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Yielding and Shear Banding in Soft Glassy Materials

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Yield stress fluids have proven difficult to characterize, and a reproducible determination of the yield stress is difficult. We study two types of yield stress fluids (YSF) in a single system: simple and thixotropic ones. This allows us to show that simple YSF are simply a special case of thixotropic ones, and to pinpoint the difference between static and dynamic yield stresses, one of the major problems in the field. The thixotropic systems show a strong time dependence of the viscosity due to the existence of an internal percolated structure that confers the yield stress to the material. Using loaded emulsions to control the thixotropy, we show that the transition to flow at the yield stress is discontinuous for thixotropic materials, and continuous for ideal ones. The discontinuity leads to a critical shear rate below which no steady flows can be observed, accounting for the ubiquitous shear banding observed in these materials.

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Many materials around us are yield stress fluids: materials that respond elastically to small applied stresses, but flow once a threshold stress (the yield stress) is exceeded. Perhaps the most ubiquitous problem encountered by scientists and engineers dealing with typical yield stress materials such as food products, powders, cosmetics, foams and concrete is that the yield stress of a given material has turned out to be very difficult to determine [1,2]. Indeed it has been demonstrated that a variation of the yield stress of more than 1 order of magnitude can be obtained depending on the way it is measured [3]. The variable nature of yield stress measurements has led to a suggestion that an absolute yield stress is an elusive property [4]. One method that has been frequently used for characterizing yield stress materials is to work with two yield stresses, one static and one dynamic [2]. The static yield stress would be the stress above which the material turns from a solid state to a liquid one, while the dynamic yield stress is the stress where the material turns from a liquid state to a solid one. The fact that these are usually found to be different again poses a problem. All of these difficulties have resulted in lengthy discussions of whether the concept of the yield stress is useful and how it should be defined and subsequently determined experimentally [5].

In this Letter we argue that in order to understand the discrepancies when determining the static or dynamic yield stress of a material, one needs to distinguish between two types of yield stress fluids: thixotropic and nonthixotropic (or simple) materials. A simple yield stress fluid is one for which the shear stress (and hence the viscosity) depends only on the shear rate, while for thixotropic fluids the viscosity—and hence also the yield stress—depends also on the shear history of the sample. The rheological behavior is then determined by the competition between a spontaneous build-up of some microstructure at rest (“aging”) and its breakdown by flow (“shear rejuvenation”). We study the flow properties of yield stress materials with variable thixotropy, allowing us to have both simple and thixotropic yield stress materials in a single system. Controlling the thixotropy is done by using loaded emulsions [6]. We show that a pure emulsion behaves as a simple yield stress material. However the same emulsion, when loaded with clay particles that induce an attraction between the emulsion droplets, becomes very thixotropic. For the thixotropic systems, we find that the existence of a structure and its interaction with flow directly implies that the transition between flow and no flow at the yield stress is discontinuous, whereas for the simple yield stress materials the transition is continuous. The discontinuous transition between flow and no flow also implies a direct relation between thixotropy and shear banding (in a homogeneous stress field): the thixotropic fluid exhibits a critical shear rate below which no homogeneous flows can be observed. We report here that this critical shear rate increases with increasing thixotropy and thus the tuning of our system allows us to demonstrate that “normal” yield stress fluids are merely a special case of thixotropic materials, with a critical shear rate that goes continuously to zero. Finally, we show that when imposing a shear rate below the critical one, shear localization appears in the thixotropic emulsion, but for the simple emulsion, the flow is homogeneous even for the lowest shear rates. One way to view the difference between both materials is then to reconsider static and dynamic yield stresses. In this picture, for thixotropic materials the static yield stress depends on time and/or flow history whereas the dynamic yield stress is an intrinsic property of the material. For simple materials, static and dynamic yield stresses are identical.

Experiments were performed on emulsions of castor oil droplets (Sigma Aldrich) dispersed in water. The emulsions are stabilized by sodium dodecyl sulfate (Sigma Aldrich). The surfactant concentration within the aqueous phase is 1 wt. % and the oil volume fraction is 80% [7]. Emulsions...
were prepared at 24 000 rpm with an IKA T18 emulsifier, and loaded emulsions by mixing the pure emulsion with different concentrations of clay (Bentonite, from Steetley) in the emulsifier. The presence of clay particles in a loaded emulsion tends to form links between neighboring droplets. This leads to flocculation of the droplets; to directly visualize this effect, a pure and a loaded emulsion for which a fluorescent dye was added to the oil were diluted with water. Confocal microscopy pictures show that isolated Brownian droplets are observed without clay, whereas for the loaded emulsion, the sample shows large aggregates of droplets (Fig. 1).

