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Yield of reversible colloidal gels during flow startup: Release from kinetic arrest[†]

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Yield of colloidal gels during startup of shear flow is characterized by an overshoot in shear stress that accompanies changes in network structure. Prior studies of yield of reversible colloidal gels undergoing strong flow model the overshoot as the point at which network rupture permits fluidization. However, yield under weak flow, of interest in many biological and industrial films, shows no such disintegration. Mechanics of reversible gels are influenced by bond strength and durability, where ongoing rupture and re-formation imparts aging that deepens kinetic arrest [Zia *et al.*, *J. Rheol.*, 2014, **58**, 1121], suggesting that yield be viewed as release from kinetic arrest. To explore this idea, we study reversible colloidal gels during startup of shear flow via dynamic simulation, connecting rheological yield to detailed measurements of structure, bond dynamics, and potential energy. We find that pre-yield stress grows temporally with the changing roles of microscopic transport processes: early time behavior is set by Brownian diffusion; later, advective displacements permit relative particle motion that stretches bonds and stores energy. Stress accumulates in stretched, oriented bonds until yield, which is a tipping point to energy release, and is passed with a fully intact network, where the loss of very few bonds enables relaxation of many, easing glassy arrest. This is followed immediately by a reversal to growth in potential energy during bulk plastic deformation and condensation into larger particle domains, supporting the view that yield is an activated release from kinetic arrest. The continued condensation of dense domains and shrinkage of network surfaces, along with decrease in potential energy, permit the gel to evolve toward more complete phase separation, supporting our view that yield of weakly sheared gels is a ‘non-equilibrium phase transition’. Our findings may be

particularly useful for industrial or other coatings, where weak, slow application via shear may lead to phase separation, inhibiting smooth distribution.

1 Introduction

Colloidal gels and other so-called yield-stress fluids exhibit a solid-like to liquid-like transition under imposed forces and fields, a behavior that forms the functional basis for an array of technological materials. The external forcing which induces yield and material deformation need not be strong; for example, in slump tests of concrete and other yield stress materials, the weight of the material itself induces yield and deformation, providing useful information about yield stress and material consistency.^{1–3} Bacterial biofilms have been recognized as viscoelastic materials⁴ and, in recent work, the formation and nature of bacterial streamers under creeping flows have received interest due to the tendency to clog or foul channels or other features in microfluidic devices.⁵ Under a wide range of flows they show an elastic response⁶ and span surfaces far away⁷; during flow these streamers can strain harden before failure and break off.⁸ Even when subjected to a fixed strain rate, it appears that fluidization is not instantaneous, but rather occurs after a finite delay during which material stress grows rapidly in time to a peak stress, and after which bulk stress and structural rearrangements are consistent with steady-state flow. While much study has been devoted to yield under strong flow,^{9,10} providing important connections between network rupture and yield, many questions still surround the solid-like to liquid-like transition in colloidal gels subjected to startup of a weak fixed shear rate, including whether network rupture accompanies such yield. The duration of the yield event, the subsequent material stress, and long-time flow behavior exhibit dependence on particle volume fraction¹¹ and the strength of interparticle bonds¹², both of which influence the initial morphology of the space-spanning network and its elastic response.^{13–18} Gel morphology and thus transient behavior are intrinsically linked to the underlying transport behavior; here, of interest is how the durability and lifetime of interparticle bonds relative to Brownian fluctuations gives rise to the formation of colloidal gels via arrested phase separation^{18–25} and thus may inform the framework with which we view transient behavior.

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Most prior strong-flow studies that attribute gel flow to network rupture focused on dilute gels formed by interparticle attractions much stronger than thermal fluctuations, $V \gg kT$, where V is the potential of interaction, k is Boltzmann's constant, and T is the absolute temperature. The bonds between particles are essentially permanent, leading to stringy or fractal gel morphology that changes only under the influence of externally applied stresses. The relatively well-understood and simple structure of such gels makes it natural view to fluidization as a cascading rupture of network strands leading directly to mechanical failure. The idea that fluidization is not instantaneous even though bulk motion is imposed emerges from observations that the gel retains solid-like, slow dynamics during early deformation. Mohraz and Solomon and co-workers^{26–29}, in a series of experimental studies, defined a three-regime characterization of gel fluidization: an early time rise in stress, a yield point, and long-time flow. The solid-like early stress response was explained as arising from alignment and immobilization of network strands,²⁹ followed by network rupture concomitant with rheological yield.²⁷ Expanding these ideas, Colombo and Del Gado³⁰ discovered important structure/yield relationships in strong gels, in an impressive computational study of startup shear flow of dilute, strongly bonded colloidal gels with a string-like microstructure. They discovered both a linear and nonlinear pre-yield regime, providing a clear picture of pre-yield structural change, showing that network chains first unbend, then align, and finally stretch and stiffen during the pre-yield rise in stress. In these and other recent simulation studies, the stringy, low-coordination number gel morphology is mimicked in simulation through strong interparticle interactions in concert with tangential or rotational forces^{9,31} or angular rigidity³⁰. In such models, bonds can form any time, but are lost only due to imposed flow or stress. Whittle and Dickinson³¹, and later Park and Ahn⁹ studied bond loss during peak stress, suggesting that the peak rate of bond loss sets structural yield. Overall, fluidization of dilute, permanent colloidal gels has been convincingly connected to the solid-like fracture of the strongly bonded network; but such models leave open questions of how fluidization occurs in denser or reversibly bonded gels where network strands are many particles thick and, in the case of the widely prevalent reversible gel, the durability of bonds leads to time-dependent behavior.

Markedly less study has been devoted to concentrated or reversibly bonded gels, owing in part to the difficulty of making detailed structural measurements of denser and higher-contact number network strands.

Vermant and coworkers^{32–34} studied structural evolution of very strongly bonded, moderate to concentrated gels undergoing gelation as well as flow utilizing microscopy to examine two-dimensional gels formed at an interface. They reported gel morphology comprising clusters of particles that percolate into a space-spanning network, and that fluidization occurs via liberation of such clusters from the network. The authors also make a connection between initial, post-gelation cluster size and the size of clusters that break free from the network, a phenomenon that may owe its origin to the nature of nearly-permanent interparticle bonds. This work makes it clear that rupture mechanisms in colloidal gels can change markedly with changes in morphology. Subsequent studies have applied the idea that permanently bonded gels yield via cluster liberation to reversibly bonded, dense gels.

Fluidization of dense, reversible gels was recently studied by Petekidis and coworkers, among others, where one of the most substantial findings was the emergence of a secondary yield event during flow startup.^{11,12} The first yield event was reported to occur at a yield strain on the order of a bond length; from this the authors inferred that particle clusters connected to one another by a few bonded particles break free from the network, producing a flowing suspension of clusters.^{11,12} This was inspired by their earlier work that showed two yields in attractive glasses^{35,36} thought to arise from both bond-scale and cage-scale yield events. Secondary yield in hard-sphere colloidal gels seems to be unique to reversibly bonded gels. Some insight into this secondary yield comes from considering sample preparation history and the role of flow strength. Recent microscopy and computational study of the structure under steady shear shows individual clusters when flow is strong.^{37,38} Flow shutoff reveals a structure and rheology dictated by the pre-cessation flow strength,^{37,38} including residual stresses under weaker flows,³⁹ similar to residual stresses and particle pair asymmetry found in soft glasses.^{40,41} Simulation study utilizing Dissipative Particle Dynamics (DPD) suggests similar structural origins of the two yielding events,⁴² but conclude that two step yield occurs at higher shear rates as opposed to the intermediate shear rates suggested in the work from Petekidis and coworkers.^{11,38} While preparation history complicates structural explanations for the secondary yield, the primary yield under strong flow has been well explained as simple structural failure. However, structural origins of weak-flow yield remain murky.

Indeed, interparticle bonds or the presence of a network need not play a role at all in yield stress or stress

overshoot behavior. Similar overshoots are well known to occur in dispersions of purely repulsive smooth, hard sphere colloids, from dilute to moderately concentrated suspensions^{43–45} to glasses.^{46–49} This behavior has been explained at the microstructural level as the time required for advection to balance diffusion to create a mature near-contact structure, a disparity that widens when diffusive rearrangements are further slowed by, e.g., hydrodynamic interactions.⁴⁴ In hard sphere glasses, the stress overshoot grows more pronounced when cage distortion can accumulate before cage breakage, and this is dependent on the free volume available, found in both simulation and experiments^{46,47,49} and predicted by mode coupling theory (MCT).⁴⁸ Interestingly, stress overshoots in reversible colloidal gels emerge at relatively weak forcing, independent of hydrodynamic interactions. Beyond just the presence of an attractive interparticle potential, what sets the response of gels apart from dispersions is the ongoing influence of slow, non-equilibrium, transient evolution of microstructure – gel aging.^{18,50} Our prior studies of quiescent aging suggest that coarsening should be viewed as ongoing but very slow phase separation – i.e., that “arrest” is not complete: particle dynamics continue to cause growth of condensed-region volume and shrinkage of surface area. The much lower-strain rate emergence of overshoots in reversible gels may indicate sudden progress in this slowed condensation when flow is weak – a release from kinetic arrest – and that subsequent structural evolution may be viewed as a non-equilibrium phase separation.

To interrogate these ideas, we conduct large-scale dynamic simulations of the deformation of a reversible colloidal gel during startup of a fixed strain rate. A primary goal is to understand the microstructural origins of yield, and how structural and rheological yield connect release from kinetic arrest. We first characterize the series of processes that transform the colloidal gel from solid-like to liquid-like rheology after flow startup, namely: pre-yield, rheological yield, and long-time deformation. Next, the evolution of the shear stress and bond dynamics are monitored for a range of imposed flow strengths, and the details of the structure are monitored as they evolve with deformation. We form connections between bond dynamics, structure, and rheology that support the idea that mechanical yield of gels can be viewed as a transition from energy storage to energy release, consistent with release from kinetic arrest and a non-equilibrium phase transition.

The remainder of this paper is organized as follows: The model system and simulation methods are

presented in §2. In §3, results are presented in order of temporal regime: the pre-yield regime in §3.1, the yield point in §3.2, and the stress overshoot in §3.3. For each regime of startup flow, first the rheological response is analyzed, followed by the accompanying evolution of energy, bond dynamics, and microstructure. Discussion and concluding remarks are given in §4.

2 Methods

2.1 Model system

The colloidal gel is formed from a dispersion of 750,000 neutrally buoyant, nearly-hard colloidal spheres of radius a , suspended in a solvent of viscosity η and density ρ . Particle concentration and interaction potentials are selected to produce a model colloidal gel that closely mimics experimental model systems where physical bonds between colloids arise from depletion interactions induced by non-adsorbing polymer depletant^{11,51–53} or temperature-responsive gelation via adhering polymer chains^{24–26,54–56}, for example. Such particle systems are typically moderately concentrated, with particulate volume fractions $0.1 \leq \phi \leq 0.4$ where $\phi \equiv 4\pi a^3 n/3$ is the particle volume fraction and n is the number density. The volume fraction selected is $\phi = 20\%$. Size polydispersity is introduced as a uniform distribution of particle sizes about the average size a with 7% variance.

Particle motion arises from interparticle forces (attractive and repulsive), thermal fluctuations (Brownian motion), and externally imposed flow. The particle interaction potential $V(r)$ was selected to mimic those reported in the experimental literature for a range of depletant-driven and thermoresponsive systems.^{11,55} To do so, we introduce a steep, hard-sphere repulsion and short-ranged attraction, via the Morse potential

$$V_{ij}(r_{ij}) = -V_0 \left(2e^{-\kappa[r_{ij}-(a_i+a_j)]} - e^{-2\kappa[r_{ij}-(a_i+a_j)]} \right), \quad (1)$$

where r_{ij} is the center-to-center distance from particle i to particle j . The attractive potential acts to bond particles together and resist thermal bond rupture; it is set by the well depth, V_0 . In addition, κ and $a_i + a_j$ provide independent control of the attraction range and particle polydispersity, given by particle sizes a_i and a_j . We selected $\kappa = 30/a$ to approximate an Asakura-Oosawa⁵⁷ attraction range $\Delta/a \equiv 0.1$ (cf. Figure 1).

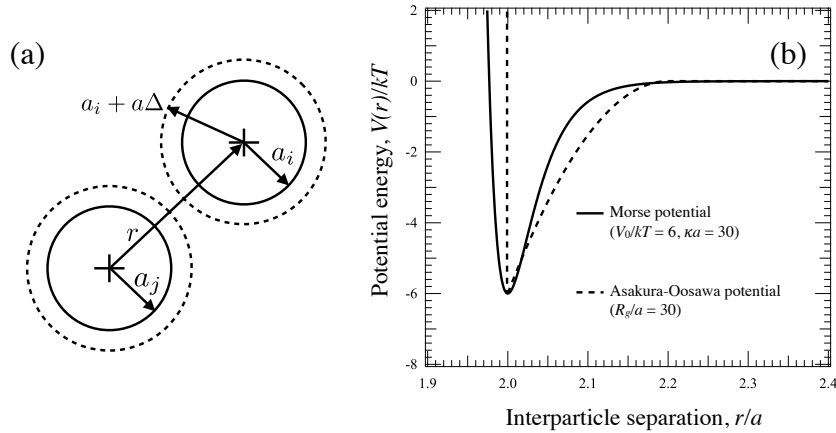


Figure 1: (a) Model system. (b) Interparticle potential given by the Morse potential (solid curve) between particles of radius a . Also shown is an Asakura-Oosawa potential with equal depth and a polymer-to-colloid size ratio of 0.1, given by the ratio of the radius of gyration of the polymer R_g to the radius of the colloid a .⁵⁷

Bonds frequently rupture and reform during and after gelation when they are of order several kT ; here, we selected $5kT \leq V_0 \leq 6kT$, a range that provides substantial difference in gel morphology and linear response rheology.¹⁸

Inertial forces are negligible and fluid motion is set by Stokes equations owing to the small size of the particles that sets a vanishingly small Reynolds number, $Re = \rho U a / \eta$, where U is the characteristic velocity of a particle during shear flow. The small particle size permits Brownian forces to play a key role in gelation and subsequent age coarsening¹⁸, set by the diffusion coefficient $D = kT / 6\pi\eta a$. In general, particles experience Stokes drag, as well as many-body hydrodynamic interactions. While such interactions influence transport rates near equilibrium, during gelation, and exert pronounced effects under strong flow, the freely draining approximation taken here provides substantial initial insight to many important rheological questions.^{43,58}

The 750,000 particles were distributed in the simulation cell and gelation was induced. Structural evolution was then permitted to proceed over time as described in detail in our prior work.¹⁸ The quiescent age-coarsening and corresponding increase in gel stiffness were also presented, revealing that gels of reversibly bonded particles evolve in time via migration of particles over the surface of the network toward lower-energy regions, permitting the slow age-coarsening of dense, glassy strands. Our recent study of delayed shear yield⁵⁰ showed that gels yield at a critical strain, that Brownian motion facilitates yield, and that gels can resolidify after flow has begun. In the present study, flow is imposed rather than arising from a fixed stress, permitting us to ask new questions about yield behavior and its connection to the kinetically arrested

state.

