Relationship between Particle Elasticity, Glass Fragility, and Structural Relaxation in Dense Microgel Suspensions

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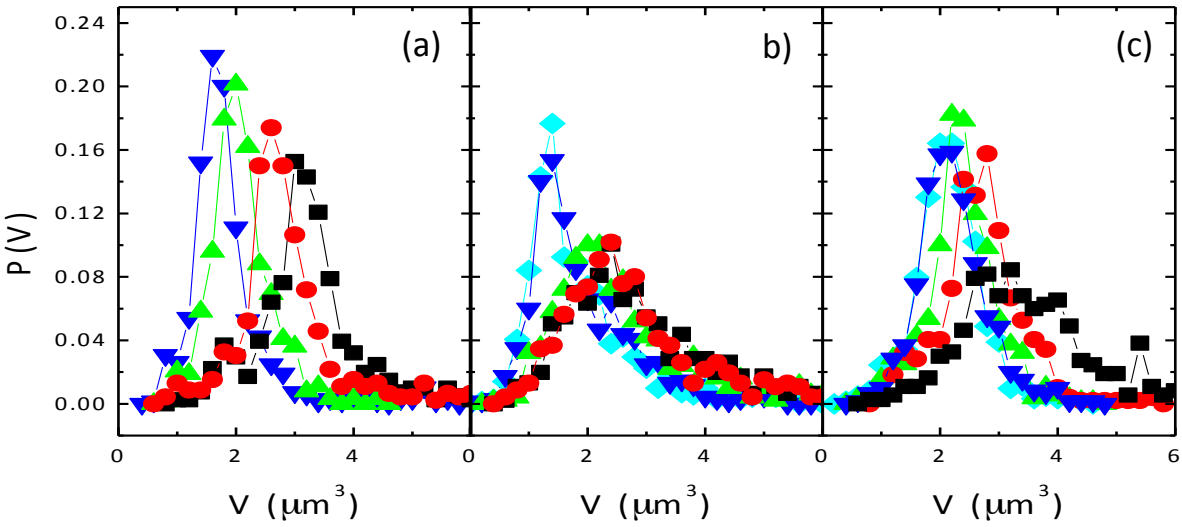
Supplemental Document

Synthesis and Characterization of microgels of varied particle elasticity. Poly(N-isopropylacrylamide) (PNIPAM) microgels of varied crosslinking densities were synthesized by free radical polymerization. Methylene-bis-acrylamide (BIS) was used as the crosslinker at different mass ratio, *CL*, to the N-isopropylacrylamide (NIPAM) monomer, $CL = \frac{[BIS]}{[BIS]+[NIPAM]}$, to control the microgel elasticity, where [BIS] and [NIPAM] are the mass concentrations of BIS and NIPAM, respectively. Five different ratios of CL=0.9%, 1.6%, 2.2%, 3.3%, and 6.6% of fluorescence-labeled PNIPAM microgels were examined in this work to vary the particle elasticity ranging from soft to model "hard" spheres. All the microgels were fluorescence labeled by the copolymerization of 2-aminoethyl methacrylate attached with a fluorescent dye, NHS-Rhodamine. After the synthesis, all the resulting suspension were purified via dialysis for two weeks at room temperature using a SpectraPor® dialysis membrane (MWCO 6-8,000, 22 mm in diameter and 34 mm in flat width) and re-dispersed in fresh deionized water (Barnstain Diamond Nanopure II) before characterization. A microgel stock suspension was concentrated by a rotavapor (Rotovap R-210) at 60 ^{o}C and re-diluted with deionized water until desired microgel concentrations were achieved.

