Metastable versus unstable transients at the onset of a shear-induced phase transition

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We measure the transient stress response at the onset of shear of a wormlike micelles solution which shows an inhomogenous banded flow pattern above a characteristic rate $\dot{\gamma}_t$. Depending on the magnitude of the excess rate above $\dot{\gamma}_t$, we identify two distinct types of stress response that correspond, respectively, to the metastable and to the unstable regimes, for the formation of the banded flow. This feature further underlines the analogy between the spontaneous formation of a banded flow and a first-order phase transition.
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A number of publications dealing with solutions of giant micelles under shear [1–5] have reported on shear-banded inhomogeneous stationary flows above some characteristic shear rate $\dot{\gamma}_t$. A mechanical signature of this behavior is an abrupt change in the slope of the evolution of the stress σ versus the rate $\dot{\gamma}$: σ suddenly levels off at $\dot{\gamma}_t$ and becomes almost independent of $\dot{\gamma}$ up to a rate $\dot{\gamma}_2$ at which the stress starts to increase again (inset in Fig. 1). Several experimental studies [2–5] involving neutron scattering under shear and flow birefringence have supported the picture of a nonuniform flow, banded along the thickness of the gap; lubricating bands of strongly oriented micelles coexist with viscous bulk regions of weakly oriented, entangled micelles. Increasing $\dot{\gamma}$ in the plateau regime mainly results in an increase in the relative proportion of the oriented fluid bands versus the bulk viscous unoriented regions at almost constant σ: in this respect, this behavior is similar to a first-order phase separation.

The considerable attention recently focused on this phenomenon is motivated by the evidence of similar behaviors for other complex fluids having sometimes completely different microstructures: semidilute solutions of polymers [6], onion textures in sheared smectic lyotropic phases [7], colloidal crystals and dense dispersions of silica spheres [8], copolymer melts and solutions [9,10]. In one case in [8], rheological measurements performed on a colloidal crystal revealed a nonmonotonic evolution of the stress response to increasing rates, which could be unambiguously assigned to an orientation transition. So, the scheme seems quite general. But still, giant micelles solutions provide most convenient model systems because the samples are cheap and easy to make, their mechanical characteristics have just the right magnitude for conventional rheometers, and, more importantly, the typical times to reach the steady state remain reasonable.

A general explanation for banded flows has been proposed [1,6] assuming a nonmonotonic constitutive equation for these materials (see inset in Fig. 1 for a schematic picture). If the applied $\dot{\gamma}$ lies in the region of decreasing σ (dotted part of the thin line), an initially homogeneous flow becomes mechanically unstable. The flow then evolves in time until a stationary state is reached where bands of highly sheared liquid ($\dot{\gamma}_2$) of low viscosity coexist with more viscous fluid subjected to a lower shear rate ($\dot{\gamma}_t$). In the banded regime, the stress is uniform throughout the material and only the relative fraction of the thickness of the gap occupied by the high *versus* the low shear-rate bands varies, so as to adjust to changes in the applied strain rate. Such description in terms of a mechanical instability of the viscous flow therefore accounts for the existence of the stress plateau.

The kinetics of the stress response associated with the formation of the banded flow after sudden onsets of the strain rate in the plateau range were studied in Ref. [4]. Immediately after the onset of shear, the material is still homogeneous in its initial viscous entangled states, so an excess stress is first measured above the late steady value. As time goes on, lubricating fluid bands progressively take place and the stress decreases towards its steady-state plateau value. At low initial excess stress (in the beginning of the plateau), sigmoidal decays for $\sigma(t)$ were found with characteristic times much longer than the viscoelastic time τ_R. Similar transients have been reported later on by Grand, Arraut, and Cates [11] for another system. Such stress evolution with zero slope at the origin is hardly compatible with a simple mechanical instability for which one would expect single exponential-like evolution with a nonzero negative initial slope. It rather suggests that the homogeneous flow is meta-

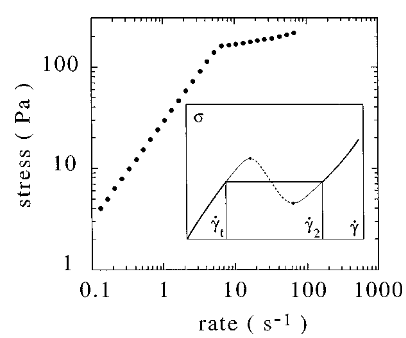

FIG. 1. Stress versus strain rate at steady state for the studied sample. In the inset, typical flow curve (thick line) corresponding to a nonmonotonic constitutive equation (thin line). The horizontal line represents the stress plateau for rates in between $\dot{\gamma}_{t-}$ and $\dot{\gamma}_2$.