2.2 Dynamic simulation

The stochastic and deterministic forces that influence the motion of microscopic particles in a continuum solvent can be modeled via the Langevin equation,

$$\mathbf{m} \cdot \frac{d\mathbf{U}}{dt} = \mathbf{F}^H + \mathbf{F}^B + \mathbf{F}^P, \quad (2)$$

where $\mathbf{m}$ is the mass or moment of inertia tensor, $\mathbf{U}$ is particle velocity, and $\mathbf{F}^H$, $\mathbf{F}^B$, and $\mathbf{F}^P$ are the hydrodynamic, Brownian, and interparticle forces, respectively. The hydrodynamic drag force is proportional to particle velocity $\mathbf{U}_i$ relative to fluid motion $\langle \mathbf{u} \rangle$, and for particle i is given by

$$\mathbf{F}_i^H = -6\pi\eta a_i [\mathbf{U}_i - \langle \mathbf{u} \rangle]. \quad (3)$$

The stochastic Brownian force arises from thermal fluctuations of the solvent, and obeys Gaussian statistics

$$\overline{\mathbf{F}_i^B} = 0, \quad \overline{\mathbf{F}_i^B(0)\mathbf{F}_i^B(t)} = 2kT(6\pi\eta a_i)\mathbf{I}\delta(t), \quad (4)$$

where the overbar denotes an average over times long compared to the solvent timescale. The Brownian impacts are instantaneously correlated, where $\delta(t)$ is the Dirac delta function. The interparticle force is derivable from a spherically symmetric potential, and a particle i will experience this force as a pairwise sum over all nearby particles,

$$\mathbf{F}_i^P = -\sum_j \frac{\partial V_{ij}(r_{ij})}{\partial r_{ij}} \hat{\mathbf{r}}_{ij}, \quad (5)$$

where $\hat{\mathbf{r}}_{ij}$ is the unit vector pointing from the center of particle j to the center of particle i . In the LAMMPS molecular dynamics software package⁵⁹, the velocity is integrated forward in time via the velocity Verlet algorithm,⁶⁰ where a Langevin “thermostat” enforces Brownian statistics.⁶¹ A small time step is selected to model Stokesian (inertialess) physics, where the Reynolds number and Stokes number must be vanishingly small. The ratio of the Stokes number to the Péclet number sets the importance of particle inertia in Verlet

integration. Although it cannot be set identically to zero, it can be made sufficiently small to faithfully model Stokesian physics,⁶² as shown in our prior work.¹⁸

To apply a sudden startup flow, a linear shear flow $u_x^\infty(x, y, z) = \dot{\gamma}y$ is imposed, where $\dot{\gamma}$ is the shear rate, by deforming the simulation cell at a prescribed rate and updating particle positions, with x as the flow direction and y , the flow gradient direction. The ratio of the shear rate to the rate of diffusion specifies a Péclet number $Pe \equiv \dot{\gamma}a^2/D$. The particular values used here $0.005 \leq Pe \leq 1$ interpolated between regimes dominated by Brownian motion and those by advection, and they compared favorably with those in experiments.⁶³

2.3 Data collection and statistical measurements

The positions and velocities of all particles are monitored throughout simulation, giving detailed information about structure, bond evolution, and stress as flow commences and deforms the gel. The total stress in a colloidal system can be expressed as a sum of contributions from the suspending solvent, $\boldsymbol{\sigma}_S$, plus that from the particle phase, $\boldsymbol{\Sigma}$ as $\langle \boldsymbol{\sigma} \rangle = \langle \boldsymbol{\sigma}_S \rangle + \langle \boldsymbol{\Sigma} \rangle$.⁶⁴ The particle-phase stress itself arises from hydrodynamic interactions arising from externally imposed flow and Brownian disturbance flows as well as interparticle forces. The latter is produced by both entropic forces (hard-sphere repulsion) and enthalpic forces (attractive bonds). In the freely-draining model, the particle-phase contribution to the stress is thence expressed as

$$\langle \boldsymbol{\Sigma} \rangle = -nkT\mathbf{I} - n\langle \mathbf{r}\mathbf{F}^P \rangle, \quad (6)$$

where the first term is the ideal osmotic pressure and the second is the pair-level elastic stress resulting from repulsive and attractive particle interactions. Here, $\mathbf{I}$ is the identity tensor and $\mathbf{r} = \mathbf{X}_i - \mathbf{X}_j$ is the center-to-center separation between an interacting pair. The angle brackets signify an average over all particles in the gel, and over times much longer than the particle momentum relaxation time. The stress is a tensor with six independent elements, where the off-diagonal elements give the shear stress in the velocity-gradient plane that, when scaled on solvent viscosity and shear rate, defines an effective viscosity of the medium.

Structural measurements taken include particle coordination number and static structure factor as they evolve with time. The former, denoted $N_{c,i}$, gives the number of particles within the bond range of particle i . This data is tracked for all 750,000 particles throughout simulation to give a continuous temporal evolution

of contact number distribution $P(N_c)$ as well as an evolving average over all particles. Change in these values are utilized to infer net bond gain and loss. The threshold for the “bonded” state is set at $r_{ij} \leq a_i + a_j + 2a\Delta$. The static structure factor $S(q)$ is computed at instants of interest throughout the simulation. It is defined as the Fourier transform of particle position,

$$S(\mathbf{q}) \equiv \frac{\rho(\mathbf{q})\rho(-\mathbf{q})}{N}, \quad \rho(\mathbf{q}) = \sum_j \exp[-i\mathbf{q} \cdot \mathbf{x}_j(t)]. \quad (7)$$

Here, $\rho(\mathbf{q})$ is the Fourier amplitude of the particle number density at wave vector $\mathbf{q}$, i is the imaginary part, and $S(\mathbf{q})$ is the static structure factor. We calculated this quantity by first binning particles into parallelepiped cells with edge vectors parallel to those of the deforming, periodic simulation box, then performing fast Fourier transforms, and finally back-interpolating from a cubic grid to the resultant Fourier amplitudes. The static structure factor was radially averaged to compute values such as the dominant length scale, $L_{S(q)}$, as discussed later.

3 Results

To interrogate the micro-mechanical origin of yield and understand its connections to energy storage and dissipation, we examine the macroscopic stress and corresponding microscopic structural evolution for each temporal regime of startup flow. We utilized dynamic simulation to subject a family of colloidal gels ($\phi = 0.20$, $5 \leq V_0/kT \leq 6$) to sudden startup of shear flow of strength $0.005 \leq Pe \leq 1$. By varying the interparticle attraction strength as well as the initial age, t_w , of the gel prior to flow startup, the effect of bond strength, network coarseness, and morphology were studied.

The temporal evolution of the shear stress is the primary macroscopic response examined; an example is shown in Figure 2 for a $6kT$ bond-strength gel. Each curve represents the response of the same gel to a flow of strength Pe , as noted in the legend. The three temporal regimes traditionally utilized to characterize macroscopic behavior²⁷ are highlighted by background color. The region highlighted blue corresponds to regime I, a “pre-yield” regime where stress growth exhibits power-law behavior, discussed in §3.1. The growth in stress is followed by a peak or “overshoot” in the stress; a green background highlights this “yield” region, regime II, in the plot. Features of interest in this regime include the value of the peak stress and the

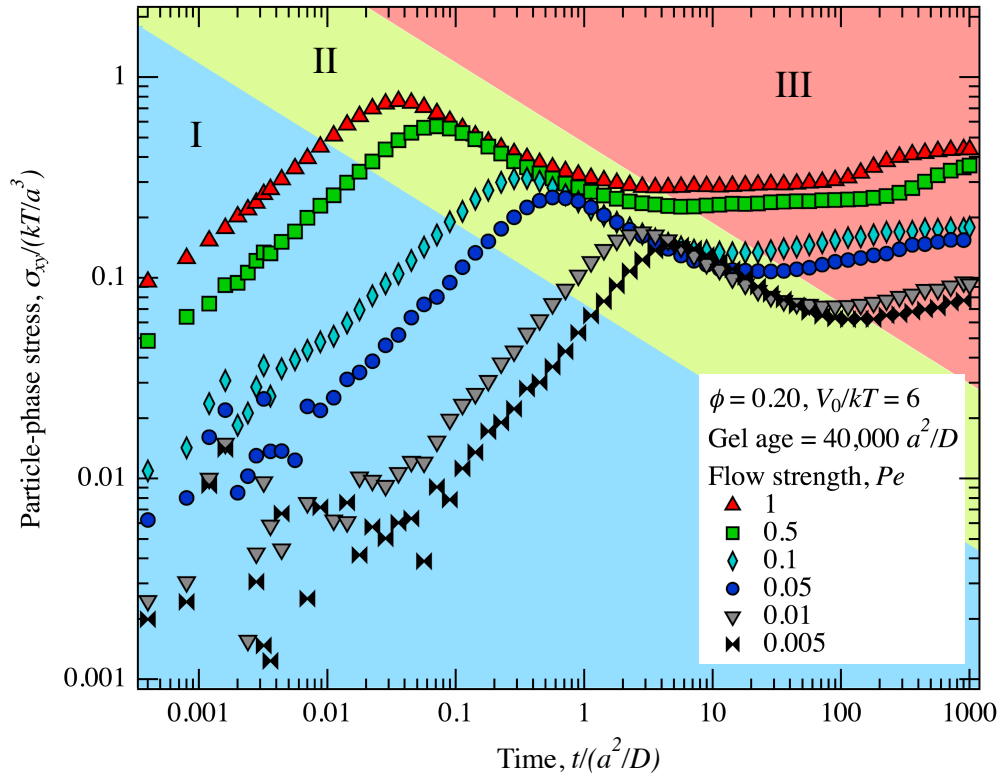


Figure 2: Three macroscopic rheological regimes of the startup shear response: Particle-phase stress in the xy plane, made dimensionless on the thermal stress, plotted over diffusively scaled time after flow startup: (I) pre-yield, (II) rheological yield, and (III) long-time deformation. All curves are for a gel of $\phi = 0.20$, attraction strength $V_0/kT = 6$, and initial age $40,000 a^2/D$. Individual curves correspond to different flow strengths Pe as shown in the legend.

time (or strain) at which it occurs; the yield stress, yield strain, and the underlying microstructural origins are discussed in §3.2. The overshoot, including the post-yield stress decay, is examined in §3.3. Regime III, highlighted in red, defines the long-time behavior of the gel, which is typically presumed to correspond to steady, viscous flow.

3.1 Pre-yield behavior: entropic and enthalpic energy accumulation

At early times after the onset of the imposed strain rate, macroscopic shear stress grows rapidly and monotonically in time (Figure 2, regime I, shaded blue), defining the “pre-yield” regime. We first examine the bulk rheology, and then the underlying microstructural evolution.

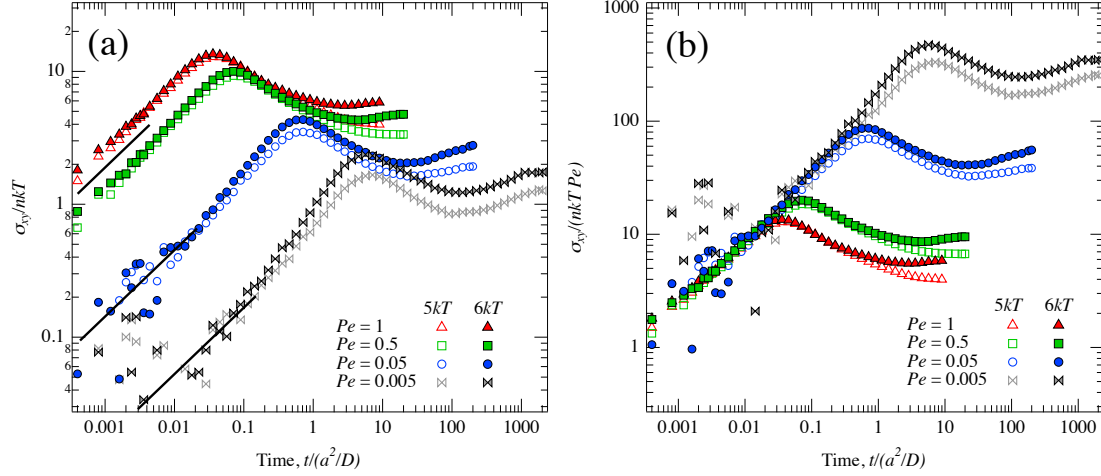


Figure 3: (a) Shear stress response scaled on the ideal osmotic pressure as a function of diffusively scaled time for a 5kT gel (open symbols) and a 6kT gel (closed symbols) and initial age 4,000 a^2/D for several flow strengths Pe . Solid black lines are $\hat{t}^{1/2}$ to guide the eye. (b) Shear stress response from data in (a) scaled on flow strength.

