Rheological behavior of a solution of particles aggregating on the containing walls

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The possibility of macroscopic shear-thickening behavior is shown for a solution containing particles that tend to stick and grow aggregates on the walls containing the solution. A simple one-dimensional model is used with two basic ingredients: shear tends to peel off the aggregate and the viscosity of the solution increases with particle concentration. In addition to shear thickening, instabilities at fixed driving velocity can also occur. In cylindrical geometries it is even possible to reach situations displaying instabilities both at fixed stress (torque) and at fixed velocity. [S1063-651X(98)13311-1]

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I. INTRODUCTION

Rheology of complex systems is a growing field of interest and much fascinating behavior has been reported ranging from shear-thinning or shear-thickening behavior to flow induced phase transitions and instabilities. This behavior can result from some underlying thermodynamic phase transitions or be purely dynamical in nature [1–5]. The difficulty in modeling even simple systems is to incorporate concomitantly the effect of the developing structures on the flow pattern, and the resulting deformation of the structures themselves [6–9].

A very simple model system is here introduced to show that complex ''effective'' rheological behavior can result from the inhomogeneity of a system due to its interaction with the walls of the measuring device. Namely, we consider a solution containing particles (suspension, emulsion, etc.) and suppose that these tend to adsorb on one of the walls in such a way that this adsorption triggers the macroscopic aggregation of the particles (heterogeneous nucleation). An applied flow can, however, peel this aggregate if it is strong enough. The peeled particles dissolve and diffuse in the neighbor solution.

We consider this simple system first in a planar shear geometry before turning to a situation where the flow is induced by the shearing of two concentric cylinders.

II. MODEL

Consider the very simple one-dimensional (1D) model of Fig. 1. A gap of thickness L separates two parallel plates, the upper one moving at $V\mathbf{x}$ while the lower one is at rest. An aggregate of thickness $h(t)$, taken rigid, limits the actually flowing region to $h(t) < z < L$, the local particle volume fraction being $\phi(z,t)$. The volume fraction of the particles in the aggregate is denoted by a constant ρ. The flowing region is taken locally Newtonian with a viscosity $\eta(\phi)$.

The dynamics are described through simple equations.

(i) Diffusion of particles in the solution:

$$\partial_t \phi = D \partial_z^2 \phi, \tag{1}$$

with boundary conditions

$$\partial_z \phi(z=L) = 0, \tag{2}$$

$$D\partial_z \phi(z=h) + [\rho - \phi(h)]d_t h = 0. \tag{3}$$

These together with Eq. (1) grant the conservation of the total number of particles $N = \phi_0 L = \rho h + \int_h^L \phi dz$, with ϕ_0 the average concentration of particles between the walls.

(ii) Mechanical equilibrium of the flowing fluid:

$$\partial_z \sigma(z) = 0, \tag{4}$$

where σ is the local shear stress given by

$$\sigma = \eta(\phi)\partial_z v, \tag{5}$$

with η the local viscosity of the solution and $v(z)$ the flow velocity. Boundary conditions for the flow are

$$v(L) = V, \quad v(h) = 0. \tag{6}$$

(iii) Eventually we describe the interface motion by a phenomenological expression:

$$d_t h = f(\phi(h)) - g(\sigma). \tag{7}$$

The first term on the right hand side describes the adsorption of the particles onto the aggregate while the second describes the peeling of the aggregate due to shear forces. This picture of course implies a local peeling of the aggregate rather than the induction of fractures within its bulk. Both f and g are typically monotonic increasing functions.
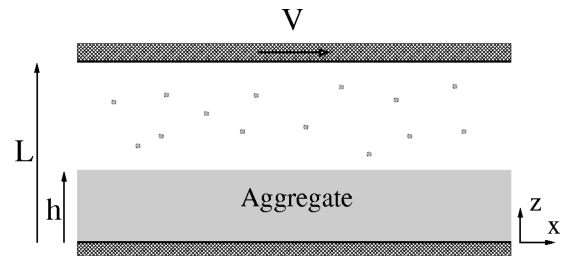

FIG. 1. The interface position is fixed by the competition between the adsorption of diffusing particles and the peeling of the aggregate due to the flow.

