Glasslike Kinetic Arrest at the Colloidal-Gelation Transition

P. N. Segrè,[1,*] V. Prasad,[1] A. B. Schofield,[2] and D. A. Weitz[1]
[1]*Department of Physics, Harvard University, Cambridge, Massachusetts 02138*
[2]*Department of Physics and Astronomy, University of Edinburgh, Edinburgh EH93JZ, United Kingdom*

(Received 5 October 2000)

We show that gelation of weakly attractive colloids is remarkably similar to the colloidal glass transition. Like the glass transition, dynamic light scattering functions near gelation scale with scattering vector, and exhibits a two-step decay with a power-law divergence of the final decay time. Like the glass transition, static light scattering does not change upon gelation. These results suggest that, like the glass transition, gelation results from kinetic arrest due to crowding of clusters, and that both gelation and the glass transition are manifestations of a more general jamming transition.

DOI: 10.1103/PhysRevLett.86.6042 PACS numbers: 82.70.Dd, 64.70.Pf, 82.70.Gg, 83.80.Hj

Colloidal dispersions exhibit a wide range of rheological behavior, which is one of the key features that makes them so useful technologically and so fascinating scientifically. They can exhibit both fluidlike and solidlike behavior, with the transition between the two taking a variety of different forms. When particles have only a repulsive interaction on contact, due to volume exclusion, they behave as hard spheres. Suspensions of hard spheres are fluidlike at low concentrations, but as the volume fraction, ϕ, increases the particles become increasingly crowded until, at $\phi \sim 0.58$, they undergo a glass transition to a disordered solid [1,2]. By contrast, colloidal particles with an attractive interparticle energy, with magnitude U on contact, exhibit a fluid to solid transformation due to gelation; this occurs at a critical volume fraction, $\phi_c < 0.58$, whose values depend on U [3–5]. At very large U, irreversible diffusion-limited cluster aggregation leads to the formation of fractal clusters [6], which can gel at arbitrarily low volume fractions, so $\phi_c \approx 0$ [7]. Both the gelation and glass transitions have important similarities [8,9]: Both are liquid to solid transitions that are thought to be kinetic, rather than thermodynamic, in origin. Thus it is intriguing to consider whether these two transitions are, in fact, fundamentally related. The distinguishing features of the colloidal glass transition are its structure and dynamics as ϕ_g is approached. Unfortunately, however, relatively little is known about the structure and dynamics of the gelation transformation, precluding direct comparison with the glass transition.

In this Letter, we show that gelation of colloidal suspensions exhibits many of the hallmarks of the colloidal glass transition. Like the colloidal glass transition, the structure factor, as probed by static light scattering, remains essentially unchanged as the gelation occurs. Like the colloidal glass transition, the intermediate scattering function (ISF), as probed by dynamic light scattering, exhibits a two-step decay. Like the colloidal glass transition, the time scale of the final decay diverges as ϕ_c is approached. Like the colloidal glass transition, for samples very close to ϕ_c, the ISF's exhibit a scaling behavior in scattering wave vector, q, with the scaling factors following the form of the static structure factor, $S(q)$. This remarkable similarity between the kinetic behavior of these two disparate transitions suggests that both are, in fact, intrinsically related, with the fluid to solid transformation driven by crowding, of single particles for colloidal glasses and of clusters for gelation.

We use polymethyl-methacrylate spheres, stearically stabilized by thin layers of poly-12 hydroxystearic acid, so that the interparticle interaction is well approximated as that of hard spheres [10]. The particles have a mean radius of $a = 212$ nm and a polydispersity of about 5% about the mean. They are suspended in a mixture of *cis*-decalin and cycloheptyl bromide which nearly matches both the index of refraction and the density of the particles to those of the solvent; this allows light scattering studies, while simultaneously reducing sedimentation due to gravity. An attractive interparticle interaction is induced by means of the depletion interaction [11] by adding polystyrene [12], a nonadsorbing polymer; we use a molecular weight of $m_w = 1.96 \times 10^6$ and mean radius of gyration of $r_g \approx 40$ nm. The range of the attraction is controlled by $\xi = r_g/a \approx 0.19$. The strength of the attraction is controlled by the concentration, and, assuming an ideal gas law for the polymer, is given by $U/k_BT \approx 0.69c_p^F$, where c_p^F is the amount of polymer added in units of milligrams per cm^3 of *free* volume of solution [12].