3.1.1 Rheological evolution during pre-yield regime

We focus on two features of the pre-yield stress growth: the magnitude of the stress response (vertical shift) and the rate at which stress grows, the latter described by a power law as $\sigma_{xy} \sim \hat{t}^m$, where $\hat{t} = t/(a^2/D)$ is the diffusively scaled time after flow startup. The shear stress is plotted as a function of time in Figure 3 (a) for a range of flow strength, Pe ; the particle-phase stress is made dimensionless on the ideal osmotic pressure and time is scaled diffusively. At early times after flow startup, each of the curves follows a temporal growth that scales as $\hat{t}^{1/2}$, regardless of bond or flow strength. This short-time growth matches freely-draining suspensions of purely repulsive hard spheres measured in dynamic simulation studies of startup shear,^{43,45} theoretical and simulation studies of microrheology,^{44,58} and experimental studies of concentrated suspensions.⁶⁵ The Brownian motion that sets this scaling initially occurs with little structural distortion; the influence of attraction strength or flow is thus negligible at short times, when structural distortion is small.

At longer times, when advection starts to play a role, temporal growth is faster, $m > 1/2$. Unsurprisingly, the transition to $m > 1/2$ growth occurs earlier as Pe increases: the temporal increase in slope occurs an order of magnitude earlier in time as Pe increases by the same order. The duration of the longer-time pre-yield regime increases as Pe decreases, and the slope continues to grow. The first of these effects, suggests that when flow is weak, additional relaxation processes emerge and delay stress buildup. Such processes may

include relaxation of stretched bonds, relaxation of stretched network strands, or diffusive motion made slower by interparticle attractions. We study their contribution by interrogating dynamics and structure in §3.1.2. Increasing flow strength also increases the magnitude of the pre-yield stress response: the curves shift upward with increasing Pe . Scaling the stress with the applied flow strength gives the viscosity, Figure 3 (b), and collapses the pre-yield regime onto a single curve for all Pe and all V_0 . This behavior can be understood by viewing the stress as energy density, where stronger flow inserts more energy into the system. The linear response suggested by the collapse supports the view that early-time behavior is set by diffusion, and the time at which the curves peel away corresponds to the time at which advection and attractive forces begin to play a role.^{44,58}

Bond strength influences the later pre-yield growth, where the power-law exponent changes with bond strength, as shown in Figures 3 (a) and (b). Stronger bonds produce faster long-time growth of pre-yield stress for all Pe . The change of m with time indicates activation of additional relaxation modes. Given sufficient time, flow distorts the structure enough that interparticle bonds play a role via two mechanisms: bond stretching and hindered Brownian diffusion, both of which slow energy dissipation. Stretched, stronger bonds produce faster stress growth, because further stretching demands more flow energy. Bond strength also sets the magnitude of the stress, the vertical offset, at a given value of Pe . In fact, the offset in stress is linear in the bond strength: $1 \leq \sigma_{6kT}/\sigma_{5kT} \leq 1.2$, where $6kT/5kT = 1.2$, suggesting that, just prior to yield, attraction strength plays only an $O(1)$ role in the magnitude of the stress, consistent with the time-invariant role of pair-level interactions on the linear viscoelastic moduli.¹⁸ More detailed discussion can be found in the Supplementary Materials §??.

Finally, we consider the influence on startup response exerted by initial network morphology and stiffness which are in turn set by pre-gelation volume fraction and the strength of interparticle attractions. As discussed in §2.1, reversible colloidal gels formed during arrested phase separation, where attractive interparticle forces are $O(kT)$, begin with a dense, bicontinuous network structure of thick, glassy strands in which average contact number is six or higher.^{18,66} In addition, ongoing network coarsening takes place as thermal fluctuations restructure the gel over time, leading to the age-stiffening of the linear viscoelastic moduli observed in both simulations and experiments.^{11,18,67–69} Figure 4 (a) gives a plot of the startup response

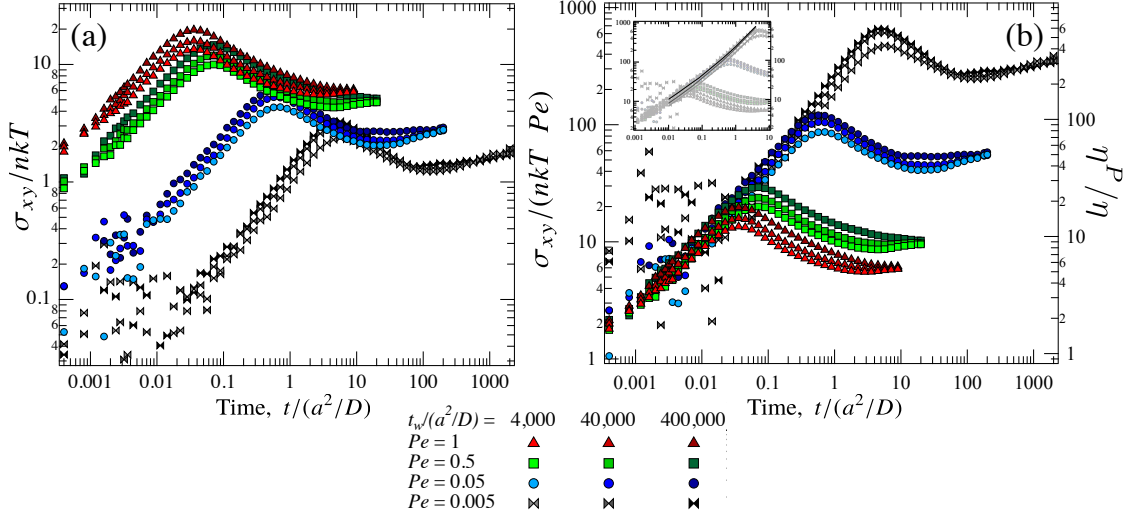


Figure 4: (a) Shear stress response as it evolves over diffusively scaled time for $6kT$ gels ranging in age from $4,000$ to $400,000a^2/D$. (b) Shear stress data from (a) scaled by flow strength, which is simply the viscosity, right axis. The inset, same axes, shows the complex viscosity, computed from the linear moduli published in Zia *et al.*,¹⁸ as solid curves with grey to black for gels of increasing age. Corresponding plots for $5kT$ gels can be found in Figure ?? in the Supplementary Materials.

of a $6kT$ gel subjected to a range of flow strengths Pe at a sequence of advancing ages. Increasing gel age leads to both an increase in the magnitude of the stress response (vertical separation) and more rapid temporal growth. Scaling the stress by Pe gives the viscosity and removes its linear influence, Figure 4 (b), but not age; curves for different ages are still well separated. Age-stiffening at early times recovers age-stiffening of the complex viscosity, shown by solid curves in the inset. The early-time transient viscosity fits well within the linear response envelope, similar to observations in experiments of concentrated suspensions undergoing weak flow.⁶⁵ Differences arise (the steeper slope and greater magnitude of the late-time pre-yield response) where we have proposed that relaxation processes absent from the linear response become activated, again suggesting structural evolution due to flow occurs prior to the yield point, reminiscent of strong, athermal gels which exhibit strong strain stiffening prior to yield.³⁰ But, we recall from our recent work¹⁸ that the high-frequency linear viscoelastic moduli of reversible colloidal gels, which grow with age, are set by the most dominant length scale $L_{S(q)}$ ¹⁸ (the length scale associated with the peak of the static structure factor, details in §2.3). The high-frequency response corresponds to short-time ($\hat{t} \rightarrow 0$) response, making it natural to scale the data from Figure 4 (b) by the dominant network length scale $L_{S(q)}$ of the initial quiescent gel for each age; the result is plotted in Figure 5. Now all early-time curves collapse together, showing that

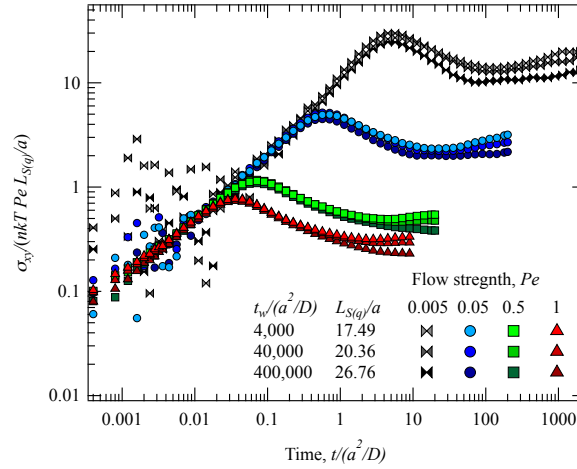


Figure 5: Shear stress scaled on both the flow strength and dominant length scale as a function of diffusive time for $6kT$ gels ranging in age from 4,000 to 400,000 a^2/D . The dominant length scale, $L_{S(q)}/a$, used to scale each curve is shown in the legend (from Zia *et al.*¹⁸). Data for $5kT$ gels is in Figure ?? in Supplementary Materials.

diffusion sets the qualitative temporal scaling, while large-scale structural relaxation sets its magnitude. At longer times, relaxation of the dominant structure gives way to a spectrum of relaxation length and time scales, and the influence of gel age prior to flow startup begins to weaken. The late pre-yield power-law exponent m increases with gel age and the underlying origins of this behavior are discussed below in §3.1.2.

In summary, stress accumulates in the gel first at a rate set by diffusion, $\hat{t}^{1/2}$, when structural distortion is small, switching to $\hat{t}^m$ with $m > 1/2$ when particle displacement begins to matter and interparticle bonds can play a role. The magnitude of the stress shifts upwards with increasing flow strength and gel coarseness, but because these rheological effects can be scaled out, we conclude that little microstructural change occurs at short times, that the network remains intact, and that interparticle bond relaxation drives the change in time scaling at later times. Combining these ideas we propose an extension of the colloidal gel Rouse theory developed by Zia *et al.*¹⁸ as

$$\sigma_{xy} \sim \hat{t}^m L_{S(q)} Pe, \quad (8)$$

$\hat{t}^m$ at early times follows $m = 1/2$, and later in time, becomes $m > 1/2$ with its exact magnitude dependent on flow strength, bond strength, and gel age. The study of the detailed structural origins of this behavior is taken up next.

3.1.2 Structural evolution during the pre-yield regime

Thus far we have focused on the macroscopic response of the gel during startup flow, and inferred from its temporal evolution that only weak, diffusive structural rearrangement occurs at early times, but not sufficient to appreciably stretch bonds on average and, at longer times, microstructural distortion commences and bond forces begin to matter. A simple measure of gel structure is the average coordination or contact number of each particle, $\langle N_c \rangle$, which gives the average number of neighbors around particles that are close enough to experience interparticle interaction. A complementary measure which details how the distance between a pair of particles results in a relaxed, stretched, or compressed bond is the average potential energy of the gel,

$$\langle V \rangle = \frac{1}{N} \sum_{i < j} V_{ij}(r_{ij}), \quad (9)$$

thus providing a monitor of the temporal evolution of “bondedness”⁷⁰ and thus structural rearrangement due to changes in pair separation arising from relative motion. In our recent work, we showed that a reversible colloidal gel formed by arrested phase separation undergoes a continued decrease in its potential energy (the absolute value of potential energy grows), a finding that supports the view that quiescent coarsening is slow, ongoing phase separation.^{18,50} When such gels are subjected to fixed, step shear stress, potential energy increases more rapidly after gel yield than under quiescent conditions, suggesting an activation of phase separation.⁵⁰

Though $\langle N_c \rangle$ and $\langle V \rangle$ are closely related, they distinguish bond rupture (or formation) versus bond stretching (or compression). One expects bonds to stretch before they break, and thus $\langle V \rangle$ gives a sensitive measure of small-scale changes in structure that can potentially exert an impact on rheology. Bond rupture, as measured by $\langle N_c \rangle$, represents a greater microstructural distortion and is the mechanism long attributed to gel yield and fluidization.^{11,12,31} To monitor the extent to which contact number and potential energy change during startup of flow, each is normalized on its initial value prior to startup, $\langle N_c \rangle_i$ and $\langle V \rangle_i$, respectively, and plotted in Figure 6 with $\langle N_c \rangle / \langle N_c \rangle_i$ on the right vertical axis and $\langle V \rangle / \langle V \rangle_i$ on the left vertical axis. Values larger than unity in the plot correspond to net bond formation (solid lines) or compression (dashed lines) while values smaller than unity correspond to net bond loss (solid lines) or stretch (dashed

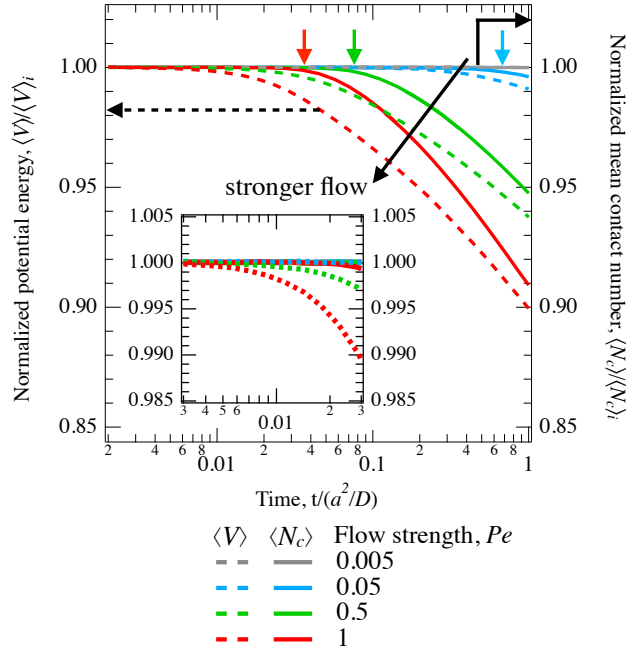


Figure 6: Bond dynamics: Normalized potential energy, left axis and dashed lines, and normalized mean contact number, right axis and solid lines, plotted as a function of diffusive time for a $6kT$ gel with initial age $4,000a^2/D$. Vertical arrows indicate the yield point. Inset zooms in to the end of the pre-yield regime. Axes labels in insets are same as main plots.

lines).^c Figure 6 illustrates the effect of flow strength, Pe , on these bond dynamics. Only the first diffusive time is shown, $t/(a^2/D) = 1$, which is long enough to capture the pre-yield regime for $Pe = 1, 0.5$, and 0.05 , and most of this regime for $Pe = 0.005$; the yield point, or stress maximum of the overshoot, is marked by a downward arrow, color-matched to the curve of each flow strength. The solid lines ($\langle N_c \rangle / \langle N_c \rangle_i$) show that almost no net bond loss occurs prior to the yield point; in fact, the first visible net loss of bonds is observed at the yield point and will be discussed in detail in §3.2.2. The absence of net bond loss prior to the yield point supports the assertion in §3.1.1 that only weak structural evolution occurs during the pre-yield regime.

