Electronic Supplementary Material (ESI) for Soft Matter.

Role of shear-induced dynamical heterogeneity in the nonlinear rheology of colloidal gels

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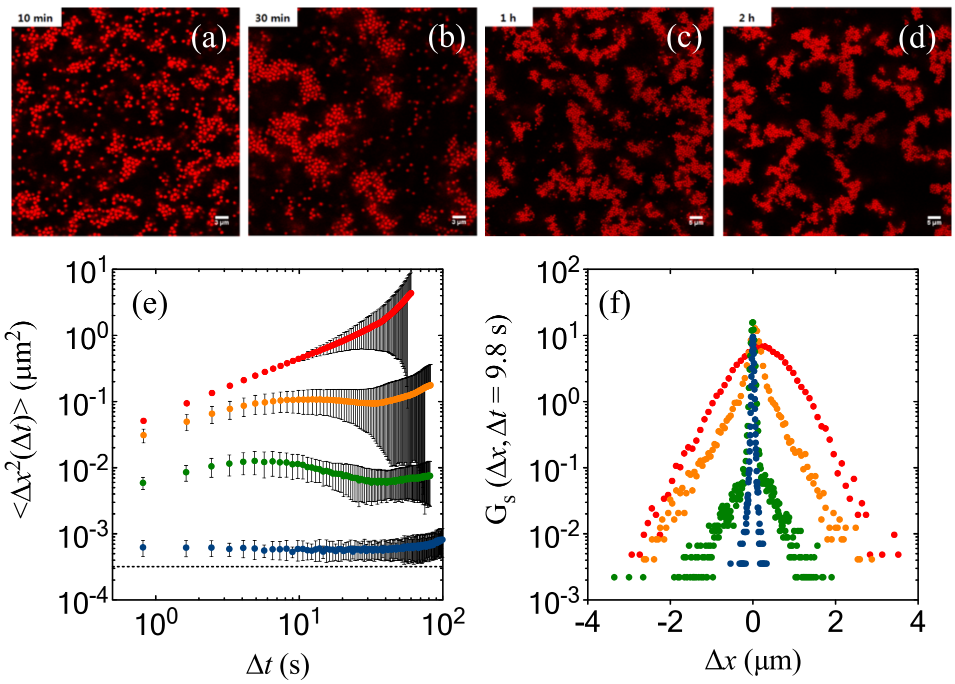
Supplemental Material

Characterization of quiescent colloidal gels prior to application of shear

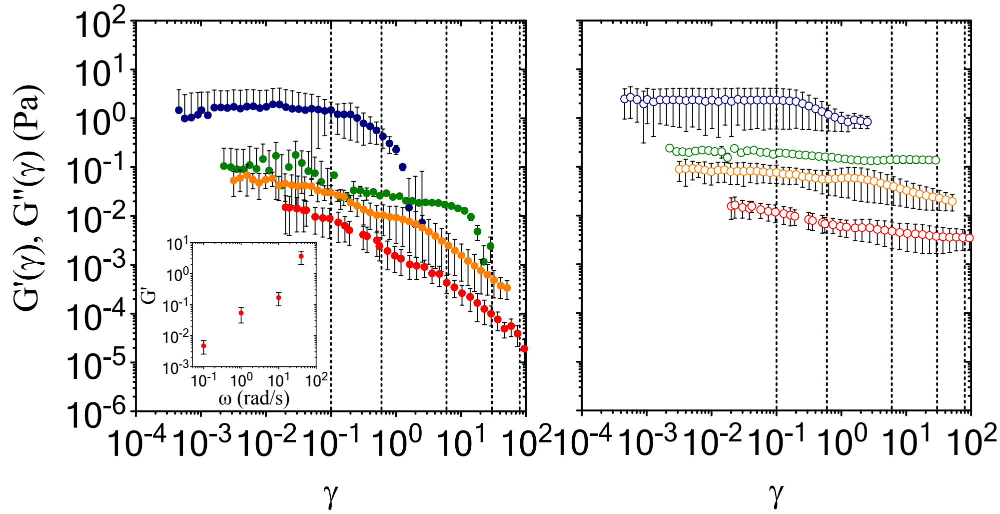
The dynamics of the quiescent gels are monitored at waiting times of t_w = 10 min, 30 min, 1 hour and 2 hours after sample loading. Representative confocal images of the effect of waiting time on the microstructure of these gels are shown in SI Fig. 1(a)-(d). The mean-squared displacement (MSD) values and the van Hove self-correlation functions plotted in the figure show that the colloids become increasingly arrested over the course of 2 hours. SI Fig. 1(e) shows that the MSD of the gels attain a plateau localization length of $\langle \Delta x^2(t) \rangle = (6.5 \pm 2.0) \times 10^{-4}$ μm^2 at t_w = 2 hours. Similarly, SI Fig. 1(f) shows that the single particle displacement probability is narrow and non-Gaussian. The asymmetry in the van Hove self-correlation function at the longest time characterized indicates that there is some center-of-mass drift occurring at that instance.



