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From shear thickening to shear-induced jamming

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We show that applying shear to a suspension may lead to either thickening or permanent jamming, depending on the volume fraction of the considered suspension. Interpreting measurements of conductivity under shear, we invoke a dynamical structural transition to explain the origin of shear thickening in suspensions of non-Brownian particles. We finally suggest that shear thickening and shear-induced jamming be regarded as two consequences of this dynamical structural transition.

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Shear thickening and jamming are questioning phenomena from both the fundamental and the industrial point of view. Both are very often observed with industrial suspensions and may cause severe problems in many processes, such as mixer blade damage or jamming in a transport pipe [1,2]. First observed in 1938 by Freundlich and Röder [3] in suspensions of hard spheres, shear thickening is the increase of apparent viscosity with increase in shear rate [1,4]. In this paper, we show that, when a sufficiently concentrated suspension of non-Brownian particles is submitted to shear, it may exhibit either shear thickening or permanent jamming (i.e., become pasty), depending on the volume fraction of the considered suspension. We subsequently measure different components of the conductivity tensor of a suspension under shear and invoke the dynamical order-disorder transition scenario proposed by Hoffman [5–7] to explain the origin of shear thickening in suspensions of non-Brownian particles. Finally, we suggest that shear thickening and shear-induced jamming be seen as two consequences of this same dynamical structural transition.

The system considered here is a suspension of bismuth oxychloride (BiOCl) in a very dilute polyelectrolyte—namely a short poly(sodium acrylate)—solution. The BiOCl particles are non-Brownian (mean equivalent diameter of 6 μm, measured with a Malvern granulometer), highly anisotropic, and have irregular shapes. The polydispersity of these particles is moderate as it corresponds to a measured uniformity of 40%. The uniformity is defined as the mean deviation to the median diameter of the size distribution. Without additive, the BiOCl particles are very hydrophobic: they strongly aggregate in pure water.

Once dispersed, BiOCl particles exhibit a rheological behavior that depends strongly on their volume fraction. At volume fractions inferior to 17%, the suspension is a Newtonian liquid. Between 17% and 22.5%, the suspension is a liquid that behaves as follows. It is shear-thinning at low shear rates; the viscosity decreases when the shear rate increases. It is then shear-thickening at higher shear rates and shear thinning again at the highest accessible shear rates. Between 22.5% and 31.5%, an amazing behavior takes place. It consists of a liquid that can be transformed into a persisting paste by moderate shearing. This phenomenon, which we have dubbed *shear-induced jamming*, is spectacular: a whole liquid sample becomes pasty in a few seconds when it is moderately stirred with a spatula. The behavior of the corresponding shear-induced jammed state is also noticeable: while this state is indefinitely stable kinetically, it breaks down and becomes liquid again if slightly vibrated. Finally, above 31.5% volume fraction, the suspension looks like a paste and behaves like a solid, symptomatic of a jammed state [2,8,9].

Let us first focus on the range of volume fraction (between 17% and 22.5%) where the suspension is a liquid that exhibits shear thickening in a limited range of shear rates. In order to study this phenomenon quantitatively, we used a stress-controlled rheometer (TA Instruments) with a plate-plate geometry and a gap of 2 mm, large compared with the particle size. We made viscosity measurements in a time scale appropriate to avoid any influence of water evaporation or particle sedimentation and scratched the inner face of the geometry to prevent any slippage. Figure 1(a) shows the measured viscosity as a function of the imposed shear stress. The two samples with the lowest volume fractions show a Newtonian behavior. At fractions higher than 22.5%, no reproducible rheology experiments could be performed. All the other samples (from 17.5% to 22.5%) display the same viscosity profile as a function of the imposed shear stress. At low stress (less than approximately 5 Pa), the suspension behaves as a shear-thinning yield-stress fluid: viscosity decreases from infinity. At higher stress, shear thickening takes place: viscosity increases with shear stress. At even higher stress, above approximately 100 Pa, the suspension becomes

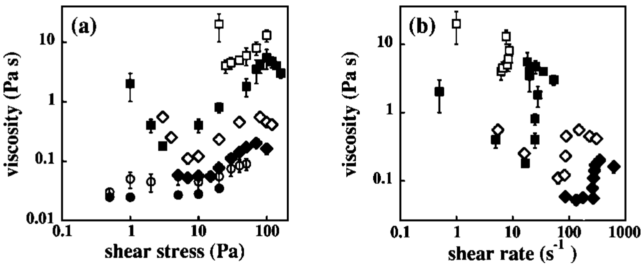

FIG. 1. Measured viscosity of a BiOCl suspension as a function of the applied shear stress (a) and as a function of shear rate (b) in a logarithmic scale. Each symbol refers to a different volume fraction; full circles, 11.5%; empty circles, 16.5%; full diamonds, 17.5%; empty diamonds, 19%; full squares, 21%; empty squares, 22.5%.

