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Yielding in colloidal gels due to nonlinear microstructure bending mechanics

Eric M. Furst* and John P. Pantina†
Colburn Laboratory, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716, USA

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We report measurements of the nonlinear micromechanics of strongly flocculated model colloidal aggregates. Linear aggregates directly assembled using laser tweezers are subjected to bending loads until a critical bending moment is reached, which is identified by a stictionlike rearrangement of a single colloidal bond. This nanoscale phenomenon provides a quantitative basis for understanding the macroscopic shear yield stresses of strongly flocculated polystyrene latex gels, based on the maximum bending moment exceeding the critical moment of the constituent colloidal bonds of the gel microstructure. These mechanics are consistent with the local bending moment overcoming the static friction force between neighboring adhesive particles. This results in a direct relationship between the rheology of these gels and the boundary friction between Brownian particles.

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The yield stress, elastic recovery, and gravitational collapse of colloidal gels are of immense interest for controlling the processing characteristics and stability of a number of economically important products and by-products, including coatings, consumer products, lubricants, and mineral extraction wastes. While substantial progress has been made in understanding these aspects of gel rheology, there is a critical need to assimilate bulk rheological behavior with the knowledge of mechanics, structure, and interactions on the colloidal scale.

Along these lines, models of colloidal gel rheology are typically based on the near-contact interactions between colloidal particles [1–4]. For instance, consider the startup of a shear deformation in a colloidal gel, illustrated in Fig. 1. The microstructure over the length scale ξ is subjected to a tensile force $F_{tens} \sim \sigma \xi^2$ [1], where $\xi = a(\phi_e/\phi)^{1/(3-d_f)}$ represents the dominant structural correlation length of a gel with fractal dimension d_f, which is determined by the gel aggregation kinetics [5]. The yield stress arises primarily due to the tensile failure of the colloidal "bonds" formed by the aggregated particles when the microstructure is subjected to a maximum tension F_{tens}. The resulting yield stress associated with tensile failure is [1]

$$\sigma_y^{tens} \sim F_{tens} a^{-2} (\phi/\phi_e)^{2/(3-d_f)}. \tag{1}$$

Under shear, the microstructure represented in Fig. 1 is also subjected to a bending moment $\Gamma \sim \sigma \xi^3$ [1]. Previously, in studies of the bending mechanics of colloidal aggregates, we found that a critical bending moment M_c marked the limit of linear elastic response [6]. Because the critical moment reflects a yielding behavior of a colloidal microstructure, its existence may be evident in the macroscopic rheology of colloidal gels as a yield stress. By substituting Γ with the critical moment of the colloidal bonds M_c, the gel microstructure would be expected to yield according to

$$\sigma_y^{bend} \sim M_c/\xi^3 \sim M_c a^{-3} (\phi/\phi_e)^{3/(3-d_f)}. \tag{2}$$

Consistent with this expectation, in this Rapid Communication, we demonstrate that the yield stress of a colloidal gel, consisting of strongly flocculated polymer latex particles, can be *quantitatively* understood based on the critical bending moment of the underlying gel microstructure. Furthermore, the mechanical characteristics of the critical moment suggest an origin in the boundary friction between the particle surfaces in the contact region. This is in distinct contrast to the more common assumption that centrosymmetric normal forces dominate colloidal interactions. To our knowledge, nonhydrodynamic interparticle friction has not been recognized previously as a significant factor in colloid-colloid interactions or colloidal gel rheology.

