Dilatant Flow of Concentrated Suspensions of Rough Particles

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The flow anisotropy of a concentrated colloidal suspension at the jamming transition is studied. It is shown that the use of rough spherical particles reduces the hydrodynamic lubrication forces between adjacent colloids and makes possible the study of the stress tensor anisotropy. At low shear rates, the suspension exerts an attractive force between two opposite surfaces, whereas at higher shear rates it becomes dilatant. Direct confocal microscopy observation of the particles organization reveal that crystallites form at high shear rate.

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When a concentrated colloidal suspension is sheared, particles organize. They exhibit an anisotropic microstructure, which in its turn modifies the flow properties of the suspension. At low shear rate, this coupling is stable, and leads to permanent ordering of the colloids under shear, for example, along planes parallel to the shear direction [1]. When the shear rate becomes high enough, the coupling may become instable. In that case, transient structures develop and lead to a huge instantaneous increase of the suspension viscosity: the suspension jams [2]. This transition may be gradual or discontinuous, and is still poorly understood, despite its industrial importance [3].

Direct observation of concentrated colloidal suspensions under flow at the jamming transition is a challenging task, and the elucidation of the microstructure is thus difficult. Nevertheless, indirect information on the anisotropic organization might be obtained by mechanical measurements. Indeed, anisotropic microstructure of the particles leads to imbalance of the bulk stress, and thus to nonzero normal stress differences. This has been evidenced by means of numerical simulations, for dilute suspensions under simple shear at low Reynolds number [4,5]. Nevertheless, normal stresses are much lower than tangential stress and experimental measurements are difficult to achieve. One must thus find a way either to measure low normal stress values or to increase the mechanisms responsible for the anisotropic structure formation.

In this Letter, we use concentrated suspensions of silica particles of controlled roughness. We show that roughness decreases the shear rate at which jamming occurs, and we measure normal stress difference as a probe of the suspension microstructure. Silica particles are prepared according to a Stöber-like synthesis [6]. Their average size, measured by dynamic light scattering, is 1 μm.

At high enough volume fractions and shear rates, suspensions of silica particles exhibit a jamming transition: the viscosity of the suspension, measured in Couette geometry, diverges at a given shear rate [2]. Nevertheless, in order to measure normal stresses, one needs to use cone-plate or plate-plate geometry. In that case, at high shear rates, the suspension is submitted to high centrifugal forces and is forced out of the shearing cell. Together with the difficulty of measuring small normal forces, this has precluded detailed experimental investigations of the normal force of concentrated colloidal suspensions under shear [7,8]. We thus chose to approach the problem with a different point of view. We slightly modified the particles' interaction so that the boundary of jamming behavior is shifted towards smaller shear rates. In order to understand the physicochemical change we performed, one first needs to understand the underlying mechanism of the jamming transition. When submitted to a simple shear, particles are compressed along the compression axis of the shear field and form particle clusters oriented at 45° from the flow direction [5]. Reducing the centrifugal force at the jamming transition may be accomplished by diminishing the shear rate at which clusters form. Now, the dynamics of cluster formation is controlled by the lubrication solvent flow of the solvent in the gap between adjacent colloids [9], and the critical shear rate at the jamming transition is reduced when the hydrodynamic drag force F_H decreases. F_H is of the form $F_H = 6\pi\eta R v(R/h) f^*$, where η is the solvent viscosity, R the radius of the particles, h the distance between the surfaces of adjacent colloids, v the speed of the colloids, and f^* a numerical factor, taking into account the degree of slippage at the particles surface. f^* is a decreasing function of the slip length [10]. Thus, an increase of the slip length induces the required decrease of the hydrodynamic drag force. This may be done by changing the wettability of the particles by the solvent, but a low wettability would greatly reduce the stability of the suspension. We chose to keep water as a solvent and to roughen the surface of the colloids. Indeed, Bonaccurso *et al.* [11] measured the hydrodynamic drainage force as a function of particle roughness. They observed that, for silica surfaces whose roughness ranged from 0.4 to

12.2 nm, the degree of slip increases as the surface roughness increases. The repulsive hydrodynamic force between two particles is reduced by as much as a factor of 2 for the roughest particles. To increase particles roughness, we add sodium hydroxide to an aqueous suspension of silica particles. At the surface of the beads, silica is dissolved [12]. We then wash the suspension several times with Millipore water. The surface roughness is measured by atomic force microscope, in tapping mode on the top of the sphere. The mean square roughness is 0.68 nm for the smooth unmodified particles and 6.2 nm for the rough ones (Fig. 1, inset). Let us insist that, for rough particles, the ratio of the roughness on the particles' radius is $6.2/500 \ll 1$, and the particles thus remain spherical.

