Limits to Gelation in Colloidal Aggregation

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We show that the dynamics of large fractal colloid aggregates are well described by a combination of translational and rotational diffusion and internal elastic fluctuations, allowing both the aggregate size and internal elasticity to be determined by dynamic light scattering. The comparison of results obtained in microgravity and on Earth demonstrates that cluster growth is limited by gravity-induced restructuring. In the absence of gravity, thermal fluctuations ultimately inhibit fractal growth and set the fundamental limitation to the lowest volume fraction which will gel.

Diffusion-limited cluster aggregation (DLCA) of colloidal particles results in the formation of tenuous, highly disordered clusters; nevertheless, their fractal nature leads to a well determined scale-invariant symmetry, which facilitates our understanding of the structure and growth kinetics of such aggregates. Growth by DLCA is predicted to result in a power-law increase in cluster size with time, $R_c \sim t^{1/d_f}$, where R_c is the average cluster radius and d_f is the fractal dimension [1]. This growth proceeds until the clusters span space, whereupon the system gels; this occurs when $R_c = a\phi_0^{1/(d_f-3)}$, where a is the colloid radius and ϕ_0 is the initial particle volume fraction [2,3]. Since the density of fractal objects decreases as their size increases, colloidal aggregates can, in principle, gel to form an elastic solid at arbitrarily low volume fractions. However, a solid in the limit of zero volume fraction is certainly unattainable; instead there should be a fundamental limit that determines ϕ_L, the lowest initial volume fraction of particles that will gel. The ultimate limitation is likely to be set by the mechanical strength of the fractal aggregates, which decreases as their size increases [4]. Ultimately, thermal fluctuations can deform and break the clusters, preventing gelation. Gravitational forces can also challenge their structural stability, since the body force due to gravity and the surface force due to hydrodynamic drag of sedimenting clusters result in a shear stress that can tear the aggregates apart. However, the elastic properties of large isolated aggregates are not well characterized experimentally, thus, the maximum stress that can be sustained by these aggregates has not been determined. As a result, the physical origin of the fundamental limitation to gelation and the value of ϕ_L are not known.

In this Letter, we report results of experiments probing the limits to gelation. We use light scattering to measure dynamics of colloidal aggregates formed both in micro-gravity and on Earth. We observe a crossover for fractal aggregates, from cluster diffusion at large length scales to internal elastic modes at short length scales. We show that gravitational stress limits the cluster growth on Earth, even under near buoyancy-matched conditions, whereas thermal fluctuations limit the growth of fractal structures in the absence of gravity. This allows us to determine the limits to colloid gelation.

