

## Shear-induced phase separation of complex fluids: The role of flow-concentration coupling

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We propose a classification scheme for the instabilities that might arise in sheared complex fluids. A central role is played by the coupling between the flow and the solute concentration, which is a combination of the parameters describing (a) the tendency of solute molecules to migrate to regions of small or high shear rates and (b) the variation of the viscosity with concentration. Using a mean field approach, we show that the nature and the geometry of the instability can be predicted from the knowledge of the coupling parameter, the diffuson coefficient, and the derivative of the stress with respect to the shear rate. We also successfully compare a description of the variation of the stress at and just beyond the instability threshold, with experimental results from a wormlike surfactant solution of CPCIO<sub>3</sub>.

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### I. INTRODUCTION

The rheology of concentrated colloidal suspensions, polymer or surfactant solutions, and many other complex fluids is often used as a tool for extracting structural information from these materials. It carries, for instance, the signature of ordering phase transitions, entanglement of long polymer chains, or breaking and recombination kinetics in self-assembled surfactant chains. Experiments are usually performed in the shear geometry depicted in Fig. 1: a steady shear is applied between two plates. The velocity is in direction 1; the velocity gradient is in direction 2:

$$\vec{v} = (\dot{\gamma}_0 x_2, 0, 0). \quad (1)$$

One defines the viscosity as the ratio of the shear stress  $\sigma_{12}$  by the shear rate. We will note the derivative of the stress with respect to the shear rate  $\eta_d(\dot{\gamma}_0)$ , which is also of interest in this paper:

$$\eta_d(\dot{\gamma}_0) = \left. \frac{d\sigma_{12}}{d\dot{\gamma}} \right|_{\dot{\gamma}=\dot{\gamma}_0}. \quad (2)$$

This “local viscosity” is measurable, as is the viscosity. While carrying a simple shear experiment, one generally assumes that the velocity profile of Eq. (1) is self-sustained in the shear: any small, randomly generated velocity fluctuation around the average profile must decay to zero. Otherwise, an instability will grow away from mechanical equilibrium. An example of such instability growth is the so-called spurt effect in polymer melts, first reported by Bagley, Cabott, and West [1] as a discontinuity in the flow curve of polyethylene. This instability

has been explained on the microscopic basis provided by the theory of Doi and Edwards for polymer melts, but it can also be viewed, at the macroscopic level, as a mechanical instability arising for a vanishing derivative of the stress with respect to the shear rate  $\eta_d(\dot{\gamma}_0) = 0$ . A linear stability analysis can be performed on the Navier-Stokes equation in one dimension,

$$\rho \frac{\partial v_1}{\partial t} = \frac{\partial \sigma_{12}}{\partial x_2}, \quad (3)$$

by considering a small perturbation in the shear velocity profile and expanding the stress around its initial value:

$$\sigma_{12}(\dot{\gamma}) = \sigma_{12}(\dot{\gamma}_0) + \left. \frac{\partial \sigma_{12}}{\partial \dot{\gamma}} \right|_{\dot{\gamma}=\dot{\gamma}_0} \delta \dot{\gamma}. \quad (4)$$

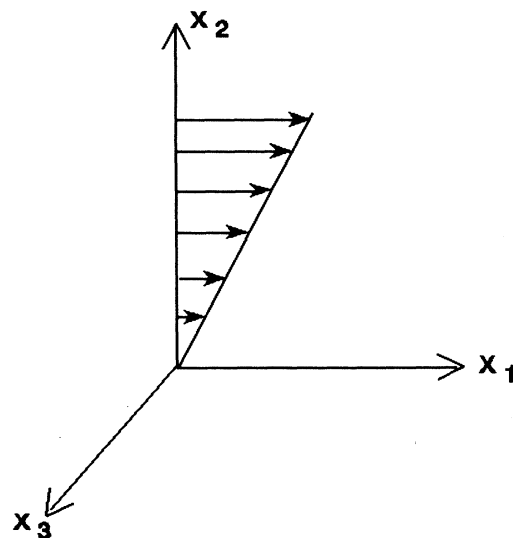


FIG. 1. Flow geometry: velocity field.