The rheological measurements presented here were done using cone-plate and plate-plate geometries in a controlled stress rheometer (SS) (Physica MCR 300) and in a controlled strain rheometer (SR) (Rheometrics ARES). For the ARES, a 25 mm of radius cone (with 4° for angle) and a 12.5 mm radius plate-plate geometry are used. A 25 mm of radius plate-plate is used for the Paar rheometer, and measurements were checked with a 25 mm 4° cone-plate geometry. All geometries had roughened walls in order to prevent wall slip effects during measurements. All results presented here are independent of the rheometer and geometry, indicating that wall slip was successfully prevented [8]. In Fig. 2, measurements on the pure emulsion show that the flow curve is independent of the rheometer used. The steady-state flow curve is that of a simple yield stress fluid; i.e., the shear stress tends to a plateau at low shear rates and a Herschel-Bulkley model represents the flow curve very well.

The rheological properties of loaded emulsions turn out to be very different. Upon increasing the clay concentration, thixotropy is observed. The key observation is summarized in Fig. 3: the flow curve of the pure emulsion is perfectly reversible: there is no difference between increasing and decreasing stress loops. However, for with clay present, a clear hysteresis in the up-and-down stress sweeps is observed, that becomes more pronounced as the clay content increases. The complex rheological behavior of thixotropic materials can be understood on the basis of their microstructure: relatively weak attractive forces between the droplets cause the formation of flocs that are weak enough to be broken by the mechanical stresses that occur during flow, leading to a viscosity decrease in time, when the sample is made to flow.

The steady-state flow curve of the clayey emulsion was also determined with the two types of rheometers. Unlike the pure emulsion, a fundamental difference between the two steady-state flow curves at imposed shear stress and imposed shear rate is observed in Fig. 4. The latter shows a flow curve that again looks very much like a typical Herschel-Bulkley material. However, under an imposed shear stress, the shear rate jumps discontinuously to zero at a critical stress, and no data points can be obtained on the stress plateau at low shear rates. This means that there exists a critical shear rate below which no stable flows are possible if one imposes the stress.

The existence of this critical shear rate is best demonstrated by the viscosity bifurcation experiment. In this experiment, a fixed stress is applied to the system, and the viscosity (or shear rate) is followed in time until a steady state is reached. This is then repeated for different stress levels. For the pure emulsion [Fig. 5(a)], we find that there is a continuous family of curves, implying that all shear rates are possible when the stress is imposed.
However, for the loaded emulsion [Fig. 5(b)] we observe that above a certain shear stress, of about 141 Pa, the material starts flowing, and through the liquefaction by the flow reaches a steady state for which the shear rate is high. On the other hand, for a stress below the critical value of about 141 Pa, the shear rate is observed to decrease. Because the stress is fixed, this corresponds to an increase of about 141 Pa, the shear rate is observed to decrease. This implies also the existence of a transition of viscosity in time ("aging"); the steady state reached by the sample may be below, and another part above the yield stress; this immediately leads to shear localization [10,11]. Second, strong localization of the flow in the near-wall-region may lead to an apparent wall slip [9] that has recently been interpreted as being due to gradients in viscosity [12]. Both of these should not be present in a cone-plate geometry (homogeneous stress) with roughened walls (no wall slip).

Confocal microscopy measurements of the velocity profiles in such a setup shows that nonetheless a third type of shear localization may be observed here, but only for the thixotropic emulsions (Fig. 7). For these experiments, similar but transparent emulsions were prepared by emulsifying silicone oil (Prolabo η = 500 mPa·s and n = 1.403) in an aqueous phase composed of a water and glycerol (Sigma Aldrich, n = 1.471)) mixture to completely index matched with the oil. The rest of the procedure is the same as for the other emulsions. Before emulsification Nile red was added to the oil phase in order to use a fast Confocal Laser Scanning Microscope (Zeiss LSM Live) to obtain velocity profiles. These emulsions had a flow behavior that was qualitatively the same as the emulsions prepared above, notably the (non-) thixotropic behavior in the presence (absence) of clays. These emulsions were sheared in a rheometer directly coupled to a confocal microscope. The confocal is an inverted microscope, and the cover slide is used as the plate of a 12 mm 2° cone-plate geometry. Both the cover slide and the cone are roughened; we found that the best way to avoid wall slip while maintaining transparency of the cover slip was a thin layer of instant transparent of the cover slip was a thin layer of instant

Varying the amount of clay, the value of the critical shear rate increases linearly with clay content in the emulsion [Fig. 4(b)], showing that this indeed allows us to interpolate between ideal and thixotropic yield stress materials. The former is then simply a special case of the latter, for which the thixotropic effects and hence the critical shear rate tends to zero.