We study the structure and dynamics of clusters using both static light scattering (SLS) and dynamic light scattering (DLS), exploring a wide range of length and time scales. For experiments in microgravity, we use the Physics of Colloids in Space (PCS) apparatus [5,6] on the International Space Station ISS. A narrow beam from a frequency-doubled Nd:YAG laser, with a wavelength $\lambda = 532$ nm *in vacuo*, passes through the sample. Scattered light is collected from a volume of approximately 10^{-5} cm^3 with a single-mode optical fiber, and detected with a solid state photon-counting detector; this fiber can be rotated to scattering angles ranging from 11° to 169°, probing scattering vectors $3~\mu\text{m}^{-1} < q < 31~\mu\text{m}^{-1}$. Additionally, a broad beam from a second Nd:YAG laser illuminates the sample in a direction perpendicular to the first beam. Scattered light from a larger volume of 0.8 cm^3 is imaged through a spherical lens onto a CCD camera to measure small-angle SLS or DLS at many wave vectors simultaneously, $0.04~\mu\text{m} < q < 1.8~\mu\text{m}$. We use polystyrene colloids with a particle size $a = 10.5$ nm and $\phi_0 = 8 \times 10^{-6}$. The solvent is a nearly buoyancy-matching mixture of H_2O and D_2O which mitigates the effects of gravity, thereby allowing complementary studies of gelation on Earth, where we measure SLS and DLS over a comparable range of angles. Aggregation is initiated by mixing a MgCl$_2$ solution with the colloidal suspension to a final concentration of 42 mM. At this concentration, we expect aggregation to
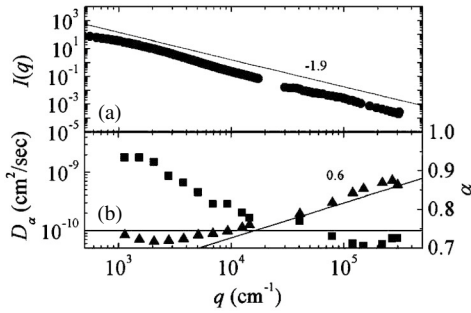
FIG. 1. (a) SLS; solid line is a guide to the eye showing that the fractal dimension is $d_f = 1.9$. (b) Effective diffusion coefficient D_a (▲); solid lines are guides to the eye, with slopes 0 and 0.6; stretching exponent, α (■), all 16 days after initialization.
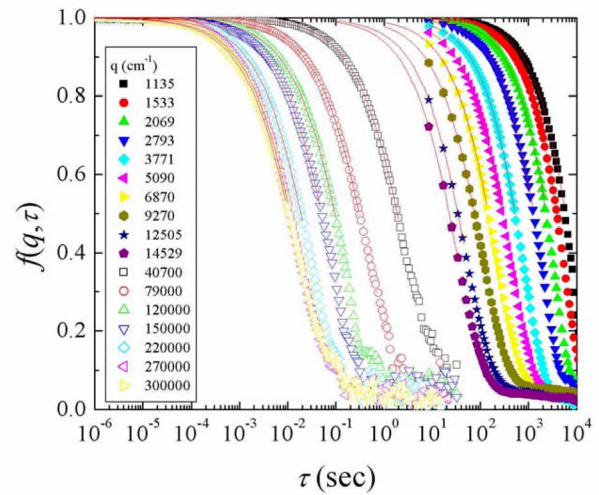

FIG. 2 (color online). Correlation functions from DLS measurements taken 16 days after initialization over a range of scattering vectors $1.1 \times 10^3 < q < 3 \times 10^5$ cm^{-1}. Solid curves are stretched exponential fits to the data.

be diffusion limited [7] and gelation to occur after $\sim$90 days [8].

Fractal clusters are formed, as evidenced by the power-law decay of the static scattering intensity, $I(q)$; as a typical example, we show in Fig. 1(a) data obtained on the ISS, 16 days after aggregation was initiated. The fractal dimension is $d_f = 1.9$, in agreement with the value expected for DLCA [9–11]. The dynamic structure factor, $f(q, \tau)$, exhibits complete relaxation at all q and at all times, for both ground and space experiments. However, there is a qualitative change in the shape of the decay as q increases; the correlation functions deviate from exponential and become increasingly stretched exponential in form. To capture this behavior, we fit the data to a stretched exponential, $f(q, \tau) \sim \exp(-[q^2 D_\alpha \tau]^\alpha)$, where D_α has the form of a diffusion coefficient, and α is the stretching exponent. This form adequately captures the shape of the dynamic structure factor at all q, as shown by the solid curves in Fig. 2, where we plot $f(q, \tau)$ for the same sample shown in Fig. 1(a).

There is a distinct crossover between the high- and low-q regimes, which is most clearly seen in the q dependence of the fitting parameters D_α and α, shown in Fig. 1(b). At low q, D_a is essentially q independent, whereas, at high q, it increases, asymptotically scaling as $D_\alpha \sim q^{0.6}$. Concurrently, there is a change in the degree of stretching of $f(q, \tau)$, characterized by α decreasing from nearly 1 at low q to about 0.7 at high q. The deviation from low-q behavior takes place at wave vectors near the limit of the fractal scaling range of the SLS data shown in Fig. 1(a). We can observe this crossover because we access a large range of scattering vectors, corresponding to length scales on the order of and smaller than the cluster size.