shear thinning again. It is worth emphasizing here that all these viscosity profiles are perfectly reversible: they can be obtained either by increasing or by decreasing the applied shear stress. This whole behavior is a general feature of all concentrated suspensions of nonaggregating solid particles [1]. In Fig. 1(b), we have represented the measured viscosity as a function of shear rate for four samples. The range of shear rate within which the suspension shows shear thickening appears extremely limited. In particular, for the two highest volume fractions (21% and 22.5%), the viscosity versus shear rate profile almost bends backward. This part of the viscosity profile would be obviously unstable at controlled shear rate [10,11], leading to a clear discontinuity in viscosity [1,6].

For the structural origin of shear thickening, two distinct theories have been proposed in the framework of hard spheres suspensions. The first one relies on Reiner's [12] concept of entire layers of particles gliding over each other [4] and has been formalized by Hoffman [6,7]. According to this theory, in the regime of low shear stress, this layered flow of particles induces a shear-thinning behavior in the suspension. At some critical level of shear stress, a flow instability causes the particles to break out of their ordered layers and jam into each other, thereby inducing the rise in viscosity that defines shear thickening [6]. This microstructural dynamical transition from ordered layers to a jammed state within the flow has been called an order-disorder transition by Hoffman [6]. Note that this theory does not involve any ordering of the particles within the layers [5]. The second theory involves a shear-induced reversible flocculation of particles, or hydrodynamic clustering, which causes the increase in viscosity with increasing shear stress as the dynamical clusters become larger and larger [5,13,14]. Hoffman and others have used light [5–7] or neutron [15] scattering techniques to demonstrate the existence, in highly monodisperse colloidal suspensions of hard spheres, of ordered layers under flow. However, for polydisperse or anisotropic particles, such experiments have all failed to detect layering [5,16], which explains why the model of hydrodynamic clustering is the most often cited in the recent literature [5], in particular for suspensions of Brownian spherical particles [17].

We have performed conductivity measurements under flow in Couette cells (with a gap of 1 mm) at controlled shear rate [18]. The conductivity at low frequency (20 kHz) of the shear-thickening BiOCl suspension has been measured in the directions of the vorticity ((S_Z)), the velocity ((S_V)), and the velocity gradient ((S_G)). The whole setup is described in detail in Ref. [18]. It enables us to measure the three diagonal components of the conductivity tensor but not the whole tensor. We have found differences between the three measured conductivity values for a certain range of shear rates. We have thus defined two anisotropies $(S_V/S_G)-1$ and $(S_Z/S_G)-1$. Figure 2(a) and 2(b) show each of these two anisotropies versus shear rate, for a system corresponding to 18% of particles in volume. In both cases, the conductivity is roughly isotropic at rest and at high shear rate, and strongly anisotropic at low shear rate. The anisotropy in the conductivity abruptly decreases for a shear rate between 200 and 300 s^{-1}. It is important to point out that, according to our rheological measurements, the viscosity of this suspension (18% volume fraction) starts increasing at a shear rate of approximately 200 s^{-1}. Consequently, a dynamical transition within the flow between anisotropic and isotropic (as far as the three measured components of the conductivity tensor are concerned) structures takes place when the suspension becomes shear thickening. The difference, at low shear rate, between the conductivity in the direction of the velocity and that in the direction of the velocity gradient and of the vorticity is compatible with the two aforementioned models invoked to explain shear thickening. Indeed, an ordered flow of adjacent layers (or at least pieces of layers), concentric with the Couette cell, gliding over each other in the direction of the velocity, would result in screening the conductivity of the ions in the direction perpendicular to the layers, i.e., in the direction of the velocity gradient. Nevertheless, one could imagine the same screening effect resulting from the presence of anisotropic hydrodynamic clusters oriented in the flow-vorticity plane. However, in this latter case, the anisotropy would go on increasing as the liquid enters the shear-thickening regime of shear rate, since the anisotropic clusters would be larger and larger. Such an increase of the anisotropy is not observed experimentally. Our conductivity measurements thus confirm the hypothesis of an at least partially layered flow at low shear rate, and of a disordered (or, at least, less ordered) flow at high shear rate. However, these experiments provide no direct insight into the structure either before or after the transition. Let us mention the slight residual difference between S_Z and S_V at low shear rate, which means that these gliding layers of particles are not perfectly concentric with the Couette cell and are slightly tilted with its surface. We interpret the anisotropy-isotropy transition of the measured conductivity as indirect but compelling evidence that a dynamical structural transition within the flow is at the origin of the phenomenon of shear thickening for suspensions of non-Brownian anisotropic particles.

