

A phenomenological model for shear-thickening in wormlike micelle solutions

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Abstract. – We present a simple phenomenological model to describe shear-thickening in a wormlike micelle solution. The solution is assumed to undergo a reaction above a critical shear stress, to form a gel-like phase. There is no flow within this “gel” phase, and it is insoluble in the solution. The amount of gel in the system is determined by a competition between a stress-dependent reaction rate, which creates gel, and a constant breakage rate, which destroys gel. We recover a re-entrant region in the stress-shear rate curve, which is only accessible under controlled stress conditions. When the apparent shear rate is fixed, the corresponding stress-shear rate relation is discontinuous. Our results are in qualitative agreement with the experimental observations of Pine *et al.*

Introduction. – Solutions of wormlike micelles show novel non-linear rheology. Shear-thinning wormlike micelle solutions are known to “shear-band” [1] such that macroscopic phases with different shear rates coexist within the same system. These observations have been attributed to a multi-valued stress constitutive relation for the solution [2]. Thus, different shear rates can correspond to the same stress such that the average shear rate of the system is held constant.

Another class of wormlike micelle solutions, however, show shear-thickening behavior [3]. Pine *et al.* [4] have found that the sudden viscosity increase that occurs upon shearing these solutions is concomitant with the growth of a new phase. This phase is difficult to characterize structurally, but is not known to exist under equilibrium conditions, and appears to possess the mechanical properties of a gel. The experiments are carried out in a Couette rheometer, with either the outer or inner cylinder rotating and the other cylinder stationary. Dramatically

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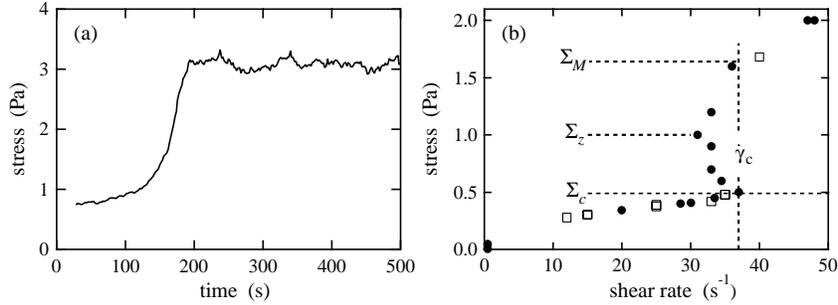


Fig. 1. – Experimental data from ref. [4]. (a) Temporal evolution of the stress after the shear rate is increased above a critical shear rate, $\dot{\gamma}_c$. The increase in stress is associated with the formation of a gel-like phase. (b) Steady-state stress *vs.* shear rate showing re-entrant behaviour under controlled stress conditions and a discontinuous stress-shear rate curve under controlled shear rate conditions. Closed circles: controlled stress; open squares: controlled (apparent) shear rate $\dot{\gamma}$.

different steady states are observed depending on whether the applied shear stress, Σ , or the apparent shear rate, $\dot{\gamma}$, is held constant. When $\dot{\gamma}$ is held fixed, a critical shear rate $\dot{\gamma}_c$ must be exceeded before the “gel” begins to form. The gel grows out from the inner cylinder, and appears to fill the gap of the cell, resulting in a substantial increase in the system stress (see fig. 1(a)). Flow visualization shows that the gel moves as a solid body (*i.e.*, there are no velocity gradients), flow in the system being confined to a thin fluid layer at the outer cylinder [4]. Under controlled stress conditions, however, the gel phase forms above a critical stress Σ_c , and coexistence between the gel and the solution is observed. The gel occupies a larger fraction of the gap with increasing stress.

Figure 1(b) shows the stress-shear rate relation for the system. Notice that the controlled stress data are continuous, exhibiting a re-entrant region for $\Sigma_c < \Sigma \leq \Sigma_z$, where $\dot{\gamma}$ is a decreasing function of Σ . By contrast, the controlled shear rate data show a jump in the stress at $\dot{\gamma}_c$, and then Σ increases monotonically with $\dot{\gamma}$. The two curves superimpose at $\{\Sigma_M, \dot{\gamma}_c\}$, beyond which the stress appears to increase linearly with apparent shear rate. (At an even higher stress, gel fracture accompanied by elastic instabilities and shear-thinning behaviour are observed: we shall not discuss this regime here.)

In this paper, we present a simple phenomenological model which qualitatively explains the experimental observations of Pine *et al.* We do not attempt to give a microscopic description of the dynamical mechanism by which the shear-induced phase forms, rather we focus on the physics underlying the non-monotonic rheological behavior and the differences between the controlled stress and controlled shear rate experiments.