For all aggregation times, D_α is nearly q independent and $\alpha \sim 1$ at low q, reflecting diffusive motion of clusters; moreover, the complete decay of $f(q, \tau)$ indicates that the sample remains ergodic. Thus, within our experimentally

accessible time, the sample does not gel, but instead remains a suspension of freely diffusing fractal aggregates. To estimate the cluster size, we determine the first cumulant of $f(q, \tau)$, Γ_1, for the small-angle scattering data and calculate the effective diffusion coefficient, $D_{\text{eff}} = \Gamma_1/q^2$ [12]. As shown in Fig. 3(a), D_{eff} exhibits pronounced q dependence. This reflects the effect of rotational motion, which makes a significant contribution to the dynamics for $q > q_c$, where $q_c = 2\pi/R_c$; because of the heterogeneous structure of the fractal clusters, the scattered intensity of a single cluster varies upon rotation, leading to a faster decay of $f(q, \tau)$ [13]. However, because
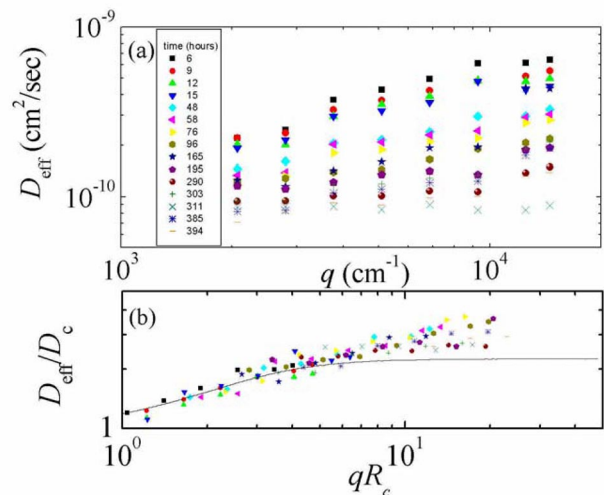

FIG. 3 (color online). (a) D_{eff} from cumulant fits at different aggregation times and (b) scaling of D_{eff} along diagonal onto a single master curve for microgravity data (symbols). Solid line shows theoretical curve from 15.

of the scale invariance of the fractal structure, the data can be scaled onto a single master curve; this is accomplished by normalizing D_{eff} by D_c, the translational diffusion coefficient of clusters with average size, R_c, and plotting them as a function of qR_c. The data scale onto a master curve remarkably well and are in agreement with the theoretical prediction at low q, as shown in Fig. 3(b), allowing an accurate measure of the average cluster size and its time evolution from the low-q dynamics.

For contributions of rotational and translational diffusion alone, we expect D_{eff} to plateau at very large q; this, however, is not observed experimentally. The deviation between the scaled experimental data and the theoretical prediction for $qR_c > 10$ must reflect the contribution of internal fluctuations within the cluster [13]. Such internal dynamics has been observed in colloidal gels [14], where the fractal clusters are constrained by the network and thus can neither translate nor rotate. In this case, $f(q, \tau)$ is well described by a stretched exponential form with an exponent $\alpha \sim 0.7$, which results in a q dependence for the apparent diffusion coefficient, $D_\alpha \sim q^{2-2\alpha} = q^{0.6}$. This is in striking agreement with the measured values of $\alpha \sim$ 0.7–0.8 and $D_\alpha \sim q^{0.6}$, and confirms that the high-q dynamics probe internal fluctuations of the clusters. It also accounts for the crossover behavior observed in Fig. 1(b). Thus, although our sample is not a gel, the incredibly slow diffusion of the clusters allows us to measure their internal dynamics.

The internal dynamics probed at high q provide previously inaccessible information about the elasticity of individual clusters. As a cluster grows larger, it also becomes floppier, resulting in internal fluctuations with larger amplitudes and slower relaxations. The motion of a segment of the cluster of size q^{-1} is determined by integrating over thermal fluctuations of all length scales greater than q^{-1} up to the cluster size. The dominant contribution to this motion stems from the elastic mode with the largest wavelength, whose length is the size of the cluster itself. In the case of fractal gels, the resultant dynamic structure factor is well approximated at short times by $f(q, t) = \exp(-q^2 D_p t^p)$, where p is the stretching exponent, and $D_p = F(R_c)\kappa_o^{-(1-p)}$, with $F(R_c)$ a function of the average cluster size [14]. Thus, D_p reflects the motion due to the internal modes and depends weakly on the particle-particle spring constant, κ_0. However, to correctly describe the dynamics of large isolated clusters at high q, we must also include the contributions of both translational and rotational diffusion, which are small but nonnegligible. We therefore refine the fitting function by adding a diffusive term, $f(q, t) = \exp[-q^2(D_p t^p + D_{\text{eff}} t)]$, where D_{eff} includes contributions from both rotational and translational diffusion of the clusters. We use the value for DLCA clusters in the high-q limit, $D_{\text{eff}} = 2.2 D_c$ [15], and allow D_p and p to vary. From the fit, we