To study the structure of the colloidal gels, we use static light scattering. Light scattered from a collimated beam from a He-Ne laser is collected on a translucent screen which is imaged onto a CCD camera. The resultant images exhibit an intense ring of scattering as ϕ_c is approached. They are radially averaged to determine $S(q)$, and typical results are plotted in Fig. 1, where we show data for a series of ϕ for a fixed $U = 4.0k_BT$. All of these data were obtained about 5 days after the sample was homogenized, allowing ample time for structures to form. All the data exhibit a pronounced peak at low qa. Except for the very lowest ϕ, this peak occurs at essentially the same value of $qa \approx 0.5$, which corresponds to a characteristic length scale of $\xi \sim \pi/q \sim 6a$, considerably larger than the size of a single particle. This reflects the existence of clusters with a characteristic spacing equal to their size, ξ.

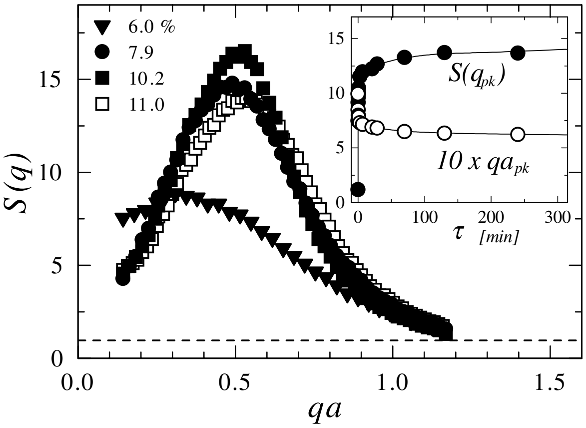

FIG. 1. Static structure factors $S(q)$, measured ~5 days after mixing, of samples with $U_d = 4.0k_BT$ and the listed volume fractions. The dark symbols are fluidlike samples, the open symbol a solid. Inset: time evolution of the peak position and intensity of a fluid sample with $\phi = 0.079$.

The existence of a peak in $S(q)$ is characteristic of a colloidal gel [7,13]. However, surprisingly, not all samples are truly gelled. At the lower volume fractions, the speckles at the peak are not static in time, but instead continue to fluctuate; thus the clusters must continue to diffuse over length scales at least as large as their size. These samples remain ergodic, and a solid gel network is not formed. Remarkably, even with this ergodic behavior, the peak in the scattering persists for very long times; this is shown in the inset of Fig. 1, which shows the time evolution of both the intensity of the scattering at the peak as well as the peak position. After an initial transient as the clusters form, both quantities remain nearly constant over extended periods of time; we have followed some fluid samples for over a month, with no significant change in the scattering. It is only at very high ϕ that the speckles cease to fluctuate in time and the sample becomes completely nonergodic, forming a true gel network. The shape of $S(q)$ does not change upon gelation, indicating that the existence of a ring is not a good measure of the transition, but instead the dynamics must be examined.

The similarity in the static light scattering between the fully ergodic and nonergodic samples implies that the structure is very similar, each consisting of clusters of nearly equal size and spacing; the main difference must be the degree of interconnectivity, with the clusters in the ergodic samples completely disconnected while those in the ergodic samples must be completely interconnected. Thus, we hypothesize that the origin of the gelation transition is the crowding of the clusters themselves as their volume fraction increases; when they form a fully connected network, gelation occurs. To check this, we use microscopy with differential interference contrast (DIC) to directly visualize the clusters as the volume fraction increases. Typical images are shown in Fig. 2, where we show images of two suspensions each of which have $U \approx 4k_BT$. The sample above the gelation transition, with $\phi = 0.12$, shows a connected network of clusters, which are clearly solidlike. By contrast, the sample below the gelation transition, with $\phi = 0.06$, shows a coexistence between single particles and clusters, and clearly does not form a connected, solidlike network, but instead remains fluidlike [14,15]. This supports our hypothesis that gelation occurs when the crowding of clusters causes them to touch, leading to an ergodic to nonergodic transition. Further support for this picture comes from the behavior of the characteristic length scale ξ_c at gelation, which is consistent with a simple structural model of close-packed fractal clusters with fractal dimension d_f [7]. Clusters of size ξ occupy a volume fraction $\phi_\xi = \phi(\xi/a)^{3-d_f}$ which is greater than ϕ. Gelation occurs when $\phi_\xi \sim 1$, with $(qa)_c = \pi a/\xi_c = \pi\phi^{1/(3-d_f)}$. For a solid sample, such as shown in Fig. 1, with $\phi = 0.11$ and $d_f = 1.8$, this model predicts $(qa)_c \sim 0.5$, in excellent agreement with the observed peak position.