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At steady state $\phi(z)$ is a constant related to h by the conservation law $\phi_0 L = \rho h + \phi(L-h)$. The steady-state equation of state $\sigma_{SS}(\dot\gamma)$ is thus given by

$$\sigma = \eta(\phi)\dot\gamma \frac{L}{L-h}, \quad f(\phi)=g(\sigma). \qquad (8)$$

To investigate the resulting rheological behavior, let us first look at a simple case (model zero) in which (i) $f(\phi)=a\phi$ and (ii) $g(\sigma)=0$ for $\sigma<\sigma_c$ and $g(\sigma)=(\sigma-\sigma_c)g'$ otherwise (with g' a constant).

III. FIRST INSIGHTS FROM MODEL ZERO

Let us consider the steady-state solution in this model. At rest ($V=0$) all the particles are in the aggregate that occupies a fraction ϕ_0/ρ of the gap.

Two limiting regimes can easily be identified. (i) For low shear ($\sigma<\sigma_c$), there is no peeling, so $h=L\phi_0/\rho$ and $\phi=0$. The observed effective viscosity is

$$\eta_{\text{eff}}=\sigma L/V = \eta(0)\frac{1}{1-\phi_0/\rho}. \qquad (9)$$

(ii) For high shear $\sigma>\sigma_M=\sigma_c+a\phi_0/g'$, all the aggregate is peeled away so that $h=0$ and $\phi=\phi_0$:

$$\eta_{\text{eff}}=\eta(\phi_0). \qquad (10)$$

The threshold shear rates $\dot\gamma=V/L$ for the two regimes are $\dot\gamma_c=\sigma_c(1-\phi_0/\rho)/\eta(0)$ and $\dot\gamma_M=(\sigma_c+a\phi_0/g')/\eta(\phi_0)$.

This simple analysis shows that the system appears (a) shear thinning if $\eta(\phi_0)/\eta_0<(1-\phi_0/\rho)^{-1}$, and (b) shear thickening in the opposite case. For low ϕ_0, one expects $\eta(\phi_0)/\eta_0 \simeq 1+2.5\phi_0$ so that regime (b) can indeed occur for $\rho>0.4$. Although in case (a) $\dot\gamma_c<\dot\gamma_M$ is always verified, case (b) leads to an additional distinction as one can have $\dot\gamma_c>\dot\gamma_M$ (for g' large enough) which automatically leads to multivaluedness in the $\sigma(\dot\gamma)$ diagram (see Fig. 2). Between the limiting regimes (i) and (ii), the $\sigma(\dot\gamma)$ curve depends on the explicit form of $\eta(\phi)$.

So, the dependence of the viscosity on concentration can induce a shear-thickening behavior with indication of possible instabilities at fixed shear rate.

IV. STABILITY ANALYSIS

More generally, i.e., independently of whether or not there is a threshold σ_c for peeling, one expects shear thickening and multivaluedness if η is a sufficiently strong function of ϕ. To investigate the relation with possible instabilities, let us discuss the linear stability of the steady-state solution (8) for this simple unidimensional model. This will clearly illustrate the difference between systems at imposed stress σ and systems at imposed velocity V (or average shear rate $\dot\gamma=V/L$). The basic features are most easily obtained supposing that diffusion is very fast ($D\to\infty$) so that the homogenization of ϕ is almost instantaneous compared to interface motion. Then, at fixed stress σ, a slight perturba-
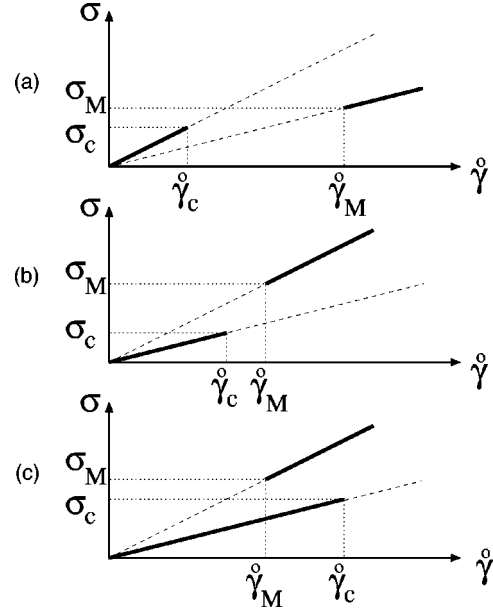