Recently, Ajdari [5] presented a model capable of exhibiting shear-thickening. He considered a solution of particles which adsorbed onto a wall, forming a solid aggregate. At low stress, the particles were completely aggregated. When a critical stress at the aggregate-solution interface was exceeded, particles began to peel off the aggregate. At high enough stresses, the aggregate was completely peeled away. Ajdari constructed an equation of motion for the aggregate height, using a concentration-dependent adsorption rate, and a stress-dependent peeling rate. Assuming a concentration-dependent solution viscosity, he found stable steady states under controlled stress conditions, where the aggregate and solution could coexist. Such steady states could go unstable for fixed apparent shear rate.

We similarly write an equation of motion for the gel height in a wormlike micelle solution under shear. In our case, a stress-dependent reaction creates gel, in competition with a constant

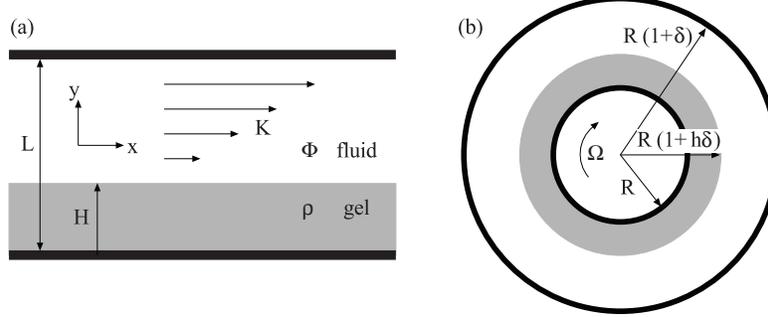


Fig. 2. – Schematics showing an insoluble gel phase (gray) in co-existence with a fluid wormlike micelle phase (white). The gel height is determined by a stress-dependent reaction in the fluid phase, which competes against gel breakage. (a) Planar geometry. (b) Couette geometry.

rate of gel breakage. Consequently, at low stress the system is completely fluid and the gel appears only when the stress exceeds some critical stress. Using a constant fluid viscosity, we find both stable and unstable coexistence states at fixed shear rate.

Flat geometry. – For simplicity, let us first consider a wormlike micelle solution in a planar shear flow. At equilibrium, a container of height L is filled with a solution of surfactant volume fraction Φ_0 . The solution is taken to be Newtonian so that

$$\Sigma(y) = \eta K(y), \quad (1)$$

where Σ is the shear stress, η is a constant viscosity, K is the shear rate in the solution and $0 \leq y \leq L$. We assume that once the local shear stress in the solution exceeds Σ_c , wormlike micelles react to form an insoluble gel of constant surfactant volume fraction, ϱ , where $\varrho > \Phi_0$. Denoting the height of the gel by H (see fig. 2), we write an equation for the dimensionless gel height $h = H/L$, which is valid for $\Sigma \geq \Sigma_c$:

$$\frac{dh}{dt} = \frac{1}{a} [\Sigma(h)\Phi(h) - b], \quad (2)$$

where $\Phi(h)$ is the solution volume fraction of surfactant at the gel-solution interface, and a is a constant which makes the equation dimensionally correct. The physical meaning of eq. (2) is this: a stress-dependent reaction produces gel, increasing h , while a constant backward rate, b , destroys gel (due to peeling of the gel surface by flow or some other mechanism—we do not specify). Let us define the scaled variables $\phi = \Phi/\Phi_0$, $\rho = \varrho/\Phi_0$, $\sigma = \Sigma/\Sigma_c$, and $\tilde{t} = at/\Phi_0\Sigma_c$. Then $dh/d\tilde{t} = \sigma\phi - 1$ and at steady state the solution surfactant volume fraction is

$$\phi_s = \frac{1}{\sigma}, \quad (3)$$

where we have set $b = \Phi_0\Sigma_c$ to guarantee continuity in Φ . An alternative form of the dimensionless equation, $dh/d\tilde{t} = \phi - 1/\sigma$, results in the same steady-state solution, but has a different physical interpretation which is similar to that proposed previously by Ajdari [5].

