Syneresis of Colloidal Gels: Endogenous Stress and Interfacial Mobility Drive Compaction

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This is a "Post-Print" accepted manuscript, which has been Published in "Physical Review Letters"

Please cite this publication as follows:

You can download the published version at:

https://doi.org/10.1103/PhysRevLett.125.208004

Syneresis of colloidal gels: Endogenous stress and interfacial mobility drive compaction

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Colloidal gels may experience syneresis, an increase in volume fraction through expulsion of continuous phase. This poroelastic process occurs when adhesion to the container is weak compared to endogenous stresses which develop during gelation. In this work, we measure the magnitude of syneresis, $\Delta V/V_0$, for gels composed of solid, rubber, and liquid particles. Surprisingly, despite a constant thermoresponsive interparticle potential, gels composed of liquid and elastic particles synerese to a far greater extent. We conclude that this magnitude difference arises from contrasting modes of stress relaxation within the colloidal gel during syneresis either by bending or stretching of interparticle bonds.

When colloidal particles in a dispersion are made attractive, they aggregate into fractal clusters which, even at low volume fraction, ϕ, grow to form a space-spanning network, or gel. These gels determine the rheology of many consumer products; their shelf-life relies on the mechanical stability of the colloidal gel network acting as scaffold to provide rigidity. Understanding the mechanical stability of such colloidal gels is thus of crucial importance for controlling the properties of many soft solids. Once a colloidal gel forms, the heterogeneous structure, often bonded through weak non-covalent interactions, is subject to body forces such as gravity [1], surface forces such as adhesion to container walls [2, 3] and shear forces[4]; the delicate balance between these forces acting on the system as a whole determines its fate. Interestingly, even in the absence of external stresses, colloidal gels undergo slow internal rearrangements that cause the network structure to gradually age and coarsen [5, 6] or densify by a mechanical instability known as syneresis [2, 7–9], which is a compaction of the gel accompanied by the expulsion of the continuous phase. While mechanical failure of gels subjected to external stresses, both shear or gravitational, has been studied in detail, there is a dearth of studies on catastrophic failure of gels due to internal stresses that accumulate during the gel formation. Furthermore, few studies have investigated gels formed by particles other than solid spheres, while differences could be anticipated [10] and most colloid-based consumer products are comprised of soft particles; interestingly, these products nearly universally exhibit syneresis. As a result, predicting the stability of colloidal gels remains prohibitively difficult as the interplay between internal stress, stiffness of particles, and adhesion to the solid container surfaces is not yet established.

In this letter, we investigate the failure of colloidal gels due to syneresis driven by internal stresses in the absence of any external stresses such as adhesion to the container walls and gravity. We find that syneresis is a poroelastic and reversible phenomenon; when the attractive forces are removed, the gel relaxes back to a dispersion of par-

ticles, indicating that neither coalescence nor irreversible aggregation occurs. Furthermore, we find that the normalized magnitude of syneresis, $(V - V_0)/V_0$, with V and V_0 the final and initial volume fraction, respectively, is highly dependent on the particle nature; gels composed of soft particles, such as liquid droplets and elastic rubber particles, display larger $\Delta V = V_0 - V$, than gels formed of rigid particles with the same interparticle attraction. In all cases, syneresis arrests before maximum compaction, which we relate to the elastic stresses that develop during syneresis which cannot relax by particle rearrangements or connectivity changes in these strongly attractive gels.

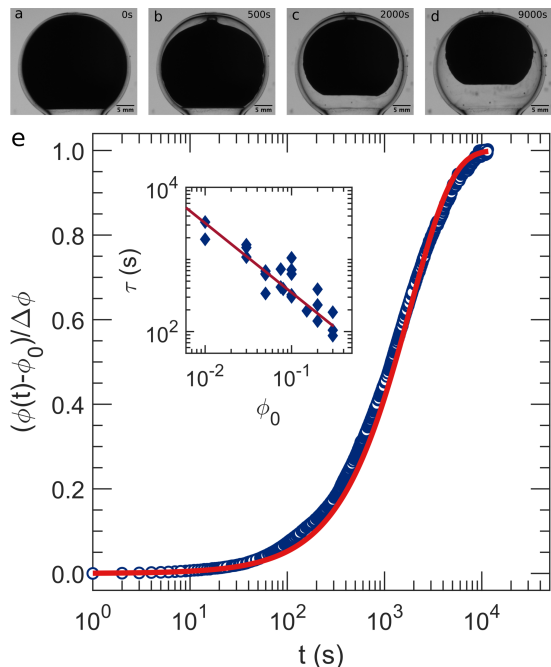To minimize external stresses on these colloidal gels,

