermodynamics point of view [27, 28]. In the approach of references [27, 28], the flow properties of a polymer fluid are determined in part by a “non-equilibrium potential” which depends on the recoverable elastic strain stored in the material. This “non-equilibrium potential” is roughly analogous to our effective potential F_s . In our approach, however, F_s also accounts for the changes in configurational entropy in a structured complex fluid induced by externally imposed flow. As such, it contains both elastically recoverable and irrecoverable contributions [39]. Note that when we associate F_s and the measured value of σ in order to define γ_s , we implicitly assume that all the energy injected by the rheometer is ultimately dissipated by the relaxation of the mesoscopic structure of the complex fluid (thus the small portion dissipated in simply shearing the neat solvent is neglected).

Our principle ansatz is that F_s is the effective potential that drives the stationary state and hence is subject to some minimization principle. There are no fundamental guidelines available to specify the appropriate form of this non-equilibrium minimization principle. One plausible candidate is the following variational principle: the integral of F_s over the whole thickness e of the sheared material must be at its absolute minimum,

$$\frac{\delta}{\delta\gamma_s} \int_0^e F_s\{\gamma_s(z)\} dz = 0 \quad (2)$$

subject to the constraint of uniform shear stress σ in the gap and a constraint on the average (macroscopic) strain rate $\bar{\dot{\gamma}}$,

$$\frac{1}{e} \int_0^e \dot{\gamma}(z) dz = \bar{\dot{\gamma}}. \quad (3)$$

In a controlled stress experiment, we must enforce an imposed shear stress $\sigma = \bar{\sigma}$ and determine $\bar{\dot{\gamma}}$; while in a controlled strain rate experiment, we fix $\bar{\dot{\gamma}}$ and determine σ . In the following, we will focus on the case of controlled strain rate.

As in the conventional equilibrium thermodynamics approach, the solution $\gamma_s(z)$ of our variational problem depends on the shape of the potential F_s as function of γ_s . If the curvature of the potential is everywhere upward, all solutions are homogeneous (constant γ_s). If on the other hand the curvature of F_s changes sign two "phase" coexistence may occur. The important point is that the characteristics of the two flow phases are uniquely determined by the particular minimization procedure employed. In particular, this procedure gives coexisting values of γ_s , along with a unique value for the transition stress σ_t . For the case of the particular variational principle introduced above, the solution of equation (2) subject to equation (3) and the requirement of uniform $\sigma = dF_s/d\gamma_s$ gives these quantities. We note that in this case, since $\dot{\gamma}$ is generally a non-linear function of γ_s , the coexistence values of γ_s are not given by a simple common tangent construction. We will not dwell here on the detailed nature of the phase selection mechanism, but rather focus on the rheological consequences of this internal phase transition.

So far we have introduced the quasi-thermodynamic potential F_s and the internal order parameter γ_s . However, a complex fluid cannot sustain a steady value of the order parameter unless energy is constantly injected into the system by steady applied shear. So, in order to describe the flow pattern, the potential must be supplemented by some expression for the rate of dissipation. This aspect can be introduced in a very conventional manner. Consider first the relaxation of the material immediately after the steady shear has been switched off. We are interested in the initial decay rate $\dot{\gamma}_s$ of the order parameter. For the purposes of illustration, we choose the simplest possible form for the dynamics of our non-conserved order parameter, namely

$$\dot{\gamma}_s = -\mu(\gamma_s) \frac{dF_s}{d\gamma_s} \quad (4)$$

where $\mu(\gamma_s)$ is a mobility factor which in principle depends on the internal state of the system, and where $dF_s/d\gamma_s$ plays the role of the driving force. Since F_s depends only on the order parameter γ_s , its initial rate of dissipation \dot{F}_s is simply

$$\dot{F}_s = -\mu(\gamma_s) \left(\frac{dF_s}{d\gamma_s} \right)^2 \quad (5)$$

Under applied shear, \dot{F}_s also includes the rate of energy density $\sigma\dot{\gamma}$ injected into the material by the motor of the rheometer. Hence for the case of externally driven rheological flows, we have

$$\dot{F}_s = -\mu(\gamma_s) \left(\frac{dF_s}{d\gamma_s} \right)^2 + \sigma\dot{\gamma}. \quad (6)$$

