A mechanorheological memory suspension

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Smart materials that can be manipulated by external stimuli [1] have wide applications, from automotive shock absorbers [2] to microfluidics [3]. Electrorheological [3] and magnetorheological [4] fluids are prototypical examples. Applying the relevant field solidifies the fluid; removing the field causes the material to re-fluidise. These fluids are monostable and lack memory; the solid state persists only when a field is applied. We report a new bistable smart material, a mechanorheological (MecR) fluid whose rheology is tuneable by mechanical stimuli. While most complex fluids are MecR in the sense that their rheology is rate-dependent, e.g. suspensions may shear thicken [5, 6], dry grains fluidise when vibrated [7], these fluids lack memory. Surprisingly, adding non-Brownian particles to a colloidal gel forms a bistable MecR suspension, which is mechanically switchable between solid and liquid states and ‘remembers’ [8] the state into which it has been switched upon removal of the stimuli.

Binary suspensions of repulsive granular (= non-Brownian) and attractive colloidal (= Brownian) particles are common in industry, from fast-moving consumer products in which colloidal gels [9] are used to prevent sedimentation of larger grains, to battery cathodes formed by depositing thin films of catholyte slurries consisting of grains of lithium-ion conductor (≈ 10 µm) dispersed in a conductive carbon-black gel [10]. In many applications it is crucial to control both the suspension rheology and microstructure, e.g. in battery cathodes the slurry rheology is key to coating efficiency while its microstructure controls battery performance [11, 12]. Granular suspensions and colloidal gels have received considerable attention individually [5, 13, 14, 15]. However, mixtures of the two have not been studied with any degree of thoroughness. While the implicit assumption seems to be that such a mixture would simply behave as ‘the sum of the parts’, we show that, in fact, a binary suspension of grains and attractive colloids show surprising novelty.

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We study a mixture of large (L) and small (S) silica spheres (diameters $d_L = 4.0 \mu m$ and $d_S = 0.48 \mu m$) in a nearly refractive-index-matching aqueous solvent. Fluorescent dyes incorporated into the small colloidal spheres and solvent enable dual-channel confocal imaging of both species, and the small particles are hydrophobised to induce attraction. See Materials and Methods for further details. The volume fractions of the large and small particles are defined as the volume ($V$) of either species relative to the total volume (all solid particles plus fluid $f$), i.e. $\phi_{L,S} = \frac{V_{L,S}}{V_L + V_S + V_f}$. The total solids volume fraction is then $\phi = \phi_S + \phi_L$.

We expect electrostatic repulsion between the large silica spheres and hydrophobic attraction between the smaller colloids [16], which we verify experimentally. Suspensions of the small colloids shear thin and possess a finite yield stress $\sigma_y$ at $\phi \gtrsim 0.07$ (Supplementary Fig. 1). Confocal imaging shows ramified networks consistent with an attractive colloidal gel. The large particles appear well-dispersed and shear thickens for $\phi \gtrsim 0.30$ (Supplementary Fig. 2), consistent with a suspension of frictional, repulsive particles [6, 17]. Individually, the large- and small-particle suspensions are MecR fluids in a weak sense: they show rate-dependent rheology but lack memory. Above the yield stress $\sigma_y$ a colloidal gel fluidises, but after shear cessation a gel with finite yield stress is always recovered [18, 19]. Shearing a granular suspension at high stress forces it into a high-viscosity frictional state, but when the stress is reduced or removed, frictional contacts vanish and the viscosity quickly drops [20].

In contrast, our binary granular-gel mixtures are MecR fluids with memory. This manifests in macroscopic changes in the flow during sample preparation (Figs. 1a-d and Supplementary Video 1). Slowly tumbling a sample with $\phi_S = 0.13$ and $\phi_L = 0.30$ on a roller mixer produces a liquid-like suspension which easily flows when the vial is tilted, Fig. 1a. Vortex mixing for $\approx 30$ s transforms the sample into a solid-like state with a yield stress sufficient to support its own weight, Fig. 1b. This transition is reversible: returning the vial to the roller mixer for $\approx 20$ min re-fluidises the suspension and subsequent vortex mixing again solidifies it. Left at rest, both the solid-like and liquid-like samples remain in their respective states for at least a week, Figs. 1c, d. Our binary mixture is therefore a memory material that can be switched between two states (liquid and solid) by external mechanical stimuli.