Rheological behavior of these suspensions is then measured using a strain-controlled rheometer (Rheometrics, RFS II), in a Couette geometry (diameter of the inner cylinder 17 mm and 0.25 mm gap). Samples are supported on a layer of perfluoro-methyl-decaline, whose density ($d = 1.95$) is higher than the density of the suspensions, poured in the bottom of the geometry in order to avoid jamming in this geometry part. The following protocol is applied: the suspension is first sheared for 1 min with a low stress, σ_{ref} below the jamming transition, and then sheared for 10 s with a constant stress, during which the shear rate is recorded. Finally, the suspension is sheared again with the previously applied stress value, σ_{ref}, to check whether irreversible aggregation or structures have been induced. The samples' volume fractions are measured by dry content weighting and are varied from 40.5% ± 0.2% up to 45.5% ± 0.2%.

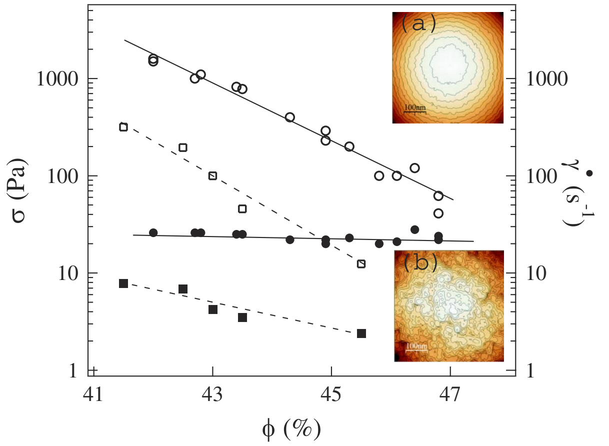

FIG. 1 (color online). Critical shear stress, σ (solid symbols), and shear rate, $\dot{\gamma}$ (open symbols), at the jamming transition for suspensions of bare silica particles (circle symbols) and roughened particles (square symbols) as a function of their volume fraction, ϕ. Lines are guides to the eye. The diameter of the particles is 1 μm. Inset: AFM images of the surface of the particles. Diameter of the particles is 1.5 μm. Distance between level lines is 5 nm. (a) Bare particle. (b) Rough particle.

Whatever the volume fraction, at low shear rates, the suspensions flow. Then, when a critical shear rate (corresponding to a critical shear stress) is reached, the viscosity of the suspension diverges: this is the jamming transition. The critical values of both shear rate and shear stress are reported in Fig. 1 as a function of the suspension volume fraction. As previously described [2], the abrupt increase of the viscosity of the suspension [Fig. 2(a)] is accompanied by stress fluctuations. One observes that the jamming transition occurs at lower shear rates, shear stresses, and volume fractions when particles are roughened. Whereas the hydrodynamic force has been reduced by a factor of 2, the critical shear stress at the jamming transition is reduced by 1 order of magnitude. This demonstrates the importance of collective effects at the transition. This result allows the measurement of the normal stress in cone-plate geometry,

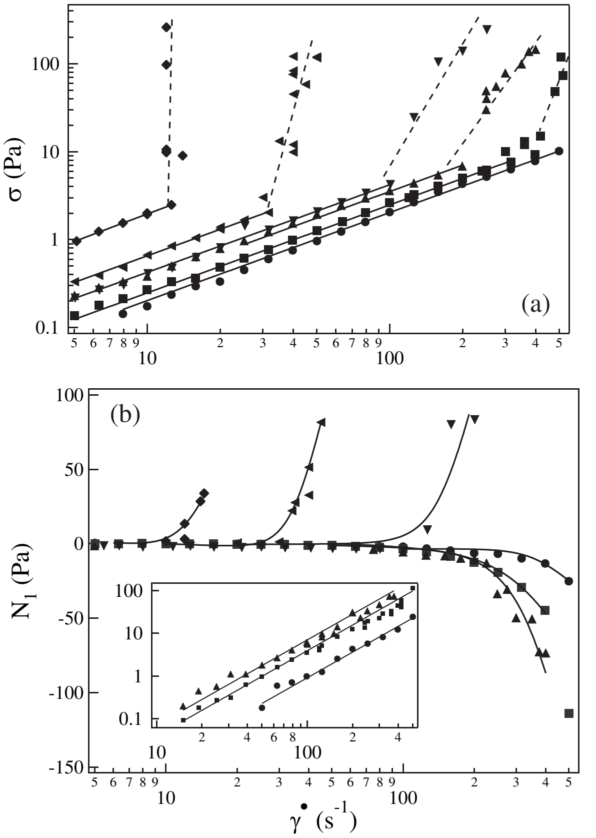

FIG. 2. (a) Shear stress increase as a function of the shear rate for different particle volume fractions (●, 40.5%; ■, 41.5%; ▲, 42.5%; ▼, 43%; ◀, 43.5%; ◆, 45.5%). Below the jamming transition, continuous lines are linear fits of the data. Above the transition, dashed lines are guides to the eye. (b) Evolution of the first normal stress difference, as a function of the applied shear rate, for the same suspensions. Inset: Absolute value of the first normal stress difference as a function of the shear rate, below the jamming transition, for $\phi = 40.5\%$ (●), $\phi = 41.5\%$ (■), and $\phi = 42.5\%$ (▲). Solid lines are quadratic fits to the data.

and all the subsequent experiments will be performed with rough particles.

