Microstructure and Rheology near an Attractive Colloidal Glass Transition

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Microstructure and rheological properties of a thermally reversible short-ranged attractive colloidal system are studied in the vicinity of the attractive glass transition line. At high volume fractions, the static structure factor changes very little but the low frequency shear moduli varies over several orders of magnitude across the transition. From the frequency dependence of shear moduli, fluid-attractive glass and repulsive glass-attractive glass transitions are identified.

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Recently, colloidal systems interacting via short-ranged attractive potentials have received considerable attention in terms of their dynamical properties [1–6]. Mode-coupling theory and computer simulation have successfully predicted two different glass transitions: the conventional repulsive colloidal glass where the ergodicity is lost due to blocking of the particle diffusion by the dense surrounding cages formed by their nearest neighbors, and the attractive glass in which the particle motion is jammed even at low volume fractions (ϕ) by the short-ranged attraction or stickiness [2]. These two glass transition lines meet at high ϕ defining a reentrant transition of repulsive glass–fluid–attractive glass as the attractive interaction is progressively increased [1,2]. The attractive glass line extends beyond the reentrant region to a higher order singular point (A_3) delineating a glass-glass transition [2]. In experiments, similar dynamical features as that predicted by theory and simulation have been observed in a diverse class of short-ranged attractive colloidal systems [7–16].

The interparticle potential, $V(r)$, in short-ranged attractive colloidal systems can be approximately described by hard-sphere repulsion (HS) with an attractive square-well (SW) [1,15]. $V(r) = \infty$, for $0 < r < \sigma$, $V(r) = -u$ for $\sigma < r < \sigma + \Delta$, and $V(r) = 0$ for $r > \sigma + \Delta$, where σ is the hard-sphere diameter, u and Δ are depth and width of the attractive well. The strength of attraction is characterized by the stickiness parameter, $\tau_B = [1/(12\varepsilon)] \times \exp(-u/k_BT)$, where $\varepsilon = \Delta/(\sigma + \Delta)$ [17]. The phase behavior and microstructure of this model can be readily obtained using the Ornstein-Zernike integral equation and the Percus-Yevick approximation (PYA) [1,17]. At low ϕ, the system shows a gas-liquid type phase separation with the liquid phase having gel-like dynamics [15].

The distinguishing features of attractive and repulsive glasses are in their dynamical behavior [2,4,5]—the mechanical properties especially have not been investigated so far. This Letter presents a study of microstructure and rheological behavior near attractive glass transitions in a thermally reversible model short-ranged interacting colloidal system. The microstructure was obtained by ultra small-angle x-ray scattering (USAXS) and the rheological properties were derived from bulk rheology. The results demonstrate subtle changes in the static structure but colossal variations in the rheological parameters in the neighborhood of the reentrant region where the two glass lines meet.

The experimental system consisted of stearyl grafted silica colloids suspended in n-dodecane. This system undergoes a reversible aggregation below a well-defined temperature, T_A, which is attributed to a lyotropic ordering transition of the grafted stearyl chains [18]. The x-ray contrast of grafted stearyl layer (thickness about 1.85 nm) is very closely matched with dodecane. As a result, the x-ray scattering essentially originates from the silica core and the core volume fraction can be determined from the absolute scattered intensity.

The USAXS measurements were performed at the High Brilliance beam line (ID2) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, using a Bonse-Hart camera [19]. The crossed analyzer configuration in the setup permitted us to obtain intensity profiles, $I(q)$, directly in an absolute scale without any smearing. Additional, SAXS measurements were made using a 10 m pinhole SAXS instrument [19]. The incident x-ray wavelength (λ) was 1 Å in all experiments. Samples for USAXS were contained in thin walled flat glass capillaries with sample thickness 0.5 mm. High resolution rheology was performed using a stress-controlled rheometer (Haake, RS300 with microtorque option) with plate-plate geometry thermostated to $\pm 0.01\,^\circ$C. Typical sample diameter and thickness were 8 mm and 0.5 mm, respectively. Special care was exercised for reducing the evaporation losses using a solvent trap and correcting for the real size of sample between the plates. However, the maximum duration of the experiment was still limited to less than 24 h. The applied low frequency oscillatory stress (τ) was well within the linear viscoelastic range.