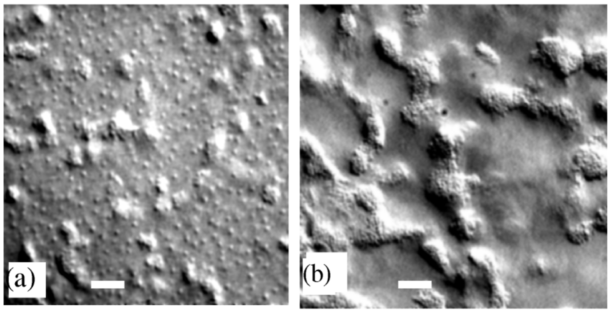

FIG. 2. DIC microscope images of (a) fluidlike and (b) solidlike phases. The attractive interactions are the same in both samples, $U \approx 4k_BT$, but the volume fractions are different, $\phi_a = 0.06$ and $\phi_b = 0.12$. The lines are 2.5 μm long.

These results suggest that gelation has many similarities to the colloidal glass transition of hard spheres. In both cases, $S(q)$ does not significantly change at the transition. Both are kinetic transitions due to crowding; in the case of hard spheres, it is crowding of single particles, while in the case of gelation, it is crowding of larger clusters. To further explore this similarity we use dynamic light scattering (DLS) to measure the intermediate scattering function, $f(q,\tau) \equiv S(q,\tau)/S(q)$ [16]. We examine the region near the peak of scattering rings, $f(q\xi \sim 1, \tau)$; this directly probes the motion of clusters themselves. In Fig. 3 we show ISF's for a series of samples at fixed $U = 4k_BT$ and different ϕ. There is a pronounced slowing down of the final decay of the ISF's as ϕ increases; moreover, a two-step decay is observed as the gelation transition is approached. In the most dilute sample, the clusters are highly mobile, with $f(q,\tau)$ similar to that of an unaggregated sample. However, the decay time increases percipitously over a very narrow range of ϕ, with more than a 300-fold increase for a small change in ϕ of only 0.102 to 0.110. Finally, for the highest concentration, $\phi = 0.110$, $f(q,\tau)$ does not completely decay over more than 2000 seconds, requiring care to ensure that a true ensemble average is determined [17]; this sample is nonergodic on lab time scales and is effectively a solid.

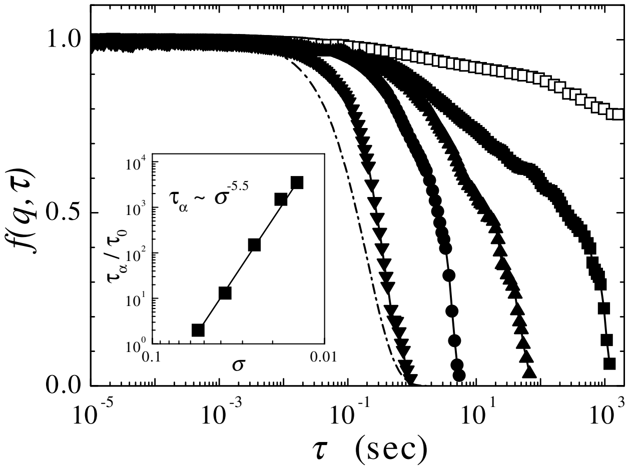

FIG. 3. Intermediate scattering functions $f(q,\tau)$ at $qa = 0.98$ for several different ϕ (same symbols as Fig. 1 and triangle, $\phi = 9.1\%$). Inset: critical behavior of the normalized decay time τ_α/τ_0 as a function of the reduced volume fraction $\sigma = (\phi_c - \phi)/\phi_c$ where $\phi_c = 0.117$.