Let us now consider normal force measurements. We use the same strain-controlled rheometer, along with a cone-plate geometry of radius of $R = 12.5$ mm and angle of 0.04 rad. With this geometry, the normal force F_N exerted by the suspension on the cone is measured. Assuming that the shear is linear along the gap of the geometry, the measured normal force is proportional to the first normal stress difference, $N_1 = 2F_N/\pi R^2$ [13]. The upper cone will thus be attracted towards the base plate for negative values of N_1 and pushed away for positive values. At low shear rates, whatever the volume fraction of the suspension, the first normal stress difference is negative [Fig. 2(b)]. Negative values of the first normal stress difference may be attributed to strong hydrodynamic forces [5], whereas Brownian forces would contribute to positive values of N_1. More quantitatively, the Péclet number of the flow is of the order of $\mathrm{Pe} = \frac{\sigma a^3}{k_B T} \sim 15$, in agreement with Pe values for which negative first normal stress differences were measured for latex particles [7]. Moreover, the absolute value of N_1 increases with the tangential stress value according to $|N_1| \sim \dot{\gamma}^2$ [Fig. 2(b), inset]. However, linearity of the Stokes flow implies that the stress tensor linearly depends on the applied shear rate, through a microstructure tensor μ_{ij} that depends on the organization of the particles under flow:

$$\sigma_{ij} = \eta \mu_{ij}(\dot{\gamma})\dot{\gamma}. \tag{1}$$

Thus, our observation implies that the microstructure itself linearly depends on the applied shear rate. In other words, the anisotropy of the particles' microstructure increases linearly with the applied shear rate. At high shear rates, stress fluctuations are observed when the jamming transition occurs. Both the mean values of the tangential stress [Fig. 2(a)] and of the normal stress diverge. Nevertheless, the behavior dramatically depends on the volume fraction of the suspension. (1) At low volume fractions ($40.5\% \leq \phi \leq 42.5\%$), close to the jamming transition, the first normal stress diverges by negative values [Fig. 2(b)]. More precisely, fluctuations of the tangential stress are accompanied by negative fluctuations of the first normal stress difference, in phase with the tangential stress fluctuations [Fig. 3(a)]. (2) Then, at higher volume fractions ($43\% \leq \phi \leq 45.5\%$), the first normal stress difference diverges by positive values [Fig. 2(b)]. In this case, the tangential stress fluctuations, observed above a critical shear rate, are associated with positive normal force fluctuations, in phase with the tangential stress fluctuations [Fig. 3(b)]. In both cases, the reversibility of the microstructure responsible for these stress fluctuations was checked by shearing the suspension at low shear rate before and after fluctuations occur.

These observations clearly demonstrate that the percolation of the stress tensor under flow is anisotropic. For a similar tangential stress fluctuation, one may observe a negative or a positive first normal stress difference, depending on the volume fraction of the suspension. The divergence of N_1 by negative values at low volume fractions may be described by an increase of the anisotropy of the suspension, similar to the mechanism described at lower shear rate values. The hydrodynamic clusters are large and concentrated enough to jam the suspension, but do not organize in such a way that the suspension becomes dilatant. On the contrary, at higher volume fractions, each tangential stress fluctuation is associated with an increase of the first normal stress difference: the suspension is dilatant.

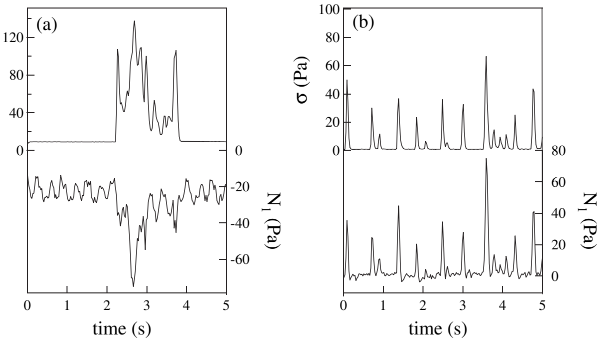

FIG. 3. Tangential and normal stress fluctuations under flow. (a) Volume fraction $\phi = 42.5\%$ and shear rate $\dot{\gamma} = 250\ \mathrm{s}^{-1}$. Tangential stress fluctuations (left scale) are accompanied by negative normal stress fluctuations (right scale). (b) $\phi = 45.5\%$, $\dot{\gamma} = 10\ \mathrm{s}^{-1}$. The normal stress fluctuates by positive value, in phase with the tangential stress.