The potential energy can elucidate how intact bonds evolve (on average) during the pre-yield regime. In contrast to $\langle N_c \rangle / \langle N_c \rangle_i$, the dashed lines for the potential energy $\langle V \rangle / \langle V \rangle_i$ depart from unity during the pre-yield regime, indicating that bonds on average begin to stretch. Bond stretch commences at the transition from $m = 1/2$ to $m > 1/2$, occurring at longer times after flow startup with decreasing Pe , showing that flow-induced bond-scale stretching and relaxation underlies late pre-yield stress evolution. That is, deformation

^cA decrease in the normalized potential energy can also be observed when bonds near the potential minimum (at $r/a = 2.0$ in Figure 1) are compressed into the steeply repulsive regime of the Morse potential. We find that at these flow strengths, bond length distribution confirms that the decrease in average, normalized potential energy near yield is not characterized by particles under strong compression.

can accumulate over time until diffusion is unable to keep up. In consequence, structure evolves at the bond length scale. When m grows larger, stress in fact accumulates more slowly since $0 < \hat{t} < 1$. It is clear from the plot that stronger flow stretches bonds farther and earlier, but how can this help explain the qualitative growth rate of σ_{xy} ?

First, we recall the inset in Figure 4 (b) and see that weaker flows give better agreement to the linear envelope at later times (lower frequency) where the gel is more viscous. For stronger flow, we find that the transient viscosity grows more rapidly than the linear envelope predicts, arising from the interparticle force that sets the interparticle stresslet (Equation 6): stronger flow stretches bonds farther than weak flow does at some instant which gives a larger value of the enthalpic stresslet. This is consistent with behavior in strong gels where stiffening via bond or chain stretching is a key mode of energy storage up to the yield point.³⁰ While others have proposed that bond stretching plays a role in the yield point (regime II),¹² we instead find that bond stretching begins to play a role well before, during the later part of the pre-yield, and alters the rate of stress accumulation prior to the yield point.

Gel age also exhibited an impact on the rate of stress growth during the pre-yield. Increasing the initial connectivity, e.g. greater number of interparticle bonds, of the gel permits a greater resistance to flow, and a greater memory of flow, producing a more rapid accumulation of energy. Discussion on this topic is provided in Supplementary Materials §??.

The arrangement of bonds – not just particles – evolves during the pre-yield regime. Dispersions of purely repulsive hard spheres undergoing steady shear flow accumulate in a compressional axis and deplete along an extensional axis.⁷¹ Attractive forces change relative particle trajectories, transferring some from the accumulation to the depleted region.^{72–74} The fabric tensor is one way to monitor the distribution of bonded neighbors:

$$\mathbf{R} = \frac{\phi}{N} \sum_{i=1}^N \sum_{j \neq i}^N \hat{\mathbf{r}}_{ij} \hat{\mathbf{r}}_{ij}, \quad (10)$$

where the normalized orientation vector $\hat{\mathbf{r}}_{ij}$ points from the center of particle i to the center of particle j , for pairs of particles within a prescribed distance (here, the bond distance, Δ , which also defines N_c). Here we have adopted the normalization of Aarons et al⁷⁵, utilizing the total number of particles N and the volume fraction ϕ , which avoids normalizing on the average bond number because $\langle N_c \rangle$ evolves during both

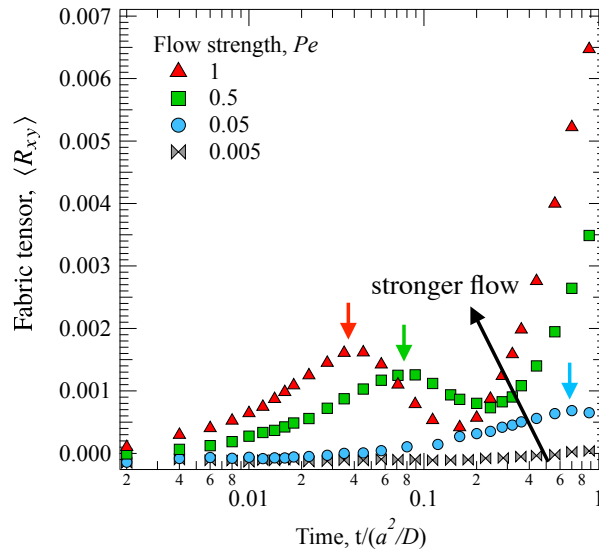


Figure 7: Orientation of bonds: Fabric tensor as it evolves with diffusively scaled time after startup for a $6kT$ gel with initial age $4,000a^2/D$. Vertical arrows mark the yield point.

quiescent conditions and under flow for reversible gels. To measure the anisotropy of the bond arrangement in the flow-flow gradient (xy) plane, we evaluate the off-diagonal component R_{xy} where $R_{xy} > 0$ indicates orientation in the positive quadrants of the plane (the extensional axis) and $R_{xy} < 0$ indicates orientation in the negative quadrants (the compressional axis). In a quiescently aged gel, off-diagonal components of $\mathbf{R}$ are vanishingly small, because neutrally buoyant gelation does not bias particle bond orientation. The fabric tensor element $\langle R_{xy} \rangle$ is computed here as an average over all particles and is monitored over time after flow startup.

Bond orientation in the plane of flow, $\langle R_{xy} \rangle$, is plotted in Figure 7 for a range of flow strengths Pe . At short times, bond orientation is isotropic, $\langle R_{xy} \rangle = 0$, but at intermediate times, $\langle R_{xy} \rangle > 0$, showing that flow induces anisotropic orientation of bonds prior to yield, i.e. that bonds not only stretch, they re-orient in the direction of the extensional axis. Bond anisotropy grows non-monotonically, with a peak emerging well after the times at which bonds begin to stretch during the pre-yield. In fact, the peak value of $\langle R_{xy} \rangle$ occurs at the same time as the macroscopic yield peak, indicated by the arrow at the yield point in Figure 7. That is, yield occurs when bond-level structural anisotropy reaches a first peak, which will be discussed further in §3.2.2. Bond anisotropy is one measure of entropic energy stored via deformed structure in the plane of flow: energy is stored in the distorted structure which in dispersions and other viscoelastic fluids permits

useful work to be done upon removal of forcing^{58,76,77} while in dense or sticky systems, stresses may be frozen in.^{39–41} For the stronger flows shown, $\langle R_{xy} \rangle$ exhibits a larger and more rapid growth leading up to the yield point, suggesting that more energy is stored at these flow strengths. In comparison, at lower Pe , $\langle R_{xy} \rangle$ shows little anisotropy leading up to the yield point: weaker flow stores less entropic energy during the pre-yield regime. Our findings are consistent with recent studies of gels undergoing strong flow^{9,10}, which also find increasing structural alignment in the extensional direction of the flow-flow gradient plane during the increase in the stress response leading up to the yield peak. While these studies use $g(r)$ or the harmonic $g(r)_2^{-2}$ show that the nearest neighbor contacts decrease in the extensional direction, the data shows a shift of bonded particles into the extensional direction, with a more pronounced increase during pre-yield.¹⁰ Here, the fabric tensor monitors the relative accumulation of particles within the range of the attraction length (counting both nearest neighbor and all more stretched but still bonded particles) which we suggest reflects how weak flow allows pair bonds to shift from the compressional axis to the extensional axis, as seen in weak flows in attractive dispersions.^{72–74} We remark that both bond stretching and bond orientation set energy storage: bonds relax faster when weak flow provides only a modest disturbance and particle cages attain a weaker anisotropy.

The influence of gel age and bond strength are far weaker than Pe on the bond orientation during the pre-yield regime. This is consistent with the idea that bond orientation signals entropic energy storage, which should be less influenced by enthalpic changes in the gel, e.g. greater connectivity or increased bond strength. A discussion can be found in the Supplementary Materials.

In summary, the pre-yield rheological evolution reveals the changing role of energy dissipation, enthalpic energy storage, and entropic energy storage. Similar to hard-sphere suspensions, structural distortion propagates via diffusive displacements that produce temporary fluctuations in structure that rapidly dissipate,^{43,58} setting a diffusive evolution as $\hat{t}^{1/2}$. But, as deformation accumulates, diffusion is unable to keep up, permitting particle interactions to change the qualitative rate of stress growth, $\hat{t}^m$ (where $m > 1/2$). Potential energy indeed confirms that bonds begin to stretch, storing enthalpic energy, and the fabric tensor indicates bonds orient along the extensional axis, signaling entropic energy storage. No net bond loss occurs during the pre-yield, suggesting an intact network stores energy. The magnitude of the pre-yield response depends

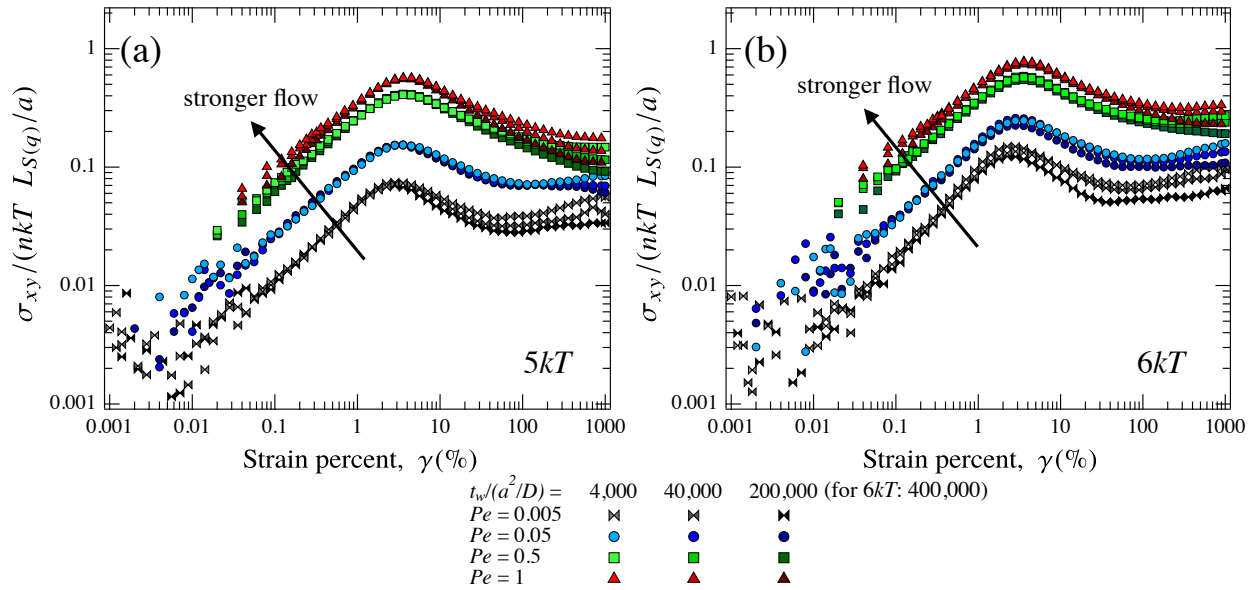


Figure 8: Shear stress scaled by the dominant length scale and the ideal osmotic pressure as a function of strain percent for (a) $5kT$ gels and (b) $6kT$ gels ranging in initial age from 4,000 to 400,000 a^2/D .

quantitatively on gel age and flow strength as $\sigma_{xy} \sim \hat{t}^m L_{S(q)} Pe$. Weaker flow permits bond relaxation, resisting flow and causing more rapid stress growth, and storing less energy as bonds are less stretched and particle cages less distorted.

3.2 The yield point: maximum energy storage

The stress reaches a peak value that grows higher and peaks earlier as flow strength increases, and then gives way to a long time evolution towards steady behavior (Figure 2, regime II, shaded green). We examine the stress maximum, with detailed interrogation of corresponding microstructure, in order to characterize rheological and structural response to this maximum energy, lending insight into the subsequent stress decay.

3.2.1 Rheology of the yield point

The view of yield as a transition where solid-like character is lost makes it natural to examine stress versus strain, rather than time. The strain, γ , represents the deformation accumulated from the applied shear flow, $\gamma = \dot{\gamma}t$. In Figure 8, stress is plotted as a function of strain, for (a) $5kT$ and (b) $6kT$ gels. In both plots, the stress is normalized on the ideal osmotic pressure nkT and the dominant quiescent length scale $L_{S(q)}$.

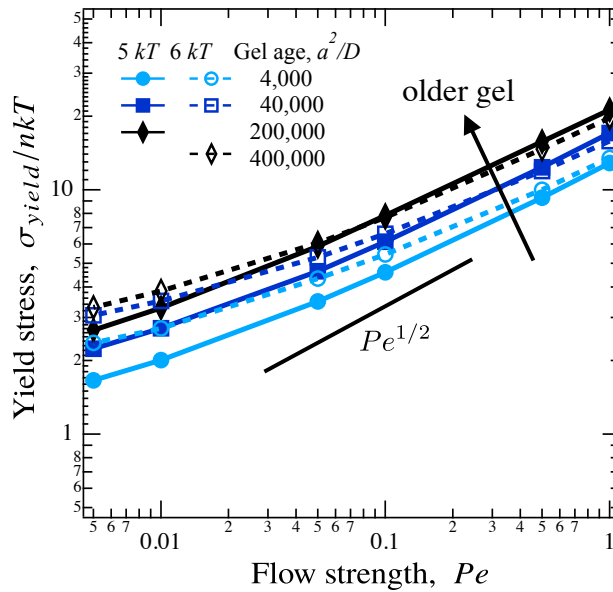


Figure 9: Yield stress scaled on the ideal osmotic pressure as a function of flow strength. Each curve represents a gel with initial age ranging from 4,000 to 400,000 a^2/D with $V_0 = 5kT$ (solid lines) and $6kT$ (dashed lines). The solid black line represents $Pe^{1/2}$ scaling for comparison.

The effect is clear immediately: the yield peaks that were widely separated in time are now brought nearly aligned with one another. Yield occurs over a narrow range of strain, $2.5\% \leq \gamma \leq 4\%$, for the gels and flow strengths examined. Together, the value of the peak or yield stress, σ_{yield} , and the yield strain, γ_{yield} , define the yield point; the influence of flow strength, gel age, and bond strength on σ_{yield} and γ_{yield} are inspected and compared with corresponding behavior in sheared dispersions.

