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Elasticity and clustering in concentrated depletion gels

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X-ray scattering and rheology are employed to study the volume fraction dependence of the collective structure and elastic moduli of concentrated nanoparticle-polymer depletion gels. The nonequilibrium gel structure consists of locally densified nonfractal clusters and narrow random interfaces. The elastic moduli display a power law dependence on volume fraction with effective exponents that decrease with increasing depletion attraction strength. A microscopic theory that combines local structural information with a dynamic treatment of gelation is in good agreement with the observations.

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Suspensions of particles and polymers are ubiquitous in diverse areas of physical and biological science and engineering [1–3]. Experimental control and theoretical prediction of competing equilibrium (fluid, crystal, phase separated) and nonequilibrium (gel, glass) states, collective structure, and dynamic properties are major challenges. The fluid-to-gel transition and viscoelastic properties are particularly important for particle processing, membrane formation, and cellular biophysics [1,3]. A model of colloidal gels as kinetically controlled aggregates which percolate and/or jam has emerged from studies of low particle volume fraction materials, where fractal clusters of dimensions much larger than the primary particle can form [2,4–6]. Power-law scaling of the elastic modulus with particle volume fraction is often observed and generally attributed to self-similar fractal structure and/or percolation effects.

Physical gelation and elasticity of concentrated particle gels is a far less explored and understood problem. Recently, a combined experiment-theory study [7,8] of the influence of polymer concentration and radius of gyration, R_g, on the structure and viscoelasticity of model hard spheres (radius R) at a *single* high particle volume fraction of $\phi=0.4$ was performed [7,8]. Gelation is induced via the depletion attraction mechanism associated with nonadsorbing polymer additives [9]. Despite the irrelevance of fractal cluster formation, the gel elastic modulus, G', was found [7] to depend on polymer-to-particle size asymmetry ratio, R_g/R, and reduced polymer concentration, c_p/c_p^*, in a power-law fashion: $G' \sim (R_g/R)^{-2}(c_p/c_p^*)^{4.4}$, where c_p^* is the dilute-to-semidilute crossover polymer concentration. A theoretical analysis [7,10] which combines the polymer reference interaction site model (PRISM) [11] for collective structure with a "naïve" [12] version of mode coupling theory (MCT) of gelation [13,14] suggests the origin of this scaling behavior is short-ranged many-body correlations between nanoparticles. MCT-PRISM theory for concentrated depletion gels has also very recently predicted power-law dependences of G' on volume fraction with effective exponents that monotonically decrease as the gel state is more deeply entered [10]. The dependence of elasticity on particle concentration is a particularly sensitive probe of the coupling of structure and mechanical properties. This Rapid Communication reports on systematic experiments to elucidate the volume fraction-dependent structure and elastic modulus of concentrated depletion gels, which also serve as a benchmark test of the theoretical predictions.

The well-characterized model polymer-particle suspensions, and the x-ray scattering and rheological tools employed to study them, have been discussed elsewhere [7,8]. The particles are $D=2R=90$ nm hard sphere octadecylsilica dissolved in decalin, to which polystyrene of $R_g \sim 3.5$ nm ($R_g/R=0.078$) is added to induce gelation. The suspension is rapidly loaded into the sample cell, and presheared prior to gelation for ~ 200 s at a rate of $450-600$ sec^{-1}. It is then allowed to reach a mechanical equilibrium state as determined by measurements of the time-dependent elastic modulus at a frequency of 1 Hz. The recovery time for all samples was on the order of a few minutes. Figure 1 shows the visually determined nonequilibrium fluid-to-gel boundary, $c_p^{gel}/c_p^*(\phi)$, which is consistent with rheological measurements for high volume fraction depletion gels [7]. The (weakly) frequency dependent elastic modulus at a fixed reduced polymer concentration is shown in the inset for several particle volume fractions.

An ultrasmall angle x-ray scattering (USAXS) study of the nanoparticle collective structure factor, $S(q)$, has been performed over a wide range of reduced polymer concentrations ($c_p/c_p^*=0.3$, 0.6, and 0.8 in the gel) and high $\phi \sim 0.2-0.4$. The collective structure factor is found to be remarkably *insensitive* to volume fraction variations in this range; the measured $S(q)$ are very similiar to the $\phi=0.4$ system [8] and hence are not presented here. Depletion attractions induce structural reorganizations on three distinct length scales: (i) strong enhancement of local cage correlations, (ii) suppression of intermediate length scale fluctuations (decreased osmotic compressibility), and (iii) a large amplitude, Porod-like upturn in $S(q)$ at small wave vectors. In accordance with confocal microscopy results [15], these