FIG. 2. The solid lines depict the small and high shear behavior as described by Eqs. (9) and (10): depending on parameters, various situations can occur (a), (b), (c). In the small shear branch the shear is too weak to peel the aggregate. In the high shear branch it is so high that the aggregate has been completely peeled off. The connecting branch linking $(\dot\gamma_c,\sigma_c)$ to $(\dot\gamma_M,\sigma_M)$ is not represented; its precise shape depends on $\eta(\phi)$ along Eq. (8).

tion δh of the interface position around a steady-state solution (8) evolves according to:

$$d_t\delta h = f'(\phi)\delta\phi = -f'(\phi)\frac{\rho-\phi}{L-h}\delta h. \qquad (11)$$

With $\rho>\phi$ the steady-state solution is thus stable [typically $f'(\phi)>0$], as a slight increase of the aggregate thickness leads to a decrease of ϕ and thus to a decrease of the adsorption of particles: peeling thus takes over inducing a stabilizing decrease of the thickness.

At fixed V things are more complex:

$$d_t\delta h = -\left[f'(\phi)-\sigma g'(\sigma)\left(\frac{d\ln\eta}{d\phi}-\frac{1}{\rho-\phi}\right)\right]\frac{\rho-\phi}{L-h}\delta h. \qquad (12)$$

The three terms on the right hand side can be easily understood, e.g., for the case of an increase of the aggregate thickness $\delta h>0$: (i) as the concentration ϕ drops adsorption decreases, (ii) as ϕ drops, so does the viscosity, resulting in a lower peeling stress, (iii) however, the fluid gap $L-h$ has also decreased resulting at fixed V in an increase of the peeling stress. The first and third term are thus stabilizing whereas the second one is destabilizing [as we clearly expect $g'(\sigma)>0$]. Thus we get an instability criterion for evolution at imposed velocity:

$$\frac{d\ln\eta}{d\phi}>\frac{1}{\rho-\phi}+\frac{f'(\phi)}{\sigma g'(\sigma)}. \qquad (13)$$

Note that from the equations (8) describing the steady-state solution $\sigma=\sigma_{SS}(V)$, one easily gets
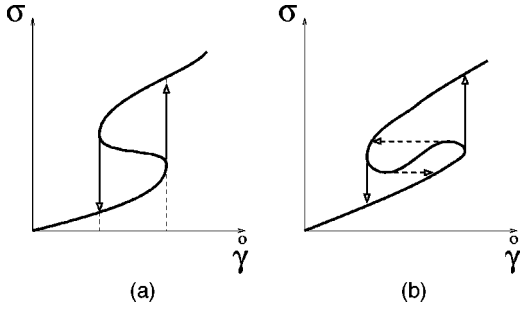
FIG. 3. Situation (a) can occur for flat and cylindrical geometries, situation (b) only in the geometry of Fig. 4(a). The full arrows indicate the stress jump of the system driven at controlled shear rate resulting in hysteretic behavior, while the dashed arrows in (b) indicate the shear rate jumps for a driving at controlled shear stress. The sections with negative slope correspond to steady-state solutions unstable under controlled shear rate, but stable under controlled shear stress. The central section of (b) which separates the two negative slope sections corresponds to solutions unstable in both situations.

$$\frac{d\sigma_{SS}}{dV} = \frac{\sigma_{SS}}{V}\left[1 - \frac{\sigma g'(\sigma)}{f'(\phi)}\left(\frac{d\ln\eta}{d\phi} - \frac{1}{\rho-\phi}\right)\right]^{-1}. \quad (14)$$