Given that liquefying the solid state involves yielding, we suppose that the control variable is stress, and construct a schematic transition diagram, Fig. 1e. A quiescent liquid state (F) subjected to high-stress vortex-mixing (F $\rightarrow$ D) transitions into a solid with finite yield stress (C) upon shear cessation. The quiescent solid (A) subjected to moderate-stress roller mixing (A $\rightarrow$ B) transitions into a liquid state (E) and remains liquid upon shear cessation. Bistability is immediately apparent in this representation.

Not surprisingly, the rheological flow curve, stress versus shear rate $\sigma(\dot{\gamma})$, is protocol-dependent, Fig. 2a. A sample with $\phi_S = 0.1$ and $\phi_L = 0.2$ is initially sheared at $\dot{\gamma} =$
1000 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 \(\sigma_y \approx 2.5\) Pa. Remarkably, the two protocols agree for a pure small-particle gel \((\phi = \phi_S = 0.1)\), both giving \(\sigma_y \approx 1\) Pa.

An important difference between the two protocols is the duration of shear, or more accurately the accumulated strain. In the transition diagram (Fig. 1b), the ramp-down protocol (Fig. 2a, blue) may be schematically represented by the path C → B′ → E′ → E → F. There must therefore be some critical stress \(\sigma_b\) (dashed vertical, Fig. 1b) at B′E′ below which the sample liquefies. Reference to Fig. 2a suggest that \(\sigma_b \approx 10\) Pa, above which the two protocols give the same results. In contrast, the step-down protocol (Fig. 2a, red) corresponds to a C → B quench. This quench is too short to liquefy the solid-like sample and therefore produces a flow curve with yield stress \(\sigma_y^H \approx 2.5\) Pa, which imposes a lower bound for the end point of this protocol (dotted vertical, Fig. 1b).

To explore these two critical stresses, we pre-shear the same sample at various stresses \(\sigma_{pre}\) and then monitor the time-dependent strain \(\gamma(t)\) at various applied stresses \(\sigma\), i.e. a creep test. We find that for \(\sigma_{pre} > \sigma_b \approx 10\) 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 \(\sigma_y^H\). Figure 2b shows data for \(\sigma_{pre} = 100\) Pa, which displays yielding between 2 and 3 Pa, agreeing with the \(\sigma_y^H = 2.6\) Pa obtained by fitting the step-down data in Figure 2a.

Applying the same protocol but with \(\sigma_y^H < \sigma_{pre} < \sigma_b\) always produces a liquid state with no yield stress (Supplementary Fig. 4) regardless of the shear history prior to applying \(\sigma_{pre}\). Novelty appears when we apply \(\sigma_{pre} < \sigma_y^H\). Now, if the sample being pre-sheared starts as a solid, then it simply creeps and remains a solid after cessation of pre-shear, Fig. 3a (●). On the other hand, a sample starting as a liquid remains a liquid as \(\sigma_y \approx 0\), Fig. 3a (○). In other words, a sample ‘remembers’ its prior shear history. We therefore have a MecR fluid in the strong sense of the term, displaying bistable memory.