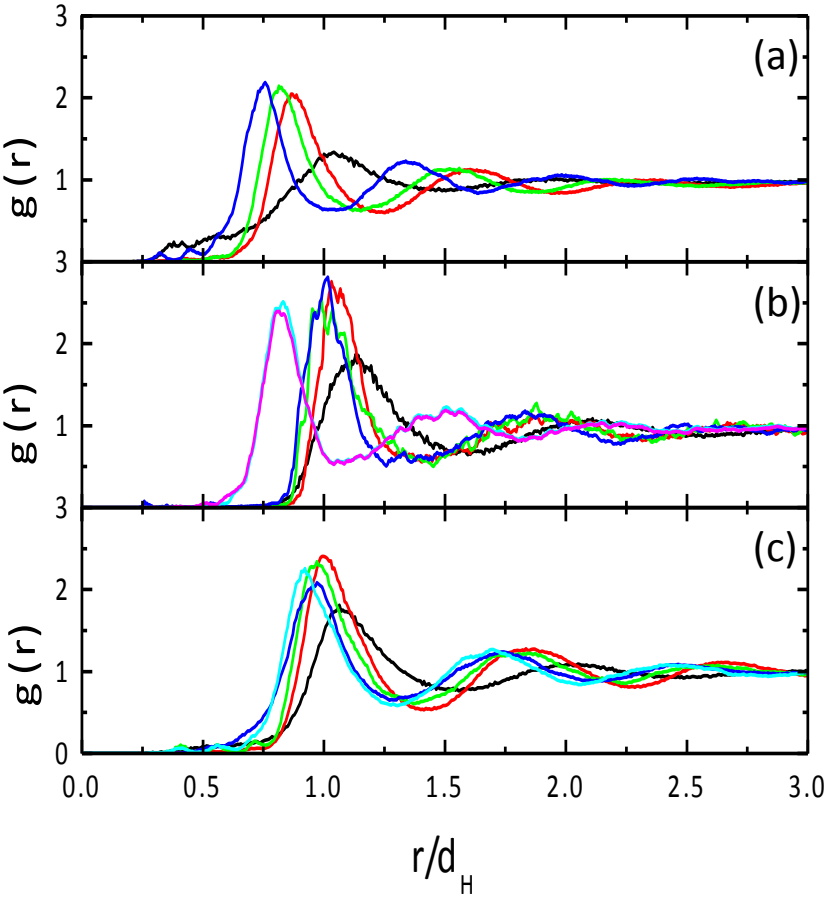
Using a simple Hertzian model, the elastic modulus, *E* (unit: Pa) of these microgel particles is estimated from g(r) following $U(r) = -k_B T \ln g(r) = \frac{4}{15} E (1 - \frac{r}{\sigma})^{5/2} V_c$ at $r \leq \sigma = 2r_{eff}$, where U(r) is the chemical potential energy, r is the radial distance from center of the particle, and V_c is the volume of the contact area and approximated as $V_c \approx \frac{4}{3}\pi(\frac{d_H - R_0}{2})^3$,

and averaged over the values at different ϕ_{eff}. This model is valid for single contact between any two adjacent particles and therefore applicable for an intermediate concentration range as explored in this work.

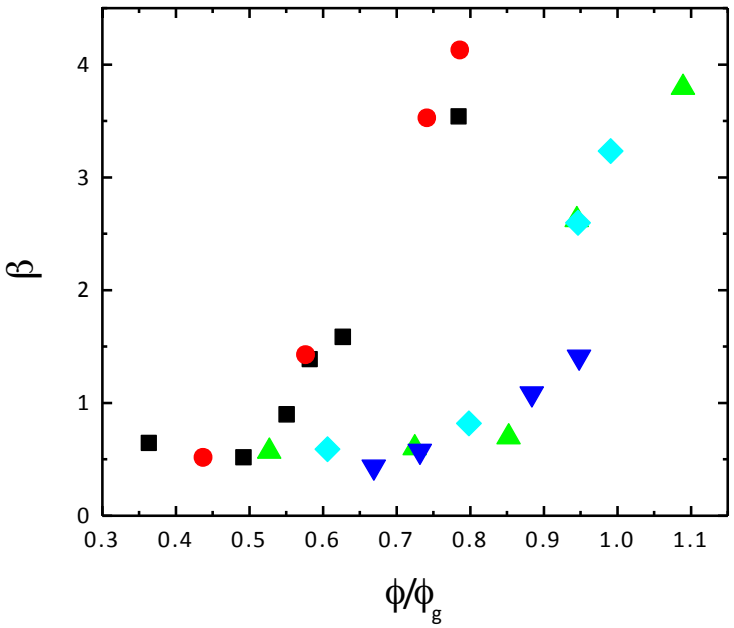
Supplemental Figure 1. Probability distribution, P(V) of volume-per-particle, V, from the Voronoi tessellation for PNIPAM microgels of (a) E= 166 Pa at ϕ_{eff}=0.69 (black squares), 0.71 (red circles), (green triangles), and 0.67 (inverted blue triangles), (b) E=179 Pa at ϕ_{eff}=0.38 (black squares), 0.47 (red circles), 0.59 (green triangles), 0.68 (inverted blue triangles), and 0.79 (cyan diamonds), and (c) E=2.6×10^4 Pa at ϕ_{eff}=0.38 (black squares), 0.49 (red circles), 0.50 (green triangles), 0.56 (inverted blue triangles), and 0.58 (cyan diamonds).The mean volume-per-particles decreases with increasing ϕ_{eff} as expected due to closer packing of particles at high concentrations as well as compressibility of softer particles. These plots show a broad distribution of V for all ϕ_{eff}, implying that the sample is in a random state and there is minimal sedimentation or crystallization at large ϕ_{eff}.