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The linearized form of Eq. (3) derived with respect to  $x_2$  corresponds then to a diffusion equation

$$\rho \frac{\partial \delta \dot{\gamma}}{\partial t} = \left( \frac{\partial \sigma_{12}}{\partial \dot{\gamma}} \right)_{\dot{\gamma}=\dot{\gamma}_0} \frac{\partial^2 \delta \dot{\gamma}}{\partial x_2^2} \quad (5)$$

for the shear perturbation with the corresponding diffusion coefficient:

$$D_{\text{visc}} = \frac{\eta_d(\dot{\gamma}_0)}{\rho}. \quad (6)$$

It is clear that an instability will appear and grow when  $\eta_d(\dot{\gamma}_0) < 0$ . From the experimental point of view this instability corresponds to a situation in which the stress first increases as a function of shear rate and then gradually levels off until a zero slope is attained. The fluid is then expected to decompose into a layered structure, with a series of strips alternatively subjected to low and high shear rates at the same stress [2]. This instability can occur in flexible unbreakable polymers and in surfactant solutions of wormlike micelles; in that case, this structure is at the origin of a stress plateau observed in some systems [3].

In some cases, these domains have different concentrations, as experimentally observed in concentrated wormlike solutions [4]. In these cases [4,5], the rheological signature is very different. This shows the importance of shear-concentration coupling. A similar instability also exists in sheared suspensions of colloidal particles where a plug forms in shear flow past a critical shear. Nozières and Quemada [6] have explained how a coupling mechanism between flow and concentration is responsible for plug formation in sheared suspension flow. By invoking a lift force (reminiscent of the magnum force in inviscid fluids) that drives the particles toward the regions of small shear rate, the increase of viscosity with concentration leads to a feedback circuit that may drive the instability: the particles migrate toward regions of small shear, increasing the concentration there and thus reducing the shear rate, which further increases the migration current.

The coupling between flow and concentration is a rather general feature of complex fluids, where the viscosity usually depends on the concentration of at least one of the constituents, and where the trajectory of the solute species is often coupled to the stress bestowed on the solution. This coupling has been described not only in concentrated colloidal suspensions but also in polymer solutions [7] and copolymer solutions [8] and binary fluids [9], where two-fluid models or stochastic dynamics concepts have been successfully applied to describe the increase of concentration fluctuations in shear flows [10] or order-disorder phase transitions [11]. In this paper, we attempt to classify some instabilities that may arise in sheared complex fluids where flow and concentration are coupled. We purposefully position our description at a phenomenological level: on the one hand, the dynamics of the concentration fluctuations will be treated by a generalized diffusion equation that explicitly accounts for the coupling between flow and concentration; on the other hand, the flow hydrodynamics will be treated with the Navier-Stokes equation, including a constitutive equation

relating the stress with both concentration and velocity field.

This approach allows us to maintain some degree of generality, clarifying the role of the coupling mechanism. In Sec. II we present a linear stability analysis for the velocity fluctuations around the average velocity profile under a shear flow, and we describe the conditions under which different instabilities may grow. Special attention is paid to the prediction of the stability geometry, an important issue related to orientation of the differently sheared domains. In Sec. III we describe the flow and stress fields when the two phases coexist in the flow and compare our predictions to experimental results from a wormlike surfactant solution of CPClO<sub>3</sub> [5]. The concluding section discusses the limitations and possible extensions of our work.

## II. LINEAR STABILITY FOR A CONSERVED ORDER PARAMETER

In the Appendix, we show that, if the order parameter coupled with shear is nonconservative (as nematic anisotropy), then the previous flow stability criterion remains exactly the same:  $\eta_d(\dot{\gamma}_0) > 0$ . Thus, we will only consider the effect of a conservative order parameter, i.e., the concentration. For many of the experimental situations that might be indicated by our description, such as binary-fluid mixtures, colloidal suspensions, surfactant solutions, polymer solutions and blends, or diblock copolymer melts, the evolution of the system can be described by two coupled dynamical equations: one equation that describes the dynamics of the order parameter and one that describes mechanical equilibrium. They can be derived with some degree of generality at the phenomenological level by considering the conservation law for the order parameter

$$\frac{\partial \Phi}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0 \quad (7)$$

and writing a generalized Fick equation for the current

$$\vec{J} = \Phi \left[ \vec{v} - \frac{1}{\zeta} \vec{\nabla} \mu \right], \quad (8)$$

where  $\mu$  is the osmotic stress acting on the order parameter (like the osmotic stress acting on the solute in a two-component solution),  $\zeta$  is a friction coefficient, and  $\vec{v}$  is the velocity field of the fluid. Enforcement of incompressibility of the fluid leads to

$$\frac{\partial \Phi}{\partial t} + \vec{v} \cdot \vec{\nabla} \Phi = \vec{\nabla} [M \vec{\nabla} \mu(\Phi, \vec{\nabla} \cdot \vec{v})], \quad (9)$$

where  $M = \Phi / \zeta$  is a positive transport coefficient. For a dilute solute ( $\mu = k_B T \ln_{10} \Phi$ ) in a quiescent solvent, one recovers the usual diffusion equation with diffusion coefficient  $D = k_B T / \zeta$ . We have assumed that the concentration is coupled with the shear rate. In an inhomogeneous flow, the concentrations of two regions sheared with different shear rates will evolve in time by a diffusion process. This has been introduced by the mean of a dependence of  $\mu$  on the shear rate.

