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Super-cooled and glassy states of charged microgel systems in the weak screening regime

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This work presents an investigation of the super-cooled and glassy states of charged colloids in the weak screening regime. Providing groups that can dissociate to a colloidal surface is a standard way to stabilize a colloidal dispersion. Upon dissociation of the surface groups the colloids acquire a net charge and the counter ions form an ionic double layer around the colloids; the colloids then interact by screened Coulomb repulsions. In this work we used negatively charged PNIPAM microgel particles suspended in water and maximized the screened Coulomb repulsions by minimizing the ion concentration of the aqueous medium.

The structures obtained after extended equilibration reveals a phase behaviour that is typical for repulsive colloids: with increasing particle volume fraction ϕ the system exhibits a fluid-crystal and a crystal-glass transition at respectively ϕ_f and ϕ_G . As a result of the long-ranged nature of the screened Coulomb interactions both transitions are shifted to significantly lower particle volume fractions as compared to ϕ_f and ϕ_G of colloidal hard sphere systems. This enabled us to access both super-cooled fluids and glassy states over a wide range of concentrations, the super-cooled fluids being obtained by shear rejuvenating the crystalline systems.

Surprisingly, we find that the structural relaxation times increase exponentially with concentration in the super-cooled fluid range. Such dependence is reminiscent of that observed in strong glass formers. It contrasts with the characteristics of fragile glass formers usually observed for purely repulsive colloidal systems, where the structural relaxation times increase critically with particle concentration. A comparison with numerical solutions of the Ornstein–Zernike equation and molecular dynamics simulations reveals that both the structural and dynamical features of our super-cooled systems can be fully described by assuming DLVO interactions. Our findings suggest that the exponential increase of the structural relaxation time with concentration is the result of the non-negligible contribution of the counter-ions to the total ion concentration of the system. A variation in the particle concentration not only leads to a variation of the free volume, but also to a variation of the screening length; both contributions have an opposite effect on structural relaxations, such that the structural relaxation time varies more slowly with particle concentration than typically observed for hard sphere colloidal systems.

Beyond the glass transition we find that residual relaxation processes persist and that the characteristic times of these processes are almost concentration independent. We argue that this characteristic may be understood by considering that imbalanced internal stresses are the source of restructuring processes within glassy systems. Upon increasing the particle concentration the internal stresses increases compensating the effect of the loss in free volume, such that the structural relaxation time becomes almost concentration independent. Almost concentration independent dynamics is also found for microgels that interact by steric repulsion only, which indicates that this behaviour is a general feature of soft particles.

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