Jamming, two-fluid behavior and ‘self-filtration’ in concentrated particulate suspensions

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We study the flow of model experimental hard sphere colloidal suspensions at high volume fraction \( \Phi \) driven through a constriction by a pressure gradient. Above a particle-size dependent limit \( \Phi_b \), 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 \( \Phi_c \), downstream of the constriction. We propose that this ‘self-filtration’ effect is the consequence of 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 the concept of 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 Osborne Reynolds’ original experiments on dilation in granular materials.

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In this paper 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. Rheometrical work on concentrated suspensions has demonstrated complicated effects such as stress-induced thickening, erratic flow response, and fluctuating viscosity.

In the rheology of very concentrated suspensions and other crowded soft matter systems a concept that has excited much recent speculation and theoretical and experimental work 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 ‘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. 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 stabilised by short grafted polymers (polyhydroxystearyl alcohol), suspended in a non-polar hydrocarbon solvent (decalin). This system is a good model of the conceptual ‘hard sphere’ suspension. The particles can be manufactured in almost monodisperse batches (polydispersities typically less than 6-7%). Here we study three batches of particles of radii \( 318 \pm 10 \text{ nm}, 656 \pm 20 \text{ nm and } 1000 \pm 50 \text{ nm respectively}, \) 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 \( \Phi_x \) with the bulk concentration \( \Phi_b \).

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. In practice we prepare pairs of samples which have been subjected to exactly the same treatment (i.e. duration and rate of centrifugation etc.) and which thus have equal \( \Phi_b \) 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 \( \Phi_x \) and then measuring \( \Phi_b \) 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 a portion not by scooping but by syringe, and similarly measure the mass fraction of this extracted portion. We convert mass fractions into volume fractions \( \Phi \) (the more common measure of concentration in studies of colloidal suspensions) assuming a particle density \( \rho_p = 1.188 \text{ g cm}^{-3} \) (the bulk density of PMMA) and solvent density \( \rho_s = 0.897 \text{ g cm}^{-3} \). If there is no effect of convergent flow in the syringe on extracted volume fraction we should find \( \Phi = \Phi_b \). A large number of experiments is carried out on rediluted and newly centrifuged pairs of samples to ensure that statistical variations due to measurement imprecision are minimised.

There are a number of ways of estimating \( \Phi \) for a colloidal suspension, none of which is without drawbacks. As is well known, the ‘mass fraction’ measure of \( \Phi \) 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-stabilised 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 so that we obtain 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 minimised by using the ‘mass fraction’ to obtain \( \Phi \); 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 \( \Phi \) 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 \( \approx 2.5 \text{ cm} \); 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 \( \approx 0.6 \text{ ml} \), so that a pressure drop \( (P_b / P_{atm} \approx 0.03) \) 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 \( \Phi_0 \) vs \( \Phi_x \) are shown in Figure 1 for the three particle sizes given above. As is clear, when \( \Phi_0 \) is above some limit volume fraction \( \Phi_x \) the sample ‘pumped’ through the contraction into the syringe barrel has a significantly reduced volume fraction \( \Phi_x < \Phi_b \). The limit concentration \( \Phi_0 \) 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 volume fractions. The reduction in extracted volume fraction is somewhat more severe with a smaller constriction geometry or with a larger initial pressure drop (see 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 drop. 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.

![FIG. 1: Bulk volume fraction \( \Phi_0 \) vs volume fraction extracted by syringe \( \Phi_x \). The line indicates \( \Phi_0 = \Phi_x \), i.e. the expected result if convergent flow into syringe has no ‘self-filtration’ effect. Filled circles, empty diamond and empty circles, particle radius 1000nm; filled triangles, radius 656nm; filled squares, 318nm. Empty circles show experiments extracting through a fine needle rather than syringe barrel; the diamond shows an experiment using a larger initial pressure drop. Error bars on \( \Phi \) are \( \approx \pm 0.005 \), i.e. approximately the size of the symbols.](image-url)
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 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 microphone 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 in the form of digitised movies are available at [15], while figures 2(a)-(c) and 3 show extracted still-images. In all but one of the movies, the height of the field of view corresponds to ∼ 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 centred ∼ 0.5 mm diagonally from the lower corner of the capillary entry; in this case the particles, 1000 nm radius, are just resolvable.

Summarising 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 speed-up, repeated re-jamming, and so on. Jamming as a transient ‘conversion’ of flowing liquid to stationary solid is strikingly apparent. In the movie of higher magnification (Ref. [15] experiment 4) the sample, blurred whilst flowing (i.e. liquid), can be seen to repeatedly momentarily freeze (become solid).

At the highest concentrations flow is localised near the entry of the capillary (Ref. [15] experiment 6). However dark lines form in arch-like shapes, often travelling in sudden ‘waves’ or ‘shocks’ out from the end of the capillary [Figs. 2(b) and (c) and Fig. 3]. The ‘shocks’ are associated with subsequent speed-up of the flow, i.e. collapses

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

FIG. 3: A sequence of images of the flow of a suspension of 318 nm colloids, volume fraction φ = 0.61. The stills (a) to (f) are each separated by 0.08 seconds. At the left extreme 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 from whose motion and distortion one may obtain an approximate idea of the velocity field flowing into the capillary entrance. Dark lines form towards the right hand side of images (b) to (e) in arch-like crossing configurations, then disappear very suddenly in (f) as the jam ‘collapses’. See movie at Ref. [15] experiment 1.
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 localised 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. More detailed study and comparison with granular density waves will be the subject of future work.

As \( \Phi_0 \) is lowered toward the limit \( \Phi_0 \), the jam-collapse-rejam behavior cycles faster (Ref. [13] 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 \( \Phi_0 \), we indeed observe smooth non-jamming flow of the suspension into the convergence [Fig. 2(a) and Ref. [14] 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 hourglass flow of sand, solid arches give way to allow flow.

Collapse of jams apparently involves a sliding-solid fracture-like 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 consequence of the combination of jamming and solvent permeation through the jam. Fractures may be localised by geometry-dependent pressure gradients driving solvent through the pores of the jams into regions of decreased particle concentration—sometimes called ‘micro-cracks’ in the rock fracture literature—which we associate with the dark lines we observe in the suspensions. The excess solvent in these regions lubricates localised sliding (‘cataclastic shear bands’ [16]) of opposing solid regions. Such a ‘lubricated slide’ picture has been proposed for 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 Osborne Reynolds, who squeezed rubber balloons filled with ball bearings and water [10]. Reynolds observed that on applying pressure, water was drawn into the balloon—quite 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 only strain 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 as follows. 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 \( \Phi \). This increase in \( \Phi \) in turn leads to jamming of the colloidal particles.

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