The yield stress, σ_{yield} , increases as flow strength increases (Figure 9), growing as Pe^δ , where $\delta \leq 1/2$. Whittle and Dickinson observed similar behavior but with $\delta = 1/2$, for nearly permanently-bonded, low-density gels, hypothesizing that the connection of Pe to relaxation timescales indicates that yield is a “de-gelation” process.³¹ No measures of the complex moduli or network order were put forth to support this intriguing hypothesis, however. Alternatively, one can recognize that stress is a measure of energy density and, given that σ_{yield} is the maximum value of stress, view yield as a transition in storage and dissipation of flow energy, rather than as a structural failure.

To interrogate the balance of energy storage and dissipation at the yield point, we compare the yield stress of the gel to the well-characterized shear thinning regime in sheared dispersions of purely repulsive hard spheres⁷⁸; this non-Newtonian behavior arises due to entropic energy storage in a distorted structure

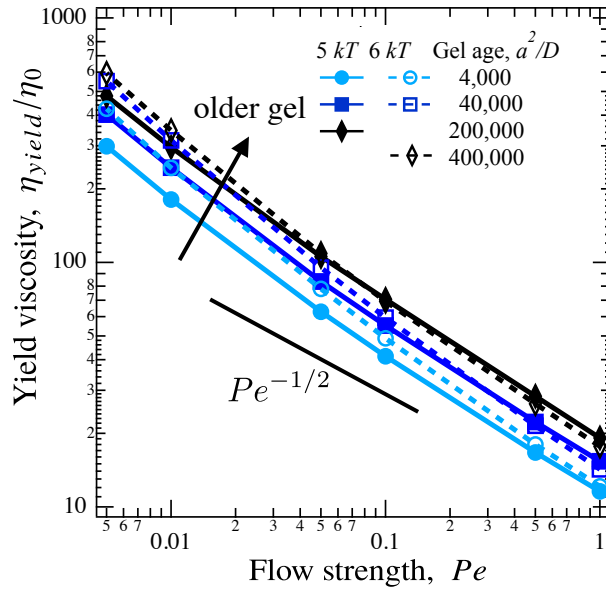


Figure 10: Yield viscosity as a function of flow strength. Each curve represents a gel with initial age ranging from 4,000 to 400,000 a^2/D with $V_0 = 5kT$ (solid lines) and $6kT$ (dashed lines). The solid black line represents $Pe^{-1/2}$ scaling for comparison.

when Brownian motion begins to weaken as Pe grows. To compare the gel with sheared dispersions, we scale the stress on flow strength to give the viscosity, $\eta \sim \sigma/Pe$ (Figure 10). The viscosity at the yield point is thus $\eta_{yield} \sim Pe^{\delta-1}$, with $\delta - 1 < 0$. We compare the yield viscosity to the steady state shear thinning regime in dispersions because when flow is weak, dispersions exhibit almost no overshoot; the maximum viscosity is the steady-state value. In the gel, the viscosity is maximum at the yield point (the maximum value of the overshoot) and an overshoot occurs even when $Pe \leq 1$. Shear thinning of hard-sphere dispersions arises from changes in the ability of microstructural dynamics to dissipate flow energy, and over the regime of interest, $0.005 \leq Pe \leq 1$, the viscosity decays with a $\Delta\eta \sim Pe^2$ weakening of the interparticle contribution.⁷⁸ For weak forcing, $Pe \leq 1$, such a quadratic weakening of the interparticle contribution is small, producing a weak decay in the total viscosity. When we estimate a decay of the interparticle contribution over the same regime of flow for the gel, we find $\Delta\eta \sim Pe^w$, where $w \leq 1/2$, which indicates that the yield point of the gel shear thins more strongly than a dispersion. Stronger shear thinning (weakened energy dissipation) reflects the greater capacity of a gel to store energy in stretched bonds prior to yield. As flow gets stronger, more energy is stored in stretched bonds, reducing the ability to dissipate energy. Weakening Brownian motion also contributes to shear thinning but exerts less influence. Measurement of bond dynamics is needed to

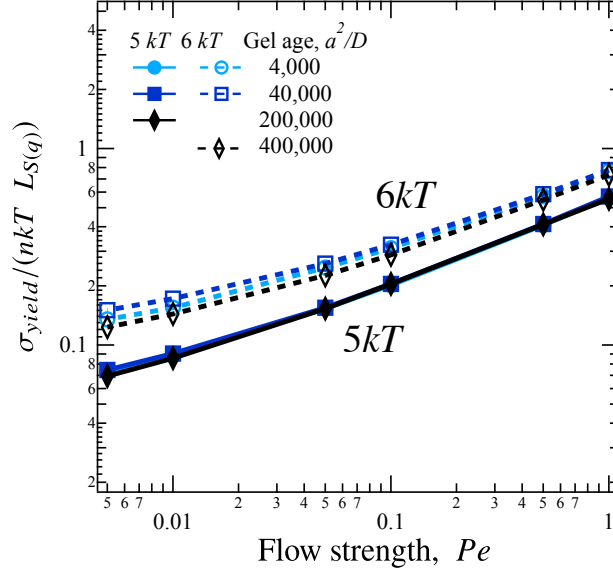


Figure 11: Yield stress scaled on the dominant length scale prior to flow startup and the ideal osmotic pressure, plotted as a function of flow strength. Initial age ranges from 4,000 to 400,000 a^2/D with $V_0 = 5kT$ (solid lines) and $6kT$ (dashed lines).

verify this hypothesis, and is presented in §3.2.2. Our observation that $\eta_{yield} \sim Pe^{\delta-1}$ is also consistent with experimental work from Petekidis and coworkers¹¹ who observe shear thinning of the yield viscosity where $\delta \rightarrow 0$ indicating strong shear thinning for the approximate range of $0.01 \leq Pe \leq 0.5$.

As gels age, they coarsen and stiffen elastically, while particle mobility decreases;¹⁸ the yield stress shown in Figure 9 also exhibits age dependence. Each curve can be scaled on the dominant network length scale, $L_{S(q)}$, as shown in Figure 11. All ages for each attraction strength collapse together^d, showing that the network length scale plays a role in the quantitative value of the stress at the yield point. Petekidis and coworkers¹¹, in a study of moderately concentrated depletion gels, also find that the peak stress grows with gel age which the authors attribute to an increase in the number of inter-cluster bonds with gel age that must break at the first yield peak to release clusters. However, the yield point occurs well beyond the $\hat{t} \rightarrow 0$ limit; one does not expect the response at intermediate times necessarily to follow that observed in the high-frequency¹⁸ or short time (§3.1) limit. A broad spectrum of relaxation scales should matter at intermediate times. It appears that bonds additively contribute to the behavior of the gel via the network

^dEven when the yield stress curves are normalized by $L_{S(q)}$ dividing the $6kT$ curves by the corresponding $5kT$ curves does not identically give 1.2, the ratio of the bond strengths. That is, there is no simple or direct effect of attraction strength. As shown in previous work,¹⁸ dynamical heterogeneity depends nontrivially on the bond strength. A quantitative discussion of the effect of attraction strength on the yield stress σ_{yield} is in §?? of the Supplementary Materials.

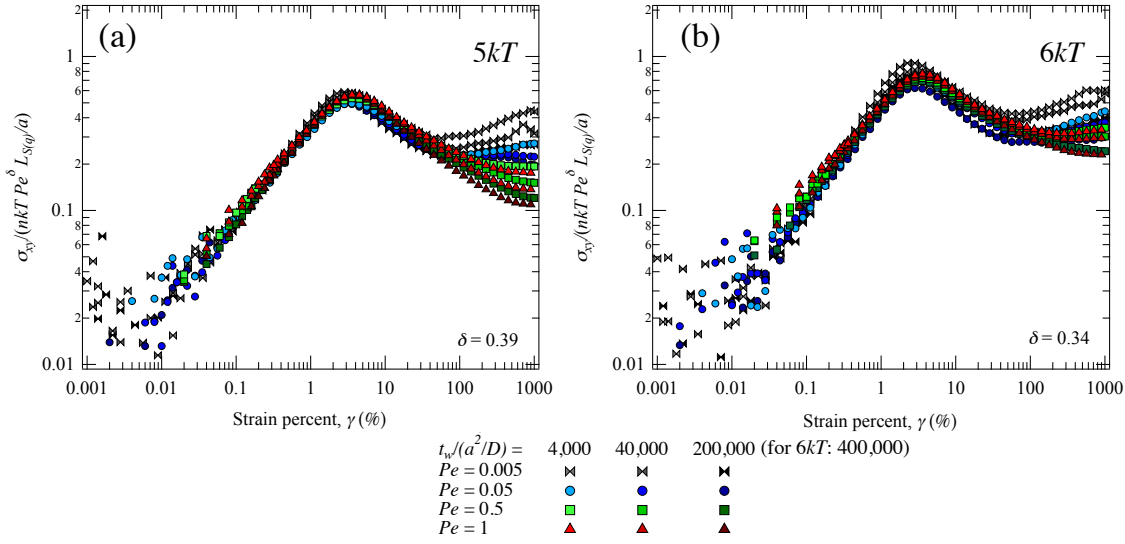


Figure 12: Shear stress scaled by the dominant length scale, the ideal osmotic pressure, and Pe^δ as a function of strain percent for (a) 5kT gels and (b) 6kT gels ranging in initial age from 4,000 to 400,000 a/D . The value of δ utilized is noted within each subfigure.

feature size, as follows: Combining the Pe -dependence of σ_{yield} with its dependence on $L_{S(q)}$ shows that interparticle bond dynamics set the qualitative scaling of yield stress (energy storage) with flow strength, and the network length scale shifts the curves, i.e. exerts a quantitative influence on energy storage. It remains to be determined whether yield is the detachment of clusters or blobs of $L_{S(q)}$ from the network, as envisioned by Petekidis and coworkers^{11,12}, or something less catastrophic, such as melting within glassy blobs. Indeed, the influence of the quiescent length scale on σ_{yield} suggests that dramatic network failure need not accompany the yield point, and that structures as large as $L_{S(q)}$ remain intact at the yield point, which we will discuss further in §3.2.2.

The cumulative effect of the above scalings is shown in Figure 12, with a scaling Pe^δ extracted from the data. These scalings collapse the yield points together vertically, highlighting the difference in the behaviors surrounding yield: the qualitative difference in the rate of stress growth during the pre-yield (§3.1) and the diverging overshoot behavior (§3.3) and post-yield response. This collapse also reveals that δ for the 6kT gels is smaller than that of the 5kT gels, suggesting stronger bonds further weaken diffusive transport and enhance the strength of shear thinning, and supporting the idea that additional energy storage at the yield point is imparted to the gel by the presence of bonds.

In addition to the the yield stress σ_{yield} , the yield strain γ_{yield} also changes with flow strength, gel age,

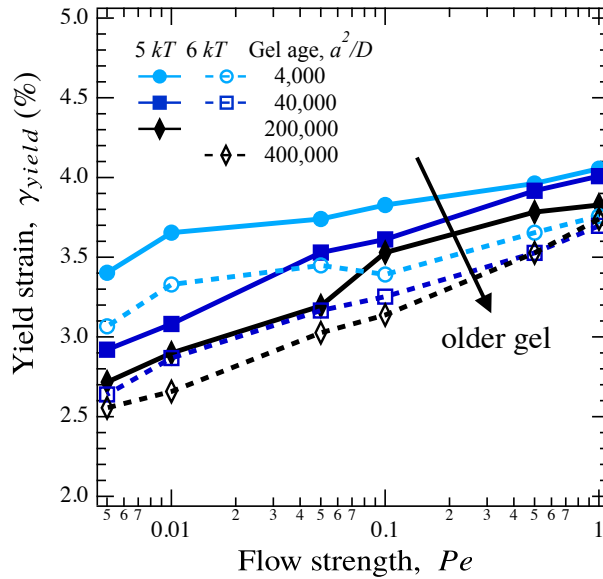


Figure 13: Yield strain as a function of flow strength. Initial age ranges from 4,000 to 400,000 a^2/D with $V_0 = 5kT$ (solid lines) and $6kT$ (dashed lines).

and attraction strength. Thus far, we have examined the yield stress as an indication of the maximum in energy stored from flow. The extent of macroscopic deformation at which this energy maximum is reached is the yield strain, γ_{yield} . The yield strain is plotted in Figure 13 as a function of Pe . For all gels shown, γ_{yield} increases with flow strength. Stronger flow increases deformation, while weaker flow exhibits both a lower energy maximum and reduced macroscopic deformation, suggesting that Brownian forces play a role in setting the energy and deformation reached at the yield point. Memory loss accompanies stress and structural relaxation in colloidal dispersions, and Brownian motion plays an important role in erasing such memory.^{44,58,79} Here, Brownian motion also erases memory storage in gels, but can play a direct role by rupturing bonds⁵⁰ and an indirect role, by making uniform the structure. How the effects combine to produce a lower macroscopic yield strain will be explored in §3.2.2.