FIG. 1. (a-d) Image sequence of syneresis in a spherical geometry for a solid particle dispersion at $\phi_0 = 0.01$ heated to $45°$C. (e) Kinetics of syneresis in a polystyrene particle dispersion at $\phi_0 = 0.01$; solid red line is a fit to an exponential function. Inset: characteristic syneresis time, showing $\tau \sim \phi_0^{-1}$.

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we prepare a dispersion of polystyrene particles of radius, $r = 275$ nm, at ϕ=0.01 in a density matched solution of 100 mM NaCl, 55/45v% D_2O/H_2O [11]. To this dispersion, 0.1wt% of a thermoresponsive surfactant is added which adsorbs onto the particle surface and induces a reversible temperature-triggered interparticle attraction when heated above 32°C [12]. The dispersion is heated to 45°C in a spherical glass geometry, the particles become attractive, with an attractive strength, $U \gg 50k_BT$ and a range of $\approx 8nm$ [12, 13], and an elastic network forms. Immediately after formation, the network contracts expelling continuous fluid. We macroscopically image this syneresis over time, see Fig. 1 (a-d). Crucially, the container walls are treated with a polyelectrolyte multi-layer which prevents colloidal particles and surfactant from adsorbing to the container surface [14]. By contrast, if the spherical container boundary is adhesive, the gel forms and remains stable with contraction balanced by adhesion to the rigid walls. Nearly all experimental studies on the mechanical failure of colloidal gels do not control adhesion; syneresis having been observed only after the container is rotated, breaking adhesive bonds to the walls [2] or by traditional means of knifing cheese curd [7]. By forming the gel network *in situ* in all experiments, endogenous contractile tension is generated by the gel network, as no shear is exerted on the network by mixing or pipetting, which is known to directly affect the gel network connectivity [15], anisotropy [16], and failure [4].

To quantify the syneresis process, we calculate the normalized change in volume fraction with time, $(\phi(t)-\phi_0)/\Delta\phi$, with $\Delta\phi$ the final change in volume fraction, $\phi(\infty)-\phi_0$, by extracting the projected area occupied by the gel from the images as shown in Fig. 1 (a-d). As the gel contracts, ϕ reaches a plateau within several hours, as seen in Fig. 1 e. The kinetics can be described accurately with an exponential function

$$\frac{\phi(t) - \phi_0}{\Delta\phi} = 1 - \exp(-t/\tau)$$

with a characteristic time scale τ that decreases with increasing initial volume fraction as $\tau \sim \phi_0^{-1}$ as seen in the inset of Fig. 1. These observations resemble the compaction of gels under the influence of external stresses, such as gravity, which was described successfully as a poroelastic relaxation process with a rate limited by the fluid flow through the elastic porous material [1, 8].

The characteristic timescale of such a poroelastic process is given by $\tau \sim \frac{\eta(1-\phi_0)R^2}{k_0 K}$ [1] with η the continuous phase viscosity, R the initial dimension of the material, which in the present case corresponds to the contracting sphere radius, K the gel bulk modulus, and k_0 the gel network permeability. For $\phi_0 \ll 1$, we thus expect $\tau \sim 1/k_0 K$. Rather than the typically used Kozeny-Carman equation, the permeability of a colloidal gel network was shown to scale as $k_0 \sim \frac{a^2}{\phi_0^{2/(3-d_f)}}$, with a the particle radius and d_f the fractal dimension [1]. For
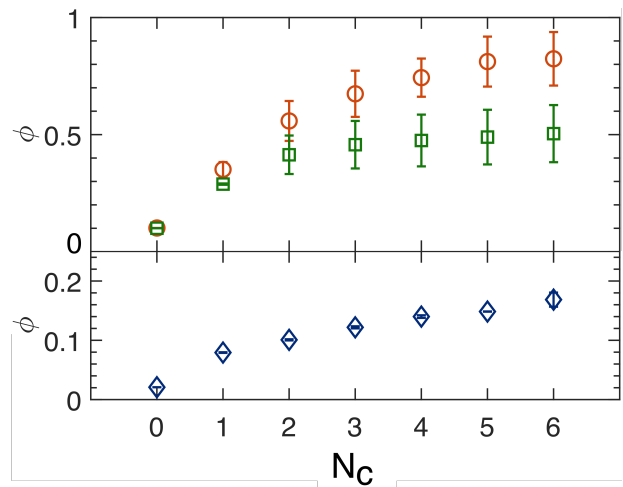