When writing equation (6), we again assume that all the energy injected by the rheometer is ultimately dissipated by the relaxation of the mesoscopic structure of the complex fluid (so that we ignore the portion dissipated in simply shearing the neat solvent). In stationary conditions, \dot{F}_s is zero and the relation between the stress σ and the potential F_s given by equation (1) is

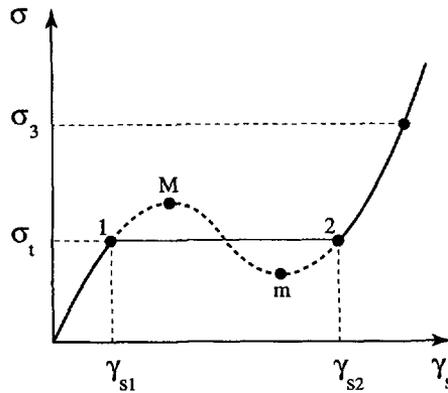


Fig. 4. — A plot of $\sigma(\gamma_s)$ vs. γ_s obtained from the $F_s(\gamma_s)$ in the two-phase region.

valid. Thus, in steady state conditions equation (6) yields the generalized viscous constitutive equation

$$\sigma = \eta(\gamma_s)\dot{\gamma} \quad (7)$$

where the effective viscosity $\eta(\gamma_s)$ is simply the inverse of the mobility factor $\mu(\gamma_s)$. Hence, using our phenomenological mesoscopic description in terms of $F_s(\gamma_s)$, we recover the usual *macroscopic* continuum description of flow based on viscous dissipation in a non-Newtonian liquid subjected to steady shear. Note however that the effective viscosity we obtain depends on the internal state of deformation γ_s of the material. This is consistent with common intuition. For instance, a solution of giant micelles in a strongly oriented state is much more fluid than in the disordered, entangled state. Hence, the viscosity η is taken to depend explicitly on the internal order parameter γ_s , which in turn depends implicitly on the local shear rate $\dot{\gamma}$.

3. Inhomogeneous Flow Patterns

In the present framework, the flow pattern depends strongly on the shape of the potential $F_s(\gamma_s)$. If F_s is concave upwards at all γ_s , then $\sigma(\gamma_s)$ from equation (1) remains monotonic. If, on the other hand, the concavity of $F_s(\gamma_s)$ changes sign in some range of γ_s , then $\sigma(\gamma_s)$ is no longer monotonic [Fig. 4] and the sheared material will undergo an “internal transition” at a unique characteristic stress σ_t , determined by the solution of equation (2) subject to equation (3) and the requirement of uniform $\sigma = dF_s/d\gamma_s$.

The consequences for the state of flow depend on specific features of the effective viscosity $\eta(\gamma_s)$. We distinguish two qualitatively different cases: shear-thinning and shear-thickening fluids. The case of shear-thinning is the most relevant to shear-banded flows of giant micelle solutions and also provides the cleanest illustration of the non-equilibrium phase transition phenomena that we wish to highlight. The case of shear-thickening is rather complex and our analysis can only touch on a few qualitative aspects of the inhomogeneous flow behavior in this limit. Each case is discussed separately in the following.

3.1. SHEAR-THINNING VISCOUS LAW. — Consider our two equivalent expressions, equation (1) and equation (7), describing the shear stress in steady flow conditions. By differentiating each equation with respect to $\dot{\gamma}$ using the implicit relation between $\dot{\gamma}$ and γ_s ,