In Eq. (9), the convection term  $\vec{v} \cdot \vec{\nabla} \Phi$  breaks the translational invariance in direction 2 of the problem because the initial velocity depends explicitly on  $x_2$ . Thus the problem is inhomogeneous and leads to Orr-Sommerfeld-like equations requiring sophisticated asymptotic analysis [12]. However, substantial simplification can be achieved if we can neglect disturbances modulated in direction 1. Any fluctuation with a characteristic relaxation rate slower than  $\dot{\gamma}_0$  is strongly convected by the flow, and the fluctuations are “layered” in a plane perpendicular to the flow direction. As the fluctuations are controlled by diffusion, which is a very slow process, it is quite reasonable to assume that all the fluctuations are layered. Actually, this assumption amounts to not taking into account the instabilities that would appear at a length scale smaller than  $(D/\dot{\gamma}_0)^{1/2}$ —typically of the order of micrometers. It is possible that these instabilities occur in some systems [13], and so we have to keep in mind that we have not considered a class of instabilities for which the samples are not layered but are instead becoming lumpy.

Therefore, we will assume that all the fluctuations are layered, and hence that the wave vector of the fluctuations can be taken perpendicular to the initial velocity, i.e., in the  $(\vec{e}_2, \vec{e}_3)$  plane. In that case,  $\vec{v} \cdot \vec{\nabla} \Phi$  vanishes, and we can perform a linear analysis.

The other ingredient of the model is the mechanical equilibrium, described by the Navier-Stokes equation

$$\rho \frac{\partial \vec{v}}{\partial t} = -\vec{\nabla} P + \vec{\nabla} \cdot \vec{\sigma}, \quad (10)$$

where we have limited ourselves to flows with low Reynolds numbers. The stress depends on both the shear and the concentration; hence it can be developed as

$$\begin{aligned} \vec{\sigma}(\vec{\nabla} \cdot \vec{v}, \Phi) &= \vec{\sigma}(\vec{\nabla} \cdot \vec{v}_0, \Phi_0) + \left[ \frac{\partial \vec{\sigma}}{\partial(\vec{\nabla} \cdot \vec{v})} \right]_{\vec{v} \cdot \vec{v} = \vec{v} \cdot \vec{v}_0} : \vec{\nabla} \cdot \delta \vec{v} \\ &+ \left[ \frac{\partial \vec{\sigma}}{\partial \Phi} \right]_{\Phi = \Phi_0} \delta \Phi. \end{aligned} \quad (11)$$

This is in fact the local constitutive equation of the fluid. The term

$$\left[ \frac{\partial \vec{\sigma}}{\partial(\vec{\nabla} \cdot \vec{v})} \right]_{\vec{v} \cdot \vec{v} = \vec{v} \cdot \vec{v}_0}$$

is an unknown fourth order tensor that can itself lead to various mechanical instabilities [14]. It contains *a priori* many terms: the study of this tensor is in fact reminiscent of all the work on constitutive equations. However, here we are only interested in instabilities that are due to the coupling, so we will not consider all the parameters but will simplify this tensor as much as possible. The simplest form of the tensor we can assume is scalar, which corresponds to the case of a Newtonian fluid. In this approximation, the only efficient perturbations possess velocity fluctuations parallel to the initial velocity. As we are interested in the coupling between the mechanical instabilities and phase separation, we have to deal with a vanishing value of  $\partial \sigma_{12} / \partial \dot{\gamma}_{12} = \eta_d$ . The possible cancellation of this term arises from the convection of the stress

by a shear parallel to the initial one. It is clear that if a secondary shear occurs in another direction, the effect will be completely different. As in the previous case of isotropic viscosity, we will allow velocity amplitude fluctuations, not velocity direction fluctuations. Hence we will keep only two terms corresponding to two directions of the perturbed velocity gradient (Fig. 2); in each case, the velocity fluctuation is parallel to the initial velocity, but the gradient of the velocity fluctuation is either in direction 2 or in direction 3. The first component is the derivative of the stress with respect to the initial shear rate and corresponds in fact to the “local viscosity”  $\eta_d(\dot{\gamma}_0)$ . This is the term that leads, without coupling, to mechanical instabilities as explained previously. The second component represents the dissipation due to a shear with a gradient in direction 3 superimposed on the initial shear rate in direction 2 (see Fig. 2) and is given by

$$\eta_3 = \left. \frac{\partial \sigma_{13}}{\partial \dot{\gamma}_{13}} \right|_{\dot{\gamma}_{12} = \dot{\gamma}_0}. \quad (12)$$

