Neutron scattering techniques shed new light on gel formation

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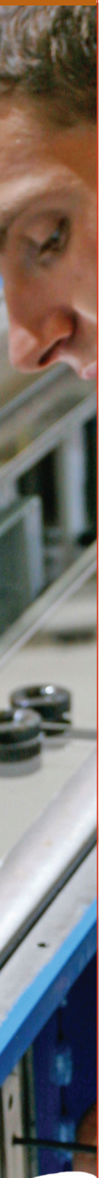

Colloidal dispersions are used in many household products ranging from paints to shaving cream to gelatin and even to foods such as salad dressings or mayonnaise. The stability and processing of these and similar products highly depend on the state of the material. Of particular interest is the phase transition from fluid to a solid, called a gel at low particle volume fractions, $\phi < \approx 0.40$, and a glass at higher volume fractions. While the phase behavior for such systems has been studied for decades, the boundary separating a fluid from a gel is still debated.

In this work we study gelation using a model nanoparticle system with thermoreversible interactions. The system consists of nanometer spheres of silica dioxide (≈ 30 nm) coated with a short carbon chain (C_{14}), and suspended in tetradecane. At high temperatures $T > \approx 32$ °C the particles are stable and the system behaves like a simple hard sphere fluid. Upon quenching the system, particles aggregate in connection with a phase transition of the molecular brush [1]. This in-turn causes a short-range attraction between particles, and if the particle volume fraction is sufficient, $\phi \geq 0.05$, the system will form a stress-supporting gel. We define gelation and determine the gel temperature (T_{gel}) to within ± 0.1 °C using a combination of rheological experiments and an experimental study of the dynamics using fiber-optic quasi-elastic light scattering (FOQELS). Finally, we study the structure of the dispersion at and around the gel transition using small-angle neutron scattering (SANS).

Small-amplitude oscillatory shear (SAOS) rheological measurements are used to identify the transition from the fluid state to the gel state employing a well-defined criterion established for cross linking polymer resins [2]. The SAOS results for a temperature ramp experiment for one dispersion, $\phi = 0.12$, can be seen in Fig. 1. At high temperatures ($T > \approx 31$ °C), in the fluid state, the suspension exhibits a negligible storage modulus G′, which defines the amount of elastic energy the fluid can store.

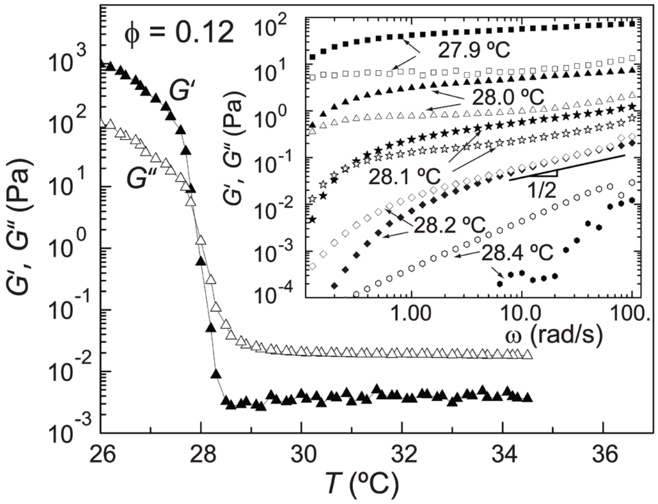

FIGURE 1: Storage, G′ (closed symbols), and loss, G″ (open symbols), moduli vs. temperature in a small-amplitude oscillatory (stress amplitude, σ_o = 17.68 mPa, frequency, $\omega = 2\pi$ rad/s) temperature ramp experiment (ramp rate 0.2 °C/min). Inset: G′ and G″ from frequency sweep measurements at temperatures around the gel-point. Data are offset vertically for clarity by factors 0.03, 0.05, 0.08, and 0.2 for temperatures (28.4, 28.2, 28.1, and 28) °C, respectively.

As the system is quenched to lower temperatures from the fluid state, the elastic modulus increases over five orders of magnitude in the narrow temperature range of 29 °C to 27 °C. This shows the suspension undergoes a transition to a strong viscoelastic solid similar to cooled Jello. Frequency sweep measurements provide a determination of the strength of the gel. Frequency sweep experiments on the same sample can be seen in the inset to Fig. 1 as a function of temperature near the gel point. At the highest temperature shown, 28.4 °C, G″ (the loss modulus) is larger than G′ over the whole frequency range tested. As the temperature is decreased to 28.2 °C, G′ and G″ become comparable at high frequencies. At lower temperatures the sample has a greater elastic modulus, characteristic of solid-like behavior. At 28.2 °C, G′ and G″ are nearly equal with power law slopes of ½, over more than a decade of frequency, which is a characteristic feature of gelation [2]. The gel temperature is confirmed using FOQELS (not shown) which provides a measure of the particles' dynamics. From FOQELS measurements it can be shown that the dynamics decrease and exhibit an entire relaxation spectrum at the gel temperature determined from rheology.

