Viscosity bifurcation in thixotropic, yielding fluids

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Synopsis

Most concentrated colloidal suspensions such as cement, drilling fluids, paints, muds, etc., have been considered until now thixotropic fluids with a flow curve of an ideal yield stress fluid. We start by showing from inclined plane tests, intended to determine the yield stress, that these systems in fact exhibit peculiar properties. Unlike ideal yield stress fluids, they stop flowing abruptly below a critical stress, and start flowing at a high velocity beyond a critical stress, which in addition increases with the time of preliminary rest. In order to clarify these features we carried out a complete set of rheometrical tests with a model fluid, a bentonite suspension. Our results show that under controlled stress, in some cases after significant flow, there is bifurcation of the behavior towards either stoppage or rapid shear, depending on the relative values of the imposed and critical stresses. As an immediate consequence, we find that no (homogeneous) steady state flows at a shear rate below a critical value can be obtained. These results can be qualitatively predicted by a simple theoretical model that assumes that the viscosity of the material results from the competition between aging and shear rejuvenation, associated to, respectively, the organization or disorganization of the network of particle interactions. This shows that the flow curve in the steady state of concentrated colloidal suspensions and, more generally, of structured fluids, is strongly affected by their thixotropy. [DOI: 10.1122/1.1459447]

I. INTRODUCTION

Many materials of industrial importance such as paints, mineral suspensions, printing inks, foodstuffs, etc., are colloidal suspensions consisting of fine particles dispersed in a liquid. Interactions among the particles may lead to the formation of microstructures in the suspension at rest. Depending on how the structure responds to the applied shear

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forces, one can observe different types of macroscopic flow behavior, such as shear thinning, yield stress behavior, thixotropy, and viscoelasticity [see, e.g., Mewis and Spaull (1976); Bird *et al.* (1982); Utracki (1988); Russel *et al.* (1989); Coussot and Ancey (1999)]. Perhaps the two most important rheological properties of suspensions, in terms of both practical and fundamental significance, are thixotropy and yield stress, which have been dealt with comprehensively by Mewis (1979) for the former, and by Barnes (1997, 1999) for both.

Thixotropy is generally understood as the time-dependent decrease in the viscosity of a fluid due to a finite, measurable, reversible change of the fluid microstructure during shear. In the absence of shear, generally a damaged structure rebuilds, i.e., it is said to *age*. Thus pseudoplastic or shear-thinning behavior might be considered a special case of thixotropy where both structural breakdown under shear and rebuilding of the structure at rest take place very rapidly. It remains that, in practice, thixotropy is often not taken into account, because of a lack of simple, systematic, relevant procedures to characterize it.

Although *a priori* it is a single physical parameter of the fluid, the yield stress as a true property of suspensions is less well understood and is more controversial. Over the last 20 years many methods have been developed for measuring yield stress, more than for any other rheological property [see, e.g., De Kee *et al.* (1980); Nguyen and Boger (1983); Uhlherr *et al.* (1984); James *et al.* (1987); Chhabra and Uhlherr (1988); Coussot and Boyer (1995); Pashias *et al.* (1996)]. While each method has its own merits and limitations [Nguyen and Boger (1992)], and although some techniques are more popular than others, none of them is accepted as the standard procedure for the determination of yield stress. In addition, it is not unusual to find different values of yield stress for a given suspension using different techniques [James *et al.* (1987)] or different procedures [Alderman *et al.* (1991)]. This led to the distinction between dynamic yield stress, i.e., the stress limit for an infinitely low shear rate, and static yield stresses which are observed after different durations of rest [Cheng (1986)]. This description will be entirely confirmed by our inclined plane tests; however we find that the behavior of the systems we study is due to the existence of a sort of instability of these fluids, leading to either abrupt stoppage or rapid flow for slowly decreasing or increasing stress, respectively.

Recently, "flow curves with a minimum," leading to somewhat similar observations, have been reported using commonly accepted rheometrical procedures for a number of thixotropic materials: bentonite, laponite, and alumina suspensions, and grease. The authors observed fracturing below a critical shear rate [Coussot *et al.* (1993)] or an effective decrease of stress as a function of the shear rate at low shear rates and in steady state, leading to a flow curve with a minimum [Mas and Magnin (1994)]; Ducerf and Piau (1994, 1996); Pignon *et al.* (1996)]. However, Pignon *et al.* (1996) demonstrated with a transparent suspension that, in the latter case, when the shear rate is decreased below a critical value, the deformation is localized in a thin region. Persello *et al.* (1994) also observed such a localization of shear in a "slip layer" within suspensions of silica in water. These effects have so far been interpreted as typical of "pathological" materials.

Another related phenomenon, *shear banding*, that takes the form of a plateau of stress as a function of the shear rate, associated with shear melting, i.e., a shear-induced phase transition and/or a transition in particle arrangement for suspensions, has been observed for various systems such as lyotropic liquid crystals [Bonn *et al.* (1998)] or colloidal crystals [Chen *et al.* (1992, 1994)]. In the present work we intend to show that this type of behavior is in fact quite general for dense, noncrystalline materials and in addition is usually strongly related to thixotropy, and to present a more comprehensive description of it. In particular we shall see that the peculiar behavior observed for all of these very different systems results from the interplay between the yielding and thixotropic character of the fluid, two effects which, we conclude from our measurements, are closely related.

This paper is organized as follows. We start by showing from inclined plane tests (Sec. II), intended to determine the yield stress, that various concentrated colloidal suspensions exhibit peculiar properties: unlike ideal yield stress fluids, they stop flowing abruptly at a critical stress. In addition, these systems start to flow at a relatively high velocity beyond a second critical stress that increases with the duration of preliminary rest. In order to clarify these features we subsequently present in Sec. III a complete set of rheometrical tests on a bentonite suspension, that we consider a model fluid. Our results show that under controlled stress bifurcation occurs in the flow behavior towards either stoppage or rapid shear, depending on the relative value of the stress imposed and the (time-dependent) critical stress. In order to provide a physical interpretation for these results, we develop a simple theoretical model (Sec. IV) assuming that the viscosity of the material results from the competition between aging and shear rejuvenation processes, respectively, associated with the organization or disorganization of the fluid microstructure.

