Droplet formation and scaling in dense suspensions

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When a dense suspension is squeezed from a nozzle, droplet detachment can occur similar to that of pure liquids. While in pure liquids the process of droplet detachment is well characterized through self-similar profiles and known scaling laws, we show here the simple presence of particles causes suspensions to break up in a new fashion. Using high-speed imaging, we find that detachment of a suspension drop is described by a power law; specifically we find the neck minimum radius, \( r_m \), scales like \( r^\alpha \) near breakup at time \( r \to 0 \). We demonstrate data collapse in a variety of particle/liquid combinations, packing fractions, solvent viscosities, and initial conditions. We argue that this scaling is a consequence of particles deforming the neck surface, thereby creating a pressure that is balanced by inertia, and show how it emerges from topological constraints that relate particle configurations with macroscopic Gaussian curvature. This new type of scaling, uniquely enforced by geometry and regulated by the particles, displays memory of its initial conditions, fails to be self-similar, and has implications for the pressure given at generic suspension interfaces.

Results and Discussion

When a highly concentrated suspension is slowly extruded through a nozzle, it will squeeze out as a plug and then begin to strain near the nozzle from gravitational stress. Eventually this stress becomes too large and the sample starts to yield. Upon failure, the suspension profile will begin to thin down to detach (Fig. 1A). Throughout this necking process, a dense suspension will maintain a vertically symmetric bridge profile with a steadily decreasing minimum neck radius. Ultimately, the thinning leaves just two particles connected by a small, vertical bridge of liquid. At this point, the particle size acts as an intrinsic cutoff scale for suspension thinning, because the rupture of the liquid thread between the two final particles proceeds within the solvent only. Our study focuses on the regime prior to this final necking for suspensions of packing fractions larger than 50%, where we show how the breakup is driven by the interplay of particles, liquid, and initial conditions.

Comparing the profile shape of a dense suspension (Fig. 1C) to that of a pure liquid (Fig. 1D), the symmetry about the minimum of the average neck profile in a suspension stands in stark contrast to the asymmetric profile of the pure liquid in its final stages. Early in detachment, high viscosity liquids can exhibit symmetric profiles (1, 2), and consequently previous authors (29) have attempted to connect the observed rate of thinning for the neck with self-similar scaling predictions for high viscosity liquids. However, while an interpretation of dense suspensions as simply very viscous fluids is appealing from a rheological point of view (31), quantitative description of detachment eliminates this perspective: As shown in Fig. 2, the neck minimum radius near breakup, \( r_m \), decreases with time to breakup, \( r \), slower than the linear scaling, \( r_m \sim \tau \), predicted near detachment for the high viscosity limit (1, 2). Instead, \( r_m(\tau) \) follows a power law \( r_m \sim \tau^\alpha \) over almost two and a half decades of time (Fig. 2).

The presence of a 2/3 scaling exponent can imply a variety of different physics. For instance, a 2/3 exponent results from the force balance between inertia and surface tension, which governs the pinch-off of inviscid liquids like water (18). Yet the simple fact that dense suspensions can have shear viscosities on the order of 1 Pa s (32, 33) makes a connection to inviscid pinch-off counter-intuitive. Further, barring an initial transient regime, the bridge profile for inviscid pinch-off is markedly asymmetric (18). Other systems displaying a 2/3 exponent that are always symmetric include clustering granular jets (34, 35) and pinching power-law

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fluids (20, 21), though in these cases the thinning mechanism is related to types of dissipation. To discern which, if any, of these systems are similar to dense suspension pinch-off, we systematically changed material properties and initial conditions searching for indicative variation in the thinning power law.

Varying these experimental conditions can delay the onset of this scaling but not eliminate it: Early time behavior of $r_m(\tau)$ can be material dependent (Fig. 3A) and/or vary with initial conditions, such as changes in nozzle size (Fig. 3B). When the packing fraction is reduced we find that the early stages of detachment mimic the behavior of a pure liquid of matched effective viscosity (Fig. 3C), in agreement with previous work (27, 29). Yet it should be noted that this regime, being far from breakup, depends strongly on initial conditions, and therefore even the pure liquid cannot be described by simple scaling arguments. Instead, where scaling arguments do describe the viscous liquid, it thins as $\tau^{1/2}$, while the suspension thins according to $\tau^{2/3}$. Independence of neck thinning from packing fraction and compatibility with $2/3$ scaling has been suggested by authors working in the more dilute limit (29). Further the presence of this exponent, even at such low packing fractions, implies that for much denser suspensions, the packing fraction is an inessential parameter in describing scaling. The data in Fig. 3 show that, close to breakup, the $2/3$ scaling exponent is even more robust and applies deep into the regime of dense suspensions, independent of particle composition or diameter, and nozzle diameter.