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SANS measurements were performed over a range of temperatures spanning the transition from the fluid-state through gelation. The low-Q scattering intensity systematically evolves for decreasing temperature in the range where aggregation occurs until T_{gel}, where structure on the length scales accessible by SANS becomes arrested. Figure 2 shows the SANS spectra at T_{gel}, as identified from rheology, for the entire concentration range.

The spectra at the gel point evolve from fractal-like scattering at low ϕ to a glass-like spectra at high ϕ. The scattering intensity is fitted (solid lines), using well established theories assuming a square-well interaction potential for the particles. From the fits we extract the strength of attraction defined by a reduced temperature, $\tau = (\varepsilon/12)\exp(-U/k_BT)$, called the Baxter temperature, where U is the square-well depth, ε is a perturbation parameter $\varepsilon = \Delta/(a+\Delta)$, where Δ is the square-well width and a is the particle diameter, and k_BT is the thermal energy. As τ decreases, the strength of attraction increases.

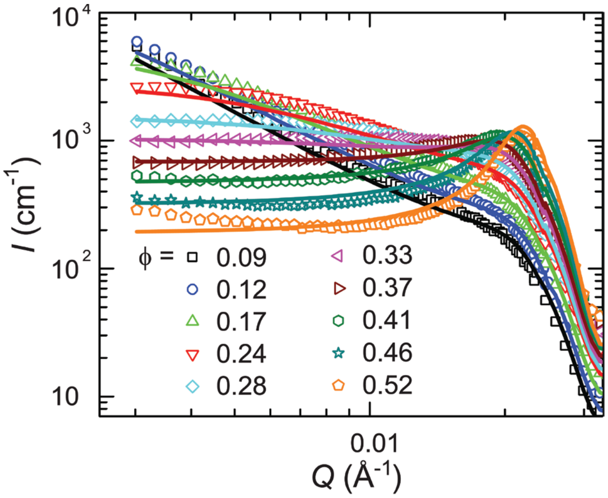

FIGURE 2: SANS measurements at the gel point for various volume fractions ϕ and the corresponding model fits.

The state diagram with our experimentally determined gel transition for the AHS system is presented in Fig. 3. At intermediate to low ϕ and high attractive strength there is a liquid / vapor coexistence region. Conversely, at high ϕ and low attractive strength there is a liquid / crystal coexistence region.

This is in addition to a repulsive driven glass (RDG) line which intersects the attractive driven glass (ADG) line with mode coupling theory (MCT) singularity, A_3. As is typically done, the location of the RDG and ADG lines calculated from MCT are shifted to higher particle densities using known experimental data, since MCT under-predicts the RDG line [6,7]. The percolation line for the AHS fluid can be seen extending from the liquid / vapor coexistence region at low ϕ to the liquid / crystal coexistence region at high ϕ. The experimentally determined points defining the gel transition (triangles) agree well with percolation theory up to $\phi \approx 0.41$. For concentrations $\phi > \approx 0.41$ the boundary for dynamical arrest tends toward and joins the ADG line. Thus, the major conclusions of this work show that for this AHS nanoparticle system: *The dynamical arrest transition extends from the dilute particle concentration side of the liquid/vapor coexistence above the critical point following predictions of percolation theory until at sufficiently high particle concentrations it subtends the predictions and joins the MCT ADG line.*

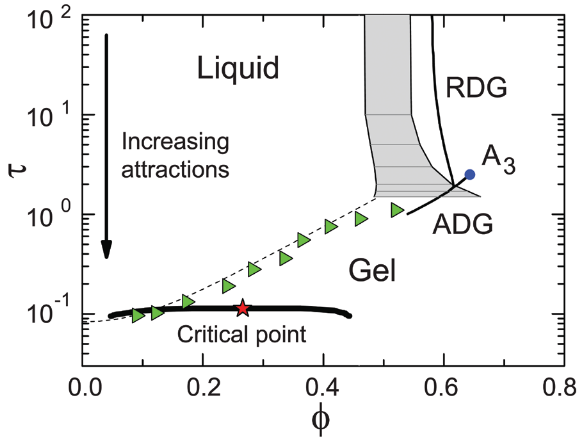

FIGURE 3: State diagram for the model adhesive hard sphere system (AHS). (━) Is the liquid/vapor coexistence region with critical point (star, $\tau = 0.1133$ and $\phi = 0.266$) as determined by Monte Carlo (MC) simulations [3]; broken line is the analytical solution to the percolation line [4]; grey shaded region is the liquid/crystal coexistence region from the modified weighted-density approximation (MWDA) theory [5]; (—) repulsive and attractive driven glass (RDG and ADG) lines from model coupling theory (MCT) with point singularity, A_3 (circle) [6]. The triangles are the experimentally determined dynamical arrest transition.

We experimentally determine the fluid-to-gel transition of a model nanoparticle dispersion with short-ranged attractions. Our experiments demonstrate a continuous boundary that extends from the gas-liquid phase separation region at low concentrations to the attractive driven glass line at high concentrations. The conclusions presented herein have implications in a wide range of colloidal systems that interact via a short range interaction. The anticipation is that this work will direct the development of advanced theory and simulation efforts. These will in turn help us to further understand the underlying mechanisms that drive gelation and ultimately allow for the optimization of products through predictive tools rather than guess and check formulation.

References

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