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Nonlinear Elasticity and Yielding of Nanoparticle Glasses

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We employ experiment and theory to explore the nonlinear elasticity and yielding of concentrated suspensions of nanoparticles which interact via purely repulsive forces. These glassy suspensions are found to exhibit high exponent power law or simple exponential dependences of the shear elastic modulus and perturbative yield stress on nanoparticle volume fraction, as well as a monotonic decrease of the perturbative yield strain with increasing concentration. Our experimental observations are in good agreement with the predictions of a recently developed microscopic statistical mechanical theory, which describes glassy dynamics based on a nonequilibrium free energy that incorporates local cage correlations and activated barrier hopping processes [(1) Schweizer, K. S.; Saltzman, E. J. *J. Chem. Phys.* **2003**, *119*, 1181. (2) Saltzman, E. J.; Schweizer, K. S. *J. Chem. Phys.* **2003**, *119*, 1197. (3) Kobelev, V.; Schweizer, K. S. *Phy. Rev. E* **2005**, *71*, 021401].$^{1-3}$

Colloidal (and nanoparticle) suspensions exhibit a wide range of rheological behavior and are often classified as “soft materials”.[4,5] One specific example is that of hard sphere suspensions, whose interactions are dominated solely by excluded volume effects. Concentrated hard sphere suspensions bear many similarities to glassy liquids,[6,7] including the presence of a yield stress, shear thinning behavior, and strain softening. Understanding and controlling these nonlinear phenomena are of critical importance for a broad range of technological applications, including the design of concentrated colloidal[8,9] and nanoparticle inks[10] for direct-write assembly of complex 3-D structures.

The structure and dynamics of concentrated glassy suspensions have been previously investigated by light scattering,[11−15] confocal microscopy,[16,17] and rheological measurements.[18−20] The onset of a glassy state is marked by a rapid rise in viscosity, the development of a yield stress, and significant recoverable strain upon removal of a transient step stress. In such systems, the dynamics of the nearest-neighbor particles that form a “cage” around a given colloid play an important role in determining their nonlinear rheological response. The goals of this Letter are to study the linear and nonlinear viscoelasticity of a hard sphere-like nanoparticle suspension of technological importance and to compare the observations with theory.

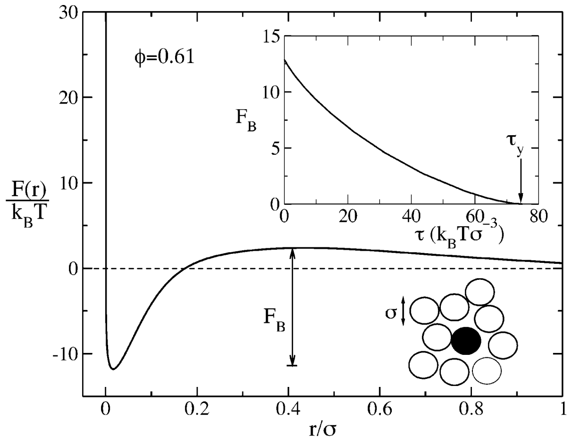

Figure 1. Nonequilibrium free energy (in units of the thermal energy) as a function of particle displacement (in units of particle diameter) for $\phi = 0.61$. The entropic barrier, F_B, decreases in a monotonic, nonlinear manner with external stress until it vanishes at the absolute yield stress.

A few theories have been recently developed to address the challenging problem of nonlinear rheology of glassy suspensions.[3,21,22] All neglect the long time consequences of many particle hydrodynamics. The coarse grained and phenomenological “soft glassy rheology” or “trap model” approach[21] postulates the existence of barriers to particle hopping transport. In this case, external deformation is assumed to reduce barriers, accelerate relaxation and flow, and ultimately drive yielding. In contrast, ideal mode coupling theory (MCT)[22,23] is a predictive microscopic approach that connects slow dynamics to structural constraints on the local cage scale. It associates shear thinning with loosening of interparticle constraints by convection of cage scale collective density fluctuations.[22] This theory is built on the idealization that a true glassy solid state exists (infinite viscosity) and ignores slow activated barrier hopping processes. Recently,

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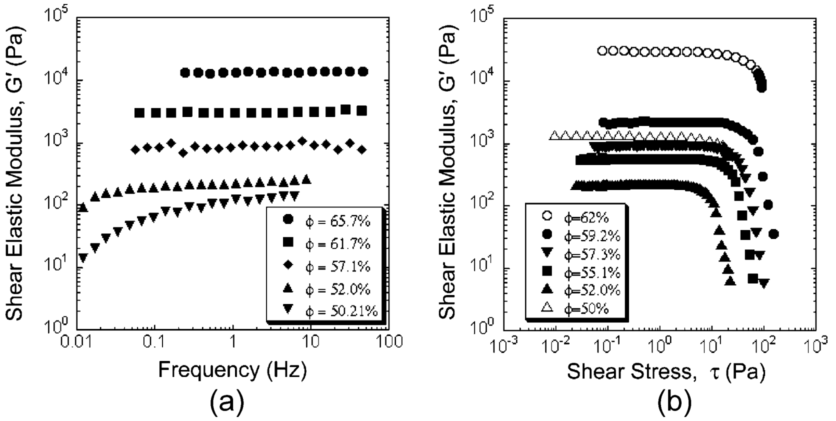