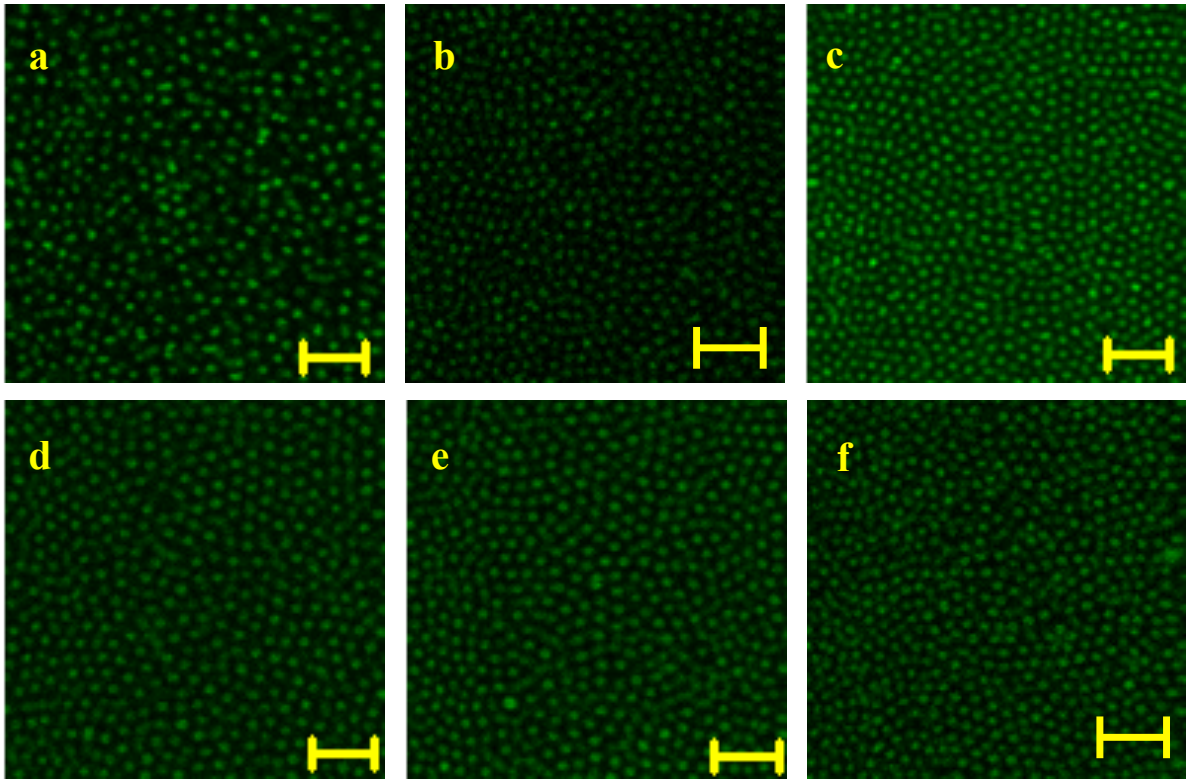
Supplemental Figure 2. Pair correlation function, *g(r),* of dense PNIPAM microgel suspensions plotted against normalized radial distance by undeformed particle diameter, r/d_H, for PNIPAM particle of (a) E=166 Pa at ϕ_{eff}=0.46 (black), 0.69 (red), 0.71 (green), and 0.95 (blue), (b) E = 179 Pa at ϕ_{eff}=0.38 (black), 0.47 (red), 0.50 (green), 0.59 (blue), 0.67 (cyan), and 0.79 (magenta), and (c) E=2.6×10^4 Pa at ϕ_{eff}=0.38 (black), 0.49 (red), 0.51 (green), 0.56 (blue) and 0.58 (cyan).



Supplemental Figure 3. Stretching exponent, β, from the Kohlrausch-Williams-Watts (KWW) fitting of the overlap order parameter, $q_s(\tau) = Aexp((\tau/\tau_\alpha)^\beta)$, is plotted against ϕ_{eff} normalized by ϕ_g for PNIPAM microgels of E = 166 Pa (black squares), 169 Pa (red circles), 179 Pa (green triangles), 436 Pa (inverted blue triangles), and 2.6×10^4 Pa (cyan diamonds).



Supplemental Figure 4. Sample micrographs of fluorescence-labeled PNIPAM particles of elasticity (i) $E = 2.6\times10^4$ Pa in aqueous suspensions of ϕ_{eff}=(a) 0.38, (b) 0.50, and (c) 0.58 and (ii) $E = 166$ Pa at ϕ_{eff}=(d) 0.47, (e) 0.75, and 0.95. Scale bar in each panel is 5 μm. All the micrographs confirm the amorphous disordered structures of PNIPAM particles in aqueous suspensions.



Supplemental Figure 5. Four-point correlation function, $g_4^*(r,\tau)$, at varied lag times, τ, for PNIPAM microgel particles of (a) E = 166Pa in aqueous suspension of ϕ_{eff}=0.61 at τ = 73 s (black), 730 s (red), 3.6×10^3 s (green), 7.2×10^3 s (blue), and 2.9×10^4 s (cyan) and (b) E = 2.6×10^4Pa, ϕ_{eff}=0.52 at τ = 76 s (black), 760 s (red), 2.9×10^3 s (green), 1.2×10^4 s (blue), and 5.3×10^4 s (cyan).