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Shear banding in reaction-diffusion models

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Presented at EuroRheo 99-1 May 3-7, 1999, Sophia-Antipolis, France Abstract Shear banding occurs in the flow of complex fluids: various types of shear thinning and shear thickening micelle solutions and liquid crystals. In order to cope with the strongly inhomogeneous interface between the bands, constitutive models used in standard rheology must be supplemented by non-local terms. This leads rather generally to non-linear partial differential equations of the reaction-diffusion type. We use this formalism in order to explain some observed experimental

features and as a guide for future research in this field.

Key words Non-linear rheology · Flow instabilities · Shear banding · Constitutive equations · Johnson-Segalman Model

Introduction

Shear banding, consisting of the formation of bands of different shear rates and apparent viscosities, occurs in the flow of wormlike micelles in water solutions of surfactants (Rehage and Hoffmann 1988; Berret et al. 1994; Callaghan et al. 1996; Grand et al. 1997; Decruppe et al. 1997; Boltenhagen et al. 1997), or in organic solutions of metallic complexes (Terech 1998), or in the flow of lyotropic liquid crystals (Bonn et al. 1998). The same type of phenomenon may be responsible for spurt and extrudate distortions of polymers (McLeish 1987). Although for each system the details of this instability vary, some general features may be emphasized. Steady flow curves have several branches: a high shear rate and low viscosity branch, a low shear rate and high viscosity branch, and a coexistence plateau corresponding to banded flow. One can imagine two types of banding and coexistence plateaus: at constant stress (shear stress is the same inside all bands that are parallel to the vorticity) and at constant shear rate (shear rate is the same for all bands that are perpendicular to the vorticity), Fig. 1. The origin of this rheological behaviour is that for the same value of the shear stress (or shear rate) the fluid can exist in different microscopic states. For instance at constant shear stress wormlike micelles in the shear thinning surfactant/salt system CPCl/NaSal 0.1/0.06 M, well known from the work of Rehage and Hoffmann (1988), can exist in either an isotropic state sustaining almost all of the total stress at a low shear rate, or in a nematic state sustaining only a small part of the total stress, the other part being sustained by the solvent at a high shear rate, (Fig. 1a). Bands perpendicular to the vorticity (Fig. 1b) were observed (Wheeler et al. 1998) in the shear thickening surfactant/salt system CPCl/NaSal 0.04/0.04 M. nevertheless these bands were not stationary and it is not yet clear if they can be related to a microstructural reorganisation.

Reaction-diffusion models and the dominance principle

We discuss here the case of bands parallel to the vorticity.

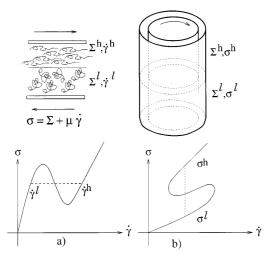


Fig. 1 Two types of shear banding: **a** bands parallel to the vorticity (here in planar shear), plateau at constant stress in a shear thinning system; **b** bands perpendicular to the vorticity (here in Couette geometry), plateau at constant strain rate in a shear thickening system

Standard local constitutive models in differential form [Johnson-Segalman (JS), Doi-Edwards, see Larson 1988] lead, in the case of simple shear, to equations of the form $\partial_t \sigma^p = \mathbf{C}(\sigma^p,\dot{\gamma})$ where $\dot{\gamma},\sigma^p$ are the shear rate and the "polymer" part of the stress, respectively. The function \mathbf{C} changes from one constitutive model to another. Because constitutive models rely on very general "material frame indifference" principles, they do not usually contain all the information on the microstructure dynamics. On the other hand microscopic models rely on a large number of stochastic variables whose dynamics is not always amenable to a deterministic low dimensional form. Obviously, the two approaches should be considered in a complementary way.

In planar shear the creeping flow momentum balance reads:

$$\sigma = \Sigma + \mu \dot{\gamma} = \text{const.} , \qquad (1)$$

where σ , Σ , μ are the total and the polymer shear stress, and the solvent viscosity, respectively.