This component should be positive on physical grounds and does not affect the stability criterion we discuss presently. Lastly, it can be shown that the modification of the osmotic stress due to a shear flow fluctuation reduces to the single term

$$M \left[ \frac{\partial \mu}{\partial(\vec{\nabla} \cdot \vec{v})} \right] : \vec{\nabla} \cdot \delta \vec{v} = M \frac{\partial \mu}{\partial \dot{\gamma}_{12}} \delta \dot{\gamma}_{12}. \quad (13)$$

For this, we use the property that the osmotic stress is a scalar and thus can only depend on the scalar invariants

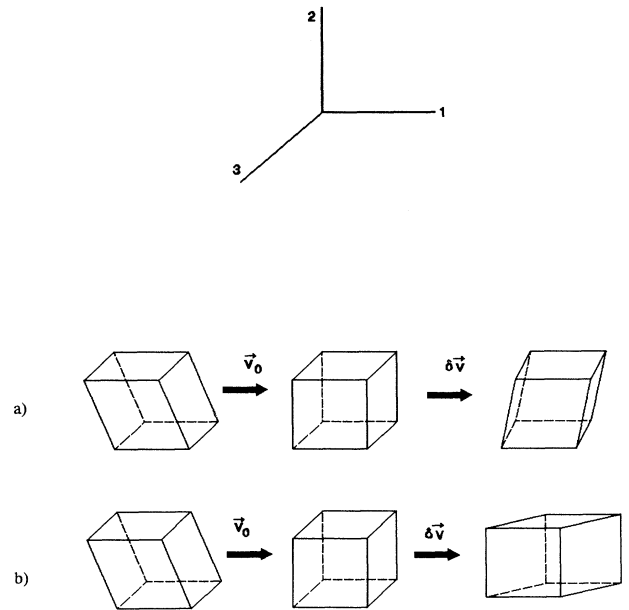


FIG. 2. Representation of the main and perturbative shear. (a) The perturbative velocity gradient is in direction 2, as the main velocity gradient; (b) the perturbative velocity gradient is in direction 3, perpendicular to the main velocity gradient.

of the flow. Then, after linearization and suppression of the irrelevant terms, we get the two coupled equations for the deviations of concentration  $\delta\Phi$  and velocity  $\delta v_1$ :

$$\frac{\partial \delta\Phi}{\partial t} = D \Delta \delta\Phi + M \frac{\partial \mu}{\partial \dot{\gamma}} \frac{\partial^3 \delta v_1}{\partial x_2^3} \quad (14)$$

and

$$\rho \frac{\partial \delta v_1}{\partial t} = \eta_d \frac{\partial^2 \delta v_1}{\partial x_2^2} + \eta_3 \frac{\partial^2 \delta v_1}{\partial x_3^2} + \frac{\partial \sigma_{12}}{\partial \Phi} \frac{\partial \Phi}{\partial x_2}, \quad (15)$$

where  $D$  is the classical diffusion coefficient and can depend on the initial shear rate

$$D = M \frac{\partial \mu(\Phi, \dot{\gamma})}{\partial \Phi}. \quad (16)$$

Taking a velocity perturbation

$$\delta v_1 = \delta v e^{i\vec{k} \cdot \vec{r} + \omega t} \quad (17)$$

with a wave vector  $\vec{k} = k \cos\theta \vec{e}_2 + k \sin\theta \vec{e}_3$ , we see that Eqs. (5) and (6) become

$$\omega \delta\Phi = -D k^2 \delta\Phi - i M \frac{\partial \mu}{\partial \dot{\gamma}} k^3 \cos\theta \delta v_1 \quad (18)$$

$$\rho \omega \delta \vec{v} = -k^2 [\eta_d \cos^2\theta + \eta_3 \sin^2\theta] \delta \vec{v} + ik \left[ \frac{\partial \sigma_{12}}{\partial \Phi} \right]_{\Phi=\Phi_0} \delta\Phi k \cos\theta \vec{e}_1, \quad (19)$$

and combining Eqs. (7) and (8), we obtain the following dispersion equation:

$$\left[ \frac{\omega}{k^2} \right]^2 + \left[ \frac{\omega}{k^2} \right] \left[ \frac{\eta_d}{\rho} \cos^2\theta + \frac{\eta_3}{\rho} \sin^2\theta + D \right] + \left[ \frac{\eta_d}{\rho} \cos^2\theta + \frac{\eta_3}{\rho} \sin^2\theta \right] D - C \cos^2\theta = 0, \quad (20)$$