Confocal rheo-imaging reveals the microstructural basis of the bistable transition. In the solid state obtained from \(\sigma_{pre} = 100\) Pa \(\gg \sigma_b\), Fig. 3b (right), the system is homogeneous with the large particles (green) uniformly distributed in a background matrix of small particles (red) that appear to percolate through space. In the liquid state obtained from \(\sigma_y^H < \sigma_{pre} = 10\) Pa \(< \sigma_b\), the small particles gather into blobs, Fig. 3b (middle). The three-dimensional scan of this state, Fig. 3b, shows the blobs to be essentially globular and disjoint, in stark contrast to the gel matrix of small particles in the solid state, Fig. 3b. Thus, liquefaction and loss of rigidity in this regime result from the collapse of the small-particle gel, a process visually similar to colloidal vapour-liquid phase separation [21]. While pure colloidal gels can coarsen under shear [18, 22], such complete phase separation has not been seen before.
Note, however, that the interior of our blobs are not in a colloidal liquid state: they
do not coalesce either at rest or under flow (Supplementary Fig. 5). These are likely
‘droplets’ of attractive colloidal glass [23] whose break-up strength constitutes the upper
critical stress \( \sigma_b \). When \( \sigma_{\text{pre}} > \sigma_b \), these glassy ‘droplets’ fragment and the homogenised
small particles re-form a ramified gel upon shear cessation. In the ‘memory’ regime, the
applied stress \( \sigma_{\text{pre}} < \sigma_y^H \) can neither drive flow in a homogeneous solid nor break up blobs
in the phase-separated liquid state. A sample in this regime therefore ‘remembers’ its
initial state.

Complete phase separation in the intermediate regime (\( \sigma_y^H < \sigma_{\text{pre}} < \sigma_b \)) requires a
total strain of \( \gamma_{\text{tot}} \approx 10^3 \), Fig. 4a (and Supplementary Video 2). Up to \( \gamma \approx 100 \), the
small-particle gel coarsens and separates into irregular flocs. 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 homogenising these blobs also requires a large strain, Fig. 4b
(and Supplementary Video 3). When sheared above \( \sigma_b \), individual particles and small
clusters are ablated off the blob surface with the overall shape maintained up to \( \gamma \approx 100 
\), indicating 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.

The need for a large total strain for both solidification and liquefaction correlates with
Figs. 1a, b. Roughly estimating (see Supplementary Information) the shear rates on the
roller mixer \( \dot{\gamma}_r \gtrsim \mathcal{O}(1 \text{s}^{-1}) \) and vortex mixer \( \dot{\gamma}_v \gtrsim \mathcal{O}(100 \text{s}^{-1}) \), we find that both 20 min
rolling mixing and 30 s vortex mixing result in an accumulated strain of \( \gamma \gtrsim 10^3 \). We
therefore add strain dependence to complete our diagram representation (Fig. 1e), with
the colour gradient indicating accumulated strain. The full diagram then summarises all
of our observations reported so far.

Finally, we map out the \( \phi_S = 0.1 \) slice of the state diagram for our binary system
varying the applied stress \( \sigma \) and large particle concentration \( \phi_L \), Fig. 4f: The pure
colloidal gel (\( \phi_L = 0 \)) exists in one of two states: a non-flowing solid state (NF) below its
yield stress or a homogeneous flowing state (H) that becomes solid after flow cessation.
Binary suspensions at \( \phi_L \ll 0.1 \) are similarly monostable. Increasing \( \phi_L \), we find the
phase-separated liquid state (PS) emerges at moderate stress. The sample is still history
independent in both the H and PS regions provided sufficient strain is applied, but the
low-stress regime is now bistable, since the suspension ‘remembers’ if it was previously in
the H or PS state. The PS region is bounded between the H-state yield stress \( \sigma_y^H(\phi_L) \) and
the blob-breaking stress \( \sigma_b(\phi_L) \), both increasing with \( \phi_L \) yet at different rates. Within
the PS region, the blob size \( d_b \approx 20 \mu m \) is remarkably insensitive to both the applied
stress, Fig. 4l, and \( \phi_L \), Fig. 4f, suggesting that the PS state is a stable fixed point of the
system. At $\phi_L \geq 0.45$, the PS regime vanishes and the binary system again behaves as a monostable gel.

