Jamming, Two-Fluid Behavior, and "Self-Filtration" in Concentrated Particulate Suspensions

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We study the flow of model hard-sphere colloidal suspensions at high volume fraction Φ driven through a constriction by a pressure gradient. Above a particle-size dependent limit Φ_0, direct microscopic observations demonstrate jamming and unjamming—conversion of fluid to solid and vice versa—during flow. We show that such a jamming flow produces a reduction in colloid concentration Φ_x downstream of the constriction. We propose that this "self-filtration" effect is due to a combination of jamming of the *particulate* part of the system and continuing flow of the *liquid* part, i.e., the solvent, through the pores of the jammed solid. Thus we link jamming in colloidal and granular media with a "two-fluid-like" picture of the flow of concentrated suspensions. Results are also discussed in the light of the original experiments of Reynolds on dilation in granular materials.

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In this Letter we consider the pressure-driven flow of concentrated suspensions of model colloidal particles. Concentrated suspensions of particles in liquid solvents are ubiquitous in "soft matter" technology (cosmetics, foods, building materials, paints, detergents, pharmaceuticals, waste management) as well as in natural phenomena (soil and wet sand, formation of porous rocks and sediments, landslip, etc.). Much industrial processing of soft matter, and many examples of natural flow phenomena, involve pressure-driven flow; moreover, the flow often features "complex" geometries where convergent and divergent elements generate extensional components of strain (e.g., constricting and widening pipes in a transport system). Fundamental studies of suspension behavior in such complex flow remain rare in comparison to the wealth of studies of soft matter under simple shear [1]. Rheometrical work on concentrated suspensions has demonstrated complicated effects such as stress-induced thickening, erratic flow response, and fluctuating viscosity [2,3].

In the rheology of very concentrated suspensions and other crowded soft matter systems a concept that has excited much recent speculation [4] and theoretical and experimental work [5–9] is that of *jamming*. Here we shall define jamming as *the conversion of a liquid system into a solid by imposed stress*. Jamming is very obvious in the "hourglass" flow of dry sand where stress-supporting solid arches form across the convergence, even though the sand typically flows more or less like a liquid in simpler geometries. "Dilation" of wet sand is a related example with a venerable history, having been considered more than 100 years ago by Reynolds [10]. However, there remains no clear picture of the generic conditions required for nor the consequences of jamming in soft matter. Our study of a model system is aimed toward such a goal.

Our experimental system consists of polymethylmethacrylate (PMMA) spheres sterically stabilized by short grafted polymers (polyhydroxystearyl alcohol), suspended in a nonpolar hydrocarbon solvent (decalin). This system is a good model of the conceptual "hard sphere" suspension [11]. The particles can be manufactured in almost monodisperse batches (polydispersities typically less than 6%–7%). Here we study three batches of particles of radii 318 ± 10, 656 ± 20, and 1000 ± 50 nm, respectively, spanning the particle-size range from "colloidal" (where Brownian motion dominates in dilute suspensions) toward "granular" where gravity is dominant.

We first demonstrate quantitatively one important and striking consequence of jamming in a concentrated suspension: that jamming in a convergent flow can induce a significant reduction in concentration downstream of the constriction, what one might call a "self-filtration" behavior by the suspension. We study the effect of convergent flow on concentration by extracting a portion of a bulk sample through a constriction—put simply, by sucking a small volume out of a bulk cell through a narrow-barrelled syringe and comparing the resulting "extracted" concentration Φ_x with the bulk concentration Φ_b.

Samples are prepared as follows. Dilute suspensions are centrifuged until the particles form "solid" sediments (see below for a discussion of jamming effects on sedimentation). To obtain given bulk volume fractions measured amounts of solvent are added to the sediments. Diluted samples are thoroughly remixed to ensure a homogeneous bulk. In practice we prepare *pairs* of samples that have been subjected to exactly the same treatment (i.e., duration and rate of centrifugation, etc.) and that thus have equal Φ_b to within the (small) uncertainties associated with measuring masses of sediment and added solvent. (We use pairs of samples for the comparison because, if $\Phi_x \neq \Phi_b$, extracting some sample by syringe to measure Φ_x and then measuring Φ_b for the *same* sample would introduce systematic errors.) For one

member of the pair we obtain the bulk colloidal *mass* fraction by scooping out a measured mass of the sample, allowing all solvent to evaporate, and measuring the mass of solids remaining. From the other member of the pair we extract not by scooping but by *syringe,* and similarly measure the mass fraction of this extracted portion. We convert mass fractions into volume fractions Φ (the more common measure of concentration in studies of colloidal suspensions) assuming a particle density $\rho_p = 1.188\ \mathrm{g\,cm^{-3}}$ (the bulk density of PMMA) and solvent density $\rho_s = 0.897\ \mathrm{g\,cm^{-3}}$. If there is no effect of convergent flow in the syringe on extracted volume fraction, we should find $\Phi_x = \Phi_b$. Large numbers of experiments are carried out on rediluted and newly centrifuged pairs of samples to ensure that statistical variations due to measurement imprecision are minimized.