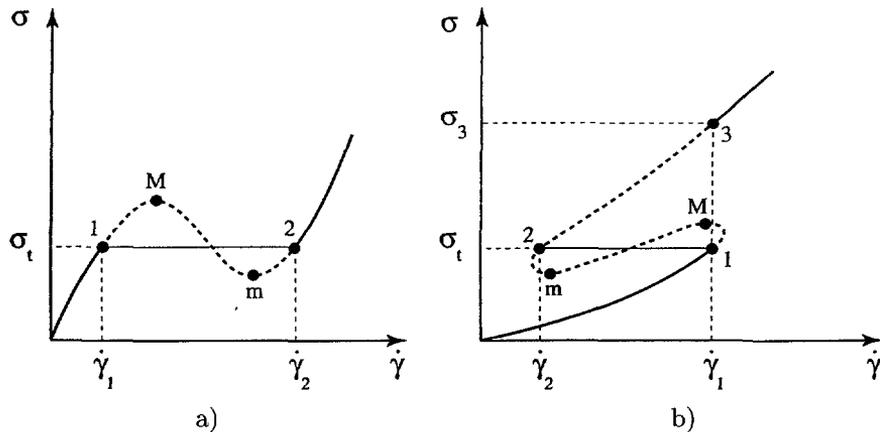


Fig. 5. — a) A generic non-monotonic $\sigma(\dot{\gamma})$ for shear-thinning fluids obtained from equation (8); b) an analogous non-monotonic $\sigma(\dot{\gamma})$ for shear-thickening fluids.

one obtains

$$\frac{d\sigma}{d\dot{\gamma}} = \eta(\gamma_s) \frac{d\sigma}{d\gamma_s} \left[\frac{d\sigma}{d\gamma_s} - \dot{\gamma} \frac{d\eta}{d\gamma_s} \right]^{-1} \tag{8}$$

For situations where the effective viscosity $\eta(\gamma_s)$ is a monotonically decreasing function of γ_s (“shear-thinning”: $d\eta/d\gamma_s < 0$), equation (8) immediately indicates that a non-monotonic constitutive relation between σ and $\dot{\gamma}$ is recovered whenever the associated mesoscopic $\sigma(\gamma_s)$ is non-monotonic. Figure 5a shows a plot of such a resulting non-monotonic $\sigma(\dot{\gamma})$.

Now, the threshold of the “thermodynamic” instability [the spinodal point M in Fig. 4] is characterized by:

$$\frac{d\sigma}{d\gamma_s} = 0. \tag{9}$$

In steady-state conditions, this point cannot be reached since the first order metastable regime described above [the binodal transition point 1 in Fig. 4] will be met before. On the other hand, the threshold of the “viscous flow” instability [the point M in Fig. 5a] is given by:

$$\frac{d\sigma}{d\dot{\gamma}} = 0. \tag{10}$$

It is clear from equation (8) that, since $d\eta/d\gamma_s < 0$, the two elastic and viscous instability conditions, equations (9) and (10), must occur together. This feature has an important consequence: since the binodal transition point of F_s is always met before the spinodal point, the viscous flow instability is always preempted by the first order “thermodynamic” transition for shear-thinning fluids (except of course at the critical point where the first-order character of the transition vanishes). Thus, the inhomogeneous flow regime of coexisting states for shear-thinning fluids is *uniquely defined* by the value of the transition stress σ_t selected above by the effective potential. In case of an experiment at controlled strain rate, the constraint on the macroscopic imposed shear rate is expressed by equation (3), which gives the relative proportions x and $1 - x$ of the high and low shear-rate bands (sketched by the classical lever rule in Fig. 5a) as