Hence the instability criterion of the steady-state solution at a fixed velocity is the usual $(d\sigma_{SS}/dV) < 0$, which results in a discrete jump in the stress upon increase of the controlled shear rate (see Fig. 3). The concordance of these two criteria results from supposing fast diffusion: the system is then completely described by two parameters among σ, V, and h (or equivalently ϕ through the conservation law). If we write formally the relaxation at fixed stress $d_t\delta h = A\,\delta h = A(\partial h/\partial V)_\sigma \delta V$, and that at fixed velocity $d_t\delta h = B\,\delta h = B(\partial h/\partial\sigma)_V \delta\sigma$, then moving along the line of steady-state solutions $\sigma_{SS}(V)$ corresponds to changing both V and σ so that $d_t\delta h = 0$, which leads to $d\sigma_{SS}/dV = -(A/B)(\partial h/\partial V)_\sigma(\partial\sigma/\partial h)_V = (A/B)(\partial\sigma/\partial V)_h$ which relates Eqs. (11) and (12) to Eq. (14), given that at fixed h (and thus ϕ), $(\partial\sigma/\partial V)_h = \sigma/V$.

Including diffusion. It is also possible to perform the linear stability analysis including the diffusion dynamics, e.g., for fixed velocity V. Writing that the perturbation δh evolves as $\delta h = \delta h_0 e^{\omega t}$, one deduces ω from

$$\frac{L-h}{\rho-\phi}(\omega-\omega_0) = f'(\phi)[1 - \Lambda\coth(\Lambda)], \quad (15)$$

with $\Lambda^2 = \omega(L-h)^2/D$ and

$$\omega_0 = -\frac{\rho-\phi}{L-h}\left[f'(\phi) - \sigma g'(\sigma)\left(\frac{d\ln\eta}{d\phi} - \frac{1}{\rho-\phi}\right)\right]. \quad (16)$$

Thus in the limit $D\to\infty$, $\Lambda\to0$, and $\omega\to\omega_0$ in agreement with Eq. (12). For a finite value of Λ, ω has the same sign as ω_0 but a smaller value. The instability criterion ($\omega>0$) is thus still Eq. (14). For small values of D, Eq. (15) leads to $\omega\simeq D$ with a prefactor dependent on the gap thickness and on the dynamics of adsorption and peeling.

Conclusion. As in the early analysis of the model zero, instabilities upon increase of the velocity are more likely to occur for a strong dependence of the viscosity on concentra-
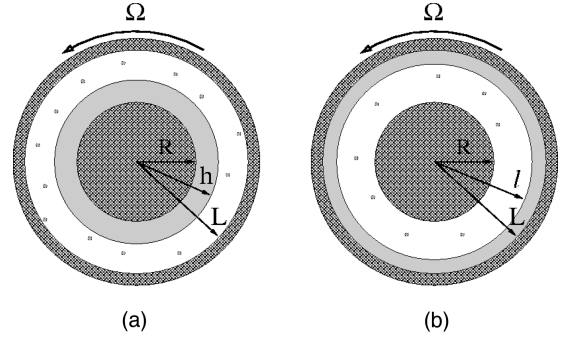

FIG. 4. The outer cylinder rotates while the inner is fixed. The aggregate is taken to form (a) on the inner cylinder (case A), (b) on the outer cylinder (case B).

tion and large increase of g with σ. Note that the occurrence of instabilities is implicitly dependent on the initial and fixed average concentration ϕ_0.