where

$$C = \frac{M}{\rho} \left[ \frac{\partial \mu}{\partial \dot{\gamma}} \right]_{\dot{\gamma}=\dot{\gamma}_0} \left[ \frac{\partial \sigma_{12}}{\partial \Phi} \right]_{\Phi=\Phi_0} = \frac{M}{\rho} \dot{\gamma}_0 \left[ \frac{\partial \mu}{\partial \dot{\gamma}} \right] \left[ \frac{\partial \eta_{12}}{\partial \Phi} \right] \quad (21)$$

is the coupling term.  $C$  is the product of the derivative of the viscosity with respect to the concentration and the derivative of the chemical potential with respect to the shear rate.  $C$  actually represents the feedback effect of the concentration: if two domains have different shear rates, their concentrations will evolve and then their viscosities. So, if  $C$  is positive, the viscosity of the domain with the higher shear rate is decreased, and vice versa if  $C$  is negative. Let us note that  $C$  is difficult to estimate from experimental measurements; however, its sign is very easy to obtain:  $C$  is positive if the shear induced phase is less viscous than the initial one, and negative otherwise. It is zero if the shear induced phase has the same concentration as the initial one.

The extrema for Eq. (20) lie at  $\theta=0$  or  $\pi/2$ . Hence the previous dispersion equation reduces either to

$$\left[ \frac{\omega}{k^2} + \frac{\eta_d}{\rho} \right] \left[ \frac{\omega}{k^2} + D \right] - C = 0, \quad \text{for } \theta=0 \quad (22)$$

or to

$$\left[ \frac{\omega}{k^2} + \frac{\eta_3}{\rho} \right] \left[ \frac{\omega}{k^2} + D \right] = 0, \quad \text{for } \theta=\pi/2. \quad (23)$$

A perturbation will grow if there is a positive solution for  $\omega$ . We have plotted a two-parameter stability diagram (Fig. 3) in the case  $D > 0$ . If  $D$  remains positive, two types of instabilities are possible; both appear with  $\vec{k} \parallel \vec{e}_2$ , i.e., with a band structure perpendicular to the shear. The first one occurs with a positive  $\eta_d$  coefficient and can be observed only while the stress is an increasing function of the shear rate [see Fig. 4(a)]. This instability appears when

$$C \geq \frac{\eta_d D}{\rho}, \quad (24)$$

and the other one occurs when

$$\eta_d \leq -\rho D. \quad (25)$$

Thus, the second instability appears if the stress is decreasing with rising shear rate, because the negative coupling stabilizes the flow with regard to the purely mechanical instability. However,  $-\rho D$  is of the order of  $10^{-7}$  Pa s, so that a negative value of  $\eta_d$  cannot be detected with rheometers. Hence, in practice the transition will occur when  $\eta_d$  is observed to vanish. The corresponding flow curve  $\sigma_{12} = f(\dot{\gamma})$  will present a vanishing derivative [Fig. 4(b)] similar to the purely mechanical instability described in the Introduction. Actually, if  $C$  is negative, thin layers with higher viscosity than that of the initial fluid appear. This situation is in fact unstable because

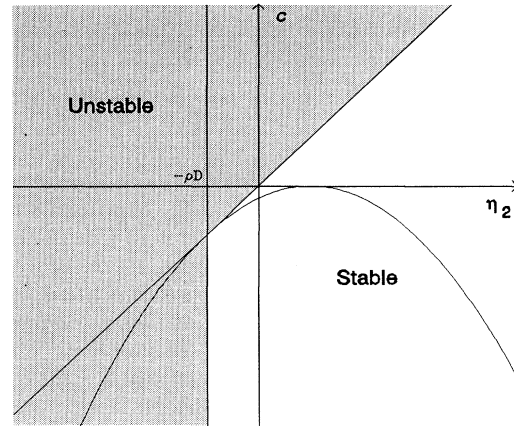





FIG. 3. Stability diagram for a positive diffusion coefficient. A perturbation is amplified in the domain noted "unstable" and softened in the domain noted "stable." The coupling term is  $C = M/\rho (\partial \mu / \partial \dot{\gamma})_{\dot{\gamma}=\dot{\gamma}_0} (\partial \sigma_{12} / \partial \Phi)_{\Phi=\Phi_0}$ .

TABLE I. Classification of the instabilities when concentration and flow are coupled.