There are a number of ways of estimating Φ for a colloidal suspension, none of which is without drawbacks. As is well known [12] the "mass fraction" measure of Φ tends to give systematically lower values compared to the other common measure in the PMMA system, that based on mapping experimental phase boundaries onto computer simulated fluid-crystal hard-sphere phase coexistence boundaries. Given the core-shell nature of the sterically stabilized particles, no simple measure can give an *absolutely* correct result in the sense of a "true hard-sphere" volume fraction. The important point for this work is that all measures are carried out in the same way giving volume fractions that are consistent and comparable with each other. In these experiments, given the small volumes (see below) of extracted suspension, the possible experimental errors are minimized by using the mass fraction to obtain Φ; dilution and mapping onto phase boundaries is simply not possible with such small sample volumes. However, care must be taken when comparing the numerical values of Φ given here with those quoted elsewhere in the literature, which are often obtained by mapping onto the computer-simulation phase diagram.

All experiments are carried out in identical geometry: the "bulk" cells are cylindrical glass cuvettes of diameter 25 mm with sediment heights ≈ 2.5 cm giving a total sample volume of $\approx 12\ \mathrm{cm^3}$; the syringes used have maximum volume 1.0 ml with an entry barrel internal diameter of 1.6 mm; volumes extracted are typically 0.4–0.5 ml, i.e., always $<5\%$ of the total bulk volume. The "sucking" procedure is as follows: the syringe plunger is pulled out quickly by hand to generate an empty barrel volume of ≈ 0.6 ml, so that a pressure drop ($P_b/P_{\mathrm{atm}} \approx 0.03$) is instantaneously applied between the outside surface of the bulk at atmospheric pressure P_{atm} and the surface inside the syringe barrel at reduced pressure P_b. In the majority of the experiments reported here, we study this limiting case of a suddenly applied initial pressure drop (the pressure drop slowly decreases as the sample is extracted and enters the syringe barrel). A few experiments have also been carried out using larger initial pressure drop and using narrower constrictions.

Results for Φ_b vs Φ_x are shown in Fig. 1, for the three particle sizes given above. As is clear, when Φ_b is above some limit volume fraction Φ_0 the sample "pumped" through the contraction into the syringe barrel has a significantly reduced volume fraction $\Phi_x < \Phi_b$. The limit concentration Φ_0 is strongly dependent on particle size, decreasing with increasing particle size. Thus the effect is more visible with larger particles (approaching the granular scale), but even for the smallest particles, very much within the *colloidal* regime, there is a clear effect at the highest bulk $\Phi_b \approx 0.62$ (Fig. 1). The reduction in extracted volume fraction is somewhat more severe with a smaller constriction geometry or with a larger initial pressure drop (see, for example, open circles and open diamond, respectively, in Fig. 1), though we have yet to carry out detailed investigations on the effect of different pressure drops. In any case, since extraction of samples from bulk for, e.g., observation in a microscope or measurement in a rheometer is very often achieved using syringes, pipettes, etc., it is important for experimentalists to be aware of the sensitivity of key parameters such as volume fraction to such "processing" prior to experiments. Of course, similar flow situations involving concentrated suspensions are common in technological applications such as product delivery, waste processing, and so on.

Although it seems that this self-filtration effect has not been reported in the colloidal literature, actually it is not too surprising if we consider the suspension as a "two-fluid" system, that is, a combination of *particulate fluid* and *liquid solvent,* where interaction between the particles

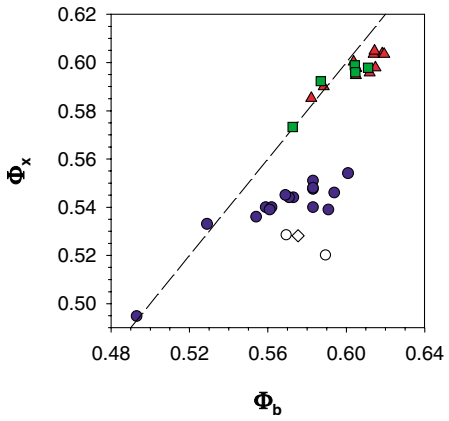

FIG. 1 (color online). Bulk volume fraction Φ_b vs volume fraction extracted by syringe Φ_x. The line indicates $\Phi_b = \Phi_x$, i.e., the expected result if convergent flow into syringe has no "self-filtration" effect. Filled circles, empty diamond, and empty circles, particle radius 1000 nm; filled triangles, radius 656 nm; filled squares, 318 nm. Empty circles show experiments extracting through a fine needle rather than a syringe barrel; the diamond shows an experiment using a larger initial pressure drop. Error bars on Φ are $\sim \pm 0.005$, i.e., approximately the size of the symbols.

