

Observation of Liquid-Glass-Liquid and Glass-Glass Transitions in the L64/D₂O Copolymer Micellar System

The glassy state of matter is ubiquitous, ranging from ordinary window glass to polymers to proteins. Yet, the nature of the transition between liquid (L) and glassy (G) states remains one of the unsolved problems in the physics of condensed matter. Mode-coupling theory (MCT), originally developed for supercooled simple liquids, makes predictions of liquid-glass (L-G) and glass-glass (G-G) transitions in a colloidal suspension. Here we present small-angle neutron scattering (SANS) and photon correlation spectroscopy (PCS) measurements confirming these predictions.

In a recent series of papers [1, 2] MCT predicts that in colloidal systems with a sufficiently short-range effective inter-particle attractive interaction one can observe two types of kinetic glass transitions (KGT). The KGT can be the result of a “cage effect,” originating from the excluded volume effect of the particles at high volume fractions and at high temperatures, or the result of a particle bonding to its nearest neighbors at low $k_B T$ and at all volume fractions.

One particularly interesting feature in this novel state of matter is the occurrence of two distinct amorphous glassy states called respectively the “repulsive glass” (G_R) and the “attractive glass” (G_A), as the result of the two

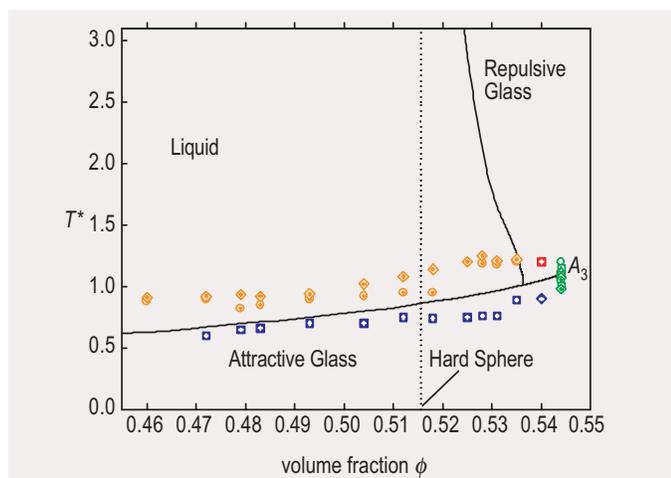


Fig. 1. The lines represent phase boundaries (in T^* - ϕ plane) determined by mode-coupling theory for a colloidal system with a short-range attraction ($\epsilon = 0.03$). The phase points shown are for the L64/D₂O micellar solution. (Liquid state: orange, glassy states: blue, red, and green.) The results confirm the existence of the attractive branch in the predicted glass-transition boundary, and the G_A - G_R transition.

distinct mechanisms for the structural arrest mentioned earlier. With PCS and SANS measurements, we succeeded in detecting both these transitions in L64/D₂O micellar system at high volume fractions [3].

L64 is a symmetric tri-block copolymer of composition (PEO)₁₃(PPO)₃₀(PEO)₁₃. Above 20 °C, the copolymers self-assemble into spherical micelles each with PPO segments packed into a compact core and PEO segments forming a corona around it. The short-range attraction arises from the overlap of PEO chains in the corona regions when two micelles approach one another. The depth of the attractive well increases with temperature

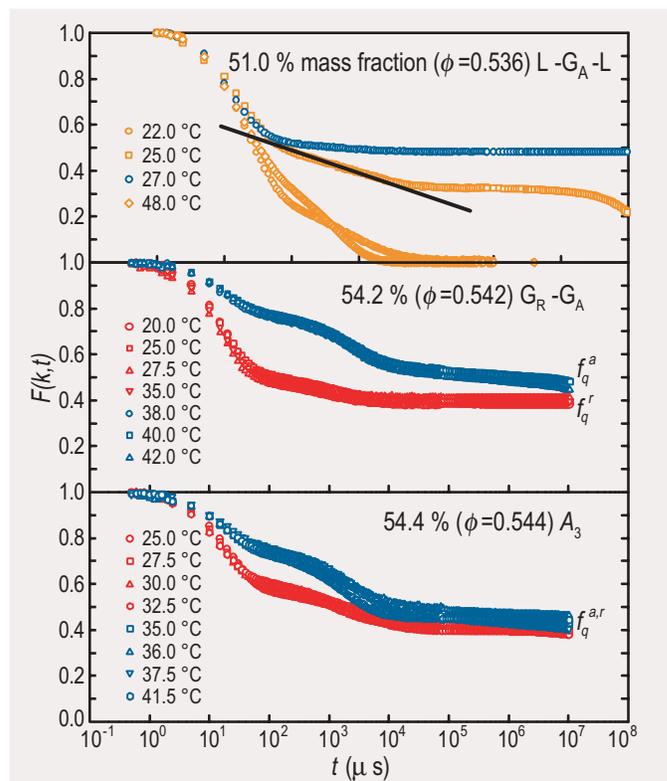


Fig. 2. The ISF as measured by photon correlation spectroscopy at three different volume fractions, ϕ , at different temperatures. (Data follow the same color scheme as in Fig. 1.) The top panel shows the re-entrant L- G_A -L transition. The line highlights a region of logarithmic time dependence preceding the plateau in the liquid state just before the transition [4]. Evidence of the G_A - G_R transition can be seen in the middle panel. By comparing the long-time limit of the ISF's with the predictions of mode-coupling theory (MCT), the two different types of the glasses can be identified by their respective Debye-Waller factors. The bottom panel is for a volume fraction of 0.544, which is the A_3 end point predicted by MCT. f_q^a and f_q^r become identical, confirming the prediction.

because water becomes an increasingly poor solvent as temperature rises.