$$x\dot{\gamma}_1 + (1 - x)\dot{\gamma}_2 = \bar{\dot{\gamma}} \tag{11}$$

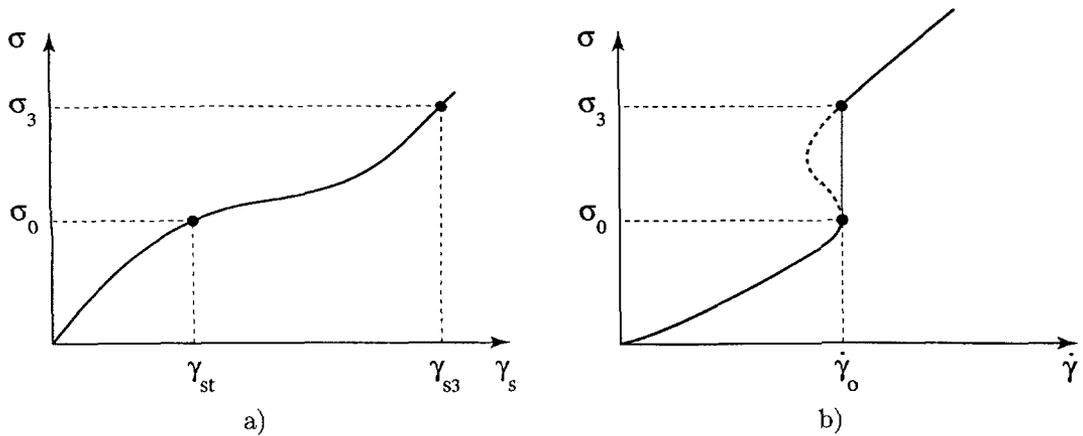


Fig. 6. — a) Monotonic $\sigma(\gamma_s)$ vs. γ_s for an elastically stable shear-thickening fluid; b) the mechanical flow instability resulting from this $\sigma(\gamma_s)$.

where the implicit relation $\dot{\gamma} = \dot{\gamma}(\gamma_s)$ is used to obtain $\dot{\gamma}_1$ and $\dot{\gamma}_2$ from γ_{s1} and γ_{s2} . Furthermore, nucleation and slow growth kinetics are in all cases expected at the plateau in connection with the “potential” barrier to be overcome in the metastable regime [cf. Fig. 4], in agreement with the experimental results discussed in the introduction.

3.2. SHEAR-THICKENING VISCOUS LAW. — Consider now an effective viscosity $\eta(\gamma_s)$ that is a monotonically increasing function of γ_s . In this case, the resulting picture of the flow behavior is completely different from the shear-thinning case. The constitutive evolution of σ versus $\dot{\gamma}$ is still given by equation (8), but with $d\eta/d\gamma_s > 0$. This situation gives rise to the generic pattern drawn in Figure 5b. There is a range of $\dot{\gamma}$ for which σ is not singled-valued but triple-valued at a given value of $\dot{\gamma}$. To understand this situation, imagine progressively increasing $\dot{\gamma}$ in a strain-controlled experiment. Below $\dot{\gamma}_1$, we remain on the lower branch and the homogeneous flow is stable. At $\dot{\gamma}_1$, σ_t is reached and the first order elastic transition takes place: germs of the viscous phase nucleate, sheared at a rate $\dot{\gamma}_2 < \dot{\gamma}_1$. However, since the total imposed shear rate is fixed, the growth of the viscous “phase” accelerates the effective shear in the more fluid “phase”, forcing an increasingly rapid phase transformation. Due to this feedback effect, the resulting stationary state is point 3 directly above point 1 on the upper branch. Once above $\dot{\gamma}_1$, we recover a stationary homogeneous flow on the upper branch. Thus, upon increasing the shear rate, we only expect a discontinuous jump of the measured stress from σ_t to σ_3 as $\dot{\gamma}$ passes through $\dot{\gamma}_1$.

When switching to decreasing imposed shear rates, just the opposite behavior is expected for the stationary state, with no hysteresis. As soon as σ decreases below σ_3 on the upper branch, we enter a metastable state since the corresponding point at the same shear rate but on the lower branch stores less elastic energy F_s . The less viscous phase will therefore nucleate and grow until the stationary homogeneous flow represented by point 1 is obtained.

Before closing this quick analysis of the shear-thickening situation, let us note in addition that an abrupt stress jump at finite shear rate may well occur even in absence of true elastic singularity. This is clear from equation (8), in which the denominator might vanish at some rate $\dot{\gamma}_0$ even if $d\sigma/d\gamma_s$ always remains positive. In such a case, the $\sigma(\dot{\gamma})$ curve would asymptotically become vertical at $\dot{\gamma}_0$ as shown in Figure 6 and a stress jump should be observed. In this case the viscous flow discontinuity takes place with no elastic singular counterpart.