FIG. 2. Cyclic syneresis in gels with ϕ, taken after each syneresis cycle for, solid particle (diamonds), rubber particle (squares), and droplets (circles). Error bars represent standard deviation (n=2).

the present case of strongly attractive particles, we expect close to diffusion-limited aggregation, leading to $d_f \approx 1.85 \pm 0.1$ [17, 18], thus $k_0 \sim \phi_0^{-1.8}$ [19]. Our observation that $\tau \sim \phi_0^{-1}$ suggests that $K \sim \phi_0^{2.8}$, which corresponds well to previous work on the compression of colloidal aggregates [20], and which, interestingly, is also of similar scaling observed for the shear modulus, $G'(\phi_0)$, discussed below. Implying that $K/G \sim \mathcal{O}(1)$, which has not been thoroughly investigated [20].

Most food products that exhibit syneresis consist of gels composed of droplets while most experimental studies on gel dynamics consist of rigid particles, similar to these polystyrene particles. To explore the effect of particle nature on the extent of syneresis, we use emulsion polymerization to synthesize monodispersed viscous droplets with the same radius, r=275nm, composed of polybutylacrylate, a low glass transition temperature polymer. Additionally, we prepare cross-linked rubber polybutylacrylate particles which are deformable and elastic, by adding 0.7mol% crosslinker during the emulsion polymerization [21]. We adsorb the same surfactant at the same concentration onto these particles as used previously, thus maintaining a near constant interparticle attraction for all three different systems. The particle radii and solution conditions are chosen to keep constant network topology for samples of comparable volume fraction which have been shown to affect gel mechanics [22], while isolating the effects of particle nature on tangential interparticle forces.

After heating, all gels exhibit arrest after an initial syneresis reaching a final volume fraction, ϕ_f, which is less than ϕ_m, the maximum possible volume fraction. To elucidate if the arrest that occurs is a stationary state, or results from kinetically arrested configuration, we perform cycling experiments: Each sample is heated, permitted to undergo syneresis until arrest, after which the

expelled fluid is removed, and the sample is cooled to 25°C. Cooling the sample removes the interparticle attraction causing particle dissociation within the gel resulting in a fluid dispersion with a now higher volume fraction $\phi_0 + \Delta\phi$. In all cases, $\langle r \rangle$ as measured using dynamic light scattering, remains constant for all cycles; emphasizing the lack of coalescence or irreversible aggregation during syneresis. Additionally, cycling experiments without removing the expelled liquid yielded consistent $\Delta\phi$, showing that the interparticle potential does not change significantly [21]. As the dispersion is heated again, the gel synereses again and additional fluid is expelled; the process is repeated N_c times and $\phi(N_c)$ determined gravimetrically after the end of each cycle, see Fig. 2. In all three colloidal gels, the observed positive $\Delta\phi(N_c)$ indicates a kinetically arrested configuration during the previous cycle; when internal stresses are released upon cooling, particles are free to find more favorable configurations when attraction is induced again in the next cycle. The droplets and rubber particles have a nearly identical volume fraction increase for N_c=1 but deviate at higher N_c, reaching different plateau values; the final cycle packing fraction is ϕ=0.82 and ϕ=0.51 for the droplets and rubber gels, respectively. This difference can be attributed to the higher deformability of droplets. Rubber particles resist deformation with elasticity originating from covalent bonds within the polymer network, while droplets only resist by Laplace pressure. This droplet final volume fraction, $\phi_m = 0.82$, is higher than $\phi(\text{hcp}) = 0.747$, which requires significant droplet deformation [23]. Clearly distinct from droplets and rubber particles, solid particles exhibit a slowly increasing $\phi(N_c)$ which remains well below $\phi(\text{rcp}) = 0.64$ during these cycling experiments. The origin of this difference must lie with how these particles respond to the emerging endogenous stress during gelation and subsequent syneresis.