II. PRELIMINARY OBSERVATIONS OF THE BEHAVIOR OF CONCENTRATED COLLOIDAL SUSPENSIONS: INCLINED PLANE TESTS

Various methods for determining the "apparent" yield stress have been proposed [Nguyen and Boger (1992)]. One of these consists of determining the critical slope at which a uniform fluid layer starts to flow [Uhlherr *et al.* (1984); De Kee *et al.* (1990)], or measuring the asymptotical thickness of a fluid layer after it has stopped flowing on an inclined plane [Coussot and Boyer (1995)]. Since these procedures still require a large volume of material (in order for edge effects to be negligible), Coussot *et al.* (1996) proposed simply determining the asymptotic thickness (h_0) in the center region of a deposit of a finite volume of material poured over the inclined plane. If slippage or other perturbing effects (sedimentation, surface tension, drying) can be neglected, and provided the thickness of the layer is much smaller than its longitudinal and lateral extent, this critical thickness is related to the yield stress by

$$h_0 = \frac{\tau_c}{\rho g \sin i}, \qquad (1)$$

where g is the gravitational acceleration, i the angle of inclination of the plane, and ρ the density of the fluid.

The response of such a yield stress fluid on an inclined plane to sudden changes of the slope during these tests appears to be a simple and rapid method by which to determine whether the fluid is thixotropic or not. For an ideal (nonthixotropic) yield stress fluid:

(1) for a fixed slope, because the thickness of the fluid layer decreases over time, the shear stress at the wall decreases also, so that the fluid velocity should progressively and continuously decrease [Coussot and Boyer (1995)];
(2) conversely, if, after stoppage on a fixed slope, the plane is further inclined, the fluid should start moving at a velocity that is a continuously increasing function of the difference in slope.

In a series of inclined plane (plywood) measurements we used various suspensions (cement, muds, clay–water mixtures, bauxite residue, paint) all containing at least a colloidal-liquid matrix (for their characteristics, see Fig. 1). After having mixed the solid fraction with water each material was gently poured over the inclined plane. The flow was generally rapid in the first few instants but each material eventually stopped. In fact,

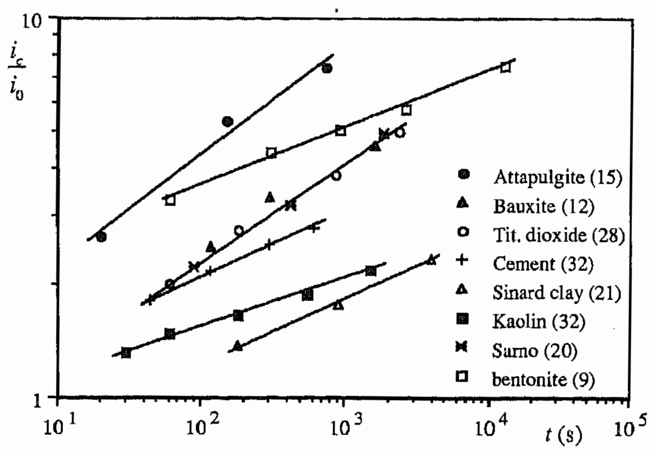

FIG. 1. Inclined plane tests with various concentrated colloidal suspensions: After stoppage the plane was inclined until a new, significant flow could be observed. Here we plot the corresponding *approximate* critical slope to the initial slope ratio as a function of the time of rest between stoppage and inclination. In the range of time considered the yield stress scales as t^p and p between 1/6 and 1/3 depending on the material. Materials [solid fraction (%), ρ (kg m^{-3})]: Attapulgite (Clarsol ATC, CECA, France), 10.2, 1160; Bentonite (Tréport deposit, Lambert-Rivière, France), 3.3, 1053; kaolin (China clay, Speswhite, Great Britain), 23.5, 1395; bauxite (red mud, Crassier-Pechiney, France), 28.8, 1576; titanium dioxide (Tronox CR-826, Kerr–McGee Chemical LLC, U.S.), 29, 1870; cement (gray cement, CPA-CEM 142, 5R, Lafarge, France), 50, 2000; Sinard clay (natural clayey soil, Isère, France), 23.8, 1405; Sarno mud (Lahar, 1998 event, Italy), 40.1-1682. The yield stress determined from fluid stoppage on the initial slope is indicated in square brackets for each fluid.

a state without visible flow was reached much more rapidly than would be the case for an ideal yield stress fluid, for which it generally takes several hours before surface tension effects become significant. For the fluids studied here, the time for stoppage typically ranged from 1 s to 1 min depending on the material and the initial conditions. More quantitative measurements showed that stoppage of our materials is quite abrupt: there is an apparent discontinuity in the derivative of the total length of the deposit as a function of time, i.e., the velocity suddenly changes from a finite value to zero.

In these experiments, when, after stoppage, we increased the slope again, these materials did not start flowing again (even if we waited a long time at an intermediate slope) before reaching a new critical slope, i_c, which was significantly larger than the initial one. This critical slope increased according to the time of rest at the initial slope. In addition, the flow generally started abruptly when i_c was reached. This behavior was reproducible: when the material was taken from the plane, mixed and poured again over the initial slope, a deposit shape similar to the initial one was obtained. Observations of i_c as a function of time of rest for the different materials are shown in Fig. 1. Note also that no slip occurred during these experiments: the upper fluid edge never moved during all these tests.

The apparent increase of yield stress over the time of rest agrees with previous observations on the yield stress of thixotropic fluids [Cheng (1986); Alderman *et al.* (1991)]. However, the abrupt stoppage on the initial slope and the abrupt start of the flow at a critical slope suggest that there is some kind of instability that happens below a critical velocity of shear rate. This instability is even clearer for long times of rest: in that case we observed that when the fluid starts flowing, the deposit develops a fracture (with a horseshoe shape as observed in certain landslides) followed by liquefaction as the material moves downwards and accelerates. It follows that there is a need to explore in more detail the rheological behavior of colloidal suspensions and in particular the relationship

between the steady state flow characteristics and possible thixotropic behavior. To this end, in the following we provide a detailed study of a bentonite suspension, whose characteristic times are convenient.