Age coarsening also influences the yield strain γ_{yield} . Gels of advancing age yield with less deformation when Brownian motion is strong ($Pe \rightarrow 0$), but this age dependence vanishes as $Pe \rightarrow 1$. While the energy maximum σ_{yield} increases with gel age for all flow strengths examined, this maximum occurs with less macroscopic deformation. It is intuitively appealing to view older gels as somehow more brittle, making it easy to understand why an older gel can deform less before yielding. But the fact that weaker flow (stronger Brownian motion) exacerbates this brittleness is puzzling. Instead, let us consider the work done to yield

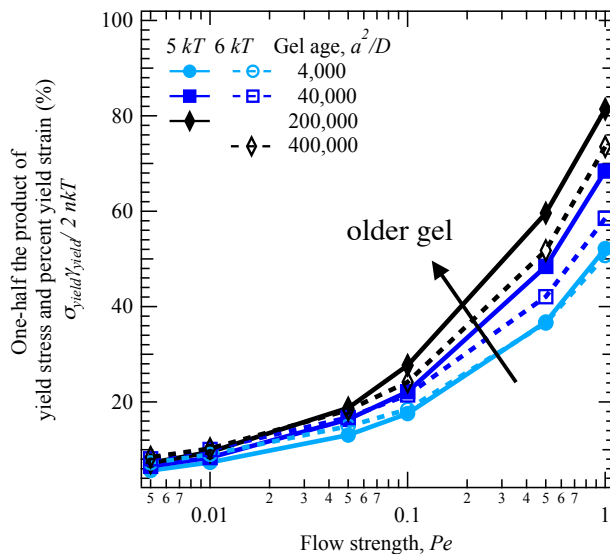


Figure 14: Work done to yield the gel: One-half the product of yield stress (scaled on the ideal osmotic pressure) and yield strain (%) as a function of flow strength. Initial age ranges from 4,000 to 400,000 a^2/D , with solid lines for $5kT$ gels and dashed lines for $6kT$ gels.

the gel. From Clapeyron's theorem, the total strain energy of a body is equal to one-half of the work done on the body by external forces. We compute one-half the product of the yield strain and the yield stress, and plot it in Figure 14 as a function of Pe . As $Pe \rightarrow 1$, the work required to yield an older gel is clearly greater than that for younger gels. As imposed flow weakens, $Pe \rightarrow 0$, the amount of work required to yield the gel becomes indistinguishable for gels of different ages; that is, the age-dependence of required work vanishes as imposed flow strength decreases, or as Brownian motion grows stronger. Age coarsening leads to net bond formation over time¹⁸; the presence of more bonds gives a greater ability to store energy enthalpically via bond stretching. Age matters for $Pe \rightarrow 1$, suggesting that this increasing enthalpic energy storage with gel age plays a role. However, enthalpic energy storage may matter less overall as flow strength weakens. To test this apparent flow-strength shift from the dominance of enthalpic energy storage mechanisms as $Pe \rightarrow 1$ to other energy storage mechanisms, such as structural distortion, when $Pe \rightarrow 0$, we will examine the underlying particle dynamics in §3.2.2.

Finally, the interparticle attraction strength also plays a role in setting the yield strain γ_{yield} : the $6kT$ gels yield at a shorter strain than the $5kT$ gels as shown in Figure 13. It has been suggested previously that the yield strain is directly related to the distance that bonds have been displaced, given that this is the distance particles must be displaced to sever a bond.^{11,12} However, here, the attraction range is held

constant, showing that changes in bond dynamics or glassy dynamics influence γ_{yield} . As shown in the quiescent aging study by Zia *et al.*¹⁸, gels with weaker interparticle bonds are coarser but more compliant at any given age; individual particle dynamics remain faster for all gel ages, compared to a gel with stronger bonds. That is, both the morphology of the gel, given by gel coarseness, and the individual particle dynamics, change when the attraction strength is increased by even $1kT$. The reduction in γ_{yield} with increasing bond strength is consistent with the idea that particle mobility affects the bulk extension; that is, recovery of $6kT$ bonds may theoretically occur more rapidly, but the loss of stronger $6kT$ bonds is more critical, further discussed in Supplementary Materials §??).

In summary, the yield point suggests a local maximum in energy density that signals a transition in the balance between energy storage and dissipation. The energy density at the yield point, represented by σ_{yield} , exhibits shear thinning behavior $\sigma_{yield}/Pe \sim \eta_{yield} \sim Pe^{\delta-1}$ where $\delta < 1/2$, showing more pronounced shear thinning, or a shift of nonlinear shear thinning to the linear response flow regime, as compared to dispersions.⁷⁸ The difference emerges from the substantially higher low- Pe plateau in gels arising from elastic bonds that can store flow energy enthalpically, as compared to dispersions, which can store flow energy only entropically via structural distortion. However, energy density at the yield point still depends on both interparticle bonds and network coarseness $L_{S(q)}$, supporting the idea that the network remains fully connected during yield. The macroscopic deformation at yield, γ_{yield} , varies with flow strength, gel age, and attraction strength, suggesting that microstructural yield may not be just a simple matter of displacing particles by the distance of the attraction range, but, rather, that bond dynamics set by Brownian motion and glassy dynamics play a central role in yield. Together, the pronounced shear thinning of the maximum energy density σ_{yield} and the flow- and age-dependence of the work required $\sigma_{yield}\gamma_{yield}/2$ highlight the proposed role played by energy storage in bonds. To interrogate this idea we next conduct a detailed study of bond dynamics and structural evolution.

3.2.2 Structure and bond dynamics at the yield point

Thus far our study of the rheology of the yield point suggests that maximum energy saturation, σ_{yield} , and work required to yield, $\sigma_{yield}\gamma_{yield}/2$, depend on microstructural energy storage mechanisms which can be

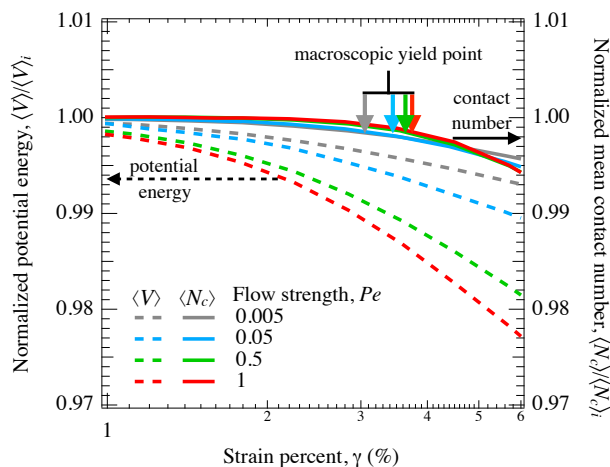


Figure 15: Bond dynamics: Normalized potential energy, left axis and dashed lines, and normalized mean contact number, right axis and solid lines, plotted as a function of strain percent for a $6kT$ gel with initial age $4,000a^2/D$. The yield point is marked for each curve with an arrow of the corresponding color.

tuned via flow strength, gel age, and attraction strength. Here, we monitor the dynamics of bond formation and rupture, along with the fabric tensor, to understand enthalpic and entropic energy storage mechanisms, respectively. As described in §3.1.2, bond dynamics reveal whether bonds are on average stretched or compressed (the normalized potential energy) or if net bond loss or gain occurs (the normalized mean contact number). These quantities are plotted in Figure 15 on the left and right vertical axes, respectively, as a function of gel deformation, γ . Both the potential energy and mean contact number have been normalized on their pre-startup values. When $\langle N_c \rangle / \langle N_c \rangle_i < 1$, flow causes net bond loss; likewise, when $\langle V \rangle / \langle V \rangle_i < 1$, bonds are, on average, stretched by the flow.^e

The first observation that connects macroscopic yield to bond dynamics is the precise alignment of bulk yield, $2.5\% \leq \gamma_{yield} \leq 4\%$, with saturation of bond stretch. An arrow points to the macroscopic yield strain; $\langle N_c \rangle / \langle N_c \rangle_i$ departs from unity at precisely the macroscopic critical strain, with a shift to the left that follows the Pe -dependent bulk yield strain. This reveals two important behaviors: first, the onset of net bond loss corresponds precisely to the onset of bulk yield. Second, the extent of bond loss is surprisingly small: fewer than tenths of one percent of bonds are lost at yield: a “critical bond loss” sets macroscopic yield, but the network remains fully intact during rheological yield. It is entirely possible, in fact probable, that strong flow

^eOnce we observe net bond loss, signaled by $\langle N_c \rangle / \langle N_c \rangle_i < 1$, a decrease in potential energy may represent both bond stretching and bond loss. The potential energy $\langle V \rangle / \langle V \rangle_i$ is a measure of how strongly particles interact, and thus when a bond is lost, effectively a particle pair cease to interact resulting in a lower value of $\langle V \rangle / \langle V \rangle_i$. Conversely, when a bond is gained, this is also reflected in the normalized potential energy as an increase in $\langle V \rangle / \langle V \rangle_i$.

ruptures a network, but evidently a flowing gel can remain intact as it yields under weaker flow. Prior studies have noted that the maximum rate of bond loss signals gel yield, and the liberation of separate aggregates from the network can occur prior to the yield point for strong flows.³¹ Indeed, experimental study of strong gels do report a maximum in bond loss but no direct connection to maximum stress.³⁴ Others have described partial network failure at the yield point, or network “softening”⁹, where some strands detach and others remain intact. In contrast, Figure 15 demonstrates that while bond dynamics and particle mobility matter, yield in dense, reversible gels can occur with little bond loss and an intact network.

It is curious that the critical bond loss does not change as the bulk yield strain changes, which suggests that bond stretching saturates at yield. Figure 15 reveals that significant bond stretching commences well before yield, and persists through the yield point. Stronger flow stretches bonds more on average at yield (more pronounced decrease of $\langle V \rangle / \langle V \rangle_i$), i.e. the flow energy stored enthalpically in stretched bonds increases with stronger flow. The fact that the same amount of bond rupture occurs regardless of the degree of bond stretching suggests that saturation of energy storage sets the yield point. Once this saturation is reached, a few bonds rupture, permitting relaxation of many others and thence bulk gel yield. When flow is very weak, we expect the memory-erasing action of Brownian motion to erode storage quickly. Even though bond stretching still saturates, the average length of a stretched bond is very small.

Overall, analysis of bond dynamics reflects the intrinsic link between yield stress, yield strain, and energy saturation. The present study suggests that the extent of bond rupture should be viewed as a proxy for a saturation of bond stretching and energy storage that signals yield, rather than as a direct cause of yield. The subsequent bond relaxation that produces yield eases glassy frustration, permitting release from kinetic arrest. This view is complementary to strong-flow yield hypotheses of Petekidis and coworkers where network rupture via bond breaking at the first overshoot accompanies fluidization.^{11,12} The value of studying weak flow yield is the ability to observe condensation of particles and changes in energy corresponding to release from kinetic arrest and further progress with phase separation.

Gel age appears to also play a role in energy management in the gel. Unsurprisingly, the extent of bondedness in a gel is most influential on the apparent energy stored (see §3.2.1 for age effects on σ_{yield}) and this is borne out by the stronger stretching observed in older gels at a set Pe at the yield point. Not

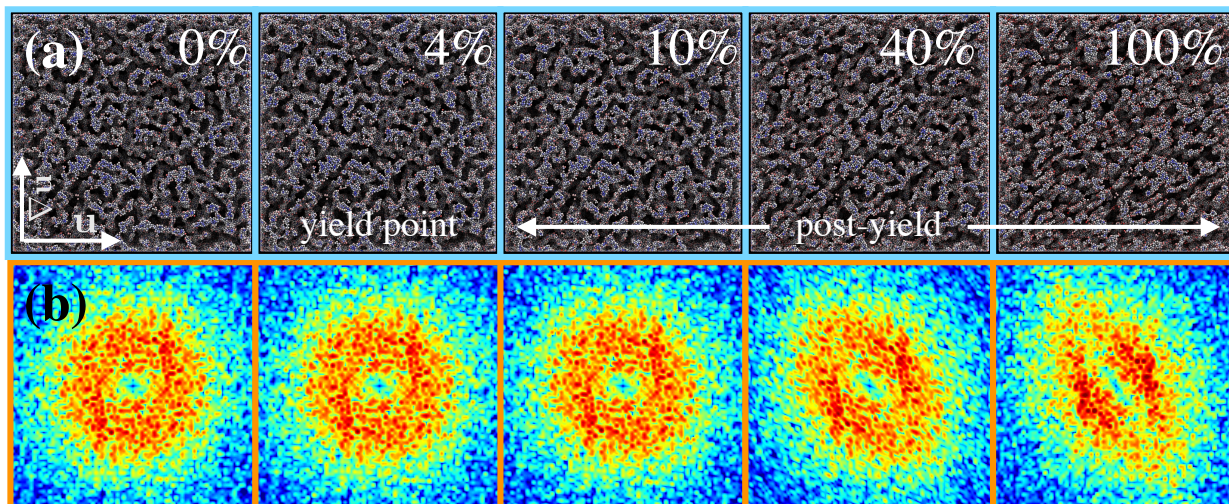


Figure 16: Evolution of structure under flow: (a) Snapshots and (b) contour plots of the static structure factor $S(q)$ of the flow-flow gradient plane at $\gamma = 0\%$, 4% , 10% , 40% , and 100% (left to right). Snapshots are colored from red for particles with few contacts to blue for particles with many. Values for the contour plots range from 0.1 (blue) to 100 or greater (red). For a $6kT$ gel, initial age $4,000a^2/D$, and flow strength $Pe = 1$.

only does an increase in the number of bonds play a role, this contributes further glassy regions that freeze in bond stretching, and the strength of bonds plays a quantitative role in bond dynamics at the yield point. Further discussion is provided in the Supplementary Materials.

Eventually, large-scale structural deformation is inevitable when a fixed rate of deformation is imposed. To examine the extent of this deformation at and following the yield point, snapshots of the gel in the flow-flow gradient plane are shown in Figure 16 (a) for a $6kT$ gel, initial age of $4,000a^2/D$ and flow strength $Pe = 1$. The leftmost image, $\gamma = 0\%$, shows the gel prior to flow. At approximately the yield point (snapshot at $\gamma = 4\%$, actual $\gamma_{\text{yield}} \sim 3.75\%$), the structure shows no visually obvious change at the network scale. Significant structural change does eventually occur, but commences only well after the yield point ($\gamma \geq 40\%$). We can quantify these structural changes via the static structure factor utilizing the method described in §2.3. Contour plots of the static structure factor corresponding to the same strains from Figure 16 (a) are shown in Figure 16 (b). Colors correspond to values ranging from 0.1 (deep blue) to 100 or greater (dark red). The dark red color surrounding the center of the plot is initially isotropically distributed, indicating strong density fluctuations over long length scales; changes in the shape of this region correspond to network length scale morphological changes. The second contour plot is virtually indistinguishable from the first,

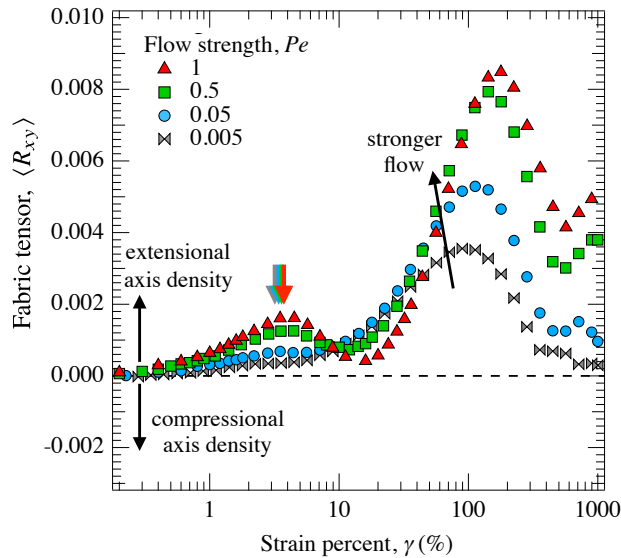


Figure 17: Orientation of bonds: Fabric tensor plotted as a function of strain percent for a $6kT$ gel with initial age $4,000a^2/D$. Vertical arrows mark the yield point for the corresponding curve.

giving quantitative confirmation that rheological yield takes place with evidently little structural change at the network length scale. Well beyond the yield point (far right contour plots), pronounced anisotropy in the static structure factor emerges; increased intensity of lower wavenumbers (longer length scale, red areas) shifts to the extensional flow axis, while the compressional region exhibits a decrease in density of large structures, evolving from an isotropic structure to a two-lobed structure, as seen in experimental study of thermoreversible gels via light and neutron scattering.^{26,80,81} Returning to the contour plot at the yield point: having established that network-scale changes do not predict yield, we turn our attention to teasing out smaller-scale precursors to large length scale changes that ultimately arise beyond the yield point.

