

Structural Similarity and Transition from Newtonian to Non-Newtonian Behavior for Clay-Water Suspensions

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(Received 12 December 1994)

Clay-water suspensions are shear-thinning yield stress fluids whose apparent viscosity increases with solid fraction. It is shown experimentally that, in a wide solid fraction range, their behavior is similar and goes through a transition from non-Newtonian to Newtonian when a nondimensional shear rate increases.

PACS numbers: 47.15.-x, 83.20.Bg, 83.50.Nj, 83.70.Hq

Flows of muds or slurries, made up of a large amount of colloidal particles suspended in water, are often encountered in industry or nature. Generally these suspensions are non-Newtonian fluids exhibiting a yield stress (τ_c) [1] which needs to be overcome for flow to take place. This parameter increases rapidly with solid volume fraction (ϕ) [1–5]. A number of rheometrical studies of clay-water mixtures have been made [4–6] but essentially for moderate solid fractions or at high shear rates (say, $>10 \text{ s}^{-1}$). In general a Bingham model has been fitted to simple shear behavior data. However, tests made in a wide shear rate range show that these fluids are shear thinning [5,7]; i.e., their apparent viscosity decreases with shear rate, and a Herschel-Bulkley model [8], for example, is consequently more appropriate [7]:

$$\tau = \tau_c + k\dot{\gamma}^n, \quad (1)$$

where τ is the shear stress magnitude, $\dot{\gamma}$ is the shear rate magnitude, and k and n (<1) are positive parameters [the Bingham model corresponds to Eq. (1) with $n = 1$]. Though it is generally considered that the fluid yield stress must be associated with a particle network (see review in [7]), there is actually no clear view of changes in microstructure and corresponding rheological parameters when ϕ varies in a wide range. In water, clay particles may develop strong interactions with each other via van der Waals attractions and double layers formed by the slight diffusion of exchangeable cations absorbed on their surfaces [9,10]. In the case of kaolin it was suggested that, due to a different net charge on particle edge and face surfaces [9], the particles form a “house of cards” structure with mainly edge-to-face links. The question remains open as to whether this holds for other clay-water systems. The influence of clay type, electrolyte concentration, pH, and solid fraction on the intensity of these interactions in relation to suspension behavior has been studied [3,4,11], providing a better but still incomplete view of the process and interactions in microstructure during flow. A systematic study of the behavior in wide shear rate and solid fraction ranges can provide further elements of understanding.

We show experimentally that, in the ϕ range (5–50)%, natural clay-water suspensions have similar simple shear behavior types, which suggest that their structures are also similar. In a (Γ, T) diagram (nondimensional shear rate and shear stress), all simple shear data gather along a master curve composed of two parts: at low Γ values, the rupture and restoration of particle links dissipate most of the energy leading to a shear thinning yield stress behavior; at high Γ values, hydrodynamic interactions are predominant, leading to a Newtonian behavior.

The suspensions were natural fine materials containing a large clay fraction, consequently referred to as “clay” henceforward, mixed with tap water at different ϕ (see Table I for detailed characteristics). For the first type of test a controlled rate rheometer (Haake RV20) equipped with parallel plates (diameter of 5 or 2 cm; gap ranging from 1 to 5 mm) was used. Thus the distance between tools was at least 25 times the size of the largest solid particles ($40 \mu\text{m}$). The temperature was 20°C ($\pm 1^\circ\text{C}$). The procedure consisted of imposing different levels of rotation rate in varying orders, waiting for a steady regime to establish itself, and recording torque at each level [7]. Thixotropic properties were negligible within the accuracy of our apparatus. Edge effects can be important with this type of material [12,13], and thus a crucial experimental precaution involved checking that the volume of unsheared material at the sample

TABLE I. Material characteristics. The solid phase density was always 2650 kg/m^3 . Kaolin is an untreated refined natural clay, St-Bernard a fraction of a debris flow deposit (French Alps), and Eybens a natural clay.