III. DETAILED RHEOLOGICAL BEHAVIOR OF A BENTONITE–WATER SUSPENSION

A. Material

The suspension used was prepared from industrial grade bentonite (Impersol poudre, Société Française des Bentonites et Dérivés, France) mixed with distilled water at a solid volume fraction of 4.5% with no chemical additives. The suspension was first agitated continuously for about 3 h to ensure complete homogenization. It was then left to rest for at least 24 h to allow hydration and dispersion of the bentonite particles. Prior to the rheological tests the suspension was gently stirred for 1 h.

B. Procedures

All rheological measurements were made using a controlled-stress rheometer (Reologica Stress-Tech). The main measuring system used was the rotating vane-in-cup geometry, which has been established as having an advantage over other geometries in that serious wall slip effects can be avoided [Barnes and Nguyen (2001)]. To further minimize possible slippage at the cup's surface, the latter was also covered with sandpaper (grade P400). The vane used had four blades with a diameter of 17 mm and length of 52 mm and the cup diameter was 27 mm. A parallel-plate fixture (40 mm diameter) with two different gap spacings (1 and 2 mm) that was roughened with sand paper on both sides was also used to obtain data for comparison with the vane-in-cup results.

After the suspension was loaded into the measuring system, it was subjected to an intense preshear at a shear stress of 26 Pa for 60 s. This level of preshearing stress generated a steady shear rate of about 400 s^{-1} which is about the maximum shear rate that the system can sustain before secondary flows (Taylor–Couette instability or turbulence) develop. Longer periods of preshear did not affect the results presented here.

After preshear, the sample rested for a given period of time before constant stress was suddenly imposed and the apparent viscosity (calculated from the apparent shear rate) was recorded as a function of time. Before the next shear stress was applied, the suspension again underwent the same preshearing and resting sequence as that above. All measurements were conducted at 20 °C. The apparent shear rate was computed by assuming homogeneous shear within the gap in the coaxial cylinder geometry, and from the relative velocity between the two disks at the periphery for the second geometry.

C. Rheometrical results

1. Viscosity bifurcation

Figure 2 shows the results obtained with the rotating vane for various constant stress levels, imposed immediately after the preshear. In fact this is the torque which is imposed in each case and the shear stress is not homogeneous but for the sake of simplicity we shall neglect this in the following and this question will be discussed subsequently. It can be observed that for very short times after start up, the shear rate response is not very sensitive to the applied stress. Except for the highest stress level, the shear rate steadily decreases over time (i.e., the viscosity increases) at a rate that is faster when the applied stress is smaller. After a certain time, which is a function of the applied stress, we observe a dramatic fall in the shear rate by more than four orders of magnitude to 10^{-4} s^{-1},

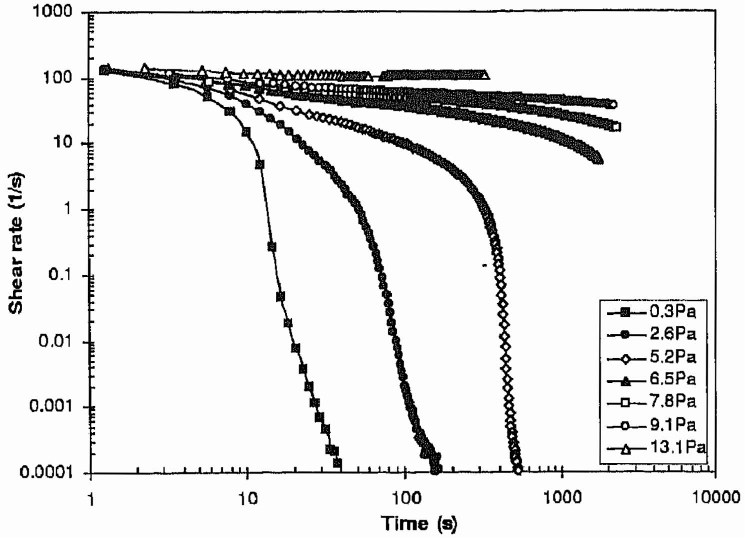

FIG. 2. Rheometry with the bentonite suspension: Change in shear rate over time for different stress levels applied immediately after preshearing (60 s at 26 Pa).

indicating that the flow rapidly decelerates and the material practically stops flowing in the rheometer. These observations could at first be mistaken for typical results of thixotropic fluids in step stress experiments [Barnes (1997)], i.e., the transient shear rate decrease (or viscosity increase) over time is associated with a partial rebuilding of the fluid microstructure previously broken down by preshear. However, the data clearly demonstrate that, for the bentonite suspension, the shear rate decrease does not eventually lead to a steady state or equilibrium condition where the rates of breakdown and recovery of the structure are equal, as would be the case of thixotropic liquids. Instead, we observe the fluid to stop flowing rather abruptly, similar to what was observed for the inclined plane tests. A shear rate of 10^{-4} s^{-1}, although not proof of the complete absence of flow, is the lowest limit of our instrument's sensitivity at which fluctuations become significant. Additionally, what is remarkable from the data is the significant flow (the strain is larger than 1000) followed by an abrupt decrease of the shear rate over many decades to reach such a low value. For the highest stress level in Fig. 3 the shear rate remains almost perfectly constant at a high value, indicating that a steady state has been reached; the corresponding viscosity is low. Although not shown in Fig. 3 this is the same for larger stress values.

To sum up, for sufficiently low stress the fluid initially flows like a liquid but eventually becomes "solid," whereas for larger stresses the material liquefies and flows rapidly (with a low viscosity). As a direct consequence, in steady state a wide range of shear rates is inaccessible. If a value in this range is (transiently) reached the shear rate subsequently evolves either towards a high value (corresponding to low viscosity) or to an infinitely small value (infinite viscosity). This viscosity bifurcation is in fact the cause of the effect of flow curve with a minimum often observed in suspensions (see Sec. I).