These results differ significantly from previous studies of similar colloidal gels which used samples that were not density matched, resulting in short-lived gels that were destroyed by gravitationally induced bond breakage [12,18]. This precluded studies over the long times that are required to measure the relaxations near the gelation transition; thus the long term persistence of a fluctuating scattering ring, and the ultimate transition to a stable nonergodic gelled solid were not observed. This suggests that the gelation transition is extremely sensitive to external stress such as gravity, which can significantly modify the behavior. Our samples are buoyancy matched as well as we can achieve, with $\Delta\rho \sim 0.005$ g/cm^3. However, even this may not be negligible, but a lower $\Delta\rho$ is not readily achievable experimentally. Thus, to ascertain that gravitational stresses can be safely neglected, we performed some corroborating experiments in microgravity, where the effects of the density mismatch are reduced by 6 orders of magnitude, corresponding to a $\Delta\rho \sim 10^{-6}$ g/cm^3 in earth's gravity. We used samples with a larger density mismatch, $\Delta\rho \sim 0.3$ g/cm^3; gels formed with these samples collapsed and sedimented on earth. Three samples, with $\phi_a = 0.05$, $\phi_b = 0.10$, and $\phi_c = 0.20$, and all with $U = 4.0k_BT$, were flown on the shuttle mission STS-95, and DLS measurements were performed. The results were completely consistent with the buoyancy-matched samples; only the highest-ϕ sample was completely nonergodic, indicating the existence of a gel, while the other two remained ergodic over the 9-day length of the flight. This confirms that gravitational stresses are sufficiently reduced in the buoyancy-matched samples to allow gelation to be probed, and corroborates the extreme sensitivity of the gelation transition to stress.

Both the shape and the extreme ϕ sensitivity of the ISF's are reminiscent of the hard-sphere colloidal glass transition, with the final decay reflecting structural relaxation, or the α decay [19]. To further explore this analogy, we determine the values of τ_α by fitting the final decay to an exponential form, $f(q,\tau) \propto \exp(-\tau/\tau_\alpha)$. For the hard-sphere glass transition, the values of τ_α exhibit a power-law divergence, $\tau_\alpha \sim \sigma^{-\alpha}$, where $\sigma = (\phi_g - \phi)/\phi_g$, and where $\phi_g = 0.58$ and $\alpha \approx 2.6$ [2]. Remarkably, a similar divergence is observed for the gelation transition, as shown in the inset of Fig. 3 where we plot the σ dependence of τ_α on a logarithmic plot. A power-law divergence is also observed here; for $U = 4k_BT$, we find $\phi_c = 0.117$ and $\alpha = 5.5 \pm 1$. Thus, the divergence of the relaxation times of the gelation transition is remarkably similar to that of the hard-sphere glass transition.

As an even more stringent comparison of gelation with glass transition, we investigate the scaling of the q dependence of the ISF's. For hard spheres near the glass transition, a remarkable scaling behavior was observed experimentally [20] and confirmed theoretically with the mode coupling model [21]. When normalized by the first cumulant, all the data for q near the peak in $S(q)$ collapse onto a single master curve for each value of ϕ, both below and above the glass transition; thus a plot of $\ln f(q,\tau)/(\chi(q)D_0q^2)$ yields a single master curve for all q, where $\chi(q)D_0 = D_s(q)$ is the short-time diffusion coefficient, obtained from the first cumulant. Moreover, for hard spheres, $D_s(q) = D_0H(q)/S(q)$, where D_0 is the free particle diffusion coefficient, given by the Stokes-Einstein relation, and $H(q)$ reflects the contributions of hydrodynamic interactions [16]; as a result, the scaling factor, $1/D_s(q)$, follows the functional form, but not the magnitude, of $S(q)$. We test for scaling in a gelling system, but restrict our attention to the intermediate and long-time decays of the ISF's, as the short-time scales are highly susceptible to distortion due to multiple scattering [22], much more so than hard spheres because of the higher scattering intensity from clusters. In Fig. 4, we plot $\ln f(q,\tau)/(\chi(q)D_0q^2)$ over a wide range of qa extending from below the cluster peak up to the monomer peak at $qa \sim 3.5$; here $\chi(q)$ is