In all cases of shear-thickening fluids discussed above, stationary inhomogeneous banded flows are suppressed. However, since we have restricted our analysis to flows with inhomogeneities in the shear gradient direction, we are unable to comment on the possible formation of shear-banded flows with inhomogeneities in the velocity or vorticity directions. Recent theoretical studies of flow instabilities in complex fluids based on the phenomenological coupling of solution flow and solute concentration dynamics [19] have predicted a class of banded-flow instabilities for shear-thickening fluids in simple shear geometries which consist of concentration and flow inhomogeneities in the vorticity direction. It is plausible that a more elaborate multi-dimensional analysis of our approach could also produce such banded structures for shear-thickening fluids, due either to viscous or elastic instabilities.

4. Discussion and Conclusion

Our work was motivated by widespread observations of unexpected features in shear-banded inhomogeneous flows of complex liquids, particularly in solutions of giant micelles. These are the robustness of the two-state banded regime and the slow nucleation and growth kinetics of these banded phases at the onset of shear. Such features of the coexisting banded states under shear are quite analogous to those of two-phase coexistence at an equilibrium first order phase transition. In analogy with the equilibrium thermodynamics of driven systems, we have proposed a phenomenological “quasi-thermodynamic” analysis of complex fluid systems in steady shear conditions. This approach is based on a effective potential whose origin is in the free energy stored in a viscoelastic material in steady shear flows. This coarse-grained potential F_s is defined on a *mesoscopic* scale as a function of a strain-like order parameter γ_s describing the effective deformation state of the medium in steady flow conditions.

This notion of an effective non-equilibrium potential which determines the multi-phase flow behavior of viscoelastic fluids is certainly not new. In particular, our approach shares many features in common with quasi-thermodynamic theories of polymer rheology based on the recoverable elastic strain stored in a deformed material [27, 28]. Since our description is based on the notion of the stored free energy, the question arises of its applicability to complex fluid systems which are not intrinsically elastic (as for the case of concentrated solutions of rigid rods, for example). However, as emphasized earlier, our non-equilibrium potential includes the changes in configurational entropy that are induced in a structured complex fluid by flow. In principle, it may contain both elastically recoverable and irrecoverable contributions. In the case of rigid rods under high shear, for instance, excess free energy is stored in the entropy reduction associated with the alignment of the rods in flow.

In our approach, we have assumed the existence a “non-equilibrium potential” and have focused our attention on the general phenomenological consequences of this ansatz on the flow behavior of complex fluid systems in steady-state flows. In this picture, a macroscopic non-Newtonian constitutive law $\sigma(\dot{\gamma})$ is slaved to an internal mesoscopic “non-equilibrium” potential. In a shear-thinning situation, this implies that a non-monotonic $\sigma(\dot{\gamma})$ necessarily reveals a hidden “internal” transition. This point of view appears fruitful at least when compared to the extensive data available for the CPSal + brine system under shear [4, 5]. In particular it predicts that for such shear-thinning systems, mechanical flow instabilities are preempted by a first-order (internal) transition. This first-order character is certainly one of the most frequently observed features of our data. On the other hand, the consequences of our quasi-thermodynamical picture in the case of shear-thickening systems are less sure and certainly deserve further consideration.

The connection between our quasi-thermodynamic formalism and the conventional rheological formulation in terms of a constitutive equation deserves to be highlighted. In principle, by

eliminating the internal order parameter γ_s between equations (1) and equation (7), one does obtain a relation directly connecting the measurable quantities, σ and $\dot{\gamma}$. This specifies the constitutive equation of the material under consideration and in this respect the two descriptions are indeed equivalent. Figures 5a and b are illustrations of non-monotonic constitutive equations built up on the basis of a quasi-thermodynamic potential which admits two-phase coexistence. If we further assume that the dependence of γ_s on $\dot{\gamma}$ is regular and monotonically increasing ($d\gamma_s/d\dot{\gamma} > 0$), the equivalence of the shear-thinning instabilities described by both approaches is apparent [since $d\sigma/d\dot{\gamma} = (d\sigma/d\gamma_s)(d\gamma_s/d\dot{\gamma})$]. Conversely, the purely viscous shear-thickening instability (without a “quasi thermodynamic transition”) discussed above would arise if γ_s changes discontinuously as a function of $\dot{\gamma}$. Nevertheless, in spite of these analogies with the classical constitutive equation approach, an essential ingredient of our point of view is absent in the classical approach, namely that the minimization principle provides a consistent mechanism of state selection from the inherently degenerate set of mechanically stable steady-state banded flow patterns. Furthermore, through equations (1) and (7), γ_s provides a useful parametrisation of σ and $\dot{\gamma}$. In some cases, σ appears in the end as a single valued function of $\dot{\gamma}$ as in Figure 5a. But our approach can also handle cases in which the dependence of σ on $\dot{\gamma}$ is not single valued.