2. Transient liquefaction followed by stoppage

Figure 3 shows the data for a sample tested following a period of rest (20 s) after preshearing over a larger number of applied stresses. The shear rates are lower for short times, and depend more sensitively on the applied shear stress than those for the material

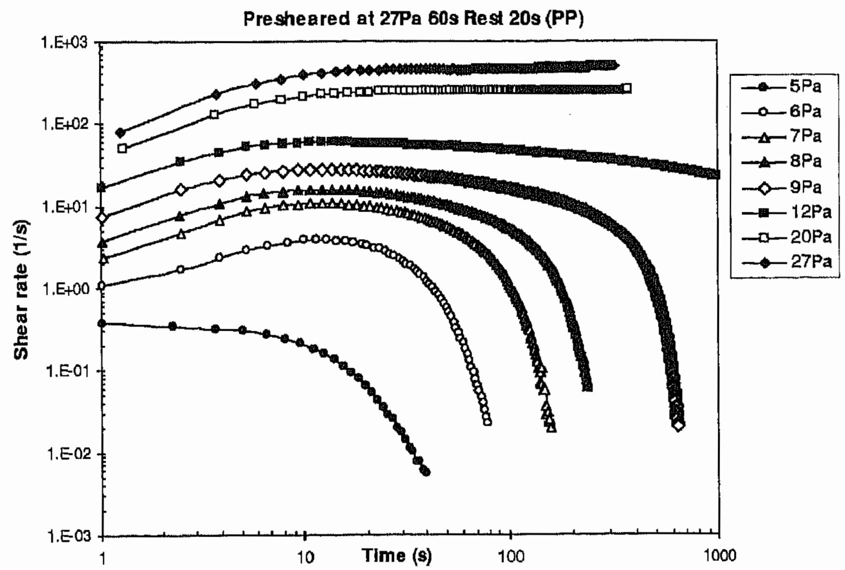

FIG. 3. Bentonite suspension: Change in shear rate over time for different stress levels applied after 20 s of rest following preshearing.

with no rest. This is an indication of the aging (i.e., the rebuilding) of the structure that was previously broken down by the preshear. For the lowest shear stress (5 Pa), the shear rate decreases over time, slowly at first and more rapidly later. For intermediate stresses (6–12 Pa), the shear rate initially increases over time to some maximum value, followed by a rather rapid decrease towards very low levels where flow can no longer be detected. The peaks are broader and the times at which flow practically ceases are longer with higher applied shear stresses. Finally, at high shear stresses, in the vicinity of the stress imposed during preshearing, the shear rate increases monotonically over time and approaches a steady state value for long times. For longer times of rest similar behavior was observed (see Fig. 4) but the shear rate maxima in the intermediate stress range are more pronounced and take longer to reach, and the subsequent drop in shear rate is more abrupt.

The data in Figs. 3 and 4 suggest that there exist two critical shear stresses, and they divide the behavior observed into three different regimes. For applied stresses that are smaller than a first critical shear stress (τ_{c1}) the shear rate always decreases over time and leads to the cessation of flow. The second critical shear stress (τ_{c2}) defines the limit above which a constant applied shear stress will cause a monotonous increase in shear rate, which will reach a steady state value at long times of shear. For an applied shear stress intermediate between the two critical limits, the shear rate first increases to a maximum, and subsequently falls off rapidly: the flow stops, and no steady state is reached. We found that it was difficult to quantify these critical shear stresses precisely. However, based on the data in Figs. 3 and 4 the value of τ_{c1} should be very close to 5 Pa (for a 20 s rest after preshearing) and 9.1 Pa (after 150 s rest) as suggested by the shear rate transient, which appears to stay approximately constant for some time before falling off. These values may imply that τ_{c1} increases according to the time of rest following the preshearing period. The second critical shear stress is harder to pinpoint.

The peculiar behavior in the intermediate stress range may originate from the recovery at rest of the structure that was previously broken down by preshearing. Basically two

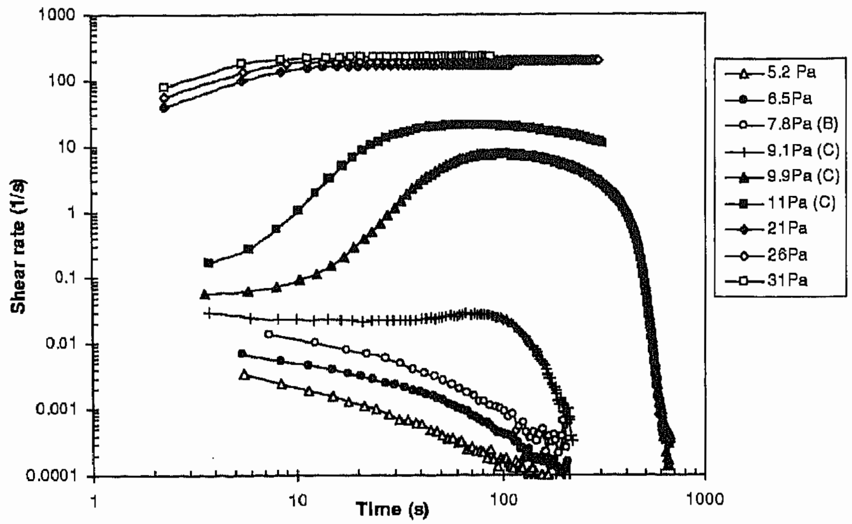

FIG. 4. Bentonite suspension: Change in shear rate over time for different stress levels applied after 150 s of rest following preshearing [(B) and (C) concern other series of experiments with ● new materials].

characteristic times of restructuring, probably associated to two different processes, i.e., low shear and high shear, are necessary for such a phenomenon to occur. Between the two critical stress levels the fluid has become restructured rather rapidly during rest but its strength cannot sustain the applied stress yet so that the fluid becomes unstructured first during shear and this unstructuring takes a certain amount of time. However after this time the usual aging under rapid shear takes place at a rate larger than rejuvenation so that the viscosity can increase rapidly.

The increase of τ_{c1} over the time of rest can be observed more clearly in the following experiment: after preshearing at a high level of stress, we impose another (high) stress after different times of rest. We observe that if the time of rest is shorter than some critical value, the viscosity always decreases. However, for a longer waiting time, the viscosity increases continuously until apparent flow stoppage in a way similar to what was observed before (see Fig. 5).