To further explore this difference, all three dispersions for different ϕ_0 are heated to 45°C; all samples exhibit syneresis of varying magnitude. This magnitude is quantified by the normalized volume change, $\Delta V/V_0$ at steady state, after 4 hours, as shown in Fig. 3. For solid particles, $\Delta V/V_0$ decreases approximately as $(\phi_0/\phi_m)^{-1.2}$. By contrast, for both droplets and rubber particles $\Delta V/V_0$ remains nearly constant for $\phi_0/\phi_m < 0.3$, then rapidly approaches 0 as $\phi_0/\phi_m \to 1$; emphasizing a nearly universal syneresis mechanism between these two particle dispersions. This difference must again originate in the stress relaxation modes during syneresis, a consequence of how the colloidal gel structure bears stress. In the absence of syneresis, an elastic gel network forms which bears stress by either bending of strands or stretching of individual interparticle bonds leading to an increase in the center to center distance between particles [24, 25]. For pair-wise particle interactions, centrosymmetric interparticle potentials such as polymeric depletion or this surfactant induced attraction, the free energy cost of relative particle rotation and, therefore bending, is near zero,
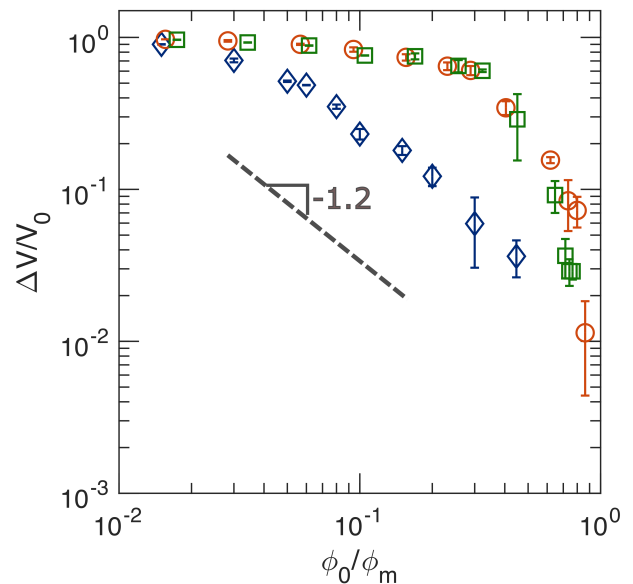

FIG. 3. Magnitude of syneresis, $\Delta V/V_0$, for solid particles (diamonds), rubber particles (squares), and droplets (circles) as a function of scaled initial volume fraction, ϕ_0/ϕ_m. Error bars represent standard deviation (N=2).

leading to stress being born only by stretching interparticle bonds. However, once the cross-section of each gel strand becomes more than one particle, bearing stress by bending energy may become appreciable [24]. The scaling of $G'(\phi)$ provides a measurement of how the gel bears any applied stress [25, 26]. In a rheometer, we form gels by heating dispersions and measure $G'(\phi)$ see Fig. 4; syneresis is eliminated due to adhesive walls. For $G' \sim (\phi)^\nu$, a small exponent value of $\nu = 1.7$ indicates gels bearing stress by stretching interparticle bonds; while a higher exponent, $\nu = 3.3$, indicates gels bearing stress by bending network strands [27–29]. Based on ν shown in Fig. 4, droplet and rubber gels bear stress by stretching predominately, while stress bearing in the solid gels is dominated by bending. Crucially, surfaces of both droplets and rubber particles are fluid and smooth permitting lateral surfactant diffusion. This surface mobility likely permits these 'soft' particles to exhibit kinetic arrest only after obtaining a higher ΔV. Due to the surface mobility, individual particles slide relative to one another with near zero free energy cost, therefore such gels only bear stress by stretching. By contrast, solid particle gels bear stress by bending and arrest at a lower volume fraction due to surface asperities and a lack of surface mobility.