To establish the short-ranged nature of attraction in this system, Fig. 1 displays the typical SAXS intensity, $I(q)$, in the vicinity of T_A for a sample with $\phi \approx 0.06$. Here, the

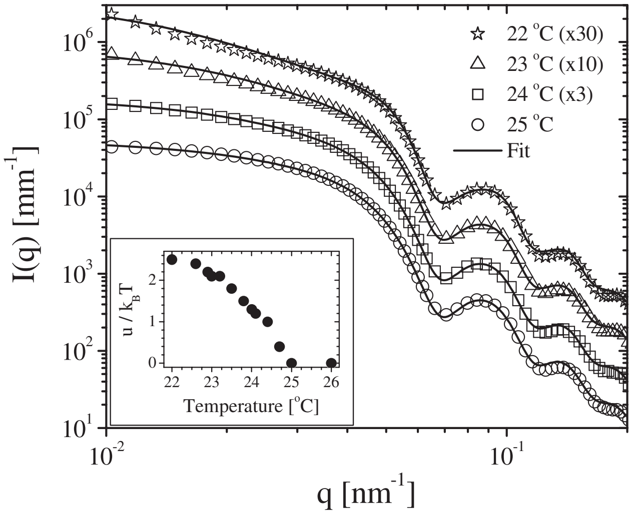

FIG. 1. Evolution of SAXS intensity in the vicinity of T_A (24 °C) for a sample of $\phi \approx 0.06$. The continuous lines are fit to the square-well model using Eq. (1), indicating a thermally reversible transition from repulsive to attractive hard-spheres. Inset shows the depth of the attractive potential (u) for fixed ε ($=0.015$). The different SAXS curves have been displaced for the sake of clarity.

scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$, with θ the scattering angle. The low q upturn of $I(q)$ as the temperature is lowered qualitatively indicates the evolution of attractive interactions. This transition is completely reversible and the attractive interaction can be switched on and off by reversing the temperature. In order to deduce the parameters of $V(r)$, $I(q)$ was modeled in terms of the structure factor, $S(q)$, of a SW system obtained using the leading order series expansion of PYA [17,20]. This analytical solution is based on the factorization of Ornstein-Zernike equation originally proposed by Baxter but with a finite depth of the attractive well [17,20]. $S(q)$ is related to $V(r)$ through the direct correlation function, $C(r)$ [21]. $S(q) = 1/[1 - NC(q)]$, where $C(q)$ is the Fourier transform of $C(r)$ and N is the colloid number density related to $\phi_{\mathrm{HS}} = \pi N\sigma^3/6$. For the SW system the effective ϕ includes the width of the potential, $\phi_{\mathrm{SW}} = \pi N(\sigma + \Delta)^3/6$. $I(q)$ of polydisperse spherical particles can be related to the effective structure factor [$S_M(q)$] and the average particle form factor [$\langle P(q)\rangle$] by the following relation [21,22],

$$I(q) = N\Delta\rho^2 V_P^2 \langle P(q)\rangle S_M(q), \qquad (1)$$

where $\Delta\rho$ is the x-ray contrast, and V_P is the average volume of the particle. $\langle P(q)\rangle$ is obtained from a dilute sample ($\phi < 0.001$) in cyclohexane and fitted to Schulz polydisperse sphere scattering function [22] with mean radius 64.5 nm and polydispersity of 7.4%. $S_M(q)$ is obtained from $S(q)$ and $\langle P(q)\rangle$ using the decoupling approximation [22]. In the fitting procedure for $I(q)$, the parameters σ, V_P, and N were constrained around their experimental values. The depth of the potential, u, was a free parameter while ε was fixed at 0.015. For stearyl silica particles, the value of ε is expected to be the overlap range of the grafted chains [18] and $\varepsilon = 0.015$ corresponds to the maximum range given by the thickness of the stearyl layer.

While the overall trend is similar for different models, the precise values of u and ε vary with the type of approximations used in the analytical expression for $S(q)$. The inset in Fig. 1 displays the depth of the attractive well derived from the fits with $\varepsilon = 0.015$ demonstrating the short-ranged character of attractive interactions in this system. In this ϕ range, with the onset of attraction particles aggregate to form clusters which sediment with time. Below T_A, this clustering process is indicated by an increase in the local ϕ and an excess scattered intensity at low q corresponding to the fractal morphology of these clusters [23]. In the concentration range $\phi \sim 0.19$ (data not shown), these clusters remain stable and the complete phase separation process is presumably interrupted by the jamming of clusters [23].

Figure 2(a) presents the behavior of $I(q)$ at high ϕ close to the reentrant transition region where the repulsive and attractive glass lines are expected to meet. The most noticeable change when transforming to an attractive system is a slight increase of $I(q)$ at low q. The inset of Fig. 2(a) illustrates a schematic phase diagram indicating attractive and repulsive glasses (AG and RG, respectively) and fluid state (F) along with the experimental path followed. Figure 2(b) shows the corresponding $S(q)$ displaying a slightly reduced peak in the attractive state. The fact that the peak position is nearly identical in both repulsive and attractive states reveals that the range of attractive potential is indeed very short ranged and justifies the value of $\varepsilon = 0.015$. The variation of $S(q)$ can be still described by Eq. (1). The decoupling approximation breaks down at this high ϕ range and the continuous lines are monodisperse $S(q)$'s for a SW system. $S_M(q)$ should lie slightly above the monodisperse $S(q)$ function at very low q values. The mismatch between the data and fits around the first peak is attributed to the effect of polydispersity as well as the limitation of the series expansion of PYA [20]. Furthermore, PYA solutions used a reduced volume fraction, $\phi' = \phi - \phi^2/16$ given by the Verlet correction [21].