find that each parameter is independent of both q and R_c; moreover, their values are quantitatively consistent with those found for gelled samples of the same particles, prepared at high ϕ_0. We estimate $\kappa_0 = 5 \times 10^3$ dyn/cm, a value in reasonable agreement with $\kappa_0 = 1.5 \times 10^4$ dyn/cm measured by rheology and light scattering on gelled samples [14,16]. These results demonstrate that the internal fluctuations of isolated clusters can be described using the same models developed for colloidal gels.

We compare the aggregation kinetics measured in space with those measured on Earth in Fig. 4. In microgravity the clusters grow at a rate in excellent qualitative agreement with that expected for DLCA, $R_c \sim t^{1/d_f}$. This cluster growth persists for the full duration of the space experiment; gelation is not observed because the duration is less than the gelation time, $t_{\text{gel}} \sim 90$ days, estimated by extrapolating the observed growth to the cluster size expected at the gel point, $R_c = 450 \ \mu$m. By contrast, the time evolution of R_c on Earth shows significant deviation from the behavior anticipated for DLCA. The initial growth of the clusters is identical to that in space, following a power-law time evolution consistent with DLCA; however, after ~ 10 h, the growth deviates from the expected behavior and reaches a plateau, with no further growth observed. Thus, this system will not gel as the maximum cluster size $R_c \sim 20 \ \mu$m is more than 1 order of magnitude lower than that needed to form a gel.

This arrested cluster growth observed on Earth suggests that gravity can ultimately limit gelation. As an aggregate sediment, its buoyant weight is balanced by hydrodynamic drag from the fluid [4]. Hydrodynamic resistance acts primarily at the surface of the cluster, but is screened in the interior, whereas gravity is a body force distributed throughout the cluster. This results in an internal shear stress across the cluster. The response of the cluster is equivalent to that of a spring, resulting in a strain of order $\gamma_g = Mg/\kappa_c R_c$ [4], where the gravitational acceleration is g, and the buoyant mass of the cluster is $M = M_0(R_c/a)^{d_f}$, with $M_0 = 4\pi a^3 \Delta\rho/3$ the buoyant mass of a single colloidal particle with a density
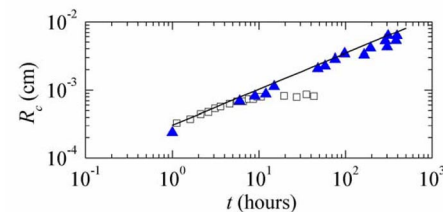

FIG. 4 (color online). Cluster size as a function of aggregation time; data at early times corrected for estimated rotational contributions for $10^{-2}g$ (□) and at late times from scaling of D_{eff} for $10^{-6}g$ (▲). Solid line shows expected growth from DLCA.

mismatch of $\Delta\rho$. The cluster spring constant is given by $\kappa_c = \kappa_0(a/R_c)^\beta$, where $\beta = 2 + d_B$ is the elasticity exponent, and d_B is the bond dimension, whose value is $d_B = 1.1$ for DLCA clusters [17]. Thus, the strain on the cluster is given by $\gamma_g = M_0 g(R_c/a)^{\beta + d_f}/(R_c\kappa_0)$. There are inevitably inherent uncertainties in matching the density of the colloidal particles to that of the fluid; in our experiment, uncertainties in the relative volumes of H_2O and D_2O, as well as ambient temperature fluctuations, lead to a buoyancy mismatch, which we estimate to be $\Delta\rho \sim 10^{-3}$ g/cm^3. Colloidal aggregate gels are found to irreversibly and catastrophically break under external strains of $\gamma > 0.45$, independent of ϕ_0 [16]. Thus, the critical strain is reached for a cluster size of $R_c \sim 35$ μm, which is in excellent agreement with the observed arrest in growth on Earth, $R_c \sim 20$ μm. Thus, gravity ultimately limits cluster growth on Earth.