	Kaolin	St-Bernard sample	Eybens clay
Mean and maximum particle sizes (μm)	1.5;15	8;40	5;40
Clay fraction mineralogy	Kaolinite	Chlorite illite	Chlorite illite
Suspension pH range (increasing ϕ)	7.9–7.3	7.9–7.5	8–7.7

peripheral free surface did not change too much during flow or from one shear rate level to another. This effect remains the predominant cause of uncertainty in results. Wall slip, which currently occurs with such materials [7,14], was avoided by using plates with rough surfaces (equivalent roughness $100\ \mu\text{m}$). Fracture within the suspension occurred especially with suspensions for the largest solid fractions at moderate and high shear rates [7]. Settling did not occur during the duration of tests for the suspensions tested with this apparatus. The present results correspond to the widest solid fraction and shear rate ranges permitted by our rheometers and for which fracture was negligible.

A capillary rheometer was used to test the less highly concentrated suspensions which could not be tested with the previous rheometer because they required low shear stresses or could flow out of the gap. It consisted in a circular conduit (diameter, 2.9 mm; length, 1 m) starting from a vessel filled with the suspension. Various pressure differences were applied between the two extremities of the conduit leading to different flow rates. Wall slip, which often affects capillary tests with mud suspensions [12], did not occur (as proved by the good agreement of results obtained with these two rheometers on the same material) because only low viscous fluids with a small yield stress were tested by this means. For parallel plate (capillary) rheometrical tests the torque (pressure difference) vs rotation velocity (flow rate) curve was used to compute the exact simple shear behavior (flow curve), with the appropriate technique taking into account the radial shear rate heterogeneity within the sample [15]. Limit suspensions for rheometer change were tested with both instruments, and a good agreement was found. Surface tension effects along air-sample interfaces were negligible compared to internal stress levels. Owing to previous observations concerning the critical Reynolds number for the transition towards turbulence for such materials [4,6], all the present data correspond to laminar regimes. Brownian movement was negligible in comparison to viscous dissipation, as is shown by high values of the Peclet number.

A typical set of results for a given material is presented in Fig. 1. For almost all solid fractions the simple shear behavior data (flow curve) seem to tend to an asymptotic shear stress value which was demonstrated to correspond quite well to the "true" yield stress, which can be defined [7,13] under controlled stress conditions as a critical stress below which the fluid strain seems to saturate asymptotically within our time scale of observation. A Herschel-Bulkley model [Eq. (1)] may easily be fitted on flow curves in the low shear rate ranges, but at higher shear rates the flow curve slope tends towards 1, precluding the relevant use of this model for the whole shear rate range.

It is generally considered [5,7,13,16–19] that within such systems solid particles aggregate in flocs which are

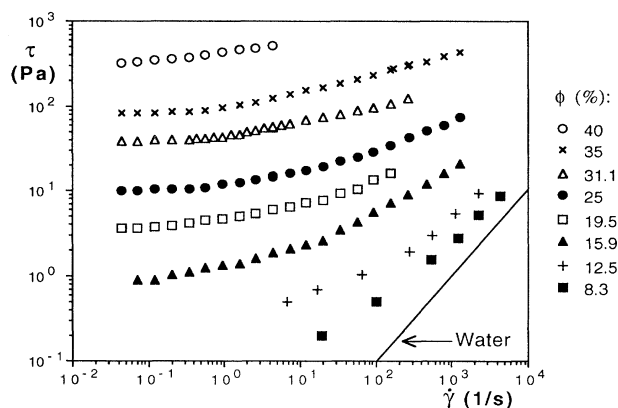


FIG. 1. St-Bernard sample-water suspensions: Experimental flow curve for different solid fractions. Only data corresponding to the two lowest ϕ were obtained with the capillary rheometer. The sets of flow curves for the two other clay-water suspensions (kaoline and Eybens clay) for different solid fractions exhibit similar trends. The uncertainty on results, which was minimized by repeating tests and taking into account all possible effects (see text), is estimated at about 20%. Results obtained for different geometry sizes were identical within this uncertainty. This value holds for other results presented in Figs. 2–4.

