

Kinetic arrest and glass-glass transitions in short-ranged attractive colloids

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1 Introduction

In self-assembly processes, the importance of short-ranged interactions of controlled magnitude has been recognized for a long time [1]. The well-known example is the crystallization of biological macromolecules in solution [2]. However, a short-ranged attraction of a few $k_B T$ often leads to gelation or glassification in lieu of the much desired crystallization. Colloidal systems interacting via a short-ranged attractive potential (square-well) allow to mimic this scenario. In recent years, these systems have received considerable interest in terms of their dynamical properties [3, 4]. Mode coupling theory (MCT)[3] and computer simulations [4] have predicted two different types of glass transitions. In the conventional repulsive colloidal glass, the ergodicity is lost due to blocking of particle diffusion by the dense cages formed by their nearest neighbors whereas in the attractive glass, the particle motion is jammed even at low volume fraction (ϕ) by the short-ranged attraction or stickiness. These two glass lines meet at high ϕ , defining a reentrant transition of repulsive glass-fluidattractive glass as the attractive interaction is progressively increased [3, 4]. The attractive glass line extends beyond the reentrant region to a higher order singular point in MCT (A_3) delineating a glassglass transition [4]. In experiments, similar dynamical arrest including the reentrant transition[5, 6] as that predicted by theory and simulation have been observed in a diverse class of short-ranged attractive colloidal systems [7, 8]. Attractive glass is a unifying term to describe the wide variety of dynamical arrest such as gelation, glassification, non-ergodicity transition, etc. induced by the stickiness.

2 Experimental

In this work, we have investigated the dynamical arrest and kinetic glass transitions in a thermoreversible model short-ranged attractive colloidal system over a wide ϕ range. The sample consisted of stearyl silica particles suspended in n-dodecane and an attractive interaction of sufficient magnitude is induced by cooling the sample below an aggregation temperature (T_A). The static microstructure across the transition was deduced by ultra small-angle X-ray scattering (*USAXS*), colloid dynamics was probed by dynamic light and X-ray scattering (*DLS* and

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DXS , respectively), and shear moduli (G' and G'' , elastic and loss moduli, respectively) were derived from high resolution stress-controlled rheology.

3 Results and Discussion

The static structure factor, $S(q)$, was modeled in terms of an attractive square-well potential using the leading order series expansion of Percus-Yevick approximation [3]. At low and intermediate ϕ , the system shows features of gas - liquid type phase separation and gelation, respectively. At high ϕ , with the onset of attraction, $S(q)$ changes only very little but the intermediate scattering function, $f(q, t)$, and shear moduli vary dramatically. From $f(q, t)$ and the frequency dependence of G' and G'' , fluid - attractive glass and repulsive - attractive glass transitions were identified [9]. The attractive glass exhibits significantly higher rigidity and frozen part of $f(q, t)$ though $S(q)$ is similar as that in the repulsive glass. The observed static and dynamic behavior is consistent with the predictions of MCT and computer simulations for a square-well attractive system [3, 4].

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