After eliminating the shear rate in the constitutive equation, a system of ordinary differential equations is obtained:

$$\partial_t \mathbf{\sigma}^p = \mathbf{C}[\mathbf{\sigma}^p, (\sigma - \Sigma)/\mu] . \tag{2}$$

Steady flow curves are obtained from:

$$\mathbf{C}[\mathbf{\sigma}^p, (\sigma - \Sigma)/\mu] = 0 . \tag{3}$$

Banding is possible at fixed σ , when Eq. (3) has at least two linearly stable solutions $\Sigma^{\ell}(\sigma)$ and $\Sigma^{h}(\sigma)$ for Σ , corresponding to low and high shear rates.

Equation (2) corresponds to the "reaction" part of the model, describing the local non-linear relaxation of the polymer stress. With only reaction terms, banded flows have discontinuous shear rate and polymer stress pro-

files, and interfaces between bands are infinitely sharp. In order to cope with the strong inhomogeneity of the shear rate and polymer stress across the interface, standard rheological models must be generalized and supplemented with non-local terms (Lu et al. 1999). This leads naturally to finite width interfaces. Non-local terms can be justified rigorously using the Fokker-Planck equation for simplified microscopic models like the dumbbell model (El-Kareh and Leal 1989). In this case, and presumably rather generally, the origin of non-local terms is the Brownian motion of the polymer chains toand-fro across the interface. Although this movement does not produce net matter flux it produces non-zero net stress flux because the chains on the low shear rate side of the interface carry more shear stress than the chains on the high shear rate side of the interface. Another mechanism for stress transfer across the interface could be the propagation of the interaction (examples include both short range van der Waals or hard core, and long range Coulomb or hydrodynamic interactions) between chains. For liquid crystals this leads to Franck elasticity, including square gradient terms in the free energy and diffusion terms in the dynamical equations. In certain cases this mechanism may be more efficient than centre of mass diffusion. The simplest non-local extension of the local constitutive equations (2) is a system of partial differential equations of the reaction-diffusion type:

$$\partial_t \mathbf{\sigma}^p = D \nabla^2 \mathbf{\sigma}^p + \mathbf{C} [\mathbf{\sigma}^p, (\sigma - \Sigma)/\mu] , \qquad (4)$$

D being deduced from the chain diffusion coefficient and/or the Frank elasticity constant.

Reaction terms (Eq. (2)) limit the Brownian excursion of the stress, because chains lose memory of their stress in a characteristic time τ . Thus, the interface width scales with $\sqrt{D\tau}$, which is typically the size of one chain.

Although for a given σ uniform high shear and low shear rate bands can both be metastable, in the interface region chains in the two states mix and generally relax differently. A stationary interface corresponds to a balance between stress diffusion and relaxation inside the interface. If the relaxation is more rapid for chains in one of the two states, then the interface moves to reestablish the balance. As shown by Eq. (2) stress relaxation is parametrized by the value σ of the total shear stress at the position of the interface. The stationarity condition for the interface provides a selection mechanism for the stress. For values of stress higher or lower than the selected one, the interface moves towards one band or towards the other. This is the dominance principle (see also Kramer 1981; Pomeau 1986; Olmsted and Goldbart 1992; Bode 1997) distinguishing, in the absence of a variational principle, between stable and metastable bands; an interface between two bands moves towards the metastable band, increasing thus the size of the stable band.

In order to fix these ideas in a more quantitative way let us consider a toy model Eq. (4) with only one stress component¹:

$$\partial_t \Sigma = D \partial_x^2 \Sigma + C[\Sigma, (\sigma - \Sigma)/\mu] . \tag{5}$$

The equation for steady flow reads:

$$D\partial_{\mathbf{r}}^{2}\Sigma = -C[\Sigma, (\sigma - \Sigma)/\mu] , \qquad (6)$$

analogous to Newton's second law for the movement of a fictitious particle in a potential $V(\Sigma, \sigma) = \int C[\Sigma, (\sigma - \Sigma)/\mu] d\Sigma$, with the following correspondences: $D = \text{mass}, \Sigma = \text{position}, x = \text{time}, -C[\Sigma, (\sigma - \Sigma)/\mu] = \text{force}$. The same analogy was used in connection with stress selection by Spenley et al. (1996) and more generally by Pomeau (1986).