The final question is then how this relates to shear banding. Basically, three types of shear localization may be observed in these systems. If the stress is heterogeneous, part of the sample may be below, and another part above the yield stress; this immediately leads to shear localization [10,11]. Second, strong localization of the flow in the near-wall-region may lead to an apparent wall slip [9] that has recently been interpreted as being due to gradients in viscosity [12]. Both of these should not be present in a cone-plate geometry (homogeneous stress) with roughened walls (no wall slip).

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stress, on the other hand, is a material parameter: the due to the aging of the microstructure. The dynamic yield stress materials, the static yield stress will depend on time, problem in defining the yield stress. For thixotropic yield the up-and-down stress sweeps in Fig. 2. Hence, there is no existence of a microstructure that confers elasticity and repulsions between bubbles, droplets and swollen microgel particles, respectively: there is no percolated structure in these materials that is destroyed by the flow. It follows that these materials for which the yield stress is due to (stable) foams, emulsions and carbopol suspensions [4]. These are all materials for which the yield stress is due to repulsions between bubbles, droplets and swollen microgel particles, respectively: there is no percolated structure in these materials that is destroyed by the flow. It follows that for ideal yield stress materials, static and dynamic yield stresses are the same, as is evident from the coincidence of the up-and-down stress sweeps in Fig. 2. Hence, there is no problem in defining the yield stress. For thixotropic yield stress materials, the static yield stress will depend on time, due to the aging of the microstructure. The dynamic yield stress, on the other hand, is a material parameter: the (cyanoacrylate) glue that wrinkles upon drying; gluing a layer of micrometric beads onto the surfaces had similar efficiency for suppressing slip.

For the pure emulsions, the flow is homogeneous even for the lowest shear rates (Fig. 7) and in the small–gap cell used here. This is nontrivial; in [12] for small gaps shear banding always happens due to a flow-concentration coupling, however others state that this need not necessarily happen [13]. Our data show that with the correct boundary condition, the shear banding effect may be suppressed completely in a simple emulsion. For the thixotropic emulsions, on the other hand, as soon as the applied shear rate is below the critical one, we clearly observe localization, in agreement with detailed MRI experiments [14].

In sum, our detailed study of thixotropic and normal yield stress fluids in a single system shows that a careful distinction needs to be made between thixotropic and ideal yield stress materials [1–5,15]. Thixotropy is due to the existence of a microstructure that confers elasticity and hence a yield stress to the material. However, more often than not, such structures are modified by the flow, leading to a yield stress that depends on the (shear) history of the material. Here are few yield stress materials that do not show thixotropy; so far ideal yield stress behavior has been reported for (stable) foams, emulsions and carbopol suspensions [4]. These are all materials for which the yield stress is due to repulsions between bubbles, droplets and swollen microgel particles, respectively: there is no percolated structure in these materials that is destroyed by the flow. It follows that for ideal yield stress materials, static and dynamic yield stresses are the same, as is evident from the coincidence of the up-and-down stress sweeps in Fig. 2. Hence, there is no problem in defining the yield stress. For thixotropic yield stress materials, the static yield stress will depend on time, due to the aging of the microstructure. The dynamic yield stress, on the other hand, is a material parameter: the up-and-down stress sweep of Fig. 4 corresponds to the steady states of the curves of Fig. 5 and hence do not depend on time. The observation that we can reach a steady state immediately implies that the competition between shear-induced breakup and spontaneous buildup of the microstructure at rest results in a steady-state structure that is independent of the (shear) history of the sample, in agreement also with the results of a number of model calculations and simulations on glassy systems [16]. The dynamic yield stress is then the lowest stress for which such a steady state can be reached, and is then a time- and preparation independent material parameter. In a shear-banded situation, there could still be a perhaps undetectably small time dependence due to the aging of the nonflowing part of the sample, which certainly evolves with time. In this case, the dynamic yield stress would in fact be time independent only in theoretical models for ideal equilibrium glasses [17]. However, in practice the time dependence, if present, is so small that it is undetectable. Thus, although indeed there is a problem defining a static yield stress for thixotropic systems, the dynamic yield stress appears to be a well-defined material property.

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