Before discussing our results, we briefly review our experimental methods, which have been reported in greater detail elsewhere [8,9]. Linear aggregates of poly(methyl methacrylate) (PMMA, $2a = 1.47 \pm 0.1$ μm, Bangs Laboratories, Fishers, IN) and polystyrene (PS, $2a = 2.84 \pm 0.1$ μm, Polysciences, Warrington, PA) particles are directly assembled using time-shared optical tweezers in solution under condi-

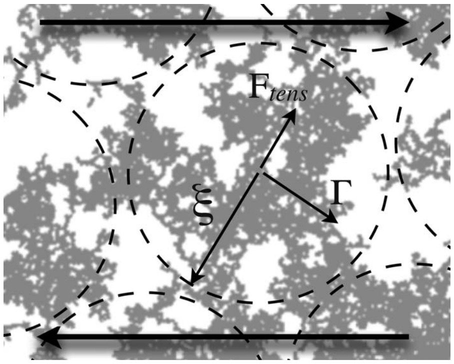

FIG. 1. Microstructure of a colloidal gel is subjected to a tensile force F_{tens} and maximum bending moment Γ over the correlation length ξ at the onset of a shear strain γ. The floc structures shown are adapted from [7].

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*Author to whom correspondence should be addressed. Electronic address: furst@udel.edu

†Current address: National Starch and Chemical Company, 10 Finderne Avenue, Bridgewater, NJ 08807.

tions that lead to aggregation. The sample cell consists of a microscope slide and cover slip separated by two adhesive spacers, which create a sample height of approximately 200 μm. The sample cell is loaded by capillary action and sealed to prevent evaporation using an uv-cure epoxy (Norland Optical, NOA 81).

Before use, particles are triple washed in ultrapurified water (>18 MΩ cm) before being diluted in the salt solution. The exact solids volume fraction is insignificant for our measurements, since each aggregate is directly assembled from individual particles. However, we find that $\phi \sim 10^{-4}$ provides the optimal number of particles in the suspension, such that it is not difficult to locate and trap a number of particles while simultaneously keeping the concentration low enough that stray particles do not interfere with the assembly process or micromechanical measurements. Salt stock solutions of $CaCl_2$, $MgCl_2$, and NaCl (Sigma Aldrich, used as received) were mixed prior to the experiment and diluted to the final concentrations ranging from 10 to 500 mM.

We measured the bending rigidity of aggregates using a three-point geometry of time-shared optical traps, in which the two end particles are held stationary and the middle particle is translated slowly (~ 20 nm/s). The mechanical response of each aggregate is measured until the onset of nonlinear behavior, after which we discard the aggregate. The traps are generated by focusing the beam of a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Coherent Compass, vacuum wavelength $\lambda = 1064$ nm) using a 63× high-numerical-aperture (NA) water immersion microscope objective (Zeiss WCorr C-Apochromat, NA 1.2). The force imparted on the aggregate is measured through the displacement of the end particles in their respective stationary traps. The maximum trap rigidity and trapping force are $\kappa_t \approx 20$ pN/μm and 15 pN, respectively, at a back aperture laser power of 280 mW. The rigidity and maximum trapping force can be controlled to tune the force sensitivity and strength of the optical traps.

As force F is applied to an individual aggregate of length L, it takes the shape of a bending beam, where the coordinates of the ith particle are given by $y_i(x_i) = (-F/EI)(Lx_i^2/4 - |x_i^3|/6)$. In this expression, E is the Young's modulus and I is the effective area moment of inertia of the aggregate [8]. From the force measurement and deflection, the aggregate bending rigidity is found, and subsequently, the bending rigidity of a single colloidal bond κ_0 can be calculated [6,8]. This characterizes the linear mechanical response of the aggregate under small stresses. When a critical bending moment M_c is reached, the aggregate yields, releasing a portion of the built-up stress.

As an example, an image sequence of an aggregate exhibiting a nonlinear mechanical response is shown in Fig. 2. The aggregate, composed of 15 PS particles in 50 mM $MgCl_2$, has a kink from the initial assembly process. The entire aggregate deforms as a rigid body from the initial frame (0:0.0) until approximately 8 s later (0:8.3). Shortly after this (0:8.10), the fourth bond from the top exhibits a failure at the site of the kink, which enables the fourth particle from the top to move to the left relative to the fifth particle, and allows the lower portion of the aggregate to relax into a more curved geometry. Note that no particle bonds are ruptured; the aggregate maintains its mechanical integrity throughout the entire process. The critical moment is typically detected through changes in the deflection and rigidity of the aggregate, as shown in Figs. 2(b) and 2(c).