Figure 2. (a) Shear elastic modulus, G', as a function of frequency for concentrated nanoparticle suspensions. (b) Shear elastic modulus as a function of shear stress for concentrated nanoparticle suspensions, comparing experimental data (filled symbols) to theoretical predictions (open symbols). [Note: Effective volume fractions are reported for the experimental data.]

a microscopic and predictive statistical dynamical theory has been developed which includes structural cage correlations in the spirit of MCT in a technically simplified manner. Most importantly, this approach goes beyond MCT to explicitly construct an effective nonequilibrium free energy that controls particle dynamics and includes ergodicity restoring activated barrier hopping within a nonlinear, stochastic Langevin equation description.[1,2] The approximate concept of an ideal glass and its associated critical volume fraction, ϕ_c, is not employed. Hence, confrontation of theory and experiment is direct and does not require the introduction of a difference volume fraction variable $\phi - \phi_c$. The technical details, approximations, and limitations of the theory have been previously discussed in depth.[1−3] An example of the nonequilibrium free energy as a function of particle displacement for a $\phi = 0.61$ volume fraction suspension is shown in Figure 1. This theory has been shown to be in good agreement with measurements of transport coefficients and other dynamical properties in glassy suspensions without the need for adjustable parameters or an ideal glass transition singularity.[1,2]

Very recently, the barrier hopping theory has been generalized[3] to include in a predictive manner the effect of external stress or strain in the spirit of trap models.[21] Specifically, external stress results in a new contribution to the nonequilibrium free energy of the form, $-\sigma^2\phi^{-2/3}\tau$, where σ is the colloid diameter and τ is the stress. Increasing stress modifies the nonequilibrium free energy resulting in a reduction of the degree of transient localization, softening of the elastic shear modulus, G', a reduction of the entropic barrier, and viscosity thinning.[3] As illustrated in the inset of Figure 1, at a critical value of strain or stress, the system is predicted to undergo an absolute yield transition, i.e, the solidlike mechanical response is lost since particles are no longer transiently trapped by the surrounding cage (local minimum of $F(r)$ disappears and the barrier $F_B \rightarrow 0$). Comparison of the theoretical predictions with the limited prior experimental[15,16] work on a polydisperse glassy poly(methyl methacrylate) (PMMA) colloidal suspension has revealed rather good agreement for strain-induced modulus softening and absolute yield stress and strain.

Here, the nonlinear elasticity and yielding behavior of concentrated nanoparticle suspensions are measured to provide a more critical test of the theoretical predictions as a function of volume fraction under preabsolute yield conditions. The experimental system under investigation is composed of barium titanate ($BaTiO_3$) nanoparticles dispersed in an aqueous solution by a comb polymer consisting of a poly(acrylic acid) (PAA) backbone with charge neutral poly(ethylene oxide) (PEO) teeth. Kirby et al.[24] have recently demonstrated that $BaTiO_3$ nanoparticles stabilized by a comb polymer adlayer remain stable over a broad range of pH and ionic strength conditions. Due to the relative size of the polymeric adlayer with respect to the nanoparticles (diameter ~ 60 nm, polydispersity index of 1.23), we invoke an effective volume fraction (ϕ_{eff}) to accurately describe the suspension concentration. To estimate ϕ_{eff}, we consider only the contribution arising from the PEO teeth, which yields an adlayer thickness approximated by its radius of gyration $R_g \approx 0.06\sqrt{MW}$, of ~2.7 nm.[25] Use of this value of ϕ_{eff} (~1.3ϕ) is expected to result in rather minor deviations from hard sphere behavior.[26,27] Concentrated suspensions are prepared by adding an appropriate amount of $BaTiO_3$ nanoparticles to an aqueous comb polymer solution (pH 9). Their rheological properties are characterized as a function of ϕ_{eff} using an oscillatory technique (C−VOR, Malvern Instruments, Malvern, UK). (See the Supporting Information for more experimental detail.)

The experimental shear elastic moduli as a function of frequency and shear stress are shown in Figure 2, panels a and b, respectively. Figure 2a indicates that, at effective volume fractions greater than approximately 52%, the colloidal suspension behaves as an elastic solid for time scales longer than roughly 100 s. For lower effective volume fractions, there is a noticeable softening at low frequencies. We note that for thermal glass formers, a relaxation time of 100 s is typically taken as the definition of a kinetic glass transition temperature. By analogy, we estimate the kinetic glass transition volume fraction of our system is ≈0.52. Interestingly, for the classic model hard sphere suspension of ≈400 nm PMMA colloids the alpha relaxation time as deduced from dynamic light scattering is ≈100 s for $\phi \approx 0.53$.[11]

Figure 2b shows the experimental elastic modulus as a function of shear stress plotted along with representative theoretical results for volume fractions on the low and high end of the range experimentally studied. Qualitatively, theory is in good agreement with experiment; the theoretical curves have similar shapes as the experimental ones, with both showing that the elastic modulus and yield stress increase with increasing volume fraction. The theory predicts a factor of ~3−4 reduction of G' with stress