If the interaction is modeled by a square-well potential, the crucial control parameters of the phase behavior are: the volume fraction, $\phi = \pi\rho d^3/6$, the effective temperature, $T^* = k_B T/u$, and the fractional well-width parameter, $\varepsilon = \Delta/d$. ρ is the number density of the spheres, d its hard core diameter, Δ its attractive well-width, and $-u$ its well-depth.

The calculated glass-transition lines, for the case of $\varepsilon = 0.03$ [2], are shown in Fig.1 in the (T^*, ϕ) plane. On

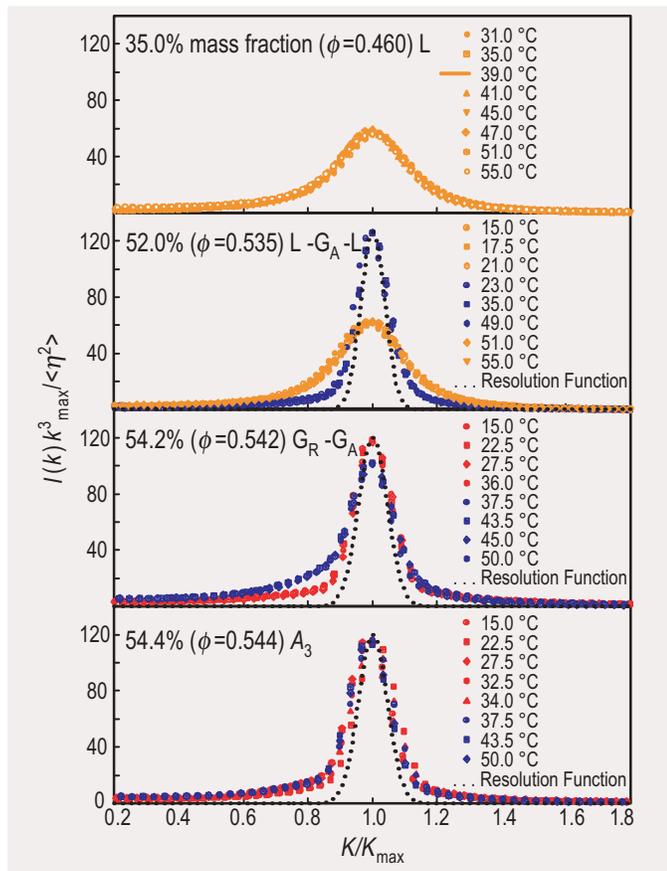


Fig. 3. SANS scaled intensity distributions vs. reduced scattering vector for the micellar solutions at four values of ϕ , at different temperatures. (Data follow the same color scheme as in Fig. 1.) The top panel is for $\phi = 0.460$. All the scaled intensities are characterized by a unique length scale and collapse into a single master curve for all temperatures. The second panel is for $\phi = 0.535$: the system is clearly characterized by two length scales. While the narrower peak is resolution limited, the broader peak is similar to the one observed in the first panel. If we identify the broader peak to represent the liquid state, then the narrower peak should represent the glassy state. The system thus shows a re-entrant L-G-L transition. The third panel is for $\phi = 0.542$. Again, two length scales characterize the system. The narrower peak is resolution-limited and the slightly broader peak is also nearly so. The results can be interpreted as showing a transition between two amorphous solid states, i.e., a G-G transition. The last panel is for $\phi = 0.544$, which is predicted as the A_3 point, at temperatures ranging from 15 °C to 50 °C. The two different types of glasses indeed become identical at this volume fraction.

going from higher to lower T^* , at volume fractions less than 0.5365 L- G_A transitions occur, and at volume fractions greater than this value, one has a possibility of observing G_R - G_A transitions.

Figure 2 shows normalized photon correlation functions (coherent intermediate scattering functions, ISF) measured at $q \approx 0.001 \text{ \AA}^{-1}$ and at three different volume fractions, as a function of temperature [3]. For the ϕ where the L- G_A transition is possible, one can see that in the L state, the long-time limit of the ISF, f_q , is zero, while in the G_A state, $f_q^a \approx 0.4$ to 0.5, which is the value of the Debye-Waller factor of the glassy state. The KGT is thus characterized by a discontinuous change of f_q . At $\phi = 0.542$, we observe the G_R ($f_q^r \approx 0.4$) to G_A transition ($f_q^a \approx .7$). At $\phi = 0.544$, which is called the A_3 singularity end point, our measured ISF's show identical values of $f_q^{r,a} \approx 0.4$ in the two glassy states, confirming the theory.

Figure 3 shows scaling plots of SANS intensity distributions at four volume fractions, and at different temperatures, spanning the regions of the phase diagram where the L, L-G-L, G-G, and two identical glasses (A_3 point) are located. The scale is set by a unique length parameter, the average inter-particle distance.

Verification of mode-coupling theory predictions through photon-correlation spectroscopy and small-angle neutron scattering measurements on a micellar system provides a basis for improved understanding of the glass transition in general.

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