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Citation for published version:
Jiang, Y, Makino, S, Royer, JR & Poon, WCK 2022, 'Flow-Switched Bistability in a Colloidal Gel with Non-Brownian Grains', Physical Review Letters, vol. 128, no. 24, 248002, pp. 1-5.
https://doi.org/10.1103/PhysRevLett.128.248002

Digital Object Identifier (DOI):
10.1103/PhysRevLett.128.248002

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Peer reviewed version

Published In:
Physical Review Letters

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Flow-Switched Bistability in a Colloidal Gel with Non-Brownian Grains

Yujie Jiang, Soichiro Makino, John R. Royer, and Wilson C. K. Poon
SUPA, School of Physics and Astronomy, The University of Edinburgh,
King’s Buildings, Peter Guthrie Tait Road, Edinburgh EH9 3FD, United Kingdom
(Dated: April 29, 2022)

We show that mixing a colloidal gel with larger, non-Brownian grains generates novel flow-switched bistability. Using a combination of confocal microscopy and rheology, we find that prolonged moderate shear results in liquefaction by collapsing the gel into disjoint globules, whereas fast shear gives rise to a yield-stress gel with granular inclusions upon flow cessation. We map out the state diagram of this new ‘mechanorheological material’ with varying granular content and demonstrate that its behavior is also found in separate mixture using different particles and solvents.

The Brownian motion of sticky colloids forms a space-spanning network with a yield stress – a gel. Such colloidal gels are ubiquitous in industry. Their physics has long been studied [1, 2], however questions remain concerning aging [3], the precise relation between structure and mechanics [4–6] and their dynamics under shear [7]. Sustained attention on the physics of suspensions of non-Brownian particles (or ‘grains’) is a more recent affair, whereby considerable work has established that their rheology is dominated by the formation of frictional inter-particle contacts [8–11]. Such contacts underlie shear thickening in suspensions of purely repulsive hard grains and the yield stress emergence with adhesive grains [12].

Colloids and grains coexist in many applications. In particular, colloidal gels are used as carriers for larger grains, e.g., grains of lithium-ion conductors (≈ 10μm) are dispersed in a conductive carbon-black gel in catholyte slurries [13, 14]. In such cases, the gel’s yield stress is desired to prevent the sedimentation of the larger grains. The physics of these ‘mixed’ suspension has not received focused attention. To date, such mixtures are typically assumed to behave as ‘the sum of the parts’, with properties predictable by extrapolating from the end members. Here, we show that a suspension of grains dispersed in a background colloidal gel may show an unexpected novelty that is not ‘readable’ from the two separate components: it can be mechanically bistable and behave as a ‘memory material’ switchable between stable solid and liquid-like states.

We mixed large (L) silica microspheres (diameter \(d_L = 4.0 \mu\text{m}\)) and small (S) hydrophobic silica colloids (\(d_S = 0.48 \mu\text{m}\)) in an aqueous solvent. For confocal imaging, dyes are incorporated into the small colloids and the nearly refractive-index-matched solvent of ethanol, water and glycerol. Imaging and rheology results are consistent with the small colloids being attractive and gel forming [2] and the large grains being repulsive and showing canonical shear thickening [8]. The partial volume fractions are defined as the volume (\(V\)) of either species relative to the total volume of particles plus fluid (\(f\)), \(\phi_{LS} = \frac{V_L + V_S}{V_L + V_S + V_f}\); the total solids volume fraction is \(\phi = \phi_S + \phi_L\). See Supplemental Material [15] for preparation and characterization details.

During initial sample preparation, we discovered that our mixture showed a unique bistable transition, Figs. 1(a)-(d). Slowly tumbling a sample with \(\phi_S = 0.13\) and \(\phi_L = 0.30\) on a roller mixer produces a liquid state that flows when the vial is tilted, Fig. 1(a). Vortexing for \(\approx 30\) s transforms the sample into a solid state with a yield stress sufficient to support its own weight, Fig. 1(b). This transition is reversible: roller mixing the solid sample for \(\approx 20\) min re-fluidises it; subsequent vortexing again solidifies it (Supplemental Video S1 [15]). A quiescent solid or liquid sample remains in its state > 7 days, Figs. 1(c),(d).