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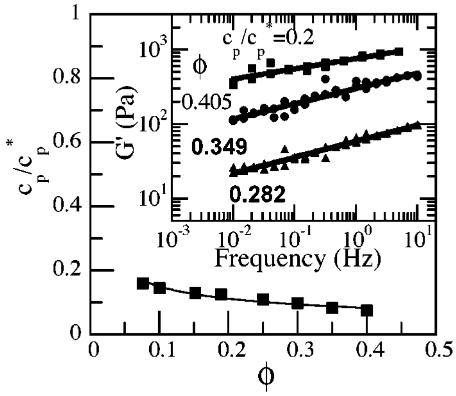

FIG. 1. Experimental gel boundary (reduced polymer concentration vs particle volume fraction) with a smooth curve drawn through the data to guide the eye. The inset shows the frequency dependent elastic modulus for $c_p/c_p^*=0.2$ and three volume fractions. The lines are power-law fits with exponents in the range of 0.15–0.2.

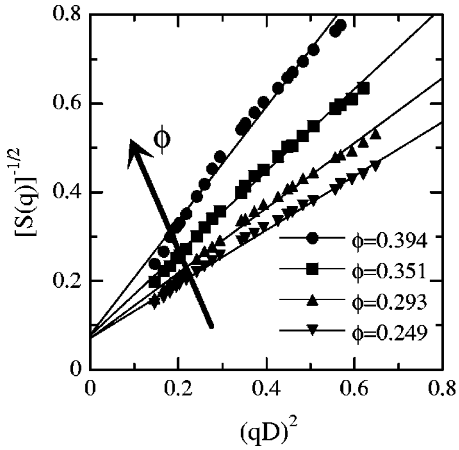

FIG. 2. Debye–Bueche (D–B) plot of the low angle USAXS data for several volume fractions at a fixed polymer concentration of $c_p/c_p^*=0.3$. The lines through the data points are the D–B fits, and indicate Porod-like or sharp interface behavior occurs.

features imply [8] the emergence of dense, nonfractal clusters and narrow random interfaces which are likely due to an annealing or compaction process on the depletion attraction scale $R_g \ll R$. Local annealing seems plausible, since the polymers are nonadsorbing and small scale relative motion of nanoparticles should not be strongly hindered.

The generic Debye–Bueche (D–B) quenched disorder model [8,16] of randomly distributed heterogeneities is employed to quantitatively analyze the low angle scattering region relevant to cluster and interface formation. The D–B real-space disorder contribution to the scattering function is $S(r) \sim \exp(-r/\xi_v)$, where ξ_v is a correlation length between voids or heterogeneities which is expected to be closely related to a typical dense cluster size. The corresponding structure factor is [8,16]

$$S_{\text{D-B}}(q) = \frac{S_{\text{D-B}}(0)}{(1+q^2\xi_v^2)^2}, \tag{1}$$

where $S_{\text{D-B}}(0)=48\phi(\xi_v/2R)^3\langle\eta^2\rangle$, and $\langle\eta^2\rangle$ is a mean-squared volume fraction difference between the diffuse "void" and dense cluster regions. Figure 2 shows that the two parameter minimalist model of Eq. (1) provides a good description of $S(q)$. Although the data display a slight downward curvature, the restricted q range probed and inherent experimental uncertainties render a more sophisticated analysis (based on more than two parameters) inappropriate in our judgment. Moreover, results obtained from a linear fit to the lower wave-vector range of data are very similiar to those obtained from fitting the entire data set. The extracted model parameters are shown in Fig. 3. $\langle\eta^2\rangle$ is essentially independent of polymer concentration, but decreases with ϕ, implying the "void" regions do contain particles as expected. The correlation length is remarkably weakly dependent on ϕ and c_p/c_p^*; its absolute magnitude is $\xi_v \sim 4\pm1$, with a mean value of ~ 3.5. The physical mechanism responsible for this insensitivity is unclear, but equilibrium suspension theories cannot provide insight. One caution is that the signifcant error bars associated with extracting the correlation length may hide subtle, but potentially important, dependences of ξ_v on ϕ and polymer concentration.

No adjustable parameter calculations of G' have been performed using MCT-PRISM theory [7,10] within the standard *dynamically* effective one-component framework [13,14,17]. In naïve MCT [12], the dynamic order parameter is the long-time limit of the mean-square particle displacement or localization length, r_{loc}. The structure of the nonergodic gel is a harmonic Einstein solid. The self-consistent equation for the localization length is [10,12]

