Flow, arrest and yielding in dense colloidal suspensions - glasses *vs.* gels

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Rheology modification in complex fluids is important for a wide range of applications including formulation of engineering fluids and consumer products. The ways in which such fluids evolve after cessation of flow and during yielding under flow have important implications for the properties and performance of the fluid in its intended application. Here we consider flow properties, dynamical arrest, and yielding in systems with repulsive and attractive interactions, i.e. systems which form soft colloidal glasses and systems which form colloidal gels, respectively. Rheological studies chart the evolution from metastable fluid-like states into arrested solid-like states as a function of time following cessation of flow for repulsively-interacting systems, or a thermal quench for thermoreversible gelation of particles with attractive interactions. We observe distinct signatures that are associated with dynamical arrest in both cases.

For colloidal glasses, arrest occurs due to a sudden onset of elasticity. The elastic component of the shear modulus grows rapidly and quickly exceeds the viscous component of the shear modulus, with a crossover that occurs concurrent with the evolution of a maximum in the viscous modulus. Arrest is delayed by the application of stress, with the arrest time τ_a diverging beyond a critical stress σ_c that is similar in magnitude to the yield stress, i.e. $\tau_a \sim \exp[1/(\sigma - \sigma_c)]$. Notably, the temporal width of the peak in the viscous modulus of the system is a strong function of the applied stress, which signals that the stress modifies the distribution of arrest timescales in the system.

In colloidal gels, arrest proceeds via the formation of a critical gel, with a clear inversion in the frequency dependence of the loss angle, $\tan\delta$, which is not observed for the colloidal glass. The scaling exponents describing the approach to the critical state can be captured through a systematic set of time-resolved measurements, revealing strong similarities to the critical behavior of many commonly studied polymer gels. The critical gel is described completely by its relaxation modulus, $G(t) = St^{-n}$ with $S = 0.33$ and $n = 0.5$. From the frequency dependence of the rate of evolution of the critical gel we extract the dynamic critical exponent, κ, as defined in Equation 1, and the relationship between the rate of growth of the elastic and viscous moduli, given by the constant of proportionality C. As shown in Figure 1, for appropriate temperatures, the system exhibits a weak power law dependence of the modulus growth rate on frequency, with a dynamic critical exponent $\kappa \approx 0.25$ and proportionality $C \approx 2$.

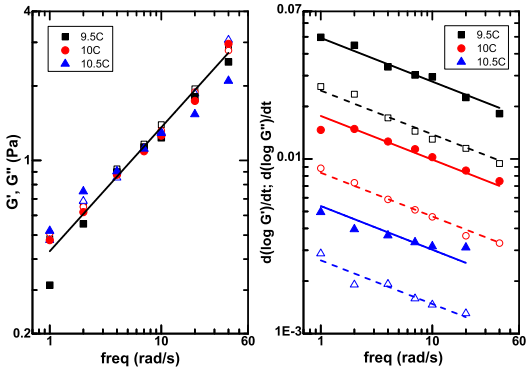

FIG. 1. Left: Elastic (G', closed symbols) and viscous (G'', open symbols) moduli in the near critical gel for 3 temperatures as shown. $G' \sim G'' \sim \omega^{0.5}$. A line of slope 0.5 is drawn as a guide to the eye. Right: Rate of change of the modulus as a function of frequency at the gel points for 3 temperatures as shown. Lines of slope $\kappa = 0.25$ are drawn as guides for the eye. Data conform to Equation 1 with $C \approx 2$.

$$\left(\frac{1}{G'}\frac{\partial G'}{\partial t}\right)_{t=t_g} \simeq C\left(\frac{1}{G''}\frac{\partial G''}{\partial t}\right)_{t=t_g} \sim \omega^{-\kappa} \qquad (1)$$

We examine the yielding response in a model suspension as the system is deliberately tuned from a soft colloidal glass to an attractive colloidal gel by adjusting ionic strength, which modulates the electrostatic interactions of the particles. The colloidal glass is marked by rapid recovery of rheological properties following yielding, whereas the gel is subject to much longer transients and exhibits path-dependence in its rheological properties due to the sensitivity of the aggregation state to shear flow. The implications of dynamical arrest and yielding are discussed in the context of formulating complex fluids and rheology modification for various applications. A novel approach to rheology modification is discussed, based on the deliberate design of systems featuring hierarchical dynamics.

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