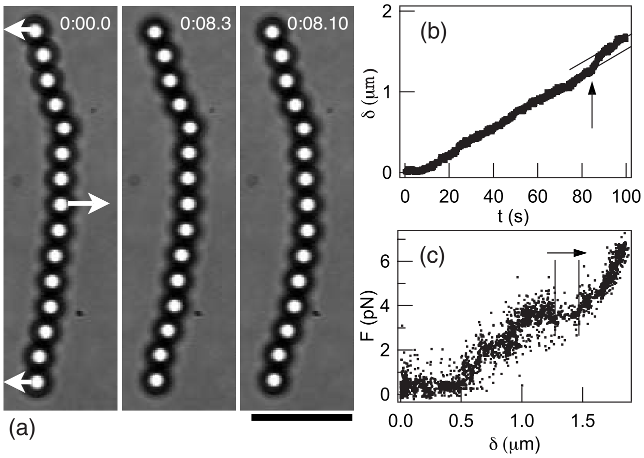

FIG. 2. (a) Image sequence demonstrating the microscopic process that characterizes the nonlinear mechanics of aggregates. A 15-particle aggregate of 2.8-μm-diameter PS particles in 50 mM $MgCl_2$ is bent using a three-point geometry, in which the middle particle is held by a translating optical trap. Two stationary optical traps holding the top- and bottommost particles exert restoring forces. The corresponding deflection of the aggregate δ and force are shown in (b) and (c), respectively.

The value of the critical moment depends on the bending force measured at the point that the aggregate rearranges F^* and the position of the yielding bond x^* relative to the aggregate center, $M_c = F^*(L/2 - |x^* - L/2|)$. As reported earlier [8], the average distance the particles translate during a rearrangement is on the order of 30 ± 15 nm. Values of M_c for several physicochemical conditions are summarized in the inset of Fig. 3.

As described above, the existence of microstructural yielding behavior characterized by the critical bending moment has important consequences for the rheology and other macroscopic properties of aggregated suspensions. By substituting Γ with the critical moment of the colloidal bonds M_c, the gel microstructure is expected to yield according to Eq. (2). This expression captures both the volume fraction and particle size dependence of the yield stress.

The overall particle size dependence of σ_y^{bend} is determined by M_c and the underlying nature of the particle contacts. The competition between the elastic deformation and the surface adhesion energy of the particle surfaces W_{SL} determines the size of the contact region between particles, as first described by Johnson, Kendall, and Roberts (JKR) [10]. In the absence of an applied normal load, $a_c = (3\pi a^2 W_{SL}/2K)^{1/3}$, where $K = 2E/3(1-\nu^2)$ is the elastic modulus of the spheres based on their Young's modulus and Poisson ratio ν. The resulting bending rigidity of a single bond between two particles is [6,8]

$$\kappa_0 = 3\pi a_c^4 E/4a^3, \tag{3}$$

leading to a direct relationship between the micromechanical bending rigidity κ_0 and the surface adhesion energy W_{SL}.