The origins of shear-driven phase separation, and therefore of bistability, in our system is yet unclear, but the behaviour is not unique. We find nearly identical phenomenology in a mixture using the same 4 $\mu$m silica spheres but changing both the smaller particles (trimethyl coated fumed silica, Aerosil R812S) and solvent (polyethylene glycol, PEG $M_w = 200$). In contrast to the colloidal spheres in our primary system, fumed silica particles are irregular aggregates ($\approx 200$ nm) of much smaller ($\approx 7$ nm) spheres sintered together [24]. These are used as rheology modifiers in a variety of industrial formulations, and their irregular shape is also similar to other gel formers such as carbon black [11, 13, 25]. Suspended in PEG on their own, the large particles again shear thicken while hydrophobic fumed silica suspensions can form yield-stress gels (Supplementary Fig. 3), again indicating the L-L repulsion and S-S attraction [26]. The solid-liquid transition observed at sample preparation for our first system, Figs. 1a-d, is also seen in this second system, Figs. 5a-d (and Supplementary Video 4). Imaging our opaque samples post-shear using cryogenic scanning electron microscopy (cryo-SEM), we once again find that solid state is homogeneous, while compact blobs of the smaller particles exist in the liquid state, Figs. 5c, d. Finally, the flow curve shows the same protocol dependence (Fig. 5e) that we observed in the primary system (Fig. 2a). It therefore appears that memory in such binary granular-gel mixtures may be generic.

Dynamic control of the mechanical properties of soft materials enables novel applications. For example, the jamming/unjamming transition in dry grains can be used to design soft grippers [27]. With the ability to reversibly switch between stable solid and liquid states, our MecR memory suspensions are a new addition to this design toolkit. The shear-driven phase separation which underlies this capability could also wreak havoc in industrial processes if not anticipated. Ramping the shear rate in a stirred suspension of this kind can, unexpectedly, produce a liquid state with no yield stress, leading to sedimentation of the granular particles. The appearance of the PS state in a cathode paste will dramatically degrade conductivity [12]. For both novel applications and the avoidance of processing mishaps requires further understanding of the bistability that we have discovered.
Materials and Methods

Particle modification and sample preparation

**Primary binary system**  The small silica spheres are synthesised using the Stöber process and fluorescently labelled by incorporating silane coupled rhodamine B isothiocyanate during synthesis. Dynamic light scattering measurement gives a hydrodynamic diameter of $d_S = 482$ nm. After synthesis, the particles are washed and mixed for 24 hours in a solution with 1:40:3:7 mass ratio of dry silica : ethanol : hexamethyl disilazane : 35% ammonium hydroxide solution to render particle surfaces hydrophobic. To incorporate the hydrophobic particles into our aqueous solvent, they are first wet with ethanol and then added to a glycerol-water mixture. The final solvent composition is 1:1:9 mass ratio of ethanol, water and glycerol, and this is dyed with 0.1 mM fluorescein sodium salt. The dye in the solvent also screens long-ranged electrostatic interactions (Debye length $\approx 10$ nm $\ll d_L, d_S$). Large silica spheres $d_L = 4.0$ µm (Angstromspheres, Blue Helix Ltd.) are received as a dry powder and first washed in pH $\approx$ 9.5 sodium hydroxide solution and probe sonicated to disperse any aggregates before transferring to our solvent. Binary suspensions are prepared by first adding a given mass of a concentrated large particle suspension along with the glycerol and water to the small particles wetted with ethanol, and then dispersing and homogenising the particles using alternating probe and bath sonication along with manual stirring.

**Fumed-silica-based binary system**  The same large silica spheres used in the primary system are dispersed as wash as before, then dried under vacuum. The particles are then dispersed in low molecular weight polyethylene glycol (PEG, $M_w = 200$) using alternating roller mixer and bath sonication. Binary suspensions are prepared by adding trimethyl-coated fumed silica particles (Aerosil R812S, Evonik) to the suspended large particles and dispersing them using vortex mixing and bath sonication. Samples are then placed under vacuum at room temperature for about 20 hours to remove any air bubbles.