ruptured during flow and subsequently restored. Previous experimental tests at different temperatures suggested that energy dissipation due to these phenomena ("particle interactions") are predominant when flow is sufficiently slow [7], while viscous dissipation due to interstitial fluid flow plays a major role at relatively high shear rates [18]. Present results provide general evidence for this. At sufficiently low $\dot{\gamma}$ and high ϕ the flow curves of clay-water suspensions are essentially of the shear thinning yield stress type which must be attributed to the particle interaction process. At sufficiently high $\dot{\gamma}$ or low ϕ the Newtonian form of flow curves along with the low viscosity obtained suggest that particles behaved as independent force-free particles suspended in water. This type of system has a Newtonian behavior with viscosity increasing with solid fraction and depending on particle form [20].

Furthermore, for a given material the geometrical similarity of flow curves at different ϕ , along with the previous considerations of predominant terms of energy dissipation, suggest that, for a given shear rate, it is mainly the intensity of particle interactions and viscous dissipation, due to water flow, which changes from one ϕ to another. τ_c is the strength of the particle interaction network at rest. Thus it appears natural to use $T = \tau/\tau_c$ and $\Gamma = \mu\dot{\gamma}/\tau_c$, where μ is the viscosity of the corresponding force-free particle suspension. To estimate the latter parameter we have selected, from a whole range of possibilities, the empirical formula proposed by Chong, Christiansen, and Baer [21] fitted to various data corresponding to monodisperse and polydisperse sphere

suspensions: $\mu = \mu_0[1 + 0.75/(\phi_m/\phi - 1)]^2$, where μ_0 is the interstitial fluid viscosity (0.001 Pa s here) and ϕ_m is the maximum packing concentration (here we took 70%, which corresponded to the critical value above which it was not possible to add more clay without separating the suspension into independent volumes). Formally Γ^{-1} is a Bingham number.

Typical results [Figs. 2(a) and 2(b)] show that, within experimental uncertainty, flow curve data plotted in a nondimensional diagram (Γ, T) fall on the same curve which comprises two main parts. At low Γ (<0.3), the flow curve corresponds to shear thinning yield stress behavior which could be well represented by Eq. (1) which now takes the general nondimensional form

$$T = 1 + K\Gamma^n, \tag{2}$$

where K and n are material parameters which depend on characteristic times of rupture and restoration processes but do not depend on ϕ . At high Γ (>50), the flow curve corresponds to a Newtonian behavior with a viscosity

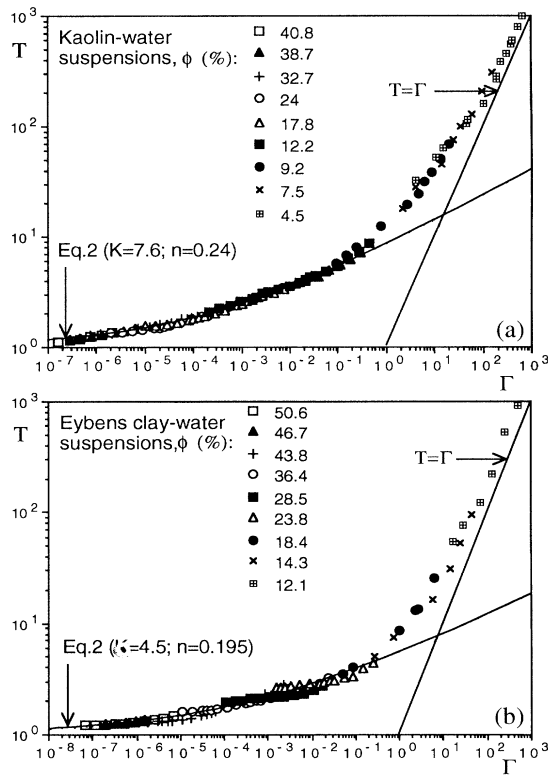


FIG. 2. (a),(b) Clay-water suspensions for different solid fractions: Flow curve in a (Γ, T) diagram. Fitting of the general semiempirical model in the range $\Gamma < 0.3$. Comparison with the flow curve corresponding to a similar suspension of force-free spheres. The three data sets corresponding to the lowest ϕ were obtained with the capillary rheometer. A similar fitting of Eq. (2) on experimental data obtained with St-Bernard sample-water mixtures can be done now with $K = 10$ and $n = 0.31$. The exact choice of expression for μ does not significantly affect these results.