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stable with respect to the band formation. Right in line with the analogy with a first-order shear-induced transition, an analysis of the slow transients was proposed in [4] assuming nucleation and growth of the fluid-oriented phase in the initial viscous entangled phase. Of course, the transients calculated so depend on the detailed specifications of the nucleation and the growth rates, but a robust feature of the approach is the parabolic ($-t^2$) asymptotic evolution at short time, which remarkably meets the data.

As a further analogy with phase transitions [4,12], at appropriate surfactant concentrations and temperatures one can meet ''critical'' conditions where the stress plateau reduces to one flat inflexion point and the transition appears second-order. Beyond critical conditions, the stress response is monotonic and no steady-state coexistence is observed. In line with these observations, one expects in subcritical conditions, for which the transition is first-order, that the above metastable regime should persist in a limited range only: it should leave its place above a characteristic excess stress (i.e., beyond some spinodal line) to a true instability. The transients should then change qualitatively from sigmoidal to exponential-like with a finite slope at the origin. With the former systems however, oscillating instabilities obscured the stress relaxation at high rates [11,13], so this conjecture could not be checked properly. These complications are direct consequences of the spectacular viscoelasticity of the materials with τ_R of the order of seconds. In the present paper, we investigate a faster system for which simple stress responses are seen at high rates. Our study provides clear evidence of the two types of transients taking place, respectively, at low *versus* high excess stresses just as expected by analogy with conventional phase transitions.

The sample under scrutiny [14] consists of cetyl pyridinium chloride (CPCl mass fraction$=0.283$) and *n*-hexanol (mass fraction$=0.046$) dissolved in D_2O-brine ($0.5M$ NaCl). All data are taken at 25 °C on a strain-controlled (Rheometrics RFS II) rheometer in the cone plate geometry. Measurements of the linear viscoelasticity of the sample revealed a Maxwellian behavior with one single viscoelastic relaxation time $\tau_R=0.17$ s. The stress versus rate flow curve in the steady state (Fig. 1) starts Newtonian at low rates and shows an abrupt kink at a rate $\dot{\gamma}_t$ about 6 s^{-1}, above which the stress σ hardly changes with $\dot{\gamma}$. Special care was taken to make sure that each point in Fig. 1 corresponds to the steady-state value. Furthermore, various shear histories have been tried systematically and so we checked the unicity and robustness of the banded steady state [15,16].

The time-resolved stress responses after startup of shear have been collected at various imposed strain rates. For rates below $\dot{\gamma}_t$, the stress quickly rises up and immediately reaches its stationary value within a time of the order of τ_R (<0.2 s). At rates above $\dot{\gamma}_t$, a stress overshoot $\Delta\sigma(t)$ is seen, which relaxes in time towards the steady value. A typical evolution of $\Delta\sigma(t)$ observed at rates just above $\dot{\gamma}_t$ ($\dot{\gamma}=7.5\,s^{-1}$) is shown in Fig. 2(a); the sigmoidal shape with zero slope at the origin is clear. The characteristic time is of the order of 90 s, very much longer than τ_R. This sigmoidal signature persists at higher rates up to 10 s^{-1}, although the characteristic time decreases markedly. At 10 s^{-1} and above [Fig. 2(b)], the stress response abruptly switches to a qualitatively different time evolution showing a finite slope at the origin. In order to exploit the two types of response within a unified quantitative scheme, all data were fitted [continuous lines in Figs. 2(a) and 2(b)] assuming stretched exponential forms,