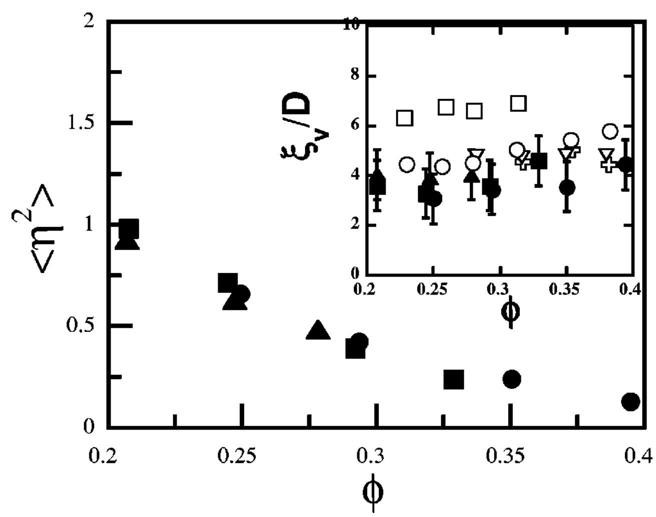

FIG. 3. Debye–Bueche fit parameters. The main panel shows the dimensionless mean-square volume fraction difference between low- and high-density regions, $\langle\eta^2\rangle$, as a function of ϕ for three reduced polymer concentrations $c_p/c_p^*=0.3$ (circle), 0.6 (square), and 0.8 (triangle). The heterogeneity correlation length or cluster size, ξ_v, is shown in the inset (solid symbols). The open symbols are the corresponding values required for the prefactor corrected MCT-PRISM calculations of G' to quantitatively agree with the experimental moduli in Fig. 4 for $c_p/c_p^*=0.15$ (plus symbol), 0.2 (diamond), 0.3 (circle), and 0.6 (square).

$$\alpha = \frac{1}{6}\int_0^\infty \frac{4\pi q^2 dq}{(2\pi)^3} q^2 \rho_s C^2(q) S(q) e^{-q^2/4\alpha[1+1/S(q)]}, \qquad (2)$$

where $\alpha \equiv 3/2r_{loc}^2$, ρ_s is the particle number density, and the effective particle-particle direct correlation function is given by $\rho_s C(q) = 1 - S^{-1}(q)$, where $S(q)$ is the two-component PRISM theory particle structure factor. The elastic modulus is [13,14]

$$G' = \frac{kT}{60\pi^2}\int_0^\infty dq q^4 \left(\frac{d \ln S(q)}{dq}\right)^2 e^{-(q^2/2\alpha)[1/S(q)]}. \qquad (3)$$

The driving force for localization, and origin of gel elasticity, is polymer-induced interparticle correlations on R_g and smaller length scales. This corresponds to large, reduced wave vectors ($qD \gg 2\pi$), where a local annealing process should be most efficient.

Before presenting the theoretical results, the differences between MCT predictions based on PRISM input and simpler approaches [9,13,14] are summarized. PRISM theory [11] explicitly contains the polymer-induced changes of collective particle structure which quantify the depletion attractions that induce gelation in MCT. The relevant structural changes depend strongly on *both* c_p/c_p^* and ϕ. It is the volume fraction dependence that defines "many-body effects," which is not included by popular effective one-component approaches based on a depletion potential of mean force (PMF) between two isolated particles ($\phi \to 0$). The particle direct correlation function is often approximated by its infinite dilution form: $C(r) \approx -1 + \exp[-\beta W(r)]$, where $W(r)$ is the Asakura-Oosawa (AO), PRISM, or another ϕ-independent PMF; MCT predictions for gel boundaries and elastic moduli at this PMF level are *not* qualitatively sensitive to the specific $W(r)$ employed [10]. However, ϕ-dependent structural changes are physically expected to be important and it is well known [18] that they strongly influence $C(q)$ at the relevant large wave vectors. This important point has been *explicitly* demonstrated for the polymer concentration dependence of the gel modulus at a single high volume fraction [7,10]. Specifically, MCT at the PMF level predicts an exponential dependence, $\ln G' \propto c_p/c_p^*$, in *qualitative disagreement* with the experimental and MCT-PRISM theory findings of a power-law behavior [7,10]. In the language of the simple approaches, the *effective* depletion potential is volume fraction *dependent*, suggesting the ϕ dependence of G' is a critical test of the importance of particle concentration dependent local structural changes.