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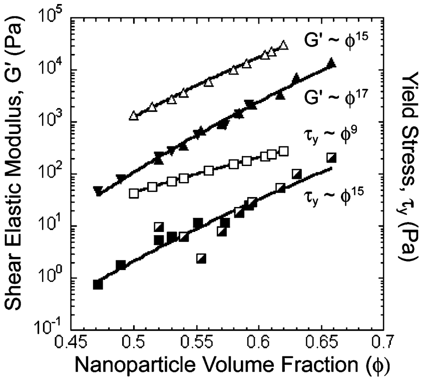

Figure 3. Elastic modulus (triangles) and perturbative yield stress (squares), for concentrated nanoparticle suspensions, comparing experimental data (filled symbols) to theoretical predictions (open symbols). The experiments were performed at both 1 Hz (▼,■) and 10 Hz (▲,◪). The solid lines are power-law fits. [Note: Effective volume fractions are reported for the experimental data.]

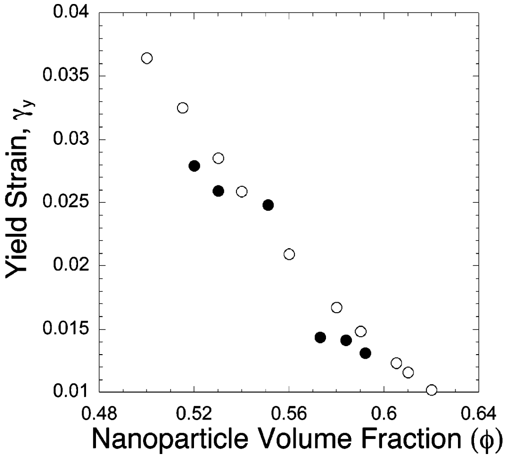

Figure 4. Yield strain as a function of volume fraction for concentrated nanoparticle suspensions, comparing experimental data at 1 Hz (filled symbols) to theoretical predictions (open symbols). [Note: Effective volume fractions are reported for the experimental data.]

before the absolute yield point. The abrupt vanishing of the theoretical zero frequency G' follows from the stress-induced destruction of the transient localized state and the neglect of strain induced structural changes.[3]

The dependence of the elastic modulus and yield stress on nanoparticle volume fraction is quantified more fully in Figure 3. Here the yield stress is defined in a standard perturbative (not absolute as in ref 20) manner to be the stress at which the elastic modulus had dropped by 10% relative to its linear response value. As predicted by the (no adjustable parameter) theory, the experimental results show interesting power law or exponential behavior with the elastic modulus exhibiting a stronger dependence than the yield stress. Although the figure indicates power law fits of the form $A\phi^x$, exponential fits of the form $Ae^{B\phi}$ were also satisfactory and resulted in B values of 15.1 and 25.9 for the theoretical yield stress and elastic modulus, respectively, and 27 and 30.8 for the experimental yield stress and elastic modulus, respectively. The same high exponent power law or simple exponential behavior was seen at both frequencies tested, 1 and 10 Hz, and the elastic modulus versus nanoparticle volume fraction curves at these two frequencies overlay well. However, at a detailed level, there are differences between theory and experiment. The theoretical elastic modulus and yield stresses are over an order of magnitude greater than the experimental values, and the theoretical perturbative yield stress is a weaker function of volume fraction than its experimental counterpart. We believe these differences may be mainly a consequence of the "soft" repulsive nature of the glassy nanoparticle suspensions studied. Although the comb polymer-coated barium titanate particles do act much like hard spheres, the steric adlayers have more compliance than the underlying rigid particles to an extent that is likely ϕ-dependent. For these concentrated suspensions, where the particles are in contact with one another, this adlayer will compress slightly under pressure, resulting in a lower elastic modulus and yield stress. If this interpretation of the origin of the differences between theory and experiments is qualitatively correct, then one might expect the yield strain will not be as sensitive to the layer softness since it is a ratio of stress to modulus.

Figure 4 shows the perturbative yield strain, $\gamma_y = \tau_y/G'$ where G' is the quiescent plateau value, for both the experimental and theoretical systems as a function of volume fraction. The experiment and theory are in remarkably good agreement in terms of both the volume fraction dependence and the absolute magnitude of the yield strain which decreases from ~3.5% to 1% with increasing ϕ. Although this level of quantitative agreement may be fortuitous, we believe it provides significant support for the theory of ref 3, which was previously shown to predict the absolute yield strain and stress of a glassy PMMA suspension quite well.[3,20]

In conclusion, we have demonstrated that a microscopic theory for the rheological properties of glassy colloidal suspensions which predicts high exponent power law or simple exponential dependences of elastic modulus and perturbative yield stress on colloid volume fraction, and a monotonically decreasing perturbative yield stress with volume fraction, are in good agreement with experiments on repulsive, hard sphere-like $BaTiO_3$ nanoparticle suspensions. New experiments to measure shear thinning of the viscosity and stress-shear rate flow curves will provide an explicit test of the dynamical predictions of the theory.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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