SI FIG. 1. Representative 2D confocal images of quiescent gels at (a) t_w = 10 min, (b) t_w = 30 min, (c) t_w = 1 hour, and (d) t_w = 2 hours after sample loading. Scale bars represent 3 μm. In (e), the MSD of the gels at t_w = 10 min (red), 30 min (orange), 1 hour (green), and 2 hours (blue) are shown. Error bars are standard deviations from independent measurements. The dashed line shows the static noise floor of the instrument. The van Hove self-correlation of the gels at t_w = 10 min (red), 30 min (orange), 1 hour (green), and 2 hours (blue) are shown in (f).

Oscillatory strain sweep data

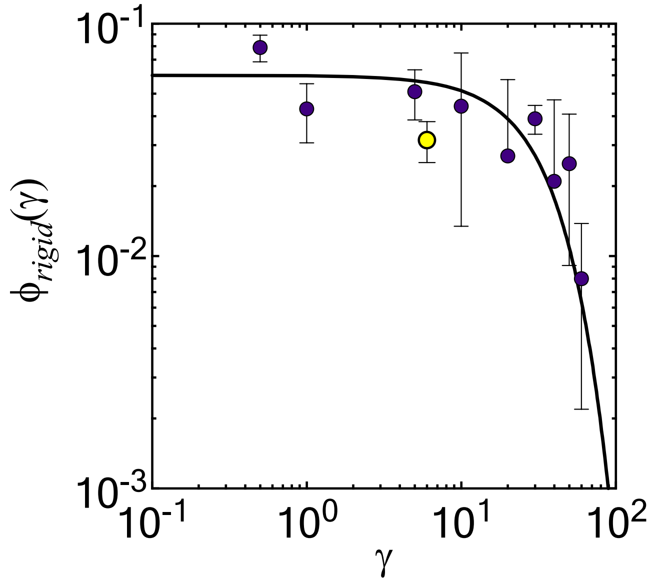
Measurements of G'(γ) and G"(γ) are carried out at angular frequency ω = 0.1 rad/s, 1.0 rad/s, 10 rad/s, and 40 rad/s to study the effect of frequency on the linear elastic modulus, G'. Experimental values of G'(γ) are normalized by G' (as characterized at low strain) to compare with MCT-PRISM.



SI FIG. 2. Oscillatory stress sweep data at an angular frequency ω = 0.1 rad/s (red), 1.0 rad/s (orange), 10 rad/s (green), and 40 rad/s (blue). Closed symbols represent G'(γ) and open symbols represent G''(γ). Inset: Linear plateau value, G', plotted as a function of ω. Error bars are standard error of the mean from 3 independent measurements.

Volume fraction of slow, rigid clusters after yielding

In equation (3) of the main text, MCT-PRISM is modified to include only the effect of the slow, rigid subpopulation of colloids in the yielded gel. The elastic modulus depends on the volume fraction of this subpopulation. These values of $\phi_{rigid}(\gamma)$ are obtained by fitting a stretched exponential function to samples used in Ref. [2]. The incorporation of $\phi_{rigid}(\gamma)$ into equation (3) addresses the effect of rapid structural relaxation of the mobile subpopulation and provides an accurate depiction of the 3D structural landscape immediately after the cessation of flow. Ref. [2] found that the decrease in ϕ_{rigid} is a general function of γ for depletion gels ($0.375 \leq c/c^* \leq 1.1$) tested at large strain deformations ($0.5 \leq \gamma \leq 60.0$) and in the volume fraction range $0.10 \leq \phi \leq 0.20$. This range of conditions includes the gel of the present study. We further checked the consistency of this relation with the gels used in this study by a direct measurement of the value of ϕ_{rigid} at $\gamma = 6.0$ using the methods of [2]. We find that the measurement for this study agrees with the full correlation of Ref. [2] to within experimental error. The exponential fit of data in SI Fig. 3 takes a compressed form of $\phi_{rigid}(\gamma) = 0.060\exp\left[-(\gamma/35)^{1.5}\right]$ and is used in equation (3) of the main text.



SI FIG. 3. Strain-dependent volume fraction of slow/rigid clusters after yielding, obtained from Ref. [2] (purple) and this work at γ = 6.0 (yellow). Error bars are standard error of the mean from 3 independent measurements. The solid line shows the exponential decay fitting for the data points.