may lead to a rheological "separation" of the two fluids. There are a few studies of *squeeze flow* where a separation between solvent and dispersed phase is discussed [13,14], but such a two-fluid picture of flow, though familiar in studies of polymer systems, is not often encountered in the colloidal literature. We propose that our results can be explained in a two-fluid spirit as an "extreme" rheological separation of the particulate and solvent parts of the suspension. The particles *jam* and form a solid that resists the pressure drop and does not flow at all. Meanwhile the solvent, remaining liquid, cannot resist the pressure gradient and continues to flow through the pores of the jammed colloid. Hence, there is an increased flow rate of solvent relative to particles, resulting in a reduced downstream particle volume fraction.

But is colloidal jamming really responsible for the measurements in Fig. 1? To elucidate directly what is actually happening in our convergent pressure-driven flow, we have carried out direct observations by optical microscope. To enable microscope observations, the PMMA particles are suspended in a mixture of solvents (decalin and tetralin) to partly match the particle refractive index and reduce multiple scattering, and samples are prepared (centrifuged) inside thin *rectangular* cuvettes. "Extraction" is achieved by inserting a cylindrical glass capillary into the sediment, internal diameter 1.0 mm, connected to a syringe whose plunger is withdrawn using a fixed-speed syringe pump. The flow in the region of the capillary tube entrance is observed with bright field microscopy, the field of view positioned at the region around the entrance to the capillary as shown in Fig. 2(d). Results

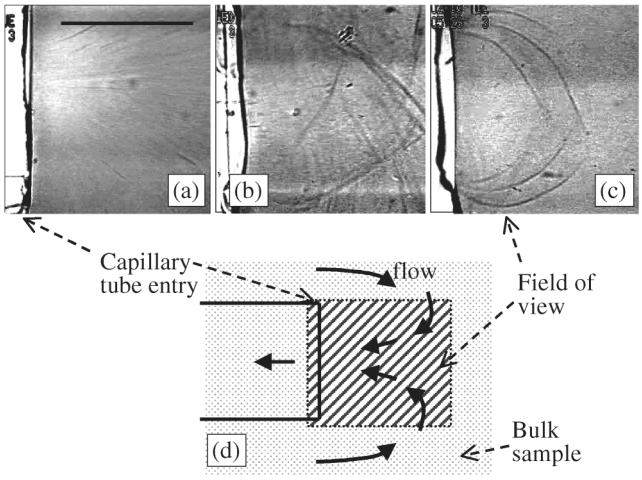

FIG. 2. Images of the flow of a suspension of 1000 nm colloids, volume fractions (a) $\Phi = 0.534$; (b) $\Phi = 0.578$; (c) $\Phi = 0.60$. The horizontal bar in (a) is 0.5 mm. At the left of each image the capillary entrance can be seen, as indicated by the schematic in (d) showing the viewing and flow geometry. In (b) and (c) dark lines form in archlike patterns around the end of the capillary, while flow in (a) is smooth. Still images are taken from digitized movies; see Ref. [15], experiments 2, 3, and 6 for (a), (b), and (c), respectively.

in the form of digitized movies are available at [15], while Figs. 2(a)–2(c) and 3 show extracted still images. In all but one of the movies, the height of the field of view corresponds to $\sim$1 mm, and the entry to the capillary can be seen at the left of the picture. At such low magnification individual colloids cannot be resolved. In one movie (Ref. [15], experiment 4) the magnification is increased by a factor of 10 and the field of view is centered $\sim$0.5 mm diagonally from the lower corner of the capillary entry; in this case the particles, 1000 nm radius, are just resolvable.

To summarize our observations, flows at high Φ are typically very erratic, demonstrating very clear *transient jamming* of the samples in the region of the tube entrance, involving slowing of flow, sudden "fracture" events followed by speedup, repeated rejamming, and so on. Jamming as a transient "conversion" of flowing liquid to stationary solid is strikingly apparent. In the movie at higher magnification (Ref. [15], experiment 4) the sample, blurred while flowing (i.e., liquid), can be seen to repeatedly momentarily freeze (become solid). Note that migration of particles to the walls of the syringe entry, which might potentially allow a central channeled flow at lower Φ, is not observed at these high volume fractions.