The values of the tangential stress and the first normal stress differences are correlated during fluctuations: the first normal stress difference increases linearly with the tangential stress (Fig. 4). In order to get insight into the structure of the suspension in the regime of high shear rate, we observed the particles' organization using confocal

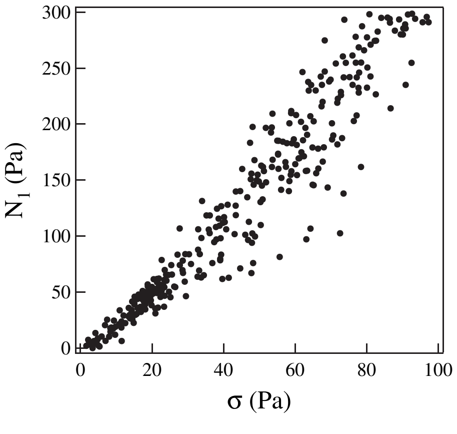

FIG. 4. Correlation between the first normal stress difference N_1 and the tangential stress σ in the jammed regime. The volume fraction is $\phi = 45.5\%$ and the applied shear rate $\dot{\gamma} = 20\ \mathrm{s}^{-1}$.

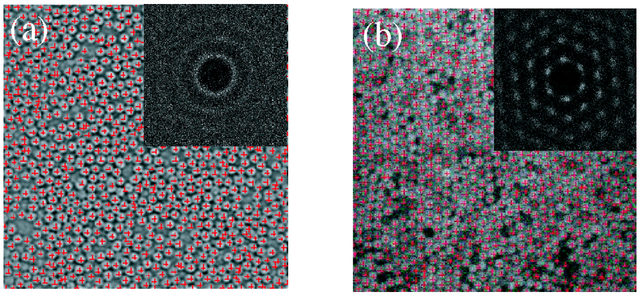

FIG. 5 (color online). Confocal images of suspensions at rest (a) and just after shear above the jamming transition (b). The Fourier transforms of the centers of the particles are inserted. Volume fraction of the particles is 50%, in a mixture water/glycerol (23/77), w/w.

microscopy. The sample is sheared with a homemade cone-plate shear cell (2°, radius 50 mm) placed on a confocal microscope (Leica TCS-4D, oil immersion × 100 objective, equipped with an Ar-Kr laser). In order to allow the particles visualization, they are rendered fluorescent by covalently grafting of fluorescein isothiocyanate (FITC, isomer I, Sigma) [14] and suspended in a mixture of water and glycerol (23/77, w/w), whose refractive index matches the particles' refractive index. The volume fraction of the suspension is $50\% \pm 0.5\%$ [16]. The image plane is parallel to the bottom plate of the shear cell and images are located 25 mm away from the cell axis. The axial resolution of the optics system is 0.45 ± 0.25 μm, lower than the diameter of one particle. Because of the acquisition time of a confocal image, images of the suspension at shear rates higher than the critical jamming shear rate $\dot{\gamma}_c$ could not be obtained. We thus used the following protocol: the suspension is sheared for 1 min at a shear rate $\dot{\gamma}$ higher than $\dot{\gamma}_c$, shear is ceased, and an image is acquired less than 1 s after shear cessation. Two images of the suspension, at rest and after shear above the jamming transition are given in (Fig. 5), as well as the Fourier transform of the centers of the particles. Whereas, at rest, the particles exhibit liquidlike order, after shear, the suspension is much more heterogeneous. High density regions exhibiting crystalline order are separated by lower density defects. Although this structure is similar to that of polycrystalline materials, the rheological response of the suspension is strikingly different. Indeed, polycrystalline materials generally exhibit plastic flow behavior, in which the tangential stress is a power-law function of slope smaller than unity, of the shear rate. The motion of the defects is responsible for this behavior. On the contrary, in the shear regime where crystallites are observed, the suspension is highly shear thickening and becomes dilatant. The origin of dilatancy when concentrated suspensions are sheared is similar to dilatancy in granular materials [17]: each particle needs to find room in order for the system to flow, and the system thus expands. Nevertheless, the elementary unit responsible for the dilatancy is the crystallite rather than the particle itself.

The use of rough particles thus allows detailed exploration of the jamming transition of colloidal suspensions under flow. At a given shear rate, giant fluctuations of the tangential stress are observed. Nevertheless, depending on the volume fraction of the suspension, they are accompanied by fluctuations of the first normal stress difference of different signs: whereas for the smaller volume fractions, the opposite surface of the shear cell are attracted, and at higher volume fractions, the suspension becomes dilatant. This last behavior is associated with the apparition of crystallites under flow.

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