Sign of $C$	Instability criterion	Instability	Geometry
$C > 0$	$C > \eta_2 \frac{D}{\rho}$	$\vec{k} \parallel \vec{e}_2$	
$C < 0$	(a) If $D > 0$ $\eta_2 \leq -\rho D$	$\vec{k} \parallel \vec{e}_2$	
	(b) $D(\dot{\gamma}) < 0$	$\vec{k} \parallel \vec{e}_3$	

the layers tend to break into small droplets. So in that case, a secondary instability will be generated simultaneously.

Let us now consider the case in which the diffusion coefficient, modified by the flow, becomes negative. Thus, a shear induced spinodal phase separation occurs. If the

coupling coefficient  $C$  is positive, the first instability previously described (24) will grow before the spinodal phase separation. However, if the coupling coefficient  $C$  is negative, the spinodal separation can occur before the mechanical instability. Then its wave vector will be parallel to direction 3.

All these results are summarized in Table I. In fact, fluids can be sorted into two types:

(i) If the coupling term  $C$  is positive, only one kind of instability can occur. Concentration fluctuations induce shear rate fluctuations, which in a feedback process generate an amplification of concentration fluctuations. The sample is then layered perpendicularly to the gradient direction.

(ii) If the coupling term  $C$  is negative, mechanical and spinodal instabilities are separate. (a) If  $D$  remains positive, a mechanical instability can be generated. It is so slightly modified and stabilized by the coupling that it can be considered a purely mechanical one. The layering remains perpendicular to direction 2. In general, the layers of the shear induced phase will not be stable, as they are more viscous and break into droplets. (b) If  $D$  is modified by the flow and becomes negative, the thermodynamical instability remains under flow but the spinodal separation is layered perpendicularly to the neutral direction.

So if  $C$  is positive, we can observe a new instability with a strong coupling between shear rate and concentration. In contrast, if  $C$  is negative, we find almost all of the usual instabilities, either purely mechanical or spinodal. Let us also remember that we have only discussed shear banded instabilities and that other instabilities (where the system becomes lumpy) can also exist. Moreover, secondary instabilities can develop, for instance, if the shear induced phase is more viscous than the initial one.

Shear induced transitions can be generated not only by instabilities but also by nucleation and growth processes. So we have two different domains in the phase diagram: the first one corresponding to the instabilities and the other to coexisting phases in flow. This is similar to a first order transition [6]. In practice, it is quite easy to distinguish between mechanical and diffusive transitions because the typical times are very different. But it will be experimentally difficult to distinguish between instability and nucleation and growth. To separate the two effects, a study of the mechanical transient behavior must be combined in the detection of the concentration and velocity fields.

### III. BEHAVIOR OF THE STRESS IN THE COEXISTING DOMAIN

The behavior of the stress in the two-phase coexisting domain is easy to estimate, from the dynamical phase diagram  $(\Phi, \dot{\gamma})$ , for both geometries. Let  $\Phi$ ,  $\eta$ , and  $\dot{\gamma}$  be the concentration, the viscosity, and the shear rate of the initial phase (indexed with  $a'$ ) and of the shear induced one (with  $a''$ ). Let  $x$  be the volume fraction of the initial fluid. We assume that the initial fluid is always kept at its instability threshold  $\dot{\gamma}_c(\Phi)$ .

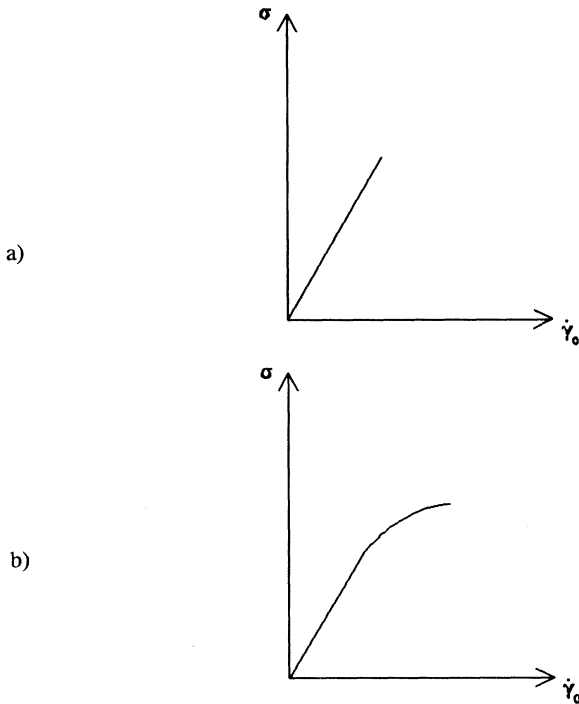


FIG. 4. Flow curve. (a) When the coupling term  $C$  is positive, the instability appears for increasing stress as a function of shear rate. (b) When the coupling term  $C$  is negative, the instability appears for a vanishing derivative of the stress with respect to the shear rate.