At the highest concentrations, flow is localized near the entry of the capillary (Ref. [15], experiment 6). However, dark lines form in archlike shapes, often traveling in sudden "waves" or "shocks" out from the end of the capillary [Figs. 2(b), 2(c), and 3]. The shocks are associated with subsequent speedup of the flow, i.e., collapses of the jammed particle structure. Collapse is followed by rejamming, generating erratic changes in flow speed. The most likely optical origin of the dark lines is small-angle scattering (their appearance is very sensitive to refractive index contrast consistent with this), indicating localized changes in volume fraction. The exact nature of these waves or shocks of dark lines is unclear. They exhibit similarities with density or kinematic waves observed in granular media, such as hourglass flow of sand [16].

As Φ_b is lowered toward the limit Φ_0, the jam-collapse-rejam behavior cycles faster (Ref. [15], experiments 3 and 4), suggesting that below some limiting concentration jams effectively collapse immediately, in other words the sample no longer jams during flow. Below Φ_0, we indeed observe smooth nonjamming flow of the suspension into the convergence [Fig. 2(a) and Ref. [15], experiment 2].

Continued flow of the reduced volume fraction (partially "self-filtered") sample downstream presumably accounts for the *transience* of the jamming: jams give way just as, in an hourglass flow of sand, solid arches give way to allow flow.

Collapse of jams apparently involves a sliding-solid fracturelike behavior (Ref. [15], experiment 5), sliding occurring at the dark lines visible in the sample. We speculate that such sliding fracturing may also be a

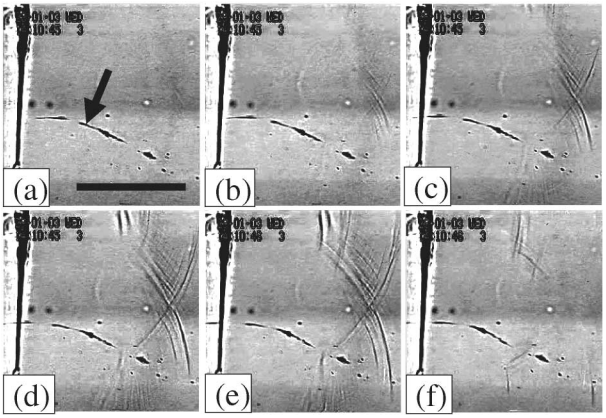

FIG. 3. A sequence of images of the flow of a suspension of 318 nm colloids, volume fraction $\phi = 0.61$. The still images (a)–(f) are each separated by 0.08 s. At the left of each image the entrance of the capillary can be seen. In the top left image, the horizontal bar is 0.5 mm, while the arrow shows a line of dust particles whose motion and distortion give an approximate idea of the velocity field at the capillary entrance. Dark lines form [toward the right hand side of images (b)–(e)] in archlike crossing configurations, then disappear very suddenly in (f) as the jam "collapses." See movie at Ref. [15], experiment 1.

consequence of the combination of jamming and solvent permeation through the jam. Fractures may be localized by geometry-dependent pressure gradients driving solvent through the pores of the jams into regions of decreased particle concentration—sometimes called "microcracks" in the rock fracture literature—which we associate with the dark lines we observe in the suspensions. The excess solvent in these regions lubricates localized sliding ("cataclastic shear bands" [17]) of opposing solid regions. Such a "lubricated slide" picture has been proposed for the slip of porous rocks in earthquakes (see, e.g., [17]). The possibility that model suspensions might ultimately be used as simple "soft" analogues of geological systems deserves further investigation.

A further demonstration of jamming is provided by simple observations of the behavior of sediments of the largest particles. Though apparently solid under careful handling, we have observed that the sediment formed after centrifugation very easily *reliquifies* under a slight deliberate *lateral* shaking. The sediment thus behaves as an example of what has been called "fragile matter" [8]: it solidifies (jams) under application of a *unidirectional* force in the centrifuge (or over a longer time period in normal gravity) but cannot support (liquifies under) small stresses applied in *any other direction*.

Finally we note that the sucking experiments may be compared to the early granular experiments of Reynolds, who squeezed rubber balloons filled with ball bearings and water [10]. Reynolds observed that on applying pressure, water was drawn *into* the balloon—the reverse of the case of a balloon completely filled with a simple fluid, which would be forced *out*. The ball-bearing system inside the balloon can strain only by decreasing its local volume fraction, i.e., by *dilation* and increase of the total volume of the flexible balloon. Water is then naturally drawn in to fill the extra volume. Our observations in colloidal suspensions may also be interpreted in terms of dilation in the zone of convergent flow. To allow flow in response to the applied pressure drop, the region of sample just downstream of the convergence must dilate, i.e., decrease its volume fraction by taking on more solvent; but this solvent must come from somewhere, i.e., from the region upstream, hence generating an increase in upstream Φ. This increase in Φ in turn leads to jamming of the colloidal particles.

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[15] See EPAPS Document No. E-PRLTAO-92-033417 for video files (digitized movies) depicting several experiments. A direct link to these videos may be found in the online article's HTML reference section. The video files may also be reached via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.
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