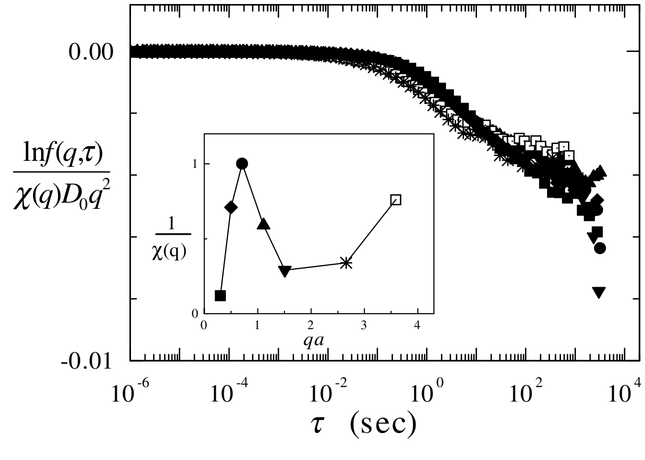

FIG. 4. The scaling form for the hard-sphere glass transition for a solid sample at $\phi \approx 0.13$. Inset: The values of $1/\chi(q)$ used to obtain the scaling behavior.

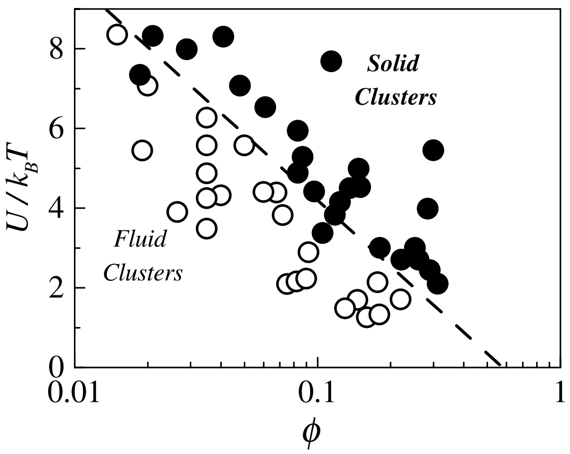

FIG. 5. Observed phases of depletion induced attractive colloidal suspensions.

the normalization factor chosen to give the best overlap for $\tau > 10^{-1}$ sec. The data can indeed be scaled together, just as for a colloidal glass. Moreover, as shown in the inset of Fig. 4, $1/\chi(q)$ exhibits a pronounced peak, qualitatively similar to $S(q)$; exact correspondence cannot be established without eliminating multiple scattering [22]. Nevertheless, these results are again in remarkable agreement with those observed for the hard-sphere colloidal glass transition [20].

Finally, the use of DLS allows us to simply determine a precise phase diagram of the transition between an ergodic fluid and a nonergodic gel as both ϕ and U are varied, and we plot the results in Fig. 5. There is a well defined boundary between fluid and solid, identifying the gelation transition. Moreover, the boundary extrapolates directly to the value of ϕ_g of the hard-sphere colloidal glass transition, providing direct evidence of the continuity of the two transitions. Interestingly, this boundary is well described by the functional form,

$$\phi_g(U) \approx (0.55\text{–}0.60)\exp(-U/2.1k_BT). \qquad (1)$$

This is a highly suggestive form which is reminiscent of a thermally activated process. It is consistent with the kinetic nature of the gelation process. When the strength of the interaction is low enough that bonds can readily be broken due to thermal fluctuations, it is conceivable that gelation occurs when the rate of bond formation exceeds that of bond breakage; this might lead to an activated functional form in Eq. (1).