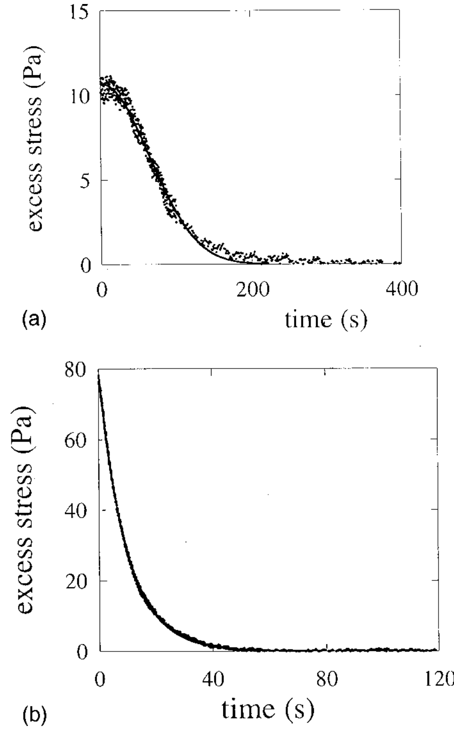

FIG. 2. Stress response at the onset of shear: (a) rate 7.5 s^{-1} just at the beginning of the plateau. (b) rate 14 s^{-1} further inside the plateau. The continuous lines represent the best fits according to expression (1).

$$\Delta\sigma(t)=\Delta\sigma(0)\exp\left[-\left(\frac{t}{\tau_N}\right)^{v}\right], \tag{1}$$

where $\Delta\sigma(0)$ is the initial excess stress, τ_N is the characteristic time, and v is the exponent characterizing the stretched exponential. Very good fits were obtained for the two types of responses [continuous lines in Figs. 2(a) and 2(b)] with this functional form. For all rates in between 6 and 9 s^{-1}, good fits are obtained for the sigmoidal evolution with an exponent v being close to 2, whereas at higher rates the exponent is close to 1. In order to emphasize the sharp change from one regime to the other around 10 s^{-1}, we have plotted in Fig. 3 the exponent v versus the rate $\dot{\gamma}$. On the other hand, the amplitude of the initial stress overshoot $\Delta\sigma(0)$ increases smoothly as a function of the rate (Fig. 4); the evolution is linear and its extrapolation to zero provides an accurate determination of the transition strain rate, $\dot{\gamma}_t=6.3\,s^{-1}$. In the inset of Fig. 4, we have plotted the inverse characteristic time τ_N^{-1} as a function of the rate $\dot{\gamma}$. We again obtain a straight line extrapolating to zero at $\dot{\gamma}=6.3\,s^{-1}$: the time scale of the transient, therefore, diverges at the transition rate $\dot{\gamma}_t$. This is in contrast with the observations of Grand *et al.* in [11] for a different system: they observed the divergence at a rate somewhat larger than the transition rate. It is also intriguing in Fig. 4 that the variation of τ_N is completely smooth over the full rate range, although the shape of the transient sharply changes at 10 s^{-1}.

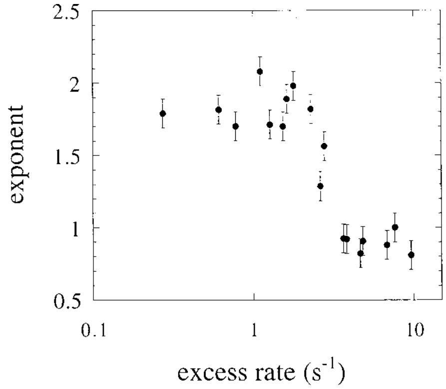

FIG. 3. The exponent ν versus the rate $\dot{\gamma}$.

All above data are for the stress response. In order to conclude on the underlying transient evolution of the coexisting phases, we must express $\Delta\sigma(t)$ in terms of the time evolution of $x(t)$ the fraction of the gap occupied by the shear-induced-oriented fluid phase. On time scales longer than τ_R and neglecting all inertial effects, the instantaneous stress $\sigma(t)$ is uniform through the gap. In contrast, due to the difference in their viscosities, the oriented and unoriented bands experience very different instantaneous rates. With these premises, it is straightforward to show that the initial excess stress $\Delta\sigma(t)$ is well approximated by

$$\Delta\sigma(t)=\Delta\sigma(0)\left(1-\frac{x(t)}{x_f}\right) \tag{2}$$

[x_f is the final plateau value of $x(t)$] provided that $\Delta\sigma(0)$, the excess initial stress, is moderate.