Examining the dependence of the prefactor of the power law shows further disagreement with any models relating the scaling behavior to viscous stress. Fig. 3A shows that altering the solvent viscosity by two orders of magnitude has little to no effect on the scaling near breakup, while decreasing the surface tension by only threefold reduces the prefactor of the power law noticeably. The independence of both exponent and prefactor from the solvent viscosity over the range investigated implies that, near breakup, viscous dissipation is inconsequential.

On the other hand, the finite particle size clearly has to come into play as the suspension neck thins down. In the images in Fig. 1 we see that the bounding surface is littered with deformations from protruding particles, and Fig. 3D clearly shows a dependence of the power-law prefactor on particle size. In fact, even at much lower packing fractions, particle-induced deformations...
surface area per particle, some characteristic area related to the contact angle and the depth of immersion (26). The tension, 4.3 mm, and 7.2 mm for 250 μm ZrO₂ suspended in water yields prefactors –25/R₀², which similarly agree with Eq. 2 (B). Data for 150 μm and 250 μm ZrO₂, exiting a 2.4-mm radius nozzle shows that the ratio of the prefactors, 0.8, is within 5% of (150/250)², the ratio predicted by Eq. 2 (D). Comparison of 33-μm polyethylene particles at packing fraction of 25% in a density matched oil with a pure silicone oil of the same effective viscosity (50 cst) (C). Early in the breakup there is strong similarity between the suspension and the pure liquid, but near detachment the two curves diverge. In particular, as shown in the inset, the pure liquid thins linearly with time, first in the Stokes then in the Eggers regime (1, 2). As a result, the ratio of the linear slopes in the inset is 2.4, as predicted. The suspension, on the other hand, thins nonlinearly, decaying like r².

dominate the local curvature in the neck region (28). Therefore, the local pressure at the surface may not be related to the macroscopic mean curvature, as in the Laplace–Young equation, but instead to particle-induced menisci.

Altogether these results suggest that available approaches (1, 2, 21, 30) based on liquid models cannot adequately describe suspension behavior near breakup (SI Text). They also call into question recent attempts to characterize thinning near breakup (37, 40). They also call into question recent attempts to characterize thinning near breakup (37, 40). Early in the breakup there is strong similarity between the suspension and the pure liquid, but near detachment the two curves diverge. In particular, as shown in the inset, the pure liquid thins linearly with time, first in the Stokes then in the Eggers regime (1, 2). As a result, the ratio of the linear slopes in the inset is 2.4, as predicted. The suspension, on the other hand, thins nonlinearly, decaying like r².

To develop such a description, we start with the force exerted by the liquid on a particle protruding through the surface of the suspension. This force scales as \( F_p = \gamma a \) where \( \gamma \) is the surface tension, \( a \) the particle diameter, and \( n \) a constant of order unity related to the contact angle and the depth of immersion (26). The pressure on the surface from \( n \) of these particles contained within some characteristic area \( A \) is then \( P = \gamma a n / S_{pp} \), where \( S_{pp} \) is the surface area per particle. \( \frac{KdA}{A} \) leads to

\[
\int KdA = \frac{1}{2} (6 - \frac{\tilde{Z}}{A}) n, \quad \text{where} \quad \tilde{Z} = n \text{ is the mean coordination number in the triangulation (37, 40). We now note that near the neck minimum radius, the curvature is roughly constant. This allows us to make the approximation } K/((6 - \tilde{Z})) = \frac{\pi}{6}. \quad \text{Identifying the right hand side of this equation as } S_{pp} \quad \text{and combining it with the pressure expression gives } P = \gamma a K/\pi (6 - \tilde{Z}). \quad \text{Simulations of locally disordered packings on curved 2D spaces reveal that } \tilde{Z} \quad \text{is set by the number of spheres that can be brought in contact around a given sphere on the surface (SI Text). That is, } \tilde{Z} \approx 2\pi \arccos \left( \frac{\cosh (\sqrt{K}a)}{1 + \cosh (\sqrt{K}a)} \right) (38, 39). \quad \text{Because both principle radii are always larger than the particle size, the pressure expression can be expanded around } \sqrt{K}a = 0. \quad \text{This leads to}

\[
P = -\gamma a \left[ \frac{1}{2\sqrt{3}a} + \frac{(6 - \sqrt{3}\pi)}{12\pi} Ka + O(\sqrt{K}a)^3 \right]. \quad [1]
\]

The first term in Eq. 1 represents the constant capillary stress that would result from hexagonal close packing on a flat surface. This term, while a crucial component in describing shear thickening in dense suspensions (32, 33), is constant everywhere and therefore does not contribute to the gradient needed to create flow. The second term, however, varies along the surface and can drive the flow causing breakup. This result, together with conservation of momentum, can now be used to create a scaling argument.