Liquefying the solid involves overcoming a yield stress. So, we surmise that our mixing protocol essentially controls stress. A schematic transition diagram, Fig. 1(e), then shows a quiescent liquid state (F) subjected to high-stress vortexing (F → D) transitions into a solid with finite yield stress (C) upon shear cessation. Likewise, FIG. 1. (a)-(d) Flow-switched transition between solid and liquid states in a binary mixture with \(\phi_S = 0.13\) and \(\phi_L = 0.3\) (see also Supplemental Video S1 [15]). After slow roller mixing, the sample flows freely when the vial is tilted (a) and remains in this liquid-like state when left undisturbed for a week (c). After brief vortex shaking (b), the sample transitions into a solid that can support itself when inverted. This solid state likewise persists when left at rest (d). (e) A schematic transition diagram, using the yield stress after shear cessation to distinguish solid (red) and liquid (blue) states. (Horizontal) dashed lines denote ‘unstable’ states, where sustained shear drives a transition to the stable state (solid lines) after a large accumulated strain.
a quiescent solid (A) subjected to moderate-stress roller mixing (A → B) transitions into a liquid state (E) and remains liquid upon shear cessation. Bistability is immediately apparent in this representation.

Not surprisingly, the system’s flow curve, stress versus shear rate \( \sigma(\dot{\gamma}) \), is protocol-dependent, Fig. 2(a). A sample with \( \phi_S = 0.1 \) and \( \phi_L = 0.2 \) is initially sheared at \( \dot{\gamma} = 1000 \text{ s}^{-1} \) for 100 s. Thereafter, measuring the steady-state stress at a series of decreasing \( \dot{\gamma} \), we find \( \sigma \to 0 \) as \( \dot{\gamma} \to 0 \), indicating a liquid with no yield stress (■). However, if we rejuvenate the sample by shearing at 1000 s\(^{-1}\) between each measurement before recording the transient stress at each stepped-down \( \dot{\gamma} \), the resulting flow curve is that of a yield-stress solid with \( \sigma_y \approx 2.5 \text{ Pa} \) (■). Importantly, the two protocols agree for a pure small-particle gel (\( \phi = \phi_S = 0.1 \)), both giving \( \sigma_y = 1 \text{ Pa} \) (■ and ◆).

A key difference between the protocols is the duration of shear, and therefore the accumulated strain. In the transition diagram Fig. 1(e), the ramp-down protocol may be schematically represented by the path C → B′ → E′ → E → F. There must therefore be some critical stress \( \sigma_b \) at B′E′ (denoted by the dashed vertical) below which the sample liquefies. Figure 2(a) suggests \( \sigma_b \approx 10 \text{ Pa} \), above which the two protocols agree. By contrast, the step-down protocol in Fig. 2(a) corresponds to a C → B quench, which does not accumulate enough strain to induce liquefaction and so produces a flow curve with yield stress \( \sigma_y \approx 2.5 \text{ Pa} \), which is therefore the lower bound for the dotted vertical in Fig. 1.

To explore these two critical stresses, we pre-shear the same sample at various stresses \( \sigma_{\text{pre}} \) and then monitor the time-dependent strain \( \gamma(t) \) at various applied stresses \( \sigma \) (a creep test). For \( \sigma_{\text{pre}} > \sigma_b \approx 10 \text{ Pa} \), we always see a transition from a creeping solid (\( d\ln \gamma/d\ln t < 1 \)) to a flowing liquid (\( d\ln \gamma/d\ln t = 1 \)) as \( \sigma \) increases beyond a yield stress \( \sigma_y^H \). Data for \( \sigma_{\text{pre}} = 100 \text{ Pa} \), Fig. 2(b), displays yielding between 2 and 3 Pa, agreeing with the \( \sigma_y^H = 2.6 \text{ Pa} \) obtained by fitting the step-down data in Fig. 2(a). Applying the same protocol with \( \sigma_y^H < \sigma_{\text{pre}} < \sigma_b \) always produces a liquid state with no yield stress (see Sec. IV of Ref. [15]) regardless of previous shear history.

Novelty appears at \( \sigma_{\text{pre}} < \sigma_y^H \), Fig. 3(a). Now, a sample starting as a solid creeps and remains a solid after shear cessation. Similarly, a sample starting as a liquid remains...
a liquid. In other words, we find history-dependent bistability in this regime ($\sigma_{\text{pre}} < \sigma^H_\gamma$).