We assume that the solution is uniform in surfactant concentration, *i.e.* that diffusion is fast on the time scale of the growth of the gel. Demanding that the total stress is divergence free ensures that the shear stress is uniform through the system. For an infinitesimally sharp gel-solution interface, mass conservation of surfactant gives

$$(1 - h)\phi + h\rho = 1. \quad (4)$$

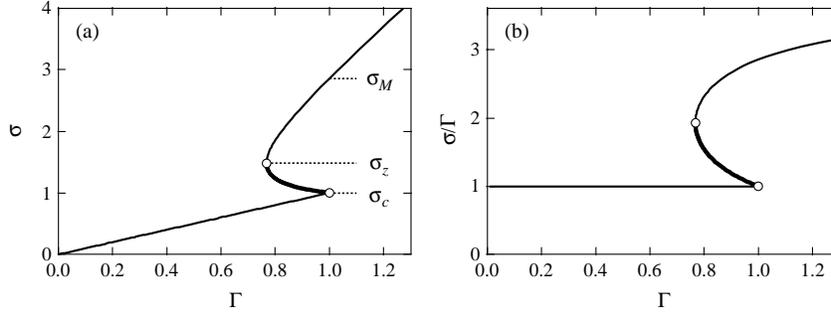


Fig. 3. – (a) Stress σ and (b) apparent viscosity σ/Γ vs. apparent shear rate Γ for $\rho \equiv \varrho/\phi_0 = 1.35$. We assume a constant (Newtonian) viscosity for $\Sigma < \Sigma_c$, and have used eq. (5) for $\Sigma > \Sigma_c$. Note the re-entrant behaviour for $\Sigma > \Sigma_c$. When stress is held constant, the entire curve can be explored. At fixed Γ , the lower branches of the multi-valued stress and apparent viscosity loops are unstable (*i.e.*, the bold region of the curves between the open circles at $\Gamma_z = (2/\rho)^2(\rho - 1) \simeq 0.77$ and $\Gamma_c = 1$).

We now make the assumption that there are no velocity gradients in the gel phase, which produces the relation $\dot{\gamma}/\dot{\gamma}_c = \Gamma/(1 - h)$, where Γ is a dimensionless apparent shear rate and $K_c = \dot{\gamma}_c \equiv \Sigma_c/\eta$. Notice that if we had made the gel formation reaction in eq. (2) shear-rate dependent (rather than stress-dependent), the gel would not be self-sustaining, because the shear rate inside the gel would vanish as soon as the gel was created.

The apparent shear rate may then be written as

$$\Gamma(\sigma) = \sigma \left[\frac{\rho - 1}{\rho - \phi_s(\sigma)} \right], \quad (5)$$

which can immediately be seen to be non-monotonic if $\rho - \phi_s(\sigma)$ increases faster than σ . This is indeed the case for the choice of reaction rates which leads to eq. (3), as is shown in fig. 3(a). The apparent viscosity for the system is shown in fig. 3(b). While we maintain a constant viscosity for convenience, allowing η to be concentration dependent produces a softer re-entrant region, not unlike that observed experimentally (fig. 1).

We can characterize the shape of the multi-valued stress region by two points: $\{\sigma_z = 2/\rho, \Gamma_z = (2/\rho)^2(\rho - 1)\}$, which measures the minimum apparent shear rate for the system, and $\{\sigma_M = 1/(\rho - 1), \Gamma_M = 1\}$, where the apparent shear rate is that of the unreacted micellar solution at the critical stress. For $\rho = 2$, the re-entrant behavior is completely lost.

Fixed stress. – When a constant stress is applied to the system, the steady-state surfactant volume fraction is given by eq. (3). Let us consider small fluctuations around the steady-state height h_s , such that $h = h_s + \varepsilon$. Then eq. (2) becomes

$$\frac{d\varepsilon}{dt} = -\sigma \frac{(\rho - 1)}{(1 - h_s)^2} \varepsilon. \quad (6)$$

Since $\rho > 1$, the entire stress-shear rate curve given by eq. (5) is stable.

Fixed shear rate. – There are two steady-state solutions to eq. (2), $\phi_{s,\pm}(\Gamma) = \rho[1 \pm \theta]/2$, which correspond to the following stresses:

$$\sigma_{s,\mp}(\Gamma) = \frac{\rho\Gamma}{2(\rho - 1)} [1 \mp \theta]; \quad \theta = \left[1 - \frac{4(\rho - 1)}{\rho^2\Gamma} \right]^{1/2}. \quad (7)$$