It is worth noting that the stress between coaxial cylinders is not homogeneous. As a possible consequence the fluid may be partially sheared and the thickness of the sheared layer could progressively decrease over time until reaching a size of the order of several particle diameters. Another complexity may result when using a vane: the material between the blades of the vane may have been somewhat perturbed during the preshear, so that the rotating geometry is not exactly cylindrical. To verify that the complex time-dependent flow behavior observed with the bentonite suspension is real and not merely an artifact caused by the rotating vane geometry used, we have also carried out similar experiments using a parallel-plate fixture with two gap settings, 1 and 2 mm. The results are compared in Fig. 6, in the form of apparent viscosity versus time plots at constant shear stresses, for a suspension presheared at 26 Pa and rested for 20 s. As can be observed, the differences between the two geometries are small and within experimental error. It is remarkable that the parallel-plate geometry with different gaps perfectly reproduces the trend of the data from the rotating vane-in-cup method. There are only some small quantitative differences between the results in steady state at high stress levels (see,

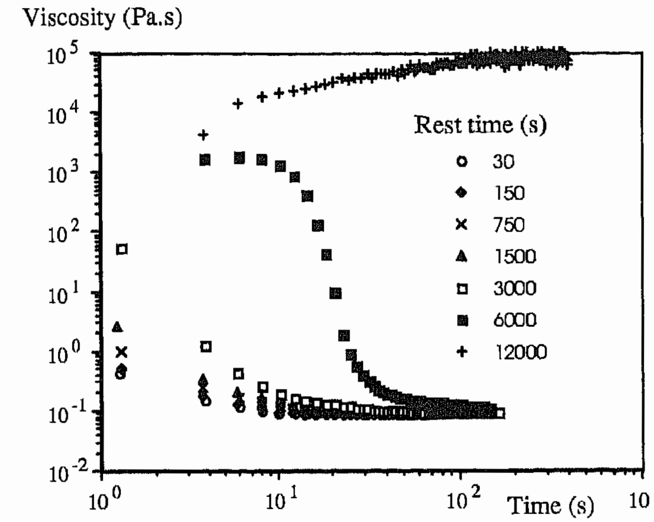

FIG. 5. Bentonite suspension: Change in viscosity over time when stress of 24 Pa is applied after preshearing and for different times of rest. Its initial level and the time necessary for significant rejuvenation liquefaction increase roughly exponentially.

for example, Figs. 2 and 3) which are probably due to significant edge effects with the parallel plates: the free surface at the periphery tends to penetrate the gap between the plates.

D. Discussion

The experimental procedure used in this work is not new. Preshearing a thixotropic fluid at a constant high shear rate or shear stress, followed by a fixed period of rest has

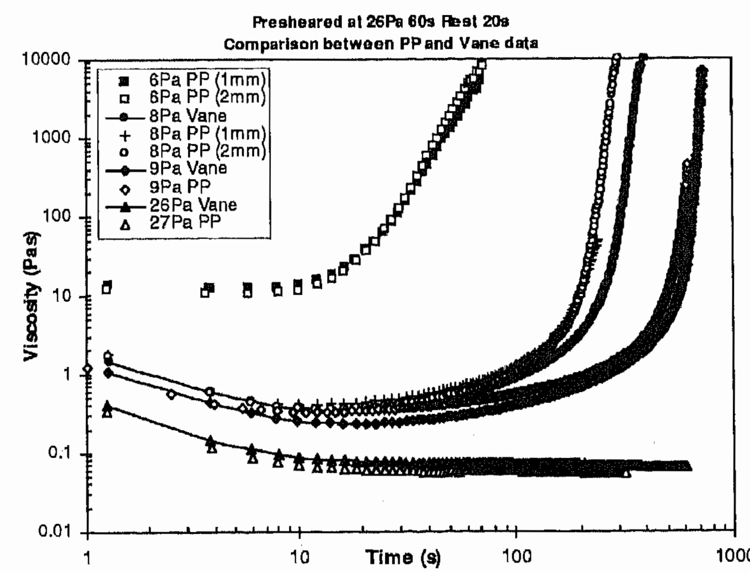

FIG. 6. Bentonite suspension: Change in viscosity over time for different stress levels applied after a rest of 20 s following preshearing in two measurement geometries (rotating vane and parallel plate).

been used by other workers as a means to create a controlled initial structural state for transient measurements [Barnes (1997)]. For example, Nguyen and Boger (1985) used the same technique with the vane method to determine the change in yield stress of red mud suspensions as a function of aging. Baravian *et al.* (1996) employed a controlled stress rheometer with Couette geometry to measure the thixotropic properties of a hydrocolloid solution. Cloitre *et al.* (2000) and Derec *et al.* (2000) studied the creep behavior of a microgel paste and a stabilized silica suspension, respectively, as a function of resting time after preshearing. However, the suspension of natural bentonite used here displays some interesting behavior, which we think is typical of thixotropic structured fluids: *in response to an applied shear stress, the suspension shows a bifurcation in flow behavior that depends on its flow history, i.e., on its current structural state.* For high stresses, the suspension exhibits the conventional characteristics of a thixotropic material: it flows with a time-dependent viscosity that decreases continuously towards a constant value in steady state. However, for low stresses, the suspension may flow initially but the flow gradually slows down and shows an apparent antithixotropic effect. In the intermediate stress range, the viscosity first decreases over time towards a minimum then rapidly increases by several orders of magnitude, leading to a more or less sudden cessation of flow. In both of the latter situations, a steady state flow condition cannot be obtained and the concept of an equilibrium viscosity is not applicable. One may thus interpret from this bifurcation behavior that there is a critical shear stress that determines whether prolonged shearing will lead to a flow or nonflow condition *in steady state.* As such, this critical stress is identifiable as a (time-dependent) *yield stress*, which is a measure of the mechanical strength of the suspension structure at a given time. However it is demonstrated here that this time-dependent yield stress is an integral and indissociable part of the thixotropic behavior of structured suspensions. In addition, apart from the behavior in the intermediate range of stresses, which might be specific to bentonite suspensions, our observations from the inclined plane tests are in complete agreement with the above picture.