Equation (6) has a first integral, corresponding to the total mechanical energy of the fictitious particle:

$$\frac{D}{2}(\partial_x \Sigma)^2 + V(\Sigma, \sigma) = \text{const} . \tag{7}$$

Stationary interfaces correspond to soliton solutions of Eq. (6), satisfying the boundary conditions $\Sigma(-\infty, \sigma) = \Sigma^h(\sigma)$, $\Sigma(\infty, \sigma) = \Sigma^\ell(\sigma)$, $\partial_x \Sigma(-\infty, \sigma) = \partial_x \Sigma(\infty, \sigma) = 0$. In order to comply with the boundary conditions and with Eq. (7), one has:

$$V[\Sigma^{h}(\sigma_{\rm sel}), \sigma_{\rm sel}] = V[\Sigma^{\ell}(\sigma_{\rm sel}), \sigma_{\rm sel}]$$
(8)

or, equivalently:

$$\int_{\Sigma^{h}(\sigma_{\text{sel}})}^{\Sigma^{\ell}(\sigma_{\text{sel}})} C[\Sigma, (\sigma_{\text{sel}} - \Sigma)/\mu] d\Sigma = 0 , \qquad (9)$$

which is the condition selecting the stress value $\sigma_{\rm sel}$.

If Eq. (8) is not fulfilled, then the interface is moving. Using a comoving frame $\tilde{x} = x - x^*(t)$, where $x^*(t)$ is the position of the interface we obtain:

$$D\partial_{\tilde{x}}^{2}\Sigma = -C[\Sigma, (\sigma - \Sigma)/\mu] - c\partial_{\tilde{x}}\Sigma ,$$
where $c = \frac{\mathrm{d}x^{*}(t)}{\mathrm{d}t}$. (10)

This equation is analogous to the movement of a particle with friction. The soliton boundary conditions are fulfilled if in the analogous mechanical system all the potential energy difference is dissipated by friction: $V[\Sigma^h(\sigma), \sigma] - V[\Sigma^\ell(\sigma), \sigma] = c \int_{\Sigma^\ell(\sigma)}^{\Sigma^h(\sigma)} (\partial_{\tilde{x}} \Sigma) d\Sigma$. Using

$$\frac{\mathrm{d}C[\Sigma,(\sigma-\Sigma)/\mu]}{\mathrm{d}\sigma} = \frac{\partial C(\Sigma,\dot{\gamma})}{\partial \Sigma} - \frac{\mathrm{d}C[\Sigma,(\sigma-\Sigma)/\mu]}{\mathrm{d}\Sigma}$$

and Eqs. (1, 7, 9), we find after some algebra that to the first order in $\sigma - \sigma_{sel}$:

$$c = -\frac{\mu\sqrt{D}(\sigma - \sigma_{\text{sel}}) \int_{\dot{\gamma}^{\ell}(\sigma_{\text{sel}})}^{\dot{\gamma}^{h}(\sigma_{\text{sel}})} \frac{\partial C}{\partial \Sigma}(\Sigma, \dot{\gamma}) d\dot{\gamma}}{\int_{\Sigma^{h}(\sigma_{\text{sel}})}^{\Sigma^{\ell}(\sigma_{\text{sel}})} \sqrt{2V[\Sigma^{h}(\sigma_{\text{sel}}), \sigma_{\text{sel}}] - V[\Sigma, \sigma_{\text{sel}}]} d\Sigma}$$
(11)

where $\dot{\gamma}$ and Σ are related via Eq. (1).

Equation (11) expresses quantitatively the dominance principle; the metastable character of the high and low shear rate band is determined by the sign of the quantity $I := \int_{\dot{\gamma}^l}^{\dot{\gamma}^h(\sigma_{\rm sel})} \frac{\partial C}{\partial \Sigma}(\Sigma,\dot{\gamma})\mathrm{d}\dot{\gamma}$. The possible situations are summarized in Table 1. The case I < 0 would correspond to shear thinning systems when an increase of the stress inclines the balance in favour of the high shear rate band, while the case I > 0 would correspond to a shear thickening system when the stress increase would favour the production of the low shear rate band. At the selected value of stress the interface is stationary, both bands are stable.