The inset of Fig. 2(b) shows the depth of SW derived from the analysis of $S(q)$. Since the overall size of the particles is the same, ϕ_{SW} can be taken as a constant (ϕ_{HS}) for small Δ. Alternatively, the observed change in $S(q)$ can be described by a repulsive HS term alone but an effective ϕ that decreases with attraction. The dotted lines in Fig. 2(b) depict the corresponding $S(q)$'s which suggest that the effect of attraction is as if the effective ϕ has decreased. This increase in the compressibility of particles is beyond what is possible by the enhanced overlap of the grafted stearyl chains. At still higher ϕ, difference between $S(q)$'s in attractive and repulsive states diminishes corresponding to a fully jammed state.

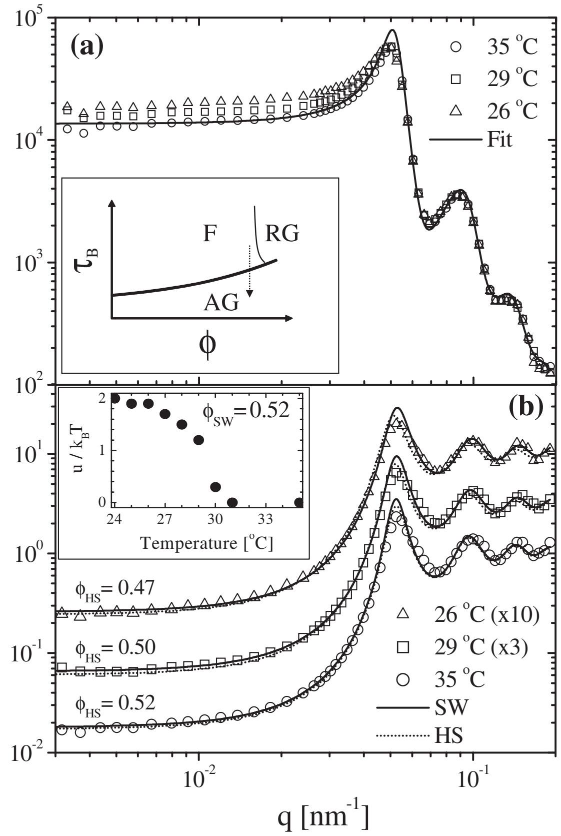

FIG. 2. (a) Typical variation of USAXS intensity across the fluid-attractive glass transition at high $\phi(\approx 0.52)$. Fitted line corresponds to Eq. (1) with a hard-sphere $S(q)$ in the fluid state. The inset shows a schematic phase diagram indicating the experimental path followed (dotted arrow). (b) $S(q)$ obtained from the above data and the corresponding fits to a variable ϕ hard-sphere (ϕ_{HS}) and square-well models. Inset depicts the depth of the square-well potential (u) for fixed ϵ ($= 0.015$) and ϕ_{SW} ($= 0.52$).

The observed features of $S(q)$ presented in Fig. 2 are somewhat different from the light scattering results on reentrant systems involving colloid-polymer mixtures [10,11] but similar to that observed in a concentrated block copolymer micellar system [12]. Key advantages in this case are that USAXS results represent the true partial $S(q)$ of colloid-colloid interactions, and $S(q)$ is properly normalized using an experimentally determined $\langle P(q)\rangle$ and the high q limit of $I(q)$.

Although $S(q)$ shows only a little variation at high ϕ ($\approx$0.52), the rheological parameters are expected to change significantly across the transition [2,24]. Figure 3 illustrates the typical evolution of elastic and loss moduli (G' and G'', respectively) with temperature for the same ϕ [dotted arrow in the inset of Fig. 2(a)]. The inset shows the angular frequency (ω) dependence at higher and lower temperatures. At higher temperatures, G' and G'' vary as ω^2 and ω, respectively, corresponding to the fluid behavior of the system [25]. As the temperature is lowered, the system transforms to an attractive glass corresponding to very high values of G' and G'', and weak ω dependence (G' or $G'' \sim \omega^{x-1}$, with $x \to 1$) as that expected near a glass transition in soft materials [7,13,25]. The transition is completely reversible but G' and G'' exhibit noticeable aging in the attractive state. Moreover, the low temperature attractive glass can be transformed to fluidlike behavior ($G' \sim \omega^2$ and $G'' \sim \omega$) by applying a τ of 200 Pa. As a result, an optimum τ ($\approx$5 Pa) without getting into instrumental limitations but well within the linear viscoelastic range was selected for all the measurements.