Thus, conventional viscometric methods may not be able to meaningfully measure the steady shear flow properties of structured suspensions at low shear stresses below a critical shear stress. Since many available direct methods for yield stress determination [Nguyen and Boger (1992)] take times on the order of minutes or more to complete, the yield stress measured may not have a unique value if the structural changes taking place in the material have characteristic times comparable to the duration of the experiments. Although this conclusion is based on stress-controlled instruments, it also applies to strain-controlled devices as well (as long as instrumental effects such as wall slip are absent). In fact there have been various reports on the difficulty of obtaining reproducible low shear rate data in the region at or below the apparent yield stress [Barnes (1999); Magnin and Piau (1990)]. The features reported here indeed show that flows of structured fluids at low or moderate shear rates cannot correspond to homogeneous flows.

IV. THEORETICAL MODELING

It is rather difficult to develop a "microstructural" approach that would be based on a detailed description of the physical phenomena at the scale of the particles. The rheology of a suspension of colloidal particles depends upon the ensemble of interactions between all the particles, which makes it impossible to predict its viscosity from first principles. A number of "structural models" have been proposed in the literature (we cite in the following) but they in fact all basically rely on qualitative concepts concerning the effects of the interactions between particles on the mechanical behavior. Therefore, in the following, in an attempt to provide some basic, physical ideas, which explain the rheological trends observed in the experiments, we prefer a phenomenological approach.

For sufficiently concentrated suspensions, the particles can interact at some distance even at rest. The strength, or more precisely the viscosity, of the material depends on the strength of these interactions in a network that extends over the entire sample. This is at the basis of the yield stress: in the absence of such a network, the material would not stop flowing below a critical stress. However, in a disordered system such as a polydisperse suspension, the local stress intensity may depend significantly on the spatial distribution of particles. At rest, the particles evolve towards an equilibrium state because of local and collective rearrangements. The strength of the corresponding network of interactions consequently increases. The effect of flow is to disperse particles in a more or less disorganized state that tends to decrease the strength of the local interactions between them, which in its turn decreases the strength of the network. On this basis we shall simply assume that the rheological behavior of the material, i.e., its apparent viscosity (η), results from the simple competition between two opposite processes, i.e., aging and rejuvenation by the shear flow. A further simplification, considering our observations in the rheometrical tests, is to consider that these two processes separately take place at rates that only depend on the instantaneous state of the material.

Under these conditions we suppose that the state of the material at a given time can be described by a single parameter λ, which represents, for instance, the degree of flocculation or aggregation [Tsenoglou (1990); Coussot *et al.* (1993); Usui (1995); Potanin *et al.* (1995); Quemada (1999)], gives the fraction of particles in potential wells for colloidal suspensions [Coussot and Ancey (1999)], or is a measure for the free energy landscape for glasses [Bouchaud *et al.* (1995)]. In a more general approach for particulate systems, including granular materials, λ can also be seen as the degree of jamming of the system [Liu and Nagel (1998)].

For an aging system, at rest, λ increases at a constant rate of $1/T_0$ where T_0 is the characteristic time of the aging, i.e., the spontaneous evolution of the microstructure. Since we are dealing with laminar flows the change in the spatial distribution of particles due to shear is a purely geometrical process, and is directly proportional to the strain undergone by the fluid. As a consequence, we assume that the rate of decrease of λ under shear rejuvenation is proportional to the shear rate $\dot{\gamma}$. This rate is also proportional to some function of the degree of "jamming," that we shall assume to be simply proportional to λ, which leads to

$$\frac{d\lambda}{dt} = \frac{1}{T_0} - \alpha\lambda\dot{\gamma}, \tag{2}$$

with α a system-dependent constant.

To relate flow and structure, we consider that the instantaneous viscosity is a function only of the instantaneous state of the material:

$$\eta = \eta_0 f(\lambda), \tag{3}$$

where η_0 is the asymptotic value of the viscosity that corresponds to a structure that is entirely destroyed ($\lambda \to 0$) or, more realistically, to a negligible role of the network of interactions.

A number of models of this type, including a viscosity equation along with a kinetic equation for the structural parameter, may be found in the literature [Moore (1959); Tiu and Boger (1974); Usui *et al.* (1984); Coussot *et al.* (1993); Billingham and Ferguson (1993); Pearson (1994); De Kee and Chan Man Fong (1994); Chan Man Fong *et al.*

(1996); Toorman (1997); Yziquel *et al.* (1999)]. However, in order to develop this simple and heuristic model, in contrast to existing models which considered *a priori* viscoelastic or viscoplastic behavior, we shall not suppose a specific form of the behavior, i.e., f is an unknown function. At this stage the only conditions on f are that it is an increasing function of λ which verifies $f \rightarrow 1$ when $\lambda \rightarrow 0$.

From Eqs. (2) and (3) the dimensionless, steady state, shear stress ($T = \tau \alpha T_0 / \eta_0$) may be written as a function of the dimensionless shear rate $\Gamma = \alpha T_0 \dot{\gamma}$) as

$$T = \Gamma f(1/\Gamma). \tag{4}$$

It is interesting that T can be a decreasing function of Γ, which corresponds to a decreasing flow curve (T vs Γ), at sufficiently small shear rates if there is some value of x for which $xf'(x) > f(x)$. This in fact occurs for a function f that increases sufficiently rapidly, i.e., a viscosity that increases rapidly with λ. For example, this is true for an exponential function or a power-law function with a power larger than 1.

Let us first examine the case in which there is no decreasing part in the flow curve (T vs Γ): here the rheological behavior of the material is that of a thixotropic fluid without yield stress. For various forms of the function f the fluid subjected to any shear stress level reaches, by competition between aging and rejuvenation, depending on its flow history, a steady state at a finite shear rate. A limiting case is encountered for $f \propto \lambda$ when $\lambda \rightarrow \infty$. In this case, the fluid exhibits both yield stress and is thixotropic; however, the yield stress is not time dependent.