To probe the microstructural basis of this bistability, we performed in situ imaging in an Anton Paar MCR 301 rheometer using a Leica SP5 confocal microscope (see Sec. II C of Ref. [15]). In the solid state obtained from $\sigma_{\text{pre}} = 100 \text{ Pa} \gg \sigma_b$, Fig. 3(b) right, the structure is homogeneous with the large grains (green) uniformly distributed in a background matrix of small colloids (red) that appear to span space. In the liquid state obtained from $\sigma^H_\gamma < \sigma_{\text{pre}} = 10 \text{ Pa} < \sigma_b$, the colloids gather into blobs, Fig. 3(b) middle. The three-dimensional scan of this state, Fig. 3(c), shows the blobs to be essentially globular and disjoint, in stark contrast to the gel matrix of colloids in the solid state, Fig. 3(d). Thus, liquefaction and loss of rigidity in this regime result from the collapse of the colloidal gel.

These ‘blobs’ are reminiscent of ‘liquid droplets’ seen in colloidal vapor-liquid phase separation [16]. Interestingly, such complete phase separation is not found in pure colloidal gels under shear [17, 18]. Note, however, that the interior of our blobs are not in a colloidal liquid state: the blobs do not coalesce either at rest or under flow (see Supplemental Material [15]). These are likely ‘droplets’ of attractive colloidal glass [19] whose break-up strength constitutes the upper critical stress $\sigma_b$. When $\sigma_{\text{pre}} > \sigma_b$, these (colloidal) ‘glass beads’ homogenize to small particles that can re-form a ramified gel upon shear cessation. In the bistable regime, the applied stress $\sigma_{\text{pre}} < \sigma^H_\gamma$ can either drive flow in a homogeneous solid nor break up blobs in the phase-separated liquid state.

Complete phase separation in the intermediate regime ($\sigma^H_\gamma < \sigma_{\text{pre}} < \sigma_b$) requires a total strain of $\gamma_{\text{tot}} \approx 10^5$, Fig. 4(a). Up to $\gamma \approx 100$, the small-particle gel coarsens and separates into irregular flocs, reminiscent of sheared pure gels [17, 20]. Between $\gamma \approx 100$ and 1000, the flocs gradually compact into disjoint blobs with a characteristic size $d_b \approx 20 \mu$m. The reverse process of homogenizing these blobs also requires a large strain, Fig. 4(b). When sheared above $\sigma_b$, individual particles and small clusters are ablated off the blob surface with the overall shape maintained up to $\gamma \approx 100$. The absence of deformation indicates the solid nature of blobs. As the breakup progresses, blobs begin to fall apart into clouds of smaller, irregular clusters and ultimately, at $\gamma \gtrsim 1000$, all blobs are broken and the small particles are homogeneously dispersed. Upon reaching a steady state in either process, further shear neither alters the microstructure nor changes the yield stress after shear cessation. This need for a large strains for both solidification and liquefaction correlates with Figs. 4(a), (b). Estimating (see Sec. II of Ref. [15]) the shear rates on the roller mixer $\dot{\gamma}_r \approx \mathcal{O}(1 \text{s}^{-1})$ and vortex mixer $\dot{\gamma}_v \approx \mathcal{O}(100 \text{s}^{-1})$, we find that both 20 min rolling mixing and 30 s vortex accumulate strains of $\gamma \gtrsim 10^3$. These results lead us to add strain dependence to complete our schematic transition diagram, Fig. 1(e), with the color gradient indicating accumulated strain.

We next map out a state diagram at $\phi_S = 0.1$ in the applied stress vs grain concentration, $(\sigma, \phi_L)$, plane, Fig. 5(a). The pure colloidal gel ($\phi_L = 0$) and mixtures at $\phi_L \leq 0.1$ are monostable: they exist either as a non-flowing solid state (NF) below their yield stress or as a homogeneous flowing state (H) that solidifies after flow cessation. Increasing $\phi_L$, we find the phase-separated liquid state (PS) emerges at moderate stress. The sample is
For each point, the sample is first high-shear rejuvenated by applying fixed stress $\sigma_{\text{ij}} = 100 \text{ Pa}$ for 100 s, then a stress $\sigma$ is applied until reaching a steady state (typically $\geq 10 \text{ min}$ for PS region and $\geq 100 \text{ s}$ for H region). The PS (■) and H (●) states are identified by imaging the 3D microstructure after shear is ceased. We do not obtain steady flow ($\times$, $\times$) below the yield stress of the high-shear rejuvenated state, in agreement with $\sigma_y^H(\phi_L)$ estimated from Herschel–Bulkley fits to flow curves measured by step-down protocol (see Sec. VI of Ref. [15]). Samples with bistability in the low-stress regime ($\times$) are highlighted in pink. (b),(c) Mean blob size measured from 3D confocal stacks, varying both $\sigma$ (b) and $\phi_L$ (c) within the PS region of the state diagram. Error bars denote standard deviation from blobs within the imaging volume.