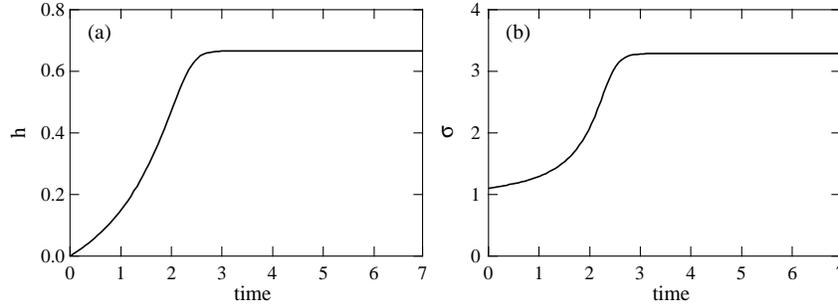


Fig. 4. – Growth of (a) the gel height and (b) the stress as a function of dimensionless time for the system in fig. 3 and fixed $\Gamma = 1.1$.

The corresponding linear stability analysis for h is

$$\frac{d\varepsilon}{dt} = -\Gamma \frac{(\rho - 2\phi_s)}{(1 - h_s)^2} \varepsilon. \quad (8)$$

Thus the system is stable for $\phi_s < \rho/2$ and $\sigma \geq \sigma_z$, *i.e.* $\phi_{s,-}(\Gamma)$, $\sigma_{s,+}(\Gamma)$ (see fig. 3). A line of unstable steady states $\sigma_{s,-}(\Gamma)$ lies between the open circles at σ_z and $\sigma_c (\equiv 1)$ in fig. 3. For $\Gamma < \Gamma_z$, no real solutions to eq. (2) for ϕ_s exist: the system is pure fluid.

Increasing Γ from the pure fluid state, the inhomogeneous states for $\sigma \geq \sigma_z$ are inaccessible, since Γ must exceed unity for the reaction to begin. At the critical shear rate $\Gamma = 1$, the unstable branch corresponds to $\{\phi_{s,+} = 1, \sigma_{s,-} = 1, h_s = 0\}$, while the stable branch corresponds to $\{\phi_{s,-} = \rho - 1, \sigma_{s,-} = \sigma_M, h_s = 2 - \rho\}$. Thus, there is a jump in the system stress, which is greater when ρ is marginally greater than Φ_0 . In this case, $\rho = 1 + \epsilon$, where $\epsilon \ll 1$ and $h_s(\Gamma_c) \approx 1 - \epsilon$, so that the gel *appears* to completely fill the system. This results in an approximately constant apparent viscosity (see eq. (5)) and is consistent with the experimental results reported by Pine *et al.* [4]. This is a conceptually different picture from that of a pure gel phase with a solvent slip layer at the wall, as suggested by Pine *et al.* [4]. In the latter case, the thickness of the solvent layer should be independent of shear rate, and gap width. For $\rho \approx 1$, however, the two descriptions may not be experimentally distinguishable.

If we prepare the system in the gelled state instead, and decrease Γ below unity, the steady states $\sigma \geq \sigma_z$ should in principle be accessible. This is not seen in experiment; decreasing Γ causes the system to revert back to the micelle solution [4].

Dynamical evolution of the gel height. – We can solve the ordinary differential equation (2), using the initial condition $h(\tilde{t} = 0) = 0$, and by writing explicitly $\phi(h(\tilde{t})) = (1 - \rho h(\tilde{t})) / (1 - h(\tilde{t}))$. Figure 4(a) shows how the gel grows to its steady-state height for fixed Γ . The corresponding evolution of the system stress is shown in fig. 4(b). Physically, the initial formation of gel increases the stress at the interface, which in turn causes further growth of gel, until the system reaches a stable steady state. The evolution of the system stress shown in fig. 4(b) is qualitatively very similar to the experimental measurements shown in fig. 1.

Couette geometry. – We briefly discuss how to extend the calculation above to the Couette case. For the stress tensor to be divergence free in both the gel and solution, the shear stress must vary as $\Sigma = C/r^2$, where C is a constant. Gel begins to form as soon as the stress at the *inner* cylinder, Σ_i , exceeds Σ_c . In the flat case, there is no mechanism to select where the

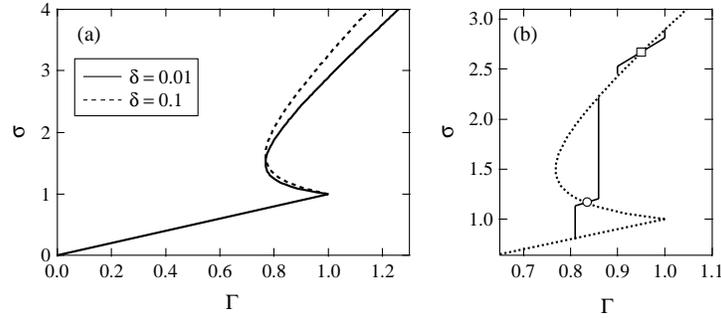


Fig. 5. – (a) Stress *vs.* apparent shear rate for the system in fig. 3, in a Couette geometry, showing the effect of varying the gap width, δ . (b) Stability at fixed Γ : A fluctuation in Γ , in the re-entrant region (*i.e.* the open circle), drives the system towards a different branch of the curve. A disturbance elsewhere (*i.e.* the open square) drives the system to the same branch.

gel is situated. The Couette geometry breaks this symmetry —the gel phase grows out from the inner cylinder, because the stress is highest there. The analog of eq. (2) is then

$$\delta \frac{dh}{dt} = \frac{1}{a} \left[\frac{C}{R^2(1+h\delta)^2} \Phi(h) - b \right], \quad (9)$$

where the radius of the inner rotating cylinder is R , and the outer stationary cylinder has a radius $R(1+\delta)$. The scaled gel height is given by $h = (H-R)/\delta R$ (see fig. 2(b)). Once more, ϕ is assumed to be homogeneous through the solution. The mass conservation constraint is

$$[(1+h\delta)^2 - 1]\rho + [(1+\delta)^2 - (1+h\delta)^2]\phi = [(1+\delta)^2 - 1]. \quad (10)$$

For fixed Σ_i , $C = \Sigma_i R^2 = (2\Omega\eta R^2(1+\delta)^2(1+h\delta)^2)/([(1+\delta)^2 - (1+h\delta)^2])$, where Ω is the angular velocity of the inner cylinder. The apparent shear rate is then

$$\Gamma = \sigma_i \frac{(1+\delta)^2 - (1+h\delta)^2}{(1+h\delta)^2[(1+\delta)^2 - 1]}. \quad (11)$$

A quadratic equation for $(1+\delta h)^2$ results from eqs. (9) and (10), which may be solved for and substituted into eq. (11). The resulting σ - Γ curve obviously depends on the gap width (see fig. 5), so that δ becomes an additional parameter in tuning the shape of the curve. For the experimentally relevant case of thin gaps, $\delta \rightarrow 0$, we recover all the results of the flat geometry.

Conclusions. – We have shown that a simple phenomenological theory can qualitatively explain the experimental observations of Pine *et al.* The essential features of our model are that a stress-induced reaction produces an insoluble gel phase, within which there is no flow. The particular form of the reaction rate can lead to re-entrant behavior in the stress-shear rate curve. Upon scaling the stress and shear rate by Σ_c and Γ_c , respectively (which are increasing functions of Φ_0 in experiment [4]), the theory contains only one adjustable parameter, ϱ/Φ_0 .

We stress that the experimental phenomenology is generic to virtually *any* macroscopic model which produces the re-entrant behavior in fig. 3. In fact, the stability criteria can be understood simply from the shape of the σ *vs.* Γ curve. Consider a steady state on the σ - Γ curve for fixed Γ , corresponding to a gel height of h^* . In the re-entrant region, fluctuations which increase Γ , increase the fluid shear rate, K , and in turn the system stress (see eq. (1)). The system thus moves off the steady-state curve, along a line with slope $\eta/(1-h^*)$. To

maintain Γ constant, the height grows, further increasing the stress until finally a steady state on the upper branch of the curve is reached (see fig. 5). Analogously, a fluctuation which decreases Γ drives the system to the constant viscosity branch. The upper branch, however, is stable, because its slope is greater than $\eta/(1-h^*)$. Here, changes in the height (in response to fluctuations in Γ) return the system to a steady state on the same branch, infinitesimally close to the original state. For fixed stress, the single-valued Γ vs. σ curve is clearly stable.

Our model is deliberately crude, since our aim has been to identify the physics necessary to reproduce the experimental phenomena. A more realistic macroscopic model would allow for a variable surfactant concentration in the gel, with its own equation of motion, coupled to one for the solution surfactant concentration. The elastic stress of the gel, the shear-thinning fluid viscosity, a stress- or shear-rate-dependent breakage rate, as well as fluctuations in the stress and concentration also need to be accounted for. The assumption of no flow in an insoluble gel phase could be relaxed to include a high-viscosity gel phase, coexisting with the fluid phase, with an interface of finite thickness. A microscopic description of the mechanisms underlying gel formation, and the shear-induced phase transition between solution and gel, still does not exist.

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