In microgravity, the gravitationally induced strains are 6 orders of magnitude smaller; consequently, the clusters can grow to be much larger. Instead, strain induced by thermal fluctuations will eventually limit growth of fractal clusters, and thus will ultimately limit gelation [4]. The elastic energy of a fractal is $E_e = \kappa_c u^2/2$ for a linear displacement u; therefore, thermal fluctuations produce a strain of $\gamma_T = (k_B T(R_c/a)^{d_B}/(a^2\kappa_0))^{1/2}$. Thermal fluctuations set the maximum cluster size to $R_T \sim 1.2 \times 10^2$ μm. This is close to the maximum cluster sizes observed in the microgravity experiment; indeed, we observe signs of a plateau in R_c near the end of the experiment.

The fractal nature of the aggregates is essential to enable a small volume fraction of colloids to form a connected solid, thus any deviation from fractal growth severely compromises gelation. On Earth, gravity limits the maximum cluster size, thereby determining the minimum volume fraction which will gel. Since the cluster size at gelation is $R_c = a\phi_0^{1/(d_f-3)}$, $\phi_L = (\gamma_m a\kappa_0/M_0 g)^{(\beta+d_f-1)/(d_f-3)}$; for our samples on Earth, $\phi_L = 9 \times 10^{-5}$. Consistent with this, visual observations of samples over a range of volume fractions, $4 \times 10^{-4} < \phi_0 < 8 \times 10^{-6}$, show that for $\phi_0 < 10^{-4}$ samples appear heterogeneous, suggesting that gelation is compromised. By contrast, in microgravity, thermally induced strains limit the cluster size, setting $\phi_L =$ $(\gamma_m^2 a^2\kappa_0/k_B T)^{(d_f-3)/d_B}$. For our microgravity experiments, this leads to $\phi_L \approx 3 \times 10^{-5}$. Similar limitations pertain for all materials, even if the individual chains are stronger. Thus, the fundamental limitation to gelation is determined by thermal fluctuations; their magnitude ultimately becomes so large that they inhibit further fractal growth of the clusters, thereby preventing gelation.

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[1] D. A. Weitz et al., Phys. Rev. Lett. **53**, 1657 (1984).
[2] M. Carpineti and M. Giglio, Phys. Rev. Lett. **68**, 3327 (1992).
[3] J. Bibette et al., Phys. Rev. Lett. **69**, 981 (1992).
[4] Y. Kantor and T. A. Witten, J. Phys. (Paris) Lett. **45**, L675 (1984).
[5] C. T. Lant et al., Appl. Opt. **36**, 7501 (1997).
[6] M. P. Doherty et al., NASA Technical Report No. NASA/TM-2002-211371, 2002.
[7] M. Carpineti et al., Phys. Rev. Lett. **42**, 7347 (1990).
[8] Collection of data at longer times was precluded due to limitations of the ISS experiment.
[9] D. A. Weitz et al., Phys. Rev. Lett. **54**, 1416 (1985).
[10] M. Carpineti and M. Giglio, Phys. Rev. Lett. **70**, 3828 (1993).
[11] D. Asnaghi et al., Phys. Rev. A **45**, 1018 (1992).
[12] B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976).
[13] H. M. Lindsay et al., Phys. Rev. A **39**, 3112 (1989).
[14] A. H. Krall and D. A. Weitz, Phys. Rev. Lett. **82**, 1064 (1998).
[15] M. Y. Lin et al., J. Phys. Condens. Matter **2**, 3093 (1990).
[16] T. Gisler, R. C. Ball, and D. A. Weitz, Phys. Rev. Lett. **82**, 1064 (1999).
[17] P. Meakin, J. Phys. A **17**, L975 (1984).