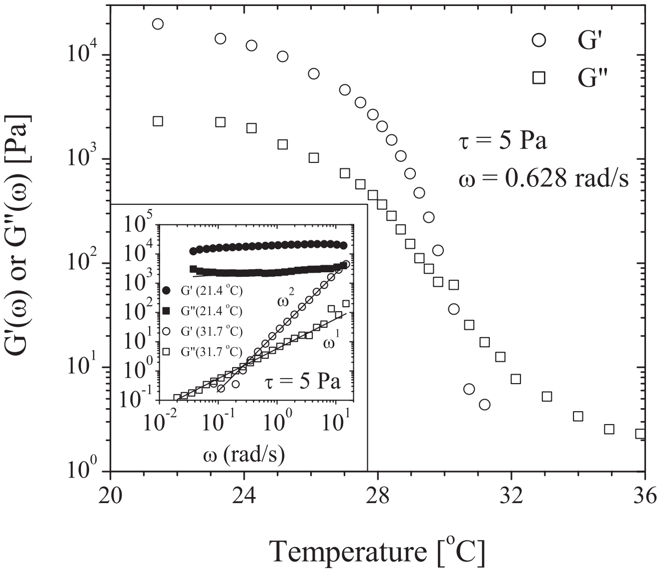

FIG. 3. Evolution of shear moduli, G' and G'' across the fluid-attractive glass transition for a sample of $\phi \approx 0.52$. The inset depicts the frequency dependence of G' and G'', illustrating the fluid and glassy behavior at 31.7 °C and 21.4 °C, respectively.

With a further increase of ϕ, $S(q)$ becomes similar at higher and lower temperatures but the shear moduli display remarkable differences. Figure 4 shows the observed variation of G' and G'' for a sample with $\phi > 0.53$. As the temperature is increased from the attractive region, the shear moduli drops by more than an order of magnitude but the system transforms to a different glassy state as suggested by the weak frequency dependence presented in the inset. This transition can be identified as an attractive-repulsive glass transition [as schematically shown in the inset of Fig. 2(a)] with the attractive glass having a higher rigidity [2]. In the repulsive state an increase of τ leads to fluidlike behavior at a lower threshold ($\sim$15 Pa). At intervening ϕ range, G' exhibits a more pronounced dip and then a slow rise reminiscent of the reentrant behavior. However, stronger dependence of parameters on τ and temperature step make the rheological characterization of the reentrant region extremely difficult. At still higher ϕ, $S(q)$ becomes indistinguishable to that of a repulsive glass while the rheological parameters remain high as in the attractive glass [23].

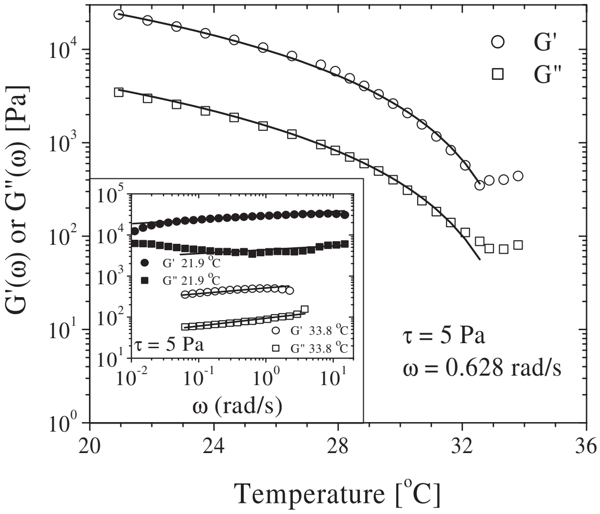

FIG. 4. Variation of shear moduli, G' and G'' with temperature for a sample of $\phi \approx 0.536$ indicating repulsive glass-attractive glass type transition. Continuous lines are guides to the eye and correspond to $(T_A - T)^2$, with $T_A = 34.3\,^\circ\mathrm{C}$. The frequency dependence of G' and G'' presented in the inset demonstrate glassy behavior above and below the transition.

In summary, static structure and rheological behavior of a model short-ranged interacting colloidal system were studied in the vicinity of fluid-attractive glass and repulsive-attractive glass transitions. The $S(q)$ showed only small variations but the shear moduli changed remarkably. The observed features are in agreement with mode-coupling theoretical predictions [2], as well as the generalized jamming phase diagram of attractive colloidal systems [9], but the sharper glass-glass transition differ from computer simulations [5]. Differences in the aging time and finite temperature dependence of u might explain this deviation from simulation results. At high ϕ range, the static structure is similar to the repulsive glass but the rheological parameters are closer to the attractive glass.

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