The fabric tensor $\langle \mathbf{R} \rangle$ (Equation 10) quantifies the arrangement of bonds, which in turn sheds light on how energy is stored entropically by a deformed particle configuration. In Figure 17, we plot the average orientation of bonded particles in the plane of flow $\langle R_{xy} \rangle$ as a function of deformation for a $6kT$ gel with age $4,000a^2/D$ and imposed flow of strength $0.005 \leq Pe \leq 1$. From the startup of flow, $\langle R_{xy} \rangle$ grows from zero to a positive local maximum at the yield point, that grows with flow strength. Positive values of $\langle R_{xy} \rangle$ indicate that, on average, bonded particles are oriented along the extensional axis in the flow-flow gradient plane. Sheared dispersions of purely repulsive hard spheres exhibit particle accumulation along the compressional axis and depletion along the extensional axis, due to entropic forces, which would appear as a negative

value of $\langle R_{xy} \rangle$.⁷¹ Attractive forces pull density from the accumulation region to the extensional axis^{72–74} which manifests in $\langle R_{xy} \rangle$ as a positive value. In fact, the yield point corresponds to a local maximum in the fabric tensor, suggesting again that energy storage, this time entropic energy storage, saturates at the yield point. Because the structural anisotropy induced by flow is smoothed by Brownian motion, the local maximum in $\langle R_{xy} \rangle$ decreases in value, or even vanishes, as flow becomes very weak. Stronger flow leads to stronger structural deformation and hence greater entropic energy storage at the yield point, viz. the increased alignment of bonded particles with flow. While flow-aligned bonds correspond to flow-aligned strands in fractal or stringy gels,²⁷ in the dense, high-contact number gels studied here, bond alignment does not cascade upward to a high degree of flow-aligned network strands. The positive value of $\langle R_{xy} \rangle$ at the yield point further suggests that bonds play a role in the entropic energy storage, permitting particles to remain in contact in the extensional direction, which may enhance entropic energy storage at yield over that of a dispersion which emerges solely on entropic exclusion. Gel yield is distinct from purely repulsive dispersions because the network of bonded particles stores energy enthalpically and produces greater and more durable entropic storage. This enhanced storage underlies the stress overshoot, allowing it to emerge for relatively weak flow owing to the new timescale of attractive transport.

In summary, the yield point, or stress maximum, is set by maximum energy storage. While strand rupture makes sense for dilute gel networks of low-coordination number chains of particles, where stress localization or strand breakage is a possible yield mechanism,³⁰ in reversible colloidal gels, strands are many particles thick with average coordination number $\langle N_c \rangle = 7$ or higher; it is unlikely for so many bonds to be lost instantaneously. While strong shear can overstretch and break entire strands in dense gels, weak flow reveals a different type of yield: a release from kinetic arrest permitted by relaxation of glassy arrest following rupture of just a few bonds.

3.3 Stress overshoot: Energy release

Stress decays following the yield point, leaving behind a stress overshoot (regime II, green shaded region in Figure 2). The presence of an overshoot suggests that the gel stores more energy than required for long-time flow. We examine the macroscopic stress alongside the microscopic structural evolution to quantify the “ex-

cess” stored energy that is released during yield, where the height and width of the overshoot correspond to the energy dissipated by one yield event.

3.3.1 Rheology and energy of the stress overshoot

We have proposed that the stress overshoot signals a transition from energy storage to energy dissipation, and here relate the magnitude of the overshoot (peak minus long-time stress value) to the decrease in potential energy. We begin with the idea proposed by Mohanty and Zia⁴⁴ that the overshoot arises because Brownian motion hinders maturation of the steady state structure. Here, we expect interparticle bonds to further hinder this process. Phenomenologically, the overshoot indicates that the gel must store more energy than the work required for steady-state flow. Even for the weakest flow studied, we find a stress overshoot which suggests that the gel stores more energy than required to permit flow.

The size of the overshoot is computed as the peak value minus the nearest post-yield minimum, $\sigma_{post-yield}$, as

$$\sigma_{overshoot} = \sigma_{yield} - \sigma_{post-yield}. \quad (11)$$

The value of $\sigma_{post-yield}$ is estimated as the stress at the transition from regime II to III, or the end of the stress overshoot, and varies with imposed flow strength, gel age, and bond strength. It would be simplest to define the overshoot as the maximum minus the long-time stress, but, as seen in the curves in Figure 8, the long-time behavior may continue to evolve; the overshoot for $Pe = 1$ persists until $300\% \leq \gamma \leq 1,000\%$ and the long-time stress is steady. In contrast, the overshoot ends at $\gamma \sim 50\%$ for $Pe = 0.005$, with a trough or local minimum in the stress response. Age and attraction strength also influence whether a trough exists, or if the end of the overshoot leads to a steady stress.

The size of the stress overshoot grows with flow strength, as shown in Figure 18, consistent with our finding that stronger flow leads to greater energy storage at the yield point that must be released to permit bulk flow. The height of the first overshoot in dense, reversible gels^{11,12} is sometimes obscured by the presence of a second peak, but the overall size of these two peaks together grows with flow strength as seen here. We also note that weaker flow leads to a long-time trough in the stress or, equivalently, possible

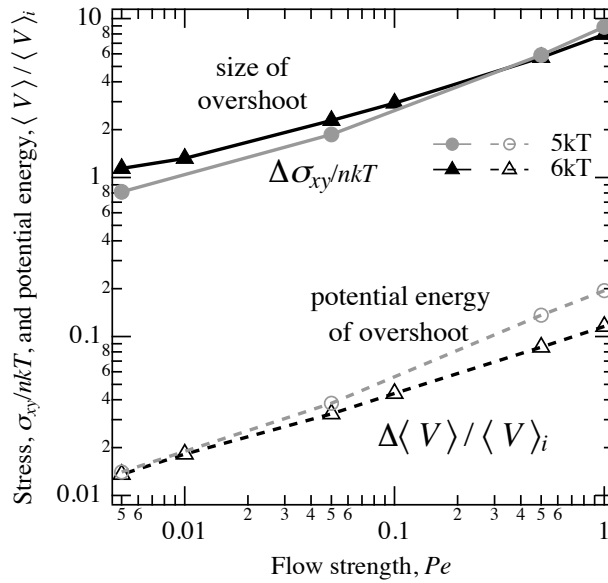


Figure 18: Size of the stress overshoot: the difference between the peak and trough value of the shear stress (solid curves, closed symbols) and the change in the normalized potential energy during the same time (dashed curves, open symbols) plotted as a function of flow strength, for $5kT$ and $6kT$ gels for initial age $4,000a^2/D$.

flow arrest and second yield event. As flow gets stronger, the trough shifts to higher strains and eventually vanishes. We do not observe a secondary overshoot or yield event, which is discussed in §3.3.2.

We have said that the overshoot height gives excess energy storage, which can be measured during yield as the post-overshoot potential energy change, $\Delta\langle V \rangle = \langle V_{yield} \rangle - \langle V_{post-yield} \rangle$. This quantity is normalized on the initial value of potential energy prior to startup of flow $\langle V \rangle_i$ and plotted in Figure 18 as a function of flow strength, and is positive because, on average, bonds stretch or rupture as stress decays. The two quantities, stress decay and decreasing potential energy, exhibit the same qualitative trend with flow strength: if greater energy was stored at the yield point (as indicated by the size of the overshoot), there is a corresponding increase in dissipation of that energy, given by the potential energy. In dispersions, setting up a steady-state microstructure under strong flow is connected to the end of the transient behavior and the onset of a steady stress, and fully formed structure, over a length scale of a particle size, and over the time required for diffusion-dominated behavior to give way to advection-dominated behavior.⁴⁴ However, in gels, bond stretching and loss also matters for the evolution of both the microstructure and the energy response because attractions hinder diffusion, one expects a longer time to reach advection-dominated behavior.

In summary, the stress overshoot signals a release of flow energy that was stored prior to yield, and

must be released to achieve so-called steady-state flow. The size of the overshoot grows with increasing flow strength: a stronger flow will release a greater percentage of the stored energy as compared to weaker flow. The underlying microscopic origin is the extent to which bond loss and the significant bond relaxation that attends such a loss helps the gel towards a release from glassy arrest, with greater and more prolonged energy dissipation occurring with stronger flow indicating a greater reactivation of the kinetically arrested progress towards phase separation. Gels, as compared to dispersions, store energy in the glassy, bonded structure and the release of this energy over the duration of the overshoot suggests a slow, plastic deformation of the still predominantly glassy structure. Further, energy release via bond loss and relaxation has other consequences for the gel, namely that bond loss may change the degree to which the gel is arrested; we conduct a study of the network-scale structure to examine the influence of this energy release.

3.3.2 Structural evolution during stress overshoot

Microstructural evolution, both as particle rearrangement and bond loss, is a key mechanism for post-yield dissipation of the energy stored prior to the yield point. Figure 19 gives snapshots of the structure and contour plots of the static structure factor prior to flow ($t = 0$), at the yield point ($\gamma = 4\%$), and post-yield ($\gamma \sim 70 - 400\%$), in the flow-flow gradient plane, for flow strength $Pe = 0.005$ (a),(b) and $Pe = 1$ (c),(d). At the yield point, the static structure factor shows little perceptible flow-induced coarsening, and no indication that structural breakup has occurred. The network apparently remains unchanged at yield.

Well after yield, following the overshoot, pronounced structural evolution at the network-length scale emerges. Flow strength influences both the alignment of the structure at the end of the overshoot, and the length scale of the network, as shown in the rightmost images. For weaker flow (thick red border in Figure 19), intense red regions near low wavenumbers align along the extensional axis, indicating that structure is oriented along the extensional axis, and grows in length scale. The structure remains connected; some decrease of structural size along the compressional axis indicates that while the network is overall intact, pores are growing larger and stretched open while strands are condensing into larger, thicker structures aligned with the flow, and corresponds to a trough in rheological stress.

In contrast, when $Pe = 1$, the structural image at the end of the overshoot (thick black border in Figure

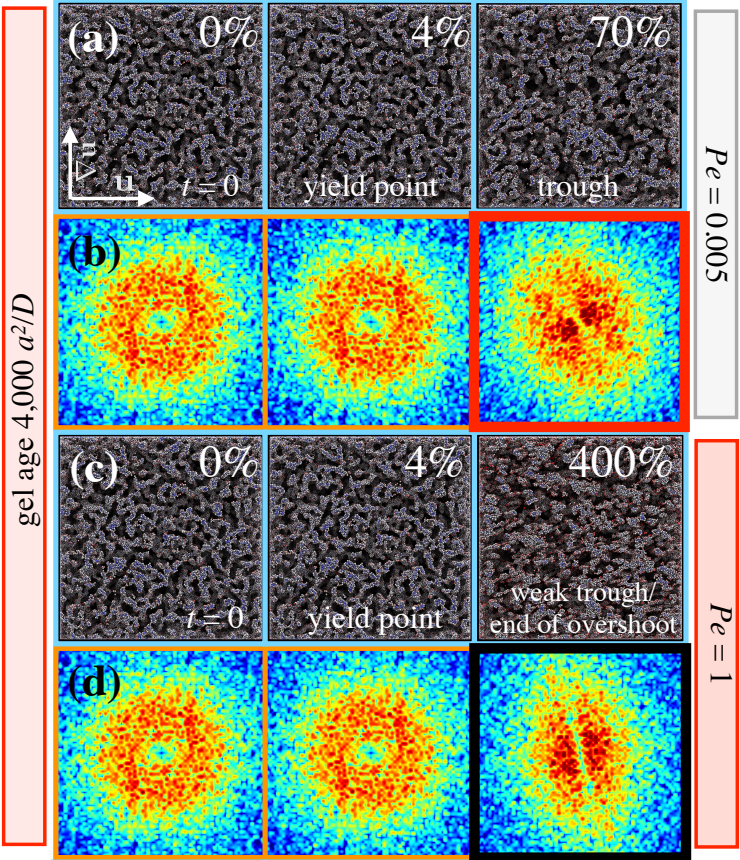


Figure 19: Evolution of structure under flow: Snapshots ((a), (c)) and contour plots of the static structure factor $S(q)$ ((b), (d)) of the flow-flow gradient plane at $\gamma = 0\%$, 4% , and the end of the overshoot or trough ($\gamma \sim 70\% - 400\%$ shown) for a $6kT$ gel. Snapshots are colored from red for particles with few contacts to blue for particles with many. Values of the contour plots range from 0.1 (blue) to 100 or greater (red). Gel age is $4,000a^2/D$ and flow strength is $Pe = 0.005$ for (a)-(b) and $Pe = 1$ for (c)-(d).