As an example let us consider the toy model with one order parameter Σ (shear component of σ^P), leading to the same flow curves as the JS model. For this purpose it is sufficient to consider (see next section):

$$C(\Sigma, \dot{\gamma}) = -\Sigma(1 + \dot{\gamma}^2) + \dot{\gamma} \tag{12}$$

Flow curves are of the shear thinning type (Fig. 1a) because Eq. (3) is of third degree in Σ for a given σ . Notice that $C(\Sigma,\dot{\gamma})$ is linear in Σ separately. A similar toy model, also linear in Σ , is discussed by Spenley et al. (1996). Shear thickening systems would imply several roots of Eq. (3) for σ at fixed $\dot{\gamma}$, and a necessary condition is the strong non-linearity of $C(\Sigma,\dot{\gamma})$ in Σ separately, in order to inflect the flow curve in the direction of the stress. Constitutive models used for polymer melts and solutions (Larson 1988) are usually either linear or of degree two in Σ . A covariant constitutive model for shear thickening could in principle be obtained if one considered appropriate combinations of higher degree invariants of the stress tensor σ^P .

The dominance principle is coherent with the shear thinning character of the flow curves, because

$$I = -\int_{\dot{\gamma}^\ell(\sigma_{
m sel})}^{\dot{\gamma}^k(\sigma_{
m sel})} (1+\dot{\gamma}^2) \mathrm{d}\dot{\gamma} < 0$$
 .

Thus high shear rate bands are stable at stresses higher than σ_{sel} and metastable at stresses lower than σ_{sel} .

Table 1 Dominance principle and state selection

$\sigma - \sigma_{\rm sel}$	I	c	$\dot{\gamma}^h$	$\dot{\gamma}^\ell$
+	_	+	Stable Metastable	Metastable Stable
+	_	_	Metastable	Stable
_	+	+	Stable	Metastable
0	Any	0	Stable	Stable

¹ To the best of our knowledge, covariant local constitutive equations or microscopic models lead to reaction-diffusion equations with at least two order parameters (shear stress and normal stress difference).

The selected shear stress is given by Eq. (9) and does not depend on D. The reason is that in Eq. (6), describing stationarity, the diffusion coefficient can be rescaled. D can be made arbitrarily small and the singular perturbation represented by diffusion terms still ensures the stress selection. Nevertheless, changing D modifies the life time of the transients, which can be very long for small D. A rather natural question is usually asked (Greco and Ball 1997); does the selected stress plateau correspond to an equal-area Maxwell construction well known from the van der Waals isotherms? However, this question implicitly assumes that the stress and the shear rate are conjugate variables, which is not a well-defined property in a non-equilibrium system. A Maxwell plateau would be defined by the equation $\int_{\dot{\gamma}^{\ell}}^{\gamma^{n}} [\sigma(\dot{\gamma}) - \sigma_{\rm sel}] d\dot{\gamma} = 0$, where the dependence $\sigma(\dot{\gamma}) =$ $\mu\dot{\gamma} + \dot{\gamma}/(1+\dot{\gamma}^2)$ follows from the flow curve equation $C(\sigma - \mu \dot{\gamma}, \dot{\gamma}) = 0$. Maxwell's condition is generally different from Eq. (9). For the toy model considered here straightforward algebra shows that the selected stress plateau is equivalent to $\int_{\dot{\gamma}^{t}}^{\dot{\gamma}^{h}} [\sigma(\dot{\gamma}) - \sigma_{sel}] (1 + \dot{\gamma}^{2}) d\dot{\gamma} = 0$, that is different from the Maxwell condition. Although the Maxwell condition would be valid after a change of variables $\dot{\gamma} \rightarrow \dot{\gamma} + \dot{\gamma}^3/3$, this is due to the one-dimensional (1D) character of the toy model and there is no reason to believe that the new variable is conjugate to the stress with respect to some general "non-equilibrium potential" (Porte et al. 1997). We should stress the fact that the dominance principle is sufficient to take into account the interface processes governing equilibrium, and there is no need for a variational principle leading to a Maxwell construction. As discussed by Lu et al. (1999), stress selection has only weak universality; changes of interfacial properties by impurities or other effects may change the value of the selected stress.