In order to check further the consistency of the analysis, we also performed step-down measurements. The data shown in Fig. 5 are collected according to the following procedure: the sample was first presheared at 15 s^{-1}, long enough to reach the steady banded state; the rate was then abruptly stepped down to 6 s^{-1} just below $\dot{\gamma}_t$. Since we start with lubricating bands, an undershoot is observed just after stepping down the rate. This negative excess stress is plotted versus time in Fig. 5. The time evolution involves two mechanisms with distinct characteristic times. The short one is of the order of $\tau_1=1$ s. We believe that it corresponds to the readjustment of the viscosity of the two coexisting phases to the new shear rate (unfortunately, we have no data on the

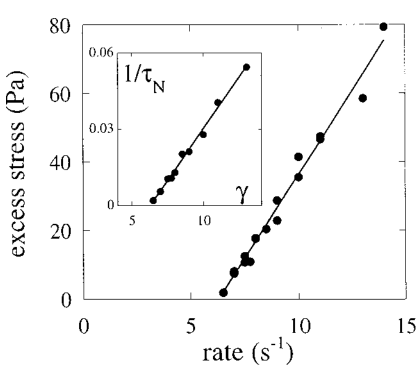

FIG. 4. The amplitude $\Delta\sigma(0)$ of the initial overshoot versus the shear rate. In the inset, the inverse characteristic time τ_N^{-1} versus the rate $\dot{\gamma}$.

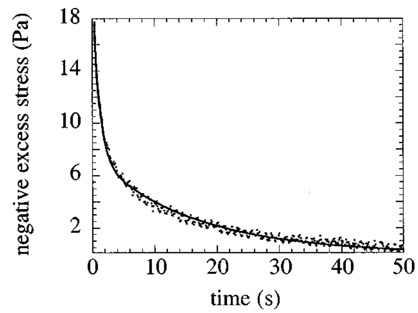

FIG. 5. Time evolution of the negative excess stress after stepping the rate abruptly from 15 s^{-1} down to 6 s^{-1}. The continuous line is a fit assuming a sum of two single exponentials of times $\tau1=1.06$ s and $\tau2=16.09$ s.

mechanical characteristics in the shear-induced aligned phase); during this fast step, the relative proportion of the two phases remains essentially constant. The longer relaxation ($\tau2=16$ s) would then correspond to the progressive thinning out and eventual disappearance of the lubricating bands. Since the interfaces between the oriented bands and the bulk-disoriented material are already present in the initial banded state, nucleation is not a necessary prerequisite for the evolution of the phases in such a step-down experiment. This is in qualitative agreement with the single exponential behavior, which we assume for the $\tau2$ component of the relaxation in Fig. 5.

Having checked this point and turning back to the above experiments at the onset of shear, the decay of the excess stress $\Delta\sigma(t)$ linearly reflects the kinetics of the formation of the inhomogeneous flow $x(t)$: the sigmoidal stress response with exponent 2 is the direct signature of the metastable regime at moderate rates and the simple exponential decay reveals the unstable regime at higher rates. The analogy with usual field-induced phase transitions at equilibrium is complete: the existence of the metastable regime suggested from previous studies is confirmed by the present evidence of the crossover to the unstable regime at higher rates. This consistent picture has an important consequence: the steady state with coexisting phases is not only uniquely defined and robust to changes in the shear history of the sample, it really acts as a *true attractor capable of driving the inhomogeneous flow pattern even when some activation barrier makes the initial homogeneous flow metastable*. These issues have been discussed at length in the current literature [15,17–19]: the unicity and robustness of the two-state coexistence can be rationalized, considering that the interface between the coexisting bands has a finite thickness within which the state variables are submitted to continuous gradients. Then the equations of motion provide [17–19] a stable interface (i.e., state coexistence) only if the stress is tuned at a uniquely defined value driving so a unique, robust steady state. But this is not enough to account for the attractor character of the steady state, which finally overcomes metastability. In equilibrium phase transition, the evolution towards equilibrium is driven by the minimization principle applied to the total free energy of the system. The analogy with equilibrium transitions observed in a situation far from equilibrium could indicate that some global out-of-equilibrium minimization principle here drives the steady state of flow [15].

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