The close packing of the grains will lead to stresses that are constant along the radial direction but vary along the axial scale due to differences in the confining pressure. This has
two repercussions: First, it implies that the dominant flow should be in the z direction. Second, it produces a flow that is largely irrotational, removing viscous stress from the flow equations, as observed in the experiments.

Balancing the remaining stress from the gradient of the pressure and the inertial force density gives (SI Text) \( \rho a^2 \rho \frac{\partial^2 r}{\partial t^2} - \gamma \frac{\partial \Lambda}{\partial t} \), where \( K_{\text{trans}} \) is the Gaussian curvature at the neck minimum, and for simplicity we absorb all the numerical prefactors and \( \alpha \) into a new constant \( \Lambda \propto \alpha \). Volume conservation, jamming, and symmetry arguments can be used to show that the axial principal radius near the minimum must converge to the initial nozzle radius, \( R_0 \) (SI Text). Therefore, \( K_{\text{trans}} = -1/(r_m R_0) \). This lets us write our scaling expression as

\[
r_m \sim \left( \frac{\Lambda a}{\rho R_0} \right) \tau_\theta^2. \tag{2}
\]

Dividing both sides of Eq. 2 by the initial nozzle radius, we obtain the nondimensional variables characterizing the intrinsic length and time scales for the breakup process,

\[
\bar{R} = r_m/R_0, \quad \tau_\theta = \tau \left( \frac{\rho R_0^4}{\Lambda a} \right)^{1/2}. \tag{3}
\]

As shown in Fig. 4, applying this scaling collapses data for a wide range of different particle types and sizes, and agrees to within a prefactor of \( \Theta(1) \).

Fig. 4 demonstrates that the remaining variation can be related to the particle-solvent chemistry. Glass, the material most easily wet by water, has the largest prefactor, polystyrene, which is the most hydrophobic material, has the smallest prefactor, and zirconium dioxide, which is mildly hydrophobic, exhibits an intermediate value. This dependence is fully consistent with our model because a more realistic representation of the force \( F_a = a \gamma a \) on a particle from the liquid treats \( a \) not as a constant but includes an explicit dependence on the solid-air contact angle, \( \theta \), and the immersion angle, \( \phi \), measured from the top of the protruding sphere to the contact point with the liquid (26). Explicitly, \( a = \sin(\phi) \sin(\theta + \phi) \). To show this quantitatively, we vertically shift representative data from Fig. 4A onto a single curve (Fig. 4B) and plot the values for \( \Lambda \) required for this collapse as a function of measured solid-air contact angle \( \theta \) (Fig. 4B, Inset). Because \( \Lambda \propto \alpha \), better wetting, and thus larger solid-air contact angle \( \theta \), increases \( \Lambda \) and thus the prefactor in Eq. 2. Moreover, a fit to \( \Lambda(\theta) \) allows us to extract estimates for the immersion angle and the numerical constant, resulting in \( \phi \sim 50^\circ \) and \( \Lambda \approx 3 \alpha \).

Inspection of Eqs. 2 and 3 allows us to establish a connection with the breakup scaling in inviscid liquids (18), where early in detachment the same 2/3 exponent is observed and the nondimensionalized variables are \( \bar{R} = r_m/R_0 \) and \( \bar{\tau}_\theta = \tau / (\gamma R_0^2)^{1/2} \). Such \( \bar{\tau}_\theta \) is reproduced by Eq. 2 when \( R_0/a = 1 \). This predicts a suspension to behave like an inviscid liquid in the limit that the particle diameter approaches the scale of the nozzle. In other words, behavior similar to a molecular liquid is recovered not for vanishing particle diameter but once the particles become clearly visible to the naked eye!

Though at first glance paradoxical, the validity of this argument emerges when the role of surface tension is considered. For a pure liquid, the characteristic length for surface tension is related to the curvature induced by the droplet hanging from the nozzle. For the suspension, surface tension creates pressure from small particle menisci. If the mean curvature from each meniscus becomes comparable to the mean curvature from the sagging pendant drop, these two pressure scales converge. Fig. 5A shows that this is indeed what happens: As the particle size approaches the nozzle diameter, in this case 0.7 mm diameter zirconium dioxide particles in a 4.7 mm nozzle, the scaling of the neck minimum conforms to that of a pure inviscid liquid.