We have carried out a preliminary mapping of the wider state space (see Sec. VII of Ref. [15]). Increasing $\phi_S$ reduces the extent of the PS region, suggesting it will vanish at $\phi_S \approx 0.2$. Decreasing $\phi_L$ until it is too low for the attractive colloids to form a space-spanning gel, we find that the solid-liquid transition disappears; however, the PS state persists. The ability of large grains to drive micro-phase separation is therefore a more general phenomenon than bistability. The reason for either of these observations is not yet clear.

The behavior we have found is likely generic. Consider, e.g., battery slurries [13, 14]. A previous study of such slurries [21] reports similar protocol-dependent rheology (their Figure 3) as well as flow-induced structures (their Figures 6 and 7). Inspired by this industrial system, we replaced our small colloids by trimethyl coated fumed silica (Aerosil R812S), which are irregular aggregates ($\approx 200 \text{ nm}$) of much smaller ($\approx 7 \text{ nm}$) spheres sintered together [22], mimicking the structure of carbon black [23]. We also replaced the solvent by polyethylene glycol, PEG, ($M_w = 200$), a widely used binder in battery manufacturing. Suspended in PEG on their own, the large particles again shear thicken while the hydrophobic fumed silica can form yield-stress gels (see Sec. III of Ref. [15]), again indicating the L-L repulsion and S-S attraction [24]. The previously observed solid-liquid transition, Figs. [1(a)-(d)], is also seen in this second system, Figs. [6(a)-(d)]. Imaging our opaque samples post-shear using cryogenic scanning electron microscopy (cryo-SEM), we once again find that the solid state is homogeneous, while compact blobs of the smaller particles exist in the liquid state, Figs. [6(c),(d)]. Finally, the flow curve, Fig. [6(e)], shows the same protocol dependence as before, Fig. [2(a)].

In summary, we have shown that adding non-Brownian grains to colloidal gels introduces a novel bistable regime in which external flow acts as a switch between two distinct states, which direct imaging reveals to have very different microstructure. We have schematized the unexpectedly complex behavior of our mixture in a transition diagram and mapped out one slice of its state diagram. The same complex behavior is also found in a second system, suggesting generic physics. So far we do not fully understand this behavior. The globular blobs in our systems somewhat resemble ‘log-rolling’ structures seen in a variety of sheared attractive suspensions [25, 26]. The hydrodynamic origin of the latter phenomena [20] may imply the important role of hydrodynamic interactions in our systems.

Though the nature of this generic physics is not yet clear, it may involve ideas from the emergent field of
memory materials [27]. Dynamic control of the mechanical properties of materials enables novel applications, e.g., the jamming transition in dry grains can be used in soft grippers [28]. Our findings add to this design toolkit by offering a 'mechanorheological material' that can be reversibly switched between solid and liquid states by stress and accumulated strain. On the other hand, the shear-driven phase separation at intermediate stresses that underlies this bistability could wreak havoc in industrial processes if not anticipated, e.g. by dramatically degrading conductivity in cathode pastes [14]. For mishaps, further understanding of the mechanistic basis of the bistability that we have discovered is required.

We thank Andy Schofield for particle synthesis and Tom Glen for cryo-SEM assistance. JRR and WCKP were funded by the Engineering and Physical Sciences Research Council (EPSRC, EP/N025318/1). YJ was funded by the EPSRC Centre for Doctoral Training in Soft Matter and Functional Interfaces (SOFI CDT, funded by the EPSRC Centre for Doctoral Training). Y.-M. Chiang and J. A. Lewis, Adv. Energy Mater. 5, 1500535 (2015).

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* yuiejiang_1994@outlook.com Now at Wenzhou Institute, University of Chinese Academy of Sciences, Wenzhou, Zhejiang 325000, China