V. CYLINDRICAL GEOMETRIES

Let us turn to the case of a Couette geometry (Fig. 4). Formally we distinguish here the case where the particles tend to aggregate on the inner cylinder (case A), from the case where they tend to aggregate on the outer cylinder (case B). The control parameters are now either the torque (per unit length) on the outer cylinder $\Gamma = \sigma_{ext}2\pi L^2$ or the velocity of this outer cylinder $\Omega = V/L$. Throughout this section we will consider fast diffusion so that the concentration ϕ in the gap is homogeneous. An effective average shear rate can be defined by comparison with the case of a uniform fluid in the gap between the inner and outer cylinders (radii R and L) for which $\sigma_{ext} = \eta[2R^2/(L^2-R^2)](V/L)$. Thus we can define $\dot\gamma = [2R^2/(L^2-R^2)](V/L)$ as an effective average shear rate and $\eta_{eff} = \sigma_{ext}/\dot\gamma$ as an effective viscosity.

A. Case A: Aggregate on the inner cylinder

Let us consider that the aggregate extends from the inner cylinder (radius R) to a radius h. Then the stress in the gap ($h<r<L$) is easily obtained, $\sigma(r) = \sigma_{r\theta} = \eta[2Lh^2/(L^2-h^2)]V/r^2$, so that the outer stress σ_{ext} and the stress on the aggregate σ_{int} are simply

$$\sigma_{ext} = \eta(\phi)\frac{2h^2}{L^2-h^2}V/L, \quad \sigma_{int} = \eta(\phi)\frac{2L^2}{L^2-h^2}V/L, \quad (17)$$

where ϕ and h are related by the conservation equation $(L^2-h^2)\phi + (h^2-R^2)\rho = (L^2-R^2)\phi_0$ with ϕ_0 the average concentration. The evolution of the interface is now given by $d_t h = f(\phi) - g(\sigma_{int})$.

Model zero. The analysis of model zero leads again to two limiting branches. For $\sigma_{int}<\sigma_c$ ($\dot\gamma<\dot\gamma_m$), no peeling occurs, the thickness is constant $h=h_0$, and the apparent viscosity is $\eta_{eff} = \eta_0(h_0/R)^2 1/(1-\phi_0/\rho)$. For large shear ($\dot\gamma>\dot\gamma_M$), the aggregate is completely peeled and $\eta_{eff} = \eta(\phi_0)$. Thus the ratio $\eta_{eff}(\dot\gamma\to\infty)/\eta_{eff}(\dot\gamma\to0)$ is smaller by a factor $(R/h_0)^2$

than in a planar geometry favoring effective shear-thinning behavior. However, the ratio $\dot{\gamma}_M/\dot{\gamma}_m$ has the same value as in the planar case.

Stability. A linear stability analysis can be performed as in Sec. IV. If Ω (or V) is fixed we get as in the planar case

$$d_t \delta h = \left[f'(\phi) - \sigma_{\text{int}} g'(\sigma_{\text{int}}) \left(\frac{d \ln \eta}{d \phi} - \frac{1}{\rho - \phi} \right) \right] \delta \phi, \quad (18)$$

with clearly $\delta \phi$ of opposite sign to δh. So the stability criterion is the same as previously. At fixed torque Γ (or σ_{ext}) there is an additional term due to the geometry:

$$d_t \delta h = \left(f'(\phi) - \sigma_{\text{int}} g'(\sigma_{\text{int}}) \frac{L^2 - h^2}{h^2} \frac{1}{\rho - \phi} \right) \delta \phi. \quad (19)$$

This additional destabilizing term is due to the inhomogeneity of the stress (it increases with decreasing distance to the center): σ_{ext} is maintained at a fixed value so that if the aggregate thickens, its interface is submitted to a weaker peeling stress, favoring further growth. This term diminishes as the curvature is reduced and vanishes in the limit $(L-h)/L \to 0$ so that Eq. (11) is recovered.

Looking now at the steady-state torque/angular velocity relation $\Gamma = \Gamma_{SS}(\Omega)$, one gets either by direct calculation or from Eqs. (18) and (19)

$$\frac{d\Gamma_{SS}}{d\Omega} = \frac{\Gamma_{SS}}{\Omega} \frac{f'(\phi) - \sigma_{\text{int}} g'(\sigma_{\text{int}})[(L^2 - h^2)/h^2][1/(\rho - \phi)]}{f'(\phi) - \sigma_{\text{int}} g'(\sigma_{\text{int}})[d \ln \eta/d\phi - 1/(\rho - \phi)]}. \quad (20)$$

There is thus the formal possibility for the interface to be unstable at both fixed torque and fixed angular velocity, in a region of parameter space where $d\Gamma_{SS}/d\Omega > 0$. This would correspond to the schematic picture of Fig. 3(b).