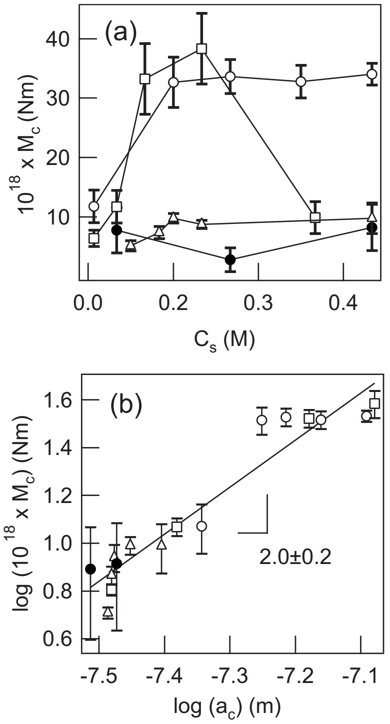

FIG. 3. (a) Critical bending moment M_c as a function of salt concentration C_s. Note that PMMA in $CaCl_2$ reverses charge, causing both a_c and M_c to decrease for $C_s > 0.3M$. Error bars reflect the average of at least three separate measurements. The symbols represent PMMA particles in NaCl (open triangles), $MgCl_2$ (open circles), and $CaCl_2$ (open squares), and PS particles in $MgCl_2$ (solid circles). (b) Values of M_c versus the corresponding contact radius a_c calculated from the measured values of κ_0 from [6] for $\zeta < 0$. The line is a best fit to the data and has a slope 2.0±0.2 and intercept −4.5±3.0.

Indeed, earlier we demonstrated that divalent ions contribute to the surface adhesion energy in a manner which significantly strengthens the bending mechanics of aggregates composed of PMMA particles [6]. For our purposes here, measurements of κ_0 from our earlier studies of the linear bending mechanics provides the contact radius a_c between particles.

Empirically, we find $M_c = m_c a_c^2$ for our measurements made in $CaCl_2$ solutions, which is in good agreement for other salts and surface chemistries. This leads to $M_c \sim a^{4/3}$ based on Eq. (3), and an expected particle size dependence of the yield stress, $\sigma_y^{bend} \sim a^{-5/3}$. The prefactor m_c is approximately 10^{-2} N m.

To test our hypothesis that non-linear bending mechanics can underlie gel yielding, we compare σ_y^{bend} to yield stress measurements reported by Buscall *et al.* for strongly flocculated polystyrene lattices in solutions of barium chloride ($BaCl_2$) for several particle sizes and volume fractions [11]. The original data are reproduced in Fig. 4(a). These values are scaled by $a^{5/3}$ according to the particle size dependence of σ_y^{bend}. Although slightly lower than the particle size scaling exponent originally reported in [11] ($\sigma_y \sim a^{-2}$), our proposed scaling collapses the experimental measurements onto a single master curve. Furthermore, using the average measured value of the critical moment for PS particles in $MgCl_2$, $M_c = 6 \times 10^{-18}$ N m, and $d_f = 1.8$ (as expected for DLCA aggregation kinetics [12–14]) we find that σ_y^{bend} shows a remarkable quantitative agreement with the experimental values, as demonstrated by the solid line in Fig. 4. In contrast, using the tensile rupture force of a colloidal bond under the same conditions, $F_{rupt} = \frac{3}{2} W_{SL} \pi a$ [10], typical yield stress values are expected to be 1–12 kPa for $0.05 \leqslant \phi \leqslant 0.25$. This is far above the experimental values reported by Buscall *et al.* Furthermore, the calculated JKR rupture forces are consistent with previous observations that aggregates do not break when subjected to tensile forces up to 15 pN [9].

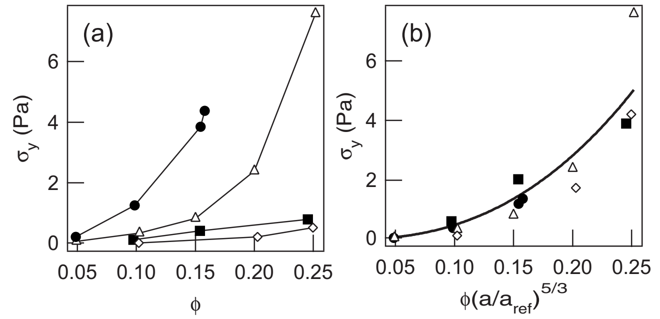

FIG. 4. (a) Bulk rheological measurements of the yield stress for polystyrene suspensions aggregated in $BaCl_2$, adapted from [11]. The symbols represent the particle diameters $2a = 0.5$ (circles), 1.0 (triangles), 2.6 (squares), and 3.5 μm (diamonds). (b) Comparison of the calculated yield stress using σ_y^{bend} [Eq. (2), solid line] to the data of Buscall *et al.* with $M_c = 6 \times 10^{-18}$ N m for polystyrene and $d_f = 1.8$, expected from DLCA aggregation kinetics. Here, $a_{ref} = 0.5$ μm.