There is another principle that is sometimes employed for state selection in non-equilibrium conditions, namely the principle of minimum entropy production. In case of a mechanical instability represented by a non-monotonic constitutive equation (such as shown in Fig. 1), this principle provides an alternative rule for selection amongst the degenerate set of mechanically stable two-state banded flows: the pair of states with the lowest value for σ (*i.e.* the horizontal line with point *b* located at *m* in Fig 1) corresponds to minimum entropy production and hence will be selected. It is clear that the principle of minimum entropy production gives different predictions from ours and hence these two approaches are mutually exclusive. Furthermore, it is plausible that a phenomenological model based on a minimum entropy production ansatz could be constructed to explain both the observed robustness of the two-state banded flows and the transient kinetics as well as our approach.

There are a number of limitations to our approach. For the sake of simplicity, we have deliberately neglected the tensorial character of shear stresses and strains in this paper. Thus our consideration is limited to uni-dimensional flow instabilities in the shear gradient direction. In order to comment upon the nature of possible flow inhomogeneities in the velocity or vorticity directions [19], our formalism must be extended to account for the multi-dimensional nature of the flows. Moreover, in order to emphasize the phenomenological consequences of a non-equilibrium effective potential, we have defined our “elastic potential” F_s and its conjugate variable, the “stored shear strain” γ_s , in a very general manner. This general framework in principle incorporates many specific internal degrees of freedom, such as the average length of the micelles and their local composition and orientation, which are usually not associated with the intuitive mechanical notion of a shear strain. A disadvantage of this generality is that we are unable to provide any guidelines for constructing F_s from first principles.

A recent hydrodynamic analysis of the shear-induced isotropic-nematic transition in thermotropic liquid crystalline fluids described an interface method for determining two-phase coexistence under flow [29]. In this approach, the structure of an interface between two bulk non-equilibrium phases is analyzed by including in the free energy appropriate gradient terms of the order parameter. At a given temperature, the selected coexistence shear stress is that for which the interface separating an isotropic phase and a nematic phase is stationary. This approach has recently been extended to analyze flow-induced transitions in lyotropic liquid crystalline fluids [40]. For the case of entangled wormlike micelles in shear flows, hydrodynamic approaches based on non-monotonic constitutive relations for stress as a function of shear rate

are also capable of predicting banded-flows of low and high shear rate fluid phases [18]. When these constitutive models are supplemented by phenomenological interfacial terms penalizing sharp spatial gradients in the viscoelastic portion of the shear stress, finite width bands at a selected value of the viscoelastic shear stress are obtained [18,20], in accordance with experiments. However, such analysis seems to predict the occurrence of a large, kink-like stress overshoot prior to achieving the coexistence stress level, a feature not observed in experiments. This behavior is presumably due in part to the lack of a nucleation mechanism in such a flow instability approach to banding. Nevertheless, this interfacial stability approach seems to be a very useful paradigm for understanding flow-induced non-equilibrium phase transitions in complex fluids. In particular, we note that in the case of field-induced phase transitions in equilibrium systems (*e.g.* an Ising-like system in an external magnetic field), the interface approach outlined above is equivalent to a variational analysis based on a bulk thermodynamic potential. We hope that future studies will demonstrate some link between the mesoscopic description of the quasi-thermodynamic approach and such kinetic approaches to the supramolecular structure under flow of model systems such as living polymers or giant micelles.

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