approximately equal to 1.5μ . Since in reality clay particles have the form of thin plates, the latter value is not surprising. Additionally it is consistent with those obtained in the case of suspension of nonspherical force-free particles [21].

τ_c can be written as the number of links per surface unit times the mean interaction intensity. Through the nondimensional number Γ , the transition from a Newtonian to a non-Newtonian behavior thus appears to be expressed in terms of the ratio of mutual interactions between clay particles to viscous dissipations due to water flow. Γ also corresponds to the ratio of a material characteristic time (μ/τ_c) to a characteristic time of flow ($1/\dot{\gamma}$).

Attempts to compute τ_c from estimations of force intensity have led [5,17] to formulas which do not predict the present exponential increase in a very wide solid fraction range (Fig. 3). Thus our quantitative knowledge of interactions between clay particles in water remains insufficient [22]. For low solid fractions the yield stress increases even faster. This probably corresponds to a percolation process: At very low ϕ (in a range for which settling occurred in our tests) clay particles are distant from each other and the corresponding homogeneous suspension does not exhibit a yield stress; around a critical solid fraction (ϕ_c) a weak continuous interacting network appears

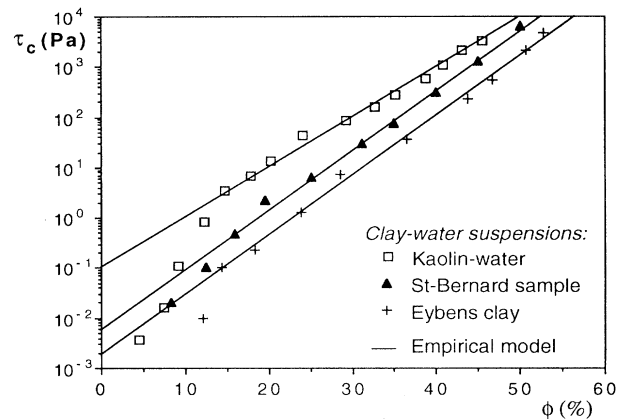


FIG. 3. Yield stress of clay-water suspensions as a function of solid fraction. Yield stress value corresponding to ϕ levels in the range of those presented in Figs. 1, 2(a), and 2(b) have been determined by fitting Eq. (2) on simple shear data. It appears that this corresponds approximately to the extrapolated yield stress towards low shear rate value and to the estimated yield stress from controlled shear stress tests [7]. Data corresponding to other ϕ levels have been roughly extrapolated from simple shear data obtained at low shear rates (using a parallel plate rheometer) because for these high solid fractions fracture occurred rapidly during tests. Above $\phi = 15\%$, we have $\tau_c = a \exp(b\phi)$ where a and b are two fluid parameters which take the following values: kaolin, $a = 0.1$ and $b = 23$; St-Bernard sample, $a = 0.006$ and $b = 27$; and Eybens clay, $a = 0.002$ and $b = 27$. τ_c increases even more rapidly with ϕ for $\phi < 15\%$. However, the corresponding points should be seen as rough estimations of a possible yield stress because our technique could not provide accurate data at such stress levels.

through the sample; and just above ϕ_c the strength of this network increases rapidly as the clay fraction increases as is the case with gels [23], for example. Far in excess of ϕ_c the network is dense, and a subsequent ϕ increase does not substantially increase the particle link number.