The critical bending moment represents a yielding point of an otherwise elastic aggregate. The suddenness of the rearrangement when the critical moment is reached suggests a stictionlike mechanism when the applied load becomes larger than the static friction force F_s between the polymer surfaces, allowing them to slide past each other. The static friction force is expected to be $F_s = \mu_s L_0$ for an effective adhesive load L_0 caused by the attractive interactions between surfaces [15]. This force must be overcome before motion is induced. The static coefficient of friction, μ_s, is typically independent of the contact area [15]. To proceed, we calculate the critical force F_c associated with M_c. Although the bending moment is experimentally identified in terms of the entire aggregate length, we expect that the stresses are focused in regions close to the particle contacts, while the majority of each particle remains elastically inactive. For each colloidal bond, the size of this deformed region is determined by the contact radius a_c and particle radius a, $\delta \approx a_c^2 / a$ [10]. Thus, the critical force for a particle bond to slip is $F_c \sim M_c / \delta$.

For the sliding mechanism to be static friction, F_c must be independent of the contact area, and thus, M_c should scale as a_c^2, in agreement with the results shown in Fig. 3. With the equations for F_s and F_c, the static coefficient of friction between polymer particles is $\mu_s = m_c a / L_0$, where $L_0 = \pi a W_{SL} / 2$ [10]. This leads to $\mu_s = 2 m_c / \pi W_{SL}$. Using this resulting expression, we find that μ_s has a physically reasonable range of values between approximately 0.1 for PMMA in low-salt-concentration solutions to 0.01 at high salt concentrations. The observation that μ_s decreases with increasing adhesion energy possibly reflects the flattening and plastic deformation of asperities on the contacting surfaces as the adhesive load increases.

Note that the dependence $M_c \sim a_c^2$ does not appear to support a rupture mechanism due to rolling friction. In this case, a maximum stress at the edge of the contact region between particles, τ_c, would need to be reached to begin rolling. This is related to the critical moment by $\tau_c \sim 4M_c/\pi a_c^3$. Thus, M_c would scale as a_c^3, giving a scaling exponent significantly higher than the experimental value. The stronger dependence on a_c would also lead to a substantially lower dependence of the yield stress with respect to the particle radius, $\sim a^{-1}$. This is not supported by the rheology experiments of Buscall *et al.*

To conclude, in this Rapid Communication, we have demonstrated the direct relationship between the yield stress of a colloidal gel and the nonlinear microscopic bending mechanics of colloidal aggregates. This can account for the low yield stress observed for gels of latex particles, as well as its dependence on particle size and volume fraction. This represents a new paradigm in thinking about the microscopic rearrangements and mechanical processes that underlie the yielding behavior of colloidal gels. The nonlinear bending mechanics of colloidal aggregates will also have significant implications for other macroscopic properties of gels, for instance, by providing energetic barriers for thermally activated rearrangements that underlie elastic recovery and gravitational collapse [16,17]. Finally, understanding the nature and implications of the interactions between Brownian particles in near-contact regimes remains a particularly important challenge for colloid science, especially as interest grows in tailoring colloidal and nanoparticle interactions to create new materials and devices, such as photonic crystals and novel sensors [18–20]. The role of boundary friction, and the ability to enhance or reduce it, provides a means for controlling the properties of industrially important suspensions and emerging colloidal materials.

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