Again we observe two contrasting dependencies between gels formed of solid particles and those formed from droplet and rubber particles, in addition to this same dependence already being observed in syneresis magnitude, i.e. Fig. 3. To explain this contrast, we hypothesize that there is an initial syneresis pressure, $P \sim \phi_0^2$; this is in analogy to the second virial approximation for the osmotic pressure of non-ideal dispersions, which scales
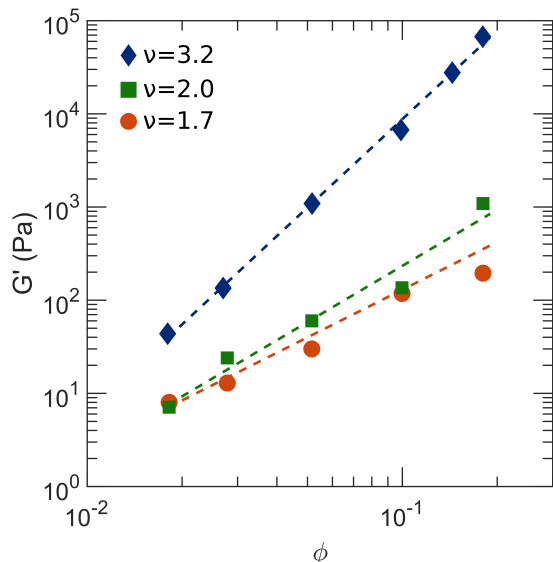
FIG. 4. Storage moduli, G', of colloidal gels for solid particles (diamond), rubber particles (square), and droplets (circle) as a function of volume fraction, ϕ.

as $\Pi \sim B_2 \phi^2$, with the second virial coefficient, B_2, being negative here as particles attract forming additional bonds [30]. This negative pressure leads to compression which is counteracted by network elasticity. Combining, K, being defined as $\Delta V/V_0 = -P/K$, and our previous result which implies $K \sim G \sim (\phi)^{\nu}$, then for solid particles with $\nu = 3.2$ suggests $\Delta V/V_0 \sim \phi_0^{2-3.2} \rightarrow \phi_0^{-1.2}$ in agreement with syneresis results, see Fig. 3. Similarly, for droplet and rubber particles, $\nu \sim 2$ suggests $\Delta V/V_0 \sim \phi_0^{2-2} \rightarrow \phi_0^0$ also in agreement with Fig. 3. For larger ϕ_0/ϕ_m there is a strong deviation from this simple scaling, as $\Delta V/V_0$ approaches zero, likely due to B_2 being no longer pair-wise additive; additionally, this scaling argument relies on a gel structure with a well-defined d_f, which no longer holds for high volume fractions. This scaling assumes that syneresis is counteracted by network elasticity, thus, arrest in droplets and rubber gels is likely a consequence of network connectivity. The gels contract until further contraction would require breaking of interparticle bonds, energetically unlikely as $U \gg 50 k_B T$ [12, 13]. We note, finally, that deviations from the predicted scaling are also observed in Fig. 3 at low ϕ_0/ϕ_m for the solid particle gels; we ascribe these deviations to the low elastic resistance of these gels, which are very close to the percolation threshold and therefore very weak.

To directly illustrate these arrest modes, syneresis is observed at the microscopic level by heating quasi-2D disks of gels within non-adhesive microfluidic chambers consisting of droplets ($\phi_0 = 0.05$) and solid particles ($\phi_0 = 0.02$) with comparable $G'(\phi_0)$; the low half of these disks are shown in Fig. 5 (a-d) with movies in [21]. The onset of syneresis is defined as the initial detachment from the chamber wall, $t_d = t = 0$; Fig. 5 (a,c) are immediately after t_d. Particle Image Velocime-

try (PIV) analysis at $t = 10$s indicates displacements are directionally disorganized in both cases. Interestingly, at t=130s, displacement vectors in the droplet gel appear radially oriented, while disordered displacements for the solid gel persist, see Fig. 5 (b) and (d) respectively. To quantify this difference, the spatially averaged vorticity is computed using PIV for an interrogation window, and its standard deviation, σ, is normalized by the averaged velocity, μ; the quantity, $\sigma(t)/\mu(t)$ is shown in Fig. 5 (e). A lower $\sigma(t)/\mu(t)$ is indicative of a uniform vorticity or arrest, while, a large $\sigma(t)/\mu(t)$, is indicative of spatial inhomogeneity of the vorticity possibly arising from non-affine motions.