Experimental elastic moduli at 1 Hz as a function of volume fraction for fixed reduced polymer concentration, and the corresponding MCT-PRISM calculations, are shown in Fig. 4. In order to compare trends, the theoretical results have been multiplied by a ϕ-independent constant (vertical shift; see below). Both experiment and theory display an effective power-law behavior, $G' \propto \phi^x$. The predicted decrease of the exponent for higher polymer concentrations (deeper in the gel) is consistent with the measurements. As suggested by the weak frequency dependences in Fig. 1, the effective scaling exponents are found to be insensitive to shear frequency. Quantitatively, the theoretical power-law

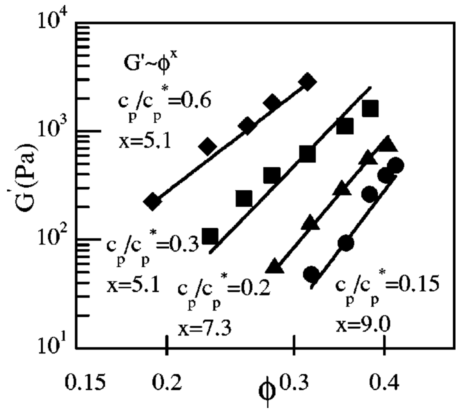

FIG. 4. Experimental elastic moduli (solid symbols) as a function of volume fraction for different polymer concentrations. Power-law fits (not shown) yield the exponents indicated. The solid lines are the prefactor corrected MCT-PRISM theory calculations with the ξ_v/D values shown in Fig. 3.

exponents are $x = 8.8$, 7.8, 6.9, and 5.1 for $c_p/c_p^* = 0.15$, 0.2, 0.3, and 0.6, respectively, which, given the experimental uncertainties and no adjustable parameter nature of the theory, is in good agreement with the observed behavior.

The theoretical results in Fig. 4 have been multiplied by a volume fraction *independent* factor, f, so that $G' = fG'_{\mathrm{MCT}}$. For a fixed $\phi = 0.4$, MCT-PRISM theory yields elastic moduli roughly a factor of 100 times larger than observed ($f \approx 0.01$) over a wide range of polymer concentrations [7,10]. Interestingly, the numerical factor required to force quantitative theory-experiment agreement for the present variable volume fraction gels is nearly constant and of the same magnitude: $f \approx 1/80$, 1/100, 1/120, 1/350 for $c_p/c_p^* = 0.15$, 0.2, 0.3, 0.6, respectively. The near independence of the prefactor correction on polymer concentration, particle volume fraction and depletion range R_g/R [7] suggests MCT-PRISM theory provides a reliable microscopic approach for describing gel elasticity as a function of the multiple experimentally controllable variables.

The reason why the prefactor correction is roughly 0.01 is not *a priori* obvious; it might be an unavoidable quantitative limitation of MCT. However, based on the USAXS measurements, one can rationally speculate its physical origin is largely the dense cluster formation process which is not accounted for by the "homogeneous" local MCT approach [10,12–14]. If MCT properly determines the elementary "bond level" elasticity [14], but macroscopically mechanical energy is stored at the cluster level, then the relevant concentration could be argued to be the cluster, not particle, number density. This simple idea suggests $G' = G'_{\mathrm{MCT}}/N_c$, where N_c is the number of colloids per cluster of radius ξ_v. N_c may be estimated as $N_c \approx 8\phi_{\mathrm{cluster}}(\xi_v/D)^3$, where ϕ_{cluster} is the particle volume fraction in a single cluster. Note that this argument is not based on fractal mechanics concepts, since the relevant clusters are dense. For $\phi_{\mathrm{cluster}} = 0.5$ and a correlation length of $(3-4)D$, $N_c \approx 100-250$. Recognizing the considerable quantitative uncertainties in the latter estimate, we can conclude the simple physical idea is at least consistent with an independent experimental estimate of cluster mass. This provides a plausible rationalization (but not proof) for the absolute magnitude of the empirically deduced prefactor. The physical picture suggests an underlying simplicity in that nonequilibrium mesoscopic structural features of the gel may enter mainly via the size of the dense nonfractal clusters which sets the length scale for mechanical energy storage and the absolute magnitude of the modulus, but does not significantly modify the microscopic origin of elasticity which occurs on the local depletion potential range scale. These ideas are admittedly speculative, and a deeper understanding should be pursued. Recent efforts to develop a "cluster level" MCT may be relevant [19]. However, at present this approach does not predict cluster size or geometry in dense gels nor any mechanical properties.

The good agreement between theory and experiment in Fig. 4, coupled with a comparable level of agreement for the polymer concentration dependence of G' [7], has important implications for understanding and controlling elasticity in concentrated depletion gels. The multiple power-law dependencies of G' on control variables emerge as a consequence of changes in the particle localization length and short-range correlations, not fractal microstructure or other mesoscopic effects. At low enough volume fractions, kinetic aggregation, percolation, and/or fractal cluster formation are expected to play a prominent role, but the "bond level" information provided by MCT remains important. The MCT-PRISM approach can be extended to treat more complex suspensions where other forces are present (e.g., Coulomb, van der Waals). By building on recent progress for predicting barrier formation and activated hopping transport in glassy colloid suspensions [20], the problems of long-time aging, sedimentation, and nonlinear response in depletion gels are also amenable to theoretical treatment [21].

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