JS model with stress diffusion term

We add a diffusion term to the local JS model (Larson 1988) in order to cope with finite width interfaces. The stress diffusion term in this extension (JS-d) of the JS model can be justified microscopically using the Fokker-Planck equation for a non-affinely deformed system of dumbbells (El-Kareh and Leal 1989).

The two order parameter dynamics arising from the JS-d model in planar shear with vorticity along the z axis and flow lines along the x axis reads (Lu et al. 1999; Olmsted et al. 1999):

$$\partial_t \begin{pmatrix} S \\ W \end{pmatrix} = D\partial_r^2 \begin{pmatrix} S \\ W \end{pmatrix} + C(S, W, \hat{\gamma}) , \qquad (13)$$

where

$$C(S, W, \hat{\gamma}) = \begin{pmatrix} -S + \hat{\gamma}(1 - W) \\ -W + \hat{\gamma}S \end{pmatrix}$$
 (14)

The creeping flow momentum balance in planar shear, reads:

$$\epsilon \dot{\hat{\gamma}} + S = \hat{\sigma} \tag{15}$$

The rescaled variables are:

$$\hat{\dot{\gamma}} = \dot{\gamma}\tau\sqrt{1 - a^2}$$

$$\hat{\sigma} = \sigma\sqrt{1 - a^2}/G_o$$

$$S = \sigma_{x,y}^p \sqrt{1 - a^2}/G_o$$

$$W = \left[\frac{1 - a}{2}\sigma_{y,y}^p - \frac{1 + a}{2}\sigma_{x,x}^p\right]/G_o$$
(16)

where τ is the linear viscoelastic time, G_o is the high frequency modulus, $\epsilon = \mu/(G_o\tau)$ is the ratio of solvent/polymer viscosities, and a the slip parameter, that equals 1 for no slip and 0 for total slip.

Flow curves and asymptotic matching

Flow curves of the JS-d model in planar shear geometry coincide with the flow curves of the 1D toy model. In order to obtain the flow curves in other geometries we should as a first step change the momentum balance, considering generally inhomogeneous total stresses:

$$\epsilon \hat{\gamma} + S = \hat{\sigma}(r) \quad ; \tag{17}$$

 $\hat{\sigma}(r) = fr$ in Poiseuille flow where f is the pressure gradient or $\hat{\sigma}(r) = \Gamma/r^2$ in Couette flow, where Γ is the torque per unit length of the cylinders. Thus, steady flow corresponds to:

$$D\hat{\sigma}_r^2 \begin{pmatrix} S \\ W \end{pmatrix} + C[S, W, (\hat{\sigma}(r) - S)/\epsilon] = 0 . \tag{18}$$

The second step is to look for matched asymptotic expansions of Eq. (18). This consists of considering an outer layer and an inner layer solution (Radulescu and Olmsted 1999). The outer layer solution corresponds to regions far from the interface where diffusion terms are negligible, and satisfies $C[S, W, (\hat{\sigma}(r) - S)/\epsilon] = 0$.

The inner layer solution is obtained after changing variables $\tilde{r}=(r-r^*)/\sqrt{D}$ in Eq. (18), and expanding the left-hand side in powers of \sqrt{D} (Lagerstrom 1988). At the lowest order, thin inner layer solutions (small D) coincide with the planar shear solution, satisfying thus Eq. (18) with constant total stress $\hat{\sigma}(r)=\hat{\sigma}(r^*)$, r^* being the position of the interface. Matching conditions represent the soliton boundary conditions for the inner layer solution, and in the limit $D\to\infty$, $\tilde{r}\to\pm\infty$, they read:

$$S(-\infty) = S^{h}, W(-\infty) = W^{h}$$

$$S(+\infty) = S^{\ell}, W(+\infty) = W^{\ell}$$

$$\partial_{r}S(\pm\infty) = 0, \partial_{r}W(\pm\infty) = 0. (19)$$

The existence of a solution satisfying these boundary conditions is equivalent to the existence of a "nontransverse" heteroclinic orbit connecting two hyperbolic fixed points of a 4D dynamical system and selects (the number of conditions exceeds the number of constants specifying an arbitrary orbit) the value of the parameter $\hat{\sigma}(r^*) = \sigma_{\text{sel}}$, i.e. the stress at the position of the interface (Lu et al. 1999). The existence and uniqueness of the selected stress can not be proven in the same way as for the 1D toy model, because the 2D JS-d dynamics is nonpotential. The mathematical techniques relevant to this situation are shooting arguments (Dunbar 1984) or topological methods (Smoller 1983; Lu et al. 1999), but will not be discussed here. Instead we determine σ_{sel} numerically, as a function of the model parameter ϵ . As for the 1D model D can be rescaled in Eq. (18), so σ_{sel} is independent of D. Because the stress selection is a property of the inner layer solution σ_{sel} does not depend on the flow geometry (as long as the flow lines stay parallel). The comparison between selected stresses in the 1D and 2D models, as well as by Maxwell construction, is shown in Fig. 2b.

Knowledge of σ_{sel} allows one to find the flow curves in the limit of a very thin interface. As an example we discuss flow curves in Couette geometry. In this geometry banded flow should have only two bands as there is only one interface in the unique position obeying $\hat{\sigma}(r^*) = \sigma_{sel}$. The normal sequence of bands is with the high shear rate band at the inner cylinder (where the total stress is maximum) but for a low curvature of the cylinders it is conceivable to have two coexistence plateaus, the second corresponding to an inverted sequence of bands. Using the relation between total stress and position $dr/r = -d\sigma/(2\sigma)$, the equation of the

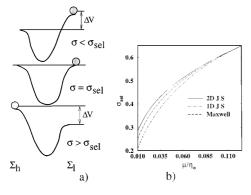


Fig. 2a, b Mechanical analogy for the dominance principle. At $\sigma=\sigma_{\rm sel}$ the interface is stationary. At $\sigma\neq\sigma_{\rm sel}$ the interface is moving with a velocity given by the energy balance for the fictitious particle: ΔV equals exactly the energy loss by friction. In all cases the particle starts and arrives at potential maxima with zero velocity and in an infinite time. This corresponds to the soliton boundary conditions. b Selected stress as a function of the ratio $\epsilon=\mu/\eta_o$, where $\mu,\eta_o=G_o\tau$ are the solvent and polymer viscosity, respectively. (JS Johnson-Segalman model)

coexistence plateau with the normal sequence of bands reads:

$$\langle \dot{\gamma} \rangle = \frac{R_1}{R_2 - R_1} \left[\int_{\Gamma/R_2^2}^{\sigma_{\text{scl}}} \dot{\gamma}^{\ell}(\sigma) \frac{d\sigma}{2\sigma} + \int_{\sigma_{\text{scl}}}^{\Gamma/R_1^2} \dot{\gamma}^{h}(\sigma) \frac{d\sigma}{2\sigma} \right] , \qquad (20)$$

where R_2 , R_1 are the outer and inner radii of the Couette cell, and $\langle \dot{\gamma} \rangle$ is the average shear rate.

The coexistence plateau corresponding to the inverted sequence of bands has the equation:

$$\langle \dot{\gamma} \rangle = \frac{R_1}{R_2 - R_1} \left[\int_{\Gamma/R_2^2}^{\sigma_{\text{sel}}} \dot{\gamma}^h(\sigma) \frac{d\sigma}{2\sigma} + \int_{\sigma_{\text{sel}}}^{\Gamma/R_1^2} \dot{\gamma}^\ell(\sigma) \frac{d\sigma}{2\sigma} \right] . \tag{21}$$