As seen in the supporting syneresis movies, both gels experience a pore size increase for $t < 0$, a process of local syneresis leading to an increasing number of interparticle bonds. Only for the droplet gel is this clearly followed by a macroscopic radial movement of gel strands. These two processes are concomitant; a large $\sigma(t)/\mu(t)$ corresponds to pore size increase and non-radial displacement, while radial bulk syneresis drives $\sigma(t)/\mu(t) \rightarrow 0$. Conversely for the solid gel at $t > 0$, no clear radial motion is observed, resulting in a large $\sigma(t)/\mu(t)$ persisting, only decreasing to 0 during arrest, see Fig. 5 (e) [21]. As these two different gels have similar $G'(\phi_0)$, see Fig. 4, this difference must originate in contrasting surface mobility. Both a decreasing pore size and radial movement imply a nearly affine deformation similar to what has been shown for networks of beams with low bending modulus [31], true for the droplet gel with interparticle sliding.By contrast, the non-radial, non-affine motion of the solid particle gel without interparticle sliding results in a lingering $\sigma(t)/\mu(t) > 0$ before arresting at approximately $t \sim 500$s.

We have shown that colloidal gels undergo syneresis when eliminating adhesive boundary conditions and forming gels *in situ*. Interestingly, we observe that the magnitude of syneresis, $\Delta V/V_0$, is highly dependent on the surface mobility and local deformability of the particle composing the gel; these two properties are nearly universally overlooked in colloidal materials, yet, they likely play key roles in rheologic responses, especially during mechanical breakdown [32]. While syneresis is more readily seen in 'soft' particle gels, especially foods, we have shown that it is still not negligible in gels composed of solid particles, but often not observed experimentally due to adhesive container walls. However, this does not preclude local syneresis within the network which may be interpreted as aging in literature [6, 33, 34].
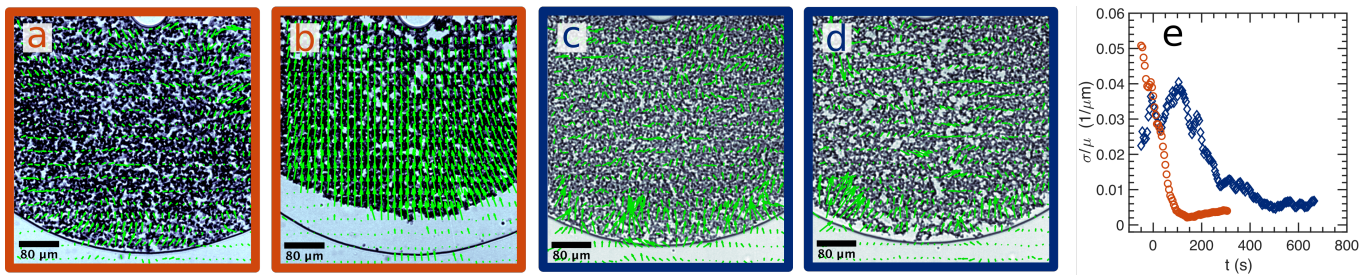
FIG. 5. Quasi-2D gels consisting of droplets, ϕ_0=0.05, at t=10 s **(a)** and $t = 130$ s **(b)**, of solid particles, ϕ_0=0.02, at $t = 10$ s **(c)** and $t = 130$ s **(d)**. Green vectors represent the velocity over 5 s; vectors are enlarged 1.5 times and 3 times in the gel consisting of droplet and solid particles respectively. **(e)** Standard deviation of vorticity normalized by average magnitude of vector, σ/μ, for droplets (circle) and solid particles (diamond) as a function of time.

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