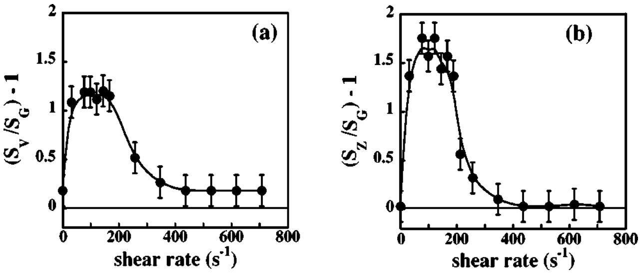

FIG. 2. Conductivity anisotropies $(S_V/S_G)-1$ (a) and $(S_Z/S_G)-1$ (b) as a function of the applied shear rate for a BiOCl suspension of 18% volume fraction. In each case, the curve is only a guide to the eye.

Between 22.5% and 31.5% volume fraction, the system can be either liquid or pasty. In this region, a moderate manual shearing of the liquid phase induces a dynamical jamming transition. However, the so-called shear-induced jammed state is only metastable. Indeed, when a tiny drop of liquid phase is put into contact with a shear-induced jammed sample at the same volume fraction, the drop instantly grows

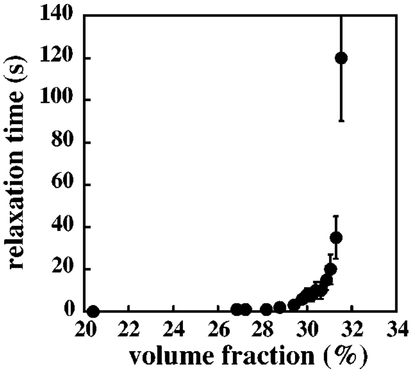

FIG. 3. Relaxation time (defined in the text) of a BiOCl shear-induced paste submitted to a constant vibration, as a function of the particle volume fraction.

and the whole sample becomes liquid in a few seconds. The metastability of the shear-induced jammed state is confirmed by another observation: the shear-induced paste breaks down when vibrated and comes back to the stable liquid state. Neither reproducible rheology measurements nor reproducible DWS (diffusing wave spectroscopy) experiments could be performed within the corresponding range of volume fraction. Finally, we could only perform a more qualitative experiment to characterize the metastability of the shear-induced jammed state. Figure 3 shows the relaxation time of this shear-induced jammed state submitted to a constant vibration, as a function of the particle volume fraction. This measurement consists of inducing the jammed state in the whole sample, putting it in contact with a vibrator set at 1000 rounds per minute, and recording the relaxation time necessary for the whole sample to become liquid again. A very strong divergence of this relaxation time appears for a volume fraction of 31.5%: above this volume fraction, the system is irreversibly trapped into the jammed (or pasty) state [2]. This measurement thus provides a means to locate precisely the border between the metastable shear-induced jammed state and the irreversible jammed state induced by an increase of the particle volume fraction.

In conclusion, the observed jamming transition, induced by an increase of the particle volume fraction (above 31.5%), can also be induced by shear at volume fractions below 31.5%. The question that remains open concerns the relation between the shear-induced jammed state and the shear-thickened state. The former is kinetically stable and has a finite lifetime, even when it is vibrated, whereas the latter is transient and persists only while the shear is applied. However, this difference is only quantitative: as can be seen in Fig. 3, the relaxation time tends towards zero continuously when the volume fraction decreases. It is thus impossible to locate precisely the border between the shear-thickening liquid state and the metastable shear-induced jammed state. We consequently suggest that the shear-induced jamming transition could result from the same structural transition invoked to explain shear thickening in our suspensions of non-Brownian anisotropic particles. Both phenomena would thus be two different consequences of the same cause. The two different outputs only come from the difference in volume fraction. If the volume fraction is in the range 22.5–31.5 %, the shear-induced jammed state is kinetically stable, whereas if the volume fraction is below 22.5%, it is unstable and only leads to shear thickening. In other words, in the former case, the volume fraction is too high and there is not enough free space for the particles to unjam. Conversely, in the latter case, there is enough space for the particles to unjam and the dynamical order-disorder transition is reversible: viscosity goes through the same profile if the shear stress is increased or decreased.

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