The results reported here clearly show that the gelation transition has many of the hallmarks of a hard-sphere colloidal glass transition. Both are kinetic phase transitions from a fluid to a solid. Both are driven by the crowding of the particles in the suspension; the crowding of the individual particles in the case of the hard-sphere glass transition, where $U = 0$, and the crowding of the aggregate clusters in the case of gelation, where $U > 0$. This continuity between gelation and the glass transition has not been recognized experimentally. However, this result is consistent with a very recent theoretical speculation [23] that attractive particles may undergo a fluid to solid transition due to jamming; this jamming transition is predicted to depend on both U and ϕ, as observed here. Thus, these results strongly support the jamming transition as a description of the phase behavior of attractive particles.

We thank M. Fuchs, A. Pao, V. Trappe, and A. Levine for useful discussions, and M. Hoffmann and the crew of STS-95 for invaluable assistance in the microgravity experiments. This work was supported by NASA (NAG3-2284) and NSF (DMR9971432 and DMR9704300).

---

*Present address: Biophysics group, NASA Marshall space flight center, MSFC, AL 35812.
Electronic address: phil.segre@msfc.nasa.gov

[1] P. N. Pusey and W. van Megen, Phys. Rev. Lett. **59**, 2083 (1987).
[2] W. van Megen and S. M. Underwood, Phys. Rev. E **49**, 4206 (1994).
[3] R. C. Sonntag and W. B. Russel, J. Colloid Interface Sci. **116**, 564 (1991); M. Chen and W. B. Russel, J. Colloid Interface Sci. **141**, 564 (1997).
[4] C. J. Rueb and C. F. Zukowski, J. Rheol. **41**, 197 (1997).
[5] J. A. Yanez, E. Laarz, and L. Bergstrom, J. Colloid Interface Sci. **209**, 162 (1999).
[6] D. A. Weitz and M. Oliveria, Phys. Rev. Lett. **52**, 1432 (1984).
[7] M. Carpineti and M. Giglio, Phys. Rev. Lett. **68**, 3327 (1992).
[8] S. Z. Ren and C. M. Sorensen, Phys. Rev. Lett. **70**, 1727 (1993).
[9] J. Bergenholtz and M. Fuchs, Phys. Rev. E **59**, 5706 (1999).
[10] S. E. Phan *et al.,* Phys. Rev. E **54**, 6633 (1996).
[11] S. Asakura and F. Oosawa, J. Polym. Sci. **32**, 183 (1958); A. Vrij, J. Appl. Chem. **48**, 471 (1976).
[12] S. M. Ilett, A. Orrock, W. C. K. Poon, and P. N. Pusey, Phys. Rev. E **51**, 1344 (1995).
[13] J. Bibette, T. G. Mason, Hu Gang, and D. A. Weitz, Phys. Rev. Lett. **69**, 981 (1992).
[14] A similar phase of very weakly coalescing polymer droplets has also been reported in H. Tanaka, J. Phys. Condens. Matter **12**, R207 (2000).
[15] M. D. Haw, M. Sievwright, W. C. K. Poon, and P. N. Pusey, Adv. Colloid Interface Sci. **62**, 1 (1995).
[16] P. N. Pusey, in *Liquids, Freezing and the Glass Transition,* edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1991), p. 358.
[17] P. N. Pusey and W. Van Megen, Physica (Amsterdam) **157A**, 705 (1989).
[18] W. C. K. Poon, A. D. Pirie, and P. N. Pusey, Faraday Discuss. Chem. Soc. **101**, 65 (1995).
[19] W. Götze, in *Liquids, Freezing and the Glass Transition* (Ref. [16]), p. 287.
[20] P. N. Segrè and P. N. Pusey, Phys. Rev. Lett. **77**, 771 (1996).
[21] M. Fuchs and M. R. Mayr, Phys. Rev. E **60**, 5742 (1999).
[22] P. N. Segrè, W. van Megen, P. N. Pusey, K. Schätzel, and W. Peters, J. Mod. Opt. **42**, 1929 (1995).
[23] A. J. Liu and S. R. Nagel, Nature (London) **396**, 6706 (1998).