If the instability appears with  $\vec{k} \parallel \vec{e}_2$ , the two phases are similarly stressed but have different shear rates. The measured shear rate is the mean shear rate

$$\dot{\gamma} = x\dot{\gamma}' + (1-x)\dot{\gamma}'' , \quad (26a)$$

$$\sigma = \eta'\dot{\gamma}' = \eta''\dot{\gamma}'' . \quad (26b)$$

Hence, we can deduce an expression of the stress variation near the threshold at the beginning of the layering ( $x \approx 1$ ):

$$\frac{d\sigma}{d\dot{\gamma}} = \eta' \left[ 1 + \frac{\dot{\gamma}_c}{\Delta\Phi \left[ \frac{\partial\dot{\gamma}_c}{\partial\Phi} \right]_{\Phi=\Phi'}} \left( 1 - \frac{\eta'}{\eta''} \right) \right]^{-1} , \quad (27)$$

where  $\Delta\Phi$  is the concentration gap.

If the instability appears with  $\vec{k} \parallel \vec{e}_3$ , then the two phases are similarly sheared but differently stressed; using the same argument, we can deduce the expression of the stress variation at the threshold

$$\frac{d\bar{\sigma}}{d\dot{\gamma}} = \eta' \left[ 1 + \frac{\dot{\gamma}_c}{\Delta\Phi \left[ \frac{\partial\dot{\gamma}_c}{\partial\Phi} \right]_{\Phi=\Phi'}} \left( 1 - \frac{\eta''}{\eta'} \right) \right] . \quad (28)$$

Both expressions can be derived from the measurement of the dynamical phase diagram, from which we can easily derive  $\dot{\gamma}_c(\Phi)$  and  $\Delta\Phi$ . Of course, if the estimated slope  $d\sigma/d\dot{\gamma}$  is negative, a secondary mechanical instability is generated.

The experimental results were obtained from the wormlike system described in [5] with two surfactant concentrations: 31% and 34% (in weight) of surfactant. The dynamical phase diagram and the flow curves were determined at equilibrium. In this specific case, the coupling term  $C$  is positive because the shear induced phase is less viscous than the initial one; hence we apply the expression (27) corresponding to the  $\vec{k} \parallel \vec{e}_2$  geometry. The results are reported in Table II.

Let us point out that these results are approximate because the term  $\partial\dot{\gamma}_c/\partial\Phi$  depends strongly on the concentration, as can be seen in the dynamical phase diagram reported in [5]. So a small uncertainty about the concentration induces a strong uncertainty about this term. Another difficulty arises from the fact that in this wormlike micellar system, the induced phase is nematic and is very shear-thinning. Hence, care must be taken to deter-

mine the value of  $\eta''$ , which has to be estimated at the relevant stress. However, these experimental results are satisfactory. Moreover, the slope obtained by using Eq. (28), i.e., assuming the orthogonal geometry, is completely incompatible with the measured one, thus confirming that the layers are perpendicular to the gradient direction.

#### IV. CONCLUSION

The model that we have developed here allows classification of the layering instabilities when flow and concentration are coupled. This approach allows us to distinguish two classes of fluids according to the sign of the coupling term  $C$ . This coupling constant is positive if the shear induced phase is less viscous than the initial one. If  $C$  is positive, we have a new type of instability, in which the mechanical and thermodynamical mechanisms are mixed. If  $C$  is negative, the two mechanisms are uncoupled and the instability is either quasi purely mechanical (and develops when the local viscosity vanishes) or thermodynamical (on the spinodal line). These instabilities appear with specific orientation of the layers. Beside these instabilities, other instabilities can occur (where the system becomes lumpy), as well as nucleation and secondary instabilities. Thus, many studies are required for an insight into the shear induced transitions, although we have also shown with a simple example that quantitative analysis of the coexisting phase domain is possible.