The present results concerning yield stress increase and the similarity of suspension behavior for a wide ϕ range suggests that the suspension structure is disordered and similar (considering the nonuniform grain size distribution and the various particle motions, an ordered structure is unlikely). When ϕ increases in this range only the mean separating distance between particles increases causing an increase in interaction forces at the origin of yield stress. Many other materials (sewage sludges, greases, paints, etc.) in the field of colloidal suspensions exhibit macroscopic properties and microstructural characteristics analogous to those of the present systems. It is likely that a similar analysis developed for these suspensions for solid fractions far above the percolating solid fraction would lead to the same kind of results concerning the transition zone and structural similarity.

- [1] J. Locat and D. Demers, *Can. Geotechn. J.* **25**, 799–806 (1988); C. Migniot, *La Houille Blanche* **1**, 11–29 (1989); **2**, 95–111 (1989); G. H. Tattersall and P. F. G. Banfill, *The Rheology of Fresh Concrete* (Pitman, Boston, 1983); C. R. Wildemuth and M. C. Williams, *Rheol. Acta* **24**, 75–91 (1985); J. S. O'Brien and P.-Y. Julien, *J. Hydr. Eng.* **114**, 877–887 (1988).
- [2] J. J. Major and T. C. Pierson, *Water Resour. Res.* **28**, 841–857 (1992).
- [3] Z. Wang, W. Xiang, and P. Larsen, *J. Hydr. Res.* **32**, 495–516 (1994).
- [4] D. G. Thomas, *Ind. Eng. Chem.* **55**, 18–29 (1963).
- [5] A. S. Michaels and J. C. Bolger, *Ind. Eng. Chem. Fundamentals* **1**, 153–162 (1962).
- [6] N. I. Heywood and J. F. Richardson, *J. Rheol.* **22**, 599–613 (1978); D. H. Caldwell and H. E. Babbitt, *Ind. Eng. Chem.* **33**, 249–256 (1941).
- [7] P. Coussot and J.-M. Piau, *Pheol. Acta* **33**, 175–184 (1994).
- [8] W. H. Herschel and R. Bulkeley, *Am. Soc. Testing Mater.* **26**, 621–633 (1926).
- [9] H. Van Olphen, *Introduction to Clay Colloid Chemistry* (Wiley and Sons, New York, 1977).
- [10] D. J. Shaw, *Introduction to Colloid and Surface Chemistry* (Butterworths, London-Wellington, 1980).
- [11] Z. Huifang, P. F. Low, and J. M. Bradford, *Soil Sci.* **151**, 196–207 (1991); B. Rand and I. E. Melton, *J. Colloid Interface Sci.* **60**, 308–336 (1977).
- [12] P. Coussot, Ph.D. thesis, INPG, Grenoble, France, 1992.
- [13] P. Coussot, A. I. Leonov, and J.-M. Piau, *J. Non-Newtonian Fluid Mech.* **46**, 179–217 (1993).
- [14] A. Magnin and J.-M. Piau, *J. Non-Newtonian Fluid Mech.* **36**, 85–108 (1990).
- [15] B. D. Coleman, H. Markowitz, and W. Noll, *Viscometric Flows of Non-Newtonian Fluids* (Springer-Verlag, New York, 1966).
- [16] F. Moore, *Trans. Brit. Ceram. Soc.* **58**, 470–484 (1959).
- [17] B. A. Firth and R. J. Hunter, *J. Colloid Interface Sci.* **57**, 266–275 (1976).
- [18] A. Tsutsumi and K. Yoshida, *J. Non-Newtonian Fluid Mech.* **26**, 175–183 (1987).
- [19] C. J. Tsenoglou, *J. Rheol.* **34**, 15–24 (1990).
- [20] G. K. Batchelor and J. T. Green, *J. Fluid Mech.* **56**, 375 (1972); M. R. Kamal and A. Mutel, *J. Polym. Eng.* **5**, 293–382 (1985).
- [21] J. S. Chong, E. B. Christiansen, and A. D. Baer, *J. Appl. Polym. Sci.* **15**, 2007–2021 (1971).
- [22] W. B. Russel, *J. Rheol.* **24**, 287–317 (1980).
- [23] P. G. de Gennes, *J. Phys. (Paris), Lett.* **37**, L1 (1976).