The analogy can be pushed even further and tested on the axial evolution of the neck. During the early stages of inviscid liquid pinch-off the axial curvature scale stays constant (18). Therefore, if a suspension of large particles in a density matched solvent truly duplicates both the radial and axial behavior of a pure liquid during the early stages of break off, images from the two situations should match up when appropriately synchronized to the same axis. Fig. 5B demonstrates this explicitly by superimposing video images from pure water and a suspension of 0.7 mm diameter polyethylene particles in water. The boundaries from the pure fluid provide an excellent envelope for the average profile of the suspension.

The fact that force and length scales are intrinsically regularized by the finite particle size leads to two very remarkable features of this detachment. First, given that the forces involved are not divergent implies that the pressure expression derived here is generic and can be used to describe the stress at arbitrary suspension interfaces. A Laplace–Young type equation, modified to describe suspensions, could facilitate progress in constructing continuum descriptions for suspensions engaging in a variety of flows. For instance, a continuum description of boundary stresses could aid modeling technologies like inkjet printing (15, 41, 42), the fabrication of DNA microarrays (43), and omnidirectional

Fig. 4. (A) Dimensionless neck minimum radius as a function of dimensionless time. Data shown are 22 μm glass (blue diamonds) in water (solid) and oil (open) exiting a 4.7-mm nozzle, zirconium dioxide in water (red) with 150- and 250-μm particles exiting a 4.7-mm nozzle (triangles and light circles, respectively), as well as an 8.8-mm nozzle (diamonds and dark circles, respectively), and 200-μm polystyrene in water exiting a 4.7-mm nozzle (gold diamonds). The data collapses to within a prefactor of \( \Theta(1) \). The remaining banding of the data demonstrates a material dependence of the power-law prefactor resulting from different particle-solvent combinations. (B) Forcing a collapse by to a single power law (see Eq. 2) shows that the prefactor is directly related to the measured contact angle. (Inset) Dependence of the parameter \( \Lambda \) in Eq. 2 on liquid-particle contact angle \( \theta \).
printing (44), or more fundamental problems like the shear-thickening in suspensions (32, 33) or jamming transitions in colloids mediated by capillary arrest (25).

Second, much like in bubble detachment (22–24), the system retains a memory of its initial conditions, specifically the initial nozzle radius, even though it undergoes a topological transition at detachment. Both systems are able to retain this memory through the help of an intrinsic length scale, which terminates the detachment before forces independent of the initial conditions diverge. In the case of bubbles this cutoff is provided by the asymmetry length scale (22) whereas for suspensions continuum modeling breaks down at the particle size. Moreover, the fact that the axial principal radius saturates implies that, also like bubble pinch-off, this type of detachment cannot be cast into a self-similar scaling class. Future work might examine the role of memory in this detachment process by imbending asymmetries in the nozzle shape and analyzing the impact these have on the droplet profile.

Our findings show that droplet formation by suspensions bears similarities to pure liquid breakup but is not encapsulated by that theory. Particle deformations of the surface are not a perturbation that can be ignored through a limit case but rather provide a crucial ingredient to the force balance. A meaningful connection to pure liquids only exists far from the eventual singularity in the pure liquid, when the forces are comparable in scale to those of the suspension and the initial conditions are still relevant. Consequently, the system retains a memory of its initial conditions and fails to be self-similar even in the moments directly before breakup.

Materials and Methods

Our experiments employed two high-speed cameras synchronized to obtain a sufficiently large field of view together with high spatial resolution in the neck region (Fig. 18). A Phantom v7.9 (Vision Research) was fitted with a Micro-Nikkor 55 mm 1:2.8 lens and Nikon PK-12 ring extender to achieve a spatial resolution of 35 μm per pixel. A Phantom v7.3 was equipped with a bellows and macros lens giving 4.4 μm per pixel. Backlighting was provided by three Dedolight units (one for the camera imaging the large scale evolution, two for the bellows camera). This lighting allowed for shutter speeds around 100 μs for the large scale camera and 50 μs for the bellows camera.

Nondensity matched suspensions were prepared from soda lime glass (MoSci), zirconium dioxide (Glen Mills), and polystyrene particles (Grinding Media Depot) suspended in water or in different viscosity silicone oils (Clear-co). For density matching, 1 g/mL polyethylene particles (Cospheric) were used in 20 cm silicone oil (Sigma Aldrich). The suspension was extruded from a variety nozzles at a constant rate by a syringe pump (Razel Scientific R99-E).

Flow rates in the range of 10−4 mL/s kept the extrusion process quasi-static. To prevent fluctuations owing to variations in ambient conditions, the laboratory was controlled to stay at (50 ± 5)% humidity and at (72 ± 1) °F.

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