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#### APPENDIX: COUPLING WITH A NONCONSERVED ORDER PARAMETER

Let us consider the case in which the flow is coupled with a nonconserved order parameter  $S$  (as nematic anisotropy, for example). This parameter takes the  $S_0$  value at equilibrium. The stress depends on both  $S$  and  $\dot{\gamma}$ , and it can then be developed as

$$\begin{aligned} \sigma_{12}(\dot{\gamma}, t) = & \sigma_{12}(\dot{\gamma}_0, t) + \left[ \frac{\partial\sigma_{12}}{\partial\dot{\gamma}} \right]_{\dot{\gamma}=\dot{\gamma}_0} \delta\dot{\gamma} \\ & + \left[ \frac{\partial\sigma_{12}}{\partial S} \right]_{S=S_0(\dot{\gamma}_0)} \delta S . \end{aligned}$$

The order parameter  $S(\dot{\gamma})$  relaxes to its equilibrium value  $S_0(\dot{\gamma})$ :

$$\frac{\partial S(\dot{\gamma})}{\partial t} = -\xi(S(\dot{\gamma}) - S_0(\dot{\gamma})) , \quad (A1)$$

where  $\xi$  is a positive microscopic relaxation rate.  $S$  can be developed as

$$\begin{aligned} S(\dot{\gamma}) = & S_0(\dot{\gamma}_0) + \delta S , \\ S_0(\dot{\gamma}) = & S_0(\dot{\gamma}_0) + \left[ \frac{\partial S_0}{\partial\dot{\gamma}} \right]_{\dot{\gamma}=\dot{\gamma}_0} \delta\dot{\gamma} ; \end{aligned}$$

TABLE II. Comparison between model and experiments on wormlike micelles.

Surfactant concentration	$\Phi = 31\%$	$\Phi = 34\%$
$\frac{d\sigma}{d\dot{\gamma}}$ estimated from the flow curve	0.58 Pa s	5.0 Pa s
$\frac{d\sigma}{d\dot{\gamma}}$ calculated from the expression (27)	0.4 Pa s	5.6 Pa s

hence Eq. (A1) can be linearized as

$$\frac{\partial \delta S}{\partial t} = -\xi \delta S - \xi \left[ \frac{\partial S_0}{\partial \dot{\gamma}} \right]_{\dot{\gamma}=\dot{\gamma}_0} \delta \dot{\gamma},$$

and the Navier-Stokes equation, derived with respect to  $x_2$ , is given by

$$\rho \frac{\partial \delta \dot{\gamma}}{\partial t} = \frac{\partial^2}{\partial x_2^2} \left[ \left[ \frac{\partial \sigma_{12}}{\partial \dot{\gamma}} \right]_{\dot{\gamma}=\dot{\gamma}_0} \delta \dot{\gamma} + \left[ \frac{\partial \sigma_{12}}{\partial S} \right]_{S=S_0(\dot{\gamma}_0)} \delta S \right].$$

Let us consider a perturbation to the initial shear rate  $\dot{\gamma}_0$  as  $\delta \dot{\gamma} = \delta \dot{\gamma}_0 e^{ikx_2 + \omega t}$ . This leads to the following disper-

sion equation:

$$\omega = -\frac{k^2}{\rho} \left[ \left[ \frac{\partial \sigma_{12}}{\partial \dot{\gamma}} \right]_{\dot{\gamma}=\dot{\gamma}_0} + \frac{\xi}{\xi + \omega} \left[ \frac{\partial S_0}{\partial \dot{\gamma}} \right]_{\dot{\gamma}=\dot{\gamma}_0} \left[ \frac{\partial \sigma_{12}}{\partial S} \right]_{S=S_0(\dot{\gamma}_0)} \right].$$

The term between brackets is the total stress variation resulting from a shear variation  $d\sigma_{12}/d\dot{\gamma}$ . Hence we find the usual stability criterion for the effective stress varia-

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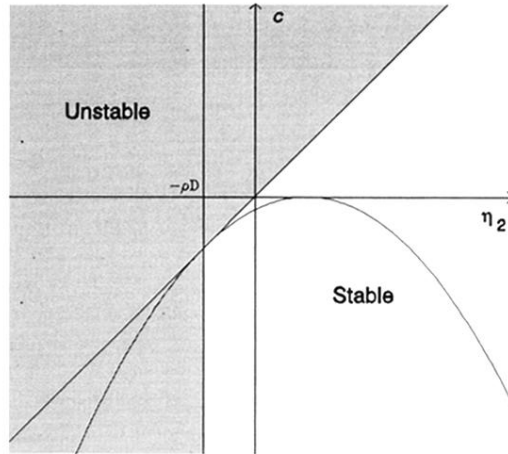


FIG. 3. Stability diagram for a positive diffusion coefficient. A perturbation is amplified in the domain noted "unstable" and softened in the domain noted "stable." The coupling term is  $C = M / \rho (\partial \mu / \partial \dot{\gamma})_{\dot{\gamma} = \dot{\gamma}_0} (\partial \sigma_{12} / \partial \Phi)_{\Phi = \Phi_0}$ .