The flow curves (including homogeneous branches) for different values of ϵ are represented in Fig. 3. The coexistence plateau becomes higher and its width decreases with ϵ , i.e. when the polymer viscosity decreases. Eqs. (20), (21) also contain implicitly the relation between the average shear rate and the position r^* of the interface. When $\langle \dot{\gamma} \rangle$ increases from one end to the other end of the plateau, r^* scans the gap from the inner $(r^* = R_1)$ to the outer $(r^* = R_2)$ cylinder for the normal band sequence and in the opposite direction for the inverted sequence. When the radius of curvature is big with respect to the gap $[(R_2 - R_1)/R_1 \ll 1]$ the dependence between r^* and $\langle \dot{\gamma} \rangle$ is approximately linear. These properties are in qualitative agreement with experiments on wormlike micelles (Decruppe et al. 1997). Birefringence techniques (Decruppe et al. 1997) always show the normal sequence of bands, although a systematic search for the inverted sequence would

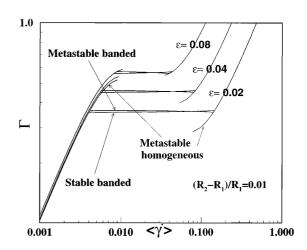


Fig. 3 Matched asymptotic flow curves in the limit $D \to 0$ for different values of the viscosity ratio ϵ , in log-log plot. Increasing ϵ corresponds to decreasing polymer viscosity η_o . The metastable plateau corresponds to a high shear rate band at the outer cylinder

be interesting. In Couette geometry the coexistence plateaus have a slight inclination, which seems also to be noticeable in experimental flow curves (Decruppe et al. 1997). Concentration effects may further increase the slope of the plateau (Schmitt et al. 1995; Olmsted and Lu 1997) and may be also responsible for multiple interface solutions. In Fig. 2b $\sigma_{\rm sel}$ increases with ϵ and thus decreases with the concentration (we suppose that the polymer viscosity, which by definition scales as $1/\epsilon$, increases with the concentration). A depletion layer near the inner wall of the Couette cell may thus create a second interface equilibrium position closer to the inner wall (at a higher stress), thus explaining the three-band structure low-high-low observed in NMR microscopy (Mair and Callaghan 1997).

Dominance principle

In order to state the dominance principle we must find the dependence of a moving interface velocity on the total stress at the position of the interface. We have numerically solved the equation:

$$D\partial_r^2 \binom{S}{W} - c\partial_r \binom{S}{W} + C(S, W, [\hat{\sigma}(r^*) - S]/\epsilon) = 0 . \tag{22}$$

Like the stress selection in the case of the stationary interface, the existence of a moving interface solution that satisfies the boundary conditions Eqs. (19) imposes a relation between the velocity c and the stress at the position of the interface $\hat{\sigma}(r^*)$. This relation is repre-

Fig. 4 a Dependence of the kink velocity on the stress. A kink-antikink germ will grow or vanish depending on the value of the stress and on the band sequence. In Couette flow, **b** the homogeneous low shear rate band is metastable at $\sigma > \sigma_{\rm sel}$, **c** banded profiles with the high shear rate band at the inner cylinder are stable, **d** banded profiles with the high shear rate band at the outer cylinder are metastable. The position r is linearly rescaled such that r = 0.1 correspond to the inner and outer cylinders, respectively

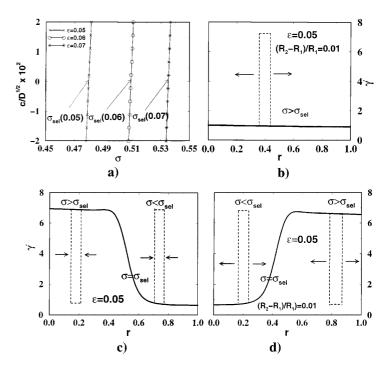
sented in Fig. 4a. We notice that c > 0 for $\hat{\sigma}(r^*) > \sigma_{\text{sel}}$ is consistent with shear thinning behaviour; the high shear rate band is stable and the low shear rate band is metastable at stresses higher than σ_{sel} .