Rheology and confocal rheoimaging

Rheological measurements on the primary binary system are carried out on a confocal-rheoimaging setup, consisting of an Anton Paar MCR 301 rheometer mounted above a Leica SP5 confocal microscope. The upper rheometer geometry is a sandblasted cone (cone angle 1°; diameter 25 mm; truncation gap 48 µm), while the bottom plate is a No. 1.0 (thickness $\approx 150$ µm) circular coverglass slide. This coverglass is roughened (roughness $\approx 5$ µm) to reduce slip and mounted on an aluminium plate to maintain a rigid bottom surface, with a small round window in the plate 10 mm from the rheometer tool centre for optical access. We image the suspension using a NA=1.4, 63× oil immersion objective, exciting the different dyes in the small particles and solvent using two diode lasers.
(emission wavelengths 488 nm and 552 nm) and the fluorescence signal collected using two detectors with differing collection ranges.

Negative images of the large particles against the fluorescent solvent are inverted to produce composite images. We measure the blob size distribution from three dimensional confocal stacks by first thresholding the small-particle channel then applying the mean shift clustering algorithm to identify individual blobs. After removing any blobs cut off by the image boundaries, we calculate an effective size $d_b$ for each from the diameter of the equivalent volume sphere.

Rheological measurements on the fumed-silica-based binary system are carried out on an Anton Paar MCR 302 rheometer with a sandblasted parallel plate geometry (diameter 25 mm, 0.5 mm gap) at 20°C.

**Cryogenic scanning electron microscopy**

Cryo SEM imaging are carried out using a Zeiss Crossbeam 550 FIB-SEM with a Quorum Technologies Ltd cryogenic attachment. Samples are first pre-sheared on the rheometer, then the upper plate slowly lifted. A small amount of the sample is collected and placed on the cryo-SEM sample holder, then rapidly plunge frozen in a liquid nitrogen slush before loading into the Quorum chamber. Prior to imaging, the frozen sample is cleaved to obtain a flat surface and sputter coated with a thin platinum layer to minimise charging.

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**Author Contributions**

J.R.R. and W.C.K.P conceived the project. Y.J. designed and performed the experiments with the primary system. S.M. performed experiments with the fumed-silica system. All authors interpreted the data and wrote the manuscript.