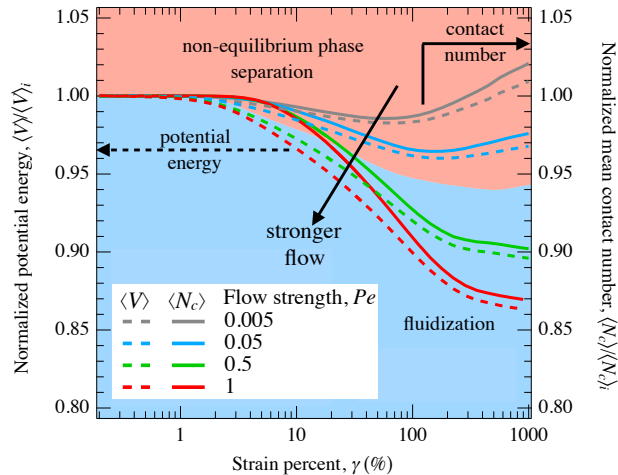


Figure 20: Bond dynamics: Normalized potential energy, left axis and dashed lines, and normalized mean contact number, right axis and solid lines, plotted as a function of strain percent for a $6kT$ gel with initial age $4,000a^2/D$ for the full range of strain examined. The background is colorized to separate the post-yield responses: fluidization or non-equilibrium phase separation.

19) shows strands oriented between the extensional axis and the flow direction, like experimental studies of thermoreversible gels⁸⁰ and, more familiarly, the reverse of dispersions, which show accumulation in the compressional axis at steady state. The dominant structural length scale set by the oriented strand is larger than in the quiescent gel. Together, these observations suggest that strands disconnect *across* streamlines to leave larger solvent pores and thicker strands that retain structural memory of the network, only slowly aligning with flow. Attainment of this structure coincides with steady-state stress. Such a structure suggests that the gel does not fully ‘fluidize’ into a dispersion-like structure but perhaps large, partially connected structures as greater bond loss (Figure 20) accompanies the structural evolution during the overshoot, in agreement with the ideas proposed by many other authors that strong flow simply breaks the gel.^{9–12,30,31} This is also consistent with our finding that the work required to yield gels depends on gel strength (stiffness due to age and from interparticle bonds, Figure 14). This is in contrast to what we find for weak flow where only modest bond loss (Figure 20) accompanies the overshoot, then bond loss turns to bond gain post-yield after a short-lived overshoot and small energy release (Figure 18). Bond gain and structural length scale growth can be viewed as signatures of flow-enhanced age-coarsening, or a speeding up of the progress towards phase separation, where such markers as growth in length scale of condensed domains is taken as the advancement of spinodal decomposition.^{18–25} We have shown previously that the application of shear

stress can reactivate the phase separation⁵⁰ and that such a continuation of phase separation is the origin of gel collapse.⁷⁰

Gel age plays a quantitative role in large-scale post-yield structure. The longer length scales produced via quiescent aging prior to the application of flow remain relevant to the length scales found post-yield; further discussion is given in the Supplementary Materials.

It is appealing to describe the post-overshoot deformation as fluidized structure ($Pe = 1$, thick black border), as suggested by Park and Ahn,⁹ but measurement of the elastic modulus or other possible indicators of a fluid-like dispersed structure or dynamics to support this description is challenging. Instead, we recall that the initial energy release at yield suggest only plastic deformation. We hypothesize an alternate mechanism where “flow” occurs over the particle scale rather than the bulk scale: formation of localized pockets of re-entrant fluid, which provide the mobility necessary for particles to advect, but not necessarily escape glassy structures. The persistence of longer length scales from quiescent aging through the end of the overshoot further suggests that significant bond loss or rupture of the network need not occur to permit flow. Later, appreciable bond loss ($\gtrsim 10\%$ of the initial bonds) occurs for $Pe \geq 0.5$ which suggest that the late-time overshoot may be dominated by the presence of less connected network features. However, no such bond loss occurs when flow is weak, and in fact bond loss turns to bond gain suggesting that continued flow is a plastic deformation of the gel permitted by this particle-scale flow, activating the continual loss and re-formation of bonds to create a more condensed structure.

A secondary yield or a second overshoot, seen experimentally in dense, reversible gels,^{11,12} is not found in the post-yield response. However, one explanation consistent with our findings is that a secondary yield may occur if the structural growth from flow-induced coarsening following first overshoot breaks, thereby forming a second overshoot. It is possible that hydrodynamic interactions, neglected here, lead to the breakup of structures formed following the first yield peak by flow-induced coarsening, although prior simulation studies utilizing DPD⁴² find that a secondary yield occurs when flow is strong, in contrast to the regimes pointed out by Petekidis and coworkers keeping that question open. In the present work, dynamics of the coarse structure appear responsible for temporal stress growth when $Pe < 1$, Figure 17). That is, the growth in stress could arise from the movement or plastic deformation of coarse structures past each other, without requiring great

bond loss to form peaks and troughs in the stress response. Recently, Petekidis and coworkers^{37,38} find that sample preparation matters for the startup response and attribute it to heterogeneous structures formed when low or moderate rates (or small strain amplitudes) are utilized to prepare the sample; we did not employ a preshear protocol in sample preparation.

In summary, the stress overshoot is an energy release, not necessarily a fluidization of the gel, characterized by the gradual evolution in the orientation and size of the network-scale structure and persistence of large-scale network features. Intuitively, stronger flow produces a greater stress energy release permitting a more aligned structure at the end of the overshoot, indicating the role of advection is to simply break the gel as one would expect. When flow is weak, yield is triggered by the saturation of a far smaller amount of stored energy, thus less energy is released during the overshoot, and the structure retains many features formed by quiescent aging, suggesting that advection plays little role besides moving forward a glassy structure at the prescribed rate. When the few bonds that rupture at rheological yield do so, they relieve local glassy frustration and allow many nearby bonds to relax, and particles to advect past each other, even within strands. These more mobile particles dissipate energy, leading to the initial decay in stress after the yield peak. An increase in the length scale suggests a larger volume of the condensed, high contact number regions consistent with a non-equilibrium phase separation activated by the energy release during the overshoot.

Weak-flow yield seems to bridge mechanical yield and a release from kinetic arrest. We thus describe this structural evolution and energy release during yielding as “phase mechanics”: While proper equilibrium phase separation involves formation of sharp interfaces, its successful completion requires a single interface between the condensed and dilute/dispersed regions. The bicontinuous structure formed by arrested phase separation has many sharp interfaces, and we propose that triggered advances in condensation are a non-equilibrium phase separation, where yield is actually an externally triggered or a ‘non-equilibrium’ phase transition. Weak flow has the ability to reactivate the underlying drivers of phase separation – bond gain and cage formation – thus enabling the continuation of this phase separation.

4 Conclusions

We have carried out a computational study of reversible colloidal gels subjected to the sudden startup of shear flow. Such reversible gels are formed by imparting $O(kT)$ attractions between colloidal particles. With the passage of time, these particles form an elastic network which continues to coarsen via particle migration across strand surfaces. Quiescent coarsening is driven by thermally-induced rupture of reversible bonds which permits particles to explore the energy landscape of the strand surface, leading to eventual bond reformation and dense, glassy strands under quiescent conditions.¹⁸ Once a gel reaches a given age after its formation, we apply a shear flow of strength $0.005 \leq Pe \leq 1$, monitoring the evolution of the rheological response, the bond dynamics, and the microstructure under flow. We connect the underlying energy and structural evolution to features of the stress response: the early-time stress growth, the peak stress value, and the stress overshoot. This transient yield event can be understood as a stress (energy-density) accumulation up to energy saturation and transition to stress (energy) release, the stress overshoot. We summarize the relevant parameters and our findings below and in Table 21.

Pre-yield stress buildup at the earliest times grows at a rate set by diffusion, scaling as $\hat{t}^{1/2}$, and at times long enough for interparticle interactions to matter, the qualitative rate of stress growth becomes $\hat{t}^m$ where $m > 1/2$. Thus, enthalpic energy storage begins to matter as energy accumulates in the interparticle bonds of the gel network; entropic energy storage, provided by anisotropic particle arrangement, also begins to grow. The quantitative strength of the stress growth during the pre-yield is set by the relaxation of the longest length scale $L_{S(q)}$ of the quiescently aged gel, and the intrinsic morphological differences set by the attraction strength V_0/kT .

The yield point, or the stress maximum of the overshoot, marks the beginning of release from kinetic arrest, a non-equilibrium phase transition triggered by a saturation of flow-energy storage in the gel network. Rheologically, σ_{yield} depends quantitatively on the dominant length scale, suggesting an intact network at yield rather than instantaneous network failure or a cascade of strand rupture events. Stronger flow clearly provides enough flow energy to stretch bonds, breaking these stretched bonds before they can relax. Weaker flow provides less energy, and yield occurs via the thermal rupture of less stretched bonds, resulting in lower

	mechanistic findings	quantitative findings	main figure
bulk strain at yield	critical bond loss, rather than bulk deformation, sets yield under weak flow	$2.5\% \leq \gamma_{\text{yield}} \leq 4.0\%$ higher with stronger flow, weaker bonds, younger gel	figures 8 & 13
structural mechanism of yield	<i>weak</i> flow: activated phase separation <i>strong</i> flow: structural breakup	$\sigma_{\text{yield}} \gamma_{\text{yield}} / 2$ work done on gel activates: bonds (weak flow) or activates strands (strong flow)	figures 14 & 20
structural origin of stress overshoot	saturation of enthalpic storage in stretched bonds, followed by minor bond loss + bond relaxation	$\Delta \sigma_{\text{overshoot}} \sim \Delta \langle V \rangle$ bond loss & bond relaxation dissipate energy - height is excess beyond that needed for flow. $Pe \lesssim 0.5$ non-eq. phase separation $Pe \gtrsim 1$ mechanical strand fracture	figures 18, 19, & 20
mechanism of shear thinning of yield stress	increasing enthalpic energy storage in stretched bonds as flow strengthens	$\sigma_{\text{yield}} / Pe \sim \eta_{\text{yield}} \sim Pe^{\delta-1}$ $\delta = \delta(V_0) < 1/2$	figures 12, 15, & 17

Figure 21: (Table) Summary of mechanisms and scalings of startup shear flow of reversible colloidal gels.

energy storage. A competition in time scales of advection, bond relaxation, and Brownian motion sets this flow strength-dependent bond stretching and controls maximal energy storage. Entropic energy storage, viz. oriented bonds, reaches a local peak at yield with a magnitude dependent on flow strength, and separate from enthalpic effects, e.g. gel age or attraction strength. The small net loss of bonds at yield is simply a manifestation of the transition to energy dissipation, rather than a symbol of network rupture.

Yield is the tipping point from net storage of flow energy to its release, producing the post-yield stress decay, the overshoot that gives way to plastic-like deformation then, for strong flow, bonds continue to break leading to a more pronounced loss in connectivity and a broken, flowing structure. However, condensation of network strands accompanies weaker flows where continued deformation is plastic and flow occurs at the particle scale: bond stretching or loss is still activated by advection or thermal rupture, forming local reentrant liquid pockets that allow the cage-migration of particles along the network. The gel now undergoes progress in phase separation, where advection and Brownian motion have triggered bond dynamics that allow attractive forces to drive particles to lower potential-energy positions. Liberation of clusters is not

necessary for yield and the subsequent post-yield deformation under weak flow, and in fact the presence of interconnected condensed phase regions and the continued growth in network length scale and number of bonds suggests that this is not a flowing suspension of loose clusters.

This energy release accompanying the stress overshoot and subsequent condensation of the particle-rich strands is consistent with a release from kinetic arrest. Quiescent aging coarsens the network, simultaneously seeking phase separation, while self-limiting its own ability to reach a fully phase-separated state by deepening the glassy arrest of progressively more particles.^{18,70} A “kick” from the externally imposed deformation introduces energy that is at first stored, then saturates, and ultimately releases to drive more rapid structural condensation. Even though a hallmark of equilibrium phase transition is establishment of new, sharp interfaces, its completion is characterized by a single such interface. Because an external perturbation is necessary to re-initiate the condensation of particle-rich regions and evolution from bi-continuous morphology to a single interface, we identify this framework as “phase mechanics” and the transition as a non-equilibrium phase transition. The influence of ongoing deformation and whether this leads to full phase separation is still an open question and is the topic of a companion work on the post-yield response.⁸²

Overshoots and yield-stress behavior in gels is distinct from that in repulsive dispersions, owing to the network of bonded particles that lends both enthalpic energy storage and enhanced material memory, viz. dramatic shear thinning of the yield stress. We have shown that flow provides energy that allows the gel to access a lower-energy configuration, reminiscent of progress towards full phase separation.

The present work sheds light on gel response to imposed flow when the flow may be varied from weak flow, where Brownian motion plays a role, to stronger flows where gel breakup can matter. By computing the work done to yield the gel, we find that more work is required to yield stronger or older gels, but under weak forcing, the work required is driven by the strength of the individual bonds. For a simple spreadable coating, weaker flows may allow a more monotonic effort to spread coating by reducing the stress overshoot. However, a gel or paste designed to be applied via spreading with the minimum amount of shear stress, may instead encourage ongoing phase separation and impair the coating functionality. Our finding that this transition from gel breakup at stronger flows to reactivation of phase separation under weaker flow occurs over only a few orders of magnitude of flow strength could inform experiments where the flow strength is

smaller than or similar to the strength of Brownian motion.

This new understanding of gel yield can be leveraged for the long-time stability and functionality of reversibly bonded gels. Future work should include the investigation of the influence of many-body hydrodynamic interactions in a colloidal gel during startup shear flow, expected play a quantitative role in gel yield. Colloidal gels formed by arrested phase separation are shown to exhibit history-dependent behavior, which may pose a challenge to predicting bulk rheological behavior via constitutive modeling approaches, however, our findings for the work required to yield the gel suggest that such approach may be a promising one to capture the range of mechanical responses of the gel from strong flow gel breakup to weak flow phase separation. Within the field of dense, reversible gels, further study of the role of volume fraction and stronger interparticle attractions are necessary to elucidate the additional influence of strong steric hindrance and structural arrest, thus denser morphologies, on the ability of the gel to store and release energy. Such dense gels are relevant to the many situations where loading of attractive particles is substantial.

Conflicts of interest

There are no conflicts to declare.

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