The dominance principle can also be used to compare the stability of different branches in the flow curve. Thus the segment corresponding to homogeneous low shear rate flow above the normal band sequence coexistence plateau is metastable. Changing $r \to -r$, $c \to -c$, does not affect Eq. (22), so an antikink interface (high shear rate band at $r = \infty$) has, for the same stress, a velocity equal in modulus and of opposite sign to the already discussed kink solution (high shear rate band at $r=-\infty$). A kink-antikink nucleus of high shear rate surrounded by low shear rate bands will grow if $\hat{\sigma}(r^*) < \sigma_{\rm sel}$ and will shrink otherwise. An antikink-kink nucleus of low shear rate surrounded by high shear rate bands has the opposite behaviour. This proves the metastability of the branch of low shear rate flow above the coexistence plateau (Fig. 4b) and of the inverted band sequence coexistence plateau (Fig. 4d). The normal band sequence plateau is stable (Fig. 4c).

Nucleation is nevertheless prevented by the existence of a critical nucleus (Kramer 1981), although the nucleation rate that determines the life of the above metastable solutions is difficult to estimate for non-potential systems like JS-d.

Non-asymptotic effects

The matched asymptotic expansion is valid only when the interface is at a distance from the wall that is much



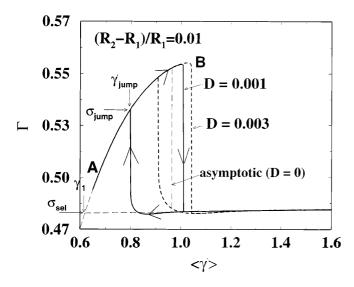


Fig. 5 Hysteresis window. Nucleation from the metastable homogeneous branch to the plateau is possible only for $\sigma > \sigma_{\text{jump}}$ in stress controlled and in shear rate controlled experiments. $|\dot{\gamma}_{\text{jump}} - \dot{\gamma}_1|$ scales with \sqrt{D}

higher than its width. This condition fails to be satisfied at the extremities of the coexistence plateaus. The typical effect, that we have studied numerically, is that the coexistence plateaus end before touching the homogeneous branches. The distance between the end of the plateau and the homogeneous branch scales with the width of the interface, i.e. like \sqrt{D} . This is seen as a trapezoidal hysteresis window in the flow curves Fig. 5. There seems to be experimental evidence of such an effect (Grand et al. 1997). In stress controlled experiments, nucleation of the high shear rate band is possible on the metastable branch AB only for stresses above a critical value σ_{jump} that is above the coexistence plateau $\sigma_{\text{jump}} > \sigma_{\text{sel}}$. Furthermore, in strain rate controlled experiments nucleation begins at shear rates $\dot{\gamma} > \dot{\gamma}_{\text{jump}}$, where $\dot{\gamma}_{\text{jump}}$ corresponds to σ_{jump} on the flow

Conclusion

We have shown why local constitutive models have to be supplemented with non-local terms in the case of shear banding, when strongly inhomogeneous interface regions are present. These non-local terms ensure the selection of the stress at the interface between bands and thus the reproducibility of the coexistence plateau. In the absence of a variational principle stress selection, the relative stability of the bands is ensured by the "dominance principle". This principle is coherent with the "weak-universality" of the selected stress, meaning that the selected stress depends on details of the stress relaxation and diffusion inside the interface; the presence of impurities may affect these processes and change the selected stress (Lu et al. 1999).

Flow curves can be obtained in various geometries in the limit of thin interfaces, by using matched asymptotic expansions. In Couette geometry, for low curvature there are two coexistence plateaus, a stable and a metastable one, corresponding to the high shear rate band at the inner and at the outer cylinder, respectively. Non-asymptotic effects, occurring when the interface between bands is near the wall at a distance of the order of its width, are responsible for the existence of trapezoidal hysteresis windows at the extremities of the coexistence plateaus, in agreement with experiments.

Using the JS constitutive model supplemented with a diffusion term could at least in principle fit flow curves for wormlike micelle systems because the right qualitative dependence of the plateau on the viscosity is predicted. Nevertheless, we do not expect this model to be a perfect substitute of a microscopic model.

Non-local terms also produce long-living flow transients that will be presented elsewhere. Shear banding in shear thickening systems should be described by more complex constitutive models that are non-linear in the polymer stress.

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