**Competing Interests statement**

The authors declare no competing interests.
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Fig. 1: A shear-switched solid-liquid transition with memory. a-d, Snapshots of a binary granular/colloidal-gel mixture with $\phi_S = 0.13$ and $\phi_L = 0.3$ in a 10 mL vial. After slow roller mixing (a), the sample flows freely when the vial is tilted and remains in this liquid-like state when left undisturbed for a week (c). Arrows in a, c highlight the air-sample interfaces. After brief vortex mixing (b), the suspension 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 after a large accumulated strain. In this schematic, solidification via vortex mixing (a→b) corresponds to the path $F \rightarrow D \rightarrow C$, while liquefaction via roller mixing (b→a) corresponds to the path $A \rightarrow B \rightarrow E$. 
Fig. 2: Protocol-dependent rheology. a, Flow curves $\sigma(\dot{\gamma})$ for a sample with $\phi_S = 0.1$ and $\phi_L = 0.2$ measured at fixed rate using two protocols. Ramp-down protocol ($\blacksquare$): the shear rate is ramped down, at each point taking the steady-state stress after shearing for 300 s. Step-down protocol (●): the sample first rejuvenated at $\dot{\gamma}_{\text{rej}} = 1000 \text{s}^{-1}$ for 100 s between each shear rate, and the transient stress is measured for 30 s. Full line: Herschel-Bulkley fit $\sigma = \sigma_y + k\dot{\gamma}^n$, giving $\sigma_y = 2.6 \text{ Pa}$, $k = 1.8 \text{ Pa s}^n$ and $n = 0.7$. Gray: flow curves for the same protocols applied to a colloidal gel with $\phi = \phi_S = 0.1$. b, Strain $\gamma$ versus time $t$ for a creep test performed on the binary sample in a. After preshear at $\sigma_{\text{pre}} = 100 \text{ Pa}$ (×: imposing 1 Pa after preshear at $\sigma_{\text{pre}} = 5 \text{ Pa}$), we impose stepwise increasing shear stress $\sigma$ and measure the evolution of strain $\gamma$. Liquid-like flow is indicated by unit slope.
Fig. 3: **State transition boundaries and microstructural changes.** a, Suspension yield stress measured via creep tests at various probe stresses $\sigma$ applied to a sample with $\phi_S = 0.1$ and $\phi_L = 0.2$. Error bars reflect the finite stress step in creep test. The sample was initially in a solid state (◆, obtained by homogenising for $100\text{ s at }1000\text{ s}^{-1}$) or a liquid state (○, obtained by homogenising for $\approx 20\text{ min at }5\text{ s}^{-1}$). b, Two-channel confocal images in the flow-vorticity ($x$-$y$) plane at a height $z = 30\mu\text{m}$, separately showing the small (red) and large (green) particles. The suspension (same composition as in a) was sheared at $\sigma_{\text{pre}}$ (indicated above each image) for sufficiently long. The top and bottom images in the left panel correspond to samples that started initially as the sample on the right and in the middle panel respectively. c, d, Volume renderings constructed by thresholding the red small-particle channel from 3D confocal stacks. These stacks run from $z = 0\mu\text{m}$ to $z = 60\mu\text{m}$ and correspond to the same $\sigma_{\text{pre}} = 10\text{ Pa}$ (c) and $\sigma_{\text{pre}} = 100\text{ Pa}$ (d) samples shown in b.
Fig. 4: Transition dynamics and state diagram. a, b, Confocal images at $z = 30\mu m$ from a time series showing the H→PS transition at $\sigma = 5$ Pa (a) and the PS→H transition at $\sigma = 50$ Pa (b), both for $\phi_S = 0.1$ and $\phi_L = 0.2$. See Supplementary Video 2 and 3 for full time series. c, State diagram in $\phi_L - \sigma$ space for fixed $\phi_S = 0.1$. For each point, the sample is first high-shear rejuvenated by applying fixed stress $\sigma_{rej} = 100$ Pa for 100 s, then a stress $\sigma$ is applied until reaching a steady state (typically $\gtrsim 10$ min for PS region and $\gtrsim 100$ 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 (×, ×) below the yield stress of the high-shear rejuvenated state, in agreement with $\sigma^H_y$ (★) estimated from Herschel–Bulkley fits to flow curves measured by step-down protocol (Supplementary Fig. 6). For our MecR fluids with memory (highlighted in pink), the low-stress regime is bi-stable (×). d, e, Mean blob size measured from 3D confocal stacks (see Materials and Methods), varying both $\sigma$ (d) and $\phi_L$ (e) within the PS region of the state diagram. Error bars denote standard deviation from blobs within the imaging volume.
Fig. 5: **Obtaining a MecR memory fluid in a second binary suspension.** a, b, Images of the fumed-silica-based binary suspension ($\phi_s = 0.02$ and $\phi_L = 0.3$) in a glass vial, showing a similar liquid-solid transition under alternating high-shear vortex mixing and gentle roller mixing as in Figs. 1a-d. c, d, Cryo-SEM images showing the solid (c) and liquid states (d) at the same composition, prepared by $\sigma = 250$ Pa and $\sigma = 10$ Pa in a rheometer, respectively. Note that individual fumed silica particles cannot be resolved, only the larger blobs of the smaller particles in the liquid state. e, Flow curves obtained using the same two protocols (indicated by arrows) as in Fig. 2a. A Herschel-Bulkley fit (solid red line) to the data from step-down protocol gives $\sigma_y = 5.2$ Pa, $k = 3.5$ Pa s$^n$ and $n = 0.7$. 

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