Within this simple model, the generic behavior of thixotropic, yielding fluids observed in these experiments corresponds to a function f such that there is a decreasing part in the flow curve. In order to simplify the following developments without affecting the qualitative conclusions, we shall simply assume that, within a sufficiently wide range of λ, $f(\lambda = \exp(\lambda)$. In this case the critical value below which the flow curve decreases is $\Gamma_0 = 1$. In this region the flows are unstable because the shear stress–shear rate curve decreases [Tanner (1988)]. Consequently, when a constant shear rate rather than constant stress is applied to the material, stable homogeneous flows can occur only when $\Gamma > \Gamma_0$. In practice, for smaller shear rates the material will either fracture, produce shear banding instabilities (shear localization) or evolve towards a stable situation of shear, either zero or at a rate equal to or larger than $\dot{\gamma}_c$ depending on the regions of the sample. such phenomena have already been observed experimentally for several systems [Coussot *et al.* (1993); Pignon *et al.* (1996)]. From the model, we consequently find that the flow curve of yielding thixotropic fluids differs from its usual representation: it is truncated below $\dot{\gamma}_c$ because no stable flows can be expected for $\dot{\gamma} < \dot{\gamma}_c$ (see Fig. 7).

Even more interesting is the behavior of the viscosity over time under controlled stress. In solving the model, we find that the fluid evolves either towards complete stoppage if the stress is smaller than a certain value which depends on previous flow history, or towards a steady flow otherwise (see Fig. 8). This critical stress can be expressed as a function of the initial state (λ_0) of the material

$$T_c = \frac{\exp(\lambda_0)}{\lambda_0}. \tag{5}$$

For a material left at rest after preshearing at high stress (leading to a low value of λ) T_c will consequently increase significantly according to the time of rest which is simply proportional to λ_0, in complete agreement with our experimental observations. However the most important prediction of this model is that *the yield stress does not have a specific*

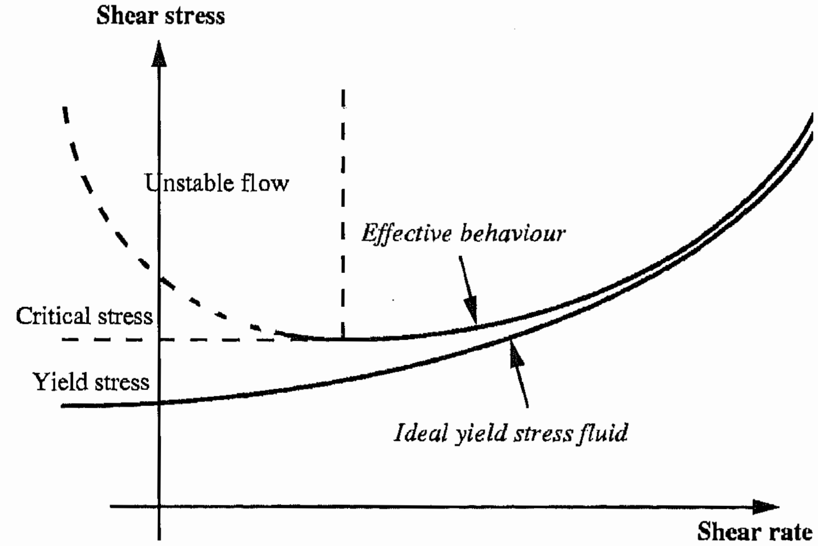

FIG. 7. Typical flow curve of a thixotropic yielding fluid predicted by the model compared to the usual representation of the flow curve for an ideal yield stress fluid.

value but results from the bifurcation, at a critical stress (that depends on the flow history of the material), between a catastrophic increase in viscosity (due to aging), leading to flow stoppage, and a shear rejuvenation ultimately leading to a steady state flow with a rather low viscosity.

The predictions of the model for the temporal evolution of the viscosity under various levels of stress are the following (Fig. 8). The viscosity can follow different paths depending on the relative values of the initial state of the system and the stress imposed. For stress larger than T_c the viscosity decreases and reaches a steady state value. For stress smaller than T_c the viscosity increases at an increasing rate and tends

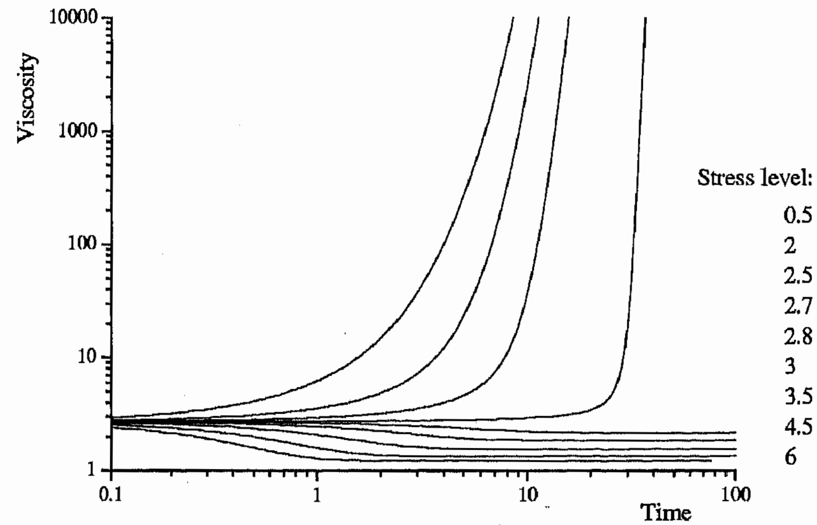

FIG. 8. Change in dimensionless viscosity (T/Γ) over dimensionless time (Θ) for different dimensionless stress levels (levels increase from top to bottom) according to the model.

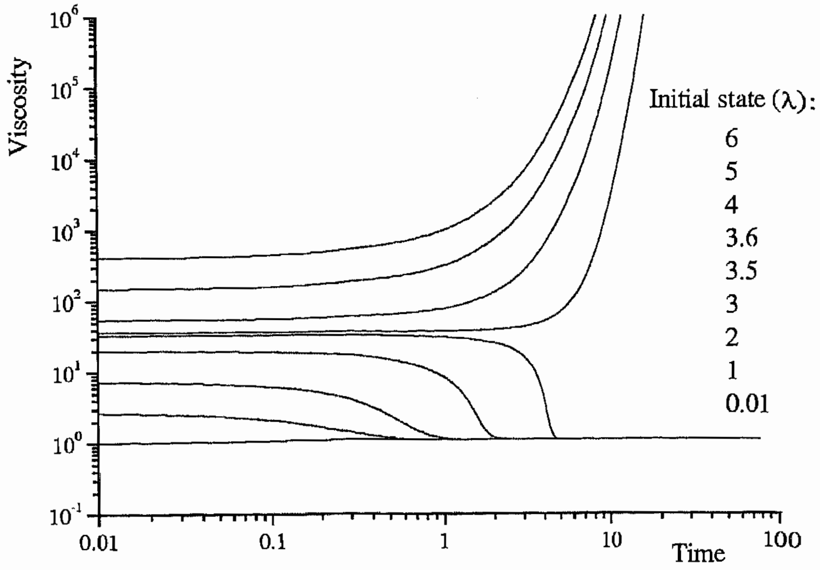

FIG. 9. Change in dimensionless viscosity over dimensionless time when a given stress is applied after different times of rest according to the model (from top to bottom: the decreasing level of the corresponding value of the structure parameter is also indicated).

towards infinity. The corresponding curves for the shear rate as a function of time are very similar to what was obtained with the bentonite suspension in Sec. III. Nevertheless we are still incapable, in this simple model, to capture the peculiar initial rejuvenation followed by dramatic aging observed for the bentonite suspension over a specific range of stresses. This is probably because we used only a single characteristic time for the aging.

If, in the model, we apply fixed stress but allow different initial states, we also obtain curves similar to those in Sec. III under similar conditions (cf. Fig. 9). For a material that is not well restructured (low values of λ) the viscosity decreases towards a low value. On the other hand, for a material that has aged a sufficient amount of time, the viscosity tends towards infinity. It is especially interesting to note the large amount of time needed before the shear rejuvenation becomes apparent when the stress approaches the critical value, which is consistent with our observations in rheometry and with the inclined plane tests.

Another typical experiment one could perform for thixotropic yielding fluids is to impose a stress ramp after different times of rest of the fluid. Under these conditions our model predicts a shear stress–shear rate curve which significantly evolves over the time of rest (or, equivalently, with the initial level of restructuring of λ_0) (cf. Fig. 10): for low values of λ_0 the curve is close to that of a simple viscous fluid; for larger values the curve exhibits an apparent yield stress whose level increases with λ_0. A second experiment consists of applying a constant shear rate after different times of restructuring. In that case, when the applied (dimensionless) shear rate is in the stable range ($\Gamma_0 > 1$) our model predicts that stress follows an exponentially decreasing curve whose initial level, which corresponds approximately to the overshoot observed in practice, increases with the initial state of the structure λ_0. The dimensionless stress follows as

$$T = \Gamma_0 \exp\left(\frac{1}{\Gamma_0}[1+(\lambda_0\Gamma_0-1)\exp(-\Gamma_0\Theta)]\right), \tag{6}$$

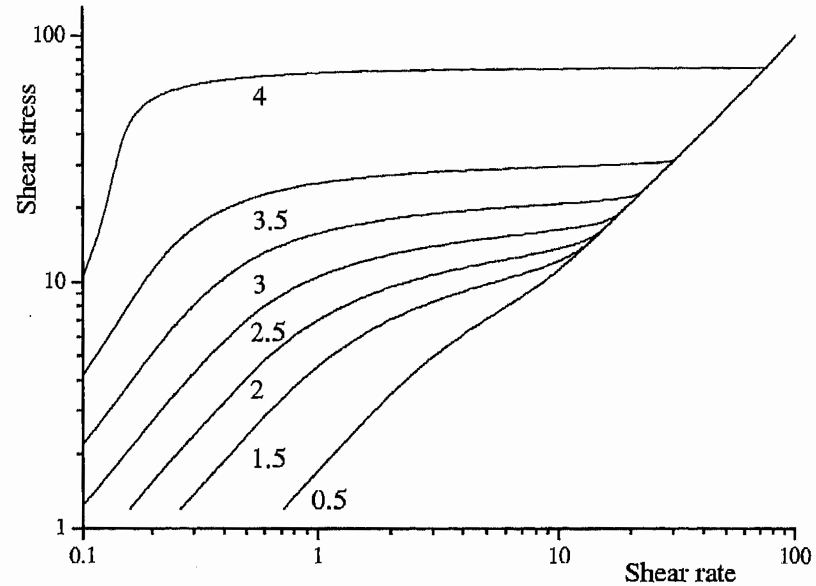

FIG. 10. Dimensionless shear stress–shear rate curve when a stress ramp ($T = 1+10\Theta$) is applied after different times of rest according to the model. The initial value of λ associated with each time of rest is indicated to the right of each curve.

where $\Theta = t/T_0$ is the dimensionless time.

In conclusion, a simple phenomenological model based on very natural physical concepts (aging and rejuvenation under shear) is capable of reproducing the very specific rheological behavior of thixotropic yielding fluids. A more complete model, possibly one that takes into account the underlying microscopic phenomena, obviously needs to be developed. However, these simple considerations clearly demonstrate that the yielding behavior of structured materials is closely linked to their thixotropy.

V. CONCLUSION

We have shown experimentally using different techniques (parallel plate and vane rheometry, inclined plane test) that the simple shear behavior of concentrated colloidal suspensions differs from what is commonly accepted. Under controlled stress they evolve either towards a rapid shear or stoppage depending on the relative values of the applied stress and a critical stress which depends on previous flow history. From a general point of view this means that thixotropy and yielding are properties of these materials that are closely linked. A reasonable physical modeling, based on very simple arguments, makes it possible to qualitatively reproduce the trends observed. In this model, in analogy to in recent models with glassy systems [Berthier *et al.* (2000)], two generic processes are taken into account: aging and shear rejuvenation, which, respectively, correspond to structuring and destructuring of the network of interactions between particles, independently of their origin (flocculation, repulsion, etc). Further physical approaches are needed to understand the processes from a more microscopic point of view. Our work, showing that very different suspensions exhibit similar peculiar rheological behavior, suggests that a general framework might be found [Liu and Nagel (1998)].

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