B. Case B: Aggregate on the outer cylinder

In this geometry it is convenient to define l such that the thickness of the aggregate is $h = L - l$ (Fig. 4). The stress on the aggregate/fluid interface reads now

$$\sigma_{\text{int}} = \eta(\phi) \frac{2R^2}{l^2 - R^2} V/L \quad (21)$$

whereas the applied stress σ_{ext} is $\sigma_{\text{ext}} = (l^2/L^2)\sigma_{\text{int}}$.

Model zero— We quote just the results: for $\dot{\gamma} < \dot{\gamma}_m$ the gap thickness is l_0 and the effective viscosity is $\eta_{\text{eff}} = \eta_0(l_0/L)^2 1/(1 - \phi_0/\rho)$, lower than its planar counterpart. For $\dot{\gamma} > \dot{\gamma}_M$, then $\eta_{\text{eff}} = \eta(\phi = \phi_0)$. The ratio $\dot{\gamma}_M/\dot{\gamma}_m$ has again the same value as in the planar case.

Linear stability. At fixed applied V Eq. (18) is again recovered and thus the same stability criterion. At fixed torque Γ (or fixed σ_{ext}) the additional term due to the geometry is now stabilizing:

$$d_t \delta h = \left(f'(\phi) + \sigma_{\text{int}} g'(\sigma_{\text{int}}) \frac{l^2 - R^2}{l^2} \frac{1}{\rho - \phi} \right) \delta \phi. \quad (22)$$

This is sound as if the aggregate grows it faces larger stresses, resulting in a stabilizing increase of the peeling.

VI. DISCUSSION

In this crude model we have shown that a rich rheological behavior can be expected when a simple solution tends to aggregate on the walls of the measuring device. Most effects are due to the variation of the viscosity with the concentration of particles in the fluid region, the latter increasing as the aggregate is peeled away. The physics at work here does not imply a close to equilibrium description of the exchanges between the aggregate and the solution but rather a crude description of the two antagonistic phenomena: adsorption and peeling. These effects point out the possible role of concentration dependence of the viscosities in more complex systems where obtaining the effective equations of motion for the interface between phases requires a careful description of the fluxes [3]. One may also want to apply the present analysis to situations where aggregation on the bottom plate is induced by gravity and where by shearing the sediment one modifies the effective viscosity of the solution.

To make our point in a clear way the model chosen is oversimplified: aggregation of particles within the solution has been neglected, the assumed form for interface motion is very simple, no elastic deformation of the aggregate has been incorporated. Also the description was limited to a 1D analysis of steady-state solutions neglecting the possible occurrence of modulations along the flow direction [9] (the two-dimensional extension of the 2D stability analysis is left for further work). Eventually we have supposed that the aggregate can appear only on one wall. Although this may be the case if the walls differ in surface chemistry or roughness, one would expect in a symmetric situation that aggregate can exist on both. In particular in the cylindrical case, once an aggregate initially on the inner cylinder has been completely peeled away under strong shear, one expects upon decreasing of the shear that nucleation occurs first on the outer cylinder where the shear stress is weaker, resulting in additional possibility of hysteretic behavior.

We also hope that this kind of analysis, beyond wall effects, can also help us understand situations where aggregates (usually fractal-like) exist in a solution due to stickiness of the particles [7,8]. Then additional mechanisms would also enter the picture: fracture in large blocks instead of peeling, and growth by coalescence of two aggregates. However the mechanism of release of particles in the interaggregate space upon increase of the flow and its consequence on the global rheology, in a geometry somewhat equivalent to Fig. 4(a) (an